

CCl_4 : mean dipole moment derivatives and core electron binding energies

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Abstract

Atomic polar tensors for the carbon tetrachloride molecule are calculated from experimental fundamental infrared intensities, a normal coordinate transformation determined from observed fundamental frequency values and experimentally determined CCl bond lengths. Dipole moment derivative sign ambiguities were eliminated by comparing the alternative mathematical solutions obtained from the experimental data with results of Hartree–Fock, Möller–Plesset 2 and Density Functional Theory calculations using a $6-31++G(d,p)$ basis set. Carbon and chlorine mean dipole moment derivatives of $1.043 \pm 0.022e$ and $-0.261 \pm 0.006e$, respectively, are determined from the preferred atomic polar tensors. These values are in excellent agreement with those obtained from the CCl_4 1s carbon atom ionization energy using a simple potential model (1.081e and $-0.270e$), from an electronegativity model proposed earlier (1.008e and $-0.252e$) and from an electronegativity equalization model (1.066e and $-0.266e$). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

For some time, our research group has been calculating atomic polar tensors from gas phase experimental intensities and frequencies of infrared vibrational fundamental bands and force fields. These calculations are important since they contribute to an increase in a database which contains only a limited number of atomic polar tensors. This limitation is directly related not only

to the small number of experimental endeavors to measure infrared intensities but also to difficulties in resolving sign ambiguities of dipole moment derivatives as well as in the calculation of their polar tensors.

Atomic polar tensor invariant quantities have been shown to be linearly related to the averages of the electronegativities of substituent atoms in the halomethanes [1,2]. Since the atomic polar tensor elements have units of charge, attempts have been made to relate tensor invariant quantities, such as the mean dipole moment derivatives and effective atomic charges, to electronic charge distributions of atoms in molecules. Cioslowski [3]

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has suggested that mean dipole moment derivatives be interpreted as atomic charges, namely General Atomic Polar Tensor (GAPT) charges, and has pointed out several advantages in their calculation from molecular orbital wave functions relative to other kinds of calculated atomic charges.

Recently [4,5], carbon mean dipole moment derivatives have been shown to be related to the 1s carbon electron binding energies using the simple potential model proposed by Siegbahn et al. [6] to interpret X-ray photoelectron spectra. This result suggests that mean dipole moment derivatives, obtained from gas phase measurements of fundamental vibrational band intensities and frequencies, might be interpreted as atomic charges. Furthermore, different potential models were shown to exist for the different hybrid forms of the carbon atom, sp^3 , sp^2 and sp . Later the results obtained for the sp^3 carbon atom were found to be extendable to the np core electrons of other group IV atoms, Si and Ge [7].

The biggest obstacle for investigating the relationships between core electron ionization energies and mean dipole moment derivatives is the small amount of atomic polar tensor data published in the scientific literature. Although core ionization energies have been measured for hundreds of atoms in molecules, the number of molecules for which complete gas phase fundamental infrared intensity measurements have been made is very small. In this work, the atomic polar tensor values for CCl_4 are reported. Even though its fundamental infrared intensities have been measured for some time [8], its atomic polar tensors have not been reported previously. As a consequence of this evaluation, the sign ambiguities in the dipole moment derivatives of the CCl_4 molecule have also been resolved.

2. Calculations

The atomic polar tensor (APT) method of analysis of infrared intensity data was introduced initially by Morcillo et al. [9]. This approach was reformulated [10] and extended, making it more consistent with commonly used spectroscopic no-

tations. These APT supply the changes in the total molecular dipole moments, $\Delta\vec{P}$, when an atom α is moved from its equilibrium position,

$$\Delta\vec{P} = \sum_{\alpha=1}^n P_r^{(\alpha)} \Delta\vec{r}_{\alpha} \quad (1)$$

with $\vec{r}_{\alpha} = x_{\alpha}\vec{i} + y_{\alpha}\vec{j} + z_{\alpha}\vec{k}$, being the position vector expressed in terms of a fixed Cartesian coordinate system.

