

Article

Carbon 1s Electron Ionization Energies and Infrared Intensities of the Chlorofluoromethanes

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São examinadas duas suposições do modelo potencial simples aplicando à energia do orbital 1s para os átomos de carbono e as derivadas dipolares médias para os fluoro-, cloro- e clorofluorometanos. Embora as variações nas energias de relaxamento dos fluorometanos sejam menores do que os erros experimentais nas medidas da energia da camada 1s nos átomos de carbono, isto não se verifica para os cloro- e clorofluorometanos. As correções do modelo potencial para o efeito de relaxamento resultam numa significativa melhoria dos resultados da regressão linear no modelo potencial. Uma análise do modelo CCFO utilizando cálculos *ab initio* com a função de onda MP2/6-311++G(3d,3p) mostra que as derivadas dipolares médias são essencialmente equivalentes à contribuição de carga para os átomos de carbono nos fluorometanos. Isto indica que essas derivadas podem ser interpretadas como cargas atômicas para essas moléculas. Por outro lado, contribuições do fluxo de carga e *overlap* são muito importantes para os cloro e clorofluorometanos. Apesar disto, as energias do orbital 1s para os átomos de carbono e as derivadas dipolares médias podem ser descritas pelo modelo potencial simples para todos os clorofluorometanos tratados. Através deste modelo, a soma das intensidades fundamentais no infravermelho para CCl₄ foi estimada em 308,9 km.mol⁻¹, um pouco abaixo da medida experimental que é de 322 km.mol⁻¹.

Two basic assumptions of the simple potential model applied to the carbon 1s electron binding energies and mean dipole moment derivatives of the fluoro-, chloro- and chlorofluoromethanes are examined. Although the relaxation energies of the fluoromethanes vary less than the experimental errors in the binding energy measurements, this is not true for the chloro- and chlorofluoromethanes. Correction of the potential model for the relaxation effects results in a statistically significant improvement in the potential model regression results. A charge-charge flux-overlap model analysis using *ab initio* results of MP2/6-311++G(3d,3p) wave function calculations shows that the total mean dipole moment derivatives are essentially equivalent to their charge contributions for the atoms in the fluoromethanes. This indicates that the mean dipole moment derivatives can be interpreted as atomic charges for these molecules. On the other hand, charge flux and overlap contributions are very important for the chloro- and chlorofluoromethanes. In spite of this complication the carbon 1s binding energies and mean dipole moment derivatives can be described by the simple potential model for all the chlorofluoromethanes treated here. Also this model leads to a theoretical prediction of the fundamental infrared intensity sum for CCl₄ of 308.9 km.mol⁻¹, slightly lower than the measured value of 322.2 km.mol⁻¹.

Keywords: core electron binding energies, mean dipole moment derivatives, infrared intensity sums

Introduction

In a recent study¹ the carbon mean dipole moment derivatives obtained from experimental infrared fundamental intensities of a diversified group of more than thirty molecules were related to their carbon 1s core electron ionization energies using the simple potential model proposed by Siegbahn and co-workers². Hybridized sp, sp² and sp³ carbon atoms of the halomethanes, of acetylenic, ethylenic, carbonylic and cyano organic compounds, as well as those of even three-membered ring compounds were investigated. In order to explain why these ionization energies and mean dipole moment derivatives are so neatly related through the potential model, two assumptions must be observed: 1) the relaxation energies of the 1s electron ionization processes of the molecules studied must be constant (or contain only slight variations), and 2) the mean dipole moment derivatives can be identified with atomic charges. In this manuscript these assumptions are closely examined for the chlorofluoromethane molecules.

The chlorofluoromethanes were chosen as the objects of this study for several reasons. They are among the simpler molecules included in the first study, having only σ -bonds and sp³ hybridized carbon atoms. As such, changes in their carbon core electron ionization energies as a function of their carbon mean dipole moment derivatives should be easier to interpret in terms of their electronic structures than those in the other molecules. Also, their mean dipole moment derivatives obtained from experimental intensity values are well-known. Furthermore, reasonably extensive molecular orbital calculations for these molecules with MP2/6-311++G(3d,3p) wave functions have been calculated by our research group³.

