An electronegativity model for vibrational intensities of substituted methanes

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The mean dipole moment derivatives of the carbon polar tensors of the halogenated methanes are shown to be linearly related to the carbon partial charges calculated using the equalization of the electronegativity principle. The relationship is quantitative and allows the calculation of mean dipole derivatives of carbon atoms from valence state ionization potentials and electron affinities of the atoms in the halogenated methanes. The methyl group electronegativity in ethane calculated from the carbon mean dipole derivative is in excellent agreement with the previously reported value obtained from electronic transition data. *Ab initio* charge, charge flux, and overlap contributions to the carbon mean dipole derivatives are shown to be useful in the interpretation of the relation between the derivatives and the partial charges.

I. INTRODUCTION

Many attempts have been made at relating vibrational intensity parameters to other parameters of chemical interest, but in all cases only relatively small groups of molecules were studied. To study any possible trends in these parameters from a broader perspective, we decided to undertake a statistical investigation of a very extensive set of intensity data. A total of 158 experimental atomic polar tensors[1] from 50 different molecules were taken from the literature and analyzed by means of the well-known statistical technique of decomposition into principal components.[2] This analysis revealed that most of the variance in the polar tensor data, as reflected in the first principal component, could be associated with the electronegativities of the atoms involved. For the carbon polar tensors belonging to the halogenated methanes, the relation is quantitative, and a strikingly good regression line was found between the coordinates of the points on the first principal component axis (the so-called PCl scores) and a linear function of the electronegativities of the substituents.

With resort to modern electronegativity concepts the regression equation of the PCl scores on the electronegativities can be reduced to a relation between mean dipole derivatives and partial atomic charges. To investigate the meaning of this relation we performed *ab initio* calculations of the polar tensors in question, and analyzed the results obtained in terms of charge, charge flux, and overlap contributions.

This equation is shown to be useful in the calculation of mean dipole derivatives of the substituted methanes from partial charges obtained from electronegativity relations. Conversely, experimental vibrational intensities can be used to calculate the electronegativities of atoms and characteristic chemical groups.

II. ELECTRONEGATIVITIES, PARTIAL CHARGES, AND MEAN DIPOLE DERIVATIVES

In the original formulation electronegativity was conceived as an invariant atomic property.[3] As the concept be-

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came more sophisticated, it was realized that the electronegativity should vary with the environment surrounding the atom in a molecule or, more specifically, with the atomic hybridization.[4] This variability now appears as a natural outcome of the density functional theory treatment of electronegativity.[5]

Over thirty years ago, Sanderson[6] postulated that upon molecular formation the atomic electronic densities will change until the electronegativities of the combining atoms become the same. In the process, electronic charge flows toward the more electronegative atoms, giving rise to partial atomic charges. A straightforward procedure to calculate these partial charges in a molecule was proposed by Huheey.[7] Here, using a slightly modified notation, we briefly review Huheey's method.

Let us assume that the energy of an atom is a function of its partial charge δ and expand it in a Taylor series around the neutral species:

$$E = E_0 + \frac{dE}{d\delta} d\delta + \frac{1}{2} \frac{d^2 E}{d\delta^2} (d\delta)^2 + \cdots . \tag{1}$$

The first two coefficients, $dE/d\delta$ and $(1/2)d^2E/d\delta^2$, are easily identified as the chemical potential[5] and the hardness[8] of the density functional theory, and can be obtained from the finite-difference approximations

$$\frac{dE}{d\delta} \approx \frac{I + A}{2} = a,$$

$$\frac{d^2 E}{d\delta^2} \approx I - A = b,$$

where I and A are, respectively, the ionization potential and the electron affinity of the atom.

Taking the energy of the neutral atom as zero and neglecting higher-order terms, Eq. (1) becomes

$$E = a\delta + (b/2)\delta^2, \tag{2}$$

where we have substituted δ, the partial charge, for $d\delta$, to recover the notation of Ref. 7. The electronegativity is now defined[7] as the derivative of Eq. (2) with respect to (partial) charge and is itself a linear function of charge

$$\chi = \frac{dE}{d\delta} = a + b\delta. \tag{3}$$

Equating these electronegativity functions for all the atoms in a molecule and including the charge conservation equation, all partial atomic charges can be determined, once the values of a and b for the atoms in question are known.

