

Revealing substitution effects on the strength and nature of halogen-hydride interactions: a theoretical study

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Abstract A quantum chemistry study was carried out to investigate the strength and nature of halogen bond interactions in $\text{HXeH}\cdots\text{XCCY}$ complexes, where $\text{X} = \text{Cl}, \text{Br}$ and $\text{Y} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CN}, \text{NC}, \text{C}_2\text{H}, \text{CH}_3, \text{OH}, \text{SH}, \text{NH}_2$. Examination of the electrostatic potentials $V(r)$ of the XCCY molecules reveals that the addition of substituents has a significant effect upon the most positive electrostatic potential on the surface of the interacting halogen atom. We found that the magnitude of atomic charges and multipole moments depends upon the halogen atom X and is rather sensitive to the electron-withdrawing/donating power of the remainder of the molecule. An excellent correlation was found between the most positive electrostatic potentials on the halogen atom and the interaction energies. For either $\text{HXeH}\cdots\text{ClCCY}$ or $\text{HXeH}\cdots\text{BrCCY}$ complexes, an approximate linear correlation between the interaction energies and halogens multipole moments are established, indicating that the electrostatic and polarization interactions are responsible for the stability of the complexes. According to energy decomposition analysis, it is revealed that the electrostatic interactions are the major source of the attraction in the $\text{HXeH}\cdots\text{XCCY}$ complexes. Furthermore, the changes in the electrostatic term are mainly responsible for the dependence of interaction energy on the halogen atom.

Keywords Distributed multipole analysis · Electrostatic · Electrostatic potential · Energy decomposition analysis · Halogen bond

Introduction

Noncovalent interactions play critical roles in many chemical and biological phenomena, such as molecular recognition, conformational transformation, and molecular packing in crystals [1–6]. Among the various types of noncovalent interactions, the hydrogen bond is, without doubt, the most widely studied one. However, other interactions such as, the dihydrogen bond [7, 8] recently have been the subject of extensive investigations. A halogen bond is a short-range $\text{R-X}\cdots\text{B}$ interaction, where X is a halogen (typically chlorine, bromine, or iodine) that is part of the molecule RX and B is a lone-pair-possessing atom, i.e., a Lewis base. The $\text{R-X}\cdots\text{B}$ angle is typically close to 180° , which suggests that the halogen bond is a highly directional interaction [9, 10]. Halogen bonds share numerous chemical and physical properties with the hydrogen bonds [11–14]. Indeed, such competition can be used to control crystallization of simple organic compounds for the synthesis of new materials [15] and protein-ligand complexation [16–18].

In halogen-bonding, the halogen atom and the electron donor usually have net negative charges; thus the existence of halogen bonding was initially viewed as surprising. A reasonable explanation for this puzzling phenomenon came from Auffinger et al. [19], Politzer et al. [20], and Clark et al. [21] who showed the existence of an electropositive crown (the region of positive charge) at the top of the halogen atom directed toward the electron donor. According to Politzer's viewpoint [22], when a half-filled p orbital participates in forming a covalent bond, its electron normally tends to be somewhat localized in internuclear region, thereby diminishing

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the electronic density in the outer lobe of that orbital. Through this positive region, which has been labeled a “ σ -hole” [22], the halogen atom can interact attractively with a negative site. This positive region is usually, but not always, surrounded by a belt of negative electrostatic potential, which accounts for the possibility of interacting laterally with a positive site. This is the reason for the highly directional nature of halogen-bonding. The directionality of the halogen bond was investigated by quantum mechanical calculations [23–26]. The calculations reveal that the directionality of the interaction in the halogen-bonded R-Br \cdots B complex is higher than that of the hydrogen bonded R-H \cdots B [27]. The electrostatic interaction is responsible for the higher directionality of halogen bond. Theoretical calculations reveal that, for a given negative site, the strengths of halogen bonds correlate with the magnitudes of the σ -hole potentials [28–32]. This may emphasize the largely electrostatic nature of these interactions. However, the combination of electrostatics and polarization is a major directional driving force in halogen-bonding [33–35]. Dispersion effects also play an important role [10, 36]. These are partially balanced by a repulsive interaction, which becomes dominant at very short X \cdots B separations. Recently, Riley et al. [37] indicated that halogens with larger, more positive σ -holes tend to exhibit weaker dispersion interactions, which are attributable to the lower local polarizabilities of the larger σ -holes.

With the progress in the study of halogen-bonding, some unconventional halogen bonds such as the π -halogen bond [38], the single-electron halogen bond [39], and the carbene-halogen bond [40, 41] have been proposed. Considering the fact that a partially negatively charged hydrogen atom can readily interact with an atom with the electron lone-pair vacancy [42, 43], a different type of halogen bonding has been established where a hydrogen atom acts as the electron donor. In such halogen – hydride interactions, the halogen atom acts as a Lewis acid center and the hydrogen atom, with an excess negative charge, like a Lewis base. Indeed, characteristics and origin of hydride – halogen interactions has already been the subject of many theoretical studies [44–47], since this type of halogen bond plays a similar role as that of dihydrogen bonds. The dominance of the electrostatic contribution in the interaction energy of a hydride – halogen bond was reported by Grabowski et al. [48] where the variation-perturbation energy decomposition scheme [49] was used. The significant importance of the dispersion energy was also indicated for very weakly bounded systems as for instance HBeH \cdots ClSiF₃ and FBeH \cdots ClSiF₃ [48]. On the basis of symmetry-adapted perturbation theory (SAPT) approach, Jabłoński and Palusiak [50] have recently found that the induction interaction play a dominant role in the interaction LiH \cdots XCF₃ and HMgH \cdots XCF₃ (X = Cl, Br and I) systems. However, this finding may be due to the close proximity of partially

negatively charge hydrogen atom and a bulky and easily polarizable halogen atom.

Xenon dihydride, HXeH, is frequently found in Xe-matrices containing hydrogen atoms [51, 52]. It is a linear centrosymmetric molecule possessing a strong antisymmetric stretching absorption doublet at 1166 and 1181 cm⁻¹ in a Xe matrix [53]. The origin of bonding in the HXeH molecule can be understood on the basis of a resonance hybrid between (H – Xe)⁺H⁻ and H⁻(Xe – H)⁺, where (H – Xe)⁺ is mainly covalent, while the interaction between (HXe)⁺ and H⁻ is mainly ionic [54]. Due to the negative partial charge on the hydrogen atoms, some literatures have verified that the XeH₂ can provide its electron and further formed the dihydrogen bond with H₂O, (H₂O)₂ [55, 56], HF, HCl and HCN [57]. Considering the similarities between the halogen bond and the hydrogen bond [9–12], we deduce the existence of the XeH₂–halogen bond. Although the structure and interaction energies for the XeH₂–halogen bond have already been investigated [58], there still remain a number of important and fundamental issues that demand deeper understanding. Herein we report our quantum chemistry study of HXeH \cdots XCCY type systems, where X = Cl and Br; Y = H, F, Cl, Br, CN, NC, NH₂, C₂H, CH₃, OH and SH (Fig. 1). Because the binding energies of halogen bonds are comparable to those of hydrogen-bonding, high level quantum chemistry calculations should be adopted to describe them. The strength and nature of the halogen bonds in these complexes are also compared with their analogue HXeH \cdots HCCY dihydrogen bonds.

