The hydrogen bond: a molecular beam microwave spectroscopist's view with a universal appeal

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In this manuscript, we propose a criterion for a weakly bound complex formed in a supersonic beam to be characterized as a 'hydrogen bonded complex'. For a 'hydrogen bonded complex', the zero point energy along any large amplitude vibrational coordinate that destroys the orientational preference for the hydrogen bond should be significantly below the barrier along that coordinate so that there is at least one bound level. These are vibrational modes that do not lead to the breakdown of the complex as a whole. If the zero point level is higher than the barrier, the 'hydrogen bond' would not be able to stabilize the orientation which favors it and it is no longer sensible to characterize a complex as hydrogen bonded. Four complexes, Ar₂–H₂O, Ar₂–H₂S, C_2H_4 -H₂O and C_2H_4 -H₂S, were chosen for investigations. Zero point energies and barriers for large amplitude motions were calculated at a reasonable level of calculation, MP2(full)/aug-cc-pVTZ, for all these complexes. Atoms in molecules (AIM) theoretical analyses of these complexes were carried out as well. All these complexes would be considered hydrogen bonded according to the AIM theoretical criteria suggested by Koch and Popelier for C-H. O hydrogen bonds (U. Koch and P. L. A. Popelier, J. Phys. Chem., 1995, 99, 9747), which has been widely and, at times, incorrectly used for all types of contacts involving H. It is shown that, according to the criterion proposed here, the Ar₂-H₂O/H₂S complexes are not hydrogen bonded even at zero kelvin and C_2H_4 – H_2O/H_2S complexes are. This analysis can naturally be extended to all temperatures. It can explain the recent experimental observations on crystal structures of H_2S at various conditions and the crossed beam scattering studies on rare gases with H_2O and H_2S .

I. Introduction

There has been a continuous debate about what a hydrogen bond is and how it is different from the more general 'van der Waals interaction', though both concepts are nearly

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a century old. Considering the importance of this debate, IUPAC has recently formed a task group to come up with a modern definition of hydrogen bonding.¹ Nevertheless, the importance of "hydrogen bonding" is well-recognized in chemistry and biology.^{2–7} It has long been known that H₂O and H₂S from the same group have remarkably different properties under ambient conditions. Due to this, it was traditionally thought that H₂O forms hydrogen bonds and



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interactions, chemical kinetics and dynamics and shock tube techniques. He is the Chairman of the IUPAC task group on hydrogen bonding and other molecular interactions and is a Fellow of the Indian Academy of Sciences. H_2S does not.⁷ However, the modern view is that both molecules have very different 'hydrogen bonding' capabilities.²⁻⁶ In any case, this difference is often rationalized due to the lower electronegativity of sulfur compared to that of oxygen which makes the former a poor hydrogen bond donor/acceptor.⁸ Thus, under ambient temperature and pressure, H₂O is a liquid and H₂S is a gas. The crystal structures of H₂O and H₂S also exhibit remarkable differences. In ice, each of the H₂O molecules is coordinated to four others in a tetrahedral arrangement. On the other hand, under ambient pressure. H₂S has been found to crystallize (freezing point -60 °C) in a close-packed fashion where each hydrogen sulfide molecule is in contact with twelve equidistant neighbors.⁷ This disorder in the crystal structure of H₂S is attributed to the isotropic nature of the interaction among the neighbours, which are essentially spherical. Does it mean that H₂S can never participate in 'hydrogen bond' formation?

Our knowledge of 'hydrogen bonding' has been evolving over the last century and we now know that a wide and versatile range of chemical entities are capable of forming hydrogen bonds. Thus, in a hydrogen bond, which is typically denoted by $X-H \cdots Y$, X and Y were initially observed to be only the most electronegative elements, N, O or F.⁷ However, Pimentel and McClellan in their authoritative book on the hydrogen bond chose not to put any restriction on X or Y.² According to them, if there is evidence that an H atom is simultaneously bonded to X and Y then there is hydrogen bond. Their conviction proved right and there have been numerous examples of hydrogen bonding beyond what was initially believed and X could be any element with an electronegativity larger than that of H, including S.⁵ Moreover, Y could be a lone pair, π pair, an unpaired electron, sigma bonding electrons, hydride ions etc. and the list is expanding.9-12 It has been shown recently that the carbon atom of methane can act as a hydrogen-bond acceptor.¹³

In the literature, there are well-accepted criteria which are widely used to characterize hydrogen bonds.²⁻⁷ These criteria, though helpful in many cases, are not without ambiguities. First and foremost was the belief that hydrogen bonding was purely electrostatic.^{7,14} Now it is well recognized that 'the electrostatic picture' is incomplete.^{15,16} Compton scattering¹⁷ and NMR¹⁸ experiments in the last decade have given unambiguous evidence for a partial covalent nature in hydrogen bonding. The next most important criterion was the red shift of the X-H stretching frequency on hydrogen bond formation.² It is a well established signature of 'hydrogen bond' formation that holds true in most cases. However, recently, it has been observed that there are 'hydrogen bonds' which cause a blue shift in the X-H stretching frequencies.¹⁹ Moreover, Joseph and Jemmis have shown that it is possible to have systems with no shift of the X-H stretch frequencies upon hydrogen bond formation.²⁰ Another popular and stringent criterion has been that the distance between the X and Y atoms should be less than the sum of their van der Waals' radii.²¹ This has been relaxed to some extent now and the distance between H and Y atoms is compared to the sum of their van der Waals radii. The stringent criterion has been strongly criticized by many as being too limiting most of the time^{3-5,22-26} and the relaxed

criterion is criticized as too generous on individual cases such as 1,2-diols.²⁶ Recently, a hydrogen bond radius has been proposed as an alternative to van der Waals radius for the atoms typically found to be involved in hydrogen bonding.^{22–25} However, one aspect about hydrogen bonding that is widely accepted is the directionality, *i.e.* X–H···Y is found to be linear in most cases. Although secondary interactions in a system could force X–H···Y away from linearity,²⁷ it is the directionality in hydrogen bonding resulting in an anisotropic intermolecular potential that separates it from the more general 'van der Waals forces', which are expected to be isotropic. There have been suggestions about energy cutoffs for hydrogen bonds and these are at best suggestive and subjective, and at worst arbitrary.

