Comparison for Electron Donor Capability of Carbon-Bound Halogens in Tetrel Bonds

Qingqing Yang, Xiaolong Zhang,* and Qingzhong Li*

1. INTRODUCTION

The tetrel bond is an attractive interaction between a group 14 element and an electron donor.1 Politzer and coauthors proposed a concept of σ-holes, referred to the electron-deficient outer lobe of a half-filled p orbital of a covalent bond, to explain the formation of a halogen bond.2 Then, this concept was extended to other groups including the group 14 element (tetrel).3 This σ-hole displays a region with positive molecular electrostatic potentials (MEPs) on the atomic surface along a covalent bond; thus, it can interact attractively with a negative site in another molecule. Subsequently, these authors named a π-hole to describe a region with positive MEPs that is vertical to a portion of a molecular framework.4 Such a π-hole is also found for the group 14 element in sp2-hybridized molecules. The presence of a σ-hole/π-hole indicates that the tetrel bond is electrostatically driven. Both the σ-hole and π-hole become larger going from the lighter to the heavier atoms in a given group of the periodic table; thus, it is expected that the tetrel bond becomes stronger. Other than electrostatic contributions, the stability of a tetrel-bonded complex is in part attributed to charge transfer from the electron donor to the acceptor.5

Like hydrogen and halogen bonds, the tetrel bond is of great importance in crystal materials,6,7 chemical reactions,8,9 molecular recognition,10–12 and biological systems.13–15 Therefore, there are lots of theoretical and experimental studies of tetrel bonds.16–32 These applications are related to the directionality and strength of tetrel bond. Owing to the anisotropic distribution of electrostatic potentials and steric hindrance of a tetravalent tetrel atom,33 the tetrel bond is sensitive to angular distortions, displaying directionality. Both the electron-donating substituents in the electron donor and the electron-withdrawing groups in the tetrel donor have an enhancing effect on the strength of the tetrel bond.16–22

Sometimes, some unexpected substitution effects are found for tetrel bonds. For example, adding a −CH3 group in formamidine could greatly increase the interaction energy of the SiH2F complex from 60 to 80 kJ/mol.21 Cooperativity can also strengthen or weaken tetrel bonds, and this effect plays an important role in constructing crystal materials.24–32 Experimental and theoretical studies show that a tetrel bond is concurrent with an agostic Pb···H–C interaction in N’-(phenyl(pyridin-2-yl)methylene)isonicotinohydrazide–PbX complexes (X=Cl, I, NCS, NO2).30

The electron donor in the tetrel bond is varied from neutral molecules with lone pairs and anions33 to molecules with π electrons,34 metal hydrides,35 radicals,36 and carbenes.37 Even so, the electron donors used in studying tetrel bonds are usually from neutral molecules with lone pairs and anions. These molecules are often nitrogen/oxygen-containing38–51 partly because some of these complexes such as SiF···NH3 and SiF···N(CH3)3 were identified experimentally.38 The N hybridization in the nitrogen electron donor affects the tetrel bond, becoming stronger in the sp < sp2 < sp3 sequence.39,40 When the carbonyl oxygen atom of malondialdehyde engages in a π-hole tetrel bond with F2SiO, the intramolecular hydrogen bond is enhanced with proton transfer within this H bond.46 NH3 is inclined to form a H bond with the −CF3 group adjoined to pyridine; however, the protonation on the nitrogen atom of pyridine promotes the formation of a tetrel
bond.\textsuperscript{59} Dong and coauthors compared $\sigma$−/$\pi$-hole tetrel bonds between TH$_3$F/T:TO and H$_2$C~X (X=O, S, Se) and found an interesting dependence of their strengths on the chalcogen electron donor.\textsuperscript{51} The $\sigma$-hole interaction is weaker for the heavier chalcogen electron donor, while the $\pi$-hole interaction involving F:TO (T=Ge, Sn, and Pb) has an opposite dependence.\textsuperscript{51}

Halogen anions have been used in studying tetrel bonds since they can be utilized in molecular recognition.\textsuperscript{52−54} Regardless of which receptors (hydrogen, halogen, chalcogen, pnictogen, and tetrel), F$^-$ is bound much more strongly than Cl$^-$ and Br$.\textsuperscript{53}$ More surprisingly, the tetrel receptor shows the greatest selectivity for F$^-$ over the other halides, as much as 10$^{13}$, an enhancement of six orders of magnitude when compared to the H-bonding receptor.\textsuperscript{53} Likely, the halogen anion in LiX forms a stronger tetrel bond than neutral molecules and the tetrel bond becomes weaker for the heavier halogen ion.\textsuperscript{55} The ionic property of HArF makes the negatively charged F atom become a good electron donor in the tetrel bond.\textsuperscript{56} The tetrel bonding interaction energy between HArF and SiH$_3$X (X = halogen) is in a range of 95−135 kJ/mol at the MP2/CBS level.\textsuperscript{56} Interestingly, the interaction energy becomes larger with the increase of X atomic mass in SiH$_3$X although the heavier X atom shrinks the $\sigma$-hole on the Si atom.\textsuperscript{56} However, hydrogen halides are seldom used as the electron donors in tetrel bonds.\textsuperscript{57,58} In the ground-state geometry, CO$_2$ forms a hydrogen bond with HCl but a tetrel bond with HBr in which the negatively charged Br atom approaches the carbon atom of CO$_2$.\textsuperscript{57} SiH$_4$, SiF$_4$, and SiCl$_4$ bind with NH$_3$ through a tetrel bond, but they form a hydrogen bond with HF where the hydrogen atom interacts with the silicon substituents.\textsuperscript{58} It was demonstrated that organic fluorine molecules have been extensively utilized in crystal engineering and functional materials.\textsuperscript{59} However, the study of tetrel bonds involving organofluorine electron donors is sporadic.\textsuperscript{50,61} CH$_3$F forms a weaker tetrel bond with SiH$_3$X (X=F and Cl) than NH$_3$.\textsuperscript{60} There is evidence for the C−F...C=O $\pi$-hole tetrel bond in protein−drug interaction although its interaction energy is less than 5 kJ/mol.\textsuperscript{61}

