# Simple potential models for carbon 1s ionization energies using infrared mean dipole moment derivatives

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## Abstract

Simple potential model relations for experimental carbon 1s ionization energies ($E_{C,1s}$) and carbon mean dipole moment derivatives ($\bar{p}_C$) obtained from experimentally measured infrared fundamental band intensities are investigated for a diverse group of 29 molecules. Positive and negative correlations of the $E_{C,1s}$ values and neighboring atom electrostatic potential contributions, $V$, with the $\bar{p}_C$ values result in large variances for the $E_{C,1s}$–$V$ values and excellent potential model fits. MP2/6-311++G(3d,3p) level Koopmans' energies are shown to provide the most precise potential model fits with correlation coefficients of 0.9996, 0.9962 and 0.9960 for $sp^3$, $sp^2$ and $sp$ hybridized carbon atoms, respectively. Potential models using experimental ionization energies adjusted by HF/6-31G(d,p) level relaxation energies are almost as precise. The slopes of the potential lines obtained using Koopmans' energies or experimental ionization energies adjusted by relaxation energies increase with increasing values of the inverse covalent $sp^3$, $sp^2$ and $sp$ radii. Relative electrostatic potentials at carbon nuclei calculated directly from electronic densities of MP2/6-311++G(3d,3p) molecular orbital wave functions are shown to be in good agreement with those estimated by mean dipole moment derivatives calculated from the same wave functions.   © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In a recent study the simple potential model proposed by Siegbahn et al. [1] has been shown to be useful in relating carbon 1s electron ionization energies observed in the X-ray region of the electromagnetic spectrum to atomic mean dipole moment derivatives determined from fundamental vibrational band intensities measured in the infrared [2,3]. Since the correlated measurements are for gas phase mole-cules and the isolated molecule approximation is appropriate, the mean dipole moment derivatives can be interpreted as atomic charges of these molecules. Of course many methods have been proposed to calculate atomic charges. Attempts have been made to relate some of them to core ionization energies via the simple potential model [4–11]. However the mean dipole moment derivatives have an important advantage over other charges. Their values can be determined experimentally and do not depend on the choice of wave function used in the expectation value integral for their calculation. Besides approximating electrostatic potentials of possible reactive centers in molecules they can also be used to test

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electronic charge distributions calculated from wave functions.

The simple potential model [1] for carbon atom 1s electron ionization energies can be expressed as

$$E_{C,1s} = k\bar{p}_C + \sum_{A \neq C} \frac{\bar{p}_A}{R_{AC}} = k\bar{p}_C + V \qquad (1)$$

where $\bar{p}_C$ and $\bar{p}_A$ are mean dipole moment derivatives of a carbon and a neighboring atom, respectively, $R_{AC}$, the internuclear distance between atoms A and C and $k$ is a constant which depends not only on the type of atom but also its hybridization state. The second term sums over all atoms in the molecule except the carbon atom being ionized and is the electrostatic potential at the carbon nucleus owing to the neighboring atomic charges, here approximated by values of mean dipole moment derivatives.

The main objective of our study is to further investigate the simple potential model relationship between 1s ionization energies and mean dipole moment derivatives for an ample selection of molecules containing sp$^3$, sp$^2$ and sp carbon atoms. As in our previous work, the molecules studied are restricted to those for which complete infrared fundamental intensity data have been measured and for which polar tensor results, necessary for calculating mean dipole moment derivatives, are available. The relationship between $E_{C,1s}$ and $\bar{p}_C$ as well as between $V$ and $\bar{p}_C$, both determined from only experimental measurements are analyzed in an attempt to better understand why the mean dipole moment derivatives provide good statistical fits for the simple potential model. Since this study contains some quite polar molecules, such as the fluorochloromethanes, the electrostatic potentials, $V$, are found to provide important contributions to the simple potential model. Also, the simple potential model description of Koopmans' energies, $E_{Koop}$, as a function of the mean dipole moment derivatives are compared with those for the corresponding experimental ionization energies. If the molecular wave functions are sufficiently accurate one can expect better fits for their Koopmans' energies than for experimental ones since relaxation effects are not included in the derivation of the simple potential model. However, inclusion of adequate relaxation energy adjustments, $E_{relax}$, to the experimental carbon atom core ionization energies is shown to provide simple potential

models that are almost as precise as those obtained with Koopmans' energy values.

