

WORKSHOP REPORT FROM THE TASK GROUP ON HYDROGEN BONDING AND OTHER MOLECULAR INTERACTIONS

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INTRODUCTION

IUPAC formed a task group towards the end of 2004 with the following objectives: 1) To take a comprehensive look at intermolecular interactions and classify them and 2) to give a modern definition of the hydrogen bond, taking in to account all current experimental and theoretical information, and including hydrogen bonded systems both in gaseous and condensed phases as well as in chemical and biological systems. The details of the project and task group are available in the IUPAC website (www.iupac.org/project/2004/2004-026-2-100.html). The task group was given a period of two years to come up with a recommendation. The task group held a Workshop on 'Hydrogen bonding and other molecular interactions' in Pisa in September 2005. Eleven of the fourteen task group members participated in the workshop (Crabtree and Kleinermanns could not attend and Scheiner had to cancel the participation due to unavoidable reasons). The workshop was followed by a meeting of the task group. This report summarizes the presentations and deliberations during the workshop. An interim recommendation on classifying hydrogen bonding and other molecular interactions has been prepared as well.

WORKSHOP

Two members of the task group, Roger Klein and Benedetta Mennucci volunteered to organize a work shop in Pisa during September 5-9, 2005. All task group members were consulted before choosing the time and during this period 12 out of the 14 task group members could participate in the meeting. All task group members were requested to give a 30 minute presentation of their recent work in related areas and offer suggestions for an interim report. The meeting was advertised in Chemistry World and Chemistry International, IUPAC website and also in some newsgroups (Cluster Science). *The Journal of Applied Rheology* included an announcement as well. It was decided to have invited talks from some experts outside of the task group and also to allow some participants. In the end, the workshop had talks from 11 task group members and 11 invited speakers and 17 other participants. The complete list of participants has been enclosed. All the talks are available in the Workshop webpage hosted by Roger Klein (http://institut.physiochem.uni-bonn.de/IUPAC_Pisa2005/meeting).

DAY 1 - 6 Sep 2005

The workshop had three morning sessions focusing on hydrogen bond, spectroscopic techniques and application. Every evening, there was a group discussion

that included some brief presentations from other participants. Arunan gave the opening remarks on the background and introduction to the IUPAC project and the Workshop. He pointed out the diverse views in the description of hydrogen bonding and van der Waals interactions.

First session on hydrogen bonding had 30-minute presentations by Desiraju, Klein, Espinosa, Alkorta, Zottola, Sordo and Gilli. Desiraju presented a comprehensive overview from a crystallographer's point of view. He classified hydrogen bonds as weak, moderate and strong depending on the energetics. He also suggested using the term hydrogen bridge instead of hydrogen bonding. He suggested the following as a modern definition of hydrogen bridge "Under certain conditions an atom of hydrogen is attracted to two atoms instead of only one, so that it may be considered to be acting as a bridge between them" Klein talked about the co-operativity in hydrogen bonding and the usefulness of electron density topology in identifying hydrogen bonds. He pointed out that 1,2-diols do not have hydrogen bonding interaction as a bond critical point is not found between O and H. He suggested that cooperativity could be a defining and exclusive feature in hydrogen bonding.

The importance of bond critical points in the electron density topology was highlighted by Espinosa and Alkorta, as well. (Dannenberg and Sadlej expressed some reservations in relying exclusively on the theoretical electron density topology). Espinosa differentiated the 'shared shell (covalent)' interactions from the 'closed shell' interactions such as hydrogen bonding. Alkorta talked about chiral recognition in hydrogen bonded systems. Sordo discussed 'Symmetry Adapted Perturbation Theory' and identified four fundamental (physical) forces in chemistry as electrostatic, exchange, dispersion and induction. (Hobza pointed out that 'hydrogen bonding' is not one of the physical forces). Gilli ended the session with his talk on leitmotifs in hydrogen bonding. He also classified hydrogen bonds as strong, moderate and weak. He pointed out five leitmotifs in hydrogen bonding as follows: charge assisted hydrogen bonds, p and s bond polarization assisted hydrogen bonds, and resonance assisted or p bond cooperative hydrogen bonds. He pointed out 'modulability' as the most striking feature in hydrogen bonding as opposed to chemical bonds. Hydrogen bonds show a great variation in terms of distances and energetics.

On 6th evening, Barbara Kirchner, Mark Rosenberg and Chandra Verma gave brief presentations. Kirchner talked about molecular dynamics simulations. Rosenberg discussed the empirical correlations between frequency shift and intensity enhancement in hydrogen bonded systems. Verma talked about the entropy of H₂O trapped in a biological cavity. After these presentations, Sadlej chaired a discussion on the reliability of theoretical bond critical points as a decisive factor in identifying hydrogen bonds. There were diverse opinions on this issue.

DAY 2 - 7 Sep 2005

Capelletti started the second day's session on "Spectroscopy" with a discussion on glory scattering results from crossed beam experiments with rare gas (Rg) and

H₂O/O₂. The intermolecular potentials were derived from glory scattering and state of the art theoretical calculations. He concluded that the Rg-H₂O interaction attains 'hydrogen bonding' nature as the rare gas is changed from He to Xe. The Rg-H-O angle was shown to be near linearity for Xe. Arunan presented rotational spectroscopic results on H₂O and H₂S complexes and argued that structurally both are similar. He pointed out that even for the interaction between Ar and H₂S, the intermolecular potential is anisotropic. The barriers for internal rotation of H₂S about the axes that break the 'hydrogen bond' are about an order of magnitude larger than that for internal rotation about the axis that does not break the hydrogen bond. He introduced hydrogen bond radii for various donors and showed that they vary between the covalent and van der Waals radii of H atom. Hobza summarized the work on improper blue-shifting hydrogen bonds and covered the results from 1998-2005. He showed that the traditional view of red-shift in stretching frequency would not hold in some hydrogen bonded systems.

