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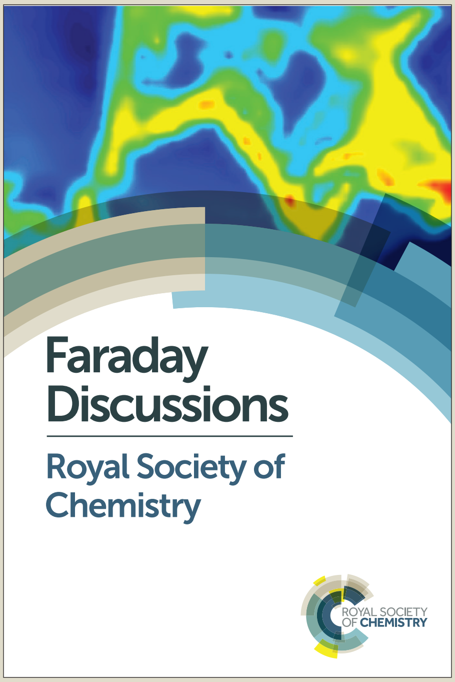

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Dynamics of the chemical bond: Inter- and intra-molecular hydrogen bond

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In this Discussion, we show that a static definition of a 'bond' is not viable by looking at a few examples for both inter- and intra-molecular hydrogen bonding. This follows from our earlier suggestion (Goswami and Arunan, *Phys. Chem. Chem. Phys.* 2009, **11**, 8974) which showed a practical way to differentiate 'hydrogen bonding' from 'van der Waals interaction'. We report results from ab initio and atoms in molecules theoretical calculations for a series of Rg•••HX complexes (Rg = He/Ne/Ar and X = F/Cl/Br) and ethane-1,2-diol. Results for the Rg•••HX/DX complexes, show that Rg•••DX could have a 'deuterium bond' even when Rg•••HX is not 'hydrogen bonded', according to the practical criterion given by Goswami and Arunan. Results for ethane-1,2-diol show that an 'intra-molecular hydrogen bond' can appear during a normal mode vibration which is dominated by the O---O stretching, though a 'bond' is not found in the equilibrium structure. This dynamical 'bond' formation may nevertheless be important in ensuring the continuity of electron density across a molecule. In the former case, a vibration 'breaks' an existing bond and in the later case, a vibration leads to the 'bond' formation. In both cases, the molecule/complex stays bound irrespective of what happens to this 'hydrogen bond'. Both these cases push the borders on the recent IUPAC recommendation on hydrogen bonding (Arunan et al. *Pure. Appl. Chem.* 2011, **83** 1637) and justify the inclusive nature of the definition.

Introduction

In September 2013, *Chemical and Engineering News* turned 90 and it chose 9 discoveries in Chemistry that 'transformed the planet'.[1] Top most among them was the 'chemical bond'. One would expect that nearly 75 years after Pauling's classic book[2] on *The Nature of Chemical Bond* was first published, chemists, if not the world, understand chemical bond. However, Ritter mentions in the lead article of this special issue '*...chemists still struggle to come up with an apt description of a chemical bond*'.[3] Hoffman was quoted in Ritter's article: '*Any rigorous definition of a chemical bond is bound to be impoverishing'*.

In this Discussion, we address a more specific, and perhaps one of the most important chemical bonds discovered by chemists, the hydrogen bond. If Hoffman felt a rigorous definition of 'a chemical bond would be impoverishing', a rigorous definition of 'a hydrogen bond' was thought to be impossible. It took 14 experts and about 25 referees (and numerous others interested in the outcome) before a modern definition of a 'hydrogen bond' was accepted by the International Union of Pure and Applied Chemistry in 2011.[4] A short definition had to be followed by 3 pages of caveats listing six criteria and six characteristics, with a warning that 'these are not exhaustive'. A technical report running to 18 pages accompanied the definition detailing the rationale behind the new definition.[5]

Why was defining the hydrogen bond such an arduous task? To understand this, we need to go back to the ideal gas law and van der Waals equation[6]. Ideal gas law was derived with two assumptions: gaseous molecules can be treated as point masses occupying no space and there is no attractive interaction between them. Van der Waals introduced two parameters, aptly denoting them *a* and *b*, and corrected the ideal gas law. The parameter *a* accounted for the attractive forces between molecules and the parameter *b* accounted for the finite volume of the gaseous molecules, which in effect reduces the volume of the container leading to the term 'excluded volume'. This led to all intermolecular forces being called 'van der Waals forces' and the intermolecular interaction being noted as 'van der Waals interaction'. However, in the early part of 20th century, the advent of x-ray diffractometers among other things, produced accurate structural information in the solid phase. It was discovered that each H_2O molecule is surrounded by four other H_2O molecules in ice but each H_2S molecule is surrounded by twelve other H_2S molecules in solid H_2S.[1] They were as different as apples and oranges, see Figure 1. Only a sphere could accommodate 12 neighbours and H_2S is effectively spherical. The difference was stunning and it clearly warranted different names for intermolecular interaction found between H_2O molecules and that found between H_2S molecules. The anisotropic interaction between H_2O molecules was christened 'hydrogen bonding' while the isotropic interaction between H_2S molecules were left as 'van der Waals interaction'.

