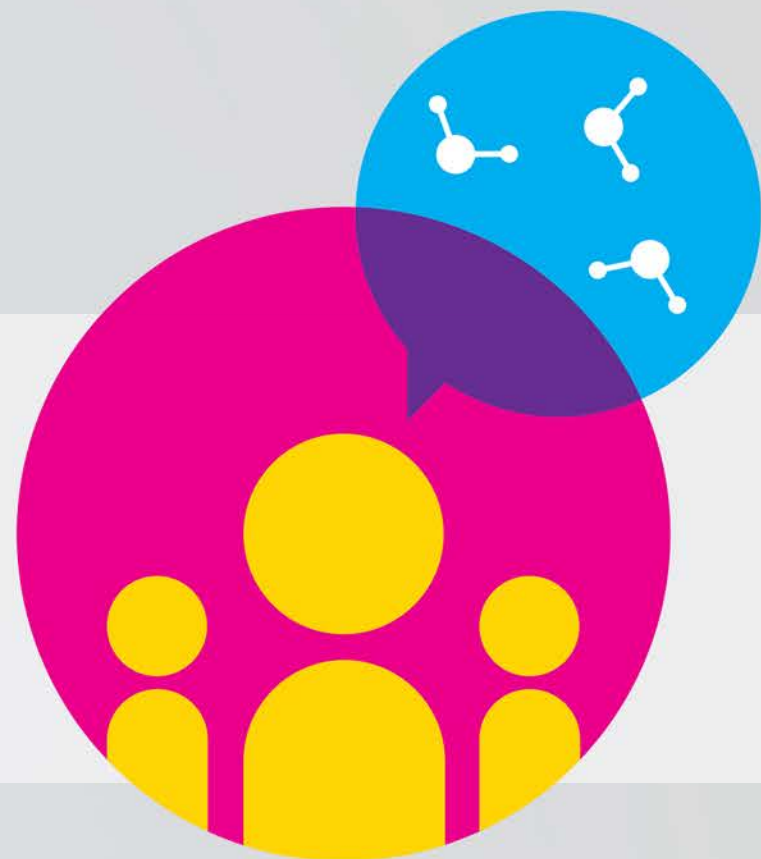


HBOND2019

Amsterdam

24-27 SEPTEMBER 2019



Conference Book

23rd International Conference on
"Horizons in Hydrogen Bond Research"



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Sponsors

We are very grateful for the generous support by our official sponsors:



Welcome to HBOND2019

On behalf of the Organizing Committee, it is a pleasure to welcome you at the 23rd International Conference on "Horizons in Hydrogen Bond Research" (HBOND2019), which takes place on September 24-27, 2019 at the OI2 Building on the campus of the Vrije Universiteit Amsterdam.

The International Conference on "Horizons in Hydrogen Bond Research" is a biennial conference series and has a long tradition with meetings being held across Europe.

1977 L. Sobczyk, Karpacz, Poland	1997 P. Schuster, Niederöblarn, Austria
1978 G. Zundel, Munich, Germany	1999 L. Sobczyk, Świeradów Zdrój, Poland
1979 D. Hadzi, Ankaran, Yugoslavia	2001 P. Ugliengo, Turin, Italy
1980 I. Olovsson, Sångy-Såby, Sweden	2003 H. H. Limbach, Berlin, Germany
1981 A. Potier, Montpellier, France	2005 P. E. Hansen, Roskilde, Denmark
1982 P. Huyskens, Leuven, Belgium	2007 K. G. Tokhadze, St. Petersburg, Russia
1985 W. A. P. Luck, Marburg, Germany	2009 M. C. Bellissent-Funel, Paris, France
1987 L. Sobczyk, Polanica Zdrój, Poland	2011 M. Suhm, Göttingen, Germany
1989 J. Kroon, Zeist, The Netherlands	2013 W. Herrebout, Antwerpen, Belgium
1993 Y. Maréchal, Autrans, France	2015 Z. Latajka, Wrocław, Poland
1995 L. Kimtys, Birstona, Lithuania	2017 J. Lundell, Jyväskylä, Finland

The series gathers scientists working in the field of hydrogen bonding research and other weak interactions, who study virtually all states of matter by a multitude of experimental and theoretical methods.

We wish you a wonderful stay in the beautiful city of Amsterdam and a pleasant and inspiring conference, with many interesting discussions, at Vrije Universiteit Amsterdam.

Célia Fonseca Guerra and F. Matthias Bickelhaupt



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Organizing Committee

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Jacek Waluk (Institute of Physical Chemistry, Polish Academy of Sciences,
Warsaw, Poland)
Karl Peter Wolschann (University of Vienna, Austria)



Program

Tuesday 24 September

08:30 - 09:30	Registration + coffee and tea
09:30 - 09:40	Opening by Célia Fonseca Guerra
	<i>Chair: F. Matthias Bickelhaupt</i>
09:40 - 10:20	E. (Bert) W. Meijer
10:20 - 10:50	Martin A. Suhm
10:50 - 11:30	Coffee break
	<i>Chair: Trevor A. Hamlin</i>
11:30 - 12:00	David Gonzalez-Rodriguez
12:00 - 12:20	Christian Jelsch
12:20 - 12:40	Stephanie C. C. van der Lubbe
12:40 - 14:00	Lunch
	<i>Chair: Tom Grossmann</i>
14:00 - 14:40	Manuel Yáñez
14:40 - 15:10	Elangannan Arunan
15:10 - 15:25	Michael Schmitt
15:25 - 16:00	Coffee break
	<i>Chair: Otilia Mó</i>
16:00 - 16:40	Jonathan Clayden
16:40 - 16:55	Giovanni Bistoni
16:55 - 17:10	Devendra Mani
17:10 - 20:00	Poster session, drinks and walking dinner
* Keynote / Invited / Contributed	



Program

Wednesday 25 September

	<i>Chair: Anja Palmans</i>
09:00 - 09:40	Han Zuilhof
09:40 - 10:10	Zdzisław Latajka
10:10 - 10:40	Roxanne Kieltyka
10:40 - 11:20	Coffee break
	<i>Chair: José A. Fernandez</i>
11:20 - 11:50	Stefania Grecea
11:50 - 12:20	Sonia Melandri
12:20 - 12:35	Venkateswara Rao Mundlapati
12:35 - 12:50	Jacek Waluk
12:50 - 14:00	Lunch
	<i>Chair: Laura Orian</i>
14:00 - 14:40	Paul Popelier
14:40 - 15:10	Tom Grossmann
15:10 - 15:25	Ilya G. Shenderovich
15:25 - 15:40	Simone d'Agostino
15:40 - 16:10	Coffee break
	<i>Chair: Poul Erik Hansen</i>
16:10 - 16:40	Sílvia Simon
16:40 - 17:10	Halina Szatylowicz
17:10 - 17:25	Vladimir D. Maiorov
17:25 - 17:40	Götz Schuck
17:45	Group photo

* **Keynote** / **Invited** / **Contributed**



Program

Thursday 26 September

	<i>Chair: Elangannan Arunan</i>
09:00 - 09:40	Erik T. J. Nibbering
09:40 - 10:10	Andrew J. Wilson
10:10 - 10:40	Aloke Das
10:40 - 11:20	Coffee break
	<i>Chair: Zdzisław Latajka</i>
11:20 - 11:50	Judy I. Wu
11:50 - 12:20	Jordi Poater
12:20 - 12:35	Ruslan E. Asfin
12:35 - 12:50	Margaret Mandziuk
12:50 - 14:00	Lunch
	<i>Chair: Wouter Herrebout</i>
14:00 - 14:40	Marcus Elstner
14:40 - 15:10	Marcin Palusiak
15:10 - 15:25	Jan Dillen
15:25 - 16:00	Coffee break
	<i>Chair: Jan Lundell</i>
16:00 - 16:30	Poul Erik Hansen
16:30 - 17:00	Henrik G. Kjaergaard
17:00 - 17:15	Mariusz P. Mitoraj
19.45 - 21.45	Dinner cruise
* Keynote / Invited / Contributed	



Program

Friday 27 September

	<i>Chair: Martin A. Suhm</i>
09:00 - 09:40	Jesús Jiménez-Barbero
09:40 - 10:10	Nicholas R. Walker
10:10 - 10:40	Wouter Herrebout
10:40 - 11:20	Coffee break
	<i>Chair: Jan Dillen</i>
11:20 - 11:50	Jan Lundell
11:50 - 12:05	Oleg A. Filippov
12:05 - 12:20	Barbara Golec
12:20 - 12:50	José A. Fernandez
12:50 - 13:00	Poster prize and closing ceremony
13:00 - 14:00	Lunch (suitable for take-away)

* **Keynote** / **Invited** / **Contributed**



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Practical Information

Where does the conference take place?

OI2 Lab Building
De Boelelaan 1108
1081 HZ Amsterdam

The conference takes place in the OI2 building (De Boelelaan 1108) of the Vrije Universiteit Amsterdam, which can be recognized by its white cubic shape with two large cut-outs. When entering the building, you will immediately see our registration desk in the hall. The lectures will take place in the Auditorium, which is on the ground floor and right behind our registration desk.





How to reach the conference venue?

The conference venue is easily accessible by public transport. Multiple busses and trams stop right in front of the OI2 building. Here, we give two examples for reaching the venue. However, several more options exist; we recommend to make use of Google maps for planning your journey.

From Schiphol airport

Take Connexxion Bus 341 in the direction of Station Zuid Amsterdam, and get out at *VU Medisch Centrum*. The bus leaves every 15 minutes and takes approximately 20 minutes. You can buy a ticket from the bus driver with debit or credit card (cash is not accepted). More information about taking a taxi from Schiphol can be found at www.schiphol.nl/en/page/regular-taxis/.

From Amsterdam Central station (Amsterdam Centraal)

Take GVB Tram 24 in the direction of VU Medisch Centrum, and get out at *VU Medisch Centrum*. The tram leaves every 10 minutes and takes approximately 32 minutes. You can buy a ticket in the tram with debit or credit card (cash is not accepted).

How to reach the conference dinner?

The conference dinner will take place on a boat while exploring the historical city center along the famous canals of Amsterdam. We will meet on Thursday 26 September at 19:45 at the Blue Boat Company, which is located at *Stadhouderskade 501* in Amsterdam. The nearest bus/tram station is at the *Rijksmuseum*, which is approximately 2 minutes walking from the meeting point. Another close-by bus/tram station is *Leidseplein*.

From the conference venue to the stop Rijksmuseum

Option 1: Take the Connexxion bus 347 or 357 at *VU Medisch Centrum*. This stop is 3 minutes walking from the conference venue and can be reached as follows: when stepping out of the OI2 building, go immediately to your right. Walk until the T-junction; you will see the bus stop at your left hand. Take the bus in the direction of the Elandsgracht Amsterdam and get out at *Rijksmuseum*. Both busses leave every 15 minutes and take approximately 17 minutes.

Option 2 (in case you would like to travel with GVB): Take GVB Tram 5 at De Boelelaan VU. This stop is about 7 minutes walking from the conference venue and can be reached as follows: when stepping out of the OI2 building, go immediately to your left. Pass the first intersection and keep going straight until the second intersection; you will see the tram stop at your right-hand side. Take tram 5 in the direction of Westergasfabriek and get out at *Rijksmuseum*. The tram leaves every 8 minutes and takes approximately 17 minutes.





From the stop Rijksmuseum to the Blue Boat Company

When stepping out of the bus or tram (i.e. when standing with your back to the bus or tram), go to the left and keep following the tracks of the tram (the street's name is *Hobbemastraat*). After approximately 2 minutes, you will come at an intersection with the *Stadhouderskade*. Cross the street, and you will see the Blue Boat Company on your right-hand side.





How to travel around?

Depending on the location of your accommodation, it might be convenient to buy a (multi)-day ticket for travelling around in Amsterdam and nearby cities. For example, a popular option is the GVB multi-day ticket, which allows you to travel with all GVB trams, buses and metros:

1 day (24 hours):	€8.00
2 days (48 hours):	€13.50
3 days (72 hours):	€19.00
4 days (96 hours):	€24.50
5 days (120 hours):	€29.50

It is also possible to buy 1-hour tickets. More information about the options, prices and selling points can be found at <https://reisproducten.gvb.nl/en/uur-en-dagkaarten>. Furthermore, we recommend to make use of Google maps for planning your journey.

Abstracts keynote speakers

The abstracts are given in alphabetical order by last name of the speaker.



Communicating information using switchable hydrogen-bonded dynamic foldamers

Jonathan Clayden^[a]

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j.clayden@bristol.ac.uk

Conformational changes are central to the function of biomolecules involved in signal transduction.^[1,2] This lecture will describe the design and utility of hydrogen-bonded **dynamic foldamers**^[3] (switchable oligomeric structures that have more than one accessible global conformation) as responsive systems that can use conformational change as a means of processing and communicating information. It will discuss the structural limitations of symmetry imposed by an ideal globally switchable structure, and show how the conformational uniformity imposed by well-defined intramolecular hydrogen bonding may be quantified spectroscopically.^[4,5] It will outline the application of alternative switching mechanisms in the design of extended molecules that respond selectively to chemical signals in solution and in the membrane phase.^[6,7]

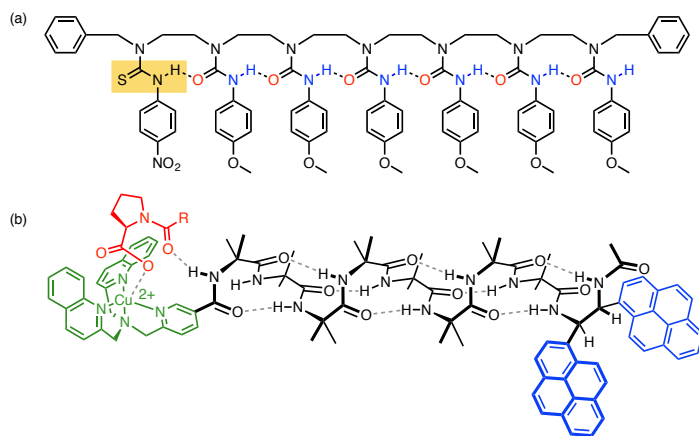


Figure 1 | Dynamic foldamers. (a) The acidic thiourea function induces a directional preference in the entire chain of directionally switchable ureas. (b) A chiral carboxylate ligand (red), bound by a Cu(II) 'cofactor', induces a screw sense preference, detectable by a remote fluorescent reporter (blue), in an otherwise achiral helical chain.

- [1] M. De Poli, W. Zawodny, O. Quinonero, M. Lorch, S. J. Webb, J. Clayden, *Science* **2016**, 352, 575.
- [2] F. G. A. Lister, B. A. F. Le Bailly, S. J. Webb, J. Clayden, *Nature Chem.* **2017**, 9, 420.
- [3] B. A. F. Le Bailly, J. Clayden, *Chem. Commun.* **2016**, 52, 4852.
- [4] M. Tomsett, I. Maffucci, B. A. F. Le Bailly, L. Byrne, S. M. Bijvoets, M. G. Lizio, J. Raftery, C. P. Butts, S. J. Webb, A. Contini, et al., *Chem. Sci.* **2017**, 8, 3007.
- [5] B. A. F. Le Bailly, L. Byrne, V. Diemer, M. Foroozandeh, G. A. Morris, J. Clayden, *Chem. Sci.* **2015**, 6, 2313.
- [6] J. Brioché, S. J. Pike, S. Tshepelevitsh, I. Leito, G. A. Morris, S. J. Webb, J. Clayden, *J. Am. Chem. Soc.* **2015**, 137, 6680;
- [7] R. Wechsel, M. Žabka, J. W. Ward, J. Clayden, *J. Am. Chem. Soc.* **2018**, 140, 3528.



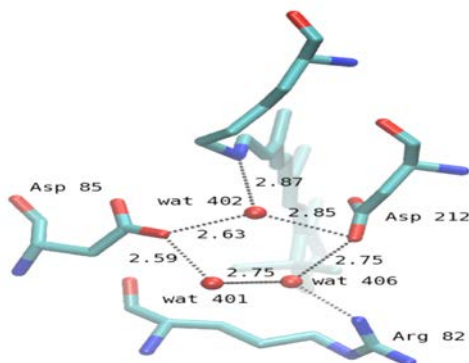
QM/MM simulations of hydrogen bonded networks in proteins

Marcus Elstner^[a]

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In the last years, we have studied the structure, dynamics and spectroscopy of retinal proteins using QM/MM approaches. For many of these systems, the strongly hydrogen bonded networks cannot be treated properly using classical force fields, therefore, already for the sampling step a QM/MM approach is needed. To compare with experimental results and clarify the details of structural models, we investigated the temperature dependence of the local hydrogen bonded networks and computed IR and UV/vis spectra, which allow to identify the dominant structural motives



Hydrogen bonded network in Bacteriorhodopsin.



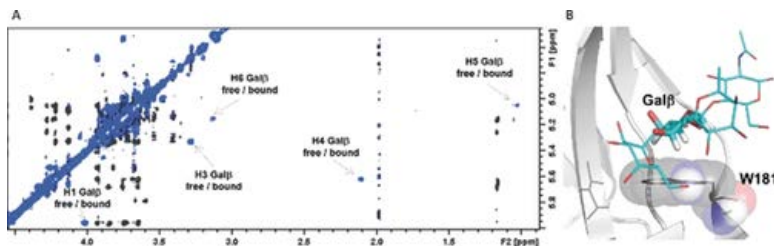
Breaking the limits in understanding glycan recognition by NMR

Jesús Jiménez-Barbero^[a]

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^[b] Ikerbasque, Basque Foundation for Science, 48006 Bilbao, Bizkaia, Spain

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Molecular recognition by specific targets is at the heart of the life processes. The interactions between proteins (lectins, enzymes, antibodies) and carbohydrates mediate a broad range of biological activities, from fertilization and tissue maturation, to pathological processes. The elucidation of the mechanisms that govern how sugars are accommodated in the binding sites is a topic of interest. Given the inherent flexibility of sugars, we use NMR as key tool for deducing at atomic resolution molecular recognition processes in which glycans are involved, also assisted by a variety of biophysical techniques.

I herein focus on the application of state-of-the-art NMR methods both from the ligand and receptor's perspective to study recognition processes between lectins of biomedical interest and glycans. Different lectins have been used to evaluate the relative importance of polar (hydrogen bonding, electrostatic) and non-polar (van der Waals, CH- π) forces in the recognition event, with especial emphasis in the application of novel NMR methods and on the analysis of the kinetics and thermodynamics.^[1-7]

- [1] A. Gimeno, et al. *ACS Chem Biol.* **2017**, 12, 1104.
- [2] A. Canales, et al., *Angew Chem Int Ed.* **2017**, 56, 14987.
- [3] B. Fernández de Toro, et al., *Angew Chem Int Ed.* **2018**, 57, 15051.
- [4] A. Ardá, J. Jiménez-Barbero, *Chem Commun.* **2018**, 54, 4761.
- [5] P. Valverde et al., *ACS Chem Biol.* **2019**, 14, 1660.
- [6] A. Gimeno et al., *Angew Chem Int Ed Engl.* **2019**, 58, 7268.
- [7] L. Unione et al., *ACS Central Sci.* **2019**, 5, doi: 10.1021/acscentsci.9b00540

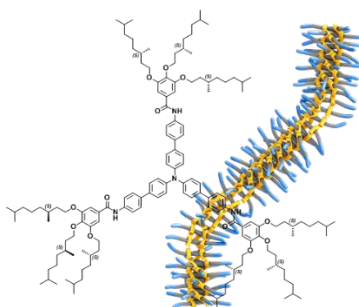


Supramolecular polymers and hydrogen bonds; “a happy marriage”

E.W. Meijer,^[a]

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Eindhoven, the Netherlands,
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Although the word polymer was already coined by Jöns Jakob Berzelius in 1833, it was through the pioneering work of Hermann Staudinger in 1920, that it was recognized that the macroscopic properties of polymers both in solution and solid state are the result of the macromolecular nature of the molecules. The impressive progress in supramolecular chemistry, however, paved the way to redesign polymers and polymeric materials that lack the macromolecular structure [1]. Instead, highly directional secondary interactions are used to assemble the many repeating units into a polymer array. By adequate design, these systems should still have all of those material properties that make polymers so valuable and on top of that we may expect some unprecedented behaviour – like self-healing - as a result of the reversibility of the supramolecular design. Multiple hydrogen bonding units will be shown to be highly attractive to produce supramolecular polymers with unique properties. Especially ordered arrays of monomers are highly interesting due to the cooperative nature of their supramolecular polymerization processes. In the lecture, the pivotal role of hydrogen bonds – both as bonding and structural element – will be demonstrated in ordered supramolecular polymers, while a proposal is made to explain some fascinating electronic properties.



[1] T. Aida, E. W. Meijer and S. I. Stupp, *Science*, **2012**, 335, 813.



Soft X-ray spectroscopy of hydrogen-bonded systems in protic and aprotic solvents

Erik T. J. Nibbering,^[a] Maria Ekimova,^[a] Carlo Kleine,^[a] Jan Ludwig,^[a] Miguel Ochmann,^[b]
Markus Kubin,^[c] Nils Huse,^[b] Philippe Wernet,^[c,d] Michael Odelius^[e]

^[a] Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Berlin, Germany

^[b] Institute for Nanostructure and Solid State Physics, University of Hamburg, Hamburg,
Germany

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Profound insight on hydrogen bonding of water in its different phases (liquid, surface, solid phase) has been acquired using soft X-ray absorption spectroscopy, probing the oxygen 1s core excitations to unoccupied molecular orbitals of the water molecule, that directly reflect the hydrogen bonding donating and accepting interactions of bulk water. To obtain information on hydrogen bonding of solvation shell water, one instead can probe solute molecules in aqueous solution, by inspection of element specific transitions associated with the functional groups directly involved in hydrogen bonding with the solvent shell water. For the latter approach we have initiated a study of the amine group using N K-edge spectroscopy of solution phase amine compounds under different charge and solvation conditions.^[1,2] For this we have used a liquid flatjet system with which solution phase soft-x-ray spectroscopy can conveniently be performed.^[3] Recent progress in flatjet technology has enabled us to probe the O K-edge of water as a solute in acetonitrile solution. This spectacular advance paves the way for probing O K-edge spectra of water selectively probing its interactions as hydration species in water-poor conditions. With this we expect new detailed insight into the nature of hydrogen bonding and its effects on the electronic structure of water.

