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Dipole Moment Derivative Signs, Polar Tensors, and Vibrational Intensities of C<sub>2</sub>F<sub>6</sub>M. M. C. Ferreira, B. B. Neto,<sup>†</sup> and Roy E. Bruns\**Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, 13081 Campinas, SP, Brazil*  
(Received: June 27, 1988; In Final Form: October 26, 1988)

The atomic polar tensors of hexafluoroethane calculated from the experimental vibrational intensities measured previously are reported. Dipole moment derivative signs were determined using STO-3G and 4-31G molecular orbital wave functions. The fluorine polar tensor invariants,  $\bar{p}$ ,  $\beta$ , and  $\chi$ , are found to be significantly smaller than those for fluorine of the substituted fluoromethanes. Transference of fluorine polar tensor elements from CH<sub>3</sub>F and CF<sub>4</sub> to C<sub>2</sub>F<sub>6</sub> results in reasonably accurate estimates for the C<sub>2</sub>F<sub>6</sub> vibrational intensities with the exception of the one for the  $\nu_7$  E symmetry CF stretching mode, which is calculated to be much too large.

## Introduction

Thirty years ago the gas-phase fundamental vibrational intensities of hexafluoroethane, C<sub>2</sub>F<sub>6</sub>, were measured by Crawford and co-workers.<sup>1</sup> The intensity data were transformed into values of dipole moment derivatives with respect to the hexafluoroethane symmetry coordinates  $\partial\bar{p}/\partial S_j$  and into the corresponding bond moment parameters. Signs for the dipole moment derivatives with respect to the normal coordinates  $\partial\bar{p}/\partial Q_i$  were attributed on the basis of bond moment criteria, although these research workers carefully considered the limitations of this procedure.

In this work two objectives are pursued. First, the dipole derivative signs are determined for C<sub>2</sub>F<sub>6</sub> on the basis of ab initio molecular orbital calculations using STO-3G and 4-31G basis sets. These determinations are particularly important because the isotopic invariance criterion can not be used in this case. Second, polar tensor values are calculated for the preferred set of signs of the  $\partial\bar{p}/\partial Q_i$ . Since complete polar tensor data are available only for a small number of molecules and vibrational intensity parameters are sensitive probes of the molecular electronic environments, an increase in this data base is naturally welcome. A knowledge of the C<sub>2</sub>F<sub>6</sub> polar tensor values permits comparisons with tensors for similar molecules, especially those of the fluorinated methane family. These comparisons can be useful in establishing criteria for the selection of reference polar tensors to be employed in transference tests for the prediction of vibrational intensities.

## Calculations

The atom numbering scheme and molecular Cartesian coordinate system for C<sub>2</sub>F<sub>6</sub> are displayed in Figure 1. Carbon-carbon and carbon-fluorine distances of 1.54 and 1.36 Å<sup>2</sup> and the normal coordinates of ref 1a, calculated with the force field of Shimanouchi,<sup>3</sup> were used. Fundamental gas-phase vibrational intensity values were taken from ref 1b. The polar tensors were calculated by use of the equation<sup>4</sup>

$$P_X = P_Q L^{-1} U B + P_\rho \beta$$

where the matrix product  $L^{-1} U B$  transforms the  $\partial\bar{p}/\partial Q_i$  values into derivatives with respect to Cartesian coordinate displacements, which are the elements of the vibrational part of the molecular polar tensor. Since C<sub>2</sub>F<sub>6</sub> does not have a permanent dipole moment,  $P_\rho$  is a null matrix and the second term in this equation (that is, the rotational part of the polar tensor) does not contribute to the  $P_X$  values.

