

Does single-electron chalcogen bond exist? Some theoretical insights

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Abstract Ab initio calculations have been carried out to investigate the σ -hole interaction in $XHY\cdots CH_3$ and $XHY\cdots CH_2CH_3$ complexes, where $X=F, Cl, Br$ and $Y=S, Se$. This interaction, termed “single-electron chalcogen bond interaction” was analyzed in terms of geometric, interaction energies and electronic features of the complexes. This interaction is a weak one, with an interaction energy that varies from a minimum of $-1.7\text{ kcal mol}^{-1}$ for $BrHS\cdots CH_3$ to $-6.0\text{ kcal mol}^{-1}$ for $FHSe\cdots CH_2CH_3$ at the CCSD(T)/aug-cc-pVTZ level of theory. Energy decomposition analysis indicated that the dominant attraction energy originates in the electrostatic term which is larger for the Se complexes than for the S counterparts. However, the attractive polarization and dispersion components also make an important contribution to the interaction energy for the single-electron chalcogen bond interactions.

Keywords Ab initio · Chalcogen bond · Interaction energy · σ -hole

Introduction

Many chemical and physical properties of materials are determined mainly by noncovalent interactions, of which hydrogen bonds are an important class [1–3]. A detailed understanding of these interactions is of great importance for rationalization

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of the effects observed in several fields, such as biochemistry and material science [4]. Hydrogen bond interaction is usually represented as an $A-H\cdots B$ attraction, where A and B are electronegative elements and B possesses one or more lone electron pairs. However, a number of unusual hydrogen bonds have been proposed with progress of the study on hydrogen bonds, such as $C-H\cdots B$ hydrogen bonds [5], blue-shifting hydrogen bonds [6], π -hydrogen bonds [7], or even single-electron hydrogen bonds [8]. In recent years, much attention has been paid to a specific intermolecular interaction involving a halogen atom as an acceptor of electron density. Such an interaction is now referred to as halogen-bonding to emphasize its striking similarities with hydrogen-bonding [9–13]. A halogen bond is defined as an attractive $RX\cdots BZ$ interaction where RX is usually an organic halide (almost always chloride, bromide, or iodide), X is an electrophilic halogen atom (typically chlorine, bromine, or iodine) and BZ is a Lewis base, B is a negative site, most often an atom such as F, O, and N with lone-pair electrons. In literature, the occurrence of the halogen bond is explained with the “ σ -hole” concept proposed by Politzer and co-workers [14–24]. This term refers to the electron deficient outer lobe of a p orbital, which can act as an electron-pair acceptor from a Lewis base. The size of the σ -hole increases with halogen size in going from the lighter to the heavier atoms, as polarizability increases and electronegativity decreases. Although not as thoroughly investigated as halogen bonds, there have been a number of theoretical and experimental studies that chalcogen atoms (O, S, Se, and Te) can serve a similar function in what might analogously be to referred as a “chalcogen bond” [25–27].

The chalcogen bond has been recognized as a new and important type of intermolecular interaction. It can be explained as an electrostatic attraction between the positive potential of the chalcogen atom and the negative site on the other molecule. As expected, the chalcogen’s σ -hole potentials become more positive (α) in going from the lighter to the heavier

atoms, as polarizability increases and electronegativity decreases ($O < S < Se < Te$), and (b) as the remainder of the molecule is more electron withdrawing [28, 29]. Thus, the σ -holes on the selenium in $SeCl_2$ are more positive than those on the sulfur in SCl_2 , but less positive than the selenium ones in SeF_2 . Like halogen bonds, one of the interesting properties of chalcogen bond interactions that shows great promise for the design of materials with novel properties is that they are highly tunable, i.e., their binding properties can be strongly controlled not only by changing the molecular environment of the chalcogen atom, but also by changing the chalcogen itself. Generally, there are two main factors that control the strength of a chalcogen bond. The first of these is the size of the σ -hole potential over chalcogen atom surface, with larger chalcogen atoms having the tendency to form larger σ -holes. The tunability of chalcogen bond by making substitutions of electron-withdrawing groups near the chalcogen has been studied extensively [30–32] and it has been shown that it is mainly attributable to modulate the electrostatic contribution to the overall interaction. The other factor affecting the strength of the chalcogen bond is the basicity of the electron donor. Such a factor has been shown to strongly modify the properties of many different types of chalcogen bond interactions [33, 34].

