

## DEFINITION OF THE HYDROGEN BOND

E. Arunan,<sup>1\*</sup> G. R. Desiraju,<sup>2\*</sup> R. A. Klein<sup>3\*</sup>, J. Sadlej,<sup>4\*</sup> S. Scheiner,<sup>5\*</sup> I. Alkorta,<sup>6#</sup> D. C. Clary,<sup>7#</sup> R. H. Crabtree,<sup>8#</sup> J. J. Dannenberg,<sup>9#</sup> P. Hobza,<sup>10#</sup> H. G. Kjaergaard,<sup>11#</sup> A. C. Legon,<sup>12#</sup> B. Mennucci<sup>13#</sup> and D. J. Nesbitt<sup>14#</sup>

<sup>1</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore. 560012, India; <sup>2</sup>Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore. 560012, India; <sup>3</sup>30, Kimberley Road, Chesterton, Cambridge, CB4 1HH, UK; <sup>4</sup>Department of Chemistry, Laboratory of Intermolecular Interactions, University of Warsaw, Warsaw, PL-02093, Poland; <sup>5</sup>Department of Chemistry and Biochemistry, 0300 Old Main Hall, Utah State University, Logan, UT. 84322 USA; <sup>6</sup>Juan de la Cierva 3, Instituto de Quimica Medicam Madrid, E-28006, Spain; <sup>7</sup>Department of Physical and Theoretical Chemistry, Oxford University, South Parks Road, Oxford OX1 3QZ, UK; <sup>8</sup>Department of Chemistry, 225 Prospect Street, Yale University, New Haven, CT 06511-8499 USA; <sup>9</sup>Department of Chemistry and Biochemistry, 695, Park Avenue, City University of New York - Hunter College, New York, NY 10065 USA; <sup>10</sup>Institute of Organic and Biochemistry, Academy of Sciences of Czech Republic, Flemingovo nam 2 Praha CZ 16610 Czech Republic; <sup>11</sup>Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark; <sup>12</sup>School of Chemistry, University of Bristol, Bristol BS8 1TS United Kingdom; <sup>13</sup>Department of Chemistry, University of Pisa, Via Risorgimento 35 Pisa I-56125 Italy; <sup>14</sup>Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO80309 USA.

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#Other members of the task group are listed alphabetically. The task group met in Pisa, Italy during September 2005 following a discussion meeting in which 12 of the members and 10 outside experts gave a talk. This meeting was followed by email discussions about the definition of a hydrogen bond. The core-group met in Bangalore in September 2006 following which the draft recommendation (Section 3 of this article) was produced. Comments from the task group and outside experts helped in refining the write-up. This was originally submitted to IUPAC in 2007 and has gone through several revisions. Names of other experts who gave valuable comments are included in the acknowledgment. All the correspondence and talks are available at the website: <http://ipc.iisc.ernet.in/~arunan/iupac/>.

*Abstract:* The term ‘Hydrogen Bond’ has been used in the literature for nearly a century now. While its importance has been realized by physicists, chemists, biologists and material scientists, there has been a continuous debate about what this term means. This debate has intensified following some important experimental results, especially in the last decade, which questioned the basis of the traditional view on hydrogen bonding. Most important among them are the direct experimental evidence for a partial covalent nature and the observation of a blue-shift in D–H stretching frequency following D–H•••A hydrogen bond formation (DH being the hydrogen bond donor and A being the hydrogen bond acceptor). Considering the recent experimental and theoretical advances, we propose a new definition of hydrogen bond as follows: *The hydrogen bond is an attractive interaction between a hydrogen atom from a fragment or molecule D–H in which D is more electronegative than H, and an atom or a group of atoms A, in the same or a different molecule, where there is evidence of bond formation.* However, the complexity of this interaction has necessitated listing a set of criteria which are found to be followed by most systems exhibiting hydrogen bonding. This list is followed by some typical characteristics that are observed in hydrogen bonding environments.

## I. INTRODUCTION

The importance of hydrogen bonding can not be overemphasized. It may best be summarized using a definition for hydrogen bonding given in the Penguin dictionary: “A weak electrostatic chemical bond which forms between covalently bonded hydrogen atoms and a strongly electronegative atom with a lone pair of electrons ... Life would be impossible without this type of bond”.<sup>1</sup> One starts wondering what an electrostatic chemical bond is and at the same time marvels at the clever juxtaposition of the words ‘electrostatic’ and ‘chemical’ to describe the hydrogen bond. Pauling, in his classic book on the Nature of the Chemical Bond, had concluded that hydrogen bonding has to be electrostatic as it cannot be chemical (covalent)!<sup>2</sup> Moreover, it is well established now that a lone pair of electrons in a strongly electronegative atom represents just one of the many types of acceptors for a hydrogen bond.

