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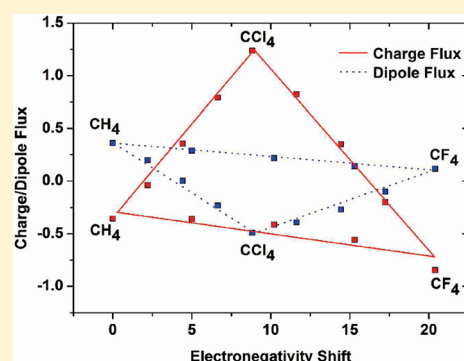
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QTAIM Charge–Charge Flux–Dipole Flux Interpretation of Electronegativity and Potential Models of the Fluorochloromethane Mean Dipole Moment Derivatives

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S Supporting Information

ABSTRACT: Infrared fundamental vibrational intensities and quantum theory atoms in molecules (QTAIM) charge–charge flux–dipole flux (CCFDF) contributions to the polar tensors of the fluorochloromethanes have been calculated at the QCISD/cc-pVTZ level. A root-mean-square error of 20.0 km mol^{−1} has been found compared to an experimental error estimate of 14.4 and 21.1 km mol^{−1} for MP2/6-311++G(3d,3p) results. The errors in the QCISD polar tensor elements and mean dipole moment derivatives are 0.059 *e* when compared with the experimental values. Both theoretical levels provide results showing that the dynamical charge and dipole fluxes provide significant contributions to the mean dipole moment derivatives and tend to be of opposite signs canceling one another. Although the experimental mean dipole moment derivative values suggest that all the fluorochloromethane molecules have electronic structures consistent with a simple electronegativity model with transferable atomic charges for their terminal atoms, the QTAIM/CCFDF models confirm this only for the fluoromethanes. Whereas the fluorine atom does not suffer a saturation effect in its capacity to drain electronic charge from carbon atoms that are attached to other fluorine and chlorine atoms, the zero flux electronic charge of the chlorine atom depends on the number and kind of the other substituent atoms. Both the QTAIM carbon charges (*r* = 0.990) and mean dipole moment derivatives (*r* = 0.996) are found to obey Siegbahn's potential model for carbon 1s electron ionization energies at the QCISD/cc-pVTZ level. The latter is a consequence of the carbon mean derivatives obeying the electronegativity model and not necessarily to their similarities with atomic charges. Atomic dipole contributions to the neighboring atom electrostatic potentials of the fluorochloromethanes are found to be of comparable size to the atomic charge contributions and increase the accuracy of Siegbahn's model for the QTAIM charge model results. Substitution effects of the hydrogen, fluorine, and chlorine atoms on the charge and dipole flux QTAIM contributions are found to be additive for the mean dipole derivatives of the fluorochloromethanes.



■ INTRODUCTION

The gas-phase infrared fundamental intensities of the fluorochloromethane molecules have been shown to be especially informative about their electronic structures. After reduction of the intensities to mean dipole moment derivative values obtained from the traces of atomic polar tensors,¹ several intriguing models have been proposed. The mean dipole moment derivatives of the fluorine, chlorine, and hydrogen atoms have been shown to be transferable within ± 0.05 *e* for all the fluorochloromethanes.² As such, the carbon mean derivative is determined almost completely by its substituent atoms and appears to vary only with their electronegativities.³ As a consequence, one might expect that the carbon mean dipole moment derivatives as well as the molecular infrared intensity sums of different halomethanes are related by sum rules. Indeed, sum rules of this nature have been observed for the fluorochloromethanes⁴ and also for the X₂CY (X = F, Cl; Y = O, S) molecules.^{5,6} Besides these interesting relations, the

carbon mean dipole moment derivatives of the halomethanes and of other molecules obtained from experimental infrared intensities⁷ have been shown to obey Siegbahn's simple potential model⁸ for the carbon 1s electron ionization energies. Because the simple potential model proposes a linear relation between these energies and atomic charges, the mean derivatives must be closely related to these charges. This is particularly relevant because mean dipole moment derivatives can be determined solely from experimental data. Indeed, usage of the mean dipole moment derivative as an atomic charge, the GAP^T (generalized atomic polar tensor) charge,⁹ has already been suggested owing

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to the similar mathematical properties of these two parameters. However, vibrational spectroscopists have long known that mean dipole moment derivatives have dynamic contributions.¹⁰

Recent studies have shown that atomic polar tensor elements and mean dipole moment derivatives can be expressed as a sum of their corresponding atomic contributions as given in the charge–charge flux–dipole flux (CCFDF) model¹¹ with atomic charges and atomic dipoles obtained from the quantum theory of atoms in molecules (QTAIM).¹² Besides a static charge contribution the mean dipole moment derivative is known to contain dynamic contributions, the charge and dipole fluxes, that are often seen to act in opposite directions, partially canceling one another. In this work the electronegativity and simple potential models for the fluorochloromethane mean dipole moment derivatives are interpreted with the QTAIM/CCFDF model. The importance of both the static and dynamic contributions to the mean dipole moment derivatives is determined for each of these models. In this way the reliability of the interpretation of the mean dipole moment derivative as an atomic charge can be assessed.

The values of the QTAIM atomic charges and dipoles depend on the quantum level used to determine their wave functions. In our exploratory work on these molecules the MP2/6-311++G-(3d,3p) level was used to calculate these parameters.¹³ Here results for the charge, charge flux, and dipole flux contributions are determined at the QCISD/cc-pVTZ level and compared with those obtained previously.

