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Internal Rotation Spectra of Methylamines. I. CH_3NH_2 and CH_3ND_2

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Infrared absorption spectra of methylamine (CH_3NH_2) and methylamine-d_2 (CH_2ND_2) have been observed in the gaseous states in the region of 500–80 cm^{-1} (20–125 μ). A complicated, irregular structure is observed all over the spectral region, which is attributable to the internal rotation coupled with an over-all rotation of the molecule. The internal and over-all rotation energy levels were calculated on the basis of the previously determined molecular parameters and a potential function for the internal rotation (x) with the form of $V(x)=\frac{1}{2}H_3(1\text{-}\cos3x)+\frac{1}{2}H_6(1\text{-}\cos6x)$. The frequencies and intensities for radiative transitions between these energy levels were then calculated. On comparing the results of the calculation with the observed spectra, it has been found that we need to revise the values of the potential constants and one of the molecular constants C_2 (the moment of inertia of the methyl group around its own symmetry axis) from what were determined previously with microwave data.The new set of values is $H_3=683.2$ cm^{-1}, $\mathrm{H}_6=-2.0$ cm^{-1}, and $C_2=5.273\times10^{-40}$ $g\cdot cm^2$ for CH_3NH_2. For CH_2ND_2, a set of values: $H_3=671.6$ cm^{-1}, $H_6=0$, and $C_2=5.273\times10^{-40}$ $g\cdot cm^2$, has been proposed. The band center of the fundamental band ($n=1\leftarrow0$) is found to be at 263.9 cm^{-1} for CH_3NH_2 and at 224.5 cm^{-1} for CH_3ND_2.

I. INTRODUCTION

Internal rotation in the methylamine molecule has been investigated mostly by the microwave method so far. The microwave absorptions of CH_3NH_2 were observed and analyzed by Shimoda, Nishikawa, and Itoh,[1–3] those of CD_3ND_2 by Lide and Kivelson,[4,5] and quite recently those of CH_3ND_2 by Takagi and Kojima.[6] These investigators determined the height of the hindering barrier in the internal rotation potential to be 691.1 cm^{-1} for CH_3NH_2,[2,3] 684.7 cm^{-1} for CD_3ND_2,[4] and about 690 cm^{-1} for CH_3ND_2.[6] The microwave spectroscopy provided very detailed and precise information of the energy levels situated around the bottom of the potential well, from which the molecular parameters and potential constants were evaluated. The positions of these energy levels, however, are less sensitive to the shape of the potential of the internal rotation and to the moment of inertia of the internal rotor than the positions of the energy levels situated near the midpoint of the potential hill. The information of the latter energy levels is obtained by an analysis of the far-infrared spectra, and, therefore, it is desirable to extend the examination into this spectral region.

The purpose of this paper is to report the results of our observations of the infrared absorption spectra of CH_3NH_2 and CH_3ND_2 in the 500–80-cm^{-1} region, and to present the result of an analysis of these spectra as well as the values of some molecular constants derived by the analysis.

Brief accounts of some of the results of this investigation have already appeared elsewhere.[7,8]

II. EXPERIMENTAL

CH_3NH_2 gas was prepared by adding saturated aqueous solution of methylammonium chloride, purified by recrystallization from ethanol, on solid sodium hydroxide. The gas, thus prepared, was found to have only a trace of ammonia as an impurity. The sample was trapped by dry ice and acetone and then placed in a gas cell, with two polyethylene windows, a pathlength of 10 cm, and potassium hydroxyde as a desiccant.

CH_3ND_2 gas was prepared by adding D_2O solution of methylammonium chloride-d_3 (CH_3ND_3Cl) on solid sodium deuteroxyde (NaOD). Here, CH_3ND_3Cl was prepared by dissolving undeuterated methylammonium chloride into D_2O, by removing the solvent in vacuum, and by repeating this procedure several times. NaOD was obtained by the reaction of metallic sodium with D_2O at a lower temperature. Before placing the CH_3ND_2 sample in a gas cell (10 cm), D_2O gas was filled in the cell several times so that the adsorbed gas on the cell wall was completely deuterated. As a desiccant, metallic sodium was placed in the cell. The purity of the sample, when filled in the gas cell, was estimated to be 93%–95% by an infrared examination. The main impurity was found to be CH_3NHD, and practically no contamination of CH_3NH_2, ND_3, nor ND_2H were found.

Infrared absorption measurements were made in the

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[2] T. Itoh, J. Phys. Soc. Japan **11**, 264 (1956).

[3] T. Nishikawa, J. Phys. Soc. Japan **12**, 668 (1957).

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[7] M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, Symposium on Infrared and Raman Spectra, Chemical Society of Japan, Tokyo, November, 20–21, 1964, Paper 20A-7; M. Tsuboi, K. Tamagake, and A. Y. Hirakawa, U.S.-Japan Cooperative Seminar on Far-Infrared Spectroscopy, The Ohio State University, Columbus, Ohio, September 15–17, 1965.

[8] M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, Proc. Japan Acad. **42**, 795 (1966).

