Research paper

Is σ-hole an electronic exchange channel in YX···CO interactions?

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HIGHLIGHTS

- The halogen bonds YX···CO are not primarily electrostatic in nature.
- The σ-hole magnitude of YX has influences on all the stabilizing components of the LMOEDA method.
- The PAEM function is a good descriptor of the covalence of the $X > \cdots C$ interactions.

ARTICLE INFO

ABSTRACT

A theoretical study of linear YX···CO complexes (in which YX are diatomic interhalogens or hydrogen halide) has been performed to high-level quantum chemical calculations. Calculations show that at the equilibrium geometry, the stabilizing effect that arises from the Pauli exclusion principle is more important than the electrostatic interactions. In addition, the stabilizing terms of the LMOEDA scheme increase with the σ-hole magnitude, being the exchange term the most affected one, followed by electrostatics, polarization and dispersion components. The PAEM function measured on the X···C interatomic interaction line gives a measure of the covalence of these interactions.

1. Introduction

The σ-hole concept explains many features of the interactions established between a covalently-bonded atom of groups IV–VII in the periodic table and a Lewis base [1]. This concept has been introduced by Clark et al. in the context of halogen bonding (XB) R—X···B (X = F, Cl, Br, I and B = Lewis base) [2]. It involves a region of positive electrostatic potential (positive σ-hole) centered around the extension of the R—X bond that interacts with a negative region [3,4]. More recently, Clark, Murray and Politzer showed that the electrostatics/polarization plus dispersion interpretation of XBs explains all of its known features, such as its directionality and the ability of the halogen atoms to interact favorably with both negative and positive sites [5–8].

There are a large number of studies that relate σ-holes magnitude of isolated halogen-donor with the stabilization energy of the respective XBs [8–12]. This has allowed us to establish that the more positive the σ-hole, the stronger interaction it creates and that XBs are primarily electrostatic in nature [13].

On the other hand, the hole-lump concept is another valuable tool that has allowed the interpretation of the XBs [14–16], especially in

those situations where the σ-hole concept is not very clear [17–20]. This concept derived from the topology of the $L(\mathbf{r}) = -\nabla^2 \rho(\mathbf{r})$ function and establishes that, the formation of XBs is the result of the interaction between the hole localized on the valence shell charge concentration (VSCC) of halogen atom, and the lump localized on Lewis base.

In principle it seems that there are no major differences between σ-hole and hole-lump concepts. Both theories establish that a Lewis acid-base interaction is due to an interaction between a region of charge depletion on the halogen atom and a region of charge concentration on another molecule. However, in the σ-hole theory only the electrostatic part of potential is considered, while in hole-lump concept the full quantum potential is used [14].

It is well known that the various methods proposed for energy decomposition analysis (EDA) can lead to contradictory interpretations [5,7,21]. However, a rational analysis of the decomposition terms and the real physical properties of the system can help us to have a bridge between chemical concepts and some quantum-mechanical magnitude.

Recently, Stone using symmetry-adapted perturbation theory based on density functional theory (SAPT-DFT) shows that while the main contribution to the interaction energy is usually the electrostatic

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component, the geometries are not always determined by electrostatics alone. In particular, the strong tendency to linearity of the XBs bond is a consequence of exchange-repulsion component, not electrostatics [22]. Moreover, in the framework of interacting quantum atoms (IQA) [23], Syzgantseva et al. [24] show that in FBr···NH$_3$ complex at long-range, the electrostatic interactions are the dominant ones (as expected from the σ-hole model) and that they are responsible for the initiation of the bond formation process, while at the equilibrium geometry, the exchange component is very important for the stabilization of the complex. In this same sense, we have shown that as the σ-hole magnitude increases the exchange term of the XBs X···N in the complexes [(FX)$_n$/NH$_3$ with n = 1–5 and X = Cl, Br] increases accordingly [12].

