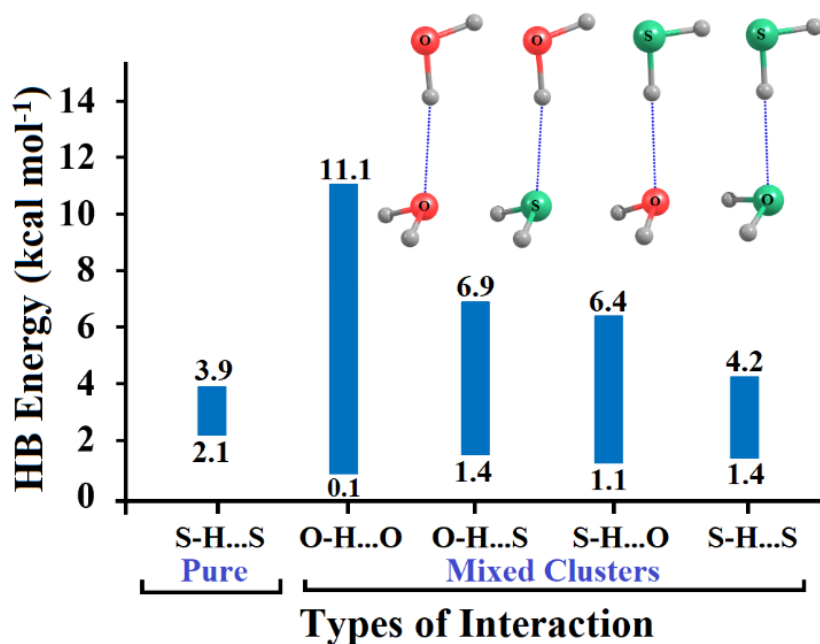# Uncovering the Individual Hydrogen Bond Strengths and Cooperativity in Pure $(H_2S)_n$ and Mixed $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) Clusters

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Abstract: The present investigation deals with the estimation individual hydrogen bond (HB) energy in pure $(H_2S)_n$ (n = 3 to 8) and mixed $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) clusters. A deeper understanding of individual interactions in these clusters are brought out in terms of energetics. Such a knowledge from the experimental studies is difficult. Therefore, the present investigation is important. The calculated results show that the hydrogen bonding strengths in these clusters range from 0.10 to 11.06 kcal mol^{-1} at the MP2(full)/aug-cc-pVTZ level. The O-H…O HB being the strongest (0.10 to 11.06 kcal mol^{-1}), followed by O-H…S HB (1.36 to 6.89 kcal/mol), S-H…O HB (1.08 to 6.39 kcal mol^{-1}), and S-H…S HB (1.35 to 4.23 kcal mol^{-1}) being the weakest. The hydrogen bonding energies in dimers follow the same rank ordering, with lower energies due to the loss of cooperativity. Thus, cooperativity contributions in the hydrogen bonding range from 0.83 to 5.96 kcal mol^{-1}. The HB energies in pure $(H_2S)_n$ clusters are similar but slightly smaller compared to those in mixed $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) clusters. These results provide important insights into the structure and energetics of hydrogen bonding in pure and mixed clusters, and sheds light on the various interactions in chemical and biological systems. Such a profound knowledge of individual energetics is missing from the literature.

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1 Introduction

Hydrogen bonds (HBs) have received a lot of attention from experimental and theoretical researchers due to their importance in many chemical and biological processes. It plays a key role to understand the structure and properties of many organic compounds, as well as the supramolecular assemblies and biomolecular reactivity.[1-8] The interconnected network of HBs formed by the molecules such as water, ammonia, hydrogen fluoride, alcohols, etc. leads to the formation of supramolecular aggregates/clusters.[9-13] Despite a large number of investigations conducted on this topic, the nature of the HBs and their energetics estimations are the very active subjects of research. There are many studies reported on water clusters.[13-25] Although, in comparison of the water clusters relatively less studies reported on the hydrogen sulphide $(H_2S)_n$ and mixed $(H_2O)_m(H_2S)_n$ clusters. Therefore, in order to understand the various properties at molecular level such as micro-solvation process, it is of utmost importance to study the structure, stability and HB strength in $(H_2S)_n$ and mixed $(H_2O)_m(H_2S)_n$ clusters. For this purpose, there are several experimental and theoretical studies have been carried out which utilizes small model molecular aggregates/clusters to represent the bulk system.

Saykally and co-workers[13-16] carried out many spectral studies to investigate the structure and dynamics of various water $(H_2O)_n$ (n=2-6) clusters. These studies revealed that cyclic trimer, tetramer and pentamer clusters of water have minimum energies structures. Water hexamer having cage-like structure with eight HB is the most stable one. Kulcke *et al.*[17] studied the absorption behaviour of small water clusters $(H_2O)_n$, (n = 2-5). The stretching frequency of O-H group involved in the HB for n = 2 to 5 were seen to be red shifted from 3601 cm^{-1} in the dimer to 3360 cm^{-1} in the pentamer. Apart from these experimental methods a number of theoretical studies which focus on the structure, stability, enthalpy and binding energies (BE) in the water clusters. For instance, Suresh and Naik,[18] reported the enthalpy of a breaking away of a single water from the liquid bulk water to be 5.6 kcal mol^{-1}. Silverstein *et al.*[19] gave HB enthalpy values in water to be 1.9 kcal mol^{-1}. These values were reported to be 1.5 kcal mol^{-1} by Smith and co-workers.[20] Iwata[21] reported the average HB energy (total binding energy divided by the number of HBs) in W_{20} and W_{25} to be 6.0 and 6.1 kcal mol^{-1} respectively. Based on the quantum theory of atoms in molecules (QTAIM) and interacting quantum atoms (IQA), Guevara-Vela et al.[22] reported the strength of HBs and cooperativity effects in pairs of dimers in water hexamers. A large number of studies have been carried out on the structural properties of water clusters; we skipped the discussion here for brevity.[23-27]

Hydrogen sulphide is the one of the interest of HB study because sulphur-centered hydrogen bonding (SCHBs) have drawn more attention due to their prevalence and importance in both materials science and biological systems.[28,29] Many different properties (*i.e.*, dipole moment, polarities, dispersion energy contribution etc.) of H_2S clusters were observed from the typical hydrogen-bonded clusters.[30–33] H_2S dimer has been the subject of a number of theoretical and experimental studies reported in the literature.[34-40] For instance, using IR-predissociation spectroscopy, Wategaonkar *et al.*[34] detected the red-shift in proton-donating S-H bond by 31 cm^{-1} in H_2S dimer. Ciaffoni *et al.*[38] reported the BE (1.68 $\pm$ 0.02 kcal mol^{-1}) for H_2S dimer where high-resolution diode laser spectroscopy has been applied for the detection of H_2S at ppm level. They utilized different transitions within the region of the $\nu_1 + \nu_2 + \nu_3$ and $2\nu_1 + \nu_2$ combination bands around 1.58 µm. Using microwave spectroscopy, Das *et al.*[39] provided the geometrical parameters (*i.e.*, S-H···S = 2.778(9)Å and ∠S-H···S = 175(7)°) of the H_2S dimer. Dreux *et al.*[35] calculated the BE for H_2S dimer at the CCSD(T)/ha(Q+d)Z (where ha(X+d)Z represents cc-pVQZ for H atoms and aug-cc-pV(Q+d)Z for S atoms) level to be 1.66 kcal mol^{-1}. Lemke[36] carried out an extensive investigation using MP2, MP4, CCSD and CCSD(T) methods and showed that the BE of the H_2S dimer at the

