

# Dipole Moment Derivatives and Polar Tensors in $\text{NH}_3$

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The dipole moment derivatives of  $\text{NH}_3$  are reexamined based on our recent intensity data. We have resolved the previous contradiction in the proper signs for the dipole moment derivatives of this molecule.

## Introduction

Determination of the preferred set of signs for the dipole moment derivatives with respect to the normal coordinates,  $\partial P/\partial Q_i$ , is the most essential step in the interpretation of vibrational intensity data<sup>1</sup>. Accordingly, preferred sets of signs for those derivatives have been determined for almost all of molecules for which complete experimental intensity data are available. However, it is of considerable concern to us that controversial results have been reported for the  $\text{NH}_3$  molecule<sup>2-4</sup>.

Although integrated IR intensities of ammonia have been reported by several authors<sup>5</sup>, all of those measurements were not in satisfactory agreement. In this respect we have remeasured recently the band intensities of this molecule<sup>6</sup>. In this paper we analyze those results.

From the observed intensities a set of dipole moment derivatives has been derived. The magnitudes and signs of the derivatives are compared with the CNDO/2 and ab initio calculated results. In addition the dipole moment derivatives have been transformed into the atomic polar tensors<sup>7</sup> in order to gain some insight into the chemical bonds of this molecule. Further, the selection of preferred signs for the dipole moment derivatives, besides allowing us to perform a comparative study of the derivatives of ammonia to other molecules, permits us to test the hypothesis of Prasad *et al.*<sup>3</sup> that the correct signs correspond to values of the atomic effective charges<sup>7</sup> which show a maximum difference for the central and terminal atoms.

## Method of Calculation

Starting with the experimental measurement, we note that the integrated molar infrared absorption coefficients,  $A_i$ , for the  $i$ th fundamental band is expressed as follows in the rigid rotor-harmonic oscillator approximation<sup>8</sup>,

$$A_i = (N\pi d_i/3c^2) |\partial P/\partial Q_i|^2 \quad (1)$$

Here,  $N$  is Avogadro's number,  $d_i$  is the degeneracy of the  $i$ th fundamental vibrational mode,  $c$  is the velocity of light, and  $\partial P/\partial Q_i$  is the vector dipole moment derivative with respect to the  $i$ th normal coordinate. Thus, the absolute values of  $\partial P/\partial Q_i$  are obtained from the measured integrated intensities. For molecules with any reasonable symmetry, the direction of  $\partial P/\partial Q_i$  is parallel to only one coordinate axis ( $X$ ,  $Y$ , or  $Z$ ), with either plus or minus sign, designated by the symbol  $\delta_i$ . Thus

we can write

$$\partial P/\partial Q_i = \delta_i (\partial P_i/\partial Q_i)^{\hat{f}} \quad (2)$$

Here  $i$  is  $X$ ,  $Y$ , or  $Z$  in the molecule-fixed Cartesian coordinate system parallel to the principal axes of inertia, and  $\hat{f}$  is the unit vector for that coordinate, with  $\delta_i = \pm 1$ . In terms of these coordinates, we can write the  $3 \times (3N-6)$  matrix of dipole derivatives with respect to the normal coordinates obtained from the experimental intensities. We call this matrix the  $P_Q$  matrix.

The normal coordinates are related to the  $3N-6$  internal symmetry coordinates  $S_j$  by<sup>9</sup>

$$S = LQ \text{ or } Q = L^{-1}S \quad (3)$$

Here  $S$  and  $Q$  are the column vectors of  $S_j$  and  $Q_i$  coordinates, respectively, and  $L$  is the  $(3N-6) \times (3N-6)$  normal coordinate transformation matrix. Thus, we can write the  $3 \times (3N-6)$  matrix of dipole derivatives with respect to symmetry coordinates ( $P_s$ ) as<sup>9</sup>

$$P_s = P_Q L^{-1} \text{ or } P_Q = P_s L \quad (4)$$

We may transform from internal symmetry coordinates  $S_j$  to the  $3N-6$  ordinary internal coordinates  $R_k$  by

$$S = UR \text{ or } R = U'S \quad (5)$$

Here  $U'$  is the transpose of  $U$ , since this transformation matrix is orthogonal<sup>9</sup>. Thus,

$$P_k = P_s U \text{ or } P_s = P_k U' \quad (6)$$

All of the coordinate transformations above have been between various molecule-fixed coordinate systems. Now let us consider the transformation to a space-fixed Cartesian coordinate system. In considering this transformation, it is necessary now to write explicitly the six "Eckart conditions" (see ref. 8) defining the translations and rotations of the whole molecule. The transformation from the internal coordinates to the  $3N$  ordinary space fixed Cartesian coordinates is given by<sup>9</sup>

$$\begin{pmatrix} R \\ \rho \end{pmatrix} = \begin{pmatrix} B \\ \beta \end{pmatrix} (X) \quad (7)$$

