

## Theoretical Analysis of Dipole Moment Derivatives in Fluoromethanes. (III) CH<sub>3</sub>F and CF<sub>4</sub>

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Received February 23, 1987

The results of an ab initio (6-31G) molecular orbital calculations of the dipole moment derivatives and gas phase IR intensities in CH<sub>3</sub>F and CF<sub>4</sub> are reported. The results are compared with corresponding values obtained from a CNDO calculation. We have also analyzed the theoretical polar tensors into the charge, charge flux, and overlap contributions. The effective term charges of hydrogen atom appeared to be transferable among the fluoromethane molecules.

### Introduction

One of the fundamental challenges facing a vibrational molecular spectroscopist is to predict the spectrum of a new molecule from a knowledge of the spectra of a set of similar model compounds. A great deal of empirical experience exist<sup>1</sup> to help us predict semi-quantitatively the frequencies of characteristic fundamental modes, and we understand how to carry out normal coordinate analyses to predict, in principle, the normal frequencies for all the fundamental modes of the new molecule using force constants transferred from model compounds. However, the prediction of the intensities is much more challenging.

This challenge has been the basis for many of the intensity studies made in the past. One of the earliest ideas was the "bond moment hypothesis" which was very soon found to be too naive<sup>2</sup>, followed by various "modified bond moment hypotheses"<sup>3</sup>, which were not widely accepted. The most successful models for predicting intensities of new molecules from intensity parameters transferred from simple model compounds were the "electrooptical parameter" model<sup>4</sup> and the "atomic polar tensor" (APT) concept<sup>5</sup>. Successful predictions of vibrational band intensities for new molecules have already been made and the possibilities for future successful extensions of these methods seem very promising, indeed<sup>6</sup>.

Newton et al.<sup>7</sup> used the APTs for H and F atoms of CH<sub>3</sub>F to predict the intensities of the fundamental vibrations of CF<sub>4</sub>, CHF<sub>3</sub>, and CH<sub>2</sub>F<sub>2</sub>. The predicted values agreed with the experimental values within a factor of 2, and often were much better. However, there is no obvious a priori reason that the APTs of H and F atoms should be transferable among the fluoromethanes. In order to rationalize these observations, and to discover their relevance to the interpretation and prediction of vibrational line strengths, the dependence of polar tensors upon molecular structure must be examined in detail. To this end, we have performed theoretical analyses on the dipole moment derivatives and the infrared intensities of the fundamental vibrations of fluoromethanes. In earlier papers in this series we have reviewed the APTs of CHF<sub>3</sub><sup>8</sup> and CH<sub>2</sub>F<sub>2</sub><sup>9</sup>. As a continuation, the results on CH<sub>3</sub>F and CF<sub>4</sub> are presented here.

### Calculations

The positions of the CH<sub>3</sub>F and CF<sub>4</sub> molecules in the Cartesian axis system are depicted in Fig. 1(a) and 1(b),

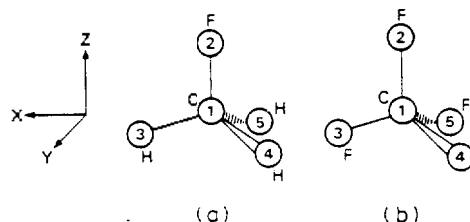


Figure 1. Definition of the Cartesian coordinate systems of CH<sub>3</sub>F (a) and CF<sub>4</sub> (b).

respectively. The dipole moment vector points from the center of negative charge to the center of positive charge. The sign of a dipole moment component is positive when the component vector points in the positive axis direction. The calculations are performed at the experimental geometry<sup>10-11</sup>. To obtain the elements of the APTs the numerical difference approximation  $\partial P/\partial \sigma \approx \Delta P/\Delta \sigma$  employed, with  $\Delta \sigma = 0.02$  Å. We have used two distinct quantum mechanical programs, one based on the CNDO method<sup>12</sup>, the other on the ab initio method. The ab initio calculations were carried out with the GAUSSIAN-70 program<sup>13</sup> using the 6-31G basis set.

The detailed description of how the fundamental intensities are derived from the atomic polar tensors (or vice versa) is given elsewhere<sup>14</sup>. Briefly, once the APTs are given in the correct molecular coordinate frames, the  $P_Q$  matrix composed of the Cartesian components of the dipole moment derivatives with respect to the normal coordinates is obtained by

$$P_Q = P_x A L, \quad (1)$$

Where  $P_x$  is the  $3 \times 3n$  ( $n$  = the number of atoms) matrix composed of the  $n$  juxtaposed  $3 \times 3$  APTs,  $A$  is the symmetrized  $A$  matrix (the inverse of the Wilson's  $B$  matrix including the six Eckart conditions), and  $L$  is the symmetrized normal coordinate transformation matrix<sup>5</sup>. The absolute intensity for the  $i$ -th fundamental band ( $A_i$ ) is related to the  $P_Q$  elements,  $\partial P/\partial Q_i$ , by<sup>15</sup>,

$$A_i = (974.8644) (\partial P/\partial Q_i)^2 \text{ (km} \cdot \text{mole}^{-1}) \quad (2)$$

if  $\partial P/\partial Q_i$  is in  $\text{eu}^{-1/2}$  ( $u$  designates atomic mass unit and  $e$  the charge on the electron:  $1e = 1.602 \times 10^{-19}\text{C}$ ).