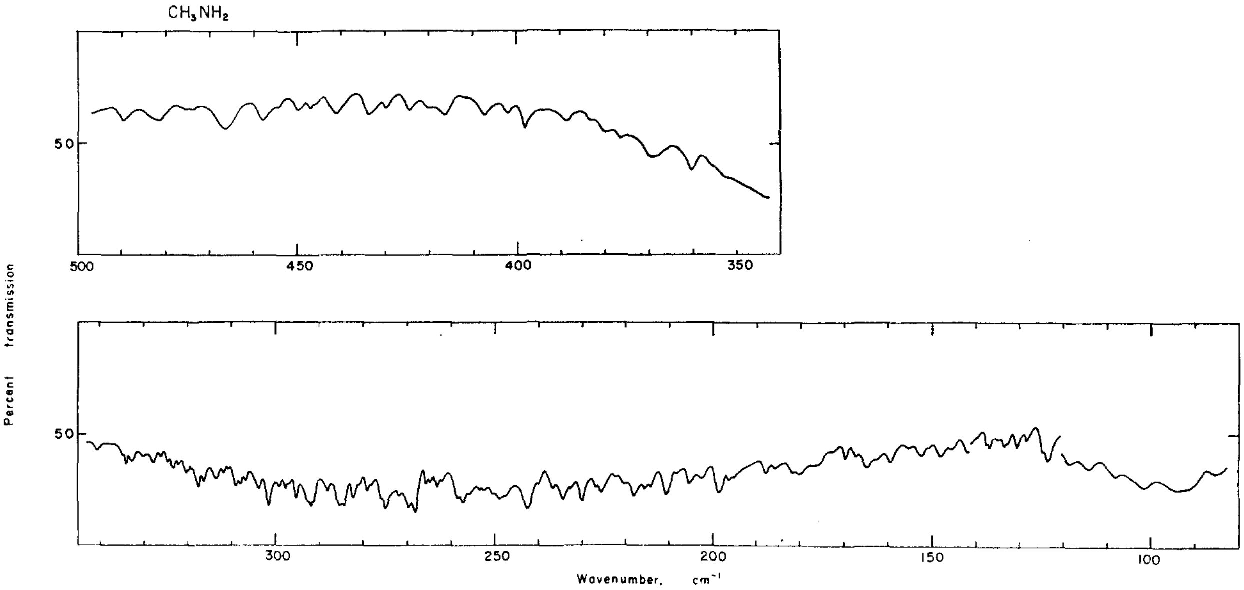

FIG. 1. Infrared absorption spectrum of methylamine (CH_3NH_2) in gaseous state in the 500–80-cm^{-1} region. Pressure, about 100 mm Hg. Path length, 10 cm.

500–80-cm^{-1} region by the use of a Hitachi FIS-1 vacuum spectrometer in the Faculty of Science, University of Tokyo. The results are shown in Figs. 1 and 2. The resolution of the instrument was about 1 cm^{-1}, and every detail given in the figures is reproducible and, therefore, significant. The wavenumber calibration was made by the use of known absorption lines of water vapor.[9]

III. GENERAL FEATURE OF THE SPECTRA AND ITS INTERPRETATION

As may be seen in Fig. 1, CH_3NH_2 shows a complicated, irregular structure in the spectral region in question. An absorption maximum in the envelope of this structure is situated at about 270 cm^{-1}. The absorptions in this spectral region are primarily attributable to the torsional oscillation of the molecule, whose fundamental frequency is considered to be around 270 cm^{-1}. The vibrational energy with this frequency, however, is comparable to the thermal energy kT. In addition, the torsional potential is anharmonic. Therefore, there should appear, in this spectral region, not only the fundamental band ($n=1\leftarrow0$, where n is the vibrational quantum number of the torsional oscillation) but also hot bands ($n=2\leftarrow1$, $3\leftarrow2$, etc.) and overtone bands ($n=2\leftarrow0$, $3\leftarrow1$, etc.) with appreciable intensities. The hot bands are considered to be situated in the frequency region lower than 270 cm^{-1}, whereas the overtone bands are expected in the higher frequency region, 500–350 cm^{-1}. Each of these bands would have a complex fine structure, because every vibration–rotation line in it should split into a few components due to the internal rotation. The amount of the splitting here should depend upon the rotational quantum number K as well as the vibrational quantum number n of the energy levels with which each vibration–rotation line is concerned.

The spectrum of CH_3ND_2, on the other hand, is much simpler. In the 280–190-cm^{-1} region, there is an absorption band with a fine structure somewhat similar to that of a perpendicular band of a rigid symmetric-top molecule with its band center at about 225 cm^{-1}. The absorptions in the overtone region, 320–280 cm^{-1}, are weaker. This is understandable because the torsional energy levels of CH_3ND_2 should be lower in the potential well than the corresponding levels of CH_3NH_2, and hence the torsional oscillation may be more harmonic in the former than that in the latter. The hot bands in the 190–80-cm^{-1} region, however, have again complicated fine structures.

IV. THEORETICAL

In considering the coupling of the internal rotation and the over-all rotations of the methylamine molecule, we adopt the so-called internal axis method[10] rather than the principal axes method.[10] The former method was developed by Dennison and his collaborators[11–14]

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[11] J. S. Koehler and D. M. Dennison, Phys. Rev. **57**, 1004 (1940).

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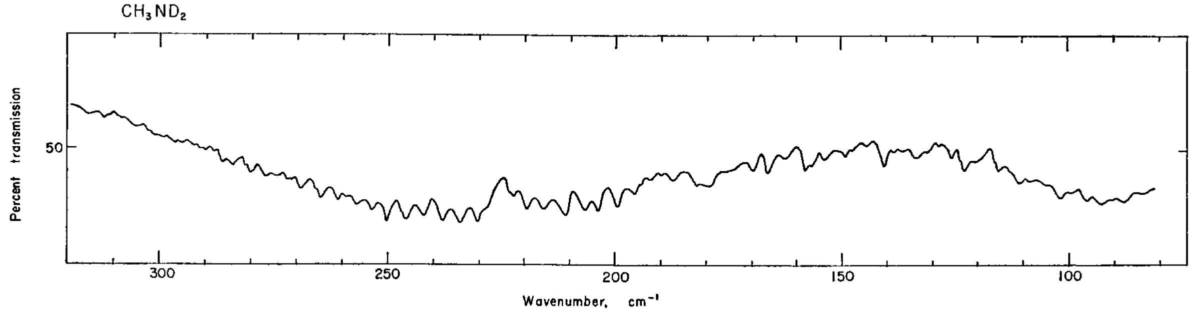

FIG. 2. Infrared absorption spectrum of methylamine-d_2 (CH_3ND_2) in gaseous state in the 320–80-cm^{-1} region. Pressure, about 100 mm Hg, path length, 10 cm.

and also by Itoh[2]; this method is more suitable than the latter for a case where the moment of inertia of the internal rotor is small and the potential barrier for the internal rotation is low as in the case of methylamine.