Theoretical values of the polar tensor elements were calculated by using the GAUSSIAN 86 computer program of Pople and co-workers.<sup>5</sup> The experimental bond distances given above were employed in these calculations to save computer time. Our experience with molecular orbital calculations on the fluorinated methane family indicates that almost identical results for the polar tensor elements are obtained by using experimental or energy

TABLE I: Comparison of Experimental and Theoretical Values for the Carbon and Fluorine Polar Tensor Elements Relative to the Molecular Cartesian Coordinate System of Figure 1<sup>a</sup>

signs of $\partial\bar{p}/\partial Q_i$	A <sub>2u</sub>				error <sup>b</sup>	
	$p_{zz}^{(F_1)}$	$p_{xx}^{(F_1)}$	$p_{yy}^{(F_1)}$	$p_{zz}^{(C_1)}$	STO-3G	4-31G
(++) <sup>c</sup>	-0.387	+0.113	+1.162		0.131	0.183
(+-)	-0.263	+0.692	+0.778		0.413	0.539
STO-3G <sup>e</sup>	-0.325	0.006	0.972			
4-31G	-0.491	0.100	1.462			
signs of $\partial\bar{p}/\partial Q_i$	E <sub>u</sub>				error <sup>b</sup>	
	$p_{xx}^{(F_1)}$	$p_{yy}^{(F_1)}$	$p_{zz}^{(F_1)}$	$p_{xx}^{(C_1)} = p_{yy}^{(C_1)}$	STO-3G	4-31G
(---) <sup>d</sup>	-0.659	-0.253	+0.483	+1.367	0.344	0.211
(-++)	-0.879	-0.007	+0.264	+1.328	0.378	0.256
(-+-)	-0.847	-0.009	+0.494	+1.284	0.397	0.306
(--+)	-0.690	-0.251	+0.253	+1.411	0.322	0.128
STO-3G <sup>e</sup>	-0.335	-0.258	+0.100	+0.896		
4-31G	-0.698	-0.377	+0.169	+1.618		

<sup>a</sup> Atomic units, 1e = 4.803 D Å<sup>-1</sup>;  $p_{\sigma\sigma}^{(a)} = \partial p_\sigma / \partial \nu_\sigma$ . <sup>b</sup> Root-mean-square errors are calculated by use of the expression  $[(1/N) \sum_i (x_{i,\text{expt}} - x_{i,\text{MO}})^2]^{1/2}$ , where the  $x$  values correspond to experimental and MO results and the sum is taken over all the polar tensor elements for the sign alternative.  $N$  is equal to the total number of nonequivalent polar tensor elements for a given symmetry species. <sup>c</sup> The signs of  $\partial\bar{p}/\partial Q_5$  and  $\partial\bar{p}/\partial Q_6$  are given in this order. <sup>d</sup> The signs of  $\partial\bar{p}/\partial Q_7$ ,  $\partial\bar{p}/\partial Q_8$ , and  $\partial\bar{p}/\partial Q_9$  are given in this order. <sup>e</sup> Polar tensor elements calculated from STO-3G and 4-31G basis set wave functions.

minimized geometries for STO-3G and 4-31G basis set calculations. The calculations were carried out on the VAX 11/750 computer of the Departamento de Química Fundamental da Universidade Federal de Pernambuco.

## Sign Determination

The absence of rotational corrections in the polar tensor of C<sub>2</sub>F<sub>6</sub> implies a given sign choice for the  $\partial\bar{p}/\partial Q_i$ 's and its reverse yield polar tensor elements identical in absolute values but with opposite

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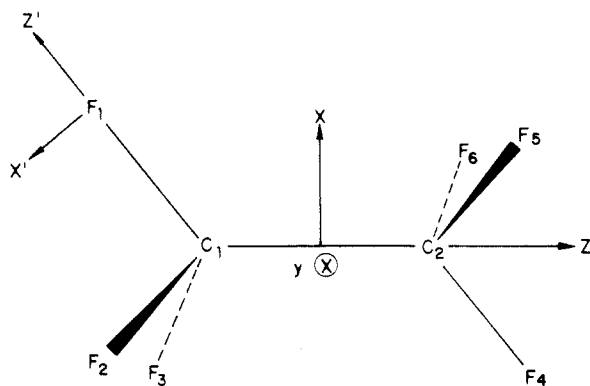
(2)  $R_{CF}$  taken from ref 1a;  $R_{CC}$  assumed equal to  $R_{CC}$  of CF<sub>3</sub>CCl<sub>3</sub>, given in: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

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**Figure 1.** Atom numbering scheme, molecular Cartesian coordinate system, and local fluorine Cartesian coordinate system for hexafluoroethane.