EXPERIMENTAL INTENSITIES AND CALCULATIONS

Care must be taken in choosing the experimental intensity results to be used for comparison with the theoretical values. For some of the fluorochloromethanes, more than a half-dozen different measurements have been made. Of course some of these were very early measurements and are not of the same quality as others that were measured later. For determining which experimental data should be included in our study three criteria were used: (1) intensities must have been measured for all the fundamental bands of the molecule, (2) error estimates from scattering of Beer's law plots must have been reported, and (3) in the case of hydrogen-containing molecules, intensity measurements and error estimates must have been made for at least two isotopomers. For the fluoro- and chloromethanes isotopomeric intensity data permits some validation of the quality of measured values by means of the G intensity sum rule¹⁴ and the isotopic invariance property of atomic polar tensor elements.¹

The selected experimental intensities and their error estimates are presented in Table 1. The methane data were taken from four different experimental studies.^{15–18} The methyl fluoride data are from Overend and co-workers,¹⁹ methylene fluoride from Kondo et al.,²⁰ and fluoroform from Kim and King.²¹ The tetrafluoromethane intensities used here are averages of results obtained by three research groups.^{22–24} The methyl chloride values are averages of results from Russell et al.,¹⁹ Dickson et al.,²⁵ and Saeki and associates.²⁶ The methylene chloride results are from Saeki and collaborators²⁷ whereas the chloroform data are averages of results from two research groups.^{28,29} For carbon tetrachloride results were taken from ref 28. Average values from several references were taken for CF₃Cl,^{4,30} CF₂Cl₂,^{31–33} and CFCF₃.^{30,31,34–36}

The molecular geometries were optimized with the Gaussian 03 program³⁷ for both the MP2/6-311G++(3d,3p) and QCISD/cc-pVTZ levels on a 64 Opteron workstation, which also generated

the wave functions to be used by the MORPHY program.³⁸ The optimized coordinates were then used to calculate the fundamental vibrational intensities, frequencies and polar tensors using Gaussian 03.

The mean dipole moment derivative is calculated from the diagonal elements of the atomic polar tensor

$$\bar{p}_\alpha = 1/3(\partial p_x/\partial x_\alpha + \partial p_y/\partial y_\alpha + \partial p_z/\partial z_\alpha) \quad (1)$$

The theoretical values of the mean derivatives were calculated from the polar tensor elements given by the quantum mechanical approach whereas the experimental values were obtained from experimentally determined intensities, normal coordinates, molecular geometries, and permanent dipole moments. The equations for the atomic polar tensors and their relations to the fundamental intensities are given in ref 1.

The MORPHY program, using the Gaussian 03 wave functions, calculated the QTAIM atomic charges and dipoles in the equilibrium geometries and also in distorted geometries obtained by displacing each atom by 0.01 Å along each Cartesian coordinate axis in the positive and negative directions. The atomic charges and atomic dipoles were then used by the PLACZEK program³⁹ to calculate the molecular dipole moment derivatives, as well as their charge, charge flux, and dipole flux contributions using the equations¹¹

$$\partial p_\sigma/\partial \sigma_A = q_A + \sum_i \sigma_i(\partial q_i/\partial \sigma_A) + \sum_i (\partial m_{i,\sigma}/\partial \sigma_A) \quad (2)$$

and

$$\partial p_\nu/\partial \sigma_A = \sum_i \nu_i(\partial q_i/\partial \sigma_A) + \sum_i (\partial m_{i,\nu}/\partial \sigma_A) \quad (3)$$

where $\sigma, \nu = x, y, z$ and the atomic charges and dipole components are given by q_i and $m_{i,\sigma}$ respectively.

During these calculations some accuracy problems in the calculated atomic charges and atomic dipoles of the central carbon atom were observed. These errors probably owe to topological irregularities of the carbon atom boundaries. Because small errors in the atomic charges and dipoles propagate into much larger ones in the derivative values, destroying the symmetry properties of the polar tensors, the carbon parameters were corrected. Atomic charge and dipole values of the terminal atoms were used in the

$$\sum q_i = 0 \quad \sum m_{i,\sigma} = p_\sigma - \sum q_i \sigma_i \quad (4)$$

relations for charge sum neutrality and the dipole moment of neutral molecules to obtain more accurate carbon atomic charges and atomic dipoles. Here p_σ is the σ -th component of the dipole moment calculated by the quantum mechanical approach and the following summation is its charge contribution (given by a sum of products between atomic charge and position for each atom).

RESULTS

The experimental intensities along with those calculated from the MP2/6-311++G(3d,3p) and QCISD/cc-pVTZ wave functions are given in Table 1. The ν_3, ν_7 , and ν_9 intensities of CH₂F₂ and the ν_2 and ν_5 intensities of CHF₃ are overlapped so only their sums are given in the table. One objective of this work is to determine whether the QCISD/cc-pVTZ level results in more accurate intensity values than those obtained at the MP2/6-311++G(3d,3p) level. For this reason the intensity sums were used in the error calculations rather than the individual estimated intensities, which could contain significant error contributions from overlapped band separation.

Table 1. Experimental, MP2/6-311++G(3d, 3p), QCISD/cc-pVTZ, MP2/QTAIM and QCISD/QTAIM Infrared Fundamental Intensities for the Fluorochloromethanes

