

25th International Conference on Horizons in Hydrogen Bond Research

11-15 September 2023, Bologna, Italy



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WELCOME TO BOLOGNA

Welcome to the 25th International Conference on “Horizons in Hydrogen Bond Research” (HBOND2023) and Graduate Research Day (GRD).

This edition is the twenty-fifth in the series of conferences on hydrogen bonding which was started by Prof. Lucjan Sobczyk in Poland in 1977 and was held biannually across Europe.

This edition is organized and supported by the Department of Chemistry “G. Ciamician” at the University of Bologna and will be hosted in the teaching buildings of the University (via Andreatta, 8, 40126 Bologna). Financial support from our sponsors is also acknowledged.

The aim of the conference is to bring together scientists working in the field of hydrogen bond and other weak interactions, who study virtually all states of matter by a multitude of experimental and theoretical methods. Non-covalently bonded systems are extremely important in many fields like biology, chemistry, astrophysics and materials sciences.

The scientific programme is organized in different sections introduced by 5 keynote plenary lectures and complemented by 10 invited talks that aim at showing the different fundamental aspects and applications of hydrogen and non-covalently bonded systems. 26 oral contributions and a poster session complete the programme.

The meeting is preceded by a Graduate Research Day (GRD) with a programme specially designed for PhD students. A conference dinner and visit to the University of Bologna Museums complement the programme and will make your stay more enjoyable.

We welcome you to the conference for interesting and entertaining discussions and experiences and we hope it will be an inspiring event that will provide plenty of opportunities for interaction and networking!



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Contents

Committees	1
Practical Information	2
Programme	4
GRD	13
Keynote Talks	29
Invited Talks	35
Contributed Talks	47
Posters	75
List of Participants	89



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CONFERENCE SITE

The conference will take place in the Teaching Complex in via Andreatta, 8, Bologna Italy.

The registration desk, coffee breaks and lunches will be located on the ground floor while the conference rooms are on the first floor.

The sessions will be held in **ROOM B** while **ROOMS C** and **D** can be used by the participants in case they need a quiet place during the breaks.

REGISTRATION DESK

The registration desk will be located at the conference site: via Andreatta 8. It will be open on Monday, September 11th and Tuesday September 12th from 8:30 to 10:00.

It will also be open throughout the conference before and after the sessions and during lunch.

SOCIAL DINNER

Thursday, September 14th, 2023, at 20:00 at SYMPO', Via delle Lame, 83, 40122 Bologna BO.

GUIDED TOUR TO THE UNIVERSITY OF BOLOGNA HISTORICAL MUSEUMS

For participants who requested it, we offer a free guided tour to the University of Bologna Historical Museums during the free afternoon on September 14th at 14:00 right after lunch.

The visit will take place in groups of twenty and the cost will be covered by the organization.

Please note that the climb up the Tower requires considerable physical effort. Please talk to the organizers if you feel you could have a heart condition or suffer from dizziness and claustrophobia.



INSTRUCTIONS FOR AUTHORS

Oral contributions

The following times are associated with the different types of talk:

- Keynote 45 minutes, 35 for presentation and 10 for discussion.
- Invited 30 minutes, 25 for presentation and 5 for discussion.
- Contributed 20 minutes, 15 for presentation and 5 for discussion.

Speakers presenting a speech are requested to arrive at least 30 minutes before the start of their oral session. Please do consider that the use of your own laptop is highly discouraged. Presentation file format includes .pptx and .pdf.

Authors are required to have a copy of their presentation on a USB drive to be able to upload it to the PC of the corresponding session. If you don't have a USB flash drive available, you can send your presentation by email to spectrameet@unibo.it by the evening before your scheduled talk. This way, the organizers of the event will have the presentation ready for your presentation slot.

Poster contribution

Poster grids will be located at the conference site. Poster size 70 x 100 cm vertical (portrait) orientation.

Internet Wi-Fi access

Participants can access the Wi-Fi infrastructure by using their personal Eduroam account. Please check the service has been activated on your devices.

If a participant does not have access to Eduroam, we can provide them with complimentary registration using the Unibo network (an identification document is required for initial access).



Programme

Monday session – 11 September

9:00 Opening Graduate Research Day

Morning Session 1 9:15-11:10

Chair W. Caminati

9:15 Keynote Talk (KTa) **D. Fazzi**

The fine interplay between weak interactions and response properties in molecular materials

10:00 Invited Talk (ITa) **S. Alessandrini**

Ab initio modeling of Noncovalent System in the gas-phase: Interaction Energy and Geometry

10:30 Contributed Talk (CTa) **S. Schweer**

Chirality and isotope effects in acid-alcohol complexes

10:50 Contributed Talk (CTb) **H. Singh**

*Unravelling the solvent role in the catalysis of the bio-renewable chemical, 6-*amyl- α -pyrone*, using rotational spectroscopy.*

11:10 Coffee break

Morning Session 2 11:40-13:00

Chair W. Caminati

11:40 Contributed Talk (CTc) **T. L. Fischer**

Vibrational Spectroscopy of Hydrate Complexes for Benchmarking with Gas Recycling

12:00 Contributed Talk (CTd) **A. Verde**

*The Duplication of the Microsolvated Complexes of *p*-Anisaldehyde*

12:20 Contributed Talk (CTe) **F. Torres Hernández**

Conformational study of 2-phenylethylamine and its aggregates using laser spectroscopy in jets

12:40 Contributed Talk (CTf) **F. Sun**

Conformations of monochloropropionic acid in isolated and solution phase

13:00 Lunch



25th International Conference on
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Afternoon Session 1 14:30-16:00

Chair R. Paciotti

14:30 Invited Talk (ITb) **A. Caracciolo**

Gas-phase and gas-surface interactions of atomic oxygen relevant for terrestrial and extra-terrestrial atmospheres

15:00 Contributed Talk (CTg) **E. Sennert**

Halogenated alcohols microsolvating closed-shell and open-shell molecules

15:20 Contributed Talk (CTh) **M. Barp**

Gas-Phase Vibrational Spectroscopy of Halide – Hexafluoroisopropanol Complexes: Hydrogen Bond Strength vs. GasPhase Basicity and Anion Proton Affinity

15:40 Contributed Talk (CTi) **P. Pinillos Pinedo**

Finding the favored interaction spots of glucose and galactose by using phenol as a probe

16:00 Coffee break

Afternoon Session 2 16:20-17:20

Chair B. Hartwig

16:30 Invited Talk (ITc) **A. Camiruaga**

Insights into the role of water in sugar-peptide molecular recognition: a gas-phase vibrational spectroscopy study of micro-hydrated mannoside-peptide complexes

17:00 Contributed Talk (CTj) **C. V. Jensen**

Infrared Spectroscopy of Room Temperature Methanol Clusters

17:20 Contributed Talk (CTk) **E. Pizzano**

Near Infrared Spectroscopy as tool for the H-Bond investigations



Tuesday session – 12 September

9:00 Opening HBOND2023

Morning Session 1 9:15-11:10

Chair P. Ugliengo

9:15 Keynote Talk (KT1) **P. Hobza**

Hydrogen Bonding with Hydridic Hydrogen – Experimental Low-Temperature IR and Computational Study: Is A Revised Definition of Hydrogen Bonding Appropriate?

10:00 Invited Talk (IT1) **F. Zerbetto**

Hydrogen bonds in molecular knots

10:30 Contributed Talk (CT1) **S. Gómez**

Modeling Hydrogen Bonding in Resonance Raman Spectroscopy

10:50 Contributed Talk (CT2) **V. Zhaunerchy**

Competition between folded and extended conformers of gas-phase chromophore-free peptides

11:10 Coffee break

Morning Session 2 11:40-13:10

Chair M. Suhm

11:40 Invited Talk (IT2) **G. Bistoni**

Computational Insights into the Role of Hydrogen Bonding in Highly Selective Catalytic Reactions

12:10 Contributed Talk (CT3) **K. Müller-Dethlefs**

Non-covalent Interactions: The Synergy of Experiment and Theory Viewed over Two Decades

12:30 Contributed Talk (CT4) **A. Fernández-Ramos**

The role of the hydrogen-bonded complexes in bimolecular reactions involving OH at ultra-low temperatures

12:50 Contributed Talk (CT5) **A. Maris**

Intra and intermolecular interactions in hydroxylamine derivatives

13:10 Lunch



25th International Conference on
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11-15 September 2023 Bologna, Italy

Afternoon Session 1 14:30-16:20

Chair J. Lundell

14:30 Invited Talk (IT3) **J. Waluk**

Nuclear Quantum Effects in Intra- and Intermolecular Hydrogen Bonds

15:00 Contributed Talk (CT6) **I. Shenderovich**

Experimentally Proven but Not Yet Explained: Examples of Obscure Mechanisms of Protonation and Proton Transfer

15:20 Contributed Talk (CT7) **I. Bakó**

Nuclear quantum effects: their relevance in topology of hydrogenbonded network and diffraction studies of hydrogen bonded liquids

15:40 Contributed Talk (CT8) **S. Blanco**

Hydrogen bond cooperativity in the pyridine... $(\text{H}_2\text{O})_n$ ($n=2-4$) adducts generated in a supersonic jet: a rotational spectroscopy study

16:00 Coffee break

Afternoon Session 2 16:50-17:40

Chair J. Lundell

16:30 Invited Talk (IT4) **C. Cappelli**

Hydrogen Bonding: a big challenge for computational spectroscopy

17:00 Contributed Talk (CT9) **S. D'Agostino**

Enabling Proton Conduction in Solid Acids Via Supramolecular Complex Formation: The Case of Crown Ethers and Alkali Hydrogensulfates

17:20 Contributed Talk (CT10) **B. Hartwig**

Combining microwave and vibrational spectroscopy: The asymmetry parameter of the nuclear quadrupole coupling constants as a possible probe for hydrogen bond strength



Wednesday session – 13 September

Morning Session 1 9:15-11:10

Chair D. Braga

9:15 Keynote Talk (KT2) **P. Metrangolo**

Orthogonal Hydrogen and Halogen Bonding in Peptide Self-Assembly

10:00 Invited Talk (IT5) **F. Grepioni**

Nature inspired crystal engineering: from interactions to applications

10:30 Contributed Talk (CT11) **E. Mendez-Vega**

Understanding Solvent Polarity: Micro- vs Macrosolvation in Reichardt's Dyes

10:50 Contributed Talk (CT12) **K. Hermansson**

Water in and on crystals – a database for ML and a knowledge-base for spectroscopic prediction

11:10 Coffee break

Morning Session 2 11:40-13:10

Chair N. Walker

11:40 Keynote Talk (Kt3) **H. Fielding**

Liquid-microjet photoelectron spectroscopy with UV light pulses

12:30 Contributed Talk (CT13) **E. Arunan**

Microwave Spectroscopic and theoretical investigations on phenylacetylene-methanol complex

12:50 Contributed Talk (CT14) **J. A. Fernández**

Experimental Determination of the Strength of Non-Covalent Interactions in Dimers

13:10 Lunch



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Afternoon Session 1 14:30-16:20

Chair E. Arunan

14:30 Invited Talk (IT6) **A. Das**

Sequence Dependent Folding Motifs of Peptides: A Comprehensive Picture from Condensed and Gas Phase Studies

15:00 Contributed Talk (CT15) **P. Carçabal**

When solvated molecules shape the solvent: sugar water interaction in the gas phase

15:20 Contributed Talk (CT16) **J. C. López**

Hydrogen Bond Interaction with Water Influence Antioxidant Properties of Flavone

15:40 Contributed Talk (CT17) **N. Walker**

Internal Rotation and Isomerisation in Monohydrates of Heteroaromatics: Insights from Rotational Spectroscopy

16:00 Contributed Talk (CT18) **J. Lundell**

Revisiting vibrational spectroscopy of the $H_2O \cdots CO$ complex

16:20 Coffee break

16:50 Poster Session

18:00 Meeting International Advisory Board

Thursday session – 14 September

Morning Session 1 9:15-11:10

Chair K. Hermansson

9:15 Keynote Talk (KT4) **M. Mas-Torrent**

Morphology and polymorphism control in organic semiconductor thin films as a tool to optimize the device performance

10:00 Invited Talk (IT7) **M. R. Chierotti**

Walking along hydrogen bonds by means of solid-state NMR

10:30 Contributed Talk (CT19) **P. Hapala**

Designing photosensitive hydrogen bonded polymer templates for molecular nanofabrication

10:50 Contributed Talk (CT20) **A. Krawczuk**

Influence of hydrogen bond formation on prediction of dipole moments of proteins – GruPol database approach

11:10 Coffee break

Morning Session 2 11:40-13:10

Chair J. A. Fernández

11:40 Invited Talk (IT8) **C. Fonseca Guerra**

Discovering in silico the uniqueness of hydrogen bonding

12:10 Contributed Talk (CT21) **S. Pothoczki**

Hydration of monosaccharide molecules

12:30 Contributed Talk (CT22) **M. Paolantoni**

Hydration properties of sugars revisited

12:50 Contributed Talk (CT23) **D. Obenchain**

Exploring the different ortho/para effects in the binding of H₂ in gas-phase complexes

13:10 Lunch

14:00 Guided tour to the UniBo Historical Museums / Free afternoon

20:00 Social dinner at SYMPO', via delle Lame 83



Friday session – 15 September

Morning Session 1 9:15-11:10

Chair M. Schnell

9:15 Keynote Talk (KT5) **H. Kjærgaard**

Hydrogen Bonds in Atmospheric Compounds and Complexes

10:00 Invited Talk (IT9) **S. Coussan**

Study of $CH_3I \cdots (H_2O)_n$ complexes. From $CH_3I \cdots H_2O$ to CH_3I in interaction with amorphous, cubic and hexagonal water ice. Atmospheric implications and nuclear risks

10:30 Contributed Talk (CT24) **S. Sobanska**

Investigation of interactions between water and organic molecules of atmospheric interest – Implication in aging of secondary organic aerosols

10:50 Contributed Talk (CT25) **E. Vogt**

The First OH-stretching Overtone Region of Water Dimer

11:10 Coffee break

Morning Session 2 11:40-13:10

Chair P. E. Hansen

11:40 Invited Talk (IT10) **P. Bolognesi**

Cyclic dipeptides as intermediates “seeds of life”? An experimental and computational model

12:10 Contributed Talk (CT26) **R. Paciotti**

DFT calculations and IRMPD spectroscopy: the relevant role of H bond for structure assignment

12:30 Poster Prizes – HBOND2023

12:50 Closing Remarks

13:10 Lunch



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GRD

KTa

The fine interplay between weak interactions and response properties in molecular materials

Daniele Fazzi

Department of Chemistry "Giacomo Ciamician", University of Bologna, via F. Selmi 2, 40126, Bologna (Italy) daniele.fazzi@unibo.it

Organic π -conjugated functional materials are soft systems whose response properties are intimately connected to the short- and long-range supra-molecular order. The energy landscape affecting the molecular organization at solid state is generally characterized by intermolecular interactions ranging from weak London dispersion forces, up to strong dipole-dipole interactions and hydrogen bonds.¹

In this contribution I will discuss the crucial role played by the intermolecular interactions in governing the charge transport properties in organic functional materials, active components for opto-electronic and energy-saving applications.² I will show how the electronic coupling, namely the electronic interaction between neighbouring molecules, is one of the crucial parameter within the context of electron transfer theory to model the charge mobility, and to design molecular systems with optimized charge and energy transfer properties.

Case studies spanning from crystalline and amorphous molecular solids, encompassing both small molecules and polymers,^{3,4} will be presented in order to provide a general overview about the structure *vs.* transfer properties of functional soft materials.

References

- [1] J.-L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, *Chem. Rev.* **104**, 4971, 2004
- [2] H. Oberhofer, K. Reuter, J. Blumberger, *Chem. Rev.* **117**, 10319, 2017
- [3] N. Gildemeister, et al., *J. Mater. Chem. C* **9**, 10851, 2021
- [4] D. Fazzi, M. Caironi, *Phys. Chem. Chem. Phys.* **17**, 2015, 8573

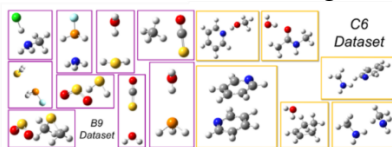
ITa

Ab initio modeling of Noncovalent System in the gas-phase: Interaction Energy and Geometry

Silvia Alessandrini¹, Jacopo Lupi², Vincenzo Barone³ and Cristina Puzzarini¹

¹*Alma Mater Studiorum – Università di Bologna, Bologna, Italy,* ²*School of Physics, Trinity College Dublin, Ireland,* ³*Scuola Normale Superiore, Italy,*
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A new model for the computation of the interaction energy (IE) in the case of noncovalent molecular complexes has been developed using explicit correlated F12 methodologies.¹ The starting point for this new model is the so-called “cheap composite scheme” (ChS)^{2,3}, which is based on the coupled cluster singles and doubles approach augmented by a perturbative treatment of triple excitations, namely CCSD(T), in conjunction with a triple-zeta basis set. This first term is then corrected for taking into account the extrapolation to the complete basis set (CBS) limit and the effect of core-valence (CV) correlation. Both these contributions are computed using second order Møller-Plesset perturbation theory (MP2) to reduce the computational cost and increase the accuracy of the model. To build the explicit correlated variant of the ChS, the CCSD(T)-F12 and the MP2-F12 methods have been considered, investigating in detail, the convergence to the CBS limit of both methodologies. Two critical aspects of the CBS extrapolation have been analyzed: the exponential formula and the family of basis set to employ for the extrapolation, with the results being compared with the accurate ones of the A14 dataset^{3,4}. Based on the results obtained for the IE, the accurate determination of the equilibrium geometries for noncovalent molecular complexes was also considered. In this case, different *ab initio* approaches, involving both standard and explicit correlation, have been used to derive the equilibrium structure of noncovalent systems and establishing the corresponding key geometrical parameters. The results of both investigations will be illustrated during my contribution, providing also new data for the B9 and C6 dataset illustrated in the following¹.