There are recent numerous studies seeking to characterize the geometrical and energetic properties of chalcogen bonds [35–38]. With the progress in the study of chalcogen-bonding, different types of chalcogen bonds have been proposed in recent years. Conventional chalcogen bonds of the sort where a chalcogen donor approaches an acceptor atom with a lone pair like O or N have been well studied over the years, and their fundamental nature is understood [30–34]. There are also so-called unconventional chalcogen bonds such as chalcogen-hydride [39]. All these interactions mentioned may be classified as Lewis acid-Lewis base interactions, and there is an electrostatic attraction between the Lewis base and Lewis acid for all of them.

Considering the fact that a partially negatively carbon atom in the CH_3 molecule can interact with a halogen atom with the positive electrostatic potential [40], a different type of chalcogen-bonding is established where a radical acts as the electron donor. Such an interaction may be referred to as a single-electron σ -hole interaction. In such chalcogen–single electron interactions, the chalcogen atom acts as a Lewis acid center and the carbon atom, with a singly occupied orbital, acts as a Lewis base. The main objective of the present study is to examine the geometry and interaction energy of various chalcogen–single electron bonded complexes. We theoretically investigated a series of chalcogen–single-electron bonded complexes between XHY ($X=F, Cl, Br$; $Y=S, Se$) and CH_3 or CH_2CH_3 radical. In order to deepen the nature of the interaction, interaction energy decomposition, molecular electrostatic potential, and electron density analyses have been performed.

Computational details

All calculations were performed using the GAMESS program [41]. The geometries of monomers and adducts have been fully optimized at UMP2/aug-cc-pVTZ level of theory. The harmonic vibrational frequencies were also calculated at the same level to confirm that the obtained structures are true minima. The interaction energy for the optimized complexes has been computed at the UMP2/aug-cc-pVTZ and UCCSD(T)/aug-cc-pVTZ levels, as the difference between the total energy of the complex and the energies of monomers. The basis set superposition error (BSSE) was corrected for interaction energies using the counterpoise method [42].

In order to gain insight into the origin and nature of the interactions we have employed the following energy decomposition scheme [43]:

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{exch-rep}} + E_{\text{pol}} + E_{\text{corr}}, \quad (1)$$

where E_{elst} , $E_{\text{exch-rep}}$, E_{pol} , and E_{corr} correspond to electrostatic, exchange-repulsion, polarization, and correlation terms, respectively. All these terms were obtained at the UCCSD(T)/aug-cc-pVTZ level.

The surface electrostatic potentials were computed with Wave Function Analysis–Surface Analysis Suite (WFA–SAS) [44]. The topological analysis of the electron charge density was performed by means of the AIM2000 program [45] with the MP2/aug-cc-pVTZ wave functions. The natural bond orbital (NBO) analysis [46] was performed by using the wave functions generated at the MP2/aug-cc-pVTZ level of theory.

Results and discussion

Electrostatic potential analysis Earlier studies [14–24] have demonstrated that the electrostatic potentials are an efficient tool for analyzing and predicting noncovalent interactions. Regarding the electrostatic nature of the chalcogen bond interaction, examination of the molecular electrostatic potentials of the various chalcogen bond donors all show a positive region in the vicinity of the chalcogen atom. In each case, we computed electrostatic potential on the molecular “surface” which we define, according to Bader et al. [47], as the 0.001 electrons/bohr³ contour of the electronic density $\rho(r)$. Figure 1 shows that there is small positive electrostatic potential cap at the end region of the S(Se) atom along the F–S(Se) bond vector of FHS(Se) molecule, which is surrounded by an electroneutral area and, next, a large electronegative domain. Such a chalcogen positive region is referred to as the “ σ -hole”, because it is centered on the F–S(Se) axis and is surrounded by negative electrostatic potential [19].

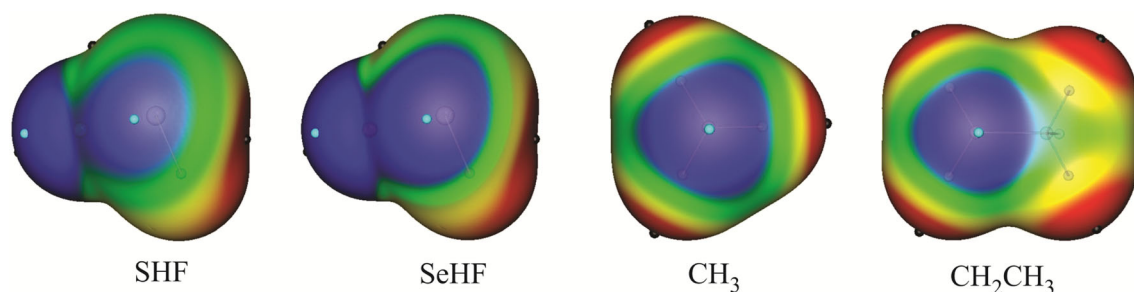


Fig. 1 Molecular electrostatic potentials of SHF, SeHF, CH₃, and CH₂CH₃ monomers. Black and blue circles are surface maxima and minima, respectively