		A_i (km/mol)				
	$\nu_{i,\text{exp}}$ (cm ⁻¹)	exptl ^a	MP2 6-311++G(3d, 3p) ^a	QCISD cc-pVTZ ^a	MP2/QTAIM ^b	QCISD/QTAIM ^b
CH ₄ ^{15–18}						
3	3019.0	67.5 ± 1.5	54.4	69.6	54.2	69.3
4	1311.0	33.5 ± 0.8	30.8	30.5	30.8	30.5
CH ₃ F ¹⁹						
1	3031.2	24.7 ± 2.5	31.9	29.3	32.0	29.4
2	1490.2	0.9 ± 0.3	1.6	3.1	1.6	3.1
3	1059.2	95.0 ± 9.5	103.7	99.3	103.7	99.3
4	3131.5	61.0 ± 6.1	46.1	70.6	43.7	68.3
5	1497.8	8.7 ± 0.9	9.0	5.4	8.8	5.3
6	1206.4	2.6 ± 0.3	2.7	3.2	2.6	3.2
CH ₂ F ₂ ²⁰						
1	2948.0	22.4 ± 11.2	37.7	43.8	37.7	43.8
2	1508.0	0.0 ± 0.3	0.4	1.4	0.4	1.4
3	1111.2					
7	1178.3	333.9 ± 41.6	365.3	350.2	365.1	350.0
9	1090.1					
4	528.5	4.8 ± 0.3	4.8	5.3	4.8	5.3
6	3014.0	42.2 ± 4.2	23.5	40.9	23.5	40.8
8	1435.0	10.3 ± 0.5	12.7	23.3	12.7	23.3
CHF ₃ ²¹						
1	3035.0	23.9 ± 0.4	22.2	35.1	22.2	35.0
2	1141.4	626.8 ± 6.6	697.4	633.5	689.2	633.7
5	1157.3					
3	700.1	12.1 ± 0.2	12.1	14.7	12.1	14.7
4	1377.8	82.0 ± 0.3	75.2	130.7	73.8	130.7
6	507.8	4.2 ± 0.1	4.2	6.0	4.0	6.0
CF ₄ ^{22–24}						
3	1298.0	1243.9 ± 38.5	1215.2	1220.2	1215.5	1220.5
4	632.0	13.0 ± 0.7	10.5	17.3	10.5	17.3
CH ₃ Cl ^{19,25,26}						
1	2966.8	19.4 ± 1.1	22.3	23.3	22.3	23.3
2	1354.9	7.6 ± 0.6	12.3	13.7	12.3	13.7
3	732.1	23.44 ± 0.7	23.7	24.3	23.7	24.3
4	3041.8	10.23 ± 0.9	5.4	12.0	5.4	11.9
5	1454.6	11.85 ± 0.7	10.1	9.8	10.1	9.8
6	1015.0	3.94 ± 0.3	4.5	4.1	4.5	4.1
CH ₂ Cl ₂ ²⁷						
1	3137.0	6.9 ± 0.5	4.9	8.2	4.9	8.2
2	1430.0	0.6 ± 0.1	0.0	0.0	0.0	0.0
3	714.0	8.0 ± 0.4	10.1	12.4	10.1	12.4
4	1155.0	0.6 ± 0.1	0.4	0.5	0.0	0.0
6	3195.0	0 ± 0	0.6	0.1	0.6	0.1
7	896.0	1.2 ± 0.1	1.4	0.9	1.4	0.9
8	1268.0	26.2 ± 1.2	41.0	42.6	41.0	42.5
9	757.0	95.0 ± 8.0	123.9	117.6	123.9	117.6
CHCl ₃ ^{28,29}						
1	3034.0	0.3 ± 0.1	1.6	0.0	1.7	0.0
2	678.0	4.4 ± 0.6	3.0	5.3	3.0	5.3
3	366.0	0.5 ± 0.1	0.1	0.4	0.1	0.4
4	1219.0	30.8 ± 2.0	44.1	47.0	44.1	47.0
5	773.0	222.4 ± 8.0	271.9	264.1	272.2	264.1

Table 1. Continued

	ν_{exp} (cm ⁻¹)	A_i (km/mol)				
		exptl ^a	MP2 6-311++G(3d, 3p) ^a	QCISD cc-pVTZ ^a	MP2/QTAIM ^b	QCISD/QTAIM ^b
6	262.0	0.1 ± 0.1	0.0	0.2	0.0	0.2
CCl ₄ ²⁸						
3	793.0	322 ± 60	408.3	412.6	408.2	412.4
4	310.0	0.2 ± 0.5	0.5	0.0	0.4	0.0
CClF ₃ ^{4,30}						
1	1109.0	493.9 ± 28	480.9	473.4	481.0	471.3
2	785.0	31.5 ± 1.8	22.8	34.3	22.8	34.3
3	476.0	0.0	0.0	0.0	0.0	0.0
4	1212.0	593.5 ± 33.6	558.3	587.6	558.4	587.7
5	562.0	3.3 ± 0.2	2.1	5.0	2.1	5.0
6	348.0	0.0	0.0	0.1	0.0	0.1
CCl ₂ F ₂ ^{31–33}						
1	1095.0	284.3 ± 4.4	279.5	293.3	280.9	293.3
2	442.0	0.2	0.0	0.1	0.0	0.1
3	665.0	12.3	7.7	11.5	9.6	11.5
4	261.0	2.6	0.2	0.0	1.6	0.0
6	1152.0	183.3 ± 3.2	192.0	211.6	192.0	211.7
7	475.0	0.1	0.0	0.0	0.9	0.0
8	915.0	324.8 ± 7.2	375.3	375.2	375.5	375.2
9	432.0	0.1	0.0	0.5	0.3	0.5
CCl ₃ F ^{30,31,34–36}						
1	1085.0	158. ± 6.3	159.8	179.3	159.8	179.4
2	539.0	1.1	0.9	1.5	0.9	1.5
3	347.0	0.3	0.4	0.0	0.4	0.0
4	846.0	394.6 ± 31.9	465.1	468.7	465.2	468.7
5	384.0	0.1	0.0	0.2	0.0	0.2
6	243.0	0.0	0.2	0.0	0.2	0.0

^a Calculated directly from the molecular wave functions. ^b Calculated from the atomic charges and atomic dipoles by the MORPHY program.

Table 2 contains the root-mean-square (rms) errors for the MP2/6-311++G(3d,3p) and QCISD/cc-pVTZ intensity values relative to the experimental intensities for each of the fluorochloromethanes. The total rms error of 20.0 km mol⁻¹ for the QCISD intensities is slightly smaller than the 21.2 km mol⁻¹ MP2 error. These errors are only about 7 km mol⁻¹ larger than the rms error of 14.4 km mol⁻¹ estimated from the scatters in the Beer's law plots from which the intensities were determined. Both the MP2 and QCISD level results for rms errors are smaller than the experimentally estimated errors for CH₃F, CH₂F₂, CF₄, and CClF₃. The QCISD/cc-pVTZ values seem to be more accurate for the fluoromethanes than the MP2/6-311++G(3d,3p) ones although this apparent difference in accuracy becomes negligible as chlorine atoms are substituted for fluorine. The QCISD results are slightly closer to the experimental values for CH₂Cl₂, CHCl₃, and CClF₃ whereas the MP2 results are slightly superior for CH₃Cl, CCl₄, CF₂Cl₂, and CFCl₃.

