Core Electron Energies, Infrared Intensities, and Atomic Charges

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Abstract: Carbon 1s electron binding energies determined by X-ray photoelectron spectroscopy and mean dipole moment derivatives obtained from experimental infrared intensities are shown to be related through the simple potential model proposed by Siegbahn and collaborators. The sp^3 carbon atoms in 13 halomethanes, 2 ethanes, 3 methylacetylenes, cyclopropane, and ethylene oxide have 1s energies, which, after correction for electrostatic potentials from neighboring atoms, are linearly related to the carbon mean dipole moment derivatives, presenting a slope of 15.50 ± 0.29 eV/e. The sp^2 carbons of ethylene, three haloethylenes, and three carbonyl compounds also exhibit a linear relationship having a significantly different slope of 17.37 ± 0.87 eV/e. The sp carbon atoms in acetylenes, cyanides, CO, CS_2, CO_2, and OCS show a third linear relationship, with a slope of 18.90 ± 0.75 eV/e. These slopes are proportional to the inverse atomic radii of sp^3, sp^2, and sp carbon atoms and according to the simple potential equation can be interpreted as estimates of Coulomb repulsion integrals involving these hybridized orbitals and the 1s core electron orbitals. Two basic assumptions of the potential model are investigated. The effect of relaxation energies on the 1s electron ionization processes is estimated as the difference between ΔSCF ionization energies and Koopmans' frozen orbital estimates obtained from 6-31G(d,p) wave functions. These results are compared with values obtained previously from the equivalent cores estimating procedure. Also the conceptual validity of identifying the carbon mean dipole moment derivatives as atomic charges is discussed within the framework of the charge−charge flux-overlap model.

1. Introduction

Many partitioning procedures have been proposed to split the total electron density distribution of a molecule among its constituent atoms, in attempts to simplify its mathematical description and achieve a model easier to interpret in chemical terms. The literature records several such schemes, which yield atomic charges labeled after Mulliken,[1,2] Coulson,[3] Jug,[4−6] Hirshfeld,[7] Bader,[8,9] Maslen,[10] and Politzer[11,12] or identified by a short description, such as natural,[13−15] density fitted,[16−25] potential derived,[26−34] and so on. Given the complexities of molecular wave functions and the ambiguities that arise in attempts to assign electron densities to individual atoms, one can expect alternate partitioning procedures to be proposed in the future.

Fortunately all existing charge scales seem to reflect one predominant underlying factor. A multivariate statistical investigation with use of principal component analysis applied to about two dozen atomic charge scales has shown that over 90% of their total data variance can be described by only one factor.[35] Other studies, based on several molecular wave functions and partitioning schemes, as well as on more empirical procedures such as electronegativity equalization[36] and charge equilibration,[37] have also produced highly correlated atomic charge values. In contrast, much less attention has been paid to charge values determined from experimental data.

Spectroscopic measurements are an important experimental source of atomic charge values. X-ray photoelectron spectros-

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copy (XPS), for example, yields a direct measure of the energy of internal core electrons,[38-43] and shifts in these energies provoked by changes in substituent atoms can be quantitatively related to atomic charges by a simple potential model. Relations between experimental core electron energies and calculated charges obtained from quantum chemical or empirical procedures have also been reported, for molecules such as the halomethanes, silanes, and germanes.[44] However, this potential model has not been tested with atomic charge parameters obtained from experimental data.

Within the harmonic oscillator and linear dipole moment approximations,[45] infrared vibrational intensities furnish dipole moment derivatives that are closely related to charge quantities.[46-50] These references, as well as one published much earlier,[51] suggest that gas-phase IR intensity data might be used to estimate atomic charge values. Surface and solid state studies have also emphasized that dipole moment variations with molecular geometry might furnish relevant information about charge distributions in chemical bonds.[52-55]

The polar tensor formalism is particularly convenient for analyzing IR intensity data because it provides derivatives associated with vibrational displacements of individual atoms. Cioslowski[56-58] has proposed that the mean values of these atomic derivatives be interpreted as generalized atomic polar tensor (GAPT) charges. However, the same electronic factors that have prohibited the successful determination of atomic charges from molecular dipole moments[59-61] appear to provide important contributions to the dipole moment derivatives as well. Besides a static charge contribution, these derivatives generally contain significant terms resulting from charge flux and overlap phenomena.[46,62,63]

Recently our laboratory has investigated the relation between infrared intensity sums and atomic charges for the fluoromethanes. This family of molecules is ideal for studying how X-ray photoelectron energies for the carbon 1s core electrons vary with atomic charges, because only their static charge contributions to the dipole moment derivatives appear to be important. Extensive molecular orbital calculations with a set of wave functions of increasing complexity have shown that the charge flux and overlap contributions essentially cancel out for the fluoromethanes, reducing their dipole moment derivatives to the static charge term.[64] These results are consistent with an electrostatic model recently proposed to explain the thermodynamic stabilities of the fluoromethanes.[65] Furthermore, Mulliken charges for the fluoromethanes, which are expected to be reasonably accurate for these polar molecules because the overlap charge is relatively small and constant, are also in excellent agreement with mean dipole moment derivative values determined from experimental infrared intensities.[64] One can anticipate, therefore, that the carbon 1s electron energies and mean dipole moment derivatives of the fluoromethanes will provide an excellent fit for the simple potential model equation, as we shall demonstrate here.

