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A theoretical analysis of atomic charge fluxes in chlorofluoromethanes and relations with bonding character descriptors

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Abstract

In this study, intramolecular electronic charge fluxes in chlorofluoromethanes, which take place during atomic stretching displacements, were analyzed in terms of bond character descriptors. Topological parameters of the electron density at the critical points of C-X bonds (X = H, F or Cl) and charge fluxes were obtained through the Quantum Theory of Atoms in Molecules (QTAIM). All calculations were done at the CCSD/cc-pVQZ level of theory. Thus, we have noticed that the covalent character of C-H, C-Cl and C-F bonds seems to increase as hydrogen atoms are replaced by halogens in other bonding sites of those molecules. This is attributed to polarizations induced over the carbon atom by the negatively charged substituents. It was also observed that the charge fluxes at the atoms of enlarged C-H bonds are linearly related to these bond character parameters. A similar pattern of charge fluxes is likewise seen for C-Cl and C-F bonds. However, the displacement of halogen atoms results in a larger delocalization of the charge fluxes (long range electronic charge transfers). This probably leads to a further observed separation into subgroups of molecules with proper linear relations between halogen charge fluxes and bond character descriptors.

Keywords: Atomic charge; charge flux; charge transfer; bond character; QTAIM; chlorofluoromethanes.

1. Introduction

The electron density (ρ) of a system is a fundamental quantity that provides information about the probability of finding an electron at each point of space, playing a major role in a variety of chemical studies. In addition, one of the simplest representations of the electron density distribution is given by the atomic charge concept. In this context, several charge formalisms, based on arbitrary ways to divide the molecular electronic charge among the constituent atoms, have been analyzed for diverse purposes [1-11].

Recently, we carried out a study comparing the use of Mulliken [12, 13], Natural Population Analysis (NPA) [14, 15] and Quantum Theory of Atoms in Molecules (QTAIM) [16-18] models in obtaining intramolecular charge fluxes during bond stretchings in diatomic and linear triatomic molecules of diverse bond character [19]. It was shown that only charge fluxes from QTAIM are consistent with simple physical arguments based on, for instance, dissociation of polar covalent bonds into neutral fragments and the existence of a harpoon mechanism in highly ionic diatomic molecules. In addition, QTAIM has been successfully used in the Charge - Charge Flux - Dipole Flux (CCFDF) partition [20] for the analysis of infrared fundamental intensities of vibrational modes in many systems.

Conversely, although the understanding of electronic cloud changes is also fundamental in, e.g., reaction coordinate [21, 22] and halogen-bonding interaction [23-26] studies, there is still a lack of deeper and more explicit investigations about these charge transfers in a representative group of molecules.

Hence, we have used the QTAIM model to analyze charge fluxes induced by stretching atomic displacements in 15 chlorofluoromethanes. This property is evaluated in terms of changes in bond character descriptors from topological analyses of the molecular electron density under substitutions of the terminal hydrogen, chlorine and fluorine atoms.

2. Computational details

Geometry optimizations were carried out with the GAUSSIAN 03 package [27]. All calculations were done at the coupled cluster level of theory with single and double excitations (CCSD) [28-31] by applying the cc-pVQZ basis sets [32, 33]. The generalized densities were obtained with the *density=current* keyword. The first-order density matrixes from these calculations were used along with the AIMALL program

[34] to determine QTAIM properties, including atomic charges (q) and atomic dipole moments (m), and also topological parameters such as the electron density (ρ), the Laplacian of ρ ($\nabla^2\rho$) and the Hessians of ρ (λ_1, λ_2 and λ_3) at the bond critical points (BCPs).

Dynamic quantities associated with atomic displacements, such as charge fluxes, were determined through a numerical estimate of derivatives from the common finite-difference technique. In this approximation, we used two slightly distorted geometries, in which bond lengths are changed through atomic dislocations,

$$\frac{\partial q_\alpha}{\partial r_{\beta C}} = \frac{q_\alpha^{(+)} - q_\alpha^{(-)}}{2\Delta r_{\beta C}}, \qquad (1)$$

where $\Delta r_{\beta C}$ is the magnitude of a β atom displacement along the bond axis with respect to the central carbon. Hence, the superscripts, (+) and (-), characterize that the properties were obtained for the α atom in the geometries given by, respectively, enlargements and shortenings of 0.01 Å [19] from the equilibrium bond length between β and carbon.

