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Vibrational Correction for Methylamine and Determination of the Zero-Point Average Structure

Takao IIJIMA
Faculty of Science, Gakushuin University, Mejiro, Toshimaku, Tokyo 171

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The method of vibrational corrections for a molecule which has a large amplitude intramolecular motion has been revised and applied to the determination of the zero-point average structure of methylamine. Necessity of torsional correction for this type of molecules has been pointed out and the method has been presented. A recent result of electron diffraction was jointly used with the effective moments of inertia obtained by microwave spectroscopy by Takagi and Kojima. The structural parameters in r_z and φ_z with the estimated limits of error in parentheses are: r(C–N)=1.471(3) Å, r(C–H)=1.101(3) Å, r(N–H)=1.019(6) Å, ∠HCH=108.4(5)°, ∠HNH=106.0(6)°, and ∠CNH=111.5(7)°. Deuterium isotope effects in the structural parameters were also determined.

Rotational constants obtained by molecular spectroscopy usually suffer complicated vibrational effects. Corrections for the effects have been successfully applied to the determination of molecular structures, especially in a joint analysis by means of a combined use of spectroscopic and diffraction data. The method is established in the small amplitude approximation for intramolecular motions.[1,2] The present author and coworker extended the method for the molecules which have a large amplitude torsional motion.[3,4] However, in an attempt to determine the structure of methylamine, it became apparent that the formulation given in the previous work[3] was not adequate for this molecule.

In Ref. 3 the formulation was based on the rigid top-rigid frame theory by Kilb, Lin, and Wilson,[5] in which the principal axes fixed to the frame were the reference axes of overall rotation of the molecule. This means that counter motion of the molecule to the internal rotation was neglected. This is an appropriate approximation for a molecule with a relatively heavy frame as compared with the top.

For CH_3NH_2, the frame NH_2 is lighter than the top CH_3, and the counter motion can not be neglected. The theory of rotation-torsion Hamiltonian of this molecule has been derived by many workers in the approximation of rigid semiasymmetric internal rotors.[6–9] Based on these works, especially on the one by Itoh[8], a revised method of vibrational corrections has been formulated in the present paper.

A correction has also been made to the expression of the n-matrix given in the appendix of Ref. 3. A transformation which projects the top-fixed coordinates onto the frame-fixed axes appears in the formulation. G and F matrices[10] are practically invariant under this transformation as assumed in Ref. 3, though it does not hold rigorously unless both the top and the frame have a common C_3 axis. However, the invariance of L matrix assumed at the same time is unacceptable.

Because of the near degeneracy of the E-type coordinates any L matrix obtained by an arbitrary rotation around the C_3 axis can be a set of eigenvectors of the vibrational equation. The assumed invariance of L means a choice among many equally valid sets.

In the calculation of n-matrix elements, evaluation of the derivative of l-matrix elements[11] with respect to the torsional angle is necessary. For this purpose the L matrix must be given as a function of the torsional angle. From the invariance of G and F alone, i.e. that of the vibrational secular equation, no answer to this question comes out. A more intuitive assumption has been introduced, and the formulation for calculating the n-matrix elements has been revised and described in the Appendix.

As a result, the method of the vibrational calculation employed in Ref. 3, in which the top and the frame were regarded as two independent molecules, has no special advantage. Therefore it has been abandoned and ordinary vibrational calculations of the GF matrix method has been employed.

The n-matrix has no effect on the vibrational corrections for the principal moments of inertia,[4] although the moments of inertia of the top around its axis are affected to a considerable extent. Most of the previously reported results of structure analyses are little affected by the present revision, because they have been obtained mainly from the principal moments of inertia.

Kinetic Energy and Vibrational Corrections

The motion of a methylamine-type molecule undergoing rotation and torsion is described by three angular velocities as discussed by Itoh.[8] The reference axes rotate by the angular velocity $\boldsymbol{\omega}$; the top, i.e. the methyl group, rotates around its C_3 axis by the angular velocity $\dot{\boldsymbol{\gamma}}$, and the molecule as a whole rotates by the angular velocity $\boldsymbol{\omega}_1$ so that the angular momentum associated with $\dot{\boldsymbol{\gamma}}$ may be canceled by the momentum of the counter motion which is associated with $\boldsymbol{\omega}_1$. The rotation of the reference axes is a constant of motion, and the corresponding total angular momenta give a set of good quantum numbers. These axes may be called the molecule-fixed axes, but do not coincide with the principal axes of the moments of inertia which are fixed to the frame, i.e., the amino group, and rotate by the angular velocity $\boldsymbol{\omega}+\boldsymbol{\omega}_1$. Several of the notations in the present paper are different from those of Ref. 8. The comparisons are given in Table 1.