To test the limitations of the mean dipole moment derivative values as a basis for extracting core electron energies from the potential model equation, our study was extended to other molecules containing sp, sp^2, and sp^3 hybridized carbon atoms. Extensive *ab initio* molecular orbital calculations performed for some of these molecules, such as the chloro- and fluorochloromethanes, have shown that all three CCFO contributions—charge, charge flux, and overlap—are important for determining the values of their mean dipole moment derivatives.[64] In spite of this apparent complication, the vast majority of the mean derivatives can still be interpreted as atomic charges and used in the potential model for calculating the carbon 1s core electron energies. The results of this analysis are reported and discussed in what follows.

2. Experimental Data and Theoretical Calculations

The carbon 1s electron energies studied in this work were taken from the literature[44,66-80] and are presented in Tables 1-3. Their error values are reported to be ±0.1 eV or less. Here we assume that all errors are equal to this maximum value. The energies are reported in separate tables, according to the hybridization of the carbon atom.

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Table 1. Experimental Mean Dipole Moment Derivatives ($\bar{p}_C$) and 1s Binding Energies (E_{1s}), for sp³-Hybridized Carbons

molecule	$\bar{p}_C/e^a$	ref	E_{1s}/eV^b	ref	V^c/eV
CH₄	0.014	84	290.90	44	−0.13
CH₃F	0.540 ± 0.012	85	293.60	66	−5.78
CH₂F₂	1.015 ± 0.026	86	296.36	67	−10.93
CHF₃	1.518 ± 0.018	87, 88	299.10	66	−16.41
CF₄	2.123	89	301.85	44	−22.45
CH₃Cl	0.272 ± 0.012	90	292.48	44	−2.19
CH₂Cl₂	0.527 ± 0.010	91	293.90	66	−4.47
CHCl₃	0.823 ± 0.007	92	295.10	66	−6.77
CFCl₃	1.367 ± 0.035	93	297.54	68	−12.42
CF₂Cl₂	1.636 ± 0.024	93	298.93	68	−16.43
CF₃Cl^d	2.033 ± 0.036	93	300.31	68	−21.71
CH₃Br	0.210 ± 0.009	90	292.12	44	−1.12
CH₃I	0.134 ± 0.003	90	291.43	69	−1.02
CH₃CH₃	0.063	94	290.74	44	−0.66
CF₃CF₃	1.328	95	299.72	70	−9.49
C₃H₆	0.017	84	290.60	71	−0.12
C₂H₄O	0.277	96	292.50	71	−2.87
C̲H₃C≡N	0.102	97	293.10	72	0.58
C̲H₃C≡CH	0.112	98	291.77	118	−0.77
C̲H₃C≡CCH₃	0.117	98	290.03	118	−1.36

^{a} Estimated errors as determined in refs 84−105. ^{b} A maximum error of 0.1 eV is assumed for these values. ^{c} V stands for the second term in eq 4. ^{d} Error estimated assuming that $s_{p_{xx}} = s_{p_{yy}} = s_{p_{zz}}$ where s is the square root of the estimated variance in one of the diagonal polar tensor element values.

Table 2. Experimental Mean Dipole Moment Derivatives and 1s Binding Energies for sp² Carbons (Notation as in Table 1)

molecule	$\bar{p}_C/e^a$	ref	E_{1s}/eV^b	ref	V/eV
H₂CO	0.593	99	294.47	73	−7.11
F₂CO	1.51 ± 0.03	100	299.64	74	−16.99
Cl₂CO	1.24 ± 0.09	100	296.75	74	−12.61
C̲H₂CH₂	−0.055	99	290.70	75	0.55
C̲H₂CF₂	−0.274 ± 0.057	101	291.33	76	7.45
CH₂C̲F₂	0.977 ± 0.043	101	296.10	76	−11.12
cis-C₂H₂Cl₂	0.182 ± 0.005	102	292.31	77	−0.40

^{a} See footnote a, Table 1. ^{b} See footnote b, Table 1.

Table 3. Experimental Mean Dipole Moment Derivatives and 1s Binding Energies for sp Carbons (Notation as in Table 1)

molecule	$\bar{p}_C/e^a$	ref	E_{1s}/eV^b	ref	V/eV
HC≡N	−0.041	103	293.5	79	0.77
CH₃C̲≡N	0.078	97	293.2	72	−1.80
CH₃C̲≡CH	−0.021	98	291.07	118	−1.26
CH₃C≡C̲H	−0.321	98	290.40	118	3.14
NC̲≡CN	0.122	103	294.5	78	−0.95
CH₃C̲≡CCH₃	−0.124	98	291.30	118	0.38
C̲H≡CH	−0.198	103	291.14	118	1.58
CO	0.228	104	296.19	69	−2.91
CS₂	0.688	105	293.10	80	−6.38
CO₂	1.073	105	297.75	79	−13.31
OCS	0.849	105	295.20	80	−9.70

^{a} See footnote a, Table 1. ^{b} See footnote b, Table 1.