signs. Thus the  $(++)$  and  $(+-)$  sign choices for the  $A_{2u}$  symmetry species, for example, give for  $\partial p_z/\partial z_{C_1}$  the values  $1.162e$  and  $0.778e$ , respectively, whereas their negative counterparts,  $(--)$  and  $(-+)$ , yield  $-1.162e$  and  $-0.778e$ . These latter values indicate a very negative carbon and may be assumed as highly unlikely in view of the strongly electronegative environment surrounding the carbon atoms in  $C_2F_6$ . The corresponding sign choices may then be discarded at the outset, leaving for this symmetry species the decision restricted to the  $(++)$  and  $(+-)$  sets. Similar considerations for the  $E_u$  species allow us to cut the sign choices down to four possibilities.

A comparison of experimental and theoretical values for the carbon and fluorine polar tensor elements relative to the molecular Cartesian coordinate system of Figure 1 is presented in Table I for the remaining sign combinations of the  $\partial \bar{p}/\partial Q_i$ 's of  $C_2F_6$ . For the  $A_{2u}$  symmetry species the  $(++)$  and  $(+-)$  sign choices lead to polar tensor element values with the same signs. The molecular orbital (MO) results using either the STO-3G or the 4-31G basis set predict signs that are identical with those of both experimental alternatives. However, the magnitudes of the polar tensor elements obtained from the MO calculations are in much better agreement with the values corresponding to the  $(++)$  sign choice for the  $\partial \bar{p}/\partial Q_i$ 's. For both the STO-3G and the 4-31G basis set calculations the root-mean-square error for this sign choice (Table I) is about one-third of the error calculated for the  $(+-)$  set. The most conspicuous discrepancy with the theoretical results occurs for the  $p_{zx}^{(F_1)}$  value of the latter set. This value is more than twice the value of the corresponding  $p_{zz}^{(F_1)}$  element, although the theoretical calculations predict an absolute value of  $p_{zz}^{(F_1)}$  which is much larger than the off-diagonal value. This result is in agreement with the relative values of these two elements in the  $(++)$  set. Hence the  $(++)$  signs are selected as the preferred ones for the  $A_{2u}$  symmetry species.

For the  $E_u$  symmetry species the MO calculations predict signs for the polar tensor elements which are in exact agreement with those for all four experimental alternative sign sets of the  $\partial \bar{p}/\partial Q_i$ 's. The smallest rms errors for both the STO-3G and the 4-31G MO results occur for the  $(--+)$  sign set, although the errors for the STO-3G theoretical values are very similar for all the experimental possibilities. The alternative  $(-++)$  and  $(-+-)$  sets appear most unlikely to be correct, since their experimental values for  $p_{yy}^{(F_1)}$  are almost zero, whereas both basis set wave functions predict large negative values for this element. The exclusion of the  $(---)$  set as the correct one can be more easily explained by examining the theoretical and experimental values in a rotated local coordinate system where the  $z$  axis is colinear with the CF bond, as in the primed system of Figure 1. These values for the  $(---)$  and  $(--+)$  alternatives are presented in Table II along with the theoretical values. The contribution from the  $A_{2u}$  species was assumed to come from the  $(++)$  sign choice. The  $(---)$  sign choice corresponds to a value of  $-0.331e$  for the  $p_{xx}^{(F_1)}$  element. Its absolute value is larger than the ones for the  $p_{xx}^{(F_1)}$  and  $p_{yy}^{(F_1)}$  elements. This result contrasts with the ones for both the STO-3G and the 4-31G calculations, which predict that this off-diagonal element has an

**TABLE II: Comparison of Experimental and Theoretical Values for the Fluorine Polar Tensor Elements Relative to the Local Fluorine Atom Cartesian Coordinate System of Figure 1<sup>a</sup>**

signs of $\partial \bar{p}/\partial Q_i$	$p_{xx}$	$p_{yy}$	$p_{zz}$	$p_{xz}$	$p_{xy}$
$(++)(-++)^b$	-0.230	-0.253	-0.816	+0.039	-0.331
$(++)(-+-)$	-0.306	-0.251	-0.771	+0.023	-0.117
STO-3G <sup>c</sup>	-0.293	-0.258	-0.367	+0.009	-0.085
4-31G	-0.429	-0.335	-0.760	-0.005	-0.074

<sup>a</sup> Atomic units,  $1e = 4.803 \text{ D } \text{\AA}^{-1}$ .  $P_{\alpha\beta} = \partial p_{\alpha}/\partial \nu_{F_1}$ . <sup>b</sup> See Table I for the sign definitions. <sup>c</sup> Polar tensor elements calculated from STO-3G and 4-31G basis set wave functions.