3. Results and discussion

3.1. Bond character considerations

The charge flux property is expected to be inherently affected by changes in the bond character driven by atomic substitutions. For example, in a nonpolar covalent bond, such as in a homonuclear diatomic molecule, the electronic charge is equally shared between the atoms independently on the distance between them. Thus, the charge flux will certainly tend to zero. Moreover, if a system with a highly ionic bond is considered, the harpoon mechanism takes place [35, 36]. This means that significant amounts of electronic charge will only be transferred in huge interatomic distances, with almost null charge fluxes for atomic displacements around the equilibrium geometry. Hence, for polyatomic systems in which the charge transfer is considerably localized over atoms of distorted bonds, large values of charge fluxes are only expected in stretchings of polar covalent interactions, since the significant amount of electronic charge exchanged on bonding should be soon restored before dissociation into neutral fragments [19]. Such preliminary arguments lead to a general pattern displayed in Figure 1.

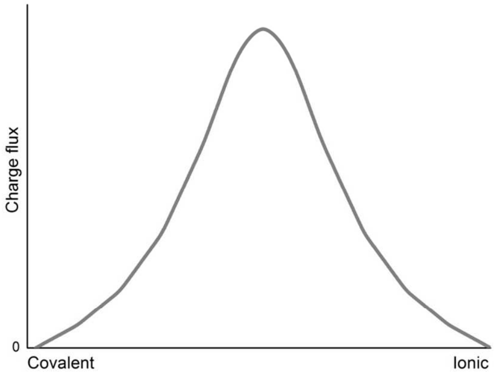

Figure 1 – General expectation of charge flux absolute values in terms of the bonding character.

In this context, an initial approximated consideration about the bond character could make use of the atomic charge concept itself. Thus, we present in Table S1 in the Supporting Information the atomic charges of 15 chlorofluoromethanes at their calculated equilibrium geometries. From these data, we observe a clear pattern of increasing carbon charges as the total electronegativity of the ligands also increases. In this manner, such analysis leads to larger absolute charge values when fluorine atoms are binding to carbon than the ones found during chlorine addition. For instance, the carbon and fluorine charges in CF_4 reach 2.8 and -0.7 *e*, respectively. Although these large absolute values in fluorinated compounds could suggest an ionic C-F bond, other parameters must be taken into account to a full characterization of the nature of this interaction.

In accordance to arguments presented by Bader and Matta [4] about the bond character in terms of electron density (ρ) contour maps, we projected the electron density over the FCF plane in the CH_2F_2 molecule. As can be seen in Figure S1 in the Supporting Information, the zero-flux surface (bifurcated bold line) does not support a closed-shell interaction picture since there is not a near spherical charge distribution around each nucleus. Besides, contour lines with electron density values as large as 0.27 a.u. already encompass both carbon and fluorine atoms. This implies in an expressive delocalization of the electron density and assigns a significant covalent character, although atomic charges of 1.36 and -0.71 *e* are determined for, respectively, carbon and fluorine in this molecule.

Moreover, according to Bader and Essén [37], a further characterization of chemical interactions in different systems can be made in terms of values determined for ρ and the Laplacian of ρ (sum of λ_1, λ_2 and λ_3 Hessians of ρ), $\nabla^2\rho$, at the BCPs. If there is an accumulation of electronic charge in the contact region between two atoms, which is a characteristic of covalent interactions, we shall observe a ρ value larger than 0.20 a.u., a ratio $|\lambda_1|/\lambda_3$ larger than unity and $\nabla^2\rho$ must be negative. The opposite should be expected for bonds of major ionic character ($\rho < 0.10$ is more indicated to qualify ionic bond [18]). Hence, we proceeded to the analysis of these density topological features by starting from the C-H bond. The calculated data are displayed in Table 1.

Table 1 – Electron density properties at the critical point of C-H bonds in chlorofluoromethanes given at the CCSD/cc-pVQZ level of calculation.[a]

Molecule	r[b]	r/r_e[c]	ρ	$\nabla^2\rho$	λ_1	λ_3	$\lvert\lambda_1\rvert/\lambda_3$
CH_4	1.275	0.621	0.286	-1.114	-0.765	0.417	1.835
CH_3Cl	1.301	0.635	0.297	-1.228	-0.844	0.437	1.930
CH_2Cl_2	1.324	0.648	0.306	-1.324	-0.897	0.454	1.975
$CHCl_3$	1.346	0.660	0.313	-1.401	-0.935	0.469	1.993
CH_3F	1.303	0.634	0.299	-1.244	-0.867	0.445	1.947
CH_2F_2	1.329	0.647	0.312	-1.373	-0.933	0.470	1.986
CHF_3	1.356	0.661	0.321	-1.475	-0.981	0.486	2.017
CH_2ClF	1.328	0.648	0.309	-1.351	-0.921	0.462	1.992
$CHCl_2F$	1.350	0.661	0.316	-1.429	-0.961	0.476	2.019
$CHClF_2$	1.354	0.661	0.318	-1.452	-0.974	0.482	2.022

[a] All the values are given in atomic units;
[b] Absolute distance from the BCP to the central atom;
[c] r_e is the calculated equilibrium bond length.

