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Characteristic Substituent-Shift Models for Carbon 1s Ionization Energies and Mean Dipole-Moment Derivatives

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Characteristic substituent-shift models for carbon mean dipole-moment derivatives are determined for the halomethanes, fluorochloroethanes, and some other small molecules. These models are analogous to those reported earlier for core ionization energies measured by X-ray photoelectron spectroscopy and are to be expected since Siegbahn's simple potential model relates these to mean dipole-moment derivatives obtained from infrared spectral data. Linear models relating carbon 1s ionization energies and mean dipole-moment derivatives to the number of fluorine, chlorine, bromine, and iodine atoms substituting hydrogen atoms in the halomethanes are reported. The regression coefficients in these models are similar to the coefficients for the fluorine and chlorine atoms found in linear models derived for the mean dipole-moment derivatives and carbon 1s ionization energies of the fluorochloroethanes. The signs of the coefficients in the fluorochloroethane model indicate that the α carbon becames more positive and the β carbon more negative upon fluorine substitution for hydrogen. Standard derivative values of −0.52 ± 0.05, −0.25 ± 0.05, −0.18 ± 0.03, −0.17 ± 0.03, and −0.01 ± 0.01 e are proposed for the fluorine, chlorine, bromine, iodine, and hydrogen atoms of saturated fluorochlorohydrocarbons. Characteristic substituent shifts for Mulliken, CHELPG, and Bader charges of the carbon atoms in these molecules are also investigated.

Introduction

It has long been the goal of chemists to understand how electronic structures of molecules change upon substitution of atoms or chemical groups. Relevant information is normally obtained by measuring molecular properties such as energies, electric and magnetic moments, acidities, NMR shifts, and ionization energies for groups of similar molecules usually differing by one or several substituents. Many experimental observables provide information about changes in the overall molecular electronic structure. Others provide information about electronic structures in specific regions of molecules, permitting conclusions about whether they have an excess or deficiency of electronic density compared with other parts of the molecule. This information is expected to be related to molecular reactivity.

Core electron ionization energies measured by X-ray photoelectron spectroscopy and mean dipole-moment derivatives obtained from infrared spectral data are both characteristic of regions that can be identified with the individual atoms in molecules. Furthermore, they have been shown to be related[1−3] by a simple potential model, first proposed by Siegbahn,[4] in which the ionization energies are a function of atomic charges and internuclear distances. In terms of mean dipole-moment derivatives, $\bar{p}_\alpha$ and $\bar{p}_\beta$, of the nucleus being ionized, α, and other nuclei in the molecule, β

$$E_{\alpha,\mathrm{core}} = k\bar{p}_\alpha + \sum_{\beta\neq\alpha}\left(\frac{\bar{p}_\beta}{R_{\alpha\beta}}\right) \qquad (1)$$

where $E_{\alpha,\mathrm{core}}$ represents the ionization energy of a core electron of the αth nucleus. $R_{\alpha\beta}$ represents the distances between the α and β nuclei, and k is a constant characteristic of the atom and its hybridization state.

Potential models obtained from experimental ionization energies and infrared spectral properties have been reported for C (sp^3, sp^2, and sp), N (sp^3 and sp), Si, Ge, O, F, B, P, and Cl, i.e., for all kinds of atoms existing in molecules for which both core ionization energies and infrared intensities have been measured.[1−3] Theoretical models based on Koopmans' energies and mean dipole-moment derivatives calculated by quantum chemical procedures have also been reported for all of the above atoms and for the 1s, 2s, 2p, 3s, 3p, and 3d electrons of the bromine atom.[3]

Siegbahn introduced the simple potential model for core electron ionization energies using atomic point charges. The fact that mean dipole-moment derivatives work so well in these models leads to the proposal that these derivatives can be identified with atomic charges.[5] Indeed, their values obtained directly from experimental infrared intensities adequately describe expected changes in charge quantities with changes in electronegativities of neighboring atoms, hybridization, and other chemical valence parameters for small molecules.[5] However, besides containing contributions from atomic charges, mean derivatives are also expected to have contributions from changes in these charges and their polarizations during molecular vibrations.[5,6] Furthermore, Sambe[7] and Lazzeretti and Zanasi[8] have showed that the atomic polar tensor, of which the mean dipole-moment derivative is one-third of the trace, is simply related to the nuclear electric shielding tensor. As such, the force exerted on an atom of a molecule placed in an external electric field is directly related to its atomic polar tensor. Also the infrared intensities can be expressed in terms of atomic nuclear-shielding tensors weighted by normal coordinate transformation coefficients.[9]

In the early seventies, several research groups showed that the shifts in atomic core electron-binding energies can be expressed as the sum of characteristic shifts of substituent atoms or chemical groups bonded to the ionizing atom.[10−15] More than

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a dozen ionizing atoms and substituent groups were included in these studies. At about the same time, studies being made by our research group noted that mean dipole-moment derivatives, $\bar{p}_\alpha$, obtained from infrared gas-phase fundamental intensities of the X_2CY (X = F, Cl; Y = O, S) molecules could be related by the equation[16]

$$\bar{p}_{\alpha_1}(Cl_2CO) - \bar{p}_{\alpha_2}(F_2CO) = \bar{p}_{\alpha_3}(Cl_2CS) - \bar{p}_{\alpha_4}(F_2CS) \quad (2)$$

for three distinct cases: (1) $\alpha_1 = \alpha_3 =$ Cl and $\alpha_2 = \alpha_4 =$ F; (2) $\alpha_1 = \alpha_2 =$ O and $\alpha_3 = \alpha_4 =$ S; and (3) $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 =$ C. This result indicates that a model of characteristic group mean dipole-moment derivative shifts also holds for these molecules. Furthermore, a matrix equation analogous to the one above was shown to hold for the atomic polar tensors of these molecules,[17] and a scalar one was also valid for the corresponding infrared intensity sums.[18] Infrared intensity sums of the halomethanes have also been shown to be related by an equation similar to eq 2.[19]

The simple potential model observed for core ionization energies and mean dipole-moment derivatives, given by eq 1, and the characteristic shifts observed for the core electron ionization energies indicate that relations of the kind observed for the infrared parameters of X_2CY molecules and expressed in eq 2 are more general. If so, characteristic group shifts might be useful for calculating mean dipole-moment derivatives and even atomic charges. In this work, these relationships for characteristic substituent-shift models are explored.