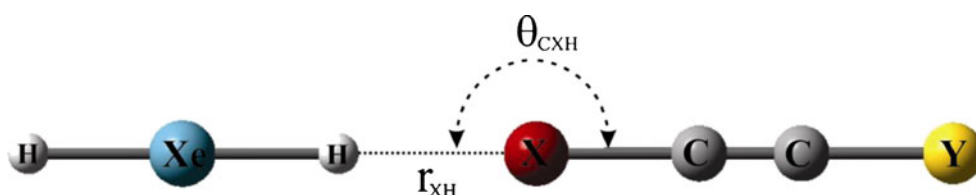
Computational details

The optimized structures of HXeH \cdots XCCY complexes were obtained using MP2 method without any symmetry constraint. For the calculations, a mixed basis set approach was used; here the Xe atom is described using the pseudopotential based aug-cc-pVTZ-PP basis [59], while the aug-cc-pVTZ is used for other atoms. The harmonic vibrational frequencies were also calculated at the same level to ensure that the optimized structures are true minima. For each complex, the interaction energy was calculated using the MP2 and CCSD (T)/aug-cc-pVTZ (–PP) methods by using the supermolecule method [60] which is defined as the difference between the energy of the complex and those of the individual molecules in isolation:

$$E_{\text{int}} = E_n - \sum_i^n E_i \quad (1)$$

where E_n is the total energy of the complex of size n , and E_i is the energy of the individual monomers in the cluster geometry. The results of Eq. 1 are subject to the basis

Fig. 1 Schematic diagram of the XeH₂⋯XCCY interaction, X = Cl, and Br; Y = H, F, Cl, Br, CN, NC, NH₂, C₂H, CH₃, OH and SH



superposition error, BSSE, as each molecule uses the basis set of the others in the complex, decreasing the energy and resulting in overestimated interaction energies. Hence, BSSE was corrected by means of Boys and Bernardi counterpoise (CP) method [61].

To gain a deeper insight into the halogen bonds properties in terms of meaningful physical components, interaction energies were decomposed using [62]:

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{exch-rep}} + E_{\text{pol}} + E_{\text{disp}} \quad (2)$$

E_{elst} gives the first-order electrostatic term describing the classical Coulomb interaction of the occupied orbitals of one monomer with those of another monomer, $E_{\text{exch-rep}}$ is the repulsive first-order exchange component resulting from the Pauli exclusion principle, E_{pol} and E_{disp} correspond to polarization and dispersion terms. The polarization term contains all classical induction, exchange-induction, etc., from the second order up to infinity. All geometry optimizations,

interaction energies and energy components were calculated using GAMESS package [63].

Results and discussion

The halogen-bonding complexes considered in the present study are formed from XCCY molecules and HXeH. The HXeH molecule was chosen for the analysis since the H atom of the HXeH possesses a meaningful negative electrostatic potential in the Xe–H bond direction, and it may act as the Lewis base center. The following section is divided into four subsections. First, a comparison of molecular geometries and halogen bonds distances of different HXeH⋯XCCY complexes is considered. Second, we present the results for halogen bonds strengths for the title complexes. Third, we discuss the interaction energy partitioning and how it varies with a given Y substitution in the XCCY molecule. Finally, we compare the properties of the halogen bonded

Table 1 Calculated surface electrostatic potential maxima $V_{\text{S,max}}$ (in kcal mol⁻¹), distributed multipole moments, atomic charge q , dipole moment μ and quadrupole moment Θ , (in au), intermolecular distances $r_{\text{X-H}}$ (in Å) and angles $\theta_{\text{C-X-H}}$ (in °) for HXeH⋯XCCY

Complex	$V_{\text{S,max}}$ /kcal mol ⁻¹	$q(\text{X})/e$	$\mu(\text{X})/ea_0$	$\Theta(\text{X})/ea_0^2$	$r_{\text{X-H}}/\text{Å}$	$\theta_{\text{C-X-H}}/^\circ$
HXeH⋯ClCCH	24.0	0.38	0.76	2.04	2.653	179.7
HXeH⋯ClCCF	25.5	0.39	0.76	2.04	2.631	179.9
HXeH⋯ClCCCl	25.9	0.39	0.75	2.03	2.626	179.4
HXeH⋯ClCCBr	32.4	0.40	0.74	2.03	2.520	179.5
HXeH⋯ClCCCN	39.1	0.45	0.72	1.98	2.585	179.4
HXeH⋯ClCCNC	30.8	0.42	0.73	2.00	2.594	179.9
HXeH⋯ClCCC ₂ H	27.7	0.41	0.755	2.04	2.617	179.6
HXeH⋯ClCCCH ₃	18.7	0.37	0.78	2.06	2.659	180.0
HXeH⋯ClCCOH	19.6	0.37	0.79	2.08	2.659	179.6
HXeH⋯ClCCNH ₂	17.1	0.36	0.79	2.08	2.651	179.6
HXeH⋯ClCCSH	24.1	0.39	0.77	2.05	2.515	180.0
HXeH⋯BrCCH	30.7	0.55	1.03	2.86	2.478	179.9
HXeH⋯BrCCF	32.5	0.55	1.04	2.85	2.478	179.8
HXeH⋯BrCCCl	32.4	0.56	1.04	2.85	2.475	180.0
HXeH⋯BrCCBr	32.6	0.56	1.03	2.84	2.443	179.7
HXeH⋯BrCCCN	45.6	0.61	0.98	2.79	2.439	180.0
HXeH⋯BrCCNC	40.1	0.58	1.00	2.82	2.481	179.9
HXeH⋯BrCCC ₂ H	33.9	0.58	1.03	2.85	2.526	180.0
HXeH⋯BrCCCH ₃	25.9	0.53	1.07	2.89	2.524	179.7
HXeH⋯BrCCOH	26.6	0.53	1.07	2.90	2.507	179.8
HXeH⋯BrCCNH ₂	24.7	0.52	1.08	2.91	2.493	180.0
HXeH⋯BrCCSH	30.7	0.55	1.04	2.87	2.515	180.0

HXeH...XCCY complexes with their analogue HXeH...HCCY dihydrogen bonds.

Surface electrostatic potentials and geometries

The electrostatic potentials have been calculated on the surface of the HXeH and XCCY moieties using WFA code [64]. Table 1 lists the most positive surface electrostatic potentials $V_{S,max}$ of halogen atom in the XCCY monomers. Previous studies indicated the efficiency of these parameters to reveal insightful trends about the surface properties of the halogen bonds [64–66]. Figure 2 shows the overall patterns of surface electrostatic potential maps for the HXeH, ClCCH and BrCCH. Of primary interest are the locations of the most negative and the most positive V_S , the $V_{S,min}$ and $V_{S,max}$, that are relevant to the approach of electrophiles and nucleophiles, respectively. For the HXeH, it is evident that the most negative $V_{S,min}$ is associated with the hydrogen atoms on the extension of the Xe – H bond. The most striking feature is the small positive electrostatic potential cap at the end region of the Cl or Br atom along the C – X bond vector, which is surrounded by an electroneutral area and, next, a large electronegative domain. The positive region can interact with an electronegative atom/group, thereby giving rise to a directional interaction. Consistent with the usual trend that σ -holes become more positive in going to the heavier elements in a group [66], the bromine $V_{S,max}$ is more positive than the corresponding chlorine (Table 1). Such halogen positive region is referred to as the “ σ -holes”, because it is centered on the C–X axis and is surrounded by negative electrostatic potential [66]. It is evident from

Fig. 2 Electrostatic potential mapped on the surface of molecular electron density at the 0.001 electrons Bohr⁻³: **a** HXeH, **b** ClCCH, and **c** BrCCH. The color ranges in kcal mol⁻¹ for HXeH: red >8.5, yellow 1.5 to 8.5, green -5.5 to 1.5, blue <-5.5; for ClCCH: red >23.5, yellow 12.0 to 23.5, green 0.4 to 12.0, blue <0.4; for BrCCH: red >23.3, yellow 11.6 to 23.3, green -0.1 to 11.6, blue <-0.1. Black and blue circles are referred to surface maxima and minima, respectively

