Electronegativity Models for the Infrared Vibrational Intensities of the Halomethanes

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Abstract: Ab initio molecular orbital calculations and empirical electronegativity models are used to understand the linear electronegativity relationships observed for the carbon mean dipole moment derivatives and atomic effective charges calculated from the experimental infrared vibrational intensities of the halomethanes. The charge–charge flux-overlap interpretation of the molecular orbital results shows that only the charge contribution is important in explaining the variations in these parameters for the fluoromethanes. For this reason a simple electrostatic model is sufficient to explain their fundamental infrared intensity sums. The mean dipole moment derivative values determined from the experimental intensities suggest the absence of a saturation effect on the ability of substituted fluorine atoms to drain electron density from the carbon atoms. A similar model has been used by others to explain the increasing thermodynamic stabilities of the fluoromethanes with increasing fluorine substitution. In contrast intramolecular charge transfer is predominant in determining the chloromethane intensities. The fluorochloromethane intensities can only be explained using models combining characteristics of the fluoro- and chloromethane models. The charge equilibration procedure introduced recently in the literature is found to be significantly superior to the simpler electronegativity equalization method for calculating atomic charges for the prediction of the infrared intensity sums of the halomethanes.

Introduction

In recent studies[1,2] the infrared vibrational intensities of the substituted methanes have been interpreted using an electronegativity model. Their infrared fundamental intensity sums are partitioned into atomic contributions that are related to the Mulliken atomic electronegativities.[3] The largest statistical variance in the halomethane intensity sum values has been clearly related to the carbon atom contributions. The carbon mean dipole moment derivatives and the atomic effective charges present strong and highly significant linear variations with the mean electronegativity values of the terminal atoms.[2] The linear behavior is most impressive for the fluoromethanes. Both the mean dipole moment derivative and atomic effective charge values increase linearly with the number of fluorine substituents. As a consequence the total infrared fundamental intensity sum contains carbon atom contributions varying from 5 km mol^{-1} for methane to 1070 km mol^{-1} for tetrafluoromethane. On the other hand, the mean dipole moment derivatives and atomic effective charges of each of the terminal atoms, H, F, Cl, Br, and I, have almost constant values consistent with results showing that their atomic polar tensors are approximately transferable within this family of molecules.[4] Furthermore, the hydrogen and halogen atomic intensity sum contributions appear to vary with their own electronegativity values. These variations are much less than those for the carbon atom, ranging from about 0.7 km mol^{-1} for iodine to around 56 km mol^{-1} for fluorine. In summary, the variations in the halomethane fundamental infrared intensities can be attributed principally to changes in the carbon atom electronic densities that are provoked by changes in the substituent atoms. The charge densities associated with the different substituent atoms are of secondary importance.

In the present study we strive to deepen our understanding of the intensity parameter–electronegativity relations in terms of the electronic structures, or more simply, the atomic charges, of the halomethanes. This is attempted at two levels, an ab initio level employing the results of molecular orbital calculations and an empirical level using the electronegativity equalization principle.

First, ab initio calculations employing wave functions at the second-order Moller–Plesset level,[5] MP2, were performed for all the fluoro- and chloromethanes as well as for the fluorochloromethanes, $CFCl_3$, CF_2Cl_2, and CF_3Cl. These wave functions are much more sophisticated than those previously employed for the calculation of the fluoromethane intensities. Although the fundamental infrared intensities have been measured for $CFCl_3$,[6] CF_2Cl_2,[7] and CF_3Cl,[8] their polar tensors have not yet been reported in the literature. As such the calculated results provide a means to test the generality of the linear relations observed earlier for the polar tensor parameters obtained from experimental intensity results of the fluoro- and chloromethanes.

The charge–charge flux-overlap model[9] (CCFO) is applied to the results of the MP2 calculations in order to understand the origin of the simple relationships between intensity and electronegativity parameters. Since ab initio calculations are performed with varying levels of sophistication, the sensitivity

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of the CCFO results to differences in the calculated halomethane wave functions can be assessed.

At the empirical level our earlier study[1] describing the variation in the electronegativities of the carbon atoms of the fluoro- and chloromethanes is extended to include CH_2Cl_2 and CCl_4 as well as the fluorochloromethanes. More importantly, however, the electronegativity equalization model[10,11] for calculating infrared intensities is critically examined. As a result, a more sophisticated electronegativity-based model for the infrared intensities of the halomethanes is employed using the charge equilibration procedure proposed by Rappé and Goddard.[12] This method has already been applied in molecular mechanics and dynamics calculations[13] using atomic charges calibrated from dipole moment values. The infrared intensity sums are also a potential source of experimental data for determining charges. Here, however, the charge equilibration method is used to calculate atomic charges for comparison with experimental intensity parameters and with atomic charges obtained from the molecular orbital calculations.

Calculations

Ab initio calculations of the polar tensors of CH_4, CH_3F, CH_2F_2, CHF_3, CF_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, CF_2Cl_2, CF_3Cl, and $CFCl_3$ were performed using the Gaussian 92 computer program.[14] Three different basis sets were used, the relatively popular 6-31G(d,p) basis, the 6-311G(3d,3p) set, and the more extensive 6-311++G(3d,3p) set. Calculations were carried out at both the Hartree–Fock (HF) and the second-order Moller–Plesset (MP2) levels. The inclusion of electronic correlation at the MP2 level in wave functions is known to be important for obtaining accurate intensity and polar tensor estimates.[15] All calculations were done using optimized geometries for all the wave functions at both HF and MP2 levels.