In the polar tensor formalism the mean dipole moment derivative is defined as one third the trace of the atomic polar tensor.[81] For the αth atom in a molecule the polar tensor is given by

$$\mathbf{P}_X^{(\alpha)} = \begin{pmatrix} \partial p_x/\partial x_\alpha & \partial p_x/\partial y_\alpha & \partial p_x/\partial z_\alpha \\ \partial p_y/\partial x_\alpha & \partial p_y/\partial y_\alpha & \partial p_y/\partial z_\alpha \\ \partial p_z/\partial x_\alpha & \partial p_z/\partial y_\alpha & \partial p_z/\partial z_\alpha \end{pmatrix} \quad (1)$$

where $\partial p_\sigma/\partial \nu_\alpha$ are the derivatives of the Cartesian components of the dipole moment ($\sigma = x, y, z$) with respect to the Cartesian displacements ($\nu = x, y, z$) of the αth atom. When juxtaposed, the 3 × 3 atomic

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polar tensors form the 3 × 3N molecular polar tensor,

$$\mathbf{P}_X = \{P_X^{(1)} \vdots P_X^{(2)} \vdots ... \vdots P_X^{(N)}\} \quad (2)$$

N being the number of atoms in the molecule. This tensor is calculated from another tensor, $\mathbf{P}_Q$, whose elements are the dipole moment derivatives with respect to the 3N − 6 normal coordinates:

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

$\mathbf{L}^{-1}$, $\mathbf{U}$, and $\mathbf{B}$ in this equation are well-known transformation matrices used in molecular vibrational spectroscopy.[82] The $\mathbf{P}_\rho \beta$ product contains the rotational contributions to the polar tensor elements.[83]

The square of each element in $\mathbf{P}_Q$ is proportional to the absolute infrared intensity if the harmonic oscillator and linear dipole moment approximations are valid.[46] To obtain a unique polar tensor from experimental intensity values, therefore, 3N − 6 sign ambiguities must be removed. Bibliographic references for these polar tensor solutions are indicated in Tables 1−3.[84−105] Errors for the $\bar{p}_C$ values, propagated from experimental intensity error estimates, are also reported where avaliable. Other sources of error for the $\bar{p}_C$ values are either difficult to assess (errors in the normal coordinates) or probably negligible (dipole moment and molecular geometry errors). Contributions from these latter sources have not been included in the $\bar{p}_C$ error estimates given in Tables 1−3.

Molecular orbital calculations were carried out with the Gaussian 92 program,[106] on RISC 6000 IBM workstations.

3. The Potential Model in XPS

The potential model used to relate XPS chemical shifts and atomic charge values,

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$$E_i = k_i q_A + \sum_{B \neq A} q_B / R_{AB} \qquad (4)$$

can be derived from purely classical electrostatic considerations[38–42] or from quantum mechanical arguments.[107] In this equation E_i is the ith core orbital energy, q_A is the net atomic charge of the atom containing this core orbital, q_B are the net atomic charges of neighboring atoms, and R_{AB} represents the internuclear distance between atoms A and B. Usually k_i is treated as an adjustable parameter and determined from least-squares fits on sets of XPS core electron energies plus estimated atomic charges for a given element in different molecules. While the core energy values are obtained directly from experimental measurements, the atomic charge values have been obtained always from theoretical—mostly molecular orbital—calculations. The k_i value can be identified with the Coulomb repulsion integral between a core and a valence electron for atom A.

The first term in eq 4 represents the ith core orbital energy of atom A caused by its own charge q_A. The second term gives the energy that this core electron experiences due to the electrostatic potential from the other atoms in the molecule and is often denoted by $V = \sum_{B \neq A} q_B / R_{AB}$. If the molecular geometry and the net atomic charges are known, the V contributions to the core electron energies can be calculated. The values of these contributions have been included in Tables 1–3.

Theoretical values of net atomic charges are usually employed as regressors for fitting the potential model equation to XPS energies. In this study the q_A and q_B values are estimated instead with use of mean dipole moment derivatives obtained from experimental polar tensors, which are determined directly from measured infrared fundamental intensities.

The carbon 1s electron binding energies for the molecules in Tables 1–3 fall between 290 and 302 eV. The neighboring atom contributions (V) are usually negative and have absolute values that are less than 10% of the binding energies. A few of these contributions have positive values, normally when the carbon atom in question has another highly positive-charged carbon atom as a nearest neighbor.

In Figure 1 the 1s electron binding energies corrected for their neighboring atom potential contributions, $E_{1s} - V$, are plotted as a function of the corresponding $\bar{p}_C$ values, for the sp³-hybridized carbon atoms of Table 1. Even though several kinds of molecules are represented in this graph—halomethanes, three-membered rings, cyano, and acetylenic compounds—a linear relationship between the potential-corrected 1s binding energies and the mean dipole moment derivatives is clearly observed. The least-squares regression line shown in the graph, which reproduces within experimental error the positions of most of the molecules, has an explained variation of 99.6%. Its slope, 15.50 ± 0.29 eV, may be taken as an estimate of k_i, the average Coulomb repulsion integral between a 1s core and a sp³ valence electron on the carbon atom. Figure 1 contains values for 20 molecules and the large number of degrees of freedom for the residuals ensures a stable regression. Of course it would be desirable to include a larger number of molecules in the regression. Experimental 1s electron energies are in fact quite abundant, but the number of molecules for which experimental carbon polar tensors have been determined is still rather small and limits such an extension.

