Book of Abstracts

XXIth International Conference on Horizons in Hydrogen Bond Research
“HBond2015”

13-18 September, 2015

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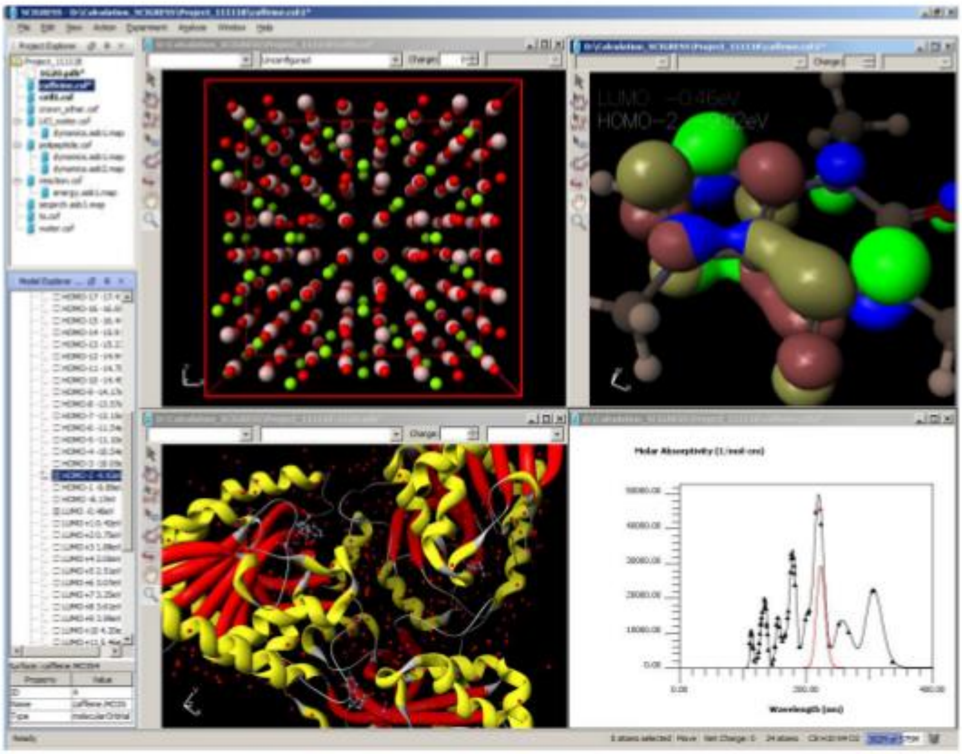

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- Polymer and functional materials
- Sol-gel process
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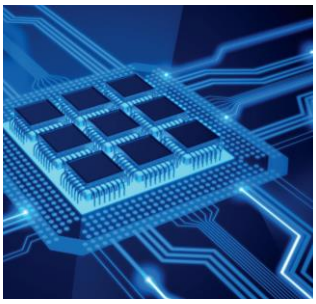
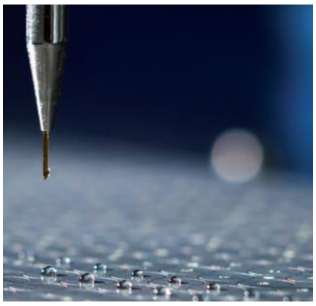
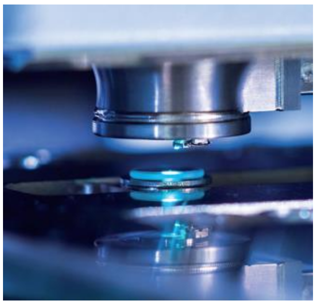
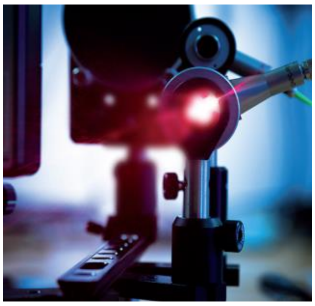
- Advanced materials characterization









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Programme

Sunday, September 13

15:00 – 21:00	**Registration – Building of the Faculty of Law, Administration and Economy (Uniwersytecka Street 7-10)**
18:30	**Get-together party**

Monday, September 14

8:00		**Registration**
8:45 – 9:00		**Opening**
Chairman:	**Henryk Ratajczak**	
9:00 – 9:50	**OL**	**Jean-Marie Lehn** (Nobel Prize in Chemistry in 1987) From supramolecular chemistry towards adaptive chemistry. Aspects of hydrogen bonding.
9:50 – 10:30	**IL-1**	**Pavel Hobza** (Prague, Czech Republic) Hydrogen and sigma-hole bonding: theoretical approach.
10:30 – 11:10	**IL-2**	**Frank Böckler** (Tübingen, Germany) Improving the applicability of halogen bonding in drug discovery.
11:10 – 11:40		**Coffee break**
11:40 – 12:20	**IL-3**	**Célia Fonseca Guerra** (Amsterdam, The Netherlands) Covalence, not Resonance-Assistance, behind cooperative hydrogen and halogen bonds.
12:20 – 13:00	**IL-4**	**Andrzej Sokalski** (Wrocław, Poland) Towards non-empirical atom-atom potentials for non-bonded interactions.
13:00 – 15:00		**Lunch**
Chairman:	**Martin Suhm**	
15:00 – 15:40	**IL-5**	**Angelos Michaelides** (London, Great Britain) Quantum nature of the hydrogen bond: Insight from ab initio path integral molecular dynamics.
15:40 – 16:00	**OC-1**	**Judy I-Chia Wu** (Houston, Texas, USA) On the nature of low barrier H-bonds in enzyme catalysis/
16:00 – 16:20	**OC-2**	**Ewa Brylska** (Wrocław, Poland) Molecular interaction of human serum albumin with meloxicam – molecular modeling studies.
Chairman:	**Austin J. Barnes**	
16:20 – 16:50		**Coffee break**
16:50 – 17:10		**FQS Poland** Presentation of research and development of new software in the field of chemistry, materials and life sciences.
17:10 – 17:30	**OC-3**	**Oleg A. Filippov** (Moscow, Russia) Role of hydrogen bonds in hydrogen transfer reaction of metal hydrides.
17:30 – 17:50	**OC-4**	**Igor E. Golub** (Moscow, Russia) A study of multifurcate dihydrogen bonded complexes with participation of boron hydrides.
17:50 – 18:10	**OC-5**	**Tomasz Masłowski** (Zielona Góra, Poland) What proton conductivity can tell us about H-bond potentials?

Tuesday, September 15

Chairman:	**Elangannan Arunan**	
9:00 – 9:40	**IL-6**	**Sammy El-Shall** (Richmond, Virginia, USA) Unconventional hydrogen bonding between organic ions and polar molecules.
9:40 – 10:20	**IL-7**	**Ibon Alkorta** (Madrid, Spain) Hydrogen bonded anion-anion aggregates.
10:20 – 11:00	**IL-8**	**Lars Pettersson** (Stockholm, Sweden) Water – a tale of two liquids.
11:00 – 11:30		**Coffee break**
Chairman:	**Poul Erik Hansen**	
11:30 – 12:10	**IL-9**	**Markus Gerhards** (Kaiserslautern, Germany) Combined IR/UV spectroscopy on hydrogen-bonded systems: from peptides to photophysical reactions.
12:10 – 12:30	**OC-25**	**Vlasta Mohaček Grošev** (Zagreb, Croatia) Evidence of polaron excitations in Raman spectra of oxalic acid dihydrate at low temperatures.
12:30 – 12:50	**OC-6**	**Barbara Golec** (Warsaw, Poland) Hydrogen bond-induced changes in photophysics and photostability of indolenaphthyridines.
12:50		**Conference photo – Leopoldian Assembly Hall, the main building of the University**
13:10 – 15:00		**Lunch**
Chairman:	**Hans-Heinrich Limbach**	
15:00 – 15:20	**OC-7**	**Erik T. J. Nibbering** (Berlin, Germany) Correlating photoacidity to hydrogen-bond structure by use of the local O-H stretching probe in hydrogen-bonded complexes of aromatic alcohols.
15:20 – 15:40	**OC-8**	**Mark Sigalov** (Negev, Israel) Structure, intermolecular and photoinduced intramolecular hydrogen bonding in 2-pyrrolylmethylidene cycloalkanones.
15:40 – 16:00	**OC-9**	**Pierre Asselin** (Paris, France) Jet-cooled high resolution infrared spectroscopy of hydrated hetero clusters.
16:00 – 16:20	**OC-10**	**Jose A. Fernandez** (Leioa, Spain) Exploring the conformational preferences of aniline aggregates in jets.
16:20 – 16:40	**OC-11**	**Michał Gil** (Warsaw, Poland) Structural distortion and fluorescence enhancement in diazatriphenylenes and their hydrogen-bonded complexes in supersonic jets.
16:40 – 17:10		**Coffee break**
17:10 – 18:40		**Poster session I (Posters: 1 – 36)**

Wednesday, September 16

Chairman:	**Wouter Herrebout**	
9:00 – 9:40	**IL-11**	**Walther Caminati** (Bologna, Italy) Tunneling dynamics, proton transfer, conformational equilibria and Ubbelohde effect in adducts of carboxylic acids.
9:40 – 10:20	**IL-12**	**Ehud Pines** (Beer-Sheva, Israel) Understanding factors affecting red-shifts for the proton stretch vibration frequency of O-H···B hydrogen bonding complexes.
10:20 – 10:40	**OC-12**	**Matthias Heger** (Göttingen, Germany) Anharmonicity and the hydrogen bond.
10:40 – 11:00	**OC-13**	**Ruslan E. Asfin** (St. Petersburg, Russia) Structure of the absorption bands of complexes in the gas phase with different hydrogen bond strengths. Fourier spectra and ab initio anharmonic calculations.
11:00 – 11:30		**Coffee break**
Chairman:	**Janez Mavri**	
11:30 – 11:50	**OC-14**	**Stéphane Coussan** (Marseille, France) From water aggregates trapped in cryogenic matrices to amorphous solid water.
11:50 – 12:10	**OC-15**	**Igor Reva** (Coimbra, Portugal) Near-infrared-induced conformational cis-trans switching in carboxylic acids isolated in cryogenic inert matrices.
12:10 – 12:30	**OC-16**	**Ragupathy Gopi** (Kalpakkam, India) Study of blue shifting hydrogen bond in fluoroform with Lewis bases (HCl, H_2O, and C_6H_6): A matrix isolation infrared and *ab initio* studies.
12:30 – 12:50	**OC-17**	**Aude Bouchet** (Berlin, Germany) Binding motifs of a microhydrated neurotransmitter: IR spectroscopy of rare gas-tagged protonated phenylethylamine and its water clusters.
12:50 – 15:00		**Lunch**
Chairman:	**Jan Lundell**	
15:00 – 15:20	**OC-18**	**Michel Mons** (Gif-sur-Yvette, France) NH – OC amide-amide H-bonds in peptides revisited in light of gas phase spectroscopy of beta-peptides.
15:20 – 15:40	**OC-19**	**Sylwia Olsztyńska-Janus** (Wrocław, Poland) Weakening of hydrogen bonds of biological structures by near infrared radiation.
15:40 – 16:00	**OC-20**	**Kasper Mackeprang** (Copenhagen, Denmark) The effect of large amplitude motions on the vibrational spectra of hydrogen bonded complexes.
16:00 – 16:30		**Coffee break**

Special session to honour prof. Lucjan Sobczyk

Chairman:	**Kazimierz Orzechowski**	
16:30 – 17:10	**IL-13**	**Aleksander Koll** (Wrocław, Poland) Polarity of hydrogen bond.
17:10 – 17:50	**IL-14**	**Hans-Heinrich Limbach** (Berlin, Germany) Acid-base hydrogen bonds in different environments: From organic solvents to enzymes.
17:50 – 18:30	**IL-15**	**Poul Erik Hansen** (Roskilde, Denmark) Isotope effects in hydrogen bond research.

Thursday, September 17

Chairman:	**Konstatin G. Tokhadze**	
9:00 – 9:40	**IL-16**	**Christoph A. Schalley** (Berlin, Germany) Multistimuli-responsive supramolecular gels.
9:40 – 10:20	**IL-17**	**Ilya Shenderovich** (Regensburg, Germany) Hydrogen bond reveals the morphology of non-crystalline solids.
10:20 – 10:40	**OC-21**	**Vytautas Balevicius** (Vilnius, Lithuania) Solid state NMR study of materials for innovative medicine: sub-nano structure and dynamics of spin clusters containing hydroxyl groups.
10:40 – 11:00	**OC-22**	**Elena Bogdan** (Nantes, France) Experimental and theoretical evidences of intramolecular OH···F hydrogen bonding in saturated acyclic fluoroalcohols.
11:00 – 11:30		**Coffee break**
Chairman:	**Zofia Mielke**	
11:30 – 12:10	**IL-18**	**Sanjay Wategaonkar** (Mumbai, India) NH···S interaction perspective.
12:10 – 12:30	**OC-23**	**Anne Schou Hansen** (Copenhagen, Denmark) Comparing second and third row elements, N, O, P and S, as hydrogen bond acceptor atoms.
12:30 – 12:50		**Patrycja Radek** (Wrocław, Poland) Wrocław Research Centre EIT+
12:50 – 14:30		**Lunch**
14:30 – 16:00		**Poster session II (Posters: 37 – 76)**
16:00 – 18:00		**Excursion**
19:30 – 23:00		**Conference dinner – HP Park Plaza Hotel restaurant** **(11-13 Bolesław Drobner street, Wrocław)**

Friday, September 18

Chairman:	**Jacek Waluk**	
9:00 – 9:40	**IL-19**	**Andrzej Katrusiak** (Poznań, Poland) Pressure-induced anomalous transformations of hydrogen-bonds and their consequences for material sciences.
9:40 – 10:20	**IL-20**	**Barbara Wyslouzil** (Columbus, Ohio, USA) The role of hydrogen bonding in phase transition.
10:20 – 10:50	**IL-21**	**Grażyna Bator** (Wrocław, Poland) The unconventional C-H···X hydrogen bonds. An application of the neutron scattering.
11:00 – 11:30		**Coffee break**
11:30 – 12:10	**IL-22**	**Jože Grdadolnik** (Ljubljana, Slovenia) Hydrogen bonding in, and structure of blocked dipeptides.
12:10 – 12:30	**OC-24**	**Agnieszka Rybarczyk-Pirek** (Łódź, Poland) N-oxide group as a proton acceptor in p-nitropyridine-N-oxide cocrystals.
12:30 – 12:50		**Closing the HBond2015** **Invitation to HBond2017**
12:50 – 14:30		**Lunch**

Opening Lecture

From Supramolecular Chemistry towards Adaptive Chemistry

ASPECTS of HYDROGEN BONDING

Jean-Marie LEHN

ISIS, Université de Strasbourg

Supramolecular chemistry aims at constructing and implementing highly complex chemical systems from molecular components held together by non-covalent intermolecular forces, in particular of hydrogen bonding type. It has relied on the development of preorganized molecular receptors for effecting molecular recognition, catalysis and transport processes, on the basis of the *molecular information* stored in the covalent framework of the components.

A step beyond consists in the design of systems undergoing *self-organization*, i.e. systems capable of spontaneously generating well-defined functional supramolecular architectures by self-assembly from their components.

Supramolecular materials, in particular *supramolecular polymers* may be generated by the polyassociation of components/monomers interconnected through complementary recognition groups.

Supramolecular chemistry is intrinsically a *dynamic chemistry* in view of the lability of the interactions connecting the molecular components of a supramolecular entity and the resulting ability of supramolecular species to exchange their constituents. The same holds for molecular chemistry when the molecular entity contains covalent bonds that may form and break reversibility. These features define a *Constitutional Dynamic Chemistry* (CDC) on both the molecular and supramolecular levels.

CDC allows for constitutional variation by reorganization and exchange of building blocks in response to either internal or external factors so as to achieve *adaptation*, thus opening perspectives towards an *adaptive chemistry*.

Hydrogen bonding plays a very important role in molecular recognition and programming, in self-organization as well as in constitutional dynamic processes. Selected examples of hydrogen bonding based discrete supramolecular entities and of supramolecular materials will be discussed.

REFERENCES

1.Lehn, J.-M., *Supramolecular Chemistry: Concepts and Perspectives*, VCH Weinheim, **1995**.

2.Lehn, J.-M., *Programmed chemical systems : Multiple subprograms and multiple processing/expression of molecular information*, Chem. Eur. J., **2000**, 6, 2097.

3.Lehn, J.-M., *Dynamers : Dynamic molecular and supramolecular polymers*, Prog. Polym. Sci., **2005**, 30, 814.

4.Lehn, J.-M., *From supramolecular chemistry towards constitutional dynamic chemistry and adaptive chemistry*, Chem. Soc. Rev., **2007**, 36, 151.

5.Lehn, J.-M., Chapter 1, in *Constitutional Dynamic Chemistry*, ed. M. Barboiu *Topics Curr. Chem*, **2012**, *322*, 1-32

Invited Lectures

IL-1

Hydrogen- and σ-hole bonding: theoretical approach

Pavel Hobza

Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Prague 6, Czech Republic

Hydrogen- and σ-hole bonding is investigated using advanced QM calculations. First, stability of hydrogen-, halogen-, chalcogen- and pnicogen bonded complexes is determined with CCSD(T)/complete basis set method. It is shown that that σ-hole bonding is comparably strong as H-bonding and when heavier elements take place the σ-hole bonded complexes can be significantly stronger. Further, the nature of bonding in these complexes is studied using the DFT-SAPT technique. While for H-bonded complexes the polarization/electrostatic term is clearly dominant, the characteristic features of σ-hole bonded complexes is due to a concert action of dispersion, polarization/electrostatic and induction/charge-transfer terms. Finally, different directionality of hydrogen- and σ-hole-bonded complexes is discussed in terms of positive electrostatic potential around proton in the former complexes and size and magnitude of the respective σ-holes in the latter ones.

IL-2

Improving the applicability of halogen bonding in drug discovery

Frank M. Boeckler, Markus O. Zimmermann, Andreas Lange, Johannes Heidrich, Manuel Ruff, Ionut Onila, Thomas E. Exner

Institute of Pharmaceutical Sciences, Department of Pharmacy & Biochemistry, Eberhard Karls Universität Tübingen, frank.boeckler@uni-tuebingen.de

With the popularity of halogen bonding[1] on the rise, particularly in life sciences and drug discovery,[2,3] there is an increasing demand for computational tools recognizing and evaluating this interaction. Several MM parameterizations and QM/MM methods[4,5] have been recently developed to facilitate the study of these interactions. In addition to these efforts, creation of a scoring function will enable the rapid assessment of halogen bond geometries and help to derive their interaction qualities.

Recently, we have used extensive QM model calculations to systematically map the relationship between strength and geometry of halogen bonds to different interaction partners (carbonyl backbone, sulfur contacts, nitrogen contacts, carboxylates, π-systems, …).[6-9] Based on a QM-derived scoring function for backbone carbonyl, we have evaluated the potential for the molecular design of halogen bonds using existing protein-ligand complexes in the PDB.[10] Based on machine learning, we have created a scoring function for methionine, which takes into account the much more complicated dependence of σ-hole deviation and spherical orientation toward the sulfur atom. We implemented all such terms into the wide used scoring function ChemPLP, which can be used in PLANTS or GOLD.

Based on the (hetero)aryl scaffold and its substituents, the σ-hole can be significantly tuned, altering interaction strength and sometimes geometry. We studied such tuning behavior extensively and created from more than 20000 diversely tuned scaffolds a model using support vector regression. Based on this model, it will be possible to account for the tuning factor with good precision, even when huge numbers of ligands are used in a virtual screening campaign. Based on a galaxy server available at www.halogenbonding.com, our tools are made freely accessible to the academic community.

REFERENCES

1. G. R. Desiraju, P. S. Ho, L. Kloo*, et al.*, *Pure Appl. Chem.* **2013**, *85*, 1711.
2. R. Wilcken, M. O. Zimmermann, A. Lange*, et al.*, *J. Med. Chem.* **2013**, *56*, 1363.
3. M. O. Zimmermann, A. Lange, R. Wilcken*, et al.*, *Future Med. Chem.* **2014**, *6*, 617
4. P. S. Brahmkshatriya, P. Dobes, J. Fanfrlik*, et al.*, *Curr. Comput.-Aided Drug Des.* **2013**, *9*, 118.
5. P. Dobeš, J. Řezáč, J. Fanfrlík*, et al.*, *J. Phys. Chem. B* **2011**, *115*, 8581.
6. A. Lange, M. O. Zimmermann, R. Wilcken*, et al.*, *J. Chem. Inf. Model.* **2013**, *53*, 3178.
7. E. Veyisoglu, M. O. Zimmermann, J. Heidrich*, et al.*, *unpublished results*.
8. R. Wilcken, M. Zimmermann, A. Lange*, et al.*, *J. Comput-Aided. Mol. Des.* **2012**, *26*, 935.
9. R. Wilcken, M. O. Zimmermann, A. Lange*, et al.*, *J. Chem. Theory Comput.* **2011**, *7*, 2307.
10. M. O. Zimmermann, A. Lange, F. M. Boeckler, *J. Chem. Inf. Model.* **2015**, *55*, 687.

IL-3

Covalence, not resonance-assistance, behind cooperative hydrogen and halogen bonds.

Célia Fonseca Guerra,[a]

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Halogen bonds are shown to possess the same characteristics as hydrogen bonds: charge transfer, resonance assistance and cooperativity. This follows from computational analyses of the structure and bonding in *N*-halo-base pairs and quartets (see Figure). The objective was to achieve understanding of the nature of resonance-assisted halogen bonds (RAXB): how they resemble or differ from the better understood resonance-assisted hydrogen bonds (RAHB) in DNA.

An accurate physical model of the RAXB based on molecular orbital theory is presented, which is derived from corresponding energy decomposition analyses and study of the charge distribution. The RAXB arise from classical electrostatic interaction and also receive strengthening from donor–acceptor interactions within the σ-electron system. Similar to the RAHB, there is also a small stabilization by π-electron delocalization. This resemblance leads to prove cooperativity in *N*-halo-guanine quartets, which originates from the charge separation that goes with donor–acceptor orbial interactions in the σ-electron system.[1-3]

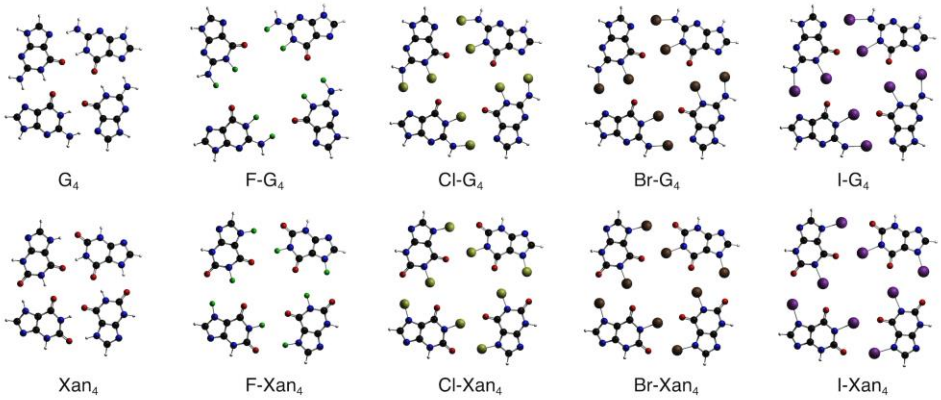

Figure 1 Hydrogen and halogen bonded quartets, X-G4 and X-Xan4 of X-G and X-Xan

REFERENCES

1. L. P. Wolters, N. W. G. Smits, C. Fonseca Guerra, *Phys. Chem. Chem. Phys.,* **2015**, *17,* 1585-1592.
2. C. Fonseca Guerra,* H. Zijlstra, G. Paragi, F. M. Bickelhaupt, *Chem. Eur. J.,* **2011**, *17,* 12612-12622.
3. L. Guillaumes, S. Simon, C. Fonseca Guerra, *ChemistryOpen* **2015**, 4, 318-327.

Towards non-empirical atom-atom potentials for non-bonded interactions

W. Andrzej Sokalski[a] , Jan K. Konieczny[a], Wiktor Beker[a],Wiktoria Giedroyć-Piasecka[a]

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The repulsion term in conventional force fields constitutes a major source of error[1] and could lead to artefact short contacts in protein-ligand complexes[2]. As this problem could originate from a too simple analytical functional form used in conventional force fields, we analyzed various analytical functions using ab initio exchange component values as the reference and obtained $(\alpha + \beta /R)\exp(-\gamma R)$ as the optimal form to represent the repulsion term over wide range of distances. Exchange, delocalization, and electrostatic penetration potentials[3] approximating the corresponding interaction energy components obtained within hybrid variation-perturbation theory (HVPT)[4] were derived using as a reference a training set of 660 bio-molecular complexes, including 230 hydrogen bond dimers[5]. The long range electrostatic multipole term was calculated using cumulative atomic multipole moments[6], whereas correlation contribution including dispersion term and first-order correlation correction was estimated from non-empirical D_{as} functions[7]. The resulting non-empirical atom–atom potentials representing electrostatic multipole and penetration, exchange, delocalization and correlation terms scaling as $O(A^2)$ were tested for several urokinase–inhibitor complexes[2] yielding improved docking results. Sum of multipole electrostatic and correlation terms yielded reasonable non-empirical scoring either for hydrophobic inhibitors of fatty acid amide hydrolase as well as for other hydrophilic systems[8]. In the case of hydrogen bonded systems electrostatic multipole term alone yields better relative stability predictions at shortened distances than MP2 and CCSD(T)[9].

Acknowledgements

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REFERENCES

1. M. Zgarbová, M. Otyepka, J. Šponer, P.Hobza, P. Jurečka, *Phys. Chem. Chem. Phys.* **2010,**12,10476.
2. R. Grzywa, E.Dyguda-Kazimierowicz , M. Sieńczyk, M.Feliks, W.A.Sokalski, J.Oleksyszyn, *J. Mol. Model.* **2007,** 13, 677.
3. J. Konieczny, W.A. Sokalski, *J.Mol.Model.* **2015**, 21:xxx DOI: 10.1007/s00894-015-2729-7
4. W. A. Sokalski, S. Roszak, M. Pecul, *Chem. Phys. Lett.*,**1988,** 153, 153.
5. J. Řezáč, K.E. Riley, P. Hobza, *J. Chem. Theor. Comput 2011,*7, 2427.
6. W.A. Sokalski, R.A. Poirier, *Chem. Phys. Lett*. **1983**, 98:86.
7. R. Podeszwa, K. Pernal, K. Patkowski, K. Szalewicz, *J.Phys. Chem.Lett*. **2010,** 1, 550.
8. W. Giedroyć-Piasecka, E. Dyguda-Kazimierowicz, W. Beker, M. Mor, A. Lodola, W.A. Sokalski, *J.Phys.Chem.B* **2014**, 118, 14727.
9. W. Beker, K.M. Langner, E. Dyguda-Kazimierowicz, M. Feliks, W.A. Sokalski, *J.Comp.Chem.* **2013**, 34, 1797.

IL-5

The quantum nature of the hydrogen bond: Insight from ab initio path integral molecular dynamics

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Hydrogen bonds are weak, generally intermolecular bonds, which hold much of soft matter together as well as the condensed phases of water, network liquids, and many ferroelectric crystals. The small mass of hydrogen means that they are inherently quantum mechanical in nature, and effects such as zero-point motion and tunneling must be considered, though all too often these effects are not considered. As a prominent example, a clear picture for the impact of quantum nuclear effects on the strength of hydrogen bonds and consequently the structure of hydrogen bonded systems is still absent. In this talk I will discuss various ab initio path integral molecular dynamics studies on the quantum nature of the hydrogen bond. Through a systematic examination of a wide range of hydrogen bonded systems we show that quantum nuclear effects weaken weak hydrogen bonds but strengthen relatively strong ones. This simple correlation arises from a competition between anharmonic intermolecular bond bending and intramolecular bond stretching. A simple rule of thumb is provided that enables predictions to be made for hydrogen bonded materials in general with merely classical knowledge (such as hydrogen bond strength or hydrogen bond length). Our work rationalizes the influence of quantum nu- clear effects, which can result in either weakening or strengthening of the hydrogen bonds, and the corresponding structures, across a broad range of hydrogen bonded materials. Furthermore, it highlights the need to allow flexible molecules when anharmonic potentials are used in force field-based studies of quantum nuclear effects.

REFERENCES

1. X.-Z. Li, B. Walker, A. Michaelides, *Proc. Nat. Acad. Sci*. **2011**, 108, 6369
2. B. Walker, A. Michaelides, *J. Chem. Phys.* 133, **2010,** 174306

IL-6

Unconventional hydrogen bonding between organic ions and polar molecules

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A special class of hydrogen bonding interactions, usually referred to as ionic hydrogen bonds (IHBs), involves hydrogen bonding between radical cations or protonated molecules and neutral polar molecules such as water, methanol, ammonia, and hydrogen cyanide. IHBs are critical in many fields such as ion induced nucleation, ion solvation, radiation chemistry, electrochemistry, and biological systems including protein folding, proton transport, self-assembly, and molecular recognition.[1] Unconventional carbon-based IHBs are formed when the hydrogen donors are ionized hydrocarbons containing CH groups and the hydrogen acceptors are electron lone pairs on hetero atoms such as O or N, olefin double bonds, or aromatic π systems.

This talk will focus on the interactions of several organic ions such as benzene, pyridine, pyrimidine, benzonitrile and naphthalene radical cations with three solvent molecules: water, hydrogen cyanide and acetonitrile. The sequential binding energies of the solvent molecules to the organic ions are determined in the gas phase using the mass-selected ion mobility method which allows measurements of thermochemical equilibria between a mass-selected ion and several solvent molecules (typically 1-6).[2-5] The results will be discussed in order to understand (1) the variation of binding energies with the structures and properties of the solvent molecules, (2) the onset of ion solvation involving a small number (four to six) of solvent molecules and whether internal or external solvation is preferred, and (3) the degree of intracluster proton transfer within the solvated ions. The combination of the experimentally measured binding energies and the computationally calculated structures and energies yields detailed insights into the basic interactions responsible for ion solvation and proton transfer processes in solution.

REFERENCES

1. “Noncovalent Forces”, *Challenges and Advances in Computational Chemistry and Physics*, Vol. 19, Editor: S. Scheiner, Springer (**2015**).
2. A. M. Hamid, A. R. Soliman, M. S. El-Shall, *J. Phys. Chem. A*, **2013**, 117, 1069.
3. I. K. Attah, S. P. Platt, M. Meot-Ner, S. G. Aziz, A. O. Alyoubi, M. S. El-Shall, *Chem. Phys. Letters* **2014**, 613, 45.
4. A. M. Hamid, M. S. El-Shall, R. Hilal, S. Elroby, S. G. Aziz, *J. Chem. Phys*., **2014**, 141, 054305.

IL-7

Hydrogen bonded anion-anion aggregates

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A theoretical study of anionic complexes formed by two partly deprotonated oxoacids joined by hydrogen bonds has been carried out at the MP2 computational level.[1] In spite of the ionic repulsion, local energy minima are found both in the gas phase and in aqueous solution. Electrostatic potential and electron density topologies, and the comparison with neutral complexes formed by oxoacids, reveal that the ionization has no significant effect on the properties of the hydrogen bonds. The stability of the complexes in the gas phase is explained by attractive forces localized in a volume situated in the hydrogen bond and defined as the electrostatic attraction region (EAR) and determined by the topological analyses of the electron density and the electrostatic potential, and by the electric field lines (Fig. 1). In solution, the strong anionic repulsion is mostly screened by the effect of the surrounding polar solvent, which only leads to a weak destabilizing interaction in the hydrogen bond region and finally favors the overall stability of the complexes. The anion−anion complexes have been compared with the corresponding neutral ones (as salts or protonated forms), showing that EAR remains unchanged along the series.

The results obtained in our work will be compared to those of other researchers.[2]

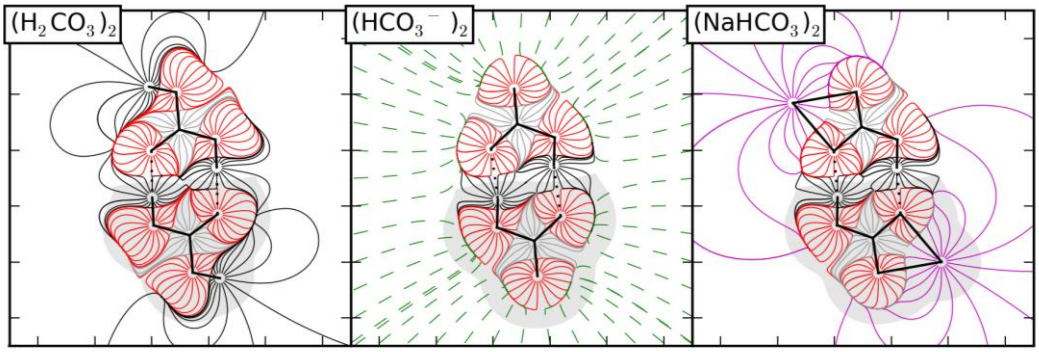

Figure 1 Electric field lines in the surroundings of neutral protic (left), anionic (center), and salt (right) complexes.

REFERENCES

1. I.Mata, I. Alkorta, E. Molins, E. Espinosa, *ChemPhysChem*, **2012**, *13*, 1421; *Chem. Phys. Lett.* **2013**, *555*, 106; *J. Phys. Chem. A*, **2015**, *119*, 183.
2. F. Weinhold, R.A. Klein, *Angew. Chem.* **2014,** *126*, 11396. G. Frenking, G.F Caramori, *Angew. Chem. Int. Ed.* **2015**, *54*, 2596.

IL-8

Water – a tale of two liquids

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I will discuss recent experimental and simulation data of liquid water and the picture of fluctuations between high-density (HDL) and low-density (LDL) liquid this has led to[1,2]. Such a two-liquid scenario would explain many anomalous properties, *e.g.*, density maximum, heat capacity and isothermal compressibility minima, but no direct connection has been found to simulations of ambient water. Here I will focus on the temperature dependence in the O-O pair-distribution function at intermediate range (< 18 Å) which has recently been measured with good statistics[3].

REFERENCES

1. Lars G.M. Pettersson and Anders Nilsson, The Structure of Water; from Ambient to Deeply Supercooled, *J. Non-Crystalline Solids* **407**, 399-417 (2015).
2. J. A. Sellberg *et al*., Ultrafast X-ray Probing of Water Structure Below the Homogeneous Ice Nucleation Temperature, *Nature* **510**, 381 (2014).
3. L. B. Skinner *et al*., The Structure of Water Around the Compressibility Minimum, *J. Chem. Phys.* **141**, 214507 (2014).

IL-9

Combined IR/UV spectroscopy on hydrogen-bonded systems: from peptides to photophysical reactions

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Peptide folding and photochemical reactions as the excited state proton transfer are of great interest due to their importance in chemical and biological processes. In several cases the reactivity and structural organization are driven by hydrogen bonds or hydrogen-bonded networks. During the last years we investigated a variety of molecular systems based on peptides, flavonols, chromones, coumarins and ethers as well as their aggregates with water or methanol (cf. e.g. [1-4]). By applying mass and isomer selective molecular beam methods on isolated species structural changes and reaction channels like proton transfers and proton wires are investigated in different electronic states of neutral and ionic species. The formation of hydrogen bonds as well as dispersion interactions are important for the observed networks within the investigated molecular aggregates. The application of double, triple and quadruple resonance combined IR/UV spectroscopic techniques in combination with (TD)-DFT calculations are very powerful tools to analyze the structures as well as reaction coordinates. Furthermore IR induced rearrangement reactions can be analyzed by a second IR excitation in combination with a resonant two (UV) photon ionization.

Acknowledgements

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REFERENCES

1. A. Stamm, K. Schwing, M. Gerhards, *J. Chem. Phys*. **2014**, *141*, 194304
2. A. Stamm, M. Weiler, A. Brächer, K. Schwing, M. Gerhards, *Phys. Chem. Chem. Phys*. **2014**, *16*, 21795.
3. M. Weiler, K. Bartl, M. Gerhards, *Journal of Chemical Physics* **2012,** *136*, 114202.
4. K. Schwing, H. Fricke, K. Bartl, J. Polkowska, T. Schrader, M. Gerhards, *ChemPhysChem* **2012**, *13*, 1576.

IL-10

Switching nucleobase fluorescence by site-selective H-bonding

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2-Aminopurine (2AP) is a fluorescent isomer of adenine with ~11 ns lifetime in room-temperature aqueous solution. It finds wide use in biochemistry as a site-specific reporter of DNA and RNA structure, base-flipping and folding; these assays assume that 2AP is intrinsically strongly fluorescent. We have shown that the lifetimes of gas-phase jet-cooled 2AP and 9-methyl-2AP (9M-2AP) are in fact short,[1,2] τ=156 ps and 210 ps, thus bare 2AP and 9M-2AP are nearly nonfluorescent. The lifetime of 2AP and 9M2AP increases dramatically by formation of H-bonds in the 2AP (and analogous 9M-2AP) microhydrate clusters $2AP{\cdot}(H_2O)_n$ and $9MAP{\cdot}(H_2O)_n$ with n=1-3. We hydrated 2AP at its sugar-edge, cis-amino or trans-amino sites, identified the cluster geometry by IR and UV/UV spectroscopy, and measured cluster-specific excited-state lifetimes. These increase by 4 times if an H_2O is attached to the sugar-edge, by 50 times if attached to the cis-amino site, and by ~100 times to ~14.5 ns if attached to the trans-amino site.[3] The 2AP lifetime exquisitely depends on the presence of H_2O molecules, the specific H-bond bond site and on the number of H_2O molecules at that site.[3] 8-vinyladenine is an adenine analogue that ist strongly fluorescent in aqueous solution,[4] and which exhibits similar behavior upon microhydration.

