

Atomic Polar Tensor Transferability and Atomic Charges in the Fluoromethane Series

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The atomic polar tensors (APT) of the fluorine and hydrogen atoms for the fluoromethanes are calculated and analyzed with respect to the charge, charge flux, and atomic and homopolar dipole fluxes. Their atomic and bonding contributions are used to discuss the transference of the fluorine and hydrogen APT among these molecules. The contributions of the APT can be written as the sum of a charge and a charge flux tensor leading to a charge-charge flux model. A novel expression for the atomic charge is obtained on the basis of this proposed charge-charge flux model. The defined atomic charge is calculated for both atoms for this series of molecules. The calculated hydrogen atomic charges vary similarly to the respective equilibrium charges obtained experimentally but in the opposite direction of the Mulliken charges.

Introduction

In a recent work,¹ a method for partitioning the dipole moment vector and the atomic polar tensor has been proposed. In the present work, that method is applied to the fluoromethanes CF_xH_{4-x} with $x = 1-4$. By the transference of the experimental polar tensors to different but related molecules, the infrared intensities of the fundamental bands in the gas phase have been predicted.²⁻⁴ The transference is especially desirable for those cases where the experimental measurements are difficult to carry out. For some molecules, the predicted intensities are exceptionally good, but for others they are quite poor. By the transference of the fluorine and hydrogen experimental tensors from methyl fluoride (CH₃F) and methane (CH₄), respectively, Person et al.² have predicted with excellent agreement the intensities of tetrafluoromethane (CF₄) but with only reasonable accuracy the intensities of methylene fluoride and fluoroform (CH₂F₂ and CHF₃). The hydrogen polar tensor for methyl fluoride is also commonly used in transference studies. Galabov et al.⁵ have also studied the experimental data of the fluorinated methanes using the bond polar parameter method and found that most of the parameters in the series CH₃F, CH₂F₂, and CHF₃ differ in magnitude, leading to the conclusion that these parameters cannot be transferred to predict intensities. On the other hand, Kim and Park⁶ found that the fluorine and hydrogen polar tensors calculated by ab-initio methods seemed to be transferable among these molecules.

To gain more information about the nature of these atomic polar tensors (APT) and their transferability, theoretical fluorine and hydrogen tensors will be calculated in the present work using ab-initio methods and interpreted through the partitioning: charge, charge flux, atomic dipole flux, and homopolar dipole flux. The different contributions of the atomic polar tensors will also be analyzed in two different ways. First, the atomic and bonding contributions are introduced to find some criteria which could be used to help us decide under what conditions the polar tensor of the fluorine and hydrogen atoms can be transferred to another structurally related molecule. Second, the contributions to the APT are taken as the sum of charge and charge flux tensors. Since the APT is an atomic quantity, a new definition of atomic charge in the molecule will be proposed on the basis of the charge tensor mentioned above. Unlike the APT, this defined atomic charge is invariant under rotation of the molecule. Atomic charges for both atoms have been calculated and compared for these molecules.

Calculations

As reported in our previous work,¹ the general expression for the atomic polar tensor partitioning for the α th atom is obtained

by taking the gradient of the dipole moment vector \mathbf{p} as

$$\nabla_{\alpha}\mathbf{p} = q_{\alpha}\mathbf{E} + \sum_{\Lambda}(\nabla_{\alpha}q_{\Lambda})\mathbf{R}_{\Lambda} - \sum_{\Lambda} \sum_{\mu < \nu} \nabla_{\alpha}(2P_{\mu\nu}\mathbf{R}_{\mu\nu}^{\Lambda}) - \sum_{A < B} \sum_{\mu} \sum_{\nu} \nabla_{\alpha}(2P_{\mu\nu}\mathbf{R}_{\mu\nu}^{AB}) \quad (1)$$

