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Vibration-rotation Spectra of Formamides

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Taking advantage of the Fourier transform infrared (FTIR) spectrophotometry in accumulating a very weak available radiation, which comes out from a multiple-reflection-type gas-cell (17 m), we have been able to record the infrared absorption spectrum of formamide ($HCONH_2$ or $DCONH_2$) at room temperature, where its vapor pressure is only 0.1 Torr (1 Torr≈133.322 Pa) in the order of magnitude. From an analysis of the rotational structure (resolution 0.5 cm^{-1}) of the C–H stretching band, a revised set of parameters has been obtained. A *Q*-branch analysis was made for the $v=2\leftarrow0$ and $v=3\leftarrow1$ bands (resolution 0.24 cm^{-1}) of the amino wagging vibration, where v is its vibrational quantum number. The rotational constants $A-B$ were determined to be 2.0269 cm^{-1} for the $v=2$ state and 1.9990 cm^{-1} for the $v=3$ state, and the transition frequencies 657.7_5 cm^{-1} for $v=2\leftarrow0$ and 769.8_5 cm^{-1} for $v=3\leftarrow1$. On the basis of these new parameter values, a discussion was made of the amino wagging coordinate of this molecule.

The molecular structure of formamide is now precisely known through a microwave study of Hirota *et al.*[1)] as well as previous investigations cited by them. The microwave spectrum was observed, not only for the ground-state molecule, but also for a few lower-lying vibrational excited states. It is desirable, however, to observe its vibration-rotation transitions directly by the infrared spectroscopy, to ellucidate intramolecular potential and vibration-rotation interaction in detail. Thanks to the recent FTIR (Fourier transform infrared spectrophotometry) technique, we have succeeded for the first time in observing vibration-rotation spectrum of formamide at room temperature. At room temperature, the vapor pressure of formamide is very low (only 0.1 Torr in the order of magnitude), and an optical path as long as 17 m which is obtained by the use of a multiple-reflection-type gas cell is needed. This causes a very low infrared radiation energy available. By accumulating (1000 times, for example) interferograms of such a weak radiation, however, we could reach a sufficiently good spectrum.

Previous works of the infrared spectrum of formamide vapor were all done at higher temperatures; for example, at 126 °C[2)] or 180 °C.[3)] At these temperatures, some disturbing emissions, hot-band absorptions, and impurity bands (from decomposition products, *etc.*) may often be generated from the sample system.

Experimental

$HCONH_2$ was purchased from Inumaru Co., Ltd. and $DCONH_2$ from Merck Sharp and Dohme, Canada Ltd. These were used after being dried in vacuum. The sample was placed in a multiple-reflection cell of Wilks Scientific Corporation. Its optical path was set at 17.25 m. Infrared absorption measurement was made with a Nicolet 7199 FT-IR system. The resolution was set at 1.0 cm^{-1} (Figs. 1 and 2), at 0.5 cm^{-1} (Fig. 3), or at 0.24 cm^{-1} (Figs. 4 and 5). For each spectral measurement, the interferometer was scanned 1000 times, and each interferogram was accumulated for Fourier transform.

Results and Interpretations

Whole Vibrational Spectrum. In Figs. 1 and 2, the whole spectra (4000—400 cm^{-1} region) of $HCONH_2$ and $DCONH_2$ are reproduced with a lower dispersion.

For many bands, the fine structures are found to be rather simple. If the band is of A-type or A-B hybrid, the central *Q*-branch is readily identified. When the *Q*-branch peaks are sharp enough, the frequencies of such peaks were determined with errors less than ±0.2 cm^{-1}. Therefore, the fundamental frequencies of such bands were determined rather precisely without any detailed analyses (although a slight difference between