CCSD(T)/CBS[D,T,Q] level of theory is 1.70 kcal mol^{-1}. Bandyopadhyay et al.[40] studied the $(H_2S)_n$ clusters (n = 2 - 4) employing high-level quantum chemical calculations and calculated the BEs (1.67 kcal mol^{-1}) at the CCSD(T)/CBS level with counterpoise corrected geometries at the MP2/aug-cc-pV(Q+d)Z level of theory. These values match excellently with the experimentally measured value by Ciaffoni et al.[38] Compared to the water clusters, limited reports have been observed on the potential energy surface (PES) of $(H_2S)_n$ clusters .[41-44] Moreover, these studies show a remarkable difference in various aspects of the two types of clusters viz., H_2O and H_2S clusters; geometrically, energetically and in terms of non-covalent interactions (NCIs). For example, H_2O tetramer prefers cyclic structure, whereas H_2S tetramer prefers cage structure. Furthermore, Wategaonkar and coworkers[31] have emphasized that dispersion plays a major role in generating a force of attraction in the O–H…S HB. Besides, this it is not yet clear how replacing individual monomeric moieties one at a time will progressively causes the pronounced change in appearance and stability of cluster. Therefore, a systematic analysis of $(H_2O)_m(H_2S)_n$ mixed clusters would be beneficial to comprehend these modifications caused by the substitution of oxygen with sulphur or vice-versa.

The mixed $(H_2O)_m(H_2S)_n$ clusters have not been studied as much as water and hydrogen sulphide clusters. In the literature, two conformers of $(H_2O)_1(H_2S)_1$ dimer, one having O–H…S and the other having S–H…O HB were proposed and observed in cryogenic matrix.[45-47] Tremblay et al.[47] shows the conformers of $(H_2O)_1(H_2S)_2$ and $(H_2O)_2(H_2S)_1$ of mixed trimers in the Ne gas matrix. Novoa et al.[48, 49] reported the BE (18.73 kcal mol^{-1}) for $(H_2O)_1(H_2S)_1$ dimer. They also studied the neutral $(H_2O)_m(H_2S)$ where m = 4 cluster and reported the zero-point corrected interaction energy (16.97 kcal mol^{-1}) at MP2/ TZ94+P level. Hillier et al.[50] reported three minimum energy structures for m = 4 cluster with relative energy (16.50 kcal mol^{-1}) at MP2/6-311++g** level. They also reported four structures for m = 7 clusters with relative energy (RE) 10.20 kcal mol^{-1} at the same level of theory. Maeda and Ohno[51] studied the Microsolvation of H_2S using ab initio potential energy surfaces by the scaled hypersphere search method. They reported the various of $(H_2O)_m(H_2S)$ where m = 5 - 7 clusters with RE 10.9 kcal mol^{-1} at the MP2/6-311++G(3df,2p) level. structures Bandyopadhyay et al.[52] reported the various conformer of $(H_2O)_m(H_2S)_n$ mixed clusters up to tetramers. They also reported the BE for $(H_2O)_m(H_2S)_n$ (m + n = 2 to 4) clusters in the range between 2.66 to 20.76 kcal mol^{-1}.

As evident from the above discussion, the studies reported on $(H_2O)_m(H_2S)_n$ mixed clusters are limited to structure determination and their BEs calculation. Furthermore, the evolution of HB energies has been carried out only in the smaller clusters (mostly in dimers). In order to understand the physical phenomenon at the molecular level, a deeper comprehension of individual HB strength is indispensable. Importantly, there is no direct information available in the literature about the energetics of these individual HBs and cooperativity in these clusters. By employing the cardinality principle, Deshmukh and Gadre[53-60] developed a molecular tailoring approach based (MTA-based) method for the estimation of individual intramolecular HB energy (IHBE) in a variety of systems. This MTA-based methodology was further extended by Deshmukh et al.,[61-65] for estimating the individual HB energy and cooperativity in various molecular clusters. Patkar and Deshmukh[66-68] utilized this method for estimation of self- and cross-associated HB energies in mixed molecular clusters. In order to explore the energetics of individual HBs in $(H_2O)_m(H_2S)_n$ mixed clusters, we employed the molecular tailoring approach (MTA) based method in the present study.

2 Methods and Computational Details

In the present work, initial geometries of $(H_2S)_n$ (n = 3 to 8) and $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) cyclic clusters, were taken from the refs. 40 and 52. We re-optimized these geometries at MP2 level of theory using the aug-cc-pVDZ (referred to as aVDZ, hereafter) basis sets. The vibrational frequency calculations confirmed the local minima nature of all the re-optimized geometries. For the optimized geometries of $(H_2S)_n$ and $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) cyclic clusters, see Figure 1-3. For the Cartesian coordinates of all the geometries, see electronic supporting information (ESI). The single point (SP) energy calculations were performed on these clusters and fragment geometries at the MP2(full) level of theory employing aug-cc-pVTZ (mentioned as aVTZ hereafter) basis sets. All the calculations were performed by using the Gaussian 16 program package.[69]
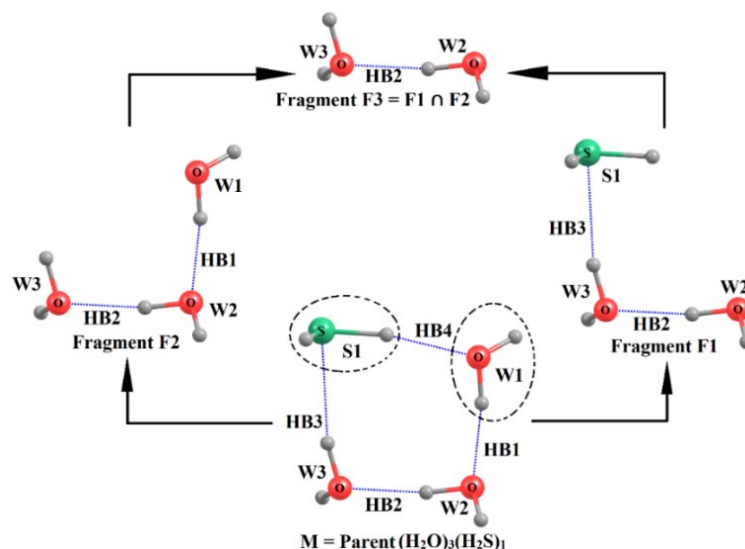
Scheme 1: Fragmentation scheme for the estimation of energy of hydrogen bond HB4 in $(H_2O)_3(H_2S)_1$ (denoted as M).

