

Trends in σ -hole strengths and interactions of F_3MX molecules ($M = C, Si, Ge$ and $X = F, Cl, Br, I$)

Ashwini Bundhun · Ponnadurai Ramasami · Jane S. Murray · Peter Politzer

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Abstract It is well-established that many covalently-bonded atoms of Groups IV–VII have directionally-specific regions of positive electrostatic potential (σ -holes) through which they can interact with negative sites. In the case of Group VII, this is called “halogen bonding.” We have studied two series of molecules: the F_3MX and, for comparison, the H_3MX ($M = C, Si$ and Ge ; $X = F, Cl, Br$ and I). Our objective was to determine how the interplay between M and X in each molecule affects the σ -holes of both, and consequently their interactions with the nitrogen lone pair of HCN. We find that the relative electronegativities of M and X are not sufficient to explain their effects upon each other’s σ -holes; consideration of charge capacity/polarizability (and perhaps other factors) also appears to be necessary. However the results do support the description of normal σ -hole interactions as being largely electrostatically-driven.

Keywords Halogen bonding · Electrostatic potentials · F_3MX molecules · Interaction energies · σ -hole interactions

Introduction: σ -Hole Interactions

In 2007, Clark et al. explained why certain covalently-bonded halogens have regions of positive electrostatic potentials on extensions of their covalent bonds [1], a feature that had been observed computationally as early as

1992 [2]. These positive regions of electrostatic potential can interact attractively with negative sites, which accounts for the existence of halogen bonds $R-X\cdots B$, where X is a halogen and B represents a negative site, such as the lone pair of a Lewis base [2–7].

Clark et al.’s explanation is a simple and straightforward one, and was originally introduced with the series F_3CX , where $X = F, Cl, Br$ and I [1]. When a halogen X forms a covalent bond, which involves its half-filled p valence orbital, that electron is largely localized in the bonding region, leaving a deficiency of electronic density in the outer (non involved) lobe of the p -type valence orbital, along the extension of the covalent bond to X . This deficiency has been labeled a σ -hole, because it is created upon the formation of a σ bond [1]. The resultant anisotropies in the electronic densities of covalently-bonded halogens have been detected both experimentally and computationally [8–13]. When the deficiency of electronic density is sufficient, a positive electrostatic potential will be created, focused along the extension of the covalent bond to X . This is the reason for the highly directional nature of halogen bonding; the $R-X-B$ angle is typically in the neighborhood of 180° . A positive σ -hole on a halogen is shown in Fig. 1 for F_3GeBr ; it is the region of positive electrostatic potential (shown in red) along the extension of the $Ge-Br$ bond.

It might be anticipated that σ -holes should be present on the extensions of other single σ bonds, not only those to halogens. Indeed, this has been found to be the case for covalently-bonded atoms of Group VI [14–17], Group V [16, 18] and Group IV [19–21]. Examples of positive σ -holes on a covalently-bonded Group IV atom are also in Fig. 1, on the extensions of $F-Ge$ and $Br-Ge$ bonds (shown in red). Such positive regions of electrostatic potential are the driving forces for the formation of stable complexes with negative sites [14–21], just as for the halogens. Interactions of covalently-bonded Group IV to VI atoms with negative sites have been

A. Bundhun · P. Ramasami (✉)
Computational Chemistry Group,
Department of Chemistry, University of Mauritius,
Reduit, Mauritius
e-mail: ramchemi@intnet.mu

J. S. Murray · P. Politzer
CleveTheoComp,
1951 W. 26th Street,
Cleveland, OH 44126, USA

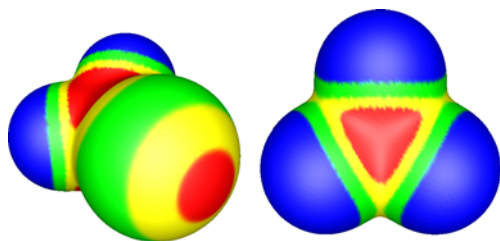


Fig. 1 Computed electrostatic potential on the 0.001 au molecular surface of F_3Ge-Br . *Left*: The bromine is in the foreground, the fluorines in the back. *Right*: The bromine is in the rear. Color ranges, in kcalmol^{-1} , are: *red*, greater than 20; *yellow*, from 10 to 20; *green*, from 0 to 10; *blue*, negative. On the left, two positive σ -holes can be seen: the one on the bromine ($V_{S,\text{max}}=25 \text{ kcalmol}^{-1}$) and one of those on the germanium, on the extension of one of the $F-Ge$ bonds ($V_{S,\text{max}}=45 \text{ kcalmol}^{-1}$). On the right is seen the germanium σ -hole on the extension of the $Br-Ge$ bond ($V_{S,\text{max}}=44 \text{ kcalmol}^{-1}$)