Here  $R$  is the  $(3N-6) \times 1$  column matrix of the internal coordinates;  $\rho$  is the  $(6 \times 1)$  column matrix of the Eckart conditions so that  $\begin{pmatrix} R \\ \rho \end{pmatrix}$  is the "augmented"  $3N \times 1$  column vector;  $B$  is a  $(3N-6) \times 3N$  transformation matrix whose elements are defined by  $B_{ij} = \partial R_i/\partial X_j$ ; and  $\beta$  is the corresponding  $(6 \times 3N)$  matrix

relating the  $\rho$  matrix to  $X$ . Thus the  $3 \times 3N$  polar tensor  $P_x$  is

$$P_x = P_{\alpha} B + P_{\rho} \beta, \quad (8)$$

Here we have defined a new tensor  $P_x$  with elements  $\partial P_x / \partial \rho_i$ . Since a translation of the whole molecule does not change the dipole moment of the molecule,  $\partial P_x / \partial \rho_i$  is zero for  $\rho_1, \rho_2$ , and  $\rho_3$ , the translations along  $X, Y$ , or  $Z$ ; for the three rotations ( $\rho_4, \rho_5, \rho_6$ ) about the principal axes of inertia ( $X, Y$ , and  $Z$ ) we may use the relationship given by Biarge *et al.*<sup>10</sup>

In this way we may obtain the so-called "atomic polar tensor",  $P_x$ , from the experimental data by transforming from  $P_Q$  to  $P_x$  using Eqs. (4), (6) and (8) to obtain<sup>11</sup>

$$P_x = P_Q L^{-1} U B + P_{\rho} \beta, \quad (9)$$

where the explicit implication of  $P_x$  for atom  $a$  in a molecule is given as the conjugate gradient of the molecular dipole moment vector,  $P$ ; that is<sup>11</sup>,

$$P_x^a \equiv \begin{pmatrix} \partial P_x / \partial X_a & \partial P_x / \partial Y_a & \partial P_x / \partial Z_a \\ \partial P_y / \partial X_a & \partial P_y / \partial Y_a & \partial P_y / \partial Z_a \\ \partial P_z / \partial X_a & \partial P_z / \partial Y_a & \partial P_z / \partial Z_a \end{pmatrix} \quad (10)$$

We note that we may also transform from  $P_x$  to  $P_Q$  by using the inverse relations. That is the usual way by which infrared intensities can be predicted from the quantum mechanical calculation.

The polar tensor values for NH<sub>3</sub> were calculated by means of Eq. (9). The cartesian coordinate axes, numbering of atoms, and orientation of the NH<sub>3</sub> molecule are shown in Figure 1.

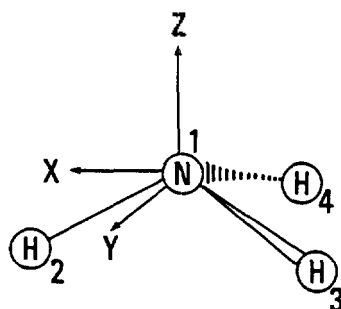


Figure 1. Coordinate axes and molecular orientation for NH<sub>3</sub> used in normal coordinate calculation.