By considering vibrational motions as well, the velocity vector of each atom is now expressed as

$$\boldsymbol{V}_i = (\boldsymbol{\omega}\times\boldsymbol{r}_i) + (\boldsymbol{\omega}_1\times\boldsymbol{r}_i)+(\dot{\boldsymbol{\gamma}}\times\boldsymbol{\sigma}_i) + \boldsymbol{v}_i, \tag{1}$$

where

$$\boldsymbol{v}_i = \dot{\boldsymbol{\rho}} - (\boldsymbol{\omega}_1\times\boldsymbol{\rho}_i) - (\dot{\boldsymbol{\gamma}}\times\boldsymbol{\varepsilon}_i), \tag{2}$$

for the i-th atom of the top, and

$$\boldsymbol{V}_j = (\boldsymbol{\omega}\times\boldsymbol{r}_j) + (\boldsymbol{\omega}_1\times\boldsymbol{r}_j) + \boldsymbol{v}_j, \tag{3}$$

where

$$\boldsymbol{v}_j = \dot{\boldsymbol{\rho}}_j - (\boldsymbol{\omega}_1\times\boldsymbol{\rho}_j), \tag{4}$$

for the j-th atom of the frame. Equations 1 and 3 are the revised expression for Eqs. 4 and 6 of Ref. 3. In the present work, however, the term for the translation of the center of gravity of the molecule is omitted from the beginning. The definitions of various symbols are summarized in Table 2.

The requirement that the angular momentum associated with $\dot{\boldsymbol{\gamma}}$ is canceled by the momentum associated with $\boldsymbol{\omega}_1$ is expressed as

$$C_2^0\dot{\boldsymbol{\gamma}} = -\boldsymbol{I}^0\boldsymbol{\omega}_1, \tag{5}$$

and therefore,

$$\boldsymbol{\omega}_1 = -(\boldsymbol{I}^0)^{-1}C_2^0\dot{\boldsymbol{\gamma}}. \tag{6}$$

where C_2 is the moment of inertia of the top around its axis and $\boldsymbol{I}$ is the tensor of the moments of inertia of the whole molecule. The superscript 0 indicates the values at the equilibrium configuration. By introducing a unit vector $\boldsymbol{\lambda}$ along $\dot{\boldsymbol{\gamma}}$, we have

$$\boldsymbol{\omega}_1 = -(\boldsymbol{I}^0)^{-1}C_2^0\boldsymbol{\lambda}\dot{\gamma} = \boldsymbol{\nu}\dot{\gamma}. \tag{7}$$

The mass-adjusted displacement vector can be expanded in terms of the vibrational normal coordinates Q_s by the use of the l-matrix[11] as

$$\sqrt{m_i}\boldsymbol{\rho}_i = \boldsymbol{l}_{is}Q_s, \tag{8}$$

where $\boldsymbol{l}_{is}$ is a vector with the components ($l_{is}^{(x)}$, $l_{is}^{(y)}$, $l_{is}^{(z)}$). The summation symbol over s is omitted by the convention that if a subscript appears only on one side of an equation twice or more in a term, the summation over it must be taken. Because of the possible dependence of $\boldsymbol{l}_{is}$ on Ω_1 and γ, the first term of Eq. 2 multiplied by $\sqrt{m_i}$, that is, the time derivative of Eq. 8 with respect to the reference axes, becomes

$$\sqrt{m_i}\dot{\boldsymbol{\rho}}_i = \boldsymbol{l}_{is}\dot{Q}_s + \frac{\mathrm{d}\boldsymbol{l}_{is}}{\mathrm{d}\Omega_1}\omega_1 Q_s + \frac{\mathrm{d}\boldsymbol{l}_{is}}{\mathrm{d}\gamma}\dot{\gamma}Q_s, \tag{9}$$

where Ω_1 is the virtual angle-variable corresponding to $\boldsymbol{\omega}_1$. It is easily conceived that