In this manuscript, we focus on the tetrel bond between TH$_3$F (T=C, Si, Ge) and organic fluorine electron donors. The organic fluorine molecules studied contain CH$_3$CH$_2$F (sp$^3$), CH$_2$CHF (sp$^3$), and CHCHF (sp). Then, the F atom in the organic fluorine is replaced by Cl, Br, and I. We systematically study the tetrel bond involving organic halogen electron donors. Can these organic halogens form a stable tetrel-bonded complex? How does the strength of tetrel bond depend on the nature of tetrel and halogen? What is the dominant origin of the tetrel bond? These tetrel bonds are characterized by means of geometries, energetics, natural bond orbital (NBO), atoms in molecules (AIM), and energy decomposition (EDA) analyses.

### 2. COMPUTATIONAL METHODS

The geometries of monomers and binary complexes were optimized at the MP2/aug-cc-pVTZ level. In addition, in order to consider the relativistic effects, the aug-cc-pVTZ-PP basis set was used for the I atom. Harmonic frequency calculations were performed at the same level to verify that the structures are local minima on their respective potential energy surfaces. The full counterpoise procedure was employed to correct for the basis set superposition error (BSSE).\textsuperscript{62} All calculations were carried out using the Gaussian 09 package.\textsuperscript{63}

The molecular electrostatic potentials (MEPs) of the monomers on the 0.001 a.u. isodensity surface were evaluated at the MP2/aug-cc-pVTZ level using the Wave Function Analysis-Surface Analysis Suite (WFA-SAS) program.\textsuperscript{64} Natural bond orbital (NBO)\textsuperscript{64} analysis was performed at the HF/aug-cc-pVTZ level to obtain orbital interaction and charge transfer (CT). The AIM2000 software\textsuperscript{66} was carried out to obtain the electron density ($\rho$), energy density ($H$), and Laplacian ($\nabla^2\rho$) at the relevant bond critical points (BCPs). The LMOEDA\textsuperscript{67} (localization molecular orbital energy decomposition analysis) was performed at the MP2/aug-cc-pVTZ level using the GAMES program.\textsuperscript{68} According to LMOEDA, the total interaction energy of a complex was decomposed into electrostatic energy ($E^{CE}$), exchange energy ($E^{EX}$), repulsion energy ($E^{RP}$), polarization energy ($E^{PO}$), and dispersion energy ($E^{DISP}$).

### 3. RESULTS

#### 3.1. MEP Analysis

The MEP maps of TH$_3$F (T=C, Si, Ge) monomers are shown in Figure 1. As indicated in Figure 1,

![Figure 1. MEP maps of CH$_3$F, SiH$_3$F, and GeH$_3$F on the $\rho = 0.001$ a.u. isodensity surface.](https://doi.org/10.1021/acsomega.1c04085)

![Table 1. Most Negative MEP ($V_{min}$, a.u.) on the X (X=F, Cl, Br, I) Atomic Surface in the Monomers](https://doi.org/10.1021/acsomega.1c04085)

![Figure 2. Schematic diagrams of three complexes.](https://doi.org/10.1021/acsomega.1c04085)

all TH$_3$F monomers possess a region with positive MEPs ($\sigma$-hole) along the extension of the T−F bond. The increase of MEP on the $\sigma$-hole follows the order of C < Si < Ge, and the maximum value of GeH$_3$F is 0.0766 a.u. According to our
previous studies, the MEP distribution of CHCF exhibits a negative region on the F end.\textsuperscript{69} Thus, the σ-hole of TH\textsubscript{3}F monomer can form a weak tetrel bond with the most negative MEP region of CHCX (X= F, Cl, Br, I; T=C, Si, Ge). In addition, the π-electrons in CH\textsubscript{3}CHX and CHCHX also participate in a tetrel bond with TH\textsubscript{3}F.\textsuperscript{34}

