A Simple Potential Model Criterion for the Quality of Atomic Charges

Anselmo E. de Oliveira, Paulo H. Guadagnini, Roberto L. A. Haiduke, and Roy E. Bruns*

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083-970 Campinas, SP, Brazil

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The simple potential model has been shown to be useful in relating core electron binding energies measured in the X-ray region with mean dipole moment derivatives obtained from experimental infrared vibrational intensities. The importance of including relaxation corrections to the experimental 1s ionization energies of sp, sp^2, and sp^3 hybridized carbon atoms are investigated here. Although relaxation energies obtained from 6-31G(d,p) and 6-311++G(3df,3p) basis sets using ΔSCF calculations show differences of about 1 eV for most molecules studied, relative differences are of the order of 0.1 eV. Exceptions are the CO, CO_2, COS, and CS_2 molecules where discrepancies are larger. Relaxation energy corrections improve simple potential model fits with mean dipole moment derivatives for all carbon atom models but is most pronounced for the sp hybridized atoms. The simple potential model corrected for relaxation energies is investigated as a criterion for testing the quality of Mulliken, CHELPG, Bader and GAPT carbon atomic charges calculated from MP2/6-311++G(3d,3p) wave functions. The GAPT charges are in excellent agreement with the experimental mean dipole moment derivatives (within 0.067*e*) and provide superior statistical fits to the simple potential model when compared with those obtained for the other charges.

Introduction

Recently, the simple potential model[1] proposed 30 years ago by Siegbahn and collaborators has been shown to be useful in relating core electron binding energies measured in the X-ray region with polar tensor invariant quantities obtained from experimental infrared vibrational intensities.[2] Separate models relating the carbon 1s core electron binding energies to their mean dipole moment derivatives were found for sp, sp^2, and sp^3 hybridized atoms. Furthermore, the models' parameter values were shown to be inversely dependent on the carbon atom covalent radii and identified with the Coulomb repulsion integrals involving core and valence electrons. This was confirmed in our later study relating 2p and 3p electron ionization energies of Si and Ge with their atomic polar tensor matrix traces.[3]

The potential model is expected to accurately relate core electron binding energies and mean dipole moment derivatives if two conditions are fulfilled: (1) the relaxation energies of the ionization process being investigated are negligible or constant and (2) the mean dipole moment derivatives can be identified with atomic charges. These two assumptions are investigated in this work.

To maintain its simplicity and usefulness for the interpretation of experimental results, the potential model was not designed to contemplate the reorganization of electron densities in molecules during the ionization process. Relaxation energies can be used to adjust the experimental ionization energies to compensate for this reorganization so that the modified energies are appropriate for use in simple potential model applications. These adjustments, whether using values calculated from either the empirical equivalent cores method[4−6] or the ΔSCF method[7−9] from 6-31G(d,p) wave functions, improve agreement of potential model fits of experimental carbon mean dipole moment derivatives to experimental 1s carbon atom ionization energies of the fluorochloromethanes.[2,10] However, the relaxation energies calculated by each of these methods are not constant. For example, 6-31G(d,p) ΔSCF relaxation energies for the fluorochloromethanes have variations, more than an order of magnitude larger than the estimated experimental errors in their measured ionization energies. Further improvement of the potential model fits might be expected, especially for molecules with sp hybridized carbon atoms since their 1s ionization energies for CO, CO_2, OCS, and CS_2 were found to result in large deviations when mean experimental dipole moment derivatives are used as atomic charges. Here more extensive wave functions, calculated with a 6-311++G(3d,3p) basis set are applied to the 1s ionization energies investigated in our previous work in order to further test the importance of relaxation effects on simple potential model applications.

The second assumption is not so easily tested. There is no universally accepted method of calculating atomic charges, and no experimental technique is available to measure them directly. The mean dipole moment derivative, on the other hand, can be determined using only experimental fundamental vibrational frequency and infrared intensity data and common molecular parameters obtained from experimental sources, such as atomic masses, molecular dipole moments, bond distances, and angles between bonds. Futhermore, it can be calculated from the same molecular orbital wave functions used to calculate other kinds of charge estimates. In fact, population analysis using mean dipole moment derivatives, also called GAPT (generalized atomic polar tensor) charges, has been proposed by Cioslowski[11] and does not require any direct reference to the basis set used to calculated the molecular wave function. However, dipole moment derivatives, just as dipole moments, have not been considered reliable sources of atomic charge values since molecules do not appear to be describable by spherical nondeformable charge distributions centered on their nuclei. Besides the static contribution, results of molecular orbital calculations

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* Corresponding author. Fax: 55-19-788-3023. E-mail: bruns@iqm.unicamp.br.

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indicate that charge flux and polarization contributions are important in determining the values of atomic polar tensor elements and consequently their corresponding mean dipole moment derivatives.[12]

In spite of theoretical arguments to the contrary, in this paper carbon mean dipole moment derivatives determined from experimentally measured fundamental infrared intensities are shown to provide accurate fits to simple potential models for experimental 1s electron ionization energies adjusted by their relaxation energies. This is even true for the sp hybridized carbon atoms in the CO, CO_2, OCS, and CS_2 molecules. Furthermore, it is suggested that the simple potential model be used as a criterion to judge the quality of atomic charge estimates of electron distributions in molecules. If atomic charges are capable of reproducing the electrostatic potentials of molecules, it is desirable that they do so at their nuclei where a convenient experimental measure of these potentials can be obtained, namely the core electron ionization energies. Whereas experimental ionization energies adjusted for neighboring atom electrostatic potential contributions and corrected for relaxation effects provide excellent fits to the simple potential model when either experimentally derived mean dipole moment derivatives or their theoretical estimates from ab initio wave functions are used as atomic charges, it is shown here that significantly inferior statistical models are obtained using more common charge measures, Mulliken,[13,14] CHELPG,[15] and Bader[16,17] charges, calculated from these same wave functions.

