ROTATIONAL SPECTRA OF WEAKLY BOUND COMPLEXES CONTAINING H₂O/H₂S: HYDROGEN BONDING VS VAN DER WAALS INTERACTION

E ARUNAN*, P K MANDAL, M GOSWAMI AND B RAGHAVENDRA

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore - 560012 (India)

Rotational spectroscopic studies on weakly bound complexes have provided accurate structural information on these complexes. This review summarizes rotational spectra of weakly bound H_2O and H_2S complexes, with C_6H_6, C_2H_4 and Ar_m (m=2,3) and the structural information obtained from the spectra. The equilibrium structures of these complexes are strikingly similar, with the O-H or S-H interacting with the p cloud in C_6H_6/C_2H_4 or with Ar_m. The Ar_3-H_2X and C_6H_6-H_2X are both symmetric tops, despite H_2X (X = O,S) being asymmetric tops. Both C_2H_4-H_2X and Ar_2-H_2X are asymmetric tops, mainly due to the lower symmetry in C_2H_4/Ar_2 compared to C_6H_6/Ar_3. In all these complexes, H_2X does not contribute to the moment of inertia along the axis perpendicular to its partner's molecular plane (for C_6H_6, C_2H_4 and Ar_3) or axis (for Ar_2). Ab initio electronic structure theory calculations at the state-of-the-art level show that the structures in which OH/SH interacts with the p cloud/Ar_m are true minima, but the structures in which O/S interacts with p are saddle points. This review summarizes data from isolated gas-phase complexes and argues that both H_2O and H_2S complexes are hydrogen bonded <u>and</u> that hydrogen bonding is just one particular type of van der Waals interaction.

Key Words: Hydrogen bond; Van der Waals interactions; microwave spectroscopy; Weakly bound complexes; Supersonic expansion

1 Introduction

Microwave spectroscopic studies on weakly bound complexes have given a wealth of information about their structure and bonding.[1-5] In general, these complexes are classified as hydrogen bonded <u>and/or</u> van der Waals complexes. In 1972, Klemperer and coworkers[6] reported the observation of $(HF)_2$ in the gas phase using molecular beam electric resonance. This was the first observation of an isolated hydrogen bonded complex by microwave spectroscopy. Shortly thereafter, Klemperer's group observed Ar-HCl complex using the same technique.[7] The structure of the complex was as written with the H of HCl 'bonded' to the Ar. A series of Rg-HX (where Rg = Ne, Ar, Kr, Xe and X = F, Cl, Br) complexes have been investigated by now and it has been found that all of them have a structure in which Rg has an attractive interaction with the H of HX.[8] Should these complexes be called hydrogen bonded is a question that needs to be answered. Bader supports such a classification as

a bond critical point is found between Rg and H in these complexes.[9] However, these complexes have been generally classified as van der Waals complexes by many.[10-13] This classification is a natural choice as van der Waals was the first to recognize the importance of intermolecular attractions and came up with his intuitively derived equation of state in 1873.[14] Hydrogen bonding was postulated later in 1920 by Latimer and Rodebush,[15] though there have been some earlier reports from 1902 invoking what is now known as hydrogen bond.[16] While the presence of hydrogen in a hydrogen bond is an obvious requirement, is there anything else that is unique in hydrogen bonding, to be differentiated from van der Waals interaction? The answer to this question appears to be quite subjective and we address this more in the Discussion section. Non-covalent interactions has been the term of choice in recent years to denote hydrogen bonding and van der Waals interactions.[17]

In a very recent paper, Kryachko *et al.*[18] discuss non conventional hydrogen bonding between clusters of gold and hydrogen fluoride. They point out that "within the classical theory of hydrogen

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*Author for correspondence
Email:* arunan@ipc.iisc.ernet.in

bonding the atoms F, N, O, C, P, S, Cl, Se, Br and I having a loan pair of sp-electrons act as proton acceptors, in forming conventional hydrogen bonds". All these elements have electronegativity higher than H. At first look, C seems misplaced in this list as it rarely has a lone pair of electrons in any molecule. However, there are experimental[19] and theoretical[20,21] reports of the unpaired electron in CH_3 acting as a hydrogen bond acceptor. A theoretical study on singlet carbenes acting as hydrogen bond acceptors has been published as well.[22] Kryachko *et al.* have classified the Au_m-HF clusters as hydrogen bonded with conventional donor and non-conventional acceptor. Nearly a century after the first suggestion about hydrogen bonds, do we still need to list the atoms or groups (exclusive!?), which can form a hydrogen bond based on what has been observed experimentally and/or theoretically till that point in time? A search in Scifinder finds close to 100,000 entries on hydrogen bond as entered and there are about 365,000 entries containing the concept (as of December 2005). Have we learnt enough about what one might call a hydrogen bond? To repeat our earlier question, would rare gases qualify as acceptors for hydrogen bonds? Quite recently, Aquilanti *et al.* reported glory scattering measurements on Rg-H_2O interactions along with state-of-the-art ab initio calculations.[23] Based on the binding energy and the equilibrium Rg-H-O angle, they concluded that as the rare gas changes from He to Xe, Rg-H_2O interaction acquires hydrogen bonding nature. For He, Ne, Ar and Kr, the equilibrium Rg-H-O angles are reported to be 144°, 160°, 165° and 180°, respectively.

In this review, we summarize microwave spectroscopic and ab initio results on H_2O/H_2S complexes with C_6H_6, C_2H_4 and Ar_m (m = 2,3). Benzene and Ar_3 complexes (C_3 or higher symmetry) are symmetric tops while the C_2H_4 and Ar_2 (C_2 symmetry) complexes are asymmetric tops. Structures of these complexes have a lot of similarity suggesting that the nature of interaction could be similar. Water and hydrogen sulphide are chosen as the former is widely accepted to be a hydrogen bonding molecule but the latter is not. Even in the case of H_2S complexes, it is shown that the preferred orientation is the one with H pointing toward C_6H_6, C_2H_4 or Ar_m (m = 2, 3).