A. Internal and Over-all Rotation Energy

We assume here that methylamine molecule has only one internal freedom, i.e., internal rotation. Let us define a rectangular coordinate system (ξ, η, ζ) fixed on the amino group of the molecule: the origin is placed at the center of gravity of the methylamine molecule, the ξ axis is directed perpendicular to the symmetry plane of the molecule, and the ζ axis is directed parallel to the symmetry axis of the methyl group. Let the elements of the inertia tensor **I** be denoted as

$$\mathbf{I}=\begin{array}{c}\xi\\ \eta\\ \zeta\end{array}\begin{pmatrix}A & 0 & 0\\ 0 & B & -D\\ 0 & -D & C\end{pmatrix}. \qquad (1)$$

Let the orientation of the ξ, η, and ζ axes with respect to the space-fixed coordinate system (X, Y, Z) be given by the Eulerian angles ϕ, ψ, and θ. We denote by x and ϕ_2 the angles of rotation of the methyl group around its symmetry axis with respect to the amino group and with respect to the space-fixed (X, Y, Z) system, respectively. Then,

$$x=\phi-\phi_2. \qquad (2)$$

We also denote by C_2 the moment of inertia of the methyl group around its own symmetry axis, and define C_1 as

$$C_1=C-C_2. \qquad (3)$$

The Hamiltonian for the present system is expressed by the sum of an internal rotation Hamiltonian $\mathbf{H}_{ir}$ and a rotation Hamiltonian $\mathbf{H}_r$:

$$\mathbf{H}=\mathbf{H}_{ir}+\mathbf{H}_r. \qquad (4)$$

As was shown by Itoh,[2] the internal rotation Hamiltonian $\mathbf{H}_{ir}$ is expressed as

$$\mathbf{H}_{ir}=(\hbar^2/2U)[(d/idx)+\lambda K]^2+V(x), \qquad (5)$$

where

$$U=C_2(BC_1-D^2)/(BC-D^2), \qquad (6)$$

and

$$\lambda=C_2(B^2+D^2)^{1/2}/(BC-D^2). \qquad (7)$$

The potential energy $V(x)$ is given by

$$V(x)=\sum_N \tfrac{1}{2}H_{3N}(1-\cos 3Nx), \qquad (8)$$

where $N=1, 2, \cdots$. In Eq. (5),

$$K=0, 1, 2, \cdots, \qquad (9)$$

is the rotational quantum number so that $K\hbar$ is the eigenvalue of the angular momentum around an axis

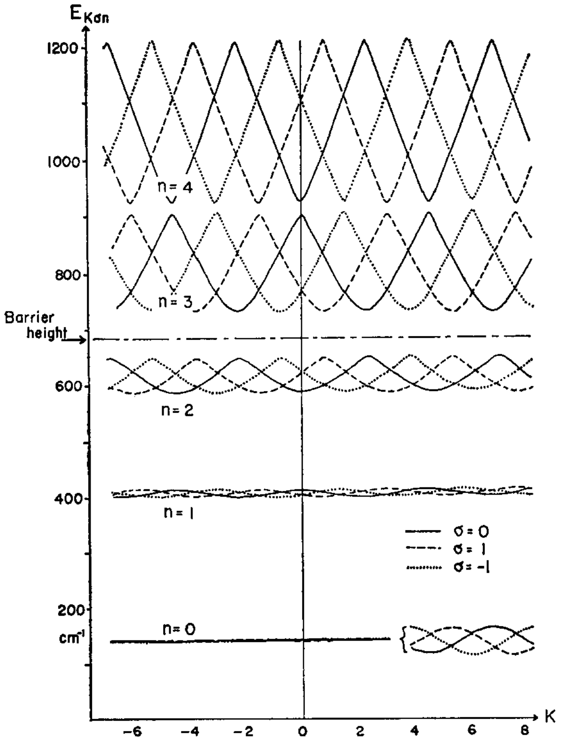

FIG. 3. Internal rotation energy $E_{K\sigma n}$ of methylamine (CH_3NH_2) calculated on an assumption that $H_3=691.1$ cm^{-1}, $H_6=H_9=\cdots=0$, $C_2=5.331\times10^{-40}$ g·cm^2, and other molecular constants are equal to what Itoh[2] gave.

ζ', which is parallel to a vector $\boldsymbol{\lambda}$:

$$\boldsymbol{\lambda}^T=[0,\ DC_2/(BC-D^2),\ BC_2/(BC-D^2)], \tag{10}$$

where ^{T} means transpose.

When $V(x)=0$, $\mathbf{H}_{ir}$ is the Hamiltonian for the free rotation, and e^{imx} are its eigenfunctions, where

$$m=0,\ \pm1,\ \pm2,\ \cdots. \tag{11}$$

If these eigenfunctions are chosen as the basis functions, the matrix elements of $\mathbf{H}_{ir}$ [when $V(x)\neq0$] are

$$(H_{ir})_{m,m}=(\hbar^2/2U)(m+\lambda K)^2+\sum_N (H_{3N}/2) \tag{12}$$

and

$$(H_{ir})_{m,m\pm3N}=-\tfrac{1}{4}H_{3N}. \tag{13}$$

For convenience, we put as

$$m=3l+\sigma, \tag{14}$$

where

$$l=0,\ \pm1,\ \pm2,\ \cdots, \tag{15}$$

and

$$\sigma=0,\ +1,\quad \text{or}\quad -1. \tag{16}$$

The $\mathbf{H}_{ir}$ matrix can be factored into three smaller matrices with $\sigma=0$, $+1$, and -1. By diagonalizing these matrices, eigenvalues $E_{K\sigma n}$ and eigenfunctions,

$$Q_{K\sigma n}(x)=(2\pi)^{-1/2}\sum_l a_{l,K\sigma n}\exp[i(3l+\sigma)x] \tag{17}$$

are to be obtained. Here,

$$n=0,\ 1,\ 2,\ \cdots \tag{18}$$

designates the eigenvalue, and corresponds to the vibrational quantum number of the torsional oscillation. In Fig. 3, are shown eigenvalues calculated on an assumption that $H_3=691.1\ \text{cm}^{-1}$, $H_6=H_9=\cdots=0$, $C_2=5.331\times10^{-40}\ \text{g}\cdot\text{cm}^2$, and other molecular parameters are equal to those given by Itoh.[2]