The assumption of constant or negligible relaxation energies is easily verified. Several methods can be used to estimate these energies. As such correction of the ionization energies for relaxation effects should provide higher quality regression results for the carbon 1s electron ionization energy and mean dipole moment derivative experimental values using the simple potential model equation, if indeed the latter parameter can be identified as an atomic charge.

Several tests of the second assumption will be presented in this manuscript. First, calculated Mulliken charges and mean dipole moment derivative values are compared. If the atomic charge interpretation of the mean dipole moment derivative is correct, one would expect excellent agreement between these quantities, at least for molecules for which approximations inherent in the Mulliken charge partitioning procedure are not expected to be critical. Second, charge, charge flux and overlap contributions to the calculated mean dipole moment derivatives are investigated. If the charge contributions are dominant compared with the combined charge flux-overlap contributions their mean dipole moment derivatives and Mulliken charges will be equivalent and the second assumption can also be expected to be valid.

Experimental Data and Theoretical Calculations

The 1s core electron energies studied here were taken from the literature⁶⁻¹⁰ and are presented in Table 1. Their error values are reported to be ± 0.1 eV or less.

Mean dipole moment derivatives are simply one third the trace of the atomic polar tensor¹¹, $P_X(\alpha)$

Table 1. Carbon 1s electron ionization energies, terminal atom potentials and relaxation energies relative to the methane values and mean dipole moment derivatives for the chlorofluoromethanes^a.

Molecule	$\Delta E_{1s,C}$ /eV	$-\Delta V$ /eV	$-\Delta E_{rel}$ /eV	$\bar{\rho}_C/e$
CH ₄	0.00	0.00	0.00	0.014
CH ₃ F	2.70	5.65	0.11	0.540 \pm 0.012
CH ₂ F ₂	5.46	10.80	0.13	1.015 \pm 0.026
CHF ₃	8.20	16.28	0.15	1.518 \pm 0.018
CF ₄	10.95	22.32	0.27	2.123
CH ₃ Cl	1.58	2.06	0.67	0.272 \pm 0.012
CH ₂ Cl ₂	3.00	4.34	1.32	0.527 \pm 0.010
CHCl ₃	4.20	6.64	2.06	0.823 \pm 0.007
CFCl ₃	6.64	12.29	2.11	1.367 \pm 0.035
CF ₂ Cl ₂	8.03	16.30	1.49	1.636 \pm 0.024
CF ₃ Cl	9.41	21.58	0.83	2.033 \pm 0.036

a) The original references for individual energy and mean dipole derivative values are Refs. 6-10 and Refs. 13-22. More specific information can be found in Table I of ref. 1. $E_{1s,C}(\text{CH}_4) = 290.90$ eV, $V(\text{CH}_4) = -0.13$ eV and $E_{rel}(\text{CH}_4) = -6.96$ eV.

$$\mathbf{P}_x^{(\alpha)} = \begin{bmatrix} \frac{\partial \bar{p}_x}{\partial \bar{x}_\alpha} & \frac{\partial \bar{p}_x}{\partial \bar{y}_\alpha} & \frac{\partial \bar{p}_x}{\partial \bar{z}_\alpha} \\ \frac{\partial \bar{p}_y}{\partial \bar{x}_\alpha} & \frac{\partial \bar{p}_y}{\partial \bar{y}_\alpha} & \frac{\partial \bar{p}_y}{\partial \bar{z}_\alpha} \\ \frac{\partial \bar{p}_z}{\partial \bar{x}_\alpha} & \frac{\partial \bar{p}_z}{\partial \bar{y}_\alpha} & \frac{\partial \bar{p}_z}{\partial \bar{z}_\alpha} \end{bmatrix} \quad (1)$$

where $\frac{\partial \bar{p}_\sigma}{\partial v_\alpha}$ are the derivatives of the Cartesian components of the dipole moment vector ($\sigma = x, y, z$) with respect to the Cartesian displacements ($v = x, y, z$) of the α^{th} atom. The atomic polar tensors are juxtaposed to form the molecular polar tensor,