References

- [1] J. Lupi, S. Alessandrini, C. Puzzarini, V. Barone, *J. Chem. Theory Comput.***17**, 6974 2021
- [2] C. Puzzarini, M. Biczysko, V. Barone, I. Pena, et. al., *Phys. Chem. Chem. Phys.***15** 16965, 2013
- [3] S. Alessandrini, V. Barone, C. Puzzarini, *J. Chem. Theory Comput.***13**, 988, 2020
- [4] J. Řezáč, P. Hobza, *J. Chem. Theory Comput.* **9**, 2151, 2013.
- [5] J. Řezáč, M. Dubecký, P. Jurečka, and Hobza, P. *Phys. Chem. Chem. Phys.***17**, 19268, 2015.



ITb

**Gas-phase and gas-surface interactions of atomic oxygen relevant
for terrestrial and extra-terrestrial atmospheres**

A. Caracciolo

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Lausanne, 1015 Lausanne, Switzerland
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Atomic oxygen (AO) in its ground state $O(^3P)$ is known to be among the most reactive species on Earth's atmosphere as well as in more exotic environments such as the interstellar medium. Here, AO may react with unsaturated hydrocarbons undergoing to myriad of different reactive channels. However, when $O(^3P)$ is involved in a high-barrier reactions or it collides with a smooth surface, these events can lead to weak interactions between the reactants. To investigate both gas-phase and gas-surface AO interactions, scattering experiments can be performed to characterize the dynamics and determine the branching ratios which can be eventually implemented in the chemical models to improve their predictability.

In this contribution, the role of $O(^3P)$ atoms will be discussed with different chemical partners in its fundamental aspects and its applications in aerospace. Furthermore, an ablation source has being designed and build at EPFL (École Polytechnique Fédérale de Lausanne, Switzerland) to eventually study and characterize $O(^3P)$ reactivity with metal atoms relevant in satellites design.

ITc

Insights into the role of water in sugar-peptide molecular recognition: a gas-phase vibrational spectroscopy study of micro-hydrated mannoside-peptide complexes

Ander Camiruaga¹, Gildas Goldsztejn¹, Pierre Çarçabal¹

¹*Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Université Paris Saclay, Orsay, France, ander.camiruaga@universite-paris-saclay.fr*

Sugars are one of the most important families of biomolecules. They act as mediators of molecular recognition processes. Among the possible biomedical applications, one example is the addition of mannosides to photosensitizers used in PhotoDynamic Therapy, targeting Mannose Receptor (MR) proteins on pathogenic cells. A precise description of the structural basis of Mannose-MR local and direct interplay, which can be provided by gas phase spectroscopy, will become a valuable insight to design PSs with improved selectivity.

In the gas phase, combining experimental mass resolved and conformer selective double resonance vibrational spectroscopy and theoretical chemistry studies,¹ we have already been able to observe several complexes between sugars and peptide models.^{2,3} We can now also observe such complexes with a controlled number of water molecules. Our most recent results on complexes of mannose with different peptide models, either hydrated or not, allow resolving the nature of the interactions between the molecules, thanks to the extensive use of isotopic substitution. These results evidence the adaptability of the sugar moiety to its peptide receptor. In particular, the study of the complexes formed with few water molecules may highlight the role of water in molecular recognition processes in an unprecedented manner.

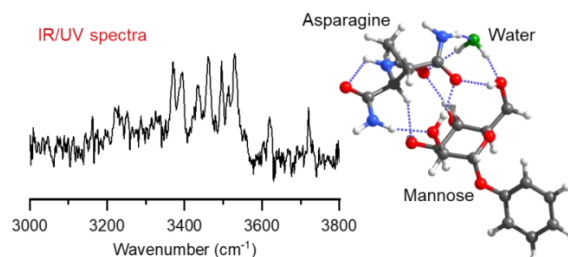


Fig. 1: Experimental conformer selective vibrational spectra of an Asparagine-Mannose-Water ternary complex.

References

- [1] Cocinero E.J.; Çarçabal P., *Top. Curr. Chem.*, 2015, 364, pp. 299-333.
- [2] Cocinero E.J.; Çarçabal P.; Vaden T.D.; Simons J.P.; Davis B.G., *Nature*, 2011, 469, 76-79.
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CTa & P12

Chirality and isotope effects in acid-alcohol complexes

Sophie M. Schweer¹, Moritz Niessner², Arman Nejad³, Martin A. Suhm⁴

¹Georg-August-University Göttingen, Germany, sschwee@gwdg.de; ²Georg-August-University Göttingen, Germany, mniessn1@gwdg.de; ³Oxford University, Great Britain, anejad@gwdg.de; ⁴Georg-August-University Göttingen, Germany, msuhm@gwdg.de

Complexes of carboxylic acids with alcohols are barely investigated. Because of the nature of the substrates, it is possible that esterification takes place.^{1,2} Pre-reactive dynamics includes vibrational couplings with dark states or a nearly degenerate double proton transfer between the constituents within the cyclic hydrogen-bonded 1:1 complex. We have already successfully investigated the formic acid-trifluoroethanol complex³ and have now moved on to the more challenging formic acid-methanol system, where we use FTIR/Raman jet spectroscopy and isotope effects combined with high level VPT2 calculations^{4,5,6} to analyze the spectral fingerprint of the OH stretching vibrations.

Another interesting aspect, which might lead to puzzle solving, is how chirality will influence such systems. We therefore use acids/alcohols with permanent chirality to perhaps favor one handedness in the transiently chiral alcohol/acid binding partner

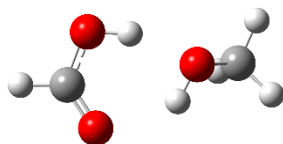


Fig. 1: The cyclic formic acid – methanol dimer.

References

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- [5] E. Miliordos, S. S. Xantheas, *J. Chem. Phys.* **2015**, *142*, 094311.
- [6] A. Nejad, M. A. Suhm, *J. Indian Inst. Sci.* **2020**, *100*, 5-19.

CTb & P13**Unravelling the solvent role in the catalysis of the bio-renewable chemical, 6-amyl- α -pyrone, using rotational spectroscopy.****Himanshi Singh^{1,2}, Mariyam Fatima^{1,3}, M. Ali Haider⁴, Melanie Schnell^{1,2}**

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Lignocellulosic biomasses are often reacted on catalysts in solvents to produce high-value chemicals. One such example is the catalytic transfer hydrogenation (CTH) of 6-amyl- α -pyrone (6PP), a biomass platform chemical, producing δ -decalactone (DDL), which is used as an aroma compound. The CTH reaction carried out in different solvents under similar conditions is reported to produce significant variation in 6PP conversion and DDL yield, ranging from 6% to 79%. These variations in yield during CTH can be attributed to numerous reasons, such as the dielectric constants of solvents or dispersive interactions during micro-solvation of 6PP.

In this work, we aim to understand the role of solute-solvent interactions in the CTH reaction using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy. This technique, coupled with supersonic expansion, reveals accurate structures of molecules and weakly bound complexes isolated in the gas phase. We first explore the conformational space of 6PP, as it is a highly flexible molecule due to the presence of a pentyl chain, and then study its complexes to understand the effect of solvent molecules on the structure of 6PP. We chose two solvents, ethanol and cyclohexane, with one yielding the best results and the other yielding moderate results in the CTH reaction, to investigate how intermolecular interactions affect the reaction yield. The conformational analysis of 6PP will be presented, along with the observed structural changes in 6PP upon complexation. Additionally, the preferred intra- and intermolecular interactions will be discussed.

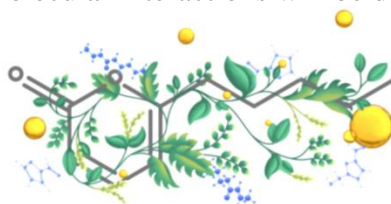


Fig.: 6-amyl- α -pyrone¹

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CTc & P14**Vibrational Spectroscopy of Hydrate Complexes for
Benchmarking with Gas Recycling****Taija L. Fischer¹, Margarethe Bödecker¹, Sophie M. Schweer¹, Ricardo A. Mata¹, Martin A. Suhm¹**¹*Georg-August-Universität Göttingen, Germany, tfische1@gwdg.de*

When testing the performance of quantum chemistry in vibrational spectroscopy, jet cooling is advantageous, FTIR gives access to many species, and not knowing the experimental results during prediction is particularly objective. One example is the so-called HyDRA (Hhydrate Donor Redshift Anticipation) blind challenge in which a prediction of the shift of the symmetric OH stretching fundamental of water, when binding to an organic molecule, was requested from different theory groups.¹ Later the theory submissions were compared to the undisclosed spectroscopic data and the results were published in a joint publication.² A novel gas recycling setup enables the usage of pricier chemicals and carrier gasses in supersonic jet expansions.³ In this work the investigation of hydrate complexes using the novel FTIR spectroscopy setup and their use for benchmarking is presented.

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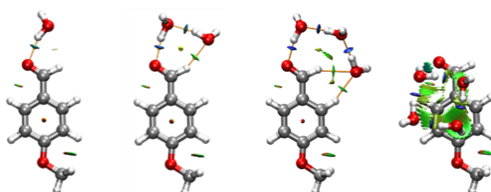
CTd & P15

The Duplication of the Microsolvated Complexes of *p*-Anisaldehyde

A. Verde¹, J.C. López¹, S. Blanco¹

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The rotational spectra of *p*-anisaldehyde, a natural product found in the anise seeds, and its microsolvated complexes generated in a supersonic jet have been studied by chirped-pulse Fourier transform microwave spectroscopy (CP-FTMW) in the 2-8 GHz region. Two conformers corresponding to the two possible relative orientations of aldehyde and methoxy functional groups have been unambiguously detected for the monomer. When allowing water vapour to expand in the supersonic jet, the spectra of five microsolvated complexes appeared for each conformer. Complexes with up to three water molecules reflect the preference of water binding to the aldehyde group instead of the methoxy one. In all these clusters, a strong hydrogen bond (HB) is established between the aldehyde’s oxygen and water. When analyzing the nature and strength of the intermolecular interactions with Bader’s Quantum Theory of Atoms in Molecules and Non Covalent Interaction analysis, σ -bond cooperativity is observed when increasing the degree of solvation. Additionally, one complex of *p*-anisaldehyde with four molecules of water has been detected for each conformer. In contrast to the previous forms where water tend to form chains, *p*-anisaldehyde captures the tetramer of water adopting a stacked configuration.



*Fig. 1: Non covalent interactions and Bader’s quantum of atoms in molecules analysis for four microsolvated complexes detected for the most stable *paa* conformer.*

CTe & P16

Conformational study of 2-phenylethylamine and its aggregates using laser spectroscopy in jets

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The study of non-covalent interactions is crucial for understanding the behavior and properties of biomolecules. One of the most important intermolecular interactions is the hydrogen bond because it is mainly responsible for the structures of proteins and DNA.¹ Among the techniques used to study this interaction, mass-resolved laser spectroscopy in combination with computational methods has successfully been applied to obtain information regarding the molecular conformation, intra- and intermolecular interactions, and relative energies.²

Following our previous investigations on 2-phenylethanethiol and 2-phenylethanol, in this work we focus on the study of 2-phenylethylamine (PEA), their nitrogen analogue, using time-of-flight mass spectrometry (TOF-MS) in combination with resonant multiphoton ionization spectroscopy (REMPI) and ion dip infrared spectroscopy (IDIR). PEA is a biologically relevant molecule that exhibits a wide range of biological activities, such as neurotransmitter and neuromodulator. Our experimental results, combined with quantum chemical calculations, provide important insights into the aggregation of PEA (Figure 1) compared to its sulphur and hydroxyl analogues.

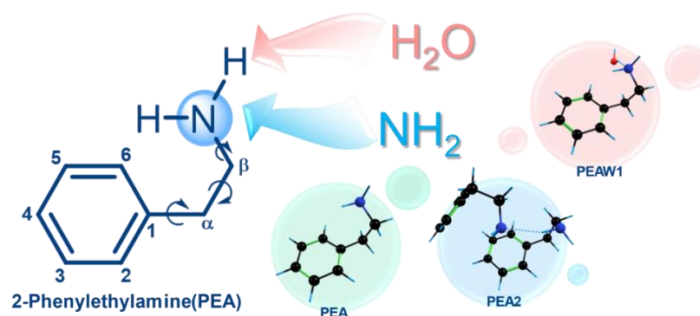


Fig. 1: 2-Phenylethylamine and its aggregates.

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CTf & P17**Conformations of monochloropropionic acid in isolated and solution phase****Fufei Sun, Assimo Maris, Luca Evangelisti, Wentao Song and Sonia Melandri**

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Monochloropropionic acids, compounds toxic to human health, have recently been found in drinking water. The reason for the enrichment of these substances in drinking water could be their water solubility and adsorption tendency. These two factors are governed by molecular polarity which in turn is determined by molecular structure. The in-depth exploration of the conformational information in isolated and solution phases is very meaningful to better understand the molecule’s condition in water. The microwave spectra of both 3-chloropropionic acid and 2-chloropropionic acid have been investigated in the gas phase using Stark-modulated free-jet absorption millimeter-wave (FJ-AMMW) spectroscopy in the 59.6-78.3 GHz region. Three conformers of 3-chloropropionic acid were observed and an additional conformer of 2-chloropropionic acid previously not observed in previous study¹ was found. To investigate the behaviour of these compounds in water, implicit and explicit solvent calculations were performed. The simulation of water with a continuous model suggests that the higher energy conformers of the molecules, those with a Z-COOH arrangement in the carboxyl group exhibit lower solvent-free energy, which is consistent with the quantum cluster growth (QCG)² calculation showing a strong interaction energy with solvent molecules of these conformers compared to others. QCG calculations indicate that the solvent shell significantly influences the conformation of monochloropropionic acid, specifically by affecting its C-C-COH dihedral angle, leading to a great conformational rearrangement compared to the gas phase structure.

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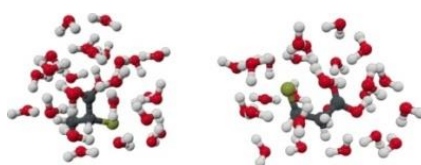


Fig.1.2-chloropropionic acid (left) and 3-chloropropionic acid (right)in the water solvent shell (number of water molecules=25).

CTg & P18

Halogenated alcohols microsolvating closed-shell and open-shell molecules

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In this work the microsolvation of different molecules by halogenated alcohols is explored by comparing cold gas phase FTIR-spectra with the results of harmonic DFT calculations. Considering possible hydrogen bonding, the OH stretching vibration of the alcohol is used as a sensitive indicator for the presence of a specific heterodimer conformer. By varying the halogenation type and degree of the alcohols the role of polarity and polarizability for the conformational solvation preferences is explored.

Besides closed-shell solutes, open-shell molecules paired with halogenated alcohols are investigated, motivated by a large dynamical nuclear polarization effect observed for nitroxyl radicals combined with halogenated solvents.¹ The gas phase microhydration of TEMPO was already explored by Brás et. al.² Following up on that study the present work investigates the solvation of TEMPO derivatives by benzyl alcohol and its *para*-halogenated derivatives³.

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CTh & P19**Gas-Phase Vibrational Spectroscopy of Halide –
Hexafluoroisopropanol Complexes: Hydrogen Bond Strength vs.
GasPhase Basicity and Anion Proton Affinity****Milena Barp¹, Jiaye Jin¹, Florian Kreuter¹, Ralf Tonner-Zech¹ and Knut R. Asmis¹**¹*Leipzig University, Wilhelm Ostwald Institute for Physical and Theoretical Chemistry, Germany, milena.barp@uni-leipzig.de; knut.asmis@uni-leipzig.de*

1,1,1,3,3,3-hexafluoroisopropanol (HFIP) is an increasingly popular organic solvent used, for example, in polymerization, epoxidation, electrochemical reactions as well as protein structure determination.¹ It exhibits several exceptional properties, one of which is to catalyse reactions as a result of its **hydrogen bond donating ability**. Understanding HFIP's solvation properties as well as the nature of the formed hydrogen bond network is, however, far from trivial. Useful insights can be gained from studying isolated, microsolvated ion complexes in the gas phase and comparing it to other solvents. Here, we study the **gas-phase vibrational spectroscopy** of the halide anion ($X^- = \text{Cl}^-, \text{Br}^-, \text{I}^-$) – **HFIP** and **d-HFIP** complexes and **compare** it to that of the corresponding complexes with **(d-)isopropanol** and **water** in order to characterize the relationship between **hydrogen bond strength, anion proton affinity and solvent gas phase basicity**. Infrared photodissociation spectra of the corresponding messenger-tagged complexes are obtained in the frequency range of O-H(D) stretching vibration (2000–4000 cm^{-1}) and analysed with support of quantum chemistry calculations. We find that the observed red-shift of the hydrogen-bonded OH(D) stretching frequency scales with anion proton affinity, as expected, but not with the solvent gas-phase basicity. The character of the hydrogen bond is also discussed in the light of results obtained from an energy decomposition analysis.