where q_{α} is Mulliken's net atomic charge of atom α and \mathbf{E} a (3 × 3) unit matrix. \mathbf{R}_{Λ} is the vector position of nucleus Λ and $P_{\mu\nu}$ a density matrix element. $\mathbf{R}_{\mu\nu}^{\Lambda}$ and $\mathbf{R}_{\mu\nu}^{AB}$ have already been defined in ref 1. ($\mathbf{R}_{\mu\nu}^{\Lambda}$) represents the center of charge of the hybrid orbital ($\mu\nu$), where μ and ν indicate orbitals of atom Λ , and $\mathbf{R}_{\mu\nu}^{AB}$ represents the bonding center of charge since μ and ν belong to different atoms, A and B , whether chemically bonded or not. These contributions in expression 1 are known, respectively, as charge, charge flux, atomic dipole flux, and homopolar dipole flux. All of the atomic polar tensors have been calculated by the SCF method using a 4-31G basis set, and the results are in good agreement with experimental values as will be seen in the next section. For the fluorine polar tensor, the CF chemical bond is parallel to the Z axis for all molecules. The hydrogen atom is in the XZ plane for the CH₃F and CHF₃ molecules, while fluorine lies in this plane for the CH₂F₂ and CF₄ molecules. The CH bond for the hydrogen polar tensors is parallel to the Z axis. The fluorine atom is in the XZ plane for the CH₃F and CHF₃ molecules. The APT elements (dipole moment derivatives with respect to Cartesian coordinates) are evaluated by calculating the molecular wave function and centers of charge at the equilibrium geometry, followed by similar calculations for fluorine shifted from its equilibrium position by 0.02 au along the x , y , and z directions, respectively. The derivatives are obtained by the finite-difference approximation, i.e., by the ratio of the difference in the dipole moment value and the 0.02-au displacement. Since the density matrix and the centers of charge are changed as the chemical bond is distorted from its equilibrium position, the gradient of the atomic and homopolar dipole flux terms of eq 1 can be partitioned into two parts each. For the homopolar dipole flux we have

$$-\sum_{B \neq \alpha} \sum_{\mu} \sum_{\nu} 2P_{\mu\nu}(\nabla_{\alpha}\mathbf{R}_{\mu\nu}^{\alpha\beta}) \quad \text{and} \quad -\sum_{A < B} \sum_{\mu} \sum_{\nu} 2(\nabla_{\alpha}P_{\mu\nu})\mathbf{R}_{\mu\nu}^{AB} \quad (2)$$

The $P_{\mu\nu}$ values are the interatomic density matrix elements. The left-hand term in eq 2 takes into account the centers of charge gradients. The movement of the frozen electronic charge is also described in this expression. Since this term involves a frozen electronic charge, it will be called the bonding charge tensor. The gradient of the density matrix (interatomic elements only), which shows in the last term of eq 2, results from a distortion of the electronic cloud while the centers of charge are maintained at their equilibrium positions. This term can be associated with a charge flux. For the atomic dipole flux, the gradient of the centers of charge is always zero, so there is only a charge flux contribution, given by

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$$-\sum_{A \mu < \nu} \sum^A 2(\nabla_{\alpha} P_{\mu\nu}) \bar{\mathbf{R}}_{\mu\nu}^A \quad (3)$$

Adding all of the charge fluxes, i.e., the charge flux with respect to the net atomic charge (eq 1) and the charge fluxes from the atomic (eq 3) and homopolar (eq 2) dipole fluxes, the atomic polar tensor for the α th atom is partitioned into the following contributions:

charge

$$q_{\alpha} \mathbf{E} \quad (4a)$$

bonding charge

$$-\sum_{B \neq \alpha} \sum_{\mu} \sum_{\nu}^B 2P_{\mu\nu} (\nabla_{\alpha} \bar{\mathbf{R}}_{\mu\nu}^{\alpha B}) \quad (4b)$$

charge flux

$$\sum_A (\nabla_{\alpha} q_A) \mathbf{R}_A - \sum_{A \mu < \nu} \sum^A 2(\nabla_{\alpha} P_{\mu\nu}) \bar{\mathbf{R}}_{\mu\nu}^A - \sum_{A < B} \sum_{\mu} \sum_{\nu}^B 2(\nabla_{\alpha} P_{\mu\nu}) \bar{\mathbf{R}}_{\mu\nu}^{AB} \quad (4c)$$

The charge and bonding charge tensors (eqs 4a and 4b, respectively) can be added to define a total charge tensor:

$$P_x^{(\alpha)} \text{ch} = q_{\alpha} \mathbf{E} - \sum_{B \neq \alpha} \sum_{\mu} \sum_{\nu}^B 2P_{\mu\nu} (\nabla_{\alpha} \bar{\mathbf{R}}_{\mu\nu}^{\alpha B}) \quad (5)$$

