

Chapter 2

Hydrogen Bonds Involving Sulfur: New Insights from *ab Initio* Calculations and Gas Phase Laser Spectroscopy

Himansu S. Biswal

Abstract The hydrogen bonds involving sulfur (sulfur center hydrogen bonds; SCHBs) are generally regarded as weak H-bonds in comparison with the conventional N–H···O, O–H···O, N–H···N and O–H···N H-bonds. One of the reasons being considered for this is the smaller electronegativity of S than O or N. However, recent high resolution laser spectroscopy in combination with quantum chemical calculations reveals that SCHBs can be as strong as conventional H-bonds. Surprisingly, in the case of methionine containing dipeptides the amide-N–H···S H-bonds are even stronger than amide-N–H···O=C H-bonds. Sulfur is not only a potential H-bond acceptor, but the S–H group is also a very good H-bond donor and capable of forming a variety of H-bonds. For example, the S–H··· π H-bond between H₂S and indole/benzene is found to be the strongest H-bond among O–H··· π , O–H··· π , and C–H··· π H-bonds. In general the SCHBs are dispersive in nature. This chapter details about few SCHB systems, many more systems need to be studied extensively and carefully to unravel many facts and facets about SCHBs. The major challenge for the experimentalists is to accurately determine the intra- and intermolecular H-bond energies and for the theoreticians to propose a universal H-bond descriptor.

2.1 Introduction

The IUPAC's new definition of hydrogen bonding (H-bonding) [1] is stated as "The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation." As is mentioned in the definition electro negativities of X and Y in X–H···Y regulates the H-bond strength, i.e. the H-bond strength increases with increasing the electronegativity values of donor and acceptor atoms [2, 3]. This is exactly followed by the H-bonds involving second row elements in general and

H. S. Biswal (✉)

School of Chemical Sciences, National Institute of Science Education and Research, Institute of Physics Campus, PO: Sainik School, 751 005 Bhubaneswar, Odisha, India
e-mail: himansu@niser.ac.in

oxygen and nitrogen in specific. In fact, $\text{N-H}\cdots\text{O}$, $\text{O-H}\cdots\text{O}$, $\text{N-H}\cdots\text{N}$ and $\text{O-H}\cdots\text{N}$ H-bonds are very essential in supramolecular chemistry, crystal engineering, designing new materials and structure and function of biomolecules [4–10]. Apart from nitrogen and oxygen, halogens (F, Cl, Br and I) are found to be potential H-bond acceptors and form weaker H-bonds with NH, OH and CH protons [11–16]. Similarly the possibility of H-bond formation by the higher group members of chalcogens (sulfur and selenium) have also been explored and documented in the literature [17–19]. As the atomic number in the chalcogen family increases, the electronegativity of the group members decreases and their metallic character increases. The electronegativities of sulfur (2.58) and selenium (2.55) in the Pauling scale are much smaller than that of oxygen atom (3.44) and comparable with the electronegativity of carbon (2.55). The CH group is regarded as a weak hydrogen bond donor [20–25] and very recently it is reported that $\text{sp}^3\text{-C}$ can be involved in non-covalent interactions very similar to halogen and hydrogen bond termed as carbon bond [26–28]. Comparable electronegativity of sulfur with that of carbon perhaps leads to the general consensus that the hydrogen bonds involving sulfur (Sulfur Center Hydrogen Bond, SCHB) are very weak. Surprisingly nature has chosen two amino acids such as cysteine and methionine bearing sulfur atom in their side chains. It is in fact observed in the protein structure data bank that sulfur can form many non-covalent interactions including H-bonds that influence structure and function of proteins [17, 29–39]. However the strength (weak or strong), nature (electrostatic or dispersive), directionality (linear or non-linear) of SCHBs are still debatable and need to be investigated at the molecular level.