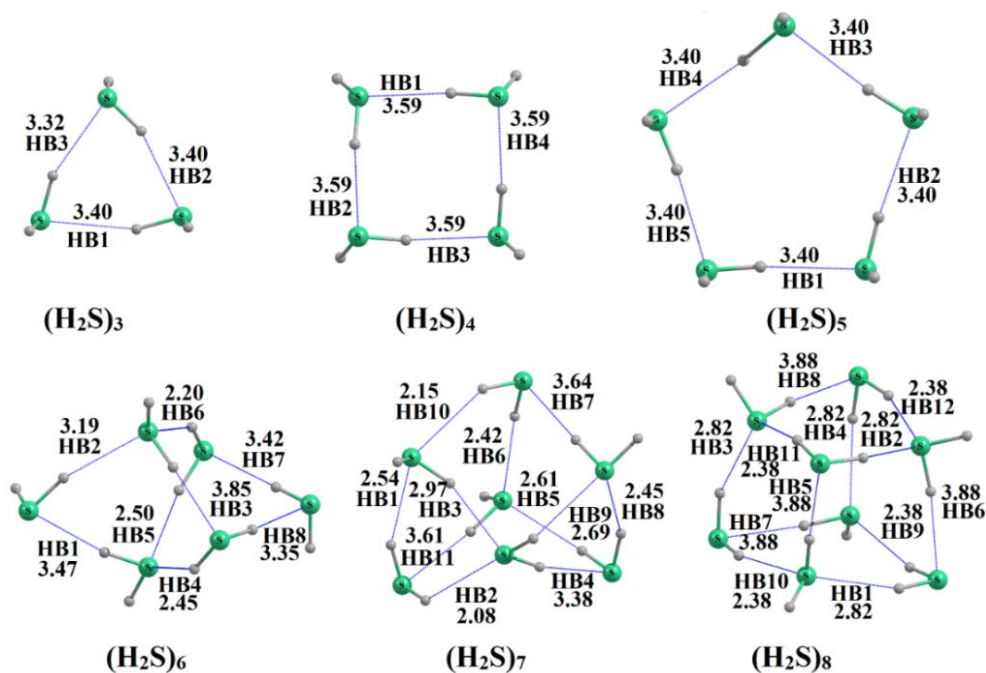**Figure 1.** The MP2/aVDZ optimized geometries of $(H_2S)_n$ (n = 3 to 8) clusters along with HB labels and their respective energies (kcal mol^{-1}) at MP2(full)/aVTZ level.
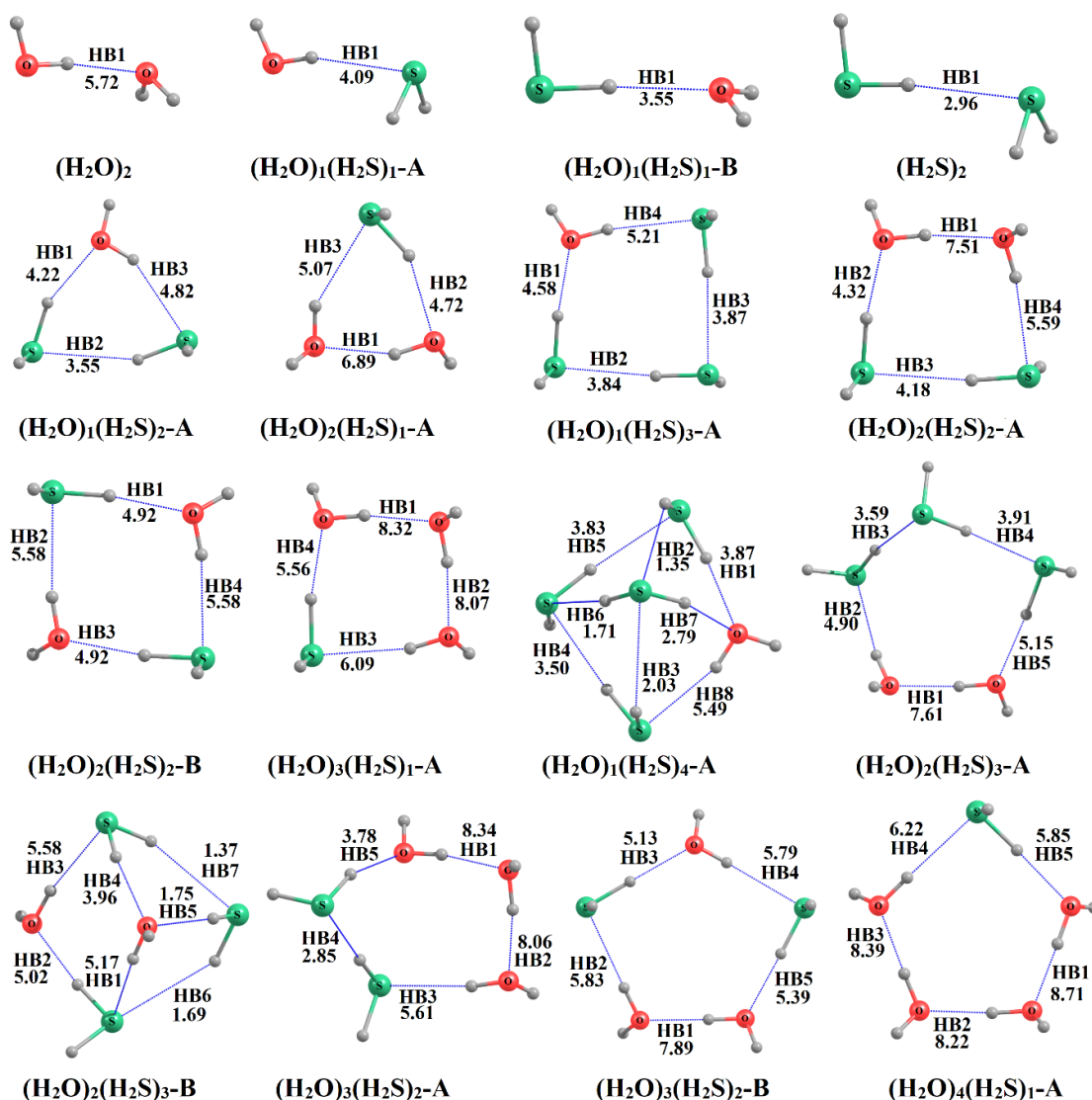
Figure 2. The MP2/aVDZ optimized geometries of $(H_2O)_m(H_2S)_n$ (m + n = 2 to 5) clusters along with HB labels and their respective energies (kcal mol^{-1}) at MP2(full)/aVTZ level.