It is interesting to learn that the concept of 'hydrogen bonding' was being discussed even before Lewis/Langmuir[7,8] defined a 'covalent bond'. The reader is referred to the IUPAC technical report[5] and references therein for historical accounts. It is important to realize that van der Waals was not aware of the physical forces involved in the interaction between molecules and did not spell them out. The several authors who invoked hydrogen bonding to explain the difference between the macroscopic properties of different molecules could not spell out what 'hydrogen bonding' was made of either. Pauling included a chapter titled 'Hydrogen bond' in his book[2]. He had concluded that the hydrogen which was already bonded to an atom could not form another bond and hence 'hydrogen bonding' must be simple electrostatic dipole-dipole interaction. We know today that intermolecular interactions between H_2O molecules as well as that between H_2S molecules arise from electrostatic forces between multipoles, inductive forces, exchange correlation, charge transfer/covalency and London dispersive forces to varying extents.

In terms of the physical forces involved, there is really no difference between 'hydrogen bonding' and 'van der Waals interactions'. It is not clear to the Authors of the present Discussion, who equated 'van der Waals forces' to London dispersive forces[9]. That dispersion is attractive at all orientations was taken to mean that dispersion is 'isotropic'. Clearly, earlier results such as evident from Figure 1 could have led to such (mis)understanding. Equating of van der Waals forces to London dispersive forces is indeed unfortunate as it has taken the due credit for dispersive forces away from London. One hopes that dispersive forces are referred as only London forces from now on.

In the next section, we refer to the recent IUPAC definition[4] and a previous criterion[10] for hydrogen bonding and provide the motive for the present work. This is followed by a brief description of theoretical methods used. Results on several test cases, which push the borders of these definitions, are discussed next followed by some concluding remarks.

Definitions of hydrogen bonding

H_2O and H_2S: Dimer and solid

The recent IUPAC recommendation[4] defines hydrogen bonding as *an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation*. During the discussion of this definition, one of the suggestions was to have 'when' instead of 'in which' before the 'evidence of bond formation' in the definition given above.

If one looks at the structures of ice and solid H_2S when they freeze, they are stunningly different, see Figure 1. Water is hydrogen bonded and H_2S has van der Waals interaction. On the other hand, if one looks at the optimized geometry of H_2O dimer and H_2S dimer, see Figure 2, they look very similar and both are hydrogen bonded. These seemingly contradicting observations were resolved by Goswami and Arunan[10] who suggested that the barriers to torsional motions which can break hydrogen bonds are more important than the barrier along the stretching coordinate which lead to the dissociation of the dimers. Nearly all prior work on hydrogen bonding[2,11-13] concentrated on the barrier along the stretching coordinate and decided on some arbitrary cut off on the dissociation energies to distinguish between hydrogen bonding and the van der Waals interaction. Goswami and Arunan[10] suggested that, *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.*

Goswami and Arunan[10] realized that the thermal motions in solid H_2S leads to an average 'spherical shape' and predicted that H_2S solid at lower temperature should exhibit anisotropic packing and hydrogen bonding. They did not realize that it had already been proved by Loveday et al.[14] who reported the crystal structure of D_2S at lower T and higher P. Loveday et al. had indeed concluded that H_2S can be a good model system where we can tune the hydrogen bond strength from "absent or very weak to structurally significant". The choice of D_2S is interesting as the heavier isotopologue would have shorter amplitude vibrations compared to the lighter isotopologue.

Rare gas•••HX complexes

The crystal structure of D_2S discussed above pegs a question. Could we have a complex in which XD•••Y has one bound level below the torsional barrier and XH•••Y does not? Could we have a 'deuterium bond' even when a 'hydrogen bond' is not possible? The complexes formed between rare gas atoms and hydrogen halides provide such a possibility. The IUPAC report[5] points out that the He•••HF complexes have HF as a nearly free rotor whereas in Kr•••HF complexes, this motion remains a bending vibration. It was decided to investigate several Rg•••HX complexes and determine the bending frequency and the barrier for internal rotation of HX within the complex. Results from these detailed calculations on a series of Rg•••HX (Rg = He/Ne/Ar and X = F/Cl/Br) show that it is indeed possible to have 'deuterium bond' when a 'hydrogen bond' does not exist according the criterion given by Goswami and Arunan.[10]