Table 1 lists the most negative MEP value \( V_{\text{min}} \) of all Lewis bases. The minimum value is only \(-0.0046 \text{ a.u.} \) When the halogen atom is fixed, due to the difference in the electron donating ability of different hybridization types C, the negative MEP value decreases according to Csp\textsuperscript{3}-X > Csp\textsuperscript{2}-X > Csp-X. When the hybrid type is the same, the most negative MEP in Csp\textsuperscript{n}-X (\( n = 2, 3 \)) molecules gradually decreases in the order of

| complexes     | \( n=1 \)          | \( n=2 \)          | \( n=3 \)          |
|---------------|-------------------|-------------------|-------------------|
| Csp\textsuperscript{3}-F--C  | 3.163             | 0.92              | 1.40              |
| Csp\textsuperscript{3}-F--Si  | 3.120             | 1.03              | 1.67              |
| Csp\textsuperscript{3}-F--Ge  | 3.098             | 0.95              | 1.32              |
| Csp\textsuperscript{3}-Cl--C  | 3.547             | 0.83              | 0.83              |
| Csp\textsuperscript{3}-Cl--Si  | 3.440             | 0.54              | 1.56              |
| Csp\textsuperscript{3}-Cl--Ge  | 3.435             | 0.54              | 1.56              |
| Csp\textsuperscript{3}-Br--C  | 3.561             | 0.76              | 1.74              |
| Csp\textsuperscript{3}-Br--Si  | 3.496             | 0.82              | 1.76              |
| Csp\textsuperscript{3}-Br--Ge  | 3.567             | 0.76              | 1.76              |
| Csp\textsuperscript{3}--I--C  | 3.728             | 0.72              | 1.75              |
| Csp\textsuperscript{3}--I--Si  | 3.679             | 0.76              | 1.75              |
| Csp\textsuperscript{3}--I--Ge  | 3.702             | 0.73              | 1.73              |

Table 2. Binding Distance (R, Å), Angles of C--X..T (\( \alpha \), °) (X=F, Cl, Br, I; T=C, Si, Ge) and X--T--F (\( \beta \), °) in Complexes

| complexes     | \( n=1 \)          | \( n=2 \)          | \( n=3 \)          |
|---------------|-------------------|-------------------|-------------------|
| Csp\textsuperscript{3}-F--C  | 3.019             | 1.06              | 1.70              |
| Csp\textsuperscript{3}-F--Si  | 2.925             | 1.10              | 1.78              |
| Csp\textsuperscript{3}-F--Ge  | 2.871             | 1.10              | 1.78              |
| Csp\textsuperscript{3}-Cl--C  | 3.434             | 0.87              | 1.70              |
| Csp\textsuperscript{3}-Cl--Si  | 3.325             | 0.88              | 1.76              |
| Csp\textsuperscript{3}-Cl--Ge  | 3.301             | 0.87              | 1.75              |
| Csp\textsuperscript{3}-Br--C  | 3.501             | 0.83              | 1.68              |
| Csp\textsuperscript{3}-Br--Si  | 3.407             | 0.84              | 1.71              |
| Csp\textsuperscript{3}-Br--Ge  | 3.404             | 0.82              | 1.74              |
| Csp\textsuperscript{3}--I--C  | 3.706             | 0.76              | 1.72              |
| Csp\textsuperscript{3}--I--Si  | 3.604             | 0.78              | 1.74              |
| Csp\textsuperscript{3}--I--Ge  | 3.613             | 0.76              | 1.73              |

F > Cl > Br > I, which is in agreement with the electronegativity trend observed for halogens. However, this is abnormal for Csp-X. The most negative electrostatic potential law is F > I > Br > Cl, probably because of the hyperconjugation effect between the π orbital on the C=C bond and the lone pair on the halogen atom.

3.2. Energetics and Geometries. Figure 2 shows the geometries of complexes between Csp\textsuperscript{n}-X and TH\textsubscript{3}F (X=F, Cl, Br, I; T=C, Si, Ge). For simplicity, CH\textsubscript{3}CHX and CHCHX are represented as Csp\textsuperscript{3}-X, Csp\textsuperscript{2}-X, and Csp-X, respectively, while TH\textsubscript{3}F is denoted as T. As shown in Figure 2, R is the distance between the X atom in Csp\textsuperscript{n}-X and the T atom in TH\textsubscript{3}F, and the related geometrical parameters are summarized in Table 2. For the sp-hybridized CH\textsubscript{3}CHX and CHCHX structures, the C--X..T (\( \alpha \)) angle varies between 69 and 104° and is largest in the Csp-F system. This may be partly due to the coulomb attraction between the C=C π electrons in Csp-X and the positive MEP near the H atoms in TH\textsubscript{3}F, which is the weakest in the Csp-F system owing to the strongest electron-withdrawing ability of the F atom.

With the increasing X electronegativity, the α (C--X..T) angles for both sp\textsuperscript{2} and sp\textsuperscript{3} cases are increased in the same order of I < Br < Cl < F. Compared with the sp hybridization, the α (C--X..T) angle increases 1--40° for the sp\textsuperscript{2} hybridization and 5--40° for the sp\textsuperscript{3} hybridization, respectively. However, the β (X--T--F) angles for the three types of
hybridized H2C
strengthening of the tetrel bond.

Figure 3 presents the relationship between the interaction energy \( E_{\text{int}} \) and the halogen substituents in different hybridization modes. For T=C complexes, the interaction energy shows a similar increasing tendency with the decrease of the electronegativity of halogen substituents. This is also the same for T=Si complexes in both sp and sp\(^3\) hybridization except for sp\(^3\) hybridization. However, for T=Ge complexes, the interaction energy decreases in the order of F < Cl < Br < I for both sp and sp\(^2\) hybridization. On the other hand, for sp\(^3\) hybridization, some inconsistent variations are found, i.e., for the X=Cl substituent, which exhibits the largest interaction energy.