The schematic fragmentation procedure for the estimation of energy of a hydrogen bond HB4 in the cyclic $(H_2O)_3(H_2S)_1$ tetramer, with three water molecules, indicated as W1, W2 and W3 and a H_2S molecule as S1, is illustrated in Scheme 1. As seen in Scheme 1, the HB4 consists of an interaction between the S-H bond of S1 and O atom of W1. By removing W1 and S1, respectively, two primary fragments F1 and F2 are generated from the parent cyclic $(H_2O)_3(H_2S)_1$ tetramer. On virtually putting F1 and F2 fragment geometries together, the geometry of the parent tetramer can be regenerated, except that: (i) the S-H…O hydrogen bond HB4 is missing and (ii) there is a double counting of structural part *viz.*, the dimer W2…W3, common to both primary fragments F1 and F2. This common dimer W2…W3 is the secondary fragment, F3 (*cf.* Scheme 1). On subtracting the energy of fragment F3 from the sum of energies of fragments F1 and F2, the energy of parent cyclic $(H_2O)_3(H_2S)_1$ tetramer may be obtained. However, thus-calculated energy of cyclic $(H_2O)_3(H_2S)_1$ tetramer misses out on the energy of HB4. With this understanding, the energy of HB4 is obtained as $E_{HB4}^{MTA} = (E_{F1} + E_{F2} - E_{F3}) - E_M = [(-551.6531867) + (-229.0530609) - (-152.6963207) - (-628.0187843)] = 0.0088574$ a.u. $= 5.56$ kcal mol^{-1} at MP2(full)/aVTZ level.
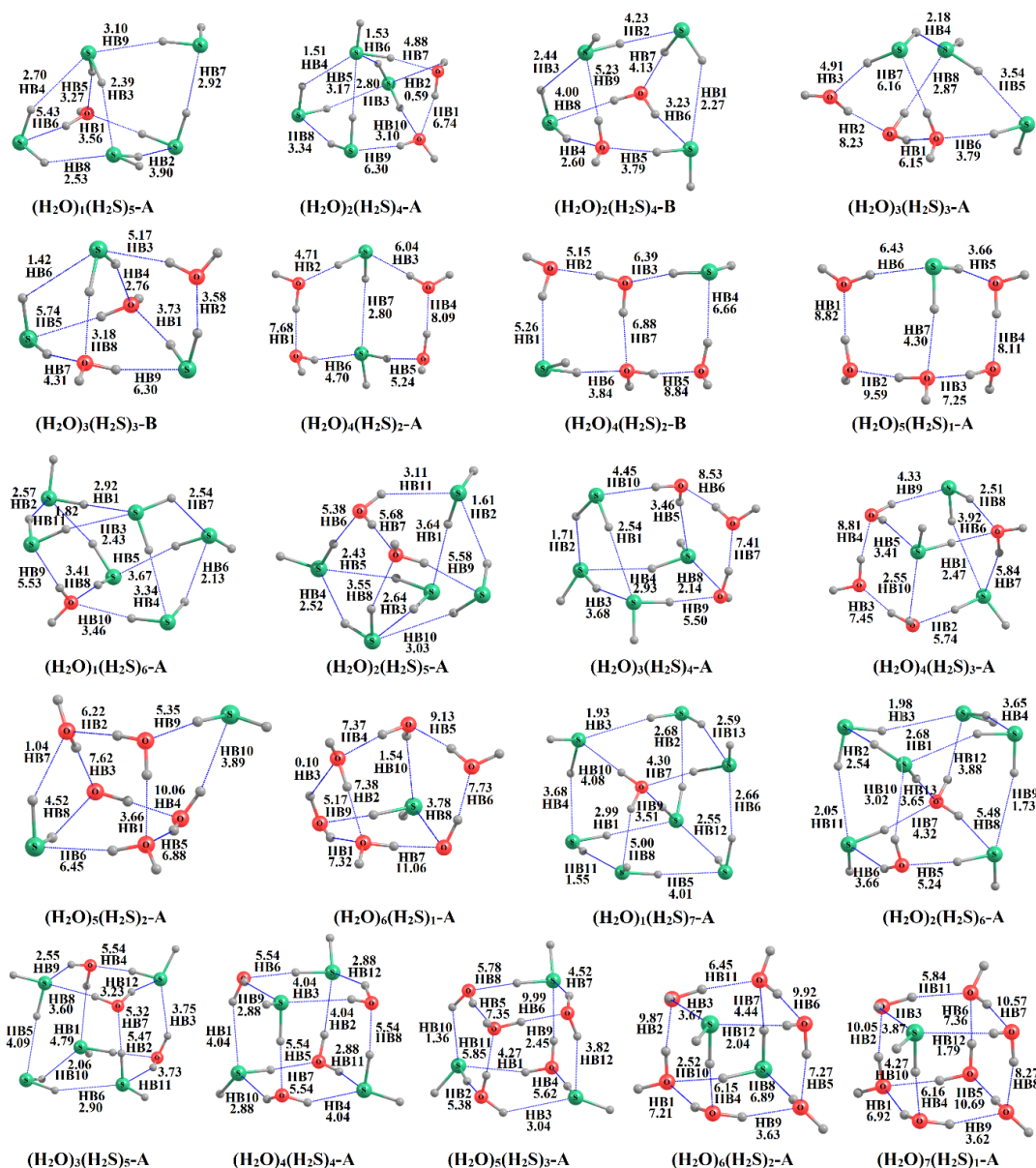
Figure 3. The MP2/aVDZ optimized geometries of $(H_2O)_m(H_2S)_n$ (m + n = 6 to 8) clusters along with HB labels and their respective energies (kcal mol^{-1}) at MP2(full)/aVTZ level.

Note that if we isolate (chopped out) HB4 from the network (as a dimer W1…S1), then it will not have the cooperativity contribution of the other HBs. The energy of the latter is obtained as $E_{HB4}^{Dimer} = (E_{W1} + E_{S1}) - E_{W1…S1}^{Dimer} = (-76.3435786) + (-398.9471068) - (-475.2960839) = 0.0053985$ a.u. $= 3.39$ kcal mol^{-1}. The geometry of W1…S1 dimer was obtained by chopping it from the cyclic $(H_2O)_3(H_2S)_1$ cluster. It ensures that this geometry of the dimer is similar to that in the parent cluster. The E_{HB4}^{Dimer} does not have the cooperativity contribution $E_{HB}^{Coop.}$. The difference between E_{HB4} and E_{HB4}^{Dimer} is the cooperativity contribution to the HB4, which is 2.17 kcal mol^{-1}.

3 Results and Discussion

3.1 Hydrogen Sulphide Clusters

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The individual HB energy (E_{HB}^{MTA}), dimer energy (E_{HB}^{dimer}), and the cooperativity contributions ($E_{HB}^{Coop.}$) in $(H_2S)_n$ (n = 3 to 8) clusters have been estimated using the aforementioned MTA-based method (*cf.* Table 1). As can be seen from Table 1, the individual HB energies are seen to fall between 2.08 to 3.88 kcal mol^{-1}. The respective S-H…S HB energies in the dimers are moderately smaller and fall in the range of 1.67 to 3.02 kcal mol^{-1}. These calculated values of cooperativity contribution towards the individual S-H…S HB in these clusters fall in the smaller dimer energies are attributed to the loss in cooperativity due to the other HBs in the network. Thus- range between -0.10 to 0.90 kcal mol^{-1}. The negative value of cooperativity indicates that the HB energy in the dimers is numerically larger in magnitude than the corresponding HB energy in the clusters (anti-cooperativity). This effect is seen to be pronounced in some of these HBs. For instance, consider hydrogen bonds HB1 and HB10 in $(H_2S)_7$ cluster. A closer look at HB1 and HB10 suggests that they are involved in the formation of anti-cooperative HBs, wherein, the direction of these two HBs are opposite to each other. Literature suggests that the formation of such an anti-cooperative network of HBs has smaller or negative contributions to the HB cooperativity.[61-68] For instance, cooperativity contribution towards HB1 is 0.01 kcal mol^{-1} and that for HB10 is -0.02 kcal mol^{-1}. For this reason, the energy of these HBs is smaller (2.54 and 2.15 kcal mol^{-1}, respectively). For similar reasons, the energy of some HBs in $(H_2S)_7$ and $(H_2S)_8$ clusters are the smallest among all the S-H…S HBs. One of the key observations from Table 1 is that the HBs in all the cyclic clusters have energies in between 3.32 and 3.59 kcal mol^{-1} suggesting

Table 1: The individual S-H…S HB energies (kcal/mol), distances (in Å) and angles (degrees), in $(H_2S)_n$ clusters calculated at MP2(full)/aVTZ level, along with the respective cooperativity contribution (kcal/mol).