The findings mentioned above lead us to thinking that the σ-hole magnitude could not be just an indicator of the electrostatic part of the interaction, but also a channel that facilitates the rest of the stabilizing factors, especially the electronic exchange between interacting atoms. Accordingly, it would also be an indicator of covalence of the XBs. To evaluate the relationship that exists between the σ-hole magnitude and the electronic exchange, we have studied the YX···CO complexes, in which YX are diatomic interhalogens or hydrogen halide, whose σ-hole magnitude on the halogen donor increases progressively.

2. Computational details

The structures of monomers and complexes were fully optimized using second-order Møller-Plesset perturbation theory (MP2) [25] with the aug-cc-pVTZ basis set. For the iodine atom the aug-cc-pVTZ-PP basis set was used. Frequency calculations were performed to establish that optimized structures correspond to true minima on their potential energy surfaces. All optimization, vibrational frequency, and single-point energy calculations at the different levels of theory were performed with the Gaussian 03 suite of programs [26]. We have calculated the interaction energies by two methods: (i) using the extrapolation scheme proposed by Helgaker et al. [27,28] following the recommendations of Hobza et al. [29], denoted as $E_{int,CBS}$ (for more details see Eqs. (1)–(6) of Ref. [30]); (ii) by means of the localized molecular orbital energy decomposition analysis (LMOEDA) [31] partition method, according to the equation below:

$$E_{int} = E_{el} + E_{ex} + E_{rep} + E_{pol} + E_{disp}$$

where E_{el} is the electrostatic term, E_{ex} and E_{rep} are the exchange and repulsion terms resulting from the Pauli exclusion principle, and E_{pol} and E_{disp} represent to polarization and dispersion terms, respectively. These calculations have been carried out with the GAMESS program (version 2013-R1) [32].

The exchange contribution [V_{ex}(IQA)] derived from IQA [23] scheme has been performed at HF/aug-cc-pVTZ level. This wave-function allows us to analyze the pure exchange (without dispersive term).

The potential acting on an electron in a molecule (PAEM) [33] and electrostatic potential (ESP) have been calculated with Multiwfn program [34].

3. Results and discussion

Table 1 shows the energetic decomposition analysis performed with LMOEDA methodology, the σ-hole magnitude ($V_{S,max}$) calculated on X in isolated YX molecule and interaction energies calculated by LMOEDA method and at CCSD(T)/CBS level. All the studied complexes are XBs and present C$_{\infty v}$ symmetry. The intermolecular distances and the interaction energies (E_{int} and $E_{int,CBS}$) of the X···C bond calculated here are in the same order of magnitude, and follow the same trend as the ones reported by Legon et al. [35] for the ClCl···CO, BrBr···CO, ClBr···CO, FCl···CO and ClI···CO complexes obtained experimentally (see Table S1). Moreover, to the best of our knowledge, the HX···CO complexes have not been observed experimentally, only the hydrogen bonded form [35]. This is probably due to the lower $E_{int,CBS}$ that XBs have, compared to their isomers. For instance, the $E_{int,CBS}$(HCl···CO) = −2.4 kJ mol^{-1} while the $E_{int,CBS}$(ClH···CO) = −7.8 kJ mol^{-1}.

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In bable 1, it can be observed that the magnitude of each stabilizing term increases simultaneously with the increase of the strength of these XBs. A good linear relationship (R^2 = 0.9777) between E_{int}(LMOEDA) and $E_{int,CBS}$ is observed (figure not shown). In addition, the strength of these interactions (as expected) follows the same trend as the σ-hole magnitude.

In all the cases the largest in magnitude stabilization term is exchange followed by electrostatic contribution, except in the weakest complexes HCl···CO and HBr···CO in which dispersive forces are stronger than electrostatic ones. It is interesting to analyze these results in percentage measures. The exchange contribution is around 50% of the stabilizing terms (between 48% and 52%). The electrostatic contribution also shows small variation (between 19% and 25%). While the polarization term increases with the strength of interactions (from 5% to 23%), and the dispersive terms follow an opposite tendency (from 27% to 6%). That is, as the strength of the interactions increases the orbital interactions related to polarization term [31], the dispersive contribution, as expected, decreases with the strengthening of the X···C interaction.