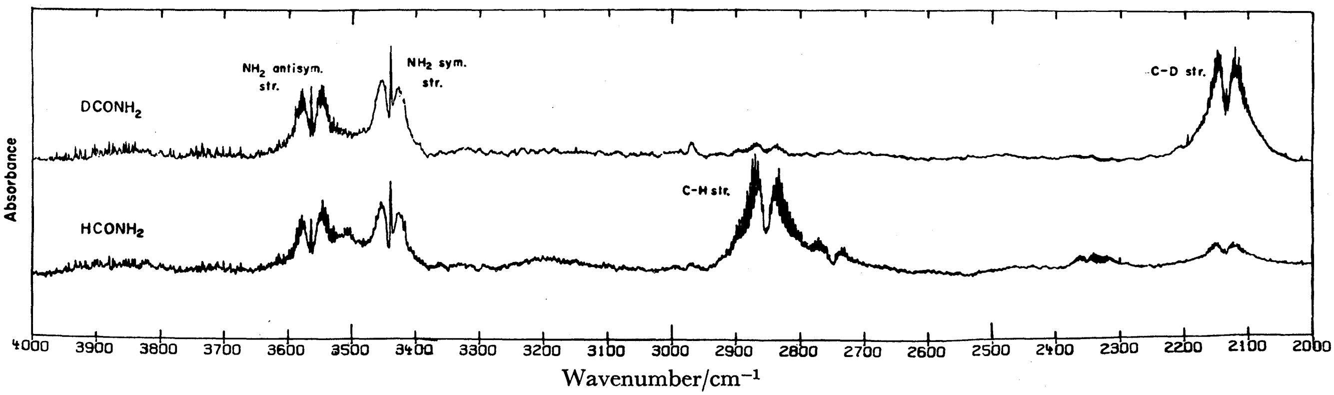

Fig. 1. Infrared absorption spectra (4000—2000 cm^{-1} range) of $HCONH_2$ and $DCONH_2$ in gaseous states. Pressure, vapor pressure at 20 °C. Optical path length, 17.25 m. Resolution, 1.0 cm^{-1}.

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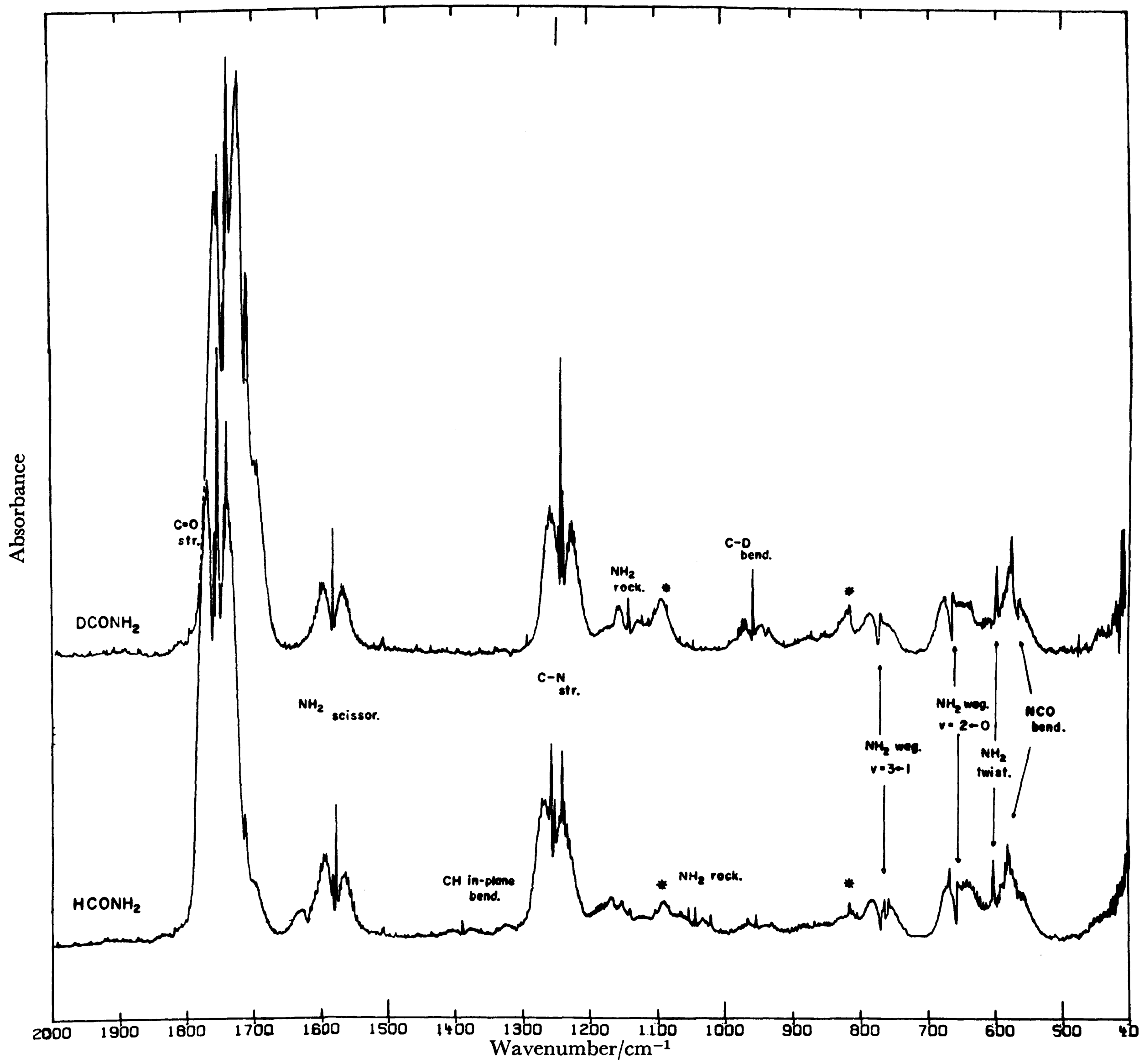