Calculations

Within the harmonic oscillator−linear dipole-moment approximations, the measured fundamental infrared intensity, A_i, is proportional to the square of the dipole-moment derivative with respect to its associated normal coordinate, Q_i

$$A_i = \frac{N_A \pi}{3c^2}\left(\frac{\partial \vec{p}}{\partial Q_i}\right)^2 \qquad i = 1, 2, ..., 3N - 6 \quad (3)$$

N_A and c being Avogadro's number and the velocity of light.[20] The dipole-moment derivatives can be transformed to atomic Cartesian coordinates using the expression[21,22]

$$\boldsymbol{P}_x = \boldsymbol{P}_Q \boldsymbol{L}^{-1} \boldsymbol{U} \boldsymbol{B} + \boldsymbol{P}_\rho \beta \quad (4)$$

where $\boldsymbol{P}_Q$ is a $3 \times 3N - 6$ matrix of dipole-moment derivatives obtained from the measured infrared intensities and $\boldsymbol{L}^{-1}$, $\boldsymbol{U}$, and $\boldsymbol{B}$ are well-known transformation matrixes commonly used in normal coordinate analysis.[23] The $\boldsymbol{P}_\rho \beta$ product provides the rotational contributions to the polar tensor elements. As such, the polar tensor elements contained in $\boldsymbol{P}_x$ are obtained using the molecular geometry (the $\boldsymbol{B}$ and β matrixes), symmetry (the $\boldsymbol{U}$ matrix), vibrational frequencies and atomic masses (the normal coordinate $\boldsymbol{L}^{-1}$ matrix), and permanent dipole-moment values ($\boldsymbol{P}_\rho$ matrix), as well as the experimentally measured intensities.

The molecular polar tensor, $\boldsymbol{P}_x$, is a juxtaposition of the atomic polar tensors (APTs)

$$\boldsymbol{P}_x = \{\boldsymbol{P}_x^{(1)} \boldsymbol{P}_x^{(2)} ... \boldsymbol{P}_x^{(N)}\} \quad (5)$$

with N being the number of atoms in the molecule. Each APT contains the derivatives of the molecular dipole moment with respect to atomic Cartesian coordinates

$$\boldsymbol{P}_x^{(\alpha)} = \begin{pmatrix} \frac{\partial p_x}{\partial x_\alpha} & \frac{\partial p_x}{\partial y_\alpha} & \frac{\partial p_x}{\partial z_\alpha} \\ \frac{\partial p_y}{\partial x_\alpha} & \frac{\partial p_y}{\partial y_\alpha} & \frac{\partial p_y}{\partial z_\alpha} \\ \frac{\partial p_z}{\partial x_\alpha} & \frac{\partial p_z}{\partial y_\alpha} & \frac{\partial p_z}{\partial z_\alpha} \end{pmatrix} = \begin{pmatrix} p_{xx}^{(\alpha)} & p_{xy}^{(\alpha)} & p_{xz}^{(\alpha)} \\ p_{yx}^{(\alpha)} & p_{yy}^{(\alpha)} & p_{yz}^{(\alpha)} \\ p_{zx}^{(\alpha)} & p_{zy}^{(\alpha)} & p_{zz}^{(\alpha)} \end{pmatrix} \quad (6)$$

The mean dipole-moment derivative of atom α, $\bar{p}_\alpha$, is simply one-third the trace of this matrix[24]

$$\bar{p}_\alpha = {}^1/_3(p_{xx}^{(\alpha)} + p_{yy}^{(\alpha)} + p_{zz}^{(\alpha)}) \quad (7)$$

Molecular orbital calculations were performed using the Gaussian 94[25] and GAMESS-US[26] programs on IBM RISC 6000 and DEC ALPHA workstations. Mean dipole-moment derivatives and Mulliken, Bader, and CHELPG charges were calculated at the Moller−Plesset 2 (MP2) level from wave functions obtained using a 6-311++G(3d,3p) basis set. All calculations were carried out at MP2 equilibrium geometries.

The calculated derivatives are found to obey the translational sum rule[21,22]

$$\sum_\alpha \boldsymbol{P}_x^{(\alpha)} = 0 \quad (8)$$

The MP2/6-311++G(3d,3p) mean dipole-moment derivatives have been found to agree with their corresponding experimental values within about ±0.055 e for a large group of molecules.[5]

Results

Experimental 1s ionization energies[27] and carbon mean dipole-moment derivatives[5,28,29] determined from infrared intensities are presented in Table 1 for the fluorochloromethanes and a variety of other molecules including some with sp- and sp^2-hybridized carbon atoms. These values were used to calculate carbon core electron ionization energies and mean dipole-moment derivatives of selected molecules using equations analogous to eq 2. The results are given in Table 2. Each line in this table identifies two or three molecules used to calculate the carbon core electron ionization energy and mean dipole-moment derivative of a test molecule. Comparison of these calculated values with those determined experimentally provides a measure of the quality of fit of characteristic substituent-shift models (CSSM). Since a natural tendency is to use smaller molecules to calculate properties of larger ones, the molecule with the largest number of electrons in each line of Table 2 was selected as the test molecule.

The first line in the table contains the X_2CY molecules mentioned previously in this paper.[16] The calculated carbon mean dipole-moment derivatives for Cl_2CS, 0.89 e, is in exact agreement with the experimental value. Unfortunately, carbon 1s ionization energies for F_2CS and Cl_2CS were not found in the literature so the analogous calculation could not be done for the Cl_2CS carbon 1s electron binding energy.

For all other test molecules in Table 2, both 1s ionization energies and mean dipole-moment derivatives can be calculated from the experimental values of the calibration molecules. The overall agreement between calculated and experimental values can be seen in Figures 1 and 2 for both the ionization energies and mean dipole-moment derivatives. The points on the graphs are close to the diagonal lines representing exact agreement. The root-mean-square (rms) error $\{\sum(x_{calc} - x_{exp})^2/n\}^{1/2}$, where $n = 32$ ($n = 31$ for ionization energy calculations) represents the number of squared terms, has values of 0.31 eV for the