There have been several books on hydrogen bonding<sup>3-15</sup> starting with the first authoritative book by Pimentel and McClellan<sup>3</sup> in 1960. This was preceded by the compilation of papers presented in the IUPAC symposium on Hydrogen Bonding published in 1959 and edited by Hadzi.<sup>4</sup> It is difficult to establish when the concept of hydrogen bond was first suggested. Before all these books, the term ‘hydrogen bond’ was brought into the mainstream by the classic book published by Pauling in 1939.<sup>2</sup> According to Pauling, Latimer and Rodebush were the first to mention the term ‘hydrogen bond’ in the published literature in 1920.<sup>16</sup> This could very well be true as the reports preceding these were in German and mentioned *Nebenvalenz*<sup>17</sup> (secondary or weak valence) and *Innere Komplexsalzbildung* (‘internal complex salt-bridge’ for describing the intramolecular hydrogen bond in 1-hydroxyanthraquinone).<sup>18</sup> Moore and Winmill<sup>19</sup> had used the term *weak union* to describe the weaker basic properties of trimethylammonium hydroxide compared to tetramethylammonium hydroxide. According to them, the trimethyl compound was a weak union between trimethylamine and water. Clearly, the concept of hydrogen bond existed before 1920; in fact Huggins from the same Department as Latimer and Rodebush (University of California, Berkeley) had apparently used this in his unpublished M.S. Thesis.<sup>20</sup>

The importance of hydrogen bonding is also amply demonstrated by the number of publications containing the terms ‘hydrogen bond’ or ‘hydrogen bonding’. For the period 2006-2008, there is on an average at least one paper published and indexed in SciFinder every hour! To be precise, on

December 26, 2005, SciFinder had 96,688 references containing the words ‘hydrogen bond’ and on December 29, 2008, this had grown to 127,793 references. That amounts to 28.3 papers a day, clearly a little more than one paper every hour. It is indeed surprising then that most authors feel that there is no universally accepted definition for the hydrogen bond.

This manuscript discusses the evolution of our understanding about hydrogen bonding. Following this discussion, we propose a definition of hydrogen bonding. This takes into account of the understanding that has resulted from the investigations of very many researchers. Indeed, the authors of this manuscript ‘were standing on the shoulders of giants’ to paraphrase Newton. While many important references have been given, it is likely that some equally or even more important references have been left out. A more comprehensive list of references on this topic is available from the books referred to above<sup>3-15</sup> and in the reviews published on hydrogen bonding in literature cutting across disciplines<sup>21-40</sup>. Our main focus in this article is to propose a modern definition for the hydrogen bond. The complexity involved in doing this has led to our proposing a short definition followed by a list of criteria and characteristics for hydrogen bonding observed under various circumstances. Many authors have in the past, resorted to providing a list of criteria in addition to or instead of providing a definition for hydrogen bond. This includes the books by Pimentel and McClellan<sup>3</sup> and Scheiner<sup>11</sup>.

Section 2 discusses several aspects of hydrogen bonding such as the nature of physical forces involved, various hydrogen bond donors and acceptors, distance and energy criteria, and spectroscopic characterization. In Section 3, the proposed definition is given. Section 4 concludes this paper and summarizes our efforts.

## 2. HYDROGEN BONDING SO FAR

### 2.1. Physical forces involved in the hydrogen bond.

All the initial examples for hydrogen bonding had FH, OH or NH as donors and this naturally led to the conclusion that only these groups can form hydrogen bonds. The three elements F, O and N are the most electronegative in the periodic table. Hence, an H atom attached to any of these three atoms will have a significant partial positive charge. Latimer and Rodebush mentioned that ‘a free pair of electrons on one water molecule exerts sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the molecules together...hydrogen nucleus held between two octets constitutes a weak “bond”’ (the double quote for bond was used by Latimer and Rodebush). During the first half of the 20<sup>th</sup> century, acceptance of the Lewis/Langmuir octet rules of valence was unquestionable.<sup>41</sup> Thus, Pimentel and McClellan applauded the audacity of the proposal by Latimer and Rodebush which showed a departure from the octet rule. As H has only one electron and it was already participating in the covalent bond formed with F, O or N, it was originally thought that it could not have another covalent bond. This led Pauling to conclude that the hydrogen bond is electrostatic (ionic) in nature. Electrostatic interactions do play a crucial role in hydrogen bonding but cannot explain several important experimental observations including the lengthening of the D-H bond with a resultant red-shift in the experimental D-H stretching frequency. Thus, defining a hydrogen bond as ‘no more than a particularly strong type of directional dipole-dipole interaction’<sup>42</sup> is certainly incomplete. As Buckingham wrote in a book ‘The hydrogen bond results from inter-atomic forces that probably should not be divided into components, although no doubt electrostatic and overlap interactions are the principal ingredients’.<sup>43</sup>

In fact, Pauling himself estimated that hydrogen bonding in O-H•••O contacts could have about 5 % covalent nature.<sup>2</sup> This was based on the H•••O distance of about 1.8 Å compared to the O-H distance of 1.0 Å which was taken to be 100 % covalent. Coulson<sup>41</sup>, Del Bene and Pople,<sup>44</sup>

Dannenberg,<sup>35</sup> Gilli et al.<sup>45</sup>, Weinhold and Landis<sup>46</sup> and many others have highlighted the importance of a partial covalent nature in the hydrogen bond. This was shown to be important in cooperative phenomena that are observed in hydrogen bonded systems.<sup>11,13,35,47</sup> The partial covalent nature of the hydrogen bond has been experimentally verified during the last decade by Compton scattering<sup>48</sup> and NMR spin-spin coupling<sup>49</sup> measurements. Moreover, the similarity between charge-transfer interaction and hydrogen bonding has been pointed out by many including Ratajczak and Orville-Thomas.<sup>50</sup> Quite recently, it has been shown that even Ng-H<sub>2</sub>O (Ng- noble gas) interactions show signs of hydrogen bonding<sup>51</sup>, and not surprisingly charge-transfer interaction as well<sup>52</sup> for heavier noble gases such as Kr and Xe.