Figure 2 is a graph of the corrected 1s carbon binding energies against the carbon mean dipole moment derivatives for sp² carbon atoms. Only seven molecules are represented, owing to the scarcity of measured intensities for molecules of this type. The least-squares line has an explained variation of 99.4%.
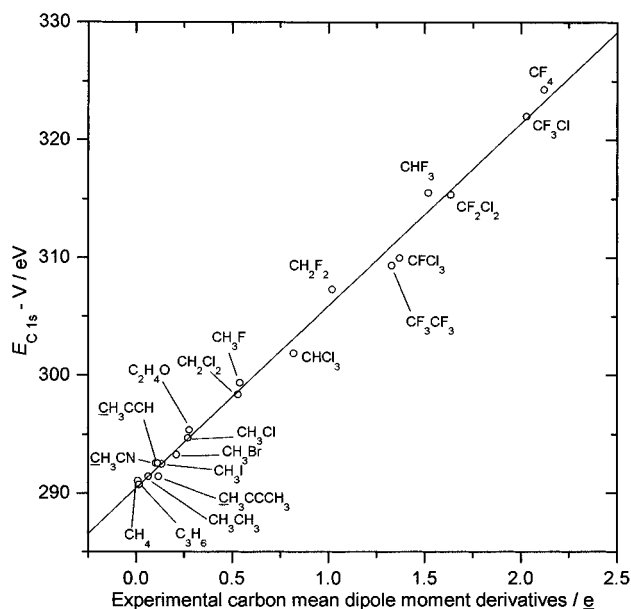
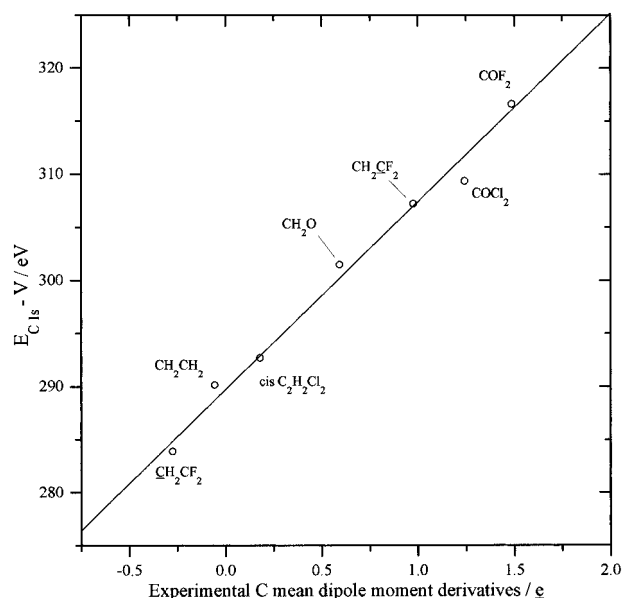(107) Gelius, U. *Phys. Scr.* **1974**, *9*, 133.

Figure 1. Graph of the carbon 1s experimental ionization energies corrected by the neighboring atom potential (eV) as a function of the carbon mean dipole moment derivatives (e) for sp³ carbon atoms.

Figure 2. Graph of the carbon 1s experimental ionization energies corrected by the neighboring atom potential (eV) as a function of the carbon mean dipole moment derivatives (e) for sp² carbon atoms.

Considering the errors propagated into the mean dipole moment derivative values, the fit is excellent. The slope of the regression line is 17.37 ± 0.87 eV/e, significantly different from the slope of the line for the sp³ carbons.

Corrected 1s electron binding energies and mean dipole moment derivatives for the sp carbon atoms listed in Table 3 are plotted against each other in Figure 3. The calculated regression line again provides an excellent fit for all the experimental data, except those of carbon monoxide. Since the carbon atom in this molecule is surrounded by a chemical moiety quite different from that of the cyano or the acetylenic carbons, it is not surprising that the CO molecule strays from the regression line. The explained variation is 99.5%, and the slope of the regression line is 18.90 ± 0.75, significantly different from the values calculated for the other two hybridizations.

Plots of the uncorrected carbon 1s electron binding energies against experimental $\bar{p}_C$ values also result in highly significant
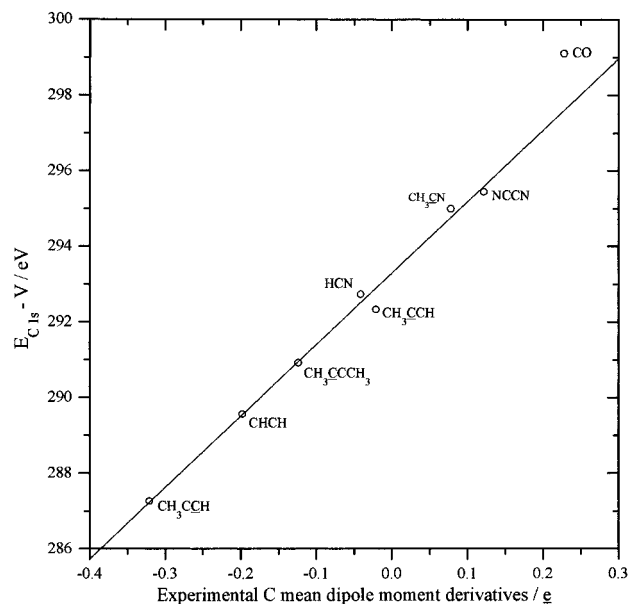
Figure 3. Graph of the carbon 1s experimental ionization energies corrected by the neighboring atom potential (eV) as a function of the carbon mean dipole moment derivatives (e) for sp carbon atoms.

Figure 4. Graph of the fluorine 1s experimental ionization energies corrected by the neighboring atom potential (eV) as a function of the fluorine mean dipole moment derivatives (e). Fluoromethanes are located with solid circles.