### 3.3. NBO Analysis

We have performed the NBO calculations to study the nature of interaction. The results of the charge transfer and the second-order stabilization energies \( E^{(2)} \) are gathered in Table 4. CT refers to the total amount of charge transfer from Csp\(^n\)-X to TH\(_3\)F, while \( E^{(2)} \) focuses on the specific orbital transfer from Lp\(_X\) to \( \sigma^{*}_{X-F} \) (Lp\(_X\) is the lone pair of electrons of halogen atoms and \( \sigma^{*}_{X-F} \) is the antibonding orbital of the T-F bond). The charge transfer leads to the better understanding of the energetics: the largest for Ge and smallest for C, and it decreases with the increase of electronegativity X. From Table 4, for different hybridization, the value of CT increases significantly from sp to sp\(^2\) to sp\(^3\).

The charge transfer of sp\(^3\) hybridization varies from a low of 0.0026e to as much as 0.0218e. Those quantities represent an 18–77% enhancement relative to the sp complexes. However, the charge transfer of sp\(^3\) hybridization is even twice that of sp.

In order to further analyze the nature of the orbital interaction, we have studied the second-order perturbation energy corresponding to the orbital interaction, and its value is estimated to in the range of 0.18–5.88 kcal/mol for all the complexes. When the X atom is the same, the \( E^{(3)} \) of the Csp\(^n\)-X···T complex increases in the order of C < Si < Ge. The \( E^{(3)} \) of the Csp\(^n\)-X···T complex increases in the order of F < Cl < Br

### Table 5. Electron Density (\( \rho \)), its Laplacian (\( \nabla^2 \rho \)), and Total Energy Density (\( H \)) at the X···T BCP in Complexes (All in a.u.)

| complexes | \( n = 1 \) | \( n = 2 \) | \( n = 3 \) |
|-----------|-------------|-------------|-------------|
| Csp\(^n\)-F···C | \( \rho \) | \( \nabla^2 \rho \) | \( H \) | \( \rho \) | \( \nabla^2 \rho \) | \( H \) | \( \rho \) | \( \nabla^2 \rho \) | \( H \) |
| Csp\(^n\)-F···Si | 0.0036 | 0.0219 | 0.0013 | 0.0052 | 0.0287 | 0.0015 | 0.0056 | 0.0331 | 0.0018 |
| Csp\(^n\)-F···Ge | 0.0054 | 0.0243 | 0.0011 | 0.0080 | 0.0332 | 0.0011 | 0.0103 | 0.0399 | 0.0010 |
| Csp\(^n\)-Cl···C | 0.0061 | 0.0266 | 0.0011 | 0.0094 | 0.0399 | 0.0014 | 0.0121 | 0.0507 | 0.0016 |
| Csp\(^n\)-Cl···Si | 0.0042 | 0.0209 | 0.0013 | 0.0043 | 0.0210 | 0.0013 | 0.0055 | 0.0242 | 0.0013 |
| Csp\(^n\)-Cl···Ge | 0.0063 | 0.0251 | 0.0011 | 0.0080 | 0.0270 | 0.0010 | 0.0092 | 0.0289 | 0.0009 |
| Csp\(^n\)-Br···C | 0.0066 | 0.0242 | 0.0011 | 0.0088 | 0.0299 | 0.0011 | 0.0103 | 0.0317 | 0.0010 |
| Csp\(^n\)-Br···Si | 0.0049 | 0.0224 | 0.0013 | 0.0061 | 0.0242 | 0.0012 | 0.0063 | 0.0257 | 0.0013 |
| Csp\(^n\)-Br···Ge | 0.0071 | 0.0236 | 0.0009 | 0.0079 | 0.0246 | 0.0007 | 0.0098 | 0.0276 | 0.0007 |
| Csp\(^n\)-I···C | 0.0073 | 0.0241 | 0.0009 | 0.0092 | 0.0280 | 0.0008 | 0.0104 | 0.0290 | 0.0007 |
| Csp\(^n\)-I···Si | 0.0053 | 0.0216 | 0.0011 | 0.0063 | 0.0221 | 0.0010 | 0.0065 | 0.0224 | 0.0010 |
| Csp\(^n\)-I···Ge | 0.0074 | 0.0212 | 0.0006 | 0.0087 | 0.0233 | 0.0005 | 0.0096 | 0.0239 | 0.0004 |

Figure 4. Laplacian contour of CH\(_2\)CHCl···SiH\(_2\)F.
of Laplacian of electron densities is confined separately to both molecules, indicative of a weak closed-shell interaction.

### 3.5. EDA Analysis

To deepen the understanding of the nature of the tetrrel bond, we performed an energy decomposition analysis for these complexes. The interaction energies were decomposed into electrostatic energy ($E_{\text{ele}}$), exchange energy ($E_{\text{ex}}$), repulsion energy ($E_{\text{rep}}$), polarization energy ($E_{\text{pol}}$), and dispersion energy ($E_{\text{disp}}$), which are collected in Table 6. This energy decomposition was performed with the GAMESS program and its energy terms have some different physical meanings from other energy decomposition schemes. The physical meanings of five terms obtained with the GAMESS program have been elaborated in the previous study; thus, they are not described here. $E_{\text{ex}}$ and $E_{\text{rep}}$ are the largest attractive and repulsive terms, respectively, but both terms are dependent and partly cancel each other; thus, they are not discussed. As shown in Table 6, among three attractive terms ($E_{\text{ele}}$, $E_{\text{pol}}$, and $E_{\text{disp}}$), the contribution of $E_{\text{disp}}$ to the stability of tetrrel-bonded complexes is greater than the $E_{\text{pol}}$ for the sp hybridization, while the $E_{\text{pol}}$ has the smallest contribution. In addition, these five kinds of energies are increased in the order of $sp < sp^2 < sp^3$. This also shows good