TABLE 1: Experimental Carbon 1s Ionization Energies and Mean Dipole-Moment Derivatives[a]

molecules	$E_{C,1s}$ (eV)	$\bar{p}_C$ (e)
CH_4	290.86	0.016
CH_3F	293.60	0.541
CH_2F_2	296.40	1.014
CHF_3	299.17	1.523
CF_4	301.88	2.049
CH_3Cl	292.44	0.277
CH_2Cl_2	293.95	0.527
$CHCl_3$	295.10	0.827
CCl_4	296.34	1.043
CF_3Cl	300.31	1.907
CF_2Cl_2	298.93	1.636
$CFCl_3$	297.54	1.367
CS_2	293.10	0.688
OCS	295.20	0.849
CO_2	297.66	1.073
CH_3C^*CH	291.07	−0.074
CH_3C^*N	292.82	0.066
C_2F_6	299.85	1.328
HCN	293.5	−0.041
C_2H_2	291.17	−0.201
F_2CO	299.64	1.514
Cl_2CO	296.75	1.243
F_2CS		1.156
Cl_2CS		0.892
CH_3I	291.43	0.134[b]
CH_3Br	291.96	0.210[b]
CF_3I	299.00	1.765[c]
CF_3Br	299.33	1.722[c]
C_2H_4	290.79	−0.055
$F_2C^*CH_2$	296.10	0.977
H_2CO	294.47	0.593
$F_2CC^*H_2$	291.33	−0.274
C_2H_6	290.70	0.063
$Cl_2C^*CH_2$	293.62	
C_2F_4	296.54	

[a] Carbon 1s ionization energies taken from ref 27. Carbon mean dipole derivatives taken from ref 5 unless indicated otherwise. [b] Reference 28. [c] Reference 29.

ionization energies and 0.09 *e* for the mean derivatives. The 0.31 eV error can be compared with expected experimental errors of about 0.1 eV in the ionization energy values and 0.17 eV in propagated error estimated for the calculated energy values. It represents about 4% of the 8-eV range in the experimental ionization energy values of the test molecules in Table 2. The 0.09 e rms error for the mean derivatives can be compared with an average error of about 0.05 e found for experimental dipole-moment derivatives.

Besides containing data for sp^3-hybridized carbon atoms of the halomethanes, Table 2 contains one set of molecules with sp^2 and two sets with sp hybrid orbitals. C_{1s} ionization energy and carbon mean dipole-moment derivative estimates of 295.96 eV and 0.87 e for 1,1-difluoroethylene are obtained from data for the C_2H_4, H_2CO, and F_2CO molecules. These results are in good agreement with the experimental values, 296.10 eV and 0.98 e. Carbon 1s ionization energy and mean derivative estimates of 292.74 eV and 0.63 e for CS_2 are obtained from the corresponding values of the CO_2 and OCS molecules. These values are close to the experimental values of 293.10 eV and 0.69 e for CS_2. The 1s ionization energy and mean dipole-moment derivative of the acetylenic carbon attached to the methyl group of the methylacetylene molecule can be calculated from methyl cyanide, hydrogen cyanide, and acetylene data. The characteristic substituent-shift estimates of 290.49 eV and −0.09 e are in good agreement with the 291.07 eV and −0.07 e experimental values.

TABLE 2: Values of 1s Carbon Ionization Energies and Carbon Mean Dipole-Moment Derivatives from Experimental Measurements and Calculated from the Characteristic Substituent-Shift Model

test molecule	calibration molecules	$E_{C,1s}^{CSSM}$ (eV)	$E_{C,1s}^{exp}$ (eV)	$\bar{p}_C^{CSSM}$ (e)	$\bar{p}_C^{exp}$ (e)
Cl_2CS	Cl_2CO, F_2CS, F_2CO			0.89	0.89
CCl_4	$CFCl_3$, CH_3Cl, CH_3F	296.38	296.34	1.10	1.04
CCl_4	$CHCl_3$, CH_3Cl, CH_4	296.68	296.34	1.09	1.04
CCl_4	CH_2Cl_2, CH_4	297.04	296.34	1.04	1.04
CCl_4	CF_3Cl, $CHCl_3$, CHF_3	296.24	296.34	1.21	1.04
CCl_4	CF_2Cl_2, CH_2F_2, CH_2Cl_2	296.48	296.34	1.15	1.04
CCl_4	$CFCl_3$, CF_2Cl_2	296.15	296.34	1.10	1.04
CCl_4	CF_2Cl_2, CF_4	295.98	296.34	1.22	1.04
CCl_4	$CFCl_3$, CF_3Cl, CF_4	295.97	296.34	1.23	1.04
$CFCl_3$	$CHCl_3$, CH_2F_2, CH_3F	297.90	297.54	1.30	1.37
$CFCl_3$	$CHCl_3$, CF_4, CHF_3	297.81	297.54	1.35	1.37
$CFCl_3$	$CHCl_3$, CH_3F, CH_4	297.84	297.54	1.35	1.37
$CFCl_3$	$CHCl_3$, CHF_3, CH_2F_2	297.87	297.54	1.34	1.37
CF_2Cl_2	CF_4, CH_2Cl_2, CH_2F_2	299.43	298.93	1.56	1.64
CF_2Cl_2	CF_3Cl, CH_3Cl, CH_3F	299.15	298.93	1.64	1.64
CF_3Cl	CHF_3, CH_2Cl_2, CH_3Cl	300.68	300.31	1.77	1.91
CF_3Cl	CF_4, CH_3Cl, CH_3F	300.72	300.31	1.79	1.91
CF_3Cl	CHF_3, CH_3Cl, CH_4	300.75	300.31	1.78	1.91
CF_3Cl	CHF_3, $CHCl_3$, CH_2Cl_2	300.32	300.31	1.82	1.91
CF_4	CHF_3, CH_3F, CH_4	301.91	301.88	2.05	2.05
CF_4	CH_2F_2, CH_4	301.94	301.88	2.01	2.05
CH_2Cl_2	CH_3Cl, CH_4	294.02	293.95	0.54	0.53
CH_2F_2	CH_3F, CH_4	296.34	296.40	1.07	1.01
CH_3C^*CH	CH_3CN, HCN, C_2H_2	290.49	291.07	−0.09	−0.07
CF_3I	CH_3I, CF_3H, CH_4	299.74	299.00	1.64	1.77[a]
CF_3I	CH_3I, CF_4, CH_3F	299.71	299.00	1.64	1.77[a]
CF_3I	CH_3I, CF_3Cl, CH_3Cl	299.30	299.00	1.76	1.77[a]
CF_3Br	CH_3Br, CF_3H, CH_4	300.27	299.33	1.72	1.72[a]
CF_3Br	CH_3Br, CF_4, CH_3F	300.24	299.33	1.72	1.72[a]
CF_3Br	CH_3Br, CF_3Cl, CH_3Cl	299.83	299.33	1.84	1.72[a]
CS_2	OCS, CO_2	292.74	293.10	0.63	0.69
$F_2C^*CH_2$	C_2H_4, H_2CO, F_2CO	295.96	296.10	0.87	0.98

[a] Experimental values from Table 1.