Figure 1 shows a graph of the MP2/6-311++G(3d,3p) and QCISD/cc-pVTZ intensity values plotted against the experimental data. The theoretical values are seen to overestimate the experimental values for both quantum levels. This has been observed for the MP2/6-311++G(3d,3p) intensity estimates for other groups of molecules.⁴⁰

The last two columns of Table 1 contain the infrared intensity values calculated with the QTAIM atomic charges and dipoles

Table 2. Root Mean Square Errors for the MP2/6-311++G(3d, 3p), QCISD/cc-pVTZ, and Experimental Intensity Values (km mol⁻¹)

molecule	MP2/6-311++G(3d, 3p)	QCISD/cc-pVTZ	exp error
CH ₄	9.5	2.6	1.2
CH ₃ F	7.6	5.0	14.7
CH ₂ F ₂	16.2	12.2	17.7
CHF ₃	31.7	22.6	3.0
CF ₄	20.4	17.0	27.2
CH ₃ Cl	3.1	3.2	0.8
CH ₂ Cl ₂	11.5	10.0	3.1
CHCl ₃	21.0	18.3	3.4
CCl ₄	61.0	64.1	42.4
CClF ₃	15.7	8.8	21.9
CCl ₂ F ₂	18.3	20.7	5.2
CCl ₃ F	28.8	31.5	23.0
total	21.2	20.0	14.4

from both quantum levels. These QTAIM/CCFDF results are almost in exact agreement with the intensity values calculated directly from the molecular wave functions. The rms differences are 0.016 and 0.018 km mol⁻¹ for the MP2/6-311++G(3d,3p) and QCISD/cc-pVTZ levels.

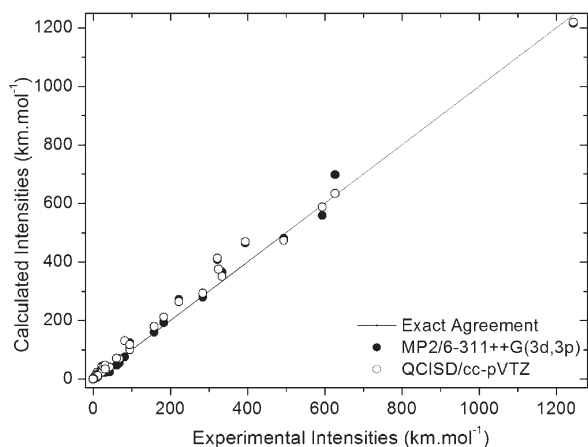


Figure 1. Graph of the MP2/6-311++G(3d,3p) and QCISD/cc-pVTZ intensities against the experimental ones for the fluorochloromethanes.

Table 3 contains values of the charge, charge flux, and dipole flux contributions to the mean dipole moment derivative for each atom of the fluorochloromethanes at both quantum levels. Mean derivatives are invariant to molecular orientation relative to the Cartesian coordinate system, permitting meaningful comparisons among values for different molecules. Of the five polar tensor invariant quantities, the mean derivative is highly correlated to three of them and together they account for about 75% of the total variance in the polar tensor data.⁴¹ The sum of the CCFDF contributions as well as the mean derivative values obtained from the experimental intensities^{20,21,26,29,42–54} are included in this table. The MP2/6-311++G(3d,3p) and QCISD/cc-pVTZ mean dipole moment derivatives agree very well with the experimental values having rms errors of 0.048 and 0.059 e , respectively. This good agreement can be observed in Figure 2 where the theoretical mean derivatives are plotted against the experimental values. As can be seen, there the points for the dipole moment derivatives calculated at both theoretical levels overlap and are close to the line representing exact agreement, although derivative values above 0.5 e tend to be overestimated by both quantum levels.

An unambiguous interpretation of the electronic densities is possible if the QTAIM/CCFDF parameters are not too sensitive to the quantum level used in their calculation. Figure 3 shows a graph of the QCISD/cc-pVTZ QTAIM/CCFDF contributions against those calculated at the MP2/6-311++G(3d,3p) level. The agreement is good although the QCISD/cc-pVTZ charge and charge flux values are seen to be systematically higher than the MP2/6-311++G(3d,3p) ones. In contrast, the dipole flux values at the MP2 level are higher than the QCISD values. As such, the results for the total mean dipole moment derivative values of these two quantum levels are in the excellent agreement as already seen in Figure 2. Therefore, some caution must be exercised in the quantitative interpretation of these parameters because the agreement between the individual QTAIM/CCFDF contributions calculated at different theoretical levels may not be as good as the ones for their total mean dipole moment derivatives.

DISCUSSION

Simple Electronegativity Model. In Figure 4 the mean dipole moment derivatives of the fluorochloromethanes are graphed as a function of their electronegativity values. The electronegativities of the terminal atoms are the Mulliken–Jaffe scale values,

12.18, 9.38, and 7.17, for the fluorine, chlorine, and hydrogen atoms, respectively. The electronegativity values used in this figure for terminal atoms are values relative to hydrogen (0 for hydrogen, -5.02 for fluorine, and -2.22 for chlorine). The hydrogen atom mean derivatives are located at the origin. The negative mean derivatives in the figure correspond to the fluorine and chlorine atoms. The carbon atom mean dipole moment derivatives are plotted against the absolute values of the sums of their terminal atom electronegativities relative to hydrogen. The darkened symbols in Figure 4 represent the experimental mean dipole moment derivatives and fall on a straight line with the carbon mean derivative for methane almost exactly on the origin. The carbon atom mean derivatives with positive values are those of the fluorochloromethanes ranging from the one for CH_3Cl close to the methane point to the one for CF_4 on the far right. In contrast, the halogen mean derivatives form tightly clustered groups, showing that they are highly transferable within the fluorochloromethanes with almost constant values of -0.532 ± 0.054 , -0.245 ± 0.045 , and -0.004 ± 0.022 e for the fluorine, chlorine, and hydrogen atoms.

These mean dipole moment derivative results suggest that a simple electronegativity model² can be used to describe the electronic structures of the CFCs. The fluorine, chlorine, and hydrogen mean derivatives are assumed to be transferable and proportional to their atomic electronegativities. Assigning the above average values for the mean derivatives of the terminal atoms of the CFCs, we can determine the carbon derivatives from the charge neutrality condition. These values have also been included in Figure 4 and are represented by the open symbols. The agreement is excellent between the electronegativity model results and the experimental mean dipole moment derivatives.

However, the QTAIM/CCFDF parameter values indicate that the electronic structures of the fluorochloromethanes are somewhat more complex. Figure 5 contains a graph of the atomic charge contributions calculated from the QCISD/cc-pVTZ wave functions, the QTAIM zero flux charges, against the electronegativity values.