Calculations

Within the harmonic oscillator−linear dipole moment aproximations 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

$$A_i = \frac{N_A \pi}{3c^2}\left(\frac{\partial \vec{p}}{\partial Q_i}\right)^2 \tag{1}$$

N_A and c being Avogadro's number and the velocity of light.[18] The dipole moment derivatives can be transformed to atomic Cartesian coordinates using the expression[19,20]

$$\mathbf{P}_X = \mathbf{P}_Q \mathbf{L}^{-1} \mathbf{U} \mathbf{B} + \mathbf{P}_\rho \beta \tag{2}$$

where $\mathbf{P}_Q$ is a $3 \times 3N-6$ matrix of the dipole moment derivatives obtained from the measured infrared intensities and $\mathbf{L}^{-1}$, $\mathbf{U}$, and $\mathbf{B}$ are well-known transformation matrices commonly used in normal-cooordinate analysis.[21] The $\mathbf{P}_\rho \boldsymbol{\beta}$ product provides the rotational contributions to the polar tensor elements. As such, the polar tensor elements contained in $\mathbf{P}_X$ are obtained using the 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, as well as the experimentally measured intensities.

The molecular polar tensor, $\mathbf{P}_X$, is a juxtaposition of the atomic polar tensors (APT's)

$$\mathbf{P}_X = \{\mathbf{P}_X^{(1)}\, \mathbf{P}_X^{(2)} ... \mathbf{P}_X^{(N)}\} \tag{3}$$

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

$$\mathbf{P}_X^{(\alpha)} = \begin{pmatrix} \partial p_x/\partial x_\alpha & \partial p_x/\partial y_\alpha & \partial p_x/\partial z_\alpha \\ \partial p_y/\partial x_\alpha & \partial p_y/\partial y_\alpha & \partial p_y/\partial z_\alpha \\ \partial p_z/\partial x_\alpha & \partial p_z/\partial y_\alpha & \partial p_z/\partial z_\alpha \end{pmatrix} \tag{4}$$

The mean dipole moment derivative of atom α, $\bar{p}_\alpha$, is simply one-third the trace of this matrix[22]

$$\bar{p}_\alpha = 1/3(\partial p_x/\partial x_\alpha + \partial p_y/\partial y_\alpha + \partial p_z/\partial z_\alpha) \tag{5}$$

Molecular orbital calculations were performed using the Gaussian 94[23] and GAMESS-US[24] programs on IBM RISC 6000 and DEC ALPHA workstations. The ΔSCF energies were carried out on molecules and their cations using HF/6-311++G(3df,3p) wave functions. Adiabatic relaxation energies were used to correct the experimental ionization energies for use in the simple potential model applications. These energies have values very similar to corresponding vertical ionization energies corrected for zero-point vibrational energies. The Mulliken, Bader, CHELPG, and GAPT charges were calculated at the Moller−Plesset 2 level from wave functions obtained with the same basis set, except that f polarization functions were removed since their inclusion in the basis set resulted in excessive memory and disk demands for our workstations. Calculated MP2 equilibrium geometries were used to obtain the charges.

Relaxation Energy

The simple potential model[1] corrected for relaxation effects for the carbon atom is given by

$$E_{C,1s} = kq_C + \sum_{A \neq C} \frac{q_A}{R_{AC}} + E_{relax} = kq_C + V + E_{relax} \tag{6}$$

where $E_{C,1s}$ is the carbon 1s core ionization energy, q_A and q_C are atomic charges, R_{AC} is the internuclear distance between atoms A and C, and E_{relax} is the relaxation energy for the ionization process. The first two terms in this equation can be derived from purely classical electrostatic considerations[1,25−27] or from quantum mechanical[28] arguments. The k parameter can be identified as the average electrostatic interaction between an electron located in a core orbital near the nucleus of an atom and a valence shell of unit charge around this nucleus, or in quantum chemical terms, as the corresponding Coulomb integral. Consistent with this interpretation the k values obtained from the slopes of $E_{C,1s} - V$ versus $\bar{p}_C$ linear plots for sp^3, sp^2, and sp hybridized carbon atoms as well as from analogous ones for sp^3, Si and Ge atoms are inversely proportional to their standard atomic radii.[2,3] This result can be expected if the relaxation energy contribution in eq 6 is negligible or constant. However, relaxation energy values calculated by the ΔSCF method using 6-31G(d,p) wave functions for the fluorochloromethanes and reported in our previous study varied from −11.9 eV for CF_4 to −14.5 eV for $CHCl_3$. The energy range of 2.6 eV is much larger than the estimated 0.1 eV measurement error for the C 1s ionization energies and 25% of the 11.0 eV variation observed in the experimental ionization energies of these molecules. Since the relaxation energies provide significant contributions to the corrected simple potential model which could affect interpretation efforts, more accurate estimates were determined in this work using the ΔSCF method with a more extensive 6-311++G(3df,3p) basis set.