The equilibrium structural data and the definition of the internal and symmetry coordinates are listed in Table 1. The normal coordinates calculated using the force fields reported in ref. (10) and ref. (16) are given in Table 2.

**Table 1. Structural Data and Definition of Internal and Symmetry Coordinates for CH<sub>3</sub>F and CF<sub>4</sub>**

Masses(u) <sup>a</sup> : m <sub>C</sub> = 12.0, m <sub>H</sub> = 1.007825, m <sub>F</sub> = 2.014102,	
m <sub>F</sub> = 18.998405	
Structure : CH <sub>3</sub> F <sup>b</sup> R <sub>CH</sub> = 0.1095 nm, R <sub>CF</sub> = 0.1382 nm,	
HCH = 110°30'	
CF <sub>4</sub> <sup>c</sup> R <sub>CF</sub> = 0.1320 nm	
Internal coordinates <sup>d</sup> :	R <sub>1</sub> = δr <sub>12</sub> R <sub>6</sub> = δα <sub>315</sub>
	R <sub>2</sub> = δr <sub>13</sub> R <sub>7</sub> = δα <sub>314</sub>
	R <sub>3</sub> = δr <sub>14</sub> R <sub>8</sub> = δα <sub>213</sub>
	R <sub>4</sub> = δr <sub>15</sub> R <sub>9</sub> = δα <sub>214</sub>
	R <sub>5</sub> = δα <sub>415</sub> R <sub>10</sub> = δα <sub>215</sub>
Symmetry coordinates <sup>e</sup> :	
CH <sub>3</sub> F(C <sub>3v</sub> )	
A <sub>1</sub>	S <sub>1</sub> = (1/√3)(R <sub>2</sub> + R <sub>3</sub> + R <sub>4</sub> )
	S <sub>2</sub> = a(R <sub>5</sub> + R <sub>6</sub> + R <sub>7</sub> ) - b(R <sub>8</sub> + R <sub>9</sub> + R <sub>10</sub> )
	S <sub>3</sub> = R <sub>1</sub>
	S <sub>4</sub> = 1/√6(2R <sub>2</sub> - R <sub>3</sub> - R <sub>4</sub> )
E <sub>x</sub>	S <sub>5</sub> = 1/√6(2R <sub>5</sub> - R <sub>6</sub> - R <sub>7</sub> )
	S <sub>6</sub> = 1/√6(2R <sub>8</sub> - R <sub>9</sub> - R <sub>10</sub> )
	S <sub>7</sub> = 1/√2(R <sub>3</sub> - R <sub>4</sub> )
E <sub>y</sub>	S <sub>8</sub> = 1/√2(R <sub>6</sub> - R <sub>7</sub> )
	S <sub>9</sub> = 1/√2(R <sub>9</sub> - R <sub>10</sub> )
A <sub>1</sub>	S <sub>red</sub> = b(R <sub>5</sub> + R <sub>6</sub> + R <sub>7</sub> ) + a(R <sub>8</sub> + R <sub>9</sub> + R <sub>10</sub> )
	a = 0.399889, b = 0.416440
CF <sub>4</sub> (T <sub>d</sub> )	
A <sub>1</sub>	S <sub>1</sub> = 1/2(R <sub>1</sub> + R <sub>2</sub> + R <sub>3</sub> + R <sub>4</sub> )
E <sub>x</sub>	S <sub>2</sub> = 1/√2(2R <sub>5</sub> - R <sub>6</sub> - R <sub>7</sub> + 2R <sub>8</sub> - R <sub>9</sub> - R <sub>10</sub> )
E <sub>y</sub>	S <sub>3</sub> = 1/2(R <sub>6</sub> - R <sub>7</sub> + R <sub>9</sub> - R <sub>10</sub> )
	S <sub>4</sub> = 1/√6(2R <sub>2</sub> - R <sub>3</sub> - R <sub>4</sub> )
F <sub>x</sub>	S <sub>5</sub> = 1/√2(2R <sub>5</sub> - R <sub>6</sub> - R <sub>7</sub> - 2R <sub>8</sub> + R <sub>9</sub> + R <sub>10</sub> )
	S <sub>6</sub> = 1/√2(R <sub>3</sub> - R <sub>4</sub> )
F <sub>y</sub>	S <sub>7</sub> = 1/2(R <sub>6</sub> - R <sub>7</sub> - R <sub>9</sub> + R <sub>10</sub> )
	S <sub>8</sub> = 1/√2(3R <sub>1</sub> - R <sub>2</sub> - R <sub>3</sub> - R <sub>4</sub> )
F <sub>z</sub>	S <sub>9</sub> = 1/√6(R <sub>5</sub> + R <sub>6</sub> + R <sub>7</sub> - R <sub>8</sub> - R <sub>9</sub> - R <sub>10</sub> )
A <sub>1</sub>	S <sub>red</sub> = 1/√6(R <sub>5</sub> + R <sub>6</sub> + R <sub>7</sub> + R <sub>8</sub> + R <sub>9</sub> + R <sub>10</sub> )

<sup>a</sup>Ref. (18), <sup>b</sup>Ref. (10), <sup>c</sup>Ref. (11), <sup>d</sup>The subscripts refer to the atoms shown in Figure 1; r<sub>ij</sub> and α<sub>ijk</sub> represent, respectively, the appropriate bond-length and bond-angle. <sup>e</sup>S<sub>red</sub> is a redundant coordinate.