On the basis of this partitioning, the APT for atom α will be interpreted as a sum of only two tensors: charge tensor (eq 5) and charge flux tensor (eq 4c), leading to a charge-charge flux model. Note that the charge tensor ($P_x^{(\alpha)} \text{ch}$) is not represented by a diagonal tensor. Consequently, a measure of an atomic charge ($Q_{(\alpha)}$) in the atom α might be defined either by the trace or by the Euclidean norm of the $P_x^{(\alpha)} \text{ch}$ matrix:

$$Q_{(\alpha)} = \frac{1}{3} \text{Tr}(P_x^{(\alpha)} \text{ch}) \quad (6a)$$

$$Q_{(\alpha)} = \sqrt{\frac{1}{3} \text{Tr}(P_x^{(\alpha)} \text{ch})(P_x^{(\alpha)} \text{ch})^T} \quad (6b)$$

It can be easily shown that the expressions defined by eqs 6a and 6b are invariant under rotation of the molecule.

A disadvantage of using the definition 6b is that for the case of a neutral molecule the sum of the atomic charges will not be zero, although very closely so. In view of this, eq 6a will be taken as a new definition of atomic charge in the molecule.

Discussion

Fluorine APT. The results discussed below refer to the partition of the APT from three points of view. Tables I, III, and IV show the numerical results for those partitions.

The results in Table I show that the Mulliken net atomic charge of fluorine becomes more negative as the F atoms are replaced by hydrogen atoms; i.e., the highly polar CF bond becomes more polar as the electronegative fluorine atoms are replaced by the much less electronegative hydrogen atoms. For the CF stretching, the charge flux vector ($\partial p / \partial Z_{\alpha}$), which is basically the P_{zz} element of the charge flux tensor, has the same sign as the net atomic charge but varies much more strongly, decreasing in magnitude with the values -0.423 , -0.418 , -0.317 , and -0.152 e for CF₄, CHF₃, CH₂F₂, and CH₃F, respectively. Consequently, with a stretching of the CF bond there is an increase in the negative character of the terminal atom and the charge fluxes are much smaller for the more polar bond. As noted before by Neto et al.,⁷ the net atomic charge of the carbon for CF₄ is 1.475 e and decreases approximately by 0.5 e for each fluorine that is being replaced (0.998, 0.504, and -0.035 e for CHF₃, CH₂F₂, and CH₃F respectively). The atomic dipole flux, like the charge flux mentioned above, is a sum over all atoms in the molecule except for the hydrogens, since hybridization is not possible. The non-negligible off-diagonal elements of the atomic dipole flux matrix shown in Table I for the CHF₃ and CH₂F₂ molecules are due to the fact that their permanent dipole moment vectors lie in the XZ plane but are not oriented along the Z direction. In spite of this, the first two diagonal elements of this contribution for all of the

TABLE I: Calculated Polar Tensor Contributions for the Fluorine Atom^a

molecule	charge	charge flux	atomic dipole flux	homopolar dipole flux	$P_x^{(\alpha)}$
CF ₄	-0.369	-0.107	-0.133	0.176	-0.437
		-0.423	-0.029	0.172	-0.436
CHF ₃	-0.405	-0.087	-0.128	0.182	-0.423
		-0.003	-0.106	0.203	-0.437
CH ₂ F ₂	-0.438	-0.008	-0.158	0.098	-0.049
		-0.418	-0.142	0.204	-0.441
CH ₃ F	-0.464	0.025	-0.126	0.196	-0.030
		-0.317	-0.228	0.068	-0.378
		-0.152	-0.262	0.196	-0.382
				0.046	-0.380
				0.162	
				0.109	
				0.119	
				0.106	
				0.042	
				0.053	
				-0.856	
				0.046	
				-0.878	
				-0.836	

^aUnits are e. Basis set 4-31G; F atom along the z axis.

TABLE II: P_{zz} Elements for the Atomic Dipole Flux of the Fluorine Tensor^a

	C	F ^b	other F atoms ^c	P_{zz}
CF ₄	-0.149	0.005	0.038	-0.029
CHF ₃	-0.205	-0.013	0.038	-0.142
CH ₂ F ₂	-0.245	-0.020	0.037	-0.228
CH ₃ F	-0.255	-0.006		-0.262

^aUnits are e. ^bF atom along the z axis. ^cPer atom.

fluorinated methanes are approximately the same. Their average values for the molecules in this series from CF₄ to CH₃F are, respectively, -0.133, -0.138, -0.139, and -0.137 e. Those values are mostly due to the rehybridization that occurs in the fluorine atom (along the Z direction) when it is moved in the X and Y axes (perpendicular to the chemical bond). Contrary to the behavior of these two diagonal terms, the P_{zz} element values, which are due to the movement of the F atom along the chemical bond, vary greatly, ranging from -0.029 e in CF₄ to -0.262 e for the CH₃F molecule. Note that this variation is opposite in direction of that of the charge flux.