The matrix elements of the total Hamiltonian $\mathbf{H}$ are given as follows[2]:

$$H_{JK\sigma n}{}^{JK\sigma n}=\tfrac{1}{4}\hbar^2\left(A^{-1}+\frac{B}{B^2+D^2}\right)[J(J+1)-K^2]$$
$$+\tfrac{1}{2}\hbar^2\left(\frac{B+C}{BC-D^2}-\frac{B}{B^2+D^2}\right)K^2+E_{K\sigma n}, \tag{19}$$

$$H_{J,K+1,\sigma,n'}{}^{JK\sigma n}=\tfrac{1}{2}\hbar^2[D/(B^2+D^2)](K+\tfrac{1}{2})$$
$$\times[(J-K)(J+K+1)]^{1/2}I_{K+1,\sigma,n'}{}^{K\sigma n}, \tag{20}$$

$$H_{J,K+2,\sigma,n'}{}^{JK\sigma n}=-\tfrac{1}{8}\hbar^2\{A^{-1}-[B/(B^2+D^2)]\}$$
$$\times[(J-K)(J-K-1)(J+K+1)$$
$$\times(J+K+2)]^{1/2}\,I_{K+2,\sigma,n'}{}^{K\sigma n}, \tag{21}$$

where

$$I_{K'\sigma n'}{}^{K\sigma n}=\int_0^{2\pi}Q_{K\sigma n}(x)^*Q_{K'\sigma n'}(x)\,dx, \tag{22}$$

and

$$J=0,\ 1,\ 2,\ \cdots \tag{23}$$

is the rotational quantum number corresponding to the total angular momentum.

For the methylamine molecule, the asymmetry is not great, and, in the analysis of the infrared spectrum, the off-diagonal elements of $\mathbf{H}$ are significant only for $K=0$ and 1.

B. Selection Rules and Intensities

The selection rules for the radiative transitions can be derived by essentially the same method as that used by Koehler and Dennison[11] for the CH_3OH molecule:

$$\Delta J=0,\ \pm1;\quad \Delta K=\pm1;\quad \Delta\sigma=0;$$

and

$$\Delta n=0,\ 1,\ 2,\ \cdots. \tag{24}$$

The intensity of each of the vibration–rotation lines in the 500–80-cm^{-1} region is given approximately by that of a perpendicular band of a rigid symmetric top multiplied by a factor I^2 where

$$I=\int_0^{2\pi}Q_{K''\sigma''n''}(x)^*Q_{K'\sigma'n'}(x)\,dx. \tag{25}$$

What are actually observed would be mostly the Q-branch absorptions, and their intensities are expressed as

$$I(E'\leftarrow E'')\propto\nu f_\sigma F_{K\pm1\leftarrow K}I^2[1-\exp(-h\nu/kT)]$$
$$\times\exp(-E''_{K\sigma n}/kT), \tag{26}$$

where

$$F_{K\pm1\leftarrow K}=\sum_{J=K}^{\infty}(2J+1)\frac{(J+1\pm K)(J\mp K)}{J(J+1)}$$
$$\times\exp\left\{-\frac{\hbar^2}{kT}\left[\frac{1}{4}\left(\frac{1}{A}+\frac{B}{B^2+D^2}\right)(J^2+J-K^2)\right.\right.$$
$$\left.\left.+\frac{1}{2}\left(\frac{B+C}{BC-D^2}-\frac{B}{B^2+C^2}\right)K^2\right]\right\}, \tag{27}$$

$$I=0,\quad \text{for}\quad \sigma'\neq\sigma'', \tag{28}$$

and

$$I=\sum_l a_{3l+\sigma,K'',n''}a_{3l+\sigma,K',n'},\quad \text{for}\quad \sigma'=\sigma''(\equiv\sigma). \tag{29}$$

f_σ in Eq. (26) is the statistical weight:

$$f_\sigma=2\quad \text{for}\quad \sigma=0 \tag{30}$$

and

$$f_\sigma=1\quad \text{for}\quad \sigma=1\ \text{or}\ -1. \tag{31}$$

In Fig. 4, the intensity factor I for the internal rotation is illustrated for $\sigma=0$.

C. Centrifugal Distortion

We remove here partly the limitation assumed that the molecule has only one internal freedom. Because

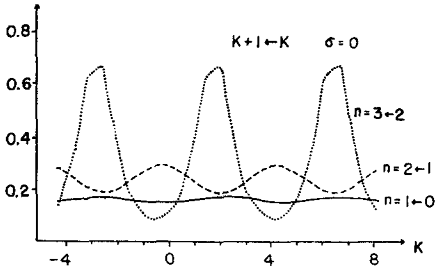

FIG. 4. The internal rotation intensity factor

$$I=\int_0^{2\pi} Q_{K+1}(x)^*Q_K(x)dx$$

for $\sigma=0$. The diagram for $\sigma=+1$ can be obtained by displacing every curve toward left by $\frac{1}{3}$ period, and for $\sigma=-1$, toward right by $\frac{1}{3}$ period.