Fig. 2. Infrared absorption spectra (2000—400 cm^{-1} range) of $HCONH_2$ and $DCONH_2$ in gaseous states. Pressure, vapor pressure at 20 °C. Optical path length, 17.25 m. Resolution, 1.0 cm^{-1}. The peaks with* are probably due to impurity.

the Q-peak and band center frequencies must be taken into account). For other bands, however, some ambiguity (given in the footnotes of Table 1) remains in locating the band centers, and therefore in fixing the fundamental frequencies with any greater accuracy than ± 1 cm^{-1}. In Table 1, the fundamental frequencies are listed with these uneven accuracies. The data in the table will be useful in a detailed study of the force field of this molecule in its completely free state.[4]

CH Stretching Band. The band at 2854 cm^{-1}, assignable to the C–H stretching vibration of $HCONH_2$, is an example of what shows relatively simple structure, as shown in Fig. 3. This is a nearly pure B-type band. This is understandable because the C–H bond is directed nearly along the B axis of the molecule. The band consists of a progression of peaks assignable to Q-branch clusters, whose J-structures are not resolved because $\bar{B}'-\bar{B}''$ is small. Evans[2] reported his analysis of this progression with a lower resolution, and we now revise it as follows: Our new K-numbering is given in Fig. 3; this was fixed by forming combination differences for a few trial sets of assignments. As may be seen in the figure, ${}^RQ_9$ and ${}^PQ_{11}$ peaks are both broader and lower than the neighboring peaks. This probably means that the upper $K'=10$ state has an anomaly. Such a correspondence (of ${}^RQ_9$ and ${}^PQ_{11}$), on the other hand, may be taken as another support to the assignment. By assuming that the rotational energy is given by $(A-\bar{B})K^2-D_KK^4$, combination relation,

$$({}^RQ_K-{}^PQ_K)/4K = (A'-\bar{B}') + D_K(2K^2+2) \qquad (1)$$

is derived, where the centrifugal distortion constant D_K is assumed to have an equal value in the upper state to that in the lower state. By the use of this relation, the upper state rotational constant $A'-\bar{B}'$ has been determined to be 2.060 ± 0.003 cm^{-1}, and $D_K=(0.38\pm0.04)\times10^{-4}$ cm^{-1}. From a similar combination relation, the lower state rotational constant $A''-\bar{B}''$ came out to be 2.070 ± 0.003 cm^{-1}, which is in agreement with what was determined by the microwave spectroscopy

