

The Structure of the Methylamine Molecule in an Excited Electronic State

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Ultraviolet absorption spectra of four isotopic methylamines, CH_3NH_2 , CH_3ND_2 , CD_3NH_2 , and CD_3ND_2 , have been observed in their gaseous states in the spectral region of 2000-2500 Å. There is an electronic band whose 0-0 peaks are observed respectively at 2397, 2376, 2392, and 2372 Å. The vibrational structure of the band was analyzed in terms of two frequencies of the ground state and two frequencies of the excited state. The two frequencies of each state were assigned to the amino-wagging and methyl-rocking vibrations. On the basis of the observed energy levels of the amino-wagging vibration in the CH_3NH_2 and CH_3ND_2 molecules, the potential function of the excited molecule along this coordinate was determined: it has a broad minimum at the position of the planar amino group, and it is nearly harmonic up to the position where the HNH plane inclines 90° from the C-N bond. On the basis of the observed vibrational frequencies, a normal coordinate treatment was made of the four methylamine molecules in the excited state. By assuming the values of two force constants (f_w and f_r), all of the seven normal frequencies observed of the four excited methylamines were explained. It was shown that the vibrational coupling of the amino-wagging and methyl-rocking modes becomes greater in the order of CH_3ND_2 , CH_3NH_2 , CD_3ND_2 , and CD_3NH_2 .

I. INTRODUCTION

The amino group of the methylamine molecule in the ground state is known to have a pyramidal structure (1). Along the amino-wagging coordinate there are two potential minima separated by a potential barrier of 1688 cm^{-1} in height (2, 3). There is an appreciable inversion doubling observed in the amino-wagging band in the infrared spectrum (2, 4).

The purpose of the present paper is to describe the corresponding wagging-inversion potential function of the methylamine molecule in an excited electronic state on the basis of the results of our examination of the vibrational structure of the ultraviolet absorption band observed in the 2000-2500 Å region.

II. EXPERIMENTAL METHODS

Four isotopic methylamines were used: methylamine (CH_3NH_2), methylamine- d_2 (CH_3ND_2), methyl- d_3 -amine (CD_3NH_2), and methyl- d_3 -amine- d_2

(CD_3ND_2). A pure CH_3NH_2 gas sample was obtained by a procedure previously described (4). The CH_3ND_2 gas was obtained by adding a small amount of purified methylamine hydrochloride (solid) into a NaOD plus D_2O solution. The NaOD was obtained by the reaction of metallic sodium with D_2O at a lower temperature. Before placing the CH_3ND_2 samples in a gas cell (10 cm), D_2O gas was filled in the cell so that the adsorbed gas on the cell wall was completely deuterated. The CD_3NH_2 and CD_3ND_2 gases were obtained from methyl- d_3 -amine hydrochloride which was supplied by Merck Sharp and Dohme of Canada Limited. This sample of hydrochloride was found to have an appreciable amount of ammonium chloride as an impurity. No purification of the hydrochloride was made, and the CD_3NH_2 gas sample had an amount of NH_3 and the CD_3ND_2 gas sample had an amount of ND_3 as impurities. This fact was properly taken into account in interpreting the experimental results.

Ultraviolet absorption measurements of these four isotopic methylamines in the 2000–2500 Å region were made by the use of a Cary 11 spectrophotometer. A gas cell with quartz windows and with an optical path length of 10 cm was used. In most experiments, the pressure of the gas was kept less than 1 mm Hg and its temperature at room temperature. Only for detecting weaker absorption bands the pressure was elevated (up to a few hundred mmHg). Also, sometimes the temperature of the sample was elevated up to 200°C for examining whether some particular bands are hot bands or not. The wavenumber calibration was made by means of known absorption peaks of ammonia (5) and known emission lines from a mercury lamp. The position of each vibrational band has been determined with an experimental error which is about $\pm 10 \text{ cm}^{-1}$. In Figs. 1–4, the absorption curves of the four isotopic methylamines are given.

III. ANALYSIS OF THE SPECTRA

The absorption spectra of methylamines in the spectral region in question were previously observed by Förster and Jungers (6) and by Tannenbaum *et al.* (7). By our present examination, however, we obtained more data on the hot bands than theirs, and we reached a different set of assignments from theirs of the vibrational bands.

The vibrational structure of the electronic bands of methylamines in the 50 000–40 000 cm^{-1} region can be analyzed in terms of two frequencies, ν_1' and ν_2' , of the excited state and two frequencies, ν_1'' and ν_2'' , of the ground state. All of the vibrational bands observed of the four isotopic methylamines are accounted for by

$$\nu = \nu_{0-0} + \nu_1' \nu_1' + \nu_2' \nu_2' - \nu_1'' \nu_1'' - \nu_2'' \nu_2''. \quad (1)$$

The frequencies, ν_{0-0} , ν_1' , ν_2' , ν_1'' , and ν_2'' , are given in Table I. The vibrational quantum numbers, ν_1' , ν_2' , ν_1'' , and ν_2'' , for the actually observed transitions are also listed in Table I. The two vibrational frequencies, ν_1' and ν_2' , of each excited