This chapter summarizes recent progress in the assessment of hydrogen bonds involving sulfur. Hydrogen sulfide dimer ($\text{H}_2\text{S-H}_2\text{S}$) is the simplest model system for intermolecular SCHBs. In this case $\text{S-H}\cdots\text{S}$ hydrogen bond is formed between the two monomer units. The computed $\text{S-H}\cdots\text{S}$ H-bond energy at semi-empirical level is 0.71 kcal/mol [40], which is much smaller than the conventional hydrogen bond energies. In this example sulfur acts as a H-bond acceptor as well as a donor. There are few matrix isolation IR spectroscopy studies on the SCHBs [41–44]. The experimental results demonstrate the sulfur atom of Methanethiol (MeSH) and dimethyl sulfide (DMS) can be a potential hydrogen bond acceptor, although a weaker acceptor than oxygen [41]. However, the work by M. Wierzejewska [42] demonstrated that the sulfur atom of DMS is better hydrogen bond acceptor than the sulfur atom of dimethyldisulfide (DMDS) and hydrogen sulfide (H_2S) and comparable to the oxygen atom of dimethylether (DME) as observed in the DMS-HNO_3 and DME-HNO_3 binary complexes [43]. Apart from the intermolecular $\text{S-H}\cdots\text{S}$ and $\text{O-H}\cdots\text{S}$ hydrogen bonds, intramolecular SCHBs are frequently observed in the crystals [45–48]. The spectroscopic evidence for intramolecular SCHB is the microwave study of the conformers of jet-cooled thiodiglycol (TDG) [49]. It is observed that intramolecular $\text{O-H}\cdots\text{S}$ hydrogen bond provides a highly compact and folded structure to the most stable conformer of TDG. Sulfur is also capable of forming $\text{S-H}\cdots\pi$ π -type H-bonds along with $\text{S-H}\cdots\text{S}$, $\text{N-H}\cdots\text{S}$ and $\text{O-H}\cdots\text{S}$ σ -type H-bonds as cited above. For instance, H_2S forms strong $\text{S-H}\cdots\pi$ H-bonded complex with benzene π -electrons. The computed H-bond energy in H_2S and benzene dimer

at CCSD(T)/CBS level is -2.85 kcal/mol. This binding energy is comparable to that of $\text{O}-\text{H}\cdots\pi$ and $\text{N}-\text{H}\cdots\pi$ H-bond energy and almost two times of $\text{C}-\text{H}\cdots\pi$ H-bond energy [50].

Many theoretical approaches have been adopted to shed light on the experimental observations on SCHBs. The main focus is to understand the directionality, nature and hydrogen bond energies of SCHBs [18, 44, 51, 52, 53–56]. One of the detailed theoretical study by Platts et al. [18] on SCHBs suggest that sulfur atoms of H_2S and H_2CS are weaker H-bond acceptor than oxygen atoms of H_2O and H_2CO . Sulfur prefers to form perpendicular H-bonds where as oxygen forms linear hydrogen bonds, the reason being $(\text{X})\text{S}\cdots\text{H}-\text{F}$ H-bond is dominated by charge (H)-quadrupole (S) interaction while charge-charge attraction is the main contributor for the $(\text{X})\text{O}\cdots\text{H}-\text{F}$ H-bonded complexes. In other words SCHBs are dispersive in nature. One of the important finding by them is that the Laplacian and charge density derived from atoms in molecules (AIM) theory is unable to predict the directionality of SCHBs in these complexes. The H-bond energy in $(\text{X})\text{S}\cdots\text{H}-\text{F}$ is almost half of that in $(\text{X})\text{O}\cdots\text{H}-\text{F}$ complexes. On contrary in the case of methanol–dimethylsulfide ($\text{OH}\cdots\text{S}$ H-bond) and methanol–dimethylether ($\text{OH}\cdots\text{O}$ H-bond), the H-bond energies are very similar. The estimated H-bond energy of $\text{OH}\cdots\text{S}$ H-bond at the coupled cluster level is -5.46 kcal/mol which is slightly smaller than the H-bond energy of -5.97 kcal/mol for $\text{OH}\cdots\text{O}$ H-bond. Similarly in a recent work on the nature of the SCHBs, Singh and co-workers [56] from the symmetry adopted perturbation theory analysis (SAPT) of variety of intermolecular H-bond complexes with DMS suggest that electrostatic component of the stabilization energy is the major contributor in the SCHBs rather than the dispersive energy component as mentioned by Barcke and co-workers [18]. One thing emerges out from these few examples is that the hydrogen bond acceptor strength of sulfur, directionality and the electrostatic/dispersive nature of SCHB are not very conclusive and still debatable.