TABLE 1: Structural Data, and Definition of Internal and Symmetry Coordinates of NH<sub>3</sub>

Masses (u) <sup>a</sup> : $m(^{14}\text{N}) = 14.003074$	$m(\text{H}) = 1.007825$
Structure <sup>b</sup> : $R_{\text{NH}} = 0.10116 \text{ nm}$	$\alpha_{\text{HNH}} = 106.67^\circ$
Dipole Moment <sup>c</sup> : $4.923 \times 10^{-30} \text{ C} \cdot \text{m}$	
Internal Coordinates <sup>d</sup> :	
$R_1 = \delta r_{12}$	$R_4 = \delta \alpha_{314}$
$R_2 = \delta r_{13}$	$R_5 = \delta \alpha_{214}$
$R_3 = \delta r_{14}$	$R_6 = \delta \alpha_{313}$

Symmetry Coordinates :

$$\begin{aligned}
 A_1: \quad S_1 &= (1/\sqrt{3})(R_1 + R_2 + R_3) \\
 S_2 &= (1/\sqrt{3})(R_4 + R_5 + R_6) \\
 E_s: \quad S_3 &= (1/\sqrt{6})(2R_1 - R_2 - R_3) \\
 S_4 &= (1/\sqrt{6})(2R_4 - R_5 - R_6) \\
 E_s: \quad S_5 &= (1/\sqrt{2})(R_2 - R_3) \\
 E_s: \quad S_6 &= (1/\sqrt{2})(R_5 - R_6)
 \end{aligned}$$

<sup>a</sup> Ref. (12). <sup>b</sup> Ref. (13). <sup>c</sup> Ref. (14). <sup>d</sup> The subscripts refer to the atoms shown in Figure 1;  $r_{ij}$  is a  $N_i H_j$  bond and  $\alpha_{ijk}$  is a  $H_i N_j H_k$  angle.

The equilibrium structural data, and the definition of the internal and symmetry coordinates are listed in Table 1. The  $L$  matrix and intensity data for NH<sub>3</sub> are given in Table 2.

## Results and Discussion

The experimental infrared intensities are proportional to the square of the dipole moment derivatives with respect to the normal coordinates of the molecule,  $\partial P / \partial Q_i$  (see eq. (1)). A principal value of MO calculations in the interpretation of infrared intensity data is the resolution of the sign ambiguity in those derivatives. Prasad *et al.*<sup>3</sup> and Bassi *et al.*<sup>2</sup> reported independently the preferred signs of those derivatives in NH<sub>3</sub>. However, since their preferred signs are not in agreement, recalculations are necessary in order to ensure that the sign conventions are consistent throughout the treatment.

The dipole moment derivatives with respect to the symmetry coordinates,  $\partial P / \partial S_i$ , in NH<sub>3</sub> calculated from the experimental data taken from the previous work<sup>6</sup> are given in Table 3 as a function of sign choice for the  $\partial P / \partial Q_i$ . For the species of  $E$  symmetry rotational corrections of 0.014 and  $-0.048 \text{ e}$  were applied to the experimental values of  $\partial P_x / \partial S_3$  and  $\partial P_x / \partial S_4$ , respectively. Table 3 contains, in addition, the calculated values from the quantum mechanical calculations, in which rotational correction is not necessary because of rotation-free distortions in a space-fixed coordinated system. A comparison of the signs of the experimental and theoretical derivatives is indeed interesting.

For the A species where two sign combinations need to be considered, Bassi *et al.*<sup>2</sup> selected the (+ +) signs, but Prasad *et al.*<sup>3</sup> the (- +) signs (we assumed that the definition of Z-axis in Prasad *et al.*'s work is opposite to ours). However, our results in Table 3 clearly suggest that only the (+ +) choice of

TABLE 2: Harmonic Force Field, Normal Coordinates, and Integrated Intensities in NH<sub>3</sub>

Harmonic Frequencies (cm <sup>-1</sup> ) <sup>a</sup> :					
$A_1$	$\nu_1$	3506	$E$	$\nu_3$	3577
	$\nu_2$	1022		$\nu_4$	1691
Harmonic Force Constants (Nm <sup>-1</sup> ) <sup>a,b</sup> :					
$A_1$	$K_{11}$	707.50	$E_s^c$	$K_{33}$	703.80
	$K_{12}$	78.90		$K_{34}$	-17.60
	$K_{22}$	54.44		$K_{44}$	68.05
Normal Coordinates (u <sup>-1/2</sup> ) <sup>d</sup> :					
$A_1$	$S_1$	1.002051	$Q_2$	-0.136272	
	$S_2$	0.078362	$Q_2$	1.169510	
$E_s^c$	$S_3$	1.040823	$Q_3$	0.028666	
	$S_4$	0.073823	$Q_4$	1.576657	
Intensities (Km <sup>2</sup> mole <sup>-1</sup> ) <sup>e</sup> :					
$A_1$	$\nu_1$	6.92	$E$	$\nu_3$	2.92
	$\nu_2$	127.2		$\nu_4$	24.77