The charge–charge flux-overlap (CCFO) model[9] was used to interpret the quantum mechanical results. For this reason finite difference calculations were made using Cartesian distortion sizes of 0.025 Å for the HF level and 0.005 Å for the MP2 level calculations. These values result from the best compromises between numerical accuracy and the accuracy of the finite difference approximation to the infinitesimal derivative.

Figure 1 contains a comparison of the intensity sums calculated for the substituted methanes using the four wave functions providing results in best agreement with the experimental intensity sums, HF/6-311++G-(3d,3p), MP2/6-31G(d,p), MP2/6-311G(3d,3p), and MP2/6-311++G-(3d,3p). Of these four the MP2/6-311++G(3d,3p) results have the smallest sum of squares error for the residuals between the calculated and experimental sums.[2] The MP2/6-311G(3d,3p) wave functions provide intensity sums almost as accurate as those obtained from the MP2/6-311++G(3d,3p) wave functions. However, Wiberg and Murcko[16] have shown that diffuse orbitals are important for calculating correct relative energies in their study of 1,2-difluoroethane and 1,2-difluoroethene. For this reason the following sections contain numerical results obtained using this wave function with diffuse orbitals.

Table 1. Mean Dipole Moment Derivatives and Atomic Effective Charge Values Obtained from the Experimental Intensities[a]

	$\bar{p}_C$	$\bar{p}_H$	$\bar{p}_F$	$\bar{p}_{Cl}$	χ_C[b]	χ_H[b]	χ_F[b]	χ_{Cl}[b]
CH_4	0.01	0.00			0.01	0.10		
CH_3F	0.54	−0.02	−0.48		0.59	0.10	0.58	
CH_2F_2	1.02	−0.02	−0.49		1.06	1.08	0.57	
CHF_3	1.52	0.00	−0.51		1.55	0.05	0.60	
CF_4	2.12		−0.53		2.12		0.63	
CH_3Cl	0.27	0.00		−0.27	0.35	0.07		0.30
CH_2Cl_2	0.53	−0.02		−0.25	0.67	0.06		0.32
$CHCl_3$	0.82	−0.03		−0.27	0.93	0.05		0.39

[a] Units of electrons, e. Values from ref 24. [b] Signs of the atomic effective charges are ambiguous. In this table positive signs are arbitrarily attributed to the effective charges.

The mean dipole derivative for atom α is simply one-third of the trace of its atomic polar tensor,[4] $\mathbf{P}_X^{(\alpha)}$,

$$\bar{p}_\alpha = {}^1/_3(\partial p_x/\partial x_\alpha + \partial p_y/\partial y_\alpha + \partial p_z/\partial z_\alpha) \tag{1}$$

This parameter is often compared with atomic charges obtained from molecular wave functions. Recently Cioslowski[17] has proposed that mean dipole moment derivatives obtained from molecular orbital calculations and called generalized atomic polar tensor (GAPT) charges be considered as an alternative to other kinds of atomic charges such as Mulliken charges,[3] Bader charges,[18] etc. Another spectroscopic parameter obtained from infrared intensity studies, the atomic effective charge, is given by

$$\chi_\alpha^2 = {}^1/_3\mathrm{Tr}[\mathbf{P}_\chi^{(\alpha)}\mathbf{P}_\chi^{(\alpha)\prime}] \tag{2}$$

Although this parameter is sometimes interpreted as an atomic charge, its main importance stems from its relationship to the infrared intensity sums via Crawford's G sum rule[19,23]

$$\sum_s^{3N-6} A_s + \Omega = 974.9 \sum_\alpha^N 3\chi_\alpha^2/m_\alpha \tag{3}$$

where A_s is the intensity of the sth fundamental band in km mol^{-1}, Ω is the rotational correction term, and the effective charge, χ_α, and the atomic mass, m_α, are given in electrons and atomic mass units, respectively. Each term on the right-hand side of eq 3 represents an atomic contribution to the intensity sum.

It should be noted that the mean dipole moment derivatives and atomic effective charges are related by the expression

$$\chi_\alpha^2 = (\bar{p}_\alpha)^2 + {}^2/_9\beta_\alpha^2 \tag{4}$$

where β_α^2 is the charge anisotropy of the αth atom. The mean dipole moment derivative and atomic effective charge values obtained from the atomic polar tensors calculated using experimental intensities were taken from previous work reported in the literature.[24] These values are listed in Table 1. For the halomethanes in this table the anisotropy values are small so that the values $\bar{p}_\alpha$ and χ_α are not very different. For