The calculated atomic polar tensor elements are also analyzed in terms of the quantum mechanical charge, charge flux and overlap (CCFO) model. Details of the charge-charge flux-overlap electronic contributions to the dipole derivatives have been described previously<sup>17</sup>. Briefly, the APT of an atom (p<sub>α</sub><sup>α</sup>) can be identified with three contributing terms.

$$P_{\alpha}^{\alpha} = \zeta_{\alpha} I + \sum_{\beta} (\nabla_{\alpha} \zeta_{\beta}) R_{\beta} - \sum_{\beta} \nabla_{\alpha} \Phi_{\beta\beta}(R), \quad (3)$$

where ζ is Mulliken's net atomic charge and

$$\nabla_{\alpha} \Phi_{\beta\beta} \equiv \sum_{i, j} \langle \psi_i(r_{\alpha}) | \nabla_{\alpha} | \psi_j(r_{\beta}) \rangle \nabla_{\alpha} N_{ij}^{\beta} \quad (4)$$

In eqn. (4), r<sub>β</sub> ≡ r - R<sub>β</sub> denotes a position vector relative to nucleus β and N<sub>ij</sub><sup>β</sup> denotes the structure dependent expansion coefficient when the electron density function is represented as a superposition of terms involving products of

**Table 2. Harmonic force field and normal coordinates of CH<sub>3</sub>F and CF<sub>4</sub>**

Harmonic force constants (Nm <sup>-1</sup> ):					
CH <sub>3</sub> F <sup>a</sup>	A <sub>1</sub>	K <sub>11</sub> = 524.8, K <sub>23</sub> = -66.8, K <sub>33</sub> = 569.2	K <sub>12</sub> = -22.2, K <sub>33</sub> = 569.2	K <sub>22</sub> = 75.7, K <sub>13</sub> = 38.5,	
	E <sub>x</sub> <sup>d</sup>	K <sub>44</sub> = 527.6, K <sub>56</sub> = -6.6, K <sub>66</sub> = 90.6	K <sub>45</sub> = -13.2, K <sub>55</sub> = 57.8, K <sub>46</sub> = 17.6,		
CF <sub>4</sub> <sup>b</sup>	F <sub>x</sub> <sup>d</sup>	K <sub>44</sub> = 622.0, K <sub>45</sub> = 110.9, K <sub>55</sub> = 176.0			
Normal coordinates (u <sup>-1/2</sup> ) <sup>c</sup> :					
	CH <sub>3</sub> F	Q <sub>1</sub>	Q <sub>2</sub>	Q <sub>3</sub>	
A <sub>1</sub>	S <sub>1</sub>	1.00478	0.08716	-0.00521	
	S <sub>2</sub>	-0.21241	1.37009	0.17050	
	S <sub>3</sub>	-0.04999	0.07428	0.35770	
		Q <sub>4</sub>	Q <sub>5</sub>	Q <sub>6</sub>	
E <sub>x</sub> <sup>d</sup>	S <sub>4</sub>	1.05086	0.01273	-0.01658	
	S <sub>5</sub>	0.11993	1.49969	-0.18062	
	S <sub>6</sub>	-0.10263	0.28246	0.95217	
	CF <sub>4</sub>	Q <sub>3</sub>	Q <sub>4</sub>		
F <sub>x</sub> <sup>d</sup>	S <sub>4</sub>	0.40020	0.05986		
	S <sub>5</sub>	-0.46728	0.31168		

<sup>a</sup>Ref. (10), <sup>b</sup>Ref. (16), <sup>c</sup>The indices labelling the normal coordinates of CH<sub>3</sub>F and CF<sub>4</sub> correspond to the labels identifying the vibrational modes given in ref. (10) and ref. (16), respectively. <sup>d</sup>The K and L elements for the E<sub>x</sub>(or F<sub>y</sub> and F<sub>z</sub>) block are identical with those of the E<sub>x</sub>(or F<sub>z</sub>) block.

complete orthonormal functions, {φ<sub>j</sub>(r<sub>α</sub>)}, centered on each nucleus. The calculated contributions of each term in eqn.(3) will be presented in the following section.

## Results and Discussion

The quantum mechanically calculated APTs for the C(1), F(2), and H(3) atoms of CH<sub>3</sub>F in Figure 1(a) and for the C(1), F(2), and F(3) atoms of CF<sub>4</sub> in Figure 1(b) are listed in Table 3 along with the corresponding APTs derived from the analysis of the reported experimental intensities<sup>7,19</sup>. The experimental values were obtained in view of the quantum mechanically calculated signs for the dipole moment derivatives with respect to the normal coordinates, ∂P/∂Q<sub>α</sub>, of CH<sub>3</sub>F and CF<sub>4</sub>. The APTs for the atoms not shown in Table 3 can be obtained by the transformation equation<sup>20</sup>, T' = R<sup>T</sup>TR. Here T is the P<sub>X</sub><sup>H(3)</sup> tensor of CH<sub>3</sub>F or the P<sub>X</sub><sup>F(2)</sup> tensor of CF<sub>4</sub>, R is the coordinate (rotation) transformation matrix, R' is its transpose, and T' is the tensor in the rotated coordinate system.

It can be seen from Table 3 that the agreement between the theoretical values and the experimental values is, in general, quite good. The signs of each elements are consistent with one another. The ab initio calculations are, however, in better agreement with experiment. One noticeable feature is that the CNDO calculated zz elements of P<sub>X</sub><sup>F(2)</sup> are significantly smaller (in absolute value) than those from experiments for both molecules, CH<sub>3</sub>F and CF<sub>4</sub>.

