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Defining the hydrogen bond: An account (IUPAC Technical Report)*

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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 continual 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 stretching frequency following X–H···Y hydrogen bond formation (XH being the hydrogen bond donor and Y being the hydrogen bond acceptor). Considering the recent experimental and theoretical advances, we have proposed a new definition of the hydrogen bond, which emphasizes the need for evidence. A list of criteria has been provided, and these can be used as evidence for the hydrogen bond formation. This list is followed by some characteristics that are observed in typical hydrogen-bonding environments.

Keywords: bonding; electrostatic interactions; hydrogen bonding; IUPAC Physical and Biophysical Chemistry Division; molecular interactions; noncovalent interactions.

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I. INTRODUCTION

The importance of hydrogen bonding cannot 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” [1]. 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 *The Nature of the Chemical Bond*, had concluded that hydrogen bonding has to be electrostatic as it cannot be chemical (covalent) [2]! 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 [3–15] starting with the first authoritative book by Pimentel and McClellan [3] 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 [4]. 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 [2]. According to Pauling, Latimer and Rodebush were the first to mention the term “hydrogen bond” in the published literature in 1920 [16]. This could very well be true as the reports preceding these used different words to describe the same phenomenon. For example, Werner had mentioned *Nebenvalenz* [17] (German for secondary or weak valence) and Pfeiffer had used *Innere Komplexsalzbildung* (“internal complex salt-bridge” for describing the intramolecular hydrogen bond in 1-hydroxyanthraquinone) [18]. Moore and Winmill [19] 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 M.S. thesis [20].

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 26 December 2005, SciFinder had 96 688 references containing the words “hydrogen bond” and on 29 December 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 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 [3–15] and in the reviews published on hydrogen bonding in literature cutting across disciplines [21–40]. 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 [3] and Scheiner [11].

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, spectroscopic characterization, and theoretical methods. In Section 3, the proposed definition is discussed. Section 4 concludes this paper and summarizes our efforts.

2. HYDROGEN BONDING: A CRITICAL SURVEY

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 among 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 20th century, the Lewis/Langmuir octet rules of valence was unquestionable [41]. 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 X–H bond with a resultant red-shift in the experimental X–H stretching frequency. Here, electrostatic is taken to mean the interaction between rigid dipoles. Thus, defining a hydrogen bond as "no more than a particularly strong type of directional dipole-dipole interaction" [42] 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" [43].

In fact, Pauling himself estimated that hydrogen bonding in O–H···O contacts could have about 5 % covalent nature [2]. 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 [41], Del Bene and Pople [44], Dannenberg [35], Gilli et al. [45], Weinhold and Landis [46], 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 [11,13,35,47]. The partial covalent nature of the hydrogen bond has been experimentally verified during the last decade by NMR spin–spin coupling [48] and Compton scattering [49] measurements. Moreover, the similarity between charge-transfer interaction and hydrogen bonding has been pointed out by many including Ratajczak and Orville-Thomas [50]. Quite recently, it has been shown that even Rg–H_2O (Rg- rare gas) interactions show signs of hydrogen bonding [51], and not surprisingly charge-transfer interaction as well [52] for heavier noble gases such as Kr and Xe. Co-operativity and charge transfer are observed in most hydrogen-bonded systems, and they are included in the list of characteristics.

There have been numerous attempts to decompose the hydrogen-bonding interaction into electrostatic, polarization, charge transfer, dispersion, and exchange repulsion [53–56]. Although the electrostatic component has often been taken to include only dipole–dipole interactions [42], several authors have shown the importance of invoking higher moments, quadrupole, octupole, etc. [57–59]. The reader is referred to a critical review by Dykstra and Lisy [60] 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-induced covalency, and exchange correlation effects from short-range repulsion due to overlap of the electron distribution. The contribution from the individual forces mentioned above varies depending on the hydrogen bond donor, acceptor, and the environment.

There have also been numerous studies in which intermolecular interaction was decomposed into various interactions including hydrogen bonding as an independent, though undefined, interaction. Curiously, some of these studies [29,42,61] list hydrogen bonding and electrostatic interactions as two different contributions despite the vast literature equating hydrogen bonding to electrostatic interactions. Hansen has successfully divided cohesion energy into contributions arising from dispersion, dipole–dipole interaction, and hydrogen bonding and derived useful solubility parameters for a large number of molecules [61,62].

