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Rotational Isomerism in Methyl-*d*-amine

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Infrared absorption spectra of methyl-*d*-amine and methyl-*d*-amine-d_2 have been observed in their gaseous states. For each of seven vibrations of the former and seven vibrations of the latter, two Q-branch peaks are observed assignable to *trans* and *gauche* forms of the molecule. In the microwave absorption spectrum of methyl-*d*-amine 60 lines assignable to the *trans* form (whose rotational constants are $A=86085$, $B=20546$, and $C=20475$ MHz) and 140 lines assignable to the *gauche* form ($A=86512$, $B=21243$, and $C=19911$ MHz) are found. Every *trans* line shows an inversion doubling which is considered to reach an observable amount only through a *trans-gauche* mixing of the vibration-rotation wavefunctions. This *trans-gauche* mixing should in turn depend upon the energy difference ΔE_{TG} between the ground vibration-rotation levels of the *trans* and *gauche* forms. On the basis of the observed amount of the inversion splitting, ΔE_{TG} has been determined to be 6.7 ± 0.4 cm^{-1}. The ΔE_{TG} value has then been refined by observing an accidental degeneracy of the *trans* and *gauche* energy levels, so that $\Delta E_{TG}=7.06\pm0.03$ cm^{-1}.

For the normal methylamine (CH_3NH_2) molecule, there are three equivalent equilibrium positions of the methyl group in the internal rotation with respect to the amino group. On substituting one of the methyl hydrogens by deuterium (*i.e.*, on going from CH_3NH_2 to CH_2DNH_2), the threefold symmetry of the torsion Hamiltonian is removed. The three potential minima are not equivalent any more; one of them corresponds to the *trans* and the other two *gauche* conformations (see Fig. 1). It should be remembered, however, that the intramolecular potential itself is not affected by an isotopic substitution. Thus, the shape of the potential function is exactly equal in the vicinity of the *trans* conformation to that in the vicinity of the *gauche* conformation even in the methyl-*d*-amine molecule. In addition, the reduced moment of inertia of the torsional oscillation would not greatly different in the *trans* form from that in the *gauche* form. Therefore, at first thought, one might guess that the energy difference between the torsional levels of *trans* and *gauche* forms would be very small and a pronounced mixing between the wavefunctions of these forms may take place so that no appreciable rotational isomerism can be observed.

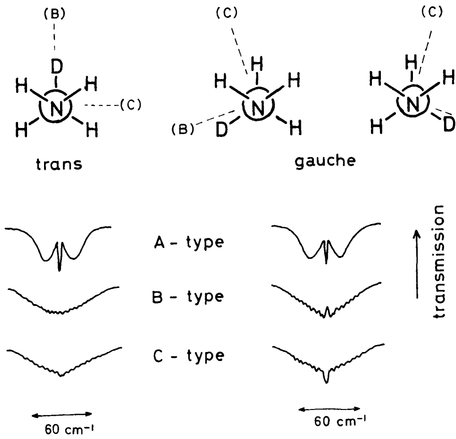

Fig. 1. Three equilibrium positions of the CH_2D group in the internal rotation with respect to the NH_2 group of the CH_2DNH_2 molecule. Of the three principal axes of inertia, A-axis is nearly along the C–N bond, while B- and C-axes are directed as shown in this figure. The band envelope of each of the A-, B-, and C-type bands expected with the resolving power 3 cm^{-1} of CH_2DNH_2 is also given on the basis of a calculation made by Ueda and Shimanouchi (*J. Mol. Spectroscopy*, **28**, 350 (1968)).

Actually, however, our analysis[1] of the far-infrared absorption spectrum of CH_2DNH_2 indicated that, in the ground torsional state ($n=0$) and in the first excited state ($n=1$), there are well-defined *trans* and *gauche* rotational isomers. Such a lack of mixing was attributed mostly to the situation that the mode of coupling of the torsional oscillation with other vibrations is different in the *trans* and *gauche* forms. Only in the higher excited states ($n\geqq2$), a pronounced mixing was found to take place between the *trans* and *gauche* torsional wavefunctions. In the present paper, we report our examination on how this isomerism appears in the infrared and microwave absorption spectra. From an analysis of the microwave spectrum, the energy difference of the rotational isomers in the vibrational ground state has been determined. This will also be reported below.

Infrared Absorption Spectra

Infrared absorption spectra of methyl-*d*-amine (CH_2DNH_2) and methyl-*d*-amine-d_2 (CH_2DND_2) have been observed in their gaseous states.