In the principal component analysis of the experimental polar tensors of carbon in different molecules, the tensor invariants[9] were used as variables, instead of the elements themselves, to avoid the problems arising from different orientations of the Cartesian frames of reference. The first principal component, corresponding to 81% of the variance in the whole set, was found to be

$$PC1 = 0.49\bar{p} + 0.49\xi + 0.32\beta + 0.44\sqrt[3]{D} + 0.48\sqrt{C},$$
(4)

where $\bar{p}, \xi, \beta, \sqrt[3]{D}, \sqrt{C}$ stand for the mean dipole derivative, the atomic effective charge, the square root of the anisotropy, the cubic root of the polar tensor determinant, and the square root of the sum of the minors of the polar tensor diagonal elements. The roots were taken in these cases to give to all variables the same unit, electronic charge. The scores of the carbon tensors in PC1, which can be easily obtained by substituting into Eq. (4) the values of the invariants, yielded for the halogenated methanes an excellent regression (correlation coefficient of 0.996) on the quantity obtained by subtracting the electronegativity of carbon from the electronegativities of each of the four atoms attached to it and then adding the results. This suggests that a good relation may be found between the carbon partial charges determined from electronegativity equalization and the PC1 scores or, better, some invariant.

Of the invariants appearing in Eq. (4), ξ, β, and $\sqrt{C}$ are defined by quadratic equations, where by convention the square root is always given the positive sign. Only $\bar{p}$ and $\sqrt[3]{D}$ may, like the atomic partial charges, assume negative values.

The mean dipole derivative is simply the arithmetic mean of the diagonal elements of the polar tensor:

$$\bar{p} = \frac{1}{3}\left(\frac{\partial p_x}{\partial x_c} + \frac{\partial p_y}{\partial y_c} + \frac{\partial p_z}{\partial z_c}\right).$$

Since all carbon polar tensors in this case are diagonal, $\sqrt[3]{D}$ reduces to the corresponding geometric mean

$$D^{1/3} = \left[\left(\frac{\partial p_x}{\partial x_c}\right)\left(\frac{\partial p_y}{\partial y_c}\right)\left(\frac{\partial p_z}{\partial z_c}\right)\right]^{1/3}.$$

The values of $\bar{p}$ for all the atoms in a molecule must add up to zero.[10] As the same holds for the atomic partial charges in a neutral species, the mean dipole derivatives have been chosen for a regression against δ_C. Table I contains the experimental $\bar{p}_C$ values for our group of CH_xX_{4-x} molecules (X being a halogen) along with values of δ_C determined from the principle of electronegativity equalization, with values of a and b in Eq. (3) taken from Ref. 7. The regression line is shown in Fig. 1. The fit is excellent, obeying the equation

$$\bar{p}_C = 0.429 + 7.218\delta_C,$$
(5)

with a correlation coefficient of 0.999. The data for CH_2F_2 were left out of the regression calculation due to the uncertainty in the sign choice for the $\partial p/\partial Q_i$ derivatives in the B_1

TABLE I. Mean dipole derivatives and partial charges[a] of carbon atoms in CH_xX_{4-x} molecules (atomic units).

Molecule	$\bar{p}_C$	δ_C
CH_4	0.013[b]	− 0.049
CH_3I	0.215[c]	− 0.031
CH_3Br	0.274,[c] 0.212[d]	− 0.026
CH_3Cl	0.331[c]	− 0.013
CH_3F	0.539,[c] 0.537[e]	0.011
$CHCl_3$	0.831[f]	0.056
CH_2F_2	0.889,[g] 1.045[g]	0.078
CHF_3	1.518,[f] 1.576[h]	0.153
CF_4	2.123[i]	0.239

[a] Values of a and b in Eq. (3) taken from Ref. 7. Hybridizations assumed as follows: carbon–sp^3; hydrogen–s; halogens: p.
[b] Reference 11.
[c] Reference 12.
[d] Reference 13.
[e] Reference 14.
[f] Reference 15.
[g] Reference 16, (+ +) and (− +) sign choices for $\partial p/\partial Q_6$ and $\partial p/\partial Q_7$, respectively.
[h] Reference 17.
[i] Calculated from the intensities reported in Ref. 18, assuming both $\partial p/\partial Q_i$'s to be negative.

symmetry block. This choice is narrowed in Ref. 16 to the (+ +) and (− +) sets, as a result of a Coriolis analysis. The (+ +) sign choice is eventually preferred, but with some reserve, for it contradicts the "CH stretching criterion," which has been observed to hold for many molecules.[16] This criterion states that upon stretching a C–H bond negative charge tends to flow toward the hydrogen. For CH_2F_2, this would require the selection of the (− +) set. It is interesting to note that this choice is indeed favored by Fig. 1, the (− +) point being closer to the regression line than the alternative (+ +) point, although both points are much too close to the line to allow a definite choice to be made only on these grounds.