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 X–H···Y interaction be more than just London dispersion forces. The main reason for this is the predominantly directional nature of hydrogen bonding as opposed to the more isotropic nature of London dispersion forces. Clear experimental evidence for this difference can be seen in the crystal structure of H_2O and H_2S, the former having 4 neighbors and the later having 12 neighbors (i.e., H_2S is nearly spherical) [2]. However, recent experimental results on H_2S offer more insight and are discussed in the next section.

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 [2]. 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 [63]. However, it was realized even in the early days that hydrogen bonding could occur with atoms other than F, O, and N as X and/or Y. 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* [13]. It discusses C–H···O hydrogen bonds and π-acceptors in detail. It points out that the C–H···N hydrogen bond was discussed in 1935 by Kumler [64] and that the O–H···π interaction was discussed by Wulf et al. in 1936 [65]. Rao and Jakkar published a paper in 1943 with the title "Evidence for H bond in benzene" [66]. Clearly, it has been realized that X [22] may be any element having electronegativity larger than that of H (F, N, O, C, P, S, Cl, Se, Br, and I) and Y [67] could be any of these elements and also π-electrons.

The range of donors and acceptors has gone far beyond what is mentioned above. For example, Crabtree and co-workers showed that another H atom itself as in metal hydrides could be the acceptor of a hydrogen bond, and it was called dihydrogen bonding [68]. Dihydrogen bonding in the gas phase was first reported by Mikami and co-workers [69]. Sadlej and co-workers have discussed the various energy components of dihydrogen bonds and compared them with that of hydrogen bonds [70]. Though C is included in the list of atoms mentioned above, it rarely acts as an acceptor atom, the one exception being CO, which has C as the negative end [71]. More often, C atoms act as acceptors only as part of π-bonds. Recently, both experimental [72] and theoretical [73] work has revealed the presence of a one-electron hydrogen bond with C in CH_3 radical as the acceptor atom. A lone pair is actually not needed for a hydrogen bond. It has also been shown that the σ-bonding electrons of H_2 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 [74]. More recently, it was shown that the global minimum in a complex between CH_4 and H_2O has OH pointing toward a tetrahedral face of CH_4 with a bond critical point between H of OH and C of CH_4 [75]. This does indeed look like the first step toward the formation of CH_5^+, and it may be pointed out that hydrogen bonding is in fact an important intermediate in proton-transfer reactions [76].

The relation between hydrogen bonding and proton-transfer reactions is widespread, and it is included as one of the characteristics of a hydrogen bond. This has been amply demonstrated by the systematic work on ammonium halides by Legon [77]. He considered the effect of methylation in the gas-phase ammonium halides $H_3N\cdots HX$ (X = F, Cl, Br, or I). Spectroscopic evidence shows that all the $H_3N\cdots HX$ are essentially simple hydrogen-bonded complexes in the gas phase but methylation to give $(CH_3)_3N\cdots HX$ causes movement of H away from HX toward N, so that the contribution of the ionic bond $NH^+–X^-$ increases. Moreover, along the series $(CH_3)_3N\cdots HX$ from X = F to X = I, there is a monotonic increase in ionic character as it becomes easier for HX to dissociate into H^+ and X^-. Thus, in gas-phase trimethylammomium iodide, there is an increased extent of proton transfer from I to N, representing a significant contribution from the ionic form $(CH_3)_3NH^+I^-$. There is also a large increase in binding strength owing to the increased ionic character.

There have been numerous reports on transition elements acting as hydrogen bond acceptors as well [78,79]. The book by Desiraju and Steiner [13] has compiled the literature up to 1997, and the recent edited volume by Grabowski [14] has a chapter authored by Calhorda [78] 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) [15,80]. Gilli and co-workers have also discussed resonance-assisted hydrogen bonding, polarization-assisted hydrogen bonding, and induction-assisted hydrogen bonding [15,32,80]. 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 rare gases (Rg = He, Ar, Ne, Kr, Xe) can act as hydrogen bond acceptors has been hotly debated. Often $Rg\cdots HX$ 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 [81]. In fact, for the $Rg\cdots HF$ series, experimental results are known for all the rare gases from He to Xe [82–86]. All these complexes have equilibrium geometry in which the Rg interacts with HF through the H side. However, in $He\cdots HF$, the HF is a free rotor [82] and in $Ne\cdots HF$, it is a nearly free rotor [83]. Clearly, it does not make any sense to identify these complexes as "hydrogen bonded" as the HF in this complex is freely rotating and there is no orientational preference for H pointing toward He/Ne. However, the heavier rare gases Ar, Kr, and Xe do show strong directional preferences and are clearly hydrogen bonded [86]. The $Ne\cdots HF$ is a particularly interesting case in that isotopic substitution of H by D makes the internal rotation somewhat hindered with the zero point energy only slightly (4 cm^{-1}) above the barrier for internal rotation of DF [87]. Hence, in the $Ne\cdots DF$ complex, there is significantly more orientational preference than in the $Ne\cdots HF$ complex.

