(13) S. E. Veazey and W. Gordy, *Phys. Rev.*, **138**, A1303 (1965).
(14) A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, *Phys. Rev.*, **96**, 629 (1954).
(15) A. J. Hebert, F. W. Breivogel, and K. Street, *J. Chem. Phys.*, **41**, 2368 (1964).
(16) F. W. Breivogel, A. J. Hebert, and K. Street, *J. Chem. Phys.*, **42**, 1555 (1965).
(17) Fluorides are notorious for anomalous behavior [see for example P. Politzer, *J. Am. Chem. Soc.*, **91**, 6235 (1969); R. S. Evans and J. E. Huhley, *Chem. Phys. Lett.*, **19**, 114 (1973)]. However the dichotomous (LiF–LiCl) f values are probably not related to abnormalities associated with fluorine. More likely, they result from a combination of factors including differential ionic radii and covalent change buildup. An examination of eq. 1 reveals that the term proportional to R in the quantum mechanically derived dipole moment model is $f + 2cz_{cv}/R$. In most of the alkali halides the covalent factor is negligible due to a combination of either a small c or small z_{cv}. However in the lithium halides both c and z_{cv} are nonnegligible. Thus in Figure 2, the appearance of the LiCl f in a position lower than would be predicted by the intersection of a vertical line and a slanted line through LiF is a result of an increasingly important covalent contribution going down a column in the lithium halides.
(18) A. von Hippel, "Dielectrics and Waves", Wiley, New York, N.Y., 1954.
(19) P. Brumer and M. Karplus, *J. Chem. Phys.*, **58**, 3903 (1973).
(20) H. E. DeWijn, *J. Chem. Phys.*, **44**, 810 (1966).
(21) R. L. Matcha, *J. Chem. Phys.*, **47**, 4595, 5295 (1967); **48**, 335 (1968); **49**, 1264 (1968); **53**, 485, 4490 (1970).
(22) R. L. Matcha and R. K. Nesbet, *Phys. Rev.*, **160**, 72 (1967).
(23) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 78.
(24) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934).
(25) P. O. Hare and A. C. Wahl, *J. Chem. Phys.*, **55**, 666 (1971).
(26) R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967).
(27) L. A. Curtiss, C. W. Kern, and R. L. Matcha, *J. Chem. Phys.*, **63**, 1621 (1975).
(28) S. Srebrenik and R. F. W. Bader, *J. Chem. Phys.*, **61**, 2536 (1974).
(29) P. Dagidigion and L. Wharton, *J. Chem. Phys.*, **57**, 1487 (1972).
(30) J. Hoeft, F. J. Lovas, E. Tiemann, and T. Toerring, *J. Chem. Phys.*, **53**, 2736 (1970).

A Localized Molecular Orbital Interpretation of the Dipole Moment Derivatives of Ammonia. A Reexamination of the Bond Moment Model Description of Infrared Intensities

Roy E. Bruns,* A. B. M. S. Bassi, and Paul M. Kuznesof

Contribution from the Instituto de Quimica, Universidade Estadual de Campinas, 13.100 Campinas, SP, Brazil.

Received August 19, 1975

Abstract: Preferred experimental values for the dipole moment derivatives of ammonia have been selected on the basis of the CNDO calculated signs for these quantities. Bond dipole moment values and directions have been calculated from the localized molecular orbital representations of the CNDO canonical MO's. The relative merits of the bond moment model assumptions pertinent to the interpretation of infrared intensities are assessed in terms of the theoretical results. The lone pair moment contributions to the dipole moment derivatives are also examined.

The comparison and interpretation of infrared gas phase intensity data have frequently been affected through use of the bond moment model. Bond moments evaluated with the aid of these data are not necessarily expected to agree with those bond moments whose vector sums are equal to the equilibrium dipole moments. Rather, a most important role of this model is to emphasize the differences between the equilibrium and the various infrared bond moments. These latter moments not only have different values for the same type of bond in different molecules, but also upon their evaluation from infrared intensities corresponding to normal coordinates of different symmetry for the same molecule.