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CTi

Finding the favored interaction spots of glucose and galactose by using phenol as a probe

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Sugars play essential roles in cellular life, they storage energy for fast consumption, they are also used as fundamental constituents of the immune system and form part of the DNA and RNA backbone. Many of their functions rely on the extensive intermolecular interactions that they can establish thanks to a collection of hydroxyl groups they present. Interestingly, modification of the position of a single hydroxyl group results in dramatic changes in the interaction landscape of a given saccharide. Here we investigate how the position of the hydroxyl group at C4, anomeric conformation, and the nature of the substituent affect these interactions using phenol as a probe. Through mass-resolved excitation spectroscopy (MRES) and density functional calculations (DFT), the structural characteristics of the aggregates are uncovered.¹

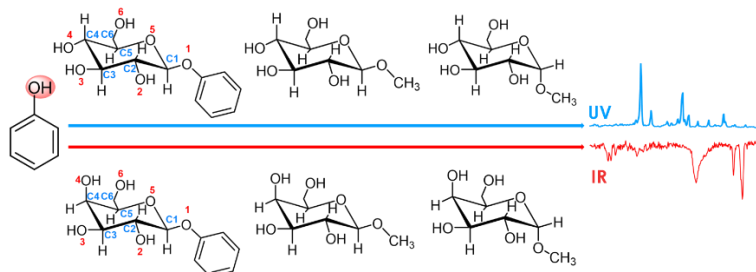


Fig. 1: Structures of phenol, phenyl- β ,D-glucopyranose, methyl- β ,D-glucopyranose, methyl- α ,D-glucopyranose and their galactose analogues.

The results obtained highlight the significant influence of the hydroxymethyl group in guiding the aggregation process. Furthermore, the position of the substituent at C4 has a stronger impact on the dimer structure than the anomeric conformation. These findings deepen our understanding of hydrogen bonding in sugars and their relevance in cellular systems.²

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CTj
Infrared Spectroscopy of Room Temperature Methanol Clusters
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Formation of hydrogen bound clusters is an important mechanism in the condensation of atmospheric volatile organic compounds. Alcohols are a prevalent functionality in the atmosphere and the cluster formation of methanol has been extensively studied in jet-cooled conditions.¹ At room temperature, the equilibrium is vastly shifted towards the monomer due to the decrease in entropy with cluster formation. This makes accurate quantification of the cluster partial pressures in experiments difficult.

We determine the formation constants of the methanol dimer, trimer and tetramer by an experimental/theoretical hybrid approach.^{2,3} Fourier transform infrared absorption experiments and spectral subtraction of the methanol monomer is used to obtain spectra of the clusters (Figure 1). By combining the experimental intensities with calculated oscillator strengths of the bands, we determine the partial pressures of the individual clusters in the gas mixture and report the associated formation constants.

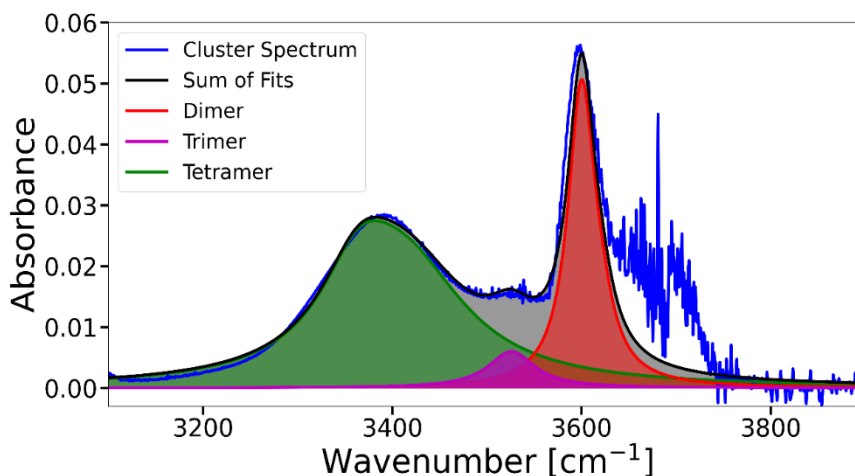


Fig. 1: OH-stretching bands of the methanol dimer, trimer and tetramer with fitted profiles.

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CTk

Near Infrared Spectroscopy as tool for the H-Bond investigations

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Hydrogen bonding is a fundamental interaction that governs various chemical and biological processes, including molecular recognition, solvation, and protein folding. However, the intricate nature of hydrogen bonding has long posed challenges in its comprehensive investigation. Near-infrared spectroscopy (NIRS) has recently emerged as a powerful tool to bridge this gap, enabling researchers to gain a deeper understanding of hydrogen bonding dynamics and behaviour. This review aims to provide a comprehensive overview of the application of NIRS in the study of hydrogen bonding, discussing its advantages over conventional methods and highlighting recent advances in the field. NIRS is a non-invasive spectroscopic technique that measures the absorption of near-infrared radiation by molecular vibrations, providing valuable information on the molecular structure, solvation, and dynamics of hydrogen-bonded systems. The NIRS technique offers several advantages over traditional methods such as infrared and Raman spectroscopy, including the ability to probe hydrogen bonding in complex environments, such as biomolecules and liquid solutions. Furthermore, NIRS can be applied in both steady-state and time-resolved experiments, allowing researchers to investigate hydrogen bonding in real-time. The lecture will show practical examples taken from both literature and laboratory works.



25th International Conference on
"Horizons in Hydrogen Bond Research"

11-15 September 2023 Bologna, Italy

Keynote Talks

KT1**Hydrogen Bonding with Hydridic Hydrogen – Experimental Low-Temperature IR and Computational Study: Is A Revised Definition of Hydrogen Bonding Appropriate?****Pavel Hobza**

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Spectroscopic characteristics of Me₃Si-H···Y complexes (Y=ICF₃, BrCN and HCN) containing a hydridic hydrogen were determined experimentally by low-temperature IR experiments based on the direct spectral measurement of supersonically expanded intermediates on a cold substrate or by the technique of argon-matrix isolation as well as computationally at harmonic and one-dimensional anharmonic levels. The computations were based on DFT-D, MP2, MP2-F12 and CCSD(T)-F12 levels using various extended AO basis sets. The formation of all complexes related to the red shift of Si-H stretching frequency upon complex formation was accompanied by an increase in its intensity. Similar results were obtained for another ten electron acceptors of different types, positive σ -, π -, and p-hole and cation. The spectral shifts, changes of intensities and stabilization energies obtained for all presently studied hydridic H-bonded complexes were comparable to those in protonic H-bonded complexes, which has prompted us to propose a modification of the existing IUPAC definition of H-bonding that covers, besides the classical protonic, also the non-classical hydridic and the dihydrogen form.

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KT2**Orthogonal Hydrogen and Halogen Bonding in Peptide Self-Assembly****Pierangelo Metrangolo**

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A halogen bond occurs between an electrophilic region associated with a halogen atom in a molecule and a nucleophilic region in another molecule. Although many modifications of amyloidogenic sequences have been utilized to tune their self-assembly behaviour, halogenation has rarely been pursued. The advantage of the introduction of halogen atoms on peptide motifs lies in the fact that halogenation is a minimal structural modification, which, on the other hand, induces a large difference in the peptide supramolecular behaviour as a consequence of the rich variety of noncovalent interactions given by halogen atoms.

In this presentation, I will show how the halogen bond can be used to promote the molecular self-assembly of peptides. We have applied this new supramolecular concept to the augmented fibrillation of amyloidogenic peptides and the control of their nanostructures (Figure 1). The obtainment of a novel unnatural amino acid functioning as strong halogen-bond donor has allowed to engineer the hydrophobic cavity of an amyloid fibril. Our results prove that selective halogenation of an amino acid enhances the supramolecular organization of otherwise unstructured biologically-relevant sequences. This method may develop as a general strategy for stabilizing highly polymorphic peptide regions.¹

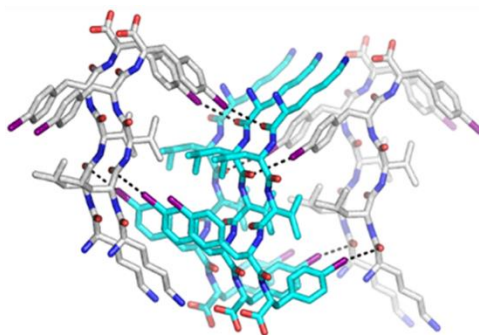


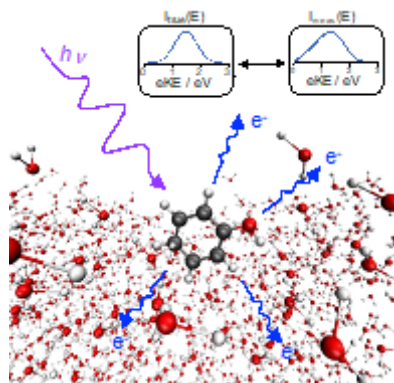
Fig. 1: Steric zipper motif formed by KLVF(I)F(I) showing halogen bonds with the carbonyl oxygens.

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KT3**Liquid-microjet photoelectron spectroscopy with UV light pulses****Helen H. Fielding¹**¹*Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K., h.h.fielding@ucl.ac.uk*

Ultraviolet (UV) photoelectron spectroscopy provides a direct way of measuring valence electronic structure; however, its application to aqueous solutions has been hampered by a lack of quantitative understanding of how inelastic scattering of low energy (<5 eV) electrons in liquid water distorts the measured electron kinetic energy distributions. We have recently developed a method for retrieving true UV photoelectron spectra of aqueous solutions.¹ Its application will be demonstrated for liquid water and organic chromophores.^{1,2} We will also demonstrate how UV liquid-jet photoelectron spectroscopy and femtosecond transient absorption spectroscopy provide complementary measurements.³

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KT4

Morphology and polymorphism control in organic semiconductor thin films as a tool to optimize the device performance

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Thin films of small molecule organic semiconductors (OSCs) have been successfully used as active layers in organic field-effect transistors (OFETs). In order to achieve an optimized performance and a high device-to-device reproducibility it is essential to control the morphology and polymorphism of these films.¹ Over the last years, we have been working on the preparation of OSC films using the bar-assisted meniscus shearing technique.² This technique results in highly crystalline thin films over large areas and is compatible with roll-to-roll manufacturing processes. Further, we investigated the influence of the deposition parameters and solution formulation on the thin film morphology and polymorphism, which in turn, has a crucial impact on the device performance.³ Here we will overview our work where we show how morphology and polymorphism determines the device stability and performance,⁴ not only in terms of charge carrier mobility but also when the devices are implemented in sensors.⁵

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KT5

Hydrogen Bonds in Atmospheric Compounds and Complexes

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Atmospheric gas-phase autoxidation, the repeated unimolecular reaction followed by uptake of molecular oxygen, has been recognized as a major pathway for volatile organic compounds (VOCs).^{1,2} It leads to highly oxygenated organic molecules (HOMs) with potentially many functional groups (typically OOH, OH, C=O), which increase hydrogen bond capabilities. The increased number of functional groups and increased size facilitates increased particle uptake.

The stability of molecules and complexes formed in atmospheric reactions depends on their ability to form hydrogen bonds. Unstable hydroperoxides (OOH) are frequently formed in the atmosphere. In cases with rapid autoxidation, formation of molecules with multiple hydroperoxide groups and even a hydrotrioxide group (OOOH) is possible (Fig 1).^{3,4} The surprising stability of the highly reactive hydrotrioxides is facilitated by multiple hydrogen bonds.

Atmospheric nucleation and aerosol growth depend on gas-phase complex formation at ambient temperatures. We have detected bimolecular complexes with hydrogen bonds, X-H...Y, for a range of different donor XH-bonds and acceptor moieties.⁵ In the best cases, we determine the Gibbs energy of complex formation, ΔG , with a precision better than 1 kJ/mol. To facilitate this, we calculate (reduced dimensionality local modes) and measure (gas phase FTIR) the oscillator strengths of vibrational bands that are characteristic to the bimolecular complex.

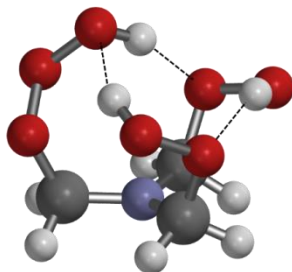


Fig. 1: Multiple hydrogen bonds stabilize the dihydroperoxide hydrotrioxide compound formed in the autoxidation trimethyl amine.

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25th International Conference on
"Horizons in Hydrogen Bond Research"

11-15 September 2023 Bologna, Italy

Invited Talks

IT1**Hydrogen bonds in molecular knots****Francesco Zerbetto**

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The investigation of knots started with the erroneous 'vortex atoms' theory of Lord Kelvin. Ever since, the study of knots has been a prerogative of mathematicians. In chemistry, in 1961, Wasserman and Frisch established the birth of the field of Chemical Topology.^[1] This event was followed, in 1967, by the discovery of the first naturally occurring catenated and knotted DNA.^[2-4] Recent work on knots^[5] has used a hybrid approach to determine the mechanical stability of some kinds of knots and tangles, highlighting how topology affects the properties of a system.

Molecular knots are therefore a reality.^[6] Their synthesis is a major achievement of synthetic chemistry, but also offers a host of opportunities because their topology forces together chemical moieties that would otherwise form structurally different configurations.

Here I will discuss the molecular dynamics of knotted molecules that are characterized by the presence of multiple hydrogen bonds. Comparison will be given with the dynamics of the unknotted counterparts. Ultimately, I will discuss if and how the chemical nature of a system is strengthened or weakened by the introduction of a knotty topology.

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IT2

Computational Insights into the Role of Hydrogen Bonding in Highly Selective Catalytic Reactions

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Using advanced computational techniques [1,2], we provide an in-depth analysis of the role played by hydrogen bonding in a series of selective catalytic transformations. Emphasis is placed on a highly relevant stereoselective reactions, including the catalytic asymmetric synthesis of cannabinoids and menthol from neral as a representative example [3]. Through different types of hydrogen bonding, catalysts can stabilize reactive intermediates, modulate transition state energies, and dictate the stereochemistry of the products. The insights gained from our computational studies deepen our understanding of the fundamental principles governing hydrogen bonding in catalysis, while providing at the same time valuable guidance for catalyst design in various fields of chemical research.

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IT3

Nuclear Quantum Effects in Intra- and Intermolecular Hydrogen Bonds

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Over several decades, we have been studying tautomerism occurring in the ground and/or excited electronic states of (i) systems with single or double intramolecular hydrogen bonds and (ii) complexes of heteroazaaromatic molecules with water or alcohols.¹ These investigations revealed that in order to properly describe the tautomerization paths, one has to take into account such phenomena as tunnelling or vibrational mode-selectivity. Tunnelling, either deep (from the zero vibrational level) or from a vibrationally excited state was found to be the dominant mechanism of proton or hydrogen transfer, even when the measurements were carried out at “normal” conditions, i.e., room temperature studies of solutions.² By using fluorescence,³ Raman,⁴ and scanning probe microscopies,⁵ it is now possible to monitor tautomerization in single molecules and observe differences in tautomerization mechanisms and rates due to the influence of the environment.

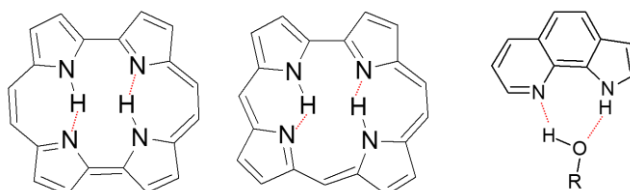


Fig. 1: Systems with intra- and intermolecular hydrogen bonds.

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IT4**Hydrogen Bonding: a big challenge for computational spectroscopy****Chiara Cappelli***¹Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy,
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Hydrogen bonding plays a crucial role in spectroscopy and influences most spectroscopic outcomes. This is for instance the case of aqueous solution, where spectral signals are often dominated by solute-water hydrogen bonding interactions.

Reliable computational models for the spectroscopy of aqueous solutions need to accurately reproduce specific hydrogen bonding effects in order to be successfully exploited in the comparison between theory and experiments. Commonly used continuum solvation approaches fail in this context,¹ and multiscale, multilayer, approaches, such as Quantum Mechanical (QM)/Molecular Mechanics (MM) approaches,² are needed.

Moreover, polarization effects are relevant for this class of systems, therefore Polarizable QM/MM approaches, where the mutual polarization between QM and MM layers is considered, are particularly successful, especially if combined with Molecular Dynamics (MD).²⁻¹⁰

I will discuss the most recent contributions of our group in this field, by also resorting to pilot applications which highlight current challenges and the methods' potentialities.

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IT5**Nature inspired crystal engineering:
from interactions to applications****Fabrizia Grepioni**

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Results will be presented obtained by applying crystal engineering to develop nature-inspired organic and organic/inorganic materials, with the intent of tackling challenges in the health and environmental fields. A number of examples will be shown to demonstrate that co-crystallization of organic/inorganic systems with organic compound can be successfully used to attain (i) inhibition of soil enzyme activity in order to reduce urea decomposition and environmental pollution, and (ii) preparation of novel antibacterial agents to tackle antimicrobial resistance. The fundamental idea is that a crystal engineering approach based on the choice of intermolecular interactions between organic and organic/inorganic compounds allows to obtain materials with collective properties that are different, and often superior to those of the separate components. It is also demonstrated that the success of this strategy depends crucially on cross-disciplinary synergistic exchange with expert scientists in the areas of bioinorganics and microbiology application-oriented developments of these novel materials.