It would be very interesting to compare the F atom polar tensors of various fluoromethanes. For that purpose, we chose the z-axis along the C-F bond. It is seen from the

Table 3. Atomic Polar Tensors of CH<sub>3</sub>F and CF<sub>4</sub> in Units of e<sup>3</sup>a

CH <sub>3</sub> F	C(1)			F(2)			H(3)		
6-31G	0.482	0	0	-0.371	0	0	-0.148	0	0.060
	0	0.482	0	0	-0.371	0	0	0.074	0
	0	0	0.945	0	0	-0.903	0.036	0	-0.014
CNDO/2	0.460	0	0	-0.293	0	0	-0.119	0	0.007
	0	0.460	0	0	-0.293	0	0	0.008	0
	0	0	0.608	0	0	-0.530	0.046	0	-0.026
Expt <sup>b</sup>	0.33	0	0	-0.26	0	0	-0.12	0	0.04
	0	0.33	0	0	-0.26	0	0	0.07	0
	0	0	0.96	0	0	-0.93	0.07	0	-0.01
CF <sub>4</sub>	C(1)			F(2)			F(3)		
6-31G	2.210	0	0	-0.434	0	0	-0.750	0	0.112
	0	2.210	0	0	-0.434	0	0	-0.434	0
	0	0	2.210	0	0	-0.790	0.112	0	-0.474
CNDO/2	1.972	0	0	-0.442	0	0	-0.578	0	0.048
	0	1.972	0	0	-0.442	0	0	-0.442	0
	0	0	1.972	0	0	-0.595	0.048	0	-0.459
Expt <sup>c</sup>	2.11	0	0	-0.33	0	0	-0.85	0	0.19
	0	2.11	0	0	-0.33	0	0	-0.33	0
	0	0	2.11	0	0	-0.92	0.19	0	-0.40

<sup>a</sup>APT's correspond to those of atoms numbered in Figure 1. <sup>b</sup>Ref. (7), <sup>c</sup>Computed from data in ref. (19).

analysis of the reported experimental intensities that the values of the *zz* elements for CF<sub>4</sub>, CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, and CH<sub>3</sub>F are -0.92, -0.95, -0.88, and -0.93e, respectively (see Table 3 of this paper and Table 5 of ref. (9)). The corresponding values for the *xx* (*yy*) elements are -0.33, -0.29, -0.25, and -0.26e. We see that the APT's of F atoms are indeed transferable among the fluoromethane molecules. The average values of the *zz* and *xx* (*yy*) elements are -0.92 and -0.28e, respectively. These values are supposed to be useful in the prediction of the band intensities in the complex fluoromolecules.

The transferability of the F-atom tensors is also confirmed from the theoretical calculations. According to the *ab initio* calculations, the *zz* elements for CF<sub>4</sub>, CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, and CH<sub>3</sub>F are -0.79, -0.89, -0.91, and -0.90e, respectively. The corresponding values for the *xx* (*yy*) elements are -0.43, -0.43, -0.38, and -0.37e. The average values of the *zz* and *xx* (*yy*) elements are -0.87 and -0.40e, respectively. Although the calculated *xx* (*yy*) element is somewhat larger than that from experiment, the *zz* elements are comparable with each other. Nevertheless, the transferability of polar tensors seems obvious for fluorine atoms.

In the CNDO limit, the *zz* elements for CF<sub>4</sub>, CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, and CH<sub>3</sub>F are found to be -0.60, -0.61, -0.58, and -0.53e, respectively. The corresponding values for the *xx* (*yy*) elements are -0.44, -0.39, -0.35, and -0.29e. The average values for the *zz* and *xx* (*yy*) elements are -0.58 and -0.37e, respectively. The transferability of the F atom tensors is again evident in the semi-empirical calculations. As noticed above, the CNDO calculated *zz* element is substantially smaller (in absolute value) than the experimental one.

The difference between the experimental and theoretical values of the tensor components is presumably a measure of the errors introduced by the particular basis set used and the

neglect of configuration interaction. The almost perfect correlation between experiment and theory suggests that, if self-consistent approximations are made, it might be possible to correct for these errors empirically, for some classes of systems.

The calculated effective charges of F atoms ( $\chi_F$ ) in the fluoromethanes fall within narrow ranges of values. The effective charge ( $\chi$ ) is defined<sup>21</sup> as the square root of one third of the sum of squares of the components of the atomic polar tensor. The observed  $\chi_F$  values are 0.60, 0.60, 0.57, and 0.58e, respectively, for CF<sub>4</sub>, CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, and CH<sub>3</sub>F. The corresponding theoretical values are 0.58, 0.62, 0.62, and 0.60e from the *ab initio* calculations and 0.50, 0.48, 0.44, and 0.39e from the semi-empirical calculations<sup>9</sup>. Although the CNDO results deviate significantly from the experimental values, the *ab initio* calculated values are in good agreement with the experimental ones. Furthermore, it is evident that the effective charge of F atom is independent of the particular fluoromethane molecule.