- [1] M. Ekimova, W. Quevedo, L. Szyc, M. Iannuzzi, Ph. Wernet, M. Odelius, E. T. J. Nibbering, *J. Am. Chem. Soc.* **2017**, *139*, 12773.
- [2] M. Ekimova, M. Kubin, M. Ochmann, J. Ludwig, N. Huse, Ph. Wernet, M. Odelius, E. T. J. Nibbering, *J. Phys. Chem. B*, **122**, 7737.
- [3] M. Ekimova, W. Quevedo, M. Faubel, Ph. Wernet, E. T. J. Nibbering, *Struct. Dyn.*, **2015**, *2*, 054301.

Paul Popelier^[a,b], Arnaldo Silva^[a,b], Mark Vincent^[a,b], James McDonagh^[a,b], Benjamin C.B.

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Diagrammatic representation of the $V_{ee,cor}^{OH}$ (in red) and $V_{ee,cor}^{OO}$ (in black) electron correlation energy terms (kJ mol^{-1}) to the hydrogen bond for the water pentamer.

Finally, we explain the new proposed Relative Energy Gradient (REG) method[8], which computes which part of molecular system is responsible for the energetic behaviour of the whole system.

- [1] R.F.W. Bader, *Atoms in Molecules. A Quantum Theory.*, Oxford Univ. Press, Great Britain, 1990.
- [2] P.L.A. Popelier, *Quantum Chemical Topology*, in: M. Mingos (Ed.), *The Chemical Bond - 100 years old and getting stronger*, Springer, Switzerland, 2016, pp. 71-117.
- [3] M.A. Blanco, A. Martín Pendás, E. Francisco, *J.Chem.Theor.Comput.*, **2005**, 1, 1096-1109.
- [4] B.C.B. Symons, D.J. Williamson, C.M. Brooks, A.L. Wilson, P.L.A. Popelier, *Chemistry Open*, **2019**, 8, 560–570.
- [5] J.L. McDonagh, A.F. Silva, M.A. Vincent, P.L.A. Popelier, *J.Phys.Chem.Letts.*, **2017**, 8, 1937-1942.
- [6] A.F. Silva, P.L.A. Popelier, *J.Mol.Mod.*, **2018**, 24, 201.
- [7] A.F. Silva, M.A. Vincent, J.L. McDonagh, P.L.A. Popelier, *ChemPhysChem.*, **2017**, 18, 3360-3368.
- [8] J.C.R. Thacker, P.L.A. Popelier, *Theor.Chem.Acc.*, **2017**, 136, 86.



Hydrogen bonds and non-covalent interactions. Cooperativity at the origin of interesting phenomena.

Manuel Yáñez,^[a] Otilia Mó,^[a] M. Merced Montero-Campillo,^[a] Ibon Alkorta,^[b]
and José Elguero^[b]

^[a] Departamento de Química, Facultad de Ciencias and Institute of Advanced Chemical Sciences (IadChem), Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

^[b] Instituto de Química Médica, IQM-CSIC. Juan de la Cierva, 3, E-28006 Madrid, Spain
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Cooperativity is responsible of the strength enhancement of hydrogen bonds and many other non-covalent interactions when several of these interactions coincide in the same chemical systems. This phenomenon just reflects the mutual perturbation of the electron densities of the compounds participating in the interaction. Cooperativity is indeed behind the high stability of the water trimer as compared with the dimer,^[1] or to the spontaneous proton transfer in certain hydrogen-bonded triads^[2] but it is recognized nowadays as a general phenomenon when dealing with non-covalent interactions.^[3] The mutual influence between beryllium bonds and intermolecular hydrogen bonds has been found to be particularly strong;^[4] but these effects are also very large when intramolecular hydrogen bonds are involved.^[4] Cooperativity effects also modulate the strengths of other non-covalent interactions such as alkaline-earth bonds and chalcogen bonds^[5] or tetrel bonds^[6] when present in different ternary molecular complexes. Importantly, it has been found that the weaker the isolated interaction, the stronger the reinforcement in the ternary complex. All these questions will be addressed and analyzed through the use of high-level *ab initio* calculations.

- [1] O. Mó, M. Yáñez, J. Elguero, *J. Chem. Phys.* **1992**, *97*, 6628.
- [2] O. Mó, M. Yáñez, J. E. Del Bene, L. Alkorta, J. Elguero, *ChemPhysChem*. **2005**, *6*, 1411
- [3] A. S. Mahadevi and G. N. Sastry, *Chem. Rev.* **2016**, *116*, 2775; b) F. Biedermann and H. J. Schneider, *Chem. Rev.* **2016**, *116*, 5216; f) A. F. Silva, M. A. Vincent, J. L. McDonagh and P. L. A. Popelier, *ChemPhysChem* **2017**, *18*, 3360.
- [4] O. Mó, M. Yáñez, I. Alkorta, J. Elguero, *J. Chem. Theory Comput.* **2012**, *8*, 2293.
- [5] O. Mó, M. M. Montero-Campillo, I. Alkorta, J. Elguero, M. Yáñez, *Chem. Eur. J.* **2019** (in press)
- [6] I. Alkorta, M. M. Montero-Campillo, O. Mó, J. Elguero, M. Yáñez, *J. Phys. Chem. A* **2019**, *123*, 7124



H-bonds in materials chemistry

Han Zuilhof^[a,b]

^[a] Lab of Organic Chemistry, Wageningen University, Wageningen, The Netherlands.

^[b] Department of Pharmaceutical Science & Technology, Tianjin University, Tianjin, P.R.
China.

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A lot is known about H-bonds in dilute solution, but much less about H-bonds at a surface. The first part will outline a novel mass-spectrometry based technique to measure H-bond strength at a surface via the kinetics of H-bond exchange. The second part will discuss a novel H-bonding moiety that forms the basis of novel self-healing, malleable materials. Such self-healing materials that hinge on H-bonding typically do not display a high mechanical strength. The novel moiety addresses this problem.



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Abstracts invited speakers

The abstracts are given in alphabetical order by last name of the speaker.



Large amplitude motions, hydrogen/carbon bonds and 3c-2e bonds

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In 2009, Goswami and Arunan proposed a condition for hydrogen bonding according to which there should at least be one bound-level along vibrational coordinates which lead to breaking of the hydrogen bond.^[1] They showed that this is the significant difference between the open tetrahedron structure of ice and the close packed structure of solid H₂S, and they are not the results of the difference between 'hydrogen bonding' and 'van der Waals interactions' as commonly assumed. When it comes to the dimers of H₂O and H₂S, there were plenty of experimental and theoretical results available for the former and very little for the latter. Recently, our group in collaboration with Newcastle University, UK and the National Institute of Standards and Technology, U.S.A. have observed the K=1 transitions of H₂S dimer which unambiguously showed that H₂S dimer is hydrogen bonded.^[2] We have now calculated the barriers along the various large amplitude motions in H₂S dimer and shown that it indeed satisfies the criterion of Goswami and Arunan. Moreover, our results indicate that when the energy along these torsional coordinates is larger than the barrier, the hydrogen bonded configurations do not contribute to the dynamic structure beyond what one can expect statistically i.e. there is no quantum localization of the hydrogen bonded geometry. Following the popular characterization of CH₅⁺ as a 3c-2e bond between the CH₃ tripod and H₂ moiety,^[3] we explored the bonding of protonated methane. Our objective was to understand whether the 3c-2e bond was 'V' shaped or 'T' shaped, as in the latter case it could resemble a 'carbon bond' between H₂ and C⁺. This investigation led to interesting findings^[4] about CH₅⁺, SiH₅⁺ and GeH₅⁺ and also the ill-defined 3c-2e bonds. The talk will highlight our recent finding on H₂S dimer and 3c-2e bonds.

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- [3] D. Marx and M. Parrinello, *Nature*, **1995**, *375*, 216 and many other papers on CH₅⁺.
- [4] S. P. Gnanasekar and E. Arunan, *J. Phys. Chem. A*, **2019**, *123*, 1168 (Featured as a cover article).

Quest for unconventional hydrogen-bonds of strength similar to conventional hydrogen-bonds

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Hydrogen-bond, in spite of being a century old concept, is still one of the most enthralling topics of research in the scientific community. Conventional hydrogen bond is generally denoted by X-H...Y where both X and Y are electronegative atoms. However, the recent redefinition of the hydrogen bonding by the IUPAC committee goes beyond the conventional wisdom on this non-covalent interaction.^[1] Consequently, there has been a growing search for finding the presence of this ever interesting non-bonded interaction considering various atoms in the periodic table as hydrogen-bond donor (X-H) and acceptor (Y). We have studied the hydrogen-bonds involving either the hydrogen-bond acceptor as a weak electronegative atom or both the hydrogen-bond donor and acceptor atoms as weak electronegative atoms. Specifically, we have explored N-H...Se hydrogen-bond by studying indole...dimethyl selenide complex^[2-3] and S-H...S, and S-H...Se hydrogen-bonds by studying 2-chlorothiophenol...dimethyl sulphide and 2-chlorothiophenol...dimethyl selenide complexes, respectively, using resonant 2-photon ionization (R2PI), IR-UV double resonance spectroscopy and quantum chemistry calculations. We have observed that the IR red-shift values in the N-H stretching frequency in the N-H...Se hydrogen-bond and the S-H stretching frequency in the S-H...S and S-H...Se hydrogen-bonds are similar to those in any conventional hydrogen-bond. Decomposition of the components of the interaction energies in the N-H...Se/S-H...S/S-H...Se hydrogen-bonded complexes indicate that the charge transfer interaction plays a significant role for these unusually strong hydrogen-bonds having relatively weaker electrostatic interaction component.

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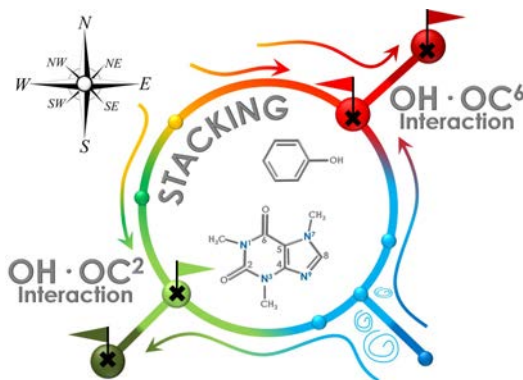
Unraveling molecular aggregation in small but complex systems using mass-resolved laser spectroscopy and calculations

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Molecular aggregation is involved in many fundamental processes: from gas condensation to molecular recognition. Thus, not surprisingly, a large number of works have been published on characterization of the intermolecular forces responsible for the aggregation. Among the many techniques used, the combination of laser spectroscopy in supersonic expansions and computational chemistry has demonstrated to be a winning couple and has enable characterization of many model systems. However, there is also a risk of over-interpretation of the results, especially in those complex systems where experimental results are limited or noisy and the molecules have a wide collection of conformational isomers energetically accessible. Here we will present some examples of such kind of systems. Our results demonstrate that special caution is required when there is not a leading interaction, such as a strong O-H $\cdots$ O hydrogen bond, but a subtle equilibrium between weaker interactions, such as C-H $\cdots$ π , $\pi\cdots\pi$, etc, and DFT computations are used.





Macroscopic assemblies via Watson-Crick pairing

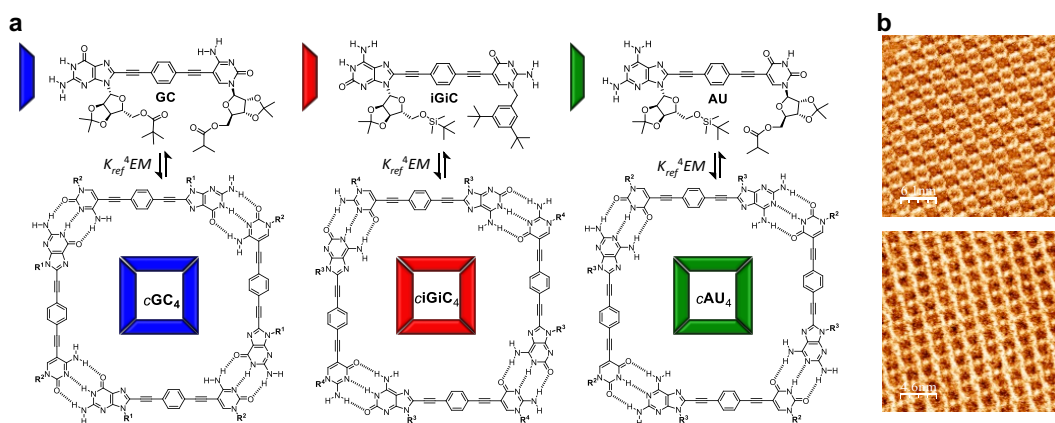
David Gonzalez-Rodriguez,^[a,b] Nerea Bilbao,^[a] Carlos Montoro-García,^[a] Sonia Romero-Pérez,^[a] Miguel Martín-Arroyo,^[a] David Serrano-Molina,^[a] Maria J. Mayoral^[a]

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A versatile strategy is described here to prepare cyclic systems whose size, shape, composition and function can be rationally predesigned and controlled at the nanoscale using concepts and tools of supramolecular chemistry. Cyclic tetramers^[1] are formed from 4 monomeric π -conjugated subunits by hydrogen-bonding interactions between nucleobase directors. A proper monomer preorganization affords high chelate cooperativities and thus high cyclization yields in solution^{2,3} and onto surfaces.⁴



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- [3] a) R. Chamorro, L. de Juan-Fernández, B. Nieto-Ortega, M. J. Mayoral, S. Casado, L. Ruiz-González, E. M. Pérez, D. González-Rodríguez, *Chem. Sci.* **2018**, 9, 4176; b) M. J. Mayoral, D. Serrano-Molina, J. Camacho-García, E. Magdalena-Estirado, M. Blanco-Lomas, E. Fadaei, D. González-Rodríguez, *Chem. Sci.* **2018**, 9, 7809.
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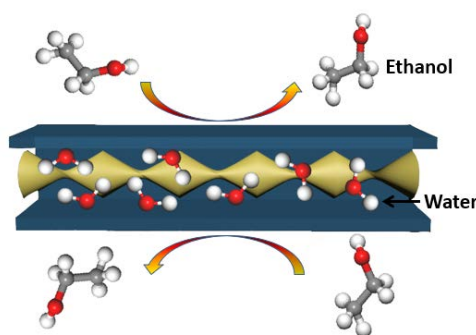
Tuning the properties of metal-organic frameworks through host-guest hydrogen bonding interactions

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Metal-organic frameworks (MOFs) is a class of porous hybrid inorganic-organic materials, consisting of metal ions or clusters of metal ions bridged by organic linkers. Their inherent properties, including high surface area, various compositions and porous networks together with their tuneable functionalities make them attractive candidates for a range of applications, including molecular storage and separation, chemical sensing as well as catalysis. Related to molecular separations, a key challenge is to design water stable MOFs having the size of the pores and their functionality tailored specifically for the selective separation of water and methanol. We will show that this challenge can be overcome by confining polymers within the pores of MOFs with specific topology to block partially the free volume accessible. The pore size and hydrophobicity of the MOF-polymer materials can be controlled by adjusting the loading of the polymer in the MOF, which in turns allows to tune the affinity of the materials towards water or alcohol molecules. Moreover, the guest polymer undergoes a transition between hydrophilic and hydrophobic phases in response to a temperature change, therefore enabling to control the adsorption and desorption of water and alcohol molecules.





Synthetic scaffolds as modulators of peptide dynamics and folding

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The design and synthesis of complex molecular scaffolds with defined physico-chemical properties present central challenges in current chemical research. Such molecules can provide access to novel therapeutics, catalysts and materials. For such agents, it is often essential to adopt defined three-dimensional structures, in which the degree of flexibility can preferably be adjusted in a controllable manner. The folding properties of peptides and proteins, usually determined by unique hydrogen bond patterns, provide an excellent basis for the design of molecules with tailored structural properties.^[1] In the group we use peptide and protein structures and combine those with non-natural small molecular scaffolds focusing on the synthesis of peptide-derived bioactive agents and the chemical engineering of proteins. Research highlights involve the structure-based design of bioactive peptidomimetics^[2,3] and the semi-synthesis of modified enzymes with enhanced activities.^[4] In addition, peptide-based molecular switches have been devised that respond to receptor binding and facilitate a homogeneous readout of this interaction in real-time.^[5]

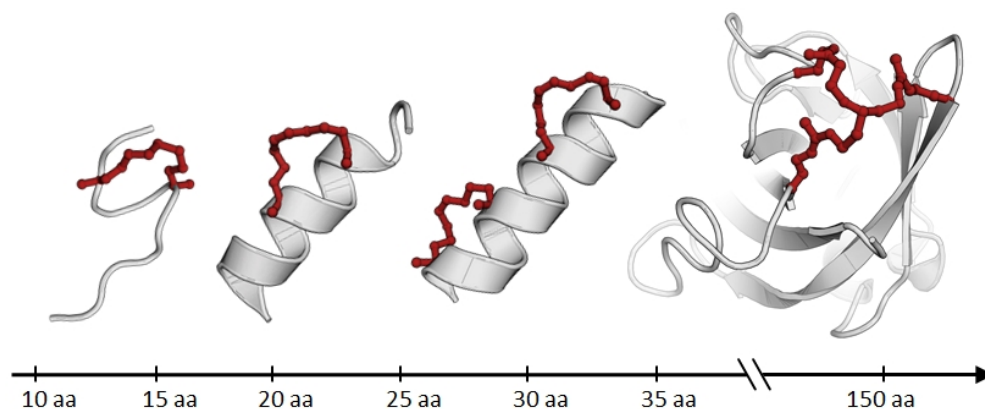


Figure: Structures of modified peptides and proteins (aa: amino acids, red: non-natural fragments).

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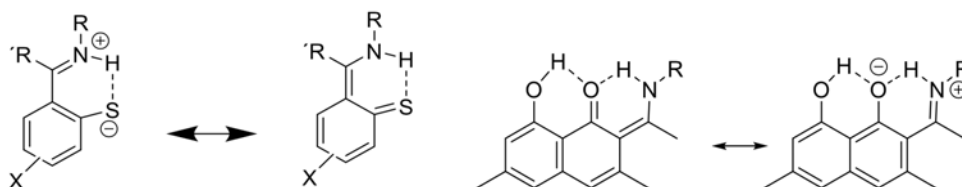
An overview of intramolecular NH...X hydrogen bonds

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A number of new compounds have been synthesized with focus on creation of compounds with high zwitter-ionic character (see Figure). These will be the basis for a discussion of a number of features.



Comparison of compounds with and without resonance assistance. Analysis of two-bond deuterium isotope effects vs. four-bond deuterium isotope effects as a measure of the importance of zwitter-ionic content (Figure). Can ^1H N chemical shifts be used to predict NH bond lengths? Do deuterium isotope effects correlate with the AIM electron densities at bond critical points and can hydrogen bond energies be determined? Can NH stretching frequencies be identified using simple calculations? Discussion of the use of $\nu\text{NH}/\nu\text{ND}$ ratios to predict NH stretching frequencies.



A novel on-the-fly hybrid QM:MM Model to predict solvent effects in IR and VCD spectra

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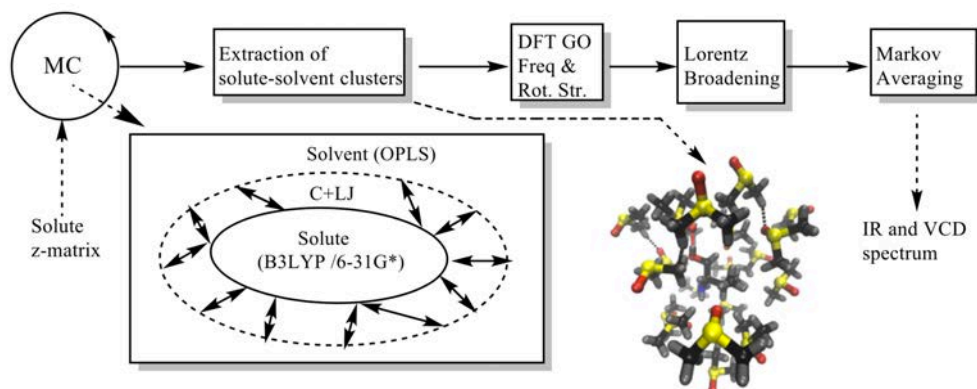
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VCD spectroscopy has proven to be a powerful method for the determination of the absolute configuration of various natural products and pharmaceutical ingredients. Differentiating between two enantiomers is rather easy, as their VCD spectra are mirror images. However, in order to identify which spectrum belongs to which enantiomer, a reliable quantum chemical prediction of these spectra is paramount. ^[1] This becomes challenging for flexible molecules that strongly interact with the solvent, as the influence of the solvent can be difficult to accurately include in these predictions. ^[2] To date, it is estimated that still in 1 out of 5 cases the absolute configuration could not be identified due to lack of a correct solvent representation within the standard VCD models and workflows.

In this presentation, we will describe an explicit solvent model which employs a QM:MM (DFT:MM) Metropolis Monte Carlo simulation to sample large explicit solute-solvent clusters, from which VCD spectra are calculated at DFT level using a frozen cage approach. The approach also allows the competition between inter- and intramolecular hydrogen bonding to be accurately described.



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Exploiting self-assembly through hydrogen-bonding for biological applications of squaramide-based supramolecular materials

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The surging interest in adaptive materials for applications from biomedicine to electronics has invigorated the search for new supramolecular materials with useful function. Because of their inherent non-covalent nature, supramolecular polymer materials show tremendous potential because they can be easily prepared with tailorable compositions, respond to their environment, overcome damage, and be recycled. In the biomaterials field, their easy processing permits the mixing of functionalized monomers with complex cargoes such as peptides or nucleic acids, and their responsiveness to different stimuli opens the door to designer materials that can be used to deliver therapeutic cargo or as scaffolds for tissue engineering. In order to realize these end-stage applications, there is a need for structurally simple monomers with high synthetic accessibility that can robustly self-assemble into polymeric architectures in the presence of complex molecular cargo. Squaramides, structurally minimal ditopic hydrogen-bonding units, show tremendous potential in this regard due to their high synthetic accessibility from commercially available precursors and robust self-assembly into supramolecular polymers. This lecture will share our exploration of the squaramide synthon as a building block for supramolecular polymers and its application to materials for biomedical applications such as *in vivo* drug delivery and 3D cell culture.