<sup>a</sup> Ref. (15). <sup>b</sup> The angle bending force constants have been weighted by  $\text{Å}^2$  and the stretch-bend interaction force constant by  $\text{Å}$ . <sup>c</sup> The K and L elements for the  $E_s$  block are identical with the  $E_s$  block. <sup>d</sup> The indices labelling the normal coordinates correspond to the labels identifying the normal frequencies above. <sup>e</sup> Ref. (6).

**TABLE 3: Comparison of Experimental and Quantum Mechanical Calculated Dipole Moment Derivatives with Respect to the Symmetry Coordinates in  $\text{NH}_3(e)^*$**

	A <sub>1</sub> symmetry species	
	$\partial P_x/\partial S_1$	$\partial P_z/\partial S_2$
+ + <sup>b</sup>	0.059	0.316
- -	-0.059	-0.316
- +	-0.107	0.296
+ -	0.107	-0.296
10s6p1d/5slp/1s <sup>c</sup>	0.004	0.379
13s8p2d/8s2p <sup>d</sup>	0.016	0.379
6-31G <sup>e</sup>	0.004	0.438
CNDO/2 <sup>f</sup>	0.011	0.303
	E symmetry species	
	$\partial P_x/\partial S_3$	$\partial P_x/\partial S_4$
+ + <sup>b</sup>	0.018	0.119
- -	-0.046	-0.023
+ -	0.028	-0.024
- +	-0.056	0.120
10s6p1d/5slp/1s <sup>c</sup>	0.044	0.091
13s8p2d/8s2p <sup>d</sup>	0.043	0.100
6-31G <sup>e</sup>	-0.022	0.095
CNDO/2 <sup>f</sup>	-0.180	0.109

\*Units of electrons, e. <sup>b</sup>The different sign possibilities for  $\partial P/\partial Q_i$ . For example, (+ -) in the A<sub>1</sub> species means that  $\partial P_x/\partial Q_1$  is positive and  $\partial P_z/\partial Q_2$  is negative. Correspondingly in the E species, those signs indicate that  $\partial P_x/\partial Q_3$  is negative. Correspondingly in the E species, those signs indicate that  $\partial P_x/\partial Q_3$  and  $\partial P_x/\partial Q_4$  are positive and negative, respectively. <sup>c</sup> Ref. (16). <sup>d</sup> Ref. (17). <sup>e</sup> Calculated in this work by using the GAUSSIAN 70 PROGRAM (see ref. 18). <sup>f</sup> Ref. (19).

signs is preferable.

Bassi *et al.*<sup>2</sup> selected their preferred signs based on the CNDO/2 calculation. Considering the notorious difficulty in quantitative prediction on dipole moment derivatives from approximate semi-empirical quantum mechanical treatment, their sign may be suspect because the small calculated magnitudes in  $\partial P_x/\partial S_1$  results from a cancellation of much larger contributions to the dipole moment derivatives arising from equilibrium charge movement and intramolecular charge transfer. Indeed, Prasad *et al.*<sup>3</sup> selected the - sign for  $\partial P_x/\partial S_1$  based on their CNDO/2 calculation. However, as shown in Table 3, all of the near Hartree-Fock ab initio calculations predict the + sign so that we choose the + sign for  $\partial P_x/\partial S_1$ , implying a flow of electronic charge toward the hydrogen atom for an increase in the NH bond length from its equilibrium value. This conclusion is consistent with our general experience that a bond stretching motion, interpreted in terms of the bond moment hypothesis, results in a transfer of negative charge to the terminal atoms, appearing to be independent of types of atoms involved in the bond. Fortunately, the calculated value of  $\partial P_x/\partial S_2$ , which is in excellent agreement with the possible experimental values, do not suffer from these uncertainties. Therefore, we assign unequivocally the (+ +) set of signs for the A species of  $\text{NH}_3$ .