Finally it is shown that the atomic mean dipole moment derivative values calculated from molecular wave functions (also called generalized atomic polar tensor charges – GAPT) [12] are capable of predicting electrostatic potentials at the carbon atom nuclei that are in excellent agreement with those obtained by integrating over molecular electronic densities corresponding to these same wave functions. This result is relevant since considerable effort has been made over many years to represent molecular electronic densities by atomic charges. As such experimental measurements of infrared intensities are useful since they provide atomic parameters which can be used to estimate accurate electrostatic potentials at reactive centers in molecules for which electronic density distributions cannot be directly measured.

## 2. 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, $Q_i$,

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

with $N_A$ and $c$ being Avogadro's number and the velocity of light [13]. The dipole moment derivatives can be transformed to atomic cartesian coordinates using the expression [14,15]

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

where $\mathbf{P}_Q$ is a 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 [16]. 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 $\boldsymbol{\beta}$ matrices), symmetry (the $\mathbf{U}$ matrix), vibrational frequencies and atomic masses (the normal coordi-

nate $\mathbf{L}^{-1}$ 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 (APTs)

$$\mathbf{P}_x = \left\{ \mathbf{P}_x^{(1)} \mathbf{P}_x^{(2)} \ldots \mathbf{P}_x^{(N)} \right\} \tag{4}$$

with $N$ being the number of atoms in the molecule. The APT corresponding to atom $\alpha$ contains the equilibrium geometry derivatives of the molecular dipole moment with respect to its cartesian coordinates

$$\mathbf{P}_x^{(\alpha)} = \begin{bmatrix} \dfrac{\partial p_x}{\partial x_\alpha} & \dfrac{\partial p_x}{\partial y_\alpha} & \dfrac{\partial p_x}{\partial z_\alpha} \\[1.5ex] \dfrac{\partial p_y}{\partial x_\alpha} & \dfrac{\partial p_y}{\partial y_\alpha} & \dfrac{\partial p_y}{\partial z_\alpha} \\[1.5ex] \dfrac{\partial p_z}{\partial x_\alpha} & \dfrac{\partial p_z}{\partial y_\alpha} & \dfrac{\partial p_z}{\partial z_\alpha} \end{bmatrix}. \tag{5}$$

The mean dipole moment derivative of atom $\alpha$, $\bar{p}_\alpha$, is simply one third the trace of this matrix [17],

$$\bar{p}_\alpha = \frac{1}{3} \left( \frac{\partial p_x}{\partial x_\alpha} + \frac{\partial p_y}{\partial y_\alpha} + \frac{\partial p_z}{\partial z_\alpha} \right). \tag{6}$$

The carbon mean dipole moment derivatives, $\bar{p}_C$, were determined from the experimental infrared fundamental intensities using Eqs. (2), (3) and (6). Theoretical estimates of these derivatives, i.e. the carbon GAPT charges, were obtained at the MP2/6-311++G(3d,3p) level using the Gaussian 94 computer suite [18]. Koopmans' energies were obtained from the corresponding Hartree–Fock wave functions.

The core ionization energies can be calculated accurately by the $\Delta$SCF method [19–21] or the unrestricted generalized transition-state model using a gradient-corrected density functional [22–24]. Here ab initio molecular orbital calculations were performed using the GAMESS-US [25] program. $\Delta$SCF energies were obtained from calculations on molecules and their cations using HF/6-31G(d,p) 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. All calculations were carried

out on an IBM RISC 6000 and DEC Alpha workstations.