Apart from spectroscopic and computational evidences, the existences SCHBs have been realized in many organic crystals, peptides and proteins [48, 57–73, 74–76]. The intrachain $\text{S}-\text{H}\cdots\text{O}=\text{C}$ H-bonds involving sulfur atom of cysteine side chain and backbone carbonyl oxygen have been observed for globular proteins [17, 77]. The strength and occurrence of SCHBs in proteins have recently been investigated by Zhou et al. [78]. By analyzing the geometrical parameters of 500 high resolution protein structures, they concluded that “(i) SCHBs regulate secondary structure of peptides, (ii) SCHBs have longer hydrogen bond length (d) and smaller hydrogen bond angle (θ), (iii) sulfur atoms in the side chain of cysteine, half-cysteine and methionine forms weaker hydrogen bond, (iv) the disulfide bonds are capable of forming SCHBs, (v) the SH group of cysteine acts as a hydrogen bond donor and forms weak $\text{S}-\text{H}\cdots\pi$ hydrogen bond, and (vi) methionine sulfur is a poor hydrogen bond acceptor.” Some of these findings are very pertinent and useful while some need to be studied at the molecular level. For example, looking at the electro negativities of acceptor atoms and distance between X and Y in $\text{X}-\text{H}\cdots\text{Y}$ H-bond systems, it is very difficult to say whether Y (in this case sulfur) will be weak or strong H-bond acceptor. A comprehensive search of crystal structure data base by Allen et al. [19] and Steiner [79] emphasizes that except for few thioethers sulfur is a poor hydrogen

bond acceptor than oxygen and the role of SCHBs in bimolecular structure function are minimal. On the contrary, Francois et al. [61] found very strong N–H...S hydrogen bond in the crystals of (Triazocyclononane)₂Fe₂S₆. They also observed that the strength of N–H...S and N–H...O H-bonds highly depend on the hydrogen bond angle (θ). For the mentioned crystal structure the N–H...S hydrogen bond strength is optimal for $\theta \sim 80^\circ$, where as N–H...O hydrogen bond is favorable for $\theta > 115^\circ$. Hence, one can conclude that the strength of SCHB is dependent on the systems and geometry of hydrogen bond. Similarly the role of SCHB in biomolecular structure and function cannot be neglected. For example, in a recent report [80] methionine is found to be very essential for the catalytic role of phosphite dehydrogenase (PTDH), that catalyses the oxidation of phosphite to phosphate. In fact, the N–H...S hydrogen bond interaction between His292 and Met53 stabilizes the transition state of the reaction, thereby lowering the activation energy barrier and increasing the catalytic activity of PTDH.