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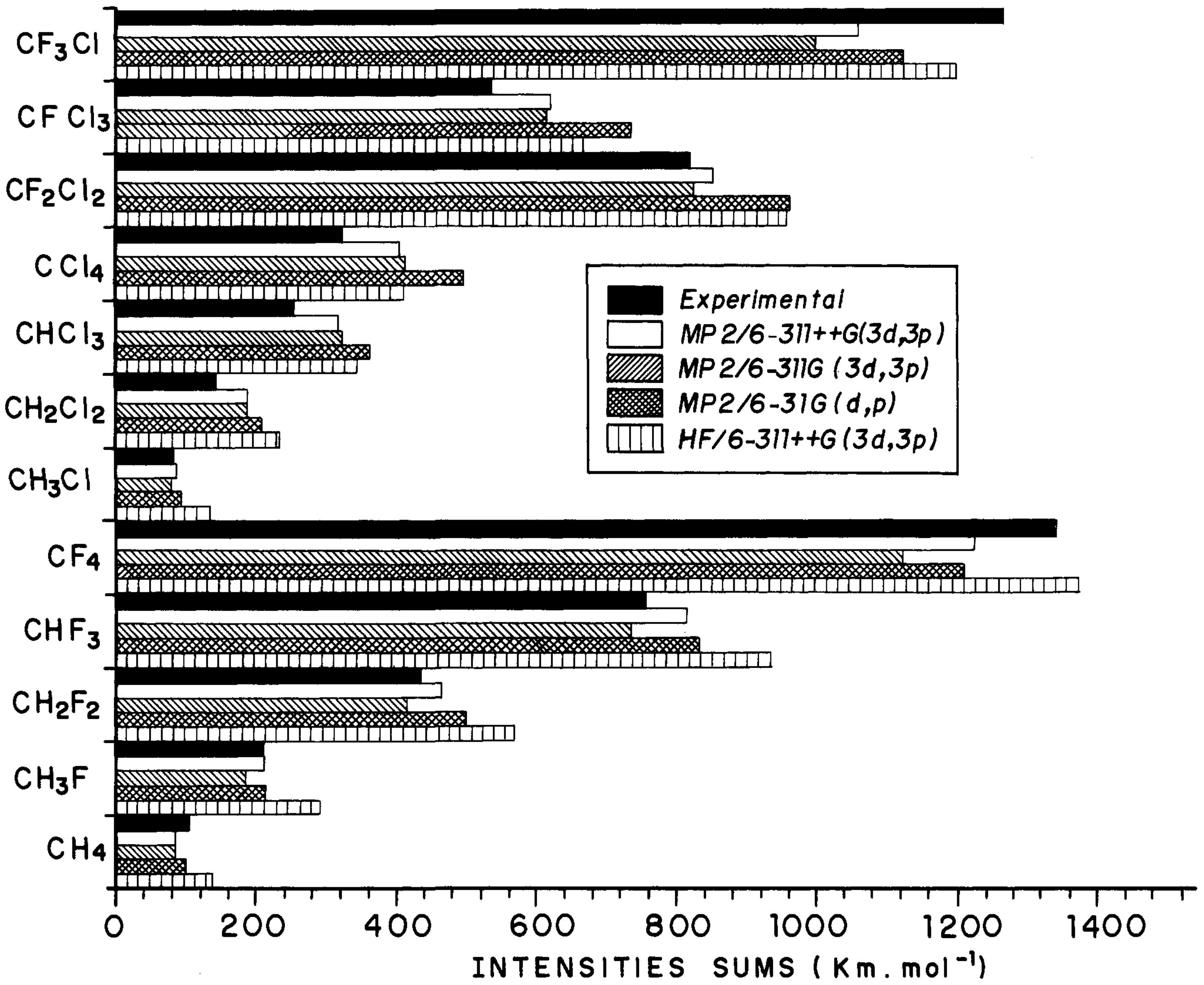

Figure 1. Comparison of the calculated fundamental intensity sums of the fluoro- and chloromethanes obtained from the HF/6-311++G(3d,3p), MP2/6-31G(d,p), MP2/6-311G(3d,3p), and MP2/6-311++G(3d,3p) wave functions with the experimental sums.

this reason both parameters have very similar linear relations with the electronegativity values of the halomethane substituent atoms.

Molecular Orbital Results

The mean dipole moment derivatives of the carbon atoms ($\bar{p}_C$) for the fluoromethanes, CH_xF_{4-x} ($x = 0$, 1, 2, 3, and 4), and for CH_3Cl, CH_2Cl_2, $CHCl_3$, CH_3Br, and CH_3I, obtained from their experimental infrared intensities,[24] are graphed as a function of the mean electronegativity values, $\bar{E}_\alpha$, of their substituent atoms in Figure 2. A linear model for $\bar{p}_C$ and $\bar{E}_\alpha$ is clearly observed for all the halomethanes. The regression line in this figure is significant above the 99% confidence level and explains 99.6% of the total variation in the $\bar{p}_C$ values.

The generality of this relation is tested using $\bar{p}_C$ values obtained from MP2/6-311++G(3d,3p) wave functions of all the fluoro-, chloro-, and fluorochloromethanes. In Figure 3 these values are plotted as a function of the mean electronegativity of the terminal atoms. Two distinct linear relations can be observed, one for the fluoromethanes and the other for the chloromethanes. Both relations are significant above the 99% confidence level and explain 99.5% of the variances in the $\bar{p}_C$ values of the fluoro- and chloromethanes. Moreover, the distinct linear behaviors are only clearly discernible for large mean electronegativity values. The presence of $\bar{p}_C$ values obtained from the experimental intensities of carbon tetrachloride and the fluorochloromethanes in Figure 2 would be useful for deciding if one or more linear relations actually exist. On the other hand, uncertainties in the $\bar{p}_C$ values due to experimental