## 3. Results and discussion

The experimental carbon 1s ionization energies [26], mean dipole moment derivatives [2,3] and electrostatic potential contributions of neighboring atoms have been given previously in Tables 1–3 of Ref. [2]. The $CH_3Br$ and $CH_3I$ data included there are not treated here since they are not as easily subjected to accurate molecular orbital calculations as the molecules containing only first or second row atoms. On the other hand, the $CCl_4$ polar tensor [27] has been determined recently from the $CCl_4$ experimental intensities so its $E_{C,1s}$ and $\bar{p}_C$ values, 296.36 eV and 1.044e, have been included in this study. The $CO_2$, OCS and $CS_2$ data are not used for modelling of sp hybridized carbon atoms since they seem to obey a different potential model than the one that appears adequate for the molecules containing the C≡C bond. Furthermore the carbon ionization energies of $CH_3CCCH_3$ have been assigned as in the original Ref. [28] and not as in Ref. [26]. Specifically 291.30 and 290.03 eV, respectively, were used for the 1s ionization energy values of the $sp^3$ and sp hybridized carbon atoms of $CH_3CCCH_3$. These changes provoke only very small changes in the regression statistics of the potential models reported in Ref. [2].

A preliminary analysis illustrates why the $E_{C,1s}-V$ vs. $\bar{p}_C$ potential models are as accurate as those reported in Ref. [2]. In Fig. 1 the experimental 1s ionization energies are plotted against the mean dipole moment derivatives determined from experimental infrared intensities. Approximate linear arrangements of points can be observed for each type of hybridized carbon atom although there exists considerable overlap for points of $sp^2$ and $sp^3$ carbon atoms. The variances in the experimental ionization energies of the $sp^2$ and $sp^3$ carbon data, given in Table 1, are about the same and more than twice the variance in the sp carbon values. Table 1 also contains the correlation coefficient, slope and intercept values of the regression lines for each type of hybridized carbon atom.
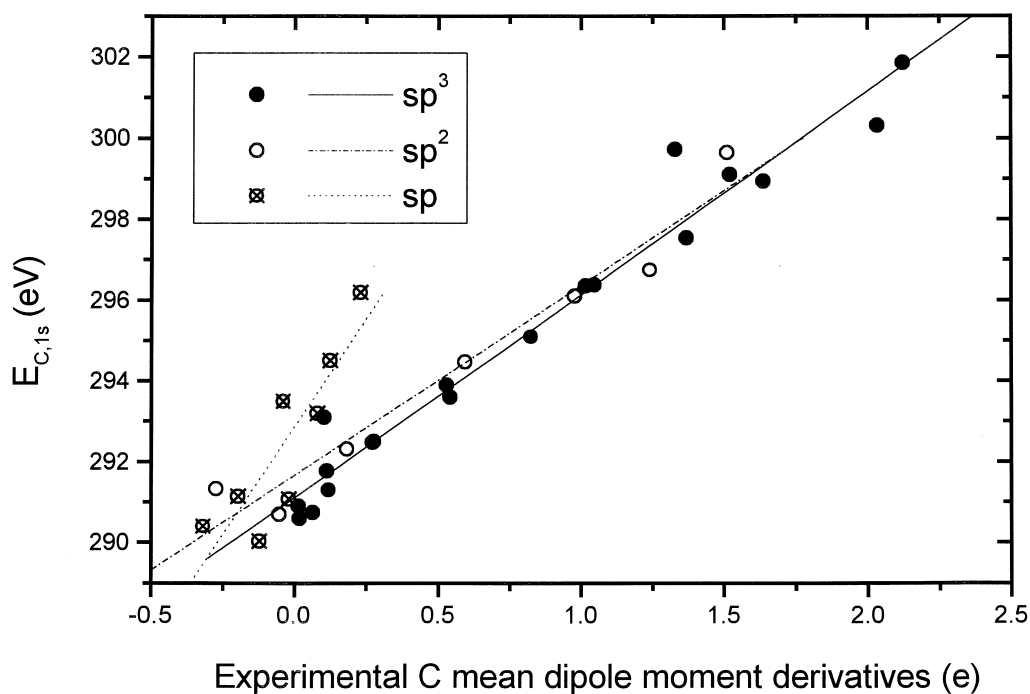
The electrostatic potentials arising from the neigh-

Fig. 1. Experimental carbon 1s ionization energies vs. experimentally determined carbon mean dipole moment derivatives.