2 Experimental Methods

Rotational spectra of the H_2O/H_2S complexes are obtained using a pulsed nozzle Fourier transform microwave spectrometer (PNFTMW) modeled after the spectrometer designed by Balle and Flygare.[24] The details of this spectrometer have been published elsewhere[2,25] and only a brief description is given here. The reagent gases diluted with a rare gas (Ar or He) are supersonically expanded into the Fabry-Perot cavity of the Fourier transform microwave spectrometer. A microwave pulse of approximately 1 MHz width is coupled to the cavity. If the molecule/complex has a rotational transition within this bandwidth, it is polarized and a free induction decay (FID) results. Double superheterodyne method is used for detection of the FID. The FID from the polarized sample is digitized and Fourier transformed to get the spectrum. The signal to noise ratio is improved by averaging over many cycles. Up to 20 FIDs can be collected per single gas pulse, significantly reducing the time required for averaging. This is possible as the residence time of the gas sample inside the cavity is a few milliseconds and the FIDs last for 50-100 microseconds.

3 Discussion

3.1 Rotational Spectra and Structure of C_6H_6-H_2X and Ar_3-H_2X Complexes

The rotational spectra of C_6H_6-H_2O,[26,27] C_6H_6-H_2S[28] and Ar_3-H_2O/H_2S[29] have a lot of similarities and some differences in details. The rotational spectra for the C_6H_6-H_2O/H_2S complexes are complicated leading to several series of transitions. However, as of now only one set of transitions has been identified for both Ar_3-H_2O and Ar_3-H_2S. All four complexes give simple symmetric top spectra for the ground state, despite H_2X being an asymmetric top. The C_6H_6-H_2X and Ar_3-H_2S complexes are prolate symmetric tops giving *a* dipole transitions and the Ar_3-H_2O complex is an oblate symmetric top giving *c* dipole transitions. The fact that symmetric top spectra were obtained for all four complexes clearly points out that the protons in H_2X unit of these complexes have free internal rotation. The C_6H_6—X/Ar_3—X acts as the frame with the protons freely rotating about the frame. The ground state rotational spectra correspond to that of the rigid frame which is a symmetric top in each case.[30] The orientation

of H_2X in the complex could be unambiguously determined from the rotational spectra for various isotopomers. By fitting the spectra, rotational and centrifugal distortion constants could be determined. Moreover, the quadrupole hyperfine splitting from the D in HDX/D_2X containing isotopomers can be used to determine the orientation of the X-D bond onto the principal axes of the complex.

The B rotational constants of various isotopomers are listed in Table I for all four complexes. The mono-^{13}C benzene containing isotopomers are asymmetric tops and their A, B and C rotational constants are given in Table II. As is evident from Table II, the A rotational constants for the $^{13}CC_5H_6$-H_2X complexes are all identical and they happen to be close to the C rotational constant of $^{13}CC_5H_6$. As $^{13}CC_5H_6$ does not have a dipole moment, adding the H_2X has made it rotationally active and H_2X could be called an electrophore.[31,2] The rotational constants for the $^{18}O/^{34}S$ isotopomers and the parent isotopomers can be used to determine the distance (a) between the center-of-mass (c.m.) of the complex and the O/S atom directly as $?I_b = ì_s a^2$, where $?I_b$ is the change in moments of inertia on substitution and $ì_s$ is the reduced mass for substitution given as $M?m/(M+?m)$.[32] Here M is the mass of the complex and $?m$ is the change in mass on substitution. The

O/S atoms lie on the symmetry axis of the complex. The symmetric top nature of the spectrum was used to determine the location of protons with a modified equation for multiple substitutions off the axis as given below:

$$\Delta I_b = \Delta m b_H^2 + [2\Delta mM/(M+2\Delta m)]a_H^2 \qquad \ldots(1)$$

Here, a_H and b_H are a and b coordinates of H, where $b_H^2 + ?a_H^2 = r_{XH}^2$ and $?a_H = a_X - a_{H'}$. The $r_{XH'}$ the X-H distance in H_2X, is assumed to be the same in the complex as in the monomer. The $?a_H$ calculated from the rotational constants for the complex can be compared to the monomer value (0.595 Å for H_2O and 0.919 Å for H_2S), in order to determine the projection angle $è$, the angle between the C_2 axis of H_2X and the principal axis a/c of the complex. The $^{13}CC_5H_6$-H_2X data have been used to locate ^{13}C in the complex and an estimate of the tilt angle, $ã$, for the benzene plane with respect to the principal axis of the complex has been made. Isotopic substitution of one of the Ar atoms could in principle give similar information about the Ar_3 plane, but so far these studies have not been done.

The structures of C_6H_6-H_2X and Ar_3-H_2X complexes are shown in Fig. 1 and the structural parameters are given in Table III. It should be kept in mind that the structural parameters correspond to the zero point energy level, averaged over all vibrational degrees of freedom. These weakly bound complexes often have several large amplitude vibrations and one should be careful about comparing these parameters with theoretical results. However, the rotational constants from the experiment can certainly differentiate between the 'hydrogen bonded' structure and the O/S bonded structure. In all these complexes H_2O and H_2S interact with C_6H_6/Ar_3 through the H atoms. The tilt angle $â$ for C_6H_6-H_2X complex is 37.0° and 28.5° for X = O and S, respectively. For the Ar_3-H_2X complexes, the corresponding $â$ values are 74° and 13°. Experimental rotational constants can not distinguish between the structures in which one or both H atoms are pointing towards the ð or Ar_m center. However, it is clear that the H atoms are closer to the other 'molecule' than the X atom is to the other molecule. Dykstra's Molecular Mechanics in Clusters (MMC) calculations led to a single 'hydrogen bonded' structure for C_6H_6-H_2S^{28} and a double 'hydrogen bonded' structure for Ar_3-H_2S^{29}.

Table I

The B Rotational Constants (in MHz) of C_6H_6-H_2X and Ar_3-H_2X Isotopomers[a]

H_2X isotopomer	C_6H_6	Ar_3
$H_2^{16}O$	1994.7735(2)	1172.1323(1)
$H_2^{18}O$	1883.7110(1)	1137.8760(1)
HDO	1956.305(1)	1155.9513(3)
D_2O	1912.0135(5)	1139.3953(3)
$H_2^{32}S$	1168.53759(5)	819.0385(1)
$H_2^{34}S$	1131.60278(6)	799.8039(1)
HDS	1160.0884(2)	813.2486(1)
D_2S	1144.3555(2)	808.7339(3)

[a] C_6H_6-H_2O : ref.[27]; C_6H_6-H_2S: ref [28]; Ar_3-H_2O/H_2S: ref. [29]; Number in parenthesis represents in the error in the last decimal.