$$\mathbf{P}_x = \{ \mathbf{P}_x^{(1)} : \mathbf{P}_x^{(2)} : \dots : \mathbf{P}_x^{(N)} \} \quad (2)$$

where there are N atoms in the molecule. The molecular polar tensor is calculated from the tensor containing elements that are the dipole moment derivatives with respect to the $3N-6$ normal coordinates, \mathbf{P}_Q

$$\mathbf{P}_x = \mathbf{P}_Q \mathbf{L}^{-1} \mathbf{U} \mathbf{B} + \mathbf{P}_\rho \beta \quad (3)$$

and \mathbf{L}^{-1} , \mathbf{U} and \mathbf{B} are well-known transformation matrices commonly used in molecular vibrational analysis¹². The $\mathbf{P}_\rho \beta$ product provides the rotational contributions to the polar tensor elements. As such, the elements of \mathbf{P}_x are obtained using molecular geometry (the \mathbf{B} and β matrices), symmetry (the \mathbf{U} matrix), vibrational frequencies and atomic masses (the normal coordinate, \mathbf{L}^{-1} , matrix) and permanent dipole moment values (\mathbf{P}_ρ), in addition to the values of the elements of \mathbf{P}_Q . The square of each element of the latter matrix is proportional to the measured infrared intensity if the harmonic oscillator and linear dipole moment function approximations are valid. Since the measured intensity-dipole moment derivative relationship is a squared one $3N-6$ sign ambiguities must be removed to obtain a unique polar tensor. Bibliographic references for the polar tensor solutions are indicated in Table 1¹³⁻²². Error values for the carbon mean dipole moment derivatives, \bar{p}_c , are also reported for most of the chlorofluoromethanes in Table 1, and were propagated using the experimental error estimates of the measured intensities. Other sources of error in the carbon mean dipole moment derivative values are either difficult to assess (errors in normal coordinate transformations) or probably negligible (dipole moment and molecular geometry errors). Contributions from these sources to the errors in the \bar{p}_c values have not been included in the values shown in Table 1.

Results and Discussion

The simple potential model equation proposed by Siegbahn and co-workers² can be written as:

$$E_{1s,C} = kq_C + \sum_{\partial \neq C} \frac{q_\partial}{r_{\partial C}} = kq_C + V \quad (4)$$

where $E_{1s,C}$ is the carbon 1s electron binding energy, q_C and q_∂ are atomic charges on the carbon atom and a neighboring atom, A , $r_{\partial C}$ is the internuclear distance between atom A and the carbon atom, and k is a proportionality constant normally determined by linear regression. V represents the electrostatic potential on the carbon nucleus due to its neighboring atoms. If the second assumption treated in this study is valid, mean dipole moment derivative values can be substituted for the atomic charge values in this equation.

The core ionization energies, corrected for the electrostatic potential of the terminal atoms, V , relative to these values for methane, are graphed against the carbon mean dipole moment derivatives obtained from the measured intensities in Fig. 1. The values used to construct this graph are presented in Table 1. The solid line is the least squares regression line obtained from all the points in the figure, those for the fluoro-, chloro- and chlorofluoromethanes. Even though this result has a coefficient of variation of 0.996 (*i.e.* 99.6% of the variance in the ionization energies is explained by the regression) there is considerable scattering of the points around the regression line. The vertical deviations of these points from the regression line are much larger than the experimental errors in the 1s ionization energies, ~ 0.1 eV. In fact, the mean square of the deviations from the regression line is 1.06, corresponding to an average error value of 1.03 eV, which seems much too large compared with the estimated experimental error. Furthermore the deviations are not random. The fluoromethane results are all located above the regression line whereas the molecules with two or three chlorine atoms tend to fall below the regression line.

