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Symmetry-adapted perturbation theory interaction energy decomposition for H_2CY-XF (Y = O, S, Se; X = H, Li, Cl) complex

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ABSTRACT

The H_2CY-XF (Y = O, S, Se; X = H, Li, Cl) complexes have been investigated at the MP2(Full)/aug-cc-pVTZ level. The formation and structures of hydrogen, lithium, and chloride bonds were studied comparatively with electrostatic potentials. The hydrogen and lithium bonds become weaker in the order O < S < Se, while the chloride bond becomes stronger in the same order. The lithium bond is the strongest in all complexes. The chloride bond is weaker than the hydrogen bond in the H_2CO complex, while the former is stronger than the latter in the H_2CS and H_2CSe complexes. The nature of three types of interactions in these complexes has been analyzed with symmetry-adapted perturbation theory (SAPT) method.

1. Introduction

It is no doubt that noncovalent interactions play a particularly important role in molecular recognition [1], crystal engineering [2], and drug–receptor interactions [3]. Thus they have been being a research focus for different fields of researchers [4]. Recently, much effort has been made to predict and characterize noncovalent interactions. Hydrogen bond varies from conventional one to π H-bond [5], dihydrogen bond [6], single-electron H-bond [7]. Mo et al. have studied the structures, energies, bonding, and spin–spin coupling constants for a series of containing B hydrogen-bonded complexes [8–10]. Lithium, analogous to hydrogen, can also form weak interactions with bases and different types of lithium bonds have been studied [11–15] although the study on them is not much. Halogen bond is another important noncovalent interaction, which is paralleling to hydrogen bond in the direction, strength, type, nature, properties, and applications in molecular recognition and crystal engineering [16–18]. Alkorta et al. have performed an *ab initio* calculation on a series of ClF binary and ternary complexes and found that the nature of the halogen bond changes from traditional, to chlorine-shared, to ion-pair [19–21].

Although there is parallelism among the above three noncovalent interactions, differences are present among them. Hence, one topic is focused on the comparison for them. It was found that the electrostatic contribution is more important in lithium bonding than in hydrogen bonding [22] and halogen bonding exhibits a higher directionality than hydrogen bonding [23]. The difference in the directionality in both interactions can be attributed to the presence of nonbonding valence electrons on the halogen and their absence on the hydrogen [24]. Raghavendra and Arunan [25] studied the H-, Cl-, and Li-bonded complexes with HF, ClF, and LiF as the respective electron acceptors, and found that a correlation between frequency shift and binding energy is present for the H-bonded complex but is not found for Li- and Cl-bonded ones. The blue-shifting halogen bond occurs more frequently in the halogen-bonded complexes than the blue-shifting hydrogen bond in the hydrogen-bonded complexes [26]. It was thought that the three lone electron pairs on the halogen atom are responsible for this difference. The bond length change and frequency shift in the H- and Li-bonded complexes have been compared and explained using a model derived from the perturbation theory [27].

Sulfur atom is present in the amino acids cysteine and methionine, thus lots of studies have been performed for H-bonding to sulfur and compared it with the oxygen analog [28–35]. In general, hydrogen bonds to sulfur not only are weaker than those to oxygen but also show a marked preference for a more “perpendicular” direction of approach to the donor atom [32]. Howard and Kjaergaard [33] compared hydrogen bonds formed between methanol and either dimethyl sulfide or dimethyl ether with infrared spectroscopy and *ab initio* calculations and thought that sulfur is weaker than, but nearly equivalent to, oxygen as a hydrogen bond acceptor. However, Raub and Marian thought that sulfur is a stronger hydrogen bond acceptor while its donor capacity is weaker [34]. Although the interaction energy is similar for S···HO H-bond in dimethylsulfide–methanol complex and O···HO H-bond in

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oxygen analog, the potential energy surfaces for the former seem to be much flatter than for the latter and the electrostatic effect is larger in the latter than in the former [35]. The lithium bonds have also been compared for O and S electron donors [36–39], and the results showed that the O is a stronger lithium bond acceptor than the sulfur analog. The case is complicated for halogen bonds with the O and S electron donors [40,41].

In this paper, we will perform a comparative computational study on H_2CY-XF (Y = O, S, Se; X = H, Li, Cl) complex with the symmetry adapted perturbation theory (SAPT) method. It is necessary to point out that most of complexes have been studied before [42–48]. Our aim is to unveil the difference of hydrogen, halogen, and lithium bonds in nature and with it to understand the difference of three interactions in strength and properties.

2. Computational methods

The H_2CY-XF (Y = O, S, Se; X = H, Li, Cl) complexes have been optimized at the MP2(Full)/aug-cc-pVTZ level. Then harmonic vibrational frequencies were calculated at the same level to ensure the optimized structures are true minima and confirm the frequency shift in X—F stretching vibration in the complexes. The interaction energies in these complexes were calculated to be the difference between the energy of the complex and the energy sum of the monomers. The interaction energies were corrected for basis-set superposition error (BSSE), which was estimated with the counterpoise method of Boys and Bernardi [49]. All calculations were performed using the Gaussian 09 suite of programs [50]. The topological analyses for these complexes were performed using Bader's atoms in molecules (AIMs) theory with AIM2000 programs [51]. The symmetry adapted perturbation theory (SAPT) calculations were carried out using the SAPT2002 program [52].