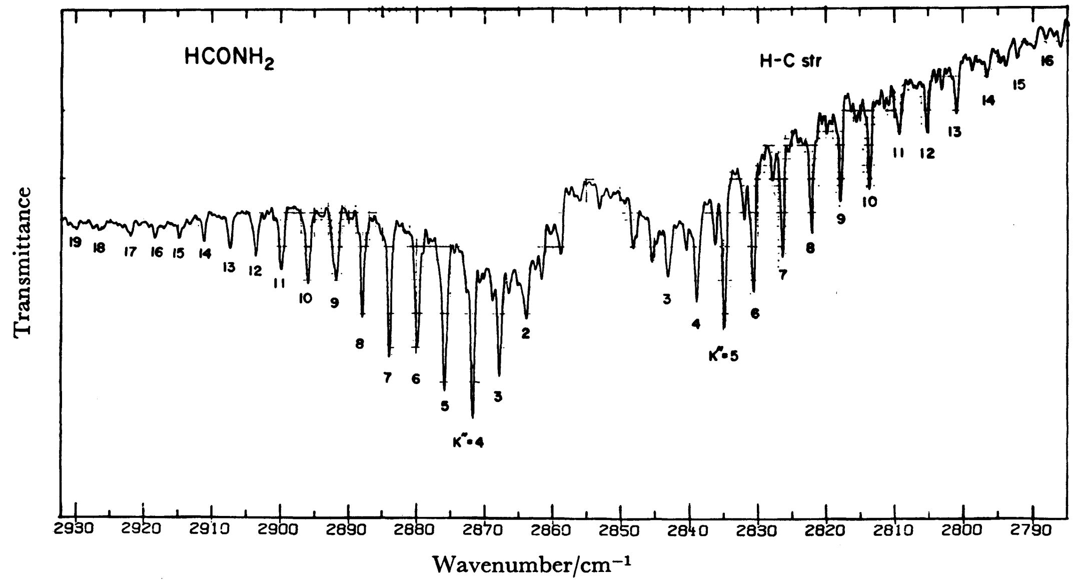

Fig. 3. Fine structure of the absorption band of $HCONH_2$ at 2854 cm^{-1} assignable to the C–H stretching vibration. At the vapor pressure of 20 °C. Optical path length, 17.25 m. Resolution, 0.5 cm^{-1}.

Table 1. Observed frequencies assignable to the fundamental vibrations of $HCONH_2$ and $DCONH_2$

Frequency ν/cm^{-1}		Assignment[a]
$HCONH_2$	$DCONH_2$	
In-plane modes		
3563.5	3563.2	NH_2 antisym. stretching
3439.3	3437.8	NH_2 sym. stretching
2853.6		CH stretching
	2135.0	CD stretching
1754.1	1739.6	CO stretching
1576.9	1582.4	NH_2 scissoring
1390.2		CH bending
	955.0	CD bending
1258.2	1241.8	CN stretching
1045.6[b]	1142.4	NH_2 rocking
581[c]	563[c]	NCO bending
Out-of-plane modes		
1021.2[d]		CH out-of-plane deformation
	——[e]	CD out-of-plane deformation
602.8[c]	591.4[c]	NH_2 twisting
(288.7)[f]		NH_2 wagging

a) Ref. 4. b) Band shape is anomalous, probably for a Coriolis coupling with the $v=3$ level of NH_2 wagging. c) NCO bending and NH_2 twisting levels are considered to be involved in a Coriolis interaction, and therefore no reliable band center determination is possible for these bands in our present resolution. d) The assignment is not sufficiently supported. e) CD out-of-plane deformation band is considered to be too weak for our present observation or hidden under another band. f) Not observed in the present study. This is what was observed by King[3].

(2.0705 cm^{-1}). Finally, the band center frequency has been determined with a considerable precision: $\nu_0 = 2853.63 \pm 0.10$ cm^{-1}.