$$\frac{\mathrm{d}\boldsymbol{l}_{is}}{\mathrm{d}\Omega_1}\omega_1 = \boldsymbol{\omega}_1 \times \boldsymbol{l}_{is}, \tag{10}$$

since the $\boldsymbol{l}_{is}$ vector changes only its direction when the whole molecule rotates by $\boldsymbol{\omega}_1$. From Eqs. 8 and 10 we have

$$\frac{\mathrm{d}\boldsymbol{l}_{is}}{\mathrm{d}\Omega_1}\omega_1 Q_s = \sqrt{m_i}(\boldsymbol{\omega}_1\times\boldsymbol{\rho}_i), \tag{11}$$

and this term divided by $\sqrt{m_i}$ is canceled by the second term of Eq. 2. For ($\mathrm{d}\boldsymbol{l}_{is}/\mathrm{d}\gamma$), however, the situation is not so simple since the configuration of the molecule changes by the torsional motion.

The third term of Eq. 2 can be rewritten as

$$\dot{\boldsymbol{\gamma}} \times \boldsymbol{\varepsilon}_i = \dot{\boldsymbol{\gamma}} \times \boldsymbol{\rho}_i - \dot{\boldsymbol{\gamma}} \times \Delta\boldsymbol{g}, \tag{12}$$

where $\Delta\boldsymbol{g}$ is the displacement vector of the center of gravity of the top and is given in terms of the normal coordinates as

$$\Delta\boldsymbol{g} = M_{\mathrm{T}}^{-1}\boldsymbol{L}_{\mathrm{T}s}Q_s, \tag{13}$$

Table 1. Comparison of the Notations

	This work	Ref. 8
Angular velocity of the reference axes	$\boldsymbol{\omega}$	$\boldsymbol{\omega}_2$
Angular velocity of the frame-fixed axes	$\boldsymbol{\omega}+\boldsymbol{\omega}_1$	$\boldsymbol{\omega}$
Angular velocity of the top relative		
to the frame: scalar representation	$\dot{\gamma}$	$\dot{x}$
vector representation	$\dot{\boldsymbol{\gamma}}$	
Angular velocity of the counter motion		
of the whole molecule	$\boldsymbol{\omega}_1$	$\boldsymbol{\omega}_1$
Vector relating $\dot{\boldsymbol{\gamma}}$ to $\boldsymbol{\omega}_1$ (Eq. 7)	$\boldsymbol{\nu}$	$\boldsymbol{\lambda}$
Unit vector along the top axis	$\boldsymbol{\lambda}$	$\boldsymbol{c}/C_2$

Table 2. Definitions of Symbols

$\boldsymbol{r}_i$, $\boldsymbol{r}_j$	Instantaneous position vector of an atom; the origin is the center of gravity of the molecule.
$\boldsymbol{\rho}_i$, $\boldsymbol{\rho}_j$	Displacement vector: $\boldsymbol{r}_i-\boldsymbol{r}_i^0$, $\boldsymbol{r}_j-\boldsymbol{r}_j^0$ [a]
$\boldsymbol{\sigma}_i$	Instantaneous position vector of an atom of the top; the origin is the center of gravity of the top.
$\boldsymbol{\varepsilon}_i$	Displacement vector: $\boldsymbol{\sigma}_i-\boldsymbol{\sigma}_i^0$ [a]

a) The superscript 0 indicates the equilibrium values.