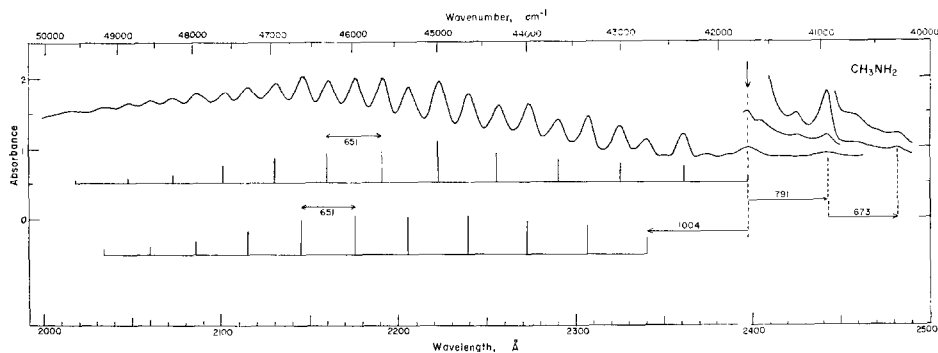


FIG. 1. The structure of the electronic $\tilde{A}-\tilde{X}$ band of methylamine (CH_3NH_2) in gaseous state. The continuous curves are reproductions of the observed absorption curves. Vertical lines indicate an interpretation of the structure (see the text). The arrow indicates the probable position of the 0-0 band.

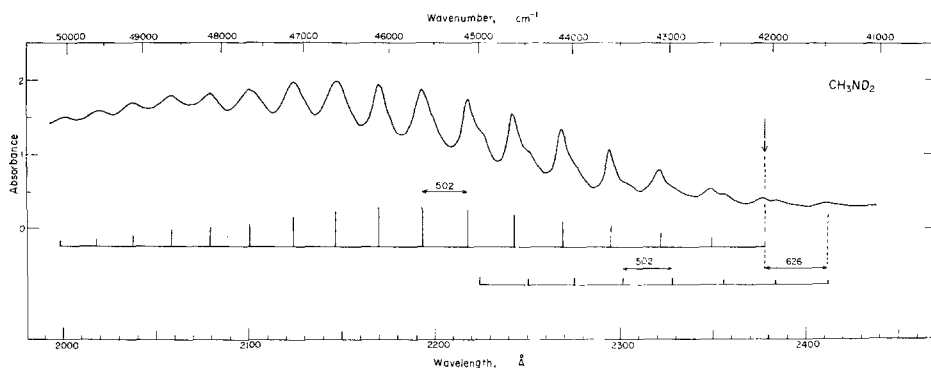


FIG. 2. The structure of the electronic $\tilde{A}-\tilde{X}$ band of methylamine- d_2 (CH_3ND_2) in gaseous state. The continuous curve is a reproduction of the observed absorption curve. Vertical lines indicate an interpretation of the structure (see the text). The arrow indicates the probable position of the 0-0 band.

methylamine are associated, respectively, with the amino-wagging and methyl-rocking modes in each excited molecule, because of the following facts:

(i) The observed ground-state frequencies, ν_1'' and ν_2'' , are what have been assigned, respectively, to the amino-wagging and methyl-rocking vibrations of the ground-state molecule (2, 4, 8, 9).

(ii) Each of the frequency values ν_1' and ν_2' is in a range acceptable for the proposed assignment on the basis of our general knowledge of the molecular vibrations of aliphatic amines (8).

(iii) The effect of deuteration on each of the frequencies is just what is expected (Table I). Thus, the change $\text{NH}_2 \rightarrow \text{ND}_2$ causes a reasonable amount of change ($651 \rightarrow 502 \text{ cm}^{-1}$ or $589 \rightarrow 479 \text{ cm}^{-1}$) in the ν_1' value, while only a small

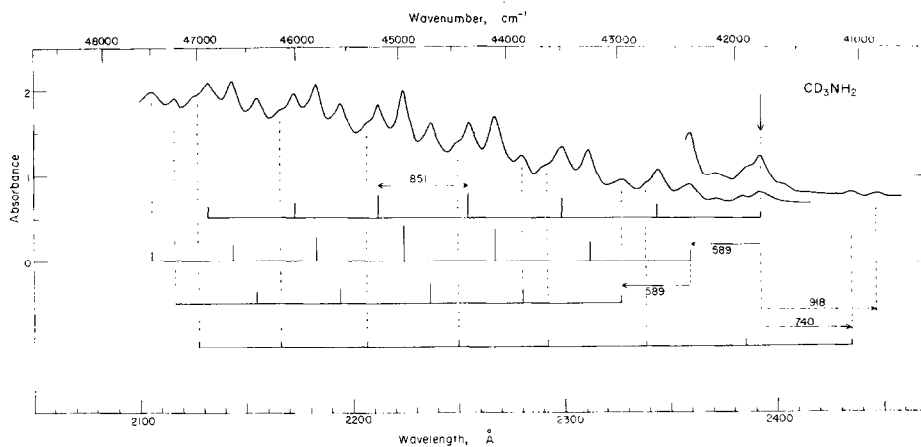


FIG. 3. The structure of the electronic \tilde{A} - \tilde{X} band of methyl- d_3 -amine (CD_3NH_2) in gaseous state. The continuous curves are reproductions of the observed absorption curves. Vertical lines indicate an interpretation of the structure (see the text). The arrow indicates the probable position of the 0-0 band.