Unfortunately, the existence of characteristic substituent shifts for carbon mean dipole-moment derivatives cannot be tested as extensively as those for ionization energies for lack of experimental intensity data. However, this concept might be useful in predicting mean dipole-moment derivatives for molecules for which intensity data are lacking. Table 3 contains several examples illustrating this for molecules whose experimental carbon 1s ionization energies do adhere well to CSSMs, Cl_2CCH_2, C_2F_4, CH_3CCl_3, CH_3CF_3, and CH_3CH_2F. In all cases, experimental ionization energies and mean dipole-moment derivatives of the calibration molecules were used to calculate values of the test molecules. The predicted ionization energies have a rms error of ±0.35 e for the test molecules in Table 3. Since the experimental $\bar{p}_C$ values have not been determined, the CSSM estimates for the mean dipole-moment derivatives are compared with molecular orbital results calculated using a 6-311++G(3d,3p) basis set at the MP2 level. The rms error for these results is 0.09 e. Considering that quantum chemical calculations at this level provide mean dipole-moment estimates within about ±0.05 e of the experimental values,[5] the agreement between the CSSM estimates and the quantum ones is quite good. Note that both these error values are similar to those obtained for the results of Table 2, ±0.31 eV and ±0.09 e.

Discussion

Characteristic atom or group substituent shifts for carbon 1s ionization energies can be expressed by the equation

$$E_{C,1s}(X_nCA_m) - E_{C,1s}(X_nCB_m) = E_{C,1s}(Y_nCA_m) - E_{C,1s}(Y_nCB_m) \quad (9)$$

where the result is the exchange of *m* A substituent atoms or

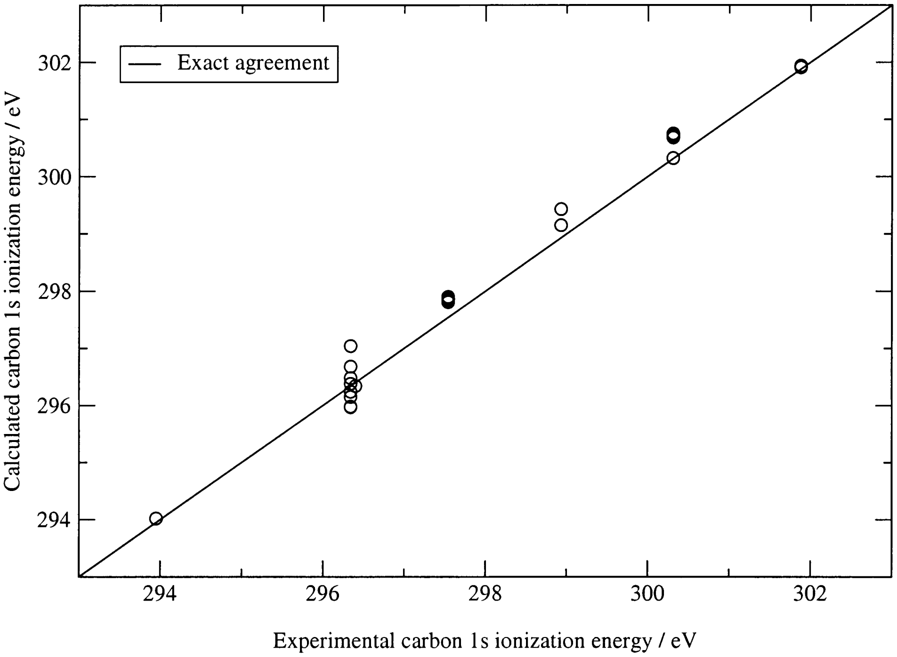

Figure 1. Graph of the experimental carbon 1s ionization energies against values obtained using a characteristic shift model.

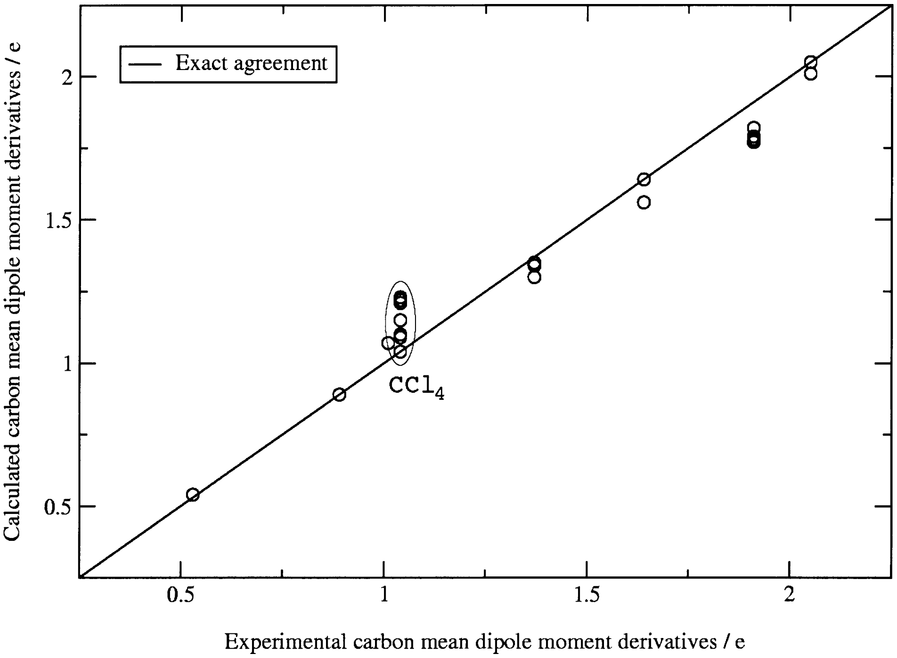

Figure 2. Graph of the experimental carbon mean dipole-moment derivatives against values obtained using a characteristic shift model.