To understand these variations, the individual contributions should be analyzed. These results for the P_{zz} elements of the atomic dipole flux are shown in Table II. There is a positive contribution of about 0.038 e from each of the fluorine atoms for the CF₄, CHF₃, and CH₂F₂ molecules. Yet, as the CF bond is stretched, there is almost no contribution from the F atom that is being moved (specially for CF₄ and CH₃F), which means that the rehybridization on this fluorine atom is negligible. The high contribution from the central atom increases as the electronegativity of the atoms attached to it is decreased. This explains why the P_{zz} contribution from the atomic dipole flux becomes more negative for the CH₃F than for the CF₄.

The last contribution to the APT in Table I is the homopolar dipole flux which is due to the interatomic interactions. As seen in the charge flux and atomic dipole flux, there are off-diagonal elements for fluoroform and methylene fluoride. The similarity between tetrafluoromethane and methyl fluoride homopolar dipole flux tensors should be noted. There is a loss of site symmetry of the fluorine atom, which is C_{3v} in CF₄ and CH₃F and C_s in CHF₃ and CH₂F₂. So, it seems that the homopolar dipole flux tensor represents the contribution to the APT which is mostly related to the site symmetry of the fluorine atom. The first two diagonal elements are approximately the same for all molecules, with average values of 0.174, 0.193, 0.198, and 0.196 for CF₄ to CH₃F. Except for the P_{zz} element, the general trend of the homopolar dipole flux elements is to cancel the correspondent atomic dipole flux elements, yielding approximately 0.06 e. The sum of these dipole fluxes—atomic and homopolar—is called the overlap contribution by Person.⁷

The atomic contribution to the APT is obtained by summing the net atomic charge, the charge flux, and the atomic dipole flux. These results are listed in Table III. The experimental tensors are also shown in this table for comparison. The experimental

fluorine tensor corresponds to the sign choice for which the terminal atom (H or F) becomes more negative with the stretching motion of the CF or CH bond. These values are in good agreement with the theoretical results. The larger differences show on the P_{xx} and P_{yy} elements, which are approximately 0.12 for all molecules. They are obtained by the sum of the respective elements of the atomic and bonding tensors. Note that there is a strong similarity among the calculated APTs for that set of molecules, and the same happens also for the experimental APTs. The off-diagonal elements are also small in magnitude. Since they are given by the sum of two numbers of approximately the same order of magnitude, the results are very sensitive with respect to the basis set.

These facts lead us to expect that the fluorine polar tensor should be automatically transferable among the molecules in this set. Now, taking a look at the individual contributions, it becomes clear that the diagonal elements of the atomic contributions are quite similar; this means that they are largely independent of the details of the molecular structure. The off-diagonal elements are small in magnitude compared to the diagonal elements. Although the bonding contributions to the APT show some variations in the off-diagonal and P_{zz} elements among the fluoromethanes, it is clear that these tensors are very similar for the CF₄ and CH₃F molecules. The results in Table III show that the transference of the fluorine polar tensor from CH₃F to CF₄ should be a good approximation (the same thing appears to occur for CHF₃ and CH₂F₂). That might be one of the reasons the infrared intensities of tetrafluoromethane are so well predicted from the transference of the fluorine polar tensor from methyl fluoride, unlike the cases for methylene fluoride and fluoroform. Transference should be done between those molecules that show strong atomic characteristics compared to the bonding and have similar patterns.

Since the homopolar dipole flux is the sum of a charge and a charge flux tensor, the fluorine polar tensor can be partitioned into three different contributions: charge (eq 4a), bonding charge (eq 4b), and the total charge flux (eq 4c). These results are shown in Table IV. The elements of the bonding charge tensors for all molecules are very small, compared with the charge tensor (Mulliken net atomic charge). There is a high total charge flux as the chemical bond is stretched, P_{zz} being the only significant element for the charge flux tensor. The P_{xx} and P_{yy} elements of the APT are essentially the net atomic charge since the contributions from the bonding charge and the total charge flux are small for these elements, which agrees with the interpretation of a diagonal APT, given by Person in ref 2. The P_{zz} elements of the APT have significant contribution from the total charge flux along with the high net atomic charge involved. The P_{zz} element of the total charge flux does not show any linear tendency from CF₄ to CH₃F, which is explained by the fact that it consists of a sum of contributions especially from the charge flux and atomic dipole flux. For example, in the case of a CF₄ molecule the rehybridization of the carbon and fluorine atoms is important, but as the F atoms are replaced, the rehybridization of the carbon becomes even more important (as seen in Table II) to the total