Recently, Koch and Popelier have proposed a set of eight criteria to detect and characterize hydrogen bonds.²⁸ These criteria are based on Bader's atoms in molecules (AIM) theory.²⁹ According to Bader himself, the presence of a bond critical point connecting the H from the donor group XH to the acceptor Y is sufficient to conclude the presence of a hydrogen bond. In the original contribution of Koch and Popelier, these criteria were used to predict if C-H...O contacts in some van der Waals complexes and the anti-AIDS drug AZT could be classified as 'hydrogen bonded' based on detailed analysis of the charge density. These have gained popularity owing to the platform it provides to differentiate 'hydrogen bonding' from other closed shell interactions through the characterization of the properties of the bond critical point found between hydrogen and the acceptor atom. It should be remembered that these criteria are based on the analysis of rigid equilibrium geometry. While the application of these criteria for crystal structures is less ambiguous, it is not clear if the conclusions reached through this analysis will hold when one considers the non-rigid/dynamic structure of the weakly bound van der Waals complexes.

Let us now turn our attention to H₂S again. Dynamics indeed decides the fate of H₂S and there is evidence in the literature that the structural behavior of H₂S changes on further cooling and compression.^{30–32} The structure becomes gradually ordered with the signature of hydrogen bond formation. As pointed out by Nelmes, Hamel and co-workers, it is interesting to note that H₂S is the only hydride which shows this behavior on compression.³¹ Further, they concluded that H₂S can be a good model system where we can tune the hydrogen bond strength from "absent or very weak to structurally significant". On the other hand, gas phase studies like scattering and spectroscopic studies in a supersonic beam are complementary to these studies in the condensed phase. These studies provide a direct or indirect estimate of the strength of the 'hydrogen bonding' interaction in smaller dimers and trimers in isolated conditions. A recent scattering experiment of Aquilanti et al. on the complexes of rare gas with H₂O and H₂S showed that for H₂O complexes, there is a progressive shift in the 'glory' pattern towards higher velocities as one moves from He to Xe. The authors concluded that this was an indication of an increase in binding strength greater than that predicted by a van der Waals' model, which, according to them, is based on polarizabilities of the interacting partners.³³ This was attributed to an onset of hydrogen bonding (O–H···Rg) and it was further supported by the *ab initio* calculations. Unlike these complexes of H₂O with rare gas atoms, in the case of the Rg···H₂S complexes, the increase in binding strength could be explained by the polarizabilities of H₂S and those of rare gas atoms and the effect due to the permanent dipole moment of H₂S.³⁴ Thus, it was concluded that the nature of interaction becomes spherical with "no measurable anisotropic effect" when the binding partner changes from H₂O to H₂S. It was further concluded that there was no signature of hydrogen bonding in the case of H₂S complexes with rare gas atoms. It should be pointed out here that an interaction involving the permanent electric dipole moment of H₂S can not lead to an isotropic potential. The difference between the Rg···H₂O and Rg···H₂S interactions has its origin elsewhere and that is the main focus of this article.

The situation may also be different when one considers a stronger acceptor rather than the rare gas atoms. Thus, there are examples of the 'hydrogen bonded' geometry of H₂S complexes characterized by microwave experiments in the supersonic beam e.g. $C_6H_6 \cdots H_2S^{35}$ and $C_2H_4 \cdots H_2S^{36}$ The ground state structures obtained from the experiments showed that these H₂S complexes are 'hydrogen bonded' similarly to their H₂O counterparts.^{37,38} Moreover, the H₂S dimer has an equilibrium geometry which is hydrogen bonded³⁹ in a manner like that of the H₂O dimer.⁴⁰ These observations do not change the fact that H₂O is a liquid and H₂S is a gas under ambient conditions. In a supersonic molecular beam, there is an extensive cooling of the translational, rotational and vibrational degrees of freedom. This facilitates the formation of these complexes which are weakly bound. However, even at these conditions, large amplitude motions of the H₂S/H₂O within these complexes lead to observable splitting in the microwave spectrum of all these complexes. Are these interactions, then, different from the Rg-H2O/H2S interactions? As it has been shown in this manuscript and elsewhere,^{13,29} the equilibrium structures of Ar \cdots H₂O, Ar...H₂S, C₂H₄...H₂O and C₂H₄...H₂S would all be hydrogen bonded according to the AIM theoretical criteria given for C-H···O contacts by Koch and Popelier.²⁸

What happens when one considers the dynamical structure i.e. the effect of the large amplitude motions in these complexes? In a supersonic expansion, the zero-point energy is the main contributor to the dynamics of the system. Hence, the question asked is what criterion one should look for to call a system 'hydrogen-bonded', while considering the zero-point energy-averaged structure. The important point to be re-emphasized here is that the 'zero-point dynamics' cannot be restricted, even at zero kelvin. The proposed answer is that the potential barriers of different motions, which take the bonded hydrogen away from the acceptor moiety, should be significantly above the zero-point energy along that co-ordinate. It should be emphasized here that this barrier is not related to the dissociation energy of the complex under consideration. These large amplitude motions have periodic potentials along vibrational coordinates that do not lead to dissociation. This can be made clear by looking at the schematic drawn in Fig. 1. Typically, both X–H···Y and X···Y–H could be below the dissociation limit corresponding to X + HY along the stretching coordinate. If it is not bound in this stretching co-ordinate, the