Table 1
Linear regression results of models for different ordinate quantities on experimental mean dipole derivatives of carbon atoms

| Hybridization | Ordinate variable | Correlation coefficient[a] | Slope, $k$ (V) | Intercept (eV) | Variance (eV)$^{2}$ [b] |
|---|---|---|---|---|---|
| sp$^3$ | $E_{C,1s}$ | 0.9816 | 5.02 | 291.12 | 12.61 |
|  | $V$ | −0.9857 | −10.30 | 0.57 | 59.31 |
|  | $E_{C,1s}-V$ | 0.9961 | 15.32 | 290.55 | 125.44 |
|  | $E_{Koop}-V$ | 0.9996 | 15.83 | 305.01 | 130.19 |
|  | $E_{C,1s}-V-E_{relax}$ | 0.9986 | 15.00 | 304.22 | |
| sp$^2$ | $E_{C,1s}$ | 0.9776 | 4.69 | 291.67 | 10.55 |
|  | $V$ | −0.9858 | −12.57 | 1.75 | 74.44 |
|  | $E_{C,1s}-V$ | 0.9941 | 17.26 | 289.93 | 138.06 |
|  | $E_{Koop}-V$ | 0.9962 | 17.23 | 304.88 | 136.89 |
|  | $E_{C,1s}-V-E_{relax}$ | 0.9955 | 16.39 | 303.75 | |
| sp | $E_{C,1s}$ | 0.8703 | 10.67 | 292.87 | 4.42 |
|  | $V$ | −0.9463 | −10.44 | −0.49 | 4.48 |
|  | $E_{C,1s}-V$ | 0.9838 | 21.11 | 293.37 | 15.41 |
|  | $E_{Koop}-V$ | 0.9960 | 17.86 | 307.77 | 11.47 |
|  | $E_{C,1s}-V-E_{relax}$ | 0.9957 | 16.88 | 305.94 | |

[a] Correlation coefficient between ordinate and abscissa values.
[b] Statistical variance calculated for each type of hybridized atom using $\{\Sigma(x_i - \bar{x})^2/(N-1)\}$.

boring atoms, $V$, and calculated using experimentally derived mean dipole moment derivatives show strong negative correlations with $\bar{p}_C$ as can be seen in Fig. 2. Furthermore the variances in the $V$ values of the $sp^2$ and $sp^3$ carbon atoms are much larger than the variances in their respective experimental ionization energies. For the sp atoms the variance in the $V$ values is almost the same as the one for the experimental $E_{C,1s}$ values. See Table 1 for the relevant statistical information.

The regression fits are clearly improved in the simple potential model graphs with correlation coefficients ranging from 0.9838 to 0.9961 compared with a 0.8703–0.9816 interval for the $E_{C,1s}$ values and $-0.9463$ to $-0.9858$ interval for the $V$ values. Also the variances in the $E_{C,1s}$–$V$ values are much larger than those for either the $E_{C,1s}$ or $V$ values for each type of carbon atom. The range in the experimental $E_{C,1s}$ energies is only about 12 eV (290.03 eV for $CH_3CCCH_3$ to 301.85 eV for $CF_4$) compared with one of about 40 eV for the $E_{C,1s}$–$V$ values. The positive and negative correlations of the $E_{C,1s}$ and $V$

values with $\bar{p}_C$ result in the large variances and excellent potential model fits of the $E_{C,1s}$–$V$ and $\bar{p}_C$ values. Furthermore the variances for the carbon nuclei electrostatic potentials owing to the neighboring atoms provide the larger contributions to the $E_{C,1s}$–$V$ variances, specially for the $sp^3$ and $sp^2$ hybridized carbons. This result is not surprising since for neutral molecules the carbon mean dipole moment derivative is related to those of other atoms in the molecule by [14,15]

$$\bar{p}_C = -\sum_{A \neq C} \bar{p}_A. \tag{7}$$

As such a partial cancellation of terms in Eq. (1) explains the small variances of the experimental 1s electron ionization energy values.