There have been numerous attempts to decompose the hydrogen bonding interaction into electrostatic, polarization, charge transfer, dispersion and exchange repulsion.<sup>53-56</sup> Although the electrostatic component has often been taken to include only dipole-dipole interactions,<sup>42</sup> several authors have shown the importance of invoking higher moments, quadrupole, octupole, etc.<sup>57-59</sup>. The reader is referred to a critical review by Dykstra and Lisy<sup>60</sup> for more details on the development of various models. Today, it is well accepted that hydrogen bonding has contributions from electrostatic interactions between permanent multipoles, polarization or induction interactions between permanent and induced multipoles, dispersion arising from instantaneous multipoles-induced multipoles, charge transfer, and exchange correlation effects from short range repulsion due to overlap of the electron distribution, in addition to partial covalent bonding. The contribution from the individual forces mentioned above varies depending on the hydrogen bond donor, acceptor and the environment. Clearly, no single physical force can be attributed to hydrogen bonding. It is suggested in the list of criteria that the forces involved in the D-H•••A interaction be more than just London dispersive forces. The main reason for this is the predominantly directional nature of hydrogen bonding as opposed to the more isotropic nature of London dispersive forces. Clear experimental evidence for this difference can be seen in the crystal structure of H<sub>2</sub>O and H<sub>2</sub>S, the former having 4 neighbours and the later having 12 neighbours (i.e. H<sub>2</sub>S is nearly spherical).<sup>2</sup> However, recent experimental results on H<sub>2</sub>S offer more insight and they are discussed in the next section.

Experimental<sup>61</sup> and theoretical (christened as Atoms in Molecules theory by Bader)<sup>62</sup> analysis of electron density topology in hydrogen bonded systems has proven to be useful and is indeed widely used. In most cases, there is a bond path connecting the H to the A atom and a (3,-1) bond critical point is found.<sup>62,63</sup> There has been a debate about the usefulness of a (3,-1) critical point between two atoms to establish the presence or absence of a bond between the two atoms.<sup>64-68</sup> One concern is that a bond critical point could be found for non-equilibrium geometries such as transition states, i.e., saddle points, rather than true global minima. It is, however, perfectly logical that a transition state in a metastable equilibrium could be partially stabilized by a hydrogen bond exhibiting a (3,-1) bond critical point<sup>69</sup>. In this instance the hydrogen bonding energy is insufficient to offset other conformational effects resulting in true minima either side of the transition state without a hydrogen bond. Klein argues that the absence of a bond critical point, corroborated by experiment and theory, does imply the absence of a bond although the presence need not necessarily indicate the presence of a bond in the normally (chemically) accepted sense.<sup>69</sup> However, as is true with many of the characteristics of the hydrogen bond, a (3,-1) bond critical point is found between H and A in most D-H•••A hydrogen bonds and is therefore included as one of the characteristics of a hydrogen bond.

## 2.2 Hydrogen bond donors and acceptors

As mentioned in the above section, the original examples of hydrogen bonding were found to involve the electronegative atoms F, O or N.<sup>2</sup> The current IUPAC definition given in the Gold

book still specifically mentions these atoms, though it adds a caveat suggesting that the phenomenon is not limited to these atoms.<sup>70</sup> However, it was realized even in the early days that hydrogen bonding could occur with atoms other than F, O and N as D and/or A. Pimentel and McClellan devote a chapter on 'What groups can form hydrogen bonds?' This chapter highlights the range of possible donors and includes CH and SH groups specifically as donors. It does not list the range of acceptors but discusses aromatic rings specifically. The book by Desiraju and Steiner has indeed been motivated by the non-conventional donors and acceptors and has the title 'The Weak Hydrogen Bond in Structural Chemistry and Biology'.<sup>13</sup> It discusses C-H...O hydrogen bonds and  $\pi$  acceptors in detail. It points out that the C-H...N hydrogen bond was discussed in 1935 by Kumler<sup>71</sup> and that the O-H... $\pi$  interaction was discussed by Wulf et al. in 1936.<sup>72</sup> Rao and Jakkar published a paper in 1943 with the title 'Evidence for H bond in benzene'.<sup>73</sup> Clearly, it has been realized that D<sup>22</sup> may be any element having electronegativity larger than that of H (F, N, O, C, P, S, Cl, Se, Br and I) and A<sup>74</sup> could be any of these elements and also  $\pi$  electrons.