From these results, it is noticeable that the C-H bond in these molecules is always highly covalent regardless of the other ligands. See that ρ lies between 0.29 and 0.32 a.u. and $|\lambda_1|/\lambda_3$ is about twice the unity, indicating a large concentration of charge in the contact region between carbon and hydrogen that results likewise in large negative values for $\nabla^2\rho$. Accordingly, hydrogen charges (see Table S1) are always small (between -0.03 and 0.11 *e*), even in the presence of more electronegative groups, as in CHF_3. Thus, these almost null hydrogen charges along with nearly invariant halogen ones also suggest that the electronic charge withdrawing effect ascribed to chlorine and fluorine appears to be restricted to those electrons of carbon directly involved in carbon-halogen bonds.

In addition, it is clear that there is a tendency of increasing the C-H covalent character as hydrogens are replaced by halogens in other bonding sites of these molecules. See the progressive increase of the electron density and the ratio $|\lambda_1|/\lambda_3$, along with a concomitant decrease of $\nabla^2\rho$ on halogenation. Such C-H covalent character strengthening is probably caused by an induced polarization effect over the C-H bond, which can be attributed to the presence of negatively charged substituent atoms at the other bonding positions around the carbon nucleus. This hypothesis is reinforced by the fact that fluorine is more effective than chlorine in increasing the C-H covalent character (Table 1) at the same time that the first halogen shows a more negative charge than the latter (see Table S1) and also that the C-F bond is shorter than the C-Cl one (calculated geometry data are found in Table S2).

Accordingly, as shown by the distances between the BCP and carbon, r, and the ratio r/r_e (r_e is the respective equilibrium bond length), the C-H BCP lies farther away from carbon as hydrogen is substituted by chlorine or fluorine. This is in agreement with a carbon basin polarization towards the C-H bond. Moreover, the topological features of the electron density given by the QTAIM model usually imply in a non-spherical charge distribution for atoms in molecular systems and, as a consequence, atomic dipole moments are defined [16]. Hence, we also analyzed the atomic dipole moments of carbon and hydrogen atoms of the C-H bonds stretched. Such C-H bonds were disposed along the z axis with the hydrogen atom placed at the positive end. In Tables S3 and S4 one finds the z components and the total magnitude of the dipole moment vector for these atoms in the equilibrium geometry of chloro-, fluoro- and chlorofluoromethane molecules. Once again, the substitution of H by F or Cl results in an increasing distortion of the carbon electronic cloud towards the positive end of the z axis. Moreover, the effect of each fluorine atom is three to four times larger than that of any chlorine (compare the values in fluoro- and chloromethanes), which is in line with the ratio of QTAIM charges of both atoms in these molecules. At the same time, the hydrogen dipole moment remains almost unaltered.

Table 2– Electron density properties at the critical point of C-F bonds in fluoro- and chlorofluoromethanes given at the CCSD/cc-pVQZ level of calculation.[a]

Molecule	r^{b}	r/r_e^{c}	ρ	$\nabla^2\rho$	λ_1	λ_3	$\lvert\lambda_1\rvert/\lambda_3$
CH_3F	0.843	0.324	0.247	-0.073	-0.481	0.888	0.541
CH_2F_2	0.828	0.325	0.272	-0.202	-0.699	1.050	0.665
CHF_3	0.818	0.326	0.296	-0.380	-0.821	1.166	0.705
CF_4	0.814	0.328	0.317	-0.575	-0.883	1.191	0.741
CCl_3F	0.826	0.329	0.296	-0.435	-0.730	1.024	0.713
CCl_2F_2	0.821	0.328	0.312	-0.477	-0.806	1.089	0.740
$CClF_3$	0.817	0.328	0.310	-0.521	-0.857	1.149	0.746
CH_2ClF	0.832	0.325	0.267	-0.179	-0.633	0.991	0.638
$CHCl_2F$	0.828	0.327	0.284	-0.304	-0.706	1.034	0.683
$CHClF_2$	0.821	0.326	0.291	-0.337	-0.774	1.113	0.695

[a] All the values are given in atomic units;
[b] Absolute distance from the BCP to the central atom;
[c] r_e is the calculated equilibrium bond length.