The above cited few examples from the literature manifest many facts and facets of SCHBs, that are still unexplored and need to be addressed very accurately. It is very clear that sulfur can form hydrogen bond and SCHBs are ubiquitous in proteins and organic crystals. For the last few years we have been trying to unravel SCHBs at molecular level using the arsenal of high resolution gas phase laser spectroscopy and computational methods. Hope our results will mark a point with respect to vexata quaestio of the acceptor strength of sulfur, directionality and nature of SCHBs. The aim is to mimic the SCHBs observed in the organic crystals, peptides, and proteins by choosing relevant simpler model compounds. The model compounds and their clusters are prepared in the supersonic jet cooled condition by exploiting isentropic phenomenon. The UV and IR spectroscopy of these compounds and their clusters are recorded in the jet cooled condition. Supersonic jet spectroscopy has many advantages over the conventional spectroscopy and used by many research groups to study molecular complexes that ranges from weakly bound van der Waal's complexes to very strongly bound ionic-hydrogen bonded complexes [81–87]. One of the major benefits of this technique is that it reduces thermal broadening of the spectra and helps the molecular complexes to form at a lower temperature that cannot be possible in the ambient temperature and pressure. Combining this with TOF-Mass spectrometer allows us to detect the complexes of our interest and studying them in isolated conditions. Many double resonance spectroscopic methods are used to record the high resolution conformer specific UV and IR spectra. The computational methods are very handy in assigning the spectra, estimating the H-bond energy and predicting the nature of the SCHBs. The experimental data are also very useful in benchmarking the computational methods and provide plenty opportunities to develop new theoretical methods to understand and correctly predict non-covalent interactions such as SCHBs. In the next few sections we will discuss how the marriage between the computational methods and high resolution laser spectroscopic methods help us to shed light on the H-bonds sulfur atoms; sulfur being a H-bond acceptor or S–H as a H-bond donor.

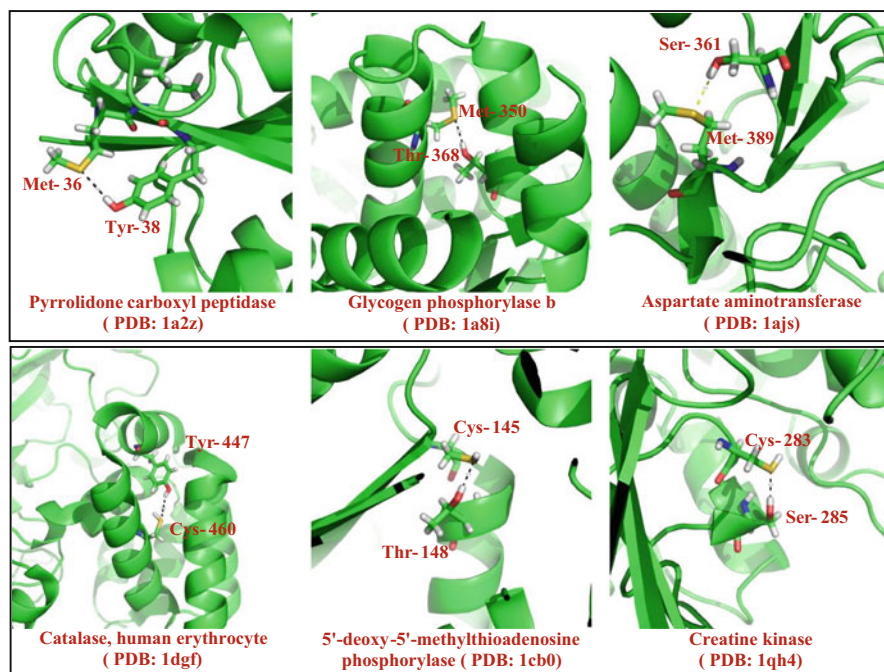


Fig. 2.1 O–H···S Hydrogen bonds involving sulfur atoms of methionine and cysteine in proteins

2.2 “Sulfur” as a H-Bond Acceptor

Sulfur can be a potential H-bond acceptor. The mostly studied H-bonds with sulfur as a H-bond acceptor are O–H···S and N–H···S H-bonds. More detail of these H-bonds will be discussed in the subsequent sections.

2.2.1 O–H···S Hydrogen Bonding

It is evident from the protein structure data bank that sulfur atoms of methionine and cysteine are capable of forming O–H···S H-bonds with the side chain OH groups of tyrosine, threonine and serine. Few selected examples are shown in the Fig. 2.1.