Consistent with the usual trend that σ -holes become more positive in going to the heavier elements in a group, the σ -hole of Se atom is more positive than the S counterpart (Table 1). Figure 1 also shows electrostatic potential map for the CH₃ and CH₂CH₃ radicals. It is evident that the methyl radical has a region of negative electrostatic potential ($V_{S,\min}$) on the outermost portion of the carbon surface. The calculated $V_{S,\min}$ for CH₃ radical is about $-8.3 \text{ kcal mol}^{-1}$, which is distinctly smaller than those of ammonia ($-39.5 \text{ kcal mol}^{-1}$) or water ($-35.6 \text{ kcal mol}^{-1}$). One can see that the $V_{S,\min}$ in the CH₂CH₃ radical is more negative than that of CH₃. Thus the carbon atom of CH₃ or CH₂CH₃ radical with negative electrostatic potential approaches the chalcogen atom and the chalcogen atom plays the role of electron acceptor. The interaction between the σ -hole and the carbon in CH₃ or CH₂CH₃ radical is called “single-electron chalcogen bond” interaction, in view of the concepts of chalcogen bond and single-electron halogen bonds.

Geometries The optimized structure of single-electron chalcogen bonded complexes is illustrated in Fig. S1 (Supporting information). Table 2 lists the bond lengths in these complexes. No imaginary frequencies were found for any of the structures determined, so they are true minima. The optimized C–H bond distance of the methyl radical is 1.075 \AA at the UMP2/aug-cc-pVTZ level, which is in good agreement with the experimental value 1.079 \AA [48]. The single electron–chalcogen binding distances are in a range of about 2.61 – 3.01 \AA and 2.57 – 2.83 \AA for the S \cdots C and Se \cdots C complexes,

Table 1 Calculated most positive ($V_{S,\max}$; kcal mol^{-1}) and most negative ($V_{S,\min}$; kcal mol^{-1}) electrostatic potentials for the optimized monomers

Monomer	$V_{S,\max}$	$V_{S,\min}$
FHS	48.2	-
CIHS	35.8	-
BrHS	33.4	-
FHSe	55.8	-
CIHSe	42.6	-
BrHSe	37.6	-
CH ₃	-	-8.3
CH ₂ CH ₃	-	-10.9

respectively, which are much smaller than the sum of the van der Waals radii of the carbon and chalcogen atoms [49]. This indicates an attractive interaction between both molecules. It is noteworthy that the S(Se) \cdots C distance becomes shorter with the increase of the chalcogen atomic radius, which implies the stronger interactions of the Se \cdots C complexes. For a given chalcogen atom donor, the CH₃ radical results in a longer binding distance than the CH₂CH₃ counterpart. An interesting aspect of the results presented in Table 2 is the fact that the binding distance of the systems tends to increase as the size of the substituted halogen increases, which corresponds to a decreasing value of the halogen atom electronegativity. Hence, the shortest binding distance is found in FHSe \cdots CH₂CH₃ complex, whereas the longest binding distance is seen in BrHS \cdots CH₃ complex. As a final note from Fig. S1, the chalcogen bond contacts are closely linear, consistent with earlier experimental [30, 31] and theoretical [32–36] data on other chalcogen-bonded complexes.

As expected, the formation of XHY \cdots CH₃ and XHY \cdots CH₂CH₃ complexes has a significant effect on the geometry of the interacting molecules. Due to the interaction

Table 2 Binding distances (in \AA), interaction energies (in kcal mol^{-1}), and interaction energy terms (in kcal mol^{-1}) for single-electron bonded complexes^a

Complexes	R_{int}	$E_{\text{int}}^{\text{MP2}}$	$E_{\text{int}}^{\text{CCSD(T)}}$	E_{elst}	$E_{\text{exch-rep}}$	E_{pol}	E_{corr}
FHS \cdots CH ₃	2.86	-2.9	-2.9	-5.8	10.0	-3.3	-3.8
CIHS \cdots CH ₃	3.00	-2.0	-1.9	-4.0	7.1	-2.0	-3.0
BrHS \cdots CH ₃	3.01	-1.9	-1.7	-4.0	7.3	-2.0	-3.0
FHSe \cdots CH ₃	2.76	-3.7	-3.7	-10.2	17.8	-3.1	-8.1
CIHSe \cdots CH ₃	2.82	-2.9	-2.7	-8.8	16.2	-5.1	-4.6
BrHSe \cdots CH ₃	2.83	-2.6	-2.4	-8.6	15.5	-4.9	-4.6
FHS \cdots CH ₂ CH ₃	2.61	-4.8	-4.7	-12.6	22.9	-8.0	-7.0
CIHS \cdots CH ₂ CH ₃	2.70	-3.7	-3.3	-9.8	18.2	-5.6	-6.3
BrHS \cdots CH ₂ CH ₃	2.72	-3.5	-3.1	-8.4	16.1	-4.5	-6.1
FHSe \cdots CH ₂ CH ₃	2.57	-6.4	-6.0	-16.2	32.4	-10.6	-11.6
CIHSe \cdots CH ₂ CH ₃	2.65	-4.4	-4.2	-14.1	28.0	-8.5	-9.6
BrHSe \cdots CH ₂ CH ₃	2.67	-3.9	-3.7	-12.6	25.1	-7.6	-8.6