Because a number of factors can produce different bond moment values, the reasons for the limited success of the bond moment model are not well understood. In its most restrictive form the model implies:[1,2] (1) when a bond is stretched by dr, a moment $(\partial\mu/\partial r)\,\mathrm{d}r$ is produced in the direction of the bond, (2) when a bond is bent through an angle dθ, a moment $\mu_0\,\mathrm{d}\theta$ is produced in the plane of bending perpendicular to the direction of the bond, and (3) when one bond is stretched or bent no changes occur in the other bonds. Differences in the bond moment values obviously can result from inaccuracies in any one of these assumptions. More realistically all three assumptions are not rigorously valid.

A quantum mechanical assessment of the relative merits of the above assumptions is clearly desirable. The approach we have taken is one in which the molecular orbitals (MO's) may be localized on the various bonds and isolated electron pairs in the molecule. Since standard SCF–MO methods yield orbitals which are delocalized over the entire molecule in a manner consistent with molecular symmetry, spatial transformations of these canonical MO's (CMO's) to localized MO's (LMO's) must be performed; a variety of techniques have been devised.[3] The LMO's can be used to calculate dipole moments for the individual bonds of the molecule at its equilibrium and vibrationally distorted geometries. Although the relative accuracies of the assumptions involved in the bond moment models are expected to vary for different molecules, the results for any one molecule should contribute to our understanding of why these models are too simple to allow an accurate general interpretation of infrared intensities.

We have chosen to study the infrared intensity data of ammonia[4] for the following reasons. First, the intensities can be interpreted in terms of the changes in the dipole moments of the NH bonds and the changes in the electronic distribution of the lone pair on nitrogen. Second, since CNDO[5] determination of the signs of the dipole moment derivatives with respect to the normal coordinates, the $\partial\mu/\partial Q_i$, have been reported for only the A_1 symmetry species,[6] it is useful to obtain CNDO estimates of the derivatives for the E species.

Calculations

The CNDO calculated dipole moment derivatives with respect to the symmetry coordinates, the $\partial\mu/\partial S_j$, were obtained in the usual manner.[6,7] Maximum displacements of 0.02 Å and 2° from the equilibrium geometry were used to determine the symmetry coordinate distortions. The symmetry coordinates were taken to be functions of the internal coordinates equal to

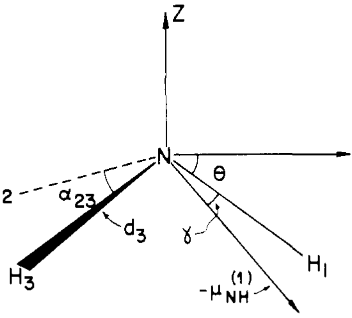

Figure 1. The Cartesian coordinate system for ammonia.

those defined by McKean and Schatz.[4] The Cartesian coordinate system used to calculate the dipole moment values is shown in Figure 1. The equilibrium geometry[4] consisted of NH bond lengths of 1.014 Å and HNH angles of 106°47′. The CNDO results were calculated using program CINDOM.[8] The localization of the CNDO CMO's was performed by incorporation of subprogram ORLOC[9] into CINDOM.

Within the CNDO framework[5] the dipole moment of ammonia can be expressed as

$$\mu_{\text{total}} = \mu_{\text{Q}} + \mu_{\text{pol}}$$

Here μ_{Q} and μ_{pol} are the contributions to the total moment calculated from the equilibrium charge distribution and the atomic sp polarizations, respectively. The latter contribution may be partitioned[10] as

$$\mu_{\text{pol}} = \sum_{i}^{\text{bonds}} \mu_{\text{pol}}^{(i)} + \mu(\text{e})$$

where $\mu_{\text{pol}}^{(i)}$, the bond polarization moment, represents the contribution to the total moment calculated from the sp polarization of the LMO describing the *i*th NH bond. The contribution from the LMO describing the lone pair of electrons on nitrogen is given by $\mu(\text{e})$. For each bond i, $\mu_{\text{Q}}^{(i)}$ can be expressed as the vector sum

$$\mu_{\text{Q}} = \sum_{i}^{\text{bonds}} \mu_{\text{Q}}^{(i)}$$

and can be calculated in a straightforward manner[10] from the electronic charge distributions of the individual LMO's.