Ethane-1,2-diol

In the previous section, we have considered the cases where a large amplitude vibration breaks a hydrogen bond existing at an equilibrium structure. Could we have a molecular system in which, a bond between two atoms is not apparent at the equilibrium structure but forms during the course of a normal mode vibration? Ethane-1,2-diol exhibits such a possibility. Whether an intra-molecular hydrogen bond is present in this molecule, commonly known as ethylene glycol, has been hotly debated. This molecule has been a text book example for 'intra-molecular hydrogen bond' finding a mention in Eliel's classic book.[15] Microwave spectroscopy reveals that the gauche conformer is more stable than the trans conformer.[16] It was attributed to the intra-molecular hydrogen bond though microwave spectroscopy cannot provide a direct evidence for the bond. After careful NMR experiments on this molecule, Roberts and coworkers[17] concluded that "*the bulk of the NMR evidence indicates that intra-molecular hydrogen bonding between the hydroxyl groups is unlikely to be a significant factor in determining that preference, except possibly in fairly non-polar solvents*". Though they did not find any evidence, they were cautious in their conclusion. Atoms in molecules (AIM) theoretical analysis on this molecule by various authors[18-20] did not show any evidence of a bond critical point between the H of one OH and the O of another OH. The ∠O-H---O angle is about 108°, even below the generously given lower limit for the hydrogen bond, ∠X-H---Y, angle of 110°, by the IUPAC recommendation.[4] The distance between H and O is less than the sum of their van der Waals radii but more than the sum of hydrogen bond radii for OH and O.[21-23] However, both the van der Waals 'radii' and hydrogen bond 'radii' do not account for the effect of anisotropy and conclusions from them are suspect. The IUAPC recommendation specifically discourages the use of van der Waals radii in deciding about hydrogen bond. An X-ray study including charge density analysis[23] of the solid sample did not find any evidence for hydrogen bond as well, though the distance between two OH groups was slightly larger than that in the gas phase, due to the strong inter-molecular hydrogen bonds. As of now, the only experimental evidence for the intra-molecular hydrogen bond is a small red-shift of about 30 cm^{-1} in the O-H stretching frequency.[24] However, this is smaller than the intercept in the frequency shift versus bond energy correlation plot for O-H•••O hydrogen bonds, 40 cm^{-1}, implying a binding energy of zero or no bond.[25] While the experimental lack of evidence remains uncontested, the lack of a bond critical point in AIM theoretical analysis, as an evidence against a bond, has been criticized severely.[26] Recently introduced 'non covalent index (NCI) plot'[27] does reveal some evidence for the intra-molecular hydrogen bond.

Are all the discussions mentioned above only semantic, as everyone agrees that the gauche conformer is more stable than the trans conformer? This debate is indeed important, as ethane-1,2-diol is part of the training set for parametrizing molecular mechanics program.[28] It is a ubiquitous synthon in sugars[29] and many pharmacologically active materials[30] and it is commonly used in step-growth polymerizations for the synthesis of polyurethanes and polyesters[31]. It is important to understand the properties of the monomer as thoroughly as one could. Moreover, the presence of a bond i.e. local concentration of electrons in between two atoms, as revealed by a bond critical point in AIM analysis is important in the concept of an 'electron wire'[32] enabling the formation of a cooperative net work as in liquid water. What if thermal vibrations bring the two atoms close enough to be 'bonded'? This could still help in the concept of an 'electron wire' and in some respect it would make more sense when such thermal motions can lead to this 'bond formation' leading to direct, continuous electron density between the two atoms. Atoms in molecules theoretical analysis has recently been employed along the reaction coordinate to understand bond formation and breaking during a reaction.[33] We report the AIM theoretical analysis as a function of the O---O stretching vibration in ethan-1,2-diol which indeed shows evidence of the intra-molecular hydrogen bond formation as the two OH groups come closer.

Computational methods

All calculations reported in this work have been carried out at MP2 level with correlation consistent triple zeta basis set, aug-cc-pvtz (aug-cc-pvdz in the case of ethane-1,2-diol), using Gaussian 09 programme suit.[34] Our main objective in carrying out these calculations are conceptual rather than accurate determination of the structure and energetics and in our experience this method provides reasonable results. All optimized structures were confirmed to be true minima using frequency calculations. Energies were corrected for basis set superposition errors using the counterpoise method[35] inherent in Gaussian09. Atoms in molecules theoretical analysis was carried out using the AIMALL program.[36]

Results and discussion

Hydrogen vs. deuterium bond: Rg•••HX complexes

The Rg•••HX complexes have been studied in detail both experimentally and theoretically. The reader is referred to a recent comprehensive study of Murdachevaew et al.[37] for a detailed discussion of the multidimensional potential surface and all the associated energy levels. Our objective in this Discussion is more conceptual and limited to determining the barrier for the internal rotation of HX which can lead to the isomerization between the Rg•••HX and Rg•••XH minima. This is compared to the zero point energy along this bending/internal rotation coordinate for both Rg•••HX and Rg•••DX to determine if the interaction is strong enough to preserve the orientation. We use one-half of the normal mode frequency as the zero point energy in this conceptual exercise. Accurate calculation of the energy levels for this vibrational motion which can change from torsion to hindered rotation to free rotation is quite involved[38] and is beyond the scope of this discussion.

Table 1 lists our results on Rg•••HX complexes for Rg = He/Ne/Ar and X = F/Cl/Br. The results are not surprising. The barrier for internal rotation decreases as Rg•••HF > Rg•••HCl > Rg•••HBr. For a given HX, the barrier increases as He•••HX < Ne•••HX < Ar•••HX. The results given in Table 1 may not be the most accurate estimates but they are reasonable. For example, the lowest bound level for Ne•••DF has been experimentally determined to be 4-6 cm^{-1} above the barrier for internal rotation[39] and Table 1 gives this to be about 8 cm^{-1}.

All the Ar•••HX complexes are 'hydrogen bonded' according to the criterion given by Goswami and Arunan[10]. They do exhibit a bond critical point between Ar and H and hence they satisfy the criteria for a bond by Bader[40] and also by Koch and Popelier[41]. According to Bader, the presence of a bond critical point between two atoms is enough to conclude the presence of a 'bond'. Koch and Popelier were trying to distinguish 'van der Waals interaction' from C-H•••O hydrogen bond and listed eight criteria based on the electron density topology for the C-H•••O hydrogen bonds.