Since the simple potential model does not contemplate relaxation effects occurring during the core ionization process one can expect that replacing the carbon 1s experimental energies by Koopmans' energies, $E_{Koop}$, would result in better fits to the mean dipole moment derivatives than those observed
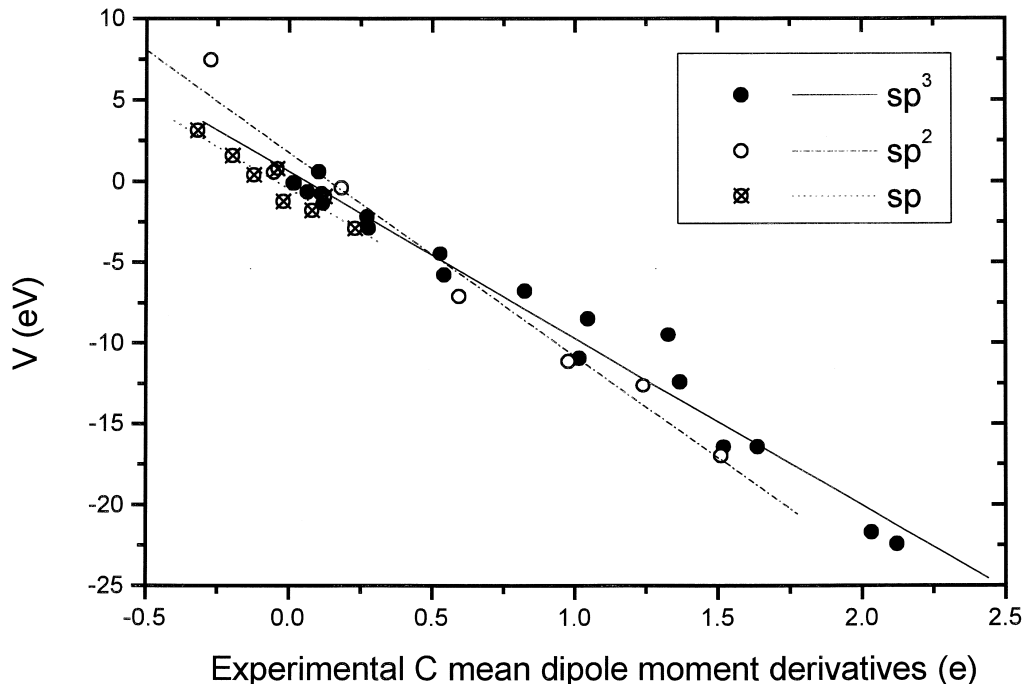


Fig. 2. Neighboring atom electrostatic potential contributions calculated from experimentally determined mean dipole moment derivatives vs. experimentally determined carbon mean dipole moment derivatives.
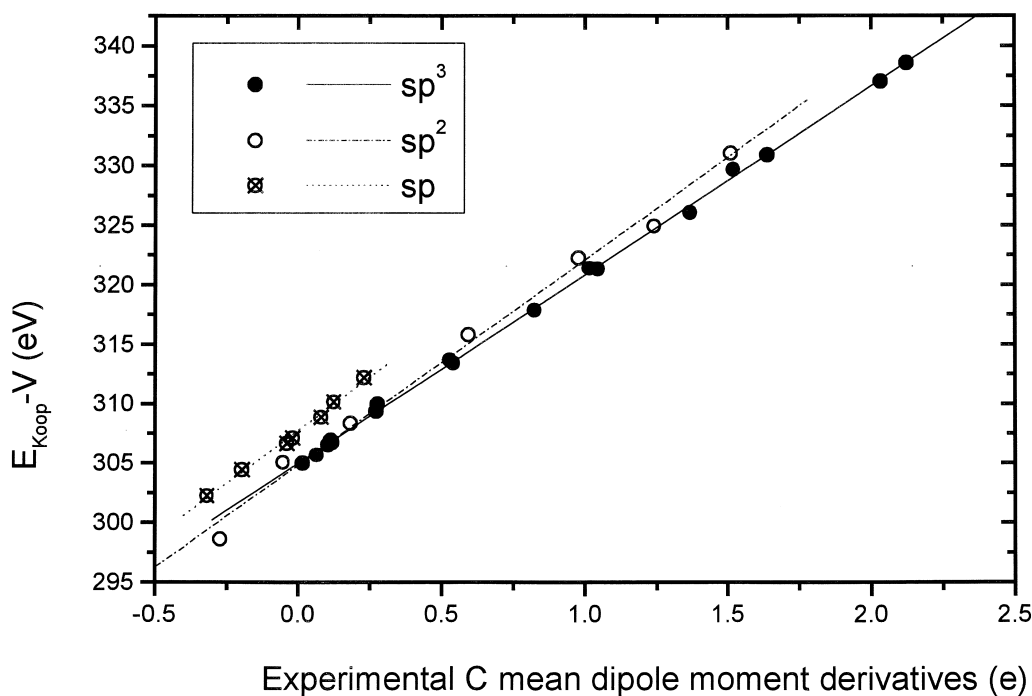
Fig. 3. MP2/6-311 + +G(3d,3p) Koopmans' energies adjusted by neighboring atom electrostatic potentials vs. experimentally determined carbon mean dipole moment derivatives.