Instead of having one linear relationship, as do the mean derivatives, three linear arrangements of points can be seen, (1) the terminal atom charges and the carbon atom charges of the fluoromethanes, (2) the carbon charges of the chloromethanes, and (3) the carbon charges of the fluorochloromethanes. The fluorine atomic charge symbols on the lower left are all superimposed. The fluorine atomic charges in the CH_xF_y and CCl_xF_y molecules are indeed very transferable, having an average value of -0.694 ± 0.009 e from the QCISD calculations (or -0.629 ± 0.015 e from the MP2 wave functions). As such, no saturation effect is found for these fluorine atoms because they gain equal quantities of electron densities at the expense of the carbon atoms independent of how many fluorine or chlorine atoms are already bound to carbon. This is not true for the chlorine atoms. The chlorine negative charges calculated at the QCISD level systematically decrease from -0.271 e in methyl chloride to -0.117 e in tetrachloromethane. Furthermore, the chlorine charges in the fluorochloromethanes are small, about -0.130 e and relatively constant. If the chlorine atoms did not suffer saturation effects in their capacities to drain electronic charge from carbon atoms that are attached to other fluorine or chlorine atoms, one would expect all the chlorine atoms to have the same charge as the one in methyl chloride, -0.271 e from the QCISD/cc-pVTZ wave functions. Assigning this value to all the chlorine atoms of the fluorochloromethanes, maintaining the constant fluorine charge of -0.694 e , and invoking the charge neutrality

Table 3. MP2/6-311++G(3d, 3p), QCISD/cc-pVTZ, and Experimental Mean Dipole Moment Derivatives and Their Charge, Charge Flux, and Dipole Flux Contributions (*e*)

	MP2/6-311++G (3d, 3p)				QCISD/cc-pVTZ				exp
	C	CF	DF	(C + CF + DF)	C	CF	DF	(C + CF + DF)	
CH ₄ ⁴²									
C	0.086	−0.485	0.400	0.002	0.013	−0.354	0.362	0.021	0.016
H	−0.021	0.121	−0.100	0.000	−0.003	0.089	−0.091	−0.005	−0.004
CH ₃ F ^{43–45}									
C	0.642	−0.491	0.399	0.550	0.650	−0.360	0.289	0.579	0.541
F	−0.644	0.158	−0.015	−0.501	−0.699	0.145	0.067	−0.487	−0.490
H	0.001	0.111	−0.127	−0.015	0.016	0.072	−0.118	−0.030	−0.017
CH ₂ F ₂ ^{20, 46}									
C	1.223	−0.546	0.411	1.088	1.314	−0.413	0.216	1.117	1.105
F	−0.644	0.157	−0.035	−0.522	−0.703	0.133	0.052	−0.517	−0.488
H	0.032	0.116	−0.170	−0.022	0.046	0.073	−0.161	−0.042	−0.018
CHF ₃ ^{21, 47}									
C	1.846	−0.692	0.418	1.572	2.021	−0.557	0.140	1.604	1.523
F	−0.641	0.183	−0.066	−0.524	−0.704	0.152	0.027	−0.524	−0.507
H	0.077	0.141	−0.231	−0.013	0.091	0.101	−0.222	−0.030	0.042
CF ₄ ⁴⁸									
C	2.512	−0.980	0.508	2.040	2.786	−0.845	0.115	2.055	2.051
F	−0.628	0.245	−0.127	−0.510	−0.696	0.211	−0.029	−0.514	−0.512
CH ₃ Cl ^{26, 49}									
C	0.191	−0.189	0.275	0.277	0.140	−0.039	0.199	0.301	0.277
Cl	−0.254	−0.080	0.058	−0.275	−0.271	−0.092	0.088	−0.276	−0.271
H	0.021	0.089	−0.111	−0.001	0.044	0.044	−0.096	−0.008	−0.002
CH ₂ Cl ₂ ⁵⁰									
C	0.271	0.232	0.081	0.585	0.255	0.357	0.002	0.614	0.531
Cl	−0.197	−0.168	0.081	−0.284	−0.214	−0.174	0.099	−0.289	−0.258
H	0.061	0.052	−0.121	−0.008	0.087	−0.004	−0.100	−0.018	−0.008
CHCl ₃ ^{29, 51}									
C	0.337	0.728	−0.168	0.898	0.363	0.792	−0.231	0.925	0.826
Cl	−0.145	−0.245	0.100	−0.289	−0.163	−0.246	0.113	−0.296	−0.267
H	0.097	0.008	−0.134	−0.029	0.124	−0.055	−0.107	−0.037	−0.022
CCl ₄ ⁵²									
C	0.397	1.251	−0.448	1.200	0.466	1.237	−0.491	1.212	1.043
Cl	−0.099	−0.313	0.112	−0.300	−0.117	−0.309	0.123	−0.303	−0.261
CClF ₃ ⁵³									
C	1.958	−0.295	0.200	1.863	2.211	−0.202	−0.103	1.906	1.907
F	−0.623	0.177	−0.093	−0.539	−0.692	0.134	0.016	−0.543	−0.590
Cl	−0.090	−0.235	0.079	−0.246	−0.135	−0.199	0.068	−0.265	−0.139
CCl ₂ F ₂ ⁵⁴									
C	1.422	0.300	−0.054	1.668	1.636	0.350	−0.268	1.718	1.636
F	−0.616	0.132	−0.069	−0.553	−0.687	0.082	0.041	−0.563	−0.585
Cl	−0.095	−0.282	0.096	−0.281	−0.131	−0.257	0.093	−0.295	−0.233
CCl ₃ F ⁵⁴									
C	0.900	0.814	−0.268	1.446	1.051	0.822	−0.389	1.484	1.352
F	−0.607	0.107	−0.055	−0.556	−0.680	0.056	0.058	−0.566	−0.514
Cl	−0.098	−0.307	0.108	−0.297	−0.124	−0.292	0.110	−0.306	−0.279
rms				0.048				0.059	

condition would result in the carbon atomic charge values represented by the open starred symbols in Figure 5. As can be seen, there all the carbon atoms in the chloro- and fluorochloromethanes would fall on the same straight line as those of the

carbon atoms in the fluoromethanes that follow a simple electronegativity model.