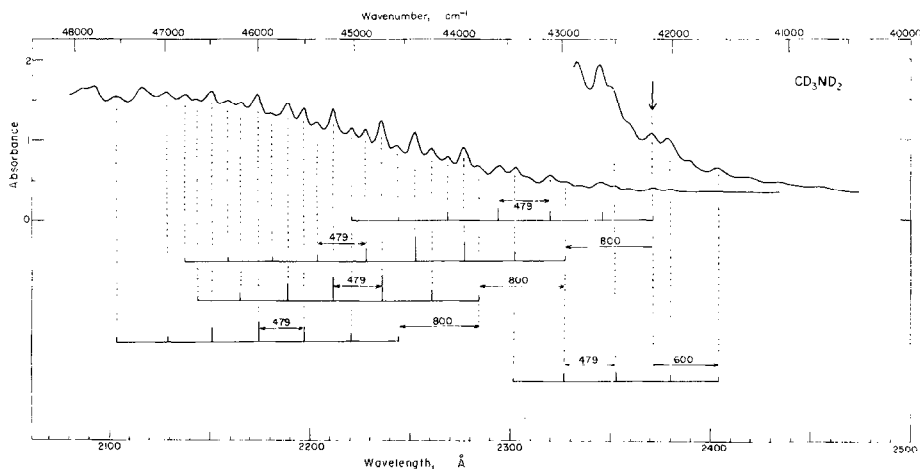


FIG. 4. The structure of the electronic \tilde{A} - \tilde{X} band of methyl- d_3 -amine- d_2 (CD_3ND_2) in gaseous state. The continuous curves are reproductions of the observed absorption curves. Vertical lines indicate an interpretation of the structure (see the text). The arrow indicates the probable position of the 0-0 band.

change ($851 \rightarrow 800 \text{ cm}^{-1}$) in the ν_2' value. The change $\text{CH}_3 \rightarrow \text{CD}_3$ causes a reasonable amount of change ($1004 \rightarrow 851 \text{ cm}^{-1}$) in the ν_2' value, but only a small change ($651 \rightarrow 589 \text{ cm}^{-1}$ or $502 \rightarrow 479 \text{ cm}^{-1}$) in the ν_1' value.

(iv) In the ground-state methylamine molecule, the amino-wagging mode

TABLE I
VIBRATIONAL FREQUENCIES (cm^{-1}) AND OBSERVED TRANSITIONS ($\nu_1', \nu_2' \leftarrow (\nu_1'', \nu_2'')$) IN
THE ULTRAVIOLET ABSORPTION SPECTRA OF FOUR ISOTOPIC METHYLAMINES
IN THEIR GASEOUS STATES^a

CH ₃ NH ₂ ($\nu_{0-0} = 41\ 715$)				CH ₃ ND ₂ ($\nu_{0-0} = 42\ 079$)			
ν_1'	ν_2'	ν_1''	ν_2''	ν_1'	ν_2'	ν_1''	ν_2''
651	1004	791 (780)	— (1130)	502	—	626 (625)	— (1117)
ν_1'	ν_2'	ν_1''	ν_2''	ν_1'	ν_2'	ν_1''	ν_2''
$\left. \begin{smallmatrix} 0 \\ \vdots \\ 12 \end{smallmatrix} \right\}$	0	0	0	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 16 \end{smallmatrix} \right\}$	0	0	0
$\left. \begin{smallmatrix} 0 \\ \vdots \\ 10 \end{smallmatrix} \right\}$	1	0	0	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 7 \end{smallmatrix} \right\}$	0	1	0
0	0	1	0				
1	0	1	0				
0	0	2	0				
CD ₃ NH ₂ ($\nu_{0-0} = 41\ 812$)				CD ₃ ND ₂ ($\nu_{0-0} = 42\ 167$)			
ν_1'	ν_2'	ν_1''	ν_2''	ν_1'	ν_2'	ν_1''	ν_2''
589	851	740 (740)	918 (913)	479	800	600 (601)	— (880)
ν_1'	ν_2'	ν_1''	ν_2''	ν_1'	ν_2'	ν_1''	ν_2''
0	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 6 \end{smallmatrix} \right\}$	0	0	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 6 \end{smallmatrix} \right\}$	0	0	0
1	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 6 \end{smallmatrix} \right\}$	0	0	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 8 \end{smallmatrix} \right\}$	1	0	0
2	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 5 \end{smallmatrix} \right\}$	0	0	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 6 \end{smallmatrix} \right\}$	2	0	0
0	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 7 \end{smallmatrix} \right\}$	1	0	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 6 \end{smallmatrix} \right\}$	3	0	0
0	0	0	1	$\left. \begin{smallmatrix} 0 \\ \vdots \\ 3 \text{ or } 4 \end{smallmatrix} \right\}$	0	1	0

^a Frequencies observed in the infrared spectra (2, 4, 8, and 9) are given in the parentheses.