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IT6**Sequence Dependent Folding Motifs of Peptides: A
Comprehensive Picture from Condensed and Gas Phase Studies****Satish Kumar¹, Kshetrimayum Borish¹, Sanjit Dey¹, Jayashree Nagesh^{2*}, and
Aloke Das^{1*}**¹*Department of Chemistry, Indian Institute of Science Education and Research
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Hydrogen bonding interactions in the backbone as well as sequence of the amino acid residues govern the folding motifs of the secondary structures of the peptides and proteins. In general, secondary structures of the peptides and proteins are stabilized by α -helix, β -sheets and several types of turns namely C6 (δ -turn), C7 (γ -turn), C10 (β -turn), C13 (α -turn), and C15 (π -turn) hydrogen-bonded rings formed through inter-residue interactions in the backbone. Out of the 22 amino acids, glycine (Gly) and proline (Pro) are quite unique because there is no side chain in the former one while the side chain of the latter one is connected with the nitrogen atom to form a five-membered ring. Thus, the most flexible amino acid Gly and the most rigid amino acid Pro are found very often in the loop region of the β -hairpin structures of the proteins. Interestingly, it has been found that the -Pro-Gly-sequence has a higher propensity of the formation of the β -turn conformation while the -Gly-Pro-sequence prefers to form an extended polyproline II type conformation. It is also known that the β -turn conformation is the requirement of the enzymatic hydroxylation of the specific proline residue of the -Pro-Gly-segment in procollagen for formation of stable triple helical structure of collagen. In this work, we have studied several Gly-Pro containing peptides i.e. Boc-D-Pro-Gly-NHBn-OMe, Boc-Gly-D-Pro-NHBn-OMe, Boc-D-Pro-Gly-Ala-NHBn-OMe etc. using FTIR, 2D-NMR, gas phase laser spectroscopy, single crystal XRD, and quantum chemistry calculations to get a comprehensive picture of the folding motifs of these peptides in the condensed and gas phases. The results show a fine interplay of the intrinsic conformational properties, crystal packing and solvation of the peptides.

IT7**Discovering in silico the uniqueness Walking along hydrogen bonds by means of solid-state NMR****Michele R. Chierotti, Roberto Gobetto, Federica Rossi, Simone Bordignon***University of Torino Department of Chemistry and NIS Centre, V. Giuria 7 Torino Italy,
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Non-covalent interactions, in particular hydrogen bonds, play a fundamental role in determining the three-dimensional arrangement of molecules in crystalline molecular solids. In Crystal Engineering these are used in a rational way to obtain new crystal forms of certain molecules that have better properties than those of the single molecules.

However, their characterization is often complicated by the fact that diffraction techniques, which are the techniques of excellence in structural characterization, often fail to accurately locate the position of the hydrogen atoms and/or encounter difficulties with crystallization and/or crystal size.

Over the last decades, solid-state NMR (SSNMR) has developed into an indispensable and complementary tool in Crystal Engineering for investigating the structure of crystalline supramolecular adducts. In particular, its ability to locate hydrogen atoms makes it a unique technique for characterization of the weak interactions. Here we present some examples of SSNMR applications on polymorphs, co-crystals and molecular salts of pharmaceutical compounds focusing on the possibility of investigating hydrogen bonds in terms of proton transfer;¹ determining the tautomeric² or zwitterionic³ character of molecules; and probing atom-atom proximities and distances.⁴

The complementarity of the SSNMR with X-Ray diffraction and computational tools will be highlighted.

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IT8

Discovering in silico the uniqueness of hydrogen bonding

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Hydrogen bonds are omnipresent in biological and supramolecular chemistry. Nevertheless, they are still mostly represented in an oversimplified manner (positively charged hydrogen attracts close-by negatively charged heteroatom) which is easy to use but often fails to explain or even qualitatively reproduce experimental findings. In my lecture, I present a state-of-the-art physical model, based on quantitative molecular orbital theory, which enables a quantum-mechanically sound, yet intuitive approach to the interesting complexity of the hydrogen bond. The latter can be dissected into understandable contributions such as covalent bonding and Pauli repulsion between occupied orbitals. Complex and seemingly exotic phenomena are unraveled and explained in a unified manner:

- cooperativity in hydrogen bonds that stabilize quadruplex structures of DNA and linear chains of urea, deltamides and squaramides,¹⁻⁴
- variations in bond lengths and energies that are not due to differences atomic charges but due to steric repulsion,⁵⁻⁶
- the legitimacy of the secondary electrostatic interaction model^{7,8}
- and the hydrogen bond donor capability of carboxamides for organo-catalysis and supramolecular chemistry.^{9,10}

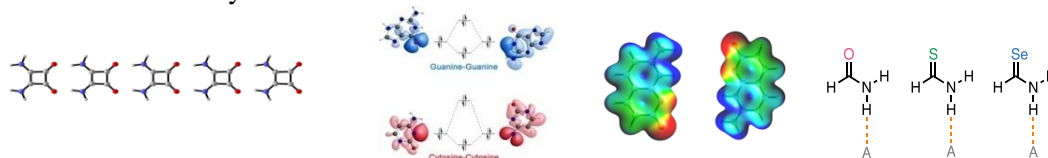


Fig. 1: Different aspects of the nature of hydrogen-bonded systems.

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IT9
Study of $\text{CH}_3\text{I}\cdots(\text{H}_2\text{O})_n$ complexes. From $\text{CH}_3\text{I}\cdots\text{H}_2\text{O}$ to CH_3I in interaction with amorphous, cubic and hexagonal water ice. Atmospheric implications and nuclear risks
Stephane Coussan¹, Christian Aupetit², Joëlle Mascetti², Sophie Sobanska²

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Gaseous iodomethane is naturally emitted in the atmosphere over oceans through the algae and phytoplankton activities. The fate of naturally emitted iodomethane is of great interest because of the oxidizing properties of iodine in the atmosphere and its impact on the catalytic destruction of the ozone layer. Additionally, iodomethane is one of the gaseous species that can be emitted in the case of severe nuclear accident. Water is one of the major species in the atmosphere which is responsible for atmospheric aerosol nucleation and thus, for cloud condensation nuclei (CCN). We have recently shown [1] that gaseous iodomethane and water will likely form aggregates of water and iodomethane polymers instead of $(\text{CH}_3\text{I})_m\text{-(H}_2\text{O)}_n$ hetero complexes. This may be explained by the low affinity of CH_3I with water. In the context of a nuclear severe accident, our work is contributing to better understanding the fate of nuclear species in the atmosphere and thus, the radionuclide dispersion. One of the aims of this work is to understand how iodomethane is dispersed in the atmospheric circulation. One of the main vectors of this dispersion is the adsorption of iodomethane on water ice, whether amorphous, cubic or hexagonal. It is therefore particularly important to understand this process and possibly its influence on the UV photochemistry of this molecule.

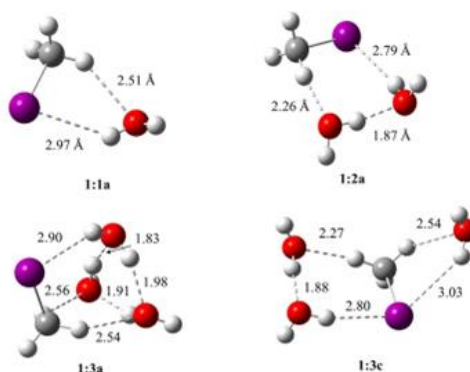


Fig. 1: The four $(\text{CH}_3\text{I})_m\text{-(H}_2\text{O)}_n$ hetero-complexes identified in cryogenic matrices

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IT10**Cyclic dipeptides as intermediates “seeds of life”?
An experimental and computational model**

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Dipeptides are the simplest peptides in nature. They are constructed out of two amino acids joined together via one (linear, l, dipeptide) or two (cyclic, c, dipeptide) peptide bonds between the carboxyl and amino groups at the opposite terminals of each amino acid. l-dipeptides represent the first step in the growing complexity of biomolecules towards proteins and enzymes made by hundreds or thousands of amino acids. c-dipeptides, despite the fact that are made only by few units, may have played a role in the evolution of life as intermediates for the survival of amino acids as well as for the formation of oligopeptides.

Based on the results of experimental and theoretical studies of the photoionization and photofragmentation of several species containing alanine and glycine (c-AlaAla [1,2], c-GlyGly and c-GlyAla [3]) we proposed that the decomposition of c-dipeptides following VUV photoionization begins with a ring opening, that can either be followed by fragmentation with the efficient release of prebiotic species, like neutral CO and HNCO [4], or stabilization of the cation into its isomeric oxazolidinone structure. Exploring the reactivity among the fragmentation products, we have theoretically predicted that two ‘reactive moieties’, the oxazolidinones and neutral aziridin molecules, can give rise to new peptide bonds, in either linear or cyclic structure.

Gas phase experiments are in excellent agreement with theoretical predictions on isolated molecules, however the experimental verification of the reactivity mechanisms requires several interacting molecules as source of reactants. To mimic the presence of an environment, we also studied the irradiation of gas phase clusters and films of selected biomolecular samples, by heavy ion beams collision, mass spectrometry and infrared spectroscopy. These new experiments will provide information on the stability of the pristine molecules under irradiation and on the formation of new species.

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Contributed Talks

CT1**Modeling Hydrogen Bonding in Resonance Raman Spectroscopy****Sara Gómez, Tommaso Giovannini, Chiara Cappelli***Scuola Normale Superiore, Piazza dei Cavalieri, 7 I-56126 Pisa (Italy)**sara.gomezmaya@sns.it*

In this contribution, we demonstrate the critical role of hydrogen bonding in determining spectral features of small amides, dipeptides, and drugs dissolved in water. We focus on a combined electronic-vibrational spectroscopy, Resonance Raman (RR), which offers diverse advantages like enhanced detection limit, high selectivity of specific chemical groups, no interfering signal of water solvent in some fingerprint spectral regions, etc.¹⁻⁴

To study the nature of solvation and its effects on the spectroscopic behavior of these systems, we perform extensive simulations using a hierarchy of solvation approaches and compare computed results with experimental data available in the literature. Our results suggest that especially for those cases where the solute exhibits strong interactions with the solvent, excitation energies, and the selective enhancement of some signals, are the results of a subtle interplay of polarization and specific interactions, that need to be appropriately included in the computational modeling.^{5,6} Indeed, a computational protocol that combines Molecular Dynamics (MD) with the Quantum Mechanics/Fluctuating Charges (QM/FQ) approach,⁵ a fully polarizable embedding model that keeps an atomistic representation of the solvent, is able to account for these effects while providing accurate results and unparalleled agreement between theory and experiment.^{5,6,7}

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CT2**Competition between folded and extended conformers of gas-phase chromophore-free peptides****Vitali Zhaunerchyk***Department of Physics, University of Gothenburg, Sweden,
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Proteins play an essential role in the functioning of living organisms. The function the protein performs is determined by its three-dimensional structure assumed upon folding. Hydrogen bonding is a key interaction in stabilizing protein structures. For example, secondary structures are stabilized by intra-molecular hydrogen bonds formed between peptide links.

Gas-phase IR spectroscopy provides a bottom-up approach to studying the structures of proteins and molecular interactions at the atomic level. In this approach, amino acids and peptides (miniature proteins) are investigated with the aim to extrapolate the obtained results to proteins. The gas phase enables the isolation of molecules from ambient species thus studying intrinsic properties. Furthermore, the obtained results from gas-phase IR spectroscopy can directly be combined with quantum chemical calculations.

A well-established way to perform IR spectroscopy for neutral gas-phase molecules is UV-IR ion-dip spectroscopy. However, it can only be implemented for molecules containing UV chromophores. As only 3 proteinogenic amino acids contain chromophores (Phe, Tyr, Trp), the applicability of this method to peptides is rather limited. To overcome this obstacle, we have developed a new approach, IRMPD-VUV spectroscopy, which can be implemented for molecules of arbitrary structure.¹

In my talk, I will present the IRMPD-VUV technique and its implementation to two dipeptides, Gly-Gly² and Ala-Ala³, and pentapeptide, Ala-Ala-Ala-Ala-Ala⁴ which aimed to investigate competition between folded and extended conformers. Our quantum chemical calculations indicate rich conformational landscapes of the studied peptides, even for Gly-Gly and Ala-Ala despite their simplicity. For the dipeptides we have experimentally observed only extended structures, while penta-Ala assumes folded conformers and we have obtained a piece of evidence for ₃₁₀-helix formation. It is interesting to note that the quantum chemical analysis predicts that the most stable Ala-Ala conformer under our experimental conditions should have a folded structure and during my presentation, I will explain this seeming contradiction to the experimental observations. I will also present the results of the hydrogen-bond analysis undertaken with the NCI method.

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CT3**Non-covalent Interactions: The Synergy of Experiment and Theory Viewed over Two Decades****Klaus Müller-Dethlefs¹ and Pavel Hobza²**¹*Photon Science Institute and Department of Chemistry, The University of Manchester Manchester, M13 9PL, UK, k.muller-dethlefs@manchester.ac.uk*²*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic Prague, Czech Republic, pavel.hobza@uochb.cas.cz*

In our *Chem. Rev.* **100**, No.1, 143-167, first issue of year 2000, **Non-covalent Interactions: A Challenge to Experiment and Theory**, Klaus Müller-Dethlefs and Pavel Hobza, a guiding focus came from the terminology "Non-covalent Interactions" and we stated: "Atoms and molecules can interact together leading to the formation of either a new molecule (reactive channel) or a molecular cluster (non-reactive channel). The former is clearly again a covalent interaction; the latter one in which a covalent bond is neither formed nor broken is termed a non-covalent or Van der Waals (vdW) interaction. This nomenclature is, however, not well defined and the term vdW interactions is sometimes used only for certain non-covalent interactions (mostly dispersion)".

In our book **Non-covalent Interactions: Theory and Experiment**, Pavel Hobza and Klaus Müller-Dethlefs, Royal Society of Chemistry, Theoretical and Computational Chemistry series, 2010, we proved that the strategy of combining theory and experiment leads to new knowledge and we also felt the need for some revision of terminology:

"we decided to use the term "*non-covalent*" to classify interactions that are *not covalent*. We are aware that this definition is again not straightforward and unambiguous since, for example, metallic interactions are also covered but we believe that the term non-covalent properly describes the origin and nature of these interactions. In the very broadest sense non-covalent interactions include *electrostatic interactions* between permanent multipoles (charge-charge, charge-dipole, charge-multipole, multipole-multipole...), *induction and/or polarization interactions* between permanent and induced multipoles, *dispersion interactions* between instantaneous and induced multipoles and also charge-transfer, ionic and metallic interactions, and interactions leading to formation of H-bonding, halogen bonding and lithium bonding."

Exploiting the synergy of theory and experiment has proven to be very powerful as demonstrated by the enormous progress in our field, *e.g.* demonstrated by the breadth of this conference. The definition of scientific terminology is also significant in order to create a clear direction and avoid confusion. A new development that could be useful comes from **Hydrogen Bonding with Hydridic Hydrogen—Experimental Low-Temperature IR and Computational Study: Is a Revised Definition of Hydrogen Bonding Appropriate?** Svatopluk Civiš*, Maximilián Lamanec, Vladimír Špirko, Jiří Kubišta, Matej Špet'ko, and Pavel Hobza*, *J. Am. Chem. Soc.* 2023, **145**, 15, 8550–8559.

This contribution will also briefly highlight some anecdotes related to the longstanding collaboration between the two authors.

CT4**The role of the hydrogen-bonded complexes in bimolecular reactions involving OH at ultra-low temperatures****A. Fernández-Ramos***Centro Singular de Investigación en Química Biolóxica e Materiales Moleculares (CIQUS) Universidade de Santiago de Compostela, Spain, qf.ramos@usc.es*

The OH radical may form strong hydrogen bonds with small molecules, leading to stable van der Waals complexes. We are focusing our attention on complexes formed before hydrogen abstraction reactions. In general, at room temperature and atmospheric pressure conditions, the pre-reactive complexes have little influence, if any, in the hydrogen transfer process. However, at ultra-low temperatures (between 10-100 K), the relative stability of the hydrogen-bond complex with respect to reactants and the pressure conditions have a decisive impact on the reaction mechanism.

Our motivation for this work is that the interpretation of the reaction mechanism at ultra-low temperatures may be of relevance in the interstellar medium. Therefore, during the past few years, we have been studying the hydrogen abstraction reactions involving the OH radical and different small neutral molecules. In this context, we present and discuss the theoretical mechanisms of the reactions of the hydroxyl radical with methanol,¹ methylamine,² and formamide, and compare our results with the available experimental data above 10 K.

For the evaluation of the thermal rate constants, we have employed the competitive canonical unified statistical (CCUS) theory¹ which considers the complex formation and the hydrogen transfer as two competitive processes. The results show that the 'surprising' increase in the thermal rate constants at ultra-low temperatures (negative temperature dependence) is due to the tunneling effect in the hydrogen abstraction step. However, tunneling is only effective after the thermal stabilization of the pre-reactive complex, a situation that is more favorable in the high-pressure regime. Therefore, the stability of the hydrogen bonded complex plays a key role in the efficiency of the OH plus neutral molecule reaction mechanism.