Table 1 contains the experimental carbon 1s ionization energies,[29] the ΔSCF energies, and the relaxation energies calculated using HF/6-311++G(3df,3p) and HF/6-31G(d,p)

TABLE 1: Experimental Ionization Energies, and ΔSCF Energies and Relaxation Energies Calculated Using HF/6-311++G(3df,3p) and 6-31G(d,p) Wave Functions (eV)

molecule	$E_{\mathrm{exp}}{}^{a}$	$E_{\Delta\mathrm{SCF}}{}^{b}$	$E_{\Delta\mathrm{SCF}}{}^{c}$	$-E_{\mathrm{rel}}{}^{b}$	$-E_{\mathrm{rel}}{}^{c}$	$\Delta E_{\mathrm{rel}}{}^{b}$	$\Delta E_{\mathrm{rel}}{}^{c}$
CH_4	290.90	290.58	291.76	14.26	13.15	0.00	0.00
CH_3F	293.60	293.52	294.61	13.97	12.90	0.29	0.25
CH_2F_2	296.36	296.55	297.63	13.62	12.55	0.64	0.60
CHF_3	299.10	299.64	300.76	13.25	12.19	1.01	0.96
CF_4	301.85	302.67	303.86	12.92	11.90	1.34	1.25
CH_3Cl	292.48	292.37	293.56	14.75	13.66	−0.49	−0.51
CH_2Cl_2	293.90	293.98	295.14	15.17	14.11	−0.91	−0.96
$CHCl_3$	295.10	295.45	296.57	15.56	14.53	−1.30	−1.38
CCl_4	296.39	296.82	297.90	15.95	14.96	−1.69	−1.81
CF_3Cl	300.31	301.00	302.23	13.95	12.97	0.31	0.18
CF_2Cl_2	298.93	299.50	300.57	14.78	13.81	−0.52	−0.66
$CFCl_3$	297.54	298.11	299.16	15.44	14.47	−1.18	−1.32
CH_3CH_3	290.74	290.35	291.55	14.62	13.51	−0.36	−0.36
C_2H_4O	292.50	292.33	293.52	14.59	13.48	−0.33	−0.33
C_3H_6	290.60		291.44		13.85		−0.70
CF_3CF_3	299.72		301.18		12.91		0.24
C^*H_3CN	293.10		293.82		13.21		−0.06
C^*H_3CCH	291.77		292.62		13.40		−0.25
$C^*H_3CCCH_3$	291.30		292.32		13.50		−0.35
CH_2CH_2	290.70		291.69		13.72		−0.57
$C^*H_2CF_2$	291.33	290.68	291.93	14.99	13.75	−0.73	−0.60
$CH_2C^*F_2$	296.10	296.21	297.43	14.59	13.42	−0.33	−0.27
COH_2	294.47		295.92		12.57		0.58
COF_2	299.64		302.00		11.74		1.41
$COCl_2$	296.75		298.78		13.48		−0.33
cis-$C_2H_2Cl_2$	292.31		293.50		14.44		−1.29
CO	296.19	296.48	298.20	12.33	10.77	1.93	2.38
CO_2	297.75	298.90	300.71	12.53	11.17	1.73	1.98
CS_2	293.10	294.47	295.90	15.59	14.42	−1.33	−1.27
OCS	295.20	296.77	298.40	14.22	13.05	0.04	0.10
HCN	293.50		294.99		12.15		1.00
HCCH	291.14		292.51		13.14		0.01
NCCN	294.50		296.50		12.45		0.70
CH_3C^*N	293.20		294.20		12.58		0.57
CH_3C^*CH	291.07		292.06		13.43		−0.28
CH_3CC^*H	290.40		291.57		13.50		−0.35
$CH_3C^*CCH_3$	290.03		291.27		13.76		−0.61

[a] Reference 29. [b] Calculated using HF/6-311++G(3df,3p) wave functions. [c] Calculated using HF/6-31G(d,p) wave functions. [d] Relative relaxation energies obtained by substracting the corresponding CH_4 relaxation energies.

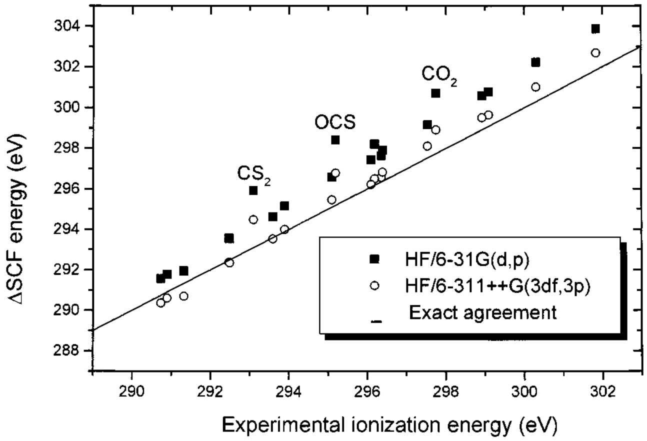

Figure 1. 6-31G(d,p) and 6-311++G(3df,3p) ΔSCF ionization energies plotted against the experimental ionization energies of the fluorochloromethanes.