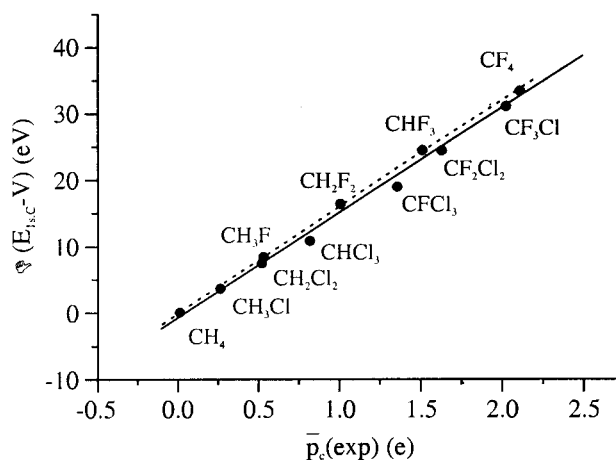


Figure 1. The carbon 1s electron ionization energies, $E_{1s,C}$, corrected for the electrostatic potentials of the neighboring atoms, V , are graphed against the carbon mean dipole moment derivative values evaluated from the experimental infrared intensities. The ordinate values are scaled relative to the value for methane, for which $E_{1s} - V = 291.03$ eV.

These deviations could be due to a break down in either of the two assumptions stated in the introduction, constant relaxation energies or inaccuracies involved in using mean dipole moment derivatives as atomic charges. Relaxation energies for the 1s electron ionization process can be expected to be smaller for the fluoromethanes than for molecules containing chlorine atoms since fluorine electron densities are not very polarizable in contrast to the chlorine ones. Assuming that the relaxation energies for the fluoromethanes are the same one might expect that only the points for the fluoromethanes would rigorously obey the simple potential model equation. The regression line for only the fluoromethanes is shown by the dashed line in Fig. 1. This line explains 99.9% of the variance in the $\Delta(E_{1s,C} - V)$ values and its mean square of the deviations corresponds to an error of 0.38 eV. Considering that the measurement errors in $E_{1s,C}$ are approximately 0.1 eV, that these energies should be corrected for relaxation or reorganization of the electron densities during the ionization processes and that the other terms in the simple potential model equation contain the mean dipole moment derivative instead of an idealized atomic charge, this regression result seems satisfactory. Note that the deviations of the chlorine-containing methanes from the dashed line depend on the number of chlorine atoms in the molecule. The larger the number of polarizable chlorine atoms the more the points deviate from the dashed line. Evidently the regression result would improve if the 1s ionization energies were corrected by the relaxation energies.

The relaxation energy values for these molecules relative to the methane value are also presented in Table 1. These values were calculated using the equivalent core method of Jolly and co-workers²⁴, and were reported in our earlier paper. As can be seen in the table, the relative relaxation energies for the fluoromethanes are all less than 0.3 eV, whereas they range from 0.7 to 2.11 eV for the chloro- and chlorofluoromethanes. The $E_{1s,C} - V$ values corrected for their relaxation energy values are graphed against the carbon mean dipole moment derivative values for the chlorofluoromethanes in Fig. 2. The corresponding regression model explains 99.9% of the total variation in the energy values. The deviations between the experimental and predicted energies correspond to an error of 0.34 eV. This value is one third of the value obtained with energy values not corrected for the relaxation phenomenon, and is about the same as the mean square of the deviations found for the regression involving only the fluoromethane data. The regression model can be considered a very satisfactory approximation to the experimental data points, since the energy measurements have an error of about 0.1 eV, the terminal atom potential and relaxation energy values are not exact, and the average error in the \bar{p}_C values of Table 1, 0.022 e, corresponds to an energy uncertainty of 0.35 eV

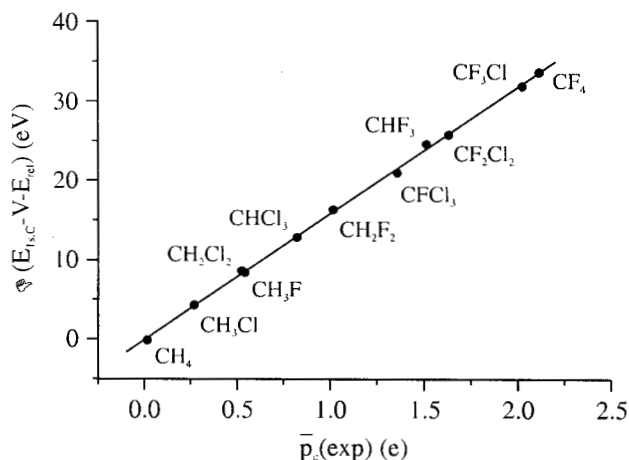


Figure 2. The energy values of Fig. 1, adjusted for the relaxation energies, are graphed against the mean dipole moment derivatives evaluated based on the experimental infrared intensities.