Table II

Rotational Constants (MHz) of Asymmetric $^{13}CC_5H_6$-H_2X Complexes[a]

H_2X	A	B	C
H_2O	2832(2)	1991.857(8)	1976.712(8)
D_2O	2832(3)	1908.916(1)	1894.985(1)
H_2S	2837(6)	1165.0628(2)	1159.8539(2)

[a] Number in parenthesis represents in the error in the last decimal.
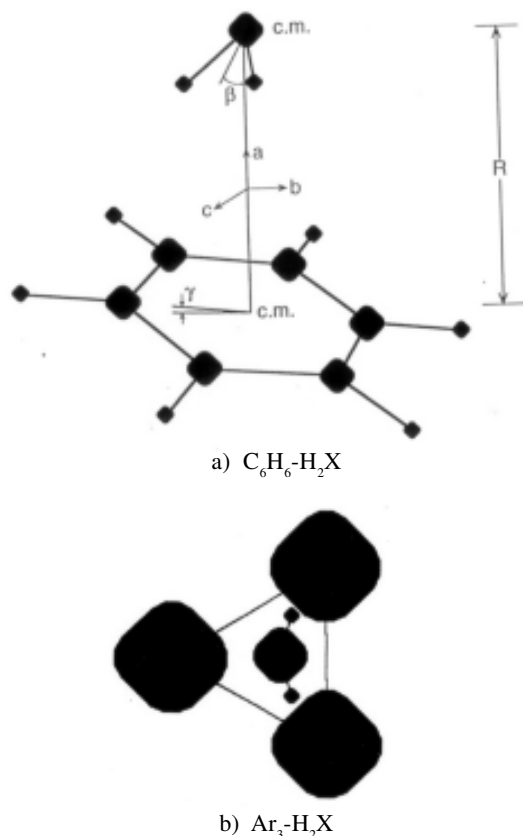
a) C_6H_6-H_2X

b) Ar_3-H_2X

Fig. 1 Structures of C_6H_6-H_2X (a) and Ar_3-H_2X. The orientation of H_2X is defined by the angles and these are given in Table III. R is the distance between the c.m. of C_6H_6 and H_2X. In Fig. 1b, all the structural parameters are similar to Fig. 1a, except the planar benzene is replaced by planar Ar_3. Virtually free internal rotation of H_2X makes both these complexes symmetric tops. (Figures reproduced with permission from American Institute of Physics. ref. [27] and [29]).

Table III

Structural Parameters for C_6H_6-H_2X and Ar_3-H_2X^a

Complex	R (Å)	è°	ā°	â°
C_6H_6-H_2O	3.329	34	0	37
C_6H_6-H_2S	3.771	26	0	28
Ar_3-H_2O	3.675	74	0	44
Ar_3-H_2S	4.112	13	0	-

^{a} R is the distance between c.m. of the two monomers i.e. H_2X and C_6H_6/Ar_3; è is the angle between the C_2 axis of H_2X and the principal axis a/c of the complex; ā is the tilt angle of C_6H_6/Ar_3. For C_6H_6, it was determined from experimental rotational constants of mono ^{13}C substituted isotopomer and for Ar_3 it is an assumption; â is the angle between the O-D bond and principal axis determined from the D quadrupole coupling constant of the HDX isotopomer.

Rotational spectra of C_6H_6-H_2X system are complicated by internal rotation/tunneling of the H_2X group and more details can be found in refs. [28, 29 and 31]. In this review, only the ground state spectra relevant for structural determination have been discussed.

3.2 Rotational Spectra and Structure of C_2H_4-H_2X and Ar_2-H_2X Complexes

As mentioned earlier, both C_2H_4-H_2X and Ar_2-H_2X are asymmetric tops. Rotational spectrum of C_2H_4-H_2O was reported by Peterson and Klemperer[33] nearly 20 years ago, and more data on several deuterated isotopomers were reported later by Andrews and Kuczkowski.[34] Rotational spectra of C_2H_4-H_2S[35], Ar_2-H_2O[36] and Ar_2-H_2S[37] were reported recently. Table IV summarizes the rotational constants of the various isotopomers for all four complexes. As noted in the previous section, H_2X does not contribute to the moment of inertia along the axis perpendicular to C_2H_4 plane/Ar_2 bond. It is evident from the fact that all isotopomers of both C_2H_4-H_2O and C_2H_4-H_2S have *A* rotational constants nearly identical to each other and to that of the *C* constant of C_2H_4. Similarly, the *A* constant of Ar_2-H_2S and the *B* constant of Ar_2-H_2O are nearly identical and close to the *B* constant of free Ar_2, 1732 MHz. Initial assignment of these asymmetric top lines is significantly more difficult than identifying the symmetric top pattern of $J+1$ lines in a Jà$J+1$ progression. However, assignment of asymmetric top spectrum yields three rotational constants which

Table IV

Rotational Constants (in MHz except for C_2H_4-H_2S A given in GHz) of C_2H_4-H_2X and Ar_2-H_2X^a

Complex	A	B	C
C_2H_4-H_2O	25960(30)	3823.617(2)	3452.099(2)
C_2H_4-$H_2^{18}O$	-	3595.366(69)	3265.219(69)
C_2H_4-HDO^b	-	3799.691	3433.905
C_2H_4-D_2O	-	3631.274(11)	3301.839(11)
Ar_2-H_2O	3457.2255(8)	1731.7811(5)	1144.5596(5)
Ar_2-$H_2^{18}O$	3178.8750(4)	1731.7465(2)	1112.0431(1)
Ar_2-HDO	3321.829(3)	1731.1607(9)	1129.4110(7)
Ar_2-D_2O	3190.924(3)	1731.472(1)	1140.609(1)
C_2H_4-H_2S	26(1)	1972.90(1)	1866.69(1)
C_2H_4-$H_2^{34}S$	26(1)	1923.11(1)	1822.05(1)
C_2H_4-HDS	26(1)	1964.68(1)	1859.50(1)
C_2H_4-D_2S	26(1)	1927.67(1)	1830.30(1)
Ar_2-H_2S	1733.115(1)	1617.6160(5)	830.2951(2)
Ar_2-HDS	1734.216(1)	1604.3268(7)	827.0668(3)
Ar_2-D_2S	1735.369(4)	1594.416(2)	824.176(1)