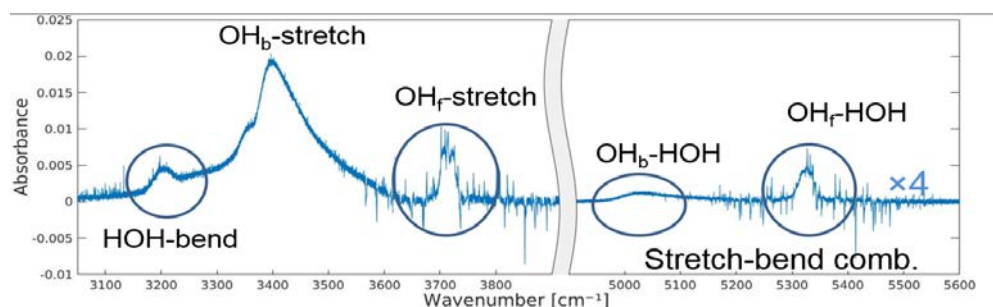
Gibbs energy of bimolecular complexes

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In atmospheric research, radiative transfer, reaction mechanisms and nucleation are all affected by complex formation. The formation of a molecular complex relies on the Gibbs energy of formation, ΔG , which is difficult to obtain accurately, from pure experimental or theoretical methods. We have developed a combined experimental and theoretical approach with which ΔG of bimolecular complex formation can be determined with an accuracy better than 1 kJ/mol.^[1]



Gas phase spectrum of the water-trimethyl amine complex and the 5 vibrational bands observed.

To facilitate this, we need to be able to calculate oscillator strengths of the vibrational transitions that are characteristic to the bimolecular complex and which can be measured. We have developed a reduced dimensionality vibrational model within the local mode framework, which can be combined with ab initio methods to calculate oscillator strengths. In bimolecular complexes, it is important to consider the effect of the 6 intermolecular modes. Our model includes modes essential to the hydrogen bond donor molecule (e.g. OH-stretching), as well as the intramolecular modes, to obtain accurate hydrogen bound OH-stretching intensities. We use this theoretical approach combined with measured spectra of several vibrational transitions observed for the same complex (see figure) to improve the ΔG determination.

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Proton transfer dynamics in strong intramolecular H-bonds – theoretical studies

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In many living systems very fast proton transfer processes occur and moreover in many cases a proton behaves as a quantum particle tunneling through the energy barrier. Despite widespread importance of tunneling effects, the quantum character of proton transfer is not frequently used in theoretical models. The Car-Parrinello Molecular Dynamics (CPMD) is very efficient scheme for description of dynamics of molecular systems. In contrary to the classical molecular dynamics the CPMD calculations do not require an a priori determined model interaction potential because the internuclear forces for each configuration of nuclei are calculated from the first principle. The quantum behavior of proton from a hydrogen bridge as well as remaining heavy atoms can be taken by means of the Path Integration Molecular Dynamics (PIMD).

The chemical systems with strong single or double O-H...O hydrogen bonds are very common in many chemical and biological systems. In the lecture results of CPMD and PIMD simulations will be presented for the examples of proton transfer in strong intramolecular O-H...O, O-H...S and N-H...N hydrogen bonds. The quantum nature of bridged proton will be discussed. Moreover, the influence of water environment on proton mobility in short intramolecular H-bond will be also presented.



Insights on hydrogen-bonded complexes involving noble gas hydrides

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In recent decades a renaissance in noble-gas chemistry has taken place, not least because of the discovery of noble-gas-containing hydrides.^[1] Some of the first molecules of this family leading the experimental way to various inorganic and organic Xe-insertion products of H₂O and HCCH forming HXeOH^[2] and HXeCCH or HXeCCXeH,^[3] respectively. Moreover, the group of such molecules has extended to other noble gases like krypton and eventually the first neutral argon-containing molecule HArF.^[4]

It has been postulated that the HNgY molecules possess both covalent and ionic nature in their bonding.^[5,6] The substantial fraction of ionicity especially in the Ng-Y bond is reflected in the exceptionally large dipole moments. As follows, the HNgY molecules are very good probes of their near chemical vicinity upon experimental studies, as has been demonstrated, for example, in the case of hydrogen-bonded complexes,^[7,8] interactions with noble gas atoms^[9] or molecular nitrogen,^[10] and when probing chemical reactivity of HNgY molecules.^[11]

Here, insights on hydrogen-bonded complexes and their properties are reviewed based on both from experimental and computational studies.

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Hydrogen bonds and other non-covalent interactions revealed by rotational spectroscopy

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The nature and driving forces of intra and intermolecular interactions can be studied to a very high degree of accuracy by free-jet rotational spectroscopy. From the detailed structural and dynamical data obtained, the site and geometry of the interaction and information on the binding energy can be inferred without ambiguity, also in the presence of conformational complexity.^[1,2] The questions usually addressed regard, the binding sites, the type of established interactions, the conformational changes caused by interactions and finally the driving forces of the interactions and how they can be influenced. When applied to molecular complexes, answers to these questions allow insight into the molecular interaction process at the molecular level, bridging the gap between gas-phase and bulk properties.

Through chosen examples of published^[3-5] and unpublished results on monomers or complexes of medium-size organic molecules formed in a supersonic expansion and characterized by rotational spectroscopy, we will show how non-covalent interactions (hydrogen bonds, weak hydrogen bonds, halogen bonds, pnictogen bonds and lp- π -hole interactions) compete to shape the conformational potential energy surfaces. We will also show how these interactions drastically change through substitution (in particular by halogen atoms) of atoms or functional group, in this way achieving an effective tuning of the interactions themselves.

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Halogen atoms interactions in view of many-body interaction theory

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The synergism of multiple intermolecular interactions may be quantified by the proper components of the interaction energy. These components are available when the many-body interaction approach can be applied explicitly. Thus, if the complex consists of molecular fragments which may be extracted from that complex and treated separately as a thermodynamically stable subsystems, not only the total interaction energy, but also its two-, three- and in general many-body components can be estimated. In that way the cooperativity or anticooperativity of the interactions can be assessed numerically, when applicable.

One of the important properties of the hydrogen bonding is the synergism of the individual H-bonds present in a more complex systems stabilized by the multiple H-bonding pattern. For instance, it was found that in case of some water clusters the cooperativity of the bonding may be of the 30% of the total interaction energy value, that is, the energy value resulting from the formation of the complex. Since the halogen bonding is often compared with the hydrogen bonding, we did an effort to check whether in the case of the X-bond the mentioned synergism is as effective as in the case of the H-bond. The set of various n-body model systems (where n is the number of the molecules in the system) being representatives of the experimentally found counterparts, will be discussed. The aspect of possible cooperativity between two types of interactions (X- and H-bond) will be considered as well.



Non-terran biosolvents model structure, stability and replication of B-DNA

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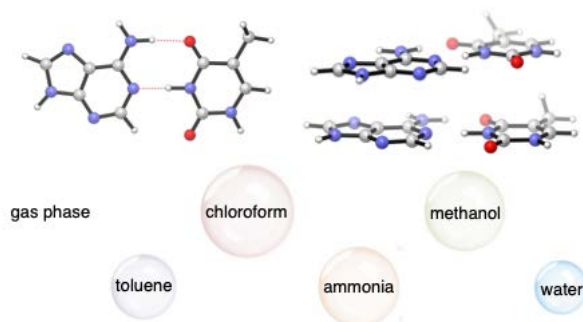
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We have computationally analyzed a comprehensive series of Watson–Crick and mismatched B-DNA base pairs,^[1–3] in the gas phase and in several solvents, including toluene, chloroform, ammonia, methanol and water, using dispersion-corrected density functional theory and implicit solvation.^[4] Our analyses shed light on how the molecular-recognition machinery behind life's genetic code depends on the medium, in order to contribute to our understanding of the possibility or impossibility for life to exist on exoplanetary bodies. Calculations show how a common non-terran environment like ammonia, less polar than water, exhibits stronger hydrogen-bonding affinities, although showing reduced selectivities towards the correct incorporation of Watson–Crick base pairs into the backbone. Thus, we prove the viability of DNA replication in a non-terran environment.



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RAHB: how resonance assist to hydrogen bond formation?

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Intra and intermolecular hydrogen bonds (HB) assisted by additional effects, e.g., resonance assisted or charge assisted, are among the strongest HBs known. Resonance assisted hydrogen bonds (RAHB) introduced by Gilli *et al.*¹ are stronger than conventional HBs because of the extra stabilization connected with the partial delocalization of the π -electrons within the so-called *quasi-ring* containing conjugated formally single and double bonds.

There are many computational and experimental works about RAHB, where the origin of the extra stabilization is in discussion. From experimental point of view, Houjou *et al.*² were studying the proton transfer in double headed salicylaldimines, showing that there is a correlation between the aromaticity of the benzene rings and the stability of the HB formed. Also, previous studies in our group³ described the interplay between RAHB strength and aromaticity of the *ipso*-ring in a series of *o*-hydroxyarylaldehydes. It is very well-known that aromaticity of condensed benzene rings, the so-called benzenoid hydrocarbons, depends on their number of rings as well as their relative position, that is, their isomeric structure.⁴ The main goal of this talk is to show how resonance, in terms of aromaticity of the *ipso*-ring, assist to the HB formation in different double-headed polycyclic aromatic hydrocarbons.

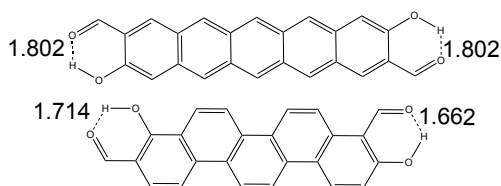


Figure 1 | Linear and kinked polycyclic aromatic hydrocarbons with double RAHB

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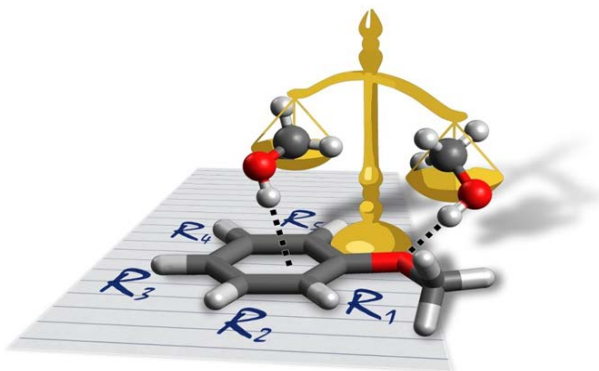


Hydrogen bonds for theory benchmarking

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Numerical solutions to the quantum mechanics of electrons and nuclei are extremely valuable to describe hydrogen bonding and their observable properties such as vibrational shifts and intensities, rotational constants, binding energies and docking preferences.^[1] The choice of a computational method is usually influenced by taste, tradition, experience, cost, and hopefully also by comparison to higher level calculations for model systems of reduced size. The latter can be misleading for contributions which grow slowly with size or are generally poorly understood. It is thus advisable to complement such theory-internal benchmarking by systematic and well-designed experimental benchmarks^[2] for realistic systems. The talk will present some current spectroscopic proposals from our group on how this can be achieved, building carefully curated experimental benchmark databases based on multi-messenger studies.^[3] This project is at the core of a new research training group in Göttingen (bench.uni-goettingen.de) which also invites contributions from all over the world.



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Interrelation between the substituent effect, hydrogen bonding and aromaticity in quartets of substituted 9H adenine tautomer

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Quartets of the 9H adenine tautomer are formed from its monomers by intermolecular hydrogen bonds between NH of the amino group at the 6 position of adenine and endocyclic nitrogen atom at the N1, N3 or N7 position of adenine rings; termed as A4N1, A4N3 and A4N7, respectively.

Selected substituents (X), varying in their electron properties, were inserted into all adenine molecules either at position C8 or N9 for tetramers A4N1 and A4N3 whereas in the case of the A4N7 quartet they were introduced either at C2 or N9 position. The strength of intermolecular interactions (H-bond energy) in the tetramer was calculated using the supramolecular approach. To describe the substituent effect, cSAR (Charge of the Substituent Active Region)^[1] concept and geometry-based aromaticity index – HOMA (Harmonic Oscillator Model of Aromaticity)^[2] were applied.

Comparison of cSAR(X) values determined for the monomer with those of the tetramer showed that H-bonding causes changes in the electron attracting/donating substituent properties. These changes are associated with the energies of the H-bond interaction in the tetramer and are also observed in the aromaticity of the five and six membered rings.

Acknowledgments: H.S. thanks the National Science Centre of Poland for supporting this work under the grant no. UMO-2016/23/B/ST4/00082.

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Exploring hydrogen bonding in gas phase molecular complexes by broadband rotational spectroscopy

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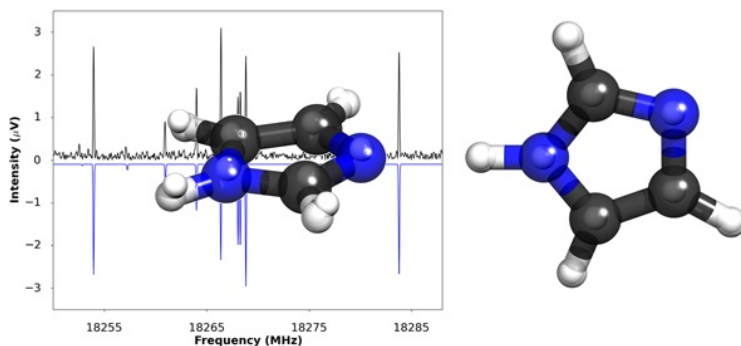
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Rotational spectroscopy provides unrivalled precision for the determination of molecular structure in isolated, gas phase species. Electronics capable of digitising waveforms at gigahertz frequencies now allows chirped-pulse Fourier transform microwave spectroscopy to be performed at high resolution, high bandwidth and with minimal or no cost to sensitivity. One focus of this presentation will be recent experiments to study intra- and intermolecular hydrogen bonds in complexes containing imidazole or methylimidazole. It will be shown that water coordinates to methylimidazole via a primary hydrogen bond to the pyridinic nitrogen atom and a secondary contact between the oxygen of water and a hydrogen atom attached to imidazole (or the methyl group). The consequences of the secondary interaction for the internal rotation of the methyl group will be described. The results of experiments that have applied broadband rotational spectroscopy to probe interactions between isolated, metal-containing molecules and simple hydrocarbons such as ethyne and cyclopropane will also be presented. These complexes are generated through laser vaporisation of a metal target in the presence of an expanding gas sample containing the hydrocarbon precursor. Precise changes in the geometry of the hydrocarbons on their attachment to copper, silver and gold atoms will be described.





Hydrogen-bonding building blocks for materials assembly and self-sorting networks

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Self-assembly is an attractive method of fabricating functional materials.^[1] A key requirement of this approach is the ready access to natural or synthetic molecular building blocks with well-defined molecular recognition behavior. This presentation will describe a series of new building-blocks capable of well-defined hydrogen-bonding interactions made in one or two steps.^[2, 3] These motifs form heterodimers with tunable associations constants (10^2 – 10^4 M⁻¹). The presentation will then describe the use of these hydrogen-bonding motifs for the assembly of polyurethanes and polymer blends.^[4, 5] Finally, a key future challenge for self-assembly is to reproduce nature's ability to assemble multiple functional entities in defined locations and at specific times. Such assemblies modulate complex adaptive networks that control biological processes (e.g. intracellular signalling cascades); multiple molecular recognition events happen simultaneously AND sequentially, requiring individual components to interact selectively with one partner at one point and then with another partner at a different point in a given process. The presentation will conclude with a discussion on how our novel hydrogen-bonding motifs together with others take from the literature can be used to carry out sequential self-sorting and develop self-sorting networks.^[6, 7]

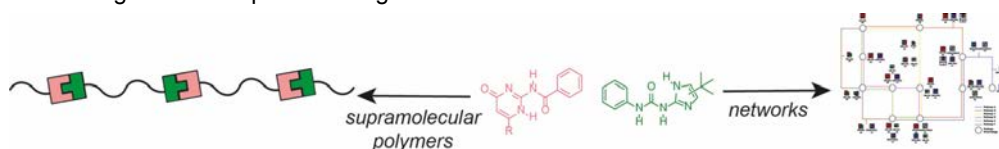


Figure 1 | Schematic illustrating novel hydrogen-bonding motifs and their use in supramolecular polymer and self-sorted network development.

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Excited-state proton transfer: molecules in a hurry to get rid of antiaromaticity

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Baird's rule explains why and when excited-state proton transfer (ESPT) reactions happen in organic compounds. Bifunctional compounds that are $[4n+2]$ π -aromatic in the ground state, become $[4n+2]$ π -antiaromatic in the first $1\pi\pi^*$ states, and proton transfer (either *inter*- or *intra*-molecularly) helps relieve excited-state antiaromaticity. Computed nucleus independent chemical shifts (NICS) for several ESPT examples (including excited-state intramolecular proton transfers (ESIPT), biprotonic transfers, dynamic catalyzed transfers, and proton relay transfers) document the important role of excited-state antiaromaticity. *o*-Salicylic acid undergoes ESPT only in the "antiaromatic" S_1 ($1\pi\pi^*$) state, but not in the "aromatic" S_2 ($1\pi\pi^*$) state. Stokes' shifts of structurally-related compounds (*e.g.*, derivatives of 2-(2-hydroxyphenyl)benzoxazole and hydrogen-bonded complexes of 2-aminopyridine with protic substrates) vary depending on the antiaromaticity of the photoinduced tautomers. Remarkably, Baird's rule predicts the effect of light on hydrogen bond strengths; hydrogen bonds that enhance (and reduce) excited-state antiaromaticity in compounds become weakened (and strengthened). Implications for proton-coupled electron transfer in DNA base pairs also will be discussed.

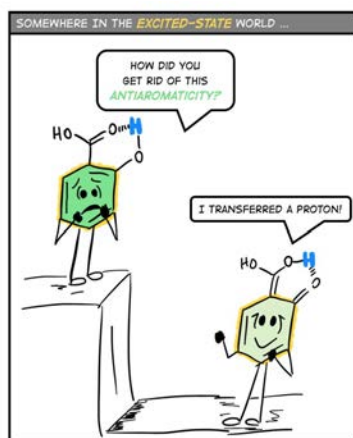


Figure 1 | Cartoon illustration of molecules getting rid of excited-state antiaromaticity through ESPT.

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HBOND2019
Amsterdam

Abstracts contributing speakers

The abstracts are given in alphabetical order by last name of the speaker.



Self-assembly and exfoliation of a novel 2D material based on B-N and hydrogen bonds

Simone d'Agostino,^[a] Luca Fornasari,^[a] Elisa Boanini,^[a] Giacomo Bergamini,^[a] Raffaello Mazzaro,^[b] Fabrizia Grepioni,^[a] Dario Braga^[a]

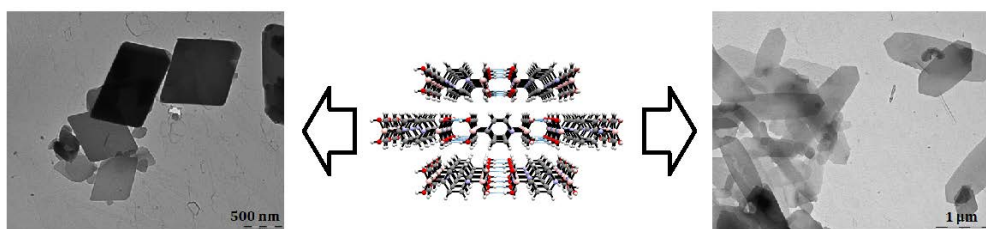
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The field of 2D materials has been the target of intense study due to the unique properties that single-atom or few-atoms thick materials exhibit compared to their bulk counterparts. The most studied 2D material is graphene, however a class of 2D materials beyond graphene is rapidly emerging, comprising a wide spectrum of organic, inorganic and hybrid materials.^[1,2] Pyridinylboronic acids have recently drawn attention in crystal engineering due to their self-complementary nature.

Herein we report the case of 4-pyridinylboronic acid. This small molecule spontaneously assembles in the solid state in a low-density structure, characterized by the stacking of 2D sheets formed by a rare cooperation of N-B and H-bonds. Crystals were characterized by means of XRD techniques and electron microscopy, while Hirshfeld surface analysis and Intermolecular Interaction Energies (IIEs) calculations were performed to probe the properties of the compound as a potential 2D material. Exfoliation was explored through liquid-phase sonication in different solvents. The nanosheets obtained by exfoliation were characterized by TEM and AFM imaging showing that the solvent has an influence on the morphology of the flakes.



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Wanted $\nu(\text{CH})$ band: IR spectra of complex of trifluoroacetic acid and acetone in the gas phase

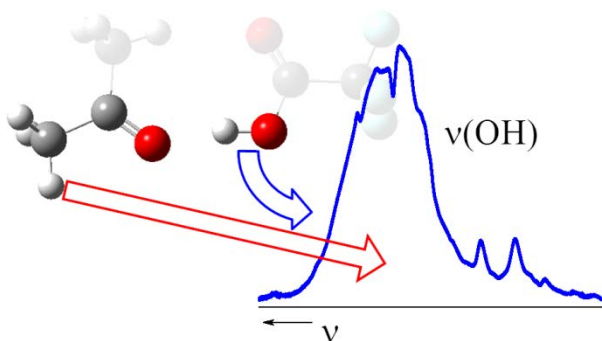
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The FTIR spectra of mixtures of trifluoroacetic acid (TFA) and acetone (H6 and D6 isotopologues) were recorded in the gas phase at temperature $T = 21\text{ }^{\circ}\text{C}$. After subtracting the bands of acid and acetone monomers and dimer of TFA, the spectra of TFA $\cdots$ acetone (H6 and D6) were obtained.^[1] Additionally, the spectra of complexes between TFA and diethyl ether (H10 and D10) were found in the same way.

All spectra have an intense broad $\nu(\text{OH})$ band located in the range of $3500 - 2100\text{ cm}^{-1}$. It was found that in the spectra of TFA $\cdots$ ether the pronounced $\nu(\text{CH})$ and $\nu(\text{CD})$ bands are observed against the background of the $\nu(\text{OH})$ band. These bands are slightly shifted from the corresponded bands in the spectra of ether monomers. In contrast, in the spectra of TFA $\cdots$ acetone complexes there are no explicit $\nu(\text{CH})$ ($\nu(\text{CD})$) bands in the region of these monomer bands. This is the signature of a strong interaction of ν_{OH} and $\nu_{\text{CH}(\text{CD})}$ vibrational modes in these complexes. Because the same effect is observed in the spectra of acetic acid dimers,^[2] the $\nu_{\text{OH}}-\nu_{\text{CH}}$ interaction can be caused by an electronic structure of the $(\text{CH}_3)-\text{C}=\text{O}\cdots\text{HO}$ fragment and should be taken into account during a $\nu(\text{OH})$ band reconstruction of similar complexes.



Acknowledgements. Author acknowledges a financial support of the Russian Science Foundation (Project 18-13-00050).