Simple Potential Model. Some years ago Siegbahn's simple potential model⁸ for the carbon atom 1s core electron energies

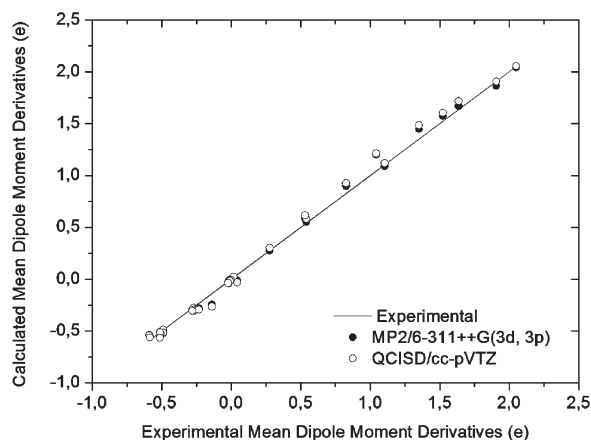


Figure 2. Graph of the MP2/6-311++G(3d, 3p) and QCISD/cc-pVTZ mean dipole moment derivatives against the experimental values.

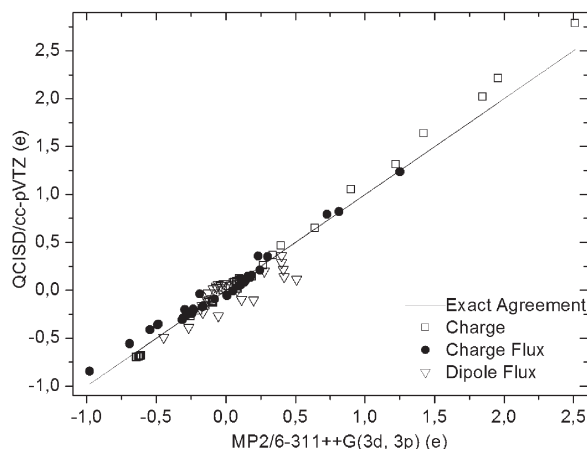


Figure 3. Graph of the QTAIM/CCFDF contributions to the mean dipole moment derivative obtained with the MP2/6-311++G(3d,3p) and QCISD/cc-pVTZ wave functions.

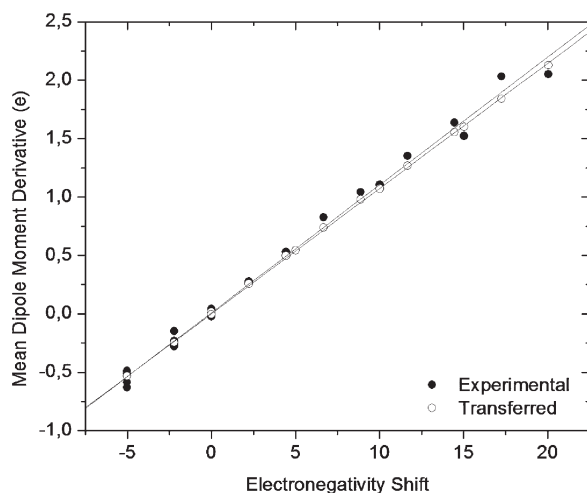


Figure 4. Experimental mean dipole moment derivative values as a function of electronegativity shifts as explained in the text (hydrogen, 0; fluorine, -5.02 ; chlorine, -2.22).

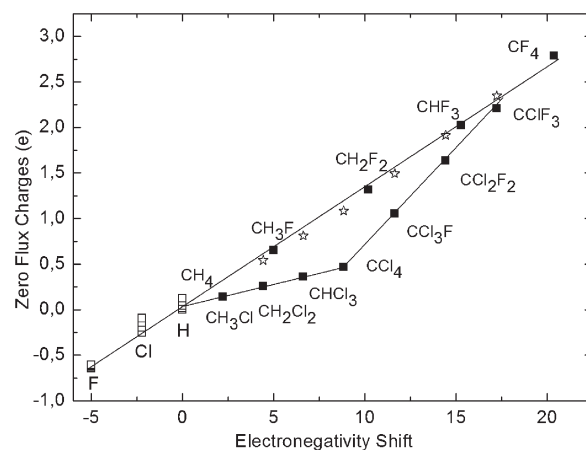


Figure 5. Graph of the QCISD/cc-pVTZ charge contributions (square symbols) to the mean dipole moment derivatives vs electronegativity shifts. The star symbols represent transferred values as explained in the text.

was shown to hold for the carbon mean dipole moment derivatives,⁷ \bar{p}_C , derived from infrared fundamental gas-phase intensities

$$E_{C,1s} = k\bar{p}_C + \sum_{i \neq C} (\bar{p}_i/R_{Ci}) + E_{\text{rel}} = k\bar{p}_C + V_{\text{charge}} + E_{\text{rel}} \quad (5)$$

where R_{Ci} is the internuclear distance between the carbon and the neighboring i -th atom, k is a constant, and E_{rel} is the core electron ionization relaxation energy.⁵⁵ Because the simple potential model was originally derived to relate core electron ionization energies to atomic charges, the good fit of this equation seems to justify the interpretation of the mean dipole moment derivative as an atomic charge. However, the mean dipole moment derivative has long been known by spectroscopists to consist of dynamic contributions as well as an equilibrium static charge contribution¹⁰ and these contributions have been quantified here by the QTAIM/CCFDF model.

Siegbahn's simple potential model applied to the fluorochloromethanes implies that a graph of the carbon 1s ionization energies adjusted for their neighboring atom electrostatic potentials and relaxation energies plotted against the atomic charges of the carbon atoms would result in a straight line. In fact, the graph of these corrected experimental ionization energies against the experimental carbon mean dipole moment derivatives of the fluorochloromethanes produces a straight line with a $r = 0.992$ correlation coefficient.⁵⁵ This seems to provide experimental evidence that the mean dipole moment derivatives do indeed have properties very similar to those of atomic charges.