An obvious application of Eq. (5) is the prediction of carbon mean dipole derivatives from partial charges, for substituted methanes not included in the regression shown in Fig. 1. This is exemplified in Table II. The agreement with the experimental values is very good for dichloromethane, and only reasonable for CH_2Br_2 and $CHBr_3$. It is worth noting, however, that the experimental values seem to be more reliable for CH_2Cl_2 than for the other two molecules. In the first case[19] the data were more complete, and isotopic information was taken into consideration in choosing the signs for the $\partial p/\partial Q_i$'s. These signs were then transferred to CH_2Br_2, a procedure which is clearly fraught with uncertainties. A similar situation occurred with $CHBr_3$, the reference molecule in this case being chloroform.[20]

The converse application, starting with the mean dipole derivative, is also interesting for it allows estimation of the electronegativity of the substituent from the vibrational intensities. We shall illustrate this by calculating the electronegativity of the methyl group in ethane. The experimental carbon mean dipole derivative in ethane[21] is $\bar{p}_C = 0.063\ e$. Substitution of this value in Eq. (5) yields $\delta_C = -0.051\ e$. Using this value in Eq. (3) with the values $a = 7.98$ and
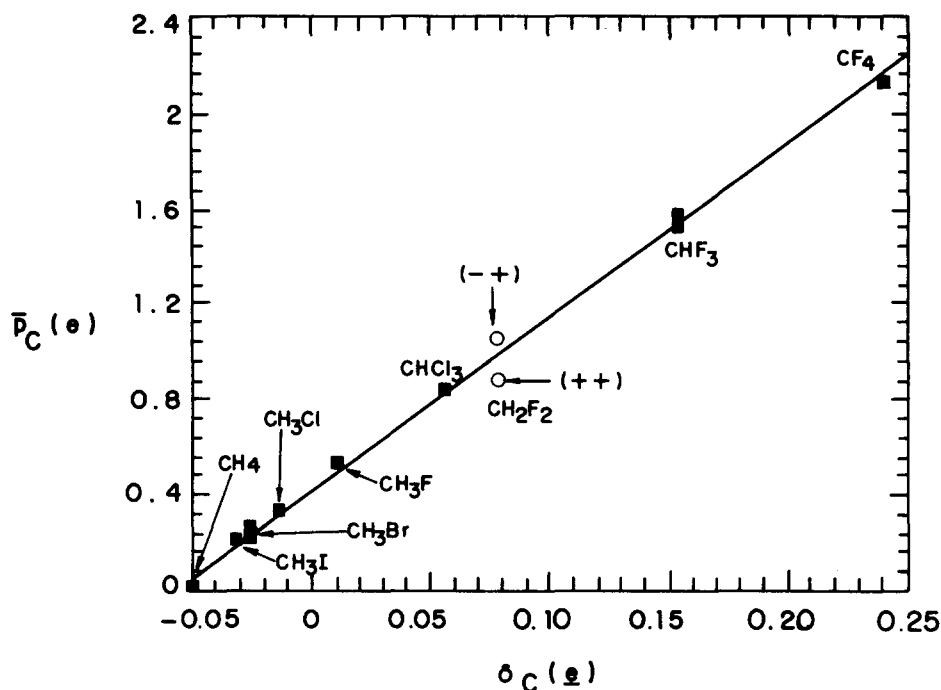
FIG. 1. Regression of mean dipole derivatives on partial charges for carbon atoms in CH_xX_{4-x} molecules (atomic units). The data corresponding to CH_2F_2 (blank circles) were not included in the regression calculation. The signs between parentheses refer to the derivatives of the molecular dipole moment with respect to the B_1 normal coordinates (see the text).

$b = 13.27$ given for carbon in Ref. 7 we obtain the electronegativity of the carbon atom in ethane, $\chi_C = 7.31$. According to the principle of electronegativity equalization, this is also the electronegativity of the methyl group (and of the remaining hydrogens, of course), the ethane molecule being regarded as CH_3Me.

Reference 7, which discusses the electronegativity of groups, assigns for the methyl group the values $a = 7.37$ and $b = 3.24$. Using these and the charge of the methyl group in ethane (zero, by symmetry) we obtain $\chi_{CH_3} = 7.37$, differing by only 0.8% from the value $\chi_{CH_3} = 7.31$. Thus, starting from an experimental infrared parameter, the mean dipole derivative, we have been able to arrive at a very good estimate of another parameter, the electronegativity, which is ultimately related to experimental electron affinities and ionization potentials.

