

Notes on the Dipole-Moment Derivatives of PF_3

Recently Levin and Adams (1) calculated the dipole-moment derivatives with respect to the symmetry coordinates $\partial \mu / \partial S_i$ for PF_3 from the absolute infrared intensities, and indicated a preferred set of derivatives through comparison with CNDO/2 calculations. However, the published L^{-1} matrix elements for the A_1 -symmetry species are not consistent with $L\bar{L} = G$,¹ and as a consequence the $\partial \mu / \partial S_i$ -values in that symmetry block are in error.

We have redetermined the normal coordinate vectors and the dipole-moment derivatives for the A_1 -species, where we used the same geometry, symmetry coordinates and force field as Levin and Adams (1). The results are listed in Table I, which may be compared with the Tables II and III of (1).

The remaining sets of sign combinations of the $\partial \mu / \partial Q_i$'s would only reverse the signs of the $\partial \mu / \partial S_i$ -values and not their magnitudes. Levin and Adams stated, that also in the E -species, where a correction for the compensating rotation of the molecule is necessary, two sets of sign combinations are enough to

¹ In fact, the error occurs in the L_{12} -element.

TABLE I. Normal coordinate vectors and $\partial \mu / \partial S_j$ -values for the A_1 -species of PF_3 .

Normal coordinate vectors ($\text{amu}^{1/2}$)			Sign-combination		Dipole-moment derivatives ($\text{D}/\text{\AA}$)	
L^{-1}	S_1	S_2	$(\partial \mu / \partial Q_1)$	$(\partial \mu / \partial Q_2)$	$(\partial \mu / \partial S_1)$	$(\partial \mu / \partial S_2)$
Q_1	+3.4941	-0.1388	+	+	+7.09 \pm 0.83	+1.57 \pm 0.05
Q_2	+1.9162	+2.3789	+	-	+4.19 \pm 0.89	-2.02 \pm 0.05
			CNDO/2		+4.88	-3.59

The values for the dispersions of the charge distribution parameters contain only the errors propagated from the dispersions in the experimental intensities.

TABLE II. Rotational corrections and the experimental and calculated $\partial \mu / \partial S_j$ -values for the E_x -species of PF_3 .

Rotational corrections		$\bar{v}_{3x} = +0.16 \text{ D}/\text{\AA}$	$\bar{v}_{4x} = +0.09 \text{ D}/\text{\AA}$
Sign-combination		Molecular charge distribution parameters	
$(\partial \mu / \partial Q_3)$	$(\partial \mu / \partial Q_4)$	$(\partial \mu / \partial S_{3x})$	$(\partial \mu / \partial S_{4x})$
+	+	+6.85 \pm 0.30 $\text{D}/\text{\AA}$	+0.84 \pm 0.01 $\text{D}/\text{\AA}$
+	-	+7.65 \pm 0.30 "	-0.87 \pm 0.01 "
-	+	-7.98 \pm 0.30 "	+0.69 \pm 0.01 "
-	-	-7.17 \pm 0.30 "	-1.01 \pm 0.01 "
		CNDO/2	-9.95 "
The values for the dispersions of the charge distribution parameters contain only the errors propagated from the dispersions in the experimental intensities.			

indicate all possible magnitudes of the $\partial\mu_x/\partial S_j$ -values. However, in our opinion, in this case not two but four sets of sign combinations are needed.

In Table II we present the rotational corrections required to correct $\partial\mu_x/\partial S_j$ for the rotation of the permanent moment and the corrected experimental and calculated dipole-moment derivatives. Comparison with the CNDO/2 results led to the following values for the $\partial\mu/\partial S_j$ -quantities.

$$\begin{aligned} A_1\text{-species: } \partial\mu_z/\partial S_1 &= +4.19 \pm 0.89 \text{ D/\AA}, & \partial\mu_z/\partial S_2 &= -2.02 \pm 0.05 \text{ D/\AA}. \\ E_x\text{-species: } \partial\mu_z/\partial S_{3z} &= -7.17 \pm 0.30 \text{ D/\AA}, & \partial\mu_x/\partial S_{4x} &= -1.01 \pm 0.01 \text{ D/\AA}. \end{aligned}$$

REFERENCE

1. I. W. LEVIN AND O. W. ADAMS, *J. Mol. Spectrosc.*, **39**, 380 (1971).

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