In order to compare the H atom polar tensors of various fluoromethanes, we chose the *z*-axis along the C-H bond. From the analysis of experimental data, it is found that the values of the *zz* elements for CH<sub>4</sub>, CH<sub>3</sub>F, and CH<sub>2</sub>F<sub>2</sub> are -0.13, -0.14, and -0.14e, respectively. The averaged values of the *xx* and *yy* elements are 0.06, 0.04, and 0.03e, respectively, for CH<sub>4</sub>, CH<sub>3</sub>F, and CH<sub>2</sub>F<sub>2</sub><sup>9</sup>. It is seen that the *zz* element of CH<sub>3</sub>F is in quite good agreement with those in CH<sub>4</sub> and CH<sub>2</sub>F<sub>2</sub>. On the other hand, the averaged value of the *xx* and *yy* elements decreases as the number of fluorine atoms bonded to the central carbon atom increases. These observations suggest that the transverse component is more sensitive to the neighbor H-F interactions. Similar trend is observed from the *ab initio* calculations. The calculated *zz* elements are -0.18, -0.16, and -0.15e for CH<sub>4</sub>, CH<sub>3</sub>F, and

Table 4. Calculated Intensities of CH<sub>3</sub>F and CD<sub>3</sub>F

	Band $\nu_i$ (cm <sup>-1</sup> )	Intensities (km·mole <sup>-1</sup> )		
		6-31G	CNDO/2	Observed <sup>a</sup>
CH <sub>3</sub> F	A <sub>1</sub> : $\nu_1$ (2910)	12.4	14.0	24.6
	$\nu_2$ (1460)	4.11	2.49	0.89
	$\nu_3$ (1049)	102	36.1	95.0
	E : $\nu_4$ (3006)	103	59.2	60.8
	$\nu_5$ (1468)	6.79	0.04	8.6
	$\nu_6$ (1182)	0.53	12.5	2.6
	SUM	229	124	193
	$\nu_1 + \nu_4$	115	73.2	85.4
	$\nu_2 + \nu_5$	10.9	2.5	9.5
	$\nu_3 + \nu_6$	103	48.6	97.6
CD <sub>3</sub> F	A <sub>1</sub> : $\nu_1$ (2110)	14.4	12.0	22.2
	$\nu_2$ (1135)	47.5	18.5	42.1
	$\nu_3$ (992)	54.7	18.0	74.1
	E : $\nu_4$ (2259)	66.0	42.2	39.6
	$\nu_5$ (1071)	1.66	0.61	4.8
	$\nu_6$ (911)	3.59	10.8	0.36
	SUM	188	102	183
	$\nu_1 + \nu_4$	80.4	54.2	61.8
	$\nu_2 + \nu_5$	49.2	19.1	46.9
	$\nu_3 + \nu_6$	58.3	28.8	74.5
	$\nu_3 + \nu_5$	56.4	18.6	78.9

<sup>a</sup>Ref. (22).

CH<sub>2</sub>F<sub>2</sub>, respectively. The corresponding values for the averaged xx and yy elements are 0.09, 0.04, and 0.02e. It thus appears that, for the prediction of infrared spectra of complex hydrocarbons containing fluorine atoms, some empirical adjustment of H-atom polar tensor can be made depending on the number of F atoms bound to certain carbon atom.

The intensities calculated for the fundamental vibrations of CH<sub>3</sub>F and CD<sub>3</sub>F are compared with the experimental values in Table 4. The ab initio calculated intensities appear, in general, to be more reasonable than the CNDO results.

The calculated intensity for the A<sub>1</sub> type CH (CD) stretching mode ( $\nu_1$ ) is about one half of the observed value. The ab initio calculated value for the E type CH (CD) stretching mode ( $\nu_4$ ) is nearly 70% larger than the experimental value. On the other hand, the CNDO calculated intensities are close to the observed ones. Nevertheless, considering that the  $\nu_1$  and  $\nu_4$  modes are somewhat overlapped, the agreement between the experimental and predicted intensities is expected to be better if they are summed. As shown in Table 4, we see that the agreement is indeed much better.

The two CH<sub>2</sub> bending modes ( $\nu_2$  and  $\nu_5$ ) are badly overlapped with each other. Once again, the summed intensity is expected to be used in the comparison of the calculated and observed intensities. The ab initio calculated intensity sum for those two bands is apparently close to the experimental data. However, the corresponding value from the semi-empirical calculations is about one fourth of the experimental intensity. The ab initio calculations are more reasonably correlated with the experimental values also for the  $\nu_2$  and  $\nu_5$  bands of CD<sub>3</sub>F. Similar trends are observed for the CF stretching ( $\nu_3$ ) and HCF (DCF) bending ( $\nu_6$ ) modes. It is noteworthy that the CNDO calculated intensities of the  $\nu_3$  and  $\nu_6$

Table 5. Calculated Intensities of CF<sub>4</sub> Fundamentals

Band $\nu_i$ (cm <sup>-1</sup> )	Intensities (km·mole <sup>-1</sup> )				
	6-31G	CNDO/2	APT 1 <sup>a</sup>	APT 2 <sup>b</sup>	Observed <sup>c</sup>
F: $\nu_3$ (1280)	1328	1017	1358	1100	1080
$\nu_4$ ( 631)	67.2	83.3	37.8	9.4	11.7

<sup>a</sup>Predicted intensities using the P<sub>x</sub><sup>F</sup> tensor of CH<sub>3</sub>F obtained from the 6-31G calculation. See Table 3. <sup>b</sup>Predicted intensities using the P<sub>x</sub><sup>F</sup> tensor of CH<sub>3</sub>F obtained from the analysis of observed intensity data. See Table 3. <sup>c</sup>Average of five independent experimental measurements found in the literature. See ref. 7.