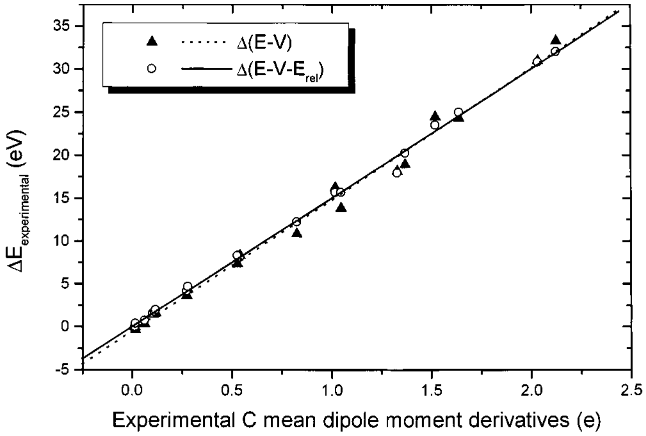

Figure 2. Experimental carbon 1s electron ionization energies adjusted by neighboring atom electrostatic potentials and relaxation energies graphed against carbon mean dipole moment derivatives calculated from experimental infrared intensities for molecules with sp^3 hybridized carbon atoms. The energy values are relative to a zero methane value ($E_{C,1s} - V - E_{relax} = 304.18$ eV for methane).

basis set wave functions. The fluorochloromethane values from the latter wave functions were previously published.[2] The HF/6-311++G(3df,3p) wave functions result in ΔSCF ionization energies for the fluorochloromethanes in much better agreement with the experimental values (standard prediction error of 0.46 eV) than do the HF/6-31G(d,p) wave functions (standard prediction error of 1.48 eV) where the error is 3 times larger. This is clearly seen in Figure 1 where the calculated ΔSCF energies from the two wave functions are plotted against the experimental ionization energies. Whereas most of the HF/6-311++G(3df,3p) energies are very close to the line representing exact agreement, the 6-31G(d,p) results are 1−2 eV above this line.

Relaxation energies were also calculated for the CO, CO_2, COS, and CS_2 molecules using both wave functions since the 6-31G(d,p) ΔSCF energies were 2−3 eV larger than the experimental ionization energies. These values seem excessively high considering the 1.48 eV prediction error for the fluorochloromethanes. The ΔSCF energies calculated with the 6-311++G(3df,3p) wave functions are in better agreement with the experimental results but are still too high by 1.2−1.6 eV and much larger than the 0.46 eV predicted error found for the fluorochloromethanes. The points for these molecules in Figure 1 are easily located since they are much farther from the line representing exact results than are the points for the other molecules calculated from the same wave function.

However, the relaxation energies relative to the methane energy are practically the same for both wave functions. This is very clear upon inspection of Figure 1 where the linear patterns of the 6-31G(d,p) and 6-311++G(3df,3p) relaxation energy results are parallel to one another. In the last two columns of Table 1 relaxation energy values relative to a zero methane value are given for both sets of wave function results. These results are almost the same with most differences being less than 0.1 eV. As a consequence, correction of the relative $E-V$ energies using relaxation energies of HF/6-31G(d,p) wave functions instead of those calculated from 6-311++G(3df,3p) wave functions hardly affects the quality of fit to the simple potential model if relative experimental ionization energies, electrostatic energies from charges on neighboring atoms and relaxation energies are used.

In Figure 2 relative $\Delta(E - V)$ ordinate values corrected by relaxation energies determined from HF/6-31G(d,p) wave functions are shown plotted against the experimental mean dipole moment derivatives for the sp^3 carbon containing molecules given in Table 1. The regression line in Figure 2, $\Delta(E - V - E_{relax}) = 15.00\bar{p}_C + 0.04$ has a correlation coefficient, *r*, of 0.9986 and is very similar to the model in ref 2 for the

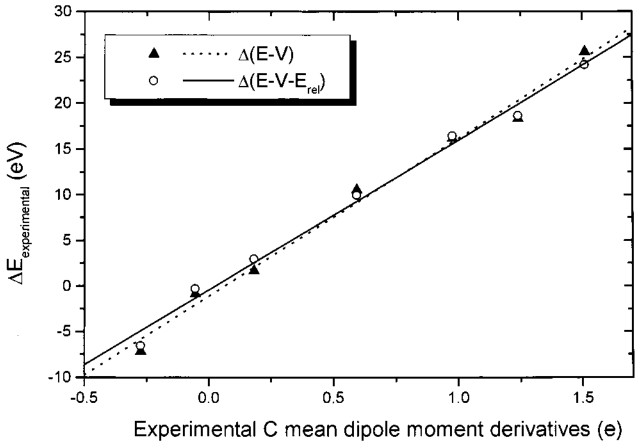

Figure 3. Experimental carbon 1s electron ionization energies adjusted by neighboring atom electrostatic potentials and relaxation energies graphed against carbon mean dipole moment derivatives calculated from experimental infrared intensities for molecules with sp^2 hybridized carbon atoms. The energy values are relative to a zero methane value ($E_{\mathrm{C,1s}} - V - E_{\mathrm{relax}} = 304.18$ eV for methane).

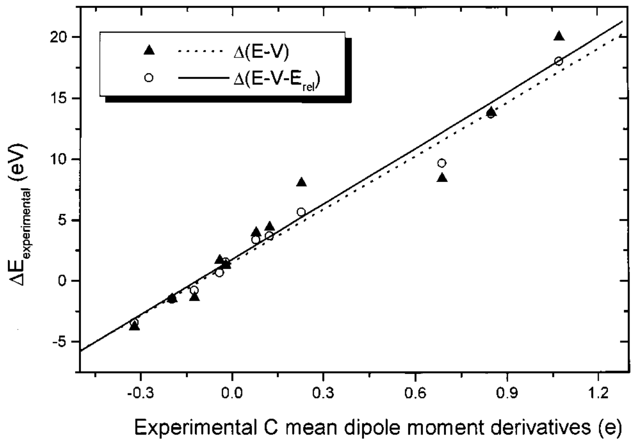

Figure 4. Experimental carbon 1s electron ionization energies adjusted by neighboring atom electrostatic potentials and relaxation energies graphed against carbon mean dipole moment derivatives calculated from experimental infrared intensities for molecules with sp hybridized carbon atoms. The energy values are relative to a zero methane value ($E_{\mathrm{C,1s}} - V - E_{\mathrm{relax}} = 304.18$ eV for methane).