For the FI···CO complex, the polarization contribution is comparable to the electrostatic one, while in the weakest complexes HCl···CO, HBr···CO, HI···CO and ClCl···CO the electrostatics terms are comparable to dispersive ones.

With the aim of comprehending what the influence of the σ-hole magnitude on the stabilizing terms of the LMOEDA scheme is, we have studied the relationship between these magnitudes (Fig. 1).
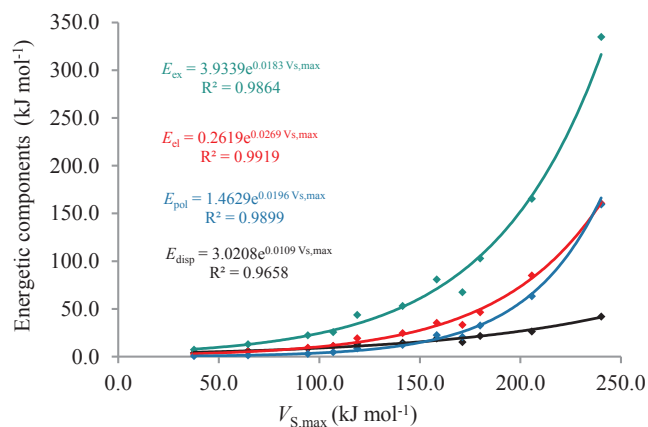
Table 1

Energy decomposition analysis of the interaction energy obtained with the LMOEDA methodology, the σ-hole magnitude and interaction energies.

Complexes	LMOEDA method						$V_{S,max}$(X)	$E_{int,CBS}$
	E_{el}	E_{ex}	E_{rep}	E_{pol}	E_{disp}	E_{int}		
HCl···CO	−2.7	−7.3	11.8	−0.7	−4.0	−2.8	37.7	−2.4
HBr···CO	−5.3	−13.0	21.5	−1.4	−5.8	−3.9	64.5	−4.7
HI···CO	−9.3	−22.4	37.6	−3.0	−8.6	−5.6	94.3	−6.2
ClCl···CO	−11.3	−25.6	44.1	−4.7	−11.0	−7.1	106.8	−6.4
BrBr···CO	−19.2	−43.8	76.9	−8.7	−13.3	−8.0	118.8	−10.4
ClBr···CO	−24.7	−53.0	94.7	−12.3	−14.6	−9.8	141.4	−11.2
BrI···CO	−35.4	−80.9	145.9	−22.5	−19.1	−12.0	158.3	−11.4
FCl···CO	−33.3	−67.5	123.8	−20.5	−15.2	−12.7	171.1	−12.6
ClI···CO	−46.4	−102.9	188.7	−32.6	−21.8	−14.9	179.9	−16.9
FBr···CO	−85.0	−165.4	321.2	−63.4	−26.3	−18.9	205.6	−22.9
FI···CO	−160.5	−334.8	668.9	−159.5	−42.0	−27.8	240.2	−35.7

All the values in kJ mol^{-1}.

Fig. 1. Relationship between stabilizing energy components of the LMOEDA method with σ-hole magnitude.

Fig. 2. Correlation between the exchange terms of IQA model and LMOEDA scheme.

It is observed that as $V_{s,max}$ increases, and so all energetic components do. The exchange term is the most affected one followed by electrostatics and polarization while dispersion term is the one that experiences the least variations with the increase of the σ-hole. It is clear that the increase in the σ-hole magnitude favors more to electronic exchange than the rest of the terms. Therefore, it appears that the existence of the σ-hole facilitates not only electrostatic interactions, as expected from the σ-hole model, but also the electronic exchange and, to a lesser extent, to the polarization and dispersion components.