The polar tensor of a molecule is defined as a juxtaposition of n 3×3 matrixes (APT), each associated with the Cartesian coordinates of just one atom,

$$\mathbf{P}_x = (\mathbf{P}_x^{(1)}; \mathbf{P}_x^{(2)}; \dots; \mathbf{P}_x^{(\alpha)}; \dots; \mathbf{P}_x^{(n)}) \quad (2)$$

where

$$\mathbf{P}_x^{(\alpha)} = \begin{pmatrix} \partial p_x / \partial x & \partial p_x / \partial y & \partial p_x / \partial z \\ \partial p_y / \partial x & \partial p_y / \partial y & \partial p_y / \partial z \\ \partial p_z / \partial x & \partial p_z / \partial y & \partial p_z / \partial z \end{pmatrix} = \begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz} \end{pmatrix} \quad (3)$$

is the polar tensor matrix of atom or, each element, $\partial\mathbf{P}_r / \partial\mathbf{r}_{\alpha}$ being interpreted as a Cartesian coordinate variation of the molecular dipole moment for an atomic displacement coordinate.

Even though the \mathbf{P}_x matrix has $3 \times 3n$ elements, many of them are equal to the same value or are equal to zero for symmetry reasons. For an atom that, for example, is on a C_3 or higher symmetry axis, the polar tensor is a diagonal matrix. In addition, some polar tensor elements are related by symmetry to other elements. For example, in the CCl_4 molecule that belongs to the T_d point group, only the tensor elements of just one chlorine atom need be calculated, since the other three chlorine atoms are related to the first one by similarity transformations. In addition, for a neutral molecule, all the APT are related,

$$\sum_{\alpha}^n P_x^{(\alpha)} = \mathbf{0}, \quad (4)$$

where $\mathbf{0}$ is the null matrix.

The complete equation for the calculation of polar tensors is

Table 1

Infrared vibrational frequencies (cm^{-1}) and intensities (km mol^{-1}), optimized force field and molecular geometry for CCl_4

ν_3 (cm^{-1})	ν_4 (cm^{-1})	$F_{33}/\text{mdynes.A}^{\circ-1}$	3.37	$r_{\text{C-Cl}}$	1.7667 Å
793	310	$F_{44}/\text{mdynes.A}^{\circ}$	1.22	$\beta_{\text{C-Cl}}$	109° 28'
A_3 (km mol^{-1})	A_4 (km mol^{-1})	F_{34}/mdynes	-0.94	—	—
322 ± 60	0.20 ± 0.05	—	—	—	—

$$\mathbf{P}_x = \mathbf{P}_r \mathbf{B} + \mathbf{P}_\rho \boldsymbol{\beta} \quad (5)$$

The $\mathbf{P}_r \mathbf{B}$ term supplies the vibrational polar tensor in fixed Cartesian coordinates of the molecule. The second term, $\mathbf{P}_\rho \boldsymbol{\beta}$, is the rotational correction that depends on the atomic weights, geometry and equilibrium dipole moment. For molecules that present zero equilibrium dipole moments, this term is a null matrix.

The polar tensors of CCl_4 can be calculated from the values of the experimental intensities and dipole moment derivatives,

$$\mathbf{P}_x = \mathbf{P}_q \mathbf{L}^{-1} \mathbf{U} \mathbf{B} \quad (6)$$

where \mathbf{P}_q contains the dipole moment derivatives and the matrix product, $\mathbf{L}^{-1} \mathbf{U} \mathbf{B}$, corresponds to the transformation of the derivatives from normal to Cartesian coordinates. The TPOLAR program [11] can be used for the calculation of these tensors.

The invariant \bar{p}_α , the mean dipole moment derivative, satisfies an equation analogous to Eq. (4) and is defined as 1/3 the trace of the α th atomic polar tensor,

$$\bar{p}_\alpha = 1/3 \text{Tr}(\mathbf{P}_x^{(\alpha)}) \quad (7)$$

The ab initio calculations were made with the Gaussian 94 [12] program at CENAPAD/SP with the 6–31G basis set supplemented by polarization functions, one set of d and p functions, and by diffuse functions on both carbon and chlorine atoms at the Hartree–Fock, Möller–Plesset 2 and density functional theory levels. For the latter, a B3LYP exchange-correlation potential was used.