A similar trend has been observed recently for the $Rg\cdots H_2O$ series. Results from molecular beam scattering experiments reported by Cappelletti and co-workers have shown that the $Rg\cdots H_2O$ interaction becomes "hydrogen bonding" as the rare gases become heavier [51], i.e., the He···H_2O interaction is isotropic whereas the Xe···H_2O interaction is very directional with the OH···Xe bond that is nearly linear. More recently, it has been shown that rare gas atoms cannot only be acceptors but also donors in hydrogen-bonded complexes. In particular, HRgF (Rg = Ar, Kr) has been shown to form strong hydrogen bonds with typical acceptors such as HF and N_2 [88–90]. It is clear that both X and Y are certainly not restricted to N, O, or F and may even include atoms not mentioned here. Hence, the proposed definition does not put any restriction on X or Y.

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 HF···ClF complex was termed as anti-hydrogen bond by Klemperer and co-workers as they expected it to form the hydrogen-bonded ClF···HF [91]. It can now easily be recognized as a halogen-bonded or more specifically a chlorine-bonded complex, and Cl is less electronegative than F (i.e., Cl carries a partial positive charge in ClF and is the acceptor of electron density from F of HF). Halogen-bonded systems have been receiving significant attention over the last decade [92,93]. It is important to realize that HF···ClF, and more importantly HF···HF, may be called fluorine-bonded except that no one uses such a terminology! Similarly, there are examples reported recently in which hydrides act as halogen bond acceptors such as LiH···$ClCF_3$ [94]. These are better characterized as halogen-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 [3]. Desiraju and Steiner [13] and Alkorta et al. [27] have used the term "inverse hydrogen bonding" to address these situations. We propose a convention in which LiH···ClF and HF···ClF are halogen (chlorine)-bonded rather than hydrogen- or fluorine-bonded, respectively. Hence, in the definition it is emphasized that the X 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 [95]. The importance of group electronegativity can be highlighted by the hydrogen-bonded complex F_3SiH···OH_2, where X is Si atom having a lower electronegativity [96].

2.3 Distance and energy criteria: Crystallographic evidence

Most of the early examples of hydrogen bonding reported distances between the X and Y atoms which were less than the sum of their respective van der Waals radii [2]. This led many, including Pauling [2], Pimentel and McClellan [3], Hamilton and Ibers [5], and Buckingham and Fowler [57], to conclude that H is immersed in the electron cloud of Y and the distance between X and Y 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 $(FHF)^-$, the distance between the two F^- is just the sum of fluoride ion radii. In bifluoride ion, one may expect a proton in between two F^- and a bare proton is indeed too small (0.66 fm) [81]. However, even in bifluoride ion, the H is not a bare proton and does occupy a finite volume in between two F. Pauling's argument was extended to neutral hydrogen-bonded complexes by Buckingham and Fowler [57] who suggested that the X—Y distance would be equal to the sum of van der Waals radii of X and Y. The recent books by Jeffrey [12], Scheiner [11], and Desiraju and Steiner [13] 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 [2]. Even without a hydrogen bond radius, based on the heavy atom distances from databases such as Cambridge Structural Database [97] and Protein Databank [98], Desiraju and Steiner [13] and Jeffrey [12] did come up with more reasonable cutoffs in terms of X—Y 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

[99]. Recently, Arunan and coworkers [100,101] and Klein [102,103] 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 XH [101]. The hydrogen bond radii for XH approach the van der Waals radii of H as the dipole moment of HX approaches zero. 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, especially of the heavy atoms, is discouraged. Indeed, Bondi in his original paper recommended that van der Waals radii be used only for estimating crystallographic volumes [104].