has a stronger vibrational coupling with the methyl-rocking mode than with any other mode. This has been shown by our normal coordinate treatment. By the use of a refined set of force constant values, which reproduces the 51 frequencies of the four isotopic methylamines with the deviations less than 1.5 %, the normal modes of vibrations of CH_3NH_2 , CH_3ND_2 , CD_3NH_2 , and CD_3ND_2 are calculated as follows:

$$\begin{aligned}\text{CH}_3\text{NH}_2, S \text{ (amino wag.)} &= 0.8377Q_1 - 0.2966Q_2 + \Sigma \pm (\leq 0.1011)Q_i; \\ S \text{ (methyl rock.)} &= 0.1643Q_1 + 0.8422Q_2 + \Sigma \pm (\leq 0.4416)Q_i; \\ \text{CH}_3\text{ND}_2, S \text{ (amino wag.)} &= 0.6578Q_1 - 0.1573Q_2 + \Sigma \pm (\leq 0.1525)Q_i; \\ S \text{ (methyl rock.)} &= 0.1004Q_1 + 0.8124Q_2 + \Sigma \pm (\leq 0.4347)Q_i; \\ \text{CD}_3\text{NH}_2, S \text{ (amino wag.)} &= 0.6764Q_1 + 0.5104Q_2 + \Sigma \pm (\leq 0.2392)Q_i; \\ S \text{ (methyl rock.)} &= 0.3659Q_1 - 0.5744Q_2 + \Sigma \pm (\leq 0.2295)Q_i; \\ \text{CD}_3\text{ND}_2, S \text{ (amino wag.)} &= 0.6087Q_1 - 0.2824Q_2 + \Sigma \pm (\leq 0.1097)Q_i; \\ S \text{ (methyl rock.)} &= 0.1829Q_1 + 0.6283Q_2 + \Sigma \pm (\leq 0.2748)Q_i;\end{aligned}$$

where S 's are the symmetry coordinates and Q_1 and Q_2 are the normal coordinates corresponding, respectively, to the frequencies, 780 and 1130 cm^{-1} for CH_3NH_2 , 625 and 1117 cm^{-1} for CH_3ND_2 , 740 and 913 cm^{-1} for CD_3NH_2 , and 601 and 880 cm^{-1} for CD_3ND_2 . The coefficients of the Q 's other than Q_1 and Q_2 are not given here; $(\leq 0.1011)Q_i$ means that the largest (in the absolute value) coefficient is 0.1011 among the coefficients which are not shown here. It is probable that the amino-wagging and methyl-rocking modes have strong vibrational coupling also in the excited methylamine molecule. In other words, the methyl-rocking vibration is considered to be the most probable one for appearing in the electronic band, if the appearance of the amino-wagging vibration has been fixed.

IV. STRUCTURE OF THE AMINO GROUP IN THE EXCITED MOLECULE

The amino group of the excited methylamine molecule now in question is considered to be nearly planar on the basis of the following pieces of evidence:

(i) In each band-progression with $v_1' = 0, 1, 2, \dots$, all the spacings between adjacent two vibrational bands are almost equal to one another (Figs. 1-4). This means that the energy levels of the amino-wagging vibration in the excited molecule are placed with almost equal intervals, and therefore that the vibrational potential is nearly harmonic for the amino-wagging mode.

(ii) The possibility of the double minimum potential along the amino-wagging coordinate is practically eliminated on the basis of the following consideration. For CH_3NH_2 , for example, the amino-wagging vibrational bands appear with equal intervals up to $v_1' = 12$ (Fig. 1). For CH_3ND_2 , the bands appear with equal intervals up to $v_1' = 16$ (Fig. 2). These facts mean that the potential function along the amino-wagging coordinate is nearly harmonic at least in the range of $\pm 90^\circ$ along the abscissa and at least up to 8032 cm^{-1} in the ordinate

(see Sec. V). Therefore, if there were two minima in the potential function along the amino-wagging coordinate, they should be separated at least 180° from each other, and the potential barrier between them should be higher than 8032 cm^{-1} (23 kcal/mole). This is quite unlikely.

(iii) The intensity of the vibrational band due to the transition $(v_1' = 0) \leftarrow (v_1'' = 0)$ is always very weak. In the band-progression with $v_1' = 0, 1, \dots$ the intensity maximum is found at $(v_1' = 5) \leftarrow (v_1'' = 0)$ in CH_3NH_2 and at $(v_1' = 7) \leftarrow (v_1'' = 0)$ in CH_3ND_2 . These facts are understandable if the potential minimum in the excited methylamine molecule is assumed to be situated at the position corresponding to the planar amino group. Since the potential minima in the ground-state molecule are situated far from the planar position (2), the intensity of the $(v_1' = 0) \leftarrow (v_1'' = 0)$ transition should be very small according to the Franck-Condon principle (see Fig. 5).

V. AMINO-WAGGING POTENTIAL

A more detailed examination of the band-progressions reveals that the amino-wagging vibration in the excited CH_3NH_2 or CH_3ND_2 molecule is not entirely harmonic; there is a slight deviation from what is expected for a harmonic vibration. As shown in Fig. 6, the interval between the $v_1' = 0$ and $v_1' = 1$ bands is always appreciably smaller than the other intervals of the successive two vibrational bands in each progression. This fact is explained by considering that the potential function of the amino-wagging coordinate has a small hump at the center.