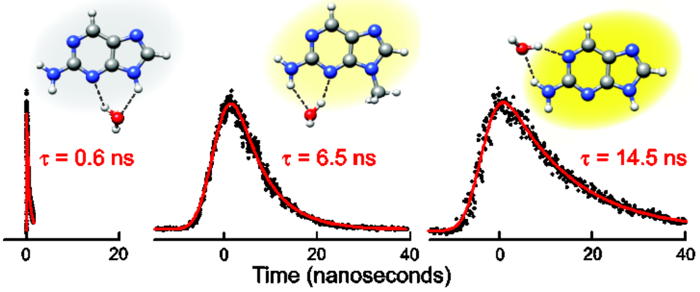

Figure 1: 2-Aminopurine-H_2O complexes and experimental lifetimes

REFERENCES

1. S. Lobsiger, R.K. Sinha, M. Trachsel and S. Leutwyler, *J. Chem. Phys.* **2011,** *134*, 114307.
2. M. A. Trachsel. S. Lobsiger, T. Schaer and S. Leutwyler, *J. Chem. Phys.* **2014,** *140*, 044331.
3. S. Blaser, H.-M. Frey, C. G. Heid and S. Leutwyler, *Chimia* **2014**, *86*, 260-263.
4. S. Lobsiger, S. Blaser, R. K. Sinha, H.-M. Frey and S. Leutwyler, *Nature Chemistry* **2014,** *6*, 989.
5. G. Kodali. K. Kistler, M. Narayanan, S. Matsika and R.J Stanley, *J. Phys.Chem. A.* **2010,** *114*, 256.

IL-11

Tunneling dynamics, proton transfer, conformational equilibria and Ubbelohde effect in adducts of carboxylic acids

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The rotational spectra of several complexes of carboxylic acids have been investigated in the last decade, which supplied plenty of information on the nature of the involved hydrogen bonds, on the internal dynamics and, occasionally, on the conformational equilibria. They can be classified as:

1) Dimers of carboxylic acids. Pairs of carboxyl groups bind cooperatively together, since both units act as proton donor and acceptor, forming a large eight-membered ring containing two hydrogen bonds. Such a kind of hydrogen bonding is the strongest one found within neutral species, with the monomers held together by more than 60 kJ/mol. To these strong hydrogen bonds a clearly sizable Ubbelohde effect is associated. Proton tunneling,[1] or other kinds of internal dynamics, or conformational equilibria[2] have been observed and described in several cases.
2) Adducts of carboxylc acids with water. The carboxyl group and water act simultaneously as proton donor and proton acceptor, leading to the formation of a six membered ring with two hydrogen bonds. Splittings of the rotational transitions have been observed, not yet satisfactorily attributed to a specific internal motion.
3) Adducts of carboxylc acids with other organic molecules. Various kinds of interactions, generally including a hydrogen bond, have been observed and described.

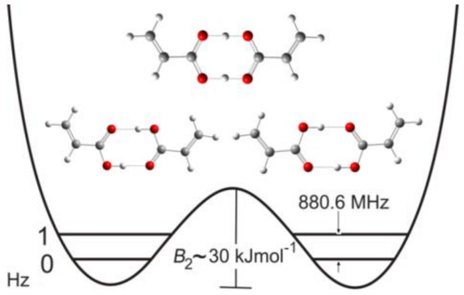

Figure 1

REFERENCES

1. G. Feng, L. B. Favero, A. Maris, A. Vigorito, W. Caminati, R. Meyer, *J. Am. Chem. Soc*. **2012**, *134*, 19281.
2. G. Feng, Q. Gou, L. Evangelisti, W. Caminati, *Angew. Chem. Int. Ed.* **2014**, *53*, 530.

IL-12

Understanding factors affecting red-shifts for the proton stretch vibration frequency of O-H···B hydrogen-bonding complexes

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We have observed almost a linear correlation between the reciprocal of the dielectric constant of the solvent and the red shift in $\nu_{O\text{-}H}$ of $RO\text{-}H\cdots B$ hydrogen bonded complexes[1-3]. In addition, for a fixed solvent and a complexing base, we report on almost a linear correlation between the proton affinity (PA) of the conjugate base of the acid and $\nu_{RO\text{-}H}$. A correlation was also found for various acids between ν_{AH} and the equilibrium constant of the acid in DMSO spanning more than 20 pK_a units on the pK_a scale. A general theoretical model for H-bonded complexes of the acid dissociation type, $AH\cdots B \rightarrow A^-\cdots HB^+$, was developed and describes the observed variation of ν_{AH} with the solvent's dielectric constant ε and the vacuum proton affinity difference $\Delta PA = PA(A) - PA(B)$ between the acid's conjugate base A^- and the base[1].

REFERENCES

1. P. M. Kiefer, E. Pines, D. Pines, J. T. Hynes, *J. Phys. Chem. B* **2014**, 118, 8330.
2. S. Keinan, D. Pines, P. M. Kiefer, J. T. Hynes, E. Pines, *J. Phys. Chem. B* **2015**, 119, 679.
3. D. Pines, S. Keinan, P. M. Kiefer, J. T. Hynes, and E. Pines, *J. Phys. Chem. B*, Just Accepted Manuscript DOI: 10.1021/jp509914w,

IL-13

Polarity of hydrogen bond

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Polarity , measuremenets of dipole moments of the systems with hydrogen bond are becoming less and less popular. It results probably from the fact, that these methods need some laboratory effort ...

In the lecture I want to describe the usefulness this technique till today and demonstrate some advances over other methods, even some sophisticated quantum mechanical calculations. This type of study was introduced into Polish science, but not only Polish science, by professor Lucjan Sobczyk. At the beginning I want to remamber basic achievements of professor Sobczyk's group. The beginning studies has demonstrated, that that polarity of hydrogen bond correlate with the strenght of interactions. It was related to the proton akceptor and proton donor abilities of interacting molecules. More precise description was based on assumption of proton transfer equilibria In function of ΔpKa. This approach needs some knowledge on the structure of complexes, which often is based only on some rational assumptions. Different approach is a direct studies on the structure of complexes with hydrogen bond In solution, applying measured dipole moments in function of concentration.

It gives a realistic information on structure of the formed aggregates. Alternative approach based on quantum mechanical calculations, in many cases, gives non proper distribution of states, because common calculations do not describe detales of specific and bulk interatcions with solvent.

IL-14

Acid-base hydrogen bonds in different environments: from organic solvents to enzymes

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This presentation is dedicated to Lucjan Sobczyk, University of Wroclaw, a pioneer in hydrogen bond research. Since the early 1950's[1] ("Complexes of proton-donor compounds with pyridine in benzene as solvent ")[1] until today[2] he studied the properties of acid-base hydrogen bonds in different environments, using dipole moment-, dielectric polarization-, nuclear quadrupole resonance-measurements, UV/Vis- and vibrational spectroscopy as well as NMR and computational methods. It was shown that all hydrogen bond properties including geometries, H/D isotope effects and proton potentials depend strongly on the polarity of the environment.

Together with the group of Gleb S. Denisov and N. S. Golubev, St. Petersburg, joined by G. Buntkowsky (now Darmstadt), Ilya G. Shenderovich (now Regensburg) and Peter M. Tolstoy (now St. Petersburg) we have applied a combination of low-temperature liquid-state and solid-state NMR spectroscopy to elucidate the properties of acid-base hydrogen bonds in different environments of increasing complexity, i.e. crystals, organic polar solution up to enzymes. Some of the results are reported here. In particular, correlations have been developed[3,4] relating hydrogen bond geometries and NMR parameters. Using the example of pyridine-acid interactions in model complexes and in alanine racemase and aspartate aminotransferase it is shown that the interior of enzymes resembles more polar wet organic solutions rather than aqueous solutions.[5] For further reading see http://userpage.chemie.fu-berlin.de/~limbach/ (go to "Publications").

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I thank my colleagues and coworkers, Shasad Sharif, Monique Chan-Huot, Benjamin Koeppe, Alexandra Dos, Ilya G. Shenderovich, Peter M. Tolstoy, Gleb S. Denisov, Gerd Buntkowsky, Michael Toney, David N. Silverman for their collaboration.

REFERENCES

1. L. Sobczyk, J. K. Syrkin, *Roczniki Chemii*, **1956**, *30*, 881.
2. A. Piecha-Bisiorek, G. Bator, W. Sawka-Dobrowolska, L. Sobczyk, M. Rok, W. Medycki, G. J. Schneider, J. Phys. Chem. A **2014**, *118*, 7159.
3. H. H. Limbach, P. M. Tolstoy, N. Pérez-Hernández, J. Guo, I. G. Shenderovich, G. S. Denisov, *Israel J. Chem.* **2009**, *49,* 199.
4. B. C. K. Ip, I. G. Shenderovich, P. M. Tolstoy, J. Frydel, G. S. Denisov, G. Buntkowsky, H. H. Limbach. *J. Phys. Chem. A.* **2012***, 116*, 11370
5. M. Chan-Huot, A. Dos, R. Zander, S. Sharif, P. M. Tolstoy, S. Compton, E. Fogle, M. D. Toney, I. G. Shenderovich, G. S. Denisov, H. H. Limbach, *J. Am. Chem. Soc.* **2013**, *135*, 18160.

IL-15

Isotope effects in hydrogen bond research

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The talk will be inspired by the work of Professor Sobczyk and will therefore concentrate on hydrogen bonding an in my case on isotope effects on chemical shifts. Examples will be Mannich bases of the type 2-(N,N-dimethylamino)methyl-x-chlorophenol (Fig. 1). Isotope effects in tautomeric systems will be treated and isotope effects on chemical shifts for these systems will be calculated and discussed.
Proton transfer and protonation are clearly important issues and will be discussed in relation to ionic liquids formed between ethyldiisopropylamine and formic acid and in relation to ΔpKa values.
Dimer formation is clearly a possibility in many of these molecules and will be treated based on NMR and UV data.

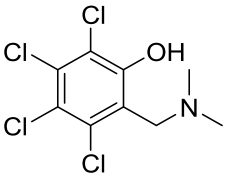

Figure 1

IL-16

Multistimuli-responsive supramolecular gels

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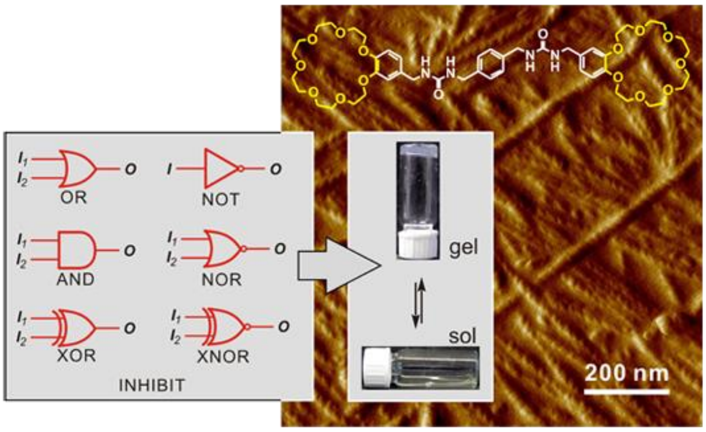
A crown ether-substituted supramolecular gelator forms gels in acetonitrile and is responsive to several stimuli. Depending on the environment in the gel, seven different logic gates have been constructed with the same gelator. Gel-sol transitions can thus be triggered by a number of different input combinations and anything immobilized within the cavities of the gel's fibrous network is released. One of the seven logic gates is a three-input INHIBIT gate.



Similar gelators have also been used to immobilize an enzyme inside the microparticles of a Pickering emulsion. As the inside phase is hydrophilic, the enzyme retains its active conformation, even when catalyzing reactions in a very unpolar reaction medium such as hexane. The gelator also gelates ionic liquids and produces ionogels with high mechanical stability, switchability and interesting self-healing properties

Finally, a quite different partially fluorinated supramolecular gelator is discussed, which forms gels on glass surfaces that are made superhydrophobic through the fluorination, but also through the micro- and nanostructure of the gel's fibrous network.

IL-17

Hydrogen bond reveals the morphology of non-crystalline solids.

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A detailed understanding of local structural patterns in non-crystalline and polycrystalline solids is often crucial for the elucidation of the mechanical and chemical properties of these materials. XRD is not capable of analysis of such materials. Instead, solid-state NMR spectroscopy can be used. Also here there are some serious constraints. Despite clear progress in solid-state NMR of protons its impact is mainly restricted to rough estimation of hydrogen bond geometry because of a narrow spread of chemical shift values. ^{13}C NMR is rarely sensitive enough to non-covalent interactions. In contrast, nitrogen and phosphorus are often actively involved in non-covalent interactions. The local morphology can be deduced from these local non-covalent interactions with or between the molecules of the system under study. The non-covalent interactions under question can be studied using proper NMR-sensors which are either present in the system or specifically induced into it. In view of all this, ^{15}N and ^{31}P NMR are particularly attractive in studies of the local morphology of amorphous materials and surfaces. In this presentation, are reviewed two areas of concern: (i) NMR study of the morphology and the chemical reactivity of surfaces and (ii) a combination of solid-state NMR and time-efficient DFT calculations in studies of complex solid-state systems.

The morphology and the effective acidity of the surfaces of parent and functionalized silica materials can be qualitatively analyzed using pyridine-^{15}N.[1-3] This approach is based on the fact that the spread of $\delta(^{15}N)$ of pyridine derivatives upon non-covalent interactions is above 120 ppm.[4] As a result, one can measure the accessibility, the proton donating ability, the surface density and the distribution of chemically active species at silica surfaces. Particularly noteworthy is the effect of water (Figure 1) and gaseous nitrogen on the chemical activity of the surfaces.[5,6]

The available experimental data showed that the effect of non-covalent interactions, such as hydrogen bond and coordination to metal center, could not be generally correlated with the isotropic ^{31}P chemical shift but tensor components, Figure 2. The latter can be reproduced quite well at relatively inexpensive levels of theory. While an increase of the basis set does not necessary bring any benefits, a correct accounting of local non-covalent interactions is crytical.[7] The latter provides a promising tool to study the local morphology of phosphorous-containing solids and surfaces. It also can be used to develop target-specific, highly sensitive ^{31}P-based NMR-sensors.

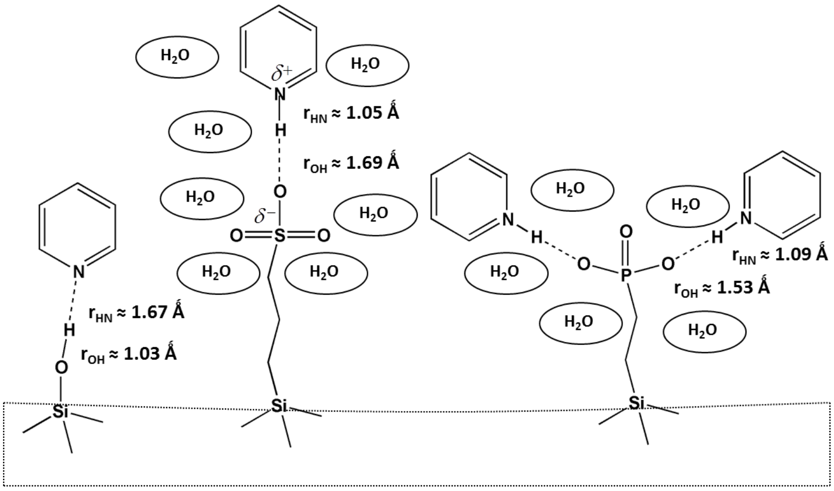

Figure 1 Schematic representation of H-bonded complexes on silica surface at 130 K

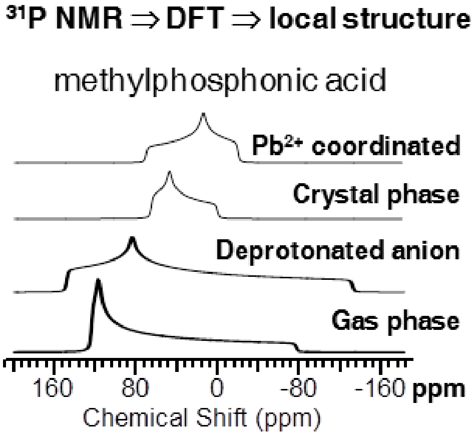

Figure 2 The effect of noncovalent interactions on the ^{31}P NMR chemical shift tensor.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Project 14-03-00716).

REFERENCES

1. I.G. Shenderovich et al. *J. Phys. Chem*. B **2003**, 107, 11924.
2. D. Mauder et al. *J. Phys. Chem. C* 2**009**, 113, 19185.
3. B.C.K. Ip et al. *Micropor. Mesopor. Mater*. **2010**, 134, 22.
4. Ph. Lorente et al. *Magn. Reson. Chem*. **2001**, 39, S18.
5. A.A. Gurinov et al. *Langmuir* **2011**, 27, 12115.
6. A.A. Gurinov et al. *ChemPhysChem* **2012**, 13, 2282.
7. I.G. Shenderovich *J. Phys. Chem. C* **2013**, 117, 26689.

IL-18

NH—S interaction perspective

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Sulfur atom by virtue of its large size and lower electronegativity has not quite been considered as the conventional hydrogen bonding partner. However, in a number of examples found in the PDB and CSD structures, based on the distance and angle constraints it has been implicated as an active hydrogen bond acceptor. We have been studying the h-bonding interactions involving sulfur as an acceptor under isolated conditions of gas phase using a variety of double resonance laser spectroscopic techniques using supersonic jet expansion method to synthesize the h-bonded complexes with XH---S (X=O,N,C) type interactions. Our work[1] has shown that the OH---S interactions do confirm to several h-bonding criteria such as directionality, influence on the OH stretching frequencies, acid-base formalism, etc. although these are strongly dominated by the dispersion interaction.

In this talk, I would like to present the characteristics of the NH---S interactions and put them in perspective with the NH---O and NH---N interactions. We have taken benzimidazole, indole as the chromophores for the NH donor and a variety of solvents containing sulfur to form the dimeric complexes. The experimental results were also corroborated with *ab-initio* quantum chemical computations.

Acknowledgements

This work was funded by Tata Institute of Fundamental Research, Mumbai, INDIA.

REFERENCES

1. H.S. Biswal, S. Bhattacharyya, A. Bhattacherjee, and S. Wategaonkar,
Int. Rev. Phys. Chem. Adv. **2015,** 34, 99.

IL-19

Pressure-induced anomalous transformations of hydrogen bonds and their consequences for material sciences

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Pressure can considerably affect the structure of hydrogen bonded crystals in several ways. Even at moderate pressure of few GPa, the hydrogen-bonded aggregates can be destabilized and new phases formed. For example, the well known structure of (+)-sucrose, the organic compound produced in the largest quantities in the pure form, is transformed to a new polymorph at 4.8 GPa.[1] A similar transformation occurs in (+)-glucose.[2] In these sugars the OH···O are destabilized, some of them broken and others formed, as they have to compete with CH···O bonds more favoured by pressure. Depending on the molecular environment, the proton position can be stabilized or destabilized in homoconjugated hydrogen bonds.[3,4] The pressure-modified preferences for the types of H-bonds open new routs for obtaining solvates and co-crystals of new compositions, such as thiourea hydrates.[5] These new multi-component compounds can be advantageous in their properties compared to the unsolvated compounds, for example in solubility in water for pharmaceutical applications.[6]

Transformations of hydrogen bonds contribute to exceptional properties of crystals, such as ferroelectric, ferromagnetic, relaxor and piezo-mechanical behaviour of exceptionally high strain.[7-10] These properties can be conveniently studied, when the crystal is monotonically compressed or when it undergoes phase transitions under pressure.

REFERENCES

1. E. Patyk, J. Skumiel, M. Podsiadło, A. Katrusiak, *Angew. Chem. Int. Ed*. **2012**, *51*, 2146.
2. E. Patyk, A. Katrusiak, *Chem.Sci.* **2015,** *6*, 1991.
3. K. Ostrowska, M. Kropidłowska, A. Katrusiak, *Cryst.Growth Des.* **2015,** *15*, 1512.
4. W. Cai, A. Katrusiak, *CrystEngComm.* **2012,** *14*, 4420.
5. H. Tomkowiak, A. Olejniczak, A. Katrusiak, *Cryst.Growth Des.* **2013,** *13*, 121.
6. W. Zieliński, A. Katrusiak, *CrystEngComm.* **2015,** *17*, 5468.
7. A. Katrusiak, M. Szafrański, *Phys. Rev. Lett.* **1999,** *82*, 576.
8. W. Cai, A. Katrusiak, *Nature Commun.* **2014,** *5*, 4337.
9. W. Zieliński, A. Katrusiak, *Cryst.Growth Des.* **2014,** *14*, 4247.
10. W. Cai, A. Gładysiak, M. Anioła, W. Smith, L. Barbour, A. Katrusiak, *J. Am. Chem. Soc*. **2015**

IL-20

The role of hydrogen bonding in phase transitions

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As molecules come together to form the first fragments of a more stable phase from a supersaturated metastable phase, hydrogen bonding can play an important role in these initial nucleation and growth stages. In vapor to liquid phase transitions, molecules that form strong hydrogen bonds can actually delay the onset and reduce the nucleation rate over that expected in the absence of this phenomenon. Here we will present our work[1] investigating the condensation of alcohols in supersonic flows, using static pressure measurements, small angle X-ray scattering and Fourier Transform Infrared Spectroscopy, under conditions for which the concentration of gas phase clusters is high. Modeling our experiments, as well as those of others,[2] can help constrain acceptable equilibrium constants for the cluster formation process.

Acknowledgements

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REFERENCES

1. H. Laksmono, S. Tanimura, H. C. Allen, G. Wilemski, M. S. Zahniser, J. H. Shorter, D. D. Nelson, J. B. McManus, B. E. Wyslouzil, *Phys. Chem. Chem. Phys.* **2011,** *13*, 5855.
2. B. Hale, G. Wilemski, Aaron Veits, AIP Conference Proceedings 1527, 27, **2013**

IL-21

The unconventional C-H···X hydrogen bonds. An application of the neutron scattering.

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The forecast of the strength of hydrogen bonds in the molecular complexes is important in the designing of the novel organic materials exhibiting polar or semiconducting properties. In such materials, besides the formation of relatively strong hydrogen bonds, we expect either the formation of infinite chains of molecules or the stacking alignment of molecules in the crystal lattice that favors the desired electrical or optical properties. Moreover the crystal structure of the molecular complexes is stabilized by the unconventional C-H…X (X = O, N, Cl…) hydrogen bonds.

Recently, the intriguing complexes have been obtained with derivatives of either pyrazine or bipyridil to form supramolecular architectures. The interaction between the acid and base molecule, mainly *via* hydrogen bond, leads to a variety of crystal structures. The complex formation in solid state substantially changes the symmetry of the molecule and the environment of methyl groups that affects their dynamics.

The parameters of the methyl (-CH_3) group rotational potential may be a probe of both the charge transfer phenomenon and the local contacts in the crystal. The most important technique we have used to determine methyl group dynamics in molecular complexes is the neutron scattering. The parameters of the -CH_3 rotational potential can be estimated on its basis. Particularly we can derive (*i*) the tunneling splitting at low temperature, (*ii*) the jump-diffusional rotation rate at moderate temperature (Quasielastic Neutron Scattering [QENS]), and (*iii*) the torsional energy (Inelastic Neutron Scattering [INS]). The number of the observed tunneling peaks for the particular molecular complex is related to the number of the inequivalent methyl groups in the crystal structure.

Several examples show an effect of the unconventional C-H···O or C-H···N hydrogen bonds on the possible tunneling of the CH_3 groups at low temperatures.

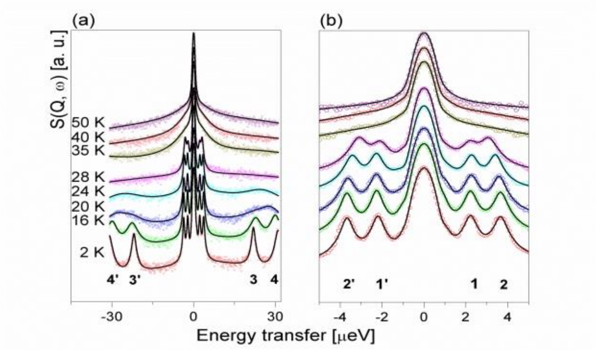

Figure 1. Tunneling splitting in tetramethylpyrazine with chloranilic acid[1].

REFERENCES

1. A .Piecha-Bisiorek, G. Bator, W. Sawka-Dobrowolska, L. Sobczyk, M. Rok, W. Medycki, G. Schneider, *J. Phys. Chem. A.*, **2014**, *118*, 7159.

IL-22

Hydrogen bonding in, and structure of blocked dipeptides

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Determination of the preferential amino acid conformations and understanding the physical basis of intrinsic preferences of amino acid residues in water are crucial for solving the protein folding problem. Dipeptides of type Ac-X-NHMe, (X is an amino acid) represent an ideal system for studying the intrinsic conformational preferences of residues. They are the smallest fragments that preserve the main characteristic of the individual amino acids within the host molecules. Moreover, the effects of neighbouring residues are absent.

Infrared spectroscopy is very suitable spectroscopic method to provide distribution of individual conformation in peptide as well as a method which probes the hydrogen network around solute. We explored the structural sensitivity of Amide I and Amide III bands in order to determine the distribution of structures of small blocked dipeptides and some larger blocked alanin peptides.

Three different conformations (P_{II}, β and α_R) define conformational space of dipeptides in water[1-4]. The distribution of these conformations strongly depends on the type of side chain. The impact of different salts or solvents on the backbone conformation will be also discussed.

The experimental results are explained by the electrostatic screening model[1,2]. The model is based on a hypothesis that the peptide conformations are affected by electrostatic dipole-dipole interactions in the peptide backbone and by screening of these interactions with surrounded water molecules. The extent of screening effect depends on nearby side chains

REFERENCES

1. J.Grdadolnik, V Mohaček-Grošev, L. R. Baldwin, F. Avbelj, *Proc. Natl. Acad. Sci. U.S.A*. **2011**, *108*, 1794.
2. F. Avbelj, S. Golič Grdadolnik, J. Grdadolnik, L. R. Baldwin, *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 1272.
3. J. Grdadolnik, S. Golič Grdadolnik, F. Avbelj, *J. Phys. Chem. B* **2008**, *112*, 2712.
4. A. Mirtic, F. Merzel, and J. Grdadolnik, *Biopolymers*, **2014**, *101*, 814.

Oral Contributions

OC-1

On the nature of low barrier hydrogen bonds in enzyme catalysis

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Low-barrier H-bonds (LBHBs), which form between donors and acceptors with matching pKa values, are strengthened *additionally* if such interactions also polarize the π-system of the H-bond donor and increase their π-electron delocalization energies. This cooperative effect explains why weak acids like imidazole and phenol can act as the general acid catalyst for many enzymatic reactions. H-bonded imidazole and phenol complexes that model representative enzyme-substrate LBHB interactions were studied computationally, both in the gas-phase and in implicit solvation (at $\varepsilon = 5, 20, 78$). According to block-localized wavefunction (BLW) analyses and other model studies, increased π-electron delocalization energies in imidazole and phenol can promote stronger than expected LBHBs by up to 8-18 kcal/mol. These effects are separate from electrostatic interactions and persist even in polar environments. H-bond donors that are saturated or are linked to the H-bond acceptor through a common π-conjugation unit do not exhibit such cooperativity.

REFERENCES

Unpublished results

OC-2

Molecular interaction of human serum albumin with meloxicam - molecular modeling studies

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Meloxicam (Fig. 1) is a non-steroidal anti-inflammatory drug (NSAID) of new generation with preferential inhibition of cyclooxygenase-2 (COX-2).[1] It is bound mostly (>99%) to albumin, the most prominent protein in plasma responsible for many drugs' efficacy and rate delivery.[2] The interaction between meloxicam and human serum albumin has been investigated by docking with AutoDock vina program.[3] Protein–ligand docking study has been performed to verify the experimental studies performed previously.[4] The theoretical study considers all potential binding sites of meloxicam presented in Fig. 2.[2]

The probable binding mechanism of the drug molecules with human serum albumin has been explored using QTAIM analysis.[5] To investigate the molecular interactions responsible for binding of the investigated drug to albumin the parameters of electron density have been analyzed for the low energy structures of meloxicam bound to human serum albumin.

In order to examine the behavior of obtained protein-ligand complexes, molecular dynamics studies have been conducted with GROMACS 5.0.4.[6] Structural changes of the ligand and its proximity as well as the stability of the system were investigated.

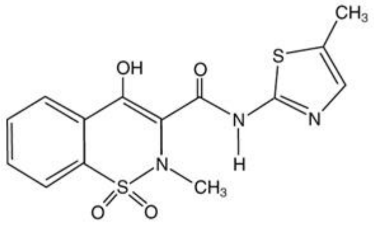

Figure 1. Structure of meloxicam

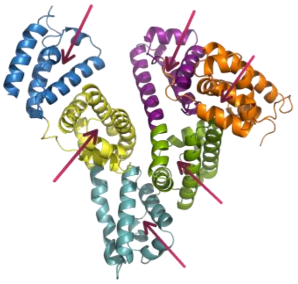

Figure 2. Human serum albumin (PDB code:1N5U), possible binding sites pointed by arrow

Acknowledgements

Calculations have been carried out using resources provided by Wroclaw Centre for Networking and Supercomputing (http://wcss.pl)

REFERENCES

1. N. M. Davies,N. M. Skjodt, *Clinical Pharmacokinetics,* **1999,** *36*
2. M. Fasano, S. Curry, E. Terreno, M. Galliano, G. Fanali, P. Narciso, S. Notari, P. Ascenzi, *Life,* **2005,** *57*
3. O. Trott, A. J. Olson, *Journal of Computational Chemistry,* **2010,** *31*
4. L. Trynda-Lemiesza, K. Wiglusz, *Journal of Pharmaceutical and Biomedical Analysis*, **2010,** *52*
5. R. F. W. Bader, *'Atoms in Molecules A Quantum Theory'*, Oxford University Press, Oxford, 1990
6. D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark H.J. C. Berendsen, *Journal of Computational Chemistry,* **2005,** *26*

Role of hydrogen bonds in hydrogen transfer reactions of metal hydrides

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Many chemical and biochemical (stoichiometric or catalytic) processes involve proton transfer reactions where formation of hydrogen bonded intermediates is a key step. In case of transition metal hydrides the formation of $M\text{-}H^{\delta-}\cdots{}^{\delta+}HA$ or $M\text{-}H^{\delta+}\cdots B$ hydrogen bonds entails an additional polarization (repolarization) of an M-H bond and, thus, tunes its reactivity. The experimental and theoretical (DFT) data show that M-H bonds are easier polarized and more reactive than $C\text{-}H^{\delta+}$ bonds of similar proton donating strength or X-Y bonds of organic bases. Consequently, the proton transfer to or from transition metal hydrides takes place at substantially lower hydrogen bond formation energy.[1]

The peculiarities of proton transfer between the two transition-metal hydrides with opposite polarities will be also considered. Formation of $M\text{-}H^{\delta-}\cdots{}^{\delta+}H\text{-}M'$ dihydrogen bond, detected only recently,[2] precedes the proton transfer and formation of very unusual $\mu,\eta^{1:1}\text{-}H_2$ species featuring an end-on coordination of hydrogen molecule between the two transition metals. Such complexes could be regarded as models for the heterolytic H_2 splitting by transition metal based frustrated Lewis pairs.

The low-energy interactions (hydrogen-bonded or Lewis complexes) activate the M—H bonds involved and stimulate further transformations. At that, the nature of the orbital interactions in the complex determines the reaction pathway: proton transfer to hydride ligand in the case of $\sigma_{MH}\rightarrow\sigma^*_{OH}$ donation, metal atom protonation in the case of $n_M\rightarrow\sigma^*_{OH}$, metal hydride deprotonation in the case of $n_N\rightarrow\sigma^*_{MH}$, and hydride transfer to Lewis acid in the case of $\sigma_{MH}\rightarrow n^*_B$. The M—H bond polarization change has the similar character upon the formation of complexes with Broensted and Lewis acids.[3]

The role of orbital interaction in comparison with the pure electrostatic attraction will be discussed on the examples of dihydrogen bonds with hydrides of different nature (transition metal hydrides, simple and polyhedral boron hydrides).

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REFERENCES

1. V. A. Levina, O. A. Filippov, E. I. Gutsul, N. V. Belkova, L. M. Epstein, A. Lledos, E. S. Shubina *J. Am. Chem. Soc.* **2010**, *132*, 11234.
2. V. A. Levina, A. Rossin, N. V. Belkova, M. R. Chierotti, L. M. Epstein, O. A. Filippov, R. Gobetto, L. Gonsalvi, A. Lledos, E. S. Shubina, F. Zanobini, M. Peruzzini *Angew. Chem.Int. Ed.* **2011**, *50*, 1367.
3. O. A. Filippov, I. E. Golub, E. S. Osipova, V.A. Kirkina, E. I. Gutsul, N. V. Belkova *Russ. Chem. Bull., Int. Ed.,* **2014**, *63*, 2428. (*Izv. Akad. Nauk, Ser. Khim.*, **2014**, *63*, 2428)

OC-4

A study of multifurcate dihydrogen bonded complexes with participation of boron hydrides

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Intermolecular interactions plays an important role in chemistry both boron and metal hydrides. The dihydrogen-bonded (DHB) complexes are known to form at the first step of proton transfer reaction. It was shown that bifurcate DHB complexes are active intermediates of this process.

Interaction of transition metals tetrahydroborate complexes[1] and dimethylamine-borane[2] with proton donors was thoroughly studied by means of combination of experimental (IR and NMR, 190-300 K) and computational methods (DFT/M06, AIM and NCI analysis). By means of QTAIM theory in multifurcate DHB complexes the (3; −1) critical point was found only for the closest contact OH···HB with the most linear O−H···H(B) angle (Figure 1). The presence of additional interactions causes deviation of the hydrogen bond geometry from linearity, which is reflected in the high values of the H···H bond ellipticity. From the NCI analysis we obtained NCI isosurfaces with two attractive areas (hydrogen bond) and on non-bonding overlap area that reveals a bifurcate character of DHB.

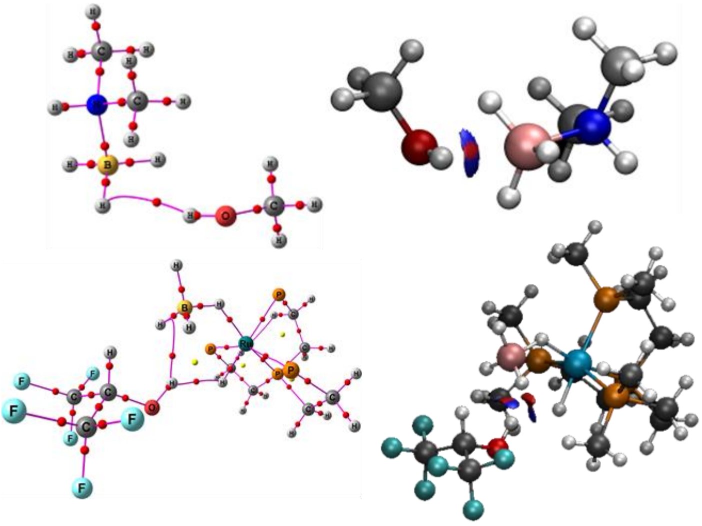

Figure 1 AIM and NCI analysis of DHB complexes

Acknowledgements

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REFERENCES

1. N. V. Belkova, E. V. Bakhmutova-Albert, E. I. Gutsul, V. I. Bakhmutov, I. E. Golub, O. A. Filippov, L. M. Epstein, E. S. Shubina, M. Peruzzini, F. Zanobini. *Inorg. Chem.* **2013***,* 53, 1080.
2. I. E. Golub; E. S. Gulyaeva; O. A. Filippov; V. P. Dyadchenko; N. V. Belkova; L. M. Epstein; D. E. Arkhipov; E. S. Shubina, *J. Phys. Chem. A* **2015**, 119, 3853.

OC-5

What proton conductivity can tell us about H-bond potentials?

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Based on the results of the kinetic Monte Carlo simulations[1] concerning the experimental data (temperature and pressure dependent) for the proton conductivity in benzimidazolium azelate[2] some general conclusions about the factors responsible for the hydrogen-bond potentials in solids are drawn.

It is demonstrated that the shape of the hydrogen-bond potential strongly results from the mutual interplay of the thermal expansion and the lattice vibrations.

Furthermore, in high-pressure regime one can anticipate the possibility of the crossover from the decreasing to increasing temperature dependence of the hydrogen-bond barrier height with increased pressure, see Figure 1.

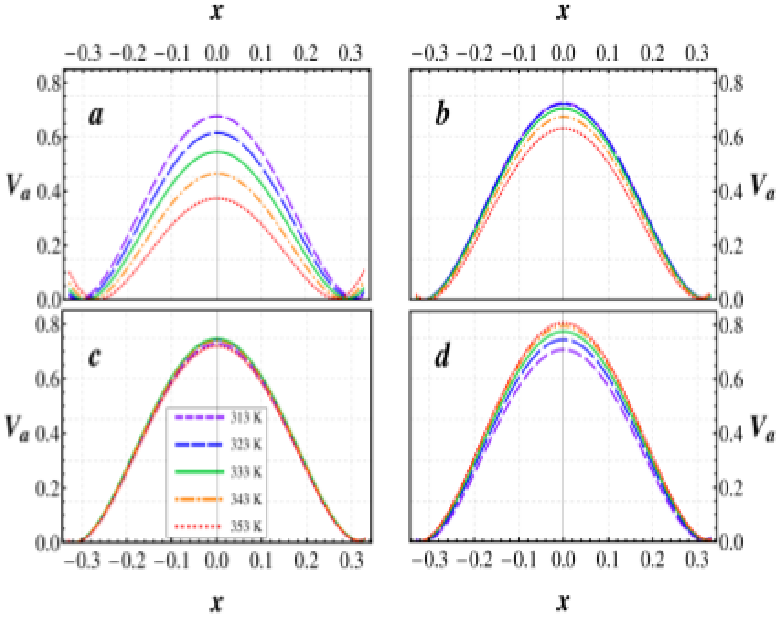

Figure 1 The evolution of the H-bond potential V_a with increasing pressure. a) A typical behavior for low pressures; b) At some pressure the slope of the temperature-dependent curves starts to reverse; c) The point where the potential hardly depends on the temperature; d) Above the enough high pressure the potential grows with the temperature in the considered range.