Pauling had suggested 8–42 kJ mol^{-1} as a typical hydrogen bond energy [2], even though this range does not cover the bifluoride anion $(FHF)^-$ included by him as an example of hydrogen bonding, or for that matter a number of other ionic hydrogen-bonded systems such as $NH_3\cdots NH_4^+$. Pimentel and McClellan were more cautious and did not put any limit on the binding energy [3]. The books by Desiraju and Steiner [13] and Jeffrey [10] recommend limits for strong (63–167 kJ mol^{-1}), medium (17–63 kJ mol^{-1}), and weak (<17 kJ mol^{-1}) hydrogen bonds, with notably no lower limit for weak hydrogen bonds. Similar limits were originally suggested by Emsley [23]. The existing IUPAC definition [63] also does not give a lower limit but suggests an upper limit of 20–25 kJ mol^{-1}.

Dissociation energy in a defined range provides a poor criterion for the existence of a hydrogen bond. As a point of reference, we first consider a series taken to represent pure London dispersion, ionic, and covalent interactions, namely, Ne_2, NaF, and F_2, for which the approximate values of D_e are 0.3, 477, and 160 kJ mol^{-1}, respectively [105]. On the other hand, the range of binding strength for the hydrogen bond can be illustrated neatly by considering the closely related, isoelectronic series Ne···HF [87], HF···HF [108], $H_2O\cdots HF$ [107], and $(F\cdots H\cdots F)^-$ [106], for which the D_e values are 1, 19, 43, and 167 kJ mol^{-1}, respectively. Although it is debatable whether there is a hydrogen bond in Ne···HF because HF is almost freely rotating, H spends more time in the region between Ne and F (and as pointed out earlier more so for Ne···DF), and for the present purpose Ne···HF can be considered the limit of a weak hydrogen bond. The bifluoride ion lies at the strong limit. Thus, the series Ne···HF, HF···HF, $H_2O\cdots HF$, and $(F\cdots H\cdots F)^-$ covers a range of hydrogen bond strengths not widely different from that of the set of London dispersion and covalent reference values.

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 distinct from the more general van der Waals interactions which are isotropic [109]. Historically, the differences in melting and boiling points for the hydrides of successive row elements (such as H_2O and H_2S and HF and HCl) [3], were helpful in identifying the presence of hydrogen bonding in H_2O and HF, and it was assumed that H_2S and HCl did not form hydrogen bonds. This was further corroborated by the fact that H_2S has 12 neighbors in the crystal (practically a sphere) as opposed to the four neighbors for H_2O in ice. This difference is rather striking, and hydrogen bonds clearly induce directional preferences and influence packing modes in crystals. This is listed as one of the characteristics of the hydrogen bond.

With the advent of cryogenic matrices [110] and supersonic beams [111] for producing exotic species, there have been several reports of hydrogen-bonded complexes involving HCl [112,113] and H_2S [114,115]. Moreover, it has been shown recently that on increasing the pressure and decreasing the temperature, H_2S has a structure similar to that of H_2O in ice [116]. In fact, Loveday et al. point out that H_2S is a model system in which the hydrogen bond goes from “absent or very weak to structurally significant” [116]. They point out that formation of a hydrogen bond involves “a change as simple as suppressing free rotation about a single axis”. It is clear then that the barriers for large amplitude motions that break the H bond in X–H···Y are more important in determining the presence of an observable hydrogen bond than the X–H···Y binding energy [117]. If this criterion is applied, one could indeed see the "border" between hydrogen-bonding and van der Waals interaction [118]. Hence, in the list of criteria no specific energy cutoff is given, and it is suggested that the X–H···Y bond must have sufficient strength to be observed under the given experimental conditions.

2.4 Spectroscopic evidence

Spectroscopy has played a crucial role in the detection of the hydrogen bonds [3]. Murthy and Rao presented a comprehensive review on spectroscopy of hydrogen bond in 1968 [21]. In particular, IR and Raman spectroscopy played important roles in the early days of hydrogen bonds. According to Pimentel and McClellan, the peak corresponding to the X–H stretch in the IR 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 X–H stretching peak disappears from the spectrum [119]. Shortly thereafter, Badger and Bauer [120] showed that the X–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 X–H···Y [11,120]. The association between intramolecular hydrogen bonding and IR red-shift for the X–H stretching frequency was made by Kuhn in a series of papers concerned with structural effects on the IR spectra of diols [121]. In general, the X–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 increase in intensity of XH stretching band [38]. Conversely, the intensity of the first X–H stretching overtone is weaker than that observed in the monomer upon hydrogen bonding [119,122,123] and the red-shift is approximately double that observed in the fundamental [3,124]. For several years, the "disappearance" of the first overtone was used as a criterion for strong hydrogen bonding [3]. Recent experiments have shown that such decrease in overtone intensity happens in both strong (O–H···O) and weak (O–H···F–C) hydrogen bonds formed within a single system, i.e., trifluoromethanol dimer formed in a supersonic jet [125].