3. Results and discussion

Fig. 1 shows the optimized structures of H_2CY-XF (Y = O, S, Se; X = H, Cl, Li) complexes at the MP2(Full)/aug-cc-pVTZ level. Here we only consider a main configuration for each type of complex although other configurations may also be present in different cases. For example, H_2CO-LiF and H_2CS-LiF complexes respectively have three and two stable isomers [47]. However, the most stable one in each complex is combined with both a lithium bond and a secondary hydrogen bond as shown in Fig. 1. It has been demonstrated that cyclic structures are more stable than chained ones. Like H_2CO-LiF and H_2CS-LiF complexes, H_2CSe-LiF complex also displays a cyclic structure. The formation of cyclic structure can be affirmed by the molecular graphs for H_2CY-LiF (Y = O, S, Se) complexes in Fig. 2, in which a ring critical point was observed.

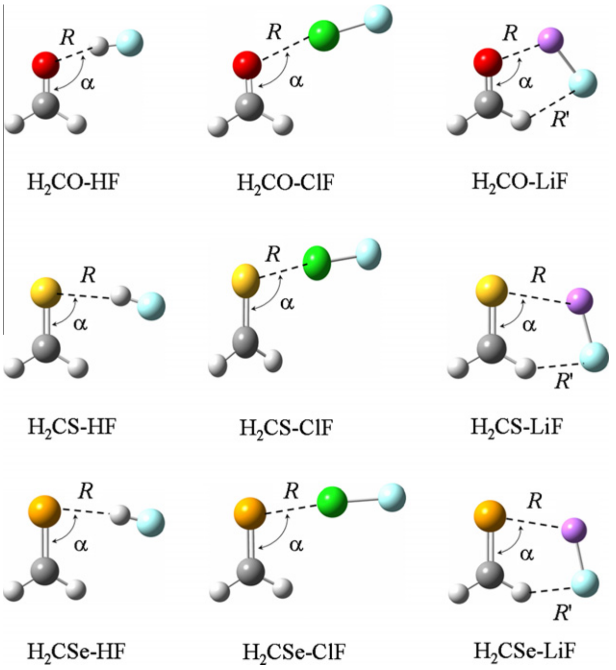

Fig. 1. The optimized structures of H_2CY-XF (X = H, Li, Cl; Y = O, S, Se) complexes at the MP2/aug-cc-pVTZ level.

All atoms in each complex are in a plane, but the angle (α) between both subunits in the same type of interaction decreases with the increase of Y atomic number. The α value is larger than 100° for the O electron donor. Due to the formation of cyclic structure, the α value in H_2CY-LiF complex is smallest in three types of complexes. The different orientation can be understood with the electrostatic potentials of Y atom. Fig. 3 presents the electrostatic potentials of H_2CO, H_2CS, and H_2CSe monomers. A positive region of electrostatic potentials is found on the outermost portion of the Se's surface along with the C=Se bond, whereas the counterpart is negative for the O and S atoms. Thus H_2CO-LiF and H_2CS-LiF complexes can also display a $C_{2,v}$ structure [47]. The most negative electrostatic potential of Y atom has a greater deviation from the $C_{2,v}$ axis along the C=Y group with the increase of Y atomic number. This supports the change of α angle in the complexes.

The binding distance and change of bond length are presented in Table 1. For the same type of complex, the binding distance is increased with the increase of Y atomic number. This is consistent with the radius of Y atom. The binding distance in the ClF complex is larger than the HF counterpart. The binding distance in the LiF complex has not a consistent change due to the presence of H···F hydrogen bond. Given the fact that the H···F hydrogen bond coexists with the lithium bond, the binding distance is a better measurement for the strength of H···F hydrogen bond. The H···F distance is 2.101, 1.950, and 1.938 Å in H_2CO-LiF, H_2CS-LiF, and H_2CSe-LiF complexes, respectively. Thus the H···F hydrogen bond becomes stronger for the heavier Y complex.

The X—F bond is lengthened in all complexes. For the chloride bond, the Cl—F bond elongation grows gradually in the order O < S < Se, but it is not suitable for lithium bond and hydrogen bond, in which the elongation of H—F and Li—F bonds holds the completely opposite order. Interestedly, the H—F bond has a smaller elongation than the Li—F and Cl—F bonds.

The X—F stretch vibration shows a red shift in all complexes. The red shift in the chloride-bonded complexes correlates with the ClF bond lengthening. Such consistent results are not found for the hydrogen- and lithium-bonded complexes. This can be explained with the presence of secondary H···F interaction in the lithium-bonded complexes. The red shift in the hydrogen bond is the largest among the three types of interactions due to the lighter mass of H atom.

The interaction energies in all complexes are also given in Table 1. The interaction energies uncorrected for BSSE do not hold the clear

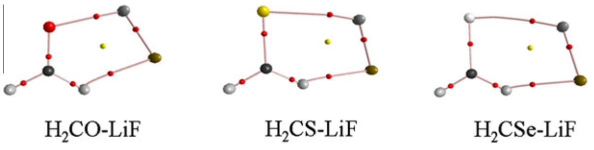

Fig. 2. Molecular graphs for H_2CY-LiF (Y = O, S, Se) complexes at the MP2/aug-cc-pVTZ level. Small red dots represent the bond critical points and yellow dots denote the ring critical points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)