TABLE III: Atomic and Bonding Contributions to the Fluorine Polar Tensor^a

molecule	atomic contribution		bonding contribution		$P_{xx}^{(F)}$		$P_{xx}^{(F)} \text{ exp}^b$	
CF ₄	-0.613		0.176		-0.437		-0.33	
		-0.608		0.172		-0.436		-0.33
				0.046		-0.775		-0.92
CHF ₃	-0.605		0.182		-0.423		-0.29	
		-0.640		0.203		-0.437		-0.29
				0.109		-0.049		-0.12
CH ₂ F ₂	-0.645		0.204		-0.441		-0.27	
		-0.570		0.192		-0.378		-0.25
				0.106		-0.030		-0.02
CH ₃ F	-0.578		0.196		-0.382		-0.26	
		-0.576		0.196		-0.380		-0.26
				0.042		-0.836		-0.93

^aUnits are e. ^bFrom ref 6.

TABLE IV: Charge, Bonding Charge, and Charge Flux Contributions^a to the Fluorine APT

molecule	charge		bonding charge			total charge flux		$P_X^{(F)}$	
CF ₄	-0.369		-0.020			-0.048		-0.437	
		-0.369		-0.027			-0.040		-0.436
			-0.369		0.031			-0.437	-0.775
CHF ₃	-0.405		0.019		0.067	-0.037		-0.423	0.053
		-0.405		0.004			-0.036		-0.437
			-0.405	0.013	0.053	-0.062		-0.504	-0.856
CH ₂ F ₂	-0.438		0.019		0.054	-0.021		-0.441	0.046
		-0.438		0.048			0.011		-0.378
			-0.438	0.011	0.037	-0.041		-0.477	-0.878
CH ₃ F	-0.464		0.051			0.031		-0.382	
		-0.464		0.050			0.034		-0.380
			-0.464		-0.010			-0.362	-0.836

^aSee eqs 4a, 4b and 4c in the text. Units are e.

TABLE V: Calculated^a Contributions of the Hydrogen^b Polar Tensor for Methane and Fluoromethanes

molecule	atomic contribution		bonding contribution			$P_X^{(H)}$		$P_X^{(H)} \text{ exp}^c$	
CH ₄	0.118		-0.040			0.078		0.062	
		0.113		-0.038			0.075		0.062
			-0.120		0.032			-0.178	-0.133
CH ₃ F	0.014		-0.028		-0.011	-0.014		0.012	0.021
		0.115		-0.047			0.068		0.073
			-0.223	-0.046	0.080	0.013		-0.142	-0.143
CH ₂ F ₂	0.056		-0.039		-0.032	0.017		0.041	0.003
		0.014		-0.031			-0.017		0.020
			-0.223	-0.072	0.114	0.029		-0.109	-0.125
CHF ₃	0.035		-0.050			-0.015		0.032	
		0.037		-0.052			-0.015		0.032
			-0.199		0.152			-0.047	-0.072

^aBasis set 4-31G. Units are e. ^bThe hydrogen along the z axis. ^cCH₄ from ref 9. CH₃F from ref 8. CH₂F₂ from ref 10 and properly rotated. CHF₃ from ref 11.

TABLE VI: Charge and Charge Flux Contributions^a to the Hydrogen Polar Tensor^b for the Fluoromethanes and Methane Molecules

molecule	$P_X^{(H)} \text{ ch}$		total charge flux			$P_X^{(H)}$	
CH ₄	0.113		-0.038			0.075	
		0.113		-0.035			0.078
			0.447		-0.625		-0.178
CH ₃ F	0.126		-0.140		0.017	-0.014	-0.009
		0.116		-0.047			0.069
			0.410	0.035	-0.552	0.013	-0.142
CH ₂ F ₂	0.131		-0.114		0.014	0.017	-0.008
		0.126		-0.142			-0.016
			0.371	0.046	-0.480	0.028	-0.109
CHF ₃	0.132		-0.147			-0.015	
		0.132		-0.147			-0.015
			0.341		-0.388		-0.047

^aBasis set 4-31G. Units are e. $P_X^{(a)} \text{ ch}$ (eq 5 in the text) is the sum of the charge and bonding charge tensors. ^bHydrogen along the z axis.

charge flux and also to the P_{zz} element of the APT. The fluorine atomic charge $Q_{(a)}$ defined in the text is obtained from this partitioning of the APT and will be discussed later.