The vector sum of the bond point charge $\mu_{\text{Q}}^{(i)}$, and bond polarization, $\mu_{\text{pol}}^{(i)}$, moment contributions

$$\mu_{\text{NH}}^{(i)} = \mu_{\text{Q}}^{(i)} + \mu_{\text{pol}}^{(i)}$$

may be regarded as the *dipole moment of the ith bond.* Since $\mu_{\text{Q}}^{(i)}$ is obliged to point in the same direction as the NH bond, this term is often used for comparison with empirical bond moments. The polarization moment, on the other hand, is free to point in any direction and thus can account for a major inaccuracy in the empirical bond moment descriptions of infrared intensities. Differences in the magnitudes of the bond moments for the various nonequilibrium geometries can also arise from the redistribution of electronic charge upon displacement from the equilibrium geometry. These changes are reflected in the altered magnitudes of $\mu_{\text{Q}}^{(i)}$.

Experimental and CNDO Derivatives

A principle value of MO calculations in the interpretation of infrared intensity data is the resolution of the sign ambiguity in the derivatives of the dipole moment with respect to the normal coordinates of the molecule, the $\partial\mu/\partial Q_i$. Since the experimental intensities are proportional to the square of these derivatives their signs for ammonia remain unknown without intensity data for the deuterated species. MO theory, even in its approximate semiempirical form, has proven its utility in the resolution of sign ambiguities in a number of cases.[6,7]

Table I. Comparison of Experimental and CNDO Calculated Dipole Moment Derivatives[a,b]

	A$_1$ Symmetry Species	
Signs of the $\partial\mu/\partial Q_i$	$\partial\mu/\partial S_1$[d]	$\partial\mu/\partial S_2$
++[c]	**0,37**	**1.56**
+−	0.42	−1.50
CNDO	+0.05	+1.46
	E Symmetry Species	
Signs of the $\partial\mu/\partial Q_i$	$\partial\mu/\partial S_{3a}$	$\partial\mu/\partial S_{4a}$[e]
++	+0.11	+0.57
+−	+0.12	+0.12
−+	**−0,25**	**+0,59**
−−	−0.24	−0.10
CNDO[f]	−0.86	+0.52

[a] The units are D/Å for S_1 and S_{3a} and D/rad for S_2 and S_{4a}. [b] The symmetry coordinates are those of ref 4: $S_1 = 3^{-1/2}(d_1 + d_2 + d_3)$, $S_2 = 3^{-1/2}(\alpha_{12} + \alpha_{13} + \alpha_{23})$, $S_{3a} = 6^{-1/2}(2d_1 - d_2 - d_3)$, and $S_{4a} = 6^{-1/2}(2\alpha_{23} - \alpha_{12} - \alpha_{13})$. [c] The (−−) and (−+) sign combinations can be obtained by reversing all of the signs in these rows. [d] The letter p is a common spectroscopic notation representing the dipole moment as μ is normally reserved for the reduced mass. We have used the greek letter to maintain consistency with other quantum mechanical treatments of the dipole moment. [e] The symmetry coordinate distortion for S_{4a} is made such that the angles between the z axis and the NH bonds are not varied. [f] The CNDO calculated values are obtained using the approximation $\partial\mu/\partial S_j \approx \Delta\mu/\Delta S_j$. Rigorously, $\partial\mu/\partial S_j = \lim_{\Delta S_j \to 0} \Delta\mu/\Delta S_j$.