Table 4. Experimental Mean Dipole Moment Derivatives ($\bar{p}_F$) and 1s Binding Energies (E_{1s}) for Fluorine Atoms

molecule	$\bar{p}_F/e^a$	ref	E_{1s}/eV^b	ref	V/eV
CH$_3$F	−0.48	85	692.92	68	5.19
CH$_2$F$_2$	−0.49	86	693.65	68	7.33
CHF$_3$	−0.51	87, 88	694.62	68	9.72
CF$_4$	−0.53	89	695.77	68	12.14
CF$_2$Cl$_2$	−0.59	93	694.68	68	10.99
CFCl$_3$	−0.49	93	694.33	68	9.88
CF$_3$Cl	−0.63	93	695.04	68	12.90
F$_2$CO	−0.45	100	695.43	69	9.50
CH$_2$CF$_2$	−0.42	101	694.44	68	6.89
CH$_3$CF$_3$	−0.44	95	695.33	68	9.69
BF$_3$	−0.51	119	694.80	120	10.34
NF$_3$	−0.40	121	694.45	76	7.29
PF$_3$	−0.58	121	694.20	122	8.95
SiF$_4$	−0.55	123	694.70	124	10.93

^{a} See footnote a, Table 1. ^{b} See footnote b, Table 1.

regressions. The regression-explained variations, though, are smaller (96.5, 97.8, and 83.7%, respectively) than those obtained when the binding energies are first corrected for contributions from the electrostatic potential of the neighboring atoms as specified by the simple potential model of eq 4.

In order to investigate if a similar relation holds for terminal atoms, fluorine was chosen for the following two main reasons. First, there exists a reasonable number of fluorine-containing molecules for which all the fundamental infrared intensities have been measured and the experimental polar tensors have been determined. Secondly, the fluorine mean dipole derivatives, compared with those of other terminal atoms, are more easily interpreted in terms of atomic charges, owing perhaps to the high electronegativity value of this element. Table 4 contains values of fluorine 1s electron binding energies and their corresponding mean dipole moment derivatives. The electrostatic potentials on the fluorine atom caused by the atomic charges of neighboring atoms result in large and positive contributions to the binding energies, again in agreement with the large electronegativity of fluorine. The corrected binding energies are plotted against the mean dipole moment derivatives in Figure 4. The range of all these potential-corrected fluorine core energies is only about 6 eV, less than the variations observed for the carbon atoms. This is consistent with the fact
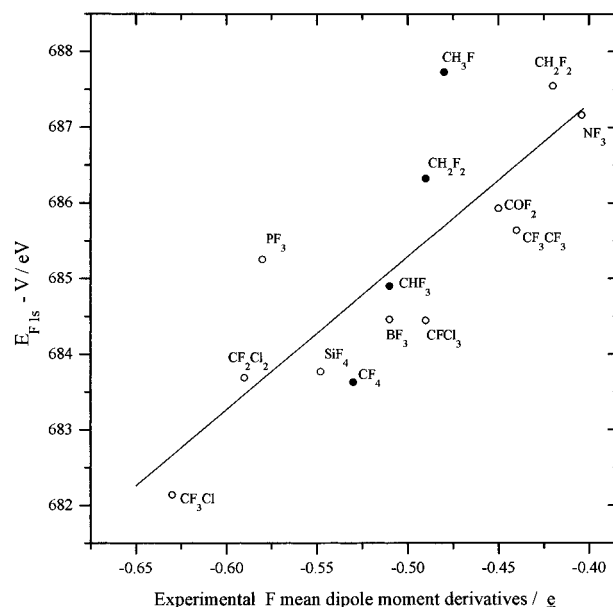
that, of all the atoms for which atomic polar tensors have been determined, fluorine presents $\bar{p}$ values that are the most resistant to changes in the molecular environment. The scatter of the points about the regression line does not provide convincing evidence for the existence of a unique linear relationship between these quantities. On the other hand, there does appear to be a linear relation for the fluorine atoms in the fluoromethanes.

4. Discussion

The derivation of the potential model (eq 4) makes use of two basic assumptions: (1) the molecular electronic structure can be approximated by net charges on the atoms and (2) charge relaxation or reorganization during the ionization process is constant. The linear relations observed in Figures 1−3 imply that the mean dipole moment derivatives can be taken as measures of atomic charges and that the relaxation energies are either negligible or constant for the molecules studied. It is shown below that both assumptions hold for the fluoromethanes. However, they do not seem to be valid for the other halomethanes.

Molecular orbital results with use of MP2/6-311++G(3d,-3p) wave functions have shown that the charge flux and overlap contributions to the carbon and fluorine mean dipole moment derivatives cancel each other for all the fluoromethanes.[64] Since the only contribution left is due to charge, one is encouraged to identify these derivatives with the net atomic charges in these molecules, and in fact the Mulliken charge values are almost the same as the fluoromethane $\bar{p}_C$ and $\bar{p}_F$ values. Electrostatic models for these molecules are capable of explaining their thermodynamic stabilities[65] and infrared fundamental intensity sums.[64] The success of these models implies that the overlap charge densities in the CF bonds are small relative to the charge densities centered on the atoms. Therefore, the way the former is divided among the atoms, a critical step in the Mulliken charge procedure, is not important for determining accurate charge values. Both procedures—Mulliken's and mean dipole moment derivatives—should provide accurate atomic charge estimates for the fluoromethanes. One may then expect the potential model to describe the relation between the experimental carbon