reported for more than half a century [22–32], but not until 2007 was it recognized that many of them are examples of σ -hole bonding. There are potentially four, three and two σ -holes on covalently-bonded Group IV, V and VI atoms, respectively (or more, if the atom is hypervalent [17, 19]),

The origins and characteristics of Group IV–VI σ -holes are similar to those of the halogens [7, 14, 17, 18, 33]. They become more positive in going from the lighter to the heavier (more polarizable) atoms in a given group, and as the remainder of the molecule becomes more electron-withdrawing. σ -Hole bonding is competitive with hydrogen bonding [34–36]. It has in fact been suggested that the latter is simply a special case of the former [7, 33, 37].

A particularly useful feature of σ -hole bonding is directional tunability. The individual σ -holes can be tuned by appropriate modification of the molecular framework bonded to the Group IV–VII atom [14, 15, 18, 19, 21, 35, 38, 39]. For example, in the molecules $XYZSi-O-N(CH_3)_2$, the $Si-O-N$ angle can be varied by changing the substituent Y that is *anti* to the nitrogen; this alters the strength of the silicon σ -hole that is interacting with the nitrogen lone pair [21].

In our earlier work involving Group VII σ -hole bonding (often referred to as halogen bonding [1, 4–7]), our focus was upon the halogen σ -holes. Likewise in demonstrating the existence of σ -holes on covalently-bonded Group IV–VI atoms, our emphasis was upon the general trends observed for the σ -holes on those atoms [14–21].

Our aim in this present study has been to make a systematic and quantitative study of *both* the Group IV and Group VII σ -holes in F_3MX molecules, where M is a Group IV atom (C, Si or Ge) and X is a halogen (F, Cl, Br or I). For comparison, we will also consider H_3MX systems. Our objectives are to examine several specific points: How does varying M and X affect the σ -hole electrostatic potentials of the Group IV atoms and of the halogens? Are the trends reported earlier [1, 6] for the surface electrostatic potentials of the halogens X in F_3CX molecules the same when carbon

is replaced by silicon or germanium? Do the σ -hole electrostatic potentials correlate with the interaction energies of these sites with a Lewis base such as HCN? These and other questions will be addressed in this paper. (The electrostatic potentials on the surfaces of the H_3MI , F_3MI and MX_4 molecules (M = C, Si, Ge, Sn and Pb) have also been determined recently by Donald et al. [38], although the local most positive and negative values were not reported. They examined factors affecting the interactions of the halogen σ -holes of $MH_{4-n}X_n$ and $MH_{3-m}F_mI$ systems.)

Procedure

All geometry optimizations of individual molecules and their complexes with HCN have been carried out with Gaussian 09 [40] at the M06-2X/6-311G(d) level. The M06-2X functional is particularly well suited for weak non-covalent interactions [41, 42], and the results have been shown to correlate well with MP2 [43].

The electrostatic potential $V(\mathbf{r})$ that the nuclei and electrons of a molecule create at any point \mathbf{r} is given by:

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|}. \quad (1)$$

In Eq. (1), Z_A is the charge on nucleus A, located at \mathbf{R}_A , and $\rho(\mathbf{r})$ is the electronic density function. An important feature of $V(\mathbf{r})$ is that it is a physical observable, which can be determined experimentally by diffraction methods [44, 45] as well as computationally. We have computed $V(\mathbf{r})$ on the molecular surfaces defined, following Bader et al. [46], by the 0.001 au (electrons/bohr³) contours of the electronic densities. $V(\mathbf{r})$ on a molecular surface is labeled $V_S(\mathbf{r})$, and its local most positive and most negative values are designated $V_{S,\text{max}}$ and $V_{S,\text{min}}$. The $V_S(\mathbf{r})$ were obtained using the Wave Function Analysis – Surface Analysis Suite (WFA-SAS) [47], which gives both the locations and the values of the $V_{S,\text{max}}$ and $V_{S,\text{min}}$.