CNDO values of the dipole moment derivatives for ammonia in terms of symmetry coordinates for the A$_1$ species have been calculated by Segal and Klein.[6] Our values for these derivatives are presented in Table I along with those obtained directly from the infrared intensities. As Segal and Klein have pointed out,[6] the sign for the CNDO value of $\partial\mu/\partial S_1$ may be suspect because its small calculated magnitude results from a cancellation of much larger contributions to the dipole moment derivative arising from equilibrium charge movement and intramolecular charge transfer. Furthermore, since the equilibrium bond length falls very close to the maximum in the calculated dipole moment function, more uncertainty is introduced in the predicted sign. Fortunately, the CNDO value for $\partial\mu/\partial S_2$, which is in excellent agreement with the possible experimental values, does not suffer from these uncertainties. The calculated positive CNDO sign indicates that the (++) or (−+) set of signs for the $\partial\mu/\partial Q_i$ is the correct one. We choose the (++) set of signs because a positive value of $\partial\mu/\partial S_1$ implies a flow of electronic charge toward the hydrogen atom for an increase in the NH bond length from its equilibrium value. For all the molecules we have tested thus far, a bond stretching motion, interpreted in terms of the bond moment hypothesis, results in a transfer of negative charge to the terminal atom. This result appears to be independent of the types of atoms involved in the bond. It must be noted that, in general, the dipole moment changes for vibrational distortions are expected to result from intramolecular charge transfer in addition to changes in sp polarizations and the movement of equilibrium charges. For the symmetrical NH stretching motion the CNDO analysis of the contributions to the dipole moment changes supports this view quite strikingly.

For the E symmetry species the CNDO value for $\partial\mu/\partial S_{4a}$ is in excellent agreement with the experimental values of the (++) and (−+) sign choices. Of these two alternatives only the (−+) choice leads to a negative sign for $\partial\mu/\partial S_{3a}$ in agreement with its CNDO calculated sign. This preferred sign

Table II. Magnitudes and Directions of the Bond Point Charge, Bond Polarization, and Total Bond Moments for the Symmetry Coordinate Distortions of Ammonia[a]

Geometry	$\lvert\mu_Q^{(i)}\rvert$[b]	$-\lvert\mu_{pol}^{(i)}\rvert$[b]	β, deg	$-\lvert\mu_{NH}^{(i)}\rvert$[b]	γ, deg
Equilibrium	0.380	1.645	1.65	1.266	2.15
S_1	0.375	1.633	2.08	1.258	2.70
S_2	0.392	1.690	2.75	1.299	3.62
S_{3a} $i = 1$	0.375	1.624	1.71	1.249	2.26
$i = 2, 3$	0.382	1.656	1.69	1.274	2.24
Av	0.380	1.645		1.266	
S_{4a} $i = 1$	0.374	1.628	1.11	1.254	1.44
$i = 2, 3$	0.383	1.654	2.16	1.271	2.87
Av	0.380	1.645		1.266	

[a] Units are in Debyes. [b] The values for $\lvert\mu_Q^{(i)}\rvert$ correspond to a charge distribution N^-H^+. The negative signs for $\lvert\mu_{pol}^{(i)}\rvert$ and $\lvert\mu_{NH}^{(i)}\rvert$ indicate that these vectors have an orientation of the sense N^+H^-.

choice indicates directions of electronic charge movement which are the same as found in the A_1 species. For the stretching derivatives, $\partial\mu/\partial S_1$ and $\partial\mu/\partial S_{3a}$, electronic charge is displaced in the direction of the moving hydrogens; i.e., the hydrogen part of the NH dipole becomes more negative as the NH bond is stretched. For the bending derivatives, the signs of $\partial\mu/\partial S_2$ and $\partial\mu/\partial S_{4a}$ imply bond moments of N^-H^+ polarity. These consistencies in the directions of charge flow between the derivatives of A_1 and E symmetry reinforces our selection of the (++) set of signs for the $\partial\mu/\partial Q_i$ of A_1 symmetry.

The CNDO magnitudes for the bending derivatives are in spectacular agreement with the experimental magnitudes for the preferred sign choices mentioned above. In fact these calculated values seem much more accurate than one would expect from an approximate molecular orbital theory, such as CNDO. On the other hand, the CNDO values for the stretching derivatives are in very poor agreement with the experimental magnitudes. Experimental error cannot be ruled out as a source of at least part of this descrepancy. The stretching fundamentals, ν_1 and ν_3, at 3337 and 3448 cm^{-1}, respectively, overlap considerably necessitating a somewhat arbitrary separation of the total band intensity into individual fundamental intensities. Attributing a larger relative intensity to ν_3 than was done previously[4] would result in a larger magnitude for $\partial\mu/\partial S_{3a}$ and a smaller one for $\partial\mu/\partial S_1$ with only very slight changes in the magnitudes of the bending derivatives, thus improving the overall agreement between experimental and theoretical results. However, an assignment of equal relative intensities for ν_1 and ν_3 instead of the 2.3:1 ratio (ν_1 more intense than ν_3) employed in ref 4 would only change the values of $\partial\mu/\partial S_1$ and $\partial\mu/\partial S_{3a}$ in Table I by about 20%. One must conclude that the major source of disagreement between the experimental and CNDO values is due to poorly calculated theoretical values for the stretching derivatives.