^{a} C_2H_4-H_2O ref. [34]; C_2H_4-H_2S ref. [35]; Ar_2-H_2O ref. [36]; and Ar_2-H_2S: ref. [37].
^{b} The rotational constants reported for C_2H_4-HDO appear to be in error. The transitions have been fit again to obtain the rotational constants listed.

are quite useful in determining the structural parameters. The distance of the substituted atom from the c.m. is readily obtained by the following equation[32]:

$$|r| = \left[\left(\frac{1}{2\mu}\right)(\Delta I_a + \Delta I_b + \Delta I_c)\right]^{\frac{1}{2}} \qquad ...(2)$$

Here, the ΔI_a terms give the change in moment of inertia about the a axis and μ is the reduced mass for substitution as defined in the last section. As already pointed out, these complexes have several large amplitude vibrations and results from their inertial analysis should be used with caution. This equation works well for heavy atoms, such as O or S, and their location could be determined with reasonable accuracy. However, for H/D substitution, the zero point vibrational amplitudes could differ significantly and it is important to look for other experimental and theoretical results to substantiate the structure determined from this equation. Hence, for the location of H atoms results from these equations will be substantiated by high level *ab initio* calculations.

Rotational constants of C_2H_4-H_2S isotopomers with HDS, D_2S and $H_2^{34}S$ can be used to locate the two H atoms and S from the c.m. of the complex. They lead to the distances 1.034 Å, 1.852 Å and 2.163 Å for H, S and H respectively. This is in excellent agreement with the structure determined by ab initio calculations at MP2 level using 6-311++G** basis set as shown in Fig. 2. Similar calculations with the rotational constants of C_2H_4-H_2O/HDO/D_2O/$H_2^{18}O$ isotopomers lead to the distances of 0.904 Å, 2.089 Å, and 2.473 Å for H, O and H, respectively. The similarity between the distances for H_2O/H_2S complexes is striking. Both H_2O and H_2S complexes have one H pointing toward the π center of C_2H_4 and the other away from it. From the A rotational constant, the location of H_2X as perpendicular to the plane of the C_2H_4 is unambiguously established. Results from substitution analysis further confirm the orientation of H_2X.

For Ar_2-H_2S, similar analysis shows that both H atoms point toward Ar_2. The distances for the two H atoms are determined to be 1.401 Å and 1.547 Å. The Ar_2-$H_2^{34}S$ spectrum is not available as of now and so the location of S is not directly established. However, ab initio calculations do support such a
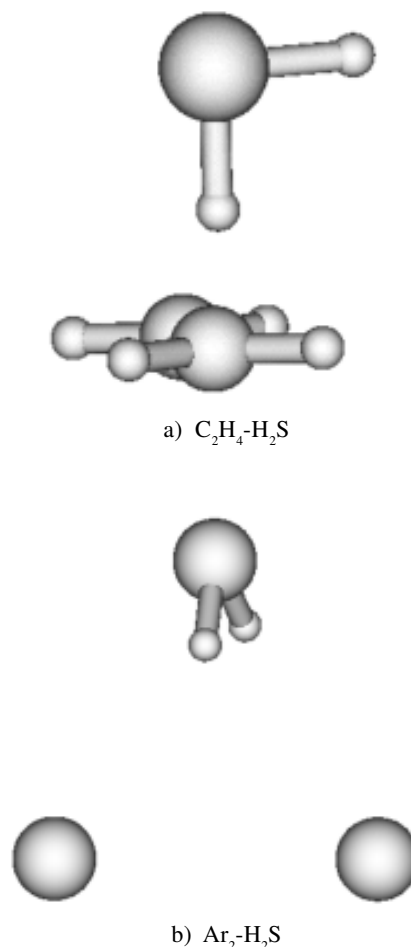

a) C_2H_4-H_2S

b) Ar_2-H_2S

Fig. 2 Structures of C_2H_4-H_2S and Ar_2-H_2S obtained from theoretical calculations. The geometry of C_2H_4-H_2S is optimized at MP2/6-311++G** level and that of Ar_2-H_2S is optimized at MP2/6-311++G(3df,2p) level. Experimental structures are in very good agreement: see text for details. Reproduced with permission from Elsevier (ref. [35]) and the Owner Societies (ref. [37])

structure with both H atoms pointing towards Ar_2 (see Fig. 2). Substitution analysis with Ar_2-H_2O leads to slightly different results and the distances from the c.m. to H, O and H are 2.453 Å, 2.559 Å and 0.949 Å, respectively. The positions of the two H atoms in this complex are reversed compared to the three other complexes discussed above. In any case, it is clear that either one or both H atoms are pointing towards Ar_2 in the Ar_2-H_2X trimers. This is in contrast to the structure considered by Scheiner and coworkers for a restricted optimization of Ar_2-H_2O.[38] They had considered a structure in which both Ar atoms interact with O of H_2O forming a distorted tetrahedron around O atom. However, MMC calculations by Dykstra did predict a geometry in which both H are pointing towards Ar_2.[36]

As already mentioned, these complexes are quite floppy and H_2X does exhibit several large amplitude motions within the complex. Comparison with Ar_2-HCl data could be useful as Cl nuclear quadrupole hyperfine coupling constants could give independent evidence for the orientation of HCl with respect to Ar_2. For Ar_2-HCl, substitution analysis using rotational constants of HCl, DCl and $H^{37}Cl$ isotopomers[39,40] leads to the values of 1.722 Å and 2.460 Å for the distance from c.m. to H and Cl atoms, respectively. Clearly, the H atom is closer to Ar_2 than Cl is. From these distances and the H-Cl distance in free HCl, the angle between the *a* axis of the complex and HCl bond axis can be determined to be 55°. The experimental[39,40] quadrupole hyperfine coupling constants for ^{35}Cl and ^{37}Cl lead to a smaller projection angle of 38.6°. This smaller projection angle implies that H is closer to Ar_2 than what is inferred from the substitution analysis, which has not been corrected for zero point vibrational amplitudes. Kisiel and coworkers[13] have reported the rotational spectrum of Ar_2-HBr recently. They have carried out a rigorous structural analysis including vibration-rotation contributions for Ar_2-HBr, Ar_2HF[10] and Ar_2HCl[39]. Though there are some subtle differences in the bond distances calculated using various methods, all of them have the H of HX pointing towards Ar_2.

