

# Cl<sup>-</sup> as the halogen bond acceptor: studies on strong halogen bonds

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**Abstract** The Cl<sup>-</sup> anion as the halogen bond acceptor, the diiodotetrafluoroethane I(CF<sub>2</sub>)<sub>2</sub>I and its derivatives I(MF<sub>2</sub>)<sub>n</sub>I (M = C, Si, Ge, Sn) as the halogen bond donor, and the strong halogen bonds could be formed. The halogen bonds between I(MF<sub>2</sub>)<sub>n</sub>I and Cl<sup>-</sup> have been designed and investigated by Moller–Plesset perturbation/aug-cc-pVDZ calculations together with the aug-cc-pVDZ-pp basis set for iodine and stannum. The halogen bonds in the I(MF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>-</sup> complexes are strong, which are apparently related to the group IV elements, becoming stronger along the sequence of M = Si, C, Ge, Sn. Accompanied with increasing number (*n*) of MF<sub>2</sub> unit, the halogen bonds (M = Si, Ge, Sn) also become stronger. The energy decomposition analyses reveal that the exchange energy contributes most in forming these halogen-bonded interactions. In the meantime, the electrostatic energy is also a significant factor for the I⋯Cl<sup>-</sup> interactions. The halogen bonds of I(MF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>-</sup> (M = C, Ge, Sn) belong to partial-covalent interactions, while they are noncovalent interactions when M = Si.

**Keywords** Halogen bond · Diiodotetrafluoroethane · Chlorine anion · Partial-covalent interactions

## Introduction

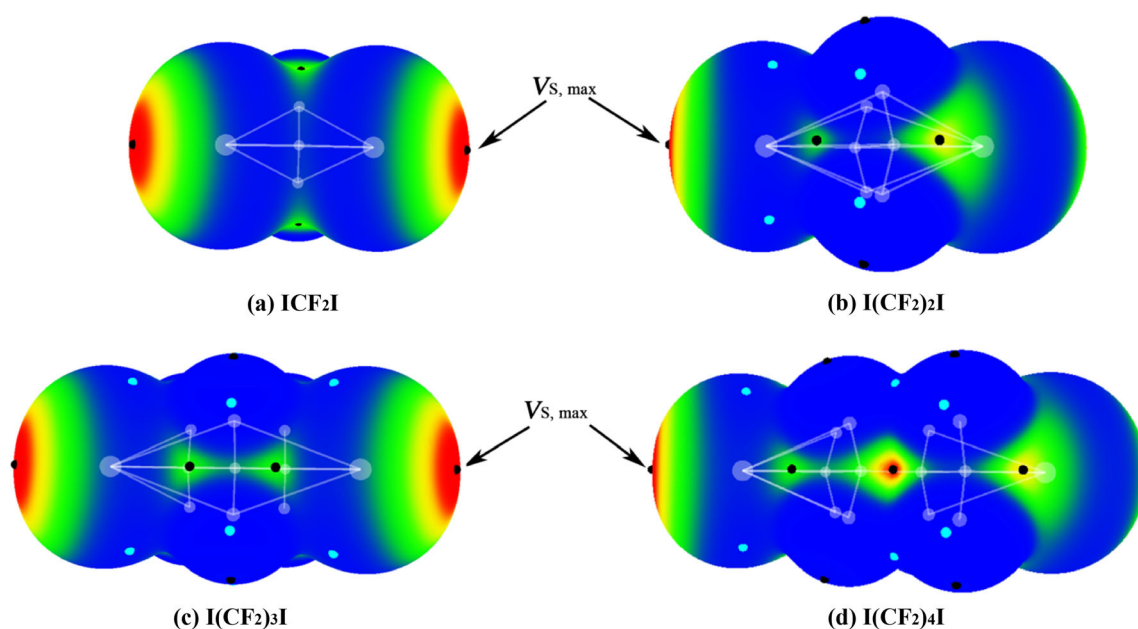
The halogen bond (XB) has special applications in many fields, such as molecular recognition [1–4], materials science, crystal engineering [1, 5–7], and biological systems [1, 8, 9]. Therefore, it has caused more and more attention [10]. The XB could be denoted as a D⋯X–Y interaction, in which X is an electrophilic halogen (Lewis acid, XB donor), D is a species donating electron density (Lewis base, XB acceptor), and Y is carbon, nitrogen, halogen, et al [11]. According to the molecular surface electrostatic potential, Politzer et al. named the halogen bond as the σ-hole bond [12, 13]. A σ-hole is a region of lower electronic density along the extension of a σ-hole bond [14]. This region of lower electronic density often leads to a positive electrostatic potential in that region, although it may be negative if the atom is much more electron-attracting (electronegative) than its bonding partner [15]. In terms of the XB-acceptor partner, with the increase of electron density, the electron-donating ability of Lewis alkaline (XB acceptor) is enhanced, resulting in the formation of strong and directional XB. Therefore, anions are more suitable as XB acceptors than neutral substances to form strong and directional XBs [16]. The chlorine anion can strongly interact with halogenated organic compounds via a specific supramolecular interaction as halogen bonding [17].

The diiodotetrafluoroethane I(CF<sub>2</sub>)<sub>2</sub>I and its derivatives are widely used in the field of liquid crystal [18] and perovskite solar cell field [17], which has caused much interest of researchers. In this work, the diiodotetrafluoroethane I(CF<sub>2</sub>)<sub>2</sub>I and its derivatives I(MF<sub>2</sub>)<sub>n</sub>I (M = Si, Ge, Sn) are selected as the XB donor, and Cl<sup>-</sup> is as the XB acceptor; the XB interactions have been constructed and investigated. The purposes of this work are the following: (1) to investigate the strength and nature of the I⋯Cl<sup>-</sup> XB interactions, (2) to compare the effects of the M replacement on the XB, and (3) to study the

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**Fig. 1** Electrostatic potentials on the 0.001 a.u. contour of the molecular electron density: **a**  $\text{ICF}_2\text{I}$ , **b**  $\text{I}(\text{CF}_2)_2\text{I}$ , **c**  $\text{I}(\text{CF}_2)_3\text{I}$ , **d**  $\text{I}(\text{CF}_2)_4\text{I}$ . Color ranges, in  $\text{kcal mol}^{-1}$ : red, more positive than 24; yellow, 13–24; green, 3–13; blue, more negative than 3. Positions of  $V_{s, \text{max}}$  are indicated by black arrows

enhancing effects with the increased number of  $\text{MF}_2$  unit on the XB interactions.