The 'hydrogen bonds' in these cases are strong enough to preferentially orient the H of HX towards Ar in the minimum. Not surprisingly, all Ar•••DX complexes are more localized than the Ar•••HX complexes and deuterium bond is stronger than hydrogen bond, a well known observation. The calculations were not carried out for Kr•••HX and Xe•••HX, for which the barriers will be significantly higher resulting in a stronger hydrogen bond. This observation is not new and has been pointed out in many earlier publications, including in a crossed beam scattering study[42] with rare gases and H_2O, aptly titled as the 'birth of a hydrogen bond'.

Clearly, none of the He•••HX complexes are 'hydrogen bonded', even though all of them exhibit a bond critical point between He and H in their optimized structure.[43] Hence, the He•••HX complexes satisfy the criterion for a bond by Bader, but these do not satisfy either the criterion given by Koch and Popelier for C-H•••O hydrogen bonds[41] or that given by Goswami and Arunan[10]. For the He•••HX (X = F/Cl/Br), the electron densities at the BCP are 0.0017/0.0012/0.0009, respectively[43], below the limit of 0.002 recommended by Koch and Popelier[41]. Even for He•••DX, the zero point energies are higher than the barrier. While for He•••DF and He•••DBr, the zero point energies are significantly higher, for He•••DCl, the zero point energy is only 2 cm^{-1} above the barrier. This implies that the DCl in He•••DCl will be more dominantly oriented as 'deuterium bonded' compared to He•••HCl as 'hydrogen bonded'. It is important to note that all the He•••HX complexes as a whole are bound even though the nearly free internal rotation can break the 'hydrogen/deuterium bond'.

The results from Ne•••HX complexes offer an interesting middle ground. All Ne•••HX complexes have zero point energy above the barrier. The Ne•••DF and Ne•••DBr complexes also have zero point energy above the barrier. However, the Ne•••DCl has the zero point energy just below the barrier. It does have one bound level below the barrier making it 'deuterium bonded' according to the criterion by Goswami and Arunan[10], even when Ne•••HCl is not 'hydrogen bonded' according to the same criterion. The potential energy scans along the bending/internal rotation coordinate for He/Ne/Ar•••HCl are shown in Figures 3, 4, and 5, respectively and these provide a nice summary of the three possibilities.

We note that the bending frequencies for the Rg•••HCl complexes and the corresponding zero point energies are lower than those of both the Rg•••HF and Rg•••HBr complexes. The barriers for internal rotation reduces by close to 50 % from Rg•••HF to Rg•••HCl, but drops by only 10 – 20 % from Rg•••HCl to Rg•••HBr. Clearly, these barriers cannot explain the unusual trend in frequencies, which indicate that the bending motion is stiffer in Rg•••HBr compared to Rg•••HCl. The reduced masses for this normal coordinate do not vary much and the changes in frequencies are dominated by the changes in force constants. For example, the reduced masses for Ne•••HF/HCl/HBr complexes for the bending vibration are 1.0374/1.0257/1.0193 amu, respectively. The force constants for these are 0.0108/0.0021/0.0060 mdyn Å^{-1}, respectively. In any case, these are floppy complexes that are very weakly bound and the one-dimensional analysis we report here are not intended for accurate description of the inter-molecular potentials.

We reiterate that these results are more conceptual than quantitative, and they can explain some experimental observations. The crystal structure of D_2S showed evidence for 'hydrogen bonding' more readily than that of H_2S.[14] Another manifestation of significant difference in vibrational averaging was seen in the example of Ar•••H_2S complex. The experimental rotational constant for Ar•••D_2S complex was higher than that of Ar•••H_2S complex.[44] It is the result of a significantly shorter intermolecular distance in Ar•••D_2S complex as compared to that in Ar•••H_2S complex, outweighing the increase in mass. Similarly, the gas phase experimental (vibrationally averaged) structure of HI dimer and DI dimer show significant differences, which can be explained by the dramatic differences in zero point vibrations.[45]

In the earlier days of hydrogen bond[2], it was considered that only H attached to F, O, and N atoms could form hydrogen bond. These molecules typically have larger dipole moment due to the larger electronegativity difference. Clearly, intermolecular potential for interaction of these molecules with hydrogen bond acceptors have significant anisotropy which could be detected readily by macroscopic experiments. On the contrary, for molecules such as H_2S, HCl, and HBr, the intermolecular potential is not isotropic, but it is much less anisotropic in comparison and their experimental manifestations could not be detected earlier. These examples show that a hydrogen bond that exists in the equilibrium structure could be broken even at zero Kelvin due to zero point vibrations. Depending on the actual difference between the barrier and zero point energy, the intermolecular potential may effectively become isotropic, leading to a structure for H_2S solid at – 60 °C in which H_2S looks spherical. At even lower temperatures, the thermal motion is restricted pushing the molecular system in to potential wells that are no longer isotropic.