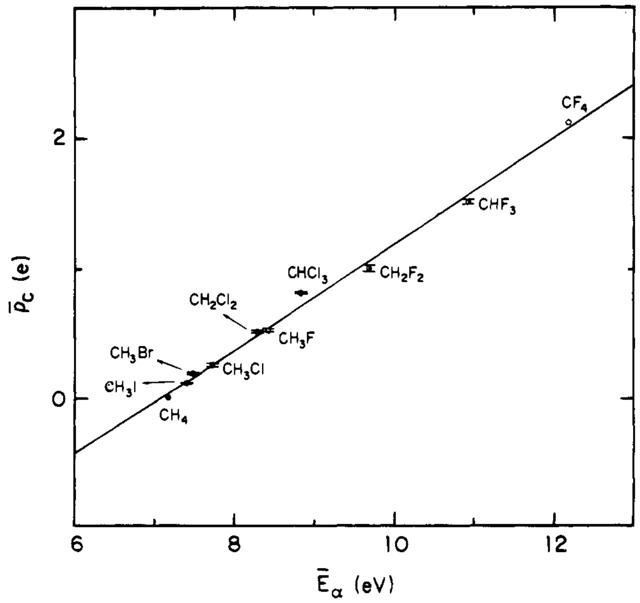

Figure 2. The experimental carbon mean dipole moment derivatives and errors of the halomethanes plotted against the mean electronegativities of the terminal atoms.

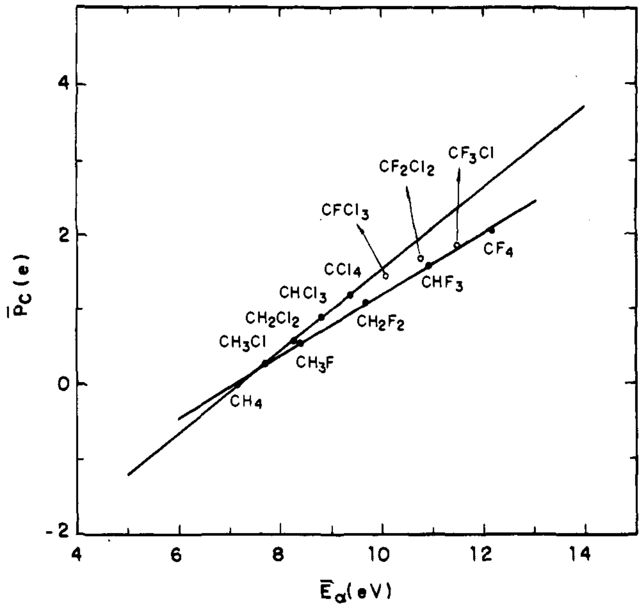

Figure 3. The carbon mean dipole moment derivatives of the fluoro-, chloro-, and fluorochloromethanes calculated with MP2/6-311++G-(3d,3p) wave functions plotted against the mean electronegativities of their terminal atoms.

errors in the measured intensities and to normal coordinate inaccuracies could obscure the observation of separate linear models.

However, the MP2/6-311++G(3d,3p) results clearly suggest separate linear relations for the fluoro- and chloromethanes with the fluorochloromethanes occupying intermediate positions between the two calculated models shown in Figure 3. As the fluorine atoms in CF_4 are substituted by chlorine atoms, the points for the fluorochloromethanes recede from the fluoromethane to the chloromethane theoretical model. In fact a separate linear relation could also be proposed for the CF_xCl_{4-x} ($x = 0, 1, 2, 3,$ and 4) theoretical results. It is also interesting to note that the methane $\bar{p}_C$ value appears to agree with both the fluoromethane and chloromethane models.

The question remains: Can the carbon mean dipole moment derivatives of the halomethanes be described by one model as the experimental results in Figure 2 seem to indicate or would separate models for the fluoro-, chloro-, and fluorochloromethanes be more appropriate as suggested by the MP2/6-311++G(3d,3p) results? The experimental measurement of the intensities of the bromo- and iodomethanes will probably be of little help since the electronegativities of the H, Br, and I are so similar. Statistics show all the models as being highly significant. The question can probably be settled only by using chemical information.

The linear relations between $\bar{p}_C$ and the mean electronegativity values can be investigated theoretically using the charge–charge flux-overlap (CCFO) model.[9] The ab initio molecular orbital results for the polar tensor elements are partitioned into contributions from the equilibrium charges on the atoms, changes in these charges upon distortion of the molecule from its equilibrium geometry, and a nonclassical overlap contribution. These are then propagated into CCFO mean dipole moment derivative contributions. The values of these contributions are partially determined by the values of the Mulliken net atomic charges and are often observed to be very dependent on the basis set used to construct the wave function as well as the level of electron correlation included in the quantum chemical calculations.[25] Although the CCFO results presented in this section of the manuscript were obtained from the MP2/6-311++G(3d,3p) wave function calculations, those obtained from all the other wave functions analyzed lead to the same qualitative interpretations unless otherwise indicated.

Figure 4 presents the variations in CCFO contributions to the mean dipole moment derivatives as a function of the mean electronegativity values. The linear behavior of the $\bar{p}_C$ values of the fluoromethanes, shown in Figure 4a, is seen to be determined almost entirely by the charge contributions to the mean dipole moment derivatives. The nonlinear dependencies of the charge flux and overlap contributions are seen to cancel one another. As such the calculated charge contribution to $\bar{p}_C$ as a function of $\bar{E}_\alpha$ is almost identical to that for the total mean derivative. It is reassuring that this same interpretation of the variation in the $\bar{p}_C$ values is obtained using the results for the other wave functions investigated in this study. Furthermore, this interpretation was reported previously[1] using the results of a very approximate wave function obtained from a 4-31G basis set at the Hartree–Fock level.

