

# The infrared fundamental intensities and polar tensor of $\text{CF}_4$

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## Abstract

Atomic polar tensors of carbon tetrafluoride are calculated from experimental fundamental infrared intensities measured by several research groups. Quantum chemical calculations using a 6-311 + + G(3d, 3p) basis set at the Hartree-Fock, Möller-Plesset 2 and Density Functional Theory (B3LYP) levels are used to resolve the sign ambiguities of the dipole moment derivatives. The resulting carbon mean dipole moment derivative,  $\bar{p}_C = 2.051 e$ , is in excellent agreement with values estimated by a MP2/6-311 + + G(3d, 3p) theoretical calculation, 2.040  $e$ , and by an empirical electronegativity model, 2.016  $e$ . The  $\bar{p}_C$  value determined here is also in excellent agreement with the one obtained from the  $\text{CF}_4$  1s carbon ionization energy using a simple potential model, 2.059  $e$ . Crawford's G intensity sum rule applied to the fundamental intensities of  $\text{CH}_4$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$  and  $\text{CHF}_3$  results in a prediction of a 1249  $\text{km mol}^{-1}$  intensity sum for  $\text{CF}_4$  in good agreement with the experimental values of  $1328 \pm 37.9$ ,  $1208.0 \pm 54.4$  and  $1194.8 \pm 7.4 \text{ km mol}^{-1}$  reported in the literature. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Infrared intensities; Atomic polar tensors; Electronegativity; G sum rule; Simple potential model

## 1. Introduction

The experimental determination of accurate absolute infrared intensity values is known to be a difficult task [1,2]. Several methods are available, however experimental measurements for the same molecule obtained using the same conceptual procedure can produce disparate results. The very

strong  $\nu_3$  band of  $\text{CF}_4$  presents a good example of this problem [3–11]. The band is quite narrow and its accurate intensity measurement requires sufficient instrumental resolution. Pressure broadening techniques are of limited use since accurate extrapolation necessitates very low partial pressure values of the absorbent. Furthermore this band is overlapped by the  $2\nu_4$  overtone.

Table 1 contains the fundamental band intensity values measured by several groups over the past fifty years [3–11]. The values of the  $\nu_3$  band intensity range from 840 to 1328  $\text{km mol}^{-1}$ . All determinations were made by absorbance measurements with the exception of the 1194.8  $\text{km}$

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$\text{mol}^{-1}$  value which was obtained from infrared dispersion studies.

Our investigation of these intensities has two main objectives. First, we determine how different intensity results affect the sizes of dipole moment derivatives. Principal component projections and quantum chemical calculations are used to determine the signs of the  $\text{CF}_4$  dipole moment derivatives and its resulting polar tensor element values. Since the  $\nu_4$  band is weak the sign of its corresponding derivative is difficult to ascertain. Second, infrared intensity results of the other fluoromethanes are used in an attempt to determine the correct intensity values for  $\text{CF}_4$ . In contrast to the  $\text{CF}_4$  data the experimental measurements of different research groups on the fundamental intensities of  $\text{CH}_4$ ,  $\text{CH}_3\text{F}$ ,  $\text{CH}_2\text{F}_2$  and  $\text{CHF}_3$  are in very good agreement. As such, electronegativity models, 1s electron ionization energy results and  $G$  intensity sum rule analysis provide strong evidence for the selection of preferred sets of intensity values.

## 2. Calculations

Atomic polar tensor elements were calculated using the equations developed by Morcillo and co-workers [12] and by Person and Newton [13]. The polar tensor is a juxtaposition of  $3 \times 3$  atomic polar tensors,

$$P_X = \{P_X^{(C)}; P_X^{(F_1)}; P_X^{(F_2)}; P_X^{(F_3)}; P_X^{(F_4)}\} \quad (1)$$

where for the  $\alpha$ th atom with atomic cartesian coordinates  $x_\alpha$ ,  $y_\alpha$  and  $z_\alpha$

$$P_X^{(\alpha)} = \begin{bmatrix} \partial p_x / \partial x_\alpha & \partial p_x / \partial y_\alpha & \partial p_x / \partial z_\alpha \\ \partial p_y / \partial x_\alpha & \partial p_y / \partial y_\alpha & \partial p_y / \partial z_\alpha \\ \partial p_z / \partial x_\alpha & \partial p_z / \partial y_\alpha & \partial p_z / \partial z_\alpha \end{bmatrix} = \begin{bmatrix} P_{xx}^{(\alpha)} & P_{xy}^{(\alpha)} & P_{xz}^{(\alpha)} \\ P_{yx}^{(\alpha)} & P_{yy}^{(\alpha)} & P_{yz}^{(\alpha)} \\ P_{zx}^{(\alpha)} & P_{zy}^{(\alpha)} & P_{zz}^{(\alpha)} \end{bmatrix}. \quad (2)$$

In this equation  $p_x$ ,  $p_y$  and  $p_z$  are the cartesian components of the dipole moment vector.