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CT5**Intra and intermolecular interactions in hydroxylamine derivatives**

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Nitrogen monoxide is a stable radical whose stability is attributed to the delocalization of the unpaired electron to form a two-centre three-electron π -type N-O bond and characterizes a series of compounds that, broadly speaking, can be considered as nitrogen monoxide derivatives. Among them, we cite the heterocyclic aminoxyl radical TEMPO, the di-tert-butyl nitroxide and Fremy's salt, whose stability is enhanced by both the steric shielding of the methyl groups surrounding the radical site and the absence of hydrogen atoms in the α -position to the nitrogen atom, that prevents hydrogen abstraction. Thanks to their stability they are not reactive towards closed-shell systems, while they are reactive towards free radicals. Hydroxylamines and alkoxyamines also contain the NO group, but they are not radical species. However, when the homolysis of the OH/OR bond takes place, the produced NO radical is quite stable, opening up the possibility for their use in several fields, including nitroxide-mediated radical polymerization and light and heat stabilization of plastics.

The interest in hydroxylamines and alkoxyamines revolves essentially around the peculiar properties of the N-O bond that are affected by the intra- and intermolecular interactions, which also determine the molecular geometry. With the purpose of modelling the properties of this class of compounds, we characterized three hydroxylamine derivatives (N,N-diethylhydroxylamine, its 1:1 water complex and its O-acetyl form) by combining molecular spectroscopy and quantum mechanical calculations.

CT6**Experimentally Proven but Not Yet Explained:
Examples of Obscure Mechanisms of Protonation and Proton
Transfer****Ilya G. Shenderovich***Institute of Organic Chemistry, University of Regensburg, Germany,
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For a structure of a given geometry, the length of linear hydrogen bonds can be estimated experimentally with high precision.¹ For such a structure, it is usually possible to estimate in detail the effect of conjugated hydrogen bonds on the geometry under discussion.² But if there is a bent hydrogen bond, or a reversible proton transfer, or the structure of the network of hydrogen bonds is unknown, an unambiguous interpretation of experimental data becomes difficult.

This report will consider examples of hydrogen bonds whose geometry has been experimentally proven, but the mechanisms responsible for its characteristics remain unclear. In particular, the following examples will be considered:

1. Rotation/tumbling of the [FHF]⁻ anion in [Collidine-H]⁺...[F...H-F]⁻ in solution.³
2. Protonation of 4-aminopyridines on silica surface.⁴
3. Counteranion-dependent intramolecular proton transfer in 2,2'-bipyridinium in solution⁵ and the conformation of 2,2'-bipyridinium in solids.

A closer look at these examples can help answer the all-important question: What is the maximum distance a mobile proton and a potential acceptor can see each other?

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CT7

Nuclear quantum effects: their relevance in topology of hydrogen bonded network and diffraction studies of hydrogen bonded liquids

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It is well established for molecular liquids that can form hydrogen bonds (HB, H-bond) that their structural and dynamical properties depend on nuclear quantum effects (NQE), too. Differences in terms of density, dynamic and thermodynamic properties between deuterated and hydrogenated forms of many liquids are well known, while the nature of deviations in terms of the atomic structure can be quite complex. The main goal of the present work is to shed some light on the structural aspects at least three different aspects.

1. The proper description of NQE effect on intra and intermolecular radial distribution function
2. Proper validation of isotopic substitution method in neutron diffraction.
3. NQE effect on different topological properties of Hydrogen bonded liquids. These properties can be represented by the local topological arrangements (Local structure index, tetrahedrality ...) or the cooperative behaviour of hydrogen bonded network. It would be also shown that a significantly different behaviour exists in the simulations, which are incorporated with the effect of polarizability (AIMD, AMOEBA)

Additionally based on extensive benchmark studies between our newly developed method ('Generalized Smoothed Trajectory Analysis' (GSTA)^{1,2}) GSTA filtered and PIMD simulation results, a reasonably good agreement between the two methods is presented.

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CT8**Hydrogen bond cooperativity in the pyridine \cdots (H₂O)_n (n=2-4) adducts generated in a supersonic jet: a rotational spectroscopy study****S. Blanco¹, J. C. López¹**

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We have explored both theoretically and experimentally the conformational behavior of the pyridine \cdots (H₂O)_n complexes. The hydrated complexes have been generated in a supersonic jet and probed using CP-FTMW spectroscopy in the 2-8 GHz range. Apart from the complicated spectrum previously studied for pyridine \cdots H₂O,^[1] and species related to complexes involving Ne, the spectra of pyridine \cdots (H₂O)_n (n=2-4) adducts have been observed. Additional exploration of the FTMW spectrum were done with a Balle-Flygare spectrometer with allows for higher resolution to solve the quadrupole coupling hyperfine structure and the tunnelling doublets observed only at high resolution for pyridine \cdots (H₂O)₃ complex. ¹³C and ¹⁵N monosubstituted species were observed for dihydrate, ¹⁸O isotopologues for all complexes and water-deuterated isotopologues for the di and trihydrates. These measurements allow to unambiguously determine the structures of the complexes. For the dihydrated form the water oxygen atoms lie in the pyridine plane and the water dimer is forming a cycle with pyridine through N \cdots H-O \cdots H-O \cdots H-C hydrogen bonds HBs. In pyridine \cdots (H₂O)₃ the water trimer forms a similar cycle with pyridine but the skeleton is no longer planar. Both the conformation and the internal dynamics leading to tunnelling doubles are similar to formamide \cdots (H₂O)₃ complex.^[2]The pyridine \cdots (H₂O)₄ complex takes the form of the book conformation similar to that of one of the (H₂O)₆ clusters. The structures show the effects of cooperativity that lead to pyridine \cdots (H₂O)_n clusters show structures and O \cdots O distances and angles close to those of (H₂O)_{n+2} as shown preciously for other hydrated molecules.^[2]

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CT9

Enabling Proton Conduction in Solid Acids Via Supramolecular Complex Formation: The Case of Crown Ethers and Alkali Hydrogensulfates

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Crystalline materials possessing dynamically disordered structures are receiving increased interest thanks to their unique physical and chemical properties and possible applications as solid-state electrolytes in fuel cells and batteries.¹ The ions or the molecules of dynamic crystals display a short-range disorder commonly derived from re-orientational motions around their center of mass or equilibrium positions, which maintain long range order. This behavior can be observed in the chemical species with bulky spherical, cylindrical, and disc like shapes, i.e., crown ethers. The dynamic phase(s) can be obtained via one or more solid-solid phase transitions.² For example, CsHSO₄ goes through a series of solid-solid transitions passing from ordered and with low proton conduction features to a disordered and highly symmetric one which is a superionic conductor.^{3,4} On the other hands, other alkali hydrogen sulfates do not display such a behavior and cannot be used for such applications. Crown ethers are paradigmatic in Crystal Engineering and Supramolecular Chemistry can be combined to obtain complex and exotic structures with improved features. In the present communication, I will discuss our latest results about synthesis and structural, thermal, and solid-state electrochemical characterization of supramolecular species obtained by reacting alkali-hydrogenates. Interestingly, supramolecular complex formation enables solid-solid phase transitions, which, as proved by Electrochemical Impedance Spectroscopy measurements, are indeed proton conductive, see Figure 1.

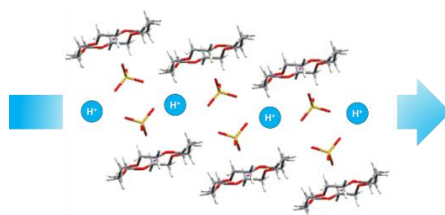


Figure 1. Proton conduction through crystal lattice is associated with phase transition promoted by temperature variations.

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CT10**Combining microwave and vibrational spectroscopy: The asymmetry parameter of the nuclear quadrupole coupling constants as a possible probe for hydrogen bond strength****Beppo Hartwig¹, Melanie Schnell^{2,3}, Martin A. Suhm¹, Daniel Obenchain¹**

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It is well established that the strength of OH hydrogen bonds can be judged by the relative downshift of OH stretching frequencies. In fact, this is one criterion of the definition of a hydrogen bond¹. The asymmetry parameter η , which can be derived from nuclear quadrupole coupling constants obtained with jet microwave spectroscopy, is sensitive towards the local electronic environment around the quadrupolar nuclei. Hence, η will also change upon the formation of a hydrogen bond towards a quadrupolar nucleus such as chlorine and bromine. By correlating the OH stretching frequencies, measured with jet-Raman spectroscopy, with η it is explored if η can be used to judge the strength of hydrogen bonds. In particular, the intramolecular hydrogen bonds formed in chloro- and bromopropanols² as well as 3-X-propane-1,2-diols (X = Cl, Br) have been investigated³. Implications for halogen bonding and OD hydrogen bonds (deuterium is quadrupolar) are also discussed.

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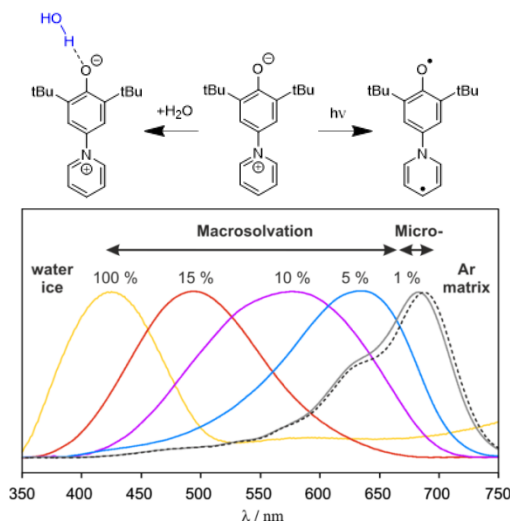
CT11

Understanding Solvent Polarity: Micro- vs Macrosolvation in Reichardt's Dyes

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Solvation is a complex phenomenon involving electrostatic and van der Waals forces as well as chemically more specific effects such as hydrogen bonding. To disentangle global solvent effects (macrosolvation) from local solvent effects (microsolvation), we studied the UV-vis and IR spectra of a solvatochromic pyridinium-N-phenolate dye (a derivative of Reichardt's dye) in rare gas matrices, in mixtures of argon and water, and in water ice at 3 K.¹ The π - π^* transition of the betaine dye in the visible region and its C–O stretching vibration in the IR region are highly sensitive to solvent effects. By annealing argon matrices of the betaine dye doped with low concentrations of water, we were able to generate 1:1 water-dye complexes. Formation of hydrogen-bonded complexes leads to small shifts of the π - π^* transition only, as long as the global polarity of the matrix environment does not change. In contrast, changes of the global polarity result in large spectral band shifts. Hydrogen-bonded complexes of the betaine dye are more sensitive to global polarity changes than the dye itself, explaining why empirical solvent polarity values ET determined with Reichardt's dyes are very different for protic and nonprotic solvents, even if the relative permittivities of these solvents are similar.



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CT12

Water in and on crystals – a database for ML and a knowledge-base for spectroscopic prediction

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Materials modelling can mean different things but typically one of the following:

- (A) **Computer simulations** that generate data about structure and phenomena based on scientific/engineering **EQUATIONS** and materials relations.
- (B) Statistical **data-driven modelling** (\approx machine-learning \approx "AI") that generates models based entirely on **DATA**.
- (C) Hybrid mixes thereof, i.e. (A) + (B)

In data-driven modelling (B), domain knowledge enters via the selection of variables (features, descriptors) and via constraints. If very many features are used, most insight is lost, but the prediction capability may be large. In this presentation we explore descriptors to **predict vibrational spectra and NMR chemical shifts for H-bonded systems, with the goal to balance predictability and insight**. We also explore differences in H-bond relations between bulk and surface OH species (Figs. 1 and 2).

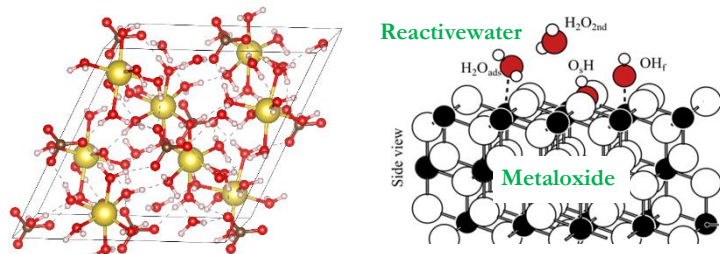
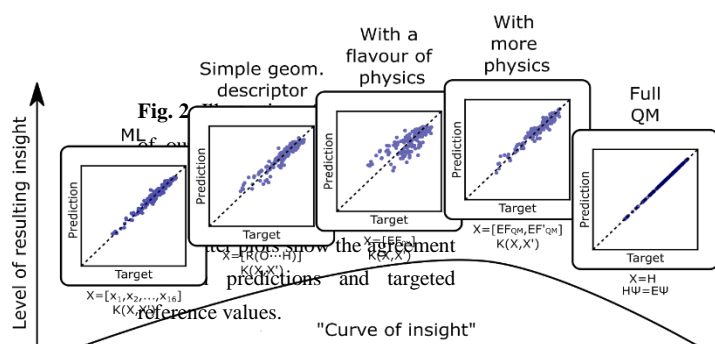


Fig. 1. We have created two databases of structures and properties of water and OH⁽ⁱ⁾ within crystalline hydrates and hydroxides [1] and (ii) on metal oxide surfaces [2]. From these we generate H-bond models/relations.

All data were generated with one and the same DFT method.



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CT13**Microwave Spectroscopic and theoretical investigations on phenylacetylene-methanol complex**Surabhi Gupta¹, Charlotte Cummins², Nicholas R Walker², Elangannan Arunan¹¹*Department of Inorganic and Physical Chemistry, Indian Institute of Science,
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Phenylacetylene (PhAc) is a multifunctional molecule and has been termed a "Hydrogen Bonding Chameleon" [1]. In 2008, Patwari and co-workers studied complexes of PhAc with various molecules, including H₂O and CH₃OH, by the IR-UV double resonance spectroscopic technique [2]. This study found that H₂O donates the H-bond to the acetylenic system, whereas CH₃OH donates the H-bond to the phenyl system. Recently, Suhm's group used FTIR spectroscopy of supersonic jet expansions to study PhAc with H₂O and CH₃OH and observed that both H₂O and CH₃OH donate H-bond to the acetylenic system [3]. The acetylenic preference in the PhAc-H₂O complex has already been confirmed by rotational spectroscopy [4]. In this work, the rotational spectrum of PhAc-CH₃OH complex has been studied. The rotational spectrum of the parent and isotopologues of PhAc-CH₃OH complex was recorded over the 2-8 GHz frequency range using the Chirped Pulse Fourier Transform Microwave (CP-FTMW) Spectrometer at Newcastle University, UK, and from 8-14 GHz using the Pulsed Nozzle Fourier Transform Microwave Spectrometer (PN-FTMW) at IISc Bangalore, India. The structure where CH₃OH donates the H-bond to the acetylenic system and CH₃OH accepts a weak H-bond through the ortho hydrogen of the PhAc was observed. The rotational transitions were split, indicating the internal motion of the CH₃ group in CH₃OH. The observed global minimum structure has been compared with several CH₃OH-containing complexes to understand the internal rotation of the CH₃ group and its effect on V₃ barrier height.

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CT14

Experimental Determination of the Strength of Non-Covalent Interactions in Dimers

Fernando Torres-Hernández, Paúl Pinillos, Ander Camiruaga, Imanol Usabiaga and José A. Fernández

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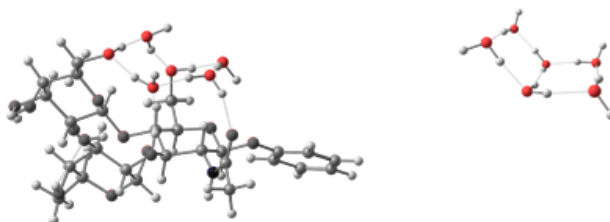
Together with structure, interaction energy value is a key parameter to understand non-covalent interactions. While important advances have been performed in structure determination, there are scarce reports on experimental binding energy values, mostly due to the complications that such experiments involve. Here we use the well-known technique of the thermodynamic cycle to estimate the binding energy values of molecules containing OH, SH and NH₂ chemical groups, which are the main responsible for formation of hydrogen bonds. Using a supersonic expansion, we form homo- and hetero-dimers, which are explored using REMPI, UV/UV hole burning and IDIR spectroscopy to determine the number of isomers and their structure. Then, the dissociation energy value of each isomer is determined by the above-mentioned method. The values obtained are compared with those predicted using several functionals and basis sets, to discuss their relative accuracy and trying to establish error bars in the values produced by each method.

CT15**When solvated molecules shape the solvent: sugar water interaction in the gas phase.****Pierre Çarçabal¹, Ander Camiruaga, GildasGoldsztein**¹*Institut des Sciences Moléculaires d’Orsay, CNRS, Université Paris Saclay, Orsay, France*

Hydrogen bonding is at the centre of the interplay between biomolecules and their environment, mostly composed of water and other biomolecules. Sugars belong to one of the most important class of biomolecules and they are key actors of a variety of biological processes, including vital molecular recognition mediated by non-covalent interactions. These especially flexible molecules encode molecular information through their chemical composition AND their conformational preferences, closely related to the direct and local environment in which they are embedded.