^a Interaction energy terms from UCCSD(T)/aug-cc-pVTZ calculations

with the XHY, the C–H bonds of CH₃ and CH₂CH₃ bonds are slightly elongated although the elongation is small. The elongation of the C–H bonds means that they become weak due to the formation of σ -hole bonding. The S–H and Se–H bond lengths are also lengthened a little upon the formation of the complexes. Meanwhile, the C–H bonds bend opposite to the chalcogen atom with the X–S \cdots C and X–Se \cdots C angles near 100°, which might be explained by the electrostatic interaction between the positively charged chalcogen atom and H atoms. Such a structural deformation indicates that the single-electron chalcogen-bonding interaction has led to rehybridization of the carbon from sp^2 to the sp^x hybridization between the ideal sp^3 and sp^2 . Not surprisingly, the largest bending is found for the FHSe \cdots CH₂CH₃ complex, which has the shortest binding distance.

Interaction energies The BSSE-corrected interaction energies in the S(Se) \cdots C bonded complexes calculated at the UMP2/aug-cc-pVTZ level are given in Table 2. The interaction energies all vary within the relatively narrow range of -1.9 to -4.8 kcal mol⁻¹ (for S \cdots C) and -2.6 to -6.4 kcal mol⁻¹ (for Se \cdots C). This range makes these complexes weak in strength. It is evident from Table 2 that the order of interaction energies of dimers for a given radical depends on the substituent X group in XHY molecule. These interaction energies decrease in the order FH Y > ClHY > BrHY. For a given X and Y, the interaction energy per S(Se) \cdots C binding distance is always greater for the C₂H₅ radical compared to the corresponding CH₃. Polynomial correlations exist between the binding distances and interaction energies of XHY \cdots CH₃ and XHY \cdots CH₂CH₃, as given by Eqs. 2 and 3:

$$E_{\text{int}} = 0.064 R_{\text{int}}^2 + 0.499 R_{\text{int}} + 3.728 \quad (R^2 = 0.945) \quad \text{for XHY}\cdots\text{CH}_3 \quad (2)$$

$$E_{\text{int}} = 0.017 R_{\text{int}}^2 + 0.227 R_{\text{int}} + 3.294 \quad (R^2 = 0.985) \quad \text{for XHY}\cdots\text{C}_2\text{H}_5. \quad (3)$$

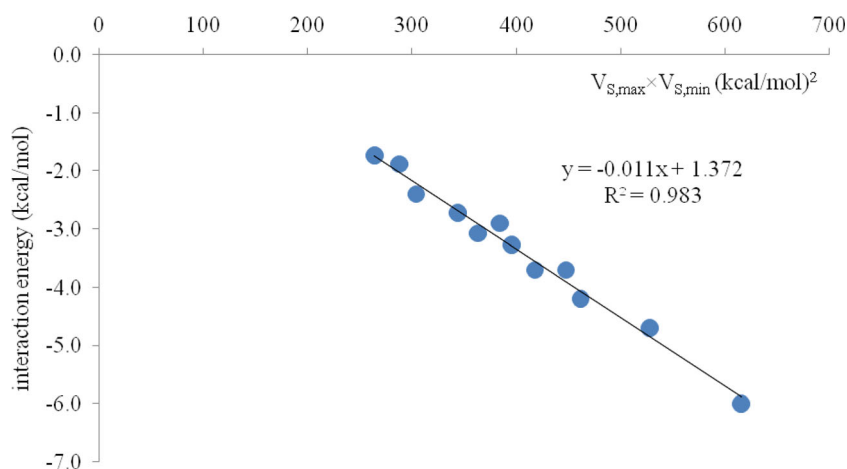
To obtain more accurate and reliable interaction energies, a single point energy was calculated at the UCCSD(T)/aug-cc-pVTZ level, which provided a less negative interaction energy of the complexes compared to that using the UMP2/aug-cc-pVTZ method (Table 2). The difference in the interaction energy at both levels is less than 0.4 kcal mol⁻¹ which shows a maximum deviation of less than 13 % from the UCCSD(T) results. This indicates that the UMP2 method is also feasible for description of single-electron chalcogen bonds. Besides, the interaction energies of the single-electron chalcogen bonded complexes are smaller than others obtained in the literature where the lone pair electrons act as electron donors [32–34]. Otherwise, the trends in interaction energies of complexes with CCSD(T) method are the same as discussed for the MP2 method.