$(H_2S)_n$	HB Label	HB Distance [a]	HB Angles	E_{HB}^{MTA}	E_{HB}^{dimer}	$E_{HB}^{Coop.}$
$(H_2S)_3$	HB1-HB2	2.74	159	3.40	2.87	0.53
	HB3	2.73	160	3.32	2.79	0.53
$(H_2S)_4$	HB1-HB4	2.65	174	3.59	3.02	0.56
$(H_2S)_5$	HB1-HB5	2.66	174	3.40	2.86	0.55
$(H_2S)_6$	HB1	2.63	169	3.47	2.85	0.63
	HB2	2.67	162	3.19	2.83	0.37
	HB3	2.58	174	3.85	2.97	0.88
	HB4	2.80	141	2.45	2.33	0.12
	HB5	2.74	161	2.50	2.56	-0.06
	HB6	2.79	147	2.20	2.12	0.08
	HB7	2.66	174	3.42	2.88	0.55
	HB8	2.65	175	3.35	2.93	0.42
$(H_2S)_7$	HB1	2.77	153	2.54	2.53	0.01
	HB2	2.94	125	2.08	1.67	0.41
	HB3	2.67	160	2.97	2.41	0.56
	HB4	2.62	169	3.38	2.65	0.73
	HB5	2.74	150	2.61	2.54	0.08
	HB6	2.72	165	2.42	2.32	0.11
	HB7	2.63	176	3.64	2.99	0.66
	HB8	2.77	154	2.45	2.42	0.03
	HB9	2.91	121	2.69	2.12	0.56
	HB10	2.86	139	2.15	2.17	-0.02
	HB11	2.63	174	3.61	2.92	0.70
$(H_2S)_8$	HB1-HB4	2.73	154	2.82	2.59	0.23
	HB5-HB8	2.59	172	3.88	2.98	0.90
	HB9-HB12	2.73	161	2.38	2.48	-0.10

[a] The S-H covalent bond distances are in the range of 1.35-1.36 Å.

that these HBs are relatively strong. These large value of HB energies in cyclic clusters may be due to formation of homodromic (positive cooperativity) cycle with all HBs in same direction. Also, the HB energies in higher-order clusters are, in general, larger. For example, the energies of all the HBs in $(H_2S)_7$ and $(H_2S)_8$ clusters are in the range of 2.08 to 3.88 kcal mol^{-1}.

3.2 Water verses Hydrogen Sulphide Clusters

Hydrogen sulphide is structurally similar to water and has the same number of valence electrons. Moreover, the electronegative atoms in both molecules belong to the same group of the periodic table. Differences in their physical properties are primarily due to their different polarities (H_2O 1.45 $x 10^{-27}$cm^3 and H_2S 3.95 $x 10^{-27}$cm^3). The dipole moment of H_2S (0.97 D) is significantly smaller than that of H_2O (1.85 D).[70-71] Both dipole-dipole and hydrogen bonding interactions between H_2S molecules are incredibly weak, whereas these interactions between H_2O molecules are quite strong. The similarities and dissimilarities between them invite comparisons.

As we discussed above, the individual S-H…S HB energies and respective dimers energies are seen to fall between 2.08 to 3.88 kcal mol^{-1} and 1.67 to 3.02 kcal mol^{-1}, respectively. These individual S-H…S HB energies are seen extremely smaller than the O-H…O HB energies (0.40 to 11.60 kcal mol^{-1}), present in the pure water clusters, reported by Ahirwar et al.[61] The O-H…O HB energies in the dimer also seen to be moderately larger (1.50 to 5.40 kcal mol^{-1}) than the respective S-H…S HB energies (1.67 to 3.02 kcal mol^{-1}) in the dimer. These small energies in the H_2S clusters are due to the smaller cooperativity contribution. On the other hand, the strong O-H…O HBs strength observed due to the strong cooperative networking effect of other HBs. The calculated values of cooperativity contribution towards the individual S-H…S HB in pure $(H_2S)_n$ clusters fall in the range between -0.10 to 0.90 kcal mol^{-1}. This cooperativity contribution towards S-H…S HB is relatively very small as compared to the O-H…O HB (-1.10 to 6.90 kcal mol^{-1}) in water. This weak cooperativity contribution could be one of the possible reasons for the formation of extremely weak HB in the $(H_2S)_n$ clusters.

3.3 Water-Hydrogen Sulphide Mixed Clusters

3.3.1 The O-H…O HB Energy and Cooperativity in Cyclic $(H_2O)_m(H_2S)_n$ Clusters

In similar fashion, the energy of self-associating O-H…O HBs by MTA in $(H_2O)_m(H_2S)_n$ (n + m = 2 to 8) clusters were calculated (cf. Tables S2-S3). Except for HB3 in $(H_2O)_6(H_2S)_1$-A), these O-H…O HB energies are found to be in the range 3.62 to 11.06 kcal mol^{-1}. These calculated O-H…O HB energies in $(H_2O)_m(H_2S)_n$ (n + m = 2 to 8) clusters are seen to be similar or of little smaller in strengths as compared to those in pure water clusters, reported by Ahirwar et al.[61] The respective O-H…O HB energy in the dimers are in the range of 3.99 to 5.69 kcal mol^{-1}. The enhancement in the O-H…O HBs strength due to the cooperative networking effect of other HBs is in between -0.62 and 5.96 kcal mol^{-1}; except HB3 in $(H_2O)_6(H_2S)_1$-A cluster. The cooperativity contribution towards HB3 in $(H_2O)_6(H_2S)_1$-A is -1.26 kcal mol^{-1}. This may be due to the weaker nature of the hydrogen bond HB3 (large O-H…O distance (2.35 Å) Also, the energy of HB3 is smallest (0.10 kcal mol^{-1}) possibly due to the structural arrangement where the acceptor water molecule simultaneously donates and accepts one hydrogen bond, while the donor water molecule also donates and accepts one hydrogen bond. This structural feature is denoted as AD(W$_D$)$\rightarrow$W$_A$(AD) and was attributed to the formation of weak HBs in water clusters.[67] Indeed, the strength of HB3 in $(H_2O)_6(H_2S)_1$-A is the lowest (0.10 kcal mol^{-1}) among all the other O-H…O HBs, it has been suggested in the literature that strong HBs have a large contribution to cooperativity.

3.3.2 The O-H…S HB Energy and Cooperativity in Cyclic $(H_2O)_m(H_2S)_n$ Clusters

The estimated O-H…S HB energies and the cooperativity contributions are summarised in Tables S4 and S5. As can be seen from Tables S4 and S5, the individual HB energies are seen to fall between 1.36 to 6.89 kcal mol^{-1}. Tables S2-S5 reveal that the individual O-H…O HBs (3.62 to 11.06 kcal mol^{-1}) are moderately stronger than the O-H…S HBs. The O-H…O HB energies in the dimer are also seen to be moderately stronger (3.99 to 5.69 kcal mol^{-1}) than the respective O-H…S HB energies (1.84 to 4.18 kcal mol^{-1}) in the dimer. The calculated values of cooperativity contribution towards the individual O-H…S HB in these clusters falls in the range between -0.83 to 3.34 kcal mol^{-1}. This cooperativity contribution indicates the favourable cross-association between water and hydrogen sulphides molecules in these clusters and also enhances the HB strength. As discussed earlier the negative cooperativity indicates that the HB energy in the dimers is numerically larger than the respective HB energy in the clusters. This effect is seen to be pronounced in some of these HBs. For instance, consider hydrogen bonds HB8 and HB9 in $(H_2O)_3(H_2S)_5$-A cluster. A closer look at these HBs (HB8 and HB9) suggests that they are involved in the formation of anti-cooperative network of HBs, where the direction of these two HBs are opposite to each other. Because of the anti-cooperative network of HBs, cooperativity contributions towards these corresponding HBs result in the smaller or negative. The cooperativity contribution towards HB8 is 0.50 kcal mol^{-1} and that for HB4 is -0.21 kcal mol^{-1}. For this reason, the energy of these HBs is smaller (3.60 and 2.55 kcal mol^{-1}, respectively). For similar reasons, the energy of HB10 in $(H_2O)_5(H_2S)_3$-A cluster is the smallest (1.36 kcal mol^{-1}) among all the O-H…S HBs in these clusters. These HB energies suggest that the O-H…S HBs, in $(H_2O)_m(H_2S)_n$ clusters are of weak to moderate strengths.