The  $\text{CF}_4$  polar tensors can be calculated from the values of the experimental intensities and frequencies from

$$P_X = P_Q L^{-1} U B \quad (3)$$

where  $P_Q$  contains the dipole moment derivatives with respect to the normal coordinates,  $\partial \vec{p} / \partial Q_j$  which are proportional to the square roots of the intensities, and  $L^{-1} U B$  corresponds to the transformation of the derivatives from normal to atomic cartesian coordinates obtained from the  $\text{CF}_4$  force field [3]. Internal and symmetry coordinate definitions, molecular orientation in cartesian coordinate space and equilibrium molecular geometry parameters were all taken from [3]. The molecular orientation has  $T_d$  symmetry. For this reason the carbon polar tensor is a diagonal matrix with identical element values and the fluorine tensor also has identical diagonal elements as well as two identical off-diagonal elements.

Principal components projections were made [14] based on polar tensor values for all possible dipole moment derivative sign alternatives for all the complete intensity data sets in Table 1. The quantum chemical calculations were made with the Gaussian 94 [15] program with 6-311G basis sets supplemented by 3-d polarization functions, and by diffuse functions on both carbon and fluorine atoms at the Hartree-Fock, Möller-Plesset 2 and Density Functional Theory levels. For the latter, a B3LYP exchange-correlation functional was used.

## 3. Results and discussion

Polar tensor values for the different intensity sets of Table 1 are presented in Table 2. The corresponding principal component projection is shown in Fig. 1. Four distinct groups of polar tensor results are clearly seen, one for each of the possible derivative sign alternatives. The quantum chemical results are positioned close to the polar tensor results for the  $(- -)$  ( $\partial \vec{p} / \partial Q_3 < 0$ ,  $\partial \vec{p} / \partial Q_4 < 0$ ) set of signs. The first principal component discriminates between the signs of the derivative for the strong  $\nu_3$  band,  $\partial \vec{p} / \partial Q_3$ . This sign affects the values of the diagonal tensor

Table 1  
Absolute infrared intensities of the CF<sub>4</sub> fundamental bands  
(km mol<sup>-1</sup>)

A <sub>3</sub>	A <sub>4</sub>	Reference
1328 ± 37.9	13.48 ± 0.49	[3]
1208.0 ± 54.4	11.81 ± 0.49	[4]
1194.8 ± 7.4	13.78 ± 0.98	[5]
1058.0 ± 100.3	13.28 ± 0.74	[6]
1038.1 ± 103.8	–	[7]
1016.2 ± 101.6	9.35 ± 0.98	[8]
934.3 ± 10.1	12.3 ± 0.25	[9]
922.7	9.35	[10]
840.8 ± 44.0	–	[11]

elements for both the carbon and fluorine atoms. The second principal component discriminates the signs of the derivative for the weak ν<sub>4</sub> band. The off-diagonal tensor element value of the fluorine atom provides the relevant information for determining the  $\partial\bar{p}/\partial Q_4$  sign. For all the experimental results in Table 2, the  $p_{xy}^{(F)}$  values for  $\partial\bar{p}/\partial Q_4 > 0$  range from  $-0.37$  to  $-0.44 e$  whereas variations from  $-0.20$  to  $-0.25 e$  are found for  $\partial\bar{p}/\partial Q_4 < 0$ . The molecular orbital results, all have  $p_{xy}^{(F)}$  values close to  $-0.20 e$  and clearly indicate a negative sign for  $\partial\bar{p}/\partial Q_4$ . As such the  $(- -)$  sign set alternative is the preferred one. This sign choice

is also confirmed by electronegativity models and carbon 1s ionization energy results although emphasis will be focused on attempts to decide which of the experimental intensity results are most likely to be the most accurate. As will be seen, quantum chemical results will also be useful for making this decision.