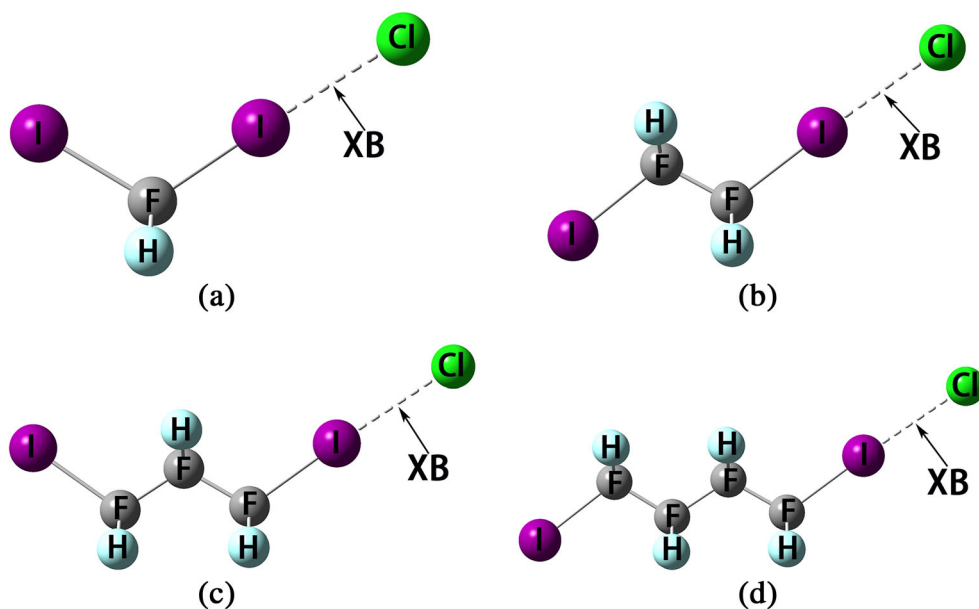
### Computational methods

All calculations were performed using the Gaussian 09 program package [19]. For all the monomers and complexes, geometrical optimizations were carried out by the second-order Moller–Plesset perturbation theory combined with the aug-cc-pVDZ [20–22] basis set. For elements Sn and I, the

aug-cc-pVDZ-pp [22, 23] basis set was used. The vibrational frequencies were calculated at the same level to confirm that the obtained geometries corresponded to the energy minima. The counterpoise method of Boys and Bernardi [24] was applied to correct the basis set superposition error.

The electrostatic potential is a well-established tool for studying the noncovalent interactions [25–28] and has been used in predicting the directionality of many noncovalent interactions. In this study, the electrostatic potentials on the 0.001 a.u. (electrons  $\text{bohr}^{-3}$ ) contour of the molecule's electronic density [27] are analyzed with the WFA program [29].

**Fig. 2** The optimized geometries of complexes. **a**  $\text{ICF}_2\text{I} \cdots \text{Cl}^-$ , **b**  $\text{I}(\text{CF}_2)_2\text{I} \cdots \text{Cl}^-$ , **c**  $\text{I}(\text{CF}_2)_3\text{I} \cdots \text{Cl}^-$ , **d**  $\text{I}(\text{CF}_2)_4\text{I} \cdots \text{Cl}^-$



**Table 1** Electrostatic potentials ( $V_{S, \max}$ ) on the 0.001 a.u. contour of the molecular electron density

Species	$V_{S, \max}$	Species	$V_{S, \max}$	Species	$V_{S, \max}$	Species	$V_{S, \max}$
ICF <sub>2</sub> I	34.05	ISiF <sub>2</sub> I	26.92	IGeF <sub>2</sub> I	30.65	ISnF <sub>2</sub> I	29.90
I(CF <sub>2</sub> ) <sub>2</sub> I	34.94	I(SiF <sub>2</sub> ) <sub>2</sub> I	26.34	I(GeF <sub>2</sub> ) <sub>2</sub> I	31.31	I(SnF <sub>2</sub> ) <sub>2</sub> I	30.91
I(CF <sub>2</sub> ) <sub>3</sub> I	35.77	I(SiF <sub>2</sub> ) <sub>3</sub> I	26.99	I(GeF <sub>2</sub> ) <sub>3</sub> I	32.65	I(SnF <sub>2</sub> ) <sub>3</sub> I	32.24
I(CF <sub>2</sub> ) <sub>4</sub> I	36.27	I(SiF <sub>2</sub> ) <sub>4</sub> I	27.35	I(GeF <sub>2</sub> ) <sub>4</sub> I	33.41	I(SnF <sub>2</sub> ) <sub>4</sub> I	33.08

**Table 2** Interaction distances (Å) of the I(MF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup>

	I(CF <sub>2</sub> ) <sub>n</sub> I⋯Cl <sup>−</sup>	I(SiF <sub>2</sub> ) <sub>n</sub> I⋯Cl <sup>−</sup>	I(GeF <sub>2</sub> ) <sub>n</sub> I⋯Cl <sup>−</sup>	I(SnF <sub>2</sub> ) <sub>n</sub> I⋯Cl <sup>−</sup>
$n = 1$	2.820	2.992	2.834	2.749
$n = 2$	2.831	3.004	2.809	2.689
$n = 3$	2.845	2.990	2.780	2.648
$n = 4$	2.846	2.980	2.759	2.619

In order to give more insight into the XB interactions in the I(MF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup> (M = C, Si, Ge, Sn;  $n = 1, 2, 3, 4$ ) complexes, the localized molecular orbital EDA (LMOEDA) Localized Molecular Orbital Energy Decomposition Analysis method was used to decompose the interaction energies via [30] using the Gamess program [31]. The density difference in molecular formation was studied by means of the Multiwfn program [32]. The quantum theory of “atoms in molecules” (QTAIM) [33] was used to investigate the electron density properties and energy density properties of the XB interactions, which was implemented with the AIMALL program [34]. To evaluate the direction and magnitude of the donor–acceptor interactions, the natural bond orbital (NBO) [35] analyses were performed within the NBO 6.0 facilities [36].