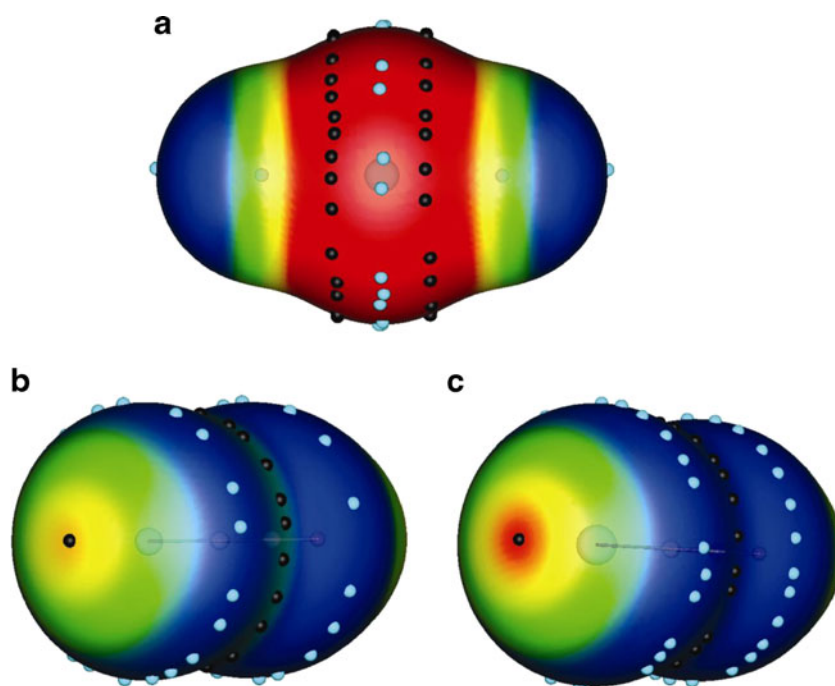


Table 2 Calculated BSSE-corrected interaction energies (in kJ mol⁻¹) for HXeH...XCCY complexes^a

Complex	E_{int}^{MP2}	$E_{int}^{CCSD(T)}$
HXeH...ClCCH	-6.77	-4.48
HXeH...ClCCF	-6.90	-5.38
HXeH...ClCCCl	-6.98	-5.16
HXeH...ClCCBr	-7.29	-5.91
HXeH...ClCCCN	-10.30	-7.51
HXeH...ClCCNC	-9.46	-6.54
HXeH...ClCCC ₂ H	-6.88	-4.75
HXeH...ClCCCH ₃	-5.96	-3.81
HXeH...ClCCOH	-5.98	-3.80
HXeH...ClCCNH ₂	-5.65	-3.52
HXeH...ClCCSH	-6.98	-4.67
HXeH...BrCCH	-10.69	-6.51
HXeH...BrCCF	-11.23	-6.83
HXeH...BrCCCl	-11.48	-7.00
HXeH...BrCCBr	-11.48	-7.48
HXeH...BrCCCN	-15.66	-10.57
HXeH...BrCCNC	-14.73	-9.29
HXeH...BrCCC ₂ H	-12.32	-7.72
HXeH...BrCCCH ₃	-9.55	-5.61
HXeH...BrCCOH	-9.19	-5.26
HXeH...BrCCNH ₂	-9.77	-5.69
HXeH...BrCCSH	-10.98	-6.69

^a CCSD(T) interaction energies were calculated at the MP2 optimized geometries

Table 1 that the magnitude of the halogen’s σ -hole depends upon the electron-withdrawing/donating power of the Y.

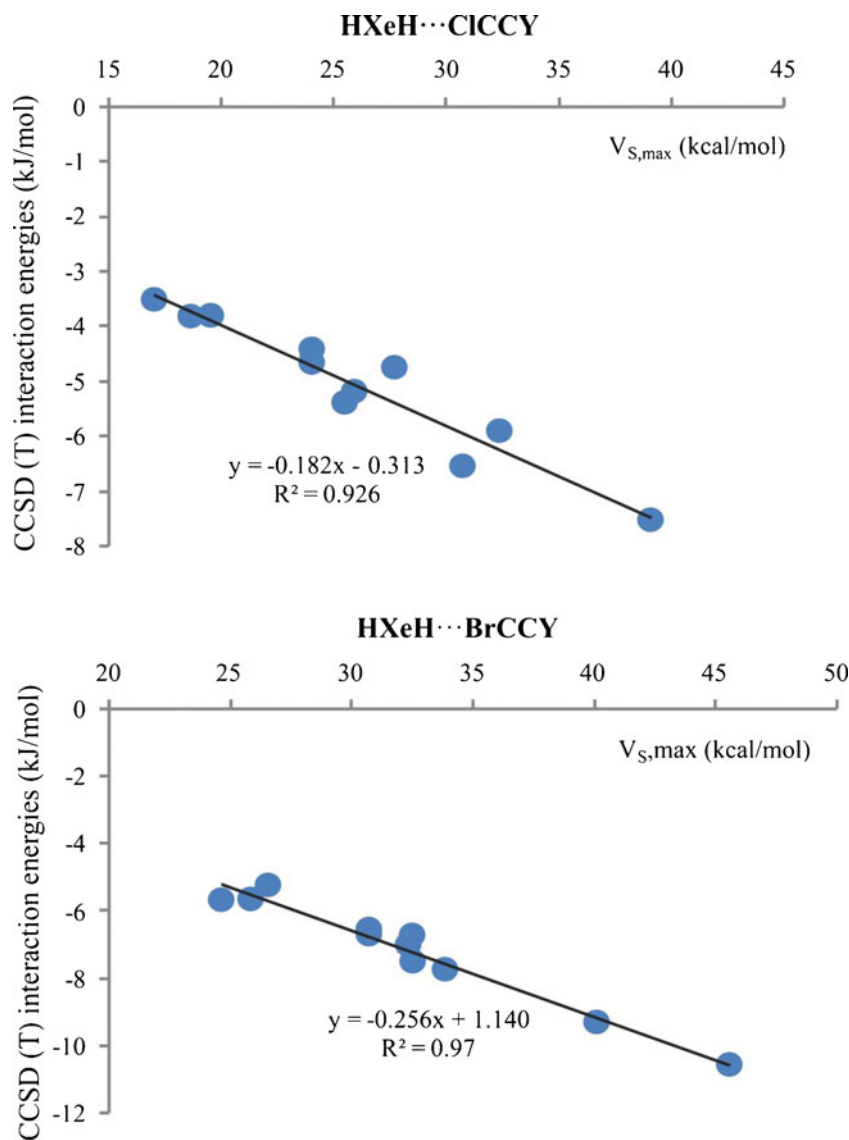
Also apparent is that the presence of electron-withdrawing groups (CN, NC, and F) on the XCCY results in higher halogen $V_{S,max}$ values while the electron-donating OH, CH₃ and NH₂ substituents lead to lower $V_{S,max}$ values.

It has been previously pointed out [67, 68] that the anisotropy distribution of electron density around a covalently bonded halogen atom can efficiently be represented by placing an electric quadrupole moment on the halogen atom. Torii and Yushida [69] indicated that the atomic quadrupole moments on the halogen atoms play a critical role in determining the geometries of halogen-bonded complexes. To examine this issue, we have carried out a distributed multipole analysis (DMA) [70, 71] of HXeH⋯XCCY using the Stone's GDMA program [72]. The evaluated atomic charges $q(X)$, dipoles $\mu(X)$, and quadrupole moments $\Theta(X)$ for chlorine and bromine atoms are given in Table 1. One immediate observation from the results is that magnitude of atomic charges and multipole moments depends upon the halogen atom X and is rather

sensitive to the electron-withdrawing/donating power of the substitution Y. Comparing the values of $\Theta(X)$ shown in Table 1, it is recognized that the magnitude of atomic quadrupole moments tend to be somewhat reduced as the H atom is substituted by an electron-withdrawing group. For a given Y substitution, the magnitude of the electric dipole and quadrupole is increasing in the order of Cl < Br, in parallel with the known general sequence of the strength of halogen-bonding. The increase of $\Theta(X)$ in the order of Cl < Br corresponds to a decreasing value of the halogen atom electronegativity and is related to the changes in the values of atomic charges $q(X)$ as well as $\mu(X)$. This suggests, not only the magnitude of the electric quadrupole but also the extent of electronegative nature of the halogen atom contributes to the enhancement of the electrostatic interaction related to halogen-bonding in the order Cl < Br.