with M_{T}, the mass of the top, and

$$\boldsymbol{L}_{\mathrm{T}s} = \sqrt{m_i}\boldsymbol{l}_{is}. \tag{14}$$

By means of Eqs. 1, 2 and Equations derived so far, we have

$$\begin{aligned}\sqrt{m_i}\boldsymbol{V}_i &= \sqrt{m_i}(\boldsymbol{\omega}\times\boldsymbol{r}_i) + \sqrt{m_i}(\boldsymbol{\omega}_1\times\boldsymbol{r}_i) + \sqrt{m_i}(\dot{\boldsymbol{\gamma}}\times\boldsymbol{\sigma}_i)\\ &\quad + \boldsymbol{l}_{is}\dot{Q}_s + \frac{\mathrm{d}\boldsymbol{l}_{is}}{\mathrm{d}\gamma}\dot{\gamma}Q_s - \dot{\boldsymbol{\gamma}}\times\boldsymbol{l}_{is}Q_s\\ &\quad + \dot{\boldsymbol{\gamma}}\times\boldsymbol{L}_{\mathrm{T}s}Q_s\sqrt{m_i}M_{\mathrm{T}}^{-1}\\ &= \sqrt{m_i}(\boldsymbol{\omega}\times\boldsymbol{r}_i) + \sqrt{m_i}(\boldsymbol{\nu}\times\boldsymbol{r}_i)\dot{\gamma}\\ &\quad + \sqrt{m_i}(\boldsymbol{\lambda}\times\boldsymbol{\sigma}_i)\dot{\gamma} + \boldsymbol{l}_{is}\dot{Q}_s + \boldsymbol{n}_{is}\dot{\gamma}Q_s,\end{aligned} \tag{15}$$

for the *i*-th atom of the top, where

$$\boldsymbol{n}_{is} = \frac{\mathrm{d}\boldsymbol{l}_{is}}{\mathrm{d}\gamma} - \boldsymbol{\lambda}\times\boldsymbol{l}_{is} + \sqrt{m_i}M_{\mathrm{T}}^{-1}\boldsymbol{\lambda}\times\boldsymbol{L}_{\mathrm{T}s}. \tag{16}$$

Similarly, Eq. 3 for the *j*-th atom of the frame is transformed to

$$\sqrt{m_j}\boldsymbol{V}_j = \sqrt{m_j}(\boldsymbol{\omega}\times\boldsymbol{r}_j) + \sqrt{m_j}(\boldsymbol{\nu}\times\boldsymbol{r}_j)\dot{\gamma} + \boldsymbol{l}_{js}\dot{Q}_s + \boldsymbol{n}_{js}Q_s\dot{\gamma}, \tag{17}$$

where

$$\boldsymbol{n}_{js} = \frac{\mathrm{d}\boldsymbol{l}_{js}}{\mathrm{d}\gamma}. \tag{18}$$

The expression for the kinetic energy T can now be obtained from Eqs. 15 and 17, and after simplification by Eckart's and Sayvetz's conditions,[12–14] as

$$\begin{aligned}2T &= (\sqrt{m_i}\boldsymbol{V}_i)^2 + (\sqrt{m_j}\boldsymbol{V}_j)^2\\ &= \boldsymbol{\omega M\omega} + 2\boldsymbol{\omega\zeta}_{ss'}Q_s\dot{Q}_{s'} + \dot{Q}_s\dot{Q}_s.\end{aligned} \tag{19}$$

In Eq. 19 the vectors $\boldsymbol{\omega}$ and $\boldsymbol{\zeta}$ are extended to include $\dot{\gamma}$ and $\zeta_{ss'}^{(\gamma)}$ as the fourth component, i.e., $\boldsymbol{\omega}=(\omega_x, \omega_y, \omega_z, \dot{\gamma})$ and $\zeta_{ss'}=(\zeta_{ss'}^{(x)}, \zeta_{ss'}^{(y)}, \zeta_{ss'}^{(z)}, \zeta_{ss'}^{(\gamma)})$. The expression is formally the same as that for the well known vibration-rotation energy of ordinary molecules,[10] except that the ordinary three-dimensional expression is extended to the four-dimensional one.

Among the components of the $\boldsymbol{M}$-tensor, $M_{\alpha\beta}(\alpha,\beta=x,y,z)$ are the ordinary instantaneous moments of inertia $\boldsymbol{I}$ with respect to the reference axes. The other components are,

$$\begin{aligned}M_{\gamma\gamma}(=U) &= \boldsymbol{\nu I\nu} + m_i\{\boldsymbol{\sigma}_i^2-(\boldsymbol{\lambda}\cdot\boldsymbol{\sigma}_i)^2\}\\ &\quad + 2m_i\{(\boldsymbol{\lambda}\cdot\boldsymbol{\nu})\boldsymbol{\sigma}_i^2-(\boldsymbol{\lambda}\cdot\boldsymbol{\sigma}_i)(\boldsymbol{\nu}\cdot\boldsymbol{\sigma}_i)\}\\ &\quad + 2\boldsymbol{\lambda}\cdot(\boldsymbol{\Lambda}_{is}\times\boldsymbol{n}_{is})Q_s^2 + 2\boldsymbol{\nu}\cdot(\boldsymbol{l}_{is}\times\boldsymbol{n}_{is})Q_s^2\\ &\quad + 2\boldsymbol{\nu}\cdot(\boldsymbol{l}_{js}\times\boldsymbol{n}_{js})Q_s^2 + \boldsymbol{n}_{is}^2Q_s^2\\ &\quad + \boldsymbol{n}_{js}^2Q_s^2 - 2\boldsymbol{\nu}\cdot(\boldsymbol{\lambda}\times\boldsymbol{L}_{\mathrm{R}s})Q_s,\end{aligned} \tag{20}$$