fluorochloromethanes, $\Delta(E - V - E_{\mathrm{relax}}) = 15.19\bar{p}_{\mathrm{C}} - 0.02$ with $r = 0.9996$. These regression results are only slightly superior to the one obtained for the uncorrected data in Figure 2, $\Delta(E - V) = 15.32\bar{p}_{\mathrm{C}} - 0.48$ with $r = 0.9961$. Note that the intercept of -0.48 eV has an absolute value much larger than the expected experimental uncertainty in the experimental ionization energies, 0.1 eV. However, the model for relaxation-corrected energies has an intercept much closer to zero, 0.04 eV, as expected for an accurate model.

In Figure 3, relaxation energy corrected and uncorrected $\Delta(E - V)$ values are graphed against the mean dipole moment derivatives of sp^2 hybridized carbon atoms. The regression model for the corrected values, $\Delta(E - V - E_{\mathrm{relax}}) = 16.39\bar{p}_{\mathrm{C}} - 0.43$ has $r = 0.9955$ and is slightly superior to the one for the uncorrected values $\Delta(E - V) = 17.26\bar{p}_{\mathrm{C}} - 1.10$, with $r = 0.9941$. Note that, although both models explain almost equivalent amounts of variance, the slope and intercept values are quite sensitive to the inclusion of relaxation corrections in the simple potential model.

Corrections for relaxation effects become important in the study of sp hybridized carbon atoms. Whereas the relative relaxation energies for HCN, HCCH, NCCN, CH_3CN, CH_3CCH, and CH_3CCCH_3 have absolute values less than 1 eV, they are about 2 eV for CO and CO_2. In Figure 4 corrected and uncorrected $\Delta(E - V)$ values for the *sp* hybridized carbon atoms are graphed against their experimental mean dipole moment derivatives. The $\Delta(E - V - E_{\mathrm{relax}}) = 14.58\bar{p}_{\mathrm{C}} + 1.54$ model has $r = 0.9932$. This is significantly larger than the 0.9694 correlation coefficient of the $\Delta(E - V) = 15.19\bar{p}_{\mathrm{C}} + 1.80$ model. The large relaxation energy correction for CO causes its point to fall close to its corresponding regression line even though the uncorrected point falls far from it.

The distribution of points in Figure 4 suggests the possible existence of two models, one for the CO_2, COS, and CS_2 molecules and another for the other sp hybridized carbon containing molecules. For the HCN, HCCH, NCCN, CH_3CN, CH_3CCH, CH_3CCCH_3, and CO molecules a $\Delta(E - V - E_{\mathrm{relax}}) = 16.88\bar{p}_{\mathrm{C}} + 1.76$ model is predicted with $r = 0.9957$. Note that the slope value of this equation is much larger than the ones for the models calculated including the CO_2, COS, and CS_2 data. Of course, one should not directly compare the correlation coefficients of the regressions with and without CO_2, OCS, and CS_2 since the numbers of degrees of freedom are not the same for both.

Unfortunately, a decision of how to model the sp carbon data is not possible based on the results presented here. Even though core ionization energy measurements are quite numerous, infrared intensities have been measured for relatively few molecules. The uncorrected data plot strongly points to the existence of two models whereas analysis of relaxation energy corrected data indicates a greater possibility for a one-model interpretation. In any case, more study is needed to resolve this problem. Perhaps higher level molecular orbital calculations on strategically chosen molecules, and not just those for which experimental polar tensor data exist as investigated here, can help resolve this problem.

Atomic Charges

Mean dipole moment derivatives can be interpreted as arising from three contributions: (1) movement of static charges about their atomic equilibrium positions, (2) atomic charge variations during molecular vibrations, and (3) quantum mechanical contributions arising from off-diagonal elements of the dipole moment matrix. This interpretation is summarized in what is called the charge−charge flux-overlap (CCFO) model[30,31] and has been frequently discussed in the chemical literature. Depending on the molecule and type of vibration involved, any one of the three contributions can be dominant. For molecules with very polar bonds, such as the fluoromethanes, the first contribution is often the most important and the mean dipole moment derivatives of its atoms can be interpreted as atomic charges.[32] Although the other contributions appear to be dominant in molecules with less polar bonds, such as the chloromethanes, all the fluorochloromethanes have been found to obey the same mean dipole moment derivative−electronegativity model.[32−34] This evidence and the excellent linear fit in the graph of Figure 2 suggest that the all fluorochloromethane carbon mean dipole moment derivatives, in spite of the theoretical CCFO arguments to the contrary, can be interpreted as atomic charges.