REFERENCES

1. T. Masłowski, A. Drzewiński, J. Ulner, J. Wojtkiewicz, M. Zdanowska-Frączek, K. Nordlund, A. Kuronen, *Phys. Rev. E* **2014**, 90, 012135.
2. T. Masłowski, A. Drzewiński, P. Ławniczak, M. Zdanowska-Frączek, J. Ulner, *Solid State Ion.* **2015,** accepted for publication, doi: 10.1016/j.ssi.2015.06.003.

OC-6

Hydrogen bond-induced changes in photophysics and photostability of indole-naphthyridines

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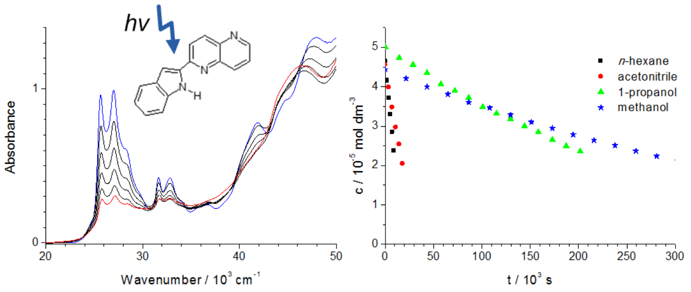
We demonstrate how the formation of hydrogen bonds can influence the photostability of the molecules that can simultaneously act as hydrogen bond donors and acceptors. It is known that this type of molecules can exhibit completely different photophysical behavior in protic and aprotic solvents.[1] Formation of multiple hydrogen bonds with, e.g., water or alcohols may lead to enhanced internal conversion; as a result, triplet formation efficiency can be reduced. These changes in photophysical characteristics may change the photostability. In order to check this hypothesis, we have investigated spectroscopy, photophysics, and changes in photostability caused by interaction with aprotic and protic solvents for 2-(1′*H*-indol-2′-yl)-[1,5]naphthyridine and 2-(1′*H*-indol-2′-yl)-[1,8]naphthyridine, molecules with hydrogen bond accepting and donating functionalities.[2] In polar and protic solvents, the presence of two species was detected and attributed to *syn* and *anti* rotameric forms; the former are dominant in all environments. The photostability of these compounds in *n*-hexane, acetonitrile and alcohols was studied in the regime of 365 nm irradiation. As a result we established that the photodegradation yield was significantly lower in alcohols than in aprotic solvents for both compounds. We also made an attempt to establish the photoproducts which are formed under 365 nm irradiation of the studied molecules in acetonitrile solution.



REFERENCES

1. J. Waluk, *Acc. Chem. Research* **2003,** *36*, 832.
2. B. Golec, M. Kijak, V. Vetokhina, A. Gorski, R. P. Thummel,J. Herbich, J. Waluk, *J. Phys. Chem.* B **2015** Accepted**.** DOI: 10.1021/jp510846w

Correlating photoacidity to hydrogen-bond structure by use of the local O-H stretching probe in hydrogen-bonded complexes of aromatic alcohols

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To assess the potential of using O–H stretching modes of aromatic alcohols as ultrafast local probes of transient structures and photoacidity, we focus in this first report on the response of the O–H stretching mode in the 2-naphthol-acetonitrile (2N-CH_3CN) complex, upon UV photoexcitation, combining femtosecond UV-infrared pump-probe spectroscopy and a theoretical treatment of vibrational solvatochromic effects based on the Pullin perturbative approach parametrized at the density functional theory (DFT) level.[1] We analyze the effect of hydrogen bonding on the vibrational properties of the photoacid-base complex in the S_0 state, as compared to O–H stretching vibrations in a wide range of substituted phenols and naphthols covering the 3000–3650 cm^{-1} frequency range.[2] Ground state vibrational properties of these phenols and naphthols with various substituent functional groups are analyzed in solvents of different polarity and compared to the vibrational frequency shift of 2N induced by UV photoexcitation to the ^1L_b electronic excited state. We find that the O–H stretching frequency shifts follow a linear relationship with the solvent polarity function $F_0 = (2\varepsilon_0-2)/(2\varepsilon_0+1)$, where ε_0 is the static dielectric constant of the solvent. These changes are directly correlated with photoacidity trends determined by reported pK_a-values,[3] and with structural changes in the O…N and O–H hydrogen-bond distances induced by solvation or photoexcitation of the hydrogen-bonded complexes.

REFERENCES

1. D. Xiao, M. Prémont-Schwartz, E. T. J. Nibbering and V. S. Batista, *J. Phys. Chem. A* **2012**, *116*, 2775.
2. B. T. Psciuk, M. Prémont-Schwartz, B. Koeppe, S. Keinan, D. Xiao, V. S. Batista and Erik T. J. Nibbering, J. *Phys. Chem. A* **2015**, *119*, 4800.
3. M. Prémont-Schwarz, T. Barak, D. Pines, E. T. J. Nibbering and E. Pines, *J. Phys. Chem. B* **2013**, *117*, 4594.

OC-8

Structure, intermolecular and photoinduced intramolecular hydrogen bonding in 2-pyrrolylmethylidene cycloalkanones

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Chemistry of bis(aryl)methylidene derivatives of cyclic ketones, due to their vast field of application and availability is an extensively growing area at present time.[1] The present contribution reports the results of X-ray, NMR, IR and UV studies supported by DFT calculations of the structure of 2,5-bis((1H-pyrrol-2-yl)methylene)-cycloalkanones and their monosubstituted 1-indanone and 1-tetralone analogues. It is shown that in both solid state and solution all studied compounds exist in the *E* (monoenones) or *E,E* (dienones) configuration, stabilized by intermolecular hydrogen bond N–H···O=C. UV irradiation leads to isomerization around the double bonds with the formation of the *Z* or *Z,E* and *Z,Z*-isomers, containing intramolecular hydrogen bonds (Fig. 1). *Z,Z*-isomers, in spite of the presence of two hydrogen bonds in the molecules, are unstable and quickly transform into the *Z,E*-isomers.

The protonation of the studied dienones with relatively weak trifluoroacetic acid results in an unexpected formation of the carbonyl oxygen protonated cations, in spite of much higher basicity of the pyrrole rings. Besides, in the acidic medium quick transformation of the *Z* (or *Z,Z*) isomers into the corresponding *E* or *E,E*-isomers takes place.

The interaction of the stidied dienones with fluoride and acetate anions leads in the first case to deprotonation of one of the pyrrole NH groups and strenghening of the remaining hydrogen bond in the *Z,E*-isomers, whereas in the secong case only formation of strong hydrogen bond of NH with AcO^- is observed. This finding allows to consider the studied compounds as potential fluoride anion sensors.

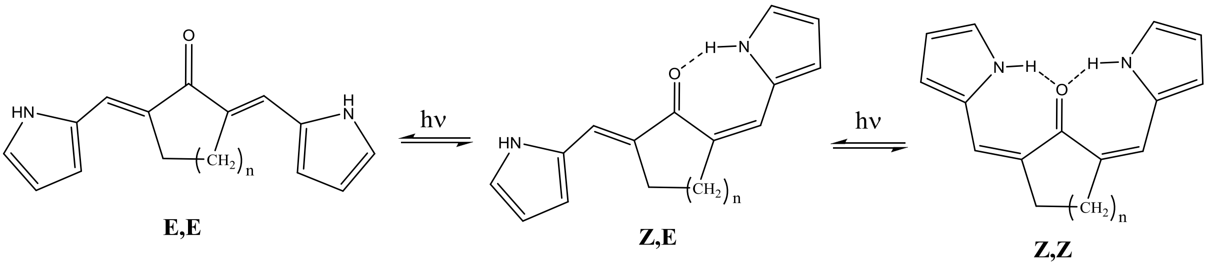

Figure 1 Products of photoisomerization of 2,5-bis((1H-pyrrol-2-yl)methylene)cycloalkanones

REFERENCES

1. S.Z.Vatsadze, A.G.Golikov, A.P.Kriven'ko, N.V.Zyk. *Russ. Chem. Rev*., 2008, 77, 661-681.

Jet-cooled high resolution infrared spectroscopy of hydrated hetero clusters

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Weakly bound complexes involving water play an essential role in many chemical, biological and astrophysical processes[1]. Cold environments such as molecular jets[2] , cryogenic rare gas matrix isolation[3] and helium droplets[4] are efficient to stabilize intermolecular weak interactions and facilitate assignments and analyses of (ro)vibrational spectra in the absence of thermal excitation. Two complementary set-ups which combine high resolution infrared spectroscopy and supersonic jets are currently exploited by our team: (i) Jet-AILES, a continuous supersonic free jet coupled to a high resolution Fourier Transform Spectrometer (FTS) equipping the AILES beam line of the synchrotron light source SOLEIL[5], (ii) SPIRALES, a pulsed supersonic jet coupled to a tunable mid-IR external cavity quantum cascade laser (EC-QCL). Two recent studies realized with Jet-AILES and SPIRALES will be presented: the first one deals with hydrogen bonded interactions of different sized $(CH_3X)_m(H_2O)_n$ heteroclusters (X = F, Cl) probed by broadband FTS in the intramolecular stretching OH region, and assigned with the support of ab initio calculations. The second one illustrates the strong sensitivity of pulsed supersonic expansions probed by high resolution laser spectroscopy to investigate van der Waals interactions between a rare gas atom and a water molecule, as shown with preliminary results obtained about $Ar\text{-}H_2O$ and $Kr\text{-}H_2O$ binary complexes in the H_2O bending mode region.

REFERENCES

1. A. Potapov and P. Asselin, *Int. Rev. Phys. Chem.* **2014**, 33, 275.
2. M. Havenith, *Infrared Spectroscopy of Molecular Clusters* (Springer, Berlin, **2002**).
3. L. Schriver-Mazzuoli, in *Molecular Complexes in Earth's Planetary, Cometary and Interstellar Atmospheres*, edited by A. Vigasin and Z. Slanina (World scientific, Singapore, **1998**).
4. J.P. Toennies and A.F. Vilesov, *Angew. Chem. Int. Ed*. **2004**, 43, 2622.
5. M. Cirtog, M.E. Alikhani, B. Madebene, P. Soulard, P. Asselin and B. Tremblay, J*. Phys. Chem*. **2011**, 115, 6688.

OC-10

Exploring the conformational preferences of aniline aggregates in jets

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Aggregation of molecules is a process related to fundamental phenomena, such as formation of aerosols, crystals, phase separation… etc. By definition, the first stages of the process are highly stochastic and are governed by weak, non-covalent interactions, which are very difficult to parameterize. Consequently, those first stages are difficult to model. Our group is engaged in the characterization of molecular aggregates whose study may yield some light on the first stages of the aggregation process. Thus, we have recently published a very detailed study on the aggregation of propofol (2,6-diisopropylphenol), demonstrating that it is able to form reverse micelles in jets.[1] We present a combined experimental (mass-resolves spectroscopy) and computational (DFT) study on the conformational preferences of aniline, from small to moderate size (containing from two to nine aniline molecules). Despite that aniline is smaller than propofol, the spectroscopy of the aggregates is significantly more complex, because aniline presents an amino group that can establish three hydrogen bonds (two as donor and one as acceptor) at the same time, but also, because the C-H···π interactions are of similar strength than the N-H···N hydrogen bonds. The structures found in the jet are therefore a subtle equilibrium, a compromise to optimize all the interactions at play, and therefore are expected to be highly dynamic.

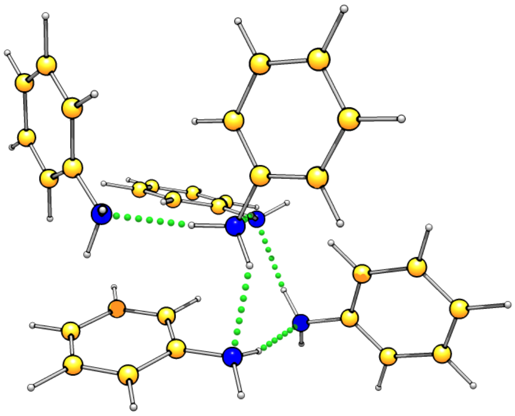

Figure 1 one of the possible structures of aniline pentamer

REFERENCES

1. Iker León, Judith Millán, Emilio J. Cocinero, Alberto Lesarri and José A. Fernández, *Angew. Chem. Int. Ed*. **2013**, *52*, 7772.

OC-11

Structural distortion and fluorescence enhancement in diazatriphenylenes and their hydrogen-bonded complexes in supersonic jets

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Diazatriphenylenes belong to a family of aza-aromatic compounds which, depending on the position of nitrogen atoms, differ significantly in such properties as pK changes in excited states, the influence of solvents and temperature on the spectra in solution, or quantum yield dependence on protonation.[1] **1,4-diazatriphenylene (1,4-DAT)** have been recently proposed as core compound in new organic light emitting materials showing thermally activated delayed fluorescence.[2] However, its photophysical properties strongly depend on the vibronic interaction between low-lying (π,π*) and (n,π*) excited states. An important source of information on such interactions is the vibronic structure of high-resolution electronic spectra obtained by supersonic jet technique.

Thus, we investigated the electronic and vibrational structure of two isomeric diazatriphenylenes, 1,4-DAT and 1,8-DAT in jet-cooled gas phase. The departure from planarity of the excited-state structure of 1,4-DAT is discussed. Distinct activity of out-of-plane vibronic modes is analyzed with the help of (TD)DFT calculations. A large increase of fluorescence intensity upon selective complexation with protic partners is reported and explained in terms of different energetics of (π,π*) and (n,π*) excited states in hydrogen-bonded species.

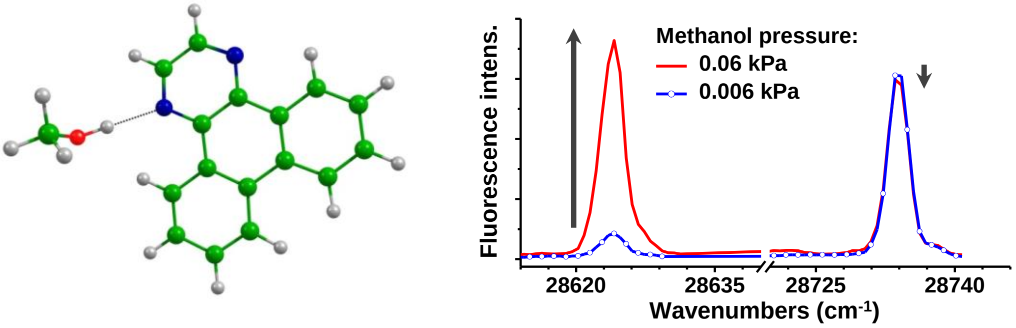

Figure 1 The structure of 1:1 complex of 1,4-DAT with methanol and, intensity changes of 0-0 vibronic transitions in LIF(E) spectra of bare and H-bonded 1,4-DAT.

REFERENCES

1. A. Grabowska, B. Pakuła, J. Sepioł, *Nouv. J. Chim*. **1979**, *3*, 287.
2. T.Takahashi, K. Shizu, T. Yasuda, K. Togashi, C. Adachi, *Sci. Technol. Adv. Mater.* **2014**, *15*, 034202

Anharmonicity and the hydrogen bond

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Despite the ever-increasing computational power available to quantum chemistry, anharmonic calculations are still often unfeasible except for rather small systems or simple methods. One is thus typically left with the harmonic approximation and all of its shortcomings to predict the spectra of hydrogen-bonded systems. This unsatisfactory situation is matched on the experimental side by the exacerbated intensity penalty of combination or overtone bands[1] which are required to deduce anharmonicity constants. Thus, gas phase studies on the role of anharmonicity in hydrogen bonding are rare, and this gap between theory and experiment remains to be closed.

The diagonal anharmonicity constant of the donor OH stretching oscillator in the methanol dimer has recently been obtained using linear jet-FTIR overtone spectroscopy.[2] We have succeeded in consistently explaining the 111 cm^{-1} red shift of this important OH···O hydrogen bond by combining the experimental data with accurate harmonic and less stringent perturbational anharmonic calculations.[3,4] In this context, the MP2 method is flawed for reliable harmonic predictions, whereas explicitly correlated local Coupled-Cluster calculations provide an accurate and feasible tool for this purpose.[3]

We further extend the analysis to the first experimental characterization of the methanol-ethene dimer.[5] Notably, the overall 45 cm^{-1} red shift in the donor OH oscillator can be explained for the most part by harmonic effects alone. Together with only minute anharmonic effects, this attests to the remarkable weakness of this prototypical OH···π hydrogen bond.

REFERENCES

1. T. di Paolo, C. Bourdéron, C. Sandorfy, *Can. J. Chem.* **1972**, *50*, 3161.
2. F. Kollipost, K. Papendorf, Y.-F. Lee, Y.-P. Lee, M.A. Suhm, *Phys. Chem. Chem. Phys.* **2014,** *16*, 15948.
3. M. Heger, R.A. Mata, M.A. Suhm, *J. Chem. Phys*. **2014**, *141*, 101105.
4. F. Kollipost, J. Andersen, D.W. Mahler, J. Heimdal, M. Heger, M.A. Suhm, R. Wugt Larsen, *J. Chem. Phys.* **2014**, *141*, 174314.
5. M. Heger, R.A. Mata, M.A. Suhm, *Chem. Sci.* **2015**, *in press*, DOI: 10.1039/C5SC01002K.

OC-13

Structure of the absorption bands of complexes in the gas phase with different hydrogen bond strengths. Fourier spectra and ab initio anharmonic calculations

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The structure of absorption bands of H-bonded complexes is the important source of information on interatomic interactions and dynamics. Our experience shows that the most complete information on the band shape formation mechanisms can be obtained from concerted experimental and theoretical studies that complement with one another. The study[1] of the ν(HF) band of gas-phase complexes $H_2O\ldots HF$, $(CH_3)_2O\ldots HF$, $(CH_3)_2CO\ldots HF$, and HCN…HF showed that its complicated form is determined by the fundamental, combination, and hot transitions involving low-frequency vibrations. To describe such bands, the calculation must accurately predict the energy values, transition frequencies and intensities, and rotational constants for many states and transitions of the complex; however, to be feasible, it should, at the same time, include a limited number of interacting modes. Once the electro-optical parameters are found, it is possible to reconstruct the spectra at different temperatures and for various isotopologues. Correctness of the theory is verified by comparison of experimental and calculated spectra. This imposes strict requirements on experiments, e.g., the gas phase, the temperature range and concentrations to ensure creation of the complexes considered, and high resolution to facilitate separation of their spectrum from the observed spectrum. Analogous studies were carried out for the trans-HONO…NH_3 complex[2].

Similar calculations were performed for the $[F(HF)_2]^-$ anion[3], which is one of the strongest H-bonded complexes. Unfortunately, gas-phase experimental spectra of this compound are unavailable. Stronger complexes of phosphinic acids have a very broad, in the region 3500 – 1200 cm^{-1}, ν(OH) band recordered[4] both in the gas phase at 400-550 K and in matrices at 12-30 K. This suggests that the band is formed due to very many combination transitions from the ground state. Solution of such multidimensional problems presents enormous difficulties for theoreticians, just as the experiment on $[F(HF)_2]^-$ is a challenge for experimenters.

Acknowledgements

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REFERENCES

1 V.P. Bulychev, K.G. Tokhadze, Vibr. Spectrosc. **2014**, *73*, 1.
2 V.P. Bulychev, M.V. Buturlimova, K.G. Tokhadze, J. Phys. Chem. A **2013**, *117*, 9093.
3 V.P. Bulychev, M.V. Buturlimova, K.G. Tokhadze, Phys. Chem. Chem. Phys. **2011**, *13*, 14019.
4 R.E. Asfin, G.S. Denisov, K.G. Tokhadze, J. Mol. Struct., **2006**, *790*, 11.

OC-14

From water aggregates trapped in cryogenic matrices to amorphous solid water

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The Hydrogen Bond, or the "Bond of Life", is ubiquitous. Its presence is key to processes on Earth – especially in water and aqueous systems, but also in the atmosphere, in mixed water/organic molecules or aggregates – as well as the Interstellar Medium (ISM), where water is predominantly observed in the form of Amorphous Solid Water (ASW). This special bond is of primary importance in the organisation of living organisms, and certainly played a fundamental role in the emergence of life. We are interested in the IR and UV photoreactivity of H-bonded molecules and aggregates trapped in cryogenic matrices. By employing a laser to perform infrared selective irradiations, and following the resulting photoreactivity using FTIR spectroscopy, we identify and discriminate isomers of a molecule or an aggregate present in cryogenic matrices, and study their vibrational relaxation pathways. Most recently, we have investigated ASW, which is one of the most widely studied H-bonded networks. Indeed, this solid presents special surface water molecules, known as "dangling OH" molecules, able to accrete small molecules such as ammonia, water, or methanol, themselves potentially involved in the formation of amino acid precursors. In this talk, we will show that these dangling bonds are able to isomerise upon IR irradiation, rather than relaxing all injected energy through the H-Bond network, and also that their bands are inhomogeneous. The OH bond facing the H-Bond network seems to evolve independently of its free surface component.

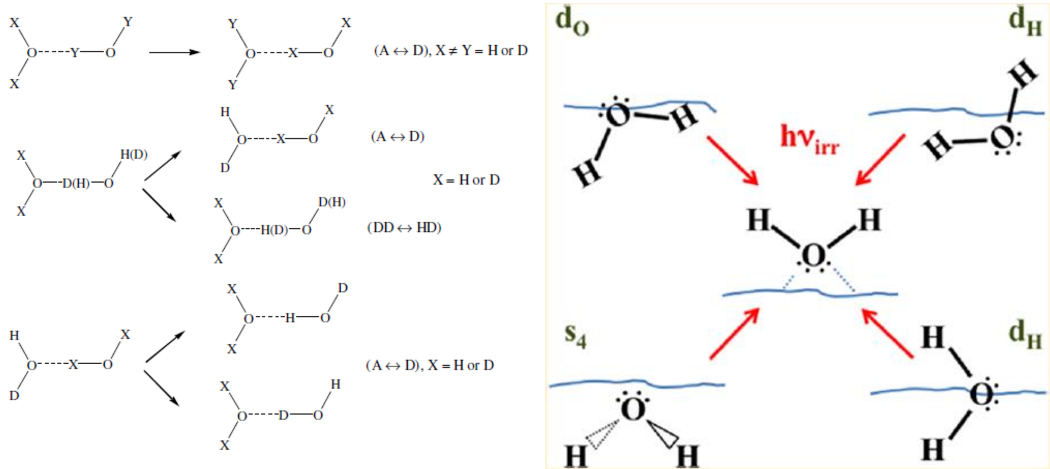

Figure 1 IR induced H-bond D-bond exchanges in water dimers[1] (left). IR induced isomerisation of ASW surface molecules[2] (right).

REFERENCES

1. S. Coussan, P. Roubin, J.P. Perchard, *Chemical Physics*, **2006**, *324*, 527.
2. J.A. Noble, C. Martin, H.J. Fraser, P. Roubin, S. Coussan, *Journal of Physical Chemistry Letters*, **2014**,*5*, 826-829.

OC-15

Near-infrared-induced conformational *cis-trans* switching in carboxylic acids isolated in cryogenic inert matrices

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It is well-known that the carboxylic acid fragment may adopt *cis* and *trans* conformations around the O=C−O−H dihedral angle. For simple aliphatic acids, the *cis* form bears the stabilizing H-bond-like OH···O interaction and is much more stable. The *trans* forms have high relative energies. Consequently, they have very small populations at room temperature and are difficult to be experimentally observed.

Using tunable narrow-band (fwhm < 1 cm^{-1}) light, it is possible to excite, in a very selective way, only a particular vibration, in molecules adopting a particular conformation. If the excitation has energy higher than the barrier for conformational isomerization, then such excitation can lead to depopulation of the initial conformer and to its transformation into another structure in the course of vibrational energy redistribution to the torsional coordinate. Usually it concerns excitation of an overtone of the OH stretching vibration with near-infrared light. If the barrier for conformational relaxation is high enough, not only the most stable structure, but also the higher-energy conformers may be trapped and stabilized in low-temperature matrices.

This contribution will cover some recent results obtained through collaboration between the Coimbra and Warsaw laboratories. Selected compounds such as squaric,[1] glycolic,[2] furoic,[3] oxamic,[4] and pyruvic[5] acids, and amino-acid alanine[6] were isolated in cryogenic inert matrices. New, previously unknown higher-energy conformers of these molecules were generated *in situ* by near-infrared excitations of the OH stretching overtones and characterized by vibrational spectroscopy. The relative stability of the *cis*- and *trans*- conformers in these systems will be correlated with the functional groups attached to the carboxylic fragment.

A spontaneous conversion of the photogenerated higher-energy conformers into the most stable forms of the studied compounds was also observed. These processes, occurring in matrices *via* proton tunneling, will be also addressed.

Acknowledgements

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REFERENCES

1. L. Lapinski, I. Reva, H. Rostkowska, et al., *J. Phys. Chem. A* **2013,** *117*, 5251.
2. A. Halasa, L. Lapinski, I. Reva, et al., *J. Phys. Chem. A* **2014,** *118*, 5626.
3. A. Halasa, L. Lapinski, I. Reva, et al., *J. Phys. Chem. A* **2015,** *119*, 1037.
4. A. Halasa, L. Lapinski, H. Rostkowska, I. Reva, M. J. Nowak, *J. Phys. Chem. A* **2015,** *119*, 2203.
5. I. Reva, C. M. Nunes, M. Biczysko, R. Fausto, *J. Phys. Chem. A* **2015,** *119*, 2614.
6. C. M. Nunes, L. Lapinski, R. Fausto, I. Reva, *J. Chem. Phys.* **2013,** *138*, 125101.

OC-16

Study of blue shifting hydrogen bond in fluoroform with Lewis bases (HCl, H_2O, and C_6H_6): A Matrix isolation infrared and *ab initio* studies

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In this work a comparative study between Fluoroform (CHF_3) and Lewis base (HCl, H_2O, C_6H_6) were carried out using matrix isolation infrared technique and *ab* initio computations. When CHF_3 and Lewis bases (HCl,H_2O,C_6H_6) were co-deposited with Ar at 12 K resulted in the formation of 1:1 CHF_3-Lewis base (CHF3-HCl,[i] CHF_3-H_2O, CHF_3-C_6H_6) adduct, which was evidenced from the shifts in the vibrational wavenumber of the modes involving the CHF_3 and Lewis base submolecules. Experimentally we observed the blue-shifting of the C-H stretching mode for the CHF_3-HCl, CHF_3-H_2O and CHF_3-C_6H_6. The experimental and computational results thus obtained will be compared with CHF_3-NH_3 [ii] adduct. To understand the nature of interaction between the CHF_3 and Lewis bases Atom in molecules (AIM) and the Natural bonding orbital analysis (NBO) were performed.

OC-17

Binding motifs of a microhydrated neurotransmitter: IR spectroscopy of rare gas-tagged protonated phenylethylamine and its water clusters

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The characterization of the three-dimensional structure of biologically relevant molecules, the role played by inter- and intramolecular interactions, especially with water which is ubiquitous in physiological media, and their ability to form charged groups, are key issues to be addressed to deepen the understanding of recognition phenomena at the molecular level in biological environments. Biomolecules are generally not neutral in physiological media, but protonated or zwitterionic. The conformation of these charged molecules and their solvation shell is thereby modified compared to neutral species. Here, vibrational spectroscopy, associated with quantum chemical calculations, has been applied to a protonated neurotransmitter, phenylethylamine (PEA), and its water clusters isolated in the gas phase. The results obtained for the rare gas-tagged PEA show that the protonation induces conformational locking of the monomer into a folded structure via a strong intramolecular NH$^+$...π interaction.[1] Monohydrated protonated PEA reveals that a very stable inclusion structure is experimentally generated, in which the water molecule is inserted between the positively charged amino group and the phenyl moiety of PEA, acting both as an hydrogen bond acceptor (NH...O) and donor (OH...π). A second isomer, for which the water is H-bonded to an external NH group is also found. The study of clusters formed by the addition of further water molecules allows for an accurate description of the first solvation shell of this protonated model neurotransmitter, mimicking its closest natural environment (Fig. 1).

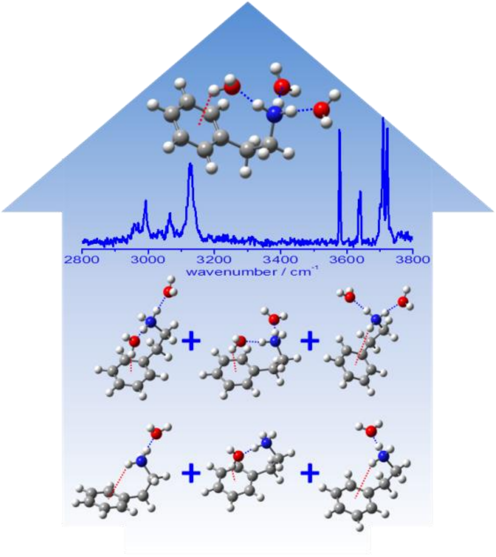

Figure 1 Most stable structures of H$^+$PEA-(H$_2$O)$_n$ (n = 1 - 3) calculated at the B3LYP-D3/aug-cc-pVTZ level of theory. The IR photodissociation spectrum of H$^+$PEA-(H$_2$O)$_3$-Ar is also represented.

REFERENCE

1. A. Bouchet, M. Schütz, B. Chiavarino, M. Elisa Crestoni, S. Fornarini and O. Dopfer, *Phys. Chem. Chem. Phys.*, 2015, DOI: 10.1039/C5CP00221D.

OC-18

NH – OC amide-amide H-bonds in peptides revisited in light of gas phase spectroscopy of β-peptides

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During the past decade, gas phase laser spectroscopy of isolated peptides obtained using sophisticated vaporization techniques and conformer-selective procedures, has generated a wealth of experimental data, documenting the strength of the H-bonding network of these species. This was done by recording the amide NH stretch spectrum on a wide variety of α-peptide conformations, identified by comparison with quantum chemistry calculations.[1-4]

Recent laser spectroscopic results obtained on β- and γ- peptides[5, 6] have demonstrated that NH – OC pure amide-amide interactions can be significantly stronger than those reported so far for isolated H-bonds in α-peptides, suggesting that H-bonds are not optimal in these biological species. In the present work, the unprecedented set of precise data on diverse H-bonds between amide groups, obtained as isolated H-bond in gas phase model systems, is used to analyze the reasons for such a frustration. The structures of these conformations, obtained from quantum chemistry (DFT-D at the RI-B97-D/TZVPP level of theory) and using theoretical tools (NBO and NCI analyses), confirm the frustrated nature of the H-bond in α-peptides, due to strong backbone constrains leading to quite distorted or elongated distances as well as NH – OC approaches with poor interactions of the NH group with the O lone pairs. In specific conformations,[1] however, or in modified β- or γ-peptides,[5, 6] constrains are gradually alleviated due to a larger number of degrees of freedom, leading to much stronger bonds.

This analysis also suggests reconsidering the assignment of the IR spectrum of $(Me\text{-}CO\text{-}NH\text{-}Me)_2$, the methyl-acetamide dimer, previously assigned to a linear NH – CO H-bond.[7] The present data suggest that, besides the H-bond, the interaction between the two acetamides could also be widely influenced by additional dispersive interactions (in particular involving the methyl groups),[8] which would be strong enough to also frustrate the formation of a strong linear H-bond, even in so simple a model system.

REFERENCES

1. W. Chin, M. Mons, J.-P. Dognon, F. Piuzzi, B. Tardivel and I. Dimicoli, *PCCP*, 2004, **6**, 2700-2709.
2. M. Gerhards, in *Principles of Mass Spectrometry Applied to Biomolecules*, eds. J. Laskin and C. Lifshitz, Wiley & Sons, Hoboken, NJ, 2006, pp. 3-62.
3. W. Chin, F. Piuzzi, I. Dimicoli and M. Mons, *PCCP*, 2006, **8**, 1033-1048.
4. E. Gloaguen and M. Mons, *Top Curr Chem*, 2014, in press; doi: 10.1007/1128_2014_1580 and ref. therein.
5. M. Alauddin, E. Gloaguen, V. Brenner, B. Tardivel, M. Mons, A. Zehnacker-Rentien, V. Declerck and D. J. Aitken, *Submitted*.
6. P. S. Walsh, R. Kusaka, E. G. Buchanan, W. H. James, III, B. F. Fisher, S. H. Gellman and T. S. Zwier, *J. Phys. Chem. A*, 2013, **117**, 12350-12362 and ref. therein.
7. M. Albrecht, C. A. Rice and M. A. Suhm, *J. Phys. Chem. A*, 2008, **112**, 7530-7542.
8. U. Adhikari and S. Scheiner, *J. Phys. Chem. A*, 2013, **117**, 489-496.

OC-19

Weakening of hydrogen bonds of biological structures by near infrared radiation

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Light causes electron excitation of atoms and molecules what may lead to activation of biological reactions. The result may be a modification of physicochemical properties of molecules, their conformational change (transformation of the structure) or even their disintegration. This may have important biomedical consequences leading to, eg., biostimulative therapeutic effects. The effects of most ranges of electromagnetic radiation on biological systems are well recognized, nevertheless, in case of near infrared radiation (NIR), the discussion still exists whether they are of photochemical or photophysical (temperature) nature.

Based on the work of Natzle *et al.*[1,2] it is clear that the absorption of NIR radiation and excitation of overtone oscillations can lead to the weakening or breakdown of the hydrogen bonds in water and an increase in the concentration of hydronium and hydroxyl ions. The authors indicate that the quantum yield of dissociation process is a function of the wavelength of the incident radiation and that the observed increase in the conductivity due to the reaction is caused by the vibrational excitation induced by a single photon. This process is not associated with a change in temperature and does not stop immediately after exposure.

It is known, that vibrational spectroscopy techniques are useful methods for examining tissues and their components, for analysis of many biological processes, as well as for diagnosis of disorders.[3] Combining Fourier Transform Infrared (FTIR) spectroscopy with the technique of Attenuated Total Reflection (ATR) has, in recent years, become a very powerful method in structural study of biological samples mainly due to important fact that the sample can be observed under physiological conditions.[4]

As energy of NIR radiation is much higher than the average energy of hydrogen bonds, it seems to be natural that hydrogen bonds between water molecules in solution or between water molecule and the membrane surface, may be modified. Spectral changes observed after NIR irradiation of a sample indicate decrease of energy of hydrogen bonds between water and polar groups of the amino acids (weakening of hydrogen bonds). It is suggested that the primary mentioned effect is action of NIR radiation on biological structures. It enhances the hydrophobic interactions. In these condition the side chains can easily aggregate.[5,6] This hypothesis is confirmed by our previous results, both on cells (erythrocytes and liposomes) and single molecules (amino acids) or macromolecules (proteins, DNA). Therefore, we suggest that this process occurs on every structure as global effect of NIR radiation on all biological media. Modifications of cell surface may result also in changes of its physicochemical properties. Such modifications can influence, for example, the mechanical resistance and fluidity of red cells.[7,8]

Acknowledgements

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REFERENCES

1. W.C. Natzle, C.B. Moore, D.M. Goodall, W. Frisch, J.F. Holzwarth, J Phys Chem **1981**, 85, 2882.
2. W.C. Natzle, C.B. Moore, J Phys Chem **1985**, 89, 2605.
3. A. Oleszko, S. Olsztyńska-Janus, T. Walski, K. Grzeszczuk-Kuć, J. Bujok, K. Gałecka, A. Czerski, W. Witkiewicz, M. Komorowska, *Biomed. Res. Int.* **2015**, art. 245607, 1.
4. M. Boulet-Audet, B. Byrne, S.G. Kazarian, Anal. Chem. 86, **2014**, 9786.
5. S. Olsztyńska-Janus, M. Komorowska, *Struct. Chem.* **2012**, *23***,** 1399.
5. S. Olsztyńska-Janus, M. Gąsior-Głogowska, K. Szymborska-Małek, B. Czarnik-Matusewicz, M. Komorowska, *Specific Applications of Vibrational Spectroscopy in Biomedical Engineering.* Chapter 4, In: Biomedical Engineering, Trends, Research and Technologies / Book 3, Edited by: M. Komorowska and S. Olsztyńska-Janus, InTech, Rijeka, Croatia, **2011**.
6. S. Olsztyńska-Janus, M. Komorowska, N. Dupuy, Appl. Spectrosc. **2006**, 60(6), 648.
7. T. Walski, L. Chludzinska, M. Komorowska, W. Witkiewicz, *Biomed. Res. Int.* **2014**, art. 162102, 1.
8. L. Chludzinska, E. Ananicz, A. Jaroslawska, M. Komorowska, Blood Cells, Mol. Dis. **2005**, 35, 74.

OC-20

The effect of large amplitude motions on the vibrational spectra of hydrogen bonded complexes

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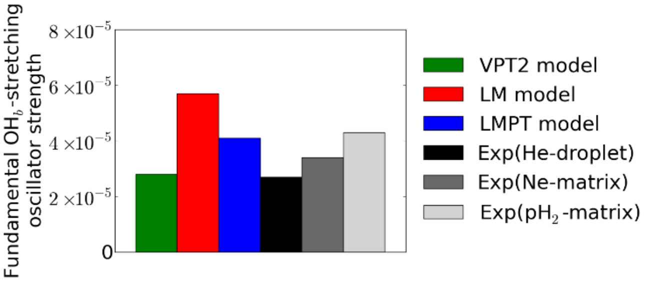
Equilibrium constants of the formation of gas-phase hydrogen bonded molecular complexes have been determined using a method combining experimental and theoretically simulated vibrational spectra. The equilibrium constants are determined from the monomer pressures and the pressure of the complex. The pressures of the monomers are measured experimentally, but the pressure of the complex is too low to be measured accurately. However, a combination of an experimentally measured integrated absorbance from Fourier-Transform Infrared spectra and a calculated oscillator strength allows us to determine the pressure of the complex and hence determine the equilibrium constant of the complex formation. We have developed a reduced dimensionality vibrational model to improve the accuracy of the calculated oscillator strengths at a reasonable computational cost. These are used to determine the pressures of the molecular complexes, thus improving the accuracy of the equilibrium constants.[1,2]

In the figure below, intensities obtained by our model on the water dimer are presented and compared with a full dimensional anharmonic vibrational calculation, a VPT2 calculation,[3] and existing experimental values. Our model, the Local Mode Perturbation Theory (LMPT) model, improves the results compared to the results of the simple Local Mode (LM) calculation at a reasonable cost compared to the full dimensional anharmonic VPT2 calculation. Application to larger bimolecular systems will be discussed.