The geometries of monomers and adducts have been fully optimized at the MP2/aug-ccpVTZ(-PP) level. Table 1 lists

Fig. 3 Correlation between CCSD(T) interaction energies and halogen's electrostatic potential maxima



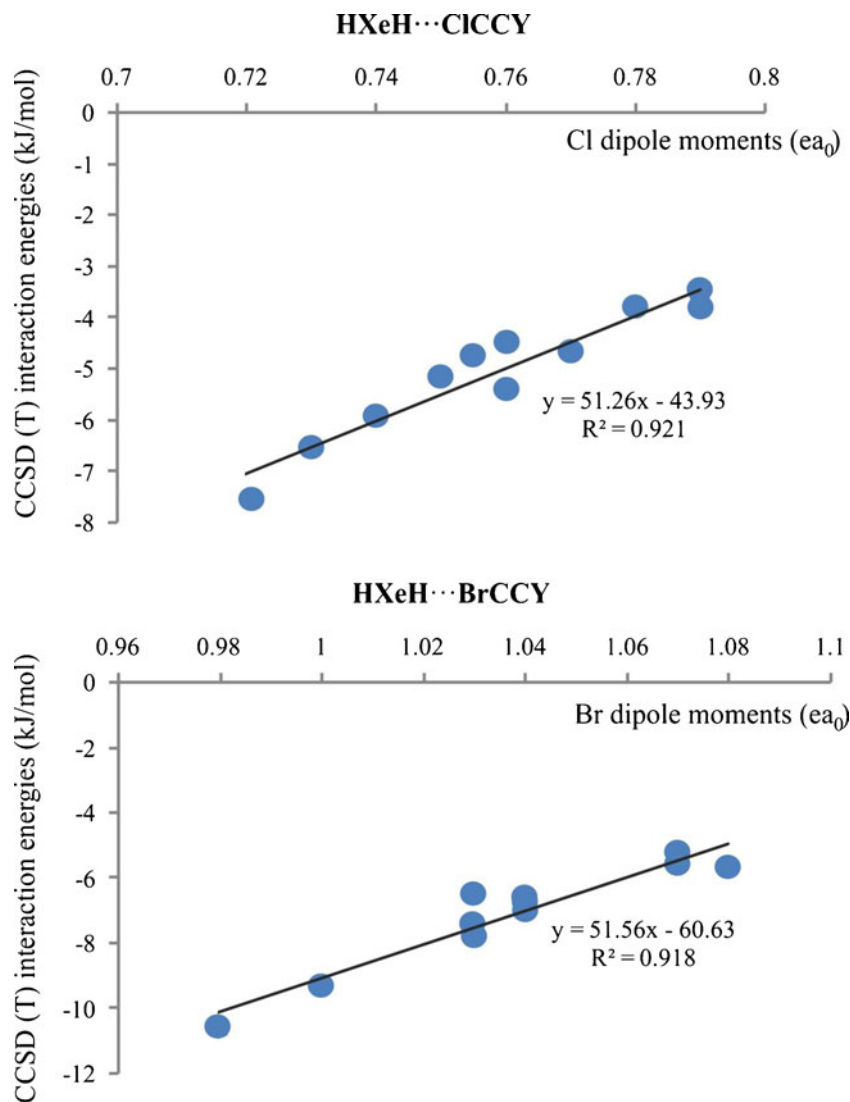
the optimized halogen⋯hydride distances/angles for all combinations of XCCY and HXeH molecules. All optimized H⋯X distances are within sum of van der Waals radii [73], 2.95 Å (for H⋯Cl) and 3.05 Å (for H⋯Br), which reveals the existence of the weak halogen-bonding interaction between halogen and hydrogen atoms. The equilibrium C – X⋯H contacts are closely linear, consistent with earlier experimental [74, 75] and theoretical [28–33] data on halogen-bonded complexes. This also corresponds to an interaction between the halogen σ -hole and the $V_{S,\min}$ located on hydrogen. For a given Y substitution, the optimized C – X⋯H angle for bromine containing complexes is slightly larger than those of chlorine. This trend may be attributable to the fact that the interaction between chlorine and HXeH is the weakest among those seen in halogen-bonding and is largely based on dispersion forces (see below). As an interesting feature of the data presented in Table 1, the bonding distance of the systems tends to increase as the size of the halogen increases. Looking at the HXeH⋯XCCH complexes, the effects of the

electron-withdrawing groups (CN, NC and F) on the optimized geometries are expressed mainly in a shortening of the H⋯X distance (r_{XH}). We noted that, however, the magnitude of these changes varies with the different types of halogen bond; it is more evident in the H⋯Br halogen bonds than in the H⋯Cl ones.

Interaction energies

Table 2 presents the BSSE-corrected interaction energies for the different HXeH⋯XCCY complexes obtained with MP2 and CCSD(T) methods. As evident from Table 2, MP2 interaction energies are calculated to be -6.77 and -10.69 kJ mol $^{-1}$ for the HXeH⋯ClCCH and HXeH⋯BrCCH, respectively. These are smaller (less negative) than the corresponding interactions in CNX⋯HMgH [46] and LiH⋯XCCH complexes (X = Cl and Br) [50]. For a given Y substitution and for a given level of theory, the interaction energies of halogen-bonded HXeH⋯XCCY complexes vary as Br > Cl. This

Fig. 4 Correlation between CCSD(T) interaction energies and halogen's dipole moments



ordering corresponds to the relative magnitudes of the polarizability of the halogen atoms and follows the expected variation in halogen interaction. The same trend is also valid for other halogen bonds and is illustrated by the increase of the magnitude of the electrostatic potential of a σ -hole of a relevant halogen atom [23–26].

Figure 3 indicates plots of CCSD (T) interaction energies versus halogens $V_{S,max}$ for the title complexes. One of the most pronounced patterns is the relationship between interaction energies and halogens $V_{S,max}$ values: higher $V_{S,max}$ (more positive σ -holes) result in complexes that are more strongly bound. The correlation is remarkably good, with a correlation coefficient of 0.926 (for the HXeH \cdots CICCY) and 0.970 (for the HXeH \cdots BrCCY). We noted, however, similar correlations have been reported for other series of halogen bond donors with a particular base (negative site) [32, 76–79]. This demonstrates the importance of the positive σ -hole, as

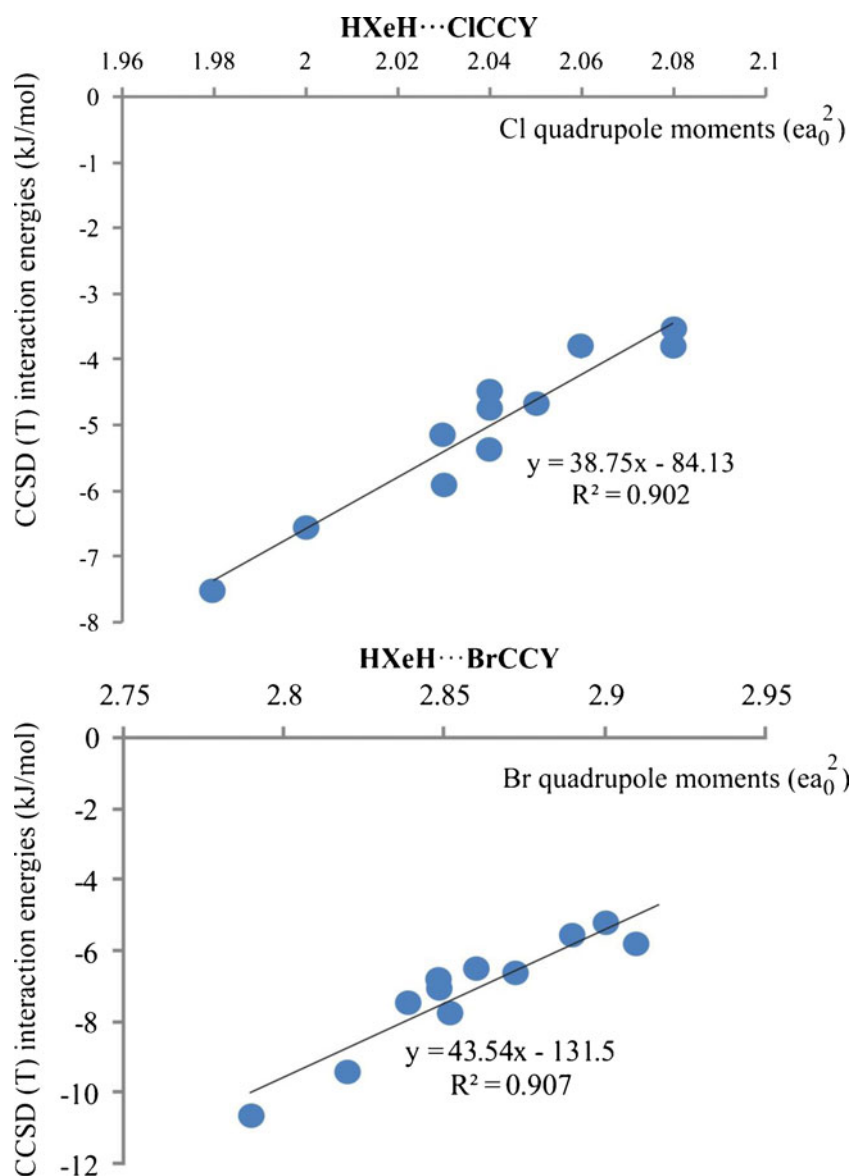
reflected by the computed chlorine and bromine $V_{S,max}$, in determining the energetics and stability of the X–H halogen bonds.