One can see that the interaction energy in the Se complexes is more negative than the S counterpart. It thus supports the general understanding that the strength of chalcogen bond correlates with the positive electrostatic potential on the extension of the bond to the chalcogen atom. The same trend is also valid for other σ -hole bonds and is illustrated by the increase of the magnitude of the electrostatic potential on the chalcogen atom [33, 34]. This result indicates qualitatively that the electrostatic interaction plays an important role in the formation of the single-electron chalcogen bond interactions. Almost perfect linear relationship is obtained between the interaction energy and the magnitudes of the product of $V_{\text{S,max}}$ and $V_{\text{S,min}}$ associated with the interacting atoms (Fig. 2). This reveals that both the negative and positive regions of the atoms in the molecules interacting can be used to predict the strength of the eventual interaction.

An important point that needs to be clarified is the mutual polarization between XHY and CH₃/C₂H₅ subunits in the title complexes. As expected from the above discussion, the formation of the chalcogen bond complexes XHY \cdots B is generally accompanied by some mutual polarization of XHY by the electric field of B (in our case CH₃ or C₂H₅) and of B by the electric field of the σ -hole on the chalcogen Y atom of XHY. This means that electron density on methyl or ethyl radical should become somewhat polarized toward the σ -hole of XHY, and that on XHY should tend to move away from the radical. We think the later effect may play a significant role in the stability of the single bond chalcogen bond interactions in the title complexes. However, the effect should be more important in the Se complexes as would be expected from the stronger σ -hole of XHSe molecule than that of XHS.

In order to gain insight into the contribution of the different energy terms of the interaction energy, interaction energy decomposition analysis was performed for the single-electron chalcogen bonded complexes (Table 2). It may be pointed out that there is no rigorous basis for defining such energy terms [50, 51], since they are not physical observable quantities. The energy components are not independent of each other, no matter what procedure is used. Although all of the energy partition schemes are arbitrary, they can provide chemical insights into energetic differences when they are applied to an analogous series of complexes, as in this case. As Table 2 indicates, electrostatic interaction has been identified as the major contributing factors for the stability of single-electron chalcogen bonded complexes. These results are consistent with those of other studies chalcogen bond interactions [33,

Fig. 2 Correlation between CCSD(T) interaction energies and magnitudes of the product of $V_{S,max}$ and $V_{S,min}$ associated with the interacting atoms in the $XHY\cdots CH_3$ and $XHY\cdots CH_2CH_3$ complexes



34, 39]. The polarization energy term also has a significant contribution to the total interaction energy, indicating a perturbation of electron density distribution arising from the weak interaction in these single-electron chalcogen bonded complexes. Another important finding is that the exchange-repulsion energy ($E_{exch-rep}$) quenches the electrostatics entirely and the first order term is repulsive. Hence, the correlation energy E_{corr} must be taken into account for the right description of the energetics of the complexes. One can see that increasing the size and positive nature of a chalcogen's σ -hole remarkably enhances the strength of the electrostatic component of the chalcogen-bonding interaction. What is notable is that the dispersion interaction weakens in the same direction. Thus, the chalcogen atom with larger, more positive σ -holes tend to exhibit larger E_{elst}/E_{disp} ratio, which is attributed to the lower local polarizabilities of the larger σ -holes. As was noted recently by Riley et al. [52], this is due to the shifting of valence electronic charge that gives rise to a positive σ -hole potential which diminishes the local polarizability of the chalcogen atom.

Electronic aspects The existence of single-electron chalcogen bonds can be further validated by the presence of S(Se) \cdots C bond critical points of electron densities in all of the title complexes. A bond critical point (BCP) is identified for each S(Se) \cdots C bond interaction, accompanied by a bond path between the two corresponding interacting points. The properties at the BCPs are analyzed in terms of the following parameters: the electron density (ρ_{BCP}), its Laplacian ($\nabla^2\rho_{BCP}$), the electron energy density (H_{BCP}), and absolute ratio of kinetic and potential energies densities ($-K_{BCP}/V_{BCP}$). Table 3 results indicate that, despite falling in a region of charge depletion with $\nabla^2\rho_{BCP} > 0$, all of the XHS \cdots CH₃ critical points are characterized by a small value of the electron density ρ_{BCP} , $H_{BCP} > 0$ and $-G_{BCP}/V_{BCP} > 1$, indicating that the kinetic energy overcomes the potential energy density at the BCPs. For the XHS \cdots CH₂CH₃ complexes, the