TABLE 3: Values of 1s Carbon Ionization Energies and Carbon Mean Dipole-Moment Derivatives Calculated from the Characteristic Substituent-Shift Model[a]

test molecule	calibration molecules	$E_{\mathrm{C,1s}}^{\mathrm{CSSM}}$ (eV)	$E_{\mathrm{C,1s}}^{\mathrm{exp}}$ (eV)	$\bar{p}_{\mathrm{C}}^{\mathrm{CSSM}}$ (e)	$\bar{p}_{\mathrm{C}}^{\mathrm{MO}}$ (e)
$Cl_2C^*CH_2$	Cl_2CO, C_2H_4, H_2CO	293.07	293.62	0.60	0.67
$Cl_2C^*CH_2$	Cl_2CO, $F_2C^*CH_2$, F_2CO	293.21	293.62	0.71	0.67
C_2F_4	$F_2CC^*H_2$, $F_2C^*CH_2$, C_2H_4	296.64	296.54	0.75	0.91
$CH_3C^*Cl_3$	C_2H_6, $CHCl_3$, CH_4	294.94	295.00	0.87	0.96
$CH_3C^*F_3$	C_2H_6, CHF_3, CH_4	299.01	298.64	1.57	1.60
$C^*H_3CF_3$	C_2F_6, CF_4, CH_3F	291.57	292.07	−0.18	−0.08
$CH_3C^*H_2F$	C_2H_6, CH_4, CH_3F	293.49	293.39	0.54	0.61

[a] Experimental values from ref 27.

groups by *n* B substituents. The rest of the substituent atoms or groups is represented by X_n on the left-hand side of the equation and Y_n on the right. Of course, the equation can be rearranged to focus on the exchange of the X_n and Y_n substituents.

Each of the 1s ionization energies can be expressed by the Siegbahn potential model. If the substitution of A for B provokes only modest changes in the various XC and YC bond lengths as well as in the X and Y mean dipole-moment derivatives, one can derive an analogous relation for the carbon mean dipole-moment derivatives on substituting Siegbahn model equations for each of the ionization energies in eq 9

$$\bar{p}_{\mathrm{C}}(\mathrm{X}_n\mathrm{CA}_m) - \bar{p}_{\mathrm{C}}(\mathrm{X}_n\mathrm{CB}_m) = \bar{p}_{\mathrm{C}}(\mathrm{Y}_n\mathrm{CA}_m) - \bar{p}_{\mathrm{C}}(\mathrm{Y}_n\mathrm{CB}_m) \tag{10}$$

This shows that if the CSSM holds for the carbon core ionization energies it can be expected to hold for carbon mean dipole-moment derivatives as well. The above assumptions, of

TABLE 4: Experimental CH, CF, and CCl Bond Lengths (Å) and Hydrogen, Fluorine, and Chlorine Mean Dipole-Moment Derivatives (e)

molecules	r_{CH}[a]	r_{CF}[a]	r_{CCl}[a]	$\bar{p}_H$[b]	$\bar{p}_F$[b]	$\bar{p}_{Cl}$[b]	$\bar{p}_C$ (exp)[b]	$\bar{p}_C$ (eq 11)
CH_4	1.087			−0.004			0.016	−0.002
CH_3F	1.095	1.382		−0.017	−0.490		0.541	0.520
CH_2F_2	1.093	1.357		−0.018	−0.488		1.014	1.043
CHF_3	1.098	1.332		0.004	−0.506		1.523	1.566
CF_4		1.323			−0.512		2.049	2.088
CH_3Cl	1.090		1.785	−0.002		−0.271	0.277	0.272
CH_2Cl_2	1.087		1.765	−0.015		−0.248	0.527	0.547
$CHCl_3$	1.100		1.758	−0.022		−0.267	0.827	0.821
CCl_4			1.767			−0.261	1.043	1.095
$CFCl_3$		1.362	1.754		−0.486	−0.296	1.367	1.344
CF_2Cl_2					−0.585	−0.233	1.636	1.592
CF_3Cl		1.325	1.752		−0.590	−0.139	1.907	1.840
average				−0.0105	−0.522	−0.245		
stand dev				0.0098	0.045	0.047		

[a] Taken from ref 30. [b] Taken from ref 5.

course, are not exact. The accuracy of calculations using the above equation should be approximately as good as that for the use of standard bond lengths to represent real interatomic distances in molecules. This implies that the concept of standard mean dipole-moment derivatives might be a useful one for terminal atoms. Indeed, for simple molecules such as the fluorochloromethanes, this is approximately correct. In Table 4, experimental values of CH, CF, and CCl bond lengths[30] are given along with the corresponding experimental mean dipole-moment derivatives. Just as standard bond lengths are useful approximations for all these molecules so are standard mean dipole-moment derivatives. Spectroscopists have already implicitly used standard mean dipole-moment derivatives by assuming polar tensors to be transferable from one molecule to another in their attempts to predict infrared intensities.[31] Of course standard derivatives are not possible for central carbon atoms since the sum of the mean dipole-moment derivatives in a neutral molecule must be zero.

If standard mean dipole-moment derivatives for fluorine, chlorine, bromine, iodine, and hydrogen accurately represent the mean derivatives in the halomethanes, regression of the carbon mean dipole-moment derivatives on the number of each of these atoms in the halomethanes should result in a highly significant linear model. The carbon mean derivative values predicted by the equation should be close to the negative of the sum of the mean derivatives of the terminal atoms. Regression of these values for the molecules given in Table 4 results in a linear model

$$\bar{p}_C = -0.002 + 0.523n_F + 0.275n_{Cl} + 0.184n_{Br} + 0.168n_I \quad (11)$$

with an excellent regression coefficient (r) of 0.9987 and a highly significant F ratio value of 1050. Carbon mean dipole-moment derivative values predicted by this equation are in excellent agreement with the experimental values as can be seen in Table 4. The regression coefficients represent the substituent-shift values for the carbon mean dipole-moment derivatives on substituting the different atoms for hydrogen. For example, by interpretation of the mean derivatives as atomic charges, each fluorine atom when substituted for a hydrogen withdraws about 0.52 e from the carbon atom whereas chlorine takes up about half this charge, 0.28 *e*. These values are opposite in sign but close in magnitude to the average dipole-moment derivatives in Table 4 for fluorine and chlorine, −0.52 and −0.25 e as expected. Since few molecules containing Br and I were included in the regression owing to lack of experimental data, the standard errors of the bromine and iodine regression coefficients, 0.034 e, are considerably larger than those for fluorine and chlorine, 0.008 and 0.010 e, respectively. However, atomic charge models do not provide a complete physical understanding of why eq 11 works so well since mean dipole-moment derivatives contain contributions from charge fluxes and electronic polarization changes besides the static equilibrium charge.

Lazzeretti has shown that nuclear electric shielding tensors, polarizabilities, and susceptibilities can be partitioned into atomic terms.[32] This partitioning was accomplished using force and torque Hamiltonians that contain $(\vec{r} - \vec{R})^{-3}$ factors where $\vec{r}$ and $\vec{R}$ are vectors locating electron density and atomic nuclei. For this reason, the electronic environment close to the nucleus is important in determining these tensors and could imply transferability of atomic terms from molecule to molecule in a series of structurally and chemically related homologues. Lazzeretti and Zanasi[33] have also shown that the nuclear electric shielding and polar tensors are closely connected.[9] As such, it is not surprising that eq 11 relates the trace of the carbon polar tensor to characteristic mean dipole-moment derivatives of the hydrogen and halogen atoms of the halomethanes.