Table 2 lists values of Mulliken, Bader, CHELPG, and GAPT carbon atomic charges calculated at the MP2/6-311++G(3d,3p) level for the fluorochloromethanes as well as for other carbon-containing molecules that were included in our earlier study.[2]

TABLE 2: Experimental Mean Dipole Moment Derivatives and GAPT, CHELPG, Bader, and Mulliken Charges Calculated Using MP2/6-311++G(3d,3p) Wave Functions (e)

molecule	q_{Mul}	q_{Bader}	q_{CHELPG}	q_{GAPT}	$\bar{p}^c$
CH_4	−0.245	0.081	−0.380	−0.005	0.014
CH_3F	0.448	0.639	0.154	0.546	0.540
CH_2F_2	1.018	1.221	0.375	1.088	1.015
CHF_3	1.507	1.844	0.549	1.581	1.518
CF_4	2.091	2.511	0.724	2.040	2.123
CH_3Cl	−0.333	0.186	−0.179	0.271	0.272
CH_2Cl_2	−0.458	0.268	−0.171	0.578	0.527
$CHCl_3$	−0.273	0.335	−0.247	0.891	0.823
CCl_4	1.278	0.395	−0.404	1.194	1.044
CF_3Cl	1.412	*a*	0.305	1.860	2.033
CF_2Cl_2	0.787	*a*	0.014	1.666	1.636
$CFCl_3$	0.428	0.896	−0.168	1.441	1.367
CH_3CH_3	−0.189	0.102	0.001	0.079	0.063
C_2H_4O	0.312	0.425	−0.110	0.265	0.277
C_3H_6	−0.054	0.014	−0.220	0.003	0.017
CF_3CF_3	*b*	*b*	*b*	*b*	1.328
C^*H_3CN	0.090	0.147	−0.245	0.108	0.102
C^*H_3CCH	−0.061	0.145	−0.025	0.125	0.112
$C^*H_3CCCH_3$	*b*	*b*	*b*	*b*	0.117
CH_2CH_2	−0.044	0.009	−0.251	−0.069	−0.055
$C^*H_2CF_2$	−0.419	*a*	−0.655	−0.323	−0.274
$CH_2C^*F_2$	1.422	*a*	0.555	1.143	0.977
COH_2	0.487	1.048	0.452	0.596	0.593
COF_2	1.408	2.327	0.881	1.606	1.51
$COCl_2$	0.435	1.262	0.431	1.363	1.24
cis−$C_2H_2Cl_2$	0.088	*a*	−0.078	0.169	0.182
CO	0.219	1.101	−0.016	0.136	0.228
CO_2	0.892	2.137	0.731	1.075	1.073
CS_2	0.040	−1.096	−0.036	0.668	0.688
OCS	0.260	0.524	0.292	0.873	0.849
HCN	0.401	0.799	0.188	−0.097	−0.041
HCCH	−0.086	−0.120	−0.221	−0.209	−0.198
NCCN	0.691	0.836	0.332	0.109	0.122
CH_3C^*N	0.312	0.748	0.402	0.025	0.078
CH_3C^*CH	−0.419	−0.159	0.051	−0.043	−0.021
CH_3CC^*H	0.184	−0.139	−0.413	−0.313	−0.321
$CH_3C^*CCH_3$	*b*	*b*	*b*	*b*	−0.124

[a] Inherent Bader charges method problems. [b] Convergence or disk space problems. [c] Reference 2.

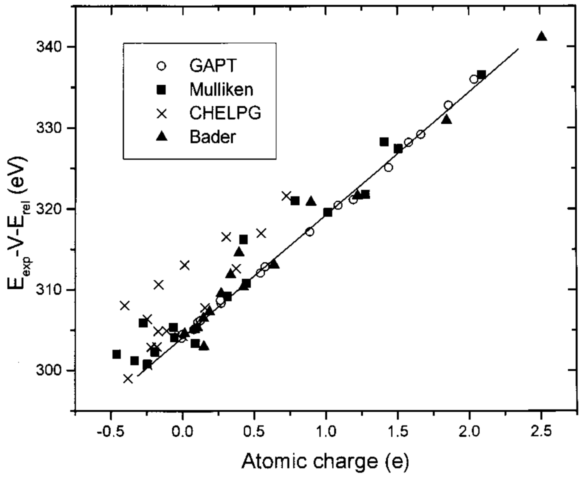

Figure 5. Experimental carbon 1s electron ionization energies adjusted by neighboring atom electrostatic potentials and relaxation energies graphed against GAPT, CHELPG, Bader, and Mulliken charges for sp^3 hybridized carbon atoms.

Experimental mean dipole moment derivative values are also included in this table for comparison with the theoretical GAPT charge values for carbon. These values have a root mean square prediction error of 0.067*e* which is less than 3% of the total variation in the carbon experimental mean dipole moment derivative values. As such, the MP2/6-311G++(3d,3p) wave functions appear to be accurately representing the carbon atom mean dipole moment derivatives in these molecules. For this reason one can expect that the theoretical values for the GAPT carbon charges will also satisfy the simple potential model corrected for relaxation energy as well as do the experimental mean dipole moment derivatives.

This is confirmed on inspection of Figure 5 where the experimental ionization energies corrected by neighboring atom potentials calculated using MP2/6-311G++(3d,3p) GAPT charges and by the HF/6-3 1G(d,p) relaxation energies in Table 1 are graphed against the calculated GAPT charges for sp^3 hybridized carbon atoms. The corresponding points fall close to the least-squares regression line shown in this figure, $E_{exp} - V - E_{relax} = 15.16q_{C,GAPT} - 304.09$, which is very similar to the analogous equation given above for the experimental mean dipole moment derivatives. The slopes are almost the same, 15.00 and 15.16 V, and the 304.09 intercept is close to the algebraic sum of the CH_4 experimental ionization, electrostatic neighboring atom potential and 6-31G(d,p) relaxation energies, 304.18 eV. Since $E_{exp} - E_{relax}$ approximates Koopmans' energy and the relative relaxation energies are accurately calculated, a graph of Koopmans' energies against GAPT charges is expected to be almost identical to the one in Figure 5. In fact, the small differences in the two graphs are not visually perceptible and for this reason the Koopmans' energy graph is not presented here.