## Results and discussion

### Geometries and energies

Figure 1 shows that there are the  $\sigma$ -holes (red region) on the contour maps of molecular electrostatic potentials of ICF<sub>2</sub>I, I(CF<sub>2</sub>)<sub>2</sub>I, I(CF<sub>2</sub>)<sub>3</sub>I, and I(CF<sub>2</sub>)<sub>4</sub>I, which are roughly along the extension of the C–I bond. It is predictable that the chlorine anion could interact with the  $\sigma$ -hole outside the iodine in I(CF<sub>2</sub>)<sub>n</sub>I ( $n = 1, 2, 3, 4$ ) along the extension of the C–I bond.

**Table 3** Interaction energies (kJ/mol) of the I⋯Cl<sup>−</sup> interactions

A⋯B	$\Delta E_{(A-B)}$	A⋯B	$\Delta E_{(A-B)}$	A⋯B	$\Delta E_{(A-B)}$	A⋯B	$\Delta E_{(A-B)}$
ICF <sub>2</sub> I⋯Cl <sup>−</sup>	−108.09	ISiF <sub>2</sub> I⋯Cl <sup>−</sup>	−87.94	IGeF <sub>2</sub> I⋯Cl <sup>−</sup>	−118.04	ISnF <sub>2</sub> I⋯Cl <sup>−</sup>	−141.63
I(CF <sub>2</sub> ) <sub>2</sub> I⋯Cl <sup>−</sup>	−107.90	I(SiF <sub>2</sub> ) <sub>2</sub> I⋯Cl <sup>−</sup>	−91.60	I(GeF <sub>2</sub> ) <sub>2</sub> I⋯Cl <sup>−</sup>	−132.72	I(SnF <sub>2</sub> ) <sub>2</sub> I⋯Cl <sup>−</sup>	−175.03
I(CF <sub>2</sub> ) <sub>3</sub> I⋯Cl <sup>−</sup>	−106.26	I(SiF <sub>2</sub> ) <sub>3</sub> I⋯Cl <sup>−</sup>	−97.77	I(GeF <sub>2</sub> ) <sub>3</sub> I⋯Cl <sup>−</sup>	−148.27	I(SnF <sub>2</sub> ) <sub>3</sub> I⋯Cl <sup>−</sup>	−205.48
I(CF <sub>2</sub> ) <sub>4</sub> I⋯Cl <sup>−</sup>	−106.23	I(SiF <sub>2</sub> ) <sub>4</sub> I⋯Cl <sup>−</sup>	−101.70	I(GeF <sub>2</sub> ) <sub>4</sub> I⋯Cl <sup>−</sup>	−159.84	I(SnF <sub>2</sub> ) <sub>4</sub> I⋯Cl <sup>−</sup>	−231.72

Therefore, the I⋯Cl<sup>−</sup> interaction make the I(CF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup> complexes formed. Figure 2 shows the optimized geometries of ICF<sub>2</sub>I⋯Cl<sup>−</sup>, I(CF<sub>2</sub>)<sub>2</sub>I⋯Cl<sup>−</sup>, I(CF<sub>2</sub>)<sub>3</sub>I⋯Cl<sup>−</sup>, and I(CF<sub>2</sub>)<sub>4</sub>I⋯Cl<sup>−</sup>. All of the I(CF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup> complexes belong to C<sub>s</sub> symmetry.

The most positive electrostatic potentials ( $V_{S, \max}$ ) on the 0.001 a.u. contour of the molecular electron density are gathered in Table 1. For IMF<sub>2</sub>I, the  $V_{S, \max}$  value outside the I atom along the M–I bond is 34.05, 26.92, 30.65, and 29.90 kcal mol<sup>−1</sup> for M = C, Si, Ge, and Sn, respectively. This trend of our work is consistent with those for the F<sub>3</sub>MX molecules (M = C, Si, Ge and X = F, Cl, Br, I) [37].

As is shown in Table 2, according to the order of I(SiF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup>, I(CF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup>, I(GeF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup>, and I(SnF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup> ( $n = 2, 3, 4$ ), the interaction length becomes shorter and shorter. From Table 3, the interaction energies of I(MF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup> are apparently related to the group IV elements, becoming more and more negative along the sequence of I(SiF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup>, I(CF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup>, I(GeF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup>, and I(SnF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup>. For M = Si, Ge, Sn, accompanied with increasing number ( $n$ ) of MF<sub>2</sub> unit, the XB interactions become stronger and stronger.

### Energy decomposition analysis

The total interaction energy ( $E^{\text{int}}$ ) consists of five fundamental physical components: exchange energy term ( $E^{\text{ex}}$ ), electrostatic energy term ( $E^{\text{ele}}$ ), repulsion energy term ( $E^{\text{rep}}$ ), polarization energy term ( $E^{\text{pol}}$ ), and dispersion energy term ( $E^{\text{disp}}$ ). From Table 3 and Table 4, the interaction energies by the supermolecular method ( $\Delta E$ ) and the LMOEDA method ( $\Delta E^{\text{int}}$ ) are very close, which verified that the result of LMOEDA is dependable.