3.3.3 The S-H…O HB Energy and Cooperativity in Cyclic $(H_2O)_m(H_2S)_n$ Clusters

As can be seen from Table S6 and S7, the energies of S-H…O HBs are smaller (1.08 to 6.39 kcal mol^{-1}) as compared to the O-H…O (*cf.* Tables S2-S3) ones. However, these S-H…O HBs are of similar or little smaller strengths to those of the O-H…S (1.36 to 6.89 kcal mol^{-1}) HBs. The similar strengths between these two types of HBs is also reflected from the respective HB energies in the dimers. For instance, the S-H…O HB energies in dimers fall in the range of 1.81 to 3.57 kcal mol^{-1}. Also, the cooperativity contribution towards these S-H…O HBs (-0.83 to 3.35 kcal mol^{-1}) is similar to O-H…S (-0.83 to 3.34 kcal mol^{-1}) HBs but smaller than O-H…O (-0.62 to 5.96 kcal mol^{-1}) HBs. A closer look at Figures 2-3 and Tables S6-S7 reveals that the energy of S-H…O HBs is a little larger when these HBs are in the immediate vicinity of stronger O-H…O and O-H…S HBs. For example, the hydrogen bonds HB1 in $(H_2O)_1(H_2S)_3$ and HB4 in $(H_2O)_3(H_2S)_1$, HB5 in $(H_2O)_3(H_2S)_2$ and HB4 in $(H_2O)_4(H_2S)_1$ etc. have either O-H…S or O-H…O HBs as their neighbours. This observation is consistent with our earlier report; HBs become stronger if there are in the immediate vicinity of stronger neighbours.[68]

3.3.4 The S-H…S HB Energy and Cooperativity in Cyclic $(H_2O)_m(H_2S)_n$ Clusters

It is evident from Table S8 and S9 that the S-H…S HBs, in these $(H_2O)_m(H_2S)_n$ clusters are of substantially weaker strengths (1.35 to 4.23 kcal mol^{-1}). In general, these S-H…S HBs are the weakest among all the interactions in the $(H_2O)_m(H_2S)_n$ clusters. Furthermore, these S-H…S HB energies, in $(H_2O)_m(H_2S)_n$ clusters, are found to be a little larger as compared to those in the pure $(H_2S)_n$ clusters (2.08 to 3.88 kcal mol^{-1}). This is because many of these S-H…S HBs in $(H_2O)_m(H_2S)$ clusters are in the vicinity of stronger O-H…O and O-H…S interactions. For instance, consider the hydrogen bonds, HB3 and HB4 in $(H_2O)_2(H_2S)_3$-A cluster; the energy of HB3 (3.59 kcal

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mol^{-1}) is a little smaller than HB4 (3.91 kcal mol^{-1}). This is because HB4 is in the vicinity of a stronger O-H…O hydrogen bond (HB1:7.61 kcal mol^{-1}). On the other hand, HB3 is in the vicinity of weaker S-H…S hydrogen bond (HB4:3.91 kcal mol^{-1}); see Figure 2. This is consistent with our earlier observation that the HB strengths are enhanced when they are in the neighbourhood of stronger HBs.[68]

The weakest strength of S-H…S HBs is also evident from the HB energies in dimers. For instance, the S-H…S HB energies in dimers fall in a much narrow range (1.54 to 3.04 kcal mol^{-1}). These S-H…S HB energies in dimers are indeed smaller than the respective ones in the dimers of the O-H…O (3.99 to 5.69 kcal mol^{-1}) and O-H…S (1.84 to 4.18kcal mol^{-1}) HBs. As discussed above, the weaker HBs have smaller cooperativity contributions. Indeed, as seen from Table S8 and S9, the cooperativity contributions toward the S-H…S HBs is much smaller (-0.90 to 1.67 kcal mol^{-1}) than the O-H…O (-0.62 to 5.96kcal mol^{-1}) and O-H…S (-0.83 to 3.34 kcal mol^{-1}) HBs. Furthermore, due to this smaller cooperativity contribution in many of these S-H…S HBs, in general, are of weaker strength. Importantly, the energetic rank ordering of these HBs in dimers is similar to that obtained by the MTA-based method.

In addition to these observations, it should be noticed here that the strong HBs in mixed $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) clusters are associated with short X−H⋯Y (X = Y= O or S) HB bond distances; see Tables S2 -S9. All these strong HB have a common structural feature, for example, whereas the double HB donor water molecule is seen to be sharing a HB with a hydrogen atom of double HB acceptor water molecule. This structural feature is denoted as AA(W$_D$)→W$_A$(DD) and was attributed to the formation of strong HBs in $(H_2O)_m(H_2S)_n$ clusters. This structural feature corresponding to the O-H…O HB having energy between 10.06 to 11.06 kcal mol^{-1}. Such strong HB significantly contribute to the HB cooperativity. The weak HB in $(H_2O)_m(H_2S)_n$ clusters also correspond to long X−H⋯Y HB distances. A common structural feature for all the weak HB is denoted as A(W$_D$)→W$_A$(D). The HB having this structural feature falls between 6.89 to 8.82 kcal mol^{-1}. The aforesaid structural features and the respective HB energies pyramid for other moderately strong/weak HB are similar to those discussed in our earlier work,[61,67] and therefore such a discussion is skipped here for brevity.
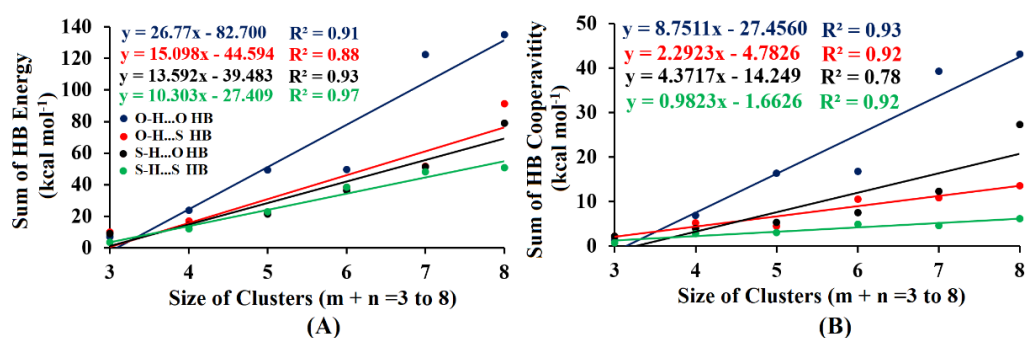

Figure 4. Correlation plots between (A) the sum of HB energies (in kcal mol^{-1}) in a cluster and the size (m + n) of $(H_2O)_m(H_2S)_n$ clusters and (B) the sum of cooperativity contributions (in kcal mol^{-1}) and the size (m + n) of $(H_2O)_m(H_2S)_n$ clusters .