Fig. 1 Schematics showing the effect of zero-point motion on the equilibrium structure of a hydrogen-bonded complex. Case I: if the barrier for the large amplitude motion is high enough compared to the zero-point energy, the dynamically averaged structure will be able to hold the 'hydrogen-bonded' configuration. Case II: when the zero-point energy along the co-ordinate is lying far above the barrier, the 'zero-point' motion becomes a 'nearly free rotation' and 'dynamic' structure will restrict any orientational preference which is characteristic of a 'hydrogen bond'.

complex does not exist. Even when the complex is bound along the stretching co-ordinate, the large amplitude motion of the HY unit within the complex can take the hydrogen away from the acceptor moiety in a vibrationally-averaged structure. In such a situation, the structure will clearly not be hydrogen bonded. This large amplitude motion of $X \cdots HY$ is described as bending or internal rotation or free rotation depending on the barrier.

In this Perspective, we analyze the effect of zero-point energy on the equilibrium structures of four complexes *e.g.* $Ar_2 \cdots H_2O$, $Ar_2 \cdots H_2S$, $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$ to test their characterization as 'hydrogen bonded' complexes. These are chosen as typical examples where the presence of a hydrogen bond is a matter of debate. The potential energy barriers for the rotation of H_2O and H_2S about their principal axes are calculated for all the complexes. The barriers were calculated using *ab initio* theory and were compared to the zero point energies along these co-ordinates. A comparison like this is useful to have an estimate of the relative strength of the interaction and it can provide important insight when one asks "is the 'hydrogen bonding', if it exists at all, strong enough to be experimentally detected and measured?"

II. Computational methodology

All four complexes were fully optimized at MP2(full)/augcc-pVTZ level of theory using the GAUSSIAN 03 suite of programs.⁴¹ Harmonic frequency calculations were performed at the same level of theory to determine the zero-point energy along the intermolecular modes. Further, the absence of any imaginary frequency ensured that the optimized geometries were true minima. However, these intermolecular frequencies are expected to be anharmonic. To check how the anharmonicity affects the frequencies of these modes, we have performed both harmonic and anharmonic frequency calculations for the $C_2H_4\cdots H_2S$ complex at a lower level of theory *i.e.* MP2(full)/aug-cc-pVDZ level. The differences in the frequency values from the harmonic and anharmonic calculations have been found to be in the range of $2-40 \text{ cm}^{-1}$. These numbers indicate that the conclusions drawn in this paper are not going to alter, as we will see later. The AIM theoretical calculations

have been performed using AIM 2000 software for the optimized geometries at this level of theory 42

Having the fully optimized geometries for all the complexes, it was decided to explore the anisotropic nature of the potential energy hypersurfaces by varying the H₂O/H₂S orientation in the complexes. For the one dimensional potential energy surface calculations for different orientations of H₂O/H₂S, we chose more symmetric structures ($C_{2\nu}$ for $Ar_2 \cdots H_2O/Ar_2 \cdots H_2S$ and C_s for $C_2H_4 \cdots H_2O/C_2H_4 \cdots H_2S$) as the starting points so that the number of parameters which are to be taken care of during the scans is reduced. Both hydrogen atoms are placed symmetrically between two Ar atoms for $Ar_2 \cdots H_2O/Ar_2 \cdots H_2S$. For $C_2H_4 \cdots H_2O$ and $C_2H_4\cdots H_2S$, the starting geometry was chosen such that the O–H··· π and S–H··· π angles were 180°. These constraints on the symmetry of the starting geometry were convenient and were also reasonable as they still represent the main features of the experimentally observed structure. The rotational spectroscopic studies on Ar2···H2O and Ar2···H2S indicated a vibrationally averaged ground state structure having $C_{2\nu}$ symmetry.^{43–45} The positions of the hydrogen atoms could not be determined from the spectra as they were affected by the large amplitude motion. However, the change in the rotational constants (change in the 'B' rotational constant of $Ar_2 \cdots H_2O$ and change in the 'A' rotational constant in case of $Ar_2 \cdots H_2S$) upon isotopic substitution indicated that both the hydrogen atoms are at almost the same distance from the center of mass. For $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$, the analysis of the experimental data showed that both H₂O and H₂S are situated on top of the π cloud of ethylene and only one of the hydrogens is pointing towards the π cloud.^{38,36} Further, for $C_2H_4\cdots H_2O$, it was also concluded that in the vibrationallyaveraged geometry, the plane of the H₂O molecule is bisecting the C=C bond of C₂H₄.⁴⁶ Furthermore, it should be pointed out that the barrier heights are not expected to be changed drastically by the assumption of the reference geometry being symmetric in the case of $Ar_2 \cdots H_2 X$ systems as the difference in energy in the symmetric and the asymmetric structures is only marginal. Thus, in the case of $Ar_2 \cdots H_2O$, this difference is only 30 cm⁻¹, whereas in case of $Ar_2 \cdots H_2S$, this difference is 44 cm⁻¹. For all four complexes, single point scans have been performed by fixing the monomer geometry as was obtained from the monomer optimization at the same level of theory. Counterpoise corrections were employed at each point to correct for the basis set superposition error (BSSE).⁴⁷ The principal axes of H₂O and H₂S are shown in Fig. 2. The structural parameters which were varied during the calculations are shown in Fig. 3. For $Ar_2 \cdots H_2O/Ar_2 \cdots H_2S$, R is defined as the distance from O/S to the mid-point of the Ar-Ar bond. The Ar \cdots Ar distance was fixed at the value obtained from the optimized geometry of the corresponding complexes. The rotation of H₂O/H₂S about its 'c' principal axis is described by the variation of angle θ . Similarly, the variation in ϕ and τ describe the rotation of H2O/H2S about it's 'a' and 'b' (C_2 symmetry axis) axes. Initially, for Ar₂···H₂O, R was varied from 2.5 to 4.0 Å in steps of 0.1 Å, whereas for $Ar_2 \cdots H_2S$, it was varied from 3.1 to 3.8 Å with the same step size, keeping all other parameters fixed. The minimum of the interaction energy was found to be at 3.4 Å for $Ar_2 \cdots H_2O$ and



Fig. 2 Principal axes system of H_2O and H_2S .