The  $E^{\text{ex}}$  term usually represents the interpenetration of electron clouds of the bonded monomers. The larger  $E^{\text{ex}}$ , the more charge transfer will occur between the related molecular orbitals. From Table 4, for all complexes, the  $E^{\text{ex}}$  contributes most in the four attractive terms, indicating that charge transfer

**Table 4** Five fundamental physical components (kJ/mol): exchange energy ( $E^{\text{ex}}$ ), electrostatic energy ( $E^{\text{ele}}$ ), repulsion energy ( $E^{\text{rep}}$ ), polarization energy ( $E^{\text{pol}}$ ), and dispersion energy ( $E^{\text{disp}}$ )

	$E^{\text{ele}}$	$E^{\text{ex}}$	$E^{\text{rep}}$	$E^{\text{pol}}$	$E^{\text{disp}}$	$E^{\text{int}}$
ICF <sub>2</sub> I⋯Cl <sup>−</sup>	− 162.00	− 255.43	463.17	− 135.94	− 18.70	− 108.87
I(CF <sub>2</sub> ) <sub>2</sub> I⋯Cl <sup>−</sup>	− 164.35	− 252.55	454.51	− 128.11	− 24.10	− 108.87
I(CF <sub>2</sub> ) <sub>3</sub> I⋯Cl <sup>−</sup>	− 158.70	− 236.77	428.53	− 123.18	− 17.20	− 107.36
I(CF <sub>2</sub> ) <sub>4</sub> I⋯Cl <sup>−</sup>	− 159.62	− 235.64	426.56	− 122.84	− 16.65	− 108.16
ISiF <sub>2</sub> I⋯Cl <sup>−</sup>	− 124.93	− 184.39	325.60	− 83.85	− 20.25	− 87.82
I(SiF <sub>2</sub> ) <sub>2</sub> I⋯Cl <sup>−</sup>	− 126.98	− 180.62	318.86	− 82.38	− 20.25	− 91.38
I(SiF <sub>2</sub> ) <sub>3</sub> I⋯Cl <sup>−</sup>	− 134.77	− 186.15	329.66	− 85.65	− 20.59	− 97.49
I(SiF <sub>2</sub> ) <sub>4</sub> I⋯Cl <sup>−</sup>	− 140.33	− 190.20	337.69	− 88.87	− 21.05	− 101.34

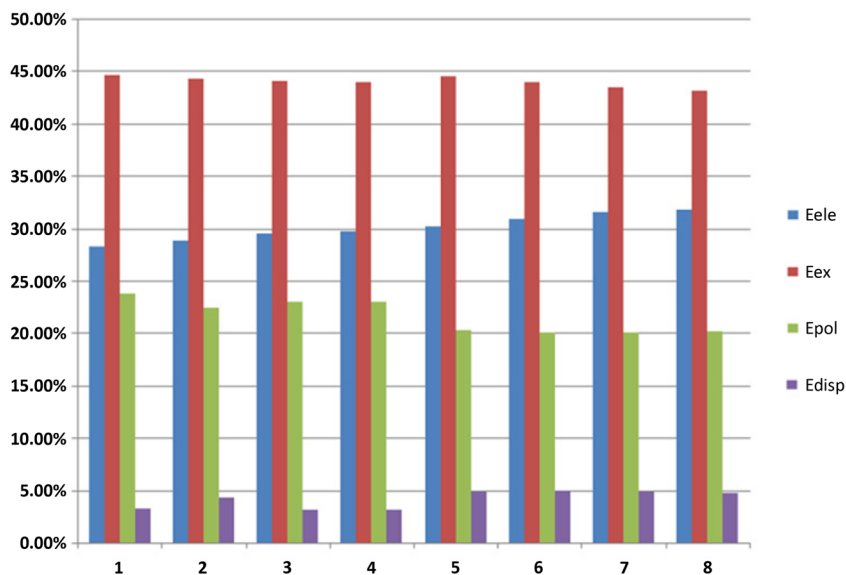
**Table 5** Percents of the electrostatic ( $E^{\text{ele}}$ ), exchange ( $E^{\text{ex}}$ ), polarization ( $E^{\text{pol}}$ ), and dispersion ( $E^{\text{disp}}$ ) terms

	$E^{\text{ele}}$	$E^{\text{ex}}$	$E^{\text{pol}}$	$E^{\text{disp}}$
ICF <sub>2</sub> I⋯Cl <sup>−</sup>	28.32%	44.65%	23.76%	3.27%
I(CF <sub>2</sub> ) <sub>2</sub> I⋯Cl <sup>−</sup>	28.88%	44.38%	22.51%	4.23%
I(CF <sub>2</sub> ) <sub>3</sub> I⋯Cl <sup>−</sup>	29.62%	44.19%	22.99%	3.21%
I(CF <sub>2</sub> ) <sub>4</sub> I⋯Cl <sup>−</sup>	29.85%	44.07%	22.97%	3.11%
ISiF <sub>2</sub> I⋯Cl <sup>−</sup>	30.22%	44.60%	20.28%	4.90%
I(SiF <sub>2</sub> ) <sub>2</sub> I⋯Cl <sup>−</sup>	30.95%	44.03%	20.08%	4.94%
I(SiF <sub>2</sub> ) <sub>3</sub> I⋯Cl <sup>−</sup>	31.55%	43.58%	20.05%	4.82%
I(SiF <sub>2</sub> ) <sub>4</sub> I⋯Cl <sup>−</sup>	31.86%	43.18%	20.18%	4.78%

between I(MF<sub>2</sub>)<sub>n</sub>I and Cl<sup>−</sup> is obvious. After the  $E^{\text{ex}}$  term, the electrostatic energy contributes the second, indicating that the electrostatic effect is very important in the XB interactions. And then, the contribution of the polarization energy is larger than dispersion energy.

From Fig. 3, for all of the I(CF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup> complexes, the exchange energy dominates the largest proportion (43–44%) among the four attractive energies. The electrostatic energy corresponds to 28–32% of the total attractive energies.

**Fig. 3** The percents of the electrostatic ( $E^{\text{ele}}$ ), exchange ( $E^{\text{ex}}$ ), polarization ( $E^{\text{pol}}$ ), and dispersion ( $E^{\text{disp}}$ ) terms of I(MF<sub>2</sub>)<sub>n</sub>I⋯Cl<sup>−</sup> (M = C, Si; n = 1, 2, 3, 4) interactions



Furthermore, the  $E^{\text{pol}}$  term (20–23%) has larger contribution than  $E^{\text{disp}}$  term (3–5%).

### NBO analysis

In order to more deeply understand the great contribution of the exchange energy to the total interaction energy, NBO analyses were implemented to investigate the charge transfer amount between the related molecular orbitals of I(MF<sub>2</sub>)<sub>n</sub>I and Cl<sup>−</sup>.