**TABLE III: Comparison between Experimental Vibrational Intensities and Those Calculated Using *ab Initio* Molecular Orbital Results and Fluorine Polar Tensors Transferred from  $CH_3F$  and  $CF_4$ <sup>a</sup>**

class	$\nu_i, \text{cm}^{-1}$	vibrational intensity			
		exptl	4-31G <sup>b</sup>	from $CH_3F$ <sup>c</sup>	from $CF_4$ <sup>d</sup>
$A_{2u}$	$\nu_5 = 1116$	237	367	208	243
	$\nu_6 = 714$	32.7	62.8	12	13
E	$\nu_7 = 1250$	820	998	1140	1370
	$\nu_8 = 522$	7.9	29.4	7.7	8
	$\nu_9 = 219$	4.3	17.6	18	20.4
rms error <sup>e</sup>			100.1	144.1	246.2
int sum		1101.9	1474.8	1385.7	1654.4

<sup>a</sup> Intensity units are  $\text{km mol}^{-1}$ . <sup>b</sup> Intensity values calculated from polar tensor elements obtained from 4-31G basis set wave functions.

<sup>c</sup> Intensity values calculated by transference of the fluorine polar tensor from  $CH_3F$ . The carbon tensor of  $C_2F_6$  is determined by the conservation of charge relation,  $\sum_{\alpha} P_{\alpha}^{(C)} = 0$ . <sup>d</sup> Intensity values calculated by transference of the fluorine polar tensor from  $CF_4$ . <sup>e</sup> The rms error is calculated as described in footnote b of Table I.

absolute magnitude much smaller than the ones for the diagonal elements. On the other hand, the  $(--+)$  set has off-diagonal elements with absolute magnitudes much smaller than those for the diagonal elements, a result that can be expected for polar tensor elements in a local coordinate system where the Cartesian system is aligned with the chemical bond containing the atom under investigation.

The  $(++)(-++)$  sign combination preferred here is in agreement with the signs chosen by Crawford and co-workers<sup>1</sup> based on bond moment hypothesis arguments. In fact, the large  $p_{xx}^{(F_1)}$  value for the  $(---)$  sign combination can be traced to bending derivatives which predict opposite signs for the CF bond moment. Although both the STO-3G and 4-31G calculated derivatives are in good agreement with the  $(++)(-++)$  experimental polar tensor element values for the  $A_{2u}$  symmetry species, the 4-31G basis set calculation for the  $E_u$  polar tensor elements is clearly superior to the one using the STO-3G basis.

### Comparison of $C_2F_6$ and Fluorinated Methanes

One of the main reasons we decided to determine the hexafluoroethane polar tensors was to test transference methods for calculating vibrational intensities. If it is found that the carbon and fluorine polar tensors of  $C_2F_6$  are similar to those of the fluorinated methanes,<sup>6-11</sup> then transference of tensors from these molecules should lead to accurate intensity predictions for  $C_2F_6$ . In Table III the experimental  $C_2F_6$  intensities are compared with values predicted by transferring the fluorine polar tensors of  $CH_3F$ <sup>6</sup> and  $CF_4$ <sup>11</sup> to this molecule. These molecules have been chosen