Indeed, this idea results in a better understanding of why core electron binding energies are highly correlated with mean dipole-moment derivatives. Electronic density distributions close to the nucleus are prominent in determining both these quantities. Of course, relaxation effects also contribute to the experimental ionization energies but they are approximately constant for the halomethanes. In fact, Siegbahn's simple potential was derived for Koopmans' energies. They appear to be more correlated with mean dipole-moment derivatives than do the experimental ionization energies, as might be suspected.

As such, a regression equation analogous to eq 11 holds for the carbon 1s experimental ionization energies of the halomethanes

$$E_{C,1s} = 291.16 + 2.62n_F + 1.30n_{Cl} + 0.56n_{Br} + 0.13n_I \quad (12)$$

This equation predicts a 291.16 eV 1s ionization energy for the carbon atom in methane compared with the 290.86 eV experimental value and implies that halogen substitution has additive effects on the carbon 1s core electron binding energies. Each fluorine substitution for hydrogen raises the carbon 1s electron ionization energy by 2.62 eV whereas as chlorine substitution raises it by about half that amount, 1.30 eV.

These arguments can be extended to the fluorochloroethanes. Table 5 contains experimental values of carbon 1s ionization energies found in the literature for fluoroethanes and chloroethanes. Carbon mean dipole-moment derivatives determined from experimental intensities are known for only ethane, 0.063 e, and hexafluoroethane, 1.328 e. For this reason, derivatives calculated from MP2/6-311++G(3d,3p) wave functions are used to model the fluoro-, chloro-, and fluorochloroethane mean dipole-moment derivative data.

Regression of the carbon 1s ionization energies on the number of fluorine and chlorine atoms bonded to the ionizing carbon, n_{F*} and n_{Cl*}, and its neighboring carbon, n_F and n_{Cl}, gives

$$E_{C,1s} = 290.80 + 2.61n_{F*} + 1.42n_{Cl*} + 0.41n_F + 0.27n_{Cl} \quad (13)$$

A regression correlation coefficient, $r = 0.9995$, and 2472.7 F value indicate that the linear model is quite precise. This can be appreciated by comparing the ionization energies predicted

TABLE 5: Experimental Carbon 1s Ionization Energies and Carbon Mean Dipole-Moment Derivatives Calculated from MP2/6-311++G(3d,3p) Wavefunctions and Corresponding Values from eqs 13 and 14

	$E_{C,1s}^{exp}$ (eV)	$E_{C,1s}^{CSSM}$ (eV)	$\bar{p}_C^{MO}$ (e)	$\bar{p}_C^{CSSM}$ (e)
CH_3CH_3	290.70	290.80	0.079	0.066
$C^*H_3CH_2F$	291.19	291.21	−0.001	0.017
$CH_3C^*H_2F$	293.39	293.41	0.605	0.584
$C^*H_3CHF_2$	291.62	291.62	−0.060	−0.032
$CH_3C^*HF_2$	296.05	296.02	1.120	1.102
$C^*H_3CF_3$	292.07	292.03	−0.079	−0.081
$CH_3C^*F_3$	298.64	298.63	1.603	1.620
CH_2FCH_2F		293.82	0.527	0.535
$C^*H_2FCHF_2$		294.23	0.474	0.486
$CH_2FC^*HF_2$		296.43	1.050	1.053
$C^*H_2FCF_3$		294.64	0.457	0.437
$CH_2FC^*F_3$		299.04	1.539	1.571
CHF_2CHF_2		296.84	1.005	1.004
$C^*HF_2CF_3$		297.25	0.991	0.955
$CHF_2C^*F_3$		299.45	1.496	1.522
CF_3CF_3	299.85	299.86	1.489	1.473
$C^*H_3CH_2Cl$	291.1	291.07	0.012	0.016
$CH_3C^*H_2Cl$	292.1	292.22	0.360	0.354
$C^*H_3CHCl_2$	291.5	291.34	−0.044	−0.034
$CH_3C^*HCl_2$	293.8	293.64	0.658	0.642
$C^*H_3CCl_3$	291.5	291.61	−0.093	−0.084
$CH_3C^*Cl_3$	295.0	295.06	0.959	0.930
CH_2ClCH_2Cl		292.49	0.318	0.304
$C^*H_2ClCHCl_2$		292.76	0.251	0.254
$CH_2ClC^*HCl_2$		293.91	0.597	0.592
$C^*H_2ClCCl_3$		293.03	0.196	0.204
$CH_2ClC^*Cl_3$		295.33	0.888	0.880
$CHCl_2CHCl_2$		294.18	0.543	0.542
$C^*HF_2CCl_3$		294.45	0.485	0.492
$CHCl_2C^*Cl_3$		295.60	0.828	0.830
CCl_3CCl_3		295.87	0.780	0.780
$CH_2FC^*Cl_2F$		296.66	1.116	1.111
$C^*H_2FCCl_2F$		294.36	0.445	0.435
$C^*H_2FCHCl_2$		293.95	0.494	0.484
$CH_2FC^*HCl_2$		294.05	0.567	0.593
$CH_2FC^*Cl_3$		295.47	0.873	0.881
$C^*H_2FCCl_3$		294.22	0.426	0.434
$C^*H_2FCClF_2$		297.85	1.345	1.341
$CH_2FC^*ClF_2$		294.50	0.470	0.436
CH_2FC^*HClF		295.24	0.814	0.823
$C^*H_2FCHClF$		294.09	0.505	0.485
$C^*H_2FCH_2Cl$		293.68	0.570	0.534
$CH_2FC^*H_2Cl$		292.63	0.267	0.305

by this equation in the third column of Table 5 with the experimental values in the second column. The differences are well within the 0.1 eV estimated experimental error for these energies. Furthermore, the constant regression value of 290.80 eV is in excellent agreement with the experimental carbon 1s ionization for ethane, 290.70 eV. The regression coefficients indicate that substitution of hydrogen by fluorine on the carbon atom being ionized raises its 1s ionization energy by 2.61 eV, essentially the same value as obtained in the halomethanes. For the Cl atom, the +1.42 coefficient in eq 13 is close to the +1.30 value in eq 12. These coefficients for fluorine and chlorine substitutions are close to the characteristic group parameter estimated by Jolly,[15] 2.75 and 1.54 eV, respectively.