From the results in Table 2, one can see that the λ_3 values of C-F bonds are approximately twice as those of C-H bonds in the same molecules, indicating a higher contribution of the depletion of ρ along the bond path that leads to less negative values of $\nabla^2\rho$ (bearing zero in CH_3F) and also provides much smaller ratios $|\lambda_1|/\lambda_3$. Such features suggest, as expected by the electronegativity of fluorine, a higher ionic character of C-F interactions when compared to the C-H ones, which indicates a polar covalent bond that stands somewhere near the central region of the curve in Figure 1.

Conversely, the values showed in Table 3 for the C-Cl bonds must be carefully analyzed. While ρ and λ_1 indicate a lower concentration of electronic charge at these BPCs than those in C-F bonds, λ_3 shows a depletion of charge even smaller than in the C-H bonds. However, these features can be attributed to the large C-Cl bond length (Table S2), which might reduce the electron concentration at the BCP and result in a smoother variation of ρ along the bond path leading to low values of λ_3. Thus, the best parameter to analyze such character among different bond types is probably $\nabla^2\rho$, as it takes into account the combined effect of the three curvatures of ρ and, because of this, may be a more robust choice. Hence, $\nabla^2\rho$ indicates a less covalent character for C-Cl bonds than that of C-H ones, which is also comparable to C-F interactions, although the

C-F bond is clearly more affected by the nature of other ligands than the C-Cl counterpart (see a larger spread of $\nabla^2\rho$ values in Table 2 compared to those in Table 3).

Table 3 – Electron density properties at the critical point of C-Cl bonds in chloro- and chlorofluoromethanes given at the CCSD/cc-pVQZ level of calculation.[a]

Molecule	r[b]	r/r_e[c]	ρ	$\nabla^2\rho$	λ_1	λ_3	$\lvert\lambda_1\rvert/\lambda_3$
CH_3Cl	1.406	0.418	0.190	-0.316	-0.302	0.288	1.048
CH_2Cl_2	1.427	0.427	0.200	-0.342	-0.331	0.311	1.067
$CHCl_3$	1.454	0.437	0.206	-0.354	-0.345	0.328	1.050
CH_2ClF	1.422	0.426	0.202	-0.360	-0.348	0.315	1.105
$CHClF_2$	1.450	0.436	0.211	-0.392	-0.371	0.339	1.097
$CHCl_2F$	1.451	0.437	0.209	-0.375	-0.362	0.334	1.083
CF_2Cl_2	1.483	0.447	0.217	-0.395	-0.377	0.352	1.072
$CClF_3$	1.484	0.448	0.221	-0.416	-0.385	0.354	1.086
CCl_3F	1.484	0.446	0.212	-0.373	-0.365	0.347	1.050
CCl_4	1.487	0.446	0.208	-0.350	-0.346	0.342	1.013

[a] All the values are given in atomic units;
[b] Absolute distance from the BCP to the central atom;
[c] r_e is the calculated equilibrium bond length.

Despite the obvious difficulties in comparing the covalent character among different bond types, the quantitative analysis of effects over a single bond on substitution is much more reliable. Hence, the substitution of hydrogen by halogens in other bonding positions of the molecule clearly leads to a likewise increment in the covalent character of these C-F and C-Cl bonds. Again, a further increase is observed as chlorine is replaced by fluorine. Thus, these variations can be also attributed to similar polarization effects as those discussed for C-H bonds.

Moreover, in order to provide additional insights about the bond character issue, we carried out an analysis based on delocalization indexes (DIs) [38], which are shown in Table S5. As expected, there is an overall tendency of increasing charge delocalization of terminal atoms during halogenation in other bonding sites. However, the substitutions of Cl by F now result in a contrary pattern to that shown by local descriptors, with larger delocalization changes on addition of chlorine than the respective ones observed with fluorine. Although, it is important to stress that the use of DIs as bond order parameters is questionable and that the DI results are difficult to interpret in polyatomic systems [39], which could be the cause for the small discrepancy observed with respect to local descriptors.

Interestingly, the absolute atomic dipole fluxes (these values are obtained similarly as the charge fluxes in Eq. 1 by using each component of the atomic dipole moment during a bond stretching) presented in Tables S6 and S7 also show a significantly large polarization change for fluorine atoms far away from the stretched C-H, C-F and C-Cl bonds, which suggests that the polarization effect is reciprocal. Hence, the fluorine basin is disturbed as the electronic cloud associated to a bond is deformed by the displacement of a terminal atom.