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TABLE IV: Comparison of Experimental Values of Polar Tensor Invariant Values for Hexafluoroethane with Those of the Fluorinated Methanes<sup>a</sup>

molecule	$\bar{\rho}^{(F)}$	$\chi^{(F)}$	$\beta^{(F)}$
CH <sub>3</sub> F <sup>b</sup>	-0.481	0.578	0.679
CH <sub>3</sub> F <sup>c</sup>	-0.474	0.555	0.610
CH <sub>2</sub> F <sub>2</sub> <sup>d</sup>	-0.423	0.565	0.793
CH <sub>2</sub> F <sub>2</sub> <sup>e</sup>	-0.500	0.591	0.668
CHF <sub>3</sub> <sup>f</sup>	-0.524	0.605	0.642
CF <sub>4</sub> <sup>g</sup>	-0.531	0.631	0.723
average	-0.489	0.588	0.686
SD <sup>h</sup>	±0.039	±0.028	±0.065
C <sub>2</sub> F <sub>6</sub>	-0.443	0.505	0.515
$\Delta^i$	0.046	-0.083	-0.171
4-31G <sup>j</sup>	-0.522	0.550	0.371

<sup>a</sup> Atomic units, 1e = 4.803 D Å<sup>-1</sup>. <sup>b</sup> Reference 6. <sup>c</sup> Reference 7. <sup>d</sup> Reference 8. <sup>e</sup> Reference 9. <sup>f</sup> Reference 10. <sup>g</sup> Reference 11. <sup>h</sup> The standard deviations are calculated by use of the expression  $[\sum_i (x_i - \bar{x})^2]^{1/2}/(N-1)^{1/2}$ , where the sum is taken over the first six entries in each column.  $N = 6$ . <sup>i</sup> Differences between the invariant quantity value for C<sub>2</sub>F<sub>6</sub> and the average value for the fluorinated methanes. <sup>j</sup> Polar tensor invariant values calculated by use of a 4-31G basis set.

because the fluorine polar tensor in methyl fluoride has already been used in a transference procedure to other fluorine-containing molecules<sup>8</sup> and, on the other hand, the electronic environment in CF<sub>4</sub> is expected to be similar to the one in hexafluoroethane. Of course appropriate rotations of the Cartesian frames were performed to ensure consistency of the reference atomic polar tensor values with the molecular Cartesian coordinate system in Figure 1. The carbon polar tensor was derived from the null condition<sup>4</sup>

$$\sum_{\alpha} \mathbf{P}_X^{(\alpha)} = \mathbf{0}$$

Intensity values calculated from the 4-31G polar tensors are also included in Table III. The intensities calculated by use of the transferred polar tensors have rms errors that are larger than the error for the 4-31G intensities. The intensities calculated for the weak bands,  $\nu_6$ ,  $\nu_8$ , and  $\nu_9$ , are almost identical whether the fluorine tensor is taken from CH<sub>3</sub>F or from CF<sub>4</sub>. On the other hand, the stronger bands,  $\nu_5$  and  $\nu_7$ , have intensity values that appear to be very sensitive to the origin of the fluorine tensor. Although the transference predictions for the  $\nu_5$  intensity value are remarkably good, the  $\nu_7$  experimental intensity of 820 km mol<sup>-1</sup> is much lower than the values of 1140 and 1370 obtained from the transference calculations. Also, the 4-31G predicted intensity for this band exceeds the experimental value by more than 20%.

The C<sub>2</sub>F<sub>6</sub> and fluorinated methane atomic polar tensor values can not be compared directly because the orientations of the molecules relative to their Cartesian coordinate systems are usually different. Although one can always define for each molecule a local atomic Cartesian system for which the  $z$  axis is aligned with the CF bond, this condition is not sufficient to fix the relative orientation of the rest of the molecule. For this reason direct comparisons of atomic polar tensor values cannot be made to explain the large errors in the calculated values of the  $\nu_7$  intensity in Table I.

The obvious procedure in such cases is to make a comparison between the polar tensor invariant quantities<sup>12</sup> rather than between polar tensor element values. In Table IV values of the mean dipole derivative  $\bar{\rho}$ , the effective charge  $\chi$ , and the square root of the anisotropy  $\beta$  are listed for C<sub>2</sub>F<sub>6</sub> and the fluorinated methanes. Average and standard deviation values are included in this table for the fluorinated methanes to facilitate the comparison with the C<sub>2</sub>F<sub>6</sub> values.