The carbon 1s ionization shifts caused by fluorine and chlorine substitutions on a neighboring carbon atom are given by the 0.41 and 0.27 eV regression coefficients in eq 13. These values are 16 and 19%, respectively, of the coefficients representing shifts for substitution directly on the ionizing atom. Group shifts for core ionization energies on neighboring atoms have been found to be about 15−25% of the values found for the substituted atoms.[15]

An analogous regression of the theoretical mean dipole-moment derivatives of Table 5 results in the equation

$$\bar{p}_C = 0.066 + 0.518n_{F*} + 0.288n_{Cl*} - 0.049n_F - 0.050n_{Cl} \quad (14)$$

In this equation, $\bar{p}_C$ refers to the carbon atom for which n_{F*} fluorine atoms and n_{Cl*} chlorine atoms substitute hydrogen atoms and n_F fluorine atoms and n_{Cl} chlorine atoms substitute hydrogens on its neighboring carbon atom. The coefficients for the fluorine terms are the same, after roundoff, as those found by Illinger and co-workers,[34] +0.52 and −0.05 for n_{F*} and n_F, respectively (see their eq 13), for MP2/6-31G(d,p) results on only the fluoroethanes. This model indicates that substitution of hydrogen by fluorine raises the mean dipole-moment derivative on the substituted carbon atom by +0.52 e. Chlorine substitution has a smaller effect, as expected, owing to its smaller electronegativity relative to fluorine raising the carbon atom charge by about half that amount, +0.29 e. These values are almost exactly the same as those found in eq 11 for the halomethanes. The model also predicts that fluorine and chlorine substitution lowers the mean dipole derivative on the carbon atom neighboring the substituted carbon. This alternating charge behavior

$$F^{\delta-} - C^{\delta+} - C^{\delta\delta-} - C^{\delta\delta+} -$$

is supported by other evidence from experimental data and theoretical results.[35] Most convincing, perhaps, is that the CH_3CF_3 experimental dipole moment of 2.347 D is much larger than the HCF_3 value, 1.651 D.[36] Alternating charge behavior is expected to produce reinforcing dipoles in $H_3{}^+C^-C^+F_3{}^-$, whereas it would result in opposing dipoles in $H^-C^+F_3{}^-$ and a smaller dipole moment. The 6-311++G(3d,3p) dipole moments of 2.372 and 1.678 D for CH_3CF_3 and HCF_3 are in almost exact agreement with the experimental values. These relative dipole-moment values and negative regression coefficients in eq 14 are not expected if fluorine substitution causes an inductive effect with positive charges steadily diminishing with distance from the fluorine substituent

$$F^{\delta-} - C^{\delta+} - C^{\delta\delta+} - C^{\delta\delta\delta+} -$$

Unfortunately, experimental mean dipole-moment derivative data, except for C_2H_6 and C_2F_6, have not been measured for the fluorochloroethanes, and regression models can only be determined for theoretical results at this time. Moreover, carbon 1s ionization energies are not available for the mixed fluorochloroethanes that would permit evaluation of possible quadratic models that might prove to be more precise than the linear model of eq 13.

Jolly[15] was able to improve the precision of his group substituent models by adding a small cross term to account for nonlinearities caused by polarizable chlorine atoms bonded to high positively charged carbon atoms. One would therefore suspect that $n_{F*}n_{Cl*}$ cross terms might be important in quadratic models for carbon 1s core ionization energies and possibly also for those predicting carbon mean dipole-moment derivatives. The variation in the chlorine mean dipole-moment derivatives of the fluorochloromethanes compared with the relatively constant values of these derivatives in the chloromethanes as shown in Table 4 indicates that this cross term may be significant for improving the linear model.

Quadratic models can be determined for the experimental mean dipole-moment derivatives and the carbon 1s ionization energies of the substituted methanes. Only data for the fluoromethanes, chloromethanes, and fluorochloromethanes are in-

TABLE 6: Mulliken, CHELPG, and Bader Charges and Mean Dipole-Moment Derivatives Calculated from MP2/6-311++G(3d,3p) Wavefunctions and Their CSSM Estimates (e)

molecule	$q_{\mathrm{Mul}}^{\mathrm{MO}}$	$q_{\mathrm{Mul}}^{\mathrm{CSSM}}$	$q_{\mathrm{CHELPG}}^{\mathrm{MO}}$	$q_{\mathrm{CHELPG}}^{\mathrm{CSSM}}$	$q_{\mathrm{Bader}}^{\mathrm{MO}}$	$q_{\mathrm{Bader}}^{\mathrm{CSSM}}$	$\bar{p}_{\mathrm{C}}^{\mathrm{MO}}$	$\bar{p}_{\mathrm{C}}^{\mathrm{CSSM}}$
Cl_2CS	0.220	−0.097	0.109	−0.055	0.422		1.016	1.097
CCl_4	1.278	−0.353	−0.404	−0.501	0.395	0.443	1.194	1.166
CCl_4	1.278	−0.361	−0.404	−0.460	0.395	0.440	1.194	1.167
CCl_4	1.278	−0.671	−0.404	0.038	0.395	0.455	1.194	1.161
CCl_4	1.278	−0.368	−0.404	−0.491	0.395		1.194	1.170
CCl_4	1.278	−0.689	−0.404	−0.532	0.395		1.194	1.156
CCl_4	1.278	0.069	−0.404	−0.350	0.395		1.194	1.216
CCl_4	1.278	−0.517	−0.404	−0.696	0.395		1.194	1.292
CCl_4	1.278	−0.251	−0.404	−0.587	0.395		1.194	1.261
$CFCl_3$	0.428	0.297	−0.168	−0.026	0.896	0.917	1.441	1.433
$CFCl_3$	0.428	0.311	−0.168	−0.072	0.896	1.002	1.441	1.350
$CFCl_3$	0.428	0.420	−0.168	0.287	0.896	0.893	1.441	1.442
$CFCl_3$	0.428	0.216	−0.168	−0.073	0.896	0.958	1.441	1.384
CF_2Cl_2	0.787	0.615	0.014	0.178		1.558	1.666	1.530
CF_2Cl_2	0.787	0.631	0.014	−0.028			1.666	1.585
CF_3Cl	1.412	1.382	0.305	0.557		1.926	1.860	1.888
CF_3Cl	1.412	1.310	0.305	0.391		2.058	1.860	1.765
CF_3Cl	1.412	1.419	0.305	0.750		1.949	1.860	1.857
CF_3Cl	1.412	1.692	0.305	0.473		1.911	1.860	1.894
CF_4	2.091	2.200	0.724	1.083	2.511	2.402	2.040	2.132
CF_4	2.091	2.281	0.724	1.130	2.511	2.361	2.040	2.181
CH_2Cl_2	−0.458	−0.421	−0.171	0.022	0.268	0.291	0.578	0.547
CH_2F_2	1.018	1.141	0.375	0.688	1.221	1.197	1.088	1.097
CH_3C^*CH	−0.419	−0.175	0.051	−0.007	−0.159	−0.171	−0.043	−0.087
CF_3Br	1.275	1.352			1.813	1.803	1.824	1.788
CF_3Br	1.275	1.243			1.813	1.912	1.824	1.696
CF_3Br	1.275	1.345			1.813	-	1.824	1.791
CS_2	0.040	−0.372	−0.036	−0.147	−1.096	−1.089	0.668	0.671
F_2C*CH_2	1.422	0.877	0.555	0.178		1.288	1.143	0.941