Fig. 3 Structural parameters of the complexes which were varied to generate the potential energy surfaces. A: for $Ar_2 \cdots H_2O/Ar_2 \cdots H_2S$, the starting reference geometry was a doubly hydrogen bonded $C_{2\nu}$ symmetric structure. B: for $C_2H_4 \cdots H_2O/C_2H_4 \cdots H_2S$, the reference geometry was a singly hydrogen bonded one having C_s symmetry. The rotation of H_2O and H_2S along ϕ , τ and θ coordinate defines the rotation of H_2O/H_2S along its own a, b and c principal axes.

for $Ar_2 \cdots H_2S$ it was found to be at 3.8 Å. For $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$, *R* is defined as the distance from the O/S to the center of π bond in ethylene. For these complexes, the minima of the interaction energy along *R* lie at 3.4 and 4.0 Å, respectively, for $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$. At this fixed value of *R*, each of θ , ϕ and τ were varied in steps of 10° to generate the one-dimensional potential curves. The barrier heights along different co-ordinates are reported by taking the lowest point as the reference point along that curve. All the curves, except the rotation of H_2O/H_2S about its 'c' principal axis in $C_2H_4 \cdots H_2O/H_2S$, are symmetric about 180° which is obvious considering the symmetry of the reference systems.

III. Results and discussion

III.1 Optimized geometries and the AIM parameters

Fig. 4 shows the optimized geometries of $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$ complexes at MP2 (full)/aug-cc-pVTZ level of theory. For $Ar_2 \cdots H_2O$, these two minima were obtained by imposing the C_s symmetry constraints. Unstrained geometry optimization also converged to C_s symmetry for both the structures of $Ar_2 \cdots H_2O$. For $Ar_2 \cdots H_2S$, both of the converged minima had C_1 symmetry as shown in Fig. 4.



Fig. 4 Fully optimized geometries of $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$ complexes at the MP2(full)/aug-cc-pVTZ level of theory. Distances between the atoms are shown in Å.

For both the complexes, Structure I is more stable than Structure II. The energy differences between the minima are 23 and 25 cm⁻¹, respectively, for $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$. BSSE correction increases this difference to 27 cm^{-1} in the case of $Ar_2 \cdots H_2O$ and to 34 cm⁻¹ for $Ar_2 \cdots H_2S$. Single point calculations at the CCSD(T)/aug-cc-pVDZ level were performed for the Structures I and II, in the case of both $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$, followed by the counterpoise correction. These calculations show the difference to be only 8 cm⁻¹ for $Ar_2 \cdots H_2O$, Structure I is still being the lower energy structure. The energy difference is 12 cm^{-1} for the two optimized configurations of Ar2···H2S at CCSD(T)/aug-cc-pVDZ level and the ordering of the energy is the same as the MP2 level. Thus, the differences of the energy between the Structure I and Structure II at CCSD(T) and MP2 levels are close enough and, hence, the level of calculation employed in this paper is adequate for the purpose. Fully optimized geometries of $C_2H_4\cdots H_2O$ and $C_2H_4\cdots H_2S$ are shown in Fig. 5. These geometries correspond to $O/S-H \cdots \pi$ interactions. Both the geometries have C_1 symmetry. For $C_2H_4 \cdots H_2O$, the $\angle O-H\cdots\pi$ is ~169°. For the optimized geometry of



Fig. 5 Fully optimized geometries of (a) $C_2H_4 \cdots H_2O$ and (b) $C_2H_4 \cdots H_2S$ complexes at the MP2(full)/aug-cc-pVTZ level. The distances of the hydrogen to the center of the ethylene π bond (Å) are shown in the figures.

Table 1 Electron density at hydrogen bond critical point (HBCP), ρ , and laplacian (*L*) of the electron density at HBCP calculated by AIM^a

Complex	ho/ m au	<i>L</i> /au	
$Ar_2 \cdots H_2O$	0.008	0.032	
$Ar_2 \cdot \cdot \cdot H_2S$	0.007	0.026	
$C_2H_4 \cdots H_2O$	0.021	0.031	
$C_2H_4\cdots H_2S$	0.017	0.023	

^{*a*} All these values are well within the range of hydrogen bonds as suggested by Koch and Popelier for C–H···O contacts. The ρ value at the BCP should lie within the range [0.002, 0.035] au and the Laplacian of the electron density at BCP should lie within the range [0.024, 0.139] au.²⁸

 $C_2H_4\cdots H_2S$ complex, the S-H··· π bond is more linear, the angle being ~178°. The intermolecular frequencies calculated for these optimized geometries were used to have the estimate of the zero point energy along a particular co-ordinate.

Bond critical points (BCPs) and the bond paths between the hydrogen of H₂O/H₂S and the Ar/C atoms could be located using AIM theoretical calculations. For both $C_2H_4 \cdots H_2O$ and $C_2H_4\cdots H_2S$, the bond critical points have been found connecting the hydrogen to the ethylene carbon instead of the center of C=C bond. The electron density and the Laplacian of the electron density at the BCP for the hydrogen bonds are given in Table 1. It can be seen that for all the complexes, both the parameters are well within the range suggested for 'C-H···O hydrogen-bonds' as suggested by Koch and Popelier.²⁸ Raghavendra and Arunan have recently shown that $Ar \cdots H_2O$ and $Ar \cdots H_2S$ complexes obey most of the criteria given by Koch and Popelier for C-H...O contacts to be classified as hydrogen bonded, including the necessary and sufficient condition.¹³ These are conclusions based on the static equilibrium structures. We now turn our attention to the dynamic structures.