Bond Moment Interpretation

The results of CNDO theory appear to be accurately reflecting the dipole moment changes for the bending motions of ammonia. Therefore, it should be fruitful to examine the CNDO wave functions expressed as LMO's, at least for these motions. As stated earlier, these orbitals allow the direct calculation of bond and lone pair dipole moments. Hence, a direct test of the various assumptions which define the bond moment model can be made.

In Table II values of the NH bond dipole moments, $\mu_{NH}^{(i)}$, are presented for ammonia at its equilibrium geometry and for geometries corresponding to the symmetry coordinate distortions. The magnitudes of the vectorial contributions to $\mu_{NH}^{(i)}$, the bond point charge moment, $\mu_Q^{(i)}$, and the polarization contribution, $\mu_{pol}^{(i)}$, in this table are of opposite sign. The angles formed by the vectors $-\mu_{pol}^{(i)}$ and $-\mu_{NH}^{(i)}$ with the chemical bonds, and hence with μ_{Q_i}, are indicated by β and γ, respectively. The angle γ, therefore, is a measure of the angular deviation of the CNDO calculated bond dipole moment from what is expected should the bond moment assumptions hold rigorously. The angles which the various NH bonds make with the xy plane of Figure 1 are given by θ. Except for the S_2 symmetry coordinate, for which θ is 20.15°, θ is equal to 22.03°.

The variation in the magnitude of the point charge moment (column one of Table II), $\lvert\mu_Q^{(i)}\rvert$, for the various symmetry distortions is less than about 0.01 D. When the NH bond length is increased by 0.02 Å the point charge moment decreases by 0.005 D. This decrease results from a reduction of the calculated positive charge on hydrogen as the NH bond is stretched from its equilibrium position. The asymmetric stretching motion shows the same decrease in the NH charge density moment as it is stretched by 0.02 Å ($i = 1$) along with compensatory increases for the bonds which are 0.01 Å shorter than the equilibrium value. The average bond point charge moment for the asymmetric distortion is equal to the equilibrium value since the dipole moment is a vector quantity. Relatively small changes in the dipole moment components in Cartesian directions other than that of the equilibrium dipole moment have a very small influence on the magnitude of the total dipole moment vector. However, these are the changes which determine the infrared intensities of the asymmetric vibrations.

For the symmetric bending motion, S_2, the bond point charge moment increases by 0.012 D as the HNH angles increase by 2°. Since each NH bond is common to two angles, there is an increase of 0.003 D for a 1° increment of any one of these angles. For S_{4a}, $\lvert\mu_Q^{(1)}\rvert$ decreases with respect to the equilibrium value by 0.006 D and the $\lvert\mu_Q^{(i)}\rvert$ ($i = 2, 3$) increase by 0.003 D. These changes correspond, respectively, to an increase of 2° in the $H_{(2)}NH_{(3)}$ angle and to decreases of 1° for the other angles.

The values in Table II can be used to provide CNDO estimates of the dipole moment derivatives, $\partial\mu/\partial S_j$, at varying levels of the bond moment approximation. The first column of Table III contains predicted CNDO values assuming that the equilibrium point charge moment does not change for vibrational distortions. Using the equilibrium value of +0.380 D and the values of θ, +0.58 and +0.32 D/rad are calculated for $\Delta\mu_{Q_0}/\Delta S_2$ and $\Delta\mu_{Q_0}/\Delta S_{4a}$. These values reflect contributions to the dipole moment derivative due to the movement of equilibrium charge for these symmetry coordinate distortions. Introducing the nonequilibrium values of $\mu_Q^{(i)}$ into the calculations is equivalent to the inclusion of intramolecular charge transfer contributions to the dipole moment derivatives. As can be seen by inspection of columns 1 and 2 of Table III, this results in relatively small decreases of 0.21 and 0.18 D/rad for the bending derivatives. The entries in column 2, the $\Delta\mu_Q/\Delta S_j$, correspond to contributions to the dipole moment derivatives from the movement of equilibrium charge and from changes in this charge as the molecule is distorted from equilibrium.