3.2. Atomic charge fluxes on substitution

Table 4 shows the charge fluxes in individual displacements of terminal atoms for all the molecules studied here. Thus, by looking only at the values attributed to carbon and hydrogen during the enlargement of C-H bonds in chloro- and fluoromethanes as a function of the increasing number of Cl and F atoms, one can notice a positive and decreasing charge flux on the hydrogen atom along with a negative and increasing charge flux on the carbon atom. This pattern is expected since, by starting from an almost nonpolar covalent bond, such as the C-H bond in CH_4 (which lies on the left of the maximum in Figure 1), the increasing covalent character detected for C-H bonds on halogenation would lead to a decreasing charge flux magnitude between carbon and hydrogen.

In order to present a clear picture of these relations between the charge flux and the covalent character, we plotted the charge flux values for the hydrogen atom of the stretched C-H bonds against $\nabla^2\rho$ at their BCPs. The result is shown in Figure 2. As can be seen, there is a linear relation between such quantities (coefficient of determination $R^2 = 0.97$). Again, it is evident that the positive charge flux values increase as the Laplacian becomes less negative. This is in line with less relevant intramolecular electronic charge transfers whereas the covalent character of C-H bonds increases as a result of halogenation.

Table 4 - Atomic charge fluxes (e Å^{-1})[a] during the enlargement of the C-X (X= H, Cl or F) bonds in chlorofluoromethanes from CCSD/cc-pVQZ calculations.

Molec.	*A*	H	Cl	F
CH_4	C	-0.595	-	-
	H*	0.451	-	-
	H	0.048	-	-
	H	0.048	-	-
	H	0.048	-	-
CH_3Cl	C	-0.554	-0.273	-
	H*	0.410	0.096	-
	Cl*	0.040	-0.011	-
	H	0.049	0.096	-
	H	0.049	0.096	-
CH_2Cl_2	C	-0.492	-0.243	-
	H*	0.364	0.094	-
	Cl	0.039	0.138	-
	Cl*	0.039	-0.081	-
	H	0.050	0.094	-
$CHCl_3$	C	-0.432	-0.221	-
	H*	0.314	0.093	-
	Cl	0.039	0.126	-
	Cl	0.039	0.126	-
	Cl*	0.039	-0.146	-
CCl_4	C	-	-0.099	-
	Cl*	-	-0.199	-
	Cl	-	0.117	-
	Cl	-	0.117	-
	Cl	-	0.117	-
CH_3F	C	-0.494	-	-1.261
	H*	0.384	-	0.230
	F*	-0.013	-	0.574
	H	0.061	-	0.230
	H	0.061	-	0.230
CH_2F_2	C	-0.394	-	-1.115
	H*	0.348	-	0.243
	F	-0.016	-	0.065
	F*	-0.017	-	0.563
	H	0.078	-	0.243
CHF_3	C	-0.257	-	-0.964
	H*	0.303	-	0.243
	F	-0.016	-	0.058
	F	-0.015	-	0.058
	F*	-0.015	-	0.589
CF_4	C	-	-	-0.846
	F*	-	-	0.668
	F	-	-	0.054
	F	-	-	0.054
	F	-	-	0.054
CH_2ClF	C	-0.429	-0.136	-1.356
	H*	0.345	0.113	0.219
	Cl*	0.048	-0.111	0.270
	F*	-0.018	0.038	0.625
	H	0.061	0.113	0.219
$CHClF_2$	C	-0.317	0.002	-1.149
	H*	0.297	0.135	0.221
	Cl*	0.059	-0.186	0.276
	F	-0.020	0.032	0.054
	F*	-0.020	0.032	0.641
$CHCl_2F$	C	-0.373	-0.088	-1.396
	H*	0.302	0.111	0.203
	F*	-0.022	0.027	0.698
	Cl	0.048	0.143	0.253
	Cl*	0.048	-0.170	0.253
CCl_3F	C	-	-0.119	-1.508
	F*	-	0.018	0.794
	Cl*	-	-0.218	0.233
	Cl	-	0.131	0.233
	Cl	-	0.131	0.233
CCl_2F_2	C	-	0.048	-1.296
	F*	-	0.023	0.744
	Cl*	-	-0.224	0.248
	Cl	-	0.150	0.248
	F	-	0.023	0.043
$CClF_3$	C	-	0.121	-1.123
	Cl*	-	-0.215	0.268
	F*	-	0.030	0.699
	F	-	0.030	0.046
	F	-	0.030	0.046

[a] Atomic charge flux for the *A* atom;

* The asterisk indicates the atoms displaced to obtain the charge flux values (the ones in the header line).