III.2 Feature of the one dimensional potentials

III.2.A $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$. Fig. 6 shows the potential energy curves for the variation of angle θ (rotation about *c* axis of H_2X) in $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$. The nature of the curve is very shallow. The minimum on the curve corresponds to 30° for $Ar_2 \cdots H_2O$ and 40° for $Ar_2 \cdots H_2S$.



Fig. 6 Potential energy curves for the rotation of H_2O/H_2S about its 'c' principal axis in $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$ complexes.

This corresponds to the geometry where both the hydrogen atoms are pointing toward the Ar...Ar moiety in an unsymmetrical fashion. This rotation has to pass over an energy barrier of 46 cm⁻¹ for Ar₂ \cdots H₂O and 64 cm⁻¹ for $Ar_2 \cdots H_2S$, corresponding to a geometry where O/S is pointing towards the Ar···Ar bond ($\theta = 180^\circ$). Another maximum was observed with a smaller barrier, for both Ar2···H2O and $Ar_2 \cdots H_2S$, when both the hydrogen atoms are placed symmetrically between two argon atoms (the reference geometry for $Ar_2 \cdots H_2 X$ systems). This barrier is very small, being 5 cm⁻¹ for Ar₂···H₂O and 7 cm⁻¹ for Ar₂···H₂S. At $\theta = 70^\circ$, one hump was observed for Ar₂···H₂O corresponding to a geometry where one of the hydrogens is interacting with one of the argon atoms and the other hydrogen atom is away from the Ar...Ar moiety. A similar characteristic was observed for $Ar_2 \cdots H_2 S$ at $\theta = 90^\circ$. A fully relaxed optimization of this geometry indeed converged to Structure I, which is more stable than the one where both the hydrogen atoms are facing the $Ar \cdot \cdot Ar$ moiety, though the difference is very small.

Variation of energy along the τ co-ordinate (rotation about the b axis of H_2X) is shown in Fig. 7. For $Ar_2 \cdots H_2O$, the lowest points along this co-ordinate lie at 0° and 180° where both the hydrogen atoms are pointing towards the Ar...Ar bond and all five atoms are in the same plane. An energy barrier of 38 cm⁻¹ separates these minima. This barrier corresponds to $\tau = 90^\circ$, where the H₂O molecular plane is perpendicular to the Ar...Ar bond. Looking at Fig. 7, it is immediately obvious that $Ar_2 \cdots H_2S$ is much floppier along this coordinate, compared to $Ar_2 \cdots H_2O$. Given the extremely floppy nature of the potential, it is not possible to locate the minima for $Ar_2 \cdots H_2S$ along this co-ordinate. However, it is noted that for $Ar_2 \cdots H_2S$, the geometry where all the atoms are in the same plane ($\tau = 0^{\circ}$, 180°) does not correspond to the lowest point along this co-ordinate, rather the lowest point lies at ~35°, just 1 cm⁻¹ below the $\tau = 0^{\circ}$ geometry. For $Ar_2 \cdots H_2S$, the energy barrier for this rotation corresponds to $\tau = 90^{\circ}$ and the barrier is only 3 cm⁻¹.

Variation of potential energy along the ϕ co-ordinate (rotation about '*a*' axis) is shown in Fig. 8. The lowest energy point on the curve corresponds to the geometry where all the



Fig. 7 Variation of potential energy for the rotation of H_2O/H_2S about its C_2 symmetry ('b' principal axis) axis in $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$ complexes.



Fig. 8 Variation of potential energy for the rotation of H_2O/H_2S about its 'a' axis in $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$ complex.

atoms are in the same plane and both the hydrogen atoms are pointing towards the Ar···Ar moiety ($\phi = 0^{\circ}$). One local minimum could be located for both Ar₂···H₂O and Ar₂···H₂S, respectively, at 40 and 57 cm⁻¹ above the lowest energy configuration along this co-ordinate. This local minimum corresponds to O-down or S-down configurations. The maximum on the curve lies at 90° and 270° for Ar₂···H₂O and 110° and 250° for Ar₂···H₂S. This corresponds to a configuration where the oxygen/sulfur lone pair is facing the Ar···Ar moiety (Ar–O/S–Ar plane is perpendicular to the H₂O/H₂S plane). The barrier separating these minima is 60 cm⁻¹ for Ar₂···H₂O and 72 cm⁻¹ for Ar₂···H₂S.

III.2.B $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$. Fig. 9 shows the variation of energy along the θ co-ordinate (rotation about 'c' axis of H_2X) for $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$. For both $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$, the lowest energy configuration along this co-ordinate is the one where one of the hydrogens is pointing towards the π system. Rotation of H_2O and H_2S along this co-ordinate faces two barriers—one is for a configuration where both the hydrogen atoms are pointing towards the π system ($\theta = 60^\circ$ for $C_2H_4 \cdots H_2O$, $\theta = 50^\circ$ for $C_2H_4 \cdots H_2S$) and the other is for the O/S down configuration ($\theta = 240^\circ$ for $C_2H_4 \cdots H_2O$, $\theta = 230^\circ$ for $C_2H_4 \cdots H_2S$). The former causes a destabilization of 426 cm⁻¹ for $C_2H_4 \cdots H_2O$



Fig. 9 Potential energy variation for the rotation of H_2O/H_2S about 'c' principal axis in $C_2H_4\cdots H_2O$ and $C_2H_4\cdots H_2S$.



Fig. 10 Potential energy variation for the rotation of H_2O/H_2S about 'b' principal axis in $C_2H_4\cdots H_2O$ and $C_2H_4\cdots H_2S$.

and 153 cm⁻¹ for C₂H₄···H₂S. For C₂H₄···H₂O, the latter configuration faces a huge barrier of 1195 cm⁻¹ and for the C₂H₄···H₂S complex this barrier is 467 cm⁻¹.