The donor and acceptor natural bond orbitals (NBO(i) and NBO(j)), the corresponding second-order perturbation energy lowering ( $\Delta^2 E$ ), and charge transfer amount between the donor and acceptor orbitals ( $q_{CT}$ ) are collected in Table 6. The values of  $q_{CT}$  were calculated using the following approximation [35, 38, 39]:

$$q_{CT} = \delta_i \frac{F_{ij}}{\varepsilon_j - \varepsilon_i}$$

where  $\delta_i$  is the electron occupancy of NBO(i),  $\varepsilon_i$  and  $\varepsilon_j$  are diagonal elements, and  $F_{ij}$  is the off-diagonal NBO Fock matrix element.

**Table 6** The NBO analyses of the complexes

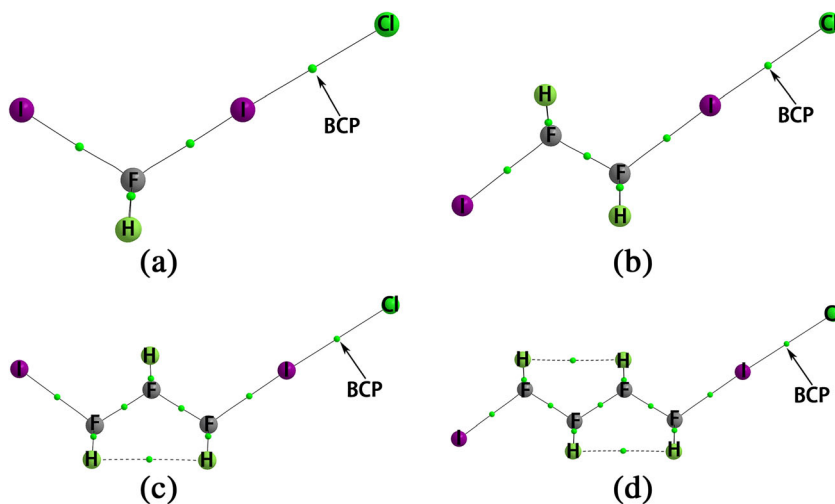
	Donor NBO (i)	Acceptor NBO (j)	$F_{ij}$	$\epsilon_j - \epsilon_i$	$\delta_i$	$q_{CT}$	$\Delta^2 E$
ICF <sub>2</sub> I···Cl <sup>-</sup>	Cl(6) lone pair	C(1)-I(5) anti-bond	0.147	0.56	1.8284	0.1260	48.39
I(CF <sub>2</sub> ) <sub>2</sub> I···Cl <sup>-</sup>	Cl(9) lone pair	C(2)-I(8) anti-bond	0.143	0.56	1.8371	0.1198	45.73
I(CF <sub>2</sub> ) <sub>3</sub> I···Cl <sup>-</sup>	Cl(12) lone pair	C(8)-I(9) anti-bond	0.139	0.57	1.8453	0.1097	42.55
I(CF <sub>2</sub> ) <sub>4</sub> I···Cl <sup>-</sup>	Cl(15) lone pair	C(11)-I(12) anti-bond	0.139	0.57	1.8455	0.1097	42.45
ISiF <sub>2</sub> I···Cl <sup>-</sup>	Cl(6) lone pair	Si(5)-I(4) anti-bond	0.093	0.58	1.9155	0.0492	18.51
I(SiF <sub>2</sub> ) <sub>2</sub> I···Cl <sup>-</sup>	Cl(9) lone pair	Si(8)-I(6) anti-bond	0.091	0.58	1.9210	0.0473	17.59
I(SiF <sub>2</sub> ) <sub>3</sub> I···Cl <sup>-</sup>	Cl(12) lone pair	Si(8)-I(11) anti-bond	0.093	0.58	1.9176	0.0493	18.5
I(SiF <sub>2</sub> ) <sub>4</sub> I···Cl <sup>-</sup>	Cl(15) lone pair	Si(11)-I(14) anti-bond	0.095	0.58	1.9146	0.0514	19.21
IGeF <sub>2</sub> I···Cl <sup>-</sup>	Cl(6) lone pair	Ge(5)-I(3) anti-bond	0.125	0.53	1.8451	0.1026	36.41
I(GeF <sub>2</sub> ) <sub>2</sub> I···Cl <sup>-</sup>	Cl(9) lone pair	Ge(7)-I(5) anti-bond	0.131	0.53	1.8338	0.1120	40.26
I(GeF <sub>2</sub> ) <sub>3</sub> I···Cl <sup>-</sup>	Cl(12) lone pair	Ge(8)-I(11) anti-bond	0.138	0.52	1.8168	0.1280	45.57
I(GeF <sub>2</sub> ) <sub>4</sub> I···Cl <sup>-</sup>	Cl(15) lone pair	Ge(11)-I(14) anti-bond	0.144	0.52	1.8027	0.1382	49.89
ISnF <sub>2</sub> I···Cl <sup>-</sup>	Cl(6) lone pair	Sn(5)-I(3) anti-bond	0.142	0.48	1.7804	0.1558	52.19
I(SnF <sub>2</sub> ) <sub>2</sub> I···Cl <sup>-</sup>	Cl(9) lone pair	Sn(8)-I(6) anti-bond	0.161	0.46	1.7252	0.2113	70.14
I(SnF <sub>2</sub> ) <sub>3</sub> I···Cl <sup>-</sup>	Cl(12) lone pair	Sn(8)-I(11) anti-bond	0.176	0.44	1.6808	0.2689	86.68
I(SnF <sub>2</sub> ) <sub>4</sub> I···Cl <sup>-</sup>	Cl(15) lone pair	Sn(11)-I(14) anti-bond	0.187	0.43	1.6461	0.3113	100.22

From Table 6, the quantities of charge transferred from the donor orbital to the acceptor orbital,  $q_{CT}$ , are large in these I···Cl<sup>-</sup> interacting complexes, which is consistent with that the exchange energy contributes most to the total interaction energy. For I(MF<sub>2</sub>)<sub>n</sub>I···Cl<sup>-</sup>, charge transfer occurs mainly from the Cl<sup>-</sup> lone pair orbital to the M-I anti-bond orbital, with the great charge transfer amount ranging from 0.091 to 0.187. From the second second-order perturbation energy lowering ( $\Delta^2 E$ ), the orbital interaction, with the Cl<sup>-</sup> lone pair as the orbital donors, is large enough in strength in I(MF<sub>2</sub>)<sub>n</sub>I···Cl<sup>-</sup> complexes. The second-order perturbation energies are consistent with the interaction energy as a whole.