As pointed out earlier, the magnitude of halogen's multipole moments are quite sensitive to the substitution effect (Table 1). This dependence on the substituent seems to be correlated to the interaction energy. Figures 4 and 5 show the relationship between the interaction energy and the halogen's dipole and quadrupole moments, respectively. For each case studied, an approximate linear relationship is evident, indicating that the electrostatic and polarization interactions are responsible for the stability of the complexes.

Energy decomposition analysis

Insights into the origin and nature of the interactions between the XCCY and the Lewis base HXeH can be found from a

Fig. 5 Correlation between CCSD(T) interaction energies and halogen's quadrupole moments



partitioning of the interaction energy into different contributions from electrostatic, exchange-repulsion, polarization and dispersion effects. It may be noted that there is no rigorous basis for defining such energy terms [80], since they are not physical observable quantities. The energy components are not independent of each other, no matter what procedure is used. For example, based on perturbation theory, the formation of $F_3C - Cl \cdots O = CH_2$, $F_3C - Br \cdots O = CH_2$ and $F_3C - I \cdots O = CH_2$ complexes, are attributed primarily to the electrostatic and dispersion effects [10]. While the method used by Palusiak [81], for exactly the same interactions, concludes that charge transfer and polarization dominate, with electrostatics contributing only “slightly”. On the other hand, Politzer et al. [26] indicated, on the basis of binding energy decomposition of halogen-bonded complexes, that the formation and observed properties of the resulting noncovalent complexes can be fully explained in terms of electrostatics/polarization plus dispersion as the driving forces.

The results of energy decomposition for the $HXeH \cdots XCCY$ complexes are given in Table 3. Based on the energy decomposition results, it is also found that electrostatic effects account for about 48 % and 50 % of the overall attraction in the $HXeH \cdots ClCCH$ and $HXeH \cdots BrCCH$ complexes, respectively. By comparison, the polarization component of these interactions represents about 16 % and 22 % of the total attractive forces, while dispersion contributes 36 % and 28 % to the

stability of these complexes, respectively. The large value of E_{elst} for the $HXeH \cdots ClCCH$ ($-13.1 \text{ kJ mol}^{-1}$) and $HXeH \cdots BrCCH$ ($-27.2 \text{ kJ mol}^{-1}$) shows that electrostatic interactions are the major source of the attraction in these complexes. The values of E_{disp} (-10.0 and $-15.2 \text{ kJ mol}^{-1}$, respectively) show that the dispersion interactions is also an important source of the attraction in the complexes. The large atomic polarizability of the bromine atom is one of the causes of the large values of E_{elst} and E_{disp} . For the same type of complex, the $E_{exch-rep}$ becomes more positive in the order $Cl < Br$, maybe this is due to the increased overlap between the orbitals of the two monomers. From Table 3, it is revealed that the changes in E_{elst} are mainly responsible for the dependence of E_{int} on the halogen atom. For either $ClCCY$ or $BrCCY$ complexes, the electrostatic interactions depend strongly on the substituent Y. The E_{elst} values for the 11 complexes of $ClCCY$ ($BrCCY$) change from -11.6 (-25.1) to -18.5 (-13.6) kJ mol^{-1} . The polarization effects also depend on the substituent, although the dependence is weaker than the electrostatic interactions. On the other hand the substituents do not largely change the dispersion contribution. For each $HXeH \cdots ClCCY$ and $HXeH \cdots BrCCY$ complexes, the electron-withdrawing groups ($Y = CN, NC, F$ and C_2H) have the largest attractive E_{elst} among the others. As seen from Fig. S1, the E_{elst} and E_{pol} have strong correlations with the total interaction energy, while the E_{disp} is weakly correlated. This reveals that the electrostatic interactions are

Table 3 Interaction energy components analyzed by MP2/aug-cc-pVDZ(-PP) method (in kJ mol^{-1}) for $HXeH \cdots XCCY$ complexes

Complex	E_{elst}	$E_{exch-rep}$	E_{pol}	E_{disp}	% E_{elst}	% E_{disp}	E_{elst}/E_{disp}
$HXeH \cdots ClCCH$	-13.14	22.34	-4.52	-10.00	48	36	1.3
$HXeH \cdots ClCCF$	-13.93	23.60	-4.98	-10.08	48	35	1.4
$HXeH \cdots ClCCCl$	-14.27	24.10	-5.06	-10.50	48	35	1.4
$HXeH \cdots ClCCBr$	-14.43	24.39	-5.10	-10.54	48	35	1.4
$HXeH \cdots ClCCCN$	-18.49	27.91	-7.07	-10.96	51	30	1.7
$HXeH \cdots ClCCNC$	-16.53	26.82	-6.02	-12.13	48	35	1.4
$HXeH \cdots ClCC_2H$	-15.02	24.89	-5.36	-10.96	48	35	1.4
$HXeH \cdots ClCCCH_3$	-11.97	21.71	-4.14	-10.13	46	39	1.2
$HXeH \cdots ClCCOH$	-12.26	22.13	-4.31	-10.04	46	38	1.2
$HXeH \cdots ClCCNH_2$	-11.59	21.51	-4.06	-10.08	45	39	1.1
$HXeH \cdots ClCCSH$	-13.68	23.47	-4.77	-10.50	47	36	1.3
$HXeH \cdots BrCCH$	-27.24	45.81	-11.80	-15.19	50	28	1.8
$HXeH \cdots BrCCF$	-29.92	50.58	-13.60	-15.69	51	27	1.9
$HXeH \cdots BrCCCl$	-30.04	50.79	-13.56	-16.15	50	27	1.9
$HXeH \cdots BrCCBr$	-30.33	51.34	-13.72	-16.28	50	27	1.9
$HXeH \cdots BrCCCN$	-36.11	57.45	-17.78	-16.65	51	24	2.2
$HXeH \cdots BrCCNC$	-34.64	57.49	-16.23	-18.70	50	27	1.9
$HXeH \cdots BrCC_2H$	-30.42	50.71	-13.72	-16.61	50	27	1.9
$HXeH \cdots BrCCCH_3$	-25.40	44.10	-10.71	-15.36	50	27	1.8
$HXeH \cdots BrCCOH$	-26.69	46.28	-11.55	-15.48	49	30	1.7
$HXeH \cdots BrCCNH_2$	-25.10	44.10	-10.54	-15.36	50	29	1.7
$HXeH \cdots BrCCSH$	-28.58	48.66	-12.59	-16.02	49	30	1.6

Table 4 Calculated BSSE-corrected interaction energies (in kJ mol^{-1}) for $\text{HXeH}\cdots\text{HCCY}$ complexes ^a