for the $E_{C,1s}–V$ data. Fig. 3 shows the graphs of Koopmans' energies, given in Table 2, corrected by the neighboring atom electrostatic potentials versus $\bar{p}_C$. Koopmans' energies were calculated using the 6-311 + +G(3d,3p) basis set whereas the $\bar{p}_C$ and $V$ values are from the experimental mean dipole moment derivatives. The regression statistics are included in Table 1. As expected the regression correlation coefficients are closer to unity for the calculated Koopmans' energies than for the experimental ionization energies. This is specially true for the sp carbon atoms where the $E_{C,1s}–V$ vs. $\bar{p}_C$ regression coefficient is 0.9838 compared to a 0.9960 value for the $E_{Koop}$ and $\bar{p}_C$ data.

In recent work [29] core ionization relaxation energies, $E_{relax}$, were calculated by the $\Delta$SCF method at the HF/6-31G(d,p) level for all the ionization energies discussed here and $E_{C,1s}–V–E_{relax}$ vs. $\bar{p}_C$ models were investigated. The graphical displays of these models for the sp$^3$, sp$^2$ and sp hybridized carbon atoms in Figs. 2–4 of this reference appear almost the same as those in Fig. 3 for the Koopmans'

energies. Regression statistics reported there have been included in Table 1. Their correlation coefficients are very close to but slightly smaller than those for the $E_{Koop}$ vs. $\bar{p}_C$ models. On the other hand the slope values are very sensitive to including relaxation effects in the simple potential model. For each kind of hybridized carbon atom there are differences of about 1 V between potential model slope values obtained using Koopmans' energies or experimental ionization energies adjusted by corresponding relaxation energies. Also relaxation effects are seen to be specially important for the sp hybridized carbons. Adjustment of the experimental sp carbon ionization energies by relaxation energies lowers the slope of the sp carbon potential model line by about 4 V whereas this effect is about 1 V for the sp$^3$ and sp$^2$ models, as can be verified in Table 1.

The slope of the simple potential model, $k$, has been interpreted as the average electrostatic interaction between an electron in a 1s orbital and an electron in a valence shell orbital. If this is correct, one can expect the size of this interaction to vary as

Table 2
Ab initio Koopmans' energies calculated using a 6-311++G(3d,3p) basis set[a]

| Hybridization | Molecules | $E_{\text{Koop}}$ (eV) | Hybridization | Molecules | $E_{\text{Koop}}$ (eV) |
|---|---|---|---|---|---|
| $sp^3$ | $CH_4$ | 304.87 | $sp^2$ | $CH_2CH_2$ | 305.61 |
| | $CH_3F$ | 307.65 | | $C^*H_2CF_2$ | 306.04 |
| | $CH_2F_2$ | 310.46 | | $CH_2C^*F_2$ | 311.11 |
| | $CHF_3$ | 313.30 | | $COH_2$ | 308.68 |
| | $CF_4$ | 316.13 | | $COF_2$ | 314.06 |
| | $CH_3Cl$ | 307.17 | | $COCl_2$ | 312.34 |
| | $CH_2Cl_2$ | 309.22 | | *cis*-$C_2H_2Cl_2$ | 307.95 |
| | $CHCl_3$ | 311.08 | | | |
| | $CCl_4$ | 312.83 | | | |
| | $CF_3Cl$ | 315.30 | | | |
| | $CF_2Cl_2$ | 314.48 | $sp$ | CO | 309.30 |
| | $CFCl_3$ | 313.66 | | HCN | 307.43 |
| | $CH_3CH_3$ | 305.02 | | HCCH | 306.00 |
| | $C_2H_4O$ | 307.11 | | NCCN | 309.19 |
| | $C_3H_6$ | 305.35 | | $CH_3C^*N$ | 307.07 |
| | $C^*H_3CN$ | 307.12 | | $CH_3C^*CH$ | 305.86 |
| | $C^*H_3CCH$ | 306.15 | | $CH_3CC^*H$ | 305.39 |