| complexes      | $E_{\text{ele}}$ | $E_{\text{ex}}$ | $E_{\text{rep}}$ | $E_{\text{pol}}$ | $E_{\text{disp}}$ |
|----------------|------------------|-----------------|------------------|------------------|------------------|
| Csp-F···C      | -0.47(22%)       | -2.02           | 3.34             | -0.15(7%)        | -1.52(71%)       |
| Csp-F···Si     | -0.74(25%)       | -2.92           | 4.91             | -0.30(10%)       | -1.95(65%)       |
| Csp-F···Ge     | -0.96(26%)       | -3.73           | 6.32             | -0.43(12%)       | -2.24(62%)       |
| Csp-Cl···C     | -0.95(28%)       | -3.26           | 5.32             | -0.25(7%)        | -2.17(64%)       |
| Csp-Cl···Si    | -1.45(27%)       | -5.76           | 9.40             | -0.74(14%)       | -3.23(60%)       |
| Csp-Cl···Ge    | -1.76(28%)       | -6.63           | 10.95            | -0.91(15%)       | -3.56(57%)       |
| Csp-Br···C     | -1.21(30%)       | -4.24           | 6.94             | -0.33(8%)        | -2.52(62%)       |
| Csp-Br···Si    | -1.99(29%)       | -7.69           | 12.62            | -1.04(15%)       | -3.76(55%)       |
| Csp-Br···Ge    | -2.29(30%)       | -8.34           | 13.84            | -1.18(16%)       | -4.04(54%)       |
| Csp···C        | -1.47(31%)       | -5.28           | 8.65             | -0.43(9%)        | -2.85(60%)       |
| Csp···Si       | -2.40(30%)       | -9.46           | 15.51            | -1.33(17%)       | -4.21(53%)       |
| Csp···Ge       | -2.63(31%)       | -9.73           | 16.14            | -1.42(17%)       | -4.48(53%)       |
| CspF···C       | -1.44(45%)       | -2.76           | 4.58             | -0.25(8%)        | -1.54(48%)       |
| CspF···Si      | -3.06(48%)       | -5.83           | 9.84             | -0.81(13%)       | -2.46(39%)       |
| CspF···Ge      | -4.07(52%)       | -7.43           | 12.75            | -1.13(14%)       | -2.67(34%)       |
| CspCl···C      | -1.09(41%)       | -2.20           | 3.58             | -0.21(8%)        | -1.35(51%)       |
| CspCl···Si     | -3.29(39%)       | -8.93           | 14.66            | -1.28(15%)       | -3.88(46%)       |
| CspCl···Ge     | -4.11(42%)       | -10.44          | 17.41            | -1.58(16%)       | -4.21(43%)       |
| CspBr···C      | -1.92(38%)       | -5.35           | 8.79             | -0.47(9%)        | -2.66(53%)       |
| CspBr···Si     | -3.35(39%)       | -9.46           | 15.62            | -1.39(16%)       | -3.76(44%)       |
| CspBr···Ge     | -4.60(41%)       | -12.31          | 20.59            | -1.88(17%)       | -4.73(42%)       |
| CspI···C       | -2.13(37%)       | -6.50           | 10.68            | -0.57(10%)       | -3.04(53%)       |
| CspI···Si      | -4.10(38%)       | -12.88          | 21.19            | -1.90(17%)       | -4.92(45%)       |
| CspI···Ge      | -6.69(39%)       | -13.54          | 22.61            | -2.07(17%)       | -5.19(43%)       |
| CspF···C       | -1.76(53%)       | -2.46           | 4.11             | -0.30(9%)        | -1.26(38%)       |
| CspF···Si      | -5.04(54%)       | -8.50           | 14.58            | -1.50(16%)       | -2.81(30%)       |
| CspF···Ge      | -6.52(56%)       | -11.03          | 19.18            | -1.96(17%)       | -3.15(27%)       |
| CspCl···C      | -1.46(35%)       | -4.13           | 6.76             | -0.41(10%)       | -2.33(55%)       |
| CspCl···Si     | -4.43(43%)       | -10.64          | 17.68            | -1.68(16%)       | -4.09(40%)       |
| CspCl···Ge     | -5.70(46%)       | -13.27          | 22.47            | -2.14(17%)       | -4.65(37%)       |
| CspBr···C      | -1.75(34%)       | -5.53           | 9.08             | -0.54(11%)       | -2.81(55%)       |
| CspBr···Si     | -4.99(43%)       | -12.86          | 21.41            | -2.04(18%)       | -4.62(40%)       |
| CspBr···Ge     | -6.07(45%)       | -14.95          | 25.33            | -2.40(18%)       | -5.10(38%)       |
| CspI···C       | -1.93(33%)       | -6.68           | 10.98            | -0.65(11%)       | -3.19(55%)       |
| CspI···Si      | -5.17(41%)       | -14.58          | 24.22            | -2.29(18%)       | -5.09(41%)       |
| CspI···Ge      | -6.01(43%)       | -16.03          | 27.10            | -2.56(18%)       | -5.55(39%)       |

< I for the same T atom, which is consistent with the change order of charge transfer CT. However, the largest amount of charge transfer does not necessarily correspond to the strongest bond. For example, Csp$^3$-I···Ge has the largest charge transfer, but the interaction energy is not the largest.