Since the $\bar{p}_C$ values of the fluoromethanes vary linearly with the number of substituent fluorine atoms, it is not surprising that the CCFO model predicts the charge contributions as being predominant. Fluorine atoms are very electronegative relative to the carbon and hydrogen atoms. The carbon atoms become proportionally more positive with each fluorine substitution. The presence of a saturation effect on the ability of the fluorine atoms to drain electronic charge from the carbon atoms would be revealed by important charge flux and overlap contributions to $\bar{p}_C$ and perhaps by pronounced nonlinearity in the $\bar{p}_C$ vs $\bar{E}_\alpha$ graph shown in Figure 2. In addition, the cancelation of charge flux and overlap terms also occurs for the $\bar{p}_F$ values. As a result the atomic mean dipole moment derivatives of the fluoromethanes are appropriately interpreted as generalized atomic polar tensor charges.

Recently Wiberg and Rablen[21] and others before[26,27] have suggested that the increasing stability of the fluoromethanes with increasing fluorine substitution can be explained by a simple electrostatic model. An alternative but more complicated explanation is based on a negative hyperconjugation effect involving the lone pair fluorine electrons and their adjacent CF σ^* orbitals.[28-31] If negative hyperconjugation were operative, large net effects of the charge transfer and overlap CCFO contributions could be expected for the dipole moment derivative values. However, the CCFO analysis shows that only the charge contribution is necessary to explain the $\bar{p}_C$ values of the fluoromethanes. Furthermore, these values vary linearly with the mean substituent electronegativity values which in turn vary linearly with the number of fluorine substituent atoms for the special case of the fluoromethanes. As such the infrared intensity sums as well as the thermodynamic stabilities of the fluoromethanes can both be explained using simple electrostatic models.

It is then logical to inquire if the atomic charges that explain the thermodynamic stabilities are related to those necessary to explain the intensity sums. Of course it is too naive to expect that the same charge values could explain quantitatively both the energy and intensity variations in the fluoromethanes since the point charge model is an extreme simplification of the

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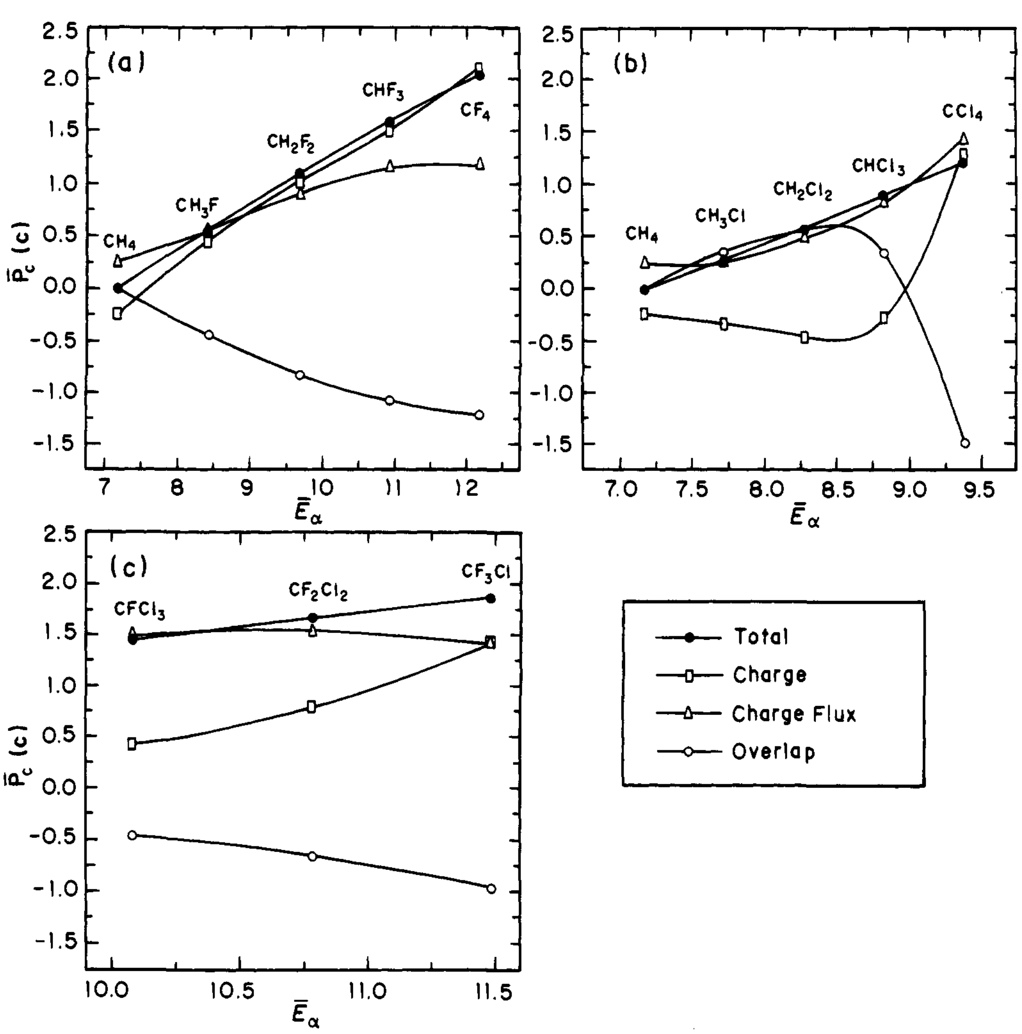