Another point to consider is how the E_{ex} and E_{el} components vary according to the intermolecular distances. In order to illustrate this competition, we compared, for FCl···CO complex, the values (in kJ mol^{-1}) of these contributions in the equilibrium geometry ($E_{ex} = -67.5$, $E_{el} = -33.3$), at 3.2 Å ($E_{ex} = -12.1$, $E_{el} = -8.5$) and 4.2 Å ($E_{ex} = -0.3$, $E_{el} = -1.5$). It is observed that the E_{ex} tends to decrease more rapidly in magnitude than E_{el} term. Consequently, E_{ex}/E_{el} ratios are equal to 2.03, 1.42 and 0.2 respectively. This proves that, when the monomers are away from each other, the electrostatic term clearly dominates (in accordance with the σ-hole model), while in the equilibrium geometry the exchange contribution is the larger in magnitude one.

Due to the multiple forms of decomposing the interaction energy, most of these methods are not free of controversy. It is known that, in all Kitaura Morokuma EDA (as the LMOEDA) derived schemes, the electrostatic and repulsion-exchange terms may be combined or divided [21]. The fact that the LMOEDA method divides the repulsion-exchange term in E_{ex} and E_{rep} components may be questioned. In LMOEDA method E_{ex} and E_{rep} are the energetic effects associated with antisymmetrization of the wavefunction. The repulsion term arises from mutual orthonormalization of monomeric orbital subspace [31], while according to Hayes and Stone EDA [36] (from which the LMOEDA method derives) E_{ex} arises from the exchange interaction of electrons with parallel spins, which is a pure electron-electron effect. In the IQA scheme the electronic exchange can be interpreted as a measurement of the pure exchange contribution between X and C atoms (when it is calculated at Hartree Fock level), derived of the Pauli exclusion principle. In order to verify the observed trend of the E_{ex}(LMOEDA) term, the exchange contribution between X and C atoms through IQA scheme, V_{ex}(IQA) has been calculated. Fig. 2 shows a very good linear relationships between these magnitudes. Therefore, we can consider that in both schemes the exchange term is a measure of the stabilizing effect that arises from the Pauli exclusion principle.

These findings are contrary to numerous previous studies [37] and to the same definition of halogen bonding established by the International Union of Pure and Applied Chemistry (IUPAC). This definition in one of its characteristics establishes that "The forces involved in the formation of the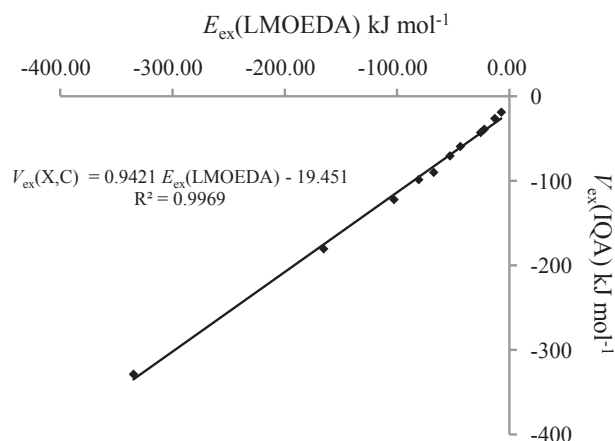 halogen bond are primarily electrostatic, but polarization, charge transfer, and dispersion contributions all play an important role" [13]. However, our results are to some extent in agreement with those reported by Stone [22] who found that the strong tendency to linearity of the XBs is a consequence of exchange-repulsion term, not electrostatics. They also agree with the results reported by Syzgantseva et al. [24] in their study on the physical nature of XBs through IQA [23] scheme. These authors have shown that at the equilibrium geometry the exchange term plays a very important role in the stabilization of the complex FBr···NH$_3$.

Fig. 3 shows a very linear correlation between the delocalization index, DI(X, C) (number of electrons exchanged or shared between X and C atoms) and the exchange term, E_{ex}. This is a clear proof of the relationship between them [38].