#### 3.4. AIM Analysis

The electron density ($\rho$), its Laplacian ($\nabla^2 \rho$), and energy density ($H$) at the bond critical point between X and T are listed in Table 5. All Csp$^n$-X···T interactions are characterized by a positive $\nabla^2 \rho$ value and a positive $H$, which are indicative of a closed-shell interaction in these systems. The electron density exhibits the relationship with the X···T binding distance. One can see, the capacity of the complex to concentrate electrons increases as T···C < Si < Ge and X···F < Cl < Br < I, which is consistent with the tetrrel bond distance as discussed above. In addition, for the different C hybridizations, the electron density is increased in the order of $sp < sp^2 < sp^3$. This has good agreement with the interaction energy discussed above. The electron density of the complexes is much less than 0.01 a.u., which means that the tetrrel bond formed is a weak interaction. The Laplacian contour of CH$_2$$\equiv$CHCl···SiH$_2$F is plotted in Figure 4, where the spatial display...
agreement with the interaction energy discussed above. For the sp² hybridization, both \( E_{\text{ele}} \) and \( E_{\text{disp}} \) have similar degrees of magnitude, except for the Csp²-F···Ge complex. This suggests that both terms make comparable contributions to the energetic stability of sp² complexes. For the sp³ hybridization, the percentage for the \( E_{\text{ele}} \) contribution is 41–56% (except for Csp³-X···C, X=Cl, Br, I), which means the \( E_{\text{ele}} \) term plays a dominant role in the energetic stability of most sp³ complexes.

4. DISCUSSION

As discussed above for each type of C hybridization, the electrostatic and dispersion energies roughly reflect the behavior of the interaction energy. Figure 5a shows the linear relationship between \( E_{\text{int}} \) and \( E_{\text{ele}} \) for all complexes, with a correlation coefficient \( R^2 = 0.95 \). In addition, the slope in Figure 5a is 2.3, which indicates that the electrostatic energy increases faster than the interaction energy, while the slope is much closer to the dispersion energy in Figure 5c. Although dispersion energy plays an important role in the total interaction energy, its correlation with \( E_{\text{int}} \) is very poor, with \( R^2 = 0.53 \). In contrast, the correlation between \( E_{\text{int}} \) and \( E_{\text{pol}} \) is not very poor, with \( R^2 = 0.84 \) as indicated in Figure 5b.

The total amount of charge from the electron donor to the acceptor is less than 0.03e for the complexes. This quantity is much smaller than the charge transfer amount of the triel bond formed by Csp³-F.⁶⁹ For three types of C hybridizations, AIM parameters suggest that the GeH₃F species is the strongest, followed by the Si and C, which corresponds to their Lewis acid strength.

The F atom has been considered as the nucleophilic source of electron density in triel bonds in the recent study.⁶⁹ However, the pertinent F was not bonded to C in the triel bond. Nonetheless, previous study can provide enlightenment for the results shown here. For example, the Csp³-F and TrR₃ (Tr=W, Al, Ga) complex is held together by a pair of triel bonds. The interaction energy of the complex varies from −0.94 to −29.74 kcal/mol at the MP2/aug-cc-pVTZ level.⁶⁹ The sp³ hybridization has a stronger effect than sp² and sp, and the interaction energy is decreased in the order of sp³ > sp² > sp.⁶⁹

5. CONCLUSIONS

The tetrel-bonded complexes between the organic halogen connected with differently hybridized C atoms and TH,X,F (T=C, Si, Ge) have been investigated by ab initio calculations. The strength of the tetrel bond is related to the C hybridization as well as the nature of both X and T. For any type of C hybridization, the GeH₃F complexes are more strongly bound than the SiH₃F analogues, which are stronger than the CH₃F analogues. For T=C complexes, the interaction energy shows a similar increasing tendency with the decrease of the electronegativity of halogen substituents. This is also same for T=Si complexes in both sp and sp³ hybridization except for the sp² hybridization.

NBO analysis shows that the principal orbital interaction of these tetrel bonds is charge transfer from the lone pair on X in the Lewis base into the empty F-T orbital. Furthermore, the values are related to the type of C hybridization, with the order of sp³ > sp² > sp. The bond critical point between T and X confirms the existence of the tetrel bond. For both sp and sp³ hybridizations, the tetrel bonds are dominated by electrostatic interaction, while for the sp² hybridization, both electrostatic and dispersion have similar degrees of magnitude, except for the \( \text{H}_2\text{C}==\text{CHF} \cdots \text{GeH}_3\text{F} \) complex, which means that those two terms make comparable contributions to the energetic stability of the \( \text{H}_2\text{C}==\text{CHX} \) complexes.

# AUTHOR INFORMATION

**Corresponding Authors**

Xiaolong Zhang — The Laboratory of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, People’s Republic of China; Phone: (+086) 535 6902063; Email: xiaolongzhang@ytu.edu.cn; Fax: (+086) 535 6902063

Qingzhong Li — The Laboratory of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, People’s Republic of China; orcid.org/0000-0003-1486-6772; Email: lqz@ytu.edu.cn

**Author**

Qingqing Yang — The Laboratory of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, People’s Republic of China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c04085

**Notes**

The authors declare no competing financial interest.