III. CCFO ANALYSIS OF CARBON POLAR TENSORS

The charge–charge flux-overlap (CCFO) model provides a useful way to analyze variations in atomic polar tensors with different molecular environments. In this model

TABLE II. Predicted carbon mean dipole derivatives for some CH_xX_{4-x} molecules (atomic units).

| Molecule | δ_C[a] | $\bar{p}_C$ | | |
		Calcd.	Exptl.	Δ[d]
CH_2Cl[b]	0.022	0.588	0.547, 0.566	0.07, 0.04
CH_2Br_2[b]	−0.006	0.386	0.518	−0.25
$CHBr_3$[c]	0.011	0.508	0.709	−0.28

[a] See footnote a in Table I.
[b] Experimental values from Ref. 19.
[c] Experimental values from Ref. 20.
[d] $\Delta = [\bar{p}_C (\text{calcd.}) - \bar{p}_C (\text{exptl.})]/\bar{p}_C (\text{exptl.})$.

the polar tensor for a C atom obtained from a molecular orbital calculation is divided into three contributions[22]:

$$P_X^{(C)}(\text{total}) = P_X^{(C)}(\text{charge}) + P_X^{(C)}(\text{charge flux})$$
$$+ P_X^{(C)}(\text{overlap}).$$

Here

$$P_X^{(C)}(\text{charge}) = Q_C \, E \qquad (6)$$

and

$$P_X^{(C)}(\text{charge flux}) = \sum_A R_A (\hat{\nabla}_C Q_A)^t, \qquad (7)$$

where R is the position vector, Q_i is a Mulliken net charge, and $\hat{\nabla}$ stands for the gradient operator. These two terms are analogous to the parameters of the "classical" charge-charge flux model,[23] whereas $P_X^{(C)}(\text{overlap})$ is a nonclassical term including contributions from the change in the lone pair atomic dipoles due to the motion of the carbon atom.

The physical meaning of the first two terms is easy to visualize. $P_X^{(C)}(\text{charge})$ is the part of the dipole derivative arising from the motion of the equilibrium charge on the carbon atom, while the charge flux contribution reflects the change in charge on all atoms due to the displacement of the carbon atom. One expects, then, that the polar tensor of an atom vibrating in a highly ionic environment will have a large charge contribution.[22]

Molecular orbital calculations of the carbon polar tensors of the CH_xF_{4-x} molecules were performed with STO-3G and 4-31G basis sets, using the GAUSSIAN 86 programs.[24] The 4-31G mean dipole derivatives, which agreed better with the experimental values, are shown in Table III along with their CCFO contributions. The charge and the charge flux terms were calculated according to Eqs. (6) and (7), and $\bar{p}_C$ (overlap) was obtained by subtracting these two terms from $\bar{p}_C$ (total).

TABLE III. CCFO analysis of 4-31G mean dipole derivatives in CH_xF_{4-x} molecules (atomic units).

Molecule	Exptl.[a]	4-31G			
		Total	Charge	Ch. flux	Overlap
CH_4	0.013	0.018	− 0.610	0.377	0.251
CH_3F	0.539	0.649	− 0.029	0.396	0.283
	0.537				
CH_2F_2	0.889	1.233	0.507	0.503	0.223
	1.045				
CHF_3	1.518	1.775	0.992	0.748	0.034
	1.576				
CF_4	2.123	2.224	1.470	0.963	− 0.209

[a] References as in Table I.

The 4-31G calculated mean dipole derivatives are consistently higher than their experimental counterparts, but the general agreement is very good, as can be more easily seen in Fig. 2, which depicts the data of Table III superimposed on the $\bar{p}_C$ vs δ_C regression line. As one would expect from the increasing overall substituent electronegativity, the charge contribution increases as one goes from CH_4 to CF_4. It is interesting, however, that it starts with a negative value, − 0.61 e for CH_4, passing through zero in the neighborhood of CH_3F, which is also close to the zero of δ_C, the carbon partial charge. The carbon atom thus progressively changes from an electron acceptor (in methane) into a strong electron donor (in CF_4). At some point around methyl fluoride the attracting and donating strengths of the substituents can-

cel out and the carbon can be regarded as vibrating in a hypothetical totally covalent average moiety.