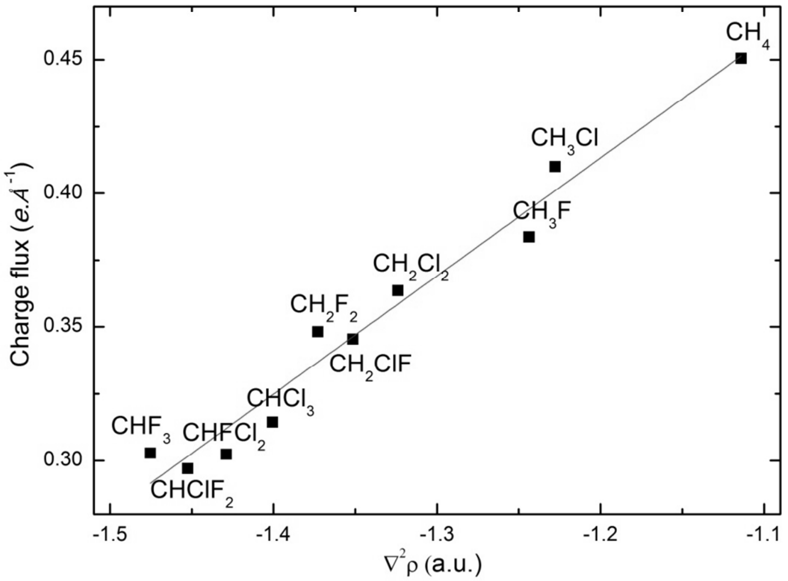

Figure 2 – Atomic charge fluxes for the hydrogen atoms displaced during C-H bond enlargements against $\nabla^2 \rho$ at the BCP of these bonds obtained at the CCSD/cc-pVQZ level of calculation.

In the same way, since the C-Cl bonds are polar covalent interactions, one should expect larger charge fluxes between the atoms of this stretched bond than those noticed for the carbon and hydrogen during C-H enlargements. However, this is not what is observed. The absolute charge flux values of the carbon and chlorine atoms of stretched C-Cl bonds are always smaller than those of carbon and hydrogen in a C-H stretching. Nevertheless, as we have been addressing throughout this paper, the simple relation between charge fluxes and bond character parameters depends also on how localized the charge fluxes are to the atoms of a stretched bond.

Hence, one can notice that the charge fluxes on the remaining atoms are quite small during C-H bond enlargements, bearing 0.08 *e* $Å^{-1}$, at most, in absolute terms. Conversely, such values reach 0.15 *e* $Å^{-1}$ when a chlorine atom is displaced. This indicates that long range electronic charge transfer effects are important for a C-Cl stretching, while a more localized picture of charge fluxes is characteristic of C-H stretchings. In addition, other factors may as well be responsible for some complications in a direct comparison of charge fluxes among different bond types, such as atomic charge values themselves, bond orders, atomic polarizabilities and distinct bond lengths.

Figure 3 shows a graph of charge fluxes on the chlorine atom of stretched C-Cl bonds against $\nabla^2 \rho$ at their BCPs. It is noticeable that, although there is a general pattern of charge fluxes becoming less negative as the Laplacian increases (which can be expected if the C-Cl bond is located at the right side of the maximum in Figure 1), there is now a clear separation of such molecules into subgroups, which depends on the remaining substituents, with distinct linear parameters associated. This separation is much probably caused by those long range electronic charge transfers already commented here. Accordingly, we can notice that these charge flux values increase almost linearly with $\nabla^2\rho$ during substitution of fluorine by chlorine. This is observed for three subgroups containing 0, 1 or 2 hydrogen atoms with a single exception, $CClF_3$.