The CNDO magnitudes for the polarization contribution, $\lvert\mu_{pol}^{(i)}\rvert$, to the bond dipole moments (Table II) are about four times larger than those of $\mu_Q^{(i)}$ and have opposite signs. Thus $\mu_{NH}^{(i)}$ is largely determined by the polarization contribution and also has a sign opposed to the one for $\mu_Q^{(i)}$. Inspection of the total bond moment values in Table II shows that their magnitudes vary over a range of 0.033 D. Thus, deviations from bond moment model results are partially accounted for by these variations. Furthermore, the polarization contributions to the bond dipole moments are not coincident with the

Table III. Contributions to the CNDO Calculated Dipole Moment Derivatives of Ammonia[a]

Symmetry coordinates	$\Delta\mu_{Q_0}/\Delta S_j$[b]	$\Delta\mu_Q/\Delta S_j$[c]	$(\Delta\mu/\Delta S_j)_{\mathrm{bonds}}$[d]	$(\Delta\mu/\Delta S_j)_{\mathrm{lone\ pair}}$[e]	$\Delta\mu/\Delta S_j$[f]
S_1		+0.17	+0.66	−0.61	+0.05
S_2	+0.58	+0.37	+0.25	+1.21	+1.46
S_{3a}		−0.11	+0.60	−1.46	−0.86
S_{4a}	+0.32	+0.14	+0.35	+0.17	+0.52

[a] The units are D/Å and D/rad for the stretching and bending derivatives. [b] Calculated using the equilibrium magnitude of $\mu_Q^{(i)}$ and the angles θ which are described in the text. [c] Calculated using the varying magnitudes of $\mu_Q^{(i)}$ and the angles θ. [d] Calculated using the values of $\mu_{NH}^{(i)}$ and the angles γ listed in Table II. [e] Calculated from changes in the sp polarization of the lone pair molecular orbital. [f] The total dipole moment derivatives which are equivalent to the sums of columns 3 and 4.

NH bonds, as indicated by the angle β, Table II. Therefore, the bond dipole moment vector is not colinear with the vector defining the NH bond. The angle between these two vectors (and hence $\mu_Q^{(i)}$ and $\mu_{NH}^{(i)}$) is given by γ in Table II. The values of $(\Delta\mu/\Delta S_j)_{\mathrm{bonds}}$ in Table III were calculated using the $|\mu_{NH}^{(i)}|$ and γ values of Table II. Thus these values include *all* the contributions to $\partial\mu/\partial S_j$ due to the localized orbitals describing the NH bonds.

Bond moment parameters are normally evaluated assuming colinearity with the NH bonds. The CNDO theory warns us against using this simple, unfortunately necessary, approach. Admittedly, the theory is known to provide some poor estimates of the magnitudes of the dipole moment derivatives, the stretching derivatives of ammonia providing two such examples. However, use of a more sophisticated theory which would result in better estimates of the dipole moment derivatives would not necessarily yield bond moments more coincident with the NH bonds.

Various groups have shown that the contribution to $\partial\mu/\partial S_j$ due to changes in the sp polarizations (sometimes referred to as the hybridization contribution) can be important. This quantity was found to have large absolute values for the CH bending derivatives of ethylene (0.6 to 1.1 D/rad). As the entries in column 3 of Table III include *all* the contributions to the dipole moment derivatives except the contributions from the lone pair, the differences between the values in columns 2 and 3 provide the *sp* polarization contributions for the bonds of ammonia. The symmetric bending derivative decreases by only 0.12 D/rad upon inclusion of these contributions whereas the asymmetric bend shows a small increase of 0.21 D/rad. Certainly, larger changes, as are found for the stretching derivatives of ammonia and the bending derivatives of ethylene, might have been anticipated.