Electronegativity models [16–18] have been proposed relating polar tensor invariant quantities of the halomethanes with the electronegativities of their substituent atoms. Table 3 contains average Müliken-Jaffe [19] electronegativity values and mean dipole moment derivative values,  $\bar{p}_C = 1/3(P_{xx}^{(C)} + P_{yy}^{(C)} + P_{zz}^{(C)})$ , for the carbon atoms of CH<sub>4</sub> [20–23], CH<sub>3</sub>F [23–26], CH<sub>2</sub>F<sub>2</sub> [26,27] and CHF<sub>3</sub> [22,28,29]. The mean dipole moment derivatives were average values of those calculated using individual intensities of the intensity sum values given in the sixth column of that table. The intensity sums as well as the individual intensities, measured by different research groups, are in very good agreement for all these molecules. Other intensity values for these molecules can be found in the literature. The values in Table 3 were selected from articles by research groups reporting intensity measurements for both the hydrogen and deuterium isotopes in an attempt to determine the most accurate  $\bar{p}_C$  values.

Table 2  
Polar tensor elements for the  $(- +)$  and  $(- -)$  dipole moment derivative sign alternatives for sets of experimental fundamental intensities reported in the literature<sup>a</sup>

$(- +)^b$			$(- -)^b$			Reference
$p_{xx}^{(C)}$	$p_{xx}^{(F)}$	$p_{xy}^{(F)}$	$p_{xx}^{(C)c}$	$p_{xx}^{(F)c}$	$p_{xy}^{(F)}$	
1.752	-0.438	-0.406	1.897	-0.474	-0.210	[6]
1.643	-0.411	-0.370	1.764	-0.441	-0.206	[10]
1.645	-0.411	-0.383	1.784	-0.446	-0.195	[9]
1.882	-0.471	-0.421	2.018	-0.504	-0.237	[4]
1.727	-0.431	-0.384	1.848	-0.462	-0.220	[8]
1.865	-0.466	-0.427	2.012	-0.503	-0.228	[5]
1.976	-0.494	-0.445	2.122	-0.530	-0.247	[3]
Average			2.051	-0.512	-0.237	[3–5]
Standard deviation			0.061	0.015	0.010	
HF/6-311++G(3d, 3p)			2.170	-0.543	-0.195	
B3LYP/6-311++G(3d, 3p)			2.039	-0.510	-0.208	
MP2/6-311++G(3d, 3p)			2.040	-0.510	-0.205	

<sup>a</sup> Units of electrons.

<sup>b</sup>  $(- +)$  Stands for  $\partial\bar{p}/\partial Q_3 < 0$  and  $\partial\bar{p}/\partial Q_4 > 0$  whereas  $(- -)$  corresponds to values obtained with both derivative signs negative.

<sup>c</sup> Since all the diagonal elements are identical  $p_{xx}^{(C)} = \bar{p}_C$  and  $p_{xx}^{(F)} = \bar{p}_F$ .

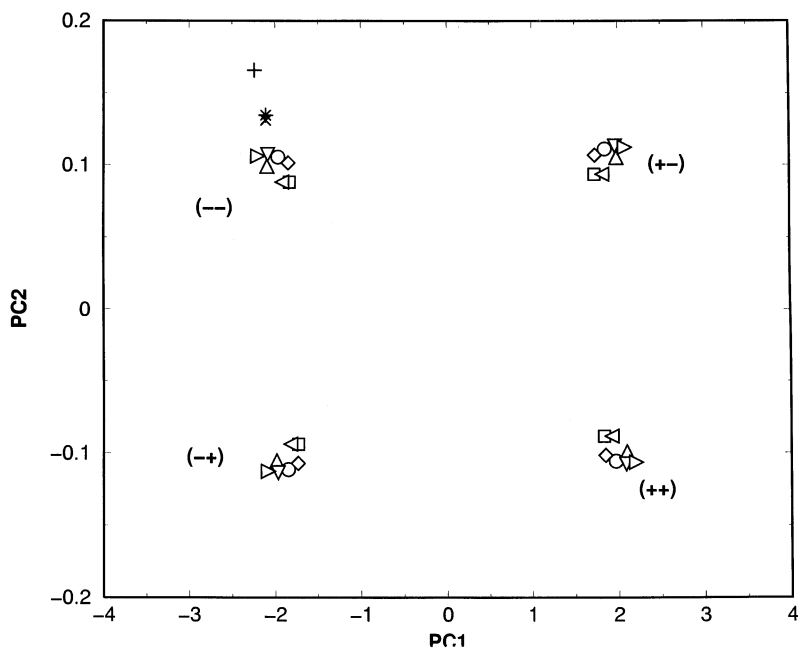


Fig. 1. Principal component score graph of the  $\text{CF}_4$  atomic polar tensor elements obtained from the experimental infrared intensity data for different dipole moment derivative sign attributions:  $\circ$  [6]; [10];  $\diamond$  [9];  $\triangle$  [4]; [8];  $\nabla$  [5];  $\triangleright$  [3]. The theoretical results with 6-311 + + G(3d, 3p) are included for comparison: + HF,  $\times$  B3LYP,  $\star$  MP2. This graph contains almost 100% of the total data variance.