Overtone Bands of Amino Wagging Vibration. King[3] observed the far-infrared spectrum of $HCONH_2$ in the 200—450 cm^{-1} region, and found three peaks at 288.7, 368.6, and 401 cm^{-1}. These were assigned by Hirota *et al.*[1] respectively to the $v=1 \leftarrow 0$, $2 \leftarrow 1$, and $3 \leftarrow 2$ transitions of the amino wagging vibration. They also proposed[1] to assign a band at 660 cm^{-1} reported by King[3] to $v=2 \leftarrow 0$ and that at 770 cm^{-1} to $v=3 \leftarrow 1$ of the amino wagging vibration. These two bands have been observed in our present study with a higher resolution (0.24 cm^{-1}) and with an expanded wavenumber scale. The results are reproduced in Figs. 4 and 5. It is readily seen that both of these are primarily A-type bands; *P* and *R* progressions with apparent average spacings of about 0.7 cm^{-1}, which is nearly equal to $2\bar{B}$, are recognized. It is noticeable that the central *Q*-branch absorption shows a distinct *K*-structure in each of these two bands. This fact means that the rotational constant $A-\bar{B}$ is appreciably different in the upper amino wagging state from that in the lower state. The *K*-numbering given in Figs. 4 and 5 was fixed by calculating simulation spectra with a number of trial sets of rotational constants, and by comparing the calculated intensity distribution among the *Q*-branch lines with what was observed. The calculation was made with a HITAC M200-H in the Computer Center, University of Tokyo, by the use of programs BC2 and ENVLOP written by Dr. T. Nakagawa, and our own plotter program. The frequency of each of these ${}^{Q}Q_K$ peaks is approximately given by

$$ {}^{Q}Q_K = \nu_0 + [(A'-\bar{B}') - (A''-\bar{B}'')]K^2, \quad (2) $$

and practically independent of the $\bar{B}'$ and $B'-C'$ values. Because the $A''-\bar{B}''$ values (for $v=0$ and 1) are known,[1] the band center ν_0 and $A'-\bar{B}'$ are readily fixed:

$\nu_0 = 657.7_5$ cm^{-1} for the $v = 2 \leftarrow 0$ band,

$\nu_0 = 769.8_5$ cm^{-1} for the $v = 3 \leftarrow 1$ band,

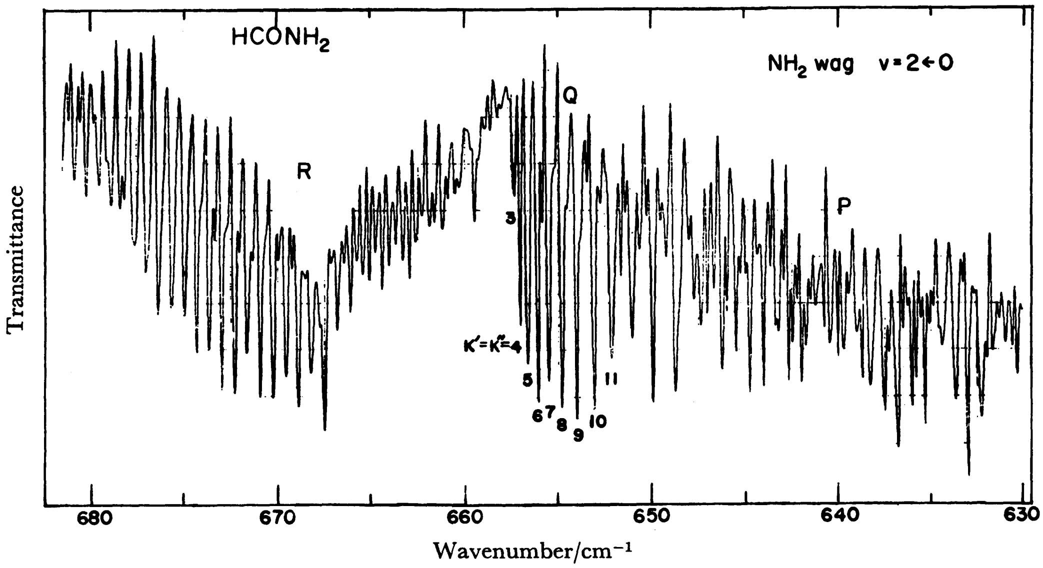

Fig. 4. Fine structure of the absorption band of HCONH$_2$ at 658 cm^{-1} assignable to the $v=2\leftarrow 0$ transition of the amino wagging vibration. At the vapor pressure of 20 °C. Optical path length, 17.25 m. Resolution, 0.24 cm^{-1}.