where

$$\boldsymbol{\Lambda}_{is} = \boldsymbol{l}_{is} - \sqrt{m_i}M_{\mathrm{T}}^{-1}\boldsymbol{L}_{\mathrm{T}s}, \tag{21}$$

and

$$\boldsymbol{L}_{\mathrm{R}s} = \sqrt{m_i}(\boldsymbol{\sigma}_i^0\times\boldsymbol{\Lambda}_{is}). \tag{22}$$

And the cross terms are

$$\begin{aligned}M_{\alpha\gamma} &= m_i\{\nu_\alpha\boldsymbol{r}_i^2-(\boldsymbol{r}_i)_\alpha(\boldsymbol{\nu}\cdot\boldsymbol{r}_i)\} + m_i\{\lambda_\alpha\boldsymbol{\sigma}_i^2 - (\boldsymbol{\sigma}_i)_\alpha(\boldsymbol{\lambda}\cdot\boldsymbol{\sigma}_i)\}\\ &\quad + m_j\{\nu_\alpha\boldsymbol{r}_j^2-(\boldsymbol{r}_j)_\alpha(\boldsymbol{\nu}\cdot\boldsymbol{r}_j)\}\\ &\quad + (\boldsymbol{l}_{is}\times\boldsymbol{n}_{is})_\alpha Q_s^2 + (\boldsymbol{l}_{js}\times\boldsymbol{n}_{js})_\alpha Q_s^2 - (\boldsymbol{\lambda}\times\boldsymbol{L}_{\mathrm{R}s})_\alpha Q_s.\end{aligned} \tag{23}$$

$$(\alpha=x,\ y,\ z)$$

In Eqs. 20 and 23 the terms of $Q_sQ_{s'}$ are omitted because they will vanish when the averaging over the vibrational state is performed. Note that for a vibrationless state ($Q_s=0$), Eq. 20 reduces to $C_2-\boldsymbol{\nu I\nu}$ and Eq. 23 to 0, to become identical with the expression given by Eq. 7 of Ref. 8, $\boldsymbol{\omega}-\boldsymbol{\lambda}\dot{x}$ in Ref. 8 being replaced by the $\boldsymbol{\omega}$ in the present work.

The expression for $\zeta_{ss'}$ are,

$$\zeta_{ss'}^{(\alpha)} = (\boldsymbol{l}_{is}\times\boldsymbol{l}_{is'})_\alpha + (\boldsymbol{l}_{js}\times\boldsymbol{l}_{js'})_\alpha,\quad (\alpha=x,\ y,\ z) \tag{24}$$

and

$$\begin{aligned}\zeta_{ss'}^{(\gamma)} &= \boldsymbol{\lambda}\cdot(\boldsymbol{\Lambda}_{is}\times\boldsymbol{l}_{is'}) + \frac{1}{2}(\boldsymbol{n}_{is}\boldsymbol{l}_{is'}+\boldsymbol{n}_{is'}\boldsymbol{l}_{is})\\ &\quad + \frac{1}{2}(\boldsymbol{n}_{js}\boldsymbol{l}_{js'}+\boldsymbol{n}_{js'}\boldsymbol{l}_{js})\\ &\quad + \boldsymbol{\nu}\cdot(\boldsymbol{l}_{is}\times\boldsymbol{l}_{is'}+\boldsymbol{l}_{js}\times\boldsymbol{l}_{js'}).\end{aligned} \tag{25}$$

The procedure of transforming Eq. 19 to the quantum mechanical Hamiltonian and the method of numerical calculation to obtain vibrational corrections for $\boldsymbol{I}$ and U, are formally the same as given in Ref. 3, and are not reproduced here. Numerical values of the vibrational corrections for the configuration of $\gamma=0$ are listed in Table 3 as ΔI_{vib}. The force constants determined by Hamada et al.[15] were used in the numerical calculations.