[a] Koopmans' energies for $C_2F_6$ were not calculated owing to limited disk capacity. Linear basis set dependence problems prohibited a successful calculation for $C_4H_6$.

the inverse of the average distance between these electrons or approximately as the inverse of the atomic radii of the atoms. In Fig. 4 the slopes of the $E_{C,1s}$–$V$, $E_{\text{Koop}}$–$V$ and $E_{C,1s}$–$V$–$E_{\text{relax}}$ simple potential model lines are plotted as functions of the inverse covalent radii [30] of the $sp^3$, $sp^2$ and $sp$ hybridized carbon atoms. In all three cases the $k$ values increase with the inverse of the covalent radii. Although only three points result from the data treated in this report it does lend support to this interpretation of the $k$ values. This is especially true for the $E_{\text{Koop}}$–$V$ and $E_{C,1s}$–$V$–$E_{\text{relax}}$ vs. $\bar{p}_C$ slopes where the points fall close to the least squares lines. Furthermore both of these lines are almost parallel since the $k$ values obtained with relaxation energy adjusted values are all about 0.9 V smaller than those obtained with Koopmans' energies for the three types of hybridizations.

Finally it is of interest to determine how well mean dipole moment derivative values can be used to calculate electrostatic potentials at the nuclei of molecules compared with those calculated directly from the electronic density distributions. These results are shown in Table 3 for the fluorochloromethanes. The first column contains electrostatic potentials ($\mathcal{V}_C$) calculated from MP2/6-311++G(3d,3p) wave functions using

$$\mathcal{V}_C = \sum_{A \neq C} \frac{Z_A}{|r_C - r_A|} - \sum_{\mu\nu} P_{\mu\nu} \int \frac{\varphi_\mu(r_1)\varphi_\nu(r_1)}{|r_C - r_1|} \, dr_1 \qquad (8)$$

where $Z_A$ is the nuclear charge of the other atoms in the molecule, $r_1$, $r_A$ and $r_C$ the position vectors of an electron and atoms A and C, $\varphi_\mu$ and $\varphi_\nu$ the atomic orbitals and $P_{\mu\nu}$ is the corresponding element of the density matrix [31]. The second column of this table contains these electrostatic potential values relative to the methane potential. Column 3 contains relative electrostatic potential values calculated using the simple potential model with a 15.83 V slope value and mean dipole moment derivatives calculated from MP2/6-311++G(3d,3p) wave functions. These values are in good agreement with those in column 2 obtained directly from integration of the corresponding molecular electronic densities.

## 4. Conclusions

Previous studies [1,7–11] have attempted to relate experimental core electron ionization energies to atomic charge values calculated by theoretical methods. This study, and others by our research group [2,3] show that mean dipole moment derivatives
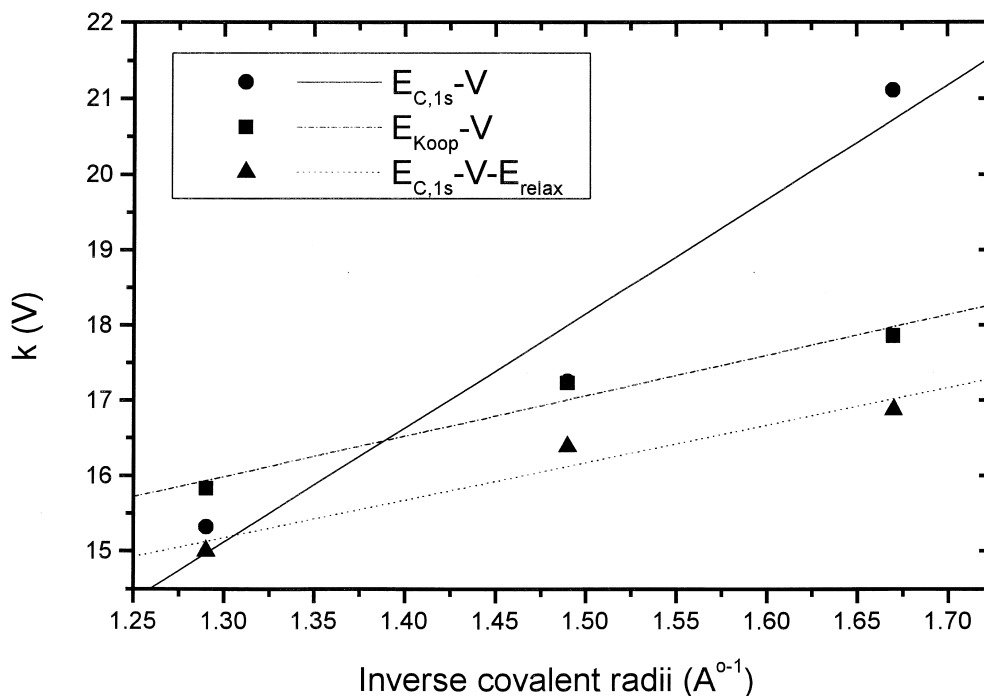
Fig. 4. Slopes of simple potential models, $k$, vs. reciprocal covalent radii for sp, sp$^2$ and sp$^3$ hybridized carbon atoms.