REFERENCES

1. K. Mackeprang, H. G. Kjaergaard, T. Salmi, V. Hänninen, L. Halonen, *J. Chem. Phys.* **2014,** *140,* 184309
2. K. Mackeprang, V. Hänninen, L. Halonen, H. G. Kjaergaard, *J. Chem. Phys.* **2015,** *142,* 094304
3. H. G. Kjaergaard, A. L. Garden, G. M. Chaban, R. B. Gerber, D. A. Matthews, J. F. Stanton, *J. Phys. Chem. A,* **2008,** *112 (18),* 4324

OC-21

Solid state NMR study of materials for innovative medicine: sub-nano structure and dynamics of spin clusters containing hydroxyl groups

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Hydroxyapatites (HA) are widely applied in implantology, orthopedic and periodontal surgery. The structural organization and dynamics of hydroxyl groups in commercial and sol-gel derived nano-structured calcium hydroxyapatites (CaHA) have been studied by means of variable (0 – 9 kHz) MAS rate and high data point density measurements of $^{1}H–^{31}P$ cross-polarization kinetics.[1,2] The setting of the sampling frequency of $5{\cdot}10^{4}$ s^{-1} chosen in the present work allowed to reveal all spin interactions having the dipolar splitting $b \leq 25$ kHz that in the case of $^{1}H–^{31}P$ interaction means that the structures with the internuclear distances $r \geq 0.125$ nm could be resolved.[1] It is seen the resolved $^{1}H–^{31}P$ spin pairs at 0.21 and 0.25 nm, respectively, as well as ^{31}P interaction with the remote (ca 0.4 nm) protons from adsorbed water **(Figure 1)**. The ^{1}H and ^{31}P relaxation time T_1 and T_2 measurements have revealed that the dynamics of $^{1}H–^{31}P$ spin interactions in nano-structured CaHA is much slower than in CaHA containing amorphous phase.

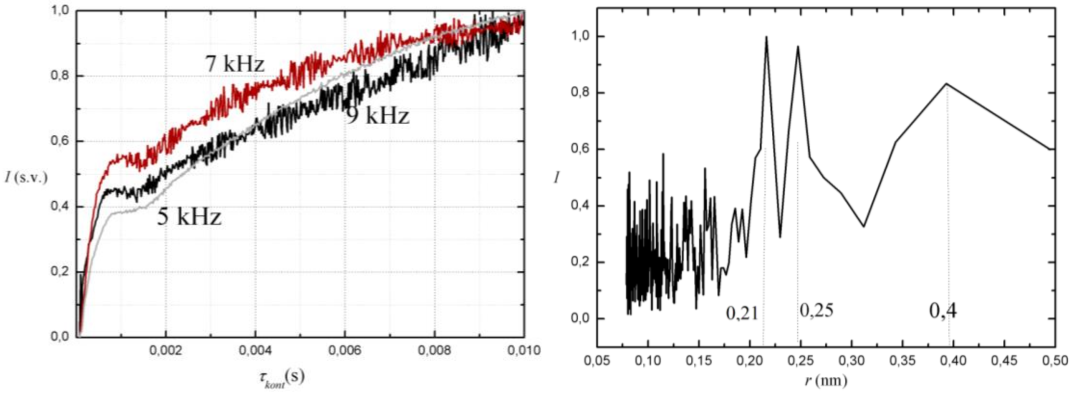

Figure 1 $^{1}H\rightarrow^{31}P$ CP MAS kinetics at the variable spinning rate and the resolved $^{1}H–^{31}P$ spin cluster structure in commercial CaHA sample.

Acknowledgements

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REFERENCES

1. V. Klimavicius, A. Kareiva, V. Balevicius, *J. Phys. Chem. C* **2014**, *118*, 28914.
2. L. Dagys, V. Klimavicius, J. Kausteklis, A. Chodosovskaja, V. Aleksa, A. Kareiva, V. Balevicius, *Lithuanian J. Phys*. **2015**, *55*, 1.

Experimental and theoretical evidences of intramolecular OH···F hydrogen bonding in saturated acyclic fluoroalcohols

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Organofluorine compounds are widely used in many different applications, ranging from pharmaceuticals and agrochemicals to advanced materials and polymers. It has been recognized that fluorine substitution can confer useful molecular properties such as enhanced stability and hydrophobicity. Another impact of fluorination is to influence the conformations of the organic molecules.

In the context of hydrogen bonding, fluorination is often considered to systematically increase the H-bond acidity, based on its electron-withdrawing effect on the vicinal H-bond donor group. We have however recently shown through FTIR measurements that an appropriate substitution can be responsible for its attenuation owing to intramolecular OH•••F interactions, in series of fluorocyclohexanols[1] and of fluorobenzyl alcohols.[2]

In this communication, we investigate the influence of fluorination on the conformational preferences and on the H-bond acidity of substituted acyclic fluorohydrins. The occurrence of intramolecular OH···F H-bonding is demonstrated trough a combined NMR and computational analysis. The relative stereochemistry of the fluorine and hydroxyl groups, the fluorination ratio and the alkyl substitution level are shown to significantly influence the occurrence of intramolecular OH···F interactions.[3]

An estimation of the intramolecular hydrogen-bond energies (E_{HB}) through Atoms in Molecules (AIM) analysis is shown to be significantly correlated to the experimental NMR $^{3h}J_{OH\cdots F}$ coupling constants. Our results show that modest conformational stabilization of the 6-membered ring hydrogen-bonded γ-fluoropropanol chair conformation is sufficient for it to be significantly populated, and that intramolecular OH•••F interactions can occur without structural rigidification.

REFERENCES

1. J. Graton, Z. Wang, A-M. Brossard, D. Monteiro, J-Y. Le Questel, B. Linclau, *Angew. Chem. Int. Ed.*, **2012**, *51*, 6176-6180.
2. E. Bogdan, G. Compain, K. Mtashobya, J-Y. Le Questel, F. Besseau, N. Galland, B. Linclau, J. Graton, *Chem. Eur. J.,* **2015,** *in press.*
3. B. Linclau, F. Peron, E. Bogdan, N. Wells, Z. Wang, G. Compain, C. Fontenelle, N. Galland, J.-Y. Le Questel, J. Graton, *J. Am. Chem. Soc.* submitted.

OC-23

Comparing second and third row elements, N, O, P and S, as hydrogen bond acceptor atoms

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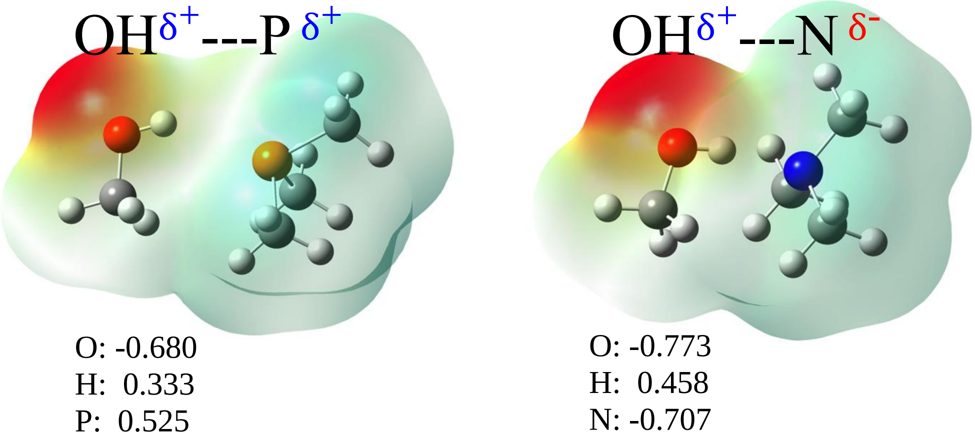
We have investigated a series of complexes containing OH-Y and NH-Y (Y = N, P, O and S) hydrogen bonds.[1-7] Fundamental XH-stretching vibrations were observed in room temperature gas phase spectra. Based on the measured XH-stretching frequency redshifts and quantum chemical calculations, we find that P, O and S are of similar acceptor strength and much weaker than N. From quantum chemical calculations we find that in the OH-N complexes the partial charges of H and N are positive and negative, respectively. However, in the OH-P complexes both H and P have positive charge. These charges are expected from the electronegativities of the atoms involved. However, the electrostatic potentials show a negative potential area on the electron density surface around the P lonepair that facilitates formation of hydrogen bonds. We correlate calculated hydrogen bonding parameters with experimental redshifts and determined equilibrium constants, in order to predict hydrogen bond strengths of complexes not yet observed.



REFERENCES

1. L. Du, H. G. Kjaergaard, *J. Chem. Phys. A.,* **2011,** 115, 12097-12104.
2. L. Du, J. R. Lane, H. G. Kjaergaard, *J. Chem. Phys.* **2012,** *136*, 184305.
3. L. Du, K. Mackeprang, H. G. Kjaergaard, *Phys. Chem. Chem. Phys.* **2013,** *15*, 10194-10206.
3. A. Hansen, L. Du, H. G. Kjaergaard, *Phys. Chem. Phys. Chem.*, **2014,** 16, 22882-22891.
5. A. Hansen, L. Du, H. G. Kjaergaard, *J. Chem. Phys. Lett.*, **2014,** 5, 4225-4231.
7. C. L. Andersen, C. S. Jensen, K. Mackeprang, L. Du, S. Jørgensen, H. G. Kjaergaard, *J. Chem. Phys. A.,* **2014,** 118, 11074-11082.

OC-24

N-oxide group as a proton acceptor in *p*-nitropyridine-*N*-oxide cocrystals

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The chemistry and applications of heterocyclic aromatic *N*-oxides recently have received much attention due to their usefulness in organic synthesis, metal organic chemistry, catalysis and pharmacy[1]. The relatively small number of multicomponent pyridine-*N*-oxide crystal structures[2], with respect to their importance is the main reason of undertaking research on this class of molecular complexes.

The main aim of this presentation concerns analysis of structural properties of *N*-oxide group and its intermolecular interactions in cocrystals of aromatic pyridine-*N*-oxides. The description of intermolecular interactions is completed by Hirshfeld surface analysis, a method which allows to identify individual types of intermolecular contacts and their impact on the complete crystal packing. A part of the presented studies is focused on theoretical DFT calculations and QTAIM[3] theory used for more detailed analysis of intermolecular interactions, i.e. hydrogen bonds in regions of *N*-oxide groups.

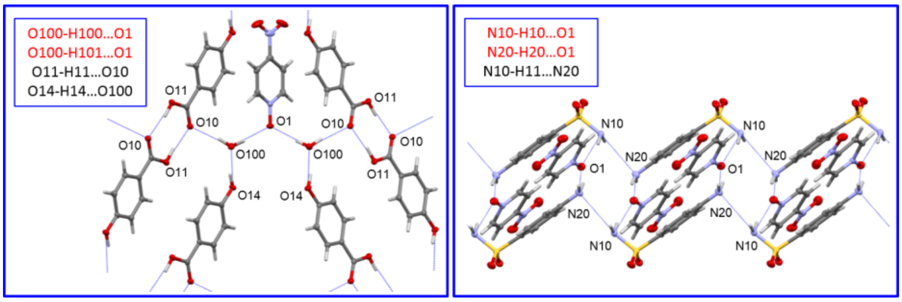

Figure 1 Net of hydrogen bonds in the hydrated structure of *p*-hydroxybenzoic acid - *p*-nitropyridine-*N*-oxide cocrystal ($C_5H_4N_2O_3 \cdot 2C_7H_6O_3 \cdot 2H_2O$) - left; structure of 4-aminobenzenosulfonamide - *p*-nitropyridine-*N*-oxide cocrystal ($C_5H_4N_2O_3 \cdot 2C_7H_6O_3$) - right

Acknowledgements

The theoretical computations with Gaussian 09 set of codes were carried out in Wrocław Center for Networking and Supercomputing (http://www.wcss.wroc.pl). Access to HPC machines and licensed software is gratefully acknowledged.

REFERENCES

1. J. A. Bull, J. J. Mousseau, G. Pelletier, A. B. Charette, *Chem. Rev*. **2012**, 112, 2642−2713.
2. F. H. Allen *Acta Crystallogr., Sect. B* **2002**, B58, 380-388.
3. R. F. W. Bader. *Atoms in Molecules - A Quantum Theory* **1994**, Oxford University Press: Oxford, UK.

OC-25

Evidence of polaron excitations in Raman spectra of oxalic acid dihydrate at low temperatures

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Oxalic acid dihydrate is an example of molecular crystal with a very strong short hydrogen bond, O···O distance being 2.49 Å at room temperature. Raman spectra revealed great richness of hydrogen bond transitions especially in the y(zz)x crystal orientation[1]. On cooling the system below 200 K one observes huge changes in the shape and position of the band observed around 1550 cm^{-1} at room temperature and moving to 1407 cm^{-1} at 10 K (Fig. 1). Also, a group of four bands occurs between 1152 and 1281 cm^{-1} below 200 K, gaining in strength on cooling, in spite of the fact that there is no phase transition reported for this crystal.

Bearing in mind the results of measurements of the proton T_1 relaxation time in the dependence of temperature, which become extremely prolonged around 200 K, we suggest that centre of inversion present in the $P2_1/c$ crystal structure of $(COOH)\cdot 2H_2O$ disappears below 200 K due to proton disorder, making it possible for strong infrared band observed at 1253 cm^{-1} at room temperature to appear as a group of bands in Raman spectra below 200 K.

Freezing of protons causes also self-trapping of an electron on one molecule inside the elementary cell, so called small polaron[2]. The energy levels of this polaron have strong directional dispersion – e.g. they appear as very broad bands in the x(zz)y direction, a bit narrower in the y(zz)x direction and comparable in bandwidth with hydrogen bond transitions in the z(yy)x and other directions. Their overlap with ν(OH) and δ(COH) as well as photo conduction properties observed for similar crystal KCOOCOOH make them extremely difficult to calculate, as their intensity depends on polarization proportional to the wave function of the crystal[3].

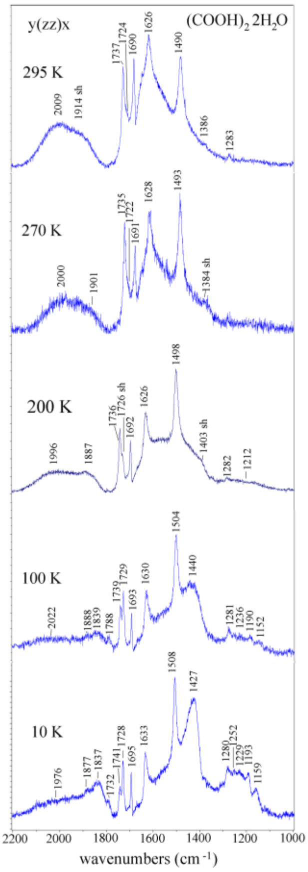

Figure 1 Broad bands at 1914 and 2009 cm^{-1} correspond to hydrogen bond transitions, while asymmetric band at 1550 cm^{-1} at 295 K which shifts to 1407 cm^{-1} at 10 K is assumed to be a polaron band.

REFERENCES

1. V. Mohaček Grošev, J. Grdadolnik, J. Stare, D. Hadži, *J. Raman Spectrosc.*. **2009,** *40*, 1605.
2. A. Levstik, C. Filipič, V. Bobnar, I. Levstik, D. Hadži, Phys. Rev. B **2006**, *74*, 153104.
3. D. Emin: Polarons, *Cambridge University Press* **2013**.

Posters

P-1

Detection of the OH-π hydrogen bond in complexes between trifluoroethanol and benzene, toluene and *m*-xylene

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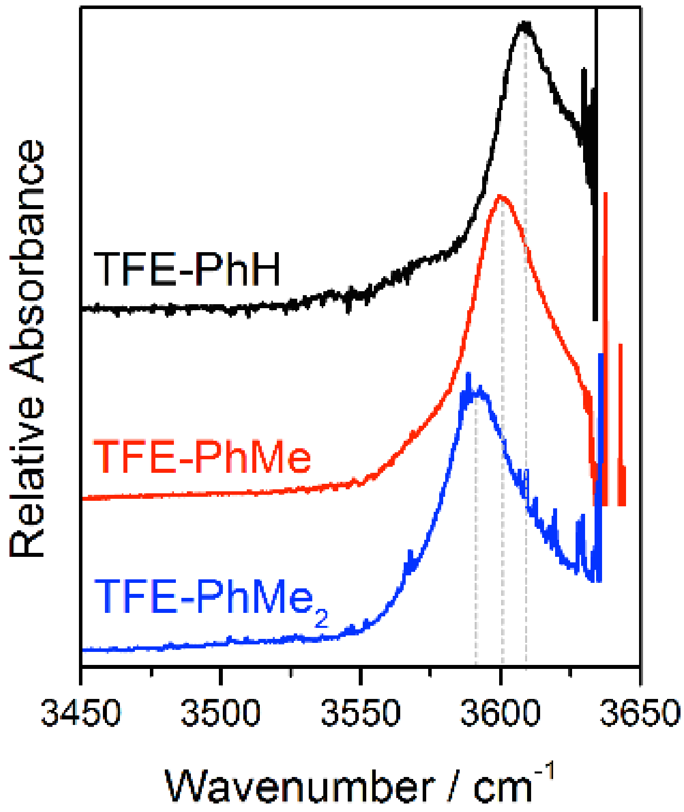
The OH-π hydrogen bond has been detected in bimolecular complexes formed between trifluoroethanol (TFE) and different phenyl groups (benzene, toluene and *m*-xylene). The OH-stretching vibration was recorded with a Fourier transform infrared spectrometer in the gas phase at room temperature. The OH-stretching vibration in the TFE-benzene complex is redshifted 50 cm^{-1} upon complexation. The addition of methyl groups in toluene and *m*-xylene add electron density to the π-cloud and result in increased OH-stretching redshifts. The equilibrium constants for complex formation are determined by combining the measured integrated absorbances and calculated intensities of the OH-stretching vibration.



P-2

FTIR study of fluoroform and methyl fluoride trapped in low temperature matrices. Evidence of a weak complex formation stabilized by blue shifting H-bond

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Fluoroform and fluoroform complexes with methyl fluoride were studied by means of infrared matrix isolation spectroscopy. Ar and N_2 were used as matrix gases. The F_3CH/M, FCD_3/M (within (0.5 – 7):1000 ratio) and $F_3CH/FCD_3/M$ mixtures were prepared by the standard manometric technique (M = Ar or N_2). The gas mixtures were sprayed onto gold-plated copper mirror held at 15 or 20 K by a closed cycle He refrigerator. FTIR spectra (resolution 0.1 cm^{-1}) were studied at 10 K in a reflection mode with a Bruker IFS 125 FTIR spectrometer. The spectra were recorded directly after matrix deposition and after its annealing to 28 – 32 K for 20 – 40 min. Results obtained for fluoroform in N_2 matrix have shown noticeable blue frequency shift effect for CH stretching vibration as compared to the gas phase[1] and Ar matrix results. Additionally lifting degeneracy effects were found which resulted in noticeable splitting the C-H bending and C-F stretching bands of *E* symmetry. Analyzing the IR spectra of F_3CH/FCD_3 mixtures in N_2 matrix it was concluded that the interaction between F_3CH and FCD_3 is of a blue shifting H-bond type, with the frequency shift $\Delta\nu^{c\text{-}m}$ of c.a. +16 cm^{-1} for CH stretching vibration of fluoroform. This value was compared with the data obtained earlier in the gas phase[1] and in liquefied noble and atmospheric (Ar, Kr, Xe, N_2) gas solutions[2,3]. The environment effect on the frequency shift has been shortly discussed.

Acknowledgements

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REFERENCES

1. K.S. Rutkowski, S.M. Melikova, R.E. Asfin, B. Czarnik-Matusewicz, M. Rospenk, J. Mol. Struct. **2014**, *1072*, 32
2. K.S. Rutkowski, S.M. Melikova, P. Rodziewicz, W.A. Herrebout, B.J. van der Veken, A. Koll, J. Mol. Struct. **2008**, *880*, 64
3. K.S. Rutkowski, P. Rodziewicz, S.M. Melikova, W.A. Herrebout, B.J. van der Veken, A. Koll, Chem. Phys. **2005**, *313*, 225

IR, Raman, and NMR spectra and X-Ray structure analysis of H-bonded complexes of $(CH_2Cl)_2POOH$

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Phosphinic acids form one of the strongest hydrogen-bonded dimers ($\Delta H \approx 25$ – 50 kcal/mol)[1,2]. The broad ν(OH) band (3500 – 1200 cm^{-1}) is observed in the IR spectra of dimers of these acids in the gas phase. To find the reason for spectrum perturbations, additional investigations of spectral, energy, and structural characteristics are required.

Different experimental methods were used to measure the spectra at room temperature in solutions and in the $(CH_2Cl)_2POOH$ crystal. The data on the structure of the acid crystal (bond lengths and angles) were obtained from the X-ray analysis of the acid crystal (Fig.1). FTIR ATR spectra and Raman spectra of the $(CH_2Cl)_2POOH$ crystal were recorded. An experiment on determination of chemical shifts in the NMR spectra was also conducted using solutions in CD_2Cl_2 at different concentration of the acid. In addition, the IR spectra of $(CH_2Cl)_2POOH$ solutions in CH_2Cl_2 with different concentrations were recorded.

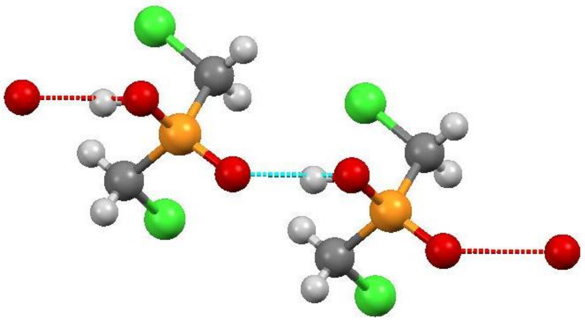

Figure 1 Geometry of the $(CH_2Cl)_2POOH$ crystal

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, project no. 15-03-04605. The IR, FTIR ATR, Raman spectra were recorded in the Center for Geo-Environmental Research and Modeling (GEOMODEL), X-Ray data were abtained in Center for chemical analysis and materials research, NMR spectra were obtained in Magnetic Resonance Research Centre of Research park of St. Petersburg State University.

REFERENCES

1. R.E. Asfin, G.S. Denisov, K.G. Tokhadze, *J. Mol. Struct.* **2006,** *790*, 11.
2. R.E. Asfin, G.S. Denisov, Z. Mielke, K.G. Tokhadze, Opt. Spectrosc. **2005**, *99*, 56.

P-4

Energetical, structural and vibrational properties of the $C_4H_6O_2$-$(H_2O)_n$ complexes by combined neon matrix / supersonic jet experiments and ab initio / DFT calculations

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The formation of non-covalent bonds and more particularly hydrogen bonds in weakly bound complexes bearing water plays a major role in many biological, atmospheric and astrophysical chemistry issues.[1] In our laboratory, we started few years ago a field of research aiming to characterize at a molecular level the hydration mechanisms within hetero-complexes by progressive solvation of water molecules.[2] In the present study, the objective is to bring deeper knowledge of intermolecular interactions between water molecules (up to twelve) and the symmetrical proton donor diacetyl ($C_4H_6O_2$) molecule by combined experimental and theoretical approaches.

In a first step, three nearly iso-energetically stable isomers (noted hereafter S1, S2 and S3) of the 1:1 $C_4H_6O_2$-H_2O complex were optimized using ab initio MP2-aug-cc-pvtz calculations and topological approaches.[3] Thanks to the observation of several isomer specific vibrational signatures from neon matrix (for all isomers) and jet-cooled experiments (for S1 and S2) coupled to infrared broadband spectroscopy, such a conformational landscape could be confirmed. Moreover, a reliable set of vibrational frequencies and anharmonic coupling constants has been derived from the spectral analysis of fundamental, harmonic and combination bands.

In a second step, the optimization of ten isomers of 1:2 $C_4H_6O_2$-$(H_2O)_2$ complex evidenced strong cooperative effects for the two most stable ones built from a water dimer interacting with a carbonyl acceptor site according to the S3 configuration. Beyond the 1:2 complex, step-by-step hydration mechanisms of diacetyl have been examined using the following theoretical strategy: (i) the choice of the appropriate DFT method able to reproduce at best geometrical and energetical properties of the CCSD(T)-F12 reference method, (ii) the searching of most stable isomers from 1:4 to 1:12, taking into account the symmetry of the diacetyl molecule.

Finally, the progressive hydration of diacetyl clearly shows that the first hydration layer was not reached with twelve water molecules. Hetero-molecular polymers having a hydration belt (diacetyl CO group surrounded by water molecules) are not the most stable ones but rather 3D geometries close to homo-molecular counterparts for which diacetyl interacts with a water polymer.

REFERENCES

1. A. Potapov and P. Asselin, *Int. Rev. Phys. Chem.* **2014**, 33, 275.
2. M. Cirtog, M.E. Alikhani, B. Madebene, P. Soulard, P. Asselin and B. Tremblay, J. *Phys. Chem*. **2011**, 115, 6688.
3. D. Dargent, E.-L. Zins, B. Madebène and M.E. Alikhani, accepted in *J. Mol. Modelling* (**2015**).

P-5

The initial stages of clustering of water molecules: matrix isolation FTIR/2DCOR study and the concept of combinatorial band broadening

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The FTIR spectra of water in argon matrix have been measured while heating the sample from T = 9 K with steps of 2K to 50 K. The main attention has been focused to the spectral range of O–H…O stretching vibrations at 2800-3800 cm^{-1} (**Figure1**). 2D correlation (2DCOR) analysis[1] of FTIR spectra as well as the non-linear band shape fitting have been carried out and the band parameters determined. The results have been compared with data on water clustering in hydrophobic solvents.[2] The combinatorial broadening has been proposed to be the most reliable factor forming diffuse O–H stretching bands in H-bond clusters at these conditions.

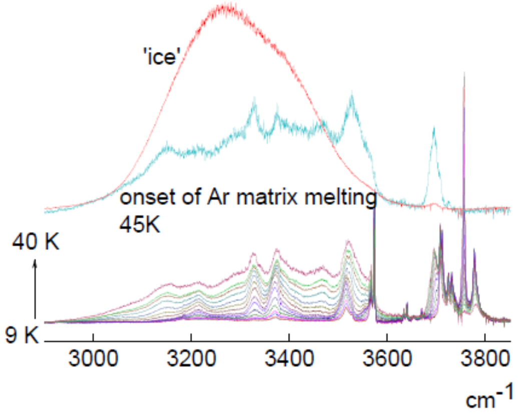

Figure 1 Temperature evolution of FTIR spectra of water in argon matrix.

Acknowledgements

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REFERENCES

1. I. Noda, Y. Ozaki, Two-Dimensional Correlation Spectroscopy - Applications in Vibrational and Optical Spectroscopy, Wiley, Chichester, **2004**.
2. T. Köddermann, F. Schulte, M. Huelsekopf, R. Ludwig, *Angew. Chem. Int. Ed.*, **2003**, *42*, 4904.

P-6

^1H, ^{13}C, ^{17}O NMR spectroscopy and X-ray study of media *versus* temperature effects on proton dynamics in hydrogen bond in picolinic acid *N*-oxide

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Continuing the studies of the large amplitude proton dynamics in the short H-bonds in liquid and crystalline phases,[1,2] we report new NMR data on picolinic acid N-oxide in the solvents of increasing polarity (from chloroform to H_2O) and temperature (– 40 ^oC to + 80 ^oC), as well as in the crystalline state obtained by ^{13}C CP/MAS and single crystal XRD. The chemical shifts of –COOH (^1H), N–O1 (^{17}O) and the ring carbon C3 (^{13}C) (see **Figure 1**) have been used for diagnostic exploring the influence of media and temperature on the location of the proton along H-bond.

It was deduced that the increasing solvent dielectric constant and temperature have an opposite effect: the H-bond proton is more and more shifted to the acceptor side (O1) going from CHL to H_2O, whereas at the heating it moves backwards to O2. The crystalline force field was found to have much stronger effect facilitating proton transfer than the solvent reaction field of any used solvents.

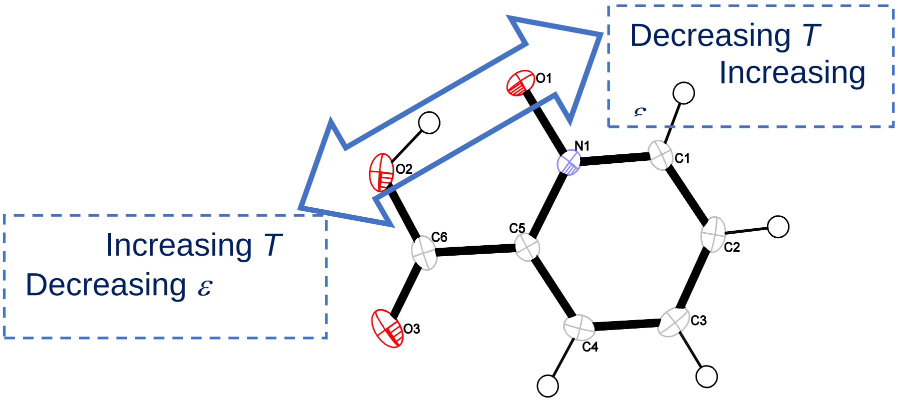

Figure 1 Picolinic acid *N*-okside (X-ray diffraction data: *T* = + 20 ^oC; Oxford Diffraction Xcalibur (TM) Single Crystal X-ray Diffractometer with Sapphire CCD Detector, TU Darmstadt).

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Funding from the European Community’s social foundation under Grant Agreement No VP1-3.1-ŠMM-08-K-01-004/KS-120000-1756 is acknowledged.

REFERENCES

1. V. Balevicius, K. Aidas, I. Svoboda, H. Fuess, *J. Phys. Chem. A* **2012**, *116*, 8753.
2. V. Balevicius, Z. Gdaniec, K. Aidas, *Physical Chemistry Chemical Physics,* **2009**, *11*, 8592.

P-7

Bonding and stability of complexes originating from sulfamic acid.

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Sulfamic acid has wide application in industry and has been suggested to act as an effective nucleation agent for the formation of aerosols and cloud particles. The ESI MS study evidenced that both singly and doubly charged hydrogen bonded clusters are formed when the acid is electrosprayed from water solutions. The largest identified clusters are built of 20 monomers. In contrast with the gas phase, aqueous solution does not favor the formation of (ASA)n aggregates.[1] Stability of the aggregates was the subject of DFT calculations whose results suggest that the doubly negatively charged anionic structures observed in electrosprayed mass spectra may be formed in the association process of smaller monocharged anions.

In the argon matrixes comprising thermolysis products of sulfamic acid, in addition to $H_3N{\cdot}SO_3$, the $H_3N\text{-}SO_3{\cdot\cdot}NH_3$ complex was also identified for the first time with the use of infrared spectroscopy.[2] So far this is the second known adduct (apart from $SO_2{\cdot}(NH_3)_2$) in which a molecule with a single acceptor center serves as an electron acceptor for two electron donor molecules. Here we present the results of a range of theoretical methods applied to explain bonding situation and relative stability of competing structures - $H_3N\text{-}SO_3{\cdot\cdot}NH_3$ adduct and $(H_3N)_2SO_3$ cyclic complex stabilized by N-H··N and N-H··O hydrogen bonds.

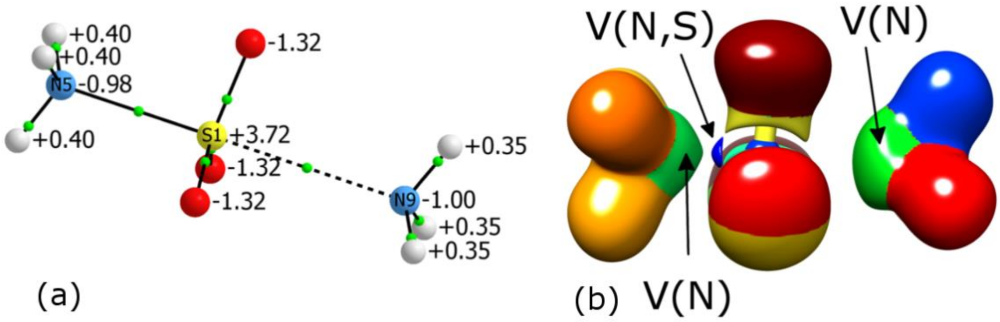

Figure 1 T Molecular graph and AIM atomic charges for the $H_3N\text{-}SO_3{\cdot\cdot}NH_3$ complex. The smallest spheres represent bond critical points (BCPs). (a) Localization domains of electron localizability indicator plotted for ELI-D(r)=1.15.(b)

REFERENCES

1. M. Pszona, K. Haupa, A. Bil, K.Mierzwicki, Z.Szewczuk, Z.Mielke *J. Mass Spect.* **2014,** *50*, 127.
2. K. Haupa, A.Bil, Z. Mielke, *to be published*.

P-8

Theoretical study of energies, structures and vibrational spectra of H(D)Cl complexed with dimethyl ether

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Interaction energies, molecular structure and vibrational frequencies of the binary complex formed between H(D)Cl and dimethyl ether have been calculated using quantum-chemical methods. Equilibrium and vibrationally average structures of the complex was calculated using DFT B3LYP and B2PLYP-D methods, as well as *ab initio* second-order Møller-Plesset scheme. Harmonic and anharmonic vibrational frequencies have been calculated for the complex. Phenomenological model describing anharmonic-type vibrational couplings within hydrogen bond was developed for explaining unique broadening and fine structure as well as an isotope effect for the HCl and DCl stretching IR absorption bands in the gaseous complexes with dimethyl ether as an effect of hydrogen bond formation. Simulations of the rovibrational structure of the HCl/DCl stretching bands were performed and results were compared with experimental spectra.

P-9

Diastereospecific conformational properties of neutral, protonated and radical cation forms of (1R, 2S)-cis and (1R, 2R)-trans amino-indanol

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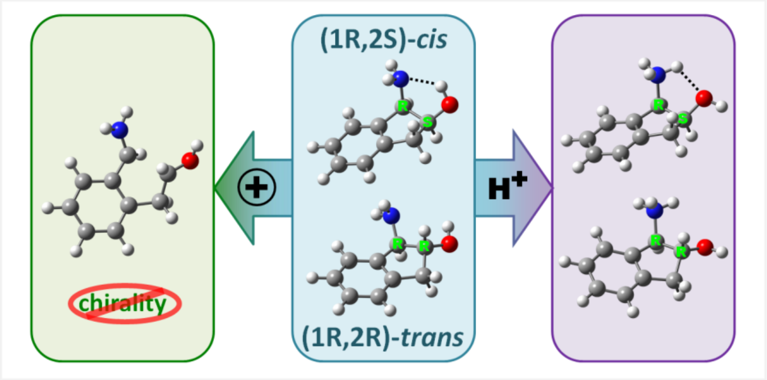
Stereochemistry plays an important role in the activity of biomolecules and their interaction with the environment. This is especially true for molecules bearing two adjacent chiral centres, which can be of identical (threo form) or opposite chirality (erythro form). *Cis*-amino-indanol is part of peptoids used as potent inhibitors of the HIV protease and the efficiency of the antiviral drug demands proper stereochemistry of this sub-unit. Moreover, since life chemistry involves species in different pH and redox states, the study of protonated or cationic species in parallel to that of the neutral is justified. The aim of this work is therefore to compare the structure of *cis*-(1S,2R) (erythro) and *trans*-(1R,2R) (threo) 1-amino-2-indanol isolated in a supersonic expansion, either neutral (AI), ionized (AI^+), or protonated (H^+AI).[1] To this end, the information gained from IR-UV double resonance experiments on neutral *cis*- and *trans*-AI is compared to those obtained by IR photodissociation for the radical cation and protonated forms. Quantum chemical calculations are conducted as a support to the interpretation of the vibrational spectra.

The two diastereomers differ by the steric constraints in the alicyclic part of the molecules: in *cis* AI and H^+AI forms, the formation of an intramolecular H-bond is sterically favoured relative to *trans* AI, whose direction changes upon protonation (OH...N vs. NH...O). Protonation is found to act as a conformational filter for *cis*-AI corresponding to a reduction of the conformational space induced by the protonation. Moreover, ionization induces disappearance of chirality effects by ring opening. This cleavage happens for both equatorial and axial conformations of the substituents, and for both *cis* and *trans* forms of the cation. It leads to the formation of a distonic ion for which the chirality of AI is lost and therefore results in the identity of the initial *cis* and *trans* forms.



REFERENCE

1. A. Bouchet, J. Klyne, G. Piani, O. Dopfer and A. Zehnacker, *Phys. Chem. Chem. Phys.*, 2015, DOI: 10.1039/C5CP00576K.

P-10

The influence of proton acceptor on the Δν$_{CH}$ complexation shift in C-H···B hydrogen-bonded complexes

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Positions of the ν(CH) stretching band for more than thirty C-H proton donors complexed with a number of proton acceptors were calculated at the B3LYP/6-311++G(d,p) level (Fig.1.). These calculations revealed that direction of the ν(CH) band shift upon complex formation, related to the charge born by the hydrogen atom of the proton donor, depends strongly on the ability of the proton acceptor to create a complex. Large positive (blue) complexation shifts were found for proton acceptors characterized by small values of proton affinity (PA), while large negative (red) shifts were observed for acceptors with high PA.