Figure 6 contains a graph of Siegbahn's simple potential model for the carbon mean dipole moment derivatives of the fluorochloromethanes calculated at the QCISD/cc-pVTZ level. The experimental ionization energies,⁵⁶ neighboring atom electrostatic potentials, and relaxation energies (obtained at the HF/6-311++G(3df,3p) level)⁵⁵ are given in Table 4. The points display a strong linear behavior with $r = 0.996$.

However, adherence of these mean dipole moment derivative values to the potential model is a mere consequence of the fact that they obey the electronegativity model. This can be demonstrated by applying the transferred carbon atomic charges that follow the electronegativity model and are shown by the starred

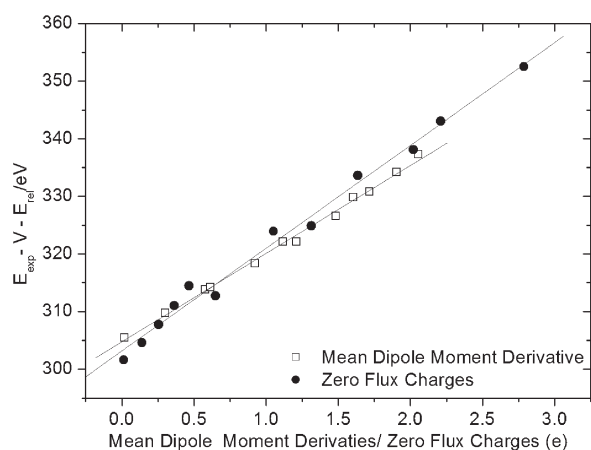


Figure 6. Graph of the 1s electron ionization energies adjusted by their neighboring atom electrostatic potentials and relaxation energies vs either the carbon mean dipole derivatives or the carbon atom zero flux charges calculated at the QCISD/cc-pVTZ level. V is a sum of the charge and dipole contributions to the neighboring atom electrostatic potential.

Table 4. Experimental Carbon 1s Electron Ionization Energies and Charge and Dipole Contributions to the Neighboring Atom Electrostatic Potentials and Relaxation Energies for the 1s Ionizations (eV)

	$E_{1s,C}^{56}$	E_{rel}^{55}	V_{charge}	V_{dipole}	V_{total}
CH ₄	290.90	−14.26	−0.18	3.74	3.56
CH ₃ F	293.60	−13.97	−6.66	1.49	−5.17
CH ₂ F ₂	296.36	−13.62	−13.77	−1.12	−14.89
CHF ₃	299.10	−13.25	−21.66	−4.10	−25.76
CF ₄	301.85	−12.92	−30.48	−7.27	−37.75
CH ₃ Cl	292.48	−14.75	−0.44	3.07	2.63
CH ₂ Cl ₂	293.90	−15.17	−1.17	2.48	1.31
CHCl ₃	295.10	−15.56	−2.31	1.94	−0.37
CCl ₄	296.34	−15.95	−3.79	1.63	−2.16
CClF ₃	300.31	−13.95	−23.74	−5.06	−28.80
CCl ₂ F ₂	298.93	−14.78	−17.05	−2.85	−19.90
CCl ₃ F	297.54	−15.44	−10.36	−0.59	−10.95

symbols in Figure 5 to Siegbahn's simple potential model for the carbon 1s ionization energies. An almost perfect straight line, shown in Figure 1S (Supporting Information), with a correlation coefficient of 0.999, results. On the other hand, the graph of $E_{C,1s} - V - E_{rel}$ vs the zero flux charges, shown in Figure 2S (Supporting Information), calculated at the QCISD level that yields chlorine atomic charges that suffer saturation effects and do not follow the electronegativity model, results in a straight line with a lower correlation coefficient, $r = 0.987$.

Equation 5 is approximate because only atomic charges have been used to estimate the neighboring atom electrostatic potentials. The model would be expected to be more realistic if the electrostatic potentials were included owing to higher order moments. The electrostatic potential contribution from the atomic dipoles is given by

$$V_{dipole} = \sum_i \vec{m}_i \cdot \vec{e}_i / R_{Ci}^2 \quad (6)$$

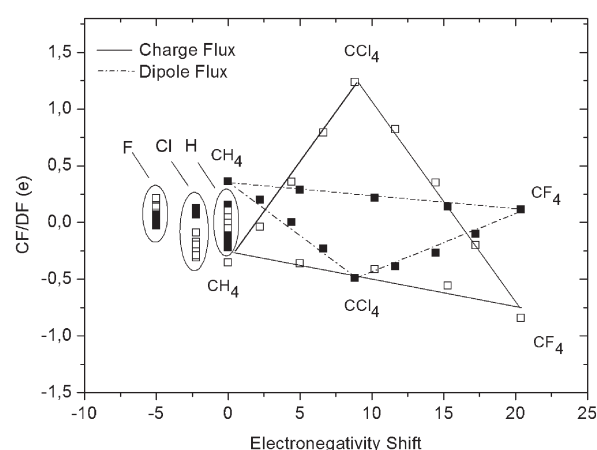


Figure 7. Graph of the QCISD/cc-pVTZ charge flux and dipole flux contributions vs electronegativity shift values. Open squares represent charge flux, and solid squares, the dipole flux contributions.

where \vec{m}_i is the atomic dipole on the i -th atom, \vec{e}_i is a unit vector directed along the bond between carbon and the i -th atom.

These potential contributions for the fluorochloromethanes were calculated with the QTAIM QCISD/cc-pVTZ atomic charges and dipole components given in Table 1S as Supporting Information and have been included in Table 4. The neighboring atom electrostatic potential contributions from the atomic dipoles relative to those from the charges are certainly not negligible. In fact, the absolute values of the dipole contributions are even larger than the charge ones for methane, methyl chloride, and methylene chloride, these being the molecules with nonpolar or slightly polar bonds for the fluorochloromethanes.

Figure 6 includes a potential model plot of the experimental 1s carbon ionization energies adjusted for the neighboring atom electrostatic potential contributions from both the QTAIM atomic charges and dipoles and for the relaxation energies. The points do fall close to a straight line with $r = 0.990$, an improvement in linearity over the one obtained by just using the atomic charge contributions from the neighboring atoms. But the points are still not as linear as those for charges following the electronegativity model. However, one can expect that including higher order multipole contributions to the electrostatic potential, V , would improve linearity for the zero flux charges even more.