---

**Figure 5.** Relationship of interaction energy (\( E_{\text{int}} \)) with (a) electrostatic (\( E_{\text{ele}} \)), (b) polarization (\( E_{\text{pol}} \)), and (c) dispersion energies (\( E_{\text{disp}} \)).
ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (21573188).

REFERENCES

(1) Bauzá, A.; Mooibroek, T. J.; Frontera, A. Tetrel-bonding interaction: Rediscovered supramolecular force? Angew. Chem., Int. Ed. 2013, 52, 12317–12321.

(2) Clark, T.; Hennemann, M.; Murray, J. S.; Politzer, P. Halogen bonding: The σ-hole. J. Mol. Model. 2007, 13, 291–296.

(3) Murray, J. S.; Lane, P.; Politzer, P. Expansion of the σ-hole concept. J. Mol. Model. 2009, 15, 723–729.

(4) Murray, J. S.; Lane, P.; Clark, T.; Riley, K. E.; Politzer, P. σ-Holes, π-holes and electrostatically-driven interactions. J. Mol. Model. 2012, 18, 541–548.

(5) Grabowski, S. J. Tetrel bond—σ-hole bond as a preliminary stage of the S22 reaction. Phys. Chem. Chem. Phys. 2014, 16, 1824–1834.

(6) Bauzá, A.; Seth, S. K.; Frontera, A. Tetrel bonding interactions at work: Impact on tin and lead coordination compounds. Coord. Chem. Rev. 2019, 384, 107–125.

(7) Mirdya, S.; Roy, S.; Chatterjee, S.; Bauzá, A.; Frontera, A. Chattopadhyay, S. Importance of π-interactions involving chelate rings in addition to the tetrel bonds in crystal engineering: A combined experimental and theoretical study on a series of amidodirecte nickel (II) complexes with (iso) nicotinohydrazide based ligands and several anions. Dalton Trans. 2016, 45, 10708–10716.

(8) Sassini, M.; Bauzá, A.; Frontera, A.; Lo, K. M.; Naseer, M. M. Structure guided or structure guiding? Mixed carbon/hydrogen bonding in a bis-Schiff base of N-allyl isatin. CrystEngComm 2018, 20, 150–154.

(9) Subramanian, R.; Yajnik, R.; Chopra, D. Characterization of the short O=C···O=C π-hole tetrel bond in the solid state. CrystEngComm 2018, 20, 3308–3312.

(10) Mahmoudi, G.; Bauzá, A.; Frontera, A. Concurrent agostic and tetrel bonding interactions in lead (II) complexes with an isonicotinohydrazide based ligand and several anions. Dalton Trans. 2016, 45, 4965–4969.

(11) Esrafili, M. D.; Mohammadmirad, N.; Solimannejad, M. Tetrel bond cooperativity in open-chain (CH3CN)2 and (CH3NC)2, clusters (n=2-7): An ab initio study. Chem. Phys. Lett. 2015, 628, 16–20.

(12) Bauzá, A.; Mohammadjam-Sabet, F. Cooperativity of tetrel bonds tuned by substituent effects. Mol. Phys. 2016, 114, 1528–1538.

(13) Esrafili, M. D.; Asadollahi, S.; Mousavian, P. Anionic tetrel bonds: An ab initio study. Chem. Phys. Lett. 2018, 691, 394–400.

(14) Mani, D.; Arunan, E. The X-C···π (X= F, Cl, Br, CN) carbon bond. J. Phys. Chem. A 2014, 118, 10081–10089.

(15) Li, Q. Z.; Zhuo, H. Y.; Li, H. B.; Liu, Y. Z.; Li, W. Z.; Cheng, J. B. Tetrel-hydride interaction between RXH(F(X= C, Si, Ge, Sn) and HM (M= Li, Na, BeH, MgH). J. Phys. Chem. A 2015, 119, 2217–2224.

(16) Li, Q. Z.; Guo, X.; Yang, X.; Li, W.; Cheng, J.; Li, H.-B. A σ-hole interaction with radical species as electron donors: Does single-electron tetrel bonding exist? Phys. Chem. Chem. Phys. 2014, 16, 11617–11625.

(17) Liu, M.; Li, Q. Z.; Li, W.; Cheng, J. Carbene tetrel-bonded complexes. Struct. Chem. 2017, 28, 823–831.

(18) Donald, K. J.; Tawfik, M. The weak helps the strong: Sigma-holes and the stability of MF3 base complexes. J. Phys. Chem. A 2013, 117, 14176–14183.

(19) Xu, H.; Cheng, J.; Li, H. B.; Li, W. Z.; Li, Q. Z. Prominent enhancing effects of substituents on the strength of π-σ-hole tetrel bond. Int. J. Quantum Chem. 2017, 117, No. e25448.

(20) Del Bene, J. E.; Alkorta, I.; Elguero, J. Exploring N–C tetrel and O–S chalcogen bonds in HN(CH)SX: OCS systems, for X= F, NC, Cl, CN, CCH, and H. Chem. Phys. Lett. 2019, 730, 466–471.

(21) Xu, H.; Cheng, J.; Yu, X.; Li, Q. Abnormal tetrel bonds between formamidine and THF: Substituent effects. ChemistrySelect 2018, 3, 2842–2849.
(44) De, V.; Nzik, P. N.; Scheiner, S. Comparison of π-hole tetrel bonding with σ-hole halogen bonds in complexes of XCN (X = F, Cl, Br, I) and NH3. J. Phys. Chem. A 2017, 121, 8017–8025.