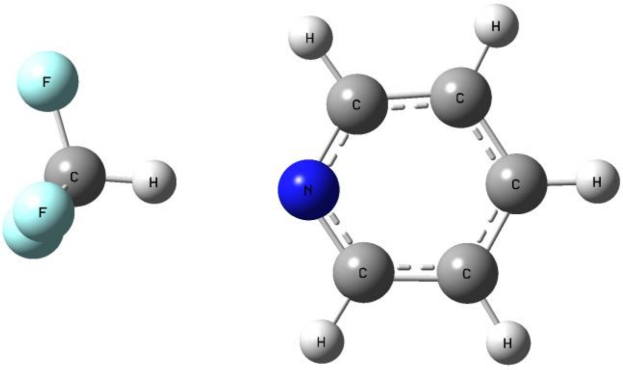

Figure 1 The optimised structure of F_3CH – pyridine complex.

REFERENCES

1. R. Szostak, *Chem. Phys. Lett.,* **2011** *516* 166.
2. R. Szostak, *J. Raman Spectrosc.*, *2011 42* 1185.

P-11

The properties of NH···O H-bonds in dehydropeptides

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The introduction of an α,β-dehydroamino acid into a peptide chain changes not only the conformational properties of the backbone and side chain but in some cases may also affect the strength of the H-bonds formed by these residues and alter the association tendency of the peptide[1,2]. It was shown, by the *ab initio* calculations, that the strength with which a peptide group can form a hydrogen bond varies with the internal conformation of the peptide chain.[3,4] The α,β-dehydroamino acids can adopt specific conformation β, characterized by the angles (ϕ, ψ = -40°, 130°), which is not too easy accessible for common amino acid residues.5 It is interesting to compare the strength of hydrogen bonds formed by model peptides and dehydropeptides in different conformations.

We calculated the energy of the NH···O hydrogen bond between a diamide and a proton acceptor molecule (Fig.1.). All calculations were carried out by the MP2/6-31++G** method. This quantum chemical technique was use to dependably reproduce the strength of the H-bonds.

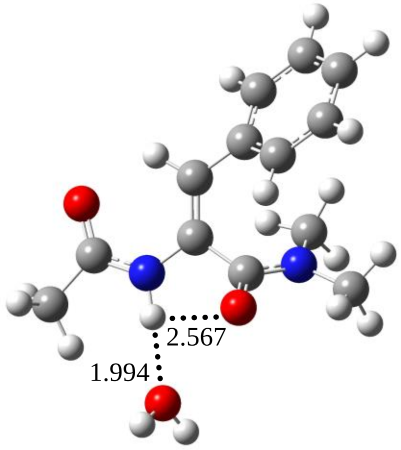

Figure 1 Example of studied system

The hydrogen bonds in the dehydropeptide - water systems are stronger than those in saturated diamide. This is probably due to larger polarizability of the N–H and C=O groups in α,β-dehydro residue. The different properties of these groups result from their participation in the π-conjugation with the $C^{\alpha}=C^{\beta}$ double bond.

REFERENCES

1. M. A. Broda, M. Rospenk, D. Siodłak, B. Rzeszotarska *J. Mol. Struct*. **2005** *740* 17.
2. M. A. Broda, B. Rzeszotarska *Acta Biochim*. *Pol*. **2006** *53* 221.
3. S. Scheiner *J.Phys.Chem.B* **2007** *111* 11312.
4. S. Scheiner *Int. J. Quantum Chem.* **2010** *110* 2775.

P-12

Intensities of sum and difference transitions in the ν(HF) absorption band of RB···HF complexes

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The ν(HF) absorption band of RB...HF complexes observed at room temperature is a superposition of the fundamental H-F transition, hot transitions from excited states of low-frequency modes, and sum and difference transitions involving high-frequency and low-frequency modes. Information on the mechanisms of band shape formation can be obtained from comparison of experimental and theoretically reconstructed spectra. An interesting problem is why the sum and difference shoulders are present in the ν(HF) band of some RB...HF complexes (e.g., $(CH_3)_2CO$…HF) and are virtually unseen in the spectra of other related complexes (e.g., water…HF). This problem can be solved using the potential energy and dipole moment surfaces and the vibrational wave functions calculated in the same approximation for different complexes. We consider the HF absorption band of complexes formed by HF with water, HCN, $(CH_3)_2O$, and $(CH_3)_2CO$. The experimental spectra are compared with the theoretical spectra reconstructed using the spectral parameters derived from variational solutions of multidimensional anharmonic vibrational equations with sufficiently accurate ab initio potential energy and dipole moment surfaces. It is found[1] that, in the spectra of these four compounds, the intensities of sum and difference transitions involving the H-F and H-bond stretching vibrations primarily depend on the degree of mixing of wave functions of these modes rather than on the behavior of the dipole moment functions. Similar effects on the combination transitions involving bending modes, as well as the role of the reduced mass of the complex and the rotational constants of monomers, are also examined.

Acknowledgements

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REFERENCES

1. V.P. Bulychev, K.G. Tokhadze, *Vibr. Spectrosc.* **2014,** 73, 1.

P-13

Manifestations of anticooperativity in energy and structural characteristics of $F^-\times(HF)_n$, $AlkF\times(HF)_n$ and $HalF\times(HF)_n$ clusters: hydrogen bond F...HF

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Mutual influence of H-bonds in the molecular systems forming multiple bonds (non-additivity) leads to their polarization and the strengthening (cooperativity) or weakening (anticooperativity). The objective of this study was to conduct a systematic study of the manifestations of anticooperativity over a large range (45 - 1 kcal/mol) of energies of H-bonding. Properties of twenty five H-bonded complexes, namely, $F^-\times(HF)_n$ (n = 1-6), $AlkF\times(HF)_n$ (Alk = *t*-Bu, *i*-Pr, Et, Me; n = 1-3), $XF\times(HF)_n$ (X = H, Br, Cl; n = 1-2), and FF…HF, in which a fluorine anion or an atom participates in H-bond formation as the acceptor, are calculated by the MP2/6-31++G** method. For the first time, the energies, geometrical parameters and vibrational harmonic frequencies are obtained for the series of the $F\times(HF)_n$ clusters, where n ranges from one to the maximum number of HF molecules in the first coordination sphere. The addition of each subsequent ligand HF in complexes with the fixed base leads to a decrease in the energy and corresponding change of the structural parameters. It was shown that non-additivity of the interaction is most strongly pronounced in the energy and vibrational frequency values. In the series of clusters $F^-\times(HF)_{1-6}$ the H-bond energy diminishes from 45 to 22 kcal/mol per bond, the relative change decreases from 17 to 12%, and remains constant in the series $AlkF\times(HF)_{1-3}$ in the energy range 8 - 5 kcal/mol per bond. For weak bonds (5 - 2 kcal/mol per bond) in complexes $CH_3F\times(HF)_{1-3}$ and $XF\times(HF)_{1-2}$ the anticooperativity increases to 18-20%. The frequency shift of the stretching vibration of a ligand decreases monotonically in the series studied. The results obtained show that the geometric parameters are less sensitive to the mutual influence, and anticooperativity is more pronounced in the hydrogen bridge length *R*(FF) than in the *r*(HF) distance of proton donor molecule. For strong bonds the length of the hydrogen bridge increases at each step by the 0.07 - 0.08 Å, the relative change slowly decreases from 3.1 to 2.8%; the magnitude of *r*(HF) is reduced by ~0.2 Å, and anticooperativity falls by more than on order of magnitude, from 13 to 0.7%. In neutral complexes $AlkF\times(HF)_n$ the *R*(FF) distance lengthens at each step by the 0.04 - 0.05 Å, anticooperativity is equal to 1.5 - 2%, and the bond *r*(HF) is reduced by 0.003 - 0.002 Å, that is 0.3 - 0.2%. For complexes $AlkF\times(HF)_n$ and $XF\times(HF)_{1-2}$ the length of the CF and XF bonds, adjacent to the hydrogen bridge, also increases systematically. For $XF\times(HF)_{1-2}$ systems the lengthening of the *R*(XF) bond is noticeably smaller, 0.3 - 0.2%. On the formation of each hydrogen bond the XF bond length changes stronger than of the HF bond. The data obtained allowed us to construct correlations between the energy, spectral and geometrical parameters of H-bonded complexes F...HF, which are still presented in the literature very poorly.

Acknowledgements

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P-14

Anharmonic calculation of HONO and its H-bonded complex with NH_3. Spectroscopic effects of H/D substitution and *cis*–*trans* transition

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Nitrous acid (HONO) is one of the simplest systems that possess different stable *trans* and *cis* isomers. This makes this compound and its complexes an attractive system for studies by theoretical methods. The purpose of our study is to perform nonempirical quantum-mechanical calculations of the frequencies and absolute intensities for fundamental transitions of HONO and HONO$\cdots$$NH_3$ complex, to examine the influence of *cis*-*trans* transition and H/D substitution on the form of vibrational modes and spectral parameters.

The equilibrium geometry, potential energy and dipole moment surfaces of these compounds are calculated in the MP2/aug-cc-pVTZ approximation. The frequencies and absolute intensities for transitions between vibrational states of the considered species are derived in the harmonic approximation and from the variational solutions of anharmonic Schrödinger equations in one to four dimensions with the potential energy and dipole moment surfaces calculated in the space of mass-weighted normal coordinates. The geometrical parameters of these systems are evaluated by averaging over the ground state or excited states with the use of vibrational wave functions. We also analyze the reasons for the changes in the band intensities on *cis*-to-*trans* passage and on H/D substitution. The calculated results demonstrate that the isotope effects on transition intensities are more significant than similar effects on frequencies. For example[1,2], the difference between the frequencies of the ν_2 fundamental mode in $NH_3$$\cdots$trans-HONO and $NH_3$$\cdots$trans-DONO is as small as 3.6%, whereas the anharmonic intensity for this transition in the lighter complex is a factor of 2.7 lower than in the heavier complex. The calculated values of fundamental frequencies and intensities are in good agreement with the available experimental results.

Acknowledgements

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REFERENCES

1. V.P. Bulychev, M.V. Buturlimova, K.G. Tokhadze, *J. Phys. Chem. A* **2013**, *117*, 9093.
2. V.P. Bulychev, M.V. Buturlimova, I.K. Tokhadze, K.G. Tokhadze, *J. Phys. Chem. A* **2014**, *118*, 7139.

P-15

Influence of enflurene, halothane, isoflurane and sevoflurane on the chain-melting phase transition of DPPC liposomes. Near-infrared spectroscopy studies supported by PCA analysis.

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The effect of four inhalation anesthetics on the chain-melting phase behavior of dipalmitoylphosphatidylcholine (DPPC) liposomes was studied using Near-infrared spectroscopy (NIR). The PCA analysis was applied to regions of NIR spectra associated with the first overtones of the symmetric and antysymmetric stretching vibrations of CH_2 groups of lipid aliphatic chains. All anesthetics significantly reduced temperature of lipid chain-melting phase transition accompanied by an increase in gauche conformers of lipid CH_2 groups and by a formation of the interdigitated lipid phase. The linear decrease in phase transition temperature as a function of a rise in anesthetic content was observed for halothane and sevoflurane. Additionally, sevoflurane induced the highest phase temperature decrease as a result of the most effective conformational membrane fluidization, which was caused by the interactions of this molecule with DPPC compounds. In case of enflurene and isoflurane, a similar character of changes of the trans-gauche isomerization was observed. Moreover, when the interdigitated lipid phase was dominated at higher enflurane and isoflurane concentrations, the phase temperatures were almost constant and independent on a further increase in admixture amount.

A good agreement with the literature data referred to the anesthetic/DPPC membranes studied by many other techniques[1,2] showed that NIR could be applied to the studies in conditions where the MIR measurements cannot be done.

Acknowledgements

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REFERENCES

1. N. Hauet, F. Artzner, F. Boucher, C. Grabielle-Madelmont, I. Cloutier, G. Keller, P. Lesieur, D. Durand, M. Paternostre, *Biophys. J.* **2003**, *84*, 3123.
2. M. Engelke, R. Jessel, A. Wiechmann, H.A. Diehl, *Biophys. Chem.* **1997**, *67*, 127.

P-16

The influence of DFT functional on AIM parameters of hydrogen bonds in crystal structures of the 2-substituted pyrroles – the benchmark studies

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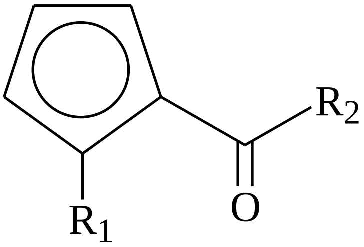
All atomic and molecular properties are governed by the electron density distribution. Thus, the methods that deal with the analysis of the electron density distribution should have a particular appeal for chemists and help to understand the electron structure of molecules and thus interactions. Nowadays, the very powerful method in investigating inter- and intramolecular interactions is Quantum Theory of Atom in Molecules (QTAIM) introduced by Bader.[1]

In this presentation we investigate the influence of type of DFT functional on QTAIM calculations. For initial studies we chose model system taken from two crystal structures of pyrrole-2-yl-dichloromethyl ketone (Scheme 1). For complexes with geometry taken from experiment we performed DFT calculations using various functionals. Additionally, results of MP2 calculations were used as a reference data.



Scheme 1.
Structure of the 2-substituted pyrroles

I *R_1=H, R_2=$CHCl_2$*
II *R_1=CH_3, R_2=$CHCl_2$*

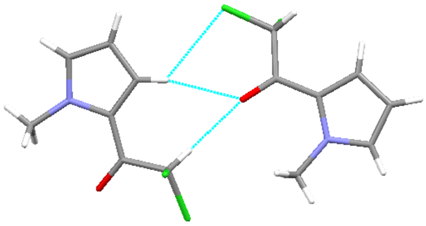


Figure 1. H-bond dimer motif in crystal structure of compound II

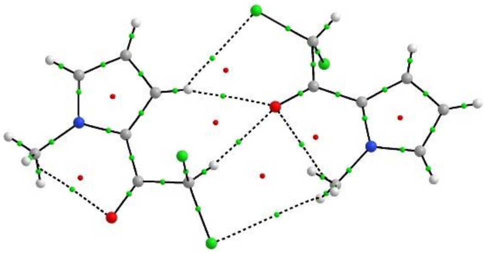


Figure 2. The molecular graph of dimer of compound II

Acknowledgements

Calculations using software Gaussian09 were made in the Wroclaw Centre for Networking and Supercomputing.

REFERENCES

1. R.F.W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, New York, **1990.**

P-17

The crystal structure of the new polymorph of methyl 3,4-dicyano-1-methyl-2,5-diphenylpyrrolidine-3-carboxylate

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Two polymorphs of *methyl 3,4-dicyano-1-methyl-2,5-diphenylpyrrolidine-3-carboxylate* were obtained in the recrystallization using two different solvent mixtures. The structure I, from petroleum ether / methylene chloride, crystallized in orthorhombic crystal system in $Pna2_1$ space group, while structure II,[1] from ethanol / methylene chloride, crystallized in monoclinic system in $P2_1/c$ space group.

The crystallographic calculations and comparative analysis of the geometry of the both structures show the clear difference in molecules organization and the formation of intra- and intermolecular interactions. A small difference in the geometry of molecules in both structures and a large difference in crystal packing, suggest a packing polymorphism. The Hirshfeld surfaces analysis[2] and the “fingerprint plots” analysis confirmed this thesis.

Moreover, for both structures of the title compound the periodic calculations in Crystal09[3] were performed. The formation energy of a molecular crystal, obtained as a difference between the energy of the bulk and the sum of the energies of isolated molecules, differs by about 3kcal/mol only.

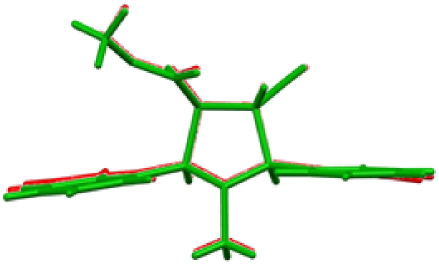

Figure 1 Superposition of molecules of both polymorphs, in red – $Pna2_1$, in green – $P2_1/c$

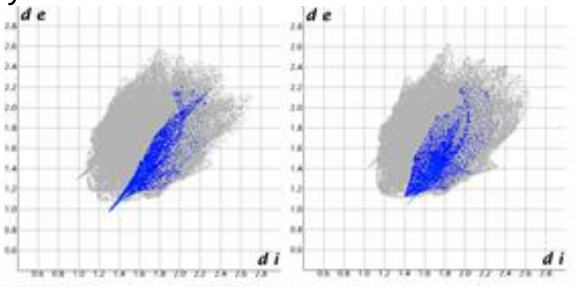

Figure 2 Fingerprint plots for O…H interactions existing in the crystal structures of both polymorphs, $Pna2_1$ (left) and $P2_1/c$ (right)

Acknowledgements

Calculations using software Crystal09 were made in the Wroclaw Centre for Networking and Supercomputing.

REFERENCES

1. G. Mlostoń, K. Urbaniak, M. Domagała, A. Pfitzner, M. Zabel and H. Heimgartner, *Helv. Chim. Acta*, **2009**, 92, 2631.
2. M.A. Spackman, D.Jayatilaka, *CrystEngComm.*, 2009, **11**, 19; M.A. Spackman, J.J. McKinnon, D. Jayatilaka, *CrystEngComm*, **2008**, 10, 377.
3. R. Dovesi, R. Orlando, B. Civalleri, C. Roetti, V. R. Saunders, and C. M. Zicovich-Wilson, *Z. Kristallogr*. 2005, **220**, 571 ; R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D’Arco, and M. Llunell, *CRYSTAL09 User's Manual*, University of Torino, Torino, **2009**.

Cooperativity of halogen – halogen bonding

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Structural motif found in crystal structure of anti α-bromoacetophenone oxime[1] (Figure 1) is a starting point for the study of halogen – halogen interactions. Recently, cooperativity of halogen – halogen bonding has been investigated for a model system being a bromomethane tetramer that reproduces the halogen – halogen bonded motif[2] (Figure 1) present in the crystal structure.

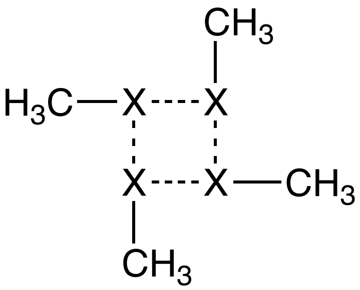

Figure 1 Structural motif in a model system.[2]

However, the source of synergy in such a system remains unknown. In the present study various model systems are investigated to reveal the origin of cooperativity in the tetramers bonded with halogen bonds.

To reach the above-mentioned goal, Morokuma-type energy decomposition analysis scheme[3] (EDA) implemented in ADF program[4] is applied. The MO analysis is also performed to fully understand the phenomenon of halogen – halogen interaction synergy in a tetramer.

REFERENCES

1. J. B. Wetherington, J. W. Moncrief, *Acta Crystallogr*. B **1973**, *29*, 1520.
2. J. Dominikowska, M. Palusiak, *Chem. Phys. Lett*. **2013**, *583*, 8.
3. K. Morokuma, *J. Chem. Phys.* **1971**, *55*, 1236.
4. ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

Matrix-isolation and *ab initio* study of the HXeCCXeH···HCCH complex

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Noble-gas hydrides (HNgY) constitute an interesting family of noble-gas compounds.[1] Due to the relatively weak bonding and large dipole moments, these molecules are strongly affected by interactions with other species and the hosts.[2] The H–Ng stretching frequency is sensitive to complex formation and can provide important insights on weak intermolecular interactions. HXeCCXeH is an unusual noble-gas hydride because it contains two noble-gas atoms,[3] and the interaction of this molecule with other species is of particular interest.

Here we report on the *ab initio* study and experimental identification of the HXeCCXeH···HCCH complex. In the most stable structure, HXeCCXeH forms a π H-bond by accepting a proton from the acetylene molecule (Fig. 1). This interaction stabilizes the H–Xe bonds and results in a calculated blue shift of the ν_{as}H–Xe mode of 22 cm^{-1} relatively to the HXeCCXeH monomer (MP2/aug-cc-pVTZ). In order to prepare the HXeCCXeH···HCCH complex experimentally, HCCH/Xe matrices are photolyzed at 250 nm and then annealed at 55–65 K. The experimentally observed blue shift of the H–Xe stretching mode is about 12-17 cm^{-1}.

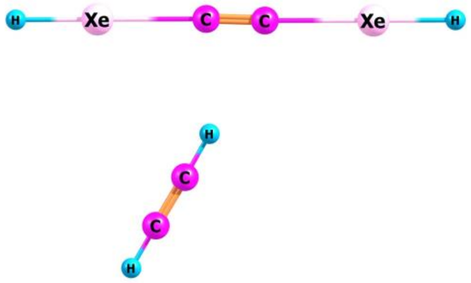

Figure 1 Optimized calculated structure of the 1:1 complex of HXeCCXeH with acetylene.

Acknowledgements
Project KUMURA of the Academy of Finland and the CSC-IT Center for Science.

REFERENCES

1. L. Khriachtchev, M. Räsänen, R. B. Gerber, *Acc. Chem. Res.* **2009**, *42*, 183.
2. A. Lignell, L. Khriachtchev, *J. Mol. Struct.* **2008**, *889*, 1.
3. L. Khriachtchev, H. Tanskanen, J. Lundell, M. Pettersson, H. Kiljunen, M. Räsänen. *J. Am. Chem. Soc.* **2003**, *125*, 4696.

P-20

Theoretical studies of the kinetic properties of the hydrogen atom elimination from chloroalkane in the radical reaction with chlorine atom

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Radical reaction of chlorine with other aliphatic hydrocarbons play very important roles in controlling the oxidation processes in trophosphere due to their high values of rate constants. Detailed experimental and theoretical studies of hydrogen atom elimination reaction mechanisms from -CH_2Cl group and from the other carbon atoms of chloroalkane revealed many previously unknown properties. As it was shown in the first paper[1], the energy barrier height for hydrogen elimination reaction from -CH_2Cl group is fast twelve times greater in case of 1,2-dichloroethane than chloroethane. It has also been shown that the value of KIE = 1.85±0.17 is temperature independent within the temperature range of 298-528.5 K in case 2-chloropropane. The most intersting influence on the whole reaction is the creation of complex R-Cl...Cl. It has been obtained model structures for 2-chloropropane and chloromethane[2,3]. We focus currently on the calculation of the rate constant including this unusual complex. We want to gain insight into this system structure and deeply know the nature of halogen and hydrogen bonding.

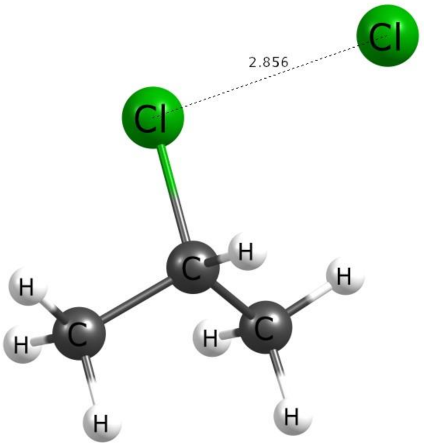

Figure 1 Obtained structure of $CH_3CHClCH_3$...Cl complex

REFERENCES

1. D.S. Sarzyński, Ł. Fojcik, A.A. Gola, R. Berkowski, J.T. Jodkowski, Z. Latajka., Chem. Phys. Lett., **2014,** 597, 86.
2. K. Brudnik, M. Twarda, D.S. Sarzyński, J.T. Jodkowski, J. Mol. Model., **2013,** 19, 1489.
3. K. Brudnik, M. Twarda, D.S. Sarzyński, J.T. Jodkowski, J. Mol. Model., **2013,** 19, 4181.

P-21

Determination of dissociation energies of sulfur centered hydrogen bonded complexes

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We have determined dissociation energies of O-H•••S hydrogen bond in the H_2S complexes of various phenol derivatives in their cationic state as well as in the ground electronic state using 2-color-2-photon photo-fragmentation spectroscopy in combination with zero kinetic energy photo electron (ZEKE-PE) spectroscopy. This is the first report of direct determination of dissociation energy of O-H•••S hydrogen bond. The ZEKE-PE spectra were used to determine the adiabatic ionization energies of the monomers as well as the complexes. The ZEKE-PE spectra of the complexes also revealed a long progression in the intermolecular stretching mode with significant anharmonicity. Recently we published a report[1] on application of Birge-Sponer (B-S) extrapolation method to estimate the dissociation energy of an O-H•••S bound complex where such anharmonicity was observed. In the present context we also validate the B-S extrapolation method to estimate the dissociation energy of the O H•••S type hydrogen bond by comparing the B-S extrapolated dissociation energy for two systems, namely, phenol-H_2S and p-cresol-H_2S with their experimental/computational dissociation energies. Experimentally determined dissociation energies were compared with a variety of ab-initio calculations. It was found that ωB97X-D functional which is a dispersion corrected DFT functional was able to predict the dissociation energies in both the cationic as well as the ground electronic state very well while all other methods failed to simultaneously predict that in both the states.

REFERENCES

1. Bhattacharyya, S.; Wategaonkar, S. *J Phys Chem A* **2014**, 118 (40), 9386-9396.
2. Biswal, H. S.; Shirhatti, P. R.; Wategaonkar, S. *J Phys Chem A* **2010**, 114 (26), 6944-6955.
3. Courty, A.; Mons, M.; Dimicoli, I.; Piuzzi, F.; Brenner, V.; Millie, P. *J Phys Chem A* **1998**, 102 (25), 4890-4898.

P-22

Theoretical and experimental studies on hydrogen-bond formation in pyrazine-2-amidoksyme.

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Theoretical calculations were performed for all possible tautomers-rotamers of pyrazine-2-amidoxime with Gaussian 09 software package at the DFT(B3LYP)/6-311+G** level. The molecular structure of the most stable conformation of pyrazine-2-amidoksyme is shown in Figure 1.

Pyrazine-2-amidoxime may display its availability to form intramolecular hydrogen bond which may stabilize the structure. For pyrazine-2-amidoxime, the hydrogen atom of the amine group (hydrogen donor) may interact with the nitrogen atom (hydrogen acceptor) in the pyrazine ring and create the intramolecular interactions. Our studies have shown that in pyrazine-2-amidoksyme can be formed two more intramolecular interactions, as in Figure 1. These three favorable interactions may explain the exceptional stability of this conformer in the gas phase.

For comparison we performed experimental IR spectra in nonpolar solvent (CCl_4). The results confirmed our theoretical investigations.

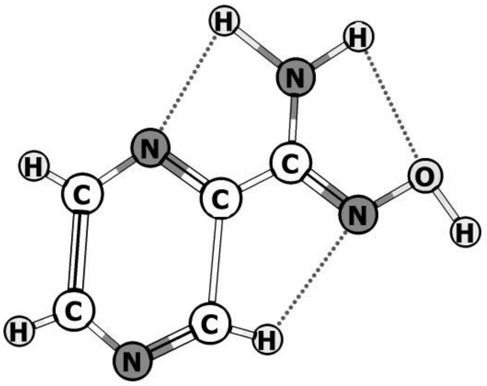

Figure 1. Structure of pyrazine-2-amidoksyme.

Acknowledgements

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Analysis of librational modes of ice XI studied by Car-Parrinello molecular dynamics

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Theoretical infrared spectra of ice XI at 4 and 40 K were obtained by Car-Parrinello molecular dynamics[1] calculations and evaluating the dipole moment using maximally-localized Wannier functions.[2] In order to improve the agreement between theoretical and experimental spectra, the Kramers–Kronig relations[3] were applied. Based on analysis of power and polarization spectra the assignment of modes was carried out. The results were compared with experimental[4] and theoretical[5,6] spectra of ice XI, performed by other authors. Such simulations can be very useful while investigating the existence of ice XI in space.

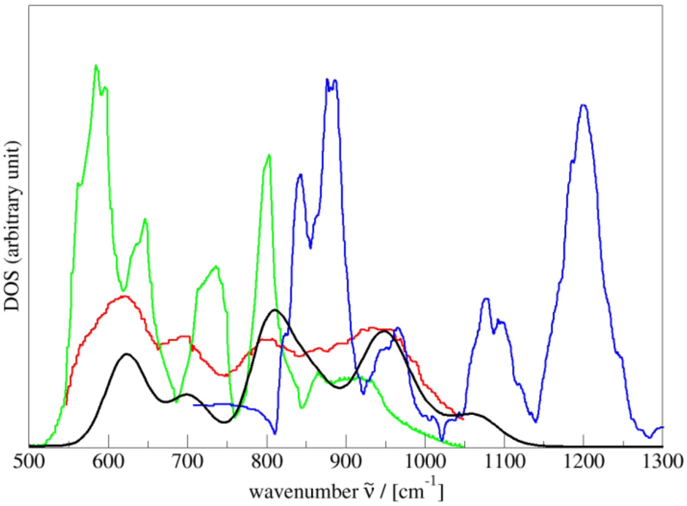

Figure 1 . Comparison of the DOS function obtained from CPMD calculations (black), IINS spectrum (red, taken from Ref. 4), DOS function obtained by model calculation (green, taken from Ref. 5), and DOS function obtained from classical MD calculations (blue, taken from Ref. 6) in the librational region of H_2O in the ice XI phase.

REFERENCES

1. R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
2. N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).
3. R. de L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926).
4. J. C. Li, J. Chem. Phys. **105**, 6733 (1996).
5. K. Iwano, T. Yokoo, M. Oguro, and S. Ikeda, J. Phys. Soc. Jpn. **79**, 063601 (2010).
6. H. Itoh, K. Kawamura, T. Hondoh, and S. Mae, J. Chem. Phys. **109**, 4894 (1998).

P-24

Effect of fluorine insertion in alcohol-amine complexes

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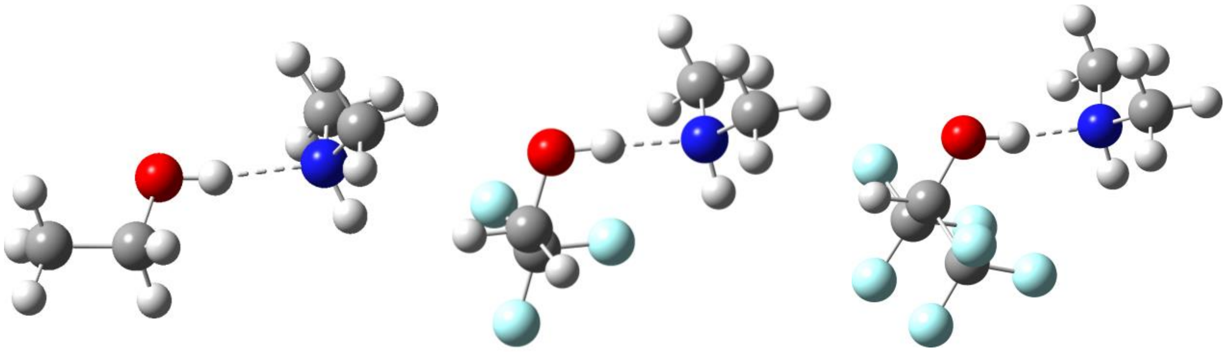
Hydrogen bonded complexes between the alcohols ethanol (EtOH), trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP), and the amines dimethylamine (DMA) and trimethylamine (TMA) were studied with a combination of vapor phase Fourier Transform InfraRed (FTIR) spectroscopy and *ab inito* calculations. The observed characteristics upon complexation include the OH-bond elongation and a frequency redshift of the OH-stretching transition. The equilibrium constant upon complexation was determined from a combination of theory and experiments. A comparison of the complexes enables insight into the affects of changing the hydrogen bond acceptor or donor.

We found that adding a methyl group to the hydrogen bond acceptor (DMA to TMA) improved the hydrogen bond slightly. Furthermore, we found that fluoronation of the hydrogen bond donor weakens the OH-bond in the donor and enhances its hydrogen bond abilities significantly. Experimentally this enhance represented a challenge.



Optimized structures of EtOH·DMA, TFE·DMA and HFIP·DMA.

REFERENCES

A. S. Hansen, L. Du, H. G. Kjaergaard. The Effect of Fluorine Substitution in Alcohol-Amine Complexes. *Phys. Chem. Chem. Phys.,* **16**, 22882-22891 (2014).

P-25

New terephthalamides: Molecular structure and co-operative interactions involving hydrogen bonds studied by polarized IR spectroscopy and DFT calculations

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Interactions *via* hydrogen bonding are recognized to be of major importance to the crystal packing, crystal structure stability, molecular recognition and self-assembly processes.[1] Some terephthalamides self-assemble to form supramolecular nanostaircase structures in crystals, which has some useful implications in supramolecular chemistry as well as in crystals engineering.[2] Poly(ester amide)s derived from natural amino acids have recently been suggested as a potential family of biodegradable polymers.[3]

Molecular structure and properties of bis-terephthalamides of methyl esters of α-amino acids including glycine (1), *β*-alanine (2) and 4-aminobutyric acid (3) ($CH_3OOC(CH_2)_nNHCOC_6H_4CONH(CH_2)_nCOOCH_3$,$n$=1-3) were experimentally investigated by X-ray diffraction technique and polarized IR spectroscopy. Experimental results on the molecular structure of (1-3) were supported with computational studies using the density functional theory, with the 6-31 G(d) basis set. Crystal structures of (1-3) formed by two intermolecular chains N-H···O hydrogen bond systems were analyzed.

The analysis of IR spectra shows that a weak *through-space* exciton coupling in (1-3) involves two closely-spaced hydrogen bonds belonging to two different adjacent chains. Moreover, the exciton coupling magnitude decreases with adding of methylene groups to terephthalamide system. The two-branch structure of the $\nu_{N\text{-}H}$ band disappears as a result of isotopic dilution of (1-3) crystals by deuterium. This proves a highly random distribution of protons and deuterons in the lattice of hydrogen bonds of isotopically diluted crystals of (1-3).

REFERENCES

1. V. Suryanti, M. Bhadbhade, R. Bishop, D. StC Black, N. Kumar, *CrystEngComm.* **2012**, *14*, 7345.
2. S. Ray, R. P. Hegde, A. Kumar Das, N. Shamala, A.Banerjee, *Tetrahedron* **2006**, *62*, 9603.
3. E. Armelin, E. Escudero, L. Campos, J. Puiggalí, *Acta Cryst. C* **2001**, *57*, 172.

P-26

"Long-distance" H/D isotopic self-organization phenomena in scope of the infrared spectra of hydrogen-bonded terephthalic and phthalic acid crystals

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Experimental and theoretical studies of abnormal properties of terephthalic acid (TAC) and phthalic acid (PAC) crystals manifested in the H/D isotopic exchange are presented. The widely utilized deuteration routine appeared to be insufficiently effective in the case of the h_6–TAC isotopomer. In the case of the d_4–TAC derivative the isotopic exchange process occurred noticeably more effectively. In contrast, both isotopomers of PAC, h_6 and d_4, appeared much more susceptible for deuteration. A suitable theoretical model was elaborated describing "*long-distance*" *dynamical co-operative interactions* involving hydrogen bonds (HBs) in TAC and PAC crystals. The model assumes extremely strong *dynamical co-operative interactions* of HBs from the adjacent $(COOH)_2$ cycles. This leads to an additional stabilization of h_6–TAC molecular chains. The interaction energies affect the chemical equilibrium of the H/D isotopic exchange. The model predicts a differentiated influence of the H and D atoms linked to the aromatic rings on to the process. In this approach the totally-symmetric C-H bond stretching vibrations and the proton stretching totally symmetric vibrations couple with the π-electronic motions. Identical hydrogen isotope atoms, H or D, in whole TAC molecules, noticeably enlarge the energy of the *dynamical co-operative interactions* in the crystals, in contrast to the case of different hydrogen isotopes present in the carboxyl groups and linked to the aromatic rings. The "*long-distance*" *dynamical co-operative interactions* in PAC crystals are found of a minor importance due to the electronic properties of PAC molecules.

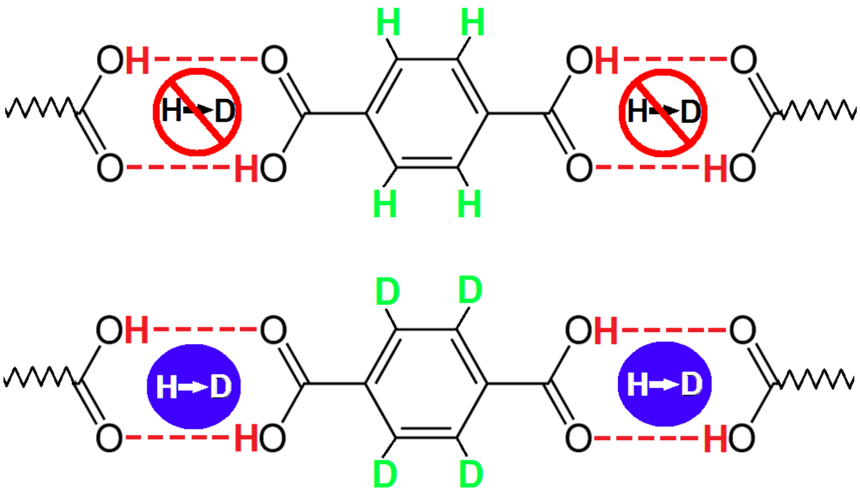

Figure 1 Influence of the H and D atoms linked to the aromatic rings of TAC molecules on to the deuteration process

P-27

Participation of xenon in hydrogen bond networks formed by simple carboxylic and sulfonic acids in different solvents

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Series of solutions of RCO_2H and RSO_3H ($R=CH_3$ and CF_3) acids saturated with Xe gas are examined by analysis of its ^{129}Xe chemical shifts extrapolated to the solvent zero concentration. Thus estimated δ_{extr} are considered as resulting from the solvent-redistributed Xe contacts with weakly self-associated acids. These results are consistent with previous predictions of the ^{129}Xe deshielding due to formation of the –O-H···Xe H-bonding-like contacts (Fig. 1).[1,2] They are also strongly dependent on the Xe contacts with the CH_3 and CF_3 structural elements of the acids.