Ethane-1,2-diol

As discussed earlier, the presence of an intra-molecular hydrogen bond in ethane-1,2-diol has been hotly debated in the recent years. Previous calculations by various authors[18-20] had concluded that there is no bond critical point between the H of one O-H group and the O of the other O-H group. Having seen the effect of even zero point vibration breaking a hydrogen bond, one wonders if a large amplitude vibration in ethane-1,2-diol could lead to a hydrogen bond. Much of the earlier work on this molecule focused on the O-H stretching frequency and the small red shift observed. An inspection of its normal mode vibrations in our calculations revealed that the nominal O---O stretching mode appears at 173 cm^{-1}. We carried out AIM theoretical analysis along this vibrational coordinate, starting from the equilibrium structure. During this vibration, the distance between the two atoms would increase and decrease compared to that in the equilibrium distance. However, when it increases, a BCP is unlikely to appear and that was indeed the case. When the distance between the two atoms decreases, a BCP does indeed appear. The potential energy curve for this vibration along with the AIM molecular graphs are shown in Figure 6. The energy levels for v = 0 and 1 are shown for comparison, assuming harmonic oscillator energies.

As evident from Figure 6, there is no BCP corresponding to intra-molecular hydrogen bond at the equilibrium structure. A BCP does not appear during zero point vibration either. However, when the value of this normal coordinate increases to just below the outer turning point of v = 1, a BCP starts appearing corresponding to an intramolecular hydrogen bond. This being a low frequency vibration, thermal population at 300 K is close to 44 % and clearly thermal vibrations can bring the two OH groups close enough to be 'bonded', even according to the AIM analysis. Interestingly, when an intra-molecular hydrogen bond is formed, a five member ring would be formed and a ring critical point has to appear to satisfy the topological requirement and it does appear. If the newly formed bond is weaker, the ring critical point would be very close to the bond critical point. A ring critical point does indeed appear and at larger values of the normal coordinate, it moves towards the centre of the ring, as expected.

Clearly, as the ethane-1.2-diol molecule vibrates, an intra-molecular hydrogen bond does appear satisfying the requirements of the proponents of AIM theory. One natural question that arises now is whether an isotopic substitution with a heavy atom would restrict the amplitude of vibration to an extent that no BCP is formed during the vibration. To test this, the calculations were repeated with ^{18}O and D substitutions. In every case, a BCP does appear during the vibration. As mentioned earlier, Roberts and co-workers[17] could not find any evidence for spin-spin coupling through the intramolecular hydrogen bond in their NMR experiments. It would be interesting to see the temperature effect on the NMR spectrum of very dilute solution of ethanle-1,2-diol in a non-polar solvent.

What then is a hydrogen bond?

This analysis of ethane-1,2-diol has led us to a contrasting conclusion. A careful analysis of the structure of H_2S dimer and crystal led us to propose a practical criterion to differentiate hydrogen bonding and van der Waals interaction. It does make sense. An analogy with internal rotation in ethane would convince a reader, if (s)he is not convinced yet. Ethane, and substituted ethanes can exist in different minima accessible by internal rotation of the C-C. These minima are characterized as trans, gauche and eclipsed depending on the dihedral angle. The barrier for this internal rotation is typically about 3-5 kcal mol^{-1}, very similar to the hydrogen bond energy. At ambient conditions, the vibrational energy along this coordinate, usually called a torsion, is limited and the molecule could exist as trans and gauche, for substituted ethanes. However, if this vibrational energy is increased, this could become a hindered rotation and eventually a free rotation. Three movie files given in supporting information show the three motions, torsion, hindered rotation and free rotation. If an ethane molecule has free internal rotation, it would not have trans, gauche or eclipsed conformers, but it would remain ethane. For it to become two methyl radicals, there has to be sufficient energy given along the C-C stretching coordinate, which is typically much larger than the barrier along the internal rotation coordinate.

The difference between barriers along torsional coordinates and the stretching coordinate for a hydrogen bond would typically be much less than that of ethane. This has led to the arbitrary classification of hydrogen bonding as different from van der Waals interaction. However, with the advent of experimental and theoretical methods, even small differences in the barriers can lead to experimentally observable manifestations. Clearly, hydrogen bonding is a specific sub set of the van der Waals interaction.

The results for ethane-1,2-diol show that an intra-molecular hydrogen bond, which does not exist in an equilibrium structure, could be formed during a vibration. While it would also be broken in this vibration, this would indeed be important in ensuring that a bond path is created for electron density to flow from O to H, through this transient bond.

Conclusions

We have considered two examples of hydrogen bonds in this Discussion. First one is formed between a rare gas and HX in its equilibrium structure. However, depending on the rare gas and X, this may not survive even the zero point vibration. We could have a strong ‘hydrogen bond’ which can ensure the directionality of a hydrogen bond in one extreme. We could have a weak hydrogen bond that does not hinder a free rotation of HX leading to an apparent isotropic interaction, often called van der Waals interaction. The second example has the potential of an intra-molecular hydrogen bond. The equilibrium structure does not have a corresponding BCP, but during thermal vibration this bond could be formed. Indeed, the recent IUPAC definition of the hydrogen bond insisting on evidence could end with ‘when there is evidence of a bond’. The dynamics due to molecular vibrations cannot be ignored. Could an experiment be carried out in which zero point vibrations can be viewed?

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† Electronic Supplementary Information (ESI) available: A power point presentation showing the torsional vibration in ethane. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Table 1. Barrier for bending/internal rotation of HX/DX in Rg•••HX/DX complexes and zero point energies (ZPE) (in cm^{-1}) along this coordinate.