As shown in Fig. 10, the rotation of H₂O about its 'b' principal axis (C_2 symmetry axis) passes through a barrier of 878 cm⁻¹ corresponding to a structure of C_s symmetry where the O lone pair is pointing towards the π cloud of ethylene ($\tau = 90^{\circ}$). For C₂H₄···H₂S, this barrier is 436 cm⁻¹. The minima along this co-ordinate lie again at the configurations where only one of the hydrogen is pointing towards the π -system of ethylene ($\tau = 0^{\circ}$) for both H₂O and H₂S complexes.

Fig. 11 shows the variation of energy along the ϕ co-ordinates (rotation about 'a' axis of H₂X) for all the complexes. Along this co-ordinate, the minimum of the energy lies at a 'singly hydrogen-bonded' ($\phi = 0^{\circ}$) structure for both C₂H₄...H₂O and C₂H₄...H₂S complexes. For C₂H₄...H₂O, the region near the maxima shows a plateau-like structure. Also, the barrier along this path corresponds to the structure where the oxygen lone pair is facing the π system of C₂H₄ and



Fig. 11 Potential energy variation for the rotation of H_2O/H_2S about its '*a*' principal axis in $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$.

III.3 Nature of the intermolecular vibrations

The zero point energies of the motions which are of interest are listed along with the barrier heights in Tables 2–5 for $Ar_2 \cdots H_2O$, $Ar_2 \cdots H_2S$, $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$, respectively. The normal modes of vibration corresponding to all these frequencies are dominated by internal rotation of the H_2O/H_2S monomer within the complex. The normal mode vibrations which relate to the rotation of H_2O or H_2S monomer about its 'c' principal axis could be readily identified in all the complexes. For $C_2H_4 \cdots H_2O$ and $C_2H_4 \cdots H_2S$, this motion is partly coupled to the movement of ethylene

Table 2 Zero point energies (ZPE) and barrier heights for different motions of $Ar_2\cdots H_2O$ complex

Nature of vibration	ZPE/cm ⁻¹ , Structure I	ZPE/cm ⁻¹ , Structure II	Barrier $1/cm^{-1}$	Barrier 2/cm ⁻¹
Rotation of H ₂ O about ' <i>a</i> '	55	125	60	_
Rotation of H_2O about 'c'	68	51	46	5
Rotation of H_2O about 'b'	126	41	38	_

Table 3 Zero point energies (ZPE) and barrier heights for different motions of $Ar_2 \cdots H_2S$ complex

Nature of vibration	ZPE/cm ⁻¹ , Structure I	ZPE/cm ⁻¹ , Structure II	Barrier $1/cm^{-1}$	Barrier 2/cm ⁻¹
Rotation of H ₂ S about ' <i>a</i> '	45	72	72	_
Rotation of H_2S about 'c'	56	43	64	7
Rotation of H_2S about 'b'	74	32	3	—

Table 4 Zero point energies (ZPE) and barrier heights for different motions of C_2H_4 ... H_2O complex

Nature of vibration	ZPE/cm^{-1}	Barrier $1/cm^{-1}$	$\begin{array}{c} \text{Barrier} \\ 2/\text{cm}^{-1} \end{array}$
Rotation of H_2O about 'a'	7	903	_
Rotation of H ₂ O about 'c'	128	1195	426
Rotation of H ₂ O about 'b'	175	878	

Table 5 Zero point energies (ZPE) and barrier heights for different motions of $C_2H_4\cdots H_2S$ complex

Nature of vibration	ZPE/cm^{-1}	$\frac{\text{Barrier}}{1/\text{cm}^{-1}}$	$\frac{\text{Barrier}}{2/\text{cm}^{-1}}$
Rotation of H_2S about 'a'	19	447	_
Rotation of H_2S about 'c'	88	465	153
Rotation of H_2S about 'b'	140	436	—

hydrogen atoms as well, but the contributions of H₂O/H₂S hydrogen atoms are more significant. The zero point energies which relate to the rotation of H₂O/H₂S around its 'b' principal axis are also listed in the tables. In case of $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$, the normal mode vibration which corresponds to this motion is such that the displacement of the hydrogen. which is away from the center of Ar...Ar bond, is more than the other hydrogen as was seen both in Structure I and Structure II. As we go from $Ar_2 \cdots H_2O$ to $Ar_2 \cdots H_2S$, the differences in the magnitude of the displacements of two hydrogen atoms decrease. This difference is 1:10 for both the structures of $Ar_2 \cdots H_2O$. These ratios are 1:3 and 1:4, respectively, for Structure I and Structure II of Ar₂···H₂S. For the normal mode vibration which relates to the rotation of H_2O/H_2S around its 'a' principal axis, the trend is reversed in all the complexes *i.e.* the hydrogen which is closer to the Ar $\cdot \cdot \cdot$ Ar center moves faster than the other, the ratio of the displacements of two hydrogen atoms being the same as the rotation around 'b'. For $C_2H_4\cdots H_2O$ and $C_2H_4\cdots H_2S$, these motions are localized on one of the hydrogen atoms of H_2O or H_2S . Rotation of H_2O/H_2S about its 'a' axis in these complexes is more like a free rotation of the non-bonded hydrogen about the hydrogen bond and the rotation about the 'b' axis is more like a dangling of the bonded hydrogen over the π system of ethylene.