Using mass resolved, conformer selective double resonance vibrational spectroscopy with systematic use of isotopic substitution,¹ we can interrogate the conformational choices of isolated sugars and the effect of a controlled number of surrounding molecules. So far, in the case of sugar-water interaction studies, we have mostly focused on the effect of water on the sugar conformer.²

We will present most recent results evidencing the symbiotic structuring behaviour of solvent molecules on sugars, and in return of sugars on the solvent. This relies on the identification of hydrated clusters of sugars structures where the OHs of the sugar and water molecules create the same H bond networks than those that have been long studied for water oligomers (Figure 1). These findings echoes to the concept that sugars can be seen as “pre-organized water oligomers”³ with the ability of shaping and affecting its own environment. This unique property of sugars could be the fundamental key to understand the basis of their central role in molecular recognition.

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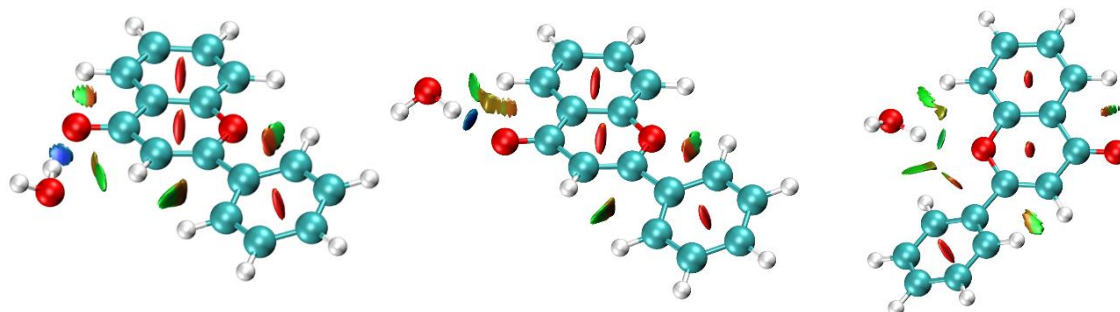
CT16**Hydrogen Bond Interaction with Water Influence Antioxidant Properties of Flavones****J. C. López¹, A. Macario,^{1,2} A. Verde,¹ S. Blanco¹**

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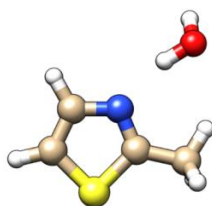
The structure and phenyl group internal rotation of the scaffold molecule flavone and its monohydrated complex have been investigated by laser ablation chirped pulse Fourier transform microwave spectroscopy on the light of DFT calculations. The observation of tunneling doublets in the rotational spectra of both species has allowed determining the periodic potential function of the phenyl torsion vibration, which SARS studies of flavones relate to their antioxidant properties. The hydrogen bond interaction with water alters substantially this potential function in an interaction site dependent way which may affect antioxidant properties. The observed data explain the flexibility and the variety of equilibrium structures of this molecule, or its derivatives observed in the condensed phases, especially when interacts with biological macromolecules.^[1-3]

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CT17**Internal Rotation and Isomerisation in Monohydrates of Heteroaromatics: Insights from Rotational Spectroscopy****Nicholas R. Walker¹**¹ Chemistry-School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom, nick.walker@newcastle.ac.uk

Broadband microwave spectra have been recorded between 2.0 and 18.5 GHz for a series of monohydrates of heteroaromatics.^{1,2} Each complex was generated by co-expansion of low concentrations of the heteroaromatic molecule and H₂O in either argon or neon buffer gas. The range of complexes studied includes monohydrates of methylimidazole (MI), methylthiazole (MT), ethylimidazole (EI), ethylthiazole (ET) and ethylfuran (EF). Multiple isomers and/or conformers of each complex have been studied. For each complex that will be discussed, the rotational spectra of five isotopologues (where the isotopic substitutions are within H₂O) have been assigned and analysed to determine rotational constants (A_0 , B_0 , C_0), centrifugal distortion constants (D_J , D_{JK}) and parameters that describe the internal rotation of the CH₃ group (where appropriate). Parameters in the (r_0) molecular geometry of complexes will be compared with r_e parameters calculated using Density Functional Theory to illustrate the trend in the molecular geometries. It will be shown that H₂O typically binds to imidazole or thiazole via a primary hydrogen bond to the pyridinic nitrogen atom of the ring, and with furan via a hydrogen bond to the oxygen atom. A secondary hydrogen bonding interaction is also possible, especially where a methyl or ethyl group is present in the 2- or 4- position of the heteroaromatic ring. It will be shown that such a secondary interaction can have a significant effect on the (V_3) barrier to internal rotation of a CH₃ group or on the conformational preferences of an ethyl group attached to the 2-position.

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CT18**Revisiting vibrational spectroscopy of the H₂O...CO complex****Jan Lundell¹, Luis Duarte², Justyna Krupa³**

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Hydrogen bonding is an important specific and directed interaction in atmospheric chemistry, catalytic reactions, surface chemistry, material science, molecular recognition and biological processes. Hydrogen bonds induce energy import and transfer channels into systems through weak chemical interactions between complex subunits like carboxylic acid dimers, water clusters or DNA acid-base pairs. High-overtone excitations on the electronic ground state may induce unimolecular chemical reactions leading to decomposition and/or isomerization. These processes open new ways to introduce novel chemistry even with the promise of controlling the outcome of light-induced chemical reactions.

It has become evident that low-temperature matrix isolation technique combined with narrow-band light sources is a powerful tool to produce and to study properties and reactivity of chemical entities.¹ Especially, formic acid has been used as a guinea pig for light-induced studies both enabling conformer interconversions² as well photo-induced formation of the hydrogen-bonded H₂O...CO complex.^{3,4}

In this study we will follow the footsteps of earlier in-situ photolysis formation of the H₂O...CO complex in low-temperature matrices, as well as an early DFT-based anharmonic vibrational calculations⁵ to elaborate our understanding of the properties of the H₂O...CO complex and its spectroscopy. Especially, we are focusing on the experimental and computational insights of the combination and overtone spectroscopy of H₂O...CO.

Acknowledgements

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CT19

Designing photosensitive hydrogen bonded polymer templates for molecular nanofabrication

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Despite the plethora of molecular switches, memories and motors developed in recent decades, fabrication of complex molecular machines comparable to living cells or silicon processors is still an elusive goal. Living nature solves this problem by encoding structural information into polymers which self-assemble in a predictable way by matching complementary sequences of hydrogen-bonded side-groups. DNA origami¹, which exploits this principle, is a rare example of scalable nano-fabrication technology. Our ambition is to computationally design photosensitive polymers which self-assemble in vacuum on the surface of ionic crystals, and can therefore be combined with photolithography, high resolution scanning probe microscopy and other tools used in surface science, molecular electronics and chip manufacturing.

In order to find molecules with the optimal structure and thermodynamic properties, we explore the configurational space of a broad variety of monomers and polymers including their interaction with different ionic substrates. The key ingredient which makes this exploration feasible is a newly developed simulation software^[2] optimized for configuration-sampling of small molecules on ionic substrate which combines GPU accelerated classical force-fields with density functional theory. This software aims to bring methodologies used in fields such as drug-design and ligand-docking into surface-science. Significant speedup is achieved by using grid-projected force-field for the description of interactions with rigid substrate and multiple replicas of the system running in parallel on a single GPU.

As hydrogen bonds are the main driving force which governs the assembling of these molecules on the surface, we also spend significant effort on developing hydrogen bonds corrections which can be efficiently implemented within this framework

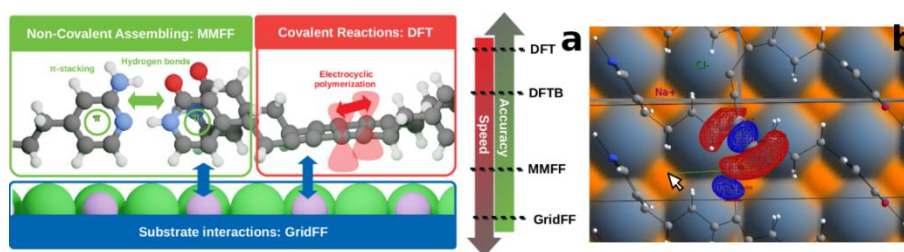


Fig. 1: (a) Schematics of the simulation framework. (b) Example of interactive QM/MM simulation of a diacetylene polymer on NaCl substrate. Molecular orbitals can be plotted in real time as the mouse pulls one of the carbon atoms.

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CT20

Influence of hydrogen bond formation on prediction of dipole moments of proteins – GruPol database approach

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Peptide bond plays a crucial role in the structure and function of biomolecules. Apart from bonding amino acid residues into peptide chains, it plays a dual role as a donor and acceptor of a hydrogen bond of N-H...O type. The geometry of the hydrogen bond is often used to distinguish between secondary structures of proteins. α -helix formation enforces a rather linear hydrogen bond formation, whereas in β -sheets the angle between acceptor and donor groups is close to 90° . Such a distinctive behavior of H-bonds results in different electrooptical response of peptides making prediction of such properties very challenging. Thus, it is of great importance to understand how the direction and geometrical parameters of the hydrogen bond influence macroscopic response of a protein.

In this work we adopt distributed atomic polarizabilities approach¹ implemented in recently introduced GruPol database.² The transferability of functional group properties, i.e. dipole moments and polarizabilities, allows for estimation of molecular dipole moment and electrostatic potential distribution in macromolecules. Recent database update³ accounts for H-bond formation involving peptide bonds and/or terminal COO^- and NH_3^+ groups, significantly increasing precision of the determination of the aforementioned electrooptic properties.

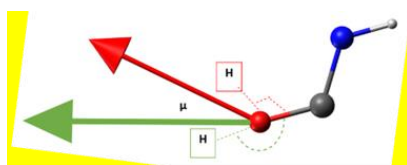


Fig. 1: Group dipole moments of the carbonyl group of the peptide bond, changing with respect to the direction of hydrogen bond formation. Dipole moment depicted in green corresponds to $\angle\text{C-O}\dots\text{H}=180^\circ$, whereas red one refers to $\angle\text{C-O}\dots\text{H}\sim 90^\circ$.

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CT21

Hydration of monosaccharide molecules

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Monosaccharides are the basic building blocks of carbohydrates, which are considered as one of the most essential biomolecules with playing principal roles in several biological processes such as molecular recognition, and structural stabilization and modification of proteins and nucleic acids that can act as cryoprotective molecules for living cells. [1]

Although monosaccharides are generally considered hydrophilic compounds, they have substantial hydrophobicity that varies with their structure. The competition of the intramolecular H-bonds with the intermolecular ones, which are formed between the monosaccharide and the water molecules, along with the hydrophobic interactions, determine the solvation shell of these molecules.

In this presentation, we consider various isomers of simple sugars (D-glucose, D-galactose, D-mannose and D-fructose) [2] whose molecular structures are very similar, yet their basic properties for example solubilities in water can be rather different. We calculated different properties that characterize the monosaccharide's molecules' hydration and reveal their differences. These include, among others the average number of acceptor and donor H-bonds, the average length of acceptor and donor H-bonds, and the properties of three and four-coordinated water molecules around carbohydrate molecules. Using classical and ab initio molecular dynamics simulations provides a very strong base for our results.

The main novelty is the quantitative characterization of the hydration shell (hydrophilic and hydrophobic) of the monosaccharides by calculating the number of water molecules below and above the plane of the studied monosaccharide molecules. The largest difference was found between the two isomers of the same monosaccharide, which is the D-glucose.

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CT22**Hydration properties of sugars revisited****Marco Paolantoni¹, Brenda Bracco², Paola Sassi³**

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Hydration properties of sugars have been subjected to a huge number of investigations due to the relevance of this class of compounds in many fields including, life and medical sciences, biology, pharmaceuticals, and food technology. Despite being a classical topic in solvation science, understanding how and to what extent sugars affect the hydrogen bonding network of water remains rather elusive, as testified by the fact that very contradictory pictures can be found in the recent literature. Often different spectroscopic approaches led to different views concerning both *H-bonding structure and dynamics* of water, such that a molecular-level understanding of the sugars' hydration features is still incomplete. In the last decade, in Perugia, the Extended frequency range Depolarized Light Scattering (EDLS) techniques has been developed to gain insights on the fast dynamics of water in aqueous solutions of different systems, including peptides, proteins and sugars.¹⁻³ EDLS has proven suitable to disentangle solute from solvent dynamics and, within the latter, hydration from bulk water contributions.¹⁻³

Here, novel structural information has been obtained on glucose and trehalose aqueous solutions by using different vibrational techniques such as Raman, Mid-IR and Near-IR spectroscopies. Other than being classical hydrophilic model systems, glucose and trehalose are also relevant in the context of biopreservation, often connected to water-mediated effects.⁴⁻⁵ Solute-correlated (SC) spectra⁶ and other analysis methods have been considered to evidence the contribution of the hydration water to the spectral profiles. We can then demonstrate that the employ of complementary approaches is mandatory to clarify some of the inconsistencies present in literature. The results of this comparative analysis will be discussed, and a coherent view will be proposed on the effect of glucose and trehalose on both *hydrogen bonding structure and dynamics* of water.

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CT23

Exploring the different *ortho/para* effects in the binding of H₂ in gas-phase complexes

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In a series of studies, we have explored the binding of molecular hydrogen to small mimics of covalent organic frameworks. Our work focuses on a series of halogenated benzaldehydes (fluoro- and chloro-), as well as a boronate ester compound meant to simulate a class of boron containing covalent organic frameworks. Several complexes between these molecules and molecular hydrogen and molecular deuterium were studied using high-resolution rotational spectroscopy. A large part of our work is dedicated to the difference in binding between the *ortho* and *para* states of molecular hydrogen when forming weakly bound complexes. The major observation is that *ortho* hydrogen seems to be more tightly bound. A range of *ab initio* and DFT calculations complements these experimentally determined structures. Further studies of the 4-fluorobenzaldehyde revealed a trimer consisting of two molecules of molecular hydrogen sandwiched on opposite sides of the aromatic 4-fluorobenzaldehyde ring. Previous high-resolutions studies of molecular hydrogen in weakly or strongly bound complexes are rare. Nevertheless, we compare the various treatments of the binding in previous IR and MW studies.

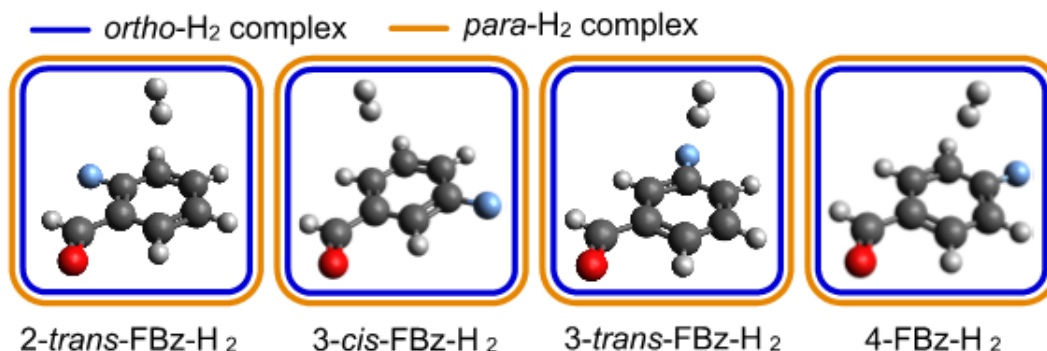


Fig. 1: Observed *ortho/para* H₂ complexes with fluorobenzaldehyde.

CT24

Investigation of interactions between water and organic molecules of atmospheric interest – Implication in aging of secondary organic aerosols

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Secondary Organic Aerosol (SOA) particles are formed in the atmosphere by gas-to-particle conversion processes involving volatile organic compounds from natural and anthropogenic origins. SOAs, which constitute 30 to 50 % of the global organic aerosol budget are recognized to affect both climate change and human health¹. To date, the formation and evolution (i.e. the atmospheric aging during air mass transport) of SOAs have been investigated by performing both field measurements and laboratory experiments, highlighting the complexity of related physico-chemical processes, due to the large diversity of their chemical makeup. Actually, interactions between atmospheric water vapor and SOAs play key roles in air quality and climate change, requiring an accurate scrutinization at the molecular scale. Indeed, a better understanding of the water – organic molecule interactions will help in predicting SOA atmospheric properties such as hygroscopicity and reactivity of SOAs.

In the presented study, molecular scale SOA-water processes were investigated using low temperature matrix isolation experiments complemented with DFT calculations. We have studied the hydration process of 3 methyl-1,2,3-butanetricarboxylic acid (MBTCA), a relevant tracer compound for monoterpene SOA formation and aging processes. This preliminary work describing the H-bond network within aggregates will help in predicting hygroscopicity, viscosity of particles and is a first step for further studying the role of H-bonds in the reactivity of water-MBTCA complexes.

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CT25
The First OH-stretching Overtone Region of Water Dimer
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Water dimer is one of the most fundamental bimolecular complexes for understanding hydrogen bonds. Its importance can hardly be overstated and water dimer has been subjected to a range of spectroscopic experiments. Due to its complex nuclear dynamics and strong coupling between high- and low-frequency vibrations, calculating an accurate rotational-vibrational spectrum of water dimer is difficult. However, with the advancements of accurate variational(-type) nuclear codes, the energy level structure in the low-energy region is today well understood. Less well understood is still the spectrum of water dimer in the OH-stretching regions.