Core Electron Energies, IR Intensities, and Atomic Charges

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Table 5. Carbon 1s Electron Ionization Energies, Neighboring Atom Electrostatic Potentials, and Relaxation Energies Relative to Their Methane Values

molecule	$\Delta E_{C,1s}$/eV[a]	$-\Delta V$/eV[b]	$-\Delta E_{rel}$/eV[c]	$-\Delta E_{rel}$/eV[d]
CH_4	0.00	0.00	0.00	0.0
CH_3F	2.70	5.65	0.11	−0.25 (−0.23)
CH_2F_2	5.46	10.80	0.13	−0.60 (−0.49)
CHF_3	8.20	16.28	0.15	−0.96 (−0.73)
CF_4	10.95	22.32	0.27	−1.25 (−0.93)
CH_3Cl	1.58	2.06	0.67	0.51
CH_2Cl_2	3.00	4.34	1.32	0.96
$CHCl_3$	4.20	6.64	2.06	1.38
$CFCl_3$	6.64	12.29	2.11	1.32
CF_2Cl_2	8.03	16.30	1.49	0.60
CF_3Cl	9.41	21.58	0.83	−0.18

[a] Experimental ESCA chemical shifts relative to methane ($E_{C,1s}(CH_4)$ = 290.9 eV). [b] Neighboring atom electrostatic potentials calculated with use of experimental mean dipole derivatives and interatomic distances ($V(CH_4) = -0.13$ eV). [c] Relaxation energies relative to the methane value calculated with use of the equivalent cores approximation ($E_{rel}(CH_4) = -6.96$ eV). [d] Relaxation energies relative to the methane value calculated with use of the ΔSCF method ($E_{rel}(CH_4) = -13.15$ eV). See text for calculational details and ref 114 for details about the values in parentheses, which were obtained with use of DZP wave functions.

1s ionization energies and the mean dipole moment derivatives of the fluoromethanes, if the ionization energies are corrected for relaxation energies.

The chloro- and fluorochloromethanes contain C−Cl bonds, which are less polar than CF bonds and result in electronic structures more complex than those of the fluoromethanes. An earlier MP2/6-311++G(3d,3p) study shows that the charge flux and overlap contributions to the carbon mean dipole moment derivatives of these molecules do *not* cancel,[64] making it difficult to interpret these derivatives as charges. In spite of this conceptual objection the chloro- and fluorochloromethane data present only small deviations from the potential model line in Figure 1, and these deviations can be explained by variations in the 1s ionization relaxation energies.

Relaxation energies can be calculated by various procedures. Jolly and colleagnes[108−110] introduced an empirical method based on the equivalent cores approximation and estimated relaxation energies of a large number of molecules. Bagus proposed the ΔSCF approach,[111] which has been used to successfully calculate these energies from SCF orbital wave functions. Applications of this approach have also been widespread.[112,113]

Table 5 contains values of the experimental 1s electron ionization energies, neighboring atom electrostatic potentials, and relaxation energies for the fluoro-, chloro-, and fluoro-choromethanes relative to the corresponding methane values. Two columns are included in this table for the relative relaxation energies, one column for values obtained with use of Jolly's empirical scheme and the other for results from ΔSCF calculations done in our laboratory using Hartree−Fock wave functions and 6-31G(d,p) basis sets. All the calculations were performed with use of theoretical equilibrium geometries. The last column of Table 5 also includes some relative relaxation energy values for the fluoromethanes obtained from the literature.[114]

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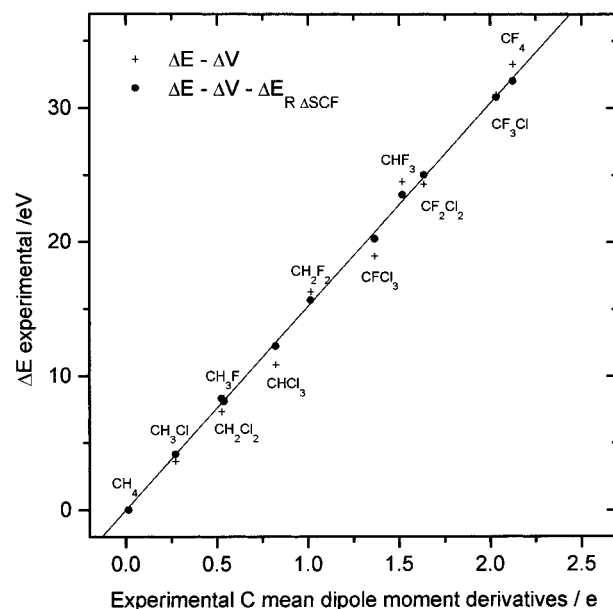

Figure 5. Experimental carbon 1s ionization energies minus the eletrostatic potentials of neigboring atoms plotted against experimental carbon mean dipole moment derivatives, (+) uncorrected values, and (●) values corrected for their relaxation energies. These values are relative to the methane $E_{C,1s} - V$ value of 291.03 eV.

The relaxation energies calculated by these methods are quite different. The empirical estimates indicate that the absolute values of the relaxation energies are smallest for methane, are only slightly changed on fluorine substitution, and increase by about half an electronvolt for each chlorine substitution. The ΔSCF results indicate that the absolute value of the relaxation energy is smallest for CF_4, increasing steadily as fluorines are substituted by hydrogen or chlorine atoms. Reasonable agreement between relaxation energies calculated in this work with HF/6-31G(d,p) wave functions and those determined in ref 114 with DZP wave functions is also evident upon inspection of the fluoromethane values in the last column of Table 5.