III.4 Zero-point energies and barrier heights

From Tables 2–5, we can see that for the $Ar_2 \cdots H_2O/$ $Ar_2 \cdots H_2S$ system, all the zero-point energies are above or comparable to the barrier heights. For both the optimized geometries of $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$, the zero-point energy for the rotation of H₂O/H₂S about the 'a' principal axis is either above or comparable to the barrier heights as can be seen from Tables 2 and 3. The situation is also similar for the rotation of H_2O/H_2S about its 'c' axis. For the rotation of H_2O/H_2S about its 'b' principal axis in the case of Structure I, the zero-point energy is three times the barrier height for $Ar_2 \cdots H_2O$ and twenty five times that of $Ar_2 \cdots H_2S$. For the Structure II, in the case of $Ar_2 \cdots H_2O$, the zero point energy for this motion (rotation about 'b') is comparable to the barrier height, whereas for $Ar_2 \cdots H_2S$, the zero point energy is almost ten times higher. Thus, the rotation of H₂O/H₂S about the C_2 symmetric axis appears to be freer in nature compared to the other two motions which take the two hydrogen atoms away from the Ar. Ar system. This certainly suggests some orientational preferences, but all these wash away when we consider the zero-point energy along the other torsional modes. The zero-point energy being above the barrier heights for all these modes clearly suggests that these vibrational motions access all possible configurations, be it the oxygen/sulfur oriented towards Ar...Ar or the hydrogen atoms towards the Ar...Ar moiety. Hence, we conclude that Ar₂...H₂O and Ar₂...H₂S complexes are 'non-hydrogenbonded' complexes, based on these results.

Let us now turn our attention towards C_2H_4 systems. The differences in barriers, as we go from H_2O to H_2S systems, are pronounced when the acceptor molecule is ethylene. The hydrogen bonding capability of the Ar \cdots Ar system is poor

enough to outweigh the relative strength of H₂O as a hydrogen bond donor compared to H₂S. However, the stronger acceptor *i.e.* the ethylene π -cloud, can distinguish between a strong hydrogen bond donor and a weaker one confirming that H₂S is a far poorer hydrogen bond donor than H₂O. For the rotation of H₂O/H₂S about its 'a' principal axis which takes both the hydrogen atoms away from the π cloud of ethylene, the barrier is one hundred twenty nine times the zero-point energy along this co-ordinate for H₂O, whereas for the H₂S complex it is twenty four times. In $C_2H_4 \cdots H_2O$, for the rotation of H₂O about its 'c' axis *i.e.* along the θ co-ordinate, the barrier energy for bringing the oxygen towards the π cloud of ethylene is nine times that of the zero-point energy. The energy barrier pertaining to a configuration where both the hydrogen atoms are pointing towards the π cloud of ethylene is less but appreciable and it is thrice the zero-point energy along that co-ordinate. Along this co-ordinate, for $C_2H_4\cdots H_2S$, the energy required to bring the sulfur towards the π cloud of ethylene is five times the zero-point energy. The energy barrier to attain a configuration where both the hydrogen atoms of H_2S are pointing towards ethylene π is twice the zero point energy along this co-ordinate (Barrier 2). The barrier for rotation of H₂O/H₂S about its 'b' axis (τ co-ordinate) is five times the zero-point energy along this co-ordinate for the $C_2H_4\cdots H_2O$ complex and three times of that for the $C_2H_4 \cdots H_2S$ complex. Thus, for both the H₂O and H₂S complexes of ethylene, the 'hydrogen bonded' geometry is more preferred compared to the oxygen/sulfur-bonded geometry. All the motions which bring the oxygen/sulfur towards the π -cloud face an appreciable barrier to be overcome by the zero point energy. Thus both $C_2H_4\cdots H_2O$ and $C_2H_4 \cdots H_2S$ are 'hydrogen bonded'. However the anisotropy of the potential energy surface is much more pronounced for $C_2H_4 \cdots H_2O$ compared to $C_2H_4 \cdots H_2S$, which makes the former a 'strong' hydrogen bonded system and the latter a 'weak' hydrogen bonded system.

IV. Discussion

The results presented above indicate that even when the equilibrium geometry is 'hydrogen bonded', the zero point dynamics can break the hydrogen bond leading to no specific orientational preference favoring a hydrogen bond. This result makes one wonder if systems like Ar...HF satisfy this criterion to be called 'hydrogen-bonded'. Bader has identified both Ar...HF and Ne...HF as hydrogen-bonded complexes.²⁹ Both Ar... HF and Ne... HF have bond critical points between Ar/Ne and hydrogen and there is a bond path which connects the hydrogen to the rare gas atom. The topological properties of the bond critical point do follow most of the criteria as was suggested by Koch and Popelier for C-H···O contacts²⁸, including the necessary and sufficient criteria of hydrogen bonding.¹³ A thorough study including both experimental and theoretical results on the potential energy surface for Ar···HF has been reported earlier⁴⁸. The barrier for the bending coordinate is about 120 cm⁻¹ and the first excited state of this mode is at 52 cm^{-1} , both from the ground level. Hence, in addition to the zero point level, we have the first excited state below the barrier for Ar...HF and it can be

classified as 'hydrogen bonded'. However, for Ne...HF, it was shown by Nesbitt and co-workers that the lowest bound state lies $4-6 \text{ cm}^{-1}$ above the saddle point and it is clearly not hydrogen bonded.⁴⁹ These authors further point out that the internal rotation of HF is virtually free in He... HF and the orientation of HF becomes more directed as we move towards Ar...HF. Thus, the inherent characteristic of hydrogen bonding *i.e.* 'directionality' becomes more pronounced as we move from He to Ar in the case of the HF complexes with the rare gases. Thus, it is of no surprise that the scattering studies for rare $gas \cdots H_2O$ reveal the 'birth of a hydrogen bond' when the binding partner changes from He to Xe. The reason is that the motions which take the bonded hydrogen away from the acceptor moiety become gradually hindered as we move from He to Xe. However, in the case of $Rg \cdots H_2S$ complexes, this must not be the case as experimental evidence for the anisotropy is not found.