The difference $\bar{p}_C$ (total) $- \bar{p}_C$ (charge), which is equal to the sum of the charge flux and overlap contributions, is nearly constant, the extreme values being 0.63 e for CH_4 and 0.78 e for CHF_3. This means that the steady increase in the total mean dipole derivative with increasing substituent electronegativity simply reflects the variation of the charge contributions. A regression of $\bar{p}_C$ (exptl) on $\bar{p}_C$ (charge) yields

$$\bar{p}_C \, (\text{exptl}) = 0.554 + 1.002\{\bar{p}_C \, (\text{charge})\}$$

with a correlation coefficient of 0.993, showing that one can obtain the experimental mean dipole derivatives for the carbon atoms in these molecules by adding the constant term, 0.554 e, to the 4-31G carbon Mulliken charges.

IV. CONCLUSIONS

The attempts to find regularities in infrared intensity data for a group of molecules have usually been restricted to the consideration of terminal atoms. In this work we present a quantitative relation involving *central* atoms (the carbons in halogenated methanes), in which the mean dipole derivatives obtained from IR spectra are related, through electronegativity, to partial charges ultimately derived from electronic transition data. This relation allows quantitative predictions of both partial charges and electronegativities for atoms or characteristic groups in similar molecules. The increase of the carbon mean dipole derivatives with increasing substituent electronegativity can be nicely interpreted in
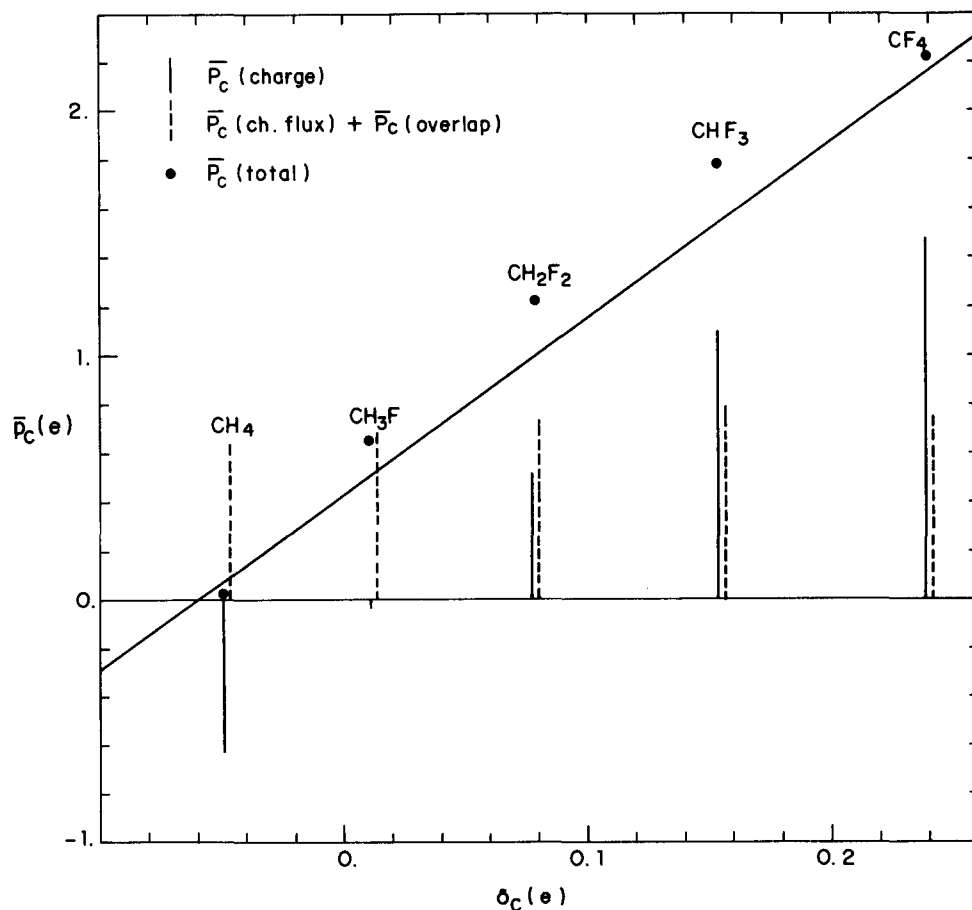

FIG. 2. 4-31G CCFO contributions of carbon mean dipole derivatives plotted against carbon partial charges (atomic units). The charge flux plus overlap contributions are slightly displaced to the right, to allow visualization. The slanted line crossing the plot is the regression line of Fig. 1.

terms of calculated charge contributions to the atomic polar tensors, confirming the usefulness of the charge–charge flux–overlap model in the interpretation of polar tensor values. The results reported here open the possibility of similar applications for other kinds of molecules.

ACKNOWLEDGMENTS

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