Figure 4. Charge, charge-flux, and overlap contributions to the carbon mean dipole moment derivatives of the fluoro-, chloro-, and fluorochloromethanes as a function of the mean substituent electronegativity values.

electronic charge densities one might expect to exist in molecules. The individual intensity values, normal coordinates, molecular geometries, and dipole moments are used to calculate the carbon mean dipole moment derivatives. For this reason their values accurately reproduce the intensity sums. The $\bar{p}_C$ values for the fluoromethanes are graphed as a function of the number of fluorine substituents in Figure 5. Included for comparison are the Mulliken charges from the MP2/6-311++G-(3d,3p) calculation, the Bader charges,[18] and the CHELPG charges.[20] Note that the values calculated for these charges all follow linear relationships with the number of fluorine substituents. This is especially noteworthy considering the different concepts involved in defining each type of charge. The Mulliken charge values are calculated from conventional orbital density analysis. The Bader charges are determined from charge densities partitioned into atomic contributions by zero-flux surfaces of gradients. The CHELPG charges are evaluated using molecular electrostatic potentials. Note that the Mulliken charges in this figure are almost the same as the $\bar{p}_C$ values obtained from the infrared intensities. This is probably a consequence of the electrostatic nature of the fluoromethanes and the excellent agreement between the polar tensor values obtained from the MP2/6-311++G(3d,3p) wave functions and from the experimental intensities.

The behavior of the charge, charge-flux, and overlap contributions of $\bar{p}_C$ as a function of the mean electronegativity values of the terminal atoms for the chloromethanes is quite different from that of the fluoromethanes as can be observed in Figure 4b. The charge and overlap contributions almost cancel one another and the charge-flux contribution determines, for the most

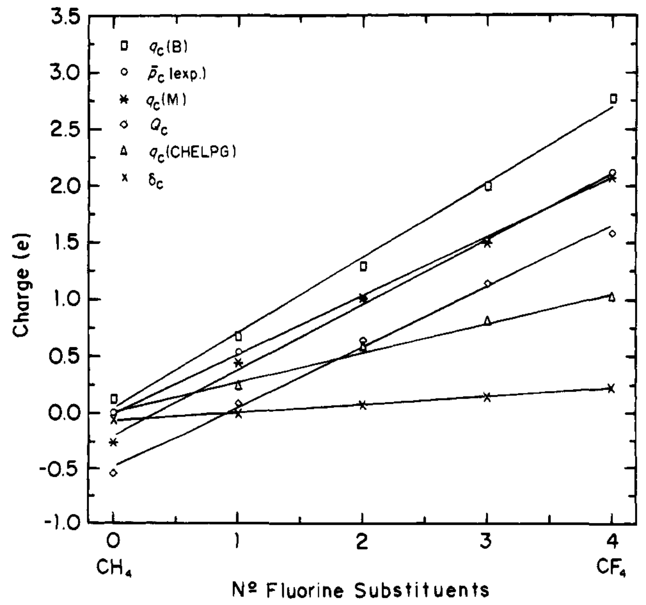

Figure 5. The experimental carbon mean dipole moment derivatives, $\bar{p}_C$, Mulliken charges, q_C(M), charges obtained from the electrostatic potential, q_C(CHELPG), Bader charges, q_C(B), charge equilibration charges, Q_C, and electronegativity equalization charges, δ_C, as a function of the number of fluorine substituents are on the fluoromethane.

part, the variation in $\bar{p}_C$ as a function of $\bar{E}_\alpha$. This cancellation is approximate but the total calculated $\bar{p}_C$ values vary almost linearly with $\bar{E}_\alpha$. The chlorine electronic charge clouds are much more polarizable than those for fluorine. As such one can expect that the charge-flux contribution increases as more chlorine atoms are substituted in the chloromethanes. CCFO analyses for the results of the other wave functions investigated in this work for the chloromethanes are quite different from that presented in Figure 4b for the MP2/6-311++G(3d,3p) function. However, the charge contribution is not predominant in determining the behavior of the $\bar{p}_C$ values with varying chlorine substitution for any these wave functions.

This CCFO interpretation is consistent with observations already reported for the chloromethanes by Wiberg and Rablen.[21] Their carbon charge values calculated using Bader's atoms-in-molecule method as well as the Mulliken charges we have calculated from the various wave functions investigated here show systematic deviations from linearity indicating that the electrostatic model is not appropriate for the chloromethanes. Also the charges calculated for the terminal chlorine atoms are not invariant with increasing chlorine substitution, contrasting with the almost constant fluorine charges obtained for the fluoromethanes. Perhaps the strongest argument against the use of an electrostatic model for the chloromethanes comes from thermodynamic stability data. For example, as pointed out in ref 21, the isodesmic reaction

$$CF_4 + 3CH_4 \rightarrow 4CH_3F$$

is endothermic by 53 kcal•mol^{-1}, indicating electrostatic stabilization in the presence of multiple CF bonds. The corresponding reaction with chlorine

$$CCl_4 + 3CH_4 \rightarrow 4CH_3Cl$$

is exothermic by about 4 kcal•mol^{-1}. This latter result is inconsistent with the use of an electrostatic model for explaining the thermodynamic stabilities of the chloromethanes. Although the mean dipole moment derivatives or the Mulliken net charges can be used to accurately calculate the fluoromethane intensity sums, their values used as parameters in an electrostatic model predict an energy of 598 kcal•mol^{-1} for the above reaction for the fluoromethanes. This value is ten times the one found experimentally. Wiberg and Rablen[21] calculated a 138 kcal•mol^{-1} electrostatic energy change for this reaction using the CHELPG charges shown in Figure 5. Although this value is in much better agreement than that calculated using the values of the intensity parameters, it is still too high by a factor of 2.5. Of course one cannot expect quantitative agreement with experimental thermodynamic and spectral intensity results using a simple point charge electrostatic model.