Table 3

Carbon 1s electron ionization energies,  $E_{C,1s}$ , in eV, mean dipole moment derivatives,  $\bar{p}_C$ , in e, electrostatic potentials, V, in eV, average substituent electronegativities,  $\bar{E}_x$ , and fundamental intensity sums,  $\Sigma A_i$ , in  $\text{km mol}^{-1}$  for the fluoromethanes

	$E_{C,1s}$ <sup>a</sup>	$\bar{p}_C$ <sup>a</sup>	V <sup>a</sup>	$\bar{E}_x$ <sup>b</sup>	$\Sigma A_i$	$\bar{p}_C$ <sup>m</sup>	$\Sigma A_i$ <sup>m</sup>
$\text{CH}_4$	290.90	0.014	-0.13	7.17	97.3 <sup>c</sup> , 100.0 <sup>d</sup> , 107.6 <sup>e</sup> , 104.0 <sup>f</sup>	0.002	85.2
$\text{CH}_3\text{F}$	293.60	0.540	-5.78	8.42	192.9 <sup>g</sup> , 194.2 <sup>h</sup>	0.550	195.2
$\text{CH}_2\text{F}_2$	296.36	1.015	-10.93	9.68	393.7 <sup>i</sup> , 413.6 <sup>j</sup>	1.089	444.8
$\text{CHF}_3$	299.10	1.518	-16.41	10.93	749 <sup>k</sup> , 784.3 <sup>l</sup>	1.584	811.4
$\text{CF}_4$	301.85			12.18		2.040	1225.8

<sup>a</sup> [31].

<sup>b</sup> Average electronegativities of substituent atoms.

<sup>c</sup> [20].

<sup>d</sup> [21].

<sup>e</sup> [37].

<sup>f</sup> [22].

<sup>g</sup> [23].

<sup>h</sup> [24].

<sup>i</sup> [26].

<sup>j</sup> [27].

<sup>k</sup> [29].

<sup>l</sup> [28].

<sup>m</sup> MP2/6-311 + + (3d, 3p), B3LYP/6-311 + + (3d, 3p) values are almost identical to these values.

Regression of the  $\bar{p}_C$  values on the average electronegativity values of the substituted atoms,  $\bar{E}_x$ , for all the molecules in Table 3 except CF<sub>4</sub> results in Eq. (4).

$$\bar{p}_C = -2.831 + 0.398 \bar{E}_x \quad (4)$$

Substitution of the fluorine electronegativity value, 12.18, in this equation gives an estimate of 2.016 *e* for the carbon mean dipole moment derivative. This value is in excellent agreement with the 2.018 and 2.012 *e* values obtained from the intensities reported by Roehl et al. [4] and by Schurin [5], respectively, and given in Table 2. Note that  $P_{xx}^{(C)} = \bar{p}_C$  for CF<sub>4</sub>, since all the diagonal elements of the carbon tensor are identical.

Recently our research group has shown that the carbon 1s electron ionization energies,  $E_{C,1s}$ , of a diverse group of molecules including the halomethanes are related to their carbon mean dipole moment derivatives [30,31] via the simple potential model proposed by Siegbahn and collaborators [32].

$$E_{C,1s} = k\bar{p}_C + \sum_{A \neq C} \frac{\bar{p}_A}{R_{AC}} \quad (5)$$

Linear regression of the carbon 1s ionization energies corrected by their neighboring atom electrostatic potential values, *V*, on the  $\bar{p}_C$  values of Table 3 results in the equation

$$E_{C,1s} - V = 290.72 + 16.31 \bar{p}_C \quad (6)$$

Substitution of the carbon 1s ionization energy [31] of 301.85 eV for CF<sub>4</sub> in this equation results in an estimate of 2.059 *e* for  $\bar{p}_C$ . This is in good agreement with the value obtained from the electronegativity model and the  $\bar{p}_C$  values obtained from the intensities of Saeki et al. [3], Roehl et al. [4] and Schurin [5] and given in Table 2.