Interaction energies ΔE with HCN have been computed from the M06-2X/6-311G(d) energy minima at 0 K using Eq. (2),

$$\Delta E = E(F_3MX \cdots NCH \text{ or } XF_3M \cdots NCH) - E(F_3MX) - E(HCN). \quad (2)$$

Our intention in computing these ΔE is to ascertain if the positive regions of electrostatic potential associated with the Group IV and Group VII atoms in the F_3MX molecules can lead to stable complexes with a Lewis base such as HCN, as has been found previously for other σ -hole donors. HCN has the feature of being linear, so that secondary interactions are insignificant.

Results

Structures of F_3MX molecules

The optimized structures and bond lengths of the F_3MX molecules are shown in Fig. 2. For each M, the M-F distances are essentially constant while the M-X increase as X goes from F to Cl to Br to I, and for each X as M goes from C to Si to Ge. This is as expected.

Electrostatic potentials of F_3MX molecules

We have dual interests in this study: the σ -holes of the Groups IV atoms and those of the halogens. Table 1 lists the most positive surface potentials, the $V_{S,max}$, associated with these σ -holes in the 12 F_3MX molecules. In addition are listed the most negative surface potentials, the $V_{S,min}$, on the halogens.

Looking first at the Group IV atoms, there are four $V_{S,max}$ on the atom M in each F_3MX molecule, on the extensions of the F–M and X–M bonds. This is consistent with what we found earlier for Group IV atoms with electron-attracting substituents [19, 20]. For any particular halogen X, the $V_{S,max}$ on the extensions of the X–M and F–M bonds increase as M becomes more polarizable, i.e., as M changes from C to Si to Ge. For example, the σ -hole $V_{S,max}$ on C, Si and Ge on the extensions of the Cl–C, Cl–Si and Cl–Ge bonds are 21.8, 47.6 and 50.3 kcalmol⁻¹, respectively. (The same trends will be seen for the H_3MX molecules in Table 2.)

For each M, the most positive $V_{S,max}$ are the four identical ones in F_3MF , increasing again with the polarizability

of M from C to Ge. It is tempting to attribute the tetrafluoro derivative having the highest $V_{S,max}$ on M to fluorine being the most electronegative halogen. However, in the F_3MX molecules that have $X \neq F$, the M $V_{S,max}$ on the extension of the X–M bond is usually more positive than those due to the F–M bonds, despite X being less electronegative than F. We will return to this point in the Discussion and summary section.

Moving on to the σ -hole potentials of the halogens, on the extensions of the M–X bonds, these are given in the third column of Table 1. For each M, the fluorines are totally negative, while the $V_{S,max}$ for Cl, Br and I increase in that order (with their polarizabilities). This is what was found earlier for the F_3CX series [1]. It is noteworthy that the “characteristic” negative ring often observed around the sides of the heavier halogens (Cl, Br and I) is seen only in the F_3CX (e.g., Fig. 3); in the F_3SiX and F_3GeX , there is instead a weakly positive ring. See Figs. 1, 4 and 5 and Table 1.

It is striking that the $V_{S,max}$ for a given halogen X are very similar in F_3CX and F_3GeX , while those for F_3SiX are lower in magnitude. For instance, the iodine $V_{S,max}$ in F_3Cl , F_3SiI and F_3GeI are 31.9, 23.7 and 31.2 kcalmol⁻¹, respectively. This variation can be seen in the surface electrostatic potentials of these molecules, in Figs. 3, 4, and 5; the sizes of the red regions on the iodines are quite similar in F_3C-I and F_3Ge-I . It can be argued that the decrease in the halogen $V_{S,max}$ in going from the F_3CX to the F_3SiX reflects the lower electronegativity of silicon compared to carbon, but the electronegativity of germanium is similar to that of silicon [48]. Why are the halogen $V_{S,max}$ higher in the F_3GeX ?