3.3 Hydrogen Bonding vs. Van der Waals Equations

In the previous sections, structural details for C_6H_6-H_2X/Ar_3-H_2X and C_2H_4-H_2X/Ar_2-H_2X obtained from their rotational spectra were presented. All these complexes have one or both H of H_2X interacting with the ð clouds of C_6H_6/C_2H_4 or Ar_m. The gas-phase dimers HF-HF[6] and Ar-HF[41] are also structurally similar. In HF-HF, the H interacts with the lone pair of F in HF and in Ar-HF, the H interacts with Ar. Such structural similarities can be found between Ar_3-HX[42,43] and C_6H_6-HX[44,45] and also between Ar_2-HX[10,39] and C_2H_4-HX[46,47] complexes for X = F and Cl. Rotational spectra for C_6H_6-HCN and Ar_3-HCN indicated that both were symmetric tops[48] and that their structures were similar with H of HCN pointing towards C_6H_6/Ar_3. In all these cases, there is an H atom that is covalently bonded to one atom, interacting with another 'molecule', through a lone pair or a ð electron cloud or just atoms. In all these cases, this hydrogen is electron deficient and there

is a net positive charge on H, however small it may be. In all these complexes, there is a structural similarity. Is this enough to conclude that all of them are hydrogen bonded complexes? Before answering this question, it is important to discuss what is generally inferred by hydrogen bonding.

Hydrogen bonding was initially observed between a hydrogen atom covalently bonded to an electronegative element and another electronegative element. It was usually represented as X-H•••Y with X and Y representing the electronegative elements. These hydrogen bonds were relatively stronger and led to significant changes in many physical properties (such as melting and boiling points) that could be readily measured in the first half of twentieth century.[49] It was followed by crystal structural data[50], frequency shifts observed in X-H stretching mode[51] and chemical shift in NMR spectra[52] and these were quite significant for hydrogen bonding involving the most electronegative atoms, such as F, O and N. This led Pauling to comment that "hydrogen bonding is formed only between most electronegative elements."[50] Pauling's influence was quite significant leading several authors[53-56] and IUPAC[57] to adopt a definition of a hydrogen bond that specifically lists these atoms as capable of hydrogen bonding. However, IUPAC in 1994 was cautious and their definition contained a caveat"…electronegative atoms are usually (but not necessarily) from the first row of the Periodic Table, i.e. N, O or F". Of course, it has been recognized much earlier and the book by Pimentel and McClellan[49] in 1960 does include examples of hydrogen bonding by other elements. It led them to suggest a definition for hydrogen bonding as follows: "A hydrogen bond is said to exist when: 1) there is evidence of a bond and 2) there is evidence that this bond specifically involves a hydrogen atom already bonded to another atom". It appears that the essence of this definition was not acceptable to many. In 1972, Kollman and Allen[58] listed the possible hydrogen bond donor groups as XH with X = C, N, O, F, P, S, Cl, Se, Br and I. This may be compared to the list of possible acceptors given by Kryachko and coworkers[18] as pointed out in the Introduction. All these elements have electronegativity higher than H. Of course, there are many more elements with higher electronegativity such as Au (2.5) and even Kr (yes, Krypton 3.0).[50,59] However, these

electronegativities are for common oxidation states of the atoms. Hence, the value for Kr may be directly relevant for this discussion. However, the value for Au is not relevant when one considers Au_m as a hydrogen bond acceptor as suggested by Kryachko and coworkers.[18] In any case, when the electronegativity difference is small, such as for C-H and S-H groups, the hydrogen bonds are relatively weaker than those formed by OH or NH groups. This made the observation of these hydrogen bonds more difficult and at times controversial. In an important paper, Taylor and Kennard provided unambiguous evidence for C-H•••O interactions using statistical analysis of data from the Cambridge Crystal Structure Database.[60] The weakness of such bonds led Desiraju and Steiner to name their recent book on these interactions as "The Weak Hydrogen Bond".[16a]

In addition to the large electronegativity of the atoms X and Y involved in hydrogen bonding, there were several initial observations about hydrogen bonding which have persisted for long as necessary conditions. These may be classified as geometrical, energetic and spectroscopic criteria. Geometrically, two observations were deemed important. Firstly, the X-H-Y angle should be close to 180°. Secondly, the X—Y distance should be less than the sum of the van der Waals radii of X and Y. These two are certainly important observations which are usually found in H bonds by FH, OH and NH. However, one should exercise extreme caution in using these criteria for exclusiveness. Legon has made systematic studies on a series of hydrogen bonded complexes using the PNFTMW spectrometer.[61] He has shown that the X-H—Y angle can deviate from linearity significantly, when secondary interactions are strong enough to tilt the X-H bond so that X can interact with a H atom in Y. Thus, even in a binary complex, secondary interactions can lead to deviations from linearity. In a crystal, it would make no sense to exclude hydrogen bonding because the X-H—Y angle is not linear. Using the van der Waals radii of the heavy atoms appears even more problematic. The two books by Desiraju and Steiner[16a] and by Jeffrey and Saenger[16c] have pointed this out extensively. Recently, we have defined a hydrogen bond radius for various donors, D-H in a D-H•••A hydrogen bond.[25,62,63] The notation has been changed to D-H•••A instead of X-H•••Y to highlight the fact that D and A may be less electronegative. In any case, the D—A distance was written as the sum of the D-H covalent bond distance, the hydrogen bond radius of D-H and the acceptor radius for A. It has been shown that the D—A distances could be considerably longer than the sum of the van der Waals radii of D and A.

The energetic criteria for hydrogen bonding involve two aspects as well. One is the bond energy and the other is the nature of the hydrogen bond. The energy limit is subjective and is usually taken as a few kcal mol^{-1}. In the early days of Lewis's covalent bond, it appeared obvious that H could not form more than one bond.[50] Hence, electrostatic interaction of the partially positive hydrogen and an electron rich region was thought to be the sole origin of hydrogen bond. It was considered to be largely dipole-dipole interaction.[64] However, Buckhingham and Fowler showed the importance of using the complete electrostatics including multipoles in explaining the geometry of a series of HF complexes.[65] Even for the simplest of the hydrogen bonded dimer HF-HF, dipole-dipole interaction can not explain the experimental geometry. It appears that the quadrupole moment also should be considered. Moreover, it has been pointed out that an electrostatic picture would completely fail in explaining the co-operativity observed in hydrogen bonded systems in condensed phase.[66] Also, partial covalent nature of hydrogen bonding has been postulated based on results from both experimental[67,68] and theoretical[69] investigations. There have been several attempts[70-72] to break up the energy of a hydrogen bond into various components such as electrostatic, polarization, exchange repulsion, overlap and dispersion. In general, it appears that electrostatics dominate for the first row hydrides and dispersion becomes important for second row hydrides.[16b,73] It is important to recognize that hydrogen bonds with different DH and A groups could have differing contributions from electrostatic, covalent, and dispersive forces.