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Coupled cluster analyses of noncovalent interactions

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Noncovalent interactions are ubiquitous in chemistry. Energy Decomposition Analysis (EDA) schemes provide in-depth insights into their nature by decomposing interaction energies into additive contributions, such as electrostatics, polarization, and London dispersion.^[1] Although modern local variants of the "gold standard" CCSD(T) method have made it possible to compute electronic energies accurately for relatively large systems,^[2-3] extracting chemically meaningful energy terms from such high level electronic structure calculations has been a long lasting challenge in computational chemistry. In this talk, I will describe basic principles, interpretative aspects and applications of recently developed coupled cluster-based EDAs for the analysis of noncovalent interactions.^[4-8] In the application part, emphasis is placed in discussing the role of the all-important H-bond interactions in determining the selectivity of organocatalytic transformations.^[9]

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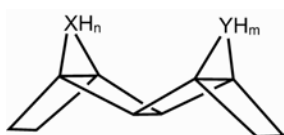


Is there a hydrogen-hydrogen bond associated with the bond path in the electron density between congested atoms?

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Four energetic criteria, all rooted in the partitioning of a molecule into atomic basins using some properties of the electron density as defined in the Quantum Theory of Atoms in Molecules,^[1] are compared and correlated with the presence of a bond path in the electron density between two non-bonded atoms in a series of sterically crowded derivatives of exo-exo-tetracyclo [6.2.1.1.^{3,6}.0^{2,7}] dodecane, shown below.



Despite the chemical differences between the congested groups, all the molecules studied display either a bond path between the congested pair of atoms in the electron density, the Ehrenfest force density,^[2] the virial^[3] and/or Coulomb potential^[4] density.

It was found that there does not exist a correlation between the presence of a bond path between the sterically congested atoms in the electron density and any of the energetic criteria considered. Nor is there a correlation between the numerical data obtained with any of the methods used.

Given that the Ehrenfest force density, the virial and the Coulomb potential density are formulated in terms of the potential energy acting on a point in the electron density or the gradient thereof, the results support the view that the “interaction line” observed between the congested atoms should be interpreted as being just a line of increasing magnitude in the value of the field, with a minimum value along the direction of the line at the line critical point, and a maximum near or at the nuclei, without any consequences on the atomic energy, as calculated by integrating over the atomic basin, of the atoms involved.

It hence appears that a similar conclusion is to be made about the bond path in the electron density.^[5]

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Acknowledgment: the Russian Scientific Foundation (grant 19-13-00459) financially supported this work.

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Influence of hydrogen bonding interactions and structure modifications on photophysics and photostability of indole derivatives

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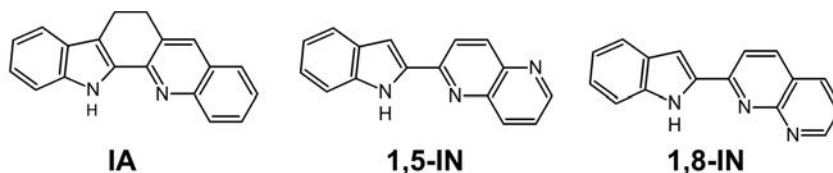
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We demonstrate how, by changing the structural properties and environment, the photophysics and photostability of molecules that can simultaneously act as hydrogen bond donors and acceptors can be modified.^[1, 2] The formation of hydrogen bonds with protic solvent leads to a significant decrease of the triplet formation efficiency and an increase of photostability of the chromophore. Two types of indole derivatives have been investigated: one that exists only in the *syn* form (**IA**) and the second, which can exist in both *syn* and *anti* rotameric structures (**1,5-IN** and **1,8-IN**)(Scheme 1).

The photodegradation yield of **IA** was found to be about 200 times lower in methanol than in *n*-hexane. This rigid molecule is also about 4 times more photostable in alcohols than similar, but non-rigid molecules. This additional photostability enhancement is due to elimination of a slower channel of excited state deactivation in alcohol complexes, $S_0 \leftarrow S_1$ internal conversion. The dominant, faster channel of S_1 depopulation, observed in the cyclic 1:1 hydrogen bonded complexes, is the excited state double proton transfer.



Scheme 1 | Structures of **IA**, **1,5-IN** and **1,8-IN**.

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Deciphering the driving forces in crystal packings by analysis of hydrogen bonds, electrostatic energies and contact enrichment ratios.

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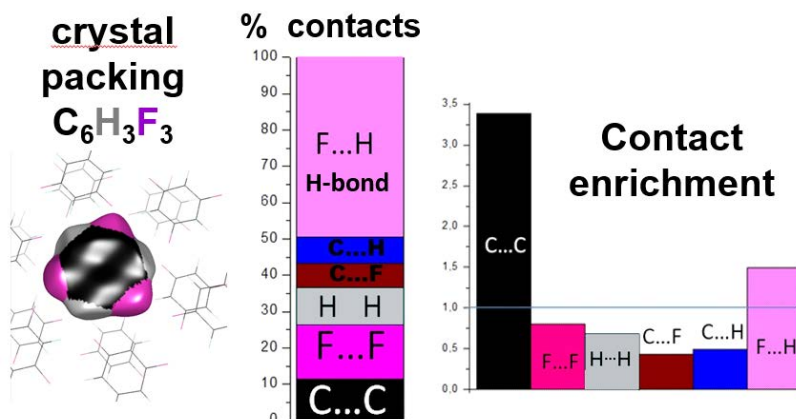
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The decomposition of the crystal contacts on the Hirshfeld surface between pairs of interacting chemical species enables to derive a contact enrichment ratio ^[1,2,3]. This descriptor yields information on the propensity of chemical species to interact with themselves and other species. The enrichment ratio is obtained by comparing the actual and equi-probable contacts. H...N, H...O and H...S as well as weak H...halogen hydrogen bonds appear generally enriched, depending on the context.

The electrostatic energy of short contacts was also computed using a multipolar atom model and compared statistically to the contact enrichment ratios.

The analyses suggest that hydrogen bonds are often the most enriched and attractive interactions and are therefore a driving force in the crystal packing formation for organic molecules. The methodology also enables to compare different types of hydrogen bonds which are in competition within crystal packings. The behaviour of weaker interactions is less contrasted and will be discussed.



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Role of weak hydrogen bonds in the structure of (co-)solvents used in cellulose dissolution

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The mechanism of cellulose dissolution has remained to be an attractive topic for researchers within the last decades. While the majority of cellulose dissolution studies are aimed at cellulose-solvent interactions, the relevant studies focusing on the cellulose solvents and co-solvents are scarce. The lack of knowledge about intermolecular interactions within these systems seriously hinders our understanding of cellulose-solvent interactions, which complicates the search for new solvents suitable for efficient cellulose processing.

To fill this gap in knowledge, the present work employs vibrational spectroscopy methods and DFT calculations to obtain new insights into the structure of the relevant compounds used in the field of cellulose dissolution. It was found that neat *N,N*-dimethylacetamide, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidone tend to form dimers as prevalent species in the liquid state. These dimers were found to be stabilized via weak hydrogen bonds between X=O and methyl groups of the adjacent molecules. These findings will be discussed in the wider context of interactions in the solvent systems employing the studied compounds, with the aim to improve our understanding of cellulose dissolution mechanism and to determine which characteristics of these systems are essential for cellulose dissolution.



Secondary electrostatic interaction model for multiply hydrogen-bonded arrays revised

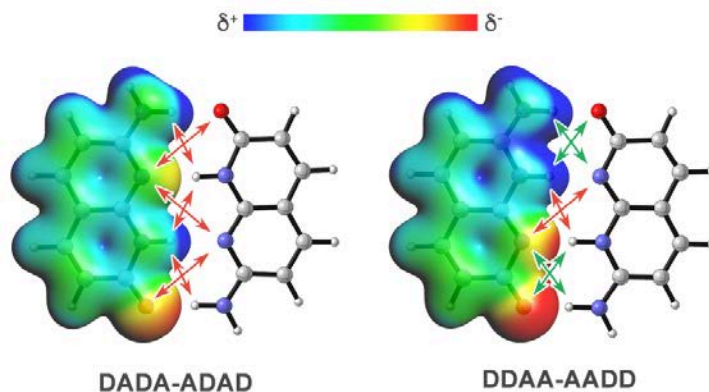
Stephanie C. C. van der Lubbe,^[a] Célia Fonseca Guerra^[a, b]

^[a] Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling, Vrije Universiteit Amsterdam, Amsterdam, The Netherlands

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The secondary electrostatic interaction (SEI) model^[1] is often used to predict and explain relative hydrogen bond strengths of self-assembled systems. The SEI model oversimplifies the hydrogen bonding mechanism by viewing them as interacting point charges, but nevertheless experimental binding strengths are often in line with the model's predictions. We therefore propose a new view on multiple hydrogen-bonded systems that is both chemically intuitive and grounded in quantum chemical analysis. Our findings explain why and how the SEI model has been predictive, and provide supramolecular chemists with meaningful understanding for tuning hydrogen bond strengths.^[2]



[1] W.L. Jorgensen, J. Pranata, *J. Am. Chem. Soc.* **1990**, *112*, 2008.

[2] S.C.C. van der Lubbe, F. Zaccaria, X. Sun, C. Fonseca Guerra, *J. Am. Chem. Soc.* **2019**, *141*, 4878.



Composition and structure of complexes formed in aqueous solutions of trifluoroacetic acid

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The composition and structure of complexes formed in aqueous solutions of trifluoroacetic acid were studied using the multiple frustrated total internal reflection IR spectroscopy and density functional theory (B3LYP/6-31++G(d,p)). Two types of molecular complexes were found in these solutions: $(\text{CF}_3\text{COOH})_2 \cdot (\text{H}_2\text{O})_2$ cyclic tetramers, in which the water and acid molecules are arranged pairwise side-by-side, and $\text{CF}_3\text{COOH} \cdot (\text{H}_2\text{O})_2$ cyclic trimers. In the concentration range from 100% acid to the $[\text{H}_2\text{O}]/[\text{CF}_3\text{COOH}] = 1:1$ ratio only the specified tetramers are observed, and all added water is bound into such hydrates. In more diluted solutions (up to the $[\text{H}_2\text{O}]/[\text{CF}_3\text{COOH}] = 2:1$ ratio), $\text{CF}_3\text{COOH} \cdot (\text{H}_2\text{O})_2$ trimers are formed along with the tetramers, and at the double excess of H_2O all components of solution are bound into such trimers. In diluted solutions (from 0 to 3.6 mol/l CF_3COOH) acid entirely dissociates into H_5O_2^+ and CF_3COO^- ions, which are hydrated by water molecules. In the intermediate region (from 3.6 mol/l to the $[\text{H}_2\text{O}]/[\text{CF}_3\text{COOH}] = 2:1$ ratio) these ions and $\text{CF}_3\text{COOH} \cdot (\text{H}_2\text{O})_2$ complexes are simultaneously present in solution. Their concentrations were estimated.



Are thermally excited isomers of a pentamer important for liquid water?

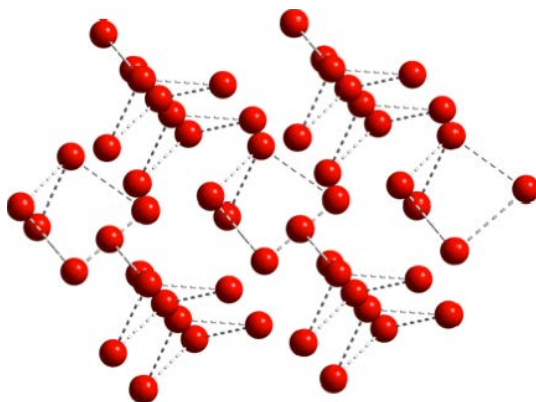
Margaret Mandziuk^[a]

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The presence of pentameric rings in liquid water has been suggested in the past. Our simple model^[1], applied to the liquid with the assumption that it contains cyclic pentamers, yields excitation energies of O–H bond stretching vibrations in surprisingly good agreement with the experimental 2-D IR spectrum of Tokmakoff's group^[2].

We have proposed that the population of thermally excited isomers of a pentamer, increasing with temperature, can be interpreted as the High Density Liquid (HDL)^[1]. In this presentation we will show how this interpretation fits experimental data. In particular, we will show that some of these structures can be considered as building blocks of ice VI and ice VII. We will examine several low energy pentameric structures and the barriers between them.

Unfortunately, with many low energy local minima, and relatively low barriers between them, it is not possible to determine with certainty the vibrationally averaged structures of the thermally excited isomers of the pentamer. Further experimental investigations should confirm or refute our interpretation of HDL.



^[1] M. Mandziuk *J. Mol. Struct.* 1177 (2019) 168

^[2] L. D. Marco *et al. J. Chem. Phys.* 145 (2016) 094501.

Acid solvation versus dissociation at ultracold temperatures: sequence matters

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Aqueous acid dissociation reactions are at the heart of numerous chemical and biological processes. These reactions also play a significant role in atmospheric chemistry, most importantly, to the processes leading to ozone layer depletion. In the past, many theoretical and experimental studies have been carried out on small HCl-H₂O clusters to understand the fundamentals of acid dissociation.^[1-3]

We have built a helium droplet machine at the FELIX laboratory^[4], which allows us to study ice particle formation and elementary reactions mimicking the star dust conditions.

Herein, we report the full dissociation of HCl on stepwise addition of ≥ 4 H₂O molecules at ultracold temperatures (0.4 K) of helium droplets.^[5] Ultrabright pulsed free electron lasers at FELIX laboratory allowed us to explore the fingerprint region^[3], 1000-1700 cm⁻¹, for HCl dissociation. Using mass- selective detection, we could unambiguously assign the spectral bands for the smallest droplet of acid, H₃O⁺(H₂O)₃Cl⁻. We also found that the dissociation of HCl is highly specific to the sequence in which molecular aggregation takes place. Accompanying ab initio-MD simulations demonstrate that not only reaction stoichiometry but in particular the reaction sequence needs to be explicitly considered to rationalize ultracold chemistry.

[1] H. Forbert et al., *J. Am. Chem. Soc.*, **2011**, 133, 4062.

[2] A. Gutberlet et al., *Science*, **2009**, 324, 1545.

[3] J. S. Mancini and J. M. Bowman, *Phys. Chem. Chem. Phys.*, **2015**, 17, 6222.

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[5] D. Mani et al., *RSC Advances*, **2017**, 7, 54318.



Carbon-hydrogen bond in an action of activation through selected non-covalent interactions

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In this contribution we will discuss the origin of C-H bond activation through various types of non-covalent interactions: starting from the elusive long-range anagostic interactions^[1] of the type C-H...M (M = a metal center, see Figure below) where metal-hydrogen distances are > 2.5 Å, going through typical hydrogen bonds e.g. C-H...S augmented by N-H...N, N-H...π, etc.^[2,3] to end up with the recently topical intermolecular London dispersion driven homopolar dihydrogen bonds C-H...H-C.^[4,5]

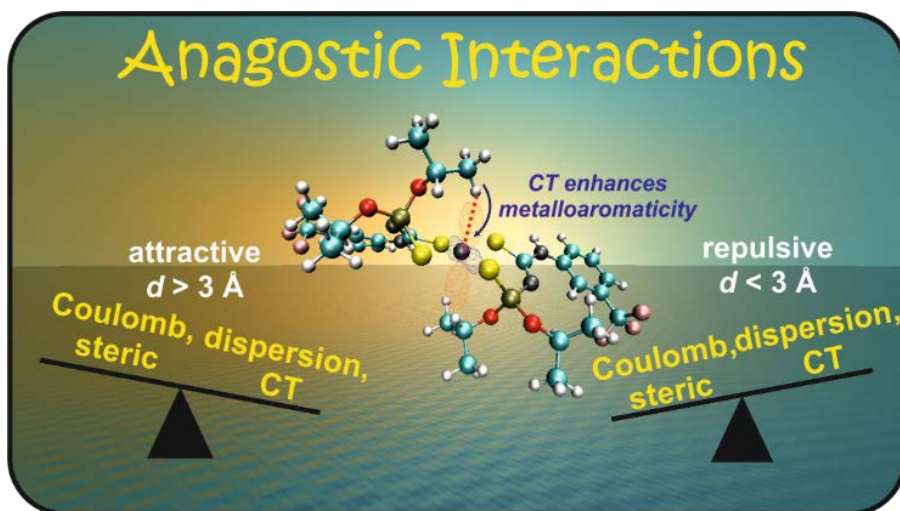


Figure: The nature of anagostic interactions C-H...Ni for various $d(\text{H}\cdots\text{Ni})$ distances ($d > 3\text{Å}$ and $d < 3\text{Å}$).

Acknowledgments: M.P. Mitoraj acknowledges the financial support of the Polish National Science Center within the Sonata Bis Project 2017/26/E/ST4/00104.

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- [2] Mariusz P. Mitoraj et al. *Cryst.GrowthDes.* **2018**, 18, 5385
- [3] Mariusz P. Mitoraj et al. *Eur. J. Org. Chem.* **2019**, 493-503
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An intra-residue NH...S H-bond stabilizes extended structures in cyclic α -peptides: a laser spectroscopy and quantum chemistry study

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In an attempt to document how the presence of a sulfur-centred hydrogen bond can provide a fine tuning of the conformational preferences in synthetic capped α -peptides, we studied in a series of short capped oligomers of a cyclic sulfur-containing α -amino acid; 3-aminothietane 3-carboxylic acid (Attc) (Figure(a)). The capped monomer, dimer and trimer (Z-(Attc)_n-NHMe, n = 1-3) were synthesized and then investigated, in isolation in gas phase using conformation-selective IR/UV double resonance laser spectroscopy and quantum chemistry (DFT-D: B97-D3/def2-TZVPPD).

- The capped monomer exhibits an original extended 5-6 γ motif, stabilized by an intra-residue five-membered ring N-H...O H-bond (C5) and an intra-residue N-H...S H-bond (C6 γ), forming a 6-membered ring between the backbone amide-N-H and the sulfur atom in γ -position (Figure(a,b)).
- In the capped dimer, the most stable conformer forms a fully extended 5-6 γ /5-6 γ structure, which can be seen as the juxtaposition of two 5-6 γ monomer motifs.
- In the capped trimer, however, the 5-6 γ motif is only preserved by the first and third residues; the central residue adopts an original folded structure, stabilized by a five-membered NH...N-amide bond, linking the two extended motifs at the extremities (5-6 γ -5 π NN/5-6 γ structure).

Since Attc is an achiral building block, the H-bonded network in its short oligomers lead to enantiomeric conformations. In future studies, insertion of a related chiral sulfur-containing α -amino acid at the central position of the tripeptide could be used to control the folding chirality.

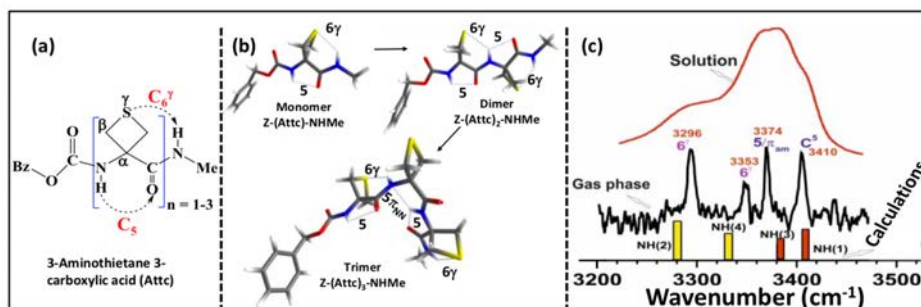


Figure (a) Structures and (b) most stable conformations of the capped monomer, dimer and trimer of the Attc α - amino acid; (c) example of a resolved IR spectrum obtained in the gas phase and its solution counterpart.



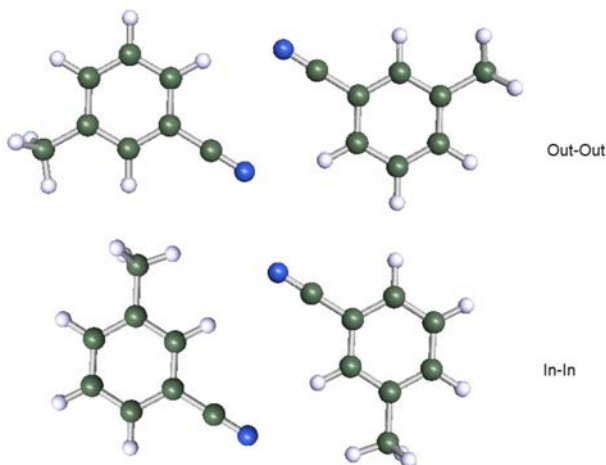
Excitonic splitting in molecular dimers: 2-tolunitrile dimer and 3-tolunitrile dimer in the gas phase

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^[a] Heinrich-Heine-University, Düsseldorf, Germany

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High resolution laser induced fluorescence spectra and fluorescence emission spectra of 2- and 3-tolunitrile, their Dimers and their water clusters, recorded through various vibronic bands in the electronically excited state, are presented. From the transition dipole moments in the individual monomers, the 2-tolunitrile dimer has shown to form J-aggregates[1], which is why the one-photon allowed transition is the S_1 state in this cluster in contrast to other symmetric dimers, which tend to form H-aggregates. The changes of the molecular structures upon electronic excitation have been determined from a Franck-Condon fit of the intensities in various fluorescence emission spectra and from a fit to the inertial parameters from rotationally resolved electronic spectroscopy. The excited state structures of the 2-tolunitrile and 3-tolunitrile have been found to be asymmetric, in contrast to the respective ground state structures. Thus, emission takes place from one of the locally excited monomer moieties in the 2-tolunitrile and 3-tolunitrile dimer.



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Combination of QENS, FTIR, EXAFS and XRD for studies of the orthorhombic-tetragonal phase transformation in $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskites

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Research interest has increasingly focused on hybrid perovskites MABX_3 like $[\text{CH}_3\text{NH}_3]^+$ (MA), $\text{B} = \text{Pb}$ and $\text{X} = \text{I}$ or Cl as a future photovoltaic material. FTIR ^[1] and QENS ^[2] studies show that chlorine substitution has a large influence on the rotational dynamics of the MA molecule in $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskites,^[1] since the chlorine substitution leads to a weakening of the hydrogen bridge bonds (these bonds connect the MA molecules with the $[\text{PbX}_6]^-$ octahedra host structure).^[2] The structural counterpart to the changes in the MA molecule dynamics caused by the chlorine substitution is the influence of the chlorine substitution on the tilting and distortion of the $[\text{PbX}_6]^-$. By a combination of EXAFS Pb L3 edge investigations (local structure) and XRD (long-range order) the influence of the chlorine substitution on the distortions of the $[\text{PbX}_6]^-$ octahedra was investigated. In order to discuss the temperature-dependence of the local structure around the Pb atom in terms of librational motions, the EXAFS Debye-Waller factor was derived from EXAFS spectra.