In the last decade, it has been realized that there could be hydrogen-bonded systems in which the X–H stretching frequency shows a small blue-shift and the reader is referred to the comprehensive review by Hobza and Havlas [30]. This was quite surprising, leading to names such as "anti hydrogen bond" [126] and "improper hydrogen bond" [127] and for a while it was considered that red- and blue-shifting hydrogen bonds were distinctly different [128]. It has now been realized that there is no fundamental difference between red- and blue-shifting hydrogen bonds [129]. Joseph and Jemmis [130] have provided a unified explanation for red-, blue-, and non-shifting hydrogen bonds based on the optimum X–H bond length in the X–H···Y hydrogen bond. They have shown that the X–H···Y energy minimum could occur at longer, equal, or shorter X–H distance compared to that in the non-hydrogen-bonded XH. Karpfen and Kryachko have pointed out that in some specific cases blue-shift in XH happens even when there is no hydrogen bonding between XH and Y [131]. Sikka has recently discussed pressure-induced blue-shifts in hydrogen bonds [132]. In any case, the vast majority of hydrogen-bonded systems show red-shifts in the XH 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 IR spectroscopy. According to Pimentel and McClellan [3] "…the IR intensity (of the X–H stretch) and the proton magnetic resonance (down shift of the H resonance) are probably the most sensitive to H bond formation…". In general, the proton magnetic resonance of XH moves toward 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 XH. 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 X and Y in a X–H···Y hydrogen-bonded system [48,133].

Though IR and NMR spectroscopy offer direct experimental criteria indicating the formation of hydrogen bonds, spectroscopy in every region of the 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 [134,135]. Moreover, in complexes containing a quadrupolar nuclei, such as ^{14}N or ^{35}Cl, the quadrupolar coupling constants can change due to the distortion of electronic environment around these atoms, following hydrogen bond formation [77,136]. The changes in quadrupolar coupling constants, in fact, provide vital clues in determining the extent of proton transfer [77]. Moreover, recent advances in far IR [137] or mm-wave [138] or terahertz [139] spectroscopy all contribute to the growing knowledge in this field. In particular, the hydrogen bond stretch, i.e., H···Y stretch, can be directly observed today [140]. Electronic spectroscopy has been traditionally used [21] in studies on hydrogen-bonded systems. Today, all modern spectroscopic techniques, such as 2D-IR [141], and other double resonance techniques (IR-UV [142], UV-UV [143]) 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 [144]. Vibrational circular dichroism spectroscopy has been used as a probe for chirality transfer in molecular interactions, including hydrogen bonding [145]. A recent experimental addition has been the use of helium nanodroplets to study molecular complexes [146]. In 2009, Raman spectroscopy has been added to this list and has been successfully used to characterize carboxylic acid dimers formed in supersonic jets [147]. 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 and intensity enhancement in the IR spectrum and a shift toward lower fields in the NMR spectrum are suggested as criteria for a hydrogen bond.

Hydrogen-bonded interactions are often responsible for specific properties of liquids. This is especially true in highly structured liquids such as water. When such a hydrogen bond network is present, specific dynamics occur over a range of time scales, from femtosecond fluctuations that involve a few molecules to sub-picosecond diffusive motions that involve the breaking and forming of hydrogen bonds. These dynamics can be experimentally investigated with time-resolved spectroscopic techniques as well as simulated with computational techniques [148–152]. These studies have provided further dynamic criteria or distinctive characteristics to identify hydrogen bonds [117,148–152]. Most of these dynamic studies investigate hydrogen bonding in water, which is of enormous importance. However, the definition provided here is quite general and would cover these and hopefully other future developments.

2.5 Theoretical/computational methods

One of the most powerful tools to study hydrogen-bonded systems, or intermolecular interactions in general, is computational chemistry. These approaches can be divided first into two broad categories. Empirical approaches make use of a predefined function that estimates the interaction energy in terms of (a) the nature of the two groups involved and (b) their relative geometry. Such methods are important to dynamics calculations but rely heavily on a number of empirical parameters, and do not lend themselves to analysis of any particular hydrogen bond.