In our previous paper (2), it was shown that the wagging-inversion energy levels of the amino group of the ground-state methylamine molecule can be accounted for by a potential function which consists of a harmonic well and an exponential hump:

$$V(Q) = \frac{1}{2}h\nu\gamma Q^2 + h\nu\alpha \exp(-\beta\gamma Q^2), \quad (2)$$

where

$$Q = \mu^{1/2}\theta. \quad (3)$$

In these equations, θ is the wagging-inversion coordinate, ν is a hypothetical frequency (cm^{-1}) if the exponential term were absent in the potential function, μ is the reduced mass, and α , β , and γ are the potential constants. A trial was made to apply the potential function of the same form [Eq. (2)] to the excited methylamine molecule now in question. By assuming a set of three potential constants, α , β , and ν , the energy levels of the amino-wagging vibration were calculated by the method previously described (2). The intervals of the successive energy levels were then calculated, and were compared with the observed intervals. After several of such trials, it was shown that the addition of the exponential hump with $\alpha = 0.167$ and $\beta = 3.0$ to the harmonic potential provides a sub-

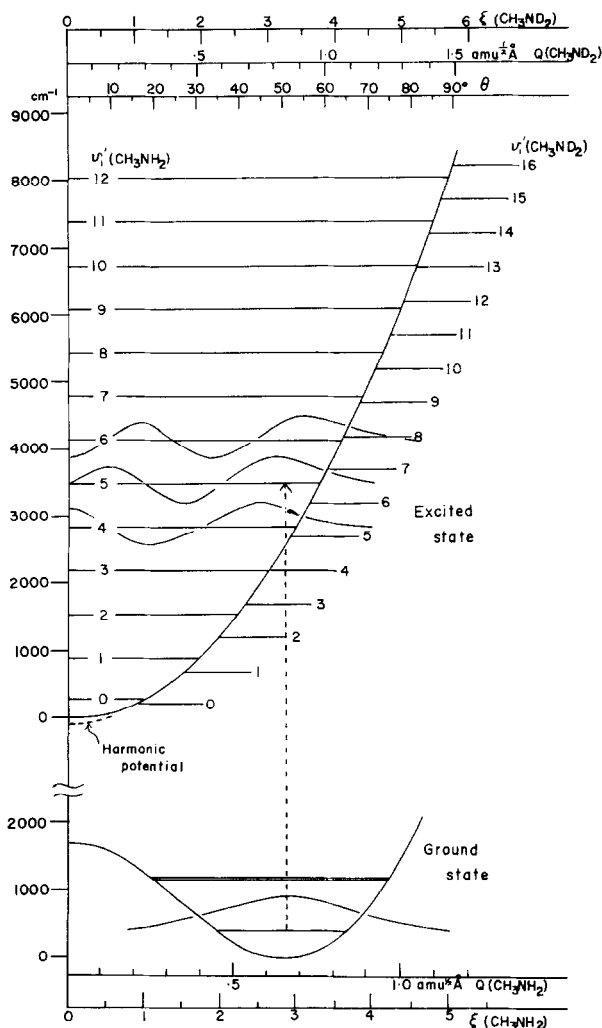


FIG. 5. Potential curves, energy levels, and wave functions of the amino-wagging vibration of the CH_3NH_2 molecule in the ground and excited states. The vertical broken line indicates the transition which should give the strongest absorption, according to the Franck-Condon principle. As is detailed in the text, the potential curve for excited CH_3NH_2 is given by Eq. (2) with $\nu = 651 \text{ cm}^{-1}$, $\alpha = 0.167$, and $\beta = 3.0$. If the scale of the abscissa ξ is properly adjusted, the same curve is almost good also for excited CH_3ND_2 . The energy levels for CH_3ND_2 are given in the right side of this common potential curve. Along the abscissa, Q and θ scales are also given.

stantial improvement in reproducing the observed energy levels of CH_3NH_2 and CH_3ND_2 (see Fig. 6). (It should be mentioned, however, that the agreement between the observed and calculated energy levels was not perfect here. It was indicated that a further additional term was needed to reach a complete agree-