Complex	$E_{\text{int}}^{\text{MP2}}$	$E_{\text{int}}^{\text{CCSD(T)}}$
$\text{HXeH}\cdots\text{HCCH}$	-6.21	-6.63
$\text{HXeH}\cdots\text{HCCF}$	-6.59	-5.41
$\text{HXeH}\cdots\text{HCCCl}$	-7.06	-5.68
$\text{HXeH}\cdots\text{HCCBr}$	-7.40	-6.16
$\text{HXeH}\cdots\text{CICCCN}$	-11.06	-9.31
$\text{HXeH}\cdots\text{HCCNC}$	-10.26	-8.07
$\text{HXeH}\cdots\text{HCC}_2\text{H}$	-7.92	-6.32
$\text{HXeH}\cdots\text{HCCCH}_3$	-5.02	-4.13
$\text{HXeH}\cdots\text{HCCOH}$	-5.28	-4.17
$\text{HXeH}\cdots\text{HCCNH}_2$	-4.81	-3.70
$\text{HXeH}\cdots\text{HCCSH}$	-6.64	-5.29

^a CCSD(T) interaction energies were calculated at the MP2 optimized geometries.

essentially responsible for the substituent effects on the magnitude of the halogen bond and the polarization interactions also contribute to the substituent effects. All above-mentioned results for hydride-halogen bond properties are compatible with those obtained at the MP2 levels for halogen-nitrogen [31, 32], halogen-oxygen [12, 37, 76], halogen-carbene [40, 41], halogen-halogen [14] and halogen- π [38] interactions.

Comparison of halogen bonds to dihydrogen bonds

In order to compare the halogen bonds properties to that of dihydrogen bonds, we have carried out calculations on the $\text{HXeH}\cdots\text{HCCY}$ complexes. The optimized $\text{H}\cdots\text{H}$ bond distances and of $\text{CC}\cdots\text{H}$ angles of the optimized geometries of the complexes are given in Table S1 (Supporting information). As expected, the majority of the complexes were found to have linear geometries. The binding distance is calculated to be 2.01 Å in the $\text{HXeH}\cdots\text{HCCH}$ complex. Similarly to what

was found for the halogen-bonded complexes discussed above, the presence of the electron-donating group (OH, NH_2 and CH_3) in the HCCY molecule makes a 0.01–0.03 Å increase of the binding distance, whereas the electron-withdrawing groups (CN, NC and F) result in a shortening of the binding distance.

Table 4 gives the interaction energy values for the $\text{HXeH}\cdots\text{HCCY}$ complexes. The binding energy of the $\text{HXeH}\cdots\text{HCCH}$ complex (-6.6 kJ mol^{-1}) is roughly comparable to that of $\text{HXeH}\cdots\text{CICCH}$ (-6.8 kJ mol^{-1}), but is less than that of $\text{HXeH}\cdots\text{BrCCH}$ ($-10.7 \text{ kJ mol}^{-1}$). It is noted, however, we found a slightly larger substitution effect on the calculated interaction energies of $\text{HXeH}\cdots\text{HCCY}$ than those of $\text{HXeH}\cdots\text{CICCY}$ and $\text{HXeH}\cdots\text{BrCCY}$. Overall, the dihydrogen bonds interaction between HXeH and HCCY moieties is less electrostatic (and more polarizable) in nature than the corresponding $\text{HXeH}\cdots\text{XCCY}$ interactions, with the electrostatic term accounting for 47–50 % of the overall interaction energy (Table 5). For each complex studied, the exchange energy term outweighs the electrostatic term, and the polarization term is rather important. The E_{elst} is largest in the $\text{HXeH}\cdots\text{HCCCN}$ complex and smallest in the $\text{HXeH}\cdots\text{HCCNH}_2$. As the size of the halogen substituent increases the electrostatic interaction would be expected to increase. Comparing the data for the fluorine, chlorine, and bromine substituted $\text{HXeH}\cdots\text{HCCY}$ systems, it can be also seen that both the dispersion and polarization components of the interaction energy increase with increasing halogen size. Interestingly, there is a larger increase in the dispersion and polarization terms, going from fluorine to bromine, than in the electrostatic interaction (Table 5).

Conclusions

We presented a quantum chemistry study on the halogen bonds interactions between HXeH and XCCY molecules, where $\text{X} = \text{Cl}, \text{Br}$ and $\text{Y} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{CN}, \text{NC}, \text{C}_2\text{H}, \text{CH}_3, \text{OH}, \text{SH}, \text{NH}_2$. The equilibrium $\text{C-X}\cdots\text{H}$ contacts are closely

Table 5 Interaction energy components analyzed by MP2/aug-cc-pVDZ(-PP) method (in kJ mol^{-1}) for $\text{HXeH}\cdots\text{HCCY}$ complexes

Complex	E_{elst}	$E_{\text{exch-rep}}$	E_{pot}	E_{disp}	% E_{elst}	% E_{disp}	$E_{\text{elst}}/E_{\text{disp}}$
$\text{HXeH}\cdots\text{HCCH}$	-10.50	16.57	-5.27	-6.40	47	29	1.6
$\text{HXeH}\cdots\text{HCCF}$	-10.96	16.86	-5.65	-6.15	48	27	1.8
$\text{HXeH}\cdots\text{HCCCl}$	-11.51	18.12	-6.11	-6.90	47	28	1.7
$\text{HXeH}\cdots\text{HCCBr}$	-11.88	19.08	-6.44	-7.11	47	28	1.7
$\text{HXeH}\cdots\text{CICCCN}$	-16.40	22.68	-9.79	-6.74	50	20	2.4
$\text{HXeH}\cdots\text{HCCNC}$	-14.10	21.46	-7.95	-8.91	46	29	1.6
$\text{HXeH}\cdots\text{HCC}_2\text{H}$	-12.22	19.00	-6.61	-7.36	47	28	1.7
$\text{HXeH}\cdots\text{HCCCH}_3$	-8.79	15.23	-4.35	-6.65	44	34	1.3
$\text{HXeH}\cdots\text{HCCOH}$	-9.04	15.36	-4.52	-6.44	45	32	1.4
$\text{HXeH}\cdots\text{HCCNH}_2$	-8.24	14.85	-4.14	-6.69	43	35	1.2
$\text{HXeH}\cdots\text{HCCSH}$	-10.84	17.66	-5.69	-7.07	46	30	1.5

linear, corresponding to an interaction between the halogen σ -hole and the $V_{S,\min}$ located on hydrogen. Halogen bonding energies, calculated at the MP2/aug-cc-pVTZ(-PP), span over a wide range, from -5.65 to -15.66 kJ mol $^{-1}$. One of the most pronounced patterns is the relationship between interaction energies and halogens $V_{S,\max}$ values: higher $V_{S,\max}$ (more positive σ -holes) result in complexes that are more strongly bound. The observed correlations between the strengths of halogen bonds and the magnitudes of the dipole/quadrupole moment also suggest that the interaction energies and the halogen multipole moments reflect the same factors. According to the energy decomposition analysis, the E_{elst} and E_{pol} have strong correlations with the total interaction energy, while the E_{disp} is weakly correlated. The dihydrogen bonds interaction between HXeH and HCCY moieties is less electrostatic (and more polarizable) in nature than the corresponding HXeH \cdots XCCY interactions.