Another observation from Tables S2-S9 is that in general, the oxygen of H_2O is a better HB acceptor as well as a better donor as compared to the sulphur of H_2S. These observations are consistent with the general energetic rank ordering of various types of HBs in these mixed $(H_2O)_m(H_2S)_n$ clusters, i.e., O-H…O (0.10 to 11.06 kcal mol^{-1}) > O-H…S (1.36 to 6.89 kcal mol^{-1}) > S-H…O (1.08 to 6.39 kcal mol^{-1}) > S-H…S (1.35 to 4.23 kcal mol^{-1}). Also, the total cooperative contribution seen to be increasing in a linear fashion with the increase in the size of

these $(H_2O)_m(H_2S)_n$ clusters. This is vividly illustrated from Fig. 4(B). This total positive cooperativity contribution also enhances the total HB strengths which increases with the size of cyclic $(H_2O)_m(H_2S)_n$ clusters; see Fig. 4(A).

4 Conclusion

In a nutshell, the present work, provides the direct estimates of individual HB strengths and cooperativity contributions in pure $(H_2S)_n$ and mixed $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) clusters. The HB energies in dimers chopped out of these clusters follow the rank ordering: O-H…O (3.99 to 5.69 kcal mol^{-1}) > O-H…S (1.84 to 4.18 kcal mol^{-1}) > S-H…O (1.81 to 3.57 kcal mol^{-1}) > S-H…S (1.54 to 3.04 kcal mol^{-1}). Similar order of HB energy by MTA is observed i.e., O-H…O (0.10 to 11.06 kcal mol^{-1}) > O-H…S (1.36 to 6.89 kcal mol^{-1}) > S-H…O (1.08 to 6.39 kcal mol^{-1}) > S-H…S (1.35 to 4.23 kcal mol^{-1}) at MP2(full)/aug-cc-pVTZ level. The strengths O–H…O HB (0.40 to 11.60 kcal mol^{-1}) and S–H…S HB (2.08 to 3.88 kcal mol^{-1}) in mixed $(H_2O)_m(H_2S)_n$ clusters were found to be quite different from those in pure $(H_2O)_m$ and $(H_2S)_n$ clusters, respectively. These HB energies suggested that very strong HBs were found when H_2O was the HB donor as well HB acceptor. On the other hand, moderately strong HBs were observed when the O–H of water is the HB donor and S of H_2S acceptor. These results suggest that the HB energies in the dimers fall in a narrow range, indicating that the large HB strengths in these mixed clusters are primarily due to the large cooperativity contributions. For instance, the cooperativity contributions of the other HBs towards the O-H…O HBs were found to be -0.62 to 5.96 kcal mol^{-1}, and those for the O-H…S HBs were found to be about -0.83 to 3.34 kcal mol^{-1}. The S-H…O and the S-H…S F HB cooperativity contributions were -0.83 to 3.35 kcal mol^{-1} and -0.90 to 1.67 kcal mol^{-1}, respectively.

We wish to emphasize here MTA-based method is indeed affordable that yields direct and reliable estimates of individual HB energy and cooperativity contributions in pure $(H_2S)_n$ and mixed $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) clusters. This work is not only shed light on the energetics of various HBs, but also illustrate the delicate effects of cooperativity among neighbouring HBs. Without quantitative assessments of individual HB strength and cooperativity one would not know that there are HBs of variable strength. The absence of quantitative assessments of individual HB strength and cooperativity in the literature underscores the significance of our results. We anticipate that these findings will be helpful to understand various physico-chemical properties of binary mixtures at molecular level.

† Electronic Supporting Information (ESI)

Molecular energies (in a.u.) of various species in $(H_2O)_3(H_2S)_1$ cluster, in Table S1 and the Cartesian coordinates of all the neutral cyclic $(H_2S)_n$ and $(H_2O)_m(H_2S)_n$ (m + n = 2 to 8) clusters studied, in the present work, in Tables S10 and Tables S11, respectively.

Conflicts of Interest: There are no conflicts of interest to declare.

Notes: The authors declare no competing financial interest.

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Reference

1. G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991.

2. G. A. Jeffrey, *An Introduction to Hydrogen Bonding*; Oxford University Press Inc., Oxford, New York, 1997.

3. G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press Oxford, New York, 1999.

4. K. Muller-Dethlefs and P. Hobza, *Chem. Rev.*, 2000, **100**, 143-167.

5. S. R. Gadre, K. Babu and A. P. Rendell, *J. Phys. Chem. A*, 2000, **104**, 8976-8982.

6. D. Herschlag and M. M. Pinney, *Biochemistry*, 2018, **57**, 3338-3352.

7. B. Kuhn, P. Mohr and M.Stahl, *J. Med. Chem.*, 2010, **53**, 2601-2611.

8. R. Ludwig, *Angew. Chem. Int. Ed.*, 2001, **40**, 1808-1827.

9. D. Rai, A. D. Kulkarni, S. P. Gejji and R. K. Pathak, *J. Chem. Phys.*, 2011, **135**, 024307.

10. S. Kazachenko, S. Bulusu and A. J. Thakkar, *J. Chem. Phys.*, 2013, **138**, 224303.

11. A. Malloum, J. J. Fifen, Z. Dhaouadi, E. S. G. Nana and N. D. Jaidane, *Phys. Chem. Chem. Phys.*, 2015, **17**, 29226-29242.

12. B. Baburao, D. P. Visco and T. V. Albu, *J. Phys. Chem. A*, 2007, **111**, 7940-7956.

13. J. D. Cruzan, L. B. Braly, K. Liu, M. G. Brown, J. G. Loeser and R. J. Saykally, *Science*, 1996, **271**, 59-62.

14. K. Liu, M. G. Brown, J. D. Cruzan, and R. J. Saykally, *Science*, 1996, **271**, 62-64.

15. K. Liu, M. G. Brown, C. Carter, R. J. Saykally, J. K. Gregory, and D. C. Clary, *Nature*, 1996, **381**, 501-503.

16. J. B. Paul, C. P. Collier, and R. J. Saykally, J. J. Scherer and A. O'Keefe, *J. Phys. Chem. A*, 1997, **101**, 5211-5214.

17. F. Huisken, M. Kaloudis, and A. Kulcke, *J. Chem. Phys.*, 1996, **104**, 1.

18. S. J. Suresh and V. M. Naik, *J. Chem. Phys.*, 2000, **113**, 9727-9732.

19. K. A. T. Silverstein, A. D. J. Haymet and K. A. J. Dill, *Am. Chem. Soc.*, 2000, **122**, 8037-8041.

20. J. D. Smith, C. D. Cappa, K. R. Wilson, B. M. Messer, R. C Cohen and R. J. Saykally, *Science*, 2004, **306**, 851-853.

21. Iwata, S., *Phys. Chem. Chem. Phys.*, 2014, **16**, 11310-11317.

22. J. M. Guevara-Vela, E. Romero-Montalvo, V. A. M. Gomez, R. Chavez-Calvillo, M. Garcia-Revilla, E. Francisco, A. Martin Pendas and T. Rocha-Rinza, *Phys. Chem. Chem. Phys.*, 2016, **18**, 19557-19566.