It is important at this juncture to point out that the absolute numbers of the barrier heights and zero point energies reported here could vary with the level of calculations. These numbers may reduce, if we perform a relaxed scan of the potential energy surface. As, for example, in $Ar_2 \cdots H_2O$, for rotation of H_2O around its 'c' axis, if we optimize the stationary points, the difference between the lowest and the highest point on the curve decreases to 31 cm^{-1} from 46 cm^{-1} . However, it is clear that a variation of this magnitude would not alter the trends or conclusions observed here. Moreover, the main purpose of this work is not to establish any benchmark, rather to testify a concept which can serve as a guideline for a system to be classified as 'hydrogen bonded'.

We realize that the procedure described above to characterize a system as hydrogen bonded is too elaborate and some general guidelines could be useful. The torsional frequencies for all these complexes are typically of the order of $50-300 \text{ cm}^{-1}$. Hence, the zero point energies are going to be at the most 200 cm^{-1} and more often less. It is suggested that for a system to be classified as hydrogen bonded, the barrier along a torsional coordinate that breaks the hydrogen bond be sufficiently above the zero point energy so that there is at least one bound level. Looking at the typical numbers given above, a barrier of 350 cm^{-1} (1 kcal mol⁻¹) could ensure that an anisotropic orientation could favour a hydrogen bonded geometry. One could reach this conclusion by optimizing only the minimum and saddle point along the torsional coordinate. It should be emphasized again that this barrier is for the large amplitude motion and not related to the binding energy of the complex as a whole.

Clearly, this conclusion could be extended to any temperature and any medium. In a crystal, if the thermal energy along a coordinate that can break the hydrogen bond is larger than the barrier along that coordinate, this orientation will not be stabilized. When the temperature reduces significantly and the pressure increases, this motion becomes restricted, leading to the observation of hydrogen bonded geometry. Thus, though H_2S remains a gas at room temperature and has 12 neighbours when it freezes at -60 °C, at lower temperatures and high pressures, it has a crystal structure exhibiting hydrogen bonding. It is interesting to find that Loveday *et al.* in their work on crystalline H_2S have observed that formation of a hydrogen bond involves 'a change as simple as suppressing free rotation about a single axis.'³¹

There have been several attempts to decompose the binding energy of a 'hydrogen bond' to probe which of the physical forces dominate in hydrogen bonding.⁵⁰⁻⁵³ As pointed out earlier, initially it was expected to be a 'simple electrostatic interaction'. However, it soon became apparent that forces due to electrostatic interaction, induction, dispersion and exchange repulsion all contribute to different extents in various hydrogen bonds and there is evidence for partial covalency as well. It has been pointed out that dispersion plays a dominant role in 'hydrogen bonded' geometries of second row hydrides compared to the first row hydrides,⁴ though dispersion is usually considered to be van der Waals forces. While these studies are useful in identifying the forces involved in different hydrogen bonding environments, it is clear that there is no single physical force that can be identified as a hydrogen bonding force. Irrespective of the forces that dominate, hydrogen bonding is directional. This directionality can manifest itself to experimental and theoretical observations, if the barriers to vibrational motions that break the hydrogen bond are significantly above the thermal energy available along these coordinates. For some systems, such as $Ar_2 \cdots H_2S$, the barrier is below the zero point energy and clearly this complex is not hydrogen bonded, even at zero kelvin.

Finally, the definition given by Pimentel and McClellan appears to be the most appropriate for a hydrogen bond. According to them, "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". We suggest that one piece of evidence for the presence of the hydrogen bond be that at least the zero point energy along any torsional degree of freedom that can break a hydrogen bond be significantly below the barrier energy along that coordinate. Unlike other evidence proposed in the literature, we submit that the evidence proposed here is absolute.

V. Conclusions

To conclude, the analysis of the potential energy barriers for different motions of H₂O/H₂S in Ar₂···H₂O/Ar₂···H₂S and $C_2H_4\cdots H_2O/C_2H_4\cdots H_2S$ complexes has been conducted and compared to the zero-point energies for the respective motions. It is found that for $Ar_2 \cdots H_2O/Ar_2 \cdots H_2S$, the barriers for different motions of H2O/H2S are comparable or even lower than the zero point energy along these co-ordinates, whereas for $C_2H_4\cdots H_2O/C_2H_4\cdots H_2S$, the barriers lie well above the zero point energy along the co-ordinates. These results indicate that, although the equilibrium structures of $Ar_2 \cdots H_2O$ and $Ar_2 \cdots H_2S$ exhibit a 'hydrogen bonded' geometry, the geometry cannot be stabilized, even at zero Kelvin. This is evidenced by the large amplitude motions of H₂O and H₂S in the microwave spectral studies where the dynamical structure of H₂O and H₂S were almost spherical in the complexes. On the other hand, both $C_2H_4 \cdots H_2O$ and $C_2H_4\cdots H_2S$ are 'hydrogen bonded' according to the present analysis. Though the magnitude of the anisotropy in $C_2H_4\cdots H_2S$ is less compared to that of the H₂O complex,

 $C_2H_4 \cdots H_2S$ emerges as a 'hydrogen bonded' complex in the present analysis and the interaction is strong enough to be detected at the low temperature of the supersonic expansion. This is indeed the case as has been evidenced by the microwave studies. Such an analysis and verification is essential to shed light on the possible existence/non-existence of a specific hydrogen-bonding interaction. It is not enough to conclude about the existence of hydrogen bonding between a donor and an acceptor from the rigid *ab initio* geometry optimization and AIM theoretical calculations. It is to be stressed that the anisotropy of the hydrogen bonding interaction should be strong enough to 'hold' the 'hydrogen bond' at least at the zero point level, otherwise it is better to think of it as non-existent. At a given temperature, the thermal energy along a coordinate that can break the hydrogen bond should be below the barrier along that coordinate.

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