The range of donors and acceptors has gone far beyond what is mentioned above. For example, Crabtree and coworkers showed that another H atom itself as in metal hydrides could be the acceptor of a hydrogen bond and it was called dihydrogen bonding.<sup>75</sup> Dihydrogen bonding in the gas phase was first reported by Mikami and coworkers.<sup>76</sup> Sadlej and coworkers have discussed the various energy components of dihydrogen bonds and compared them with that of hydrogen bonds.<sup>77</sup> Though, C is included in the list of atoms mentioned above, it rarely acts as an acceptor except as part of a  $\pi$  bond. Recently, both experimental<sup>78</sup> and theoretical<sup>79</sup> work has revealed the presence of a one-electron hydrogen bond with C in CH<sub>3</sub> radical as the acceptor atom. A lone pair is actually not needed for a hydrogen bond. It has also been shown that the  $\sigma$  bonding electrons of H<sub>2</sub> could act as hydrogen bond acceptors, though the authors of the paper had suggested that it be classified as van der Waals interaction despite the similarity with the hydrogen bonding.<sup>80</sup> More recently, it was shown that the global minimum in a complex between CH<sub>4</sub> and H<sub>2</sub>O has OH pointing towards a tetrahedral face of CH<sub>4</sub> with a bond critical point between H of OH and C of CH<sub>4</sub>.<sup>81</sup> This does indeed look like the first step towards the formation of CH<sub>5</sub><sup>+</sup> and it may be pointed out that hydrogen bonding is in fact an important intermediate in proton transfer reactions.<sup>82</sup> This relation between hydrogen bonding and proton transfer reactions is widespread and it is included as one of the characteristics of a hydrogen bond.

There have been numerous reports on transition elements acting as hydrogen bond acceptors as well. The book by Desiraju and Steiner<sup>13</sup> has compiled the literature up to 1997 and the recent edited volume by Grabowski<sup>14</sup> has a chapter authored by Calhorda<sup>83</sup> specifically devoted to transition elements as acceptors. Hydrogen bonding involving ionic systems is found to be stronger than found in neutral systems and has been christened ion-assisted/charge assisted hydrogen bonding (CAHB).<sup>15,84</sup> Gilli and coworkers have also discussed resonance-assisted hydrogen bond, polarization assisted hydrogen bonding, and induction assisted hydrogen bond.<sup>15,32,84</sup> As already mentioned, hydrogen bonding in different environments relies on varying contributions from physical and chemical forces and these classifications are useful to some extent. In this manuscript, our main focus is to define a hydrogen bond that would be appropriate for all environments. Our aim is to give a definition that is both general and accurate.

Whether noble gases (Ng = He, Ar, Ne, Kr, Xe) can act as hydrogen bond acceptors has been hotly debated. Often Ng...HX interactions have been categorized as van der Waals interactions. The electronegativity of Kr has been estimated as 3.0 and it would not be surprising if it does indeed form a hydrogen bond.<sup>85</sup> Through a series of molecular beam scattering experiments, Cappelletti and co-workers have shown that the Ng...H<sub>2</sub>O interaction shows strong evidence for hydrogen bonding as the noble gases become heavier<sup>51</sup>, i.e., the He...H<sub>2</sub>O interaction is isotropic

whereas the  $\text{Xe}\cdots\text{H}_2\text{O}$  interaction is very directional with the  $\text{OH}\cdots\text{Xe}$  bond that is nearly linear. More recently, it has been shown that noble gas atoms can not only be acceptors but also donors in hydrogen bonded complexes. In particular,  $\text{HNgF}$  ( $\text{Ng} = \text{Ar}, \text{Kr}$ ) has been shown to form strong hydrogen bonds with typical acceptors such as  $\text{HF}$  and  $\text{N}_2$ .<sup>86-88</sup> It is clear that both D and A are certainly not restricted to N, O or F but may even include atoms not mentioned here. Hence, the proposed definition does not put any restriction on D or A.

The diboranes are excluded from the list of hydrogen bonded systems for the simple reason that B is less electronegative than H. In diboranes the H atoms are negatively polarized when compared to B. It is suggested that this criterion be used as a convention to avoid diverse nomenclature to describe the same systems. For example, the  $\text{HF}\cdots\text{ClF}$  complex was termed as anti-hydrogen bond by Klemperer and coworkers as they expected it to form the hydrogen bonded  $\text{ClF}\cdots\text{HF}$ .<sup>89</sup> It can now easily be recognized as a chlorine bonded complex and Cl is less electronegative than F (i.e. Cl carries a partial positive charge in ClF). Chlorine bonded systems have been receiving significant attention over the last decade.<sup>90,91</sup> It is important to realize that  $\text{HF}\cdots\text{ClF}$  may be called fluorine bonded except that no one uses such a terminology! Similarly, there are examples reported recently in which hydrides act as chlorine bond acceptors such as  $\text{LiH}\cdots\text{ClCF}_3$ .<sup>92</sup> These are better characterized as chlorine bonded rather than hydrogen bonded, though H is indeed bonded to two atoms here as well and it would fit Pimentel and McClellan's definition of a hydrogen bond.<sup>3</sup> Desiraju and Steiner<sup>13</sup> and Alkorta et al.<sup>27</sup> have used the term 'inverse hydrogen bonding' to address these situations. We propose a convention in which  $\text{LiH}\cdots\text{ClF}$  and  $\text{HF}\cdots\text{ClF}$  are chlorine bonded rather than hydrogen bonded or fluorine bonded, respectively. Hence, in the definition it is emphasized that the D atom is more electronegative than the H atom. It is important to realize that electronegativity of an atom can be very different in different environments. Also, one may need to look at group electronegativities rather than that of atoms.<sup>93</sup>