(0.022 e \times 15.8 eV/e, where 15.8 eV/e is the slope of the line in Fig. 2). As such, correction for inadequacies in the constant relaxation energy assumption, used to derive the simple potential model, leads to significantly better regression results.

Now our attention can be turned to the assumption that the mean dipole moment derivatives can be interpreted as atomic charges. Table 2 presents Mulliken charges and mean dipole moment derivatives for the carbon atoms of the chlorofluoromethanes calculated using MP2/6-311++G(3d,3p) wave functions. Furthermore, charge, charge flux, and overlap contributions are also included in this table. The excellent agreement observed between these theoretical values and the experimental mean dipole moment derivative values of Table 1 attests to the high quality of these wave functions for the present study.

The charge contribution and sum of the charge flux and overlap contributions are presented in graphic form in Fig. 3 for the fluoro-, chloro- and chlorofluoromethanes. The fluoromethane data are the simplest of these molecules to interpret. For the more polar fluoromethanes, CH_2F_2 , CHF_3 and CF_4 , the calculated Mulliken charges and mean dipole moment derivatives of the carbon atoms are almost exactly the same. This can also be seen in Fig. 3a. The \bar{p}_C charge contribution is actually the carbon atom Mulliken charge, which is in excellent agreement with the calculated value of the total carbon mean dipole moment derivative. Furthermore, these values are almost identical to the experimental values. So, the high polarities of the CF bonds result in charge flux and overlap contributions which cancel each other out and permit the total mean dipole moment derivative of the carbon atom to be identified with the charge contribution. For these polar molecules the Mulliken charge partitioning of electron density among the various atoms is expected to work quite well, since the electron densities are clearly distributed on the atoms with low

Table 2. Mulliken charges, mean dipole moment derivative values, and charge, charge-flux, and overlap contributions to the mean dipole moment derivatives obtained from MP2/6-311++G(3d,3p) wave functions. Units of electrons.

Molecule	q_C^a	\bar{p}_C^a	\bar{p}_C (charge) ^b	\bar{p}_C (charge flux) ^b	\bar{p}_C (overlap) ^b
CH ₄	-0.245	-0.005	-0.25	0.24	0.00
CH ₃ F	0.448	0.546	0.45	0.54	-0.44
CH ₂ F ₂	1.018	1.088	1.02	0.90	-0.83
CHF ₃	1.507	1.581	1.51	1.15	-1.08
CF ₄	2.091	2.040	2.09	1.17	-1.22
CH ₃ Cl	-0.333	0.271	-0.33	0.25	0.36
CH ₂ Cl ₂	-0.458	0.527	-0.46	0.48	0.56
CHCl ₃	-0.273	0.891	-0.27	0.82	0.34
CCl ₄	1.28	1.666	1.28	1.41	-1.49
CFCl ₃	0.428	1.441	0.43	1.48	-0.47
CF ₂ Cl ₂	0.787	1.666	0.78	1.54	-0.66
CF ₃ Cl	1.412	1.860	1.41	1.41	-0.96

a) Calculated from MP2/6-311++G(3d,3p) wave functions.

b) Charge, charge-flux, and overlap contributions to the carbon mean dipole moment derivative calculated using MP2/6-311++G(3d,3p) wave functions.

densities at the centers of the CF bonds. Note that this situation is not maintained for the methane molecule, where \bar{p}_C is almost zero, resulting from a cancellation of the contributions of the charge, charge flux, and overlap terms. Although the methane charge contribution to \bar{p}_C is calculated to be -0.25 e, the charge flux contribution is +0.24 e and the overlap term is zero. Since the absolute magnitudes of these contributions for methane are small compared to those of the other substituted methanes, the deviation between the charge contribution to \bar{p}_C and the total mean derivative is also small. For these reasons, as well as for the relaxation energy arguments discussed earlier, one can expect the carbon mean dipole moment derivatives to be useful for predicting carbon 1s electron energies via the simple potential model for the fluoromethanes.