For the E symmetry species, the calculated values for the  $\partial P_x/\partial S_3$  and  $\partial P_x/\partial S_4$  are in good agreement with the experimental values of the (+ +) and (- +) sign choices. Of these

two alternatives the (- +) choice leads to a negative sign for  $\partial P_x/\partial S_3$  in agreement with the CNDO/2 and *ab initio* (6-31G) calculated signs. However, the (+ +) choice is in good agreement with the sign set from the more reliable near Hartree-Fock ab initio calculations. Based on the CNDO/2 estimates, Bassi *et al.*<sup>2</sup> selected the (- +) sign set. On the other hand Prasad *et al.* chose the (+ +) set of signs based on their unjustifiable criterion. It appears from Table 3 that the derivatives with respect to the bending modes are only slightly sensitive to considerable changes in the basis set whereas the stretching derivatives are strongly dependent on the size and structure of the basis set. However, it seems to be that the basis set dependency of the dipole moment derivatives strongly decreases as the basis set gets close to near Hartree-Fock wave functions.

Although the (+ + + +) set of signs seems to be more preferable based on the extended ab initio calculations, we have calculated the atomic polar tensors of  $\text{NH}_3$  for both possible sets of signs, (+ + + +) and (+ + - +). Here, (+ + + +) means that all of the  $\partial P/\partial Q_i$ 's are positive. Correspondingly, (+ + - +) indicates that  $\partial P/\partial Q_3$  is negative and that other  $\partial P/\partial Q_i$ 's are positive. The results are represented in Table 4, which also includes the theoretical estimates.

The *ab initio* results in Table 4 show a reasonable correspondence with the experimental values obtained from the (+ + + +) set of signs, whereas the CNDO/2 results lead to quite different values from both sets of signs, as might be expected from the derivative values of Table 3. This clearly illustrates the usefulness of large basis set ab initio calculations to support the interpretation of IR intensity data.

The preference of the (+ + + +) set of signs may be confirmed by the comparison of the predicted intensities of  $\text{ND}_3$  with the experimental values. By using the atomic polar tensors of  $\text{NH}_3$  we have calculated the expected intensities of  $\text{ND}_3$  for both sets of signs in Table 4. For the (+ + + +) set of signs, the predicted intensities are 2.1, 74, 3.8, and 15 km/mole for the  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  modes of  $\text{ND}_3$ , respectively. On the other hand, the (+ + - +) set of signs results in the values of 2.1, 74, 0.34, and 16 km/mole for the  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  modes, respectively. Koops *et al.*<sup>4</sup> reported the intensities of  $\text{ND}_3$ . Their values are 2.1, 76, 5.0 and 16.6 km/mole for the  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$  modes of  $\text{ND}_3$ , respectively. Comparing these experimental results with above estimates, the (+ + + +) set of signs is believed to be the appropriate choice in  $\text{NH}_3$  for the dipole moment derivatives with respect to the normal coordinates.

The polar tensors for the hydrogen atom in the XZ plane of Figure 1 show off-diagonal elements as large or larger than the diagonal elements. This observation indicates that in  $\text{NH}_3$  the charge flux contribution resulting from the rehybridization during vibration is as significant as the effect from the point charge displacement. This may occur from the nitrogen nonbonded electron pair. Such an influence of the lone pair of ammonia on the infrared intensity values has long been recognized<sup>21,22</sup>.

It has been well known that the hydrogen atom polar tensors are transferable among various hydrocarbons<sup>1</sup>. In this respect it may be interesting to compare the polar tensor elements of hydrogen atom in  $\text{NH}_3$  with those in typical hydrocarbons like  $\text{CH}_4$ . Let's define the molecular geometry of  $\text{CH}_4$  similarly to that of  $\text{NH}_3$  in Figure 1 except that the fourth

TABLE 4: Comparison of Experimental and Theoretical Atomic Polar Tensors of NH<sub>3</sub> in Units of e<sup>a</sup>