Complex	*Barrier*	*ZPE(HX)*	*ZPE(DX)*
He•••HF	20.7	48.7	35.4
He•••HCl	12.2	20.5	14.9
He•••HBr	9.7	41.6	30.1
Ne•••HF	39.9	66.6	47.8
Ne•••HCl	21.8	29.4	21.0
Ne•••HBr	18.7	49.9	35.5
Ar•••HF	130.8	98.8	70.5
Ar•••HCl	76.2	48.9	34.2
Ar•••HBr	63.9	56.5	40.2

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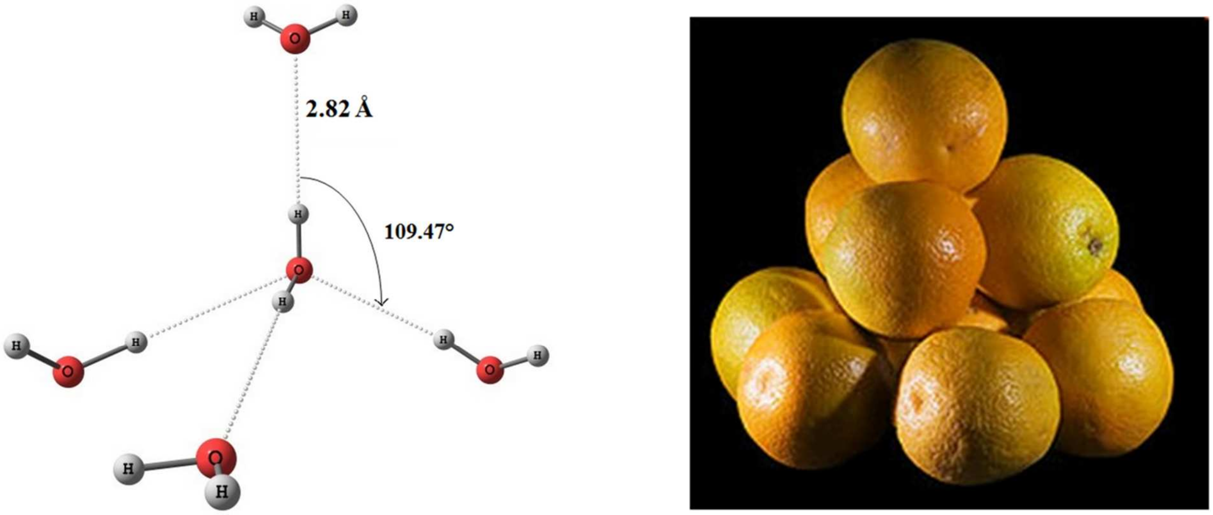

Figure 1. Comparison of the structures of solid H_2O (left, close to real) and solid H_2S (right, cartoon). The pack of oranges is from Wikipedia. Packing of H_2O is anisotropic influenced by the O-H•••O 'hydrogen bonds' and packing of H_2S is isotropic having 'van der Waals interaction'.

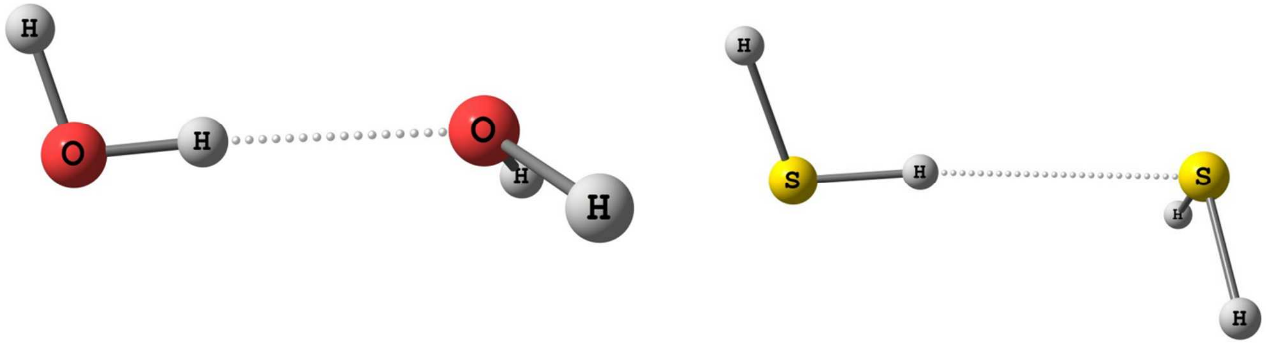

Figure 2. Optimized structures of H_2O dimer and H_2S dimer, with hydrogen bonds shown by dotted lines.