The MP2/6-311++G(3d,3p) mean derivative values are very similar to those calculated at the QCISD level, as already seen, and their use in the potential model plot results in graphs very similar to the ones in Figure 6 with $r = 0.997$ for the mean derivatives and $r = 0.984$ and $r = 0.980$ for the zero flux atomic charges with and without the atomic dipole contributions to the electrostatic neighboring atom potentials.

Dynamic Contributions. The description of the charge flux and dipole flux parameters is conveniently represented as functions of electronegativity, as can be seen in Figure 7. QCISD level values are given although the MP2 results provide a very similar description. The charge flux and dipole flux contributions of the hydrogen, fluorine, and chlorine atoms are relatively constant, forming tight groups of points on the left of the figure. There are tendencies for the charge flux values to have opposite signs to the dipole flux contributions, but there are some exceptions.

The charge and dipole flux contributions of the carbon atoms show much larger variations than those of their substituent atoms. The charge flux points in Figure 7 approximate a triangle

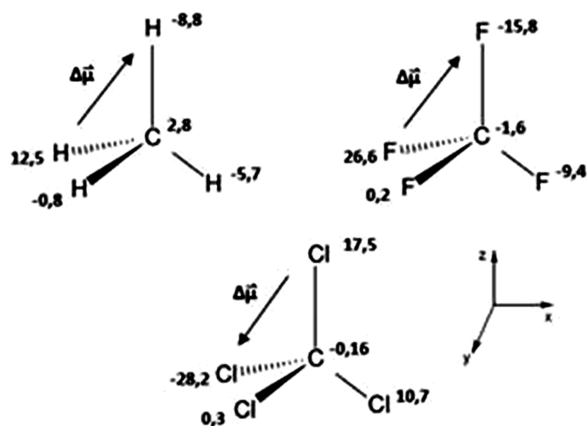


Figure 8. Net atomic charge (QCISD/cc-pVTZ) transfers on simultaneously displacing the carbon atom 0.01 Å in the positive x , y , and z directions for CH_4 , CF_4 , and CCl_4 . The arrows represent the net atomic dipole changes with polarity $- \rightarrow +$.

with the CH_4 , CF_4 , and CCl_4 molecules at the vertices. The base of the triangle is formed by the fluoromethane points whereas the chloromethane and fluorochloromethane points delineate the sides. The dipole flux points form an inverted and flatter triangle.

The carbon charge and dipole flux contributions show very regular changes on substitution within the chloromethanes and the fluorochloromethanes. The fluoromethanes show monotonic but somewhat less regular changes in the charge fluxes on fluorine substitution. The slopes of the lines in Figure 7 can be used to obtain average substitution effect values. When fluorine is substituted for hydrogen in the fluoromethanes the charge flux decreases on average by about $-0.123 e$ for each additional fluorine while the dipole flux decreases by about half that amount, $-0.062 e$. When chlorine is substituted for hydrogen, the charge flux on carbon increases by $0.398 e$ for each chlorine substitution. For each chlorine substitution for hydrogen, the dipole flux decreases by $-0.213 e$. These effects are additive, as indicated by the closed triangular forms. The average effect of substituting fluorine by chlorine on the carbon charge flux, $0.523 e$ per substitution, is almost exactly the sum of the fluorine by hydrogen substitution effect, $0.123 e$ and the hydrogen by chlorine substitution effect, $0.398 e$. This is also true for the carbon dipole flux. The hydrogen by chlorine substitution effect, $-0.213 e$, is the sum of the effects of substituting hydrogen by fluorine, $-0.062 e$ and fluorine by chlorine, $-0.152 e$.

Molecular diagrams illustrating the charge flux and dipole flux contributions to the carbon mean dipole moment derivatives of CH_4 , CF_4 , and CCl_4 are shown in Figure 8. The numbers in the figures are the quantities of net electronic charge ($\times 10000$) transferred to the atoms for simultaneous displacement of the carbon atom by $+0.01 \text{ Å}$ along the x , y , and z axes. The CX bonds in the xz plane become shorter; the one pointing in the positive y direction hardly changes length whereas the CX bond in the negative y direction becomes longer.

The charges on the terminal atoms of the shortened bonds of CH_4 and CF_4 become more negative mostly at the expense of the terminal atoms of the lengthened bonds that become more positive. The carbon atom charge is hardly changed, remaining almost the same as at equilibrium. Furthermore, the changes in charge on the terminal atoms are proportional to the sizes of their atomic displacements from equilibrium. When small angular

changes are neglected, $\partial q/\partial R$ values of $+0.08$ and $+0.16 e/\text{Å}$ are obtained for CH_4 and CF_4 , respectively. The net atomic dipole change vectors are represented by the arrows. Their polarities are opposite to the changes in polarity owing to intramolecular electronic charge transfer in these molecules. The polarities of both the charge flux and dipole flux contributions in CCl_4 are opposite to those in CH_4 and CF_4 . Note that the sizes of the charge transfers in CCl_4 are about the same as those in CF_4 but opposite in sign. For CCl_4 $\partial q/\partial R$ is $-0.18 e/\text{Å}$ compared to $+0.16 e/\text{Å}$ in CF_4 .

CONCLUSIONS

In summary, three main conclusions can be made on the basis of the results presented in this manuscript. First, although the experimental mean dipole moment derivative values suggest that the fluorochloromethanes have electronic structures consistent with an electronegativity model, QTAIM/CCFDF models at the QCISD/cc-pVTZ and MP2/6-311++(3d,3p) levels show this to be only true for the fluoromethanes. Second, the carbon mean dipole moment derivatives of the fluorochloromethanes are consistent with Siegbahn's simple potential model for the carbon 1s ionization energies because they obey the electronegativity model, not necessarily because of their similarities to atomic charges. Finally, terminal atom substitution effects on the charge and dipole fluxes are seen to be additive for the hydrogen, fluorine, and chlorine atoms.

ASSOCIATED CONTENT

S Supporting Information. Tables of QTAIM atomic charges and dipole components determined at the QCISD/cc-pVTZ level. Graphs with transferred and actual carbon zero flux charges vs the respective 1s electron ionization energies adjusted by their neighboring atom electrostatic potentials and relaxation energies without corrections due to atomic dipoles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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