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Spectral manifestations of hydrogen-bonding as a tool for condensed matter studies.

Ilya G. Shenderovich

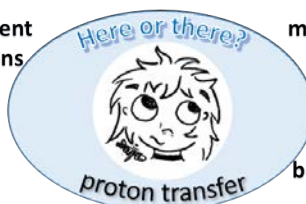
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The progress made in the study of hydrogen-bonding (H-bonding) opens up new horizons in understanding properties of condensed matter. There are many illustrative examples of using the spectral manifestations of H-bonding as a tool for the analysis at the atomic scale of the local structure and property-defining interactions in solutions, in amorphous materials, and at surfaces. The effectiveness of this approach is based on the fact that a given H-bond spectroscopic parameter is often depend on only a few or even one structural variable. The latter can thus be obtained from the former.

This presentation reviews some of the examples that have been studied by NMR. The considered topics are sketched on the picture. Specifically, it will be shown which NMR parameters are the most discriminative to:

solute-solvent
interactions
Games
Duties
(ΔpK_a)



matrix effects
School
Friends
hydrogen
bond network

- (i) the structure of the first solvation shell in organic solvents^[1,2] and polycrystalline solids^[3,4];
- (ii) the chemical reactivity of surfaces^[5,6];
- (iii) mechanisms of proton transfer in organic solvents^[7];
- (iv) H-bond network patterns in solids^[8,9].

- [1] I.G. Shenderovich, G.S. Denisov, "Solvent effects on acid-base complexes...", *J. Chem. Phys.*, **2019**, 150, accepted.
- [2] I.G. Shenderovich, *J. Chem. Phys.*, **2018**, 148, 124313.
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- [4] I.G. Shenderovich, *J. Phys. Chem. C*, **2013**, 117, 26689.
- [5] A.A. Gurinov, D. Mauder, D. Akcakayiran, G.H. Findenegg, I.G. Shenderovich, *ChemPhysChem*, **2012**, 13, 2282.
- [6] D. Mauder, D. Akcakayiran, S.B. Lesnichin, G.H. Findenegg, I.G. Shenderovich, *J. Phys. Chem. C*, **2009**, 113, 19185.
- [7] S.B. Lesnichin, P.M. Tolstoy, H.-H. Limbach, I.G. Shenderovich, *Phys. Chem. Chem. Phys.*, **2010**, 2, 10373.
- [8] E.Yu. Tupikina, M. Bodensteiner, P.M. Tolstoy, G.S. Denisov, I.G. Shenderovich, *J. Phys. Chem. C*, **2018**, 122, 1711.
- [9] R. Manriquez, F.A. Lopez-Dellamary, J. Frydel *et al.*, *J. Phys. Chem. B*, **2009**, 113, 934.



Hydrogen bond and tautomerism in porphyrin isomers

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Free base porphyrin and its structural isomers: porphycene, hemiporphycene, and corphycene (Figure 1) possess two intramolecular NH...N hydrogen bonds. Different size and symmetry of the inner cavity lead to completely different H-bond characteristics for each isomer. This, in turn, has a profound impact on the kinetics and thermodynamics of intramolecular tautomerization.^[1-4] I will present examples illustrating these differences, obtained for molecules in condensed phases, seeded in supersonic jets, and studied in the regime of single molecules.

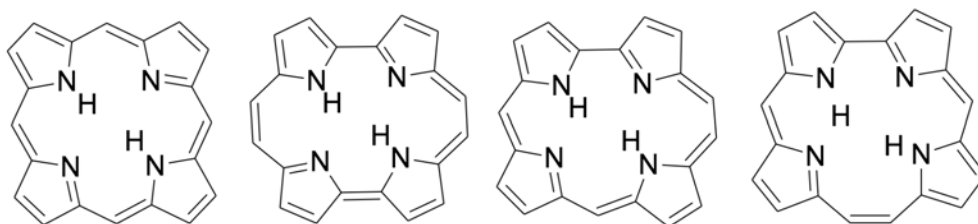


Figure 1 | From left to right: porphyrin, porphycene, hemiporphycene, corphycene.

- [1] J. Waluk, *Chem. Rev.* **2017**, 117, 2447.
- [2] J. Ostapko, K. Nawara, M. Kijak, J. Buczyńska, B. Leśniewska, M. Pietrzak, G. Orzanowska, J. Waluk, *Chem. Eur. J.* **2016**, 22, 17311.
- [3] L. Piatkowski, C. Schanbacher, F. Wackenhut, A. Jamrozik, A. J. Meixner, J. Waluk, *J. Phys. Chem. Lett.* **2018**, 9, 1211.
- [4] S. Peukert, M. Kijak, J. Ostapko, J. Sepioł, C. Le Bris, A. Zehnacker-Rentien, M. Gil, J. Waluk, *J. Chem. Phys.* **2018**, 149, 134307.

Abstracts posters

The abstracts are given in alphabetical order by last name of the presenter;
the poster numbers are given at the top of the page.



Hydride affinities of cationic main group-element hydrides

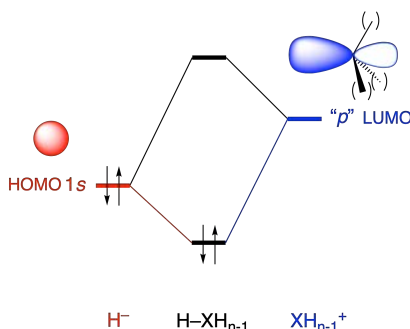
Eva Blokker,^[a] Carolina Groen,^[a] Martijn van der Schuur,^[b] Auke G. Talma,^[b] F. Matthias Bickelhaupt^[a,c]

^[a] Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam, Amsterdam, The Netherlands.

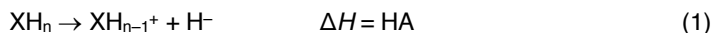
^[b] Polymer Chemistry, Nouryon, Deventer, The Netherlands.

^[c] Institute of Molecules and Materials, Radboud University, Nijmegen, The Netherlands.

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The hydride affinity (HA) is defined as the enthalpy change associated with the heterolytic dissociation of the complex between the hydride ion and the Lewis acid (here XH_{n-1}^+):



We have systematically computed the HAs in gas phase of archetypical anionic bases across the periodic table using relativistic density functional theory (DFT) at ZORA-BP86/QZ4P.^[1,2] We established a consistent set of values of the 298-K hydride affinities of all cationic maingroup-element hydrides (XH_{n-1}^+) in which we have varied the central atom X along groups 14–17 and periods 2–6. The main purpose of this study is to get insight into the underlying physical features behind the periodical HA trends by using Kohn-Sham molecular orbital (MO) theory together with a quantitative bond energy decomposition analysis (EDA).^[3] The orbital interaction, or more specifically, the HOMO-LUMO energy gap, nicely determines the trend in hydride affinities across the periodic table.

[1] E. Blokker, et al., *Results in Chemistry*, **2019**, *1*, accepted.

[2] a) G. te Velde, et al., *J. Comput. Chem.* **2001**, *22*, 931; b) C. Fonseca Guerra, et al. *Theor. Chem. Acc.* **1998**, *99*, 391.

[3] F.M. Bickelhaupt, et al., In: *Reviews in Computational Chemistry*; K.B Lipkowitz et al.; Wiley-VCH: New York, **2000**, Vol. 15, pp. 1.



Poster 2

Investigation of isolated aggregates of coumarin derivatives in the gas phase by applying combined IR/UV spectroscopy

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Coumarin and its derivatives are well known for their photo-induced reactivity leading to their importance as photobiological and photochemical substances. Here we report on 7-Hydroxy-4-methylcoumarin (7-H4MC) and its amino analogue 7-amino-4-methylcoumarin (7-A4MC). The examination of 7-A4MC is of great interest because these compounds show an intramolecular charge-transfer (ICT) between the amino group and the benzopyrone unit in solvents of moderate to high polarity.

In order to investigate intrinsic effects with respect to ICT and structure of the 7-A4MC dimer in the neutral ground and partly the excited state, mass and isomer selective combined IR/UV spectroscopy is applied in molecular beam experiments. By applying DFT and SCS-CC2 calculations a comparison of the measured IR transitions with the calculated frequencies and optimized structures is performed. This allows clear structural assignments, including binding motifs which are able to undergo ICT processes.

Furthermore the 7H4MC dimer and its mono- and dihydrate both in their neutral and cationic ground state are investigated. The dimer undergoes a structural rearrangement from a doubly hydrogen-bonded structure in the electronic ground state of the neutral species to a singly hydrogen-bonded structure in the ionic ground state. This rearrangement does not occur if one or two water molecules stabilize the doubly hydrogen-bonded arrangement.

The tendency of coumarins for self-aggregation observed in aqueous solution are investigated in detail on isolated species giving (in combination with hydration) a closer look on structure and function of coumarins.



Behaviors of halogen F---H bonds in potassium trifluoroborate salts

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In this work, the influence of halogen F---H bonds on the properties of seven potassium 3-furoyl-trifluoroborate (FTFB), 2-isonicotinoyl-trifluoroborate (ITFB), 5-hydroxypentanoyl-trifluoroborate (HTFB), 5-Br-2-isonicotinoyl-trifluoroborate (Br-ITFB), 6-chloro-2-isonicotinoyl-trifluoroborate (Cl-ITFB), 4-fluorobenzoyl-trifluoroborate (FBTFB) and 2-phenylacetyl-trifluoroborate (PTFB) salts¹⁻⁴ were studied in gas phase and in aqueous solution by using NBO and AIM calculations and the hybrid B3LYP/6-311++G** method. The structures of these salts are presented in Figures 1 and 2.

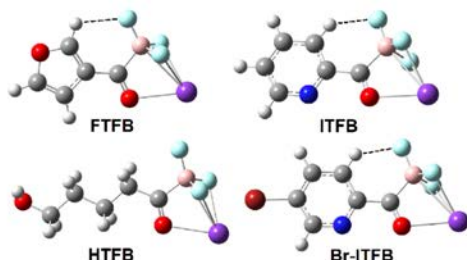


Figure 1 | Theoretical structures of FTFB, ITFB, HTFB and Br-ITFB showing the F---H bonds.

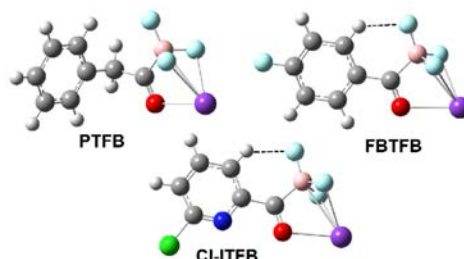


Figure 2 | Theoretical structures of PTFB, FBTFB and Cl-ITFB showing the F---H bonds.

Additionally, the corrected solvation energy, volumes and gap values were evaluated as function of molecular weights of salts by using the same level of theory. The AIM studies show that the IFTB salt present the lower F---H distances in the two medias. Evidently, the presence of a pyridine ring linked to C of C=O groups in IFTB favors the formation of halogen interaction, as compared with furyl and phenyl rings. NBO studies show that the higher delocalizations energies of halogen F---H interactions are observed in the Br-ITFB salt in both media together with the ITFB and Cl-ITFB salts. This study evidence clearly that the halogen F---H interaction play a important role in the reactivity and properties of trifluoroborate salts showing that the FTFB salt has lower volume, low corrected solvation energy and is the less reactive while the most reactive Br-ITFB, Cl-ITFB and IFTB salts present high stabilization energies of halogen F---H interactions and high corrected solvation energies.

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- [2] Iramain et al, J. Mol. Struct. 1163 (2018) 41-53.
- [3] Iramain et al, J. Mol. Struct. 1176 (2019) 718-728.
- [4] Iramain et al, J Mol. Struct. 1184 (2019) 146-156.



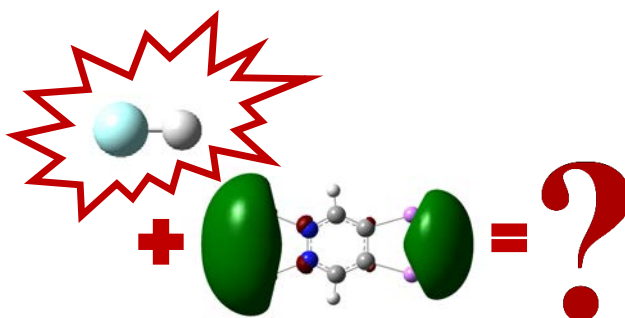
Poster 4

**Hydrogen-bonded complexes formed by the HF molecule and an
electride-like molecule $\text{Li}_4\text{C}_4\text{H}_2\text{N}_2$**

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Electrides are a new class of molecules in which anionic electrons are spatially separated from a positively charged framework. These compounds possess large values of hyperpolarizabilities and are promising for applications in nonlinear optics. They are extensively studied and new molecules are predicted and synthesized. It was shown recently^[1] that a molecule $\text{Li}_4\text{C}_4\text{H}_2\text{N}_2$ with electride properties can be obtained from a pyridazine molecule by adding four lithium atoms. In this molecule with high hyperpolarizability values the electrons of a highest occupied molecular orbital are loosely bound and significantly shifted from the nuclear framework. The IR spectrum of the $\text{Li}_4\text{C}_4\text{H}_2\text{N}_2$ molecule was calculated^[2] using the perturbation theory and different ab initio approximations. It was shown that this molecule possesses absorption bands with very high transition intensities. It is possible that due to the presence of loosely bound electrons such molecules can be partners in H-bonded complexes. In the present study H-bonded complexes formed by HF and $\text{Li}_4\text{C}_4\text{H}_2\text{N}_2$ are calculated ab initio. Geometries of complexes, their binding energies, electro-optical parameters, and changes in the electronic structure are studied.



Acknowledgements. The work was supported by the Russian Foundation for Basic Research (Project 18-03-00520).

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[2] V.P. Bulychev, M.V. Buturlimova, accepted in *Opt. Spectrosc.*, **2019**



Hydrogen bonding of protonated benzonitrile with protic and aprotic ligands

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The hydrogen bond (H-bond) is a fundamental element of chemical structure and reactivity. We address such an intermolecular force involving protonated benzonitrile (H^+BN , $\text{C}_6\text{H}_5\text{CNH}^+$) and protic as well as aprotic ligands ($\text{L}=\text{H}_2\text{O}/\text{Ar}/\text{N}_2$). This is further relevant toward understanding prebiotic chemistry involving BN because of its recent interstellar discovery.^[1] Our IR investigation confirms -CN nitrogen protonation, and the characteristic NH stretch frequency is determined from the IR action spectrum of the tenuous π -bound Ar complex.^[2] The solvent prefers the linear $\text{NH}\dots\text{L}$ H-bond motif. The H-bond strength increases with increasing proton affinity (PA) of the solvent ($\text{Ar}<\text{N}_2<\text{H}_2\text{O}$), which results in a progressive perturbation of the NH group. The larger aprotic Ar/N_2 cluster ($n>1$) features a single $\text{NH}\dots\text{L}$ H-bond along with $(n-1)$ π -bound ligands, resulting in internal ion solvation. In contrast, the larger protic $(\text{H}_2\text{O})_{n>1}$ cluster favours external ion solvation, which helps to understand its astrochemical reactivity with ice surface. For $(\text{H}_2\text{O})_2$ cluster, an intracluster proton transfer (PT) from H^+BN to the $(\text{H}_2\text{O})_2$ dimer occurs, despite the higher PA of BN. This is rationalized by the substantial $\text{H}^+(\text{H}_2\text{O})_2$ solvation energy with BN. The higher PA of the $(\text{H}_2\text{O})_{n\geq 3}$ ligands facilitates this PT and the resulting clusters feature a solvated H_3O^+ ion.



Figure: Optimized structures of (a) $\text{H}^+\text{BN}-\text{H}_2\text{O}$, (b) $\text{BN}-\text{H}^+(\text{H}_2\text{O})_2$

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Poster 6

**Quantitative Kohn-Sham MO analysis of strongly
chalcogen-bonded complexes**

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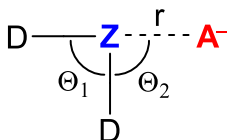
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In recent years, the relevance of noncovalent interactions, such as Hydrogen Bonds (HB) and Halogen Bonds (XB), to catalysis, molecular recognition, crystal structure of matter and self-assembly materials has sparked the need to truly understand their nature and underlying bonding mechanism.^[1] Towards this end, chemists have attributed the strength of XB to an electrostatic model, coined the “ σ -hole”.^[2] However, quantitative Kohn-Sham molecular orbital (KS-MO) theory has revealed that orbital interactions and Pauli repulsion play an important role in XB and that the electrostatics contribution to these interactions does not follow the expected behavior, as suggested by the “ σ -hole” model.^[3]



Scheme 1 | Chalcogen-bonded $D_2Z \cdots A^-$ model complexes ($Z = O, S, Se, Te$; $D, A = F, Cl, Br$).

In this work, we have quantum chemically analyzed another, related non-covalent interaction, known as Chalcogen Bonds (ChB), using KS-MO theory and a matching, canonical energy decomposition analysis (EDA). The strength of ChBs is commonly rationalized in terms of the “ σ -hole” model. Interestingly, using archetypal model systems, as shown in Scheme 1, we have identified the key role of electrostatic attraction, Pauli repulsion and orbital interactions in ChBs. Our work reveals yet another breakdown of the “ σ -hole” model by systematically outlining how it is unable to predict and explain the trends in strengths of these noncovalent interactions.

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Halogen-halogen bonding in crystals

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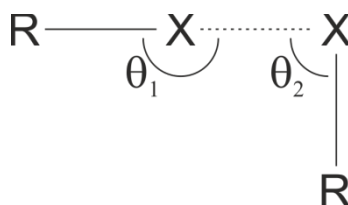
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Type II halogen-halogen contacts (Scheme 1) may form cyclic structural motifs in which each halogen atom acts simultaneously as an electrophile and as a nucleophile.



Scheme 1 | Type II halogen-halogen contact ($\theta_1 \approx 180^\circ$, $\theta_2 \approx 90^\circ$).

The simplest of such cyclic species are halogen-halogen bonded trimers. In the crystal structure one may easily find such a structural motif – the X_3 synthon.^[1] The interactions in the motif are sometimes considered cooperative^[1] but is there really any cooperativity, similarly to the case of halogen-halogen bonded tetramers of bromo- and iodoamine?^[2]

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Poster 8

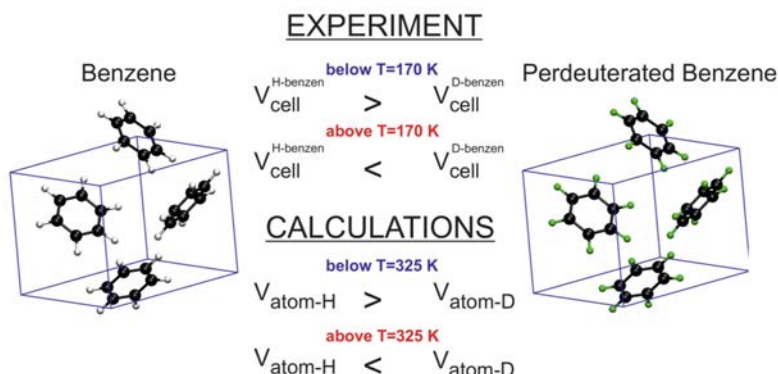
Temperature driven interchange of effective size of benzene with perdeuterated benzenePrzemysław Dopieralski,^[a] Rafał Topolnicki^[b]^[a] Faculty of Chemistry, University of Wrocław, Wrocław, Poland^[b] Faculty of Physics and Astronomy, University of Wrocław, Wrocław, Poland

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For crystalline system isotope effect is manifested through different temperature expansion of unit cell volume containing distinct isotopes of the same element, as has been observed i.e. for benzene crystal and its perdeuterated counterpart.^[1] The differences in temperature expansion of the cell are commonly attributed to changes of atomic effective size of isotopes due to atomic masses.

We propose to employ an innovative procedure to determine the effective atomic size, based on three- step routine in which the problem of finding an effective size of each atom is reduced to determination of volume inside which atom can be find with suitably high probability.

Our procedure is repeated for *ab initio* trajectories^[2,3] computed with different target temperatures for benzene and perdeuterated benzene crystal and enables us to study temperature-driven changes of the effective size of H and D atoms.



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Is it there hydrogen bond in (H₂S)₂?

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Hydrogen bond (HB) is one of the most important non-covalent interactions^[1]. Despite the importance of HB, its definition has been corrected many times depending on our capacities of measurement and our understanding of this interaction. Our experience allows us to predict which systems are likely to exhibit HBs. Hereof, the water dimer is an important reference system in the study and description of HBs^[2] but, on the other hand, few workers would affirm that there is an HB interaction in the cluster (H₂Se). Recently, some researchers have proposed that the intermolecular interaction in the dimer of hydrogen sulfide is an HB.^[3]

This work further addresses the occurrence of an HB in (H₂S)₂ by comparing the interactions in the dimers (H₂O)₂, (H₂S)₂ and (H₂Se)₂ by several quantum chemical topology tools (such as IQA and QTAIM) to increase our understanding of the nature of the existing intermolecular interactions in these clusters. Our results indicate that the interactions inside the dimers (H₂S)₂ and (H₂Se)₂ are considerably alike. In conclusion, the assertion that the H₂S molecules form HBs among themselves might imply that H₂Se molecules are also capable to form these interactions.

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Peculiarities of quasi-aromatic hydrogen bonding

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The analysis of the topological and energetic characteristics calculated for the o-hydroxyaryl Schiff, o-hydroxyaryl Mannich bases and dipyrins is presented. The quantum theory of atoms-in-molecules was used to explore the topology of the electron density at the bond and ring critical points in the studied compounds with the intramolecular hydrogen bonding. The studies of the dependencies between electron-topological, aromatic and energetic parameters under the tautomeric equilibrium were carried out. The calculated non-adiabatic potential curves showed the difference between the unconjugated, π -conjugated and ionic hydrogen bonds. The calculated dependency between the binding energy of hydrogen bonding (ΔE_{HB}) and the aromaticity of chelate chain (the HOMA aromaticity index) revealed the difference between the three types of compounds. The different behaviour of the chelate chains' aromaticity in the analyzed compounds was demonstrated. The results obtained made it possible to reveal a basic divergence between unconjugated, π -conjugated and ionic hydrogen bonds. The prevailing of the ionic impact over the π -electronic coupling in the strengthening of the hydrogen bonding was shown on the basis of the calculated structural, electron-topological and spectral data as well as the potential energy surface.

First-principles Car-Parrinello molecular dynamics was used to explore the tautomeric equilibrium in the studied compounds. A significant dynamics of the bridged proton and the bent vibration of pyrrole fragments in dipyrromethane was exposed by the CPMD calculations.