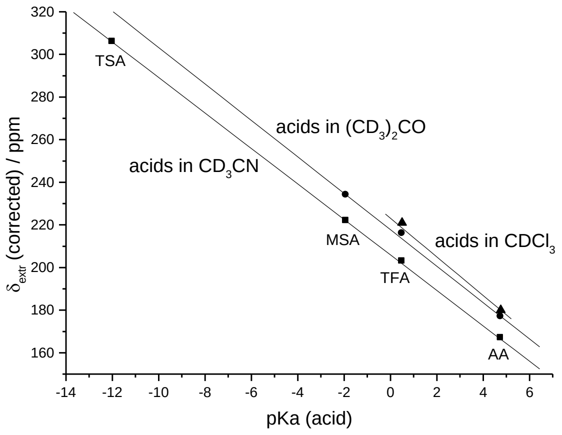

Figure 1 Extrapolated and corrected ^{129}Xe chemical shifts of the Xe-acid-solvent solutions vs. pKa of the acids: AA – acetic, TFA – trifluoroacetic, MSA – methanesulfonic, TFA – trifluoromethanesulfonic.

Acknowledgements

We thank the National Centre for Research and Development (NCBiR) for ERA–CHEMISTRY–2009/01/2010 grant.

REFERENCES

1. D. Gąszowski, M. Ilczyszyn, *Chem. Phys. Lett*. **2013,** 556, 59.
2. E. M. Arnett, P. C. Wernett, *J. Am. Chem. Soc.* **1993**, *115*, 12187.

P-28

First principle molecular dynamics study on “Zwitterionic proton sponge”

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1,8-bis(dimethylamino)-4,5-dihydroxy-naphthalene (“zwitterionic proton sponge”)[1] has been investigated on the basis of Car-Parrinello molecular dynamics[2]. The simulations were performed in the gas phase and in the solid state. The studied compound possesses two, short intramolecular hydrogen bonds classified as Low Barrier Hydrogen Bonds (LBHBs). The compound exists as a “zwitterion” in solution and in the solid state[3], thus the intramolecular hydrogen bonds belong to the class of charge-assisted interactions. The applied AIMD method enabled investigations of metric and spectroscopic parameters. The time-evolution investigations of the hydrogen bonds showed a strong delocalization of the bridge protons and their high mobility, reflected in the low barriers on the free energy surfaces. Proton transfer phenomena were noticed. The power spectra of atomic velocity were computed to discuss the vibrational features associated with O-H and N-H stretching - a broad absorption was indicated for both hydrogen bridges.

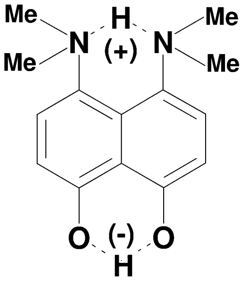

Figure 1 Structure of 1,8-bis(dimethylamino)-4,5-dihydroxy-naphthalene

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The Authors would like to express their thanks to the Wrocław Centre for Networking and Supercomputing (WCSS), Academic Computer Center CYFRONET-KRAKÓW and Centre at the ICM, University of Warsaw (grant no. G52-7) for generous grants of the computing time and use of file storage facilities. The Authors would also like to thank the National Science Centre (Poland) for supporting this study under the grant no. UMO-2011/03/B/ST4/00699.

REFERENCES

1. H. A. Staab, C. Krieger, G. Hieber, K. Oberdorf, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1884.
2. R. Car, M. Parrinello, *Phys. Rev. Lett*. **1985**, *55*, 2471.
3. V. A. Ozeryanskii, A. A. Milov, V. I. Minkin, A. F. Pozharskii, *Angew. Chem. Int. Ed*. **2006**, *45*, 1453.

P-29

Excited state intramolecular proton transfer in 2,5-bis(6-methyl-2-benzoxazolyl)phenol

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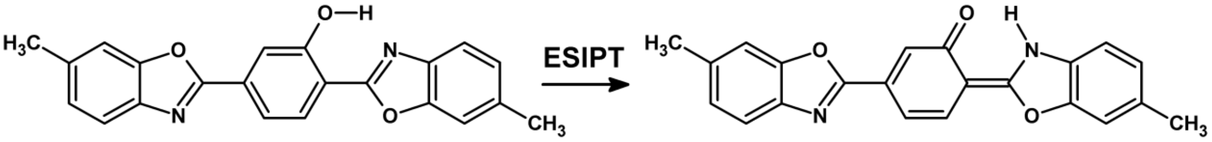
The subject of this study is 2,5-bis(6-methyl-2-benzoxazolyl)phenol (BMP). In solutions, excited BMP emits dual fluorescence: the “blue” one observed at 25000 cm ^{1} and the “red” one with the maximum at 20000 cm^{-1}.[1] Both emissions are observed in a large temperature range, down to 10 K. The high-energy fluorescence originates from the primarily excited “enol” form, whereas the low-energy emission occurs from the “keto” form, which is generated via the excited state intramolecular proton transfer (ESIPT). In contrast, when the molecule is isolated in cold supersonic jets, only one emission is detected, corresponding to the phototautomer.[1] This is consistent with very broad lines observed in the laser induced fluorescence excitation spectrum, indicating an extremely short lifetime of the initially excited species.

To understand the origin of different behavior in the two regimes the following experimental techniques were applied:

- NMR spectroscopy was used to check the possibility of the presence of different ground state conformers,
- stationary and picosecond time-resolved fluorescence and absorption spectra were recorded as the function of temperature to establish the excited state energy degradation scheme.

Stability of possible conformers, variations in the energy of electronic transitions, oscillator strengths and dipole moments upon ESIPT reaction were explored by quantum chemical modelling of the ground and excited states of BMP at the DFT and TD-DFT levels, respectively.



Acknowledgements

This work has been financed by the funds from the Polish National Science Center 2011/03/B/ST4/02621 and the computing grant G17-14 from the Interdisciplinary Centre for Mathematical and Computational Modeling of the Warsaw University.

REFERENCES

1. E. Luzina, J. Sepioł, Y. N. Svartsov, A. Grabowska, J. Chem. Phys. **2007**, *126*, 194308.

P-30

Librational vibrations of OH···O hydrogen bonded dimers

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Librational vibrations emerge in hydrogen bonded clusters from hindered rotations and torsions of the isolated monomers, resulting in a spectroscopic blueshift. They are a sensitive for the intermolecular potential of the hydrogen bond, and their inherently high anharmonicity makes them challenging benchmarks for theoretical predictions. Additionally, their anharmonic interaction with the OH stretching vibrations is key to understanding the redshift of the latter in hydrogen bonded systems. With the harmonic contribution to the OH stretching redshift in methanol dimer having been determined on a high theoretical level[1] and the diagonal anharmonic contribution in alcohol dimers obtained from experiment[2], unveiling the off diagonal contribution of the OH libration is the next step to understanding the spectral effects of these systems. The first iteration to assessing this vibrational cross talk is investigating the librational fundamentals of hydrogen bonded clusters.

As the librational modes of alcohol trimers and tetramers have been assigned formerly[3,4], we present the libration spectra of OH···O bonded dimers that stem from the frustrated torsion of the hydrogen bond donor group. They were recorded via FTIR spectroscopy of supersonic jet expansions of helium seeded with methanol[5], *t*-butyl alcohol, formic acid or methyl lactate. The assignment of the alcohol dimer vibrations is confirmed by complementary experiments in cryogenic neon matrices.

REFERENCES

1. M. Heger, M. A. Suhm, R. A. Mata, *J Chem. Phys.* **2014,** *141*, 101105.
2. F. Kollipost, K. Papendorf, Y.-F. Lee, Y.-P. Lee, M. A. Suhm, *Phys. Chem. Chem. Phys.* **2014,** *16*, 15948.
3. R. Wugt Larsen, M. A. Suhm, *J Chem. Phys.* **2006,** *125*, 154314.
4. R. Wugt Larsen, M. A. Suhm, *Phys. Chem. Chem. Phys.* **2010,** *12*, 8152.
5. F. Kollipost, J. Andersen, D. W. Mahler, J. Heimdahl, M. Heger, M. A. Suhm and R. Wugt Larsen, *J Chem. Phys.* **2014,** *141*, 174314.

P-31

Structural, energetic and electric properties of spatially confined hydrogen bonded complexes

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The phenomenon of spatial confinement is of a great importance in many areas of science as the significant part of physical and chemical processes occurs in spatially limited environments. This includes, for instance, the matter under high pressure or molecules embedded in chemical cages such as zeolites sieves, nanotubes, fullerenes, *etc*. As it has been already demonstrated the presence of spatial confinement (orbital compression) strongly influences the stability, electric properties, absorption spectra, dielectric constant as well as reactivity of atoms and molecules[1,2]. However, there is only a limited number of studies concerning the properties of hydrogen bonded complexes exposed to the orbital compression.

In the present contribution we report on the structural, energetic and electric properties of model hydrogen bonded complexes confined by the repulsive harmonic oscillator potential of cylindrical symmetry, mimicking a topology of nanotube-like carbon cages. The computations were performed at several levels of theoretical approximation including *ab initio* MP2 and CCSD(T) methods as well as the Kohn–Sham formulation of density functional theory. Additionally, a symmetry adapted perturbation theory was applied to study the interaction energy components in the presence of spatial confinement. The results of our calculations indicate that the shortening of hydrogen bond distances, observed experimentally in various high-pressure experiments, may be attributed to the confinement effects[3]. Moreover, according to the obtained data the orbital compression leads to the substantial drop of electric dipole moment, polarizability and first hyperpolarizability of the analyzed complexes. Interestingly, the energetic analyzes performed for the confined hydrogen bonded complexes demonstrate that changes in the interaction energy values, arising from the presence of spatial restriction, differ for each of the studied complexes and strongly depend on the strength of applied repulsive potential.

Acknowledgements

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REFERENCES

1. J. R. Sabin, E. Brändas, S. A. Cruz (Eds.), in Advances in Quantum Chemistry: Theory of Confined Quantum Systems, Academic Press: Waltham, MA, **2009**, vols. 57-58.
2. D. A. Britz, A. N. Khlobystov, Chem. Soc. Rev., **2006**, 35, 637.
3. P. Lipkowski, J. Kozłowska, A. Roztoczyńska, W. Bartkowiak, Phys. Chem. Chem. Phys., **2014**, 16, 1430; A. Roztoczyńska, J. Kozłowska, P. Lipkowski, W. Bartkowiak, Chem. Phys. Lett., **2014**, 608, 264–268.

Conformational and photochemical transformations of guaiacol.

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Guaiacol (*o*-methoxyphenol, GU) is a biologically active phenol derivative with an intramolecular –OH···OCH_3 hydrogen bond. This compound is used in medical and dental practices due to its analgesic, anti-inflammatory and anesthetic properties. GU is also a potent scavenger of reactive oxygen radicals.

The molecular structure and photochemistry of guaiacol were studied in argon and xenon matrices by infrared spectroscopy and DFT calculations. The performed calculations revealed the presence of three stable conformers of GU. Only the most stable structure, presented in Figure 1, was identified in the experimental GU/Ar and GU/Xe spectra.

The UV photolysis of the studied compound was also observed, with initial O–H bond cleavage and formation of the *o*-methoxyphenol radical, followed by radical recombination to form cyclohexadienone derivatives. The latter molecules transform by ring opening into the long-chain conjugated ketenes. The photoproduced ketenes were found to undergo subsequent photo-decarbonylation. *o*-Methoxyphenol radical recombination was also detected leading to the cyclopentadienone molecule.

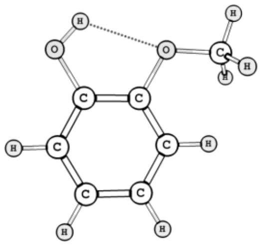

Figure 1. Most stable conformer of guaiacol (GU).

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P-33

Solute-solvent hydrogen bond formation influence on the spectral and photophysical properties

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Intermolecular hydrogen bond formation, as a site-specific interaction between hydrogen donor and acceptor molecules, is an important type of solute-solvent interaction. Identification of these interactions in the ground and in the excited electronic states and their influence on the spectral and photophysical properties can help *e.g.* in designing new fluorophores for different applications.[1]

The results reported for 4-aminophthalimide (4AP),[2] 6-aminocoumarin (6AC)[3,4] and thioxanthone (TX)[5] very well explain the complex effect of solvents on the absorption and emission spectra of molecules of different properties. According to the results, the proper choice of the solvent for solvatochromic studies is very important for accurate and separate determination of non-specific and specific (hydrogen-bonding) solute-solvent interactions.

The results of photophysical studies of 4AP and 6AC (donor-acceptor molecules) clearly show that in protic solvent, intermolecular hydrogen-bonding interactions between solute and solvent molecules facilitate the nonradiative deactivation processes of S_1-excited state. It was found for 6AC that the energy gap dependence on radiationless deactivation in an internal conversion process from S_1-ICT excited state can be observed not only for molecules but also for hydrogen-bonded complexes. On the other hand, the S_1-complexes formed via hydrogen bond by TX with protic solvent molecules deactivate from $S_1(\pi,\pi^*)$ state in fluorescence process with high quantum yield and in intersystem crossing process to T_1-state.

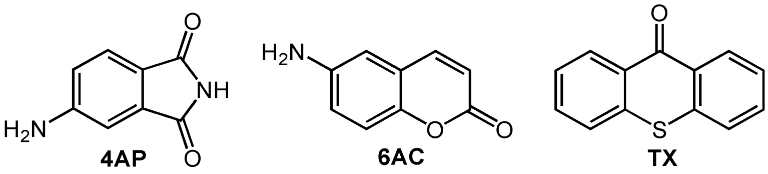

Figure 1 Molecular structures of 4-aminophthalimide (4AP), 6-aminocoumarin (6AC) and thioxanthone TX

REFERENCES

1. K. –L. Han, G. –J. Zhao, *Hydrogen bonding and transfer in the excited state*, **2011**, Wiley.
2. E. Krystkowiak, K. Dobek, A. Maciejewski, *J. Photochem. Photobiol. A: Chem.* **2006,** *184*, 250.
3. E. Krystkowiak, A. Maciejewski, *Phys. Chem. Chem. Phys.* **2011,** *13*, 11317.
4. E. Krystkowiak, K. Dobek, A. Maciejewski, *Photochem. Photobiol. Sci.* **2013,** *12*, 446.
5. E. Krystkowiak, A. Maciejewski, J. Kubicki, *ChemPhysChem* **2006,** *7*, 597.

P-34

Hydrogen bond effects on 4*H*-1-benzopyrane-4-thione S_2-excited state deactivation

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Intermolecular and intramolecular hydrogen bonds influence important properties of molecules in the ground as well as in the electronic excited states.[1]

Unexpected results of spectral emission and photophysical study for S_2-excited 4*H*-1-benzopyrane-4-thione (BPT) in water solution are reported. The careful analysis of fluorescence spectra, emission excitation spectra, quantum yield and fluorescence lifetime of S_2-state together with computational study results[2] clearly show that in the ground S_0 as well as excited S_2 electronic states almost all BPT molecules in the water solution form solute-solvent complexes via strong hydrogen bonds. There are at least two types of BPT-water complexes that participate in the S_2-fluorescence. They both deactivate with high efficiency in an internal conversion S_2~~>S_1 and in intersystem crossing process S_2~~>T_1.

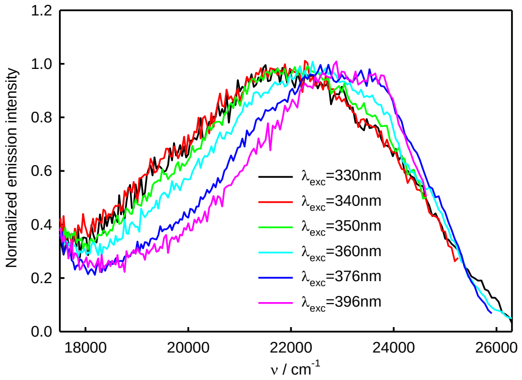

Figure 1 Normalized S_2-fluorescence spectra of 4*H*-1-benzopyrane-4-thione (BPT) in water.

Acknowledgements

Calculations were performed at the Poznań Supercomputer Centre PCSS.

REFERENCES

1. K. –L. Han, G. –J. Zhao, *Hydrogen bonding and transfer in the excited state*, **2011**, Wiley.
2. E. Krystkowiak, J. Koput, A. Maciejewski, *Phys. Chem. Chem. Phys.* **2012,** *14*, 8842.

P-35

Intramolecular proton transfer in *ortho*-substituted pyridine *N*-oxide derivatives

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The fact that the derivatives of pyridine *N*-oxide can form intermolecular hydrogen bonds, where the oxygen atom of *N*-oxide group in an acceptor of proton, rises no doubts. In the CSD crystallographic data base are many structures supporting such a conclusion[1-6]. It is interesting if the same class of compounds can form intramolecular hydrogen bonds with proton donating groups substituted in pyridine ring, in *ortho* position in respect to *N*-oxide group. The search through CSD shows that, in the case of non-oxidized pyridine rings, usually there is the proton transfer to the pyridine nitrogen atom[7-11], less commonly the intramolecular hydrogen bond is formed. In the case of pyridine *N*-oxides it is hard to put an unambiguous conclusion, because we can find both structures with hydrogen atom connected with *N*-oxide group and structures in with the proton transfer is observed[13-14].

The aim of our research was to determine location of hydrogen atom deriving from group substituted in *ortho* position in respect to *N*-oxide group in the derivatives of hydroxypyridine, aminopyridine and mercaptopyridine. The quantum-chemical calculations were made with the use of the Gaussian 09[15] at B3LYP/aug-cc-pVTZ level of theory. The results obtained from theoretical calculations were compared with experimental data from X-ray measurements.

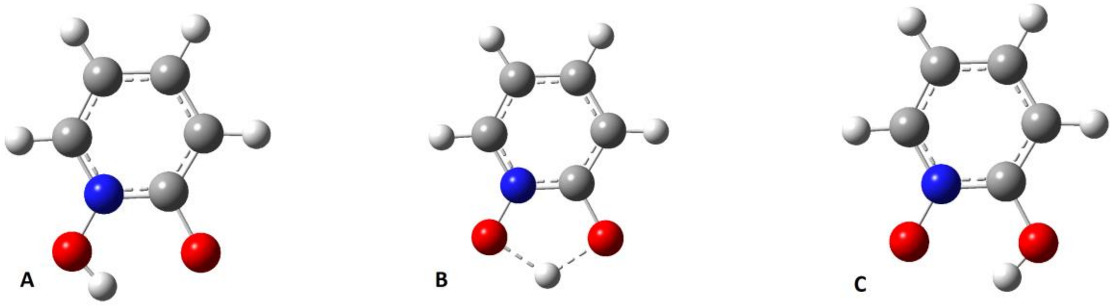

Figure 1 Tautomeric forms (A, C) and transition state (B) of *o*-hydroxypyridine *N*-oxide

REFERENCES

1. R. Moreno-Fuquen, R.H. De Almeida Santos, R.H.P. Francisco, *Acta Crystallogr., Sect. C* **1998**, *54*, 513.
2. N.J. Babu, L.S. Reddy, A. Nangia, *Mol. Pharm.* **2007**, *4*, 4, 417.
3. J.R. Lechat, R.H. De Almeida Santos, A. Bueno, *Acta Crystallogr., Sect. B*, **1981**, *37*, 1468.
4. R. Moreno-Fuquen, J.R. Lechat, R.H. De Almeida Santos, *Acta Crystallogr., Sect. C*, **1991**, *47*, 2388.
5. J.G. Planas, G.G. Mohamed, R. Sillanpaa, R. kivekas, F. Teixidor, C. Vinas, *J. Mol. Struct.*, **2006**, *787*, 121.
6. E. Bermejo, R. Carballo, A. Castineiras, R. Dominguez, C. Maichle-Mossmer, J. Strahle, D.X. West, *Polyhedron* **1999**, *18*, 3695.
7. C.D. Antoniadis, S.K. Hadjikakou, N. Hadjiliadis, M. Kubicki, I.S. Buter, *New J. Chem.* **2005**, *29*, 714.
8. J. P. Declercq, A. Schanck, G. Germain, J. M. Dereppe, M. van Meerssche, *Acta Crystallogr., Sect. B*, **1977**, *33*, 3876.
9. Z. Soldin, D. Vikic-Topic, G. Pavlovic, M. Vinkovic, D. Matkowic-Calogovic, Z. Popovic, *Croat. Chem. Acta*, **2012**, *85*, 515.
10. B.-M. Kukovec, Z. Poppovic, M. R. Linaric, *J. Mol. Struct.*, **2008**, *882*, 47.
11. J. Almlof, A. Kvick, I. Olovsson, *Acta Crystallogr., Sect. B.*, **1971**, *27*, 1201.
12. P. Ballesteros, R. M. Claramunt, T. Canada, C. Foces-Foces, F. H. Cano, J. Elguero, A. Fruchier, *J. Chem. Soc., Perkin Trans.*, **1990**, *2*, 1215.
13. R. Venkatraman, F. R. Fronczek, **2009**, *Private Communication*.
14. R. A. Hollins, L. H. Merwin, R. A. Nissan, W. S. Wilson, R. Gilardi, *J. Heterocycl. Chem.*, **1996**, *33*, 895.
15. Gaussian 09, Revision A.1, M. J. Frisch et al., Gaussian Inc., Wallingford CT, **2009**.

Solvent influence on stability of the fenamic acids dimers.

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Fenamic acids are non-steroidal anti-inflammatory drugs (NSAIDs) that are used for variety of symptoms including anticancer activity. They inhibit both cyclooxygenase-1 (COX-1) and cyclooxygenase-2 (COX-2).[1,2] Fenamic acids are typical benzoic acids existing as dimers in solid state, solute and gas phase. Stability of the dimers of fenamic acids is an important question for interaction of these drugs with biological systems.

Using the PCM method in Gaussian 09 it has been determined whether the structures of dimers would be disrupted by the influence of a variety of solvents presenting different permeability: acetonitryle, butanol, dimethylsulfoxide, formamide, heptane and water.[3]

What is more, the behavior and stability of dimers of fenamic acid and its derivatives in water have been examined using molecular dynamics studies conducted with GROMACS 5.0.4.[4]

The objects of investigation are fenamic acid as a model compound and its substituted analogues commonly used as drugs: mefenamic-, meclofenamic-, flufenamic-, tolfenamic- and clofenamic acid (Fig. 1).

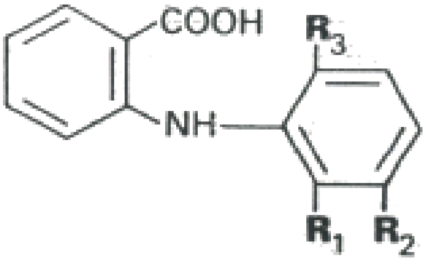

Figure 3. General formula of fenamic acids. mefenamic acid: R_1 – CH_3, R_2 – CH_3, R_3 – H, flufenamic acid: R_1 – H, R_2 – CF_3, R_3 – H, clofenamic acid: R_1 – Cl, R_2 – Cl, R_3 – H, meclofenamic acid: R_1 – Cl, R_2 – CH_3, R_3 – Cl, tolfenamic acid: R_1 – CH_3, R_2 – Cl, R_3 – H.

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Calculations have been carried out using resources provided by Wroclaw Centre for Networking and Supercomputing (http://wcss.pl)

REFERENCES

1. Z. Jia et al., *Cancer Res.,* **2010**, 70
2. A. D. Soriano-Hernandez et al., *International Urology and Nephrology,* **2012**, 44
3. M. J. Frisch et al. *Gaussian, Inc.: Pittsburgh, PA,* **2010**
4. D. Van Der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark H.J. C. Berendsen, *Journal of Computational Chemistry,* **2005,** *26*

P-37

Effects of xenon insertion into hydrogen bromide. Comparison of the electronic structure of the $HBr\cdots CO_2$ and $HXeBr\cdots CO_2$ complexes using quantum chemical topology methods: Electron Localization Function, Atoms in Molecules and Symmetry Adapted Perturbation Theory

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Quantum chemistry methods have been applied to study the influence of the Xe atom inserted into the hydrogen␣bromine bond (HBr→HXeBr), particularly on the nature of atomic interactions in the $HBr\cdots CO_2$ and $HXeBr\cdots CO_2$ complexes. Detailed analysis of the nature of chemical bonds has been carried out using topological analysis of the electron localization function, while topological analysis of electron density was used to gain insight into the nature of weak nonbonding interactions. Symmetry-adapted perturbation theory within the orbital approach was applied for greater understanding of the physical contributions to the total interaction energy.[1]

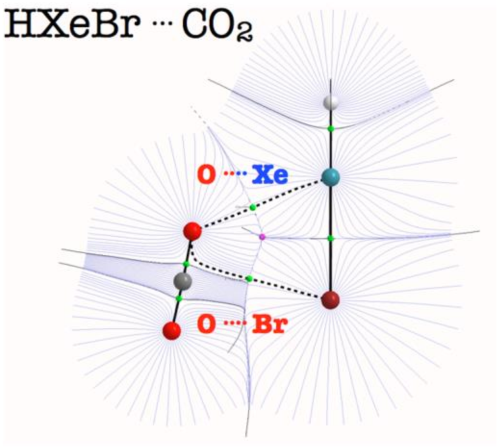

Figure 1

REFERENCES

1. Makarewicz E., Gordon A., Berski S.: *J. Phys. Chem. A*, **2014**, 118 (22), 3980–3989

P-38

Protonated AA/TT base-pair step

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The coupling between proton transfer and stacking interaction in a neutral AA/TT step was investigated theoretically by Villani.[1] However, the structures and energetics of protonated AA/TT steps were not yet reported. In the studies of protonated A:T base pairs, Noguera at al.[2] showed that the protonation of thymine's O4, or O2, leads to structures with a single proton transfer from N3 of thymine to N1 of adenine.

In this work we present result of our computations of an AA/TT step, protonated at different sites. The full optimization of the structures was performed at the M06-2X/6-31+G(d,p) level in the Gaussian 09 suite of programs. The lowest energy structure is protonated at N3 of adenine at the 3' end. In this structure, O2 of thymine at the 3' end is strongly attracted to the hydrogen on N3.

Proton affinity (PA) of this step, 245.2 kcal/mol, is significantly increased relative to the PA of the single base pair at 226.2 kcal/mol, as reported by Noguera et al.[2]

An intriguing result of our studies is a shifted pattern of hydrogen bonding in the lowest energy structure protonated at O4 of thymine. In this structure one hydrogen bond is formed between O2 of thymine and N1 of adenine (with the shifted proton from thymine's N3). The second one is present between N3 of thymine (lost proton) and the amino group of adenine.

Although the computations involving nucleic acid base pairs without hydration are not expected to yield experimentally observed structures, the analysis of the trends should guide further research. For example, the significant increase of PA, upon increasing the system size from one base pair to a base pair step, warrants further studies of protonation in longer A-tracts. A relatively rigid "spine of hydration" of A-tracts may be due to the stronger hydrogen bonding, induced by the presence of extra protons in the spine and an instantaneous protonation of bases.

Acknowledgements

The computer time at the HPC center at NYU is acknowledged.

REFERENCES

1. G. Villani *ChemPhysChem* **2013,** *14*, 1256.
2. M. Noguera, M. Sodupe, J. Bertran *Theor Chem Acc* **2007,** *118*, 113.

P-39

Equilibrium constant of formic acid dimerization

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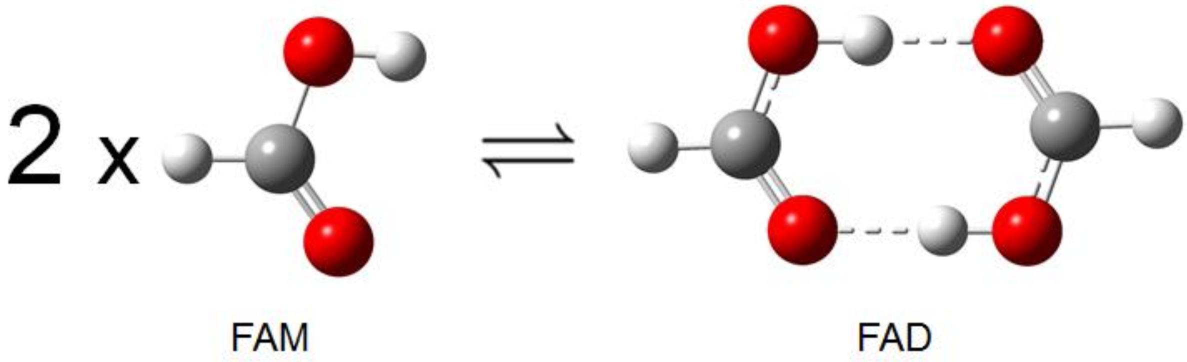
The gas-phase infrared spectrum of formic acid constitutes a great challenge both experimentally and theoretically. The two hydrogen bonds of the cyclic formic acid dimer (FAD) are very strong and FAD is formed even at very low formic acid monomer (FAM) pressures. The vibrational modes of FAD are strongly coupled which makes the calculations challenging. FAM and FAD have been studied by gas-phase Fourier transform infrared (FTIR) spectroscopy and the fundamental as well as the first overtone region of FAM and FAD were recorded. A two-dimensional local mode model was used to calculate the vibrational frequency and the oscillator strength of the OH- and CH-stretching transition frequencies in FAM and FAD. On the basis of the measured and calculated intensity of the OH-stretching transition of FAM and the CH-stretching transition of FAD, the equilibrium constant of dimerization at room temperature was determined. Assignment of spectral features in the fundamental region has been supported by molecular dynamics simulations.



P-40

Stepwise solvation of a bulky π-bond by a bulky alcohol

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The bicyclic alkene norbornene offers two faces for π-bond solvation by *t*-butyl alcohol – a cyclopentene face and a boat-shaped cyclohexene face. FTIR spectroscopy of supersonic jet coexpansions reveals distinct OH stretching signatures for both dimers as well as for trimers involving two alcohol units. Addition of a second norbornene unit to the mixed dimer increases the bathochromic shift of the OH group by coordinating an oxygen lone electron pair and coordination of the second lone electron pair by a third norbornene approximately doubles the shift increment. The findings are corroborated by analogous complexes of *t*-butyl alcohol with cyclopentene and cyclohexene and by remarkably close harmonic B3LYP-D3 and B2PLYP-D3 predictions.[1]

REFERENCES

1. R. Medel, M. Heger, and M. A. Suhm, Molecular Docking via Olefinic OH-π Interactions: A Bulky Alkene Model System and its Cooperativity, *J. Phys. Chem. A,* **2015**, *119 (9)*, 1723–1730.
DOI: 10.1021/jp508424p

P-41

Isomers of the acetic acid-water complex trapped in an argon matrix.

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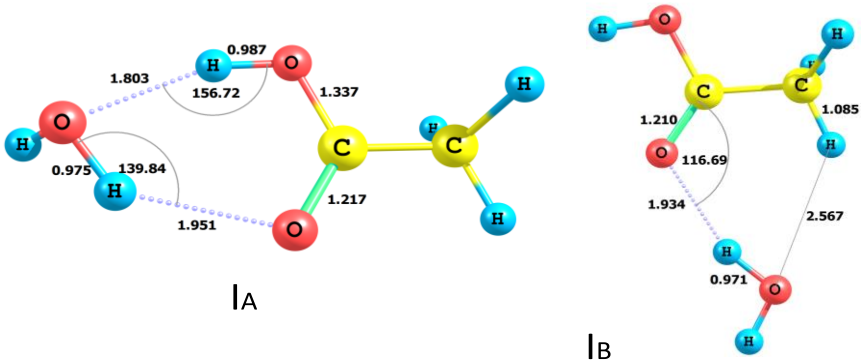
Atmospheric aerosols are one of the major environmental problems. Although they have been in the center of interest of many research groups, the formation of aerosols, at the molecular level is still far from being understood. It is generally accepted now that in the first step of new particle formation the molecular complexes and prenucleation clusters are formed. The forces responsible for the formation of atmospherically relevant complexes are mainly hydrogen bonding interactions. One of the recent discoveries in the field of aerosols is the possible participation of organic acids in their formation. However, how organic acids participate in the nucleation process is far from being understood.

Here we present the results of an infrared matrix isolation and theoretical study of the binary and ternary complexes between two relevant atmospheric molecules, acetic acetic and water. We applied a nonconventional technique of trapping acetic acid complexes in solid argon[1] by depositing AcOH vapor, above a solid acid sample cooled to 203 K, diluted with H_2O/Ar mixture. This method of matrix preparation strongly favors the formation of the higher energy complex, I_B, compared with the "conventional" method that uses deposition a gaseous AcOH/H_2O/Ar mixture at room temperature. The latter method leads mainly to formation of the more stable I_A complex. The possible atmospheric impact of the AcOH temperature on the complex structure is discussed.



I_A I_B

Figure 1. DFT/B3LYP/aug-cc-pVTZ optimized structures of the AcOH-H_2O complex.

REFERENCES

1. K. Haupa, A. Bil, A. Barnes, Z. Mielke, *J. Phys. Chem. A,* **2015**, *119, 2522-2531.*

P-42

On the multiple B-O bonding using the topological analysis of Electron Localisation Function (ELF)

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Topological analysis of the Electron Localisation Function (ELF) within the framework of Quantum Chemical Topology (QCT) has been applied to study the nature of the boron–oxygen bonds. A series of 16 compounds has been chosen, with the experimental BO bond length in the range of 1.481 Å (B–O) –1.179 Å (B≡O). Topological results obtained for the DFT(M062X), DFT(B3LYP), MP2 and CCSD(T) optimised geometrical structures show that all the boron–oxygen bonds in the investigated compounds are described by the disynaptic bonding basin, V(B,O). All these bonds have a covalent-polarised character. The mean electron population of V(B,O) varies from 1.6e ($B(OH)_4^-$) to about 3.5e (HN=CH–CH=CH–NH–B≡O)
The polarity index values, p_{BO}, lie between 0.77 (ClBO) and 0.89 (H_2BOCH_3), thus all boron–oxygen bonds are essentially polarised by the oxygen atom. According to the Lewis formula, four types of the bonds have been recognised. These are: a single bond with a mixture of the ionic hybrid (BO, B^+O^-), a single bond (B–O), a single bond with a small contribution of the dative O→B bond and a single bond
with a large contribution of the dative O→B bond (depleted B=O bonds). There is a clear distinction between a group of 11 molecules chosen for this study, with the basin population value of the boron–oxygen bond between 1.6e and 2.4e, and the HB≡O, FB≡O, ClB≡O, HN=CH–CH=CH–NH–B≡O and trans-$[(Me_3P)_2BrPt(BO)]$ molecules that exhibit the basin population in the range: 3.3e–3.5e. The second
group was postulated to have a triple bond, B≡O, but this statement has not been confirmed by our research.[2]

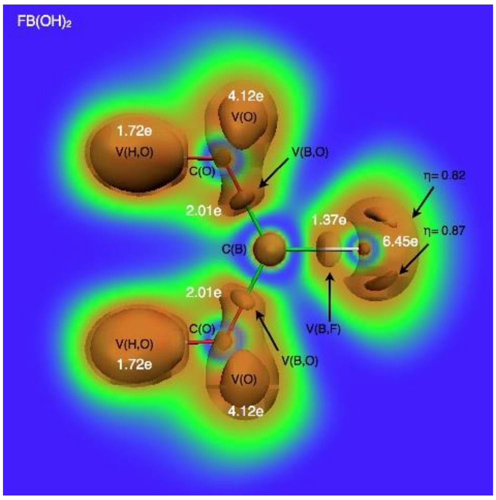

Figure 1

REFERENCES

1. J G. Mierzwa, A. J. Gordon, Z. Latajka, S. Berski *Comp. Theo. Chem*. 1053 (**2015**) 130–141.

P-43

Conformational equilibrium as a tool in supramolecular chemistry: Dibutyltriuret case

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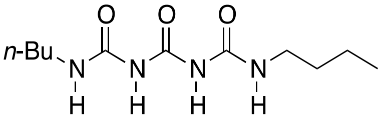
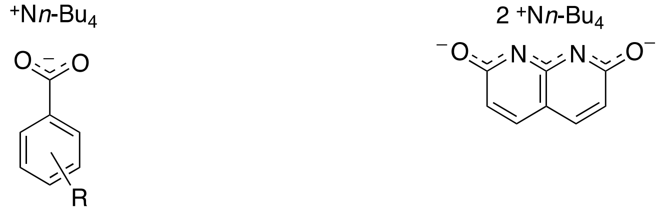
Supramolecular chemistry relies on noncovalent intermolecular interactions. In order to achieve some predictability the design of interacting molecules is highly desirable. One choice is to use compounds, which are stabilized by intramolecular hydrogen bonds. There are many examples of such molecules that can isomerize (break intramolecular hydrogen bond) in forming associates.[1] The question arises if an existence of two intramolecular hydrogen bonds would allow forming associates by breaking both of them. For that purpose *N,N'*-dibutyl diimidotricarbonic diamide (Scheme 1) was synthesized.

This imide forms two intramolecular hydrogen bonds in $CDCl_3$ solution. Its self-association was studied by NMR using dilution experiments. Its ability to form heterocomplexes with substituted benzoates and a naphthyridine bisanion (Scheme 2) was studied by NMR titration. Also variable temperature (VT) ^1H NMR has been used. The results show that neat **1** exists as symmetric structure but the symmetry is broken upon association.



Scheme 1. Dibutyltriuret (**1**)



R = 4-NMe_2, 4-OMe, 4-Me, H, 4-F, 4-Cl, 4-CF_3, 4-NO_2

Scheme 2. Titrants used in NMR experiments

REFERENCES

1. B. Ośmiałowski, K. Mroczyńska, E. Kolehmainen, M. Kowalska, A. Valkonen, M. Pietrzak, K. Rissanen, *J. Org. Chem.,* **2013**, *78*, 7582-7593.