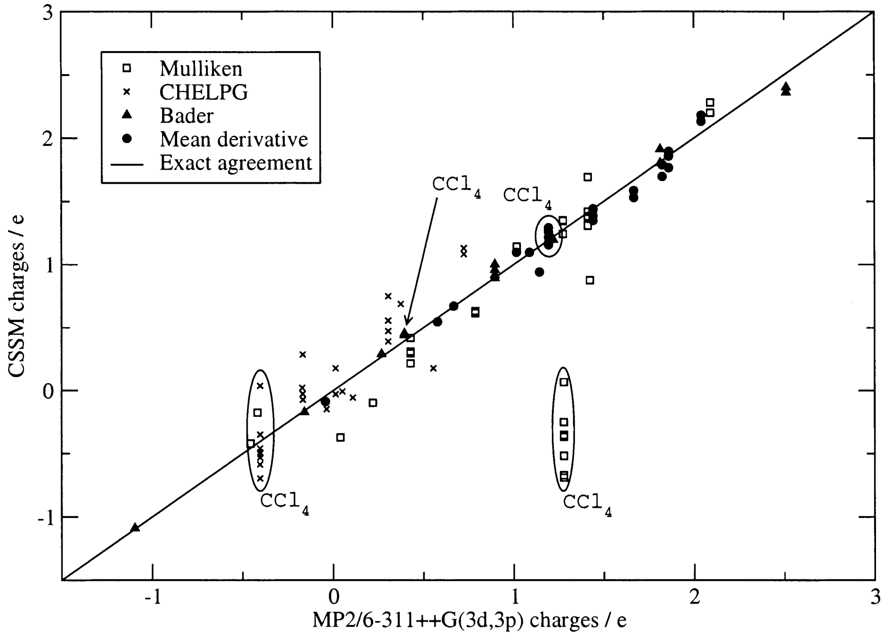

Figure 3. Graph of the MP2/6-311++G(3d,3p) charges and mean dipole-moment derivatives against values obtained using a characteristic shift model.

cluded in the modeling. These models, including only statistically significant terms, are

$$\bar{p}_{\mathrm{C}} = 0.020 + 0.494 n_{\mathrm{F}} + 0.266 n_{\mathrm{Cl}} + 0.026 n_{\mathrm{F}} n_{\mathrm{Cl}} \quad (15)$$

and

$$E_{\mathrm{C,1s}} = 290.805 + 2.78 n_{\mathrm{F}} + 1.67 n_{\mathrm{Cl}} - 0.13 n_{\mathrm{F}} n_{\mathrm{Cl}} - 0.08 n_{\mathrm{Cl}}^{2} \quad (16)$$

The $n_F n_{Cl}$ cross terms are both significant well above the 95% confidence level. Models for the theoretical results of both the fluorochloromethanes and fluorochloroethanes, however, do not contain significant $n_F n_{Cl}$ terms. It is unfortunate that more experimental data for substituted methanes containing both fluorine and chlorine atoms are not available, especially infrared intensities, for investigating whether this cross term contribution is a real effect or not.

On the other hand, either linear or quadratic models determined from either experimental ionization energy or theoretical mean derivative data for the fluorochloroethanes predict linear terms with coefficients very similar in values to those of eqs 13 and 14. Fluorine and chlorine substitution for hydrogen substantially increases the mean dipole-moment derivatives on the substituted carbon whereas it slightly decreases this derivative for the neighboring atoms. However, this sign inversion for substituted and neighboring carbon atoms is not observed for the 1s ionization energies, modeled by eq 13, since, besides depending on relaxation effects for the ionizing process, they depend on the electrostatic potential, owing to both the charge of the ionizing atom and the charges of the neighboring atoms as given by the simple potential model of eq 1.

Shift Models for Calculated Atomic Charges

Table 6 contains the results of applying the CSSM to three widely used atomic charge quantities, the Mulliken,[37,38] CHELPG,[39] and Bader[40,41] charges, calculated at the MP2/6-311++G(3d,3p) level. Mean dipole-moment derivatives calculated at this same level are also included in Table 6. The calibration molecules used in the CSSM estimates are the same as the ones in Table 2. The agreement between the MO values and those obtained from the CSSM can be seen in Figure 3 where these quantities are plotted against one another for the charges and theoretical mean dipole-moment derivatives. The calculated derivatives and their CSSM estimates are in agreement with about the same accuracy as observed for their corresponding experimental values graphed in Figure 2. All the Bader charges are also close to the line representing exact agreement. Unfortunately, we were not successful calculating Bader charges for CF_2Cl_2 and CF_3Cl. The CSSM estimates of the CHELPG carbon charges, in general, show more scatter about the exact result line than do the Bader charges. It should be noted that the 6-311++G(3d,3p) CHELPG charges on the carbon atoms of CCl_4 and $CFCl_3$ are negative, contrary to chemical intuition and opposite in sign to the results for the Bader charges and the mean dipole-moment derivatives. The Mulliken CSSM estimates show a similar dispersion about the exact result line as do the CHELPG estimates. It is interesting that the MO values for the Mulliken carbon charges on $CFCl_3$ and CF_2Cl_2 are less positive than the carbon charge predicted for CCl_4. This is not expected based on electronegativity arguments. More reasonable behaviors are predicted by the Bader charges and the mean dipole-moment derivatives. Furthermore, the CSSM breaks down badly for all estimates of the CCl_4 carbon Mulliken charge.

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