Fig. 2 Computed bond lengths in F_3MX molecules (M = C, Si, Ge; X = F, Cl, Br, I). Units for bond lengths are Å

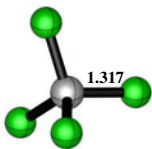
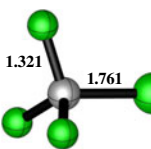
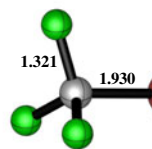
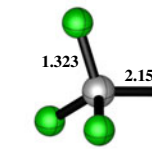
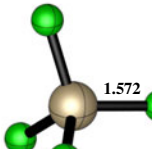
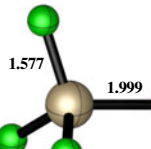
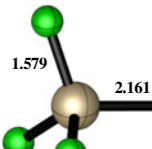
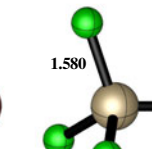
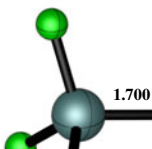
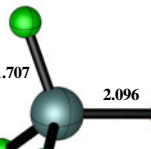
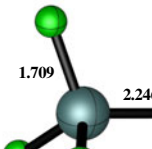
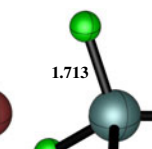
M	MF_4	MF_3-Cl	MF_3-Br	MF_3-I
C	 1.317	 1.321 1.761	 1.321 1.930	 1.323 2.157
Si	 1.572	 1.577 1.999	 1.579 2.161	 1.580 2.389
Ge	 1.700	 1.707 2.096	 1.709 2.246	 1.713 2.460

Table 1 Computed M06-2X/6-311G(d) surface electrostatic potential data for molecules F_3MX , where $M = C, Si$ and Ge , and $X = F, Cl, Br$ and I . Values of $V_{S,max}$ and $V_{S,min}$ are in $kcal\ mol^{-1}$. Only positive $V_{S,max}$ are listed

Molecule	$V_{S,max}$ of M^a	$V_{S,max}$ of X	$V_{S,min}$ of X
F_3C-F	F-C: 23.7 (4)		F: -2.8
F_3C-Cl	Cl-C: 21.8 (1) F-C: 16.7 (3)	Cl: 19.9	Cl: -0.8 F: -3.4
F_3C-Br	Br-C: 21.6 (1) F-C: 16.0 (3)	Br: 25.3	Br: -2.0 F: -3.9
F_3C-I	I-C: 19.3 (1) F-C: 15.6 (3)	I: 31.9	I: -1.9 F: -4.5
F_3Si-F	F-Si: 52.7 (4)		F: -10.4
F_3Si-Cl	Cl-Si: 47.6 (1) F-Si: 40.7 (3)	Cl: 12.2	Cl: +1.7 F: -11.3
F_3Si-Br	Br-Si: 45.0 (1) F-Si: 39.0 (3)	Br: 18.3	Br: +2.1 F: -12.1
F_3Si-I	I-Si: 43.3 (1) F-Si: 37.3 (3)	I: 23.7	I: +1.8 F: -12.7
F_3Ge-F	F-Ge: 60.7 (4)		F: -11.9
F_3Ge-Cl	Cl-Ge: 50.3 (1) F-Ge: 47.4 (3)	Cl: 17.7	Cl: +5.0 F: -14.9
F_3Ge-Br	Br-Ge: 44.5 (1) F-Ge: 45.3 (3)	Br: 25.0	Br: +6.1 F: -16.4
F_3Ge-I	I-Ge: 39.7 (1) F-Ge: 43.0 (3)	I: 31.2	I: +6.6 F: -18.1

^a The numbers in parentheses denote the number of σ -hole potentials of that value on a particular atom

Electrostatic potentials of H_3MX molecules

In order to better understand the diminished halogen $V_{S,max}$ in the F_3SiX molecules compared to those of F_3CX and F_3GeX , we have computed the surface electrostatic potentials for the series H_3MX , where again $M = C, Si$ and Ge and $X = F, Cl, Br$ and I . Our results are listed in Table 2. We find that the halogen $V_{S,max}$ in the H_3MX series are much less than those in the F_3MX . This is to be expected: for each M , F_3M is more electron-attracting than H_3M , due to the presence of the three fluorines in the former. In fact only the bromines in H_3CBr and H_3SiBr and the iodines in the three H_3MI have positive $V_{S,max}$ (Table 2). These decrease as M goes from C to Si to Ge ; for example, the iodine $V_{S,max}$ in H_3Cl , H_3SiI and H_3GeI are 13.0, 6.5 and 4.7 $kcal\ mol^{-1}$, respectively. Thus we do not see the seemingly anomalous $V_{S,max}$ for the H_3GeX that are observed for the F_3GeX .