The rotationally invariant quantities have values that do not vary greatly for the fluorinated methanes. The standard deviation for each invariant is less than 10% of its average value. On the

other hand, the absolute values of the invariant quantities of C<sub>2</sub>F<sub>6</sub> are all substantially smaller than the average values for the fluorinated methanes. In fact, the C<sub>2</sub>F<sub>6</sub> values are smaller in absolute value than almost all the other corresponding values in Table IV, the only exception being the  $\bar{\rho}$  value of the first entry for CH<sub>2</sub>F<sub>2</sub>. The largest discrepancies occur for the square root of the anisotropy: the C<sub>2</sub>F<sub>6</sub> value of -0.515 differs from the average value by 0.17e. This difference is almost three times the standard deviation of  $\beta$  for the fluorinated methane values in Table IV. As for the fluorine effective charge, the value for C<sub>2</sub>F<sub>6</sub> is 0.083e smaller than the average of this invariant quantity for the fluorinated methanes. This difference is significantly larger than the standard deviation of ±0.028e for  $\chi$  of the fluorinated methanes. Since the fundamental intensity sum of C<sub>2</sub>F<sub>6</sub> is proportional to the sum of the squares of its carbon and fluorine effective charges, as expressed by Crawford's  $G$ -sum rule,<sup>13</sup> it is not surprising that the C<sub>2</sub>F<sub>6</sub> intensity sums predicted by transference of fluorine polar tensors from CH<sub>3</sub>F and CF<sub>4</sub> are much larger than the experimental one. This overestimation is mostly due to the very large predicted values of the  $\nu_7$  band, which accounts for about 75% of the total C<sub>2</sub>F<sub>6</sub> intensity.

A recent investigation of the experimental carbon polar tensors of a set of nine substituted methanes revealed a strikingly good empirical relation between the carbon mean dipole derivatives and the carbon partial charges in these molecules.<sup>14</sup> The resulting regression equation

$$\bar{\rho}^{(C)} = 0.429 + 7.218\delta_C$$

where  $\delta_C$  stands for the carbon partial charge,<sup>15</sup> was employed to calculate, with remarkable accuracy, the electronegativity of the carbon atom in ethane.

Symmetry requires that  $\bar{\rho}^{(C)} = -3\bar{\rho}^{(F)}$  in hexafluoroethane. Thus, with the value of  $\bar{\rho}^{(F)}$  in Table IV, we obtain for  $\bar{\rho}^{(C)}$  the experimental value of 1.329e. The carbon partial charge in C<sub>2</sub>F<sub>6</sub>, as given by the principle of electronegativity equalization,<sup>15,16</sup> is  $\delta_C = 0.220e$ . Assuming, as it was done for ethane, that C<sub>2</sub>F<sub>6</sub> obeys the regression equation above, we predict for the carbon mean dipole derivative a value of 2.017e. This is about 50% higher than the corresponding experimental value and almost 0.50e higher than the 4-31G calculated values (1.566e). It may be, contrary to the behavior observed for ethane, that C<sub>2</sub>F<sub>6</sub> does not behave like a substituted methane and in this case the predictions based on the regression equation above are meaningless for this molecule. An analogous argument holds for the overestimated C<sub>2</sub>F<sub>6</sub> intensity values in Table III obtained by the transferability tests if the fluorine polar tensor in C<sub>2</sub>F<sub>6</sub> is not similar to those of the fluorinated methanes. In a review Person<sup>17</sup> has shown that although transferability of the fluorine polar tensor in the fluoromethanes is surprisingly successful, the elements of this tensor may be different for the CF<sub>3</sub>X (X = Cl, Br, I, and CF<sub>3</sub>) molecules since the polarizabilities of the X entities are very different from that of the hydrogen atom. Golden, Horner, and Overend<sup>18</sup> have shown that the parallel CF stretching intensity of CF<sub>3</sub>Cl is badly underpredicted by transference of the fluorine polar tensor from CH<sub>3</sub>F whereas the perpendicular one is accurately calculated. Certainly more research on transferability calculations is necessary before criteria for successful intensity calculations are established.

**Acknowledgment.** We express our gratitude to FAPESP, CNPq, and FINEP for partial financial support.

**Registry No.** C<sub>2</sub>F<sub>6</sub>, 76-16-4.

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