In contrast, the Mulliken, Bader, and CHELP carbon charges do not present expected linear relationships as can be clearly seen in Figure 5. Whereas the correlation coefficient, for the regression of the GAPT charges, is 0.9990, these values for the other charges are much further from the desired value of one (Mulliken 0.9778, CHELPG 0.8443, and Bader 0.9841).

The Mulliken charges for carbon are very similar to the GAPT ones for the fluoromethanes with more than one fluorine atom. For CH_2F_2, CHF_3, and CF_4 the Mulliken and GAPT charge values are in agreement within 0.1*e*. One could expect that the Mulliken charges would be more accurate for highly polar molecules since charge attributions to individual atoms of bonds are more easily assessed. Indeed the Mulliken carbon charges do satisfy eq 6 and obey a simple potential model for these fluoromethanes. On the other hand, the less polar CH_4 and CH_3F molecules show calculated Mulliken and GAPT charge differences of more than 0.1*e*. The Mulliken charges show much larger deviations from the simple potential model line. The Bader carbon charges for the fluoromethanes obey a simple potential model but they are not in as good agreement with the experimental mean dipole moment derivatives as are the Mulliken carbon charges. The carbon CHELPG charge values for the fluoromethanes are very different from the Mulliken, Bader, and GAPT values. For example, the carbon CHELPG charge in CF_4 is 0.724*e* whereas it is above 2*e* for all the other charges as well as for the experimental mean dipole moment derivative.

For the chloromethanes only the GAPT charges present a linear relationship for the simple potential model plot of Figure 5 in agreement with the linear one for the fluoromethanes. The CHELPG carbon charges for the chloromethanes do not result in a linear plot at all whereas the Bader carbon charges do present an approximate linear behavior but with a much different slope from the one found for the fluoromethanes. The Mulliken carbon charge values for the chloromethanes are very difficult to accept as reasonable since the carbon charges in CH_3Cl, CH_2-

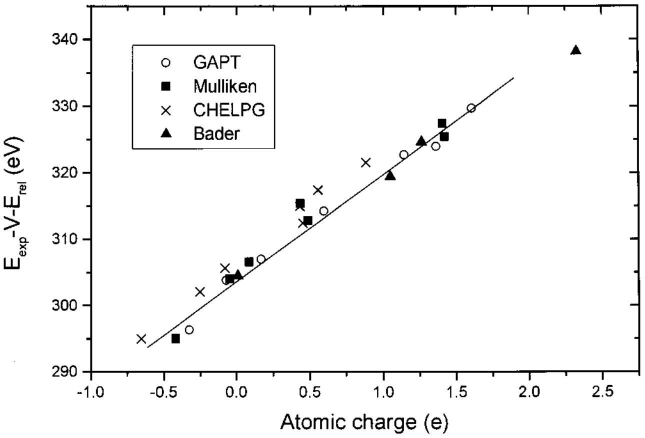

Figure 6. Experimental carbon 1s electron ionization energies adjusted by neighboring atom electrostatic potentials and relaxation energies graphed against GAPT, CHELPG, Bader, and Mulliken charges for sp^2 hybridized carbon atoms.

Cl_2, and $CHCl_3$ are $-0.333e$, $-0.458e$, and $-0.273e$ and contrary to electronegativity arguments pointing to positive carbon atomic charges.

The deviations of the Mulliken carbon atomic charges for the fluorochloromethanes from the simple potential model line in Figure 5 become more severe as chlorines are substituted for fluorines and the molecules have less polar bonds. The CHELPG charges for these molecules are also very difficult to accept since the carbon charge in CF_2Cl_2 is almost zero and its value in $CFCl_3$ is $-0.168e$, contrary to expectations from electronegativity arguments for each of these molecules. Analysis of the Bader charges for the fluorochloromethanes were hampered since computational problems were encountered for CF_3Cl and CF_2Cl_2. Even though a MP2/6-311++G(3d,3p) Bader carbon charge could be calculated for $CFCl_3$, it shows a large deviation from the simple potential model line in Figure 5.

Experimental 1s core ionization energies and infrared intensities have been measured for relatively few molecules with sp^2 hybridized carbon atoms. For this reason only H_2CO, F_2CO, Cl_2CO, C_2H_4, 1,1-$C_2H_2F_2$, and *cis*-$C_2H_2Cl_2$ could be treated in our previous study and it is possible to make only a limited investigation of the simple potential model behavior. In Figure 6 experimental ionization energies adjusted by their respective potentials and relaxation energies are graphed against GAPT, CHELPG, Bader, and Mulliken charge values. The regression model for the energy values on the GAPT charges has $r = 0.9941$ and slope and intercept values 16.14 V and 303.59 eV, in close agreement with those obtained for the experimental $\bar{p}_C$ values, 16.39 V and 303.75 eV (after adjusting for the methane values). The CHELPG charge values seem to obey a different potential model with a 17.40 V slope with $r = 0.9938$. When Mulliken charges are used in the modeling, r is only 0.9831. The model for Bader charges is not directly comparable with the above ones since we were not successful in calculating them for 1,1-$C_2H_2F_2$ and *cis*-$C_2H_2Cl_2$, as indicated in Table 2. For this reason there are only four points corresponding to Bader charges in Figure 6 whereas the other charges each have seven points in the graph. Inspection of Figure 6 clearly shows that the simple potential model is not sufficiently sensitive to permit deductions as to which charge quantity is superior for these sp^2 carbon containing molecules. Perhaps the inclusion of more sp^2 carbon containing molecules in the study would clarify the situation. However, our present efforts are limited to molecules for which *both* experimental 1s ionization energies and infrared intensities have been measured.