measured from infrared fundamental intensities can be related to carbon 1s ionization energies using the simple potential model. Other simple potential models [32] have also been found between these derivatives and np level ionization energies of Si and

Table 3
Electrostatic potentials at the carbon nuclei calculated directly from the molecular wave function and from mean dipole moment derivatives at the MP2/6-311++G(3d,3p) level

| Molecules | $\mathcal{V}_C$ (eV) | $\Delta\mathcal{V}_C$ (eV) | $\Delta(k\bar{p}_C + V)^a$ (eV) |
|---|---|---|---|
| CH$_4$ | −401.49 | 0.00 | 0.00 |
| CH$_3$F | −398.67 | 2.82 | 3.08 |
| CH$_2$F$_2$ | −395.78 | 5.71 | 5.70 |
| CHF$_3$ | −392.80 | 8.69 | 8.11 |
| CF$_4$ | −389.75 | 11.74 | 10.08 |
| CH$_3$Cl | −399.18 | 2.31 | 2.11 |
| CH$_2$Cl$_2$ | −397.09 | 4.40 | 4.32 |
| CHCl$_3$ | −395.17 | 6.32 | 6.59 |
| CCl$_4$ | −393.38 | 8.11 | 9.11 |
| CF$_3$Cl | −390.67 | 10.82 | 9.92 |
| CF$_2$Cl$_2$ | −391.57 | 9.92 | 9.93 |
| CFCl$_3$ | −392.48 | 9.01 | 9.70 |

[a] A $k$ value of 15.83 V from Table 1 used in these calculations.

Ge. Work in progress in our laboratory indicates that simple potential models are also adequate to represent core ionization energies and mean dipole moment derivatives of B, N, P, and O. The model might not be useful for the fluorine atom since variances in the $E_{F,1s}$–$V$ and $\bar{p}_F$ values are small [2]. Indeed fluorine polar tensors have been found to be approximately transferable from one molecule to another in attempts to predict infrared intensities [33,34].

One might expect to relate other electron spectroscopic energies, such as inner shell transition energies, to infrared mean dipole moment derivatives. Although infrared spectra have been determined for many gas phase molecules, absolute infrared intensities have been measured for the bands of very few of them. This limits attempts to relate electronic spectral data with infrared parameters. Quantum chemical calculations should be helpful for indicating which molecules are the most appropriate for future measurements of fundamental intensities for the development of these models.

The most intriguing question however is why dipole moment derivatives are so simply related to

the core ionization energies. The simple potential models reported here and in Refs. [2,3,32] indicate that the mean dipole moment derivatives can be interpreted as atomic charges. It cannot be expected that these charge values will be useful in accurately representing molecular electronic distributions for all kinds of applications, such as those for predicting electric moments in molecules. However mean dipole moment derivatives should be helpful for calculating electrostatic potentials at nuclei in molecules. This could permit considerable simplification in studying gas phase chemical reactions for which these electrostatic potentials are important.

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