The most important spectroscopic criterion for hydrogen bonding used to be the red-shift in D-H stretching frequency.[74] However, blue-shifting hydrogen bonds have been observed now and intriguingly some of the examples today involve the C-H bond as the donor.[75a] Blue-shifting hydrogen bonds appear to be more common now and they have received significant attention in the last few years.[75a-75e]

It is clear from the above discussion that many of the features that were thought to be the defining characteristics of a hydrogen bond are applicable only to the strong hydrogen bonds formed by NH, OH and FH donors. As these were the initial examples found, it seems natural that these features were thought to be essential. From the early days, there has been a debate whether a particular D-H•••A contact should be called a hydrogen bond or not. If the chosen answer was in the negative, the interaction was deemed to be van der Waals. For example, Badger and Bauer[74] in 1937 were wondering if o-chlorophenol (intramolecular) and HCN and HCl (intermolecular) could qualify as hydrogen bonding molecules. They concluded that these intra- and intermolecular interactions should be considered as van der Waals interactions. Today, these are generally accepted as hydrogen bonds

Grabowski and coworkers[76] reported extensive theoretical calculations on dihydrogen bonding and D-H•••ó interactions. Dihydrogen bonding describes the interaction between a hydridic hydrogen such as in a metal hydride MH and a strong H bond donor such as OH.[77] The D-H•••ó interaction describes the interaction of the H from the donor D-H with the ó bonding orbital in an acceptor. The complex between OH and H_2 is a very good example of this interaction.[78] In both these cases, there is an electron deficient H interacting with an electron rich region in the acceptor. Though, the authors did comment about the arbitrary nature of classifying these interactions, they nevertheless concluded that dihydrogen bonding may be considered as hydrogen bonded and D-H•••ó interaction may be classified as van der Waals interaction.[76]

Recently, Munshi and Guru Row[79] reported experimental and theoretical electron densities in substituted coumarins and identified C-H•••O and C-H•••ð contacts. Based on the necessary and sufficient condition given by Popelier for detecting a hydrogen bond,[80] they concluded that C-H•••O contact is a hydrogen bond and C-H•••ð contact is van der Waals interaction. Popelier's condition is that if there is penetration of electron density between the two groups, there is a hydrogen bond. It may be noted that this condition is far from the complete electrostatic picture of earlier days. However, the criterion used for penetration is that the distance between the H and A (acceptor) should be less than the sum of the van der Waals radii of

H and A. This appears rather arbitrary. The van der Waals radii for the various atoms are usually taken from Pauling's[50] or Bondi's[81] work. Bondi had warned that these radii should only be used to estimate an approximate volume and should not be used otherwise. These van der Waals radii are useful ball-park figures and their use for quantitative conclusions can be misleading.

The three examples discussed above are by no means exhaustive and at best they may be representative. It is clear that whenever there was some doubt about the existence of a hydrogen bond, van der Waals interaction was invoked. One begins to wonder what is meant by van der Waals interaction. If one considers van der Waals equation as the origin of this term, then <u>all</u> intermolecular interactions (including hydrogen bonding) should be treated as van der Waals. Hydrogen bonding is certainly a subset of van der Waals interactions. However, perceptions on what is van der Waals interaction appear to be as divided as those on hydrogen bonding. Bernstein in a review[82] states that "a van der Waals complex is a collection of two or more atoms or molecules held together by van der Waals or dispersion force**s".** Here, van der Waals equals dispersion. According to Desiraju and Steiner[16a], "the isotropic terms are exchange repulsion and dispersion, the sum of which is often called van der Waals interaction". Here van der Waals has to be isotropic and dispersion and repulsion are thought to be isotropic. Aquilanti *et al.*[23] in their recent paper write the following: "The standard picture – size repulsion and induction plus dispersion attraction – is commonly referred as the van der Waals interaction." It seems that the hydrogen bonding was taken to be interaction of permanent multipoles and everything else was van der Waals. Stone's description looks reasonable in our view and he says[54]: "The forces of attraction and repulsion between molecules are called van der Waals forces." May be one should include atoms along with molecules. Koperski in his book[83] is more explicit and according to him "van der Waals interaction relies on the long-range weak attraction between permanent and induced electric dipole (and higher) moments as well as instantaneous asymmetric charge distributions in atoms and molecules (dispersion interaction)." Koperski's description could very well be used to define hydrogen bonding with the additional requirement that a hydrogen atom is

directly involved in the interaction.

Despite the complete spectrum of views shown above, one thing seems certain. Almost everyone considers that hydrogen bonding is directional and van der Waals forces are isotropic. While the former may be largely true, the latter need not be. There seems to be a common perception that dispersion, at times equated to van der Waals forces[82], should be isotropic.[16a] A careful consideration of dispersive forces can immediately point out that dispersion can not be isotropic. Dispersion is the correlated interaction between instantaneous multipoles. In other words it is an induced multipole-induced multipole interaction. Only a few molecules have isotropic polarizability (molecules with Td, Oh, or Ih symmetry) and most molecules have anisotropic polarizability. The case of CH_4-H_2O complex highlights this dramatically. In this, CH_4 has isotropic polarizability and H_2O does not. Theoretical calculations initially pointed out that this complex has a minimum showing C-H•••O interaction.[84] A bond critical point has been found between H and O.[85] However, rotational spectroscopic studies identified the geometry in which the O-H group was interacting with one of the tetrahedron planes.[86] This appears to be general as CH_4-HX (X=F[87], Cl[88], and CN[89]) all have similar geometries. Clearly, the electron deficient H is interacting with the electron rich region in CH_4, which is perpendicular to the tetrahedron planes. Methane does not have a lone pair or ð electron cloud, which are typical hydrogen bond acceptors. However, in all these complexes CH_4 molecule is a hydrogen bond acceptor. Theoretical calculations did find this geometry to be a global minimum, though the C-H•••O interaction yields a local minimum.[90] Results from Szczêœniak et al.'s theoretical work[90] are noteworthy for another reason. They point out that the dispersion energy is important for the overall anisotropy of the potential energy surface. These results for CH_4-H_2O complex are very relevant when looking at Ar-H_2O interaction. The charge distribution of the CH_4 molecule is very close to spherical, as the lowest non-vanishing multipole moment is octupole.[90] How about H_2S complexes? We address this in the next section.