P-44

Hydrogen bonds in complexes of secondary amines with dimethyl sulfoxide as studied by solution NMR, DFT and AIM calculations

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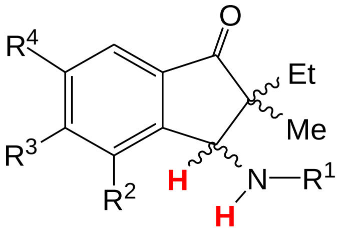
Dimethyl sulfoxide is the NMR solvent (as DMSO-d_6) of choice for many organic compounds due to its excellent solubility properties for protic and charged molecules, which are insoluble in $CDCl_3$. Although the effects of modification of ^1H NMR spectra of hydroxy compounds in DMSO-d_6 solutions are well recognized,[1] the nature of the formed complexes is not finally established. Similar interactions with amines are still less known. In the works on *N*-substituted isoindolinones some amino derivatives **1a-c** (see Fig. 1) were unexpectedly obtained,[2,3] forming 1:1 complexes of type $>N–H\cdots O=S(CD_3)_2$ as was evidently manifested by the relative large $^3J_{\mathbf{H}\text{-C-N-}\mathbf{H}}$ couplings (of ~10 Hz) observed in their ^1H NMR spectra.

An intermolecular H-bonding in these complexes was analyzed in detail for the mixture of two diastereomeric amines **1a** isolated with a *trans*/*cis* ratio of ~1.4:1. The results of our investigations [DFT-level molecular modeling followed by calculations of NMR data (δ_H, δ_C and $^3J_{HH}$) and topological 'Quantum Theory of Atoms in Molecules' analysis of existing H-bond networks] will be presented on the poster.



1 (diastereomeric mixtures)

a: R^1 = Ph, R^2 - R^4 = H
b: R^1 = Ph, R^2 - R^4 = OMe
c: R^1 = 4-$MeOC_6H_4$, R^2 - R^4 = OMe

Figure 1 The family of compounds under study

Acknowledgements

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REFERENCES

1. R. J. Abraham, J. J. Byrne, L. Griffiths, M. Perez, *Magn. Reson. Chem.* **2006**, *44***,** 491.
2. A. Jóźwiak, M. Ciechańska, R. B. Nazarski, E. A. Skorupska, *57rd Annual Meeting of the Polish Chemical Society*, Częstochowa, 14-18.09.2014, poster No. S01-P127; Abstracts, p. 117.
3. M. Ciechańska, A. Jóźwiak, R. B. Nazarski, E. A. Skorupska, *in preparation*.

P-45

Static and dynamic calculations of acetic acid dimer inside single-walled carbon nanotube

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Carbon nanotubes (CNT) play a very important role in materials chemistry and are the subject of many experimental and theoretical studies.[1] Open-ended single-walled carbon nanotubes (SWCNT) are considered in many studies as a model system in nanoconfined chemistry. Due to their special structure (tubular morphology) CNTs might be considered as “nanoreactors” for chemical reactions.[2]

The cyclic acetic acid dimer (AAD) is one of the simplest hydrogen bonded system. The possible double proton transfer, also important from the biological point of view, is the reason of widespread interest of experimental and theoretical studies.

Our previous study of formic acid dimer[3] shows that for this type of compounds we can use DFT calculations with D3 dispersion correction to obtain good results for interaction energies of cyclic organic acid dimers with large conjugated π -systems such as CNTs.

Preliminary investigation of double proton transfer inside SWCNT was carried with Car-Parrinello Molecular Dynamics. It shows influence of SWCNT on AAD by reducing barrier height.

Acknowledgements

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REFERENCES

1. N. Karousis, N. Tagmatarchis, D. Tasis, *Chem. Rev.* **2010,** 110, 5366.
2. X. Pan, X. Bao, *Acc. Chem. Res.* **2011,** 44, 553.
3. P. Okrasinski, Z. Latajka, Ch. Hättig, *J. Phys. Chem. C* **2014**, 118, 4483.

P-46

Behavior of hydrogen bonds in lithium grease during its shearing and stress relaxation

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The performance of lubricating greases largely depends on the physico-chemical and mechanical properties of materials (thickener, solid additives and base oil) used in their composition. Knowledge and understanding of the lubricants, and their properties depending on their structural composition and interactions, is essential in industry, e.g. for engineering reliable rolling bearing applications.

The three main types of molecular bonds involved in the water/soap/grease systems are: dipole-dipole (including hydrogen bonding), van der Waals and ionic interactions (electrostatic). Water (specifically one of the positively charged hydrogen atoms on the water molecule) attaches to the negatively charged oxygen ion at the end of the carboxylate head of the soap molecule. The van der Waals forces, which attach the soap molecules to grease, are based on the shifting polarities of otherwise neutral atoms. The microstructure of grease with soap thickeners consists on cross-linked particles referred to as fibers, floccules or ribbons. The effectiveness of above-mentioned forces depends on how fibers contact each other,[1] and consequently, on the physico-chemical, mechanical, and thixotropic properties of greases.[2,3] The latest is defined as a isothermal decrease in the structural viscosity of a substance during shearing, and characteristic increase in the viscosity and the resolidification of the material once shearing ends.[4,5] The increase in viscosity is caused by the formation of a spatial cross-linked structure during the relaxation of the substance.

FTIR-ATR spectroscopic analysis was performed to study the physicochemical interactions between the associated molecules of lithium 12-hydroxystearate. As a very sensitive method it enables detection of even the smallest changes in the chemical properties of the samples tested, and modifications of interactions at the molecular level.[6,7]

The spectroscopic studies of grease degradation and resolidification consisted in the analysis of changes in absorption of a grease sample before and immediately after shearing, during relaxation and after 24-h relaxation of the grease. During the shearing the bands responsible for free OH groups appeared. Most probably they come from the condensation of the OH groups at C_{12} in the carbon chains of the acid radicals. Simultaneously, concentration of hydrogen-bonded OH decreased. Therefore, from the ATR spectra one can conclude that the hydrogen bonds with the OH groups undergo destruction. This phenomenon is accompanied by a reduction in the intensity of the vibration bands of CH_2 and CH_3 groups originating from lithium 12-hydroxystearate. This is probably the result of the binding of the hydrocarbon chains of single associated molecules. After shearing (during relaxation of the grease) the number of intermolecular hydrogen bonds with the –OH groups is increasing.

As the grease is being sheared, the cross-linked microstructure of the thickener is destroyed. During the relaxation of stresses in the grease, the molecular associates try to return to the initial state, causing an increase in the structural viscosity of the grease.

Acknowledgements

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REFERENCES

1. P.M. Lugt, Tribol. Tran. **2009**, 52, 470.
2. M. Paszkowski, S. Olsztyńska-Janus, Ind. Lub. Tribol. **2014**, 2(66). 223.
3. M. Paszkowski, S. Olsztyńska-Janus, I. Wilk, Tribol. Lett. **2014,** 56, 107.
4. M. Paszkowski, Some aspects of grease flow in lubrication systems and friction nodes, Tribology – fundamentals and advancements, ed. J. Gegner, InTech, Rijeka, **2013**, pp. 77–106.
5. M. Paszkowski, *Proc. Inst. Mech. Eng. J J. Eng. Tribol.*; 2012, 227(3), 209.
6. S. Olsztyńska-Janus, M. Komorowska, Struct. Chem. **2012**, 23, 1399.
7. S. Olsztyńska-Janus, N. Dupuy, L. Vrielynck, M. Komorowska, Appl. Spectrosc. **2006** 60(9), 1040.

The equilibrium between *cis*- and *trans*-*N*-methylformamide in the gas phase

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One of the simplest and yet realistic model systems for peptide bonds is *N*-methylformamide. Like true peptide bonds, it allows for *cis*/*trans* isomerism with a high interconversion barrier. In order to benchmark quantum chemical calculations, it would be valuable to have accurate experimental values for the isomerization enthalpy and entropy in the isolated gas phase. Previous estimates based on quenching the hot gas phase equilibrium in an Ar matrix yielded isomerization enthalpies of 5.4 kJ/mol[1] and 7.4(7) kJ/mol.[2] No experimental isomerization entropies have been reported so far, although it was occasionally assumed that the entropy change is negligible.[2] In contrast, calculations indicate that the entropy of the *cis* form is lower by 7–8 J/(mol K) than that of the trans form.

By quenching the hot gas phase equilibrium in a supersonic jet expansion and probing the cooled isomers in a spontaneous Raman scattering setup,[3] we obtain estimates for both enthalpy and entropy of isomerization, using as an additional input robust relative scattering strengths of the two isomers in the NH stretching region from quantum chemical calculations. We find evidence for smaller isomerization enthalpies than measured before and for more negative isomerization entropies than harmonically predicted. The entropy of the *cis* form is clearly smaller than that of the *trans* form, in line with its higher internal rotation barrier.

We also report on the Raman spectra of singly hydrogen-bonded *trans*-*trans* dimers[4] and the search for *cis*-*cis* dimers, which are predicted to be much more stable, but kinetically hindered due to the high isomerization barrier. Finally, we give an outlook on kinetic isomerization studies.

REFERENCES

1. S. Ataka, H. Takeuchi, M. Tasumi, *J. Mol. Struct.* **1984,** *113*, 147.
2. S. Shin, A. Kurawaki, Y. Hamada, K. Shinya, K. Ohno, A. Tohara, M. Sato, *J. Mol. Struct.* **2006,** *91*, 30.
3. K. E. Otto, Z. Xue, P. Zielke, M. A. Suhm, *Phys. Chem. Chem. Phys.* **2014,** *16*, 9849.
4. M. Albrecht, C. A. Rice, M. A. Suhm, *J. Phys Chem A.* **2008,** *112*, 7530.

P-48

The case of charge assisted hydrogen bonds – QTAIM and SAPT analysis

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The hydrogen bond (H−bond) has been probably most thoroughly investigated among different so-called “weak interactions”. This is due to the fact that H−bond plays an essential role in many physical, chemical and biological processes. The strongest and, therefore, the most effectively affecting physical and chemical properties of interacting molecules, are those assisted by some additional effects, e.g. the resonance-assisted H−bonds (RAHBs) or the charge-assisted H−bonds (CAHBs). The latter occurs when the distribution of formal charges additionally favors H−bonding. A good example of such interaction may be the $NH_4(+)\cdots Cl(-)$ CAHB(+/−) which can be found in the crystal structure of ammonium chloride.

The charge-assisted hydrogen bond (CAHB) was investigated for a set of H−bridges of D−H⋯X (D=N, P, X=Cl, Br) type by the use of computational methods: QTAIM[1] and SAPT[2]. The properties of these bonds, i.e. the interaction energy and its components and the electron density measured in a characteristic point of the chemical bond (bond critical points), were represented as functions of H⋯Cl distance. This gives an opportunity to estimate and discuss the influence of formal charge on the energetic and topological characteristics of H−bonds. We found that the energy of interaction is strongly affected by formal charges, which is caused by the presence of effective interaction between formal ions. However, the electron density measured in the H-bond critical point seems to be totally independent of the formal charges. The decomposition of interaction energy performed for all studied CAHBs systems shows that the electrostatic interaction is obviously the main attractive force in CAHB(+/−) and CAHB(−) H-bridges. The contribution of induction effect plays a crucial role in the stabilities of CAHB(+) H-bridge and the dispersion contribution is the main factor stabilizing *non-charge-assisted* $H_3N\cdots HCl$ complex. Results of interaction energy decomposition were confronted against QTAIM characteristics of H−BCPs. All computations were done at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels.

REFERENCES

1. R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press,**1994**.
2. B. Jeziorski, R. Moszyński, K. Szalewicz, *Chem. Rev.*, **1994**, *94(7)*,1887.

P-49

The shape of the halogen atom – the study on anisotropy of electron density distribution

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A detailed statistical analysis of the data obtained in the CSD search (namely distances in contacts of X···N/O, X···H−N/O, X···C_{any} and the information on spatial arrangement of interacting fragments) shows that the shape of halogen atom cannot be estimated merely on the basis of interatomic distances in crystals. Although originally the concept of anisotropic charge distribution around halogen nuclei was postulated on the basis of such an analysis. It occurs that the virtual shape of the halogen atom estimated in such a way strongly depends on the type of interacting center. Therefore, it was postulated that the shape of the halogen atom can be estimated for the unperturbed (due to intermolecular interactions) halogen atom.[1-3]

Since intermolecular interactions are not a sufficient source of information about the anisotropy of halogen atom, an alternative way in which this physical property can be quantified, was proposed. The analysis of electron distribution was performed within the framework of QTAIM for Y_3C-X (X=Cl, Br and Y=H, F). Densities from DFT−B3LYP and MP2 methods and several different basis sets were investigated.

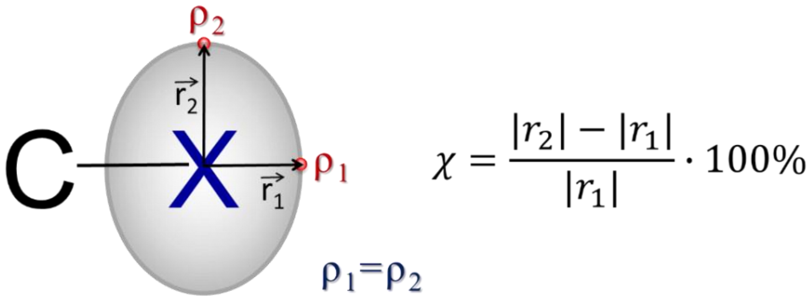

Figure 1 Spatial interrelation between the r_1 and r_2 vectors used to define the χ parameter – degree of anisotropy of the halogen atom

REFERENCES

1. J. P. M Lommerse, A. J. Stone, R. Taylor, F. H. Allen, *J. Am. Chem. Soc.* **1996**, *118*, 3108.
2. S. C. Nyburg, C.H. Faerman, *Acta Cryst. B* **1985**, *41*, 274.
3. S. L. Price, A. J. Stone, J. Lucas, R.S. Rowland, A.E. Thornley, *J. Am. Chem. Soc.* **1994**, *116*, 4910.

P-50

Static DFT investigations of selected quinoline derivatives in the ground and excited states

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Quinoline derivatives are interesting objects to investigate internal molecular reorganizations due to the observed excited-state-induced intramolecular proton transfer (ESIPT). Here, we report on DFT computations for selected 12 quinoline derivatives[1] possessing three kinds of intramolecular HBs. The metric and electronic structure simulations were performed for the ground state and first excited singlet and triplet states. Concluding, the computed potential energy profiles do not show a spontaneous proton transfer in the ground state, whereas excited states exhibit this phenomenon. The application of Harmonic Oscillator Model of Aromaticity (HOMA index)[2] showed that the aromaticity of both rings is strongly dependent on the location of the bridge proton. The ESIPT occurrence was analyzed and compared for the three studied kinds of hydrogen bridges, and competition between two bridges in one molecule was studied as well.

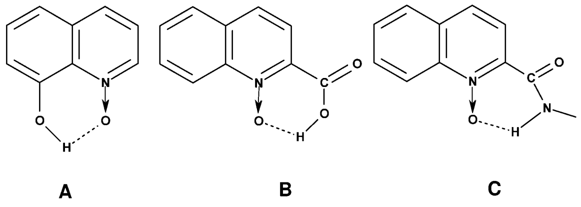

Figure 1 Kinds of intramolecular hydrogen bonds in the studied quinoline *N*-oxide derivatives

Acknowledgements

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REFERENCES

1. T. Dziembowska, Z. Rozwadowski, P. E. Hansen, *J. Mol. Struct.* **1997**, *436-437*, 189.
2. J. Kruszewski, T. M. Krygowski, *Tetrahedron Lett.* **1972**, *13*, 3839.

OH–O versus OH–π hydrogen bonds in binary methanol complexes

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Besides forming the classical OH···O hydrogen bond, alcohols can dock onto more polarizable π clouds. A competitive study introducing both docking sites in a single hydrogen bond acceptor can be used to gauge weak intermolecular forces such as London dispersion. In phenyl ethers and furan derivatives the oxygen bonding site is sufficiently unattractive (due to aromatic delocalization) to render π docking an attractive alternative. The comparison of experimental findings to quantum chemical calculations offers rigorous tests for the performance of the latter in describing dispersion interactions.

A balanced case between oxygen and π docking has lately been observed and predicted for benzofuran.[1] Here, this is further explored by FTIR-analyzed supersonic expansions. The phenyl ether anisole exhibits a slight preference for the oxygen docking site.[2] However, electronic structure theory up to CCSD(T) level with augmented triple zeta basis sets does not predict this energy sequence. Only extension to quadruple zeta basis sets starts to match experiment.

For a more complete and systematic picture further furan derivatives and phenyl ethers are studied by jet-FTIR spectroscopy.

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REFERENCES

1. H. Sasaki, S. Daicho, Y. Yamada and Y. Nibu, *J. Phys. Chem. A*, **2013**, *117*, 3183.
2. M. Heger, J. Altnöder, A. Poblotzki, M. A. Suhm, *Phys. Chem. Chem. Phys.*, **2015**, *17*, 13045.

P-52

Universal thermochemical basicity scale of solvent.

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Intermolecular interactions are of particular interest because they appear only in certain systems and can lead to a significant change in the properties of the interacting molecules, as well as have a significant influence on realization of various physic-chemical and biological processes. For the quantitative estimation influence of solvation effects on the reactivity of the molecules necessary determination thermodynamic parameters of hydrogen bonding solute - solvent. One method of determining these quantities is the thermodynamics of solvation.

In the present work we have carried out a calorimetric study of hydrogen bonding of methanol, chloroform and pyrrole with proton acceptors. Based on the data analyzed the influence of the structure and properties of interacting molecules on the enthalpy of the hydrogen bonds.

In this work, we measured the enthalpies of solution at the limit dilution of methanol, chloroform and pyrrole in 40 solvents belonging to different classes of organic compounds. Based on experimental and literature data by the method [1] were calculated of enthalpy of specific interaction in various systems solute - solvent. Comparing the enthalpies of specific interaction OH, NH and CH groups in the aprotic solvents, were found linear dependence, suggesting that additivity of the thermodynamic parameters of hydrogen bonding in the complexes 1:1. On the basis of found regularities between the enthalpy of specific interaction introduced a scale of basicity aprotic solvents (S_{HBA}). The proposed parameter was tested to describe the enthalpy of hydrogen bonding of phenol and amides with aprotic solvents. In all cases, observed linear correlation of good quality, indicating about correct description of the properties of solvents by this parameter. A comparative analysis of the proposed scale of basicity and the published parameters of the solvent.

It is known that the formation of hydrogen bonds can be determined from the shift of the absorption frequencies in the infrared spectra. The value of the frequency shift is proportional to the strength of hydrogen bonding.

In the present work we have compared the frequency shifts of the absorption of O-H and N-H groups of methanol, phenol, pyrrole and diphenylamine with proton acceptors in complexes 1:1 in the environment carbon tetrachloride on the parameter basicity S_{HBA}. It was found that the spectral characteristics are well described by this parameter.

Acknowledgemets

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REFERENCES

1. B.N. Solomonov, V.B. Novikov, M.A. Varfolomeev, N.M. Mileshko *J. Phys. Org. Chem*. **2005**, 18, (1), 49-61.

P-53

The mechanisms of self-association of N,N'-diallyl derivatives of urea and thiourea

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Self-association process of the N,N'− allyl urea and thiourea was followed using IR spectroscopy, with two gradual aggregation constants determined. Previous work[1,2] demonstrated that a minimum of two equilibrium constants are necessary to describe the association of N,N'− disubstituted derivatives. The first constant, K_1, describes dimerization and a second constant, K_2, describes subsequent multimer formation. The average molecular weight and dipole moments were shown to depend on the concentration, and the form of aggregation was analyzed through study of the dipole moments. Density-functional theory calculations accurately reproduce the experimental data and was used to show the effects resulting from the differences in structure between both N,N'− disubstituted derivatives. N,N'-diallylurea demonstrated an increase in dipole moment with increased concentration, resulting in stronger NRH···O H-bond interactions and leading to linear-type aggregation. Contrastingly, the dipole moments of the N,N'− diallylthiourea decreased with concentration and suggest that cyclic dimers are formed by $C{=}S\cdots(HR)_2N\text{-}C{=}S$ interactions.

Optical properties of N,N'-diallylurea have been spectroscopically investigated by means of IR-LD spectroscopy of oriented samples as a suspension in nematic liquid crystals. Eg.:

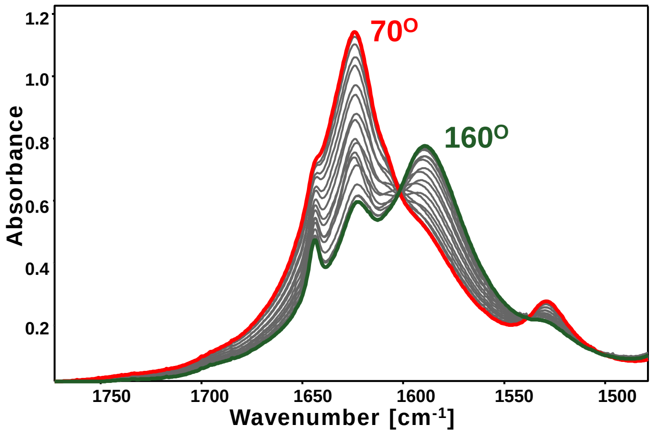

Figure 1 IR-LD spectra of N,N'-diallylurea in the 1750-1500 cm^{-1} frequency range, in function of polarization angle rotation

Acknowledgements

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REFERENCES

1. M. Obrzud, M. Rospenk, A. Koll; *J. Phys. Chem. B* **2010**, 114, 15905.
2. M. Obrzud, M. Rospenk, A. Koll; *J. Mol. Struct*. **2012,** 1018, 54.

Cryosolution infrared study of isoflurane and hydrogen bonded isoflurane•dimethyl ether complex.

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Isoflurane (CF_3-CHCl-O-CHF_2) is a structural isomer of enflurane (CHFCl-CF_2-O-CHF_2). As in the case of enflurane, two CH groups of this volatile anesthetic can act as proton donors of different energetic and spectroscopic features. In the present report, the combined experimental and theoretical studies have been performed to analyze the IR spectrum of isoflurane and, preliminary, isoflurane/dimethyl ether (DME) mixtures. The spectra of the systems studied were registered in low temperature cryogenic solvent Kr at T ~ 120 – 160 K. The data obtained for isoflurane/DME mixtures suggest that the H atom of CHCl group forms a red shifting H – bond with DME. Ab initio calculations utilizing MP2 level of theory with Pople-type 6-311++G(d,p) basis set have been performed to find geometric and spectroscopic parameters of stable conformers and H-bonded complexes of the systems studied. The conformational analysis based on the relaxed PES scan calculations predicts (as in the case of enflurane) 6 stable conformers of isoflurane. However, only two the most stable conformers have perceptual population and contribute to the IR spectrum of isoflurane at $T < 300$ K. Spectroscopic parameters of H–bonded isoflurane/dimethyl ether complex have been experimentally measured and analyzed in comparison with the calculations.

Acknowledgements

The work was supported by the National Science Centre for research funding (grant no. 2012/05/B/ST/02029). S.M.M. and K.S.R. thank RFBR (grant no 14-03-00716) for support. The calculations have been performed using the computer resources of the Resource Center of SPbGU (http://cc.spbu.ru) and of the Wrocław Center for Networking and Supercomputing (http://www.wcss.wroc.pl).

REFERENCES

1. D. Michalska, D.C. Bienko, B. Czarnik-Matusewicz, M. Wierzejewska, C. Sandorfy, Th. Zeegers-Huyskens, *J. Phys. Chem*. **2007**, B 111, 12228.
2. S.M. Melikova, K.S. Rutkowski, E.Telkova, B.Czarnik-Matusewicz, M. Rospenk, W. Herrebout, *Chem. Phys*. **2015**, 453-454, 26.

P-55

The FTIR spectrum of desflurane and desflurane / dimethyl ether mixture in low temperature Kr solvent. Conformational analysis and evidence of H bonded complex formation.

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Desflurane ((CF_3-CHF-O-CHF_2) is a third generation very volatile anesthetic, with the vapor pressure being close to atmospheric at room temperature. Three single bonds in the C – C – O – C skeleton, suggests possible existence of several conformational forms. This might result in the vibrational spectrum, with numerous bands assigned to the same normal vibration. As in the case of enflurane[1,2] and isoflurane, two CH groups of this volatile anesthetic can act as proton donors. In the present report, the combined experimental and theoretical studies have been performed to analyze the vibrational spectrum of desflurane and desflurane/dimethyl ether (DME) mixtures. The IR spectra of the systems studied were registered in liquid Kr. The assignment of a set of fundamental vibrational bands of desflurane has been made by comparison of experimental data obtained by mixed IR/Raman technique and the results of ab initio calculations utilizing MP2/6-311++G(d,p) level of theory. The conformational analysis suggests that only two the most stable conformers have perceptual population and contribute to the IR/Raman spectra of desflurane at $T < 300$ K. Spectroscopic parameters of H–bonded desflurane/DME complex have been experimentally measured and analyzed in comparison with the calculations.

Acknowledgements

The work was supported by the National Science Centre for research funding (grant no. 2012/05/B/ST/02029). S.M.M. and K.S.R. thank RFBR (grant no 14-03-00716) for support. The calculations have been performed using the computer resources of the Resource Center of SPbGU (http://cc.spbu.ru) and of the Wrocław Center for Networking and Supercomputing (http://www.wcss.wroc.pl).

REFERENCES

1. D. Michalska, D.C. Bienko, B. Czarnik-Matusewicz, M. Wierzejewska, C. Sandorfy, Th. Zeegers-Huyskens, *J. Phys. Chem*. **2007**, B 111, 12228.
2. S.M. Melikova, K.S. Rutkowski, E.Telkova, B.Czarnik-Matusewicz, M. Rospenk, W. Herrebout, *Chem. Phys*. **2015**, 453-454, 26.

P-56

In the search of the most appropriate DFT method for electron density distribution analysis – comparative experimental and theoretical studies on 2,5-diacethylhydroquinon

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The quantum theory of Atoms in Molecules (QTAIM) provides a powerful tool for topological analysis and interpretation of electron density distribution. Such analysis can be performed on the basis of experimental X-ray diffraction data and theoretical wavefunctions determined by high level quantum theoretical calculations. The latter can be obtained by various types of theoretical methods including *ab initio* Hartree-Fock (HF) and post HF (for example MP2) studies as well as density functional calculations (DFT). DFT is among the most popular methods currently available in computational modeling but the variety of possible functionals gives the reason for searching the most convenient and fast method which provides results consistent with experimental data. In turn, high resolution X-ray diffraction, has many limitations including quality of crystal, special equipment, high brilliance X-ray source and usually long time of experiment - such experiments in comparison with standard measurements are characterized by very high costs. Therefore, it seems that combination of standard X-ray crystallographic studies with modern quantum chemistry computations will be the most appropriate, relatively easy achievable way of obtaining reliable electron density distribution of molecular structures. However, it raises the relevant question about the most appropriate level of theoretical calculations, including time.

In this study we have analyzed results of various theoretical methods and functionals in order to compare obtained data with experimentally determined topology of electron density. 2,5-Diacethylhydroquinon was chosen as an object of the study because of simplicity its molecule as well as because of existence of interesting intramolecular O-H…O hydrogen bond. Therefore, a relevant crystallographic problem with proper determination of hydrogen atom positions was analyzed from the point of view of QTAIM theory.

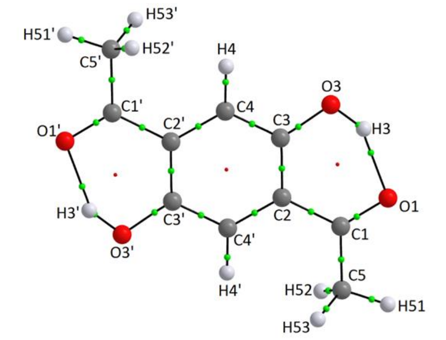

Figure 1 Bond paths and bond critical points according to QTAIM in the molecule of 2,5-diacethylhydroquinon

Acknowledgements

The theoretical computations with Gaussian 09 set of codes were carried out in Wrocław Center for Networking and Supercomputing (http://www.wcss.wroc.pl). Access to HPC machines and licensed software is gratefully acknowledged.

P-57

Proton donor and acceptor properties of *N*-hydroxyurea

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N-hydroxyurea (HU) is a representative of hydroxamic acids with the N(OH)CONH$_2$ grouping occurring in numerous biologically active compounds. It demonstrates a complex pharmacological profile and is used as a human chemotherapeutic agent. I have recently studied the isomerical and structural properties of *N*-hydroxyurea and showed that HU trapped from the gas phase into solid argon exists in the matrix preferentially in the 1*E* keto form.[1] Hydroxamic acids are *N*-hydroxy substituted derivatives of amides and involve the fragment of the simplest protein structure HNC=O. In addition to the two basic centres characteristic for the HNC=O group, hydroxamic acids have the third basic centre which is the oxygen atom of the hydroxyl group. In order to evaluate proton donor and acceptor abilities of the acidic and basic centres of the *N*-hydroxyurea molecule the infrared matrix isolation and theoretical studies of the self-association of *N*-hydroxyurea and complexes with strong proton donors: HCl and HF were performed.

The 1:1 HU···HX complexes, identified for both hydrogen halide molecules, have the cyclic structures stabilized by the X-H···O and N-H···X bonds; for the HU···HF system another isomeric 1:1 complex is also observed in which the F-H···O and (H)N-H···F bonds are present. Two 1:2 complexes were identified for the *N*-hydroxyurea–hydrogen chloride system characterised by the Cl-H···O and N-H···Cl bonds. In the first complex HU interacts with the HCl dimer, one HCl molecule acts as a proton donor toward the oxygen atom of the carbonyl group, whereas the second HCl molecule acts as a proton acceptor for the NH$_2$ group of HU. In the second complex the carbonyl group of HU acts as a double proton acceptor toward two HCl molecules.[2]

The obtained results evidence that in the matrix are formed two (HU)$_2$ dimers stabilized by a strong OH···O hydrogen bond. There is an additional weak interaction between the oxygen atom of the OH group of the proton donor molecule and the NH or NH$_2$ group of the proton acceptor in both dimers, respectively. The presence of the structures not characterised by the lowest values of the binding energy in the studied matrices indicates that the formation of *N*-hydroxyurea dimers is kinetically and not thermodynamically controlled.[3]

Acknowledgements

The author acknowledges the Wrocław Supercomputer Centre (WCSS) for providing computer time and facilities.

REFERENCES

1. M. Sałdyka, *Phys. Chem. Chem. Phys.* **2010,** *12*, 15111.
2. M. Sałdyka, *Chem. Phys.* **2014,** *444*, 15.
3. M. Sałdyka, sent for publication in *Spectrochimica Acta A.*

Formaldoxime hydrogen bonded complexes with ammonia and hydrogen chloride

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Oximes are important biological and chemical systems. The >C=NOH group involves the OH hydrogen bond donor and two hydrogen bond acceptor sites, namely the C=N nitrogen and the O-H oxygen, so, oximes may form a variety of hydrogen bonds. The intermolecular hydrogen bond motifs involving oximes play an important role in molecular design. Oximes exhibit significant molecular association even in the dilute gas phase which is relatively rare phenomenon. The ability of oximes to form hetero-aggregates with various proton donors and acceptors was much less studied than oximes homo-aggregation. Formaldoxime complexes with nitrogen,[1] nitrous acid[2] and water[3] were recently studied by help of matrix isolation technique and quantum chemistry methods. Ammonia and hydrogen chloride serve as archetypal strong proton acceptor and strong proton donor, respectively, in the studies of hydrogen bonding. The study of the formaldoxime complexes with these two molecules shall provide information on the proton acceptor and proton donor abilities of the >C=NOH group.

An infrared spectroscopic and MP2/6-311++G(2d,2p) study of the complexes of formaldoxime with NH_3 and HCl trapped in argon matrices is presented.[4] Both 1:1 and 1:2 complexes have been identified in the $CH_2NOH/NH_3/Ar$, $CH_2NOH/HCl/Ar$ matrices, respectively, their structures were determined by comparison of the spectra with the results of calculations. In the 1:1 complexes present in the argon matrices the OH group of CH_2NOH acts as a proton donor for NH_3 and a nitrogen atom acts as a proton acceptor for HCl. In the 1:2 complexes ammonia or hydrogen chloride dimers interact both with an OH group and a nitrogen atom of CH_2NOH to form seven membered cyclic structures stabilized by three hydrogen bonds. The theoretical spectra generally agree well with the experimental ones, but they seriously underestimate the shift of the OH stretch for the 1:1 $CH_2NOH\cdots NH_3$ complex.

Acknowledgements

The authors acknowledge the Wrocław Supercomputer Centre (WCSS) for providing computer time and facilities.

REFERENCES

1. B. Golec, J. Grzegorzek, Z. Mielke, *Chem. Phys.* **2008**, *353*, 13.
2. B. Golec, A. Bil, Z. Mielke, *J. Phys.Chem. A,* **2009,** *113*, 9434.
3. B. Golec, M. Mucha, Z. Mielke, *Spectrochim. Acta. Part A,* **2012**, *86*, 461.
4. B. Golec, M. Mucha, M. Sałdyka, A. Barnes, Z. Mielke, *Spectrochim. Acta. Part A,* **2015**, *136*, 68.

Role of electrostatics in Hydrogen Bonding and π–π stacking

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Non-covalent interactions such as hydrogen bonding, π–π stacking, lone pair-π, ion-π interactions, play significant role in the field of chemistry, biology and material science. In our lab we have investigated the C–H and O–H vibrational stretching frequency of several X–H···Y (X=C, O; Y = N, O) hydrogen-bonded complexes of phenylacetylene, fluorine substituted phenylacetylenes and phenol with different ligands. It has been shown that the red-shifts in the X–H stretching frequency are linearly correlated with the electrostatic component of the total energy while the stabilization energy is modulated by the dispersion component. The π-stacked homo-dimers of phenylacetylene, singly fluorine substituted phenylacetylenes and propargylbenzene were also investigated. Energy decomposition analysis suggests that dispersion plays pivotal role in π–π stacking with appreciable contribution from electrostatics. The stabilization energies of fluorophenylacetylene dimers follow the same ordering as their dipole moments, which suggests that dipole moment enhances the ability to form π–stacked structures. The analysis of propargylbenzene dimer shows the synergy between the π–π stacking and C–H···π interactions on the overall interaction energy.

Acknowledgements

Debashree Ghosh, Arghya Dey, Sohidul Islam Mondal, Aniket Kundu.

REFERENCES

1. A. Dey, S. I. Mondal, S. Sen, D. Ghosh, G. N. Patwari, *Phys. Chem. Chem. Phys.* **2014**, *16*, 25247-25250.
2. S. I. Mondal, A. Dey, S. Sen, G. N. Patwari, D. Ghosh, *Phys. Chem. Chem. Phys.* **2015**, *17*, 434-443.
3. A. Kundu, S. Sen, G. N. Patwari, *Phys. Chem. Chem. Phys.* **2015**, *17*, 9090-9097.

P-60

The charge assisted halogen bonding – complexes of quinuclidine derivatives

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Quinuclidine is an organic compound from the group of bicyclic heterocyclic compounds. It consists of the backbone bicyclo[2.2.2]octane, wherein one of the carbon node is nitrogen. Based on the analyzed model systems with single (I) and double (II) bonds in the backbone bicyclo[2.2.2]octane different from each other substituents of the cation and anion quinuclidine derivatives (where: X = Cl, Br; R = H, CN; A = CN, F, Cl, Br). In the first stage of the study the geometries of 32 systems were optimized at ωB97XD/aug-cc-pVTZ, using the Gaussian 09 program[1]. The energetic and structural properties of all complexes were tested against the topological parameters of the electron density distribution obtained by means of a Quantum Theory of „Atoms in Molecules"[2]. Interaction energies in investigated complexes, estimated with supermolecular method, appeared to be drastically larger than in classic (non-charge-assisted) halogen bonds, being in some cases above the 100 kcal/mol. Characteristics of topological and structural parameters follow the large values of energies, indicating very strong interaction of electrostatic nature in the first line.

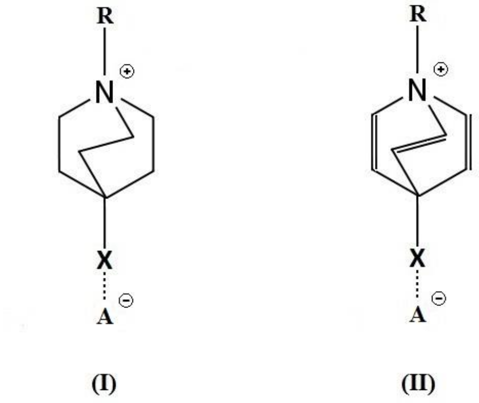

Figure 1 Forms quinuclidine with single bonds in the ring (I) and the double bonds within the cage (II).

REFERENCES

1. M.J. Frisch, et. al., *Gaussian 09; Gaussian, Inc*.: Wallingford, CT, **2009**.
2. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press: New York, **1990**.

P-61

The cooperativity of halogen- , hydrogen- and chalcogen-bonds : the dual role of sulfur atom in dimeric and trimeric intermolecular complexes.

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In recent times a growing interest on halogen and chalcogen bond increases. This type of interaction is of noncovalent type[1,2] acting between the electron-acceptor fragment (Lewis acid) and electron-donor fragment (Lewis base). We analyzed complexes stabilized by two or three different types of noncovalent interactions, that is, hydrogen bond, halogen bond and chalcogen bonds, respectively. The three-component complexes $(C_2XS)(HCN)(CX_3Br)$ and $(C_2XS)(H_2O)(CF_3Br)$, where X = H, F, are schematically illustrated in Figure 1. In addition two-complexes of C_2X_6S/ HCN, NCH, CX_3Y where X=H, F and Y=Br, F type, being fragments of larger counterparts, were also investigated. The model systems were chosen such that the sulfur atom would play the dual role of electron donor and acceptor.