References

- Desiraju GR, Steiner T (1999) The weak hydrogen bond. Oxford University Press, Oxford
- Ran J, Wong MW (2006) Saturated hydrocarbon – benzene complexes: theoretical study of cooperative CH/ π interactions. *J Phys Chem A* 110:9702–9709
- Riley KE, Hobza P (2011) Noncovalent interactions in biochemistry. *Wiley Interdiscip Rev Comput Mol Sci* 1:3–17
- Guardigli C, Liantonio R, Mele ML, Metrangolo P, Resnati G, Pilati T (2003) Design and synthesis of new tectons for halogen bonding-driven crystal engineering. *Supramol Chem* 15:177–188
- Esrafil MD, Behzadi H, Beheshtian J, Hadipour NL (2008) Theoretical ^{14}N nuclear quadrupole resonance parameters for sulfa drugs: sulfamerazine and sulfathiazole. *J Mol Graph Model* 27:326–331
- Esrafil MD, Behzadi H, Hadipour NL (2008) ^{14}N and ^{17}O electric field gradient tensors in benzamide clusters: theoretical evidence for cooperative and electronic delocalization effects in N–H \cdots O hydrogen bonding. *Chem Phys* 348:175–180
- Alkorta I, Blanco F, Elguero J (2010) Dihydrogen bond cooperativity in aza-borane derivatives. *J Phys Chem A* 114:8457–8462
- Custelcean R, Jackson JE (2001) Dihydrogen bonding: structures, energetics, and dynamics. *Chem Rev* 101:1963–1980
- El-Sheshtawy HS, Bassil BS, Assaf KI, Kortz U, Nau WM (2012) Halogen bonding inside a molecular container. *J Am Chem Soc* 134:19935–19941
- Parker AJ, Stewart J, Donald KJ, Parish CA (2012) Halogen bonding in DNA base pairs. *J Am Chem Soc* 134:5165–5172
- Metrangolo P, Carcenac Y, Lahtinen M, Pilati T, Rissanen K, Viji A, Resnati G (2009) Nonporous organic solids capable of dynamically resolving mixtures of diiodoperfluoroalkanes. *Science* 323:1461–1464
- Ke R, Hobza P (2008) Investigations into the nature of halogen bonding including symmetry adapted perturbation theory analyses. *J Chem Theory Comput* 4:232–242
- Aakeröy CB, Fasulo M, Schultheiss N, Desper J, Moore C (2007) Structural competition between hydrogen bonds and halogen bonds. *J Am Chem Soc* 129:13772–13773
- Esrafil MD (2012) Investigation of H-bonding and halogen-bonding effects in dichloroacetic acid: DFT calculations of NQR parameters and QTAIM analysis. *J Mol Model* 18:5005–5016
- Wang F, Ma N, Chen Q, Wang W, Wang L (2007) Halogen bonding as a new driving force for layer-by-layer assembly. *Langmuir* 23:9540–9542
- Metrangolo P, Neukirch H, Pilati T, Resnati G (2005) Halogen bonding based recognition processes: a world parallel to hydrogen bonding. *Acc Chem Res* 38:386–395
- Jiang Y, Alcaraz AA, Chen JM, Kobayashi H, Lu YJ, Snyder JP (2006) Diastereomers of dibromo-7-epi-10-deacetylcephalomannine: crowded and cytotoxic taxanes exhibit halogen bonds. *J Med Chem* 49:1891–1899
- Lopez-Rodriguez ML, Murcia M, Benhamu B, Viso A, Campillo M, Pardo L (2002) Benzimidazole derivatives. 3. 3D-QSAR/CoMFA model and computational simulation for the recognition of 5-HT4 receptor antagonists. *J Med Chem* 45:4806–4815
- Auffinger P, Hays FA, Westhof E, Ho PS (2004) Halogen bonds in biological molecules. *Proc Natl Acad Sci U S A* 101:16789–16794
- Politzer P, Lane P, Concha MC, Ma YG, Murray JS (2007) An overview of halogen bonding. *J Mol Model* 13:305–311
- Clark T, Hennemann M, Murray JS, Politzer P (2007) Halogen bonding: the σ -hole. *J Mol Model* 13:291–296
- Murray JS, Lane P, Clark T, Riley KE, Politzer P (2012) σ -Holes, π -holes and electrostatically-driven interactions. *J Mol Model* 18:541–548
- Politzer P, Murray JS, Concha MC (2007) Halogen bonding and the design of new materials: organic bromides, chlorides and perhaps even fluorides as donors. *J Mol Model* 13:643–650
- McAllister LJ, Bruce DW, Karadakov PB (2011) Halogen bonding interaction between fluorohalides and isocyanides. *J Phys Chem A* 115:11079–11086
- Duarte DJR, de las Vallejos MM, Peruchena NM (2010) Topological analysis of aromatic halogen/hydrogen bonds by electron charge density and electrostatic potentials. *J Mol Model* 16:737–748
- Politzer P, Riley KE, Bulat FA, Murray JS (2012) Perspectives on halogen bonding and other σ -hole interactions: Lex parsimoniae (Occam's Razor). *Comput Theor Chem* 998:2–8
- Shields ZP, Murray JS, Politzer P (2010) Directional tendencies of halogen and hydrogen bonds. *Int J Quantum Chem* 110:2823–2832
- Politzer P, Murray JS, Concha MC (2008) σ -hole bonding between like atoms; a fallacy of atomic charges. *J Mol Model* 14:659–665
- Murray JS, Concha MC, Lane P, Hobza P, Politzer P (2008) Blue shifts vs red shifts in σ -hole bonding. *J Mol Model* 14:699–704
- Li Q, Yuan H, Jing B, Liu Z, Li W, Cheng J, Gong B, Sun J (2010) Theoretical study of halogen bonding between $\text{F}_n\text{H}_{3-n}\text{CBr}$ ($n=0, 1, 2, 3$) and HMgH . *J Mol Struct (THEOCHEM)* 942:145–148
- Esrafil MD, Ahmadi B (2012) A theoretical investigation on the nature of $\text{Cl}\cdots\text{N}$ and $\text{Br}\cdots\text{N}$ halogen bonds in F-Ar-X \cdots NCY complexes (X = Cl, Br and Y = H, F, Cl, Br, OH, NH_2 , CH_3 and CN). *Comput Theor Chem* 997:77–82
- Bundhun A, Ramasami P, Murray JS, Politzer P (2013) Trends in σ -hole strengths and interactions of F3MX molecules (M = C, Si, Ge and X = F, Cl, Br, I). *J Mol Model* doi:10.1007/s00894-012-1571-4
- Awwadi FF, Willett RD, Peterson KA, Twamley B (2006) The nature of halogen \cdots halogen synthons: crystallographic and theoretical studies. *Chem Eur J* 12:8952–8960
- Metrangolo P, Murray JS, Pilati T, Politzer P, Resnati G (2011) The fluorine atom as a halogen bond donor, viz. a positive site. *Cryst Eng Commun* 13:6593–6596
- Tsuzuki S, Wakisaka A, Ono T, Sonoda T (2012) Origin of the attraction and directionality of the halogen bonds of the complexes of $\text{C}_6\text{F}_5\text{X}$ and $\text{C}_6\text{H}_5\text{X}$ (X = I, Br, Cl and F) with Ppyridine. *Chem Eur J* 18:951–960
- Lu Y, Zou J, Wang Y, Jiang Y, Yu Q (2007) Ab Initio investigation of the complexes between bromobenzene and several electron donors: some insights into the magnitude and nature of halogen bonding interactions. *J Phys Chem A* 111:10781–10788
- Ke R, Murray JS, Fanfrlík J, Řezáč J, Solá RJ, Concha MC, Ramos FM, Politzer P (2013) Halogen bond tunability II: the varying roles