calculated ρ_{BCP} value is 0.029, 0.025, and 0.024 au for X=F, Cl, and Br, respectively. These values are larger than those of XHS \cdots CH₃, which are in accordance with the evidence for the stabilization of the S \cdots C interactions by the presence of the methyl group in CH₂CH₃. One can see that all values of electron density and its Laplacian are within the range proposed by Koch and Popelier for hydrogen-bonding interactions [53]. For the S \cdots C complexes, the calculated values of ρ_{BCP} vary from 0.012 to 0.029 au, while the corresponding Laplacian values are all positive with a range of 0.037–0.058 au. The electron density values for the Se-bonded complexes are slightly larger than for the S counterparts. This finding has also been found for other types of chalcogen bonds [54]. The QTAIM results indicate the capacity of the single-electron chalcogen bonded complexes to concentrate electrons at the S(Se) \cdots C critical points enhance considerably with the size of chalcogen atom. This also supports the conclusion that the strength of S(Se) \cdots C interactions correlates with the magnitude of the surface electrostatic potential maxima on the chalcogen atom. It is revealed that for a given chalcogen atom, the H_{BCP} value at the S(Se) \cdots CH₂CH₃ critical point is more negative than that in the corresponding S(Se) \cdots CH₃. This result confirms that the chalcogen bond interactions in the S(Se) \cdots CH₂CH₃ are more covalent than with respect to the S(Se) \cdots CH₃ systems. In Fig. 3, we represented the calculated values of ρ_{BCP} versus the corresponding S(Se) \cdots C distances. They show an exponential relationship, which is similar to what is found in halogen-bonded complexes [55].

Many well-known noncovalent interactions, such as hydrogen-bonding and halogen-bonding, are stabilized by charge transfer from an occupied orbital of the electron donor to a low-lying virtual orbital of the electron acceptor [46]. Thus, to investigate the single-electron chalcogen bond formation can be related to charge transfer between different moieties in the title complexes, NBO analysis has been

Table 3 QTAIM parameters (ρ_{BCP} , $\nabla^2\rho_{\text{BCP}}$, H_{BCP} , and $-K_{\text{BCP}}/V_{\text{BCP}}$), natural charge change ($\Delta q_{\text{S(Se)}}$) of S and Se atom with respect to the isolated XHS(Se) monomer, net charge transfer (q_{CT}) and Wiberg bond index (WBI) for single-electron chalcogen bonded complexes ^a

Complexes	ρ_{BCP}	$\nabla^2\rho_{\text{BCP}}$	H_{BCP}	$-K_{\text{BCP}}/V_{\text{BCP}}$	$\Delta q_{\text{S(Se)}}$	q_{CT}	WBI
FHS...CH ₃	0.018	0.045	0.001	1.15	0.024	0.020	0.007
ClHS...CH ₃	0.012	0.038	0.001	1.09	0.016	0.014	0.004
BrHS...CH ₃	0.012	0.037	0.001	1.09	0.014	0.014	0.003
FHSe...CH ₃	0.032	0.056	-0.011	0.90	0.030	0.034	0.018
ClHSe...CH ₃	0.022	0.046	-0.001	0.91	0.022	0.033	0.010
BrHSe...CH ₃	0.021	0.046	-0.001	0.92	0.020	0.033	0.007
FHS...CH ₂ CH ₃	0.039	0.058	-0.004	0.85	0.044	0.042	0.074
ClHS...CH ₂ CH ₃	0.025	0.054	-0.002	0.87	0.035	0.036	0.032
BrHS...CH ₂ CH ₃	0.024	0.053	-0.002	0.89	0.034	0.034	0.030
FHSe...CH ₂ CH ₃	0.063	0.065	-0.019	0.80	0.052	0.049	0.086
ClHSe...CH ₂ CH ₃	0.057	0.062	-0.014	0.84	0.048	0.043	0.046
BrHSe...CH ₂ CH ₃	0.056	0.060	-0.012	0.86	0.044	0.041	0.041

^a All ρ_{BCP} , $\nabla^2\rho_{\text{BCP}}$, H_{BCP} , $\Delta q_{\text{S(Se)}}$, and q_{CT} results in au