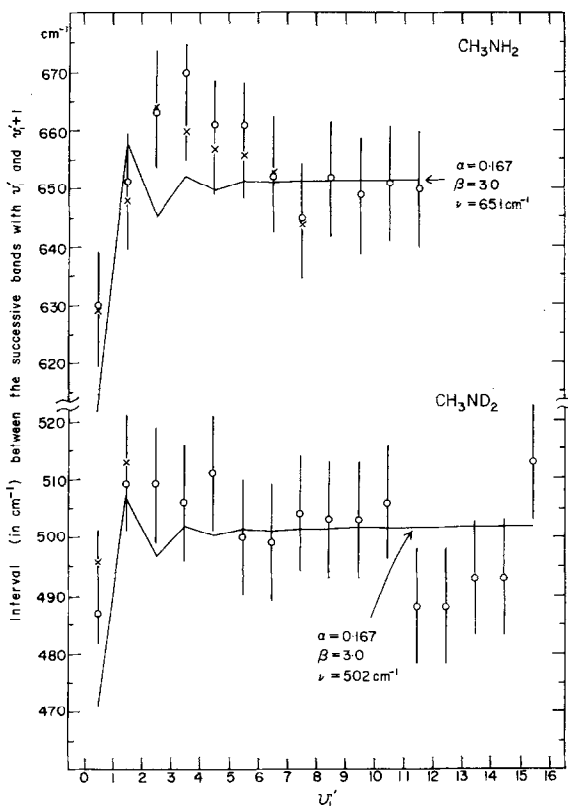


FIG. 6. Intervals (cm^{-1}) between the successive two vibrational bands (with the upper-state vibrational quantum numbers of v_1' and $v_1' + 1$) in the band progressions: ($v_1' = 0, 1, \dots; v_2' = 0$) \leftarrow ($v_1'' = 0; v_2'' = 0$) of CH_3NH_2 (O, in the upper half), ($v_1' = 0, 1, \dots; v_2' = 1$) \leftarrow ($v_1'' = 0; v_2'' = 0$) of CH_3NH_2 (X, in the upper half), ($v_1' = 0, 1, \dots; v_2' = 0$) \leftarrow ($v_1'' = 0; v_2'' = 0$) of CH_3ND_2 (O, in the lower half), and ($v_1' = 0, 1, \dots; v_2' = 0$) \leftarrow ($v_1'' = 1; v_2'' = 0$) of CH_3ND_2 (X, in the lower half). Continuous lines show the calculated intervals on the basis of Eq. (2) with $\alpha = 0.167$ and $\beta = 3.0$.

ment.) By substituting $\nu = 651 \text{ cm}^{-1}$, $\alpha = 0.167$, and $\beta = 3.0$ in Eq. (2), the amino-wagging potential curve of CH_3NH_2 was drawn (Fig. 5) with

$$\xi = \gamma^{1/2}Q, \quad (4)$$

along the abscissa. Since γ is known as $4\pi^2\nu c/h$ (2), the scale of Q is also obtained and is given in Fig. 5. The reduced mass μ was obtained by the following method. As given previously (2), the potential minimum is located at $Q = 0.655 \text{ amu}^{1/2} \text{ \AA}$ in the CH_3NH_2 molecule. This position should correspond to $\theta = 51^\circ$ on the basis of the known geometry of this molecule (1). Here, θ is defined as the angle between the HNH plane of the planar amino group and the HNH plane of a

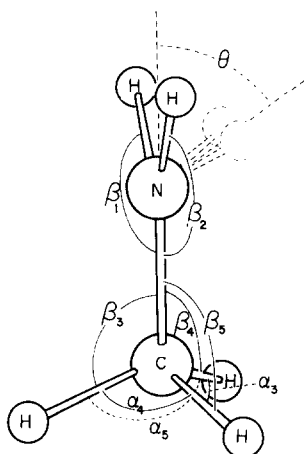


Fig. 7. Structure of the methylamine molecule with a planar amino group. Angles θ , α 's, and β 's are defined as shown here.

pyramidal amino group which is reached by a deformation of the planar amino group along the amino-wagging coordinate (Fig. 7). By substituting these values in Eq. (3), the value of μ (whose dimension is mass \times length² here) at $\theta = 51^\circ$ is obtained. By assuming that this value remains constant over the amino-wagging coordinate, the scale of θ is given along the abscissa (Fig. 5). Such a relation between the potential energy and θ should be approximately valid not only for CH_3NH_2 but also for CH_3ND_2 , because the vibrational coupling between the amino wagging and other modes is not great in both of these isotopic methylamines. By assuming that $Q = 0.845 \text{ amu}^{1/2} \text{ \AA}$ corresponds to $\theta = 51^\circ$ in CH_3ND_2 (2), the scales of Q and ξ were calculated and are given in Fig. 5.

As shown in Figs. 1 and 2, and as given in Table I, the vibrational bands can be observed up to $v_1' = 12$ for CH_3NH_2 and up to $v_1' = 16$ for CH_3ND_2 in the band-progression of $(v_1' = 0, 1, 2, \dots; v_2' = 0) \leftarrow (v_1'' = 0, v_2'' = 0)$. As is seen in Fig. 5, the energy level with $v_1' = 12$ of CH_3NH_2 or that with $v_1' = 16$ of CH_3ND_2 corresponds to a classical vibration with the amplitude of $\pm 90^\circ$. It is interesting that the amino-wagging potential is almost harmonic up to such a great amplitude.