Table 6. Comparison of Fluorine Atom Polar Tensors in CH<sub>3</sub>F and CF<sub>4</sub> in Atomic Units(e)<sup>a</sup>

		$\partial P_x / \partial X_{F_2}^b$ ( $= -\partial P_y / \partial Y_{F_2}$ )		$\partial P_x / \partial Z_{F_2}^b$		
		CNDO	6-31G	CNDO	6-31G	
CH <sub>3</sub> F	charge		-0.194		-0.194	
		6-31G	-0.455		-0.455	
	charge-flux	CNDO		-0.026		-0.332
		6-31G		0.025		-0.404
	overlap	CNDO		-0.073		-0.004
		6-31G		0.059		-0.044
	APT <sup>c</sup>	CNDO		-0.293		-0.530
		6-31G		-0.371		-0.903
		Expt'l		-0.26		-0.93
	charge	CNDO		-0.202		-0.202
6-31G			-0.346		-0.346	
charge-flux	CNDO		-0.084		-0.370	
	6-31G		-0.021		-0.136	
overlap	CNDO		-0.156		-0.023	
	6-31G		-0.067		-0.308	
APT <sup>c</sup>	CNDO		-0.442		-0.595	
	6-31G		-0.434		-0.790	
	Expt'l		-0.33		-0.92	
CF <sub>4</sub>						

<sup>a</sup>The charge, charge-flux, and overlap contributions correspond to the first, second, and third terms, respectively, in equation (3).

<sup>b</sup>APTs for the F(2) atoms in Figure 1. <sup>c</sup>See Table 3.

modes in both molecules, CH<sub>3</sub>F and CD<sub>3</sub>F, are significantly different from the observed values. In order to gain more information on the cause of such differences, the theoretical results are analyzed for the charge-charge flux-overlap electronic contributions to the dipole derivatives. Those results will be discussed later.

In Table 5 the calculated infrared band intensities of the fundamentals of CF<sub>4</sub> are compared with the experimental values. The experimental values reported here are the averages of five independent measurements found in the literature<sup>7</sup>.

The predicted intensities for the CF stretching mode ( $\nu_3$ ) are in fair agreement with the observed value. On the other hand, the quantum mechanically calculated intensities for the CF<sub>2</sub> bending mode are six to seven times larger than the experimental intensity. It is, however, very interesting to notice that the intensities predicted by using the P<sub>x</sub><sup>F</sup> tensor of CH<sub>3</sub>F obtained from the ab initio calculations are in better agreement with the observed values. Moreover, the P<sub>x</sub><sup>F</sup> ten-

sor derived from the analysis of the experimental intensities of  $\text{CH}_3\text{F}$  reproduces the  $\text{CF}_4$  band intensities within experimental errors,  $\pm 177$  and  $\pm 2.2$  km/mole for the  $\nu_3$  and  $\nu_4$  bands, respectively<sup>7</sup>. Thus, the transferability of the F-atom tensor between  $\text{CH}_3\text{F}$  and  $\text{CF}_4$  seems to be quite good. This suggests that the C-F bonds in  $\text{CH}_3\text{F}$  and  $\text{CF}_4$  are very similar, so that the substitution of three fluorine atoms for the hydrogen atoms in  $\text{CH}_3\text{F}$  does not significantly distort the electron density of the remaining C-F bond. For more detailed information, the CCFO electronic contributions to the dipole derivatives are computed. The results are represented in Table 6.

The transverse component of the fluorine atom polar tensor  $P_{xx}^F(P_{yy}^F)$  is almost entirely due to the equilibrium net charge on the F atom. The net charge effect estimated from the ab initio method is, however, considerably larger than that from the semi-empirical method.

For the longitudinal component  $P_z^F$  of  $\text{CH}_3\text{F}$ , both the net charge and the charge flux contributions are equally dominant. The quantum-mechanical overlap interaction is, in turn, less important. The ab initio calculations exhibit that the overlap contribution becomes important as the number of fluorine atoms bonded to the central carbon atom increases. Above observation represents a large charge transfer along the C-F bond during the stretching, and is indicative of the considerable electronic rearrangement that takes place as this bond is broken. In addition, it is suggested that the F-F neighbor interaction is rather strong.

In order to assess the relative importance of each of three CCFO contributions for a given tensor we may define the following quantity.

$$\xi_a^2 = \frac{1}{3} \sum_{\sigma} \left[ (\partial P_{\sigma} / \partial x_{\sigma})^2 + (\partial P_{\sigma} / \partial y_{\sigma})^2 + (\partial P_{\sigma} / \partial z_{\sigma})^2 \right] \quad (5)$$

as the square of the "effective term-charge"<sup>9</sup>. According to the ab initio calculations, the effective term-charges of fluorine atom in  $\text{CH}_3\text{F}$  are 0.46, 0.23, and 0.05e, respectively, for the net charge, charge flux, and overlap contributions. The corresponding values in  $\text{CF}_4$  are 0.35, 0.08, and 0.19e. It was reported previously<sup>9</sup> that the corresponding values for  $\text{CH}_2\text{F}_2$  are 0.42, 0.30, and 0.07e and for  $\text{CHF}_3$  0.38, 0.37, and 0.26e. It is seen that the net charge effect decreases smoothly as H-atom is replaced with F-atom. The effective term charge of the charge flux term in  $\text{CF}_4$  is considerably smaller than those of other fluoromethanes. Otherwise, the charge flux contribution increases smoothly along with the number of F atoms bound to the central carbon atom. It thus appears that overestimation of the ab initio calculation for the fundamental intensities of  $\text{CF}_4$  arises mainly from the underestimated charge-flux contribution. The observation that the predicted intensities of  $\text{CF}_4$  by using the fluorine atom polar tensor of  $\text{CH}_3\text{F}$  derived from the ab initio calculations are in better agreement with the observed values compared with those from the direct application of the ab initio method to  $\text{CF}_4$  seems to support above argument.