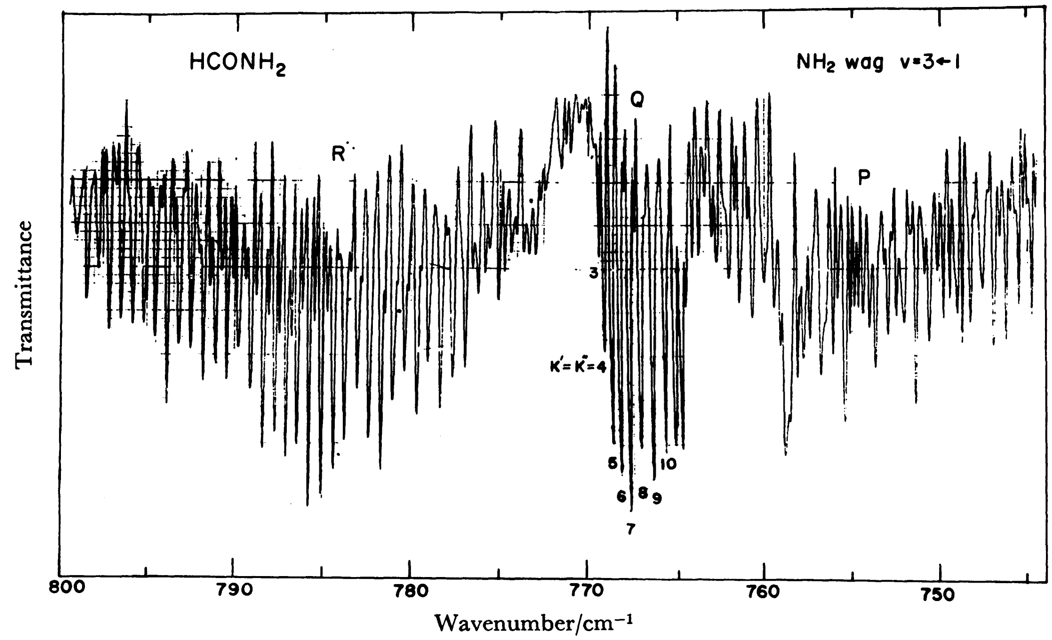

Fig. 5. Fine structure of the absorption band of HCONH$_2$ at 770 cm^{-1} assignable to the $v=3\leftarrow 1$ transition of the amino wagging vibration. At the vapor pressure of 20 °C. Optical path length, 17.25 m. Resolution, 0.24 cm^{-1}.

$$A-\bar{B}=2.0269\ \mathrm{cm}^{-1} \quad \text{for the } v=2 \text{ state,}$$

and

$$A-\bar{B}=1.9990\ \mathrm{cm}^{-1} \quad \text{for the } v=3 \text{ state.}$$

It should be pointed out that an anomaly in the Q-branch progression of the $v=3\leftarrow 1$ band is apparent at $K=11$, 12, and a few subsequent K values. Here, the spacings are smaller than they ought to be and intensity distribution is also different from what is expected (see Fig. 5). This is considered to be caused by an A axis ($\Delta K=0$) Coriolis coupling between the $v=3$ level (A'', at 1058 cm^{-1}) of the amino wagging vibration, now in question, and the first excited state (A', at 1045 cm^{-1}) of the amino rocking vibration. If the $A-\bar{B}$ value in the latter state is assumed to be 2.0719 cm^{-1} (equal to the $A-\bar{B}$ value of the ground vibrational state), the accidental coincidence of the unperturbed rotational levels should take place at about $K=14$ of the two vibrational states. The observed band shape of the 1045 cm^{-1} band is also anomalous.