	$P_x^N$	$P_x^{H(2)}$	$P_x^{H(3)}$
+++ <sup>b</sup>	$\begin{pmatrix} -0.316 & 0 & 0 \\ 0 & -0.316 & 0 \\ 0 & 0 & -0.509 \end{pmatrix}$	$\begin{pmatrix} 0.070 & 0 & 0.133 \\ 0 & 0.140 & 0 \\ 0.106 & 0 & 0.170 \end{pmatrix}$	$\begin{pmatrix} 0.123 & 0.031 & -0.066 \\ 0.031 & 0.088 & 0.115 \\ -0.053 & 0.092 & 0.170 \end{pmatrix}$
++- <sup>b</sup>	$\begin{pmatrix} -0.233 & 0 & 0 \\ 0 & -0.233 & 0 \\ 0 & 0 & -0.509 \end{pmatrix}$	$\begin{pmatrix} 0.013 & 0 & 0.155 \\ 0 & 0.142 & 0 \\ 0.106 & 0 & 0.170 \end{pmatrix}$	$\begin{pmatrix} 0.110 & 0.056 & -0.078 \\ 0.056 & 0.046 & 0.135 \\ -0.053 & 0.092 & 0.170 \end{pmatrix}$
10s6p1d/5slp/1s <sup>c</sup>	$\begin{pmatrix} -0.359 & 0 & 0 \\ 0 & -0.359 & 0 \\ 0 & 0 & -0.655 \end{pmatrix}$	$\begin{pmatrix} 0.076 & 0 & 0.121 \\ 0 & 0.164 & 0 \\ 0.091 & 0 & 0.218 \end{pmatrix}$	$\begin{pmatrix} 0.142 & 0.038 & -0.061 \\ 0.038 & 0.098 & 0.105 \\ -0.046 & 0.079 & 0.218 \end{pmatrix}$
13s8p2d/8s2p <sup>c</sup>	$\begin{pmatrix} -0.370 & 0 & 0 \\ 0 & -0.370 & 0 \\ 0 & 0 & -0.646 \end{pmatrix}$	$\begin{pmatrix} 0.072 & 0 & 0.118 \\ 0 & 0.175 & 0 \\ 0.098 & 0 & 0.215 \end{pmatrix}$	$\begin{pmatrix} 0.149 & 0.045 & -0.059 \\ 0.045 & 0.098 & 0.102 \\ -0.049 & 0.085 & 0.215 \end{pmatrix}$
6-31G <sup>c</sup>	$\begin{pmatrix} -0.389 & 0 & 0 \\ 0 & -0.389 & 0 \\ 0 & 0 & -0.755 \end{pmatrix}$	$\begin{pmatrix} 0.058 & 0 & 0.237 \\ 0 & 0.201 & 0 \\ 0.105 & 0 & 0.252 \end{pmatrix}$	$\begin{pmatrix} 0.165 & 0.062 & -0.119 \\ 0.062 & 0.094 & 0.206 \\ -0.053 & 0.091 & 0.252 \end{pmatrix}$
CNDO/2 <sup>c</sup>	$\begin{pmatrix} -0.133 & 0 & 0 \\ 0 & -0.133 & 0 \\ 0 & 0 & -518 \end{pmatrix}$	$\begin{pmatrix} -0.097 & 0 & 0.183 \\ 0 & 0.185 & 0 \\ 0.077 & 0 & 0.173 \end{pmatrix}$	$\begin{pmatrix} 0.115 & 0.122 & -0.091 \\ 0.122 & -0.026 & 0.158 \\ -0.039 & 0.067 & 0.173 \end{pmatrix}$
CH <sub>4</sub> <sup>d</sup>		$\begin{pmatrix} -0.115 & 0 & 0.063 \\ 0 & 0.064 & 0 \\ 0.063 & 0 & 0.041 \end{pmatrix}$	

<sup>a</sup> See eq. (10) and fig. 1; <sup>b</sup> See text and note b in Table 3; <sup>c</sup> Calculated from the data in Table 3; <sup>d</sup> Taken from ref. (20).

hydrogen atom in CH<sub>4</sub> is located on the positive Z-axis. Then, the polar tensor for the hydrogen atom in CH<sub>4</sub>, corresponding to the H(2) of NH<sub>3</sub> in Figure 1, can be represented as shown in Table 4. It can be noticed from Table 4 that the elements of hydrogen atom polar tensors in NH<sub>3</sub> and CH<sub>4</sub> are much different from each other in their absolute values. Noticeably, the signs of the XX elements are opposite. The environments of both hydrogen atoms are almost the same except that N atom in NH<sub>3</sub>, which is directly (simply in single bond) bonded to the terminal hydrogen atoms, has one more electron (also one more proton) than C in CH<sub>4</sub>, so that there are more flexible electrons (*i.e.*, non-bonded electron pair) around N atom. It seems to be remarkable that small change of intra-molecular environment results in such a large effect in the electronic charge redistribution during vibration. Such an observation may be correlated with the previous findings that HCN behaves exceptionally to other hydrocarbons<sup>23</sup>. The NH bond in NH<sub>3</sub> is, however, more covalent than the CH bond in HCN. This can be confirmed from the value of atom anisotropy relative to effective charge (see ref. (1) for the definitions of effective charge and atom anisotropy). The relative value for NH<sub>3</sub> obtained from Table 4 is 0.64, which is close to that of CH<sub>4</sub>(~1) rather than that of HCN(~0).<sup>24</sup> More ionic hydrogen should have value near to 0. Once again, the lone pair of N in NH<sub>3</sub> may reflect the difference in the above relative values between NH<sub>3</sub> and CH<sub>4</sub>.