Interactions with NCH

In Table 3 are the M06-2X/6-311 G(d) interaction energies ΔE and separations for the complexes **1** and **2** between the positive σ -hole regions on the Group IV or Group VII atoms

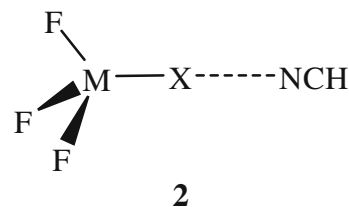
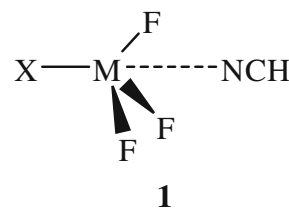
Table 2 Computed M06-2X/6-311G(d) surface electrostatic potential data for molecules H_3MX , where $M = C, Si$ and Ge , and $X = F, Cl$, and Br . Values of $V_{S,max}$ and $V_{S,min}$ are in $kcal\ mol^{-1}$; only positive $V_{S,max}$ are listed

Molecule	$V_{S,max}$ of M^a	$V_{S,max}$ of X	$V_{S,min}$ of X
H_3C-F	F-C: 20.1 H-C: b		F: -25.4
H_3C-Cl	Cl-C: 17.1 H-C: b		Cl: -15.6
H_3C-Br	Br-C: 15.5 H-C: b	Br: 5.7	Br: -14.9
H_3C-I	I-C: 12.9 H-C: b	I: 13.0	I: -13.0
H_3Si-F	F-Si: 34.7 (1) H-Si: 21.8 (3)		F: -26.2
H_3Si-Cl	Cl-Si: 34.1 (1) H-Si: 19.9 (3)		Cl: -13.4
H_3Si-Br	Br-Si: 32.8 (1) H-Si: 18.5 (3)	Br: 0.5	Br: -11.8
H_3Si-I	I-Si: 31.3 (1) H-Si: 18.4 (3)	I: 6.5	I: -10.6
H_3Ge-F	F-Ge: 43.0 (1) H-Ge: 24.2 (3)		F: -33.3
H_3Ge-Cl	Cl-Ge: 41.2 (1) H-Ge: 21.4 (3)		Cl: -15.6
H_3Ge-Br	Br-Ge: 38.5 (1) H-Ge: 20.3 (3)		Br: -13.4
H_3Ge-I	I-Ge: 35.8 (1) H-Ge: 20.1 (3)	I: 4.7	I: -11.4

^a The numbers in parentheses denote the number of σ -hole potentials of that value on a particular atom

^b The surface is positive, but there is no $V_{S,max}$

of the F_3MX and the nitrogen lone pair of NCH . In all instances, the $M\cdots N$ or $X\cdots N$ separations are less than the sums of the respective van der Waals radii [49].



Do the interaction energies of these $XF_3M\cdots NCH$ and $F_3MX\cdots NCH$ systems correlate with the respective σ -hole

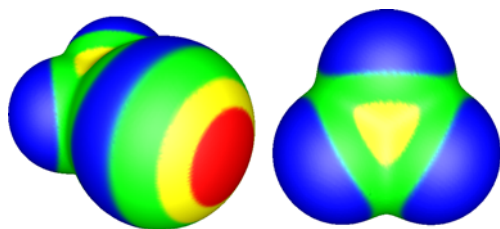


Fig. 3 Computed electrostatic potential on the 0.001 au molecular surface of F_3C-I . *Left*: The iodine is in the foreground, the fluorines in the back. *Right*: The iodine is in the rear. Color ranges, in kcal mol^{-1} , are: *red*, greater than 20; *yellow*, from 10 to 20; *green*, from 0 to 10; *blue*, negative. On the left, two positive σ -holes can be seen: the one on the iodine ($V_{S,\text{max}}=32 \text{ kcalmol}^{-1}$) and one of those on the carbon, on the extension of one of the F–C bonds ($V_{S,\text{max}}=16 \text{ kcalmol}^{-1}$). On the right is seen the carbon σ -hole on the extension of the I–C bond ($V_{S,\text{max}}=19 \text{ kcalmol}^{-1}$)

$V_{S,\text{max}}$, also given in Table 3, as was found in other recent studies of halogen-bonded systems [35, 37, 39]?