the moment of inertia of methylamine molecule around the ζ' axis is small, the effect of the centrifugal distortion upon the over-all and internal rotation energy is appreciable when the K and n are large. The effect is approximately proportional to the fourth power of the momenta of the amino and methyl groups (p_1 and p_2, respectively), around the ζ' axis. Since p_1 and p_2 are expressed as

$$p_1=(\hbar/i)(d/dx)+\hbar K, \tag{32}$$

and

$$p_2=-(\hbar/i)(d/dx), \tag{33}$$

the average values of $p_1{}^4$ and $p_2{}^4$ are given as

$$\langle p_1{}^4\rangle=\int Q^*\left(\frac{\hbar}{i}\frac{d}{dx}+\hbar K\right)^4 Qdx$$
$$=\hbar^4\sum_m (m+K)^4a_m{}^2 \tag{34}$$

and

$$\langle p_2{}^4\rangle=\int Q^*\hbar^4\frac{d^4}{dx^4}Qdx$$
$$=\hbar^4\sum_m m^4a_m{}^2. \tag{35}$$

The correction ΔE is given as

$$\Delta E=a\hbar^4\sum_m (m+K)^4a_m{}^2+b\hbar^4\sum_m m^4a_m{}^2, \tag{36}$$

where

$$a\hbar^4=-\sum_k [\hbar^4/8(C_1{}^0)^4f_k](\partial C_1/\partial Q_k)^2, \tag{37}$$

and

$$b\hbar^4=-\sum_k [\hbar^4/8(C_2{}^0)^4f_k](\partial C_2/\partial Q_k)^2. \tag{38}$$

In Eqs. (37) and (38), Q_k is the kth normal coordinate, f_k is the force constant for the displacement along Q_k, and $C_1{}^0$ and $C_2{}^0$ are the values of C_1 and C_2 for the case where the centrifugal distortion is absent.

In the problem of the internal rotation, we need to take another factor into consideration, i.e., the slight alteration of the potential function due to the centrifugal distortion. The correction in the energy $\Delta E'$ due to this factor is given by Burkhard and Dennison[14] in their analysis of the internal rotation spectrum of CH_3OH. $\Delta E'$ can be given by

$$\Delta E'=c'\{\sum_m (m+K)^2a_m{}^2\}\langle 1-\cos 3x\rangle, \tag{39}$$

where constant c' involves $\partial H_3/\partial Q_k$, etc., and has the value of $-0.14\ cm^{-1}$ in the case of CH_3OH.

V. ANALYSIS OF THE SPECTRUM OF CH_3NH_2

A. Need of Revision of the Molecular Constants

First, the energy levels and wavefunctions were calculated by assuming the molecular constants given by Itoh[2] on the basis of the microwave data (see Column 1 of Table I). From these, theoretical positions and intensities of the absorption lines (${}^PQ$ and ${}^RQ$ lines) were calculated and compared with the observed spectrum. It was found that the theoretical and observed spectra do not agree at all. If the theoretical spectrum is shifted by 4 cm^{-1} towards lower frequency, however, the theoretical and observed fine structures in the 300–200-cm^{-1} region (this is considered to be the $n=1\leftarrow 0$ region as stated in Sec. III) come in a reasonably good agreement with each other. The theoretical spectrum in the other spectral region was found to be quite different from the observed one even after the 4-cm^{-1} shift. These facts clearly indicate a characteristic of the values of the molecular constants determined from the microwave analysis: They are good enough for reproducing the positions of the energy levels of $n=0$ with respect to one another, and they are also good enough for reproducing the positions of the energy levels of $n=1$ with respect to one another. They are not always good, however, for reproducing the positions of the energy levels of $n=1$ with respect to those

TABLE I. Molecular constants for CH_3NH_2.

	No. 1[a]	No. 2[b]	No. 3[c]
$A(10^{-40}\ g\cdot cm^2)$	37.085		
$B(10^{-40}\ g\cdot cm^2)$	38.662		
$C(10^{-40}\ g\cdot cm^2)$	8.136		
$D(10^{-40}\ g\cdot cm^2)$	−0.120		
$C_2(10^{-40}\ g\cdot cm^2)$	5.331	5.247	5.273±0.020
$H_3\ (cm^{-1})$	691.1	681.9	683.2±1.2
$H_6\ (cm^{-1})$	0	0	−2.0±1.5

[a] Given by Itoh (Ref. 2). The calculated spectrum on this set does not agree with the observed spectrum.

[b] The values of A, B, C, and D in this set are equal to those in set No. 1. This set gives a good agreement between the calculated and observed spectra, if the centrifugal distortion is neglected.

[c] The values of A, B, C, and D in this set are equal to those in set No. 1. This set gives a good agreement between the calculated and observed spectra, if it is assumed that $a\hbar^4=-1.6\times 10^{-3}\ cm^{-1}$, $b\hbar^4=-0.5\times 10^{-1}\ cm^{-1}$, and $c'=-0.1\ cm^{-1}$ in Eqs. (36) and (39). In addition, this set gives a better agreement between the calculated and observed frequencies of the $7_{3,4}\leftarrow 8_{2,6}$ line in the microwaves spectrum (Ref. 3) than set No. 2 and also than set No. 1.

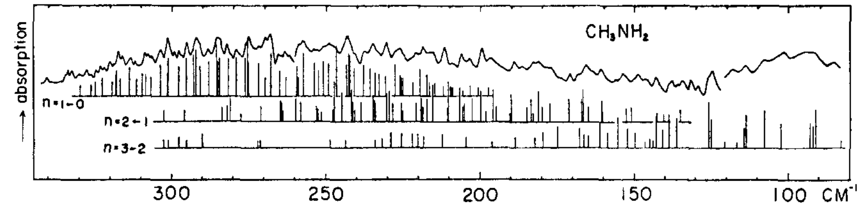

FIG. 5. A comparison of the calculated and observed infrared absorption spectra CH_3NH_2 in the 330–90-cm^{-1} region.

of $n=0$. They are not always good for reproducing the higher energy levels, namely those of $n=2$, 3, and so forth. In the present case, the positions of the energy levels of $n=1$ with respect to those of $n=0$ are considered to be newly fixed by the infrared data. Some pieces of information of the positions of the energy levels of $n=2$, and 3 have also been obtained. We now revise the values of the molecular constants by taking these new data into account.