For the chloromethanes, the behavior of the mean dipole moment derivative contributions is much different than for the fluoromethanes. The carbon atom Mulliken charges obtained from the MP2/6-311++G(3d,3p) wave functions have substantial negative values for CH₃Cl, CH₂Cl₂, and CHCl₃, whereas the \bar{p}_C values calculated from these functions are large and positive. Figs. 3b and 3c clearly show that the total \bar{p}_C values for both the chloromethanes and chlorofluoromethanes, respectively, are very different than those for their charge contributions. The almost linear behavior observed for the \bar{p}_C values as a function of the number of substituent chlorine atoms for CH₄, CH₃Cl, CH₂Cl₂, and CHCl₃, parallels the sum of the charge flux and overlap contributions, and is quite different from the trend observed for the charge contributions to \bar{p}_C . Based on these results it appears as though the carbon mean dipole moment derivatives cannot be identified as atomic

charge, and one would not be expected to be the simple relation given by the potential model adequate for describing the 1s electron binding energies of the chloro- and chlorofluoromethanes (see Table 2 and Fig. 3c). In spite of this, the chlorine-containing molecules, including the chlorofluoromethanes, have experimental 1s electron ionization energy values that provide excellent fits for the simple potential model when the carbon mean dipole moment derivative is interpreted as an atomic charge.

Estimation of Intensity Sums

The 1s electron binding energies can be used to estimate infrared fundamental intensity sums using the simple potential model. Here CCl₄ is used as an example. Its fundamental intensities have been measured, but since its polar tensors have not been calculated the regression lines in Figs. 1 and 2 were obtained without its data. The infrared fundamental intensity sum of CCl₄ can be calculated using the G intensity sum rule²³:

$$\sum A_i = \sum \frac{\chi_\alpha^2}{m_\alpha} \quad (5)$$

where $\sum A_i$ represents the fundamental intensity sum, and χ_α and m_α are the effective charge and the atomic mass of the α^{th} atom. Since CCl₄ does not have a permanent dipole moment, the rotational contribution to the polar tensor, Ω , is zero and is not included in the above equation.

The square of the effective charge of the α^{th} atom is given by:

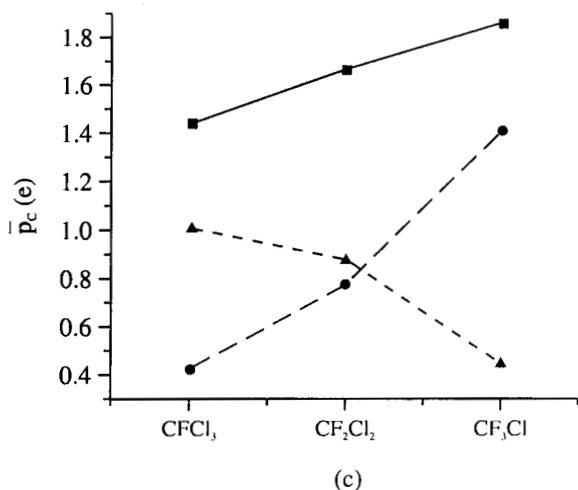
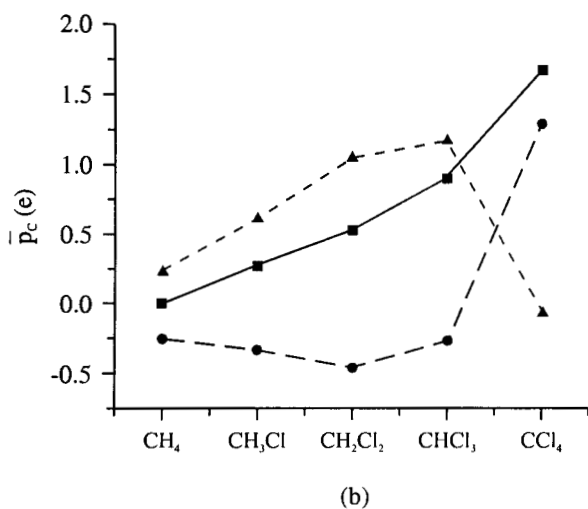
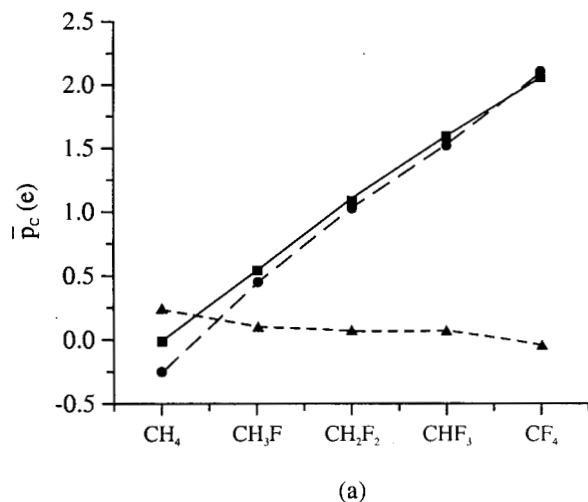


Figure 3. Charge, charge-flux + overlap, and total carbon mean dipole moment derivative values are shown for the a) fluoromethanes, b) chloromethanes, and c) chlorofluoromethanes.

$$\chi_{\alpha}^2 = \bar{p}_{\alpha}^2 + \frac{2}{9} \beta_{\alpha}^2 \quad (6)$$

where β_{α}^2 is the atomic anisotropy of the α^{th} atomic polar tensor. The use of $(\bar{p}_{\text{C}})^2$ instead of χ_{α}^2 in Eq. 5 results in a lower limit for the experimental intensity sum.

The use of the regression equation obtained from the data in Table 1 (corresponding to the regression line in Fig. 2),

$$\Delta(E_{1s,C} - V - E_{\text{rel}}) = 0.027 + 15.780 \bar{p}_{\text{C}} \quad (7)$$

the carbon 1s electron binding energy of CCl₄, 296.3 eV, its estimated neighboring atom potential, -9.06 eV, obtained by extrapolation from the other chloromethane values, and the -2.72 eV relative relaxation energy calculated using the method of Jolly and co-workers²⁴, leads to a \bar{p}_{C} value of 1.0810 e. Since the mean dipole moment derivatives must sum up to zero, $\bar{p}_{\text{Cl}} = -\bar{p}_{\text{C}}/4 = -0.2703$ e. The atomic anisotropy of the carbon atom in CCl₄ is zero by symmetry, and here we assume the anisotropies of the chlorine atoms to be negligible. Substituting these values in Eqs. 5 and 6 results in a estimated fundamental intensity sum of 308.9 km.mol⁻¹. The experimental result measured by Tanaka and Saëki²⁵ is slightly higher at 322.2 km.mol⁻¹.

Conclusions

The excellent regression fit obtained for the carbon 1s electron ionization energies and mean dipole moment derivatives using the simple potential model encourages the interpretation of these derivatives as atomic charges. Although the charge-charge flux-overlap analysis of the mean dipole moment derivatives obtained from the molecular orbital results indicates that this interpretation is naive, except for the case of the fluoromethanes, the linear regression results show that the experimental points for the carbon atoms of the chloro- and chlorofluoromethanes are in equally good agreement with the model equation as are those of the fluoromethanes.

More investigation is necessary to explain why these data fit the simple potential model equation so well. Specifically, higher quality wave functions should be used to calculate the mean dipole moment derivative contributions and atomic charges of the chloro- and chlorofluoromethanes. Perhaps methods other than Mulliken's should be considered to estimate the atomic charges of these molecules.

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