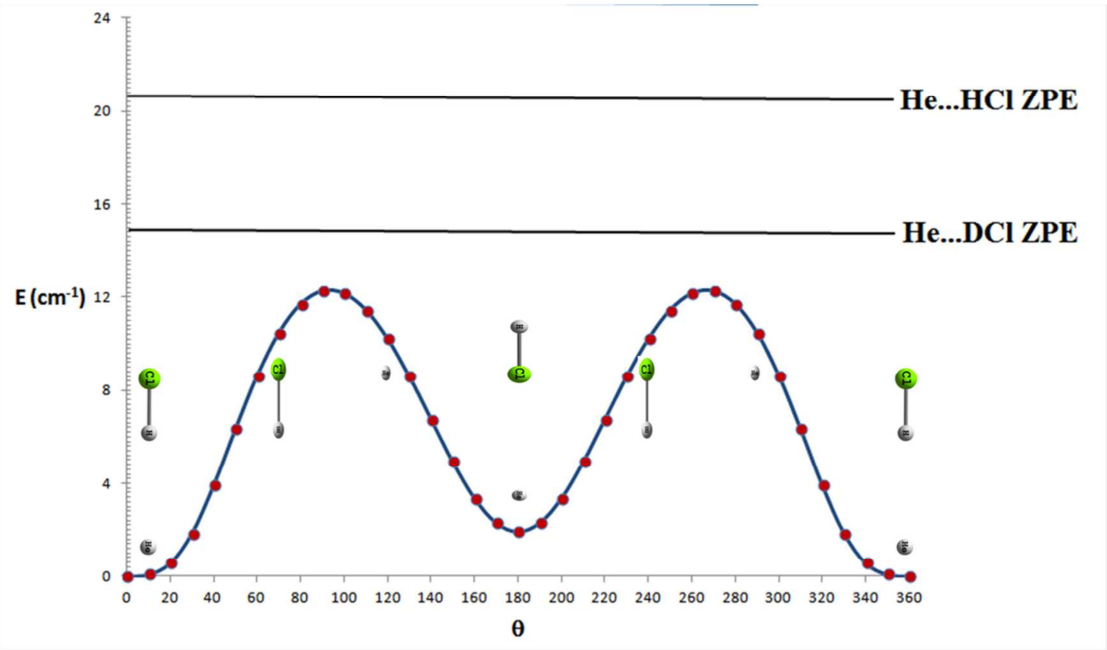

Figure 3. The potential energy curve along the bending/internal rotation coordinate for He-HCl, with the zero point energy marked for He---HCl and He---DCl. The ‘hydrogen/deuterium bond’ is not strong enough to restrict internal rotation.

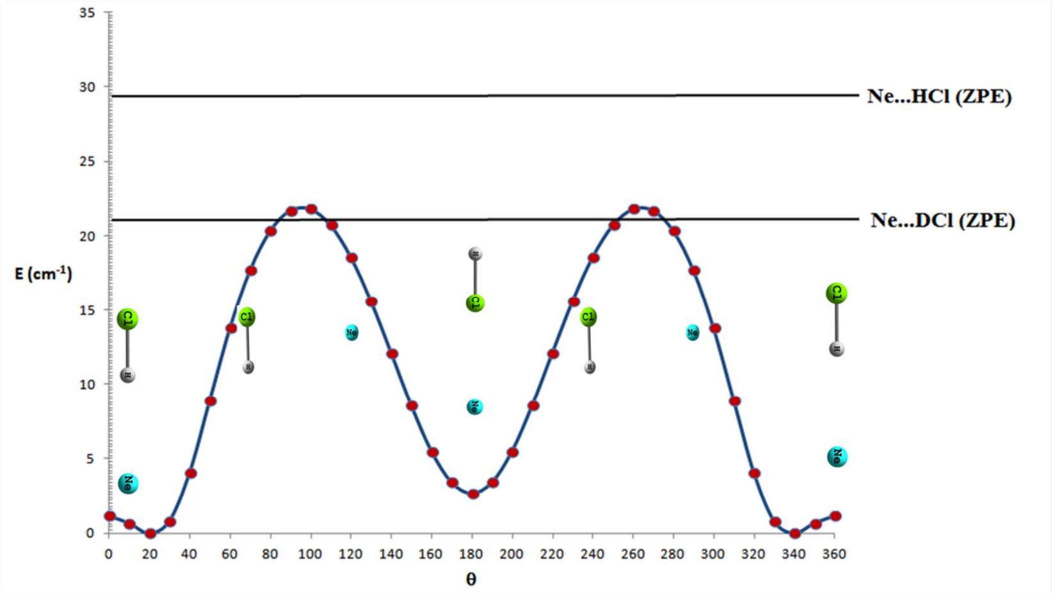

Figure 4. The potential energy curve along the bending/ internal rotation coordinate for Ne-HCl, with the zero point energy marked for Ne---HCl and Ne---DCl. The ‘hydrogen bond’ is not strong enough to restrict internal rotation but ‘deuterium bond’ is. It may be noted that the frequencies were calculated at the hydrogen bonded minimum.

