Hydrogen bonding and other molecular interactions*  

The International Union of Pure and Applied Chemistry (IUPAC) formed a task group of fifteen international experts to categorize hydrogen bonding and other molecular interactions, co-chaired by E. Arunan (Indian Institute of Science (IISc), Bangalore, India) and S. Scheiner (Utah State University, USA). This followed the initiative by Arunan and appears to be the first IUPAC project initiated from India. The details about the project and task group members may be found in the IUPAC website: http://www.iupac.org/ projects/2004/2004-026-2-100.html. The objective of the task group is ‘To take a comprehensive look at intermolecular interactions and classify them, and to give a modern definition of the hydrogen bond, taking into 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’. A workshop was held in Pisa, Italy during 5–9 September 2005, in which 11 task group members and 11 other experts each gave a 30-minute presentation on their recent work relevant to the project. The details of this workshop are available in the website: http://institut.physio.chem.uni-bonn.de/IUPAC_Pisa2005/Workshop.html. R. A. Klein (University of Bonn, Germany) and B. Mennucci (University of Pisa, Italy) from the task group took care of the local organization and Klein and Arunan put together the programme. A report from the meeting was submitted to IUPAC earlier and is available at the IUPAC website: http://www.iupac.org/projects/2004/2004-026-2-100.html.

A core group consisting of Arunan, G. R. Desiraju (Hyderabad University), R. A. Klein and J. Sadlej (University of Warsaw, Poland) met in Bangalore on 17 and 18 September 2006 to finalize the recommendation. Co-chairman Scheiner was available through video-conferenc-
tive effects exceed Pauli exchange (steric) repulsion at the optimum geometry for hydrogen-bonded systems. Naresh Patwari presented a talk titled "Is hydrogen bonding analogous to hydrogen bonding?" He showed the strong correlation between proton affinity of the acceptor and the shift observed in O–H stretching frequency in a series of hydrogen-bonded complexes. However, for dihydrogen-bonded complexes, this correlation worked only with an empirical correction of 0.84, i.e. dihydrogen-bonded systems are similar to hydrogen bonds, but 16% weaker.

Viswanathan spoke about hydrogen bonds in cryogenic matrices. He presented infrared spectra of several hydrogen-bonded complexes observed in a matrix and showed that the experimental frequency shifts had a good correlation with the computed frequency shifts and also the binding energies of the hydrogen-bonded complexes. Arunan gave the last talk of the day titled "Hydrogen bond radii: From microwave spectroscopic, ab initio and AIM studies". He presented microwave spectroscopic results on several H₂O and H₂S complexes and showed the structural similarities between these complexes. He also showed that the H–Y distance could be written as a sum of hydrogen bond radius for X–H donor and an acceptor radius for Y. He presented theoretical results from ab initio and AIM calculations and showed that both the donor and acceptor radii increase from strong to medium to weak hydrogen bonds. He presented a set of "hydrogen bond radii" that may be used instead of the single set of van der Waals radii for all atoms in confirming/ruled out the presence of hydrogen bonds.

There was panel discussion at the end that involved all the participants (about 100). The discussion centered around the use of experimental and theoretical electron density topology in confirming/ruling out hydrogen bonds. Arunan presented the evolving definition of hydrogen bonding and sought comments from everyone. After the meeting, the core group finalized the recommendation and started working on a manuscript that will justify their recommendation. This recommendation was circulated within the task group and was revised based on suggestions/criticisms.

There was a unanimous view among the task group and the participants in both meetings that there is no single physical force that can be characterized as hydrogen bonding or van der Waals interaction. This may be contrasted with covalent bonding (as in H₂ molecule), ionic bonding (as in KCl molecule in the gas phase) and London dispersion forces (as in Ar). Hydrogen bonding is used by various scientists to describe interactions in extremes that can be well summarized by an isoelectronic series, (HF), HF–HF and Ne–HF, suggested by A. C. Legon (member of the task group from University of Bristol). In (HF), we have a very strong hydrogen bond with a binding energy of 167 kJ mol⁻¹ (Elgobashi, N. and González, L., J. Chem. Phys., 2006, 124, 174308) that borders a covalent bond. In HF–HF, we have a typical hydrogen bond with a binding energy of 19 kJ mol⁻¹ (Klopper, W., Quack, M. and Suhrm, M. A., J. Chem. Phys., 1998, 108, 10096) that is dominated by electrostatic forces. Finally in Ne–HF, we have a weak interaction with a binding energy of 1 kJ mol⁻¹ (Meuwly, M. and Hutson, J. M., J. Chem. Phys., 1999, 110, 8338) dominated by dispersive and inductive forces.

For hydrogen bonding, the proposed definition follows closely the one given by Pimentel and McClellan (Pimentel, G. C. and McClellan, A. L., The Hydrogen Bond, W. H. Freeman and Co, San Francisco, 1960). It was decided to propose a short definition and a list of criteria and characteristics for hydrogen bonding.

The short definition would be: The hydrogen bond is an attractive interaction between the hydrogen from a group X–H and an atom or a group of atoms Y, in the same or different molecule(s), where there is evidence of bond formation. The most important criteria for a hydrogen bond are: (i) the H in the X–H group is more electropositive than X and (ii) the physical forces involved in hydrogen bonding should include attractive electrostatic forces, i.e. it should not be primarily dispersive forces. A detailed recommendation for classification of intermolecular forces and the rationale for the proposed definition of hydrogen bonding will be submitted to IUPAC shortly. Any comments/criticisms can be sent to arunan@ipc.iisc.ernet.in or scheiner@cc.usu.edu.

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