For the complexes $XF_3M \cdots NCH$ formed through the σ -holes on the extensions of the X–M bonds, we find excellent correlations for $M = Si$ and $M = Ge$ taken separately (Fig. 6). The correlation coefficients are both 0.999. The interactions via the carbon σ -holes, which have weaker and more similar $V_{S,\text{max}}$, fall into a very small range, with ΔE between -2.0 and $-2.2 \text{ kcalmol}^{-1}$. The $\Delta E-V_{S,\text{max}}$ relationships for the Si and Ge σ -hole-bonded complexes are nearly parallel, with the interactions through germanium being more negative than the corresponding ones for silicon (Fig. 6).

For the complexes formed through the halogen σ -holes, the correlation between interaction energy and $V_{S,\text{max}}$, shown in Fig. 7, is also very good. The correlation coefficient is 0.989. Figure 7 shows that chloro-, bromo- and iodo- systems fit a single correlation for interactions with a particular base, as was also demonstrated recently for a series of fluorinated halobenzenes interacting with acetone [39]. Figures 6 and 7 support the interpretation of these interactions as electrostatically-driven, although the importance of a dispersion component should be recognized [35, 50].

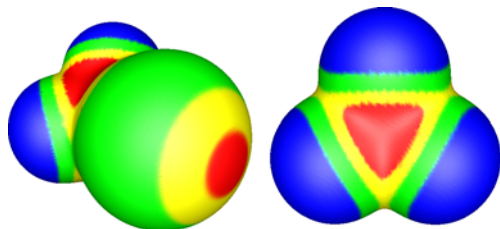


Fig. 4 Computed electrostatic potential on the 0.001 au molecular surface of F_3Si-I . *Left*: The iodine is in the foreground, the fluorines in the back. *Right*: The iodine is in the rear. Color ranges, in kcal mol^{-1} , are: *red*, greater than 20; *yellow*, from 10 to 20; *green*, from 0 to 10; *blue*, negative. On the left, two positive σ -holes can be seen: the one on the iodine ($V_{S,\text{max}}=24 \text{ kcalmol}^{-1}$) and one of those on the silicon, on the extension of one of the F–Si bonds ($V_{S,\text{max}}=37 \text{ kcalmol}^{-1}$). On the right is seen the silicon σ -hole on the extension of the I–Si bond ($V_{S,\text{max}}=43 \text{ kcalmol}^{-1}$)

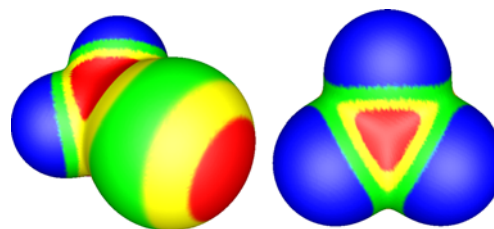


Fig. 5 Computed electrostatic potential on the 0.001 au molecular surface of F_3Ge-I . *Left*: The iodine is in the foreground, the fluorines in the back. *Right*: The iodine is in the rear. Color ranges, in kcal mol^{-1} , are: *red*, greater than 20; *yellow*, from 10 to 20; *green*, from 0 to 10; *blue*, negative. On the right, two positive σ -holes can be seen: the one on the iodine ($V_{S,\text{max}}=31 \text{ kcalmol}^{-1}$) and one of those on the germanium, on the extension of one of the F–Ge bonds ($V_{S,\text{max}}=45 \text{ kcal mol}^{-1}$). On the right is seen the germanium σ -hole on the extension of the I–Ge bond ($V_{S,\text{max}}=40 \text{ kcalmol}^{-1}$)

The fallacy of atomic charges

A time-honored, although highly flawed concept, is that of assigning charges to atoms in molecules. It is well known that there is no rigorous physical basis for this, and the many

Table 3 Computed M06-2X/6-311 G(d) interaction energies ΔE and M---N, X---N separations for F_3MX σ -hole-bonded complexes **1** and **2** and computed $V_{S,\text{max}}$ corresponding to σ -hole donor in each complex. Units for ΔE and $V_{S,\text{max}}$ are kcalmol^{-1} ; M---N and X---N separations are in Å