Hydrogen APT. The contributions to the hydrogen polar tensors have been calculated for the fluoromethanes and also for the methane. They are listed in Tables V and VI. The former shows the atomic and bonding contributions, while in Table VI the hydrogen tensors are partitioned into charge and charge flux. The calculated APTs are in excellent agreement with the experimental results, shown in Table V. It is interesting to note in this table that, as the CH bond is stretched, the atomic contributions given by the P_{zz} elements are almost the same for all of the molecules (the P_{zz} elements, if not zero, are small compared to P_{zz}). This does not occur with the other contributions of the atomic tensors. The elements of the bonding tensor are small in magnitude, except for P_{zz} , which increases by approximately 0.04 e as the number of fluorine atoms in the molecule increases by one. The small

bonding tensor contribution for the CH₄ molecule suggests a very strong atomic characteristic, while for the CHF₃ molecule the bonding tensor is equally important as the atomic tensor. So, the transference of the hydrogen polar tensor from the CH₄ to CHF₃ molecule should not give a good prediction for the CH stretch (ν_1). The predicted intensity of 51.5 km/mol, and the experimental value is 23.9 km/mol.² The hydrogen polar tensor of the CH₃F transferred to CH₂F₂ or CHF₃ should give a better prediction for the ν_1 stretch, since their P_{zz} atomic and bonding tensors behave similarly.

The charge tensors shown in Table VI are also very similar for all of the fluoromethanes, excluding the P_{zz} elements as expected from the previous table. Also in this case, the charge decreases by 0.04 e as we go from CH₄ to CHF₃. For methane, the hydrogen is bonded to a central atom which has a similar electronegativity. Consequently, for this weak polar bond, a reasonable charge flux is expected when the CH bond is stretched. This charge flux

TABLE VII: Total Charge for Fluorine, Hydrogen, and Carbon Atoms^a

molecule	Mulliken net charge $q_{(a)}$	this work ^c $Q_{(a)}$	Cioslowski ^d	Gussoni ^b	exp ^b
fluorine					
CF ₄	-0.369	-0.374	-0.550		
CHF ₃	-0.405	-0.380	(-0.572)		
CH ₂ F ₂	-0.438	-0.404	(-0.566)		
CH ₃ F	-0.464	-0.434	-0.534		
hydrogen					
CHF ₃	0.217	0.202	(-0.026)		
CH ₂ F ₂	0.186	0.209	(-0.036)		
CH ₃ F	0.166	0.217	-0.025	0.109	0.064
CH ₄	0.153	0.224	-0.0012	0.120	0.065
carbon ^e					
CF ₄	1.475	1.496	2.202		
CHF ₃	0.998	0.938	(1.742)		
CH ₂ F ₂	0.504	0.390	(1.204)		
CH ₃ F	-0.035	-0.217	0.608		
CH ₄	-0.611	-0.896	0.005		

^aUnits are (e). ^bCalculated by the ab-initio method with 4-31G basis set. ^cFrom ref 12. ^dSee eq 6a in the text. ^eFrom ref 15; the values in parentheses have been calculated in this work. ^fCalculated from difference since the sum of all atomic charges in the molecule vanishes.

decreases in magnitudes with the increase in the number of fluorine atoms. As can be seen in both tables, the contributions to the hydrogen polar tensor for methyl fluoride and methane are similar, except for the P_{xx} element in the atomic contribution (Table V) or in the charge flux tensor (Table VI). Since in the atomic contribution the charge and some of the charge flux are included, the difference in P_{xx} elements is due to a charge flux, as can be seen from Table VI.