In this work, Prasad *et al.*'s criterion<sup>3</sup> for the selection of preferred signs for the dipole moment derivatives was found not to be valid for NH<sub>3</sub>. According to them the difference in the effective charges for the central atom and the sum of these values for the terminal atoms is maximum for the preferred sign combination. However, it has been noticed in the course of this work that several sign combinations other than the our preferred (++++) choice of NH<sub>3</sub> yielded larger values in those dif-

ferences. Since we do not believe there is any physical reason to prefer Prasad *et al.*'s criterion, we suggest once again that such a criterion be abandoned<sup>25</sup>.

In conclusion, we have resolved the previous contradiction in the proper signs for the dipole moment derivatives of NH<sub>3</sub>. When the sign conventions are consistent, the values of  $\partial P/\partial S_j$  or of polar tensor elements calculated by the *ab initio* method are in good agreement with experiment. It has been shown, in addition, that the proper signs of a molecule should result in the reliable prediction of vibrational intensities of its isotopically substituted ones. We believe that results in this work support the precise measurement of IR intensities of NH<sub>3</sub> in our recent work<sup>6</sup>. Finally, it may be prudent to mention that we need to study more nitrogen compounds in order to understand further the nature of lone pair electrons in the interpretation of vibrational intensity data.

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(9) This Eq. (4) is just the matrix expression of the chain rule for partial differentiation:

$$\frac{\partial P}{\partial S_i} = \sum_j \left( \frac{\partial P}{\partial Q_j} \right) \left( \frac{\partial Q_j}{\partial S_i} \right).$$

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## Nucleophilic Substitution Reaction of Dansyl Chloride with Substituted Anilines<sup>1</sup>

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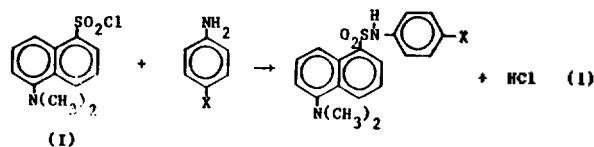
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Nucleophilic substitution reaction of dansyl chloride with anilines in various solvents have been investigated. The Brønsted  $\beta$  and Hammett  $\rho_N$  values indicated that the bond formation is advanced more than the bond breaking at the transition state. Solvatochromic correlations also predicted the importance of bond formation at the TS, showing a greater contribution of polarity ( $\pi^*$ ) compared to hydrogen bond donor acidity ( $\alpha$ ). The effect of solvent on rate was found to violate the reactivity-selectivity principle.

The nucleophilic substitution at a sulfur atom has been a subject of long-standing interest for organic chemists. Studies on sulfonyl halides in particular have led to propose two types of mechanisms,  $S_N2^2$  and  $S_N1^3$  for this reaction, the former being preferred lately. 5-Dimethylaminonaphthalene-1-sulfonyl chloride (dansyl chloride) (I) is an important compound in determination of amino-terminal amino acid, since it can be advantageously used when only a small quantity of a polypeptide is available for analysis.<sup>4</sup> In this type of reaction,  $NH_2$  groups in a polypeptide displace chloride at the sulfur atom of dansyl chloride.

As an extension of our work on the nucleophilic substitution reaction at sulfur center,<sup>1</sup> we carried out kinetic studies

on the reaction of dansyl chloride with substituted anilines (I) in various solvents.



X = p-MeO, p-Me, H, p-Cl.

### Experimental

**Materials.** Dansyl chloride and *para*-substituted anilines were obtained from Tokyo Kasei and used after purification by the