The cause of the sudden increase of the overlap contribution in  $\text{CHF}_3$  is not certain. In this respect, we may need more extended calculation including the configuration interaction. It is supposed that the overlap effect in  $\text{CF}_4$  is also somewhat overestimated in the ab initio calculation.

In the CNDO limit, the effective term charges of fluorine atom in fluoromethanes are calculated to be almost the same for each CCFO contribution. The values are 0.19, 0.19, and

0.06e in  $\text{CH}_3\text{F}$  and 0.20, 0.22, and 0.13e in  $\text{CF}_4$  for the net charge, charge flux, and overlap contributions, respectively. The corresponding values<sup>9</sup> for  $\text{CH}_2\text{F}_2$  are 0.20, 0.21, and 0.09e and for  $\text{CHF}_3$  0.20, 0.23, and 0.11e. Both the net charge and the charge flux contributions are nearly comparable to each other regardless of particular fluoromethane molecule. Those two terms are dominant in the CNDO limit. Although the non-classical overlap term contributes less significantly to the APT of F atom, it seems interesting to notice that its effective term charge shows monotonous increase along with the number of F atoms bound to the central carbon atom.

Quantitative prediction of dipole moment derivatives is difficult, in general, from approximate quantum mechanical treatments<sup>23</sup>. However, the fact that each kind of CCFO terms is not strongly dependent on the molecule in the CNDO limit may be informative. We believe that the abrupt changes in the effective term charges found in the ab initio calculations are somewhat erroneous. It seems to be worth, indeed, to carry out the more extended calculations including the configuration interactions.

As far as the hydrogen atom is concerned, the calculated CCFO contributions are consistent with one another along with the fluoromethane molecules. According to the ab initio calculations, the effective term charges of hydrogen atom in  $\text{CH}_3\text{F}$  are 0.16, 0.10, and 0.12e for the net charge, charge flux, and overlap contributions, respectively. On the same basis set, the corresponding values<sup>8,9,24</sup> are 0.16, 0.11, and 0.09e for  $\text{CH}_4$ , 0.17, 0.09, and 0.16e for  $\text{CH}_2\text{F}_2$ , and 0.20, 0.09 and 0.20e for  $\text{CHF}_3$ . Both the net charge and the charge flux contributions are nearly comparable among the molecules. The overlap contribution increases smoothly as the number of F atoms bound to the central carbon atom increases. None of the three groups of terms can be completely neglected.

In the CNDO limit, the effective term charges of hydrogen atom in  $\text{CH}_3\text{F}$  are 0.01, 0.07, and 0.06e for the net charge, charge flux, and overlap contributions, respectively. The corresponding values<sup>8,9,24</sup> for  $\text{CH}_4$  are 0.01, 0.07, and 0.07e, for  $\text{CH}_2\text{F}_2$  0.01, 0.08, and 0.06e, and for  $\text{CHF}_3$  0.02, 0.08, and 0.04e. Although the net charge contribution is far less than those from the remaining two terms, each CCFO contributions are almost transferable between molecules considered here. From both calculations, ab initio and semi empirical, it appears that the effective charge of hydrogen atom is rather insensitive to the details of the molecular structure.

It has been mentioned previously that the CNDO calculated intensities of the  $\nu_3$  and  $\nu_6$  modes in  $\text{CH}_3\text{F}$  and  $\text{CD}_3\text{F}$  are considerably different from both the ab initio results and the observed values. The underestimation of the  $\nu_3$  band intensities is due to the relatively smaller value (absolute) of the zz element in the F atom polar tensor. The overestimation of the  $\nu_6$  band intensities is due to the small value (absolute) of the yy element in the H atom polar tensor. According to the CCFO analysis, such discrepancies seem to arise from the relatively smaller net charge contributions compared with those from the ab initio calculations.

In conclusion, we have performed ab initio and semi empirical calculations for the dipole moment derivatives of  $\text{CH}_3\text{F}$  and  $\text{CF}_4$ . We have also analyzed the theoretical polar tensors into the charge, charge-flux, and overlap contribu-

tions. The major discrepancy between semi-empirical and ab initio calculated tensors seemed to arise from the differences in the net charge contributions. The effective term charges of hydrogen atom appeared to be transferable among the fluoromethane molecules. In the CNDO limit, the effective term charges of fluorine atom seemed also to be insensitive to the detailed molecular structure. It is hope that this is confirmed by the more extended calculations including the configuration interactions.