Table 3. Vibrational and Torsional Corrections for the Moments of Inertia of CH_3NH_2 (in uÅ² units)

	$I^{(\mathrm{eff})\,\mathrm{a)}}$	ΔI_{tor}	ΔI_{vib}	$I^{(z)}$
A	22.331_6	-0.011_4	0.084_8	22.405_0
B	23.279_8	0.012_3	0.061_1	23.353_2
C	4.899_7	—	0.035_1	4.934_8
D	0.106_5	—	-0.001_3	0.105_2
U	1.114_7	—	0.006_6	1.121_3
$C_2(=I_\gamma)$	3.184_0 b)			3.211_3 b)

a) Effective values by Takagi and Kojima.[17] Conversion factor 505376 MHz·uÅ² was used. b) Obtained by solving Eq. 31.

Torsional Average

It seems that Itoh[8] did not pay much attention to the difference among the reference axes and the frame-fixed axes. His Hamiltonian (Eq. 11 of Ref. 8) is actually expressed in terms of the angular momentum conjugate to the angular velocity of the frame-fixed axes. In fact his expression for kinetic energy, the unnumbered equation before the Eq. 11, is easily shown to be equivalent to Eq. 3 by Hecht and Dennison.[6]

Itoh's skillful presentation succeeded in introducing the coupling between the torsional motion and the rotational quantum number K without a discussion on the boundary conditions for the wave function.[16] However his formulation did not include the additional rotation of the newly chosen axes around the axis in the direction of $\boldsymbol{\omega}_1$. This rotation would bring about the dependence of the rotational constants on the torsional angle γ, as is fully described by Hecht and Dennison.[6]

Because of the γ-dependence of the rotational constants, the effective values of the rotational constants determined by the analysis of microwave spectra, e.g. those by Takagi and Kojima[17], become slightly different from those values at γ=0. In the case of a methylamine-type molecule, this effect must be also corrected for in addition to the vibrational corrections.

The rotational constants tensor can be expressed as

$$\begin{pmatrix} b & 0 & 0 \\ 0 & c & d \\ 0 & d & a \end{pmatrix}, \tag{26}$$

with respect to the reference axes and for γ=0. The γ-dependence is derived by Hecht and Dennison[6] as

$$\begin{pmatrix} b\cos^2\nu\gamma + c\sin^2\nu\gamma & (b-c)\sin\nu\gamma\cos\nu\gamma & -d\sin\nu\gamma \\ (b-c)\sin\nu\gamma\cos\nu\gamma & b\sin^2\nu\gamma + c\cos^2\nu\gamma & d\cos\nu\gamma \\ -d\sin\nu\gamma & d\cos\nu\gamma & a \end{pmatrix}. \tag{27}$$

By expanding each element by γ to the order of γ^2 and taking average over γ, we find

$$\begin{aligned} b^{\mathrm{eff}} &= b - \Delta, \\ c^{\mathrm{eff}} &= c + \Delta, \end{aligned} \tag{28}$$

where

$$\Delta = (b-c)\nu^2\langle\gamma^2\rangle. \tag{29}$$

Corrections to other terms are minor.

The relation between b^{eff} and b (also c^{eff} and c) can be transferred to the relation between the moment of inertia A^{eff} and A (B^{eff} and B) with respect to the initially chosen conventional axes as

$$A = A^{\mathrm{eff}}\left(1-\frac{\Delta}{b}\right), \quad B = B^{\mathrm{eff}}\left(1+\frac{\Delta}{c}\right). \tag{30}$$

Numerical values for these torsional corrections are shown in Table 3 as ΔI_{tor}. The value of $\langle\gamma^2\rangle$ was estimated from the torsional frequency in the harmonic approximation.

The symbols A, B, C, etc. are usually used for rotational constants. However in the case of methylamine they are customarily used for the moments of inertia with respect to the conventional x, y, z axes; z axis is chosen parallel to the top axis and z-y plane is the symmetry plane of the molecule at γ=0. The components of the inertia tensor of this coordinate system are denoted as $I_{xx}=A$, $I_{yy}=B$, $I_{zz}=C$ and $I_{yz}=-D$. The rotational constants a, b, c, etc. are related to A, B, C, etc. as in Eq. 27 of Ref. 8 or in Table XII of Ref. 17.