B. Jacobian Matrix for Directing the Revision

Our problem is considered to be the determination of the values of the following seven molecular constants: A, B, C, C_2, D, H_3, and H_6. Itoh[2] assumed that $H_6=0$ and $C_2=5.331\times10^{-40}$ g·cm² (set equal to the values of moment of inertia of methane), and determined the values of the other five constants on the data:

$$\nu(4_{22}\leftarrow5_{14})\,(\sigma=0,\ n=0)=20\,408\ \text{Mc/sec}, \tag{40}$$

$$\nu(4_{23}\leftarrow5_{15})\,(\sigma=0,\ n=0)=33\,509\ \text{Mc/sec}, \tag{41}$$

$$\nu(6_{15}\leftarrow5_{23})\,(\sigma=0,\ n=0)=26\,381\ \text{Mc/sec}, \tag{42}$$

origin of the $J_1\leftarrow J_0(\sigma=1,\ n=1)$ series

$$=30\,187\ \text{Mc/sec}, \tag{43}$$

Stark coefficient for $3_1\leftarrow3_0$ $(\sigma=1,\ n=1)$ transition

$$=0.0228\times10^{-24}\,(M/h)\ \text{Mc/sec}. \tag{44}$$

The energy levels are labeled by the asymmetric-rotor designation $J_{K_{-1}K_{+1}}$ in Eqs. (40)–(42). In Eq. (44), M is the rotational quantum number which labels the levels split through the Stark effect. One of our new data from the infrared spectrum is written as

$$E_{001}-E_{000}=268.2\pm0.5\ \text{cm}^{-1}, \tag{45}$$

where the band center ν_0 of the fundamental band is found at 263.9 cm⁻¹). Here, the suffix of E indicates the values of the three quantum numbers, K, σ, and n.

Among the seven constants given above, four constants A, B, C, and D are not sensitive to the infrared data while the other three C_2, H_3, and H_6 are sensitive. Therefore, we fixed the values of the former four constants at what were determined by the microwave analysis[2] (see Table I), and attempted to determine

TABLE II. Molecular constants for CH_3ND_2.

	No. 1[a]	No. 2[b]	No. 3[c]
A (10^{-40} g·cm²)	41.571		
B (10^{-40} g·cm²)	44.881		
C (10^{-40} g·cm²)	10.775		
D (10^{-40} g·cm²)	1.214		
C_2 (10^{-40} g·cm²)	5.331	5.273	5.273
H_3 (cm⁻¹)	691.1	683.2	671.6
H_6 (cm⁻¹)	0	−2.0	0

[a] Based upon the values given by Itoh (Ref. 2) for CH_3NH_2. The calculated spectrum on this set does not agree with the observed spectrum.

[b] The values of A, B, C, and D in this set are equal to those in set No. 1. The values of C_2, H_3, and H_6 are equal to those in set No. 3 for CH_3NH_2 (Table 1). The calculated spectrum on this set does not agree with the observed spectrum.

[c] The values of A, B, C, and D in this set are equal to those in set No. 1. This set gives a good agreement between the calculated fine structure and observed one of the fundamental $(n=1\leftarrow0)$ band.

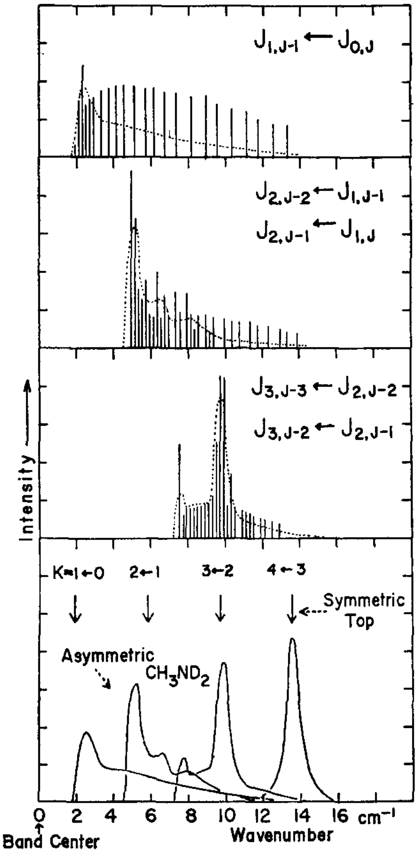

FIG. 6. Positions and intensities of the absorption lines corresponding to the transitions $J_{K_{-1}+1,K_{+1}-1}\leftarrow J_{K_{-1},K_{+1}}$ in the B-type band of CH_3ND_2.

the values of the latter three so that both of the infrared and microwave spectra are well explained. On the assumption that A, B, C, and D are equal to the values given in Table I, the five relations (40)-(44) are now reduced to one relation:

$$\tfrac{1}{3}h^{-1}(E_{200}-E_{100})-h^{-1}(E_{111}-E_{011})=52\,648 \text{ Mc/sec}. \tag{46}$$

Our problem is now to find a set of values of C_2, H_3, and H_6 which fulfills the two relations (45) and (46). If $C_2=5.331\times10^{-40}$ g·cm², $H_3=691.1$ cm⁻¹, and $H_6=0$ (No. 1 in Table I); $E_{001}-E_{000}$ is 4 cm⁻¹ higher than the value given in (45), while the relation (46) is fulfilled. We therefore need to reduce the $E_{001}-E_{000}$ value by 4 cm⁻¹ without causing any change of the $\tfrac{1}{3}(E_{200}-E_{100})-(E_{111}-E_{011})$ value. As a guide for how to reach a satisfactory set of values of C_2, H_3 and H_6, a knowledge of the derivatives of energy with respect to these parameters $[(\partial E/\partial C_2)$, $(\partial E/\partial H_3)$, and $(\partial E/\partial H_6)]$ would be useful. These are calculated as follows.