3. Results and discussion

The frequencies and intensities of fundamental vibrational bands, optimized force field and CCl

bond lengths necessary for the calculation of the CCl_4 atomic polar tensors are given in Table 1 and were taken from [8]. The symmetry coordinates and molecular orientation in Cartesian coordinate space used are the same as those of this reference except for the fact that the bending symmetry coordinates were not bond length-weighted. The values calculated for each group of signs of dipole moment derivatives is given in Table 2.

To determine the correct APT solution, a principal component analysis was made and results of ab initio calculations for the CCl_4 molecule were compared with those obtained from the experimental data in Table 1. The theoretical results are included in Table 2.

The principal component graph for the CCl_4 tensor elements is shown in Fig. 1. The first principal component, PCl, explains almost 100% of the variance of the tensor elements and is described mainly by the $P_{xx}^{(C)}$ term. This means that the signs of the dipole moment derivatives are almost directly related to that term. Observation of the plot in Fig. 1 leads to the elimination of the (+ +) and (+ -) groups of signs. The

Table 2

CCl_4 polar tensor element values obtained from experimental data and their theoretical estimates, in units of electrons

	$P_{xx}^{(C)}/e$	$P_{xx}^{(Cl)}/e$	$P_{xy}^{(Cl)}/e$
(+ +)	-1.059	0.265	-0.201
(- -)	1.059	-0.265	0.201
(+ -)	-1.028	0.257	-0.258
(- +)	1.028	-0.257	0.258
Average	1.043	-0.261	0.230
HF/6-31++G(d,p)	1.301	-0.325	0.181
MP2/6-31++G(d,p)	1.294	-0.323	0.193
B3LYP/6-31+	1.436	-0.359	0.224
+ G(d,p)			

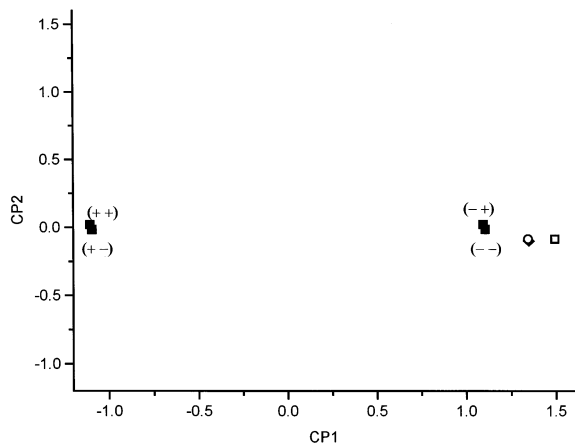


Fig. 1. Principal component score graph of the CCl_4 atomic polar tensor elements obtained from the experimental data for different dipole moment derivative sign attributions. The theoretical results are included for comparison: \circ , HF/6-31++G(d,p); \star , B3LYP/6-31++G(d,p); \square , MP2/6-31++G(d,p).

other sets of signs, $(--)$ and $(-+)$, have points close to the theoretical points and values in good agreement with the theoretical ones as can be seen in Table 2. Both sets of element values are almost identical. They only differ owing to the sign of the A_4 bending intensity, which is very small, less than 1% of the A_3 stretching intensity. Since determination of the sign of the bending derivative is not possible because of its small magnitude, the average of the $(--)$ and $(-+)$ polar tensor elements are taken as the correct values.