Complex	ΔE	$V_{S,\text{max}}$ of σ -hole donor	M---N/X---N separation ^a
Group IV donor (1):			
$F-F_3C \cdots NCH$	-2.1	23.7	3.17 (3.25)
$Cl-F_3C \cdots NCH$	-2.1	21.8	3.18 (3.25)
$Br-F_3C \cdots NCH$	-2.1	21.6	3.18 (3.25)
$I-F_3C \cdots NCH$	-2.0	19.3	3.19 (3.25)
$F-F_3Si \cdots NCH$	-5.9	52.7	2.84 (3.65)
$Cl-F_3Si \cdots NCH$	-5.2	47.6	2.88 (3.65)
$Br-F_3Si \cdots NCH$	-4.8	45.0	2.89 (3.65)
$I-F_3Si \cdots NCH$	-4.6	43.3	2.90 (3.65)
$F-F_3Ge \cdots NCH$	-9.7	60.7	2.52 (3.70)
$Cl-F_3Ge \cdots NCH$	-7.6	50.3	2.62 (3.70)
$Br-F_3Ge \cdots NCH$	-6.5	44.5	2.69 (3.70)
$I-F_3Ge \cdots NCH$	-5.7	39.7	2.74 (3.70)
Group VII donor (2):			
$F_3C-Cl \cdots NCH$	-2.0	19.9	3.05 (3.30)
$F_3C-Br \cdots NCH$	-2.9	25.3	3.06 (3.40)
$F_3C-I \cdots NCH$	-4.0	31.9	3.16 (3.53)
$F_3Si-Cl \cdots NCH$	-1.3	12.2	3.21 (3.30)
$F_3Si-Br \cdots NCH$	-2.0	18.3	3.24 (3.40)
$F_3Si-I \cdots NCH$	-2.8	23.7	3.34 (3.53)
$F_3Ge-Cl \cdots NCH$	-1.9	17.7	3.15 (3.30)
$F_3Ge-Br \cdots NCH$	-2.7	25.0	3.17 (3.40)
$F_3Ge-I \cdots NCH$	-3.8	31.2	3.27 (3.53)

^a The sums of the respective van der Waals radii are given in parentheses [49]. The van der Waals radius of Ge was estimated [19]

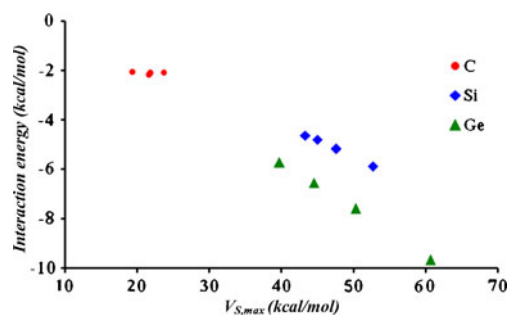


Fig. 6 Plot of interaction energy vs. $V_{S,max}$ for the σ -bonded complexes $\text{XF}_3\text{M} \cdots \text{NCH}$ (1) listed in Table 3. Red circles correspond to $\text{M} = \text{C}$, blue diamonds to $\text{M} = \text{Si}$, green triangles to $\text{M} = \text{Ge}$. The correlation coefficients R for the $\text{XF}_3\text{Si} \cdots \text{NCH}$ and $\text{XF}_3\text{Ge} \cdots \text{NCH}$ complexes are both $R=0.999$

procedures that have been proposed are arbitrary and of questionable value. To demonstrate this, Table 4 presents the atomic charges of the M and X in the molecules F_3MX , as given by the widely-used “natural population analysis” (NPA) approach [51].

It is immediately obvious, as was pointed out earlier [4, 16], that single atomic charges cannot predict the existence of halogen bonding, since the halogens are normally described as negative (Table 4). It cannot explain why the iodines in the H_3MI and the bromine in H_3CBr can interact attractively with both positive and negative sites (Table 2).

Furthermore, for a given X , the silicon and germanium are predicted to have essentially the same charges. This is inconsistent with the finding that the germaniums interact significantly more strongly with HCN (Table 3, Fig. 6). In addition, assigning a single atomic charge to M cannot account for its having σ -holes with different $V_{S,max}$ that can interact in specific directions with different strengths (Tables 1 and 2).