As may be seen in Eq. (5), C_2 is related to the energy through U and λ. Therefore,

$$\frac{\partial E}{\partial C_2}=\left(\frac{\partial E}{\partial U}\right)_\lambda\frac{\partial U}{\partial C_2}+\left(\frac{\partial E}{\partial \lambda}\right)_U\frac{\partial \lambda}{\partial C_2}, \tag{47}$$

where

$$\begin{aligned}\left(\frac{\partial E}{\partial U}\right)_\lambda&=\left\langle\left(\frac{\partial H_{ir}}{\partial U}\right)_\lambda\right\rangle=\left\langle-\frac{1}{U}\left[\frac{\hbar^2}{2U}\left(\frac{d}{idx}+\lambda K\right)^2\right]\right\rangle\\&=-U^{-1}\{E-\langle V(x)\rangle\}\\&=-U^{-1}\{E-\tfrac{1}{2}H_3(1-\langle\cos3x\rangle)\},\end{aligned} \tag{48}$$

and

$$(\partial E/\partial\lambda)_U=-\tfrac{2}{3}\pi K\,e_n'\sin\Omega-\tfrac{4}{3}\pi K\,e_n''\sin2\Omega-\cdots. \tag{49}$$

Equation (49) is obtained from an approximate expression of the eigenvalues of $\mathbf{H}_{ir}$:

$$E_{K\sigma n}=e_n+e_n'\cos\Omega+e_n''\cos2\Omega+\cdots, \tag{50}$$

given in our previous paper,[15] where $\Omega=\tfrac{2}{3}\pi(\lambda K+\sigma)$. From Eqs. (6) and (7),

$$\partial U/\partial C_2\doteqdot(C_1-C_2)/C \tag{51}$$

and

$$\partial\lambda/\partial C_2\doteqdot 1/C, \tag{52}$$

if D is neglected here in an approximation. On substituting Eqs. (48), (49), (51), and (52) into Eq. (47),

$$\begin{aligned}\frac{\partial E}{\partial C_2}=\frac{C_2-C_1}{C_1C_2}&\{E-\tfrac{1}{2}H_3(1-\langle\cos3x\rangle)\}\\&-(2\pi K/3C)(e_n'\sin\Omega+2e_n''\sin2\Omega+\cdots).\end{aligned} \tag{53}$$

The derivatives of the energy with respect to the potential constants are calculated as

$$\partial E/\partial H_3=\tfrac{1}{2}(1-\langle\cos3x\rangle) \tag{54}$$

and

$$\partial E/\partial H_6=\tfrac{1}{2}(1-\langle\cos6x\rangle). \tag{55}$$

The values of

$$\begin{aligned}\langle\cos3Nx\rangle&=\int_0^{2\pi}Q(x)^*\cos3NxQ(x)\\&=\sum_{m=-\infty}^{+\infty}a_ma_{m+3N}\end{aligned} \tag{56}$$

are rather easily calculated for any set of $(K\sigma n)$. By the use of these $\langle\cos3Nx\rangle$ values, the desired Jacobian matrix at set No. 1 (Table I) is obtained as

$$\frac{\partial\{(E_{200}-E_{100}),\,(E_{011}-E_{111}),\,(E_{001}-E_{000})\}}{\partial(C_2,\,H_3,\,H_6)}$$

$$\begin{array}{r|lll} & \Delta C_2 & \Delta H_3 & \Delta H_6\\ \hline \Delta(E_{200}-E_{100}) & 2870\text{ Mc}/10^{-40}\text{ g}\cdot\text{cm}^2\cdot\text{sec} & -29.7\text{ Mc/cm}^{-1}\cdot\text{sec} & -18.6\text{ Mc/cm}^{-1}\cdot\text{sec}\\ =\Delta(E_{011}-E_{111}) & 22\,370\text{ Mc}/10^{-40}\text{ g}\cdot\text{cm}^2\cdot\text{sec} & -196.8\text{ Mc/cm}^{-1}\cdot\text{sec} & 51.3\text{ Mc/cm}^{-1}\cdot\text{sec}\\ \Delta(E_{001}-E_{000}) & 21.3\text{ cm}^{-1}/10^{-40}\text{ g}\cdot\text{cm}^2 & 0.2111\text{ cm}^{-1}/\text{cm}^{-1} & 0.376\text{ cm}^{-1}/\text{cm}^{-1}\end{array}. \tag{57}$$

C. A Proposed Set of C_2, H_3, and H_6 Values

A trial set of C_2, H_3, and H_6 values is obtained on the basis of the Jacobian matrix (57). By diagonalizing $\mathbf{H}_{ir}$ [Eq. (5)] with these values, a new set of $E_{K\sigma n}$ values is calculated. By comparing these calculated $E_{K\sigma n}$ values with the observed values given in Eqs. (45) and (46), and by inspecting the Jacobian (57), another trial set of C_2, H_3, and H_6 values is obtained. On repeating the procedure a few times, it is found that the following relations are valid in the vicinity of the good set of values:

$$H_3=681.9\text{ cm}^{-1}-0.66\text{H}_6, \tag{58}$$

and

$$C_2=5.247\times10^{-40}\text{ g}\cdot\text{cm}^2-0.013H_6\times10^{-40}\text{ g}\cdot\text{cm}^3. \tag{59}$$

We first assumed tentatively that $H_6=0$, and obtained the set No. 2 given in Table I by the use of Eqs. (58) and (59). The calculated spectrum on this set of

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[15] M. Tsuboi, A. Y. Hirakawa, T. Ino, T. Sasaki, and K. Tamagake, J. Chem. Phys. **41**, 272 (1964).