The resulting mean dipole moment derivatives for CCl_4 are

$$\bar{p}_C = 1.043 \pm 0.022e$$

and, from Eq. (4),

$$\bar{p}_{\text{Cl}} = -0.261 \pm 0.006e.$$

3.1. Atomic polar tensors and core binding energy relationships

As stated in the introduction, carbon mean dipole moment derivatives, \bar{p}_C , of a group of molecules, have been related to their 1s core electron binding energies, $E_{1s,C}$, using the potential model proposed by Siegbahn et al. [6],

$$E_{1s,C} = k_C \bar{p}_C + V, \quad \text{with} \quad V = \sum_{B \neq C} \bar{p}_B / R_{BC}. \quad (8)$$

In this equation, mean dipole moment derivatives calculated as previously described, substitute the atomic charges used in the original model. The second term on the right side represents the electrostatic potential (V) at the nucleus of the carbon atom owing to the charges of the neighboring atoms, with R_{BC} corresponding to the distance between the B and C atoms. According to the simple potential model, the k_C value can be identified with the Coulomb integral between a core electron and an electron of the valence shell of the atom involved in the ionization process. Adding to this model the estimated relaxation energy of the electrons in the ionized molecule, one has

$$E_{1s,C} = k \bar{p}_C + V + E_{\text{rel}}. \quad (9)$$

The relaxation energy of the ionization process is obtained here as

$$E_{\text{rel}} = \Delta E_{\text{ioniz}}^{\text{ASCF}} - E_{1s,C}^{\text{Koop}}$$

where $\Delta E_{\text{ioniz}}^{\text{ASCF}}$ is the ASCF ionization energy [13] calculated using a 6-31++G(d,p) basis set and $E_{1s,C}^{\text{Koop}}$ the Hartree-Fock Koopman's energy of the 1s carbon orbital.

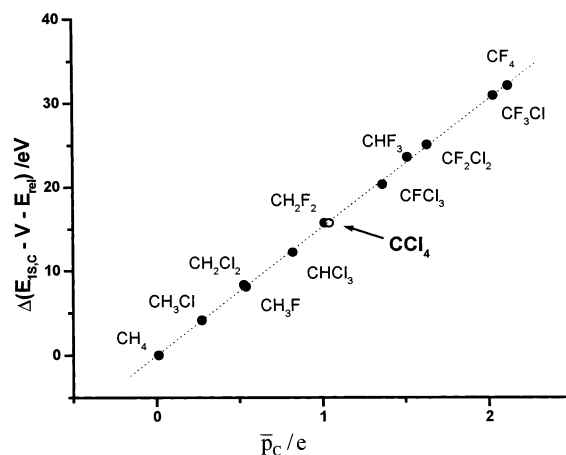


Fig. 2. The simple potential model graph for the fluorochloromethanes including the point for the CCl_4 results obtained in this work.

Fig. 2 shows a simple potential model for the fluorochloromethanes [4,5] calculated from a data base not containing the carbon CCl_4 mean dipole moment derivative. Using the CCl_4 experimental 1s ionization [14] and relaxation energy values results in a \bar{p}_C value of 1.081e in excellent agreement with the value determined from the experimental intensities.

3.2. Electronegativity models

The mean dipole moment derivatives for the C and Cl atoms in CCl_4 can also be predicted using the electronegativity models proposed earlier [1,2]. Huheey's equations [15] for the equalization of electronegativity applied to the CCl_4 molecule are

$$\chi_{C_{te}} = 7.97 + 13.27\delta_C = \chi_{Cl} = 9.39 + 11.30\delta_{Cl}$$

and

$$\delta_C + 4\delta_{Cl} = 0$$

where $\chi_{C_{te}}$ and χ_{Cl} are the electronegativities of a tetrahedrally bonded carbon atom and a p-orbital bonded chlorine atom, and δ_C and δ_{Cl} are called partial charges. The partial charge has been shown to be related to the mean dipole moment by [1]

$$\bar{p}_C = 0.429 + 7.218\delta_C.$$

Solving these equations leads to values of \bar{p}_C and \bar{p}_{Cl} of 1.066e and $-0.266e$, respectively. They are in excellent agreement with the results obtained from the experimental intensities, 1.043e and $-0.261e$.

An alternative electronegativity model [16] uses Jaffe–Mulliken electronegativity values [15], E_x for halogen atoms,

$$\bar{p}_x = 0.634 - 0.0945E_x.$$

Since $E_{Cl} = 9.38$, \bar{p}_{Cl} can be calculated to be $-0.252e$ and $\bar{p}_C = 1.008e$. Again, both values are in excellent agreement with those determined in this work.

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