3.4 Two Test Cases: C_6H_6-H_2S and Ar_2-H_2S

Both C_6H_6-H_2S and Ar_2-H_2S complexes have an H interacting with the other partner. Recently, Tauer et al. reported extensive ab initio calculations on C_6H_6-H_2S.[91] Their results are in reasonable agreement with the structure determined by rotational spectroscopy.[28] That H_2S is not generally considered as a hydrogen bonding molecule is evident from the way C_6H_6-H_2S complex has been characterized by Tauer et al.[91] as a model for aromatic-S interaction. The main objective of their calculations seems to be the study of sulfur-p interactions. However, all available results, experimental and theoretical, show that C_6H_6-H_2S system does not exhibit any attractive sulfur-p interaction to be considered as a model for such interactions. Results from experiment, MMC and ab initio calculations show that the interaction between H_2S and C_6H_6 is through the H atoms in H_2S. Tauer et al.[91] have rightly concluded that the attraction in C_6H_6-H_2S arises from electrostatic interaction between partially positive H atoms in H_2S with the negatively charged p cloud of benzene. This description is equivalent to saying that H_2S forms a 'hydrogen bond' with C_6H_6. Moreover, both ab initio[91] and MMC[28] calculations predict a barrier in the torsional potential corresponding to the geometry in which S is pointing towards the p cloud. Tauer et al. have noted that this geometry is lower in energy compared to the sum of monomer energies, though its energy is higher than that for the 'hydrogen bonded' geometry. However, they have not optimized the S down geometry or reported frequency calculations to confirm if it was a true minimum in the intermolecular potential. In order to verify the nature of the hydrogen bonded and S down structures, both structures were fully optimized at MP2/6-311++G** level. Gaussian 98 suite of programs were used for calculations.[92] Frequency calculations were carried out as well. At this level, the optimized geometry is similar to the doubly hydrogen bonded minimum reported by Tauer et al[91], though H_2S is slightly asymmetrically bound to benzene. In fact, full optimization with Dunning's correlation consistent basis set (aug-cc-pVDZ) at MP2 level leads to a structure in which only one hydrogen of H_2S is pointing towards the p-center, similar to the results from MMC calculations[28]. The three structures are shown in Fig. 3. Both hydrogen bonded geometries are true minima with all positive values in the Hessian. However, the S down geometry is a saddle point of order 2. The calculated frequencies for all three structures are given in Table V. Clearly the S down geometry is a saddle point and it is also evident from the
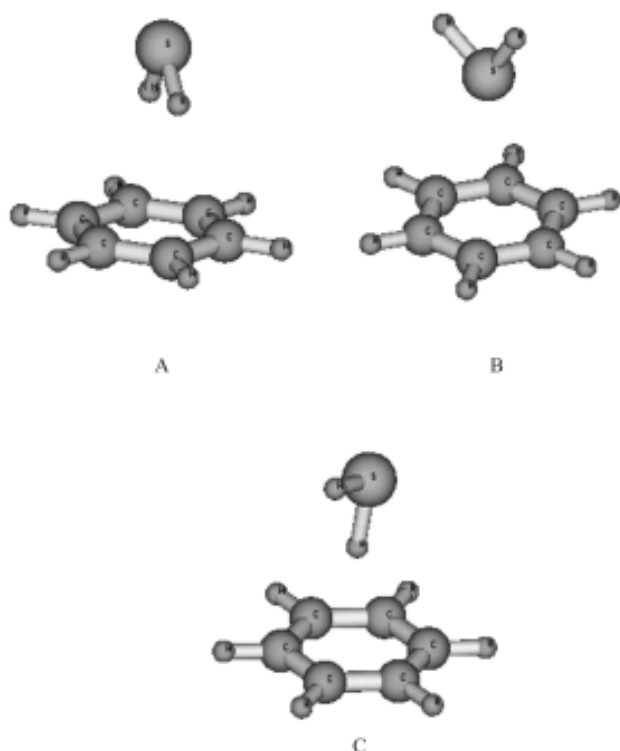
Fig. 3 Optimized structures of C_6H_6-H_2S obtained at (a) MP2-6-311++G** level for the doubly 'hydrogen bonded' geometry, a true minimum, (b) MP2-6-311++G** level for the S down geometry, saddle point of order 2 and, (c) MP2/aug-cc-pVDZ level for the single hydrogen bonded geometry, a true minimum

Table V

Vibrational Frequencies Calculated for Hydrogen Bonded C_6H_6-H_2S and the S Down Geometry C_6H_6-SH_2 (See Fig. 3 for the structures)

C_6H_6-H_2S (6-311++G**)	C_6H_6-H_2S (aug-cc-pVDZ)	C_6H_6-SH_2 (6-311++G**)
36	23	63i
57	38	60i
59	66	25
84	82	58
95	130	69
155	166	72
370	394	363
382	394	379
609	595	609
609	595	610
651	636	633
672	686	660
844	853	831
846	855	835
926	948	895
945	952	935
980	953	962
1008	989	1010
1018	1004	1018
1060	1050	1060
1060	1051	1061
1173	1156	1172
1199	1183	1198
1200	1183	1199
1223	1185	1227
1375	1334	1374
1451	1472	1453
1506	1472	1506
1506	1474	1506
1634	1621	1636
1635	1622	1637
2800	2743	2797
2825	2770	2818
3197	3199	3194
3206	3209	3204
3209	3210	3206
3222	3225	3220
3224	3226	3222
3232	3235	3230

potential energy curves obtained by partial optimization in Tauer *et al.*'s work. Dykstra's MMC calculations also revealed that the S down geometry would be a saddle point. May be it is not surprising to find that the intermolecular potential is anisotropic for C_6H_6-H_2S interaction, favoring the orientation of SH towards ð cloud in benzene. What about Ar$_m$ interaction with H_2S?