The *G* intensity sum rule [33,34] provides one more way to obtain another estimate of the more accurate intensity values. The *G* sum rule can be expressed as

$$\sum A_i + \Omega = 3 \left\{ \frac{\chi_C^2}{m_C} + n_F \frac{\chi_F^2}{m_F} + n_H \frac{\chi_H^2}{m_H} \right\}, \quad (7)$$

where  $\chi_C$ ,  $\chi_F$  and  $\chi_H$  are atomic effective charges as defined by King [34], i.e. 1/3 the trace of the matrix product  $P_X^{(z)} P_X^{(z)'}$ ,  $m_C$ ,  $m_F$  and  $m_H$  are atomic

masses and  $n_F$  and  $n_H$  are the number of fluorine and hydrogen atoms in the molecule where  $n_F + n_H = 4$ .  $\Omega$  is a rotational contribution and is zero for CH<sub>4</sub> and CF<sub>4</sub> and 14.62, 6.4 and 6.6 km mol<sup>-1</sup> for CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub> and CHF<sub>3</sub>, respectively [35]. Approximating the atomic effective charges,  $\chi_x$ , by mean dipole moment derivatives,  $\bar{p}_x$ , and recalling that  $\bar{p}_F$  is almost constant and  $\bar{p}_H$  is close to zero for the fluoromethanes one has  $\bar{p}_C = -n_H \bar{p}_F$  and Eq. (8).

$$\sum A_i + \Omega = 3 \left\{ n_F \frac{\bar{p}_F^2}{m_F} + n_F^2 \frac{\bar{p}_F^2}{m_C} \right\} \quad (8)$$

Indeed regression of the intensity sum plus rotational contribution values on the number of fluorine atoms in the CH<sub>4</sub>, CH<sub>3</sub>F, CH<sub>2</sub>F<sub>2</sub> and CHF<sub>3</sub> molecules gives an excellent fit for a quadratic model,

$$\sum A_i + \Omega = 105.28 + 28.83 n_F + 64.25 n_F^2 \quad (9)$$

with a statistically significant *F* ratio value of 609 compared with the tabulated value of 200 at the 95% confidence level. Note that the intercept of 105 is close to the CH<sub>4</sub> intensity sum (average of 102 km mol<sup>-1</sup>, see Table 3) and the  $n_F$  coefficient is smaller than the  $n_F^2$  one since  $m_F > m_C$ . For CF<sub>4</sub>,  $n_F = 4$  and a 1249 km mol<sup>-1</sup> intensity sum is predicted, in between the values obtained by Saeki et al. (1341 km mol<sup>-1</sup>) and those measured by Roehl et al. (1219 km mol<sup>-1</sup>) and Schurin (1209 km mol<sup>-1</sup>).

Quantum chemical results could also provide a criterion to choose the most accurate intensity values. Caution must be used however since even electron correlation level calculations with sophisticated basis sets do not always provide results accurate enough to substitute experimental values. Table 3 contains theoretical estimates of carbon mean dipole moment derivatives (also called GAP charges [36]) and intensity sums calculated from MP2/6-311++G(3d,3p) level wave functions for all the fluoromethanes. The result for CF<sub>4</sub> is 2.04 *e* and is identical to the  $\bar{p}_C$  value obtained using B3LYP/6-311++G(3d,3p). These results are in excellent agreement with the  $\bar{p}_C$  values predicted by the empirical models discussed earlier. The average error of the calculated  $\bar{p}_C$  values for the other

fluorocarbons in Table 3 is  $0.05 e$  which might be applicable to the calculated value for  $\text{CF}_4$  since all these molecules are in the same family. Finally the  $\text{CF}_4$  intensity sum obtained from the quantum chemical calculations is  $1226 \text{ km mol}^{-1}$ . This is also in good agreement with the  $1249 \text{ km mol}^{-1}$  value predicted by the  $G$  sum rule application.

In light of the above evidence it seems reasonable to consider the intensity results of [3–5] as the most accurate measurements of the  $\text{CF}_4$  fundamental band intensities. It is interesting that the recent results of Roehl et. al. [4] determined from absorption measurements are in such good agreement with the intensities calculated from the dispersion measurements of Schurin more than 40 years ago. As stated in [5], dispersion measurements provide accurate fundamental intensity values for intense bands of molecules with light atoms. The lower intensity values in Table 1 for  $A_3$  could stem from experimental difficulties associated with measuring the absorbance of an extremely strong and narrow band with an instrument with insufficient resolving power [4].

#### 4. Conclusions

The averages of the mean dipole moment derivatives,  $\bar{p}_C = 2.051 e$  and  $\bar{p}_F = -0.512 e$  given in Table 2 and obtained from the intensities of [3–5] are taken as best estimates in this work. Their standard deviations provide estimates of errors for these values. It should be remembered that the  $A_3$  intensity values used to calculate the polar tensor elements in this work contain contributions from the  $2\nu_4$  overtone. Golden et al. [6] estimated its intensity as about  $50 \text{ km mol}^{-1}$  or about 4% of our estimated  $A_3$  fundamental intensity. For this reason the average  $\bar{p}_C$  values recommended here might be upper limits to the correct values.

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