The amino-wagging energy levels were determined not only for ground-state methylamine but also for ground-state aniline (10, 11) and formamide (12). The potential constants of these molecules were calculated by adopting the potential function Eq. (2). The results are given in Fig. 8 for comparison. It is apparent here that the exponential hump becomes smaller in the order of $\text{CH}_3\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{HCONH}_2 \rightarrow \text{excited CH}_3\text{NH}_2$. The size of the hump may be related with the electron density in the lone pair orbital on the nitrogen

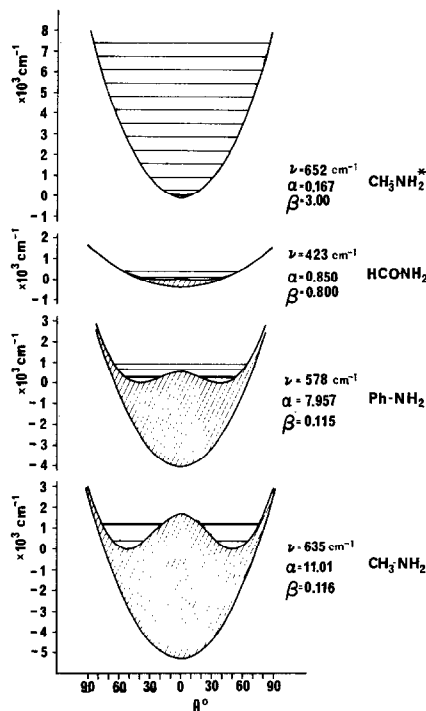


FIG. 8. Amino-wagging potentials in the methylamine, aniline, formamide, and excited methylamine molecules.

atom. Thus, in aniline, the lone pair electrons are considered to migrate partly towards the π -electron system. This trend is known to be greater in formamide. In the excited methylamine, one of the lone pair electrons is considered to be taken up from its original orbital onto the $3s$ orbital of the nitrogen atom (13).

VI. A NORMAL COORDINATE TREATMENT

If the excited methylamine molecule is assumed to have the C_s symmetry with the HNH plane as the symmetry plane (Fig. 7), there should be nine A' type and six A'' type normal vibrations. Of the A'' type vibrations, no information has been obtained in the present experiment. For the A' type vibrations, the inverse kinetic energy matrix (\mathbf{G} matrix) was first calculated by the standard method (14). In this calculation, bond lengths r 's and bond angles α 's and β 's are assumed as follows: $r_{\text{NH}} = 1.08 \text{ \AA}$, $r_{\text{CN}} = 1.540 \text{ \AA}$, $r_{\text{CH}} = 1.093 \text{ \AA}$, $\alpha_{\text{HNH}} = 120^\circ$, $\alpha_{\text{CNH}} = 120^\circ$, $\beta_3 = \beta_4 = \beta_5 = \alpha_3 = \alpha_4 = \alpha_5 = 109^\circ 28'$ (see Fig. 7. The r_{NH} is assumed to be equal to the r_{NH} of excited ammonia (15). This means that the covalent radius of the nitrogen atom is $0.066 \text{ \AA} = (1.08 - 1.014) \text{ \AA}$ longer in the excited state than that in the ground state. Therefore, the r_{CN} is assumed to be $1.474 \text{ \AA} + 0.066 \text{ \AA} = 1.540 \text{ \AA}$.) The \mathbf{G} matrix of the methylamine mole-

cule with the planar amino group is essentially similar to that of a molecule having the C_{2v} symmetry, and the \mathbf{G} matrix for the A' type vibrations is factored into 4×4 and 5×5 matrices. The former has a CH_3 stretching coordinate in its base. The CH_3 stretching frequency is considered to be so high that the vibrational coupling with other modes can be neglected. Thus, the \mathbf{G} matrix in question becomes a 3×3 matrix with the three symmetry coordinates,

$$\mathbf{S} = \begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} \theta \\ 2\Delta\alpha_3 - \Delta\alpha_4 - \Delta\alpha_5 \\ 2\Delta\beta_3 - \Delta\beta_4 - \Delta\beta_5 \end{pmatrix}, \quad (5)$$

as its base. By a transformation,

$$\mathbf{S}' = \mathbf{T}\mathbf{S}, \quad (6)$$

where

$$\mathbf{T} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/1.018 & -0.19/1.018 \\ 0 & 0.19/1.018 & 1/1.018 \end{pmatrix}, \quad (7)$$

\mathbf{G} matrix is approximately factored into 1×1 and 2×2 matrices; both of the two off-diagonal elements of the new \mathbf{G} matrix, $G(S_1', S_2')$ and $G(S_2', S_3')$, are less than one fifth of the other off-diagonal element $G(S_1', S_3')$ for every of the four isotopic species. Let us call $S_1' (\equiv S_w)$ as "amino-wagging" coordinate and $S_3' (\equiv S_r)$ as "methyl-rocking" coordinate.

The potential energy matrix, \mathbf{F} , on the basis of the symmetry coordinates S_w and S_r is assumed to be a diagonal matrix and to be the same for all of the four isotopic methylamines. The values of the two elements, f_w and f_r , were determined by a trial and error method, so that an agreement is obtained between the observed and calculated frequencies. The calculated normal frequencies on $f_w = 0.155$ millidyne-Å and $f_r = 0.650$ millidyne-Å are given in the second column of Table II. They are in a satisfactory agreement with the observed frequencies. The vibrational mode in each normal vibration is shown in the fourth and fifth columns of Table II by the elements of the \mathbf{L} matrix,

$$\mathbf{S}' = \mathbf{L}\mathbf{Q}, \quad (8)$$

where \mathbf{Q} is the normal coordinates. As a comparison of the values of these elements shows, the vibrational coupling between the amino-wagging and methyl-rocking modes is greatest in CD_3NH_2 , next greatest in CD_3ND_2 , smaller in CH_3NH_2 , and smallest in CH_3ND_2 .