Next an estimation of the $\bar{B}'$ values was made. The $\bar{B}'$ value is reflected in the apparent spacing of the P branch progression. Because of the K-structure of each P branch ($\Delta J=-1$) transition, however, the apparent spacing is not simply correlated to the rotational constants $\bar{B}'$. We have to repeat trial calculation with a

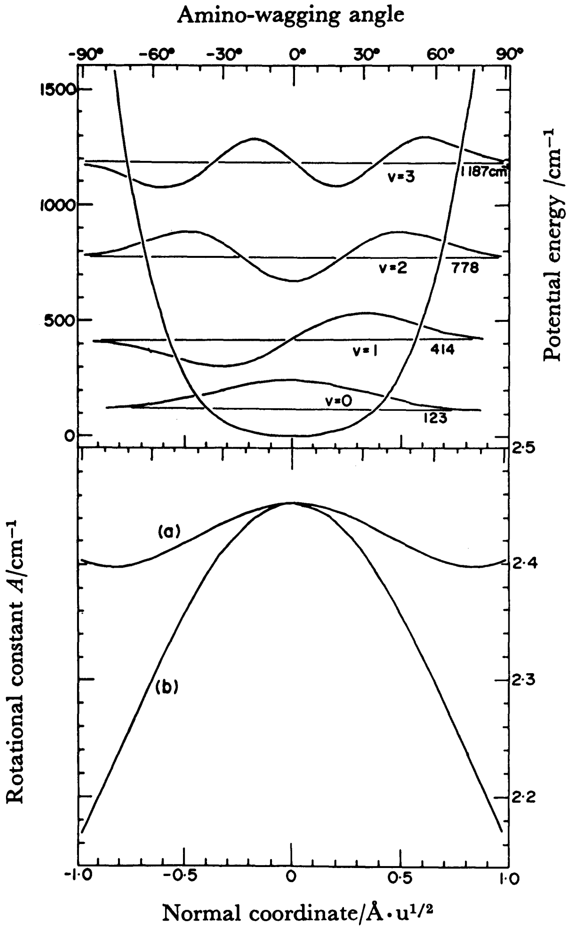

Fig. 6. (Upper) Amino wagging potential function, energy levels, and eigenfunctions of $HCONH_2$. (Lower) Rotational constant A as a function of amino wagging coordinate τ. (a) Calculated on an assumption that, in the "amino wagging motion," only the angle between the OCN plane and the bisector of $\angle$HNH changes, while all the bond lengths and bond angles (except CNH's) are kept unchanged. (b) Calculated by Eq. 5, which was derived to fit the calculated A_v's to the observed (A_v's).

trial $\bar{B}'$ value and with the known $A'-\bar{B}'$ value. Calculation indicates, for example, that in the 670—680 cm^{-1} spectral range 20 main spacings should be involved if $\bar{B}$ (at $v=2$) is assumed to be 0.3505 cm^{-1}, 17 spacings for $\bar{B}$ $(v=2)=0.3518$ cm^{-1}, 15 for $\bar{B}$ $(v=2)=0.3537$ cm^{-1}, and 14 for $\bar{B}$ $(v=2)=0.3547$ cm^{-1}. In the observed spectrum, there are 15 spacings involved in this spectral range (see Fig. 4). In this way we may reach a conclusion that $\bar{B}$ (at $v=2$)$=0.3537\pm0.0005$ cm^{-1}. Likewise, by examining the P branch progression in the 780—790 cm^{-1} spectral range, we know that $\bar{B}$ (at $v=3$)$=0.3534\pm0.0005$ cm^{-1}.

Discussion

One of the interesting problems in the formamide molecule is concerned with the large amplitude motion along the amino wagging coordinate. It has nearly been established that the equilibrium conformation of the molecule is planar.[1)] The arrangement of the amino wagging levels (which has now been precisely determined) indicates, however, that the potential function (V) of this out-of-plane motion is severely anharmonic. It involves the fourth power of the amino wagging coordinate (τ) besides the quardratic term, and it is approximately given as,