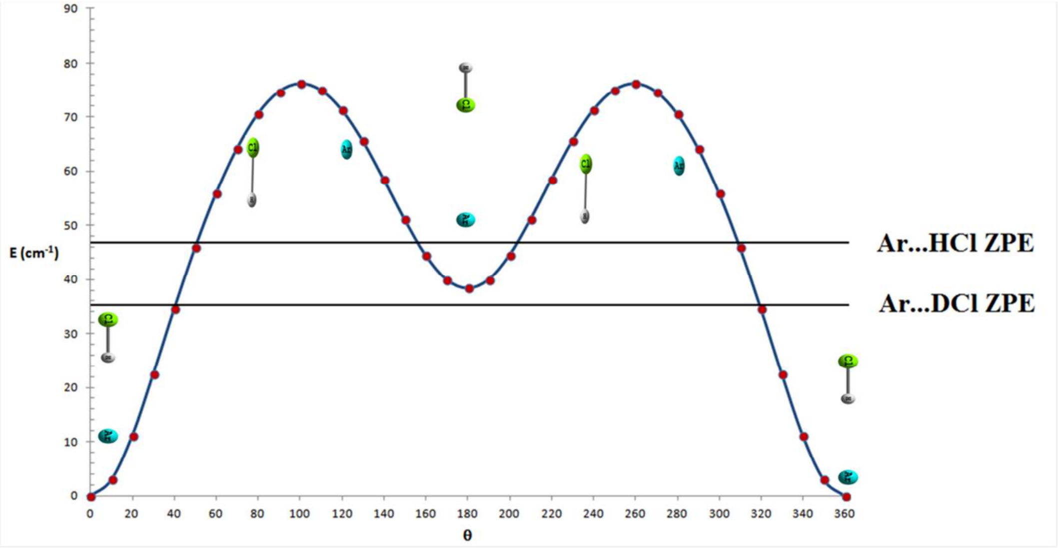

Figure 5. The potential energy curve along the bending/ internal rotation coordinate for Ar-HCl, with the zero point energy marked for Ar---HCl and Ar---DCl. The 'hydrogen/deuterium bond' is strong enough to restrict the internal rotation. It may be noted that the frequencies were calculated at the hydrogen bonded minimum.

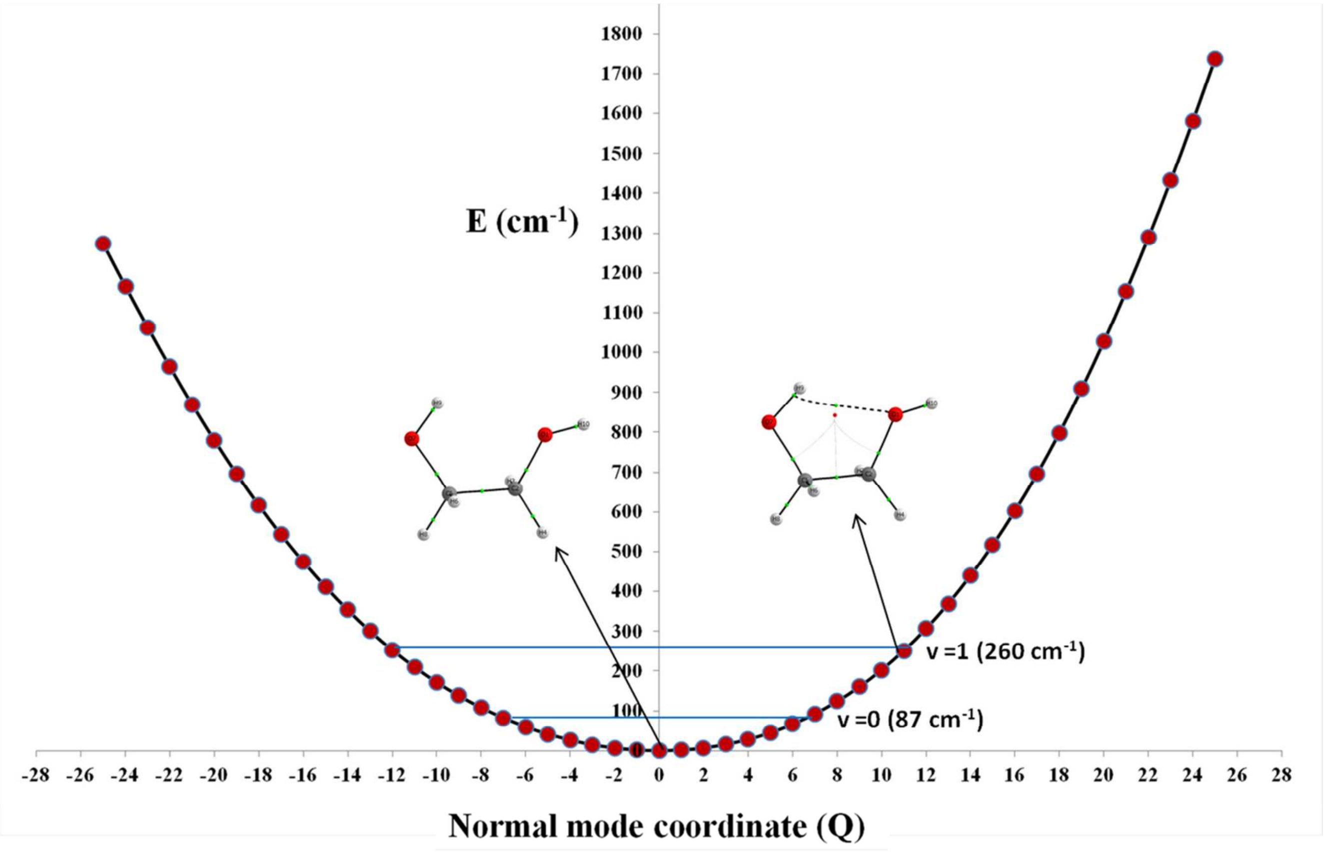

Figure 6. The potential energy along the nominal O---O stretching coordinate. At the equilibrium structure, the AIM molecular graph shows no BCP between H of one OH and the O of the other OH. As the O---O distance reduces, a bond critical point corresponding to the intra-molecular hydrogen bond appears along with a ring critical point, starting from step 11 in this coordinate. This is below the outer turning point for the v =1 level.