We have calculated the spectrum of water dimer in the first OH-stretching overtone region at $T=10$ K, corresponding to the temperature in the two previously published jet-expansion experiments.^{1,2} The first OH-stretching overtone region is rich in features, due to contributions from multiple vibrational-rotational-tunneling sub-bands originating from the different OH-stretching transitions. The calculated spectrum is obtained by combining results from a full-dimensional vibrational model and a reduced-dimensional vibrational-rotational-tunneling model.^{3,4} We assign all sub-bands observed in the two jet-expansion experiments, which subsequently leads to new band origins for some of the dominant OH-stretching transitions. Our work provides a step forward in understanding the spectroscopy of water dimer, and it emphasizes the importance of theory to obtain vibrational band origins from experimental spectra.

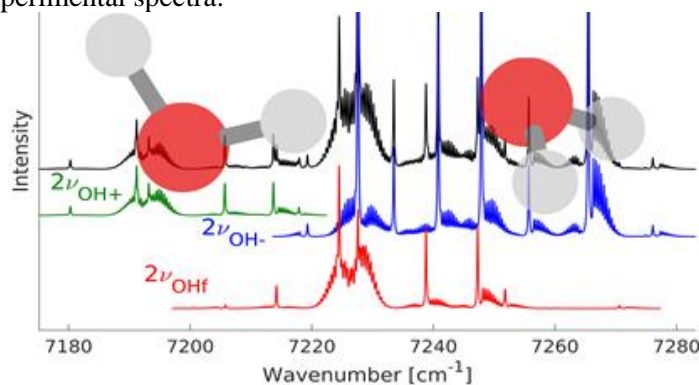


Fig. 1: Calculated spectrum (black trace) of water dimer at $T=10$ K in parts of the first OH-stretching overtone region. The colored traces show the dominant contributions.

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CT26

DFT calculations and IRMPD spectroscopy: the relevant role of H bond for structure assignment

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The Infrared multiple-photon dissociation (IRMPD) spectroscopy allows recording the “action” spectrum of mass-selected naked ions in gas phase.¹ Due to the absence of the solvent, the IRMPD spectrum is highly sensitive to hydrogen bonds which can shift the typical bands of functional groups present in the sampled ion. These bands become therefore extremely diagnostic for the structural assignment. In this scenario, density functional theory (DFT) calculations are employed to explore the potential energy surface of the putative ions and to compute the corresponding theoretical IR spectra, which are used for the detailed interpretation of the IRMPD spectrum. This approach was applied to determine geometries and anharmonic vibrational properties of low-lying isomers of deprotonated form of genistein, [geni-H]⁻, at the B3LYP/6-311+G(d,p) level of theory, suggesting that the conjugate base of genistein exists as a single isomeric form characterized by a strong intramolecular H-bond between 5-OH and the adjacent carbonyl oxygen (Fig. 1).² DFT calculations combined with IRMPD spectroscopy were also applied to study the non-covalent encounter complex formed by *cis*-[PtCl(NH₃)₂(H₂O)]⁺ and neutral cysteine, providing useful insights on the reaction mechanism of cisplatin with cysteine in solution.³

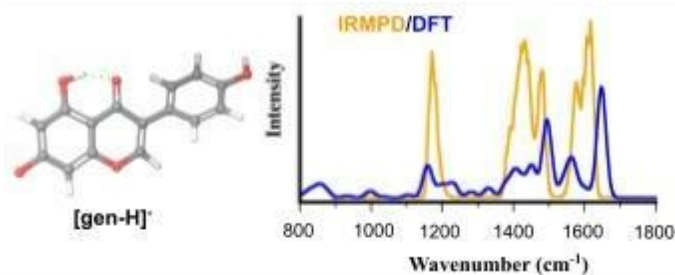


Fig. 1: the computed lowest energy structure of [geni-H]⁻ and its IRMPD/DFT spectra

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Posters

Complete poster contribution list

P1: Revealing Molecular insights Into Mixing Thermodynamics by THz Calorimetry. *Sampad Bag, Simone Pezzotti, Debasish Das Mahanta, Simon Schulke, Gerhard Schwaab, Martina Havenith*

P2: Fatty acid and alcohol base eutectic mixtures: the role of intermolecular interactions by infrared spectroscopy. *Fabio Ramondo, Giulia Adriana Bracchini, Simone Di Muzio, Oriele Palumbo, Annalisa Paolone*

P3: Highly Localized H₂O vibrational Motion as a Sensitive Far-Infrared Spectroscopic Probe for the Micro-Solvation of Thiols and Sulfides. *Dmytro Mihrin, Karen Louise Feilberg and René Wugt Larsen*

P4: Neon matrix infrared spectroscopic and ab initio investigations of methylamine-CO₂ and methylamine-CO₂-water complexes. *P. Soulard and B. Tremblay*

P5: Hydrogen bonding in deep eutectic solvents: spectroscopic and computational characterization. *Simone Di Muzio, Oriele Palumbo, Francesco Trequattrini, Annalisa Paolone*

P6: The Structural Behavior and Partial Molar Volumes of Ions in Aqueous Solution. *Marta M. Onuk, Jaroslaw Poznański*

P7: H-bond modeling in polytetrafluoroethylene on polyethylene glycol. *Ivan S. Osmushko, Vasily I. Nemtinov*

P8: First infrared spectra of the methyl carbamate-water hydrogen-bonded complexes isolated in solid neon. *B. Tremblay, P. Soulard*

P9: OH \cdots O hydrogen bond competition in the interactions between p-tyrosol and water. *J. C. López, A. Verde, A. Macario, R. Castillo, S. Blanco*

P10: Microhydrated PAHs in molecular clouds: H-bond reorientation kinetics and photoabsorption at low temperatures. *Murillo H. Queiroz, Tiago V. Alves, Roberto Rivelino*

P11: Hydrogen bonding and tunneling in H₂O···H₂S clusters. *Stefan Henkel, Philipp Meyer, Svenja Jäger, Jai Khatri, Gerhard Schwaab and Martina Havenith*

P12: Chirality and isotope effects in acid-alcohol complexes. *Sophie M. Schweer, Moritz Niessner, Arman Nejad, Martin A. Suhm*

P13: Unravelling the solvent role in the catalysis of the bio-renewable chemical, 6-*amyl- α -pyrone*, using rotational spectroscopy. *Himanshi Singh, Mariyam Fatima, M. Ali Haider, Melanie Schnell*

P14: Vibrational Spectroscopy of Hydrate Complexes for Benchmarking with Gas Recycling. *Taija L. Fischer, Margarethe Bödecker, Sophie M. Schweer, Ricardo A. Mata, Martin A. Suhm*

P15: The Duplication of the Microsolvated Complexes of *p*-Anisaldehyde. *A. Verde, J.C. López, S. Blanco*

P16: Conformational study of 2-phenylethylamine and its aggregates using laser spectroscopy in jets. *Fernando Torres Hernández, Paúl Pinillos, Ander Camiruaga, Imanol Usabiaga, José A. Fernández*

P17: Conformations of monochloropropionic acid in isolated and solution phase. *Fufei Sun, Assimo Maris, Luca Evangelisti, Wentao Song and Sonia Melandri*

P18: Halogenated alcohols microsolvating closed-shell and open-shell molecules. *Elisabeth Sennert, Martin A. Suhm*

P19: Gas-Phase Vibrational Spectroscopy of Halide – Hexafluoroisopropanol Complexes: Hydrogen Bond Strength vs. GasPhase Basicity and Anion Proton Affinity. *Milena Barp, Jiaye Jin, Florian Kreuter, Ralf Tonner-Zechl and Knut R. Asmis*

P1**Revealing Molecular insights Into Mixing Thermodynamics by
THz Calorimetry**

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We report the results of THz measurements (30-450 cm⁻¹) of aqueous acetic acid solutions over the full mixing range ($X_{AcAc}=0-1$). We recorded spectroscopic observables as a function of acetic acid concentration in the frequency range of the intermolecular stretch at 150 cm⁻¹ and of the librational modes at 350-450 cm⁻¹. This allowed us to unravel changes in hydrophobic and hydrophilic hydration motifs, respectively. By means of a novel THz-calorimetry approach, we quantitatively correlated these changes in local hydration motifs to excess mixing entropy and enthalpy. We find that ΔH_{mix} is determined by both, hydrophobic as well as hydrophilic solvation contributions. In contrast, ΔS_{mix} is governed by the hydrophobic cavity formation. Our results further suggest that acetic acid – water mixtures are systems at the edge of phase separation, due to endothermic contributions from both hydrophilic and hydrophobic solvation in a large portion of the miscibility range. Our work establishes a quantitative relationship between the balance of local hydrophobic and hydrophilic solvation motifs and the macroscopic mixing thermodynamic properties.

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P2**Fatty acid and alcohol base eutectic mixtures: the role of intermolecular interactions by infrared spectroscopy****Fabio Ramondo¹, Giulia Adriana Bracchini,¹ Simone Di Muzio^{2,3}, Oriele Palumbo³, Annalisa Paolone³**

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Fatty acid/alcohol-based hydrophobic deep eutectic solvents (DESs) were considered to be eco-friendly alternatives to replace conventional hydrophobic organic solvents (i.e., halogenated solvents) in a wide number of applications[1, 2]. Various techniques were utilized to investigate two hydrophobic mixtures, both containing tetrabutylammonium triflate (TBATFO) and octanoic acid or 1-octanol, with the aim to investigate the differences due to the different capabilities of two OH type (alcoholic or acidic) to establish hydrogen bonds with different strengths.

Since knowledge of the phase behaviour is essential for their use as solvents, the experimental SLE diagrams were measured by means of differential scanning calorimetry (DSC) and the results correlated and interpreted on basis of the microscopic arrangement of the components. The thermal stability of mixtures and components were evaluated by thermogravimetry measurements (TGA). As well known, a significant factor contributing to the differences in melting points between the mixtures and the starting materials is the formation of intermolecular contacts: the strength of secondary interactions, particularly hydrogen bonds, has a substantial role on the chemical and physical properties of these materials. The comparison between carboxylic and alcohol-based mixtures allows to modulate the strength of intermolecular interaction and investigate the role of hydrogen bonding in these mixtures. With this aim, the structure of the starting materials and mixtures were investigated by experimental infrared spectroscopy and the spectra were interpreted by appropriate models by quantum chemical (DFT). All the spectral regions revealed the presence of an intense H-bond network between the components involving the OH group of alcohol and acid which acts as donor. The role of temperature on the structure of the mixtures was further evaluated by measuring infrared spectra at different temperatures in all the spectral regions, observing the variations in intermolecular contacts and hydrogen bonding during the phase transitions.

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P3**Highly Localized H₂O Librational Motion as a Sensitive Far-Infrared Spectroscopic Probe for the Micro-Solvation of Thiols and Sulfides****Dmytro Mihrin^{1,2}, Karen Louise Feilberg² and René Wugt Larsen¹**¹*Department of Chemistry, Technical University of Denmark, 2800 Lyngby, Denmark*
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The specific far-infrared spectral signatures associated with highly localized large-amplitude out-of-plane librational motion of water molecules have recently been demonstrated to provide *direct* probes for the micro-solvation of aliphatic alcohols and ethers.^{1,2} The present work extends this far-infrared cluster spectroscopy approach for the exploration of the non-covalent forces involved in micro-solvation of thiol and sulfide analogues with systematically varied alkyl substituents. The observed out-of-plane water librational band origins for thiol and sulfide monohydrates embedded in neon matrices at 4 K provide information about the complex interplay of non-directional, long-range London dispersion forces and short, more localized hydrogen bond contacts.

The accurate interaction energies for the series of thiol and sulfide monohydrates have been predicted by the DLPNO-CCSD(T) approach followed by a local energy decomposition analysis of the total energy components. While the observed mid-infrared intramolecular donor OH-stretching spectral red-shifts significantly exceed the expectations from the conventional Badger-Bauer relationship with the total interaction energies, the corresponding absolute band origins associated with intermolecular out-of-plane water librational motion are shown to correlate strongly with the non-dispersive components of these interaction energies. In general, these far-infrared observables are demonstrated to be excellent spectroscopic probes of the local non-dispersive components of monohydrate interaction energies for a wide range of hydrogen bond acceptors among both alcohols, ethers, thiols and sulfides.

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P4**Neon matrix infrared spectroscopic and ab initio investigations of methylamine-CO₂ and methylamine-CO₂-water complexes****P. Soulard and B. Tremblay**

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The chemistry of the interstellar medium implies a large amount of molecules from the diatomic ones to the polyatomic molecules and with different spectroscopic techniques more than 250 molecules have been detected [1-3]. Three of them, methylamine (MA), CO₂ and H₂O coexist and are abundant especially in the icy grains [2-4]. For the first time the investigation of MA-CO₂ and MA-CO₂-H₂O complexes in solid neon was performed in the mid and far infrared range spectroscopy. From concentration effects and with the help of theoretical harmonic calculations performed at the MP2/aug-cc-pVTZ level, we have identified several vibrational transitions for MA-CO₂ and MA-CO₂-H₂O complexes. For the last one, MA and water molecules interact through hydrogen bonding where the water plays the role of the proton donor. Comparison between experimental and theoretical data allows us to deduce structures of observed complexes in solid neon. All the calculated vibrational data agree very well with the observations and we show once again [5,6] that the complementarity between calculations and experience is essential to carry out a vibrational study of hydrated complexes. Finally, to our best knowledge, this is the first vibrational study of complexation between three molecules in neon matrix.

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P5**Hydrogen bonding in deep eutectic solvents: spectroscopic and computational characterization****Simone Di Muzio^{1,2}, Oriele Palumbo², Francesco Trequattrini^{2,3}, Annalisa Paolone²**

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The search for new greener and eco-friendly solvents sparked growing interest in last years. Deep eutectic solvents (DESs) are one of the most promising class of studied materials¹. The main concept behind these systems is to achieve a stable liquid phase by combining two or more compounds². The significant factor contributing to the differences in melting points between the mixtures and the starting materials is the formation of intermolecular contacts. The microscopic arrangement of the components and the strength of secondary interactions, particularly hydrogen bonds, have a substantial role on the chemical and physical properties of these materials³. We aimed to investigate intermolecular contacts by preparing several binary mixtures composed by Choline Acetate (ChAc) and Tetrabutylammonium Acetate (TBAAC) with three different natural organic acids, namely Maleic (MA), Citric (CA) and Ascorbic (AA). The studied acids exhibit variations in the number and type of OH groups, which are expected to impact their capacity to donate hydrogen bonds. The structure of the starting materials and mixtures were investigated by experimental infrared spectroscopy at the AILES beamline of SOLEIL Synchrotron in Paris, conducting the measurements both in the far- and mid-infrared range (FIR and MIR). The obtained results were interpreted performing quantum chemical calculations (DFT) and classical molecular dynamics simulations.

All techniques show the presence of an intense H-bond network between the components of the studied mixtures. In the FIR spectra (30-600 cm⁻¹) we observed the bands of H-bonds (stretching and bending), especially at low temperatures. In the MIR measurements we observed the effect of the coordination: the bands of $\nu_{C=O}$ and ν_{OH} result progressively shifted when the ratio of acids changes, sign that the interactions occur between OH and C=O groups. The coordination between ChAc or TBAAC takes place by the donation of the H-bond by the acids to the oxygens of the acetate anions, which acts as an acceptor (HBA).

As expected the acids predominantly exploit their more acidic hydrogens: these results were confirmed by the analysis of MD trajectories. The structural differences between the two studied cations influence the spatial distribution of the components in the mixture bulk phases, as observable by the theoretical structure function $I(q)$: TBAAC-based systems show the presence of important pre-peaks at low q , sign of the formation of apolar domain, due to the nano-segregation of the alkyl chains.

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P6**The Structural Behavior and Partial Molar Volumes of Ions in Aqueous Solution****Marta M. Onuk^{1,2}, Jaroslaw Poznański²**¹Taras Shevchenko National University of Kyiv, Ukraine, MartaOn379@gmail.com;²Institute of Biochemistry and Biophysics PAS, Poland, jarek@ibb.waw.pl

Ion–water interactions are crucial throughout biophysics, biochemistry, and pharmaceutical industries.¹ We have studied the structural behavior and volumetric properties of some salts in water at 20–40°C and low concentrations.

The partial molar volume could be a measure of the interaction of the dissolved molecule with the solvent. The more significant the difference between molecular volume V_{mol} (calculated *in silico* from the structure) and V_2^0 (the experimental partial molar volume), the greater the hydrophobic effect.² The partial molar volume, V_2^0 , was estimated directly from the density data:

$$V_2^0 = \frac{M}{\rho_0} - \frac{10^3}{\rho_0^2} \left. \frac{\partial \rho}{\partial m} \right|_{m=0}$$

where m is the molar concentration of the solute (mol/kg), M is the molar mass, ρ_0 , and $\partial\rho/\partial m$ are the intercept and slope in the linear approximation of $\rho(m)$.²

The partial molar volumes of KCl, MgCl₂, NaCl, KBr, NaBr, MgBr₂, K₂SO₄, MgSO₄, and Na₂SO₄ solutions in water were estimated based on linear interpolation of the density–molarity relation at molar concentrations of the components from 1 to 10 mM kg⁻¹ and determined at solution temperature 25°C.