### 2.3 Distance and energy criteria: Crystallographic and computational evidence

Most of the early examples of hydrogen bonding reported distances between the D and A atoms which were less than the sum of their respective van der Waals radii.<sup>2</sup> This led many, including Pauling,<sup>2</sup> Pimentel and McClellan,<sup>3</sup> Hamilton and Ibers<sup>5</sup> and Buckingham and Fowler,<sup>57</sup> to conclude that H is immersed in the electron cloud of D and the distance between D and A is not in any way affected by the presence of H atom. This amounted to ignoring the H atom in the hydrogen bond but this view did prevail for a long time. In fact Pauling suggested that in the bifluoride anion ( $\text{FHF}^-$ ), the distance between the two  $\text{F}^-$  is just the sum of fluoride ion radii. In bifluoride ion, one expects a proton in between which is indeed too small (0.66 fm).<sup>85</sup> However, even in bifluoride ion, the H is not a bare proton and does occupy a finite volume in between two  $\text{F}^-$ . Pauling's argument was extended to neutral hydrogen bonded complexes by Buckingham and Fowler<sup>57</sup> who suggested that the D---A distance would be equal to the sum of van der Waals radii of D and A. The recent books by Jeffrey,<sup>12</sup> Scheiner,<sup>11</sup> and Desiraju and Steiner<sup>13</sup> highlight the inadequacy of this criterion.

As locating the H atom was difficult in the early days, it was not possible to define a hydrogen bond radius, as Pauling did successfully for other interactions such as covalent radii, ionic radii, metallic radii and van der Waals radii.<sup>2</sup> Even without a hydrogen bond radii, based on the heavy atom distances from data bases such as Cambridge Structural Database<sup>94</sup> and Protein Databank,<sup>95</sup> Desiraju and Steiner<sup>13</sup> and Jeffrey<sup>12</sup> did come up with more reasonable cutoffs in terms of D---A distances for strong, medium and weak hydrogen bonds.

Wallwork did define the hydrogen bond radii at a time when hydrogen atoms could not be located accurately but was disappointed not to find any correlation with other properties such as binding energy.<sup>96</sup> Recently, Arunan and coworkers<sup>97,98</sup> and Klein<sup>99,100</sup> have independently shown

that using van der Waals radii to confirm/rule out hydrogen bonding can lead to erroneous conclusions both at short and long distances for strong and weak hydrogen bonds, respectively. Hydrogen bond radii have been proposed for strong, medium and weak hydrogen bonds based on electron density studies and a strong correlation of these radii has been shown with the dipole moment of DH.<sup>98</sup> These suggestions are new and will be tested in the future. However, in the list of criteria given in this manuscript, the use of van der Waals radii is strongly discouraged. Indeed, Bondi in his original paper recommended that van der Waals radii only be used for estimating crystallographic volumes.<sup>101</sup>

Pauling had suggested 8 – 42 kJ mol<sup>-1</sup> as a typical hydrogen bond energy,<sup>2</sup> even though this range does not cover the bifluoride anion (FHF)<sup>-</sup> included by him as an example of hydrogen bonding, or for that matter a number of other ionic hydrogen bonded systems such as NH<sub>3</sub>•••NH<sub>4</sub><sup>+</sup>. Pimentel and McClellan were more cautious and did not put any limit on the binding energy.<sup>3</sup> The books by Desiraju and Steiner<sup>13</sup> and Jeffrey<sup>10</sup> recommend limits for strong (63-167 kJ mol<sup>-1</sup>), medium (17-63 kJ mol<sup>-1</sup>) and weak (< 17 kJ mol<sup>-1</sup>) hydrogen bonds, with notably no lower limit for weak hydrogen bonds. Similar limits were originally suggested by Emsley.<sup>23</sup> The existing IUPAC definition<sup>70</sup> also does not give a lower limit but suggests an upper limit of 20-25 kJ mol<sup>-1</sup>.