Several computational and spectroscopic studies have been devoted to mimic and understand such interactions at the molecular level [18, 41–43, 88–99]. The matrix isolated FTIR spectroscopy in combination with ab initio calculation provides valuable information to categories and characterize SCHBs. Maes and coworkers used the extent of the red shift of H–Cl frequency in 1:1 complexes of HCl and YR₂ (Y = O, S, Se and R = CH₃, C₂H₅) as the measure of the strength of H-bond, more is the red shift stronger is the H-bond [90]. The red shift in H–Cl stretching frequency is

higher for S than O acceptors and it correlates with the proton affinity of the acceptor. Similar studies have been performed for intermolecular and intramolecular H-bonds involving S as an acceptor and various proton donors such as H_2O , HF, HCl, HNO_2 , HNO_3 , and CF_3CCH [42, 43]. The $\text{O-H}\cdots\text{S}$ H-bond between the OH group of the HNO_3 and sulfur atoms of dimethylsulfide (DMS), dimethyldisulfide (DMDS) and H_2S was observed. In these binary complexes $\text{O-H}\cdots\text{S}$ H-bond strength increases in the order as $\text{H}_2\text{S-HNO}_3$, DMDS-HNO_3 and DMS-HNO_3 , suggesting that the sulfur atom of DMS is the strongest H-bond acceptor among them. The conclusion is purely based on the frequency shift in the O-H stretching frequencies of HNO_3 . One of the inherent problems in the matrix isolation studies is the effect of matrix on the O-H frequencies, which prohibits precise determination of vibrational frequencies. Computational efforts have also been put forward to determine the H-bond strength of O and S acceptors. Wennmohs et al. [52] computed the interaction energies of the DMS-MeOH , DME-MeOH and dimethylthiocarbonyl- MeOH at the CCSD (T)/aug-cc-pVQZ level of theory. The interaction energies are -5.46 , -5.97 and -5.33 kcal/mol respectively. It suggests that the $\text{O-H}\cdots\text{S}$ H-bond strength is very similar to that of $\text{O-H}\cdots\text{O}$ H-bond strength in these complexes. The authors also found that in case of $\text{O-H}\cdots\text{S}$ H-bonding the dispersion energy contribution is about $\sim 70\%$ to the total interaction energy. However, the electrostatic component controls the H-bond geometry. The theoretical predication of S as potential H-bond acceptor as O in DMS-MeOH and DME-MeOH complexes was confirmed experimentally by Daryl L. Howard and Henrik G. Kjaergaard [99]. From the vapor phase infrared spectroscopic study of the complexes of MeOH it was claimed that S is nearly equivalent to O as H-bond acceptor. The problem with the vapor phase IR spectra is that they are very broad and no control over mass selectivity. Hence it is very difficult to obtain precise information about the shift in O-H vibrational frequency in DMS-MeOH and DME-MeOH complexes.

The importance of SCHBs and some debatable conceptions about SCHBs prompted us to study them systematically. A combined experimental and computational approach has been deployed to extract molecular level information about SCHBs. The computational methods and experimental techniques are complementary to each other. For example computed vibrational frequencies and structure of molecules are very helpful in assigning the experimental spectral features while the experimental data can be used for bench marking and developing computational methods. To mimic the $\text{O-H}\cdots\text{S}$ interaction between the side chain of tyrosine and S of methionine, para-cresol (p-CR) and thioethers are taken as the respective model compounds. As shown in Fig. 2.2, the alkyl chain length of the thioethers is systematically varied to see its effect on the nature and strength of the SCHBs.

Laser spectroscopy of jet-cooled molecules and molecular clusters is very handy to extract precise experimental data on non-covalent bonded clusters, in this case the H-bonded clusters. In most of the cases double resonance spectroscopy such as fluorescence dips infrared (FDIR) spectroscopy and resonant ion dip infrared spectroscopy (RIDIR) coupled with mass spectrometry are used to get the X-H stretching frequencies (here, O-H , N-H , S-H stretching frequencies) of the monomers and their H-bonded complexes. The relative changes in the X-H stretch in the complexes are