- of electrostatic and dispersion contributions to attraction in halogen bonds. *J Mol Model* doi:10.1007/s00894-012-1428-x
38. Li RY, Li ZR, Wu Y, Li Y, Chen W, Sun CC (2005) Study of π – halogen bonds in complexes $C_2H_4-nF_n - ClF$ ($n=0-2$). *J Phys Chem A* 109:2608–2613
 39. Wang YH, Zou JW, Lu YX, Lu QS, Xu HY (2007) Single-electron halogen bond: ab initio study. *Int J Quantum Chem* 107:501–506
 40. Li QZ, Wang YL, Liu ZB, Li WZ, Cheng JB, Gong BA, Sun JZ (2009) An unconventional halogen bond with carbene as an electron donor: an ab initio study. *Chem Phys Lett* 469:48–51
 41. Esrafil MD, Mohammadirad N (2013) Insights into the strength and nature of carbene···halogen bond interactions: a theoretical perspective. *J Mol Model* doi:10.1007/s00894-013-1804-1
 42. Jabłoński M (2009) Binding of X–H to the lone-pair vacancy: charge-inverted hydrogen bond. *Chem Phys Lett* 477:374–376
 43. Jabłoński M (2010) Intramolecular charge-inverted hydrogen bond. *J Mol Struct (THEOCHEM)* 948:21–24
 44. Li QZ, Dong X, Jing B, Li WZ, Cheng JB, Gong BA, Yu ZW (2010) A new unconventional halogen bond C – X···H – M between HCCX (X = Cl and Br) and HMH (M = Be and Mg): an ab initio study. *J Comput Chem* 31:1662–1669
 45. Li Q, Yuan H, Jing B, Liu Z, Li W, Cheng J, Gong B, Sun J (2010) Theoretical study of halogen–hydride halogen bonds in $F_3CL \cdots HM$ (L = Cl, Br; M = Li, BeH, MgH) complexes. *Mol Phys* 108:611–617
 46. Mohajeri A, Alipour M, Mousaee M (2011) Halogen – hydride interaction between Z – X (Z = CN, NC; X = F, Cl, Br) and H – Mg – Y (Y = H, F, Cl, Br, CH₃). *J Phys Chem A* 115:4457–4466
 47. Mohajer A, Baresh I, Alipour M (2013) Prediction and characterization of halogen–hydride interaction in $Cu_nH_n \cdots ClC_2Z$ and $Cu_nH \cdots ClC_2Z$ complexes ($n=2-5$; Z = H, F, CH₃). *Struct Chem* 24:339–348
 48. Lipkowski P, Grabowski SJ, Leszczynski J (2006) Properties of the halogen – hydride interaction: an ab initio and “atoms in molecules” analysis. *J Phys Chem A* 110:10296–10302
 49. Sokalski WA, Roszak S, Pecul K (1988) An efficient procedure for decomposition of the SCF interaction energy into components with reduced basis set dependence. *Chem Phys Lett* 153:153–159
 50. Jabłoński M, Palusiak M (2012) Nature of a hydride–halogen bond. A SAPT-, QTAIM-, and NBO-based study. *J Phys Chem A* 116:2322–2332
 51. Feldman VI, Sukhov FF (1996) Formation and decay of transient xenon dihydride resulting from hydrocarbon radiolysis in a xenon matrix. *Chem Phys Lett* 255:425–430
 52. Feldman VI, Sukhov FF, Orlov AY (1997) Further evidence for formation of xenon dihydride from neutral hydrogen atoms: a comparison of ESR and IR spectroscopic results. *Chem Phys Lett* 280:507–512
 53. Pettersson M, Lundell J, Rasanen M (1995) Neutral rare-gas containing charge–transfer molecules in solid matrices. II. HXeH, HXeD, and DXeD in Xe. *J Chem Phys* 103:205–210
 54. Pettersson M, Lundell J, Räsänen M (1999) New rare-gas-containing neutral molecules. *Eur J Inorg Chem* 1999:729–737
 55. Lundell J, Pettersson M (1999) The dihydrogen-bonded complex XeH_2-H_2O . *Phys Chem Chem Phys* 1:1691–1697
 56. Lundell J, Berski S, Latajka Z (2000) Dihydrogen-bonded complexes of xenon dihydride with water: ab initio calculations and topological analysis of electron localisation function (ELF). *Phys Chem Chem Phys* 2:5521–5527
 57. Solimannejad M, Mohammadi Amlashi L, Alkorta I, Elguero J (2006) XeH_2 as a proton-accepting molecule for dihydrogen bonded systems: a theoretical study. *Chem Phys Lett* 422:226–229
 58. Solimannejad M, Malekani M, Alkorta I (2010) Theoretical study of the halogen – hydride complexes between XeH_2 and carbon halogenated derivatives. *J Mol Struct (THEOCHEM)* 955:140–144
 59. Peterson KA, Figgen D, Goll E, Stoll H, Dolg M (2003) Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post-d group 16–18 elements. *J Chem Phys* 119:11113–11123
 60. Hobza P, Zahradnik R (1998) Intermolecular interactions between medium-sized systems. Nonempirical and empirical calculations of interaction energies. Successes and failures. *Chem Rev* 88:871–897
 61. Boys SF, Bernardi F (1970) The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol Phys* 19:553–566
 62. Su P, Li H (2009) Energy decomposition analysis of covalent bonds and intermolecular interactions. *J Chem Phys* 131:014102
 63. Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, Koseki S, Matsunaga N, Nguyen KA, Su SJ, Windus TL, Dupuis M, Montgomery JA (1993) General atomic and molecular electronic structure system. *J Comput Chem* 14:1347–1363
 64. Bulat FA, Toro-Labbe A, Brinck T, Murray JS, Politzer P (2010) Quantitative analysis of molecular surfaces: areas, volumes, electrostatic potentials and average local ionization energies. *J Mol Model* 16:1679–1691
 65. Politzer, Murray JS, Peralta-Inga Z (2010) Molecular surface electrostatic potentials in relation to noncovalent interactions in biological systems. *Int J Quantum Chem* 85:676–684
 66. Esrafil MD (2013) A theoretical investigation of the characteristics of hydrogen/halogen bonding interactions in dibromo-nitroaniline. *J Mol Model* 19:1417–1427
 67. Torii H (2002) Locally strong polarity in the solvent effect of nonpolar solvent carbon tetrachloride: the role of atomic quadrupoles. *Chem Phys Lett* 365:27–33
 68. Torii H (2004) Atomic quadrupolar effect in the methanol–CCl₄ and water–CCl₄ intermolecular interactions. *Chem Phys Lett* 393:153–158
 69. Torii H, Yoshida M (2010) Properties of halogen atoms for representing intermolecular electrostatic interactions related to halogen bonding and their substituent effects. *J Comput Chem* 31:107–116
 70. Stone AJ (1981) Distributed multipole analysis, or how to describe a molecular charge distribution. *Chem Phys Lett* 83:233–239
 71. Price SL, Stone AJ, Alderton M (1984) Explicit formulae for the electrostatic energy, forces and torques between a pair of molecules of arbitrary symmetry. *Mol Phys* 52:987–1001
 72. Stone AJ (2005) Distributed multipole analysis: stability for large basis sets. *J Chem Theory Comput* 1:1128–1132
 73. Bondi A (1964) van der Waals volumes and radii. *J Phys Chem* 68:441–451
 74. Saha BK, Nangia A, Nicoud JF (2006) Using halogen···halogen interactions to direct noncentrosymmetric crystal packing in dipolar organic molecules. *Cryst Growth Des* 6:1278–1281
 75. Zhu S, Xing C, Xu W, Jin G, Li Z (2004) Halogen bonding and hydrogen bonding coexist in driving self-assembly process. *Cryst Growth Des* 4:53–56
 76. Riley KE, Murray JS, Politzer P, Concha MC, Hobza P (2009) Br···O complexes as probes of factors affecting halogen bonding: interactions of bromobenzenes and bromopyrimidines with acetone. *J Chem Theory Comput* 5:155–163
 77. Riley KE, Murray JS, Fanfrlík J, Řezáč J, Solá RJ, Concha MC, Ramos FM, Politzer P (2011) Halogen bond tunability I: the effects of aromatic fluorine substitution on the strengths of halogen-bonding interactions involving chlorine, bromine, and iodine. *J Mol Model* 17:3309–3318
 78. Politzer P, Murray JS, Clark T (2013) Halogen bonding and other σ -hole interactions: a perspective. *Phys Chem Chem Phys* doi: 10.1039/c3cp00054k
 79. Politzer P, Murray JS (2013) Halogen bonding: an interim discussion. *ChemPhysChem* 14:278–294
 80. Hobza P, Zahradnik R, Muller-Dethlefs K (2006) The world of non-covalent interactions: 2006. *Collect Czechoslov Chem Commun* 71:443–531
 81. Palusiak M (2010) On the nature of halogen bond—The Kohn–Sham molecular orbital approach. *J Mol Struct (THEOCHEM)* 945:89–92