Although the bond moment models do not formally consider changes in the lone pair contribution to the dipole moment derivatives, the influence of the lone pair of ammonia on the infrared intensity values has long been recognized.[1,4] In column 4 of Table III the lone pair moment contributions to the derivative, which are calculated from changes in the sp polarization of the LMO describing the nitrogen nonbonded electron pair, are presented. The sum of this contribution with the one resulting from the LMO's describing the NH bonds yields the total dipole moment derivative.

For the bending motions, chemical intuition points to a large contribution to $\Delta\mu/\Delta S_2$ and a much smaller one for $\Delta\mu/\Delta S_{4a}$. This is borne out by inspection of the CNDO results. The lone pair contribution to $\Delta\mu/\Delta S_2$ is more than six times larger than the contribution to $\Delta\mu/\Delta S_{4a}$. In fact, the bond dipole moments account for less than 20% of the CNDO calculated value of $\Delta\mu/\Delta S_2$. Thus, the theory indicates that reorientation of the nitrogen lone pair determines this value. On the other hand, the bond dipole moments account for 66% of the estimated value for $\Delta\mu/\Delta S_{4a}$.

Somewhat surprisingly, the largest CNDO lone pair contribution occurs for $\Delta\mu/\Delta S_{3a}$. As this contribution is of opposite sign to the one calculated from the LMO's describing the NH bonds, it determines the sense of $\Delta\mu/\Delta S_{3a}$. For the symmetric stretching derivative, the nearly complete cancellation of a positive contribution from the NH bonds by a negative one from the lone pair underlines the uncertainty in the sign of the CNDO calculated derivative.

In summary, the CNDO theory indicates that the polarization contribution to the total bond dipole moment can account for the inaccuracies observed from results predicted on the basis of the bond moment hypotheses. The calculated bond moments have been shown to vary both in magnitude and direction for the various symmetry coordinate distortions although these variations have relatively small effects on the calculated values of the bending derivatives of ammonia. The lone pair contributions to the CNDO derivatives are substantial for all of the symmetry coordinates of this molecule.

Acknowledgment. Financial support from the Fundacão de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and the Financiadora de Estudos e Projetos (FINEP) is gratefully appreciated. Computer time made available by the Centro de Computação of the Universidade Estadual de Campinas is also acknowledged.

References and Notes

(1) D. F. Hornig and D. C. McKean, *J. Phys. Chem.*, **59**, 1133 (1955).
(2) L. A. Gribov, "Intensity Theory for Infrared Spectra of Polyatomic Molecules", Consultants Bureau, New York, N.Y., 1964.
(3) C. Trindle and O. Sinanoglu, *J. Chem. Phys.*, **49**, 65 (1968); C. Edmiston and K. Reudenberg, *ibid.*, **43**, S97 (1965); C. Edmiston and K. Reundenberg, *Rev. Mod. Phys.*, **35**, 457 (1963); W. England, L. S. Salmon, and K. Reudenberg, *Top. Curr. Chem.*, **23**, 31 (1971); W. Von Niessen, *Theor. Chim. Acta*, **29**, 29 (1973).
(4) D. C. McKean and P. N. Schatz, *J. Chem. Phys.*, **24**, 316 (1956).
(5) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
(6) G. A. Segal and M. L. Klein, *J. Chem. Phys.*, **47**, 4236 (1967).
(7) R. E. Bruns and W. B. Person, *J. Chem. Phys.*, **53**, 1413 (1970).
(8) R. E. Bruns, Quantum Chemistry Program Exchange, Indiana University, QCPE 240.
(9) P. M. Kuznesof, Quantum Chemistry Program Exchange, Indiana University, QCPE 267.
(10) M. S. Gordon and W. England, *J. Am. Chem. Soc.*, **94**, 5168 (1972); P. M. Kuznesof, F. B. T. Pessine, R. E. Bruns, and D. F. Shriver, *Inorg. Chim. Acta*, **14**, 271 (1975).
(11) B. Golabov, S. Suzuki, and W. J. O. Thomas, *J. Chem. Soc., Faraday Trans. 2*, **71**, 162 (1975); D. Steele and W. Wheatley, *J. Mol. Spectrosc.*, **32**, 265 (1969); R. E. Bruns and W. B. Person, *J. Chem. Phys.*, **57**, 324 (1972).