Discussion and summary

Our focus in this work is upon the interplay between two categories of atoms in the same molecules – the

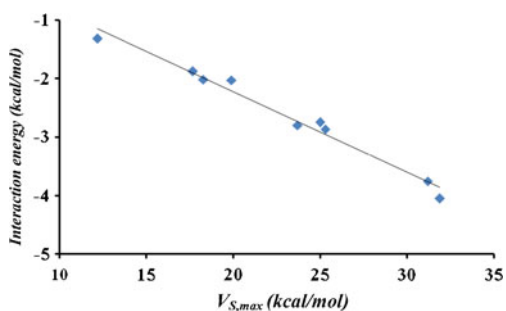


Fig. 7 Plot of interaction energy vs. $V_{S,max}$ for the σ -bonded complexes $\text{F}_3\text{MX} \cdots \text{NCH}$ (2) listed in Table 3. Correlation coefficient $R=0.989$

Table 4 NPA atomic charges for M and X in F_3MX ($\text{M} = \text{C}, \text{Si}, \text{Ge}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), computed at the M06-2X/6-311G(d) level. Units for atomic charges are in e

X	NPA charge on M	NPA charge on X
CF_3X		
F	1.39	-0.35
Cl	1.08	-0.04
Br	1.03	0.00
I	0.96	0.09
SiF_3X		
F	2.52	-0.63
Cl	2.25	-0.37
Br	2.20	-0.31
I	2.12	-0.23
GeF_3X		
F	2.52	-0.63
Cl	2.25	-0.37
Br	2.19	-0.30
I	2.09	-0.19

Group IV, M , and the halogens X – and how this interplay affects the σ -holes of M and X . In each molecule, the atoms X and M plus those attached to M (F or H) are all competing for the available electronic charge. We have seen that consideration of electronegativity alone does not suffice to explain the trends that are observed. For instance, in the molecules F_3MCl , F_3MBr and F_3MI , why are the σ -hole $V_{S,max}$ on the extensions of the Cl-M , Br-M and I-M bonds usually more positive than those on the F-M , despite fluorine being the most electronegative halogen? Why do the X σ -holes have higher $V_{S,max}$ in the F_3GeX than in the F_3SiX ?

We suggest that, besides electronegativity, an additional factor to take into account (perhaps among others) is what Huheey labeled as “charge capacity” [52, 53]. This refers to the ability of an atom to accommodate the gain or loss of electronic charge. While there are a variety of examples of the significant effects that charge capacity can have [53], a particularly striking one involves the electron affinities of the halogens. The experimental values show that fluorine, despite its ranking as by far the most electronegative [48], has a considerably lower electron affinity than chlorine, and only slightly higher than bromine [54]. While fluorine does have the strongest initial attraction for additional electronic charge, this is rapidly countered by repulsion from its own relatively concentrated electrons [55], i.e., it has a much lower charge capacity than the other halogens [53]. In physical observable terms, charge capacity can be regarded as related to polarizability [53, 56]. In general, therefore, its variation among the atoms tends to be opposite to that of

electronegativity. The importance of charge capacity/polarizability in the context of σ -holes was already pointed out when it was noted that these become more positive within a given group of the periodic table in going to the heavier, more polarizable atoms.

Can charge capacity/polarizability help to explain the seemingly anomalous features of Tables 1 and 2? We can offer some speculations. Consider the surprisingly high $V_{S,max}$ of the X atoms in the F_3GeX series. In terms of the electronegativities of silicon and germanium [48], the $V_{S,max}$ of the halogens X in F_3SiX and F_3GeX should be approximately the same, as are those of the iodines in H_3SiI and H_3GeI (Table 2). In the F_3MX series, however, there is an important additional influence: the electron-attracting power of the three fluorines in the F_3M groups. This accounts for both the silicon and the germanium $V_{S,max}$ being more positive in the F_3MX than in the corresponding H_3MX . Furthermore, since germanium is more polarizable than silicon [54], it is better able to transmit electronic charge from X to the three fluorines, resulting in the halogens X having higher $V_{S,max}$ in the F_3GeX than in the F_3SiX . (Note that the three fluorines have more negative $V_{S,min}$ in the F_3GeX than in the F_3SiX .)

With regard to the observation that the M σ -holes on the extensions of the X–M bonds in the molecules F_3MX are generally more positive than those of the F–M bonds, when X = Cl, Br or I: This may mean that the much greater polarizabilities/charge capacities of the three heavier halogens, compared to fluorine, render them better able to accept charge from the atom M.

This discussion has clearly been highly speculative. Both electronegativity and charge capacity/polarizability (and possibly other factors) appear to play roles in determining the trends in σ -hole $V_{S,max}$ in these series of molecules, but establishing their relative effects will require further investigation. However while this dual study of M and X σ -holes has revealed complexities (not unexpectedly), it has reaffirmed the electrostatically-driven nature of normal σ -hole bonding (keeping in mind the dispersion component [35, 50]).

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