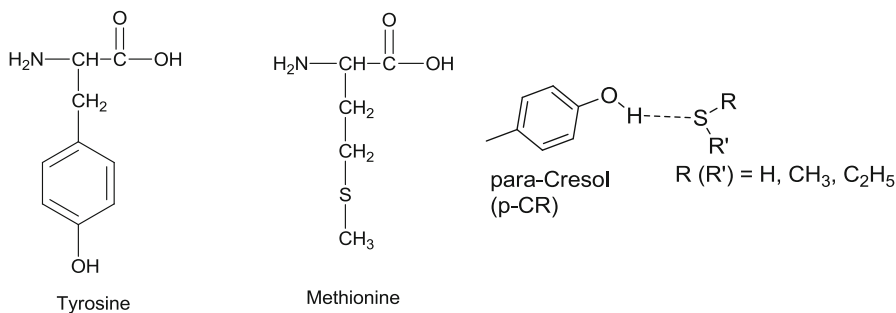


Fig. 2.2 Model compounds used to study O–H...S H-bond between OH group of tyrosine and sulfur atoms of methionine and cysteine

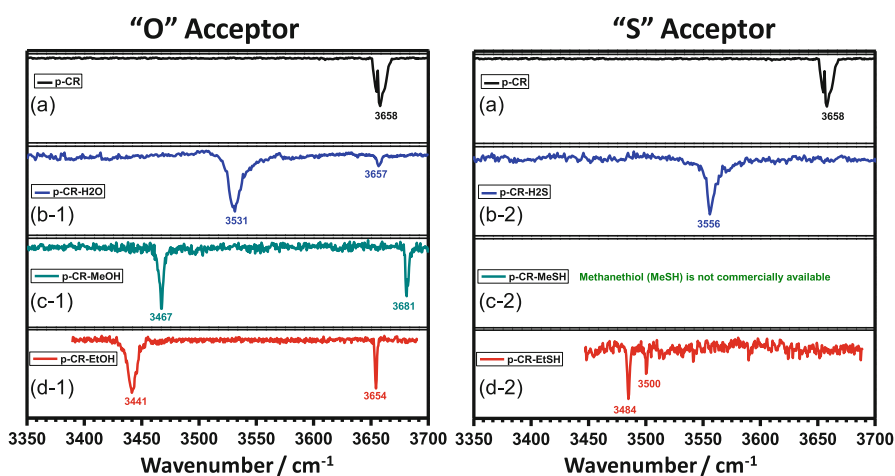


Fig. 2.3 FDIR spectra of 1:1 complexes of p-CR and YHR (Y = O, S and R = H, CH₃, and C₂H₅). H₂O, MeOH and EtOH are used as "O" H-bond acceptors and H₂S and EtSH are used as "S" H-bond acceptors

generally taken as a measure of the H-bond strength. It is a general practice for the conventional H-bond that more red shift in the X–H stretch, stronger is the X–H...Y H-bond. The X–H...Y H-bonds becomes stronger if Y becomes more basic.

Figure 2.3 presents the FDIR spectra of 1:1 complexes of p-CR and YHR (Y = O, S and R = H, CH₃, and C₂H₅). Here the OH group of p-CR acts as a H-bond donor and alcohols and thiols as H-bond acceptor.

The OH stretching frequencies of p-CR are red shifted in the complexes irrespective of the acceptor atoms, suggesting formation of O–H...O(S) H-bonds. The formations of O–H...O(S) H-bonds are also confirmed by DFT calculations [100, 101]. If one goes by the red shift of OH stretch, it is very clear from the figure that O of H₂O and alcohols are better H-bond acceptors than the S of H₂S and corresponding thiols. There are multiple conformers observed experimentally.

In such situations computed vibrational frequencies are very helpful in assigning the spectra. The computed H-bond energy and vibrational frequencies along with the experimental frequencies are tabulated in Table 2.1. As one can see the H-bond energy of O–H···S H-bonds are smaller compared to that of O–H···O H-bond. However, with increasing alkyl chain length in the acceptor moiety the O–H···S H-bond becomes stronger. One more thing can be noticed from the table; the gas phase basicities of alcohols are smaller than their corresponding thiols; however the red shifts of O–H stretching frequencies for thiols as H-bond acceptors are less compared to their oxygen counterpart, suggesting that SCHB does not follow the acid base formalism.