It is clear that specifying an energy cutoff is arbitrary and does not help in identifying or excluding the possibility of a hydrogen bond being present. Directionality rather than energy is the discriminative attribute for a hydrogen bond. Desiraju and Steiner have shown that even the weakest hydrogen bonds are distinctive from the more general van der Waals interactions which are isotropic.<sup>102</sup> Historically, the differences in melting and boiling points for the hydrides of successive row elements (such as H<sub>2</sub>O and H<sub>2</sub>S and HF and HCl)<sup>3</sup>, were helpful in identifying the presence of hydrogen bonding in H<sub>2</sub>O and HF and it was assumed that H<sub>2</sub>S and HCl did not form hydrogen bonds. This was further corroborated by the fact that H<sub>2</sub>S has 12 neighbours in the crystal (practically a sphere) as opposed to the four neighbours for H<sub>2</sub>O in ice. However, with the advent of cryogenic matrices<sup>103</sup> and supersonic beams<sup>104</sup> for producing exotic species, there have been numerous examples of hydrogen bonded complexes involving HCl and H<sub>2</sub>S. Moreover, it has been shown recently that on increasing the pressure and decreasing the temperature, H<sub>2</sub>S shows a structure similar to that of H<sub>2</sub>O in ice.<sup>105</sup> In fact, Loveday et al. point out that H<sub>2</sub>S is a model system in which the hydrogen bond goes from 'absent or very weak to structurally significant'.<sup>105</sup> They point out that formation of a hydrogen bond involves 'a change as simple as suppressing free rotation about a single axis'. It is of interest to discuss the Ng•••HX systems again. Bader suggests that Ne•••HF is hydrogen bonded as it has a bond path connecting H and Ne with a bond critical point along the bond path.<sup>62</sup> However, Nesbitt and coworkers have shown that the lowest bound level (zero point level) for Ne•••HF has an energy above the barrier for rotation of HF within the complex i.e. HF is a nearly free rotor in Ne•••HF.<sup>106</sup> Clearly, the strength of the Ne•••H bond is not enough to force the orientational preference and HF is a nearly free rotor even at 0 K. This explains the recent experimental observation of the 'birth of a hydrogen bond' as one goes from He•••H<sub>2</sub>O to Xe•••H<sub>2</sub>O.<sup>51</sup> Although there could be a Ng•••H bond path in all these cases, only for the heavier rare gases is the zero point level below the barrier for internal rotation of H<sub>2</sub>O and thus the existence of a hydrogen bond can be observed experimentally. It is clear then that the barriers for large amplitude motions that break the H bond in D-H•••A are more important in determining the presence of an observable hydrogen bond than the D-H•••A binding energy.<sup>107</sup> Hence, in the list of criteria no specific energy cutoff is given and it is suggested that the D-H•••A bond must have sufficient strength to be observed under the given experimental conditions.

## 2.4 Spectroscopy

Spectroscopy has played a crucial role in the detection of a hydrogen bond.<sup>3</sup> Murthy and Rao presented a comprehensive review on spectroscopy of hydrogen bond in 1968.<sup>21</sup> In particular,

infrared and Raman spectroscopy played important roles in the early days of hydrogen bonds. According to Pimentel and McClellan, the peak corresponding to the D-H stretch in the infrared spectrum offers the 'most sensitive, the most characteristic and one of the most informative manifestation of H bond'. Hilbert et al. had concluded in 1936 that following the hydrogen bond formation, the D-H stretching peak disappears from the spectrum.<sup>108</sup> Shortly thereafter, Badger and Bauer<sup>109</sup> showed that the D-H stretching peak does not disappear but gets red-shifted to a lower wave number, the shift correlating with the strength of the hydrogen bond in D-H...A.<sup>11,103</sup> The association between intramolecular hydrogen bonding and IR red-shift for the D-H stretching frequency was made by Kuhn in a series of papers concerned with structural effects on the IR spectra of diols<sup>110</sup>. In general, the D-H stretching peak shows decrease in frequency, increase in bandwidth and increase in intensity. Iogansen has shown the strong correlation between hydrogen bonding energy and the intensity of DH stretching peak.<sup>38</sup> These observations have remained true for most of the hydrogen bonded systems.

In the last decade it has been realized that there could be hydrogen bonded systems in which the D-H stretching frequency shows a small blue-shift and the reader is referred to the comprehensive review by Hobza and Havlas.<sup>30</sup> This was quite surprising leading to names such as 'anti hydrogen bond'<sup>111</sup> and 'improper hydrogen bond'<sup>112</sup> and for a while it was considered that red- and blue-shifting hydrogen bonds were distinctly different.<sup>113</sup> It has now been realized that there is no fundamental difference between red- and blue-shifting hydrogen bonds.<sup>114</sup> Joseph and Jemmis<sup>115</sup> have provided a unified explanation for red-, blue- and non-shifting hydrogen bonds based on the optimum D-H bond length in the D-H...A hydrogen bond. They have shown that the D-H...A energy minimum could occur at longer, equal or shorter D-H distance compared to that in the non hydrogen-bonded DH. In any case, the vast majority of hydrogen bonded systems show red-shifts in the DH stretching frequency and an increase in its intensity. Hence, it is included as a criterion for hydrogen bonding with a caveat given as a footnote.