values and on Eqs. (19)–(22) and Eq. (26) gave a reasonably good agreement with the observed spectrum in the 330–90-cm^{-1} region. Here, however, the effect of the centrifugal distortion was neglected. For including this effect, an estimation of $a\hbar^4$ and $b\hbar^4$ values [Eqs. (37) and (38)] was made on the basis of a normal coordinate treatment of the methylamine molecule[16]:

$$a\hbar^4 = -1.6\times10^{-3}\ \text{cm}^{-1}, \qquad (60)$$

$$b\hbar^4 = -0.5\times10^{-4}\ \text{cm}^{-1}. \qquad (61)$$

For obtaining $\Delta E'$ [Eq. (39)], c' was assumed as

$$c' = -0.1\ \text{cm}^{-1}, \qquad (62)$$

because it has probably the same order of magnitude with the c' value for CH_3OH.[14] The correction by the use of Eqs. (36) and (39) with these values of a, b, and c' causes a shift of each absorption line with $n=2\leftarrow1$, and $n=3\leftarrow2$ in the calculated spectrum. For restoring the agreement with the observed spectrum, it was required to assume that $H_6=-2.0$ cm^{-1}. By substituting this value into Eqs. (58) and (59), the final set of values (No. 3 in Table I) was obtained. The positions and intensities of the absorption lines calculated on Eqs. (19)–(22), (26), (36), and (39) with set No. 3 are shown in Fig. 5 by means of the vertical lines. As may be seen here, most of the absorption peaks observed are well correlated to the theoretically expected absorption lines.[17]

VI. ANALYSIS OF THE SPECTRUM OF CH_3ND_2

For CH_3ND_2, the elements of the inertia tensor, A, B, C, and D are calculated as given in the second column of Table II, on the basis of the molecular constants determined by Itoh[2] for CH_3NH_2. On these values, the splitting of the energy levels with $n=1$ through the internal rotation should be much smaller than the separations of two adjacent ^PQ or ^RQ branch absorption peaks. Thus, the $e'_{n=1}$ value of Eq. (50) is calculated to be about 0.8 cm^{-1}, whereas $(h/4\pi^2c)(C^{-1}-\frac{1}{2}A^{-1}-\frac{1}{2}B^{-1})$ value about 4.0 cm^{-1}. The limit of the resolving power of our present experiment is slightly greater than 0.8 cm^{-1}. Therefore, the fundamental ($n=1\leftarrow0$) band of CH_3ND_2 is expected to consist of somewhat broad ^PQ or ^RQ peaks arranged with almost equal spacings (4.0 cm^{-1}). This is just what is actually observed in the 280–190-cm^{-1} region (Fig. 2).

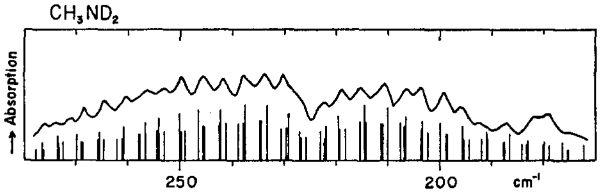

FIG. 7. A comparison of the calculated and observed infrared absorption spectra of CH_3ND_2 in the 280–170-cm^{-1} region.

From the values of the molecular constants given in Table II, it is also found that the CH_3ND_2 molecule has a greater asymmetry than the CH_3NH_2 molecule. This asymmetry should cause appreciably smaller intensities for the $K=1\leftarrow0$, $K=2\leftarrow1$, $K=0\leftarrow1$, and $K=1\leftarrow2$ peaks than those in the corresponding symmetric-top molecule (see Fig. 6). The actually observed absorption gap (see Fig. 2) at about 225 cm^{-1} can be used, therefore, for fixing the band center of the $n=1\leftarrow0$ band. The position of the band center ν_0 is determined as

$$\nu_0 = 224.5\ \text{cm}^{-1}. \qquad (63)$$

The calculated ν_0 value on the set of the molecular constants No. 1 in Table II was found to be 4 cm^{-1} higher than the observed value. Therefore, it is again indicated that C_2, H_3, and/or H_6 values determined from the microwave data[2] should be revised. The set No. 2, which has the same values of C_2, H_3, and H_6 with those proposed for CH_3NH_2, does not account for CH_3ND_2. The calculated $E_{001}-E_{000}$ value on this set is about 2 cm^{-1} higher than the observed value. To reach an agreement of the calculated and observed values of $E_{001}-E_{000}$, the potential constants H_3 and H_6 are required to have a certain set of values in which the two values are related with each other as

$$H_3 = 671.6\ \text{cm}^{-1} - 1.96H_6, \qquad (64)$$

provided that $C_2=5.273\times10^{-40}$ g·cm^2 (the same value for CH_3NH_2). The calculated spectrum with set No. 3 in Table II ($H_3=671.6$ cm^{-1} and $H_6=0$) is shown in Fig. 7 with the observed spectrum. It has been found that any set with a small H_6 value and the H_3 value derived by Eq. (64) can explain fairly satisfactorily the fine structure of the fundamental band in the 280–190-cm^{-1} region. No set with $H_6=-20$ to $+20$ cm^{-1}, however, was found to explain the spectrum in the 190–80-cm^{-1} region. Therefore, it may be concluded that the internal rotation energy levels of CH_3ND_2 with $n\geqq2$ are coupled with some other energy levels (for example with ND_2 wagging levels), so that no satisfactory account can be expected from a mere revision of the potential constants of the internal rotation. It may also be concluded that, probably because of such a coupling, the effective barrier height ($=671.6$ cm^{-1}) of the internal rotation potential in CH_3ND_2 is is slightly lower than that (683.2 cm^{-1}) in CH_3NH_2.

ACKNOWLEDGMENTS

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[16] A. Y. Hirakawa, M. Tsuboi, and T. Shimanouchi (unpublished).

[17] The value (-2.0 ± 1.5 cm^{-1}) of the sixfold coefficient H_6 in the potential function [Eq. (8)] determined by our present analysis may be useful in testing the theories of hindered rotation. J. P. Lowe and R. G. Parr [J. Chem. Phys. **44**, 3001 (1966)], for example, predicted that $H_6 \doteqdot -0.005H_3$ for the methylamine-type molecule from their theory by the use of a semiempirical electrostatic model. What was predicted is now found to be essentially in agreement with the experimental value in the case of methylamine.