The situation is little different in case of ethers and thioethers as H-bond acceptor. The FDIR spectra of 1:1 complexes of p-CR with ethers and thioethers are shown in Fig. 2.4.

The red shifts of O–H stretching frequency of p-CR•DES is larger compared to that of p-CR•DEE, suggesting the acyclic thioethers can be better H-bond acceptors than the ethers [102, 103]. Comparing the H-bond acceptor quality of cyclic thioether and cyclic ether, the cyclic ether is found to be better acceptor than its sulfur counterpart. Thioethers are better H-bond acceptors than the thiols [104]. Multiple conformers are observed for the ethers and thioether complexes [102–104]. In those cases DFT calculations are very useful to assign the experimental spectral features. Two conformers in the complex of cyclic ether, tetrahydrothiophene (THT), with p-CR are found experimentally. The two O–H stretching frequencies are observed for p-CR•THT complex while probing different electronic transitions. The FDIR spectra of p-CR•THT are shown in Fig. 2.5 with C2 and Cs symmetry in THT. These two conformers have different electronic transitions, but same IR transitions. In this case it is difficult to assign the IR spectra without the help of quantum chemical calculations. The non-covalent interaction (NCI) plots [105, 106] and atoms in molecules (AIM)[107–111] molecular graph assist the assignment. As shown in the figure conformer A of p-CR•THT does not show any vibronic coupled band in the FDIR spectra, while conformer B shows a strong vibronic coupled band. The vibronic couple band arises because of the coupling between the O–H oscillator of p-CR and C–H oscillator of THT. This is in fact happens for the p-CR•THT (Cs) conformer as predicted by NCI as well as AIM topology.

The binding and the red shift in O–H in the H-bonded complexes are the net result of several fundamental interactions, such as charge-dipole, dipole-dipole, dipole-induced dipole and the higher order multipole interactions. The magnitudes of these interactions are very difficult to determine experimentally. However theoretical insights are useful to account for the individual energy contribution to the total interaction energy. Various energy decomposition analyses such as. Natural energy decomposition analysis (NEDA) [112–114], Kitaura and Morokuma (KM) [115, 116], and reduced variational space self-consistent field (RVS) [117] decomposition analyses are used to solve the purpose. It is noticed that dispersion energy component is very important in SCHBs [100–104]. Table 2.2 summarizes dispersion energy contribution to the total interaction energy in the O–H···O and O–H···S H-bonded intermolecular complexes.

Table 2.1 Experimental red shifts of O–H stretching frequencies, red shifts of band origin (*BO*) positions, gas phase basicity of acceptors (*GB*), computed O–H shifts, changes in the O–H bond lengths (Δr) and bond dissociation energies (D_0) of p-CR•YRR' (Y = O and S, R(R') = H, CH₃ and C₂H₅) complexes

Species	O–H Shift (Expt) in cm ⁻¹	BO shift (Expt) in cm ⁻¹	GB in kJ/mol	O–H shift (B3LYP/aDZ) in cm ⁻¹	Δr (B3LYP/aDZ) in Å	BE ^a (MP2/aDZ) in kcal/mol
"O" Acceptors	p-CR•H ₂ O	-127	660.0	-192	0.0095	-4.29
	p-CR•MeOH	-191	724.5	-246	0.0120	-5.76
	p-CR•EtOH	-217	746.0	-256	0.0125	-6.33
	p-CR•DEE	-280	801.0	-292	0.0140	-7.67
	p-CR•THF	-315	794.7	-335	0.0160	-7.42
"S" Acceptors	p-CR•H ₂ S	-102	673.0	-138	0.0064	-2.49
	p-CR•MeSH		742.0	-210	0.0096	-4.08
	p-CR•EtSH	-174	758.4	-219	0.0102	-4.70
	p-CR•DES	-292	827.6	-299	0.0146	-6.23
	p-CR•THT	-285	819.3	-296	0.0142	-6.15