In a previous work, we have shown that the XBs (FX)$_n$/NH$_3$ (with n = 1–5 and X = Cl, Br) for large values of DI(X, N) and small d(X···N) correspond to a large absolute value for the exchange term calculated with IQA approach [V_{ex}(X, N)] and a considerable covalent character of the X···N interaction [12]. Similarly, in the present work we can establish that the covalence of these interactions increase in the same sense of DI(X, C). In addition, an exponential relationship between the σ-hole magnitude and DI(X, C) ($R^2 = 0.9817$) has been found (figure not shown).

Recently the potential acting on an electron in a molecule (PAEM) [33] has been applied to XBs [39]. It is defined as the interaction energy of one electron at position **r** with the remaining charges of the molecular system (electrons and nuclei) and it expresses itself as

$$V_{PAEM}(\mathbf{r}) = -V_{ESP}(\mathbf{r}) + \frac{V_{EX}(\mathbf{r})}{\rho(\mathbf{r})}$$

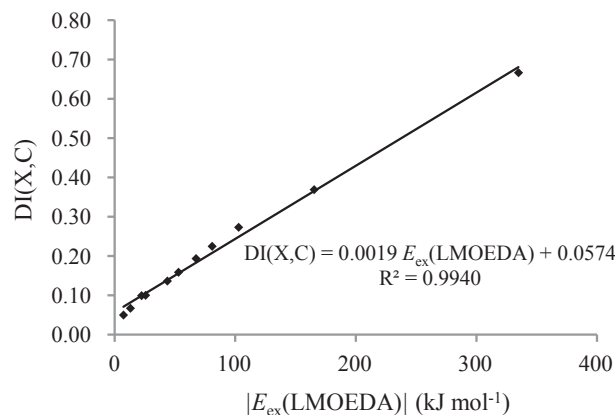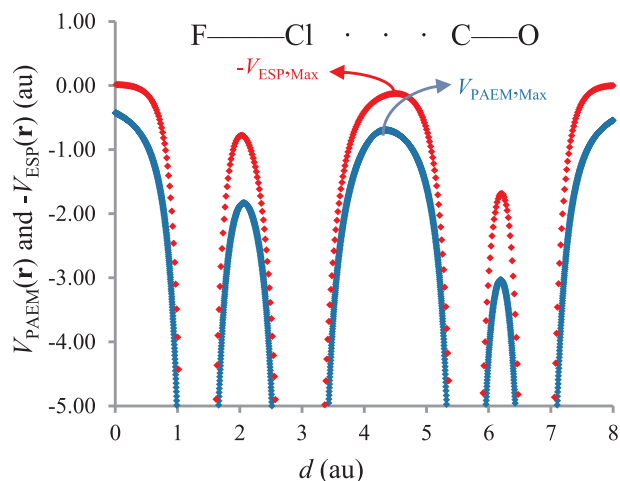**Fig. 3.** Correlation between the exchange term and the delocalization index.

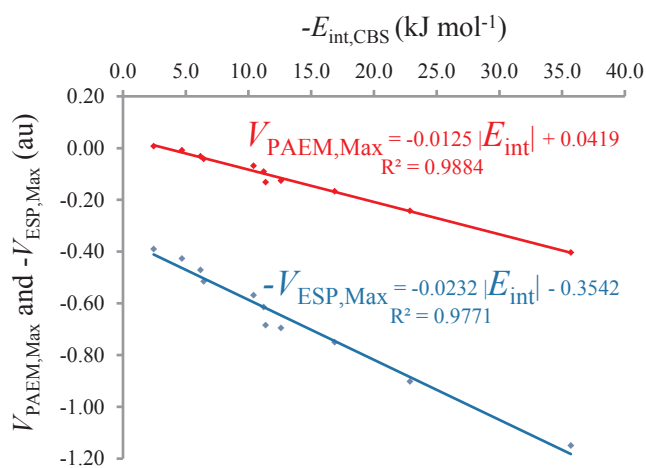**Fig. 4.** Variation of $V_{PAEM}(r)$ and $-V_{ESP}(r)$ functions along the atomic interaction line.