### QTAIM analysis

The QTAIM theory is very important to study the nature and strength of conventional and unconventional interactions, which have been suggested by a lot of studies [40–42]. The presence of a bond critical point (BCP) connecting the two bond paths is necessary for the two interacting atoms. In discussing the strength of a chemical bond, the electron density ( $\rho_b$ ) at the BCP could be used as the crucial criterion [33, 43, 44]. From Fig. 4, for the I(MF<sub>2</sub>)<sub>n</sub>I···Cl<sup>-</sup> XB interaction, a BCP exists between the iodine atom and chloride anion of the complexes ICF<sub>2</sub>I···Cl<sup>-</sup>, I(CF<sub>2</sub>)<sub>2</sub>I···Cl<sup>-</sup>, I(CF<sub>2</sub>)<sub>3</sub>I···Cl<sup>-</sup>, and I(CF<sub>2</sub>)<sub>4</sub>I···Cl<sup>-</sup>.

**Fig. 4** Molecular graphs of the complexes. **a** ICF<sub>2</sub>I···Cl<sup>-</sup>. **b** I(CF<sub>2</sub>)<sub>2</sub>I···Cl<sup>-</sup>. **c** I(CF<sub>2</sub>)<sub>3</sub>I···Cl<sup>-</sup>. **d** I(CF<sub>2</sub>)<sub>4</sub>I···Cl<sup>-</sup>





**Table 7** Electron density properties and energy density properties at the bond critical points of the I $\cdots$ Cl $\Gamma$  interactions

	$\rho_b$	$\nabla^2\rho_b$	$H_b$	$-G_b/V_b$	$DI(A/B)$
ICF <sub>2</sub> I $\cdots$ Cl $\Gamma$	0.035	0.081	-0.002	0.915	0.485
I(CF <sub>2</sub> ) <sub>2</sub> I $\cdots$ Cl $\Gamma$	0.034	0.081	-0.002	0.923	0.472
I(CF <sub>2</sub> ) <sub>3</sub> I $\cdots$ Cl $\Gamma$	0.033	0.079	-0.002	0.931	0.460
I(CF <sub>2</sub> ) <sub>4</sub> I $\cdots$ Cl $\Gamma$	0.033	0.079	-0.002	0.931	0.460
ISiF <sub>2</sub> I $\cdots$ Cl $\Gamma$	0.026	0.071	0.001	1.039	0.355
I(SiF <sub>2</sub> ) <sub>2</sub> I $\cdots$ Cl $\Gamma$	0.027	0.068	0.000	1.002	0.346
I(SiF <sub>2</sub> ) <sub>3</sub> I $\cdots$ Cl $\Gamma$	0.027	0.071	0.001	1.037	0.353
I(SiF <sub>2</sub> ) <sub>4</sub> I $\cdots$ Cl $\Gamma$	0.026	0.072	0.001	1.030	0.361
IGeF <sub>2</sub> I $\cdots$ Cl $\Gamma$	0.035	0.084	-0.002	0.936	0.455
I(GeF <sub>2</sub> ) <sub>2</sub> I $\cdots$ Cl $\Gamma$	0.037	0.086	-0.002	0.918	0.472
I(GeF <sub>2</sub> ) <sub>3</sub> I $\cdots$ Cl $\Gamma$	0.039	0.088	-0.003	0.897	0.497
I(GeF <sub>2</sub> ) <sub>4</sub> I $\cdots$ Cl $\Gamma$	0.041	0.089	-0.004	0.880	0.517
ISnF <sub>2</sub> I $\cdots$ Cl $\Gamma$	0.042	0.088	-0.004	0.870	0.541
I(SnF <sub>2</sub> ) <sub>2</sub> I $\cdots$ Cl $\Gamma$	0.047	0.089	-0.006	0.820	0.607
I(SnF <sub>2</sub> ) <sub>3</sub> I $\cdots$ Cl $\Gamma$	0.052	0.088	-0.008	0.784	0.662
I(SnF <sub>2</sub> ) <sub>4</sub> I $\cdots$ Cl $\Gamma$	0.056	0.087	-0.010	0.755	0.632

For the BCP of the XB interactions, the properties based on the electron density and energy density are given in Table 7.

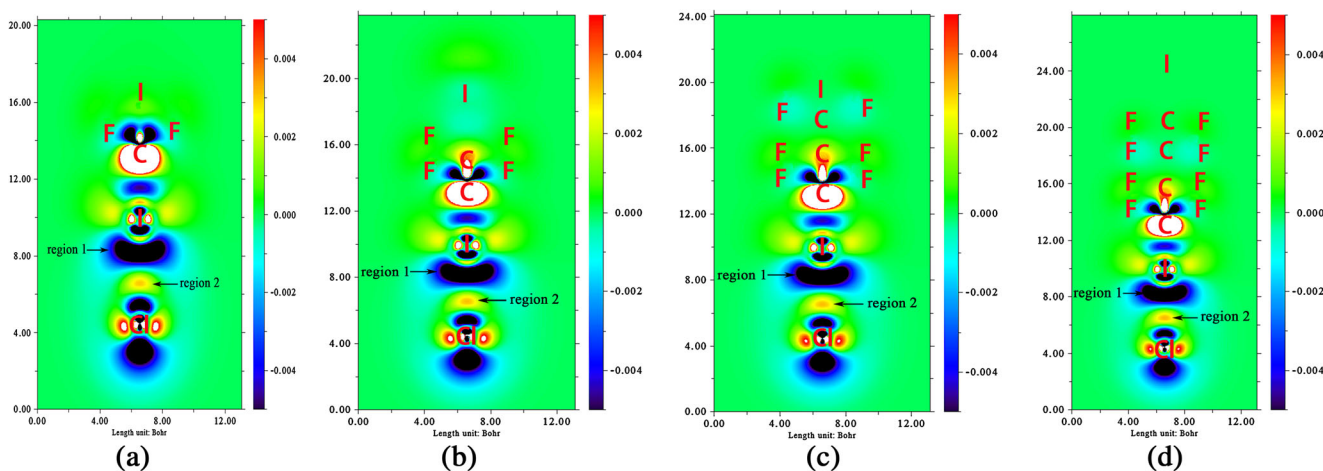
According to QTAIM, the larger the value of  $\rho_b$ , the stronger the bond is [33]. From Table 7, the  $\rho_b$  values at the BCPs for the I $\cdots$ Cl $\Gamma$  interactions are 0.026 ~ 0.056 a.u., which are larger than the  $\rho_b$  values of 0.002 ~ 0.004 a.u. for hydrogen bond [45], indicating that the I $\cdots$ Cl $\Gamma$  interactions are strong. For M = Si, the  $\rho_b$  values range from 0.026 to 0.027 a.u.; For M = C, Ge, Sn, the  $\rho_b$  values range from 0.033 to 0.035, 0.035 to 0.041, and 0.042 to 0.056, respectively. That is to say, the strength of the XB interactions become stronger along the sequence of M = Si, C, Ge, Sn.