Since the results of analysis of microwave spectra are reported in terms of A, B, C, etc., the vibrational and torsional corrections evaluated in the present work are reported in terms of the values applicable to A, B, C, etc. The observed effective values were first corrected for the torsional effect to yield the effective values for the configuration of γ=0. Then the vibrational corrections evaluated for γ=0 were applied, and the values of A, B, C, etc. corresponding to the zero-point average structure were obtained, as summarized in Table 3.

Zero-Point Average Structure

The moments of inertia for methylamine and its deuterated species CD_3ND_2 and CH_3ND_2 were reported by Takagi and Kojima.[17] The torsional and vibrational corrections as discussed in the preceding sections were applied to the reported values and the moments of inertia $I^{(z)}$ for the zero-point average structure were obtained as shown in Table 3 and 4. The zero-point moments of the methyl top around its axis, $C_2^{(z)}$ or $I_\gamma^{(z)}$, were also obtained from $U^{(z)}$ by solving the equation,

$$U^{(z)} = \frac{C_2^{(z)}[B^{(z)}(C^{(z)}-C_2^{(z)})-(D^{(z)})^2]}{B^{(z)}C^{(z)}-(D^{(z)})^2}. \tag{31}$$

The zero-point average structure, i.e. a set of structural parameters which give a best fit to $I^{(z)}$, was determined. The structural parameters are the

Table 4. Zero-Point Moments of Inertia for CD_3ND_2 and CH_3ND_2 (in uÅ^2 units)

	CD_3ND_2	CH_3ND_2
A	30.594_7	24.984_3
B	32.536_1	26.967_4
C	9.740_8	6.582_5
D	1.000	0.959_3
U	2.187_9	1.635_7
C_2	6.380_4	3.18—3.37

distances C-N, C-H, N-H, and the angles ∠HCH, ∠HNH, ∠CNH and the tilt of the methyl top. For the deuterated species, the parameters may be slightly different from those of the parent species. The difference (deuterated-parent) is called the isotope effect. The isotope effects in the C-N and C-H distances were fixed at the calculated values by assuming the Morse parameter a to be 2.0 Å^{-1}.[1,2] The isotope effects in N-D and ∠DND of CH_3ND_2 were assumed to be equal to those of CD_3ND_2. The isotope effects in ∠HCH and the tilt of CH_3ND_2 were assumed to be zero.

For the C-N distance, the result of electron diffraction[18] was transferred. Otherwise a rather wide range of structural parameters would have been permissible. The r_g-r_z correction for the C-N distance was evaluated to be 0.0010 Å which includes the centrifugal distortion 0.0005 Å, by assuming the Morse parameter a to be 2.0 Å^{-1}.

The results are summarized in Table 5. The uncertainties in parentheses correspond to the uncertainty of the C-N distance, ±0.003 Å and the assumed uncertainties of $I^{(\omega)}$, ±0.01 uA^2. The C_2 of CH_3ND_2 was not used, because in this case the two solutions of the parabolic equation (Eq. 31) become very close and the uncertainties of B, C, and U are amplified and lead to a very uncertain value of C_2. It was attempted to adjust also the isotope effects in ∠DND and the tilt of CH_3ND_2. A better fit was obtained but the results were physically unacceptable because the values of the isotope effects were in contradiction to the naturally expected trend that the isotope effects for this species must be in between those of CD_3ND_2 and zero.

The determined N-H distance and its isotope effect are in agreement with those of ammonia by Morino et al.[19]; r_z 1.024(1) Å and δ(N-D) −0.002(2) Å. The HNH angle is smaller than that of ammonia 107.3(1)°. This result is examined as follows.

By considering the wagging-inversion potential determined by Tsuboi et al.[20] the zero-point average of the wagging-inversion normal coordinate Q_6 was estimated. From the L^{-1}-matrix elements it was found that major contribution to Q_6 came from the symmetry coordinates S_4, the C-N stretching, and S_6, the amino-wagging given by

$$S_6 = \frac{1}{\sqrt{3}}(\Delta\beta_1+\Delta\beta_2+\Delta\alpha), \tag{32}$$

where β_1 and β_2 are the two CNH angles and α is the HNH angle. The zero-point average of S_4 was estimated by the use of the mean square amplitude and the Morse parameter, and $\langle S_6\rangle_0$ was obtained from $\langle Q_6\rangle_0$. Then the zero-point average of $\Delta\beta_1+\Delta\beta_2+\Delta\alpha$ was evaluated to be 2.0°. The isotope effect for this sum of angles was then estimated to be −0.7°. The corresponding quantity from Table 5 becomes −1.2±0.8°, which is comparable to the estimated value from the wagging-inversion potential.