23. T. Kar and S. Scheiner, *J. Phys. Chem. A*, 2004, **108**, 9161-9168.

24. N. Kobko and J. J. Dannenberg, *J. Phys. Chem. A*, 2003, **107**, 10389-10395.

25. Y. Chen and J. J. Dannenberg, *J. Am. Chem. Soc.*, 2006, **128**, 8100-8101.

26. V. S. Znamenskiy and M. E. Green, *J. Chem. Theory Comput.*, 2007, **3**, 103-114.

27. N. Dominelli-Whiteley, J. J. Brown, K. B. Muchowska, I. K. Mati, C. Adam, T. A. Hubbard, A. Elmi, A. J. Brown, I. A. W. Bell and S. L. Cockroft, *Angew. Chem., Int. Ed.*, 2017, **56**, 7658-7662.

28. I. Errea, M. Calandra, C. J. Pickard, J. R. Nelson, R. J. Needs, Y. Li, H. Liu, Y. Zhang, Y. Ma and F. Mauri, *Nature*, 2016, **532**, 81-84.

29. H. S. Biswal, S. Bhattacharyya, A. Bhattacherjee and S. Wategaonkar, *Int. Rev. Phys. Chem.*, 2015, **34**, 99-160.

30. H. S. Biswal, P. R. Shirhatti and S. Wategaonkar, *J. Phys. Chem. A*, 2010, **114**, 6944-6955.

31. H. S. Biswal and S. Wategaonkar, *J. Phys. Chem. A*, 2009, **113**, 12774-12782.

32. A. Bhattacherjee, Y. Matsuda, A. Fujii and S. Wategaonkar, *J. Phys. Chem. A*, 2015, **119**, 1117-1126.

33. V. R. Mundlapati, S. Ghosh, A. Bhattacherjee, P. Tiwari and H. S. Biswal, *J. Phys. Chem. Lett.*, 2015, **6**, 1385.

34. A. Bhattacherjee, Y. Matsuda, A. Fujii, and S. Wategaonkar, *ChemPhysChem*, 2013, **14**, 905.

35. K. M. Dreux and G. S. Tschumper, *J. Comput. Chem.*, 2019, **40**, 229.

36. K. H. Lemke, *The Journal of Chemical Physics,* 2017, **146**, 234301.

37. M. A. Perkins, K. R. Barlow, K. M. Dreux and G. S. Tschumper, *J. Chem. Phys.*, 2020, **152**, 214306.

38. L. Ciaffoni, B. Cummings, W. Denzer, R. Peverall, S. Procter and G. Ritchie, *Appl. Phys. B*, 2008, **92**, 627.

39. A. Das, P. K. Mandal, F. J. Lovas, C. Medcraft, N. R. Walker and E. Arunan, *Angew. Chem.*, 2018, **57**, 15199.

40. S. Sarkar, Monu and B. Bandyopadhyay, *Phys. Chem. Chem. Phys.*, 2019, **21**, 25439.

41. C. Ibargüen, D. Guerra, C. Hadad, A. Restrepo, *RSC Advances*, 2014, **4**, 58217.

42. Monu, B. K. Oram and B. Bandyopadhyay, *Phys. Chem. Chem. Phys.*, 2021, **23**, 18044.

43. S. Sarkar, Monu and B. Bandyopadhyay, *Phys. Chem. Chem. Phys.*, 2019, **21**, 25439.

44. J. M. Hermida-Ramon, E. M. Cabaleiro-Lago and J. Rodríguez-Otero, *J. Chem. Phys.*, 2005, **122**, 204315.

45. B. Nelander, *J. Chem. Phys.*, 1978, **69**, 3870.

46. A. Barnes, R. Bentwood and M. Wright, *J. Mol. Struct.*, 1984, **118**, 97.

47. P. Soulard and B. Tremblay, *J. Chem. Phys.*, 2019, **151**, 124308.

48. C. Lee, C. Sosa, M. Planas, and J. J. Novoa, *J. Chem. Phys.* 1996, **104**, 7081.

49. M. Planas, C. Lee, and J. J. Novoa, *J. Phys. Chem.*, 1996, **100**, 16495-16501.

50. A. Smith, M. A. Vincent, and I. H. Hillier, *J. Phys. Chem. A*, 1999, **103**, 1132-1139.

51. S. Maeda and K. Ohno, *J. Phys. Chem. A*, 2008, **112**, 2962-2968.

52. Monu, B. K. Oram and B. Bandyopadhyay, *Comput. Theor. Chem.*, 2022, **1213,** 113740.

53. V. Ganesh, R. K. Dongare, P. Balanarayan and S. R. Gadre *J. Chem. Phys.* 2006, **125**, 104109−104110.

54. M. M. Deshmukh, S. R. Gadre and L. J. Bartolotti, *J. Phys. Chem. A*, 2006, **110**, 12519-12523.

55. M. M. Deshmukh, C. H. Suresh and S. R. Gadre, *J. Phys. Chem. A*, 2007, **111**, 6472-6480.

56. M. M. Deshmukh, L. J. Bartolotti and S. R. Gadre, *J. Phys. Chem. A*, 2008, **112**, 312-321.

57. M. M. Deshmukh and S. R. Gadre, *J. Phys. Chem. A*, 2009, **113**, 7927-793.

58. M. M. Deshmukh, L. J. Bartolotti and S. R. Gadre, *J. Comput. Chem.*, 2011, **32**, 2996-3004.

59. J. K. Khedkar, M. M. Deshmukh, S. P. Gejji and S. R. Gadre, *J. Phys. Chem. A*, 2012, **116**, 3739-3744.

60. M. M. Deshmukh and S. R. Gadre, *Molecules*, 2021, **26**, 2928.

61. M. B. Ahirwar, S. R. Gadre and M. M. Deshmukh, *J. Phys. Chem. A*, 2020, **124**, 6699-6706.

62. M. B. Ahirwar, D. Patkar, I. Yadav and M. M. Deshmukh, *Phys. Chem. Chem. Phys*., 2021, **23**, 17224-17231.

63. M. B. Ahirwar, N. D. Gurav, S. R. Gadre and M. M. Deshmukh, *J. Phys. Chem. A*, 2021, **125**, 6131-6140.

64. M. B. Ahirwar, S. R. Gadre and M. M. Deshmukh, *Phys. Chem. Chem. Phys*., 2022, **24**, 15462-15473.

65. D. Patkar, M. B. Ahirwar, S. R. Gadre and M. M. Deshmukh, *J. Phys. Chem. A*, 2021, **125**, 8836-8845.

66. D. Patkar, M. B. Ahirwar, S. P. Shrivastava and M. M. Deshmukh, *New J. Chem.*, 2022, **46**, 2368-2379.

67. D. Patkar, M. B. Ahirwar, and M. M. Deshmukh, *ChemPhysChem*, 2022**, 23**, e202200143.

68. D. Patkar, M. B. Ahirwar, and M. M. Deshmukh, *ChemPhysChem*, 2022, 23, e202200476.

69. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, et al., Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.

70. CRC Handbook of Chemistry and Physics, ed. D. R. Lide, CRC Press, Boca Raton, 90th edn, 2009.

71. D. Wang and A. Fujii, *Phys. Chem. Chem. Phys.*, 2017, **19**, 2036.