Here our main concern is to use relaxation energies to explain small deviations of the core ionization energies from the simple potential model line in Figure 1. Correction of the $E_{C,1s} - V$ values for the chlorofluoromethanes, using either set of relaxation energies, the one obtained from the equivalent cores approximation or the one calculated with use of the HF wave functions, results in significant statistical improvements in the regression line of Figure 1.

Figure 5 contains a graph of the ΔSCF relaxation energy corrected $E_{C,1s} - V$ values for the fluorochloromethanes against the experimental carbon mean dipole moment derivatives. These values, indicated by blackened circles, form an almost perfect straight line. The regression line shown there has an explained variation of 99.96% and an extrapolated intercept of −0.02 eV. The latter value is close to zero as expected. The uncorrected $E_{C,1s} - V$ values represented by the + symbol show considerable scatter about the regression line. This explains why the regression line in Figure 1 is of lower quality than the one in Figure 5. The former explains less variance, 99.61%, and has an extrapolated intercept of −0.65 eV, which is much larger than the 0.1 eV estimated experimental error in the observed core ionization energies. Use of equivalent core estimated relaxation energies instead of ΔSCF values leads to a regression line also explaining 99.96% of the experimental data variance. Its calculated intercept, +0.03 eV, is also very close to zero. The slopes of these lines are different, however, 15.19 (ΔSCF) and 15.78 (equivalent cores) eV·e^{-1}. This
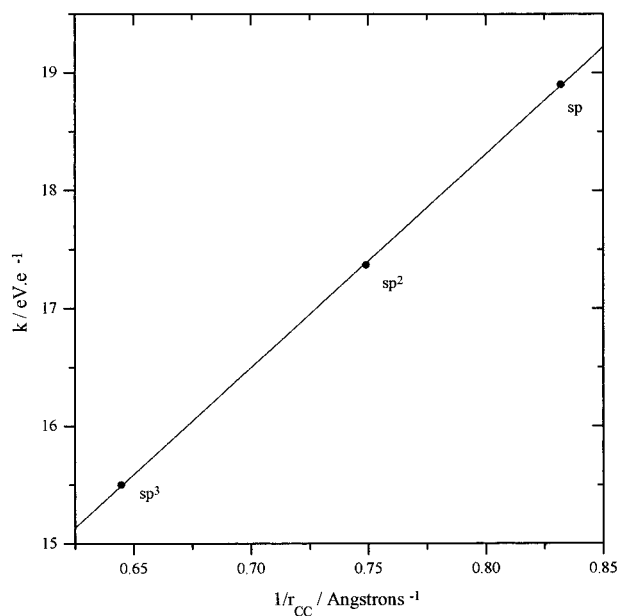
Figure 6. Plot of the slopes of the potential model regression lines (k) vs inverse average experimental atomic radii for sp^3, sp^2, and sp carbon atoms.

illustrates the importance of using correct relaxation energies in interpretating simple potential model results.

Similar arguments might be employed to explain other deviations from the regression lines in Figures 1−3, since the simple potential model ignores the relaxation phenomena, and these contribute with varying degrees of importance to the experimental ionization energies. For example, COCl$_2$ and CS$_2$, whose points fall below the regression line in Figure 2, have relaxation energies also estimated to be 1−2 eV higher than those of the other molecules in the same plot. The most striking deviation from the simple potential model lines is that of CO in Figure 3. Unlike the other deviating cases, the relaxation energy of carbon monoxide is several electronvolts *lower*, not higher, than those of the other molecules represented in the plot. The point locating CO should therefore fall *above* the regression line, and indeed this is what is observed in Figure 3.

The slopes determined for the regression lines in Figures 1−3 are also consistent with the simple potential model. Since k in eq 4 is interpreted as the value of the Coulomb repulsion integral between the core electron being ionized and a valence electron on the same atom,[38] the three slopes should have values similar to those of the 1s-valence electron repulsion integrals for sp^3, sp^2, and sp carbon atoms. Furthermore, since the electrostatic interactions are inversely proportional to the distance between the electrons, a linear relation between the slopes and the inverse of the atomic radii of the hybridized carbon atoms would not be surprising. In Figure 6 the slopes are plotted against the inverse atomic radii of the sp^3, sp^2, and sp carbon atoms, 1.55, 1.34, and 1.20 Å,[115] respectively. The points form a straight line with positive slope, validating the simple potential model interpretation employed in this work. A more precise analysis of the variations in the slopes of the potential model lines can be made after accurate relaxation energies are calculated for all the molecules treated here.