Atomic Charges. According to eq 6a, the atomic charge $Q_{(a)}$ was calculated for the fluorine, hydrogen, and carbon atoms, with the results reported in Table VII. The atomic charge for the fluorine atom given by the trace (or even the norm) falls within a narrower range of values than the Mulliken net atomic charge, suggesting that this total atomic charge is practically independent of the molecule in this set. The average value for the total charge is 0.398 e. Further calculations with other aliphatic fluorinated hydrocarbons will have to be carried out to verify this independent behavior for other molecules. The total charge of hydrogen for fluoromethanes and methane is also in Table VII. The results show that the total charge is in a rather narrow range of values, indicating that the hydrogen bonded to a carbon atom is insensitive to the presence of the fluorines. Note that the hydrogen atomic charge decreases from methane to CHF₃, that is, in the opposite direction of the Mulliken net atomic charge but similar to the tendency observed for the experimental values of the equilibrium charge.¹² The atomic charge for the carbon can be easily calculated from a difference, since its values for all atoms in a molecule must add up to zero. As can be seen in Table VII, this atomic charge decreases by approximately 0.6 e for each fluorine that is being replaced (1.496, 0.938, 0.390, -0.217, and -0.896 e from CF₄ to CH₄). This result is in agreement with that obtained by Neto.⁷ If the carbon atomic charges obtained in the present work are plotted against the carbon partial charges (δ_c), obtained by the equalization of the electronegativity principle,^{13,14} a straight line is obtained. The plot is shown in Figure 1. The experimental mean dipole derivatives⁷ which are the arithmetic mean of the diagonal elements of the experimental polar tensors are also shown in Figure 1 (the solid line). If the carbon atomic charge from methane is not included in the regression, a straight line with a high correlation is obtained, and it is parallel to the experimental line. The carbon atomic charge for the methane, and consequently the hydrogen atomic charge, should be smaller in magnitude as expected experimentally.

A new population analysis based on the APT has been proposed recently by Cioslowski.¹⁵ His definition of atomic charge is given by one-third of the trace of the calculated APT (which is known as the mean dipole derivative). However, since the APT is defined

TABLE VIII: Calculated Fluorine Polar Tensor for Methyl Fluoride^a

basis set	charge		charge flux		atomic dipole flux		homopolar dipole flux		$P_x^{(F)}$
	charge	flux	charge flux	flux	atomic dipole flux	flux	homopolar dipole flux	flux	
4-31G	-0.464	0.023	0.025	-0.137	-0.137	0.196	-0.381	-0.382	-0.381
4-21G (C)	-0.458	0.030	0.028	-0.157	-0.157	0.200	0.196	0.196	-0.391
4-31G (F,H)	-0.458	0.030	0.029	-0.077	-0.077	0.202	0.203	0.203	-0.328
4-31G* (F)	-0.484	0.030	0.029	-0.076	-0.076	0.202	0.203	0.203	-0.328
4-31G (C,H)	-0.484	0.030	0.029	-0.054	-0.054	0.202	0.203	0.203	-0.328
atomic charge									
		basis set		Mulliken		norm ^b		trace ^b	
		4-31G		-0.464		-0.435		-0.434	
		4-21G (C)		-0.458		-0.450		-0.447	
		4-31G (H,F)		-0.484		-0.460		-0.460	
		4-31G* (F)		-0.484		-0.460		-0.460	
		4-31G (C,H)		-0.484		-0.460		-0.460	
$P_x^{(F)} \text{ exp} = \begin{matrix} -0.26 \\ -0.26 \\ -0.93 \end{matrix}$									

^aUnits are (e). ^bSee text eqs 5a and 5b.