Fig. 5. Correlation between $-E_{int,CBS}$ and $V_{PAEM,Max}$ and $-E_{int,CBS}$ and $-V_{ESP,Max}$.

in which the first term is the classical electrostatic potential (ESP) with negative sign, and the second term is the interaction potential given by all the remaining electrons that contain both Coulomb and exchange interaction, provided that the wavefunction is calculated at Hartree-Fock level.

$$V_{EX}(\mathbf{r}) = \int \frac{\rho_{EX}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}$$

In this expression $\rho_{EX}(r, r')$ represents the two-electron density function. That is, the probability function of finding one electron at $\mathbf{r}$ and another electron at $\mathbf{r}'$ simultaneously.

In Fig. 4 it is observed that $V_{PAEM}(r)$ and $-V_{ESP}(r)$ functions show a maximum along the interatomic line connecting the X and C atoms, $V_{PAEM,Max}$ and $-V_{ESP,Max}$ respectively. According to the interpretation of Bartashevich et al., the lower the barriers, the easier it is to share electrons between linked atoms and the more significant covalence of the bond between becomes [39].

Fig. 5 shows the linear relationship between $-E_{int,CBS}$ and $V_{PAEM,Max}$ and $-E_{int,CBS}$ and $-V_{ESP,Max}$ measured on the X···C interatomic interaction line. It is observed that both potential barriers decrease with the strengthening of the intermolecular interactions, independently of the pair of interacting atoms. Therefore, we can establish that the covalence of these interactions increase in the same sense of the strength and, consequently with the σ-hole magnitude.

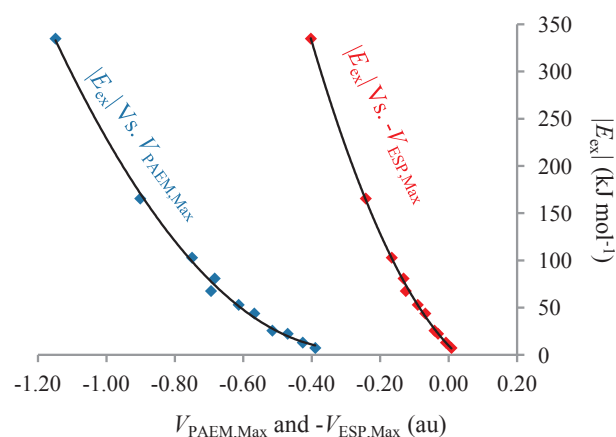Finally, Fig. 6 shows the quadratic relations between $V_{PAEM,Max}$ and

Fig. 6. Quadratic correlation between $V_{PAEM,Max}$ and $-V_{ESP,Max}$ with $|E_{ex}|$.

$|E_{ex}|$ ($R^2 = 0.9973$) and $-V_{ESP,Max}$ and $|E_{ex}|$ ($R^2 = 0.9973$). Similarly, as it is expected very good quadratic relations are found between $V_{PAEM,Max}$ and $DI(X, C)$ ($R^2 = 0.9948$) and $-V_{ESP,Max}$ and $DI(X, C)$ ($R^2 = 0.9984$) (figures not shown). That is, the electronic exchange increases with the decrease of both potential barriers ($V_{PAEM,Max}$ and $-V_{ESP,Max}$). Therefore, the height of these barriers is directly related with the covalence of the X···C interactions.

4. Conclusions

The relationship between the σ-hole magnitude and energetic terms derivative of LMOEDA method in the complexes YX···CO (in which YX are diatomic interhalogens or hydrogen halide) has been evaluated. Calculations reveal that in all the complexes studied here the stabilizing effect that arises from the Pauli exclusion principle is larger in magnitude than the electrostatic interactions.

The σ-hole magnitude has influences on all the stabilizing terms of the LMOEDA scheme. The exchange term is the most affected one, followed by electrostatics, polarization and to a lesser extent dispersion.

The joint analysis of $V_{PAEM,Max}$ and $-V_{ESP,Max}$ with the exchange term of LMOEDA method shows that the height of these barriers is directly related with the covalence of the X···C interactions.

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