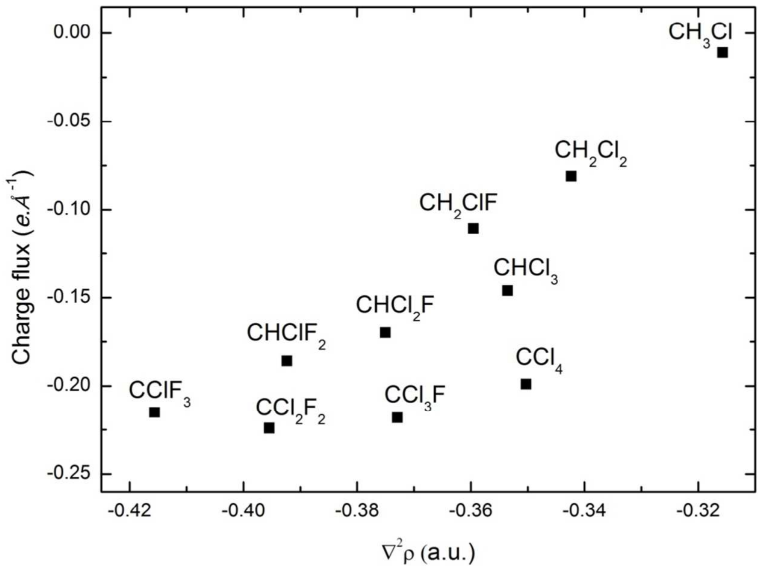

Figure 3 – Atomic charge fluxes given for the displaced chlorine atoms during C-Cl bond enlargements against $\nabla^2\rho$ at the BCP of these bonds obtained at the CCSD/cc-pVQZ level of calculation.

Moreover, the substitution of chlorine or fluorine by hydrogen also tends to result in a similar pattern. The electronic charge donation from other atoms of the molecule also explains the fact that both carbon and chlorine atoms of enlarged C-Cl bonds present negative charge flux values in almost all chlorofluoromethanes (the exceptions are those molecules containing two or three fluorine atoms). However, positive charge fluxes are still expected to occur for chlorine in larger bond lengths than the equilibrium distance to be in agreement with further dissociation into neutral fragments [19].

Finally, by analyzing the charge flux during the C-F bond enlargements, one can see that the polar covalent character of this bond results in much larger charge flux values than those obtained during displacements of hydrogen and chlorine. Absolute values up to 1.51 *e* Å^{-1} are now associated to the carbon atom. The signs seen for charge fluxes of carbon and fluorine of these bonds are also in agreement with dissociation arguments [19]. In addition, the charge donation effect from the remaining atoms is even more pronounced than those found in C-Cl stretchings. Positive charge fluxes up to 0.28 *e* Å^{-1} may now arise from a single non-displaced terminal atom. Again, as shown in Figure 4, these long range transfers affect the relation between charge flux and bond character parameters, contributing to an even clearer separation into subgroups than that seen for the C-Cl case.

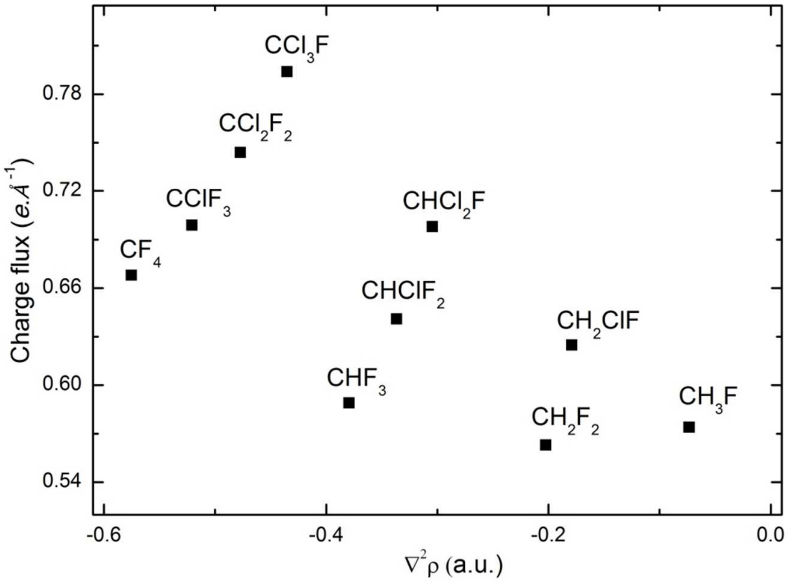

Figure 4 – Atomic charge fluxes for the displaced fluorine atoms during C-F bond enlargements against $\nabla^2\rho$ at the BCP of these bonds obtained at the CCSD/cc-pVQZ level of calculation.

In addition, the exchange of fluorine by hydrogen in subgroups with 0, 1 or 2 C-Cl bonds provides smaller charge fluxes as $\nabla^2\rho$ increases, except for CH_3F, a member of the first group. This is also observed in substitutions of Cl by H. Conversely, the substitution of fluorine by chlorine in series with 0, 1 or 2 hydrogen atoms has a contrary outcome and leads to higher charge flux values as $\nabla^2\rho$ increases. Here, a complicated interaction effect between fluorine and chlorine probably takes place. Thus, except by the values in substitutions of F by Cl, overall results also place the C-F bond in the right side of the maximum in Figure 1.