NMR spectroscopy offers the next best evidence for hydrogen bonding after infrared spectroscopy. According to Pimentel and McClellan, the IR intensity of the D-H stretch and proton magnetic resonance of the H in the hydrogen bonded DH are probably the most sensitive to H bond formation. In general, the proton magnetic resonance of DH moves towards lower field (downfield – terminology originating from the early days of NMR when the magnetic field was scanned and superconducting magnets were not available) compared to non-hydrogen bonded DH. This is the result of strong deshielding of the protons which is a direct consequence of electron redistribution around the H atom following the H bond formation. Moreover, as mentioned earlier, NMR spectroscopy has provided direct evidence for through-bond coupling between D and A in a D-H...A hydrogen bonded system.<sup>48,116</sup>

Though IR and NMR spectroscopy offer direct experimental criteria indicating the formation of hydrogen bonds, spectroscopy in every region of electromagnetic spectrum has contributed to the growing knowledge of the hydrogen bond phenomenon. Microwave spectroscopy in a supersonic beam has provided a wealth of structural information of isolated hydrogen bonded complexes.<sup>117,118</sup> Moreover, recent advances in far infrared<sup>119</sup> or mm-wave<sup>120</sup> or terahertz<sup>121</sup> spectroscopy all contribute to the growing knowledge in this field. In particular, the hydrogen bond stretch i.e. H...A stretch, can be directly observed today.<sup>122</sup> Electronic spectroscopy has been traditionally used<sup>21</sup> in studies on hydrogen bonded systems. Today, all modern spectroscopic techniques, such as 2D-IR,<sup>123</sup> and other double resonance techniques (IR-UV<sup>124</sup>, UV-UV<sup>125</sup>) are employed in investigations of hydrogen bonded systems. Moreover, mass detected IR spectroscopy, such as resonant 2 photon ionization (R2PI) detection, are also employed for investigating hydrogen bonds.<sup>126</sup> A recent experimental addition has been the use of helium nanodroplets to study molecular complexes.<sup>127</sup> Clearly, numerous spectroscopic techniques are used in the study of the hydrogen bond and many more are likely to be added. In any case, only the red-shift in the IR and a shift towards lower fields in NMR are suggested as criteria for a hydrogen bond.

### 3. DEFINITION OF A HYDROGEN BOND

In this section, we address the main objective of this manuscript. A short definition is given here which is followed by some explanation of the terms. A list of criteria, both experimental and theoretical, is given next. Finally, some characteristics that can be typically found in hydrogen bonded systems are given. In some of the places, a footnote indicated by a number F# has been added and these are given at the end of this section. These are intended to give more explanation for the sake of clarity and completeness.

#### 3.1 Definition

**The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or fragment D–H in which D is more electronegative than H, and an atom or a group of atoms A in the same or a different molecule, where there is evidence of bond formation.**

A typical hydrogen bond may be depicted as D–H•••A–B, where the three dots denote the bond. D–H represents the hydrogen bond donor. The acceptor may be an atom or an anion A, or a fragment or a molecule A–B, where A is bonded to B. In any event, the acceptor is an electron rich region such as a lone pair or a  $\pi$  cloud.

The evidence may be experimental or theoretical, or ideally, a combination of both. Some criteria and characteristics for hydrogen bonding, not necessarily exclusive, are listed below.<sup>F1</sup> The greater the number of criteria satisfied, the more reliable is the characterization as a hydrogen bond.

#### 3.2 List of criteria

For a hydrogen bond D–H•••A–B:

- (1) The forces involved in the formation of a hydrogen bond include those of an electrostatic origin,<sup>F2</sup> those arising from charge transfer between the donor and acceptor, those originating from dispersion and additionally those that are responsible for the formation of a partial covalent bond between H and A.
- (2) The atoms D and H are covalently bonded to one another and the D–H bond is polarized, the H•••A bond strength increasing with the increase in electronegativity of D.<sup>F3</sup>
- (3) The stronger the hydrogen bond, the more linear is the D–H•••A angle<sup>F4</sup> and the shorter is the H•••A distance.<sup>F5</sup>
- (4) The length of the D–H bond increases on hydrogen bond formation leading to a red shift in the infrared D–H stretching frequency and an increase in the infrared absorption cross section for the D–H stretching vibration. The greater the lengthening of the D–H bond in D–H•••A, the stronger is the H•••A bond. Simultaneously, new vibrational modes associated with the formation of the H•••A bond are generated.<sup>F6</sup>
- (5) D–H•••A–B hydrogen bonding leads to characteristic NMR signatures that typically include pronounced proton deshielding for H in DH and through H-bond spin-spin couplings between D and A and nuclear Overhauser enhancements.
- (6) The Gibbs interaction energy per hydrogen bond should be greater than the thermal energy of the hydrogen bond for it to be detected experimentally.<sup>F7</sup>

### 3.3 Some characteristics of hydrogen bonds

- (1) The  $pK_a$  of D–H and  $pK_b$  of A–B correlate strongly with the energy of the hydrogen bond formed between them.
- (2) Hydrogen bonds are involved in proton transfer reactions.
- (3) Networks of hydrogen bonds show the phenomenon of co-operativity, leading to deviations from pair wise additivity in hydrogen bond properties.
- (4) Hydrogen bonds show directional preferences and influence packing modes in crystal structures.<sup>F8</sup>
- (5) Estimates of charge transfer in hydrogen bonds show that the interaction energy correlates well with the extent of charge transfer between the donor and the acceptor.
- (6) Analysis of the electron density topology of hydrogen bonded systems shows a bond path connecting H and A and a (3,-1) bond critical point between H and A.