^a Bond dissociation energies (D_0) are computed at MP2/aug-cc-pVDZ//B3LYP-aug-cc-pVDZ level of theory, the basis set superposition error (*BSSSE*) and zero point energy (*ZPE*) corrections are also applied. aDZ: aug-cc-pVDZ, *DME* dimethylether, *DEE* diethylether, *THF* tetrahydrofuran, *DMS* dimethylsulfide, *DES* diethylsulfide, and *THT* tetrahydrothiophene

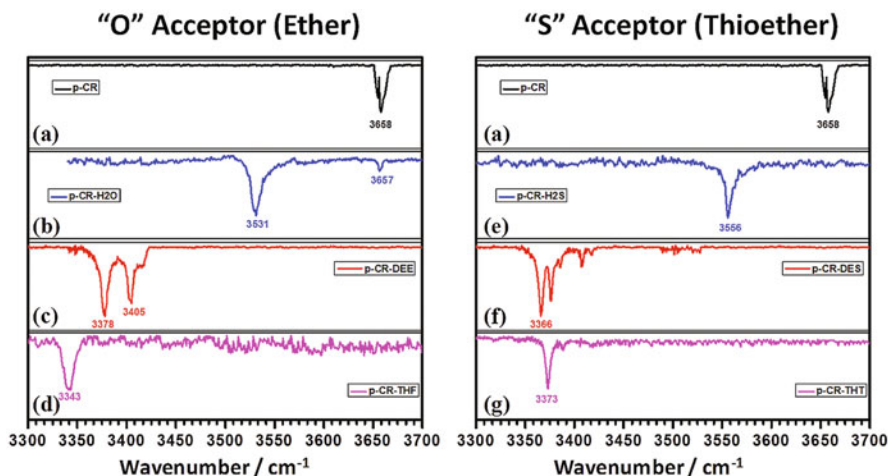


Fig. 2.4 FDIR spectra of 1:1 complexes of *p*-CR and YR (Y = O, S and R = H, CH₃, and C₂H₅). H₂O, DEE and THT are used as “O” H-bond acceptors and H₂S, DES, and THT are used as “S” H-bond acceptors

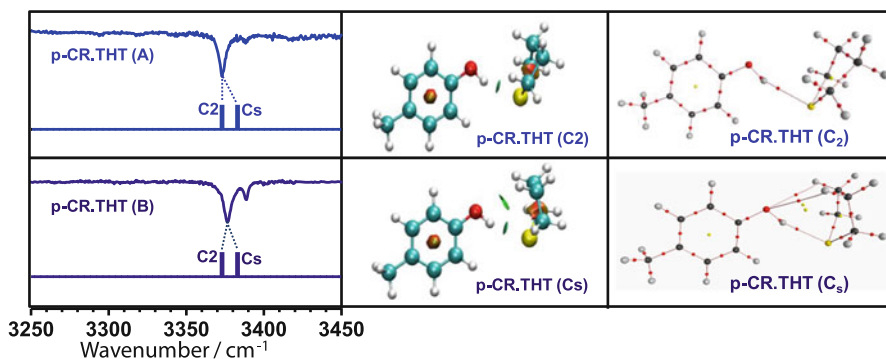


Fig. 2.5 Left panel: FDIR spectra of *p*-CR•THT conformers probed at their respective band origins. The stick diagrams in the spectra are the computed OH stretching frequencies obtained at B3LYP/aug-cc-pVDZ level of theory. Middle panel: Non-covalent interaction (NCI) plot of two conformers of *p*-CR•THT, showing O–H···S interactions in both the conformers and C–H···O interaction only in *p*-CR•THT (*C_s*) conformer. Right panel: Molecular graph of generated using atoms in molecules (AIM) electron density topology. Bond critical points are located for O–H···S and C–H···O interactions

In general the O–H···S HBs are dispersive in nature while O–H···O HBs are electrostatic. However, the dispersion energy contribution in the O–H···O HB case increases with the increase of alkyl chain length of the hydrogen bond acceptors. In the case of the O–H···S HB, the dispersion energy contribution decreases from H₂S



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