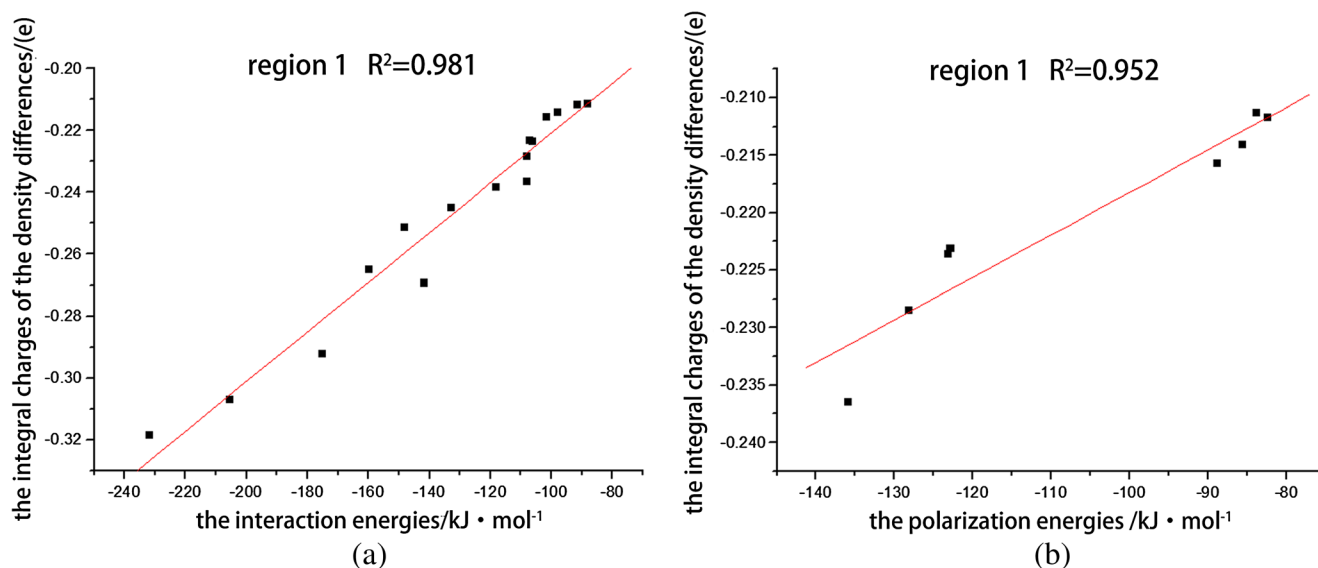
The Laplacian of electron density at the BCP,  $\nabla^2\rho_b$ , indicates the type of interaction. The negative  $\nabla^2\rho_b$  value corresponds to

**Table 8** The integral charges of region 1 (the region of increased electron density) and region 2 (the region of decreased electron density)

Complexes	Region 1	Region 2
ICF <sub>2</sub> I $\cdots$ Cl $\Gamma$	-0.2365	0.0069
I(CF <sub>2</sub> ) <sub>2</sub> I $\cdots$ Cl $\Gamma$	-0.2285	0.0081
I(CF <sub>2</sub> ) <sub>3</sub> I $\cdots$ Cl $\Gamma$	-0.2236	0.0092
I(CF <sub>2</sub> ) <sub>4</sub> I $\cdots$ Cl $\Gamma$	-0.2231	0.0095
ISiF <sub>2</sub> I $\cdots$ Cl $\Gamma$	-0.2113	0.0164
I(SiF <sub>2</sub> ) <sub>2</sub> I $\cdots$ Cl $\Gamma$	-0.2117	0.0197
I(SiF <sub>2</sub> ) <sub>3</sub> I $\cdots$ Cl $\Gamma$	-0.2141	0.0192
I(SiF <sub>2</sub> ) <sub>4</sub> I $\cdots$ Cl $\Gamma$	-0.2157	0.0203
IGeF <sub>2</sub> I $\cdots$ Cl $\Gamma$	-0.2384	0.0055
I(GeF <sub>2</sub> ) <sub>2</sub> I $\cdots$ Cl $\Gamma$	-0.2451	0.0057
I(GeF <sub>2</sub> ) <sub>3</sub> I $\cdots$ Cl $\Gamma$	-0.2515	0.0051
I(GeF <sub>2</sub> ) <sub>4</sub> I $\cdots$ Cl $\Gamma$	-0.2651	0.0047
ISnF <sub>2</sub> I $\cdots$ Cl $\Gamma$	-0.2694	0.0013
I(SnF <sub>2</sub> ) <sub>2</sub> I $\cdots$ Cl $\Gamma$	-0.2923	0.0008
I(SnF <sub>2</sub> ) <sub>3</sub> I $\cdots$ Cl $\Gamma$	-0.3071	0.0007
I(SnF <sub>2</sub> ) <sub>4</sub> I $\cdots$ Cl $\Gamma$	-0.3186	0.0008