VII. INTENSITIES OF THE VIBRATIONAL BANDS

The relative intensities observed of the bands in each band system are explained on the basis of the structure, internal potential, and the vibrational modes determined of the excited methylamine molecules.

TABLE II
NORMAL FREQUENCIES AND NORMAL MODES OF VIBRATIONS^a OF THE EXCITED MOLECULES
OF FOUR ISOTOPIC METHYLAMINES

	$\nu_{\text{calc}} \text{ cm}^{-1}$	$\nu_{\text{obs}} \text{ cm}^{-1}$	\tilde{L}^a	
			Amino wag.	Methyl rock.
CH_3NH_2	644	651	1.238	-0.099
	1014	1004	0.318	0.953
CH_3ND_2	500	502	-0.967	0.060
	1013	—	0.250	0.956
CD_3NH_2	623	589	1.108	-0.241
	801	851	0.636	0.697
CD_3ND_2	488	479	0.920	-0.117
	790	800	0.389	0.728

^a The mode of each normal vibration is directly given by the elements of the L matrix. However, if one needs to know the amplitude of each normal vibration caused by a given amount of deformation along the amino-wagging coordinate, for example, one should refer to the element of the L^{-1} matrix, instead of the L matrix itself. For calculating a two-dimensional Franck-Condon overlap integral in the space of the amino-wagging and methyl-rocking coordinates, for example, one needs also the elements of the L^{-1} matrix rather than the L matrix.

For CH_3ND_2 , in the first place, only the ν_1' and ν_1'' frequencies appear in the spectrum, but no ν_2' and ν_2'' frequencies. In other words, no transitions with $\Delta v_2 \neq 0$ are observed with appreciable intensities. This fact is related to our conclusion that, in CH_3ND_2 , the vibrational coupling between the amino-wagging and methyl-rocking is very little. The ν_1' or ν_1'' is an almost pure amino-wagging vibration, and the change in the equilibrium position of the nuclei in going from the ground state to the excited state is represented almost only by the vibrational mode of ν_1 . Therefore, the vibrations whose modes are orthogonal to this mode (for example ν_2) should not appear in the band in question.

In the spectrum of CH_3NH_2 , only one progression (11 transitions) with $\Delta v_2 \neq 0$ appears. For CD_3ND_2 , three progressions (23 transitions all together) with $\Delta v_2 \neq 0$ are observed, and for CD_3NH_2 , 25 transitions with $\Delta v_2 \neq 0$ (see Table II). How many transitions with $\Delta v_2 \neq 0$ can have observable intensities should depend upon how much coupling takes place between the amino-wagging and methyl-rocking vibrations. It has been shown that the vibrational coupling now in question becomes greater in the order of CH_3ND_2 , CH_3NH_2 , CD_3ND_2 , and CD_3NH_2 (Sect. VI). This order is the same with the order in which the transitions with $\Delta v_2 \neq 0$ become stronger.

The relative intensity of each band in a band-progression should be determined, according to the Franck-Condon principle, by the overlap integral of the

vibrational state of upper and lower electronic states. For CH_3NH_2 and CH_3ND_2 , in which vibrational coupling between the amino-wagging and methyl-rocking modes is little, only the one-dimensional overlap integral,

$$R(v_1' \leftarrow v_1'') = \int_{-\infty}^{\infty} \psi_{v_1'}(Q_1)^* \psi_{v_1''}(Q_1) dQ_1, \quad (9)$$

may be taken into consideration. In Fig. 5, the vibrational wave functions $\psi_{v_1'}(Q_1)$ for $v_1' = 4, 5$, and 6 and $\psi_{v_1''}(Q_1)$ for $v_1'' = 0$ are illustrated as curves. These curves show that the overlap integral $R(v_1' \leftarrow 0)$, where $v_1' = 0, 1, 2, \dots, 12$, takes a maximum value at $v_1' = 5$. (For the ground state CH_3NH_2 molecule, there are two levels for $v_1'' = 0$ located very close to each other; the separation is less than 0.2 cm^{-1} . The wave function of one of these two levels is symmetric with respect to the operation $Q_1 \rightarrow -Q_1$, whereas the wave function of the other level is antisymmetric. The overlap integral (Eq. 9) should be calculated by the use of the symmetric $\psi_0(Q_1)$ if $v_1' = \text{even}$ and antisymmetric $\psi_0(Q_1)$ if $v_1' = \text{odd}$). Thus, the fact that the intensity maximum appears at $v_1' = 5$ in the band-progression $(v_1' = 0, 1, 2, \dots, 12) \leftarrow (v_1'' = 0)$ of CH_3NH_2 has been explained. As shown in Fig. 5, the energy level with $v_1' = 7$ of CH_3ND_2 is what is situated nearest to the energy level with $v_1' = 5$ of CH_3NH_2 . Therefore, the fact that the intensity maximum appears at $v_1' = 7$ in the band-progression $(v_1' = 0, 1, 2, \dots, 16) \leftarrow (v_1'' = 0)$ of CH_3ND_2 is understandable.

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