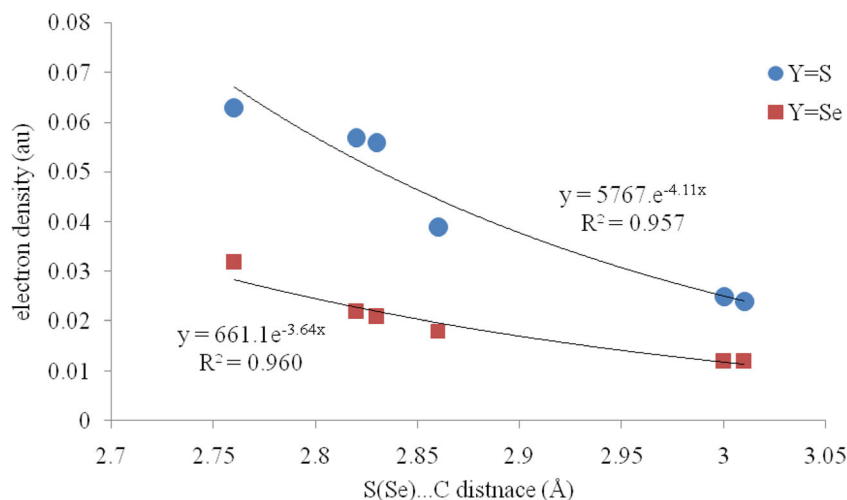
performed on the optimized structures. Figure 4 indicates the computed electron density difference plot for the FHS...CH₃ and FHSe...CH₃ complexes, where loss of electrons is indicated in yellow, and electron enrichment is indicated in blue. It is seen that there is an increase in electron density between the CH₃ and FHS(Se) surfaces, indicating the formation of the single-electron chalcogen bond interaction. The electric field of the positive σ -hole on the S(Se) atom of FHS(Se) tends to produce a rearrangement of electronic charge within the CH₃ molecule. It should be noted that the electric field created by the FHS is relatively weaker than that of FHSe, due to its smaller σ -hole (48 kcal mol⁻¹). This accordingly results in smaller electronic density shifts around the FHS molecule compared to the FHSe. At the same time, the electron density around the area of chalcogen atom which interacts with the CH₃ unit is decreased. This means that electron density on S(Se) should tend to move away from the CH₃, while the electron density around the carbon atom of CH₃ becomes somewhat polarized toward the positive portion of S or Se atom. A similar polarization effect has been previously

reported for hydrogen and halogen bonds by Politzer and Clark groups [21, 23, 56].

Table 3 lists the natural charge change ($\Delta q_{\text{S(Se)}}$) of S(Se) atom due to the chalcogen bond formation in the title complexes. Whether in the S...C or Se...C bonded complexes, it is evident that the chalcogen atom becomes less positively charged due to chalcogen bond formation. The amount of decreased atomic charge in a given complex depends on the interaction strength. As a result, the Δq enhances on going from S to Se complexes, due to the stronger Se...C interactions. On the other hand, the carbon atom in CH₃ or CH₂CH₃ subunit becomes negative from the isolated molecule to complexes. Although the chalcogen positive charge decreases in the complexes, we think that the electrostatic interaction is of importance in this interaction because the increase of the C negative charge is much larger than the decrease of the chalcogen positive charge.

In the formation of single-electron chalcogen bonded complexes, a charge transfer (0.014–0.049 e) happens from the CH₃ or CH₂CH₃ subunit to the chalcogen atom (Table 3).

Fig. 3 Correlation between electron density at the S(Se)...C critical point and binding distance in the XHY...CH₃ and XHY...CH₂CH₃ complexes



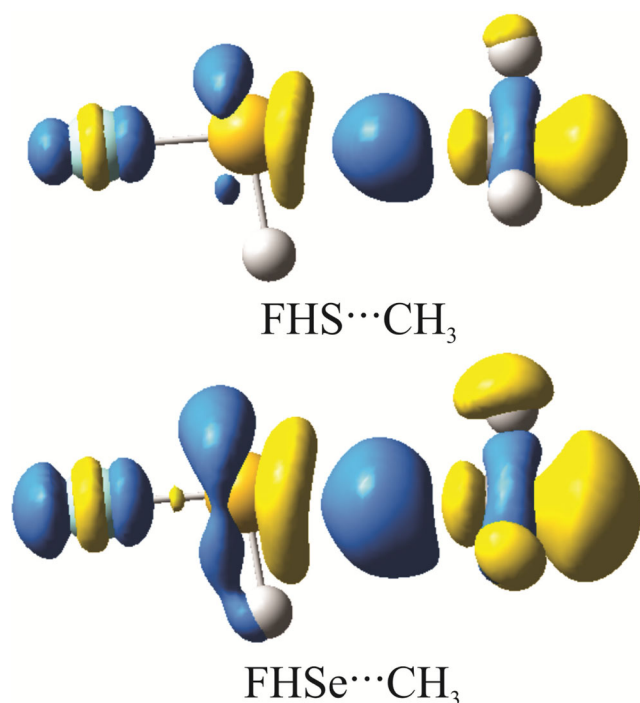


Fig. 4 Electron density shifts in $\text{FHS}\cdots\text{CH}_3$ and $\text{FHSe}\cdots\text{CH}_3$ complexes. Blue regions indicate increased density, yellow regions indicate decreased density. Contours are shown at the 0.0001 au level