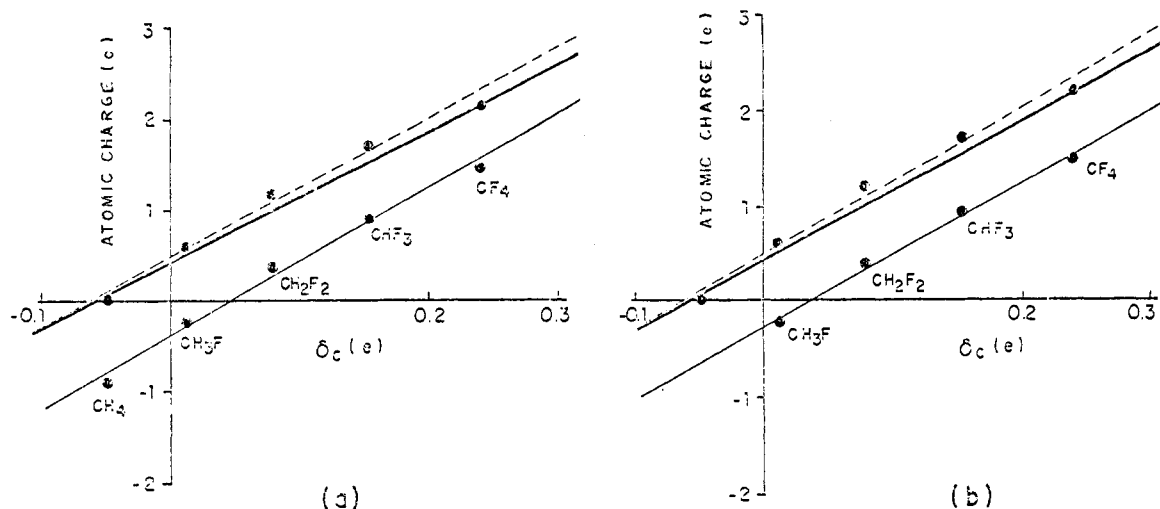


Figure 1. Plot of the carbon atomic charges against carbon partial charges (δ_c). The solid line is the regression for the experimental mean dipole derivatives. (a) — and --- are the regression lines for the atomic charges given by this work and Cioxlowski (ref 15), respectively. (b) $Q_{(c)}$ from methane has been excluded.

as a gradient of a product of the center of charge (over the atomic orbitals) by the electronic densities, it will be given by a sum of two terms, which we have identified in our work as charge and charge flux tensors. Since the gradient of the electronic densities cannot be considered as always null, this definition seems not appropriate in general.

To get a well-balanced wave function for the F atom, two additional calculations were performed besides the 4-31G basis set for the methyl fluoride, the first using a 4-21G basis set on the carbon set keeping the hydrogens and fluorine functions unchanged. In the second calculation, one polarization function was used for the fluorine (4-31G*), but the carbon and hydrogen functions were left unchanged. The results are in Table VIII. The largest changes occur for the charge flux tensor. The largest changes occur for the charge flux tensor. The Mulliken net atomic charges also show some variations (from -0.458 to -0.484 e). The fluorine atom should be represented better with respect to the carbon with these two basis functions, which appear to be more flexible to represent the charge fluxes. In the case where the carbon is represented by a 4-21G basis set, the significant changes occur in the P_{zz} charge flux element due to the changes in the net atomic charge and the homopolar dipole flux, since this term represents the bonding contributions. For the 4-31G* basis set where the polarization function is included on the F atom, some variations are observed in the net atomic charge as are large variations in the atomic dipole flux term, especially from the flux due to the stretching of the CF bond, as can be seen in Table VIII. From these calculations it becomes clear that the use of the 4-21G basis set for the carbon atom is not justified since the fluorine APT turns not worse when compared to the experimental tensor. On the other hand, it is quite clear that the inclusion of a polarization function on the fluorine is a good choice. The fluorine atom is better represented and the APT closer to the experimental tensor. Although some variations on the charge flux elements are observed as the basis set is changed, neither the total charge for the F atom nor the Mulliken net atomic charge (in this case) is sensitive. These results are also shown in Table VIII.

Conclusions

Before one engages in attempts to transfer an APT from one to another chemically similar molecule, the atomic and bonding contributions of both should be analyzed to see if they show similar patterns. In this work, the results have shown that the fluorine tensors for the CF_4 and CHF_3 molecules provide one of those cases.

The hydrogen polar tensor from CH_4 has a strong atomic characteristic with a small bonding tensor while for CHF_3 the atomic and bonding tensors are equally important, so the trans-

ference of the hydrogen APT from methane does not give a good prediction for the CH stretch.

The fluorine total charge falls within a narrow range of values, suggesting that it is independent of the molecular structure for this set of molecules. Also, this total charge appears to be rather nonsensitive to the changes in the basis set. Even the inclusion of the polarization function on the F atom leads to a different representation of the hybridization. Further calculations on longer fluorinated hydrocarbons will be necessary to measure that the fluorine charge on this CF bond is independent of the molecule of which it is a part. The hydrogen atomic charge also appears to be rather nonsensitive to the presence of the fluorine atoms. The hydrogen atom becomes a little more positive when going from CHF_3 to CH_4 , i.e., in the opposite direction to the Mulliken net atomic charge but similar to the tendency observed experimentally.

The carbon atomic charge is linearly related to its partial atomic charge and consequently to the electronegativity of the substituent. This straight line is parallel to the experimental values of the mean dipole derivatives for the fluoromethanes, which supports this novel definition for the atomic charge.

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Registry No. CH_3F , 593-53-3; CH_2F_2 , 75-10-5; CHF_3 , 75-46-7; CF_4 , 75-73-0; F, 14762-94-8; H, 12385-13-6.

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