5. An Application: IR Intensity Sums

The simple relationship between 1s electron binding energies and mean dipole moment derivatives, eq 4, can be used for

estimating infrared fundamental intensity sums, and this is of interest because experimental core ionization energies are much more abundant than complete intensity measurements. For molecules containing only carbon and one other type of symmetrically equivalent atoms, like CCl$_4$ or C$_2$Cl$_6$, the carbon mean dipole moment derivatives can be determined from 1s electron binding energies and the mean dipole moment derivative value of the remaining equivalent atoms, using the null sum relationship involving all the mean dipole moment derivatives in the neutral molecule.[46] The infrared fundamental intensity sum can be calculated by using Crawford's G sum rule,[116]

$$\sum A_i + \Omega = \sum \chi_\alpha^2/m_\alpha \tag{5}$$

where $\sum A_i$ represents the fundamental intensity sum, χ_α is the King effective charge[46] of atom α, m_α is the mass of the αth atom, and Ω is a constant easily calculated from the molecular geometry and the permanent dipole moment. For CCl$_4$ and C$_2$Cl$_6$, for example, $\Omega = 0$ because these molecules have null dipole moments. The square of the effective charge of the αth atom is also related to the mean dipole derivative by

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

where β_α^2 is the atomic anisotropy of the αth atomic polar tensor. Substitution of $\bar{p}_\alpha^2$ for χ_α^2 in the sum rule equation yields a lower bound to the experimental fundamental intensity sum. Since the weight of the anisotropy term in eq 6 is less than one fourth of the weight of the mean dipole moment derivative term, and considering that the atomic anisotropy is often very small compared with the mean dipole moment derivative, this lower limit can also be an accurate estimate of the fundamental intensity sum. For CCl$_4$ the carbon anisotropy is zero, due to molecular symmetry. Since this atom is expected to account for about 80% of the fundamental sum, the lower limit to the fundamental sum obtained with use of eqs 4, 5, and 6 could provide a good estimate of the real intensity sum.

The infrared fundamental intensities of CCl$_4$ have been measured by Tanaka and Saeki,[117] who obtained $A_3 = 322.0$ km mol^{-1} and $A_4 = 0.2$ km mol^{-1}, but did not calculate polar tensors from these values. With use of the carbon 1s electron binding energy in CCl$_4$ in the regression of Figure 1,[118] 296.3 eV, together with a terminal atom potential of −9.06 eV extrapolated from the potential values of the other chloromethanes, the mean dipole moment derivative value of the CCl$_4$ carbon atom is estimated as 0.965 e. Since the mean dipole moment derivatives must sum to zero, $\bar{p}_{Cl} = \bar{p}_C/4 = -0.241$ e. Substituting these values into eqs 5 and 6 and assuming that $\beta_{Cl}^2 = 0$ results in a predicted infrared fundamental sum of 246 km mol^{-1}. This value is almost three-fourths of the experimental sum of 322.2 km mol^{-1}.

It should be added that the above calculation is only approximate since the relaxation energy of CCl$_4$ was not used to correct its 1s binding energy. Also the regression equation for the line in Figure 1 is not completely appropriate for this

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calculation since it was determinded from energy values not corrected for relaxation. The inclusion of relaxation energy in the above estimate is expected to increase the predicted value and better its agreement with the experimental sum. For purposes of comparison with our estimate, the CCl_4 intensity sum predicted by molecular orbital calculations with use of the MP2/6-311++G(3d,3p) wave function is 405 km mol^{-1}.

Molecules with atoms from the second and lower rows of the periodic table should also be studied for relations between 2p, 3p 3d, etc. electron ionization energies and their mean dipole moment derivatives. These relations might prove to be useful for intensity sum estimations such as those presented here with 1s electron energies.

Of course many molecules contain hydrogen atoms, for which ESCA or X-ray photoelectron energies cannot be obtained. If all the heavier atoms in the molecule have known core electron ionization energy−mean dipole moment derivative relations and the hydogen atoms are symmetrically equivalent, the $\bar{p}_H$ value can be obtained via the null relationship. If more than one kind of hydrogen atom exists in the molecule and these hydrogens are not very different (hydrogen atoms in saturated hydrocarbons, for example), the use of the null relationship might still be useful for intensity sum estimates.

6. Conclusions

The experimental carbon 1s electron ionization energies have been shown to be linearly related to the experimental carbon mean dipole moment derivatives for a wide variety of molecules. This result implies that carbon mean dipole moment derivatives can be interpreted as net charges on the carbon atoms, in spite of the conflicting theoretical evidence that these derivatives have important charge flux and overlap contributions for most molecules considered here.

Since the charges evaluated from fundamental infrared intensities accurately predict the energies of the 1s core electrons, it is tempting to speculate that they might be useful to describe electrostatic potentials in regions around molecules. An accurate description of these potentials is of course important for understanding the interactions between reagent molecules.

More rigorous theoretical calculations of relaxation energies would be useful to provide explanations for the small deviations

from the simple models observed in our work. Furthermore, one should investigate how well commonly used theoretical charges, such as Mulliken's, Bader's, CHELPG, etc., describe core electron ionizations energies using the simple potential model. These studies should use accurate wave functions, which provide mean dipole moment derivative estimates in good agreement with derivatives determined from experimental intensity measurements.

Finally, these studies should be extended to molecules not included in our investigation. Although ESCA measurements of core ionization energies are quite numerous, complete gas-phase fundamental intensity measurements have been reported for relatively few polyatomic molecules. Most have been included in this paper. However, some studies are possible on molecules for which intensity measurements are avaliable and polar tensors have been or can be evaluated. Halosilane spectral data, perhaps supplemented by theoretical results, would be important for investigating further the dependency of the simple potential model line slopes as a function of the atomic radii of the ionized atoms.

The most frustrating aspect of this work concerned the lack of the polar tensor data avaliable to permite more extensive tests of the simple potential model. For a few molecules, such as CCl_4, conspicuously absent from our result and discussion sections, complete gas-phase fundamental intensity data exist. We are in the process of determining its polar tensor. However, the most serious difficulty for continuation of these studies is the lack of experimental results in measuring intensities. Hopefully our study will stimulate activity in this direction.

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