

## DEFINING HYDROGEN BOND

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During the four years from 2006 to 2009, SciFinder has added 44262 papers containing the term 'hydrogen bond'. To be precise, these many papers were added between December 26, 2005 and January 13, 2010, when the searches were made. This amounts to about 30 papers a day, a few more than 1 every hour. Hence, it is surprising to find that most authors still feel uncertain about what is a hydrogen bond. Considering the enormous interest, following our suggestion, IUPAC formed a task group to come up with a modern definition of the hydrogen bond. The task group consisting of fourteen international experts has submitted its recommendation to IUPAC recently.<sup>1</sup> It has also produced a technical report<sup>2</sup> which summarizes our understanding about what is a hydrogen bond based on literature reports covering more than a century and provides the rationale behind the proposed definition. The details of the task group activities can be found in the following websites:

IUPAC: <http://www.iupac.org/web/ins/2004-026-2-100>

IISc: <http://ipc.iisc.ernet.in/~arunan/iupac/>

Both the recommendation and technical report will be published in the IUPAC Journal Pure and Applied Chemistry shortly. These have been reviewed by about 25 experts before reaching this stage. The recommendation will also be put on IUPAC website as provisional recommendation for comments by any chemist (or anyone interested in hydrogen bonding) from all over the world for a period of six months, before IUPAC would adapt the definition. Both the technical report and the recommendation are available from the Author. Once these are published online, a link will be provided in this website as well.

A brief description of the project, also available in the IUPAC website is given below:

Hydrogen bonding has fascinated chemists and biologists for several decades now and it is central to chemistry and biology. The original definition of hydrogen bonding invoked two electronegative atoms (X and Y) interacting through a hydrogen atom as in X-H•••Y. Initially X and Y were found to be mostly N, O and F which led to the mentioning of these atoms as part of the definition of hydrogen bonds in various sources (including the Gold book of IUPAC).

Hydrogen bonding was inferred by the difference in physical properties between otherwise chemically similar systems such as found between H<sub>2</sub>O and H<sub>2</sub>S. However, now it is well known that both H<sub>2</sub>O and H<sub>2</sub>S form a hydrogen bonded (H<sub>2</sub>X)<sub>2</sub> dimer in the gas phase. Spectroscopic red shift in XH stretching frequency was among the first experimental evidence used for inferring hydrogen bonds. Now there are several hydrogen bonded systems that appear to show blue shift in XH stretching frequency. More interestingly, these systems have CH as the hydrogen bond donors, which was against conventional wisdom. The CH•••O interactions have been well established now in organic and biological systems by crystal structure analysis and NMR methods. Traditionally, hydrogen bond acceptors interact through a lone pair or  $\pi$  bonded pair electrons. However, optically active hydrogen bonded complexes involving radicals have been found in the atmosphere. Matrix experiments and theoretical studies have shown that CH<sub>3</sub> radical could form a complex with H<sub>2</sub>O, which could be represented as C•••HO? Are these one electron hydrogen bonds with C as the acceptor? There have been reports on X-H••• $\sigma$  interactions where  $\sigma$  electrons act as hydrogen bond acceptors. Dihydrogen bonds have been observed in which H in XH (X=electronegative) interacts with another hydrogen in MH (typically a metal hydride) with partial negative charge. Moreover, there have been numerous reports on H<sub>2</sub> molecular complexes in the literature – should these be regarded as containing hydrogen bonds?

Electrostatic interaction was identified as the dominant factor for hydrogen bonds. Recent NMR and Compton scattering experiments have given evidence for partial covalency in hydrogen bonds. Dispersion forces have been shown to dominate hydrogen bonded complexes of second row hydrides (HCl and H<sub>2</sub>S). Chlorine monofluoride (ClF) has been shown to form weakly bound complexes with bases very much like HF and these have been identified as chlorine bonded complexes. Such chlorine bonding interactions have been observed in crystal structures as well. Hydrogen bonding, electrostatic interactions and van der Waals interactions are all loosely and interchangeably used in the field. Often van der Waals forces are equated to dispersion forces, though the origin of van der Waals forces (from the equation named after him) should include all intermolecular forces. Should rare gas complexes such as Ar-Ne be called London molecules instead of van der Waals molecules, as only London dispersion forces contribute to stabilization of Ar-Ne? Should Ar-HF be called hydrogen bonded or van der Waals complex? This project will attempt to give a modern definition of a hydrogen bond that is as inclusive as possible. Also, intermolecular interactions will be categorized logically considering the physical forces involved.

## References:

1. E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. J. Nesbitt, "Definition of the Hydrogen Bond" *Pure Appl. Chem.* xx, xxxx (2010).
2. E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. J. Nesbitt, "Defining the Hydrogen Bond: An Account" *Pure Appl. Chem.* xx, xxxx (2010).