**Acknowledgement.** This work was supported in part by the Korea Science and Engineering Foundation.

### References

1. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Vol. 1 and 2, Methuen, London (1975 and 1981).
2. D. F. Hornig and D. C. Mckean, *J. Phys. Chem.*, **59**, 1133 (1955).
3. W. B. Person and S. R. Polo, *Spectrochim. Acta*, **17**, 101 (1961).
4. L. A. Gribov, *Intensity Theory for Infrared Spectra of Polyatomic Molecules*, Consultants Bureau, New York (1964).
5. W. B. Person and J. H. Newton, *J. Chem. Phys.*, **61**, 1040 (1974).
6. W. B. Person and G. Zerbi, *Vibrational Intensities in Infrared and Raman Spectroscopy*, Elsevier, Amsterdam (1982).
7. J. H. Newton, R. A. Levine, and W. B. Person, *J. Chem. Phys.*, **67**, 3282 (1977).
8. K. Kim, *Bull. Kor. Chem. Soc.*, **7**, 488 (1986).
9. K. Kim, *Bull. Kor. Chem. Soc.*, **8**, 10 (1987).
10. J. L. Duncan, D. C. Mckean, and G. K. Speirs, *Mol. Phys.*, **24**, 553 (1972).
11. L. H. Jones, B. J. Krohn, and W. C. Kennedy, *J. Mol. Spectrosc.*, **70**, 288 (1978).
12. J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York (1970).
13. W. J. Hehre, W. A. Latham, R. Ditchfield, M. D. Newton, and J. A. Pople, *Quantum Chemistry Program Exchange, QCPE* **10**, 236 (1974).
14. K. Kim, *J. Phys. Chem.*, **88**, 2394 (1984).
15. K. Kim, R. S. McDowell, and W. T. King, *J. Chem. Phys.*, **73**, 36 (1980).
16. J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 1089 (1964).
17. K. Kim and H. G. Lee, *Bull. Kor. Chem. Soc.*, **6**, 79 (1985).
18. A. H. Wapstra and N. B. Gove, *Nucl. Data Tables*, **A9**, 265 (1971).
19. I. W. Levin and T. P. Lewis, *J. Chem. Phys.*, **52**, 1608 (1970).
20. W. B. Person and J. H. Newton, *J. Chem. Phys.*, **64**, 3036 (1976).
21. K. Kim and W. T. King, *J. Chem. Phys.*, **80**, 983 (1984).
22. J. W. Russell, C. D. Needham, and J. Overend, *J. Chem. Phys.*, **45**, 3383 (1966).
23. W. B. Person and D. Steele, *Molecular Spectroscopy*, Vol. 2, p357, The Chemical Society, London (1974).
24. K. Kim and C. W. Park, *Bull. Kor. Chem. Soc.*, **7**, 380 (1986).

## Synthesis and Dissociation Constants of Cationic Rhodium (I)-Triphenylarsine Complexes of Unsaturated Nitriles and Aldehyde

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Reactions of  $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2$  with unsaturated nitriles and aldehyde, L, produce a series of new cationic rhodium (I) complexes,  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4$  (L =  $\text{CH}_2 = \text{CHCN}$ ,  $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CN}$ , *trans*- $\text{CH}_3\text{CH} = \text{CHCN}$ ,  $\text{CH}_2 = \text{CHCH}_2\text{CN}$ , *trans*- $\text{C}_6\text{H}_5\text{CH} = \text{CHCN}$ , and *trans*- $\text{C}_6\text{H}_5\text{CH} = \text{CHCHD}$ ) where L are coordinated through the nitrogen and oxygen, respectively but not through the  $\pi$ -system of the olefinic group. Dissociation constants for the reaction,  $[\text{RhL}(\text{CO})(\text{AsPh}_3)_2]\text{ClO}_4 \rightleftharpoons \text{Rh}(\text{ClO}_4)(\text{CO})(\text{AsPh}_3)_2 + \text{L}$ , have been measured to be  $1.20 \times 10^{-4}$  M (L =  $\text{CH}_2 = \text{CHCN}$ ),  $1.05 \times 10^{-4}$  M (L =  $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CN}$ ),  $3.26 \times 10^{-5}$  M (L = *trans*- $\text{CH}_3\text{CH} = \text{CHCN}$ ) and  $6.45 \times 10^{-5}$  M (L =  $\text{CH}_2 = \text{CHCH}_2\text{CN}$ ) in chlorobenzene at 25°C, and higher than those of triphenylphosphine complexes,  $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  where L are the corresponding nitriles that are coordinated through the nitrogen atom. The differences in dissociation constants seem to be predominantly due to the differences in  $\Delta H$  (not due to the differences in  $\Delta S$ ). The weaker Rh-N (unsaturated nitriles) bonding in  $\text{AsPh}_3$  complexes than in  $\text{PPh}_3$  complexes (based on  $\Delta H$  values) suggests that the unsaturated nitriles in **2**–**5** are good  $\sigma$ -donor and poor  $\pi$ -acceptor.

### Introduction

Transition metal complexes of triphenylphosphine ( $\text{PPh}_3$ ) have been much more studied in general than the triphenylarsine ( $\text{AsPh}_3$ ) complexes although  $\text{AsPh}_3$ , through coordination, would increase the basicity of the central metal more effectively than  $\text{PPh}_3$ , and consequently  $\text{AsPh}_3$  complexes would undergo oxidative addition reaction more readily than  $\text{PPh}_3$

complexes, which could be the most important step for the catalytic hydrogenation of olefins. Physical properties and catalytic activities of rhodium(I)-triphenylphosphine complexes,  $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  (L = unsaturated nitriles,<sup>1,5</sup> and aldehydes<sup>6,7</sup> coordinated through the nitrogen and oxygen atom, respectively) have been recently investigated. It would be interesting to compare the physical properties and catalytic activities of  $\text{PPh}_3$  complexes with those of  $\text{AsPh}_3$