Table 5. Zero-Point Average Structure of Methylamine

	r_z, φ_z[a)]	$\delta_{CD_3ND_2}$[b)]	$\delta_{CH_3ND_2}$[b)]
C-N	1.471(3)[c)]	[−0.000$_4$][d)]	[−0.000$_2$][d)]
C-H	1.101(3)	[−0.002][d)]	[0.0][e)]
N-H	1.019(6)	−0.003(3)	[−0.003][e)]
∠HCH	108.4(5)	−0.2(1)	[0.0][e)]
∠HNH	106.0(6)	0.4(2)	[0.4][e)]
∠CNH	111.5(7)	−0.8(3)	−0.6(3)
θ[f)]	2.97(4)	0.00(3)	[0.00][e)]

a) Distance in Å and angles in degrees units. 1Å=100 pm. Uncertainties in parentheses are the estimated limits of error. b) Isotope effects: deuterated−parent. c) The result of electron diffraction.[18] d) Calculated. e) Assumed. f) Tilt angle of the methyl group away from the hydrogen atoms of the amino group.

It is noted that the isotope effect for ∠CNH is negative while that for ∠HNH is positive. This suggests that the initial stage of the wagging-inversion motion is composed of a decrease in ∠HNH and an increase of ∠CNH, showing a repulsive effect of the methyl group. A slightly smaller value for the HNH angle of methylamine as compared with that for ammonia is consistent with this view of the repulsive interaction.

Appendix

n-Matrix Elements. In methylamine molecule each normal mode is well localized to the corresponding symmetry coordinate. Thus an assumption was made that the E-type symmetry coordinates change direction as the methyl group rotates relative to the frame, and the other types of symmetry coordinates are invariant. Then we have for the displacement vector of the i-th atom of the top,

$$\boldsymbol{\rho}_i = \begin{pmatrix} \mathfrak{R}(\gamma) & \\ & 1 \end{pmatrix}\{\boldsymbol{A}_{ir}L_{rs}Q_s+\boldsymbol{A}_{it}L_{ts}Q_s\} + \boldsymbol{A}_{iq}L_{qs}Q_s, \tag{A. 1}$$

where the notation follows Ref. 3. The γ-dependence of $\boldsymbol{l}_{is}$ is explicitly given by Eq. A.1, and the n-matrix elements are obtained by the definition given by Eq. 16 simply as

$$\boldsymbol{n}_{is} = -\sqrt{m_i}\boldsymbol{\lambda} \times \boldsymbol{A}_{iq}L_{qs} + \sqrt{m_i}M_T^{-1}\boldsymbol{\lambda} \times \boldsymbol{L}_{Ts}. \tag{A. 2}$$

Note that the γ-dependent terms in the first and the second term of Eq. 16 cancel each other.

Similarly for the j-th atom of the frame,

$$\boldsymbol{\rho}_j = \boldsymbol{A}_{jr}L_{rs}Q_s + \boldsymbol{A}_{jt}\mathfrak{R}(\gamma)L_{ts}Q_s + \boldsymbol{A}_{jq}L_{qs}Q_s, \tag{A. 3}$$

and by Eq. 18 we have

$$\boldsymbol{n}_{js} = \sqrt{m_j}\boldsymbol{A}_{jt}\frac{d\mathfrak{R}(\gamma)}{d\gamma}L_{ts}. \tag{A. 4}$$

The derivative is given as

$$\frac{\mathrm{d}\mathscr{R}(\gamma)}{\mathrm{d}\gamma}=\begin{pmatrix}-\sin\gamma & -\cos\gamma\\ \cos\gamma & -\sin\gamma\end{pmatrix}, \tag{A. 5}$$

and for the configuration at $\gamma=0$,

$$\left(\frac{\mathrm{d}\mathscr{R}(\gamma)}{\mathrm{d}\gamma}\right)_{\gamma=0}=\begin{pmatrix}0 & -1\\ 1 & 0\end{pmatrix}. \tag{A. 6}$$

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