Furthermore, by analyzing the electronic charge donation capacity of the atoms far away from those involved in the C-F or C-Cl bond enlarged, one can see that the overall order of donation capacity is the same for both C-F and C-Cl stretchings: Cl ≈ H > F.

4. Conclusions

We studied the covalent/ionic character of C-H, C-F and C-Cl bonds in chlorofluoromethanes and provided relations with charge fluxes from the QTAIM model during stretchings of these bonds. Topological parameters, such as the electron density Laplacian at bond critical points, showed that there is an increasing covalent character of the C-H bonds along with the substitution of other hydrogen atoms by chlorine or, mostly, by fluorine. This is attributed to an inductive effect over the carbon electronic cloud towards the C-H bond as negatively charged substituent atoms are placed at the other bonding positions. Changes observed in that component of the atomic dipole moment of carbon along the C-H bond axis corroborate such proposition. Furthermore, this increasing covalent character presented a linear relation with the charge flux values on the hydrogen atom that is displaced.

Similar covalent character changes on substitution and relations of these parameters with charge fluxes are also found for the C-F and C-Cl bonds. However, the charge fluxes observed in these stretchings are more delocalized than those noticed in C-H stretchings. Hence, we can infer that the long range electronic charge transfers taking place in such organic molecules during enlargements of C-Cl and C-F bonds are responsible for the separation of molecules into subgroups, with distinct linear relations between bond character descriptors and charge fluxes on the displaced halogen atoms. In addition, the overall charge donation capacity of the atoms not involved in these C-F and C-Cl stretchings is Cl ≈ H > F.

Hence, this study provides a new interpretation of the effect of substituents such as fluorine and chlorine in organic molecules. We showed that, although chlorine and, mostly, fluorine are strong electronic charge withdrawing substituents, the charge removed from carbon seems to be donated from a very specific site, that is, from those atomic orbitals directly involved in carbon-halogen bonds. However, the remaining electronic charge of carbon is polarized away from these carbon-halogen bonds. In addition, Shi and Boyd [40] found that a halogen atom (X) in halomethanes creates a depletion of electron density localized directly at the opposite side of the C-X bond and, as a consequence, nucleophilic attacks directed to such regions can take place. Thus, our findings, along with the conclusions from Ref. [40], strongly suggest that the polarization induced by halogen atoms occurs specifically along the bond paths.

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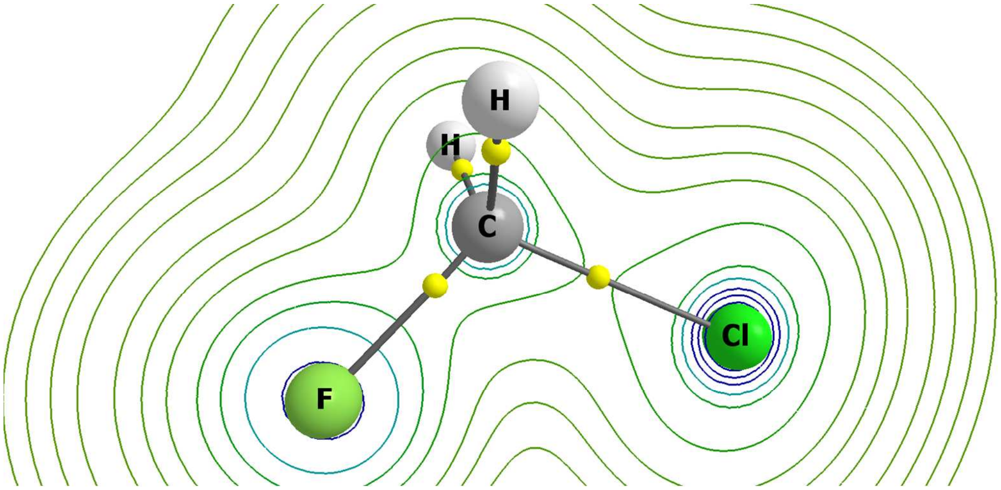

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Atomic substitutions in chlorofluoromethanes were analyzed through changes in the bond character descriptors and the related effect on electronic charge fluxes, given by the QTAIM model, which occur during atomic stretching displacements. Such interpretations of these H ↔ F ↔ Cl substitutions can provide new insights on further reaction coordinate and halogen-bonding interaction, among other studies.