the shared interaction and the positive  $\nabla^2\rho_b$  corresponds to the closed-shell interaction systems. Furthermore, combined with  $\nabla^2\rho_b$ , the total energy density ( $H_b$ ) at the BCP also could be used an index to character the type of interaction. Positive  $\nabla^2\rho_b$  and positive  $H_b$  values indicate the noncovalent interactions; positive  $\nabla^2\rho_b$  and negative  $H_b$  values reflect partial-covalent interactions. Later, the ratio  $-G_b/V_b$  is to describe the interaction. The potential energy density ( $V_b$ ), kinetic energy ( $G_b$ ), and total energy density ( $H_b = V_b + G_b$ ) at BCPs of XB interactions are also listed in Table 7. For the XBs of I(MF<sub>2</sub>)<sub>n</sub>I $\cdots$ Cl $\Gamma$  (M = C, Ge, Sn),  $\nabla^2\rho_b > 0$ ,  $H_b < 0$ , the ratios of  $-G_b/V_b$  are less than 1; these indicate that the I $\cdots$ Cl $\Gamma$  XB interactions of I(MF<sub>2</sub>)<sub>n</sub>I $\cdots$ Cl $\Gamma$  (M = C, Ge, Sn) complexes are stabilized by partial-covalent interactions. However, for the I $\cdots$ Cl $\Gamma$  interactions of I(SiF<sub>2</sub>)<sub>n</sub>I $\cdots$ Cl $\Gamma$  complexes,  $\nabla^2\rho_b > 0$ ,  $H_b > 0$ , the ratios of  $-G_b/V_b$  are more than 1; they belong to noncovalent interactions.

**Fig. 5** Computed density difference plots for the complexes ICF<sub>2</sub>I $\cdots$ Cl $\Gamma$ , I(CF<sub>2</sub>)<sub>2</sub>I $\cdots$ Cl $\Gamma$ , I(CF<sub>2</sub>)<sub>3</sub>I $\cdots$ Cl $\Gamma$ , and I(CF<sub>2</sub>)<sub>4</sub>I $\cdots$ Cl $\Gamma$ . Blue region (region 1) denotes the decrease region of electron density outside I(CF<sub>2</sub>)<sub>n</sub>I. Yellow region (region 2) denotes the increase region of electron density outside the Cl $\Gamma$  anion



**Fig. 6** Linear correlations between the integral charges of the density differences and the interaction energies (a) as well as with the polarization energies (b)

Table 7 also lists the calculated *DI*. The formal bond order can be estimated using the delocalization index (*DI*) in a selective way [46]. The *DI* values become larger along the sequence of  $M = \text{Si}, \text{C}, \text{Ge}, \text{Sn}$ , which agree well with the interaction energies.

### Density difference of molecular formation analysis

In the recent years, the idea of density difference by Daudel and Roux [47–49] has been applied to study the molecules and weak interactions [50–53]. Polarization is a real physical phenomenon, corresponding to the electron density shifts from one molecule to the electric field of another, which could be observed physically from the electronic density [54].

For the  $A \cdots B$  intermolecular interaction, the definition of the MFDD is:

$$\rho_d(\mathbf{r}) = \rho_{\text{complex}}(\mathbf{r}) - (\rho_{\text{molA}}(\mathbf{r}) + \rho_{\text{molB}}(\mathbf{r}))$$

The polarization effect of the XBs could be expressed by plotting the difference of the electron density between the complex ( $A \cdots B$ ) and the monomers (A and B). Taking  $\text{I}(\text{CF}_2)_n\text{I} \cdots \text{Cl}^-$  for example, the computed density difference plots are presented in Fig. 5. The electric field of the lone pair of  $\text{Cl}^-$  causes an increase in the electric field of the  $\sigma$ -hole region of  $\text{I}(\text{MF}_2)_n\text{I}$  and a decrease of the electron density outside  $\text{Cl}^-$ , indicating that polarization is a significant factor in the formation of the XB interactions. From  $\text{Cl}^-$  to  $\text{I}(\text{MF}_2)_n\text{I}$ , the integral charges of region 1 (the region of decreased electron density) and region 2 (the region of increased electron density) were obtained and collected in Table 8. For  $\text{I}(\text{MF}_2)_n\text{I} \cdots \text{Cl}^-$  ( $M = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ ), comparing the integral charges of region 1 with the interaction energies of Table 3,

linear correlation was found with the correlation coefficient 0.981, which is displayed in Fig. 6a. Furthermore, the integral charges of region 1 also have good relations with the polarization energy term in Table 4, with the correlation coefficient 0.952, which is displayed in Fig. 6b.

### Conclusions

1. There is a region of positive electrostatic potentials outside the iodine in  $\text{I}(\text{MF}_2)_n\text{I}$  ( $M = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ ) along the extension of the C-I bond, which can form  $\text{I} \cdots \text{Cl}^-$  XB interaction with chlorine anion. These halogen bonds are very strong.
2. The XB interaction energies of  $\text{I}(\text{MF}_2)_n\text{I} \cdots \text{Cl}^-$  are apparently related to the group IV elements, becoming more and more negative along the sequence of  $M = \text{Si}, \text{C}, \text{Ge}, \text{Sn}$ . Accompanied with increasing number ( $n$ ) of  $\text{MF}_2$  unit, the XB interactions ( $M = \text{Si}, \text{Ge}, \text{Sn}$ ) become stronger and stronger.
3. The energy decomposition analyses demonstrate that the exchange energy contributes most in forming these XB interactions. In the meantime, the electrostatic energy is also an important factor for the  $\text{I} \cdots \text{Cl}^-$  interactions.
4. The XB interactions belong to partial-covalent interactions in the  $(\text{MF}_2)_n\text{I} \cdots \text{Cl}^-$  ( $M = \text{C}, \text{Ge}, \text{Sn}$ ) complexes, while they are noncovalent interactions when  $M = \text{Si}$ .

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**Compliance with ethical standards** The manuscript has full control of all primary data, and the authors agree to allow the journal to review their data if requested.

**Competing interest** The authors declare that they have no competing interest.

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