Acknowledgments: This work has been supported by the National Science Centre (Poland) under the grant no. UMO-2016/22/M/ST4/00226. P.T. thanks Russian Science Foundation (RFBR No. 18-13-00050) for financial support. The authors gratefully acknowledge the Wrocław Centre for Networking and Supercomputing (WCSS) for computational facilities.



A recycling concept for the jet-FTIR spectroscopy of gas phase intermolecular energy balances

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The combination of a supersonic jet expansion with Fourier transform infrared (FTIR) spectroscopy is a well-established method to investigate hydrogen-bonded clusters of small molecules.^[1] Due to the low abundance of these clusters, several hundred jet pulses have to be probed to gain a single spectrum with satisfactory S/N ratio. As the gas mixture is discarded after the jet expansion at the *fillet* jet setup, this results in a high consumption of chemicals.^[2] Therefore, a new setup where the gas is recycled after the expansion, the so-called *gratin* jet (gas-recycling atom-economic infrared jet) spectroscopy, is introduced. It reduces the consumption of carrier gases and analytes by 1-2 orders of magnitude.

Carbonyl compounds with two different substituents, $R-(C=O)-R'$, offer two similar docking sites for hydrogen bond donors such as water or alcohols – the two lone pairs at the oxygen atom. By changing R and R' , the binding preference for one or the other lone pair can be tuned on a kJ to sub-kJ/mol scale, giving rise to an intermolecular energy balance.^[1] This provides a first application of the *gratin* jet.

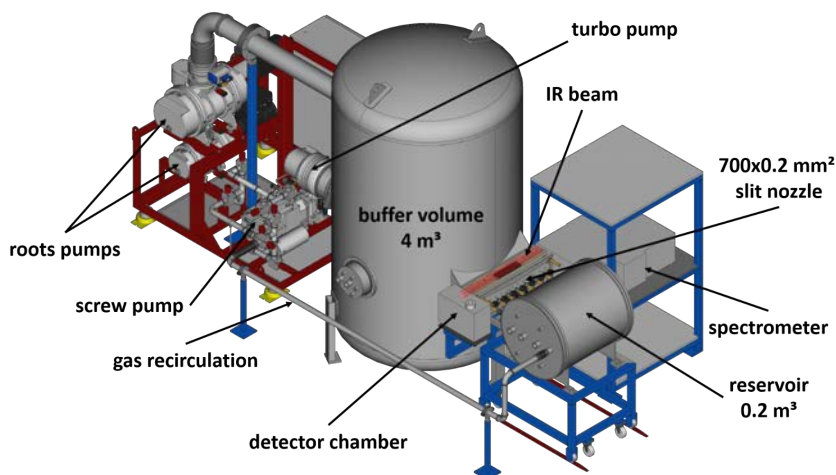


Figure 1 | The new gas-recycling setup for jet-FTIR spectroscopy (*gratin* jet).

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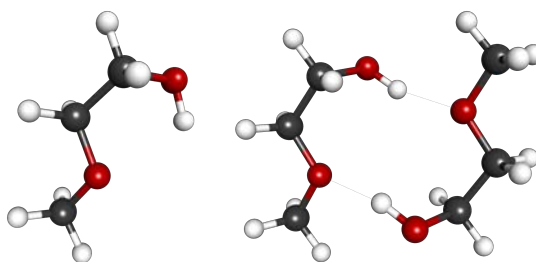
Aggregation and conformation of methoxy ethanol: two jet-raman spectra for the cost of one

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Ethane diol is known to prefer an achiral S_4 -symmetric four-fold H-bonded dimer containing monomers with opposite chirality, which leads to chirality synchronization if the racemization barrier can be overcome.^[1] But what happens if one of the four OH groups is blocked by methylation? Before investigating the mixed dimers of ethane diol and methoxy ethanol, results for monomer and dimer structures of pure methoxy ethanol from Raman spectra in supersonic expansions have to be explored. The competition between molecular conformation, which is controlled by weak and strained intramolecular hydrogen bonding, and molecular aggregation, which is driven by strong hydrogen bonding, is investigated computationally and spectroscopically. Experimental details about the setup that allows for the simultaneous recording of two Raman spectra in different spectral regions (in this case backbone and OH stretching vibrations) will be provided. This proves to be helpful when linking conformational changes with aggregation.



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Molecular recognition of blood group antigens: minimizing the entropy penalty

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Weak interactions such as hydrogen bonding, CH- π interactions and coordination to divalent cations are at the heart of sugar recognition by protein receptors. In addition, ligand conformational entropy is generally claimed as an important contribution in carbohydrate recognition events. Glycans are characterized by an intrinsic flexibility around the glycosidic linkages, and thus, except for isolated cases,^[1] the loss of conformational entropy of the sugar upon complex formation strongly impacts the energy of the binding process.

Herein, by employing a multidisciplinary approach combining structural, conformational, binding energy and kinetic information, we have disclosed the role of the protein-sugar interactions and the conformational entropy in the recognition of the histo blood group antigens A and B by human galectin-3, a lectin of biomedical interest.^[2] NMR experiments provided structural information at the atomic level and combined with ITC and modeling protocols revealed that these rigid natural antigens are pre-organized ligands for hGal-3, being locked in the bioactive conformation. The restriction of the conformational flexibility modulates the thermodynamics and kinetics of the binding process, providing the impetus for the high affinity interaction.

Thus, this study highlights the effect of glycan flexibility on the kinetics and thermodynamics of the binding process and provides inspiration for the design of high affinity ligands as antagonists for hGal-3 or other lectins of biomedical relevance.^[3]

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Manipulating the hydrogen-bonded network preference in dimers of vicinal diols

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In a previous study our group was able to show computationally as well as experimentally (FTIR and Raman jet-spectroscopy), that the simplest organic diol, namely ethane-1,2-diol (ED), exhibits a strong energetic preference for a hetero-chiral pairing with regards to the gauche + and – OCCO dihedral angle.^[1] Although ED is transiently chiral, relaxation in a supersonic jet expansion of the homo-chiral conformers to the more stable hetero-dimer is largely suppressed due to the large interconversion barrier, which we are able to show by comparing it to the permanently chiral cyclic homologue *trans*-cyclohexane-1,2-diol (CD).^[2] Building on the computational and experimental results for ED and CD we now explore ways of influencing the energetic gap between homo- and hetero-chiral dimers by means of chemical substitution. Both permanently as well as transiently chiral systems are discussed.

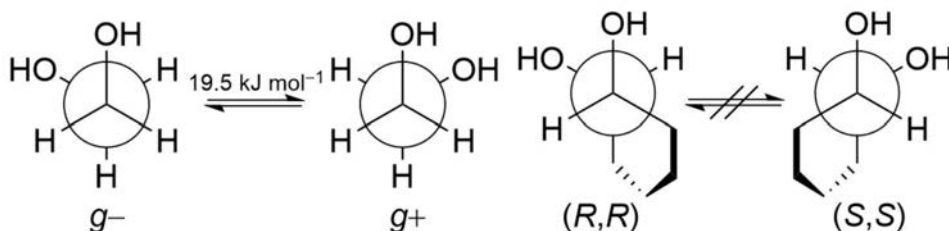


Figure 1 | Newman projections of ethane-1,2-diol (left) and *trans*-cyclohexane-1,2-diol (right) illustrating the transient and permanent chirality.

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Car-Parrinello molecular dynamics study on intramolecular hydrogen bonding in anthracene derivatives

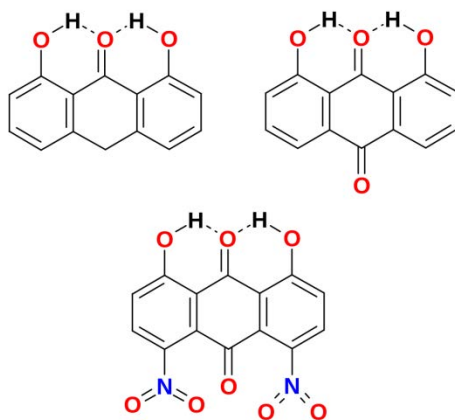
Aneta Jezierska^[a], Andrzej Pihut^[a], Jarosław J. Panek^[a]

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Proton dynamics is an important and widely discussed issue in contemporary science. Here, we report our results obtained for three anthracene derivatives^[1-3] based on Car-Parrinello molecular dynamics^[4]. These compounds possess strong, short intramolecular hydrogen bonds. Therefore, the dynamics of both protons in the hydrogen bridges was studied taking into account the internal molecular reorganization related to the presence of the hydrogen bridges and substituents in the anthracene ring. Special attention was paid to the hydrogen bridges metric parameters time-evolution during the simulation time. Additionally, spectroscopic properties of the investigated compounds were studied on the basis of power spectra of atomic velocity. The obtained results were compared with the experimental data available.

A.J. and J.J.P. express their gratitude to the National Science Centre (Poland) for supporting this work under the grant no. UMO-2015/17/B/ST4/03568.



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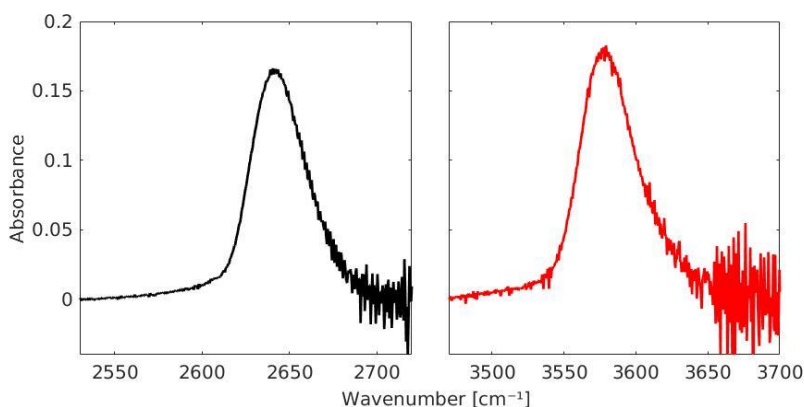


Room temperature Gibbs energies of deuterated hydrogen bonds in the gas-phase

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The hydrogen and deuterium bonded bimolecular complexes of methanol (MeOH), methanol-*d*1 (MeOD) and methanol-*d*4 (MeOD-*d*4) as the hydrogen donor unit and dimethylether (DME) as the acceptor unit, have been observed at room temperature with gas- phase FTIR spectroscopy. The Gibbs energy of complex formation have been determined for each of these complexes, by combining calculated and observed intensities. A Gibbs energy of about 9.6 kJ/mol was found for MeOH·DME, while for MeOD·DME and MeOD- *d*4·DME, it is about 7.6 kJ/mol. The observed difference in Gibbs energy between the hydrogen and deuterium bonded complexes, is partly explained by the difference in zero point vibration energy between the complex and the monomers, being smaller in the deuterium bonded complexes^[1]. This effect is primarily caused by frequencies of the intermolecular modes associated with displacements of the bound hydrogen/deuterium atom being lowered upon deuteration.^[1]



Recorded FTIR spectrum of the deuterium and hydrogen bonded complexes: MeOD·DME (Black) & MeOH·DME (Red).

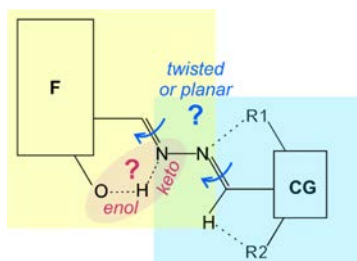
[1] S. Scheiner, M. Cuma, *J. Am. Chem. Soc.*, **1996**, *118*, 1511.



Theoretical studies on intramolecular interactions determining conformational preferences of selected Schiff base ligands in ground and excited states

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In recent years 2-hydroxy aromatic Schiff bases have been highly explored both experimentally and theoretically and considered as promising candidates for fluorescent sensors.^[1,2] It has been demonstrated that due to the existence of intramolecular O-H...N type hydrogen bonds a photodeactivation process may occur over the excited state intramolecular proton transfer (ESIPT) or rotation of the fragment (CG or F) of a molecule (TICT), ^[2,3] see Figure 1. Non-classic weak interactions (e.g. R1...N or R2...H, Figure 1) might additionally be crucial not only in terms of modulation of the equilibrium between naphthol-imine and keto-amine forms, but also for determining the planar or twisted molecular isomers. To this end, the selected results for a series of 2-hydroxy-1-naphthaldehyde Schiff base ligands will be presented primarily from quantum-chemical (time-dependent DFT) perspective, focusing on the relationship between the intramolecular interactions and conformational preferences in the ground and S1 excited state, and consequently, luminescence properties. The observed trends will be rationalized with the aim of CC2 method, as well as bonding analyses based on the Non-Covalent-Index (NCI), Interacting Quantum Atoms (IQA) energy decomposition scheme and the extended transition state coupled with natural orbitals for chemical valence (ETS-NOCV) scheme.



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FTIR spectroscopy of hydrogen bond-mediated chirality induction effects

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Chirality plays a crucial role in our daily life. Not only do vital building blocks of life show uniform chirality, but many drugs show chirality-dependent activity.

This poses a major challenge in the synthesis of these compounds. One possible strategy used in modern asymmetric organic synthesis is the concept of chirality induction^[1] where a permanently chiral molecule induces chirality on a transiently chiral or prochiral reactant through non-covalent interactions. The induced stereogenic center or axis can then be stabilized by follow-up reactions.

We present FTIR spectra of jet-cooled complexes between methyl lactate as a permanently chiral, multifunctional and flexible unit^[1] and transiently chiral or prochiral alcohols with aromatic dispersion centers like benzyl alcohol^[2] and 1-naphthol. We focus on the preference for cooperative or competitive hydrogen bonding patterns at the carbonyl group and on the induction of a more or less subtle chirality in the alcohol. This predicted energy preference is correlated with spectral fingerprints in the OH stretching fundamental region and the latter are compared to experiment. Evidence for insertion of the alcohol into the intramolecular hydrogen bond of methyl lactate^[3] and for a low complexity of the conformational manifold realized in a supersonic jet is found. This invites further studies on related compounds to unambiguously unravel the chirality induction preference.

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Understanding hydrogen bonds from a Kohn-Sham molecular orbital perspective: Pauli matters

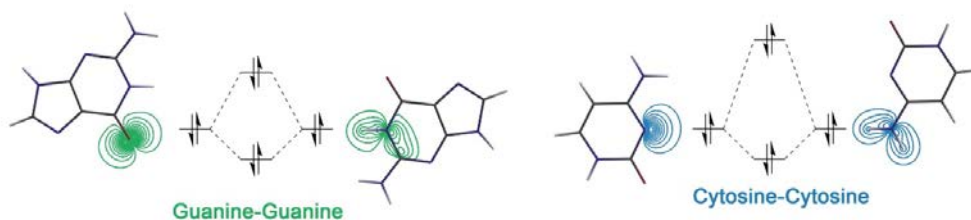
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It is known from theoretical and experimental studies that hydrogen bonds are not purely electrostatic, but also exhibit other interaction components such as polarization, charge transfer and dispersion interactions. However, a component that is often overlooked to tune hydrogen bond strength is the Pauli (steric) repulsion. Here, we demonstrate that the Pauli repulsion can be a decisive factor for relative hydrogen bonds and lengths, and highlight the importance of quantum chemical software to shed light on their bonding mechanism.^[1]



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Hydrogen bonds in phthalic acid cocrystals

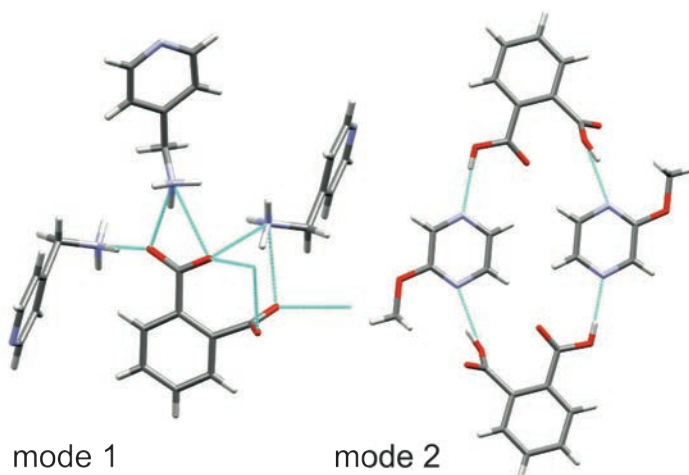
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Crystal engineering, through the analysis of supramolecular synthons, is the most common tool used to design co-crystals. Depending on the properties of the components, above all those related to the type of intermolecular interactions that they can form, molecular or ionic co-crystals can be obtained. Phthalic acid is a very interesting molecule, which by the presence of two carboxylic groups gives the opportunity to create numerous hydrogen bonds. In this contribution results of the design methods and structural studies of new co-crystals with a particular emphasis on factors affecting the possibility of proton transfer in the studied systems will be presented. The simplified calculations showing energy minima for the most preferred mutual arrangement of carboxyl groups in the acid molecule will be also shown.





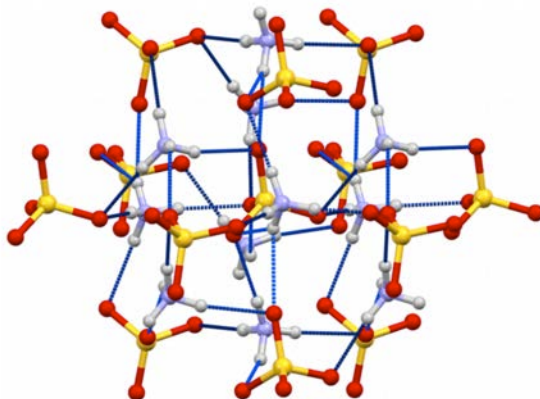
BOMD study of H-bonds in ammonium sulphate

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The giant caloric effects within ferroic materials are a subject of intense study due to their possible applications in environmental-friendly and efficient cooling devices.^[1] Lloveras et al. found that relatively small changes in hydrostatic pressure induce the largest ever known inverse barocaloric effect (BCE) in powdered ferroelectric ammonium sulphate (AS).^[2] The origin of BCE in AS was ascribed to order-disorder phase transition, which is in contrary to our recent XRD and QTAIM studies.^[3] To obtain the precise description of thermal evolution in AS structure, the Born- Oppenheimer molecular dynamics calculations (BOMD) were performed in the NVT ensemble with several conditions applied. Three different cluster sizes were used in computations. Time and space correlations between the anion and cation reorientations were analyzed through the careful study of interaction changes along the obtained trajectories. Additionally, the calculated power spectra were used to study the spectroscopic features and the dynamics of considered H-bond systems.



H-bond system in the ferroelectric, low-temperature phase of ammonium sulphate

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Does hydrated glycine act as solidification nucleus at multi-kilobar conditions?

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The investigation of aqueous solutions containing biomolecules as a function of thermodynamic parameters, such as the pressure, is crucial for understanding biological processes. Here we report the first low frequency spectra of 1.5 M aqueous glycine from ambient pressure up to 8 kbar, i.e. in the pressure range which is crucial for understanding biological processes under extreme conditions.

We observe a linear pressure dependent blue shift of the specific N-C-C-O open/close mode at ~ 320 cm⁻¹ indicating an increasing compression of the solvated glycine. In contrast, the characteristic peak of the hydrogen bond hydration water network centered, at ambient conditions, at ~ 184 cm⁻¹ non-linearly blue shifts with increasing pressure, as well, but with a slower rate than the intramolecular peak.

This indicates that the macroscopic liquid-solid phase transition observed above 8 kbar pressure is driven by hydrated glycine as solidification nucleus. The details will be presented in the poster.



Halogen bonds in ligand-protein systems: molecular orbital theory for drug design.

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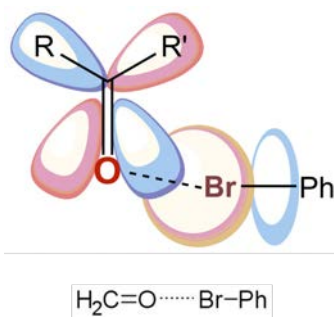
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Halogen bonds^[1] are highly important in medicinal chemistry as drugs' halogenation, generally, improves both selectivity and efficacy towards protein active sites^[2,3]. However, accurate modelling of halogen bond interactions remains a challenge, since a thorough theoretical investigation of the bonding mechanism, focusing on the realistic complexity of drug-receptor systems, is lacking. Our systematic quantum chemical study on ligand/peptide-like systems reveals that halogen bonding is driven by the same bonding interactions

as hydrogen bonding^[4]. Besides the electrostatic and the dispersion interactions, our bonding analyses, based on quantitative Kohn–Sham molecular orbital theory together with the energy decomposition analysis^[5], reveal that donor-acceptor interactions between the halogenated ligand and the protein need to be considered more carefully within the drug design process.

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Dispersion controlled docking preference: analyzing isolated dibenzofuran–solvent complexes with IR/UV spectroscopy

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The structural preferences within a series of dibenzofuran–solvent complexes has been investigated by electronic, vibrational and rotational spectroscopic methods within supersonic jet experiments. The experimental study is accompanied with a detailed theoretical analysis including dispersion corrected density functional theory, symmetry adapted perturbation theory as well as coupled cluster approaches.

The complementary, multi-spectroscopic results of microwave, FTIR and by combined IR/UV spectroscopy reveal a preferred OH $\cdots$ O structure for dibenzofuran–water as the smallest complex, whereas for the methanol complex two coexisting OH $\cdots$ O and OH $\cdots$ π isomers are revealed. Furthermore, for dibenzofuran–*tert*-butanol as the largest complex within this study, only a π -bound structure is observed. This trend is complementary to the trends observed in case of diphenyl ether–solvent complexes ^[1]. This is partly a function of the rigidity of the ether molecule. A general trend regarding the binding preference is deduced, which is driven by the interplay of London dispersion and hydrogen-bonding interactions.

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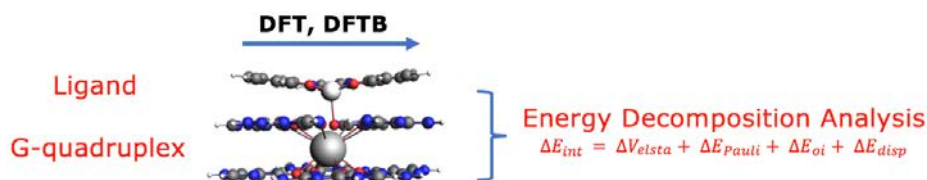


Computationally aided rational design of G4-ligands

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G-quadruplex DNA is a specific folding of guanine-rich nucleic acid sequences which has been considered as an attractive target for anticancer drug design.¹ The G-quadruplex structure is built up from G-quartets which are planar motifs generated from four guanine residues pairing together through Hoogsteen type hydrogen bonds. The formation of the G-quadruplex structure in the promotor regions of numerous genes can down-regulate transcription and suppresses oncogene expression.