The behavior of each of the charge, charge-flux, and overlap contributions for the fluorochloromethanes is different from that of the fluoro- and chloromethanes. As shown in Figure 4c, the charge contribution increases with increasing fluorine substitution as was observed for the fluoromethanes. However, both the charge-flux and overlap contributions decrease from $CFCl_3$ to CF_3Cl, partially cancelling the charge contribution and resulting in a small net increase in $\bar{p}_C$ with increasing fluorine substitution.

Table 2. Atomic Charges of the Substituted Methanes Calculated Using the Electronegativity Equalization (δ) and Charge Equilibration (Q) Methods[a]

	δ_C	δ_H	δ_F	δ_{Cl}	Q_C	Q_H	Q_F	Q_{Cl}
CH_4	−0.05	0.01			−0.54	0.13		
CH_3F	0.01	0.07	−0.23		0.09	0.15	−0.55	
CH_2F_2	0.08	0.14	−0.18		0.65	0.16	−0.49	
CHF_3	0.15	0.22	−0.13		1.15	0.16	−0.44	
CF_4	0.24		−0.06		1.59		−0.40	
CH_3Cl	−0.01	0.05		−0.14	−0.05	0.16		−0.43
CH_2Cl_2	0.02	0.09		−0.10	0.31	0.16		−0.32
$CHCl_3$	0.06	0.12		−0.06	0.59	0.16		−0.25
CCl_4	0.09			−0.02	0.81			−0.20
CF_2Cl_2	0.15		−0.13	0.05	0.99		−0.43	−0.16
CF_3Cl	0.19		−0.10	0.19	1.17		−0.45	−0.18
$CFCl_3$	0.12		−0.15	0.10	1.35		−0.41	−0.12

[a] Units of electrons, e. The δ values were obtained using only the first two terms in eq 3 for the electronegativity values whereas the Q values used the complete equalization.

The Charge Equilibration Method and Vibrational Intensities

If the electronic structures of the fluoromethanes can be described using an electrostatic model and the carbon mean dipole moment derivatives are linearly related to the mean electronegativity values as shown in Figure 2, one might expect that electronegativity models for calculating atomic charges could be used for predicting infrared intensity sums. In order to describe the variations in the electronegativity values of the carbon atoms, which are known to account for a large majority of the infrared intensity sums of the halomethanes, the electronegativity equalization principle[10,11] has already been applied to the fluoromethane molecules. Using this principle and the charge conservation condition, atomic charges, designated by δ and called partial charges,[11] can be calculated. Although the carbon atomic charges calculated in this way are much smaller than those obtained by other methods, they are almost perfectly correlated with the mean dipole moment derivatives obtained from the experimental intensity data (see Figure 5). However, charges calculated for the hydrogen and fluorine atoms are not approximately constant for the fluoromethanes (see Table 2) as would be expected from the experimental[1,2] and theoretical[2,11] evidence. In an attempt to obtain a more reliable but still simple model for predicting atomic charges for infrared intensity predictions, the charge equilibration method proposed by Rappé and Goddard[12] was investigated.

The total electrostatic energy of a molecule with N atoms in the charge equilibration procedure is given by

$$E(Q_1,Q_2,...,Q_N) = \sum_{A=1}^{N} (E_A^0 + \chi_A^0 Q_A + \eta_A^0 Q_A^2) + \sum_{A<B} J_{AB} Q_A Q_B \tag{5}$$

where the first term is a sum of atomic energies and the second is the interatomic electrostatic energy. χ_A^0 and η_A^0 are the generalized Mulliken–Pauling electronegativity and hardness[12,22] of the isolated neutral atom A. J_{AB} represents the form of the potential between charges on atoms A and B. The derivative of this equation with respect to the atomic charge, Q_A, gives an expression for the electronegativity of atom A

$$\chi_A(Q_1,Q_2...Q_N) = \chi_A^0 + 2\eta_A^0 Q_A + \sum_{B \neq A} J_{AB} Q_B \tag{6}$$

in the molecular environment. The simplest application[11] of the electronegativity equalization principle employs only the first two terms in eq 6. As such, the atomic charges calculated using this equation depend only on the types of atoms in the molecule and not on their spatial arrangement. For example, geometrical isomers are calculated to have identical atomic charge values. The charge equilibration method remedies this situation by introducing the interatomic electrostatic energy term. The form of the potential between atoms A and B, J_{AB}, is simply