Quantum mechanical methods consider each system and geometry individually, and compute the interaction via the fundamental forces that guide the motion of the electrons. The most approximate quantum mechanical methods are known as semi-empirical because they simplify the calculations by making use of a number of empirical parameters, such as ionization energy of a given atom, sometimes derived from experiment, but also evaluated so that the final results more closely mimic certain experimental quantities. While widely used to study hydrogen bonds in the 1960s and 1970s [22,153,154], semi-empirical methods are seldom applied nowadays, due to their well-known deficiencies in this area.

Semi-empirical procedures were succeeded by ab initio methods which do not employ adjustable parameters. As such, they are far more demanding in terms of computer resources, but modernization of the latter made such approaches more accessible and even routine, at least for systems of moderate size. The level of reliability of these methods can be systematically improved in stages by enlargement of the basis set, coupled with application of more complete treatments of electron correlation. Indeed, some of the most accurate calculations of hydrogen-bonded systems to date [155–158] have been accomplished in this manner.

The most recent addition to this arsenal of theoretical methods is density functional theory (DFT), which is typically much less computationally demanding than ab initio, and thus may be applied to larger systems [159,160]. These methods are similar in some ways to ab initio approaches, with the major distinction that DFT considers all molecular orbitals at one time, via the total electron density, which leads to their greater efficiency. They have been applied to hydrogen bonds at an accelerating pace [161–167], beginning in the early 1990s. Their major deficiencies lie first in their failure to include dispersion forces in a systematic manner; there are ongoing efforts [168–170] to correct this problem, particularly since dispersion can be one of the major contributors to hydrogen bonding. Also of some concern is the proliferation of many different variants of DFT, with each having undergone various levels of testing with respect to hydrogen bonds.

Regardless of the choice of method, the computation is capable of providing a good deal of information about each interaction. Most important in some ways, the strength of the hydrogen bond is typically equated with the energy required to separate the two species, the so-called hydrogen bond energy. This quantity must be corrected for basis set superposition error, usually by the counterpoise procedure [171]. Unfortunately, there is no clear definition of the hydrogen bond energy for intramolecular hydrogen bonds since the two partners cannot be fully separated. There have been some theoretical attempts recently to overcome this limitation for intramolecular hydrogen bond energy [172,173]. It is generally useful from a fundamental perspective to partition the total interaction energy into various components, e.g., electrostatic, exchange repulsion, polarization, etc. Care must be exercised here as there are multiple formalisms that have been developed for such partitioning [53–56,174–177], and each computes the components in different ways, which can lead to differing interpretations.

Quantum calculations allow determination of the lowest-energy structure of a given complex, which provides structural data that complement microwave and X-ray structures, but also provide a more complete description of the potential energy surface, which include secondary minima and the energy barriers that separate them. They are also capable of computing vibrational spectra, and of providing unambiguous pictures of the atomic motions accompanying each normal mode. These analyses are usually carried out at the harmonic level, which can be at odds with experimental data, particularly for the weak hydrogen bonding interactions which typically contain significant anharmonic contributions. NMR chemical shifts are also readily computed [178], as are coupling constants [179].

As a supplement to experimental information, the computed electron distributions lend themselves to analysis to aid in understanding the hydrogen-bonding phenomenon. Charges can be assessed to each atomic center, but as with energy decomposition methods, there are a variety of different means of computing these charges. One of the more widely used method, natural bond orbital analysis [180], provides information about specific chemical bonds and lone pairs, in analogy to Lewis structures, as well as their interactions with vacant anti-bonds.

Theoretical analysis of electron density topology (christened as Atoms in Molecules theory, AIM theory, by Bader) [181] in hydrogen-bonded systems has proven to be useful and is indeed widely used. This complements the experimental [182] electron density topology studies very well. The AIM theoretical approach [181,183] considers the electron density functional, and its Laplacian, adding bond paths and critical points to the overall picture, which contain information about ionic vs. covalent contributions to a given interaction. For a hydrogen bond system, in most cases, there is a bond path connecting the H to the Y atom and a (3,–1) bond critical point is found [181–184]. There has been a debate [185–191] 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. 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 meta-stable equilibrium could be partially stabilized by a hydrogen bond exhibiting a (3,–1) bond critical point [190]. 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 [190]. However, as is true with many of the characteristics of the hydrogen bond, a (3,–1) bond critical point is found between H and Y in most X–H•••Y hydrogen bonds and is therefore included as one of the characteristics of a hydrogen bond.