Most V_2^0 values are positive. These positive values indicate the dominance of solute–solvent interactions in solution, consistent with the literature³. The observed order of V_2^0 values in salts aqueous solutions with common cation is NaBr > NaCl > Na₂SO₄, KBr > K₂SO₄ > KCl, MgBr₂ > MgCl₂ > MgSO₄. This trend showed that intermolecular interactions in aqueous Na₂SO₄ and MgSO₄ solutions are the most significant and minor in aqueous NaBr, KBr, and MgBr₂ solutions. SO₄²⁻ shows the most potent interactions with surrounding water molecules, which a charge on oxygen can justify, and SO₄²⁻ bears a double negative charge.¹ Cl⁻ exhibits a lower affinity for water owing to its small charge-to-size ratio, but this attraction is far better than Br⁻. Bromine is less electronegative as compared to chlorine and thus forms weaker bonds. Due to stronger interactions of SO₄²⁻ anions with water molecules, they are termed structure maker ions¹ as they strengthen the H-bonds with surrounding water molecules. While Cl⁻ and Br⁻ are structure breaker ions¹ as they destroy a structural arrangement of proximal water molecules.

We observe that in the case of MgSO₄, the apparent partial molar volume is negative. An example of this appears in the dissolution of a strong electrolyte in water. Because the water molecules in the solvation sphere of the ions are physically closer together than they are in pure bulk water, there is a volume decrease when the electrolyte dissolves.⁴

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P7**H-bond modeling in polytetrafluoroethylene on polyethylene glycol****Ivan S. Osmushko^{1,2}, Vasiliy I. Nemtinov²**

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Hydrogen bonding plays a significant role in physicochemical processes. Theoretical works on the study of hydrogen bonding using the DFT method are presented quite widely. Also, the influence of hydrogen bonding on the electronic structure is appeared in the XPS spectra of the core levels.

In order to better understand the structure of polytetrafluoroethylene on polyethylene glycol, the XPS spectra of the polymers system surface were analyzed in our work, as well as the modeling of hydrogen bonding was carried out by the DFT method.

The spectra were obtained at the Institute of Chemistry of the Far Eastern Branch of the Russian Academy of Sciences using an X-ray photoelectron spectrometer Specs (Germany) with a Phoibos-150 analyzer (radius 150 mm). The results on the composition and chemical states of atoms correspond to the structure of polymers. Detailed analysis of the F1s line indicates the presence of two close fluorine states with energy splitting about 1 eV. We attributed this result to the influence of H-bond on the electronic structure of fluorine atoms oriented to the hydrogen atoms of polyethylene glycol.

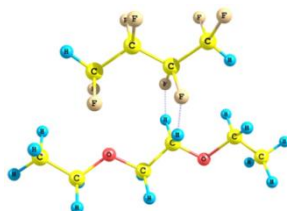


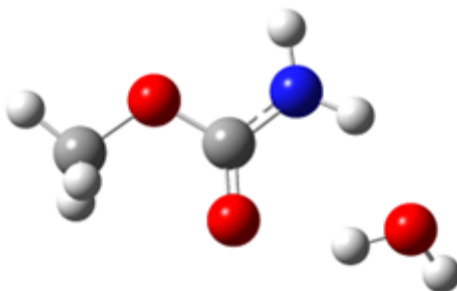
Fig. 1: Model of hydrogen bonding of a polymer system.

To clarify the effect of the H-bond on the chemical shift of the F1s line, we simulated of the electronic structure of the polymer system. Calculations were carried out by the DFT method. Model compounds (Fig. 1) are represented by limited chains. The analysis was carried out for the central fragments' atoms. Geometry optimization was carried out for each polymer. For the total polymer system, the distances of hydrogen bonds -F...H- varied.

The correspondence between the experimental data of the XPS and the results of calculations of the electronic structure of the model complexes has been established. With a high degree of confidence, we can talk about the noticeable effect of the hydrogen bond on the structure of the polymer system.

P8**First infrared spectra of the methyl carbamate-water hydrogen-bonded complexes isolated in solid neon****B.Tremblay, P.Soulard***benoit.tremblay@sorbonne-universite.fr, Sorbonne Université, CNRS, MONARIS, Case courrier 49, 4 place Jussieu, F-75005, Paris, France*

The methyl carbamate molecule is a structural isomer of the simplest amino acid, glycine, and can interact with other molecules by hydrogen bonds. The experimental study of the complexation of methyl carbamate molecule (MC) with water has been undertaken from a vibrational point of view in solid neon at 3 K from 80 to 6000 cm^{-1} using Fourier transform infrared spectroscopy. Theoretical calculations at the MP2/AVTZ level have been performed to obtain their equilibrium geometries and vibrational spectra at the harmonic level and comparison with experimental data allows us to give structures of these complexes. From concentration effects we have identified several vibrational transitions for MC dimer and MC-H₂O complex. In the MC-H₂O complex, the water molecule interacts with the amide group closing a cycle through C=O \cdots H₂O \cdots H-N hydrogen bond network.



MP2/aug-cc-pVTZ geometry of the most stable MC-H₂O complex.

P9**OH···O hydrogen bond competition in the interactions between p-tyrosol and water****J. C. López,¹ A. Verde,¹ A. Macario,^{1,2} R. Castillo,¹ S. Blanco¹**¹*Depto. Química Física y Química Inorgánica, Facultad de Ciencias, IUCINQUIMA, Universidad de Valladolid, 47011 Valladolid, Spain, juancarlos.lopeza@uva.es, andres.verde@estudiantes.uva.es,**roger.castillo@estudiantes.uva.es, susana.blanco@uva.es.*²*Present Address Univ. Rennes, CNRS, IPR (Institut de Physique de Rennes) – UMR 6251, F-**35000 Rennes, France; alberto.macario@univ-rennes1.fr*

We have explored the conformational landscape of the tyrosine analogue, 4-hydroxy phenyl ethanol (p-tyrosol) and its hydrated complexes using CP-FTMW spectroscopy. This molecule is a natural antioxidant polyphenol present in virgin olive oil which has diverse biological and pharmacological activities. The antioxidant activity seems to be related to the presence of hydroxyl groups, conjugation and resonance effects improving the stability of the corresponding phenoxy radical, formed by the hydrogen-transfer reaction. Three conformers of the monomer have been detected, the two most abundant, previously observed by (MS-R2PI), fluorescence excitation and UV hole-burning spectroscopy,^[1] being stabilised by O-H··· π hydrogen bonds between the methanol moiety and the phenol ring. The less abundant conformer presents the typical tunnelling doublets associated to phenol. Five monohydrated species and two dihydrated species have been observed up to now. For the two most abundant monomers, its monohydrated species have been observed to occur with water linked to each one of the two hydroxyl groups. For the less abundant conformer only the complex with water linked to the phenol OH group was detected. In all cases water acts as hydrogen bond acceptor. The dihydrated complexes show to form homodromic O-H···O-H···O-H cycles with the phenol hydroxyl group. The observed behaviour shows the preference of water to interact with the phenol OH associated to the formation of phenoxy radicals by proton transfer.

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P10**Microhydrated PAHs in molecular clouds: H-bond reorientation kinetics and photoabsorption at low temperatures****Murillo H. Queiroz¹, Tiago V. Alves², Roberto Rivelino³**¹*Institute of Chemistry UFBA, Brazil, murillo.halo@ufba.br;* ²*Institute of Chemistry UFBA, Brazil, tiagova@ufba.br;* ³*Institute of Physics UFBA, Brazil, rivelino@ufba.br*

Recent discoveries of organic molecules in space conditions [1], as well as the detection of water in the interstellar medium (ISM), have motivated studies of the hydration mechanism under interstellar conditions. The underlying process of aggregation with water can be driven by H-bonding [2]. In this sense, we have theoretically [3] investigated the formation and photodissociation of water complexes involving molecules recently detected in the ISM [4], such as cyanonaphthalene [1], and the kinetics of the water trimer on acenaphthylene [5]. Here, we extend these studies to (1) benzonitrile-water (neutral and cationic) and (2) benzonitrile-ammonia (neutral and anionic). The resulting complexes work as models for investigating other molecular processes occurring in the ISM. Thus, we have carried out calculations using density functional theory (DFT) considering the meta-hybrid DFT (HMDFT) and the dispersion-corrected DFT (DFT-D) approaches to find the possible complexes. Furthermore, we employ time-dependent DFT (TDDFT) methods to probe the limit of photoionization in the presence of water/ammonia. Our results indicate that for neutral complexes, O-H \cdots π , O-H \cdots O, O-H \cdots N, N-H \cdots N, and N-H \cdots π bonds are responsible for stabilizing the species. On the other hand, O \cdots π and C-H \cdots O bonds appear to stabilize the cationic complexes, whereas the N-H \cdots π bond appears to stabilize the anionic species. Regarding the kinetics, we have proposed, for the benzonitrile-water and benzonitrile-ammonia complexes, an H-bond reorientation mechanism. Our results suggest that the process exhibits the largest barrier height for benzonitrile-ammonia complexes, larger than 2.07 kcal/mol compared to a barrier height for the benzonitrile-water complexes. The thermal rate constants values indicate that the complexes stabilized by O-H \cdots N and N-H \cdots N are more likely to be ionized. Furthermore, the molecular orbitals mixing analysis reinforces that the charge transfer excitations near the α -Ly radiation field related to the photodissociation process depend on the formed H-bond pattern in the complexes. Finally, the VUV spectra appear to be rather sensitive to photoionization, with remarkable absorption bands between 200 and 300 nm for neutral complexes, and between 200 to 450 nm for the ionized species.

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P11**Hydrogen bonding and tunneling in H₂O⋯H₂S clusters****Stefan Henkel, Philipp Meyer, Svenja Jäger, Jai Khatri, Gerhard Schwaab
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We have studied the IR spectrum of H₂S and H₂O in helium nanodroplets at 0.37 K by laser spectroscopy. We have found only one isomer (HOH⋯SH₂), for which we probe the bound and unbound OD stretching vibrations of DOD⋯SH₂, D¹⁸OD⋯SH₂ and DOD⋯SD₂. The bound OD stretching vibration is divided into four signals with one very large splitting (>30 cm⁻¹), and the signals can be assigned to vibrational rotational tunneling (VRT) transitions. Some of these bands show a rotationally resolved structure. All bands were assigned to parallel transitions (K = 0 ← 0) from the four VRT levels of A₁, B₁, B₂ and A₂ symmetry. This is in line with earlier microwave studies.¹ For the unbound OD stretch only two vibrations were observed.

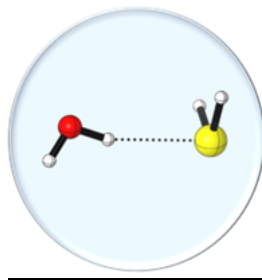


Fig. 1: Calculated HOH⋯SH₂ hydrogen bond (B3LYP-D3/6-311+G(d,p)).

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Antonio Fernández-Ramos	University of Santiago de Compostela	Spain
Helen Fielding	University College London	UK
Taija Lena Fischer	University of Göttingen	Germany
Célia Fonseca Guerra	Vrije Universiteit Amsterdam	Netherlands
Sara Gómez	Scuola Normale Superiore di Pisa	Italy
Jens-Uwe Grabow	Leibniz University Hannover	Germany
Fabrizia Grepioni	University of Bologna	Italy
Sahar Hafizi	Technical University of Denmark	Denmark
Poul Erik Hansen	Roskilde University	Denmark
Prokop Hapala	Institute of Physics of the Czech Academy of Sciences (FZU)	Czech Republic
Beppo Hartwig	University of Göttingen	Germany



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11-15 September 2023 Bologna, Italy

Stefan Henkel	Ruhr University Bochum	Germany
Kersti Hermansson	Uppsala University	Sweden
Pavel Hobza	Institute of Organic Chemistry and Biochemistry	Czech Republic
Casper Vindahl Jensen	University of Copenhagen	Denmark
Henrik Kjaergaard	University of Copenhagen	Denmark
Anna Krawczuk	University of Göttingen	Germany
Juan Carlos López	University of Valladolid	Spain
Jan Lundell	University of Jyväskylä	Finland
Andrea Maggio	University of Bologna	Italy
Assimo Maris	University of Bologna	Italy
Marta Mas-Torrent	Institute of Materials Science of Barcelona	Spain
Sonia Melandri	University of Bologna	Italy
Enrique Méndez-Vega	Ruhr University Bochum	Germany
Pierangelo Metrangolo	Politecnico di Milano	Italy
Dmytro Mihrin	Technical University of Denmark	Denmark
Klaus Müller-Dethlefs	Photon Science Institute and Department of Chemistry	UK
Daniel Obenchain	University of Göttingen	Germany
Samet Ocak	University of Bologna	Italy
Marta Onuk	Polish Academy of Sciences - Institute of Biochemistry and Biophysics	Poland
Ivan Osmushko	FEB RAS - Institute of Chemistry	Russian Federation
Roberto Paciotti	University of Chieti–Pescara	Italy
Marco Paolantoni	University of Perugia	Italy
Paúl Pinillos Pinedo	University of the Basque Country	Spain
Emanuele Pizzano	University of Bologna / BASF Italy	Italy
Szilvia Pothoczki	Wigner Research Centre for Physics	Hungary
Murillo Halo Queiroz	Federal University of Bahia	Brazil
Fabio Ramondo	University of Rome La Sapienza	Italy
Giovanna Salvitti	University of Bologna	Italy
Melanie Schnell	Deutsches Elektronen-Synchrotron (DESY)	Germany
Sophie Schweer	University of Göttingen	Germany
Elisabeth Sennert	University of Göttingen	Germany
Ilya Shenderovich	University of Regensburg	Germany
Himanshi Singh	Deutsches Elektronen-Synchrotron (DESY)	Germany
Sophie Sobanska	CNRS - Institute of Molecular Science, University of Bordeaux	France
Wentao Song	University of Bologna	Italy
Pascale Soulard	Sorbonne University / CNRS - Monaris Lab.	France



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Martin Suhm	University of Göttingen	Germany
Fufei Sun	University of Bologna	Italy
Fernando Torres Hernández	University of the Basque Country	Spain
Benoît Tremblay	Sorbonne University / Monaris Lab.	France
Piero Ugliengo	University of Torino	Italy
Andrés Verde	University of Valladolid	Spain
Emil Vogt	University of Copenhagen	Denmark
Nicholas Walker	Newcastle University	UK
Jacek Waluk	Polish Academy of Sciences - Institute of Physical Chemistry	Poland
René Wugt Larsen	Technical University of Denmark	Denmark
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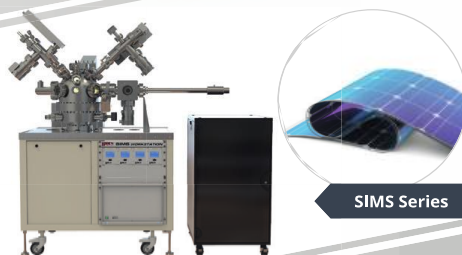
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HBOND2023						
Graduate Research Day		Tuesday 12/09/23	Wednesday 13/09/23	Thursday 14/09/23	Friday 15/09/23	
9:00	Monday 11/09/23	9:00	9:00	9:00	9:00	
	Opening GRD	Chair P. Ugliengo	Chair D. Braga	Chair K. Hermansson	Chair M. Schnell	
9:15	KTa D. Fazzi	KT1 P. Hobza	KT2 P. Metrangolo	KT4 M. Mas-Torrent	KT5 H. Kjaergaard	
10:00	ITa S. Alessandrini	IT1 F. Zerbetto	IT5 F. Grepioni	IT7 M. R. Chierotti	IT9 S. Coussan	
10:30	CTa S. Schweer	CT1 S. Gómez	CT11 E. Mendez-Vega	CT19 P. Hapala	CT24 S. Sobanska	
10:50	CTb H. Singh	CT2 V. Zhaunerchy	CT12 K. Hermansson	CT20 A. Krawczuk	CT25 E. Vogt	
11:10	Coffee break	Coffee break	Coffee break	Coffee break	Coffee break	
	Chair T. Chakraborty	Chair M. Suhm	Chair N. Walker	Chair J.A. Fernández	Chair P. E. Hansen	
11:40	CTc T. L. Fischer	IT2 G. Bistoni	KT3 H. Fielding	IT8 C. Fonseca Guerra	IT10 P. Bolognesi	
12:00	CTd A. Verde	CT3 K. Müller-Dethlefs		CT21 S. Pothoczki	CT26 R. Paciotti	
12:20	CTe F. Torres Hernández	CT4 A. Fernandez-Ramos	CT13 T. Chakraborty	CT22 M. Paolantoni	Poster prizes - HBOND2023	
12:40	CTf F. Sun	CT5 A. Maris	CT14 J. A. Fernández	CT23 D. Obenchain	Closing remarks	
13:00	Lunch	Lunch	Lunch	Lunch	Lunch	
	Chair R. Paciotti	Chair J. Lundell	Chair E. Arunan			
14:30	ITb A. Caracciolo	IT3 J. Waluk	IT6 A. Das	FREE		
15:00	CTg E. Sennert	CT6 I. Shenderovich	CT15 P. Çarçabal	or		
15:20	CTh M. Barp	CT7 I. Bakó	CT16 J. C. López			
15:40	CTi P. Pinillos Pinedo	CT8 S. Blanco	CT17 N. Walker			
16:00	Coffee break	Coffee break	CT18 J. Lundell	Guided tour to University of Bologna Historical Museums (1h)	DEPARTURE	
	Chair B. Hartwig	Chair J. Lundell	Coffee break			
16:30	ITc A. Camiruaga	IT4 C. Cappelli				
17:00	CTj C. V. Jensen	CT9 S. D'Agostino	Poster session			
17:20	CTk E. Pizzano	CT10 B. Hartwig	Meeting IAB			
				Social Dinner		