(45) Alkorta, I.; Elguero, J.; Del Bene, J. E. Azines as electron-pair donors to CO2 for N−C tetrel bonds. J. Phys. Chem. A 2017, 121, 8017–8025.

(46) Wei, Y.; Li, Q.; Scheiner, S. Pi tetrel bonds, and their influence on hydrogen bonds and proton transfers. ChemPhysChem 2018, 19, 736–743.

(47) Chandra, S.; Bhattacharya, A. Attochemistry of ionized halogen, chalcogen, pnictogen, and tetrel noncovalent bonded clusters. J. Phys. Chem. A 2016, 120, 10057–10071.

(48) Zierkiewicz, W.; Michalczyk, M.; Scheiner, S. Implications of monomer deformation for tetrel and pnictogen bonds. Phys. Chem. Chem. Phys. 2018, 20, 8832–8841.

(49) Liu, M. X.; Li, Q. Z.; Scheiner, S. Comparison of tetrel bonds in neutral and protonated complexes of pyridineTF3 and furanTF3 (T = C, Si, and Ge) with NH3. Chem. Phys. Chem. 2017, 19, 5550–5559.

(50) Xu, H.-L.; Cheng, J.-B.; Li, H.-B.; Yang, X.; Liu, Z.-B.; Xiao, B.; Li, Q.-Z. Tetrel bonds between PhSiF3/PhTH3 (T = Si, Ge, Sn) and H2O (Z = N, P, As): A pentacoordinate silicon (IV) complex. Int. J. Quant. Chem. 2018, 118, No. e25660.

(51) Dong, W.; Niu, B.; Liu, S.; Cheng, J.; Liu, S.; Li, Q. Comparison of σ−π-hole tetrel bonds between TH,F/F,TO and H2CX (X=O, S, Se). ChemPhysChem 2019, 20, 627–635.

(52) Scheiner, S. Highly selective halide receptors based on chalcogen, pnictogen, and tetrel bonds. Chem. − Eur. J. 2016, 22, 18850–18858.

(53) Scheiner, S. Comparison of halide receptors based on H, halogen, chalcogen, pnictogen, and tetrel bonds. Faraday Discuss. 2017, 203, 213–226.

(54) Esrafili, M. D.; Mousavian, P. Strong tetrel bonds: Theoretical aspects and experimental evidence. Molecules 2018, 23, 2642.

(55) Mani, D.; Arunan, E. The X−C⋅⋅⋅Y (X= O /F, Y= O/ S/ F/ Cl/ Br /N /P) ‘carbon bond’ and hydrophobic interactions. Phys. Chem. Chem. Phys. 2013, 15, 14377–14383.

(56) Liu, M.; Li, Q.; Li, W.; Cheng, J.; McDowell, S. A. C. Comparison of hydrogen, halogen, and tetrel bonds in the complexes of HArF with YH3X (X= halogen, Y=C and Si). RSC Adv. 2016, 6, 19136–19143.

(57) Legon, A. C. Tetrel, pnictogen and chalcogen bonds identified in the gas phase before they had names: A systematic look at noncovalent interactions. Phys. Chem. Chem. Phys. 2017, 19, 14884–14896.

(58) Alkorta, I.; Rozas, I.; Elguero, J. Molecular complexes between silicon derivatives and electron-rich groups. J. Phys. Chem. A 2001, 105, 743–749.

(59) Berger, R.; Resnati, G.; Metrangolo, P.; Weber, E.; Hulliger, J. Organic fluorine compounds: A great opportunity for enhanced materials properties. Chem. Soc. Rev. 2011, 40, 3496–3508.

(60) Borisenko, K. B.; Gould, R. O.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. A theoretical and experimental study of weak silane−electron donor interactions. J. Mol. Struct. 2000, 554, 163–172.

(61) Corminich, R. A.; Rittner, R.; Hagan, D. O.; Bühl, M. Inter-and intramolecular CF−CO interactions on aliphatic and cyclohexane carbonyl derivatives. J. Comput. Chem. 2016, 37, 25–33.

(62) Boys, S. F.; Bernardi, F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Mol. Phys. 1970, 19, 553–566.

(63) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A. et al. Gaussian 09; Revision A.02, Gaussian, Inc.: Wallingford, 2009.

(64) Bulat, F. A.; Toro-Labbé, A.; Brinck, T.; Murray, J. S.; Politzer, P. Quantitative analysis of molecular surfaces: Areas, volumes, electrostatic potentials and average local ionization energies. J. Mol. Model. 2010, 16, 1679–1691.

(65) Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. Chem. Rev. 1988, 88, 899–926.

(66) Bader, R. F. W. AIM2000 Program; V.2.0 McMaster University: Hamilton, Canada, 2000.

(67) Su, P.; Li, H. Energy decomposition analysis of covalent bonds and intermolecular interactions. J. Chem. Phys. 2009, 131, No. 014102.

(68) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. General atomic and molecular electronic structure system. J. Comput. Chem. 1993, 14, 1347–1363.

(69) Yang, Q.; Chi, Z.; Li, Q.; Steve, S. Effect of carbon hybridization in C−F bond as an electron donor in triel bonds. J. Chem. Phys. 2020, 153, No. 074304.