3. DEFINING THE HYDROGEN BOND

We are now ready to define the hydrogen bond. For reasons mentioned in Sections 1 and 2, we have chosen to provide a short, inclusive, and accurate definition for the hydrogen bond. This is followed by a list of criteria that can be used as evidence for the hydrogen bond. Some typical characteristics of the hydrogen bond have also been listed. More explanations have been given as footnotes for the sake of clarity and completeness. The document that contains all these have been submitted to IUPAC as our recommendation and it appears as the next article in this issue of *Pure and Applied Chemistry* [192].

The short definition follows the one given by Pimentel and McClellan [3] which is very general in scope but insists on some evidence for the hydrogen bond formation. One significant difference between our definition and that of Pimentel and McClellan is that the hydrogen bond donor X–H should have an X which is more electronegative than H for reasons elaborated in Section 2.2. The short definition is reproduced below from the recommendation [192]: **The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.**

As this definition requires some evidence for hydrogen bond formation, it was felt necessary to provide some criteria that can be used as evidence. Six such criteria have been given. One criterion is based on the geometry and it points out that the three atoms X–H•••Y usually tend toward linearity. This directionality is indeed the hallmark of hydrogen bonding as already pointed out in Section 2.3. Two of the criteria relate to the nature of the physical forces involved in hydrogen bonding. As outlined in Section 2.1, there is no single physical force that can be ascribed to hydrogen bonds, and hence one criterion requires that the interaction should not be primarily due to dispersion force, which is not highly directional. Electrostatic forces do play a significant role in the directionality of hydrogen bonding, and this is connected with the requirement that X be more electronegative than H. The historic criterion based on the sum of van der Waals radii of X and Y has not been recommended.

Two of the criteria are based on spectroscopy. As mentioned earlier, the red-shift in X–H vibrational frequency observed in IR and deshielding of H in XH observed in NMR have been included. The fact that there are blue-shifting hydrogen bonds has been pointed out in a footnote. An energetic limit for the binding energy has not been specified as it is very subjective. However, it has been pointed out that the thermal vibrational energy along all the coordinates that can break the hydrogen bond should be less than the potential barriers for breaking the hydrogen bond along those coordinates [117]. The importance of considering both kinetic energy and potential energy has been pointed out in several recent publications [117,188]. As one needs to worry about both enthalpy and entropy changes on hydrogen bond formation, the criterion mentions Gibbs energy explicitly.

The definition is concluded with the listing of some typical characteristics observed in hydrogen-bonded systems, and five of these have been explicitly mentioned in Section 2. These are: (1) co-operativity observed in hydrogen bonded network, (2) proton transfer as an intermediate between X–H•••Y and X•••H–Y, (3) directionality and the resultant influence in crystal packing, (4) the correlation between the extent of charge transfer and the hydrogen bond strength, and (5) the observation of a (3,–1) bond critical point between H and Y in the electron density topological analysis. In addition, the strong correlation observed between pK_a of X–H and pK_b of Y–Z with the energy of the hydrogen bond formed between them has been included as one of the characteristics [80].

4. CONCLUSIONS

The hydrogen bond is a complex phenomenon. It is inherently difficult to provide a simple definition for a complex phenomenon. Based on the experimental and theoretical evidence available today, a short definition for the hydrogen bond has been recommended. This report has summarized our existing knowledge on hydrogen bonding and provided the rationale for the definition proposed [192]. Therefore, this 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 evolve. 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 [3], and the emphasis on the *evidence* of bond formation is crucial.

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The task group met in Pisa, Italy in September 2005 following a discussion meeting in which 12 of the members and 10 outside experts gave presentations. This meeting was followed by E-mail discussions about the definition of a hydrogen bond. The core group (E. Arunan, S. Scheiner (by web-camera), G. R. Desiraju, R. A. Klein, and J. Sadlej) met in Bangalore in September 2006 following which the draft recommendation was produced. Comments from the task group and outside experts helped in refining the write-up. Names of other experts who gave valuable comments are included in the acknowledgments. All of the correspondence and presentations are available at the web site <http://ipc.iisc.ernet.in/~arunan/iupac/>.

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