These important biological implications have led to a new field devoted to the design of G4-ligands to selectively interact and stabilize the G-quadruplex folding.² Especially molecular dynamics (MD) simulations, in conjunction with automated docking, are preferred methods to study the dynamic G-quadruplex/G4-ligand interactions.³ However, such classical mechanic methods are not suitable to fully unravel and quantify these interactions.

In order to truly understand the physical principles behind the interactions between G-quadruplex DNA and G4-ligands we switched to a semi-empirical method: the density-functional theory-based tight-binding (DFTB) method in addition to density functional theory (DFT).⁴ With the use of these methods we aim for a better understanding of the interactions which can eventually contribute to more rational design of G4-ligands that efficiently stabilize G-quadruplex DNA.

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Benchmarking quantum chemistry with O-H-stretching vibrations in carboxylic acids

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The ability of quantum chemical methods to describe isolated molecules and clusters can be tested very sensitively for weakly bound systems and accidental degeneracies. The IR or Raman spectrum of the OH stretching fundamental provides a suitable experimental handle. This is explored in the present work for gas phase complexes of formic and acetic acid with molecular nitrogen and oxygen and for the nearly degenerate alcoholic and carboxylic O-H stretching vibrations in glycolic acid. The latter have remained unresolved in matrix isolation^[1] and gas phase^[2] infrared investigations and the former have not been investigated at all until recently^[3].

FTIR spectra in a pulsed supersonic expansion of a mixture of formic acid or acetic acid with nitrogen^[3] or oxygen now allow to benchmark the ability of harmonic and anharmonic treatments of the OH stretching mode for a range of electronic structure approximations to describe the experimental finding. It is found that for the N₂ complex, most methods significantly overestimate the hydrogen bond-induced shift and those which perform better often fail in correctly predicting the monomer OH stretching mode.

The accidentally degenerate O-H-stretching dynamics of glycolic acid offers an opportunity to benchmark not only the ability to accurately predict fundamental frequencies for oscillators of different rigidity in different bonding constellations, but also their relative spectral intensities. This requires a spectral separation by rotational cooling, which we achieve in a supersonic jet Raman experiment.

The most stable conformer of glycolic acid reveals two closely spaced O-H-stretching bands, which are compared to a range of harmonic and anharmonic predictions and to a recent prediction based on chemical homology^[4].

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Competition between σ - and π -holes in hexacoordinated complexes between TF_4 (T=Si, Ge, Sn, Pb) and NCH stabilized by tetrel bonds

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The insight into origin of tetrel bonds has been provided in our theoretical study (MP2 and DFT levels of theory) where a set of tetrahedral TF_4 molecules (T=Si, Ge, Sn, Pb) in trimers with two NCH bases were modelled and thoroughly described^[1]. It has been shown that TF_4 molecule significantly distorts from its starting geometry to accommodate to the approaching Lewis base. Therefore, two possible patterns of complexation were analyzed. First – through the two equivalent σ -holes (conformer *cis*) and second, through the two equivalent π -holes (conformer *trans*, see Figure 1). Although *trans* complexes were characterized by higher interaction energies, the *cis* complexes were more stable in terms of binding energies. The difference between these two energetic parameters was a consequence of the deformation of the Lewis acid molecule. The square planar geometry of TF_4 in *trans* dimers offers an unobstructed path of the bases to the π -holes of tetrel atom what causes higher interaction energy of *trans* arrangement than the *cis* one. This situation is reversed when we include deformation energies and calculate the total binding energies of systems studied. This advantage of *cis* structures is greatest for T=Si and diminishes in line with tetrel atom size growth.

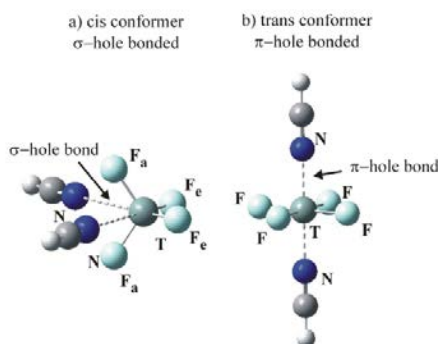


Figure 1 | Optimized structures of a) *cis* and b) *trans* conformers of TF_4 complexes with HCN.

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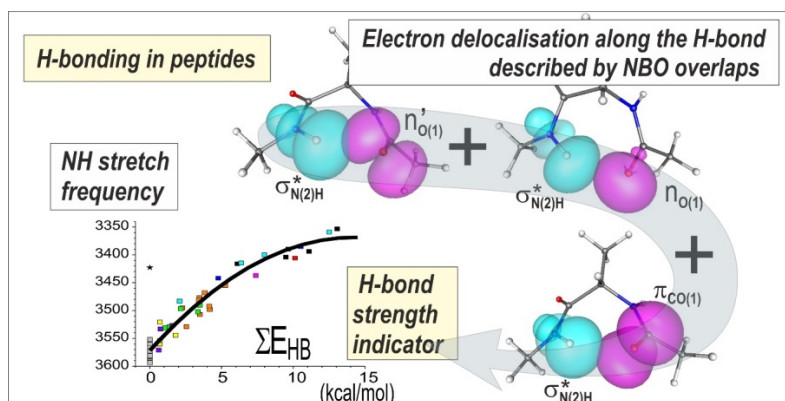
Rationalizing the diversity of amide-amide H-bonding in peptides using the Natural Bond Orbital method

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Natural Bond Orbital (NBO) analysis of electron delocalization in a series of capped isolated peptides is used to diagnose amide-amide H-bonding and backbone-induced hyperconjugative interactions, and to rationalize their spectral effects. The sum of the stabilization energies corresponding to the interactions between NBOs that are involved in H-bonding is demonstrated as an insightful indicator for the H-bond strength. It is then used to decouple the effects of the H-bond distance to that, intrinsic, of the donor/acceptor relative orientation, *i.e.*, the geometrical approach. The diversity of the approaches brought by the series of peptides studied enables us to illustrate the crucial importance of the approach when the acceptor is a carbonyl group. Remarkably, efficient approaches can be achieved despite not matching the usual picture of a proton donor directly facing a lone pair of the proton acceptor, *i.e.*, that encountered in intermolecular H-bonds. The study also illustrates the role of backbone flexibility, partly controlled by backbone-amide hyperconjugative interactions, in influencing the equilibrium structures, in particular by frustrating or enhancing the HB for a given geometrical approach. Finally, the presently used NBO-based HB strength indicator enables a fair prediction of the frequency of the proton donor amide NH stretching mode, although this simple picture is blurred by ubiquitous hyperconjugative effects between the backbone and amide groups, whose magnitude can be comparable to that the weakest H-bonds.





Modulation of HOMO–LUMO gap: broad applications

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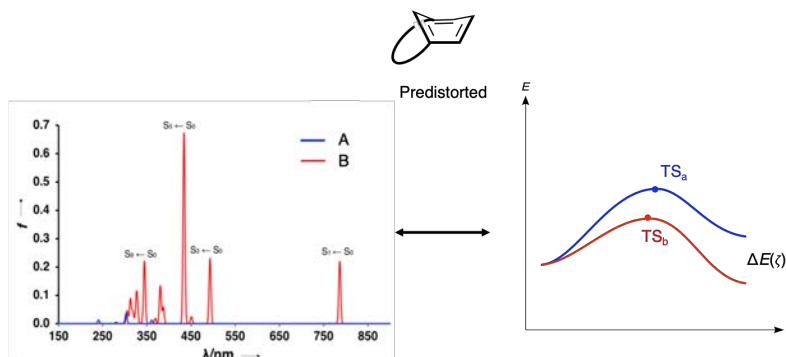
[d] Leiden Institute of Chemistry, Leiden University (The Netherlands)

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Strain in bent conjugated molecules can significantly alter the electronic structure, which, as a result, leads to changes in their optoelectronic properties and reactivity as well. Hereby, we aim to rationally understand and leverage the use of strain to tune the light-harvesting properties of organic dye molecules. We perform our analyses on model bent systems. The understanding gained is applied to more complex molecules. Quantitative Kohn-Sham molecular orbital analysis^[1] is used to study and manipulate the influence of structural distortions on the HOMO–LUMO gap while Time-Dependent DFT is used to obtain more accurate values for the corresponding excitation energies (see Figure 1). The insights obtained from spectroscopic calculations are applied to tune the Diels-Alder cycloaddition reactivity of aromatic molecules.^[2]



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- [2] A. K. Narsaria, T. A. Hamlin, K. Lammertsma, F. M. Bickelhaupt, *Chem. Eur. J.* **2019**, *25*, 9902.



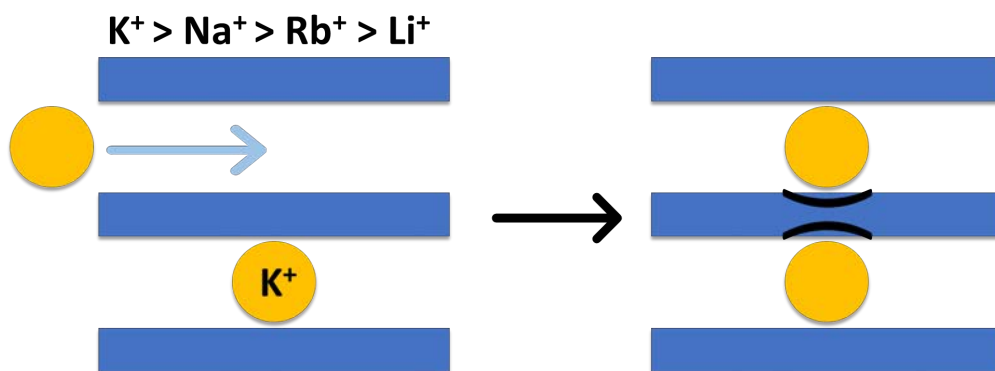
The role of alkali metal cations in the stabilization of multi-layer guanine quadruplex DNA

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To gain better understanding of the stabilizing non-covalent interactions between metal ions and DNA, dispersion-corrected density functional theory (DFT-D) based calculations were performed on triple-layer guanine quadruplexes interacting with alkali metal cations. All computations were performed in aqueous solution that mimics artificial supramolecular conditions where guanine bases assemble into stacked quartets as well as biological environments in which telomeric quadruplexes are formed.^[1]

Analysis of the stabilizing interactions between alkali cations and the DNA base pairs in triple-layer guanine quadruplex DNA reproduced the experimental affinity trend of the order $\text{Li}^+ < \text{Rb}^+ < \text{Na}^+ < \text{K}^+$. The desolvation and the size of alkali metal cations are thought to be responsible for the order of affinity. However, the magnitude of the bond energy shows to decrease for binding of a second cation, compared to the first binding event as was found by DFT-D calculations on double-layer quadruplexes.^[2] This diminished bond energy shows to be the result of the destabilizing electrostatic repulsion between the two hosted alkali metal cations.



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Benchmarking quantum chemical methods with spectroscopic data of weakly bound complexes

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Guidance for quantum chemical methods should originate from a multitude of experiments, because involved approximations have different implications for different experimental observables. For large molecular systems highly accurate theoretical reference data are typically not available, therefore the popular benchmarking against more rigorous theoretical calculations is often not sufficient. Experimental benchmark data sets offer an alternative.^[1] To be practical, they have to make educated selections in the chemical space and in the space of observables. To illustrate strategies and limitations of experimental benchmarking, we pick a relatively small subspace of compounds and observables. Specifically, we focus on three well-studied strong hydrogen bond donors (formic acid,^[2] acetic acid^[2] and hexafluoroisopropanol^[3,4]) and on their hydrogen-bonded dimers and trimers as well as complexes with very weak hydrogen bond acceptors (dinitrogen and dioxygen^[5]). We thus span the weakest and the strongest among the regular hydrogen bonds. In terms of observables, we concentrate on rotational constants for structure, on OH fundamental frequencies for dynamics, and on conformational preferences for the energetics. The intention is to make electronic structure and harmonically estimated dynamics calculations directly comparable to experiment, such that a large number of quantum chemical methods can be tested.

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Proton dynamics in symmetric and asymmetric “proton sponges” in light of the Car-Parrinello molecular dynamics approach

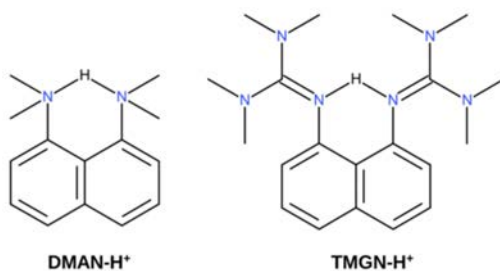
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Proton sponges, derivatives of prototypic 1,8-bis(dimethylamino)naphthalene^[1,2] exhibit remarkable basicity caused by steric strain. Details of proton dynamics in these compounds can be efficiently studied computationally with the use of Car-Parrinello Molecular Dynamics (CPMD) approach^[3]. This study reports analysis of proton dynamics for the protonated DMAN, its nitro and amino derivatives, as well as 1,8-bis(tetramethylguanidino)naphthalene^[4] (TMGN). Particular attention is paid to the effects of symmetry of the molecular skeleton and the type of substituent on the proton residency statistics and dynamics. Vibrational signatures, obtained from the power spectra of atomic velocity, are also presented. In particular, proton migration events in TMGN-H⁺ are less numerous than in the DMAN-H⁺, which can be rationalized by noticing the slower dynamics of large substituents at positions 1 and 8 of TMGN with respect to the smaller –N(Me)₂ groups of DMAN.

The Authors express their gratitude to the National Science Centre (Poland) for supporting this work under the grant no. UMO-2015/17/B/ST4/03568.



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Selective ion recognition by melamine and ammeline sextuplexes

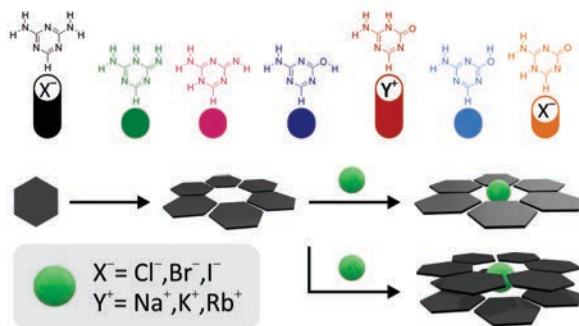
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Ion recognition is still an emerging topic in supramolecular chemistry and has aroused a great attention in the last years.^[1] In a previous work,^[2] we have found that ammeline has better self-assembling capabilities than melamine when they form six membered rosettes. In this work, we have examined the assemblies of selected hexameric rosettes of melamine and ammeline tautomeric forms, and their capacities to host halide and alkali ions in the gas phase and in water. By using relativistic dispersion-corrected density functional theory (DFT-D), we first studied the stability and the effect of introducing monovalent anions (Cl^- , Br^- , I^-) and cations (Na^+ , K^+ , Rb^+) in the center of the rosettes cavity. Finally, we explored the interactions in two stacked rosettes with an interlayer ion. Our computations reveal that amine-substituted triazines are promising candidates for anion and cation recognition either in self-assembled monolayers or pillar arrays structures. In addition, melamine and ammeline could constitute a potent mixture for dual ion recognition strategies.



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Conformational analysis of butanol and its complexes with water in low temperatures

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Butanol occurs in five isomeric forms, though the term is usually used for the straight chain primary alcohol 1-butanol. The molecule has been analyzed before but its complexes with water and their possible structure is still a question worthy of discussion^[1]. Here this system has been studied in low temperature argon and nitrogen matrices.

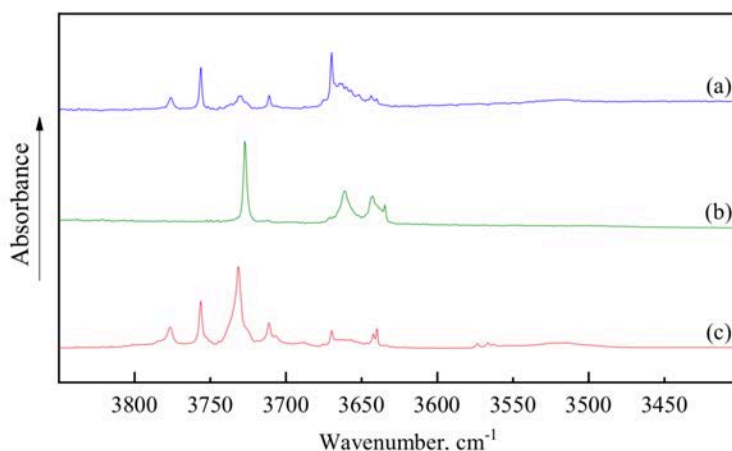


Figure 1 | IR absorption spectra of 1-butanol in (a) argon, (b) nitrogen and (c) 1-butanol and water in argon matrix.

The region of 3680-3630 cm^{-1} corresponding to butanol OH stretching vibration in spectra of butanol in argon and nitrogen (fig. 1 a, b) exhibits enough differences to conclude that the more interactive nitrogen matrix might stabilize different conformers than the argon environment. Upon addition of water, new bands appear in both argon (fig. 1 c) and nitrogen matrix spectra. They can be assigned to stretching vibrations of both water and butanol OH groups that participate in the formation of intermolecular hydrogen bond. It can be confirmed that butanol and water molecular complexes form in both matrices. DFT calculations were also performed in order to evaluate the energies and vibrational spectra of the conformers and the butanol-water complexes.

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The *gauche* effect in 2-fluorocyclohexanone analogs

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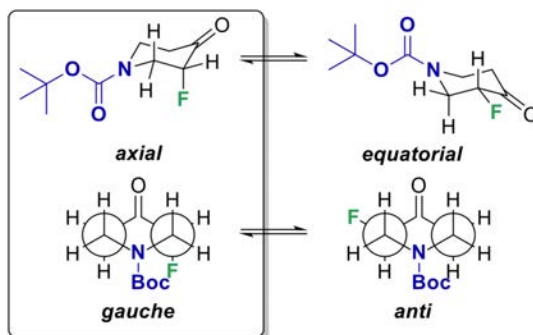
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The *gauche* effect is observed in structures containing two electron withdrawing groups in a 1,2-disubstituted ethane fragment (i.e. X–C–C–Y), which preferentially adopt the more sterically hindered *gauche* orientation ($\phi_{\text{X-C-C-Y}} \approx 600$) instead of the *anti* orientation ($\phi_{\text{X-C-C-Y}} \approx 1800$). Structural modifications focusing on inducing the *gauche* effect has recently been exploited in the design of fluorinated organic compounds with specific molecular properties.^[1] Herein, we have investigated whether such effect could also be observed in the backbone of 2-fluorocyclohexanone by the introduction of an endocyclic group (the *N*-Boc group, see scheme below) using a combined approach of nuclear magnetic resonance and density functional theory calculations. The 2-fluorocyclohexanone has a well-defined conformational equilibrium in which the axial conformer is dominant only in the gas phase. It is rather envisaged that the orbital interactions used to rationalize the *gauche* effect^[2] would further stabilize the axial fluorine conformer due to the *gauche* arrangement with the endocyclic *N*-Boc group, even in solution.



The support of the CAPES, CNPq and FAPEMIG agencies is gratefully acknowledged.

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**The FTIR spectrum of methoxyflurane and
methoxyflurane/dimethyl ether mixtures in cryosolutions.
Conformational analysis and evidence of H bonded complex
formation**

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Methoxyflurane ($\text{CHCl}_2\text{CF}_2\text{OCH}_3$), i.e. 2,2-dichloro-1,1-difluoro-1-methoxyethane according to IUPAC name, is a powerful anesthetic and analgesic agent, presently used as analgesic predominantly. In this report, IR spectra of methoxyflurane and methoxyflurane/dimethyl ether ($(\text{CD}_3)_2\text{O}$) mixtures are studied with the help of FTIR cryospectroscopy and ab initio calculations. The spectra are measured in liquefied Kr at $T \sim 140 - 160$ K and in liquefied Xe at $T \sim 165 - 195$ K. The most characteristic changes of the IR spectrum are observed in $\sim 3100 \div 2800$ cm^{-1} region, where stretch CH and CH_3 group vibrations of methoxyflurane are registered. A new band situated at low wave number side of CH stretch is detected in mixtures with $(\text{CD}_3)_2\text{O}$. Temperature behavior of this band suggests complex formation stabilized by weak H bond. Enthalpy of formation is estimated in series of temperature measurements of the spectra. DFT calculations with wb97xd functional and a set of Pople-type basis sets are performed to find the most stable conformers, geometric and spectroscopic parameters of the systems studied. The most stable heterodimer corresponds to the structure stabilized by C-H...O contact of H-bond-type predominantly. Weaker contacts stabilize additionally the methoxyflurane/dimethyl ether system. The calculated spectroscopic and energetic parameters are in reasonable agreement with those found experimentally.



An extension of the charge and energy decomposition scheme (ETS-NOCV) – On the importance of kinetic and potential energy contributions in chemical bonding

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A chemical bond being "...of the fundamental territories of chemistry..." [1] is not an observable quantity in a quantum mechanical sense; accordingly, several quantum methods and models [1], which are suitable for descriptions of chemical bonds exist. Although these approaches apply various criteria leading to the division of electron density into atoms and bonds, [2] unarguably the two fundamental quantities used in quantum chemistry and often discussed in the context of chemical bonding are the kinetic and potential energy terms.

Accordingly, in this work we have further extended our charge and energy decomposition scheme ETS-NOCV [3] by decomposition of the orbital interaction energy term (associated with electron density reorganization due to formation of a chemical bond) into kinetic and potential energy contributions. It provides for the first time direct relation between the NOCV-based deformation density components $\Delta\rho_i$ (e.g. σ , π , etc.) and the corresponding changes in kinetic and potential energy terms ΔT_i and ΔV_i .

It has been found [4] that interfragment dative and covalent-type electron charge reorganizations upon formation of a series of strong and weak bonds employing main-group elements are due to lowering of the negative kinetic energy contributions, as opposed to the intrafragment polarizations (e.g., hyperconjugations in ethane), which are, in contrary, driven by the potential energy (electrostatic) component. Moreover, a ligand to metal donation and metal $\rightarrow$ ligand back-donation known universally from a Dewar-Chatt-Duncanson model, have been found to be driven by the opposite $\Delta T_i/\Delta V_i$ mechanisms. Hydrogen and dihydrogen bonds, as well as other types of con-covalent interactions have been also characterized in terms of $\Delta T_i/\Delta V_i$.