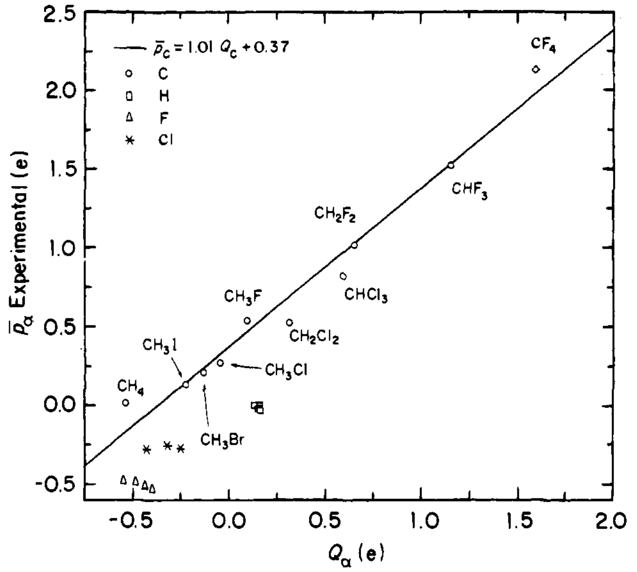

Figure 6. The mean dipole moment derivatives obtained from experimental intensity data as a function of the charges calculated using the charge equilibration method.

the Coulomb integral approximated using Slater-type s orbitals centered on atoms *A* and *B*. The exponential coefficients in the orbitals were chosen so that the calculated atomic charges reproduced the dipole moments of 20 diatomic neutral hydrides.[12] The presence of the third term in eq 6 results in the calculation of atomic charge values that depend on the molecular geometry and the connectivity of the atoms in the molecule.

In Table 2 atomic charges for the substituted methane molecules calculated using the electronegativity equalization principle (δ) and the charge equilibration procedure (Q) are compared. Although the absolute values of δ_C are much different than the Q_C values, they are highly correlated. Both models predict positive carbon charges for all molecules except CH_4 and CH_3Cl. Another notable difference between the δ and Q charges occurs for the H, F, and Cl atoms. The simplest form of the electronegativity equalization principle results in very different charge values for each of these atoms whereas the more complex charge equilibration method furnishes nearly constant values for each kind of terminal atom. For example, the δ_H values for the fluoromethanes vary between 0.01 for CH_4 and 0.22 e for CHF_3. The corresponding Q_H values range between 0.13 and 0.16 e and depend much less on the number of fluorine atoms in the molecule. Similar observations are in order for F and Cl atomic charges calculated using these two methods.

The $\bar{p}_C$ values obtained from the experimental intensities are graphed in Figure 6 against the Q_C values calculated using the charge equilibration method. The $\bar{p}_C$ dependence on Q_C is given by the diagonal regression line

$$\bar{p}_C = 1.01 Q_C + 0.37 \tag{7}$$

which has a regression correlation coefficient of 0.986. Included in this graph are points for the H, F, and Cl atoms. Contrary to the large variations in the carbon atom values, each type of terminal atom has $\bar{p}_\alpha$ and Q_α values restricted to very small and discrete areas of the graph. The analogous graph of the $\bar{p}_C$ values calculated from the MP2/6-311++G(3d,3p) wave functions is almost identical to that in Figure 6. The regression equation for the theoretical values,

$$\bar{p}_C = 1.03 Q_C + 0.40 \tag{8}$$

with a correlation coefficient of 0.991, is almost the same as that for the experimental $\bar{p}_C$ values. The above equation was obtained using theoretical results for all the fluorochloromethanes, i.e. including results for CH_4, CF_3Cl, CF_2Cl_2, and $CFCl_3$. Also the small discrete regions occupied by hydrogen, fluorine, and chlorine atom results in Figure 6 are almost identical to those in the corresponding graph of the molecular orbital values.

Conclusions

The linear behavior previously observed between the carbon mean dipole moment derivatives calculated from the experimental infrared intensities and the average of the terminal atom electronegativities of the fluoromethanes and some chloromethanes (CH_3Cl, CH_2Cl_2, and $CHCl_3$) has been critically analyzed using the results of relatively sophisticated molecular orbital wave functions. Three separate models appear to be most appropriate for the fluoromethane, chloromethane, and fluorochloromethane intensity parameters. The charge–charge flux–overlap analysis indicates that the carbon and fluorine mean dipole moment derivatives of the fluoromethanes can be identified with carbon and fluorine atomic charges. These fluorine mean dipole moment derivatives have constant values of about 0.5 e. The carbon mean dipole moment derivatives increase by about 0.5 e for each additional fluorine substitution in this series. Assuming the CCFO interpretation for the fluoromethanes to be correct, their infrared intensities provide evidence of an experimental origin confirming the simple electrostatic model description used to explain their thermodynamic stabilities. However, the atomic charge parameters which reproduce the experimental thermodynamic results are much smaller than those consistent with the fluoromethane intensity sums. This is not unexpected since the representation of molecular electronic charge densities by means of point charges on the atoms is a gross, although useful, approximation.

The apparent linear behavior of the carbon mean dipole moment derivatives obtained from the experimental infrared intensities of the chloromethanes cannot be explained using a simple point charge model. Intramolecular charge transfer during the molecular vibration seems to be important in determining the polar tensor parameters. However, this contribution to the total dipole moment change for molecular vibrations may also be linearly dependent on the mean substituent electronegativities. Certainly the more polarizable chlorine charge densities are more susceptible to modifications in the molecular geometry than are the fluorine densities. The measurement of the infrared fundamental intensities of carbon tetrachloride would be useful in quantifying the relationship between the chloromethane polar tensor parameters and the number of chlorine substituents. Finally polar tensor values for the fluorochloromethanes should be calculated from their experimental intensities to see how these values are related to those of the fluoro- and chloromethanes. It appears as though the infrared intensity parameters of these molecules might be explained using a model containing characteristics describing the fluoromethane and chloromethane intensities.

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