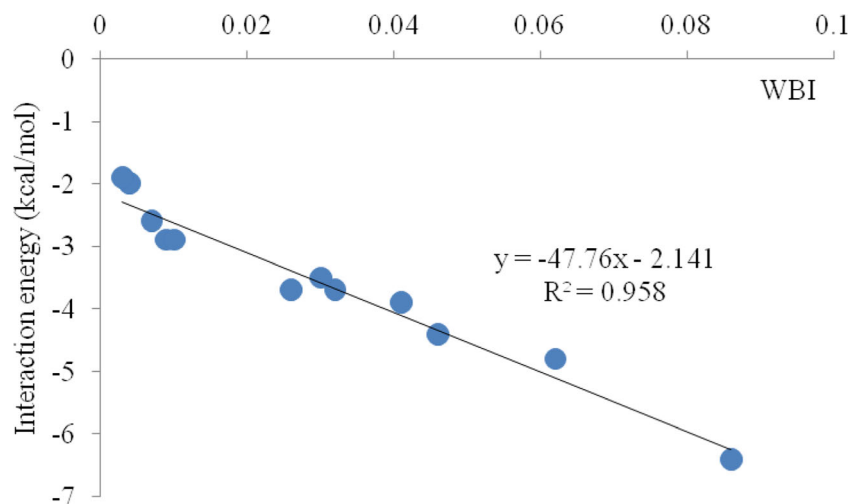
The largest charge transfer happens in the $\text{FHSe}\cdots\text{CH}_2\text{CH}_3$ complex, whereas the smallest charge transfer is seen in the $\text{BrHS}\cdots\text{CH}_3$ complex. For a given chalcogen bond acceptor, the amount of charge transfer of $\text{Se}\cdots\text{C}$ is larger than that the $\text{S}\cdots\text{C}$. Table 3 also list the Wiberg bond index (WBI) at the $\text{S}(\text{Se})\cdots\text{C}$ bonds. This is the sum of squares of off-diagonal density matrix elements between the two atoms, which gives a measure of the bond interaction. For our purposes, it shows the extent of bond overlap associated with each $\text{S}(\text{Se})\cdots\text{C}$ and it also weighs covalent character of the bond. One can see from Table 3 that the WBI at the $\text{Se}\cdots\text{C}$ bonds is larger than

that at $\text{S}\cdots\text{C}$ ones. Moreover, the WBI value associated with $\text{S}(\text{Se})\cdots\text{CH}_2\text{CH}_3$ bond is slightly greater than that in the $\text{S}(\text{Se})\cdots\text{CH}_3$ counterparts. This supports the fact that the former interaction is stronger than in the later one. In fact, good linear correlations are found between the magnitudes of interaction energy and WBI values in the complexes (Fig. 5). This means that the charge transfer interaction is a main contribution in the single-electron chalcogen bonds.

Conclusions

An ab initio study of the complexes between XHY ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) and CH_3 or CH_2CH_3 radical has been carried out at the UMP2/aug-cc-pVTZ and UCCSD(T)/aug-cc-pVTZ levels of theory. The single-electron chalcogen bond interaction is weak with small interaction energy, where the dispersion and electrostatic interaction makes the major contribution to the $\text{S}(\text{Se})\cdots\text{C}$ bond. A linear relationship is obtained between the interaction energy and the magnitudes of the product of $V_{\text{S,max}}$ and $V_{\text{S,min}}$ associated with the interacting atoms. The results of QTAIM and NBO analyses are consistent with the formation of the single-electron chalcogen bond. The QTAIM results indicate the capacity of the $\text{XHY}\cdots\text{CH}_3$ complexes to concentrate electrons at the $\text{S}(\text{Se})\cdots\text{C}$ critical points enhances considerably with the size of chalcogen atom. This supports the conclusion that the strength of $\text{S}(\text{Se})\cdots\text{C}$ interactions correlates with the magnitude of the surface electrostatic potential maxima on the chalcogen atom. An acceptable linear correlation is found between the magnitudes of interaction energy and WBI values in the complexes, which reveals that charge transfer plays an important role in the stability of the single-electron chalcogen bonds.

Fig. 5 Correlation between cooperative energy and WBI



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