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Multifaceted interactions of pyrrole

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Hydrogen bonding plays a significant role in the structural stabilization of different conformers, protein folding, cross-links in polymers and crystal packing.

Pyrrole (C_4H_5N), a simple heterocyclic molecule is of immense importance in chemistry and biochemistry due to its presence as a building block in several biomolecules like, chlorophyll, haemoglobin, and other protein moieties. Pyrrole acts as a proton donor and acceptor due to the acidic N-H bond and the electron rich π -cloud on the aromatic ring, respectively. Although pyrrole is an appropriate candidate to model biomolecular interactions, yet the studies on weak interaction of C_4H_5N are limited in the literature. Hence, some of the important types of hydrogen bonding such as $N-H\cdots\pi$, $N-H\cdots O$, and $N-H\cdots N$ interactions of C_4H_5N molecule are explored using matrix isolation infrared technique and *ab initio* computations. The $N-H\cdots\pi$ interaction is studied in C_4H_5N dimers (PD_a/PD_d) and C_4H_5N -acetylene ($PA-A/B$), C_4H_5N -ethylene ($PE-A/B/C$) and C_4H_5N -benzene (PB) Heterodimers. The $N-H\cdots O$ interaction is probed in pyrrole-water ($PW-A$), C_4H_5N -methanol ($PM-A$), C_4H_5N -phenol ($PP-A/B/C$) and C_4H_5N -diethyl ether ($py-DEE-tt/tg$) systems and the $N-H\cdots N$ interaction is explored in C_4H_5N -ammonia ($PAM-A$), C_4H_5N -pyridine ($PPY-A$) and C_4H_5N -quinoline ($PQ-A$) dimeric systems. Interestingly, the $\pi\cdots\pi^*$, $C-H\cdots\pi$ and $O-H\cdots\pi$ interactions were also observed to compete along with $N-H\cdots\pi$ and $N-H\cdots O$ hydrogen bonding interactions. These multifaceted interactions of C_4H_5N can be used as a model in biomolecules and organic crystal frameworks.

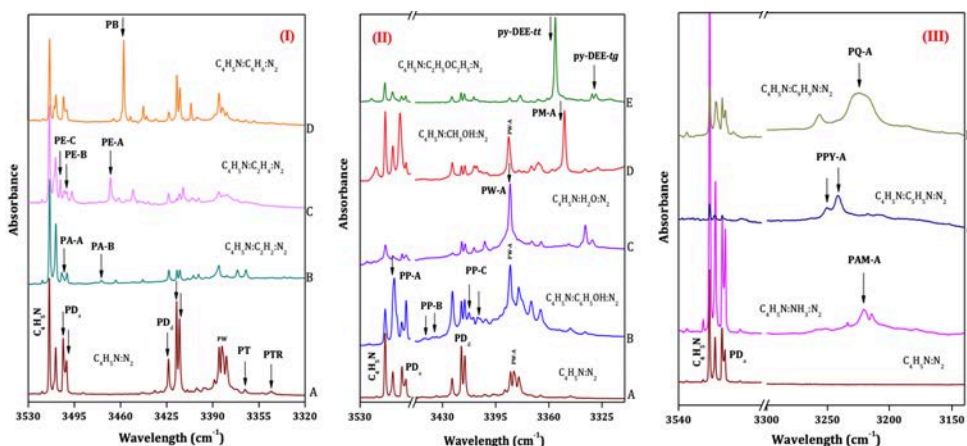


Figure illustrates the matrix isolated infrared spectra of N-H stretching region of C_4H_5N in N_2 matrix. Trace A in Grid I, II and III shows C_4H_5N alone spectra. (I) C_4H_5N with (B) C_2H_2 , (C) C_2H_4 (D) C_6H_6 ; (II) C_4H_5N with (B) C_6H_5OH , (C) H_2O , (D) CH_3OH and (E) $C_2H_5OC_2H_5$; (III) C_4H_5N with (B) NH_3 , (C) C_5H_5N and (D) C_9H_7N . All the Spectra shown here were annealed at 30 K.

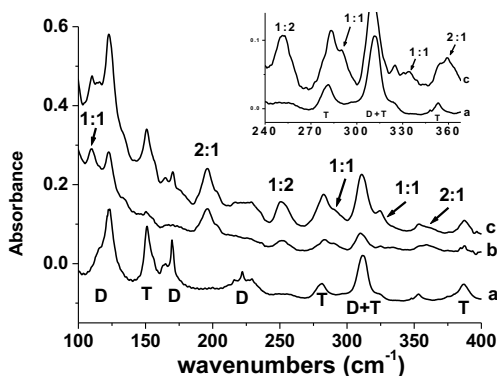


First vibrational study in neon matrix of $(\text{H}_2\text{S})_{1-2}$ - $(\text{H}_2\text{O})_{1-2}$ complexes from the far to the near infrared spectral region: identification of HOH-SH₂ and HSH-OH₂ isomers.

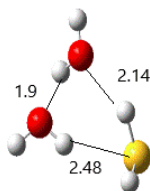
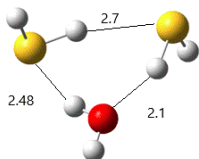
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For the first time the investigation of water molecules complexed with sulfur dihydrogen in solid neon using FTIR spectroscopy was performed from 80 to 4000 cm^{-1} . In a first step we have identified the ν_1 and ν_3 frequencies of the proton donor in the H_2S dimer. From concentration effects and help of theoretical results we have highlighted the presence of the two most stable 1:1 isomers, HOH-SH₂ where H_2O is proton donor and HSH-OH₂ where H_2S is proton donor. We have also identified several transitions for H_2S - $(\text{H}_2\text{O})_2$ (1:2) and $(\text{H}_2\text{S})_2$ - H_2O (2:1) complexes and proposed structures for these two complexes.



Spectra in the 100-400 cm^{-1} region at 3 K deposition with $\text{H}_2\text{S}/\text{H}_2\text{O}/\text{Ne}$ concentration (a) 0/2/1000, (b) 6/0.5/1000, (c) 6/2/1000. D and T are for H_2O dimer and trimer.



Geometries of the most stable form of 2:1 and 1:2 at the MP2 level. The distances are in Å.



Poster 40

Teaching Fe to behave like Pd in catalytic bond activation based on the activation strain model

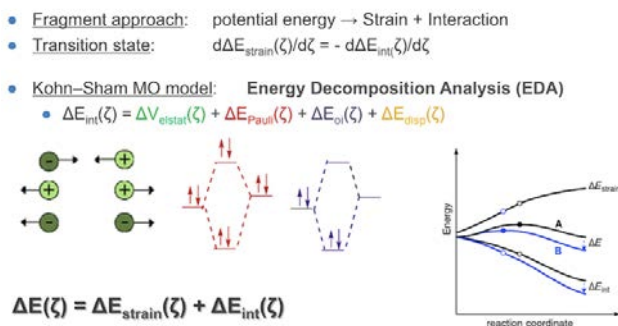
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A systematic approach for first-principle catalyst design is presented in which potential energy surface is obtained, followed by the activation strain analysis to study the steric and electronic effect separately and determine which is the key factor to influence the energy barrier.^[1,2] Based on these insights, we tried to develop a new type of iron-based catalysts that mimic the behavior of palladium catalysts in cross-coupling reactions. Firstly, we have investigated the activity of the model catalyst complexes $\text{Fe}(\text{CO})_4$ toward CH_3X (with $\text{X} = \text{H}, \text{Cl}, \text{CH}_3$) C-X oxidative addition, including different charges and spin states. Secondly, such different reactivity between $\text{Fe}(\text{CO})_4$ and Pd in activating these model reactions are compared and reasons can be explained by electronic-structure and activation strain analysis. Finally, by applying the aforementioned approach the behavior of palladium can be mimic by iron complex. Our long-term purpose is to find ways to replace palladium for bond activation and cross-coupling reactions.

Activation Strain Model (ASM)



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Matrix isolation IR spectra of 1:1 hydrogen-bonded complexes of [H,C,N] and [H,C,N,O]

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1,2,5- and 1,3,4-oxadiazoles were photolyzed at 213, 220 and 235 nm in solid argon at 12 K. The products were investigated by IR spectroscopy. In order to distinguish between different complexes, annealing experiments and selective NIR excitations of the NH and CH stretching overtones were performed. The spectrum analysis and the identification of the structures were aided by quantum chemical computations. Among the primary photolysis products HCN·HNCO and HCN·HCNO complexes could be identified. Secondary photolysis by a H-lamp (121.6 nm) resulted in new complexes, possessing HNC monomers.

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- 107



The advantages of the neon matrix to the vibrational study of van der Waals and hydrogen bonded molecular complexes

B. Tremblay, P. Soulard

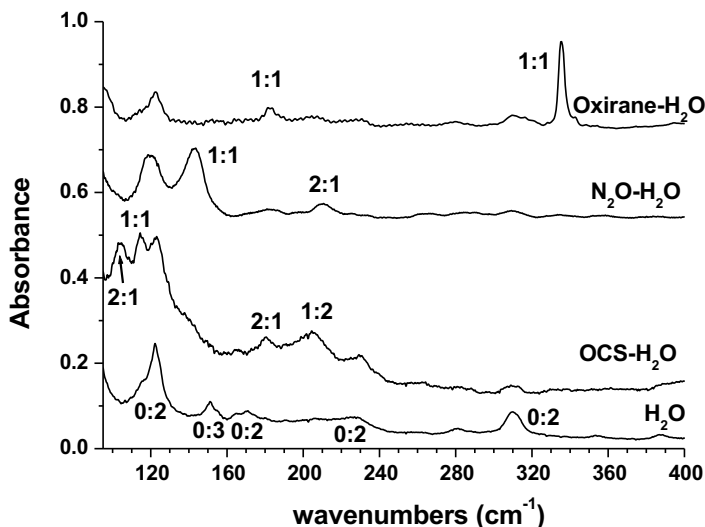
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Studies of weakly bonded complexes formed between water and atmospheric molecules can give important information on molecular interactions in atmospheric chemistry. Van der Waals and hydrogen bonded molecular complexes have motivated both theoretical and experimental studies.

In the absence of gas phase data, essentially in the near and far infrared, matrix isolation can bring pertinent information on several-quanta transitions or weak fundamentals. Also, the use of a more inert matrix, neon, causes less perturbation than N_2 or Ar on the frequencies shifts.

The purpose of this communication is to illustrate the advantages of the matrix isolation with neon to study the van der Waals and hydrogen bonded molecular complexes. Some examples are done with $L_n-(H_2O)_m$ complexes, noted $n:m$, with $L = N_2O$, OCS, diacetyl, CO_2 , oxirane, and H_2O .



Far-infrared spectrum of $n:m$ complexes in neon matrix



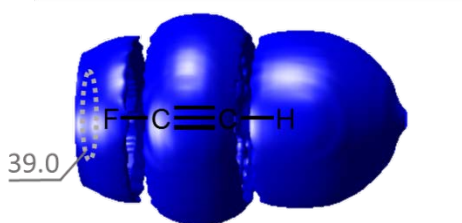
Outer electronic shell visualization by the Laplacian of helium chemical shift

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In the toolbox of a modern quantum chemist there are a few methods of outer electronic shells visualization, among them are constructing and analysis of maps of molecular electrostatic potential (MESP),^[1] and electron localization function (ELF).^[2] We propose a different visualization method which can be briefly described as follows: the space around a studied species is probed by ³He atom, and in each point helium chemical shift is calculated. It has previously been shown, that for fluorine-containing molecules^[3,4] Laplacian of ³He chemical shift is sensitive to such features of electronic shells as lone pairs. Proposed approach has significant advances compared with standard quantum mechanical approaches – Laplacian of helium chemical shift preserves its sensitivity to lone pair regions at significantly larger distances (>1.5–2 Å), and its maximal values could be used to quantitatively estimate the electron-rich character of lone pairs. In this work, we extend a set of studied objects to the “classical” molecules with localized lone pairs – NH₃, H₂C=NH, HCN, H₂O, H₂C=O, H₃P, H₂S etc.



3D isosurface of Laplacian of ³He chemical shift $V^2\delta_{\text{He}}$ near fluoroacetylene ($V^2\delta_{\text{He}} = 8 \text{ ppm}/\text{\AA}^2$). Dashed line indicates maximum values of $V^2\delta_{\text{He}}$.

Acknowledgements: This work is supported by Russian Foundation for Basic Research (RFBR) grant № 17-03-00497.

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Cooperative self-assembly in linear chains based on halogen bonds

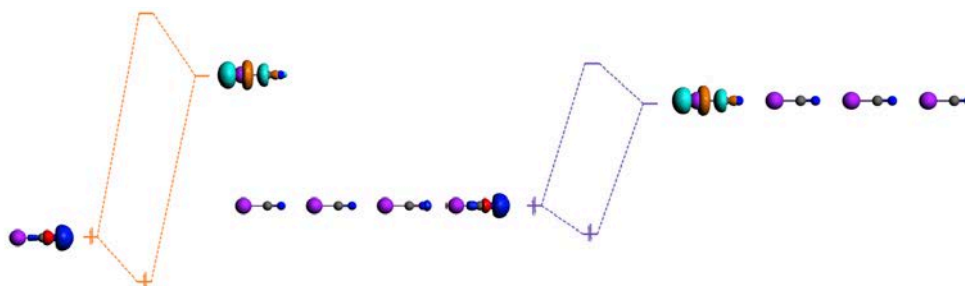
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Computational experiments based on dispersion-corrected density functional theory were carried out on linear chains of two till twelve units of cyanogen halide (X-CN), halocyanoacetylene (X-CC-CN) or 4-halobenzonitrile (X-C₆H₄-CN) to examine the cooperative properties of halogen bonds for X = F, Cl, Br, I.^[1] Energy decomposition analysis, together with Kohn-Sham molecular orbital theory and the Voronoi Deformation Density charge analysis were applied to capture the bonding mechanism of the investigated systems.^[2,3] Cyanogen halide and halocyanoacetylene linear chains possess an extra stabilization with increasing size of the chain, whereas the 4-halobenzonitrile chains do not. This cooperativity can be traced back to charge transfer within the σ electronic system between the lone-pair orbital of the nitrogen (σ_{HOMO}) on one unit and the acceptor orbital of the C-X (σ^*_{LUMO}) on the adjacent unit. The amount of cooperativity is determined by the difference in energy between the donating and accepting orbitals of the two interacting moieties.

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A novel on-the-fly hybrid QM:MM Model to predict solvent Effects in IR and VCD spectra

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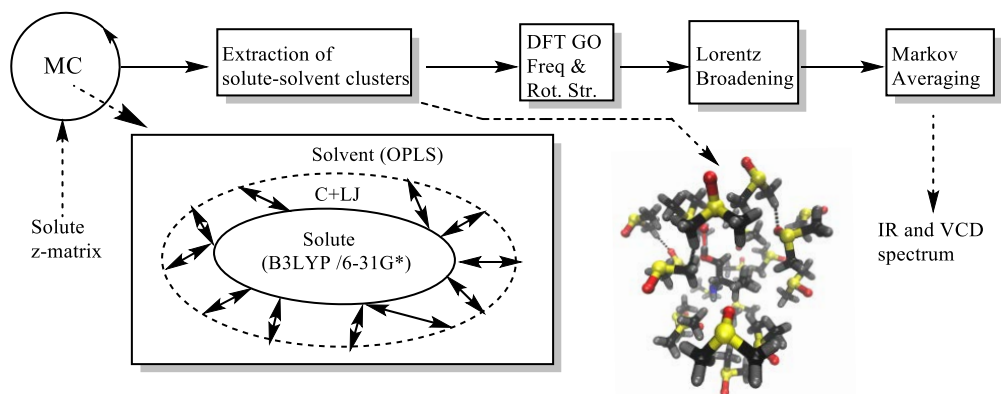
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VCD spectroscopy has proven to be a powerful method for the determination of the absolute configuration of various natural products and pharmaceutical ingredients. Differentiating between two enantiomers is rather easy, as their VCD spectra are mirror images. However, in order to identify which spectrum belongs to which enantiomer, a reliable quantum chemical prediction of these spectra is paramount. ^[1] This becomes challenging for flexible molecules that strongly interact with the solvent, as the influence of the solvent can be difficult to accurately include in these predictions. ^[2] To date, it is estimated that still in 1 out of 5 cases the absolute configuration could not be identified due to lack of a correct solvent representation within the standard VCD models and workflows.

For this reason, we have started developing a new explicit solvent model which employs a QM:MM (DFT:MM) Metropolis Monte Carlo simulation to sample large explicit solute-solvent clusters, from which VCD spectra are calculated at DFT level using a frozen cage approach.



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Vibrational transitions in hydrogen bound complexes

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Vibrational calculations form the basis for understanding hydrogen bonds (XH...Y) in the gas phase. We calculate vibrational transition frequencies and intensities of XH-stretching vibrations in hydrogen bound bimolecular complexes and their associated monomers.^[1] For monomers, XH-stretching vibrations are accurately modelled with reduced dimensionality local mode theory. For example, for alcohols we find that including the O-H, C-O and C-O-H oscillator (and the coupling between these) is sufficient to reproduce transition frequencies of the OH-oscillator to within 5 cm⁻¹ and intensities to within 10% (see figure).^[2]

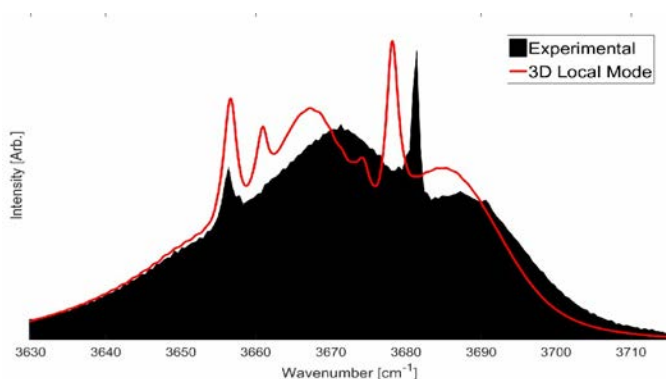


Figure: Calculated and experimental band profiles for the $\Delta\nu_{\text{OH}}=1$ region of 1-ProH. Five distinct conformers contribute to the observed band profile.

The benefit of local mode theory, compared with the conventional used normal mode models, is the reduced computational cost inherent from the reduced dimensional models. When a bimolecular complex is formed, six new low-frequency intermolecular vibrations arise, due to the collective loss of three rotational and three translational degrees of freedom for the monomers. An accurate description of the XH-stretching vibration directly involved in the hydrogen bond is challenging due to effects of these low-frequency intermolecular modes.^[3] Including these in our LM model significantly improves agreement with observed spectra of bimolecular complexes.

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Factors controlling the Diels–Alder reactivity of hetero-1,3-butadienes

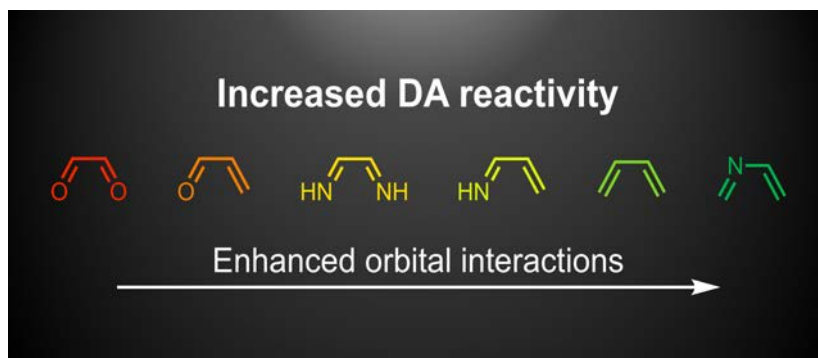
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We have quantum chemically explored the Diels–Alder reactivities of a systematic series of hetero-1,3-butadienes with ethylene by using density functional theory at the BP86/TZ2P level.^[1,2] Activation strain analyses provided physical insight into the factors controlling the relative cycloaddition reactivity of aza- and oxa-1,3-butadienes.^[3] We find that dienes with a terminal heteroatom, such as 2-propen-1-imine (**NCCC**) or acrolein (**OCCC**), are less reactive than the archetypal 1,3-butadiene (**CCCC**), primarily owing to weaker orbital interactions between the more electronegative heteroatoms with ethylene. Thus, the addition of a second heteroatom at the other terminal position (**NCCN** and **OCOC**) further reduces the reactivity. However, the introduction of a nitrogen atom in the backbone (**CNCC**) leads to enhanced reactivity, owing to less Pauli repulsion resulting from polarization of the diene HOMO in **CNCC** towards the nitrogen atom and away from the terminal carbon atom. The Diels–Alder reactions of ethenyldiazene (**NNCC**) and 1,3-diaza-butadiene (**NCNC**), which contain heteroatoms at both the terminal and backbone positions, are more reactive due to less activation strain compared to **CCCC**.



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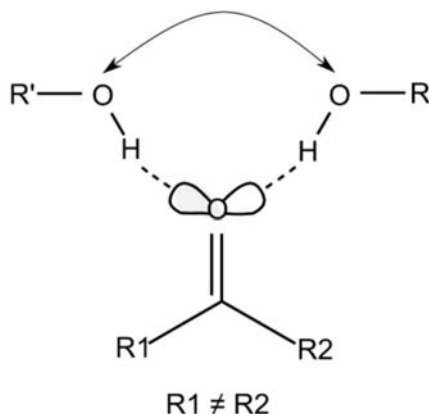


Influencing the hydrogen bond competition in ketone alcohol complexes via alkylation

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Intermolecular docking between alcohols and asymmetrically substituted ketones such as acetophenone derivatives or pinacolone occurs via an $\text{OH}\cdots\text{O}$ contact with the free electron pairs of the carbonyl oxygen, generating two competing isomers. By probing a supersonic jet expansion with FTIR spectroscopy, the abundance ratio of the two isomers at low temperature is determined. This allows for the experimental benchmarking of theoretically predicted relative conformational energies on a kJ mol^{-1} scale^[1,2]. Previously presented anisole^[3,4] and furan^[5] complexes, where the docking of an alcohol takes place via an $\text{OH}\cdots\text{O}$ or $\text{OH}\cdots\pi$ contact with an oxygen atom or an aromatic π -cloud as the competing sites for the alcohol interaction, showed a systematic favoring of one docking site by ZPVE (zero-point vibrational energy). This non-electronic correction is minimized in the ketone systems due to the more comparable docking environments, which therefore allows for a more direct benchmark of different electronic structure methods with less need for an accurate vibrational treatment beyond the double harmonic approximation. The interplay of London dispersion interactions, steric hindrances and their respective influence on the favored hydrogen bonding site is explored by varying the ketone and alcohol alkylation.



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