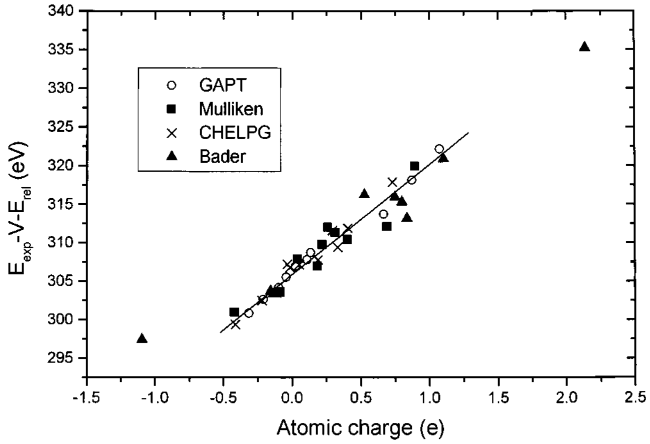

Figure 7. Experimental carbon 1s electron ionization energies adjusted by neighboring atom electrostatic potentials and relaxation energies graphed against GAPT, CHELPG, Bader, and Mulliken charges for sp hybridized carbon atoms.

Of the molecules containing sp hybridized carbon atoms included in our previous study all except CH_3CCCH_3 were successfully treated with MP2/6-311++G(3d,3p) wave functions on our workstations. Their charge values are presented in Table 2 and are plotted against the adjusted ionization energies in Figure 7. Assuming that one potential model is adequate to describe the *sp* hybridized carbon 1s ionization energies, GAPT, CHELPG, Mulliken, and Bader charges can be compared for these molecules. The regression model for GAPT charges is very similar to the one discussed earlier for mean dipole moment derivatives values, with slopes of 14.34 V for the GAPT charges and 14.58 V for the experimental mean dipole moment derivatives, respectively. The model for GAPT charges has $r = 0.9931$ compared with 0.9932 for the $\bar{p}_C$ values. The Mulliken, Bader, and CHELPG charges have significantly smaller r values, 0.9389, 0.9741, and 0.9789, respectively. It is interesting to point out that the Bader charges for the carbons of CS_2 and CO_2 occupy the extreme positions in the graph in Figure 7.

Previously, the slopes of the $E-V$ vs $\bar{p}_\alpha$ relations for the sp^3, sp^2, and sp hybridized carbon atoms have been shown to be linearly related to the inverses of their standard atomic radii.[2] Later, this relationship was shown to be extendable to Si and Ge sp^3 hybridized atoms.[3] In those studies, data for CO, CO_2, COS, and CS_2 were not used to calculate slopes since their data points clearly deviate from the simple potential model if relaxation energy corrections are not made. Here their corrected values are used to investigate the linear inverse radii dependence. As shown in the last section, assuming that one potential model can accurately describe all the sp hybridized carbon atom data, a slope of 14.85 V is obtained. This value is less than the corresponding slope values obtained for the sp^3 and sp^2 data, 15.00 and 16.39 V, respectively, and does not support the inverse radii dependence of the simple potential model k parameter. On the other hand, treatment of all the relaxation energy corrected sp hybridized carbon atom ionization data except for those of CO_2, COS, and CS_2 results in a slope value of 16.88 V lending support to the inverse atomic radii dependence interpretation of the k parameter in eq 6. It should be remembered that the slope values can be quite sensitive to the relaxation energy corrections and more accurate calculations are necessary to provide a sounder basis for interpreting the k parameter.

Conclusion

Several workers[1,25,35−41] have shown that the potential model of eq 6 is useful for atomic charge analysis. Some of the earlier investigations[1,25,37,38] employed approximate semiempirical or ab initio Hartree−Fock level calculated charges and were unable to identify different models for the hybridized states of the carbon atoms. However, the graphs of the experimental ionization energies and mean dipole moment derivatives clearly show the existence of different models for the sp, sp^2, and sp^3 carbon atoms. Although the above treatment only mentions experimental errors in the ionization energies since conventional least-squares regression was used for model calculations, the errors in the mean dipole moment derivatives are commonly on the order of a few hundredths of an electron[2] since infrared intensities are difficult to measure with great accuracy.[18] It is encouraging that the intensity values, including many that were measured 30 years ago are precise enough to clearly show the existence of the separate models. Furthermore, as shown here, the quality of the least-squares fits of experimental mean dipole moment derivatives is as good as those obtained from MP2/6-311++G(3d,3p) wave functions. The above results will hopefully stimulate infrared intensity measurements for molecules with heavier atoms than those in the molecules treated here. Molecular orbital calculational efforts are less accurate for such molecules and infrared intensities can provide valuable information about the electron density distributions in these molecules.

This work proposes the use of the simple potential model as a criterion for atomic charge quality. Certainly other criteria are also important. The capabilities of reproducing electric moments, especially dipole moments,[42−45] are commonly used to judge the quality of calculated charges. For example, the dipole moments calculated using CHELPG point charges for the fluoromethanes are much closer to the experimental values than are those obtained by using Bader or GAPT point charges. Charges satisfying these criteria have been found to be important in describing intermolecular interactions. The GAPT charges, on the other hand, should be useful for studying reactions which predominantly depend on the electrostatic potentials of reactive centers in molecules such as those involving acid−base transformations, hydrogen bonding, acid- and base-catalyzed reactions, and electrophilic substitutions.[46]

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