### 3.4 Footnotes to Section 3

F1. It is understood that there will be borderline cases for which the interpretation of the evidence might be subjective. In any case, there should be no gross deviations from the above mentioned criteria. It may be noted that a given donor/acceptor may form hydrogen bonds with more than one acceptor/donor respectively, in a hydrogen bonded network. With further progress in experimental and theoretical methods, new criteria for hydrogen bonding could evolve.

F2. Attractive interactions arise from electrostatic forces between permanent multipoles, inductive forces between permanent and induced multipoles and London dispersive forces. If an interaction is primarily due to dispersive forces, then it would not be characterized as a hydrogen bond. Thus neither  $\text{Ar}\cdots\text{CH}_4$  nor  $\text{CH}_4\cdots\text{CH}_4$  are hydrogen bonded systems. The importance of various components of hydrogen bonding may vary quite widely from system to system.

F3. It should be remembered that the electronegativity of the elements could change depending on the chemical environment. This is particularly true of organometallic and other highly polarizable systems. However, no system in which D is less electronegative than H should be considered as being hydrogen bonded.

F4. The hydrogen bond angle tends toward  $180^\circ$  and should preferably be above  $110^\circ$ . For example, the hydrogen fluoride dimer has  $\text{F}-\text{H}\cdots\text{F}$  linear and is a hydrogen bonded system. However, the lithium fluoride dimer has both LiF molecules oriented anti-parallel because of dipole-dipole interactions and would not be considered as being (analogously) lithium bonded.

F5. Historically, the D to A distance was found to be less than the sum of the van der Waals radii of D and A and this shortening of the distance was taken as an infallible indicator of hydrogen bonding. However, this empirical observation is true only for strong hydrogen bonds. This criterion is strongly discouraged. The hydrogen bond is not a van der Waals interaction and one should not apply a criterion based on van der Waals radii of the atoms D and A to evaluate hydrogen bonding.

F6. In general, for the donor, the D–H bond length increases and there is an associated red shift in the D–H stretching frequency. There are, however, certain hydrogen bonds in which the D–H

bond length decreases and a blue shift in the D–H stretching frequency is observed. It is conceivable that a hydrogen bond could exist without a red or a blue shift. To a lesser extent, in the acceptor, the A–B bond deviates from the length of the A–B bond in the isolated subunit. The A–B bond vibrational frequencies and spectral band intensities also show corresponding changes on hydrogen bond formation.

F7. For hydrogen bonding to have any practical significance, it should be thermally stable. Hence, a hydrogen bonded complex, between donor and acceptor molecules, produced in a supersonic beam or a cryogenic matrix, may not be found in a room temperature mixture of the two molecules. Moreover, the thermal energy along vibrational coordinates that can destroy the orientational preference should be less than the barrier along those coordinates. This explains why H<sub>2</sub>S has 12 neighbours and is not hydrogen bonded when it freezes at – 60° C but shows features of hydrogen bonding at much lower temperatures.

F8. Hydrogen bonds are directional and influence crystal packing modes in chemically understandable ways. The crystal packing of a non-hydrogen bonded solid (say naphthalene) is determined by the principle of close-packing, and each molecule is surrounded by a maximum number of other molecules. In hydrogen bonded solids, there are deviations from this principle to a greater or lesser extent depending upon the strengths of the hydrogen bonds that are involved. Correspondingly, the hydrogen bond geometries are conserved with fidelities that depend on their strengths.

#### 4. CONCLUSIONS

Based on the experimental and theoretical evidence available today a short definition for the hydrogen bond has been provided in this article. The hydrogen bond is a complex phenomenon. It is inherently difficult to provide a simple definition for a complex phenomenon. Therefore, our definition while simple, must be considered in the light of the criteria proposed for its validity. These criteria are found to be satisfied in most hydrogen bonded systems. Some typical characteristics have also been included. However, it is understood that with the advent of experimental and theoretical techniques that may not exist today, the list of criteria and characteristics could change. It is hoped that the short definition given based on all the existing information today will stand the test of time. It closely follows the definition given by Pimentel and McClellan<sup>3</sup> and the emphasis on the *evidence* of bond formation is crucial.

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A hydrogen bond (often informally abbreviated H-bond) is a primarily electrostatic force of attraction between a hydrogen (H) atom which is covalently bound to a more electronegative atom or group, particularly the second-row elements nitrogen (N), oxygen (O), or fluorine (F)â€”the hydrogen bond donor (Dn)â€”and another electronegative atom bearing a lone pair of electronsâ€”the hydrogen bond acceptor (Ac). Such an interacting system is generally denoted  $Dn \text{---} H \text{---} A \text{---} Ac$ , where the solid line denotes a fully