$$V = V_2\tau^2 + V_4\tau^4. \qquad (3)$$

A Hamiltonian with this potential was solved as will be detailed below, and by a least squares fit for the four energy levels ($v=0$, 1, 2, and 3) the coefficients were fixed as $V_2=156$ $cm^{-1}/radian^2$ and $V_4=410$ $cm^{-1}/radian^4$. This is close to what Hirota *et al.*[1)] gave, but this gives a slightly better fit for the observed levels with $v=2$ and 3. The eigenvalues and eigenfunctions $\psi_v(\tau)$. of the amino wagging Hamiltonian with the potential energy of Eq. 3 are illustrated in the upper half of Fig. 6. In the calculation, the Hamiltonian matrix was represented by the use of proper harmonic oscillator basis functions. If the order of matrix is taken sufficiently large, the eigenvalues and eigenfunctions of lower levels are found independent of the frequency of the basis harmonic oscillator itself. For example, the eigenvalues and eigenfunctions of the lower four levels, shown in Fig. 6, were obtained by diagonalizing a 40×40 Hamiltonian matrix in the representation of the harmonic oscillator with its frequency 156 cm^{-1}. These were found to be exactly equal (over the four significant figures) to those obtained by diagonalizing a 40×40 matrix in the representation of the harmonic oscillator with 300 cm^{-1}.

Let us now proceed with an examination of the amino wagging coordinate, τ. Let us assume, for trial, that τ is equal to the angle between the OCN plane and the bisector of $\angle$HNH. The rotational constant A has been calculated, for trial, at various τ values (0°—90°) by keeping all the bond lengths and bond angles (other than $\angle$CNH's) at the values given by Hirota *et al.*[1)] The result is shown in the lower portion of Fig. 6 (curve (a)). On the basis of this $A-\tau$ relation, the average rotational constant at each wagging level can be calculated by

$$A_v = \int_{-\pi}^{\pi} \psi_v(\tau)A(\tau)\psi_v(\tau)\mathrm{d}\tau, \qquad (4)$$

where $v=0$, 1, 2, and 3. The result is given in the fifth column of Table 2. As may be seen here, the calculated A_v's show desperate disagreement with the observed A_v's. This means that the actual amino wagging motion is greatly different from the mere out-of-plane motion of the NH_2 triangle.

We next inquire: what $A-\tau$ relation can fit the observed A_v values (for $v=0$, 1, 2, and 3)? By expressing A by a power series of τ, a least squares fit resulted in the following expression:

$$A = 2.4520 - 0.1555\tau^2 + 0.01667\tau^4, \qquad (5)$$

where A is given in cm^{-1} and τ in radian. This $A-\tau$ relation is shown by curve (b) in Fig. 6. The A_v values obtained by Eq. 4 with this $A-\tau$ relation (Eq. 5) are given in the last column of Table 2. The fit of the calculated A_v values to the observed A_v has certainly been improved. Comparing the curve (a) with (b) in Fig. 6, we now conclude that a large displacement along the amino wagging coordinate causes a great lowering of

TABLE 2. ROTATIONAL CONSTANTS (IN cm^{-1}) OF $HCONH_2$

Vibrational level a)	$A-B$ observed	B observed	A observed	A calculated (a) c)	A calculated(b) d)
$v=0$	2.071873 b)	0.3537024 b)	2.425575 b)	2.4435	2.4298
1	2.039523 b)	0.3534253 b)	2.392948 b)	2.4314	2.3955
2	2.0269	0.353$_7$	2.380$_6$	2.4254	2.3737
3	1.9990	0.353$_4$	2.352$_4$	2.4206	2.3557

a) v is the vibrational quantum number of the amino wagging vibration. b) Determined by Hirota *et al.*1) by microwave spectroscopy. c) Calculated from the A-τ relation given by the curve (a) of Fig. 6 by Eq. 4. d) Calculated from the A-τ relation given by the curve (b) of Fig. 6 by Eq. 4.

A value (*i.e.*, a great increase of the moment of inertia I_A); the amount of lowering is much greater than that expected for a simple out-of-plane bending of the NH_2 triangle. In other words, this bending motion must be accompanied by appreciable amounts of stretching of some bonds and opening of some angles. Such a coupling of the out-of-plane wagging and in-plane modes may be mainly caused, as Hirota *et al.*1) pointed out, by anharmonic potential constants. As they also showed, a coupling may partly be caused by a Coriolis force. It should be pointed out, however, that the partner level of an A axis Coriolis coupling should have A'' symmetry for the $v=2$ wagging level (A'), whereas A' symmetry for the $v=3$ wagging level (A'').

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