Kjaergaard presented the applications of overtone spectroscopy in hydrogen bonded complexes. He argued that the overtone spectroscopy is a sensitive probe of inter and intra-molecular interactions. He presented data from 3rd, 4th and 5th overtone spectra of ethylene glycol (ethane-1,2-diol) and pointed out the red-shift observed in all these overtones for the 'hydrogen bonded' OH group relative to the free OH group. Legon presented rotational spectroscopic studies on series of hydrogen and chlorine bonded complexes: B•••HCl and B•••ClF. He showed that the secondary interactions between the partially negative Cl and partially positive H in B, can make the hydrogen bond non-linear. This does not happen in halogen bonded complexes in a similar series of complexes as the other atom (F in this case) is relatively far away. His work highlights the importance of looking beyond 'linearity' in hydrogen bonds. Even in an isolated complex, secondary interactions could lead to detectable non-linearity. Results on ClF complexes clearly showed that chlorine bonding is quite analogous to hydrogen bonding.

Zottola presented some theoretical results on 'dihydrogen bonded' complexes. He concluded that dihydrogen bonds do not show cooperativity similar to hydrogen bonds and so could not be classified as hydrogen bonds. This was at variance with the detailed results presented by Sadlej on the same day. She showed that dihydrogen bonding exhibits very similar properties as traditional hydrogen bonding in terms of structure and energetics. According to her, strong and weak dihydrogen bonds resemble similar hydrogen bonds and very weak ones resemble van der Waals interactions. Her conclusion indicates that there is no fundamental difference between dihydrogen bonds and 'traditional' hydrogen bonds with lone pair or p acceptors.

Alonso presented more microwave results on hydrogen bonded complexes. His talk highlighted the conformational isomers in hydrogen bonding i.e. axial and equatorial hydrogen bonds in cyclic systems with non-equivalent lone pairs. He also presented experimental data on 'weak hydrogen bonds' with C-H•••O and C-H•••F interactions. Herrebout presented experimental data on blue-shifting hydrogen bonds and also showed that due to Fermi resonance there could be pseudo-blue shifting hydrogen bonds. The 'pseudo' label is used as the blue-shift is not due to bond shortening.

On 7th evening, there was a discussion session with short presentations by Müller-Dethlefs, Frey, and Tribello. Müller-Dethlefs talked about p-stacking vs hydrogen bonding in aromatic systems. He also pointed out that phenol-Ar could be classified as O-H...Ar hydrogen bonded complex. Frey continued the discussion on p-stacking vs hydrogen bonding. Tribello discussed packing energetics of ice and pointed out that all the potentials used for simulation of water are not appropriate for ice. Herrbeout gave an impromptu lecture on frequency shifts and showed that there need not be any correlation between bond length and frequency shift. Müller-Dethlefs led a discussion on the proceedings from that day. Klein started by asking if a hydrogen bond radius is needed. Müller-Dethlefs responded by answering that it could be useful. Arunan pointed out that the hydrogen bond radii would be more appropriate than using the van der Waals radii for excluding hydrogen bonds. There was some consensus on this latter point. Most of the members felt that there was no fundamental difference between red-shifting and blue-shifting hydrogen bonds.

DAY 3 - 8 Sep 2005

Clary started the session on 8th morning and presented his work on quantum simulation of biomolecules and clusters. He pointed out that it would be useful to consider hydrogen densities in weakly 'hydrogen bonded' complexes such as benzene-water dimer. He also discussed the tunneling path integral method for biomolecules. Dannenberg talked about the importance of cooperativity in hydrogen bonding interactions. However, he opined that cooperativity is not exclusive for hydrogen bonding interactions. He also pointed out that hydrogen bonding could have contributions from electrostatic, polarization and covalent forces. Mennucci discussed continuum solvation models for describing solvation. Nesbitt talked about hydrogen bond dynamics from simple to complex. He started the discussion with H₃O⁺ as the 'simplest hydrogen bond' and continued with the complex topic of RNA folding.

Caminati presented microwave and mmwave spectroscopic results on hydrogen bonded complexes. He suggested that dipole-dipole interactions may lead to an equilibrium structure in which 'H bonding' may not be present. He suggested a cutoff of 1 kcal mol⁻¹ stabilization energy for hydrogen bonded complexes. If the binding energy is less, the complex could be thought of having a 'hydrogen contact' rather than a bond. It is similar to the term hydrogen bridge Desiraju proposed on the first day and Huggins used in 1936. Rozas presented the final talk on hydrogen bonding and other interactions on biological systems. She described results from NBO and AIM calculations and pointed out the correlation between hydrogen bond distances and electron density parameters at the bond critical point.

The final session started with some recommendations by Legon which were presented by Arunan. It included a summary of the workshop as well, given by Rapporteurs chosen from participants other than task group members. Kitchner, Rickien and Zottola acted as the Rapporteurs. The Rapporteurs suggested using 'chemical' knowledge for defining a hydrogen bond as opposed to physical forces. They felt a

definition should include properties such as cooperativity. This was followed by a meeting of the task group members. The task group felt that the physical forces should be the governing principle in definitions and classifications of the various interactions. Arunan pointed out that the mandate from IUPAC was for classification based on physical forces. The Workshop ended with this meeting of the task group. It was decided to present the recommendations to the larger body of chemists for comments and suggestions.

List of registered participants at the IUPAC Workshop “Hydrogen Bonding and Other Molecular Interactions” Pisa 5-9 September 2005

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