Theoretical calculations at MP2/6-311++G(3df,2p) level were carried out to determine the potential energy curves for internal rotation of H_2S about all its' inertial axes in Ar$_2$-H_2S complex.[37] The results are shown in Fig. 4. The barriers for rotation about a, b and c axes of H_2S are calculated to be 10, 53 and 47 cm^{-1}. Though these barriers are small, clearly the potential is anisotropic. Table VI summarizes the barriers for internal rotation of H_2O/H_2S in C_6H_6-H_2S/H_2O and Ar$_2$-H_2O/H_2S complexes. For Ar$_2$-H_2S, the barriers are ab initio estimates at MP2/6-311++G(3df,2p) level calculations. For the other three complexes, the barriers are results from MMC calculations by

Dykstra. In all these cases rotation about b axis has the smallest barrier as the 'H bonding' is least perturbed in this motion. Clearly, whether it is C_6H_6 or Ar$_2$, it prefers to interact with H_2X through the H atoms and not X.

4 Conclusions

From the structural and energetic data discussed here, it appears that both H_2O and H_2S have similar interactions with C_6H_6, C_2H_4, Ar$_2$ and Ar$_3$. The H atoms in H_2X play a crucial role in the attractive

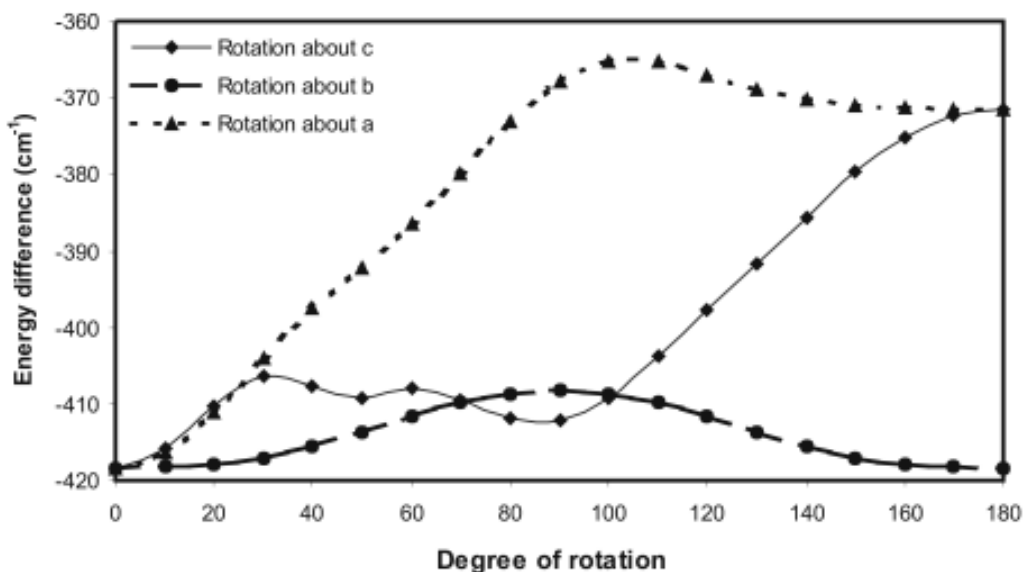Fig. 4 Potential energy surface scan at MP2/6-311++G(3df,2p) level for internal rotation of H_2S about its inertial axes within the Ar_2-H_2S complex. The S atom was held fixed in the calculations. The binding energy is 418.3 cm^{-1} with respect to Ar + Ar + H_2S limit. Reproduced with permission from The Owner Societies (ref. [37])

Table VI
Barriers for Internal Rotation (in cm^{-1}) of H_2X about its Inertial Axes a, b, and c in C_6H_6-H_2X and Ar_2-H_2X Complexes#

Complex	a	b	c	ref.
C_6H_6-H_2O	365	298	590	28
C_6H_6-H_2S	227	121	356	28
Ar_2-H_2O	80	54	80	36
Ar_2-H_2S	50	14	50	37

For the first three rows, the results are from Dykstra's MMC calculations. The last row has results from *ab initio* calculations at MP2/6-311++G(3df,2p) level. In all these complexes, the 'H bonded' geometry is the global minimum and there is a finite barrier for internal rotation of H_2X about all its' inertial axes. Note that the C_2 axis for the H_2X is its' *b* axis. Rotation about the *b* axis has the lowest barrier in all cases as it does not lead to breaking of the 'H bond'. Rotation about *a* and *c* axes involves breaking of the 'H bonds' and the barriers are significantly higher than that for the rotation about *b* axis.

interaction between the two bonding partners. All the examples discussed in this review have electron deficient H interacting with some electron rich region. It is true for both C-H•••O and O-H•••? (tetrahedron plane) interactions in the CH_4-H_2O complex. Clearly, the electron rich region could be a lone pair, ð or ó electron pairs, or unpaired electrons which are nominally attached to an atom or a bond within a molecule. It could also be an electron rich region in the molecule that is not nominally attached to any atom or a bond as in the case of CH_4. It could even be a rare gas atom such as Ar or Kr or a cluster Rg_m. It could be Au or Au_m

clusters. The donor could be any electron deficient H either from a moderately polar C-H group or a strongly polar H-F. There are not many examples in which the really non-polar H_2 interacts with an electron rich region in a similar fashion. We have not considered the interaction in diboranes where one H is shared between two B atoms having a lower electronegativity than H. The definition given by Pimentel and McClellan would include diboranes as hydrogen bonded systems. We would favor a definition of hydrogen bond as follows: Hydrogen bonding exists when an electron deficient hydrogen in a molecule interacts with an electron rich region either within the same molecule or another atom/ molecule/cluster. How does one determine whether there is any interaction between the H and the electron rich region? For the gas phase complexes, structural information appears sufficient. Obviously, the complex is bound and the presence of H in between is facilitating the complex formation. It is in agreement with the definition of a chemical bond given by Pauling[50]. However, for intramolecular hydrogen bonds and inter-atomic 'contacts' in a crystal, there needs to be some evidence that there is an interaction between H and the acceptor. Using geometric criteria such as D—A distance or D-H—A angle could be misleading. Theoretical[9,80,93] and experimental[94,79] electron density distribution appear to be well suited for this purpose. In closing, we

refer to a recent article by McDowell on the 'hydrogen bonded' complexes formed between FArH and acetylene.[95] Both C-H•••F and Ar-H•••ð interactions have been found in this complex. It is clear that the definition of a hydrogen bond should not just rely on what has been observed so far with a list of possible donor and acceptor atoms! Rather, it should rely on what we have learned about hydrogen bonding over a century.

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