In the first stage of the study the geometries of studied systems were optimized at ωB97XD/6-311++G**, using the Gaussian 09 program[3]. In the next step the topological analysis of the electron density distribution was done by means of a Quantum Theory of „Atoms in Molecules" (QTAIM)[4]. A thorough analysis of the most important energy components and topological parameters at bond critical points (BCP), allowed to perform the direct interrelation between individual interactions (cooperativity/anticooperativity effect).

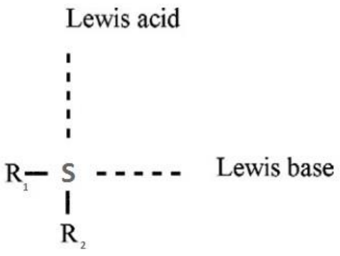

Figure 1 Caption spatial arrangement of interacting fragments in Lewis acid/base complexes of halogen atom.

Acknowledgements

Calculations using the Gaussian 09 set of codes were carried out in Wroclaw Centre for Networking and Supercomputing (http://www.wcss.wroc.pl). Access to HPC machines and licensed software is gratefully acknowledged.

REFERENCES

1. P. Politzer, J.S. Murray, T. Clark, *Halogen bonding: an electrostatically-driven highly directional noncovalent interaction, Phys. Chem. Chem. Phys.* **2010,** *12*, 7748–7757.
2. A.C. Legon, *The halogen bond: an interim perspective, Phys. Chem. Chem. Phys.* **2010,** *12,* 7736–7747.
3. M.J. Frisch, et. al., *Gaussian 09; Gaussian, Inc*.: Wallingford, CT, **2009**.
4. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press: New York, **1990**.

P-62

Complexation of two polymers as a result of hydrogen bonding and fractionation

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Formation of a complex of two polymers, i.e. of an interpolymer or macromolecular complex, is a process resulting in structures that can be exploited e.g. as drug-delivery systems, biosensors or adhesives.

Complexation is controlled by diffusion and is also dependent on the composition of the two polymers involved, their concentration and the nature of the solvent used. It is generally assumed that complex may only form if the molar masses of the two macromolecules exceed a certain value, i.e. if a minimal chain length exists. The complexation process can be driven by Coulombic forces, hydrogen bonding interactions, van der Waals forces, charge transfer interactions and hydrophobic interactions. This means that interacting sites exist in the two macromolecules, the intrinsic binding energy of which is lower than binding energy of a covalent bond, but the total binding energy may exceed that of a single covalent bond. In addition, the specific interactions leading to complexation also affect mixing of two polymers in a blend: e.g. hydrogen-bonded complexes are a special class of miscible polymer blends.

We have studied miscible blends of poly(N-methyldodecano-12-lactam) (PMDL) and poly(4-vinylphenol) (PVPh), which were soluble in tetrahydrofuran (THF) by differential scanning calorimetry and attenuated-total-reflection FTIR spectroscopy.[1] We found that the miscibility was mediated by hydrogen bonds between hydroxyl groups of PVPh and carbonyl groups of PMDL. However, when PMDL and PVPh of higher molecular mass were used, two types of a hydrogen-bonded associate formed: a gel-like interpolymer complex and a soluble blend.[2] Since all the factors, except for the higher molecular mass, were the same as for the polymers with lower molecular mass, it was expected that the process of complexation was either preceded or accompanied by fractionation. The complexes and the soluble blends were characterised by elemental analysis, differential scanning calorimetry, size exclusion chromatography and thermogravimetric analysis. The gel-like inter-polymer complex is usually assumed to have a ladder-like structure of co-operative H-bonds; on the other hand a soluble blend is thought to have a loose random H-bond structure. Thus, we also used FTIR spectroscopy and DFT calculations to answer the question whether there was any additional factor, e.g. higher density of the intermolecular H-bonds that would contribute to the observed complexation.[3]

REFERENCES

1. J. Kratochvíl, A. Šturcová, A. Sikora, J. Dybal, *J. Polym. Sci. Part B: Pol. Phys.* **2011**, *49*, 1031
2. J. Kratochvíl, A. Šturcová, A. Sikora, J. Dybal, *Polym. Int.* **2014**, *63*, 1406.
3. A. Šturcová, J. Kratochvíl, A. Sikora, J. Dybal, *Eur. Polym. J.* **2014**, *59*, 200.

Strong H-bonds formed by CH acids: changes of geometric and NMR parameters along the proton transfer pathway

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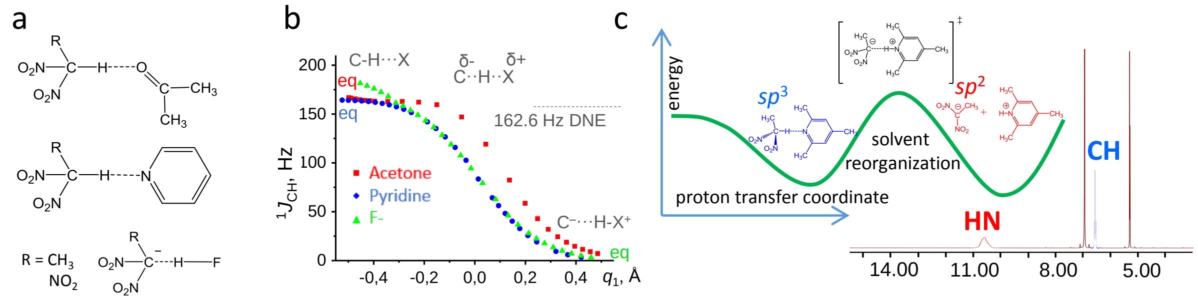
In the first part of this work we present the results of quantum-chemical calculations performed for a series of H-bonded complexes formed by strong CH acids, namely, trinitromethane and 1,1-dinitroethane (DNE), with acetone, pyridine and fluoride anion (see Fig. 1a). The geometric changes and changes of NMR parameters – chemical shifts and coupling constants of all three atoms involved in H-bond – were calculated along the quasi-adiabatic proton transfer pathway. In Fig. 1b see f.e. the dependence of $^1J_{CH}$ on $q_1 = ½ (r_{CH} – r_{HN})$ for DNE/pyridine complex.

In the second part we attempt to investigate by experimental NMR spectroscopy the structure of zwitterionic species on the example of 1,1-dinithoethane/2,4,6-collidine complex in CD_2Cl_2. The question of the existence of H-bond between NH group of the protonated base and the carbon atom of the anion (planar carbanion, $sp^3 \rightarrow sp^2$ rehybridization) is being addressed (see. Fig. 1c).

This work is continuation of the research presented on the previous conference on “Horizons in Hydrogen Bond Research” (Antwerp 2013)[1] and it follows up our recent publication.[2]



Acknowledgements

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REFERENCES

1. E. Tupikina, P. Tolstoy, G. Denisov, „Hydrogen bonds formed by CH-acids: structure and NMR properties of complexes of 1,1-dinitroethane with various proton acceptors”, XX International Conference on Horizons in Hydrogen Bond Research, Antwerp, 2013, Book of Abstracts, p. 25.
2. E.Yu. Tupikina, G.S. Denisov, P.M. Tolstoy, *J. Phys. Chem. A.* **2015**, *119*, 659.

P-64

Intramolecular hydrogen bonding in methyl lactate

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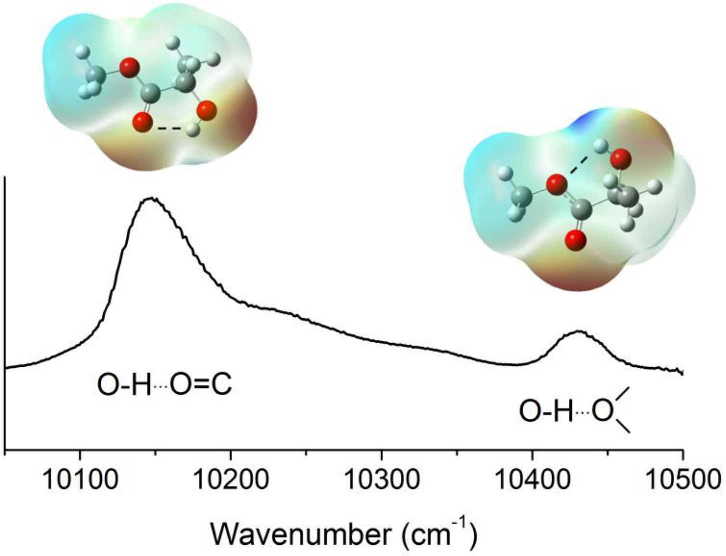
Intramolecular hydrogen bonds are of great importance as they determine the structure of several biomolecules, including the secondary and tertiary structure of proteins. Not only the possibility of forming an intramolecular hydrogen bond is important but also the competition between hydrogen bonds of different strengths. Methyl lactate (ML) forms an OH-O hydrogen bond to either a carbonyl oxygen or an ester oxygen. We present experimental and theoretical results that suggest that the carbonyl oxygen in methyl lactate is a better hydrogen bond acceptor than the divalent ester oxygen. Gas phase spectra of the Δv = 1-4 vibrational transitions of the OH-stretch were recorded using Fourier transform infrared spectroscopy (FTIR), intracavity laser photoacoustic spectroscopy (ICL-PAS) and cavity ringdown spectroscopy (CRD). Interpretation of the spectra was guided by vibrational local mode calculations. Interpretation of the complicated Δv = 4 region was further aided by deuteration and CRD spectra recorded at different temperatures. Furthermore, the hydrogen bond formation was examined theoretically using atoms in molecules (AIM), non-covalent interactions (NCI) and natural bond orbital (NBO) analyses.



ICL-PAS spectrum of the Δv_{OH} = 3 region including the calculated structure of the two most abundant conformers of ML along with the electrostatic potential energy plotted on the electron density isosurfaces

P-65

Spectroscopic and theoretical studies on the S(^{3}P)···HCN complex

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Photo-transformations of HNCS induced by tunable UV laser were studied using low-temperature matrix isolation coupled with the FTIR spectroscopy. Upon irradiation with wavelength $\lambda \geq 290$ nm the main process observed is the HNCS photo-isomerization leading to its isomers: thiocyanic acid HSCN and isothiofulminic acid HSNC. The UV photolysis at $\lambda < 290$ nm of matrix isolated HNCS results in formation of a hydrogen bonded complex between hydrogen cyanide and a ground state (^{3}P) sulfur atom. The vibrational bands of the S···HCN species are observed at 3217.0 and 746.5 cm^{-1} in an argon matrix and 3223.5 and 764.5/752.0 cm^{-1} in solid N$_2$. Based on the kinetic profiles found for the key species it was possible to conclude that the main source that gives rise to formation of the S···HCN complex was thiocyanic acid HSCN but a small impact of HSNC into the process was also evident. In solid nitrogen, HCN monomers are observed besides S···HCN indicating the hydrogen bond breaking and efficient escape of atomic sulfur out of the matrix site. Differences in the extent of the observed processes are discussed in relation to sulfur atoms mobility and the type of matrices. Results of the computational studies performed on the S···HCN geometry and infrared spectrum are presented and compared with the experimental data.

Acknowledgements

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P-66

The role of hydrogen-bonds in drug design. Study of idelalisib fluorine derivatives.

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Idelalisib (Zydelig) is a phosphoinositide 3-kinase delta (PI3Kδ) inhibitor that has been recently approved (in 2014) for the treatment of several hematological malignancies, especially as a second line drug for patients whose chronic lymphocytic leukemia (CLL) has relapsed.

The drug works as a competitive inhibitor of the ATP-binding pocket in the PI3Kδ kinase. Several additional biochemical and biophysical assays showed that the compound binding to the kinase is non-covalent and reversible. A crystal structure of idelalisib bound to the p110δ subunit of PI3Kδ deepens our understanding of the binding interactions that confer the potency and selectivity of idelalisib.

We have established the binding modes of mono-, di- or trisubstituted idelalisib derivatives by fluorine atom in their respective binding sites of PI3Kδ kinase on the basis of intermolecular interactions such as H-bonding. It is found that the hydrogen-bond intermolecular interactions, along with the π-π stacking, play the most important role in binding the ligands into the binding pocket. The significant influence of fluorine substituent on hydrogen-bond network has been observed. Furthermore, the calculated pair-wise interaction energies between each inhibitor and a specific residue in the binding pocket exhibited the changes in the binding strength are dependent on the derivatives.

The molecular docking and molecular dynamics simulations were performed to find out a binding site and to study the time evolution of binding process in the pocket. The strengths of all intermolecular interactions are quantified by means of *ab initio* electronic structure calculations.

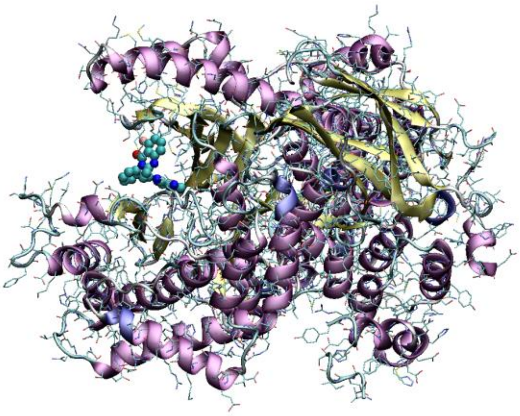

Figure 1 Idelalisib (pdb code: 4XE0) bound to the p110 subunit of PI3Kδ inhibitor.

P-67

Structural consequences of dehydration of bis(betainium) *p*-toluenesulfonate monohydrate crystal

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The water molecule, from hydrogen bonding point of view, is unique in having both double-donor and double-acceptor hydrogen-bond functionality. In organic solid hydrates water molecules are involved in hydrogen bond networks and affect the crystal structure of hydrates and their packing. On the other hand, the dehydration of organic solid hydrates leads to their changes involving a structural rearrangement and physical or biological properties. The dehydration of crystalline hydrates of organic compounds is an important process, particularly in the pharmaceutical industry. Since of this an understanding of the dehydration process, details of its mechanism as well as a nature of a product formed by this process seem to be very important and desirable.

In this contribution the structural consequences of water removed from bis(betainium) *p*-toluenesulfonate monohydrate (BBTSH) are considered[1]. Our consideration have been based on the single crystal XRD and powder sample XRD data of BBTSH crystal and its dehydrated form (BBTS) collected at various temperature and on the temperature dependent vibrational spectra of both forms, BBTSH and BBTS. DSC studies of the BBTSH crystal reveal anomaly at about 349 K which corresponds to water escape from the crystal.

- The most interesting results and conclusions are as follows:

1. The asymmetric unit of BBTSH comprises *p*-toluenesulfonic anion, monoprotonated betaine dimer and water molecule. Two O-H···O hydrogen bonds are present in the crystal: very strong (O···O distance of 2.463(2) Å), almost linear linking betaines into a dimer and weak (O_w···O distances of about 2.8 Å) in which the water molecules are involved.
2. BBTSH belongs to the $P2_1/c$ space group of a monoclinic system. Dehydration results in change of a crystal system. BBTS belongs to the *P*-1 space group of a triclinic system.
3. The dehydration process is accompanied by the breakage of the strong O-H···O hydrogen bonds in betaine dimers, rearrangement inside half of the betaine dimers and subsequently, formation of the new dimers in which very strong O-H···O hydrogen bonds are also apparent (O···O distances are equal to 2.451(4) and 2.519(5) Å). These findings are very well corroborated by the vibrational data. In the temperature dependent infrared spectra the most prominent changes are noted in two regions: (1) in the $\nu_a H_2O$ and $\nu_s H_2O$ stretching vibrations (3600-3200 cm^{-1}) and (2) in the νC=O stretching vibration (1800-1600 cm^{-1}). However no changes are noted in the ν_aOHO hydrogen bond stretching vibration region (below 1500 cm^{-1}).

REFERENCES

1. Ł. Wołoszyn, M. M. Ilczyszyn, V. Kinzhybalo, *Vib. Spectrosc.* **2015**, *76*, 6.

P-68

HXeI complexes in a Xe matrix: correlation between the H−Xe stretching frequency and photostability

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Noble-gas hydrides HNgY (Ng=noble-gas atom and Y=electronegative fragment) have weak bonding and large dipole moments. This leads to a strong complexation effect on various properties of these molecules (e.g., structure and vibrational frequency).[1] HXeI is one of the least stable HXeY molecules identified experimentally. Thus, the complexation effect on the properties of HXeI is interesting to study.

In the present work, we study IR spectra and photostability of the HXeI···HY complexes (Y=Cl, Br, I, and CCH) in a Xe matrix. The ab initio calculations reveal several HXeI···HY structures. The most stable structure with the Y−H···I hydrogen bond is experimentally observed for all complexes.[2, 3] In addition, structures with the Xe−H···Br and Xe−I···I−H interactions are probably formed for the HXeI···HBr and HXeI···HI complexes, respectively.[2]

HXeI can be decomposed by IR radiation in the 2950–3800 cm^{-1} region.[4] Figure 1 shows the lifetime of HXeI in different complexes under IR radiation of the spectrometer as a function of the shift of the H−Xe stretching mode. It is seen that the photostability of HXeI increases with the complexation-induced shift. Two contributions can be responsible for the observed effect. The first contribution is due to an increase of the harmonicity of the H–Xe stretching mode upon complexation, which decreases the intensity of the H–Xe stretching overtones. The second contribution originates from the different excess energies available for the H atom after photodissociation, which changes the cage exit probability.

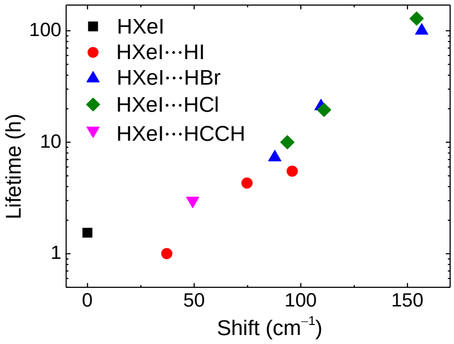

Figure 1 Lifetime of HXeI in different complexes under broad-band IR irradiation as a function of the shift of the H−Xe stretching mode.

Acknowledgements

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REFERENCES

1. A. Lignell, L. Khriachtchev, *J. Mol. Struct.* **2008,** *889*, 1.
2. M. Tsuge, S. Berski, M. Räsänen, Z. Latajka, L. Khriachtchev, *J. Chem. Phys.* **2013,** *138*, 104314.
3. C. Zhu, M. Tsuge, M. Räsänen, L. Khriachtchev, *J. Chem. Phys.* **2015,** *142*, 144306.
4. M. Pettersson, J. Nieminen, L. Khriachtchev, M. Räsänen, *J. Chem. Phys.* **1997,** *107*, 8423.

P-69

Blue-shifting C-H···O hydrogen bonds and the origin of unusual intensity changes in the infrared spectra of enflurane···acetone complexes

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Numerous authors reported that the formation of the blue-shifting C-H···O hydrogen bond was accompanied by a decrease of the IR intensity of the ν(C-H) stretching mode. Our experimental and theoretical studies on the volatile anesthetic enflurane and its complexes with deuterated acetone revealed the striking effect. For the two blue-shifted ν(C-H) stretching frequencies of enflurane the corresponding two infrared bands showed the opposite changes of their intensity, one was decreasing and the other was significantly increasing upon formation of the hydrogen bonding.[1]

The origin of this phenomenon has been investigated by using ab initio MP2 method combined with the 6-311++G(d,p) basis set. For the two enflurane-acetone complexes the interaction energies were evaluated at the CCSD(T)/CBS level of theory.

It is known that the infrared intensity of the normal mode is proportional to the square of the dipole moment derivatives of a molecular system with respect to the corresponding normal coordinate. In our study, for each of the two C-H stretching modes, the derivatives of the components of the dipole moment along the $Q_{C\text{-}H}$ normal coordinate were calculated for enflurane and its complexes with acetone.[2] We have found that a key factor responsible for the different behavior of the IR intensities of the two C-H stretching modes is the change of the angle between the molecular dipole moment and the *z* axis (along which the $Q_{C\text{-}H}$ normal coordinate is defined) caused by complexation. Thus, in the hydrogen bonded complexes studied, the change of this angle causes the changes of the components of the dipole moment derivatives (and their squares) which in consequence, leads to different IR intensities of the corresponding ν(C-H) stretching vibrations.

REFERENCES

1. W. Zierkiewicz, B. Czarnik-Matusewicz, D. Michalska, *J. Phys. Chem. A*, **2011**, *115*, 11362.
2. W. Zierkiewicz, R. Zaleśny, P. Hobza, *Phys. Chem. Chem. Phys.*, **2013**, *15*, 6001.

P-70

Analysis of conformational and polymorphic states of nitro-acetophenone.

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The nitro derivative of ortho-hydroxy acetophenone has been studied by experimental and theoretical methods. Two polymorphic forms of this compound have been obtained by evaporation of polar and non-polar solutions. Both polymorphs have been investigated by Infrared (IR), Raman, Incoherent Inelastic Neutron Scattering (IINS), Nuclear Quadrupole Resonance (NQR), differential scanning calorimetry (DSC) and density functional theory (DFT) methods. In one of the polymorphs the existence of a phase transition has been shown by NQR and DSC methods. The potential energy curves on rotation and isomerization have been calculated by DFT method for estimation of barriers of the conformational change and adjustment. A complete spectral analysis of vibrational spectra has been accomplished. The infrared spectra have been measured in a wide temperature range in order to reveal the spectral bands most sensitive to a phase transition. On the basis of the abovementioned studies the nature of the phase transition has been explained.

Effect of hydrogen bonding on electron-attracting ability of the nitro group

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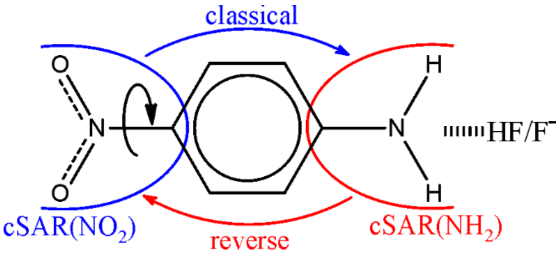
The model termed as “charge of substituent active region” (cSAR, defined as a sum of atomic charges at the substituent and the *ipso* carbon atom)[1,2] has been used to characterize electron-attracting ability of the nitro group. The cSAR model has been applied to *para*-nitroaniline complexes in which properties of the amino group (reaction site) are modified by intermolecular H-bonding (see Scheme 1). Additionally, for all studied systems properties of the nitro group are also changed by its rotation from coplanar to perpendicular orientation with respect to the benzene ring. It has been shown that electron-attracting ability of the nitro group and its rotamers can be significantly changed by intermolecular interactions of the reaction site.[3] A quantum chemistry modeling and cSAR approach allow to document the reverse substituent effect, showing the influence of reaction site on the properties of substituent.



Scheme 1 Schematic representation of the studied H-bonded complexes

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REFERENCES

1. N. Sadlej-Sosnowska, *Polish J. Chem*. **2007**, *81*, 1123.
2. N. Sadlej-Sosnowska, *Chem. Phys. Lett*. **2007**, *447*, 192.
3. O.A. Stasyuk, H. Szatylowicz, C. Fonseca Guerra, T.M. Krygowski, *Struct. Chem.* **2015,** doi: 10.1007/s11224-015-0608-6

P-72

Gas phase laser spectroscopy reveals hyperconjugation effects in hydrazide molecules

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NH stretch frequencies are often used as a spectroscopic indicator for H-bond strength. This indicator, however, is also sensitive to other specific electronic effects capable of weakening the NH bond, such as hyperconjugation, in which nearby molecular orbitals can significantly overlap with the NH bond σ^* orbital. The corresponding partial charge transfer is usually small and difficult to evidence experimentally. We here present results related to hydrazides, a family of molecules based on a –CO-N$^{(1)}$H-N$^{(2)}$< chemical group (Figure 1), especially interesting as building blocks for molecular design. In these flexible systems, the lone pair of the N$^{(2)}$ nitrogen atom can strongly interact with the σ^*_{NH} orbital providing that the conformation of the hydrazide group allows such a spatial overlap.[1] As a result the NH stretch frequency is highly sensitive to hyperconjugation, making it an efficient probe of the conformation of the neighboring nitrogen atom.

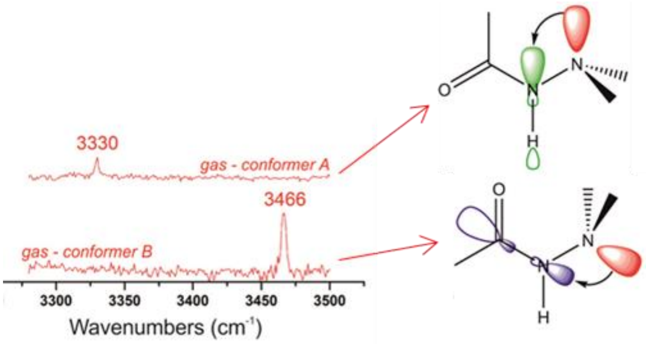

Figure 1 *Left*: Gas phase conformer-selective IR spectra (NH stretch region) of a model hydrazide molecule obtained in the by IR/UV double resonance spectroscopy; *right*: illustration of the hyperconjugation phenomena taking place in these conformations.

This property has been used in conformer-selective laser spectroscopic experiments carried out on model molecules isolated in the gas phase to identify the most stable hydrazide conformers (Fig. 1), leading us to propose a rationalization of the hydrazide conformational landscape.[1] In a second step, it has been used to probe the H-bonding properties of a β-amino acid dipeptide exhibiting such an hydrazide group, in particular for characterizing the so-called hydrazino turn folding feature occurring in these synthetic biomimetic systems.[2]

REFERENCES

1. E. Gloaguen, V. Brenner, M. Alauddin, B. Tardivel, M. Mons, A. Zehnacker-Rentien, V. Declerck and D. J. Aitken, *Angewandte Chemie-International Edition*, 2014, **53**, 13756-13759.
2. M. Alauddin, E. Gloaguen, V. Brenner, B. Tardivel, M. Mons, A. Zehnacker-Rentien, V. Declerck and D. J. Aitken, *Submitted*.

P-73

Interactions of clindamycin with the fragment of ribosome – quantum mechanics/molecular mechanics study

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Clindamycin is an antibiotic from lincosamide class, which binds to the large ribosomal subunit (50S) and inhibits protein synthesis. Lincosamides are used to treat diseases caused mostly by Gram-positive bacteria as well as some protozoal diseases. Modifications of the place of antibiotic action (mutations: G2057→A, A2058→G, A2059→G, A2059→C C2452→U, C2611→U, C2611→G, methylations: A2058 is transformed into N6-methyladenine or N6,N6-dimethyladenine) are one of the common reasons that lead to bacterial resistance because such alterations typically prevent proper binding of the antibiotic in its targeted site. The understanding of antibiotics actions on a molecular level is needed to improve their properties like selectivity and/or reduce their side effects.

The main goal of this study was to compare the dynamic properties of the clindamycin binding site in the 50S subunit with and without the A2058→G mutation to understand why this nucleotide substitution blocks the binding of lincosamides. To achieve this aim we obtained eight 50ps QM/MM simulations using the CP2K package.

To prepare the starting systems for the simulations, we chose the 3OFZ[1] 50S subunit structure from *Escherichia coli,* which consists of ribosomal RNA, ribosomal proteins, one clindamycin molecule, magnesium and zinc ions and crystal waters. For our simulations, we cut a sphere with the radius of about 15Å around clindamycin to account for the long-range interactions of the antibiotics in the 50S subunit. We added 51 K^+ ions to neutralize the charge and approximately 16000 TIP3P water molecules to solvate the system. The system was divided info two parts (Fig. 1): quantum (clindamycin and selected fragment of neighbouring/interacting nucleotides) and classical (RNA, protein, ions, water).

We analysed structure properties such as root mean square deviation (RMSD), root mean square fluctuation (RMSF), radius of gyration (GR), selected distances and angles as well as the hydrogen bond network. The hydrogen bonds are essential kind of interactions between the neutral clindamycin molecule and rRNA[2,3]. The results show the influence of clindamycin on the antibiotic binding site flexibility. The (A2058→G) mutation of the binding site also influences its flexibility, and, surprisingly, we observed better stability of the mutated clindamycin-ribosome complex.

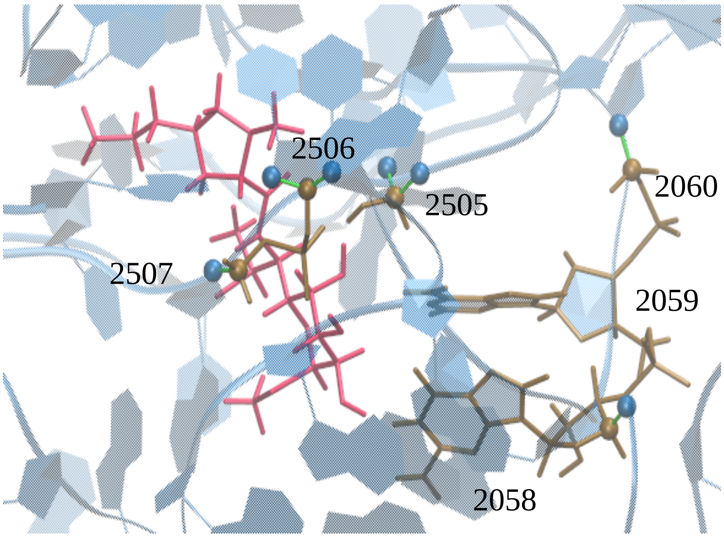

Figure 1 Fragment of the simulated system: dark blue ribbons: rRNA and protein described by classical MM, red sticks: clindamycin (QM description), brown sticks: QM nucleotides and green sticks: pseudobonds connecting QM and MM parts of simulated system.

Acknowledgements

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REFERENCES

1. J. A. Dunklea, L. Xiongb, A. S. Mankinb, J. H. D. Catea, *PNAS*, **2010,** 107(40), 17152
2. F. Schlunzen, R. Zarivach, J. Harms, A. Bashan, A. Tocilj, R. Albrecht, A. Yonath, F. Franceschi, *Nature*, **2001,** 413, 8143.
3. D. Tu, G. Blaha, P.B. Moore, T.A. Steitz. *Cell*, **2005,** 121(2), 257

P-74

Gas-phase Microsolvation of an Adenine Analogue

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Understanding the excited state relaxation pathways of nucleobases is of great importance to understand the underlying protection mechanisms of the DNA radiation-induced damage.[1] Lobsiger et al. have shown for another adenine analogue that the site specific hydration is of great importance.[2]

The mass-selective two-color resonant two-photon ionization (2C-R2PI) and UV-UV hole-burning (UV-UV HB) spectra of supersonic jet-cooled 9-methyl-8-vinyladenine·$(H_2O)_n$ clusters (9M8VA·$(H_2O)_n$) with n=0-3 have been measured to investigate the hydration pattern of an adenine analogue. Our results show several isomers for each cluster size, the cis orientation of the vinyl group is more stable than the trans. Most microhydrate isomers involve H-bonds to the N(1) position and 2-amino group, a less stable isomer exhibits an analogous H-bond pattern at the N(7) position, as shown in figure 1.

Delayed ionization measurements of 9M8VA as well as of the different water clusters have been recorded to investigate the excited state lifetimes and deduce the relaxation pathways.

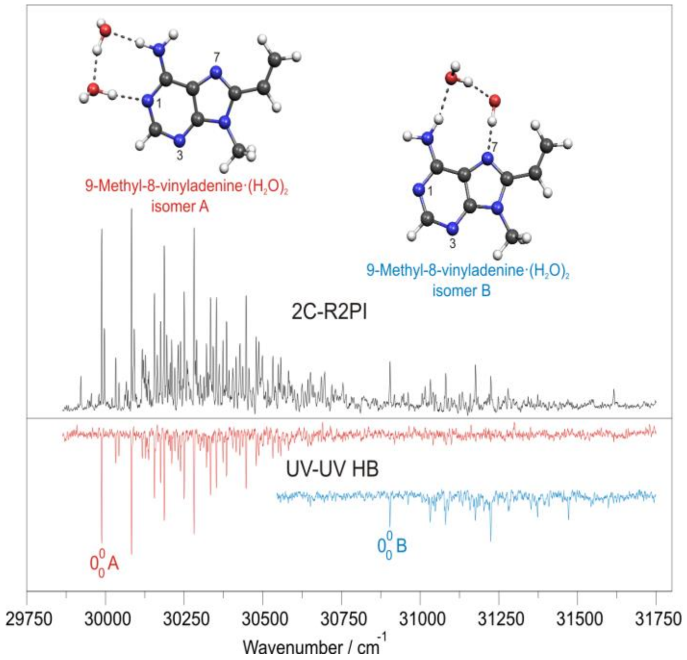

Figure 1 UV-UV hole-burning spectra of 9-methyl-8-vinyladenine·$(H_2O)_2$ isomers A and B

REFERENCES

1. K. Kleinermanns, D. Nachtigallova, M. S. de Vries, Int. Rev. Phys. Chem., 2013, 32, 2, 308-342.
2. J. S. Lobsiger, S. Blaser, R. K. Sinha, H.-M. Frey, S. Leutwyler, Nature Chemistry, 2014, 6, 998-993.

P-75

Weak interactions of noble gases and molecular hydrogen with aromatic structures

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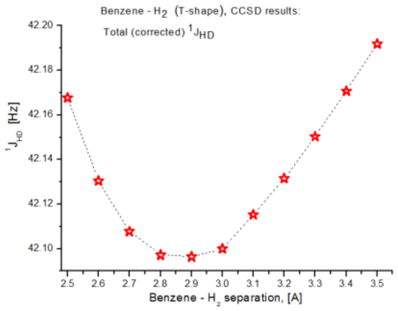
Since the discovery of carbon nanotubes (CNTs) the ordered carbon based materials have been intensively studied experimentally and theoretically. These systems are obtained as mixtures containing several impurities, for example amorphous carbon and remaining metal catalyst and physico-chemical characterization of such samples is based on various microscopic, X-ray diffraction and on IR/Raman studies. The latter technique also allows to estimate the nanotube diameter using a position of Raman breathing mode (RBM) in the recorded spectrum. Unfortunately, due to above mentioned problems, the NMR technique is of very limited use in studies of carbon nanomaterials.

Here we propose to use small magnetic probes (molecular hydrogen, H_2 and HD, as well as noble gases) to probe the cavities and walls of such porous structures. The probe atom or small neutral molecule could interact with pi-electrons of multiple carbon-carbon bonds or aromatic rings. These long range interactions could be significantly weaker than traditional H-bonds. However, the distortion of electron cloud of the probe atom/molecule could be measured as difference in nuclear magnetic shielding. Contrary to typical density functionals (for example B3LYP) which cannot reproduce energy minima due to dispersion, the calculated nuclear shielding of the probe nuclei calculated at Hartree-Fock, DFT or CCSD(T) levels of theory provide information on the surrounding. This is similar to taking images of the structure of porous system (imagine Swiss cheese with different distribution of large, middle and small pores) using water or gas as the only source of information in the external magnetic field.



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REFERENCES

1. M. Saunders, R. J. Cross, H. A. Jimenez-Vazquez, R. Shimishi, A. Khong, Science, 271 (1996) 1693-1697.
2. M. Straka, P. Lantto, J. Vaara, J. Phys. Chem. A, 112 (2008) 2658-2668.
3. T. Kupka, M. Stachów, L, Stobiński and J. Kaminsky, Magn. Reson. Chem, 51 (2013) 463-468.
4. M. Jankowska, T. Kupka, L. Stobiński, J. Mol. Graph. Model., 62 (2015) 26-37.

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The role of Hydrogen Bond in estimation of acidity of selected saccharides' derivatives

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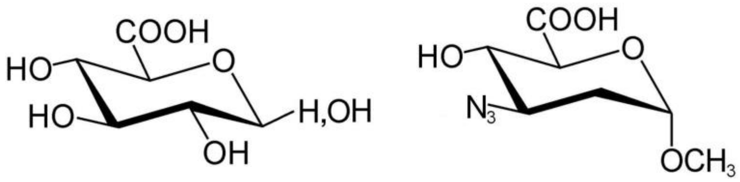
Process of determination of acidity constants of saccharide derivatives consist of potentiometric, spectrophotometric and roentgenostructural measurements. Three researched compounds (Figure 1) was taken under research: D-glucuronic acid (GlcA), (the methyl 3-azido-2,3-dideoxy-α-D-*arabino*-hexopyranoside)uronic acid (AAraCOOH) and the methyl 3-azido-2,3-dideoxy-α-D-*arabino*-hexopyranoside (AAra)[1], which do not belong to the group of uronic acids. The difference in type of functional groups decides upon acid-base properties.

The spectro-potentiometric measurements give values of deprotonation constants. Based on the general knowledge we are able to identify the group with the acidic constant it present. However, in the molecule where functional groups are vicinal, there can appear some complications in constants' values. That is why we support the research with roentgenostructural measurements. These measurements confirm that there are hydrogen bond present in crystals of saccharides and these datas are helpful to evaluate basicity and acidity of functional groups in molecules. Furthermore, it can be assumed that intramolecular hydrogen bonds appear causing proton transfer between functional group on carbon C-4 and C-6 (O-6 and O-4 atoms acting as donors on one side and deprotonated hydroxyls $[O\text{-}4]^-$ and $[O\text{-}6]^-$ acting as proton acceptors on the other side[1,2].



GlcA **AAraCOOH** **AAra**

Figure 1 Studied saccharide derivatives.

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REFERENCES

1. A. Dąbrowska, P. Dokupno, A. Konitz, Z. Smiatacz, *Carbohyd. Res.* **2000,** *323*, 230.
2. A. Dąbrowska, D. Jacewicz, A. Sikorski, L. Chmurzyński, *Carbohyd. Res.* **2005,** *340*, 2201.
3. A. Dąbrowska, A. Sikorski, D. Jacewicz, L. Chmurzyński, *Carbohyd. Res.* **2005,** *339*, 1195.

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