The sample of CH_2DNH_2 gas used is the same as what was used in our previous work.[1] The sample was placed in a gas cell, with two KBr windows, a path-length of 10 cm, and potassium hydroxide as a desiccant. CH_2DND_2 gas was obtained by adding D_2O solution of methyl-*d*-ammonium-d_3-chloride (CH_2DND_3Cl) on solid sodium deuteroxide (NaOD). Here, CH_2DND_3Cl was prepared by dissolving methyl-*d*-ammonium chloride into D_2O, by removing the solvent in vacuum, and by repeating this procedure several times. Before introducing the CH_2DND_2 sample in a gas cell (10 cm^{-1}), D_2O gas was filled in the cell several times so that the absorbed gas on the cell wall was completely deuterated. As a desiccant, metallic sodium was placed in the cell.

Infrared absorption measurements were made in the

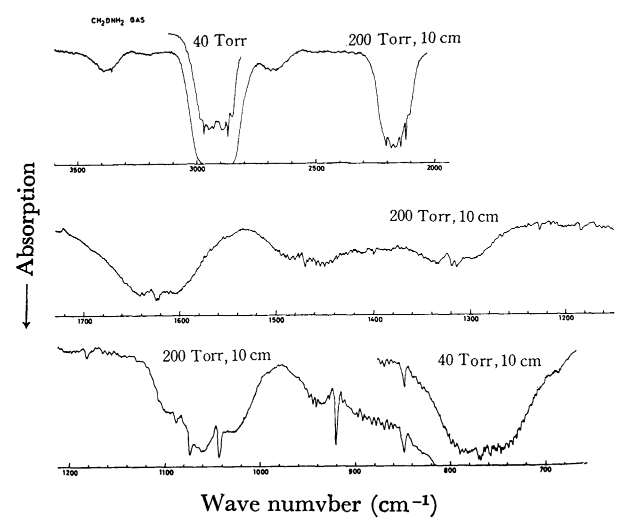

Fig. 2. Infrared absorption spectrum of CH_2DNH_2 (gas).

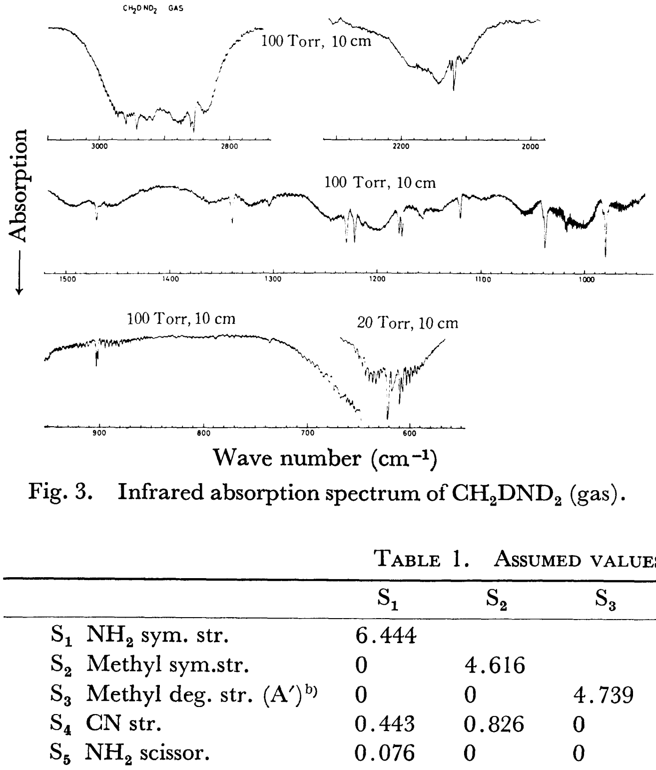

Fig. 3. Infrared absorption spectrum of CH_2DND_2 (gas).

4000—400 cm^{-1} region by the use of a Perkin-Elmer 621 spectrophotometer. The results are shown in Figs. 2 and 3.

A Normal Coordinate Treatment

In an attempt to obtain a guide in our interpretation of the infrared spectra, we have made a calculation of the vibrational frequencies and normal modes of vibration of *trans* and *gauche* forms of CH_2DNH_2 and CH_2DND_2 molecules. The relation between the force constants and the vibrational frequencies is given by the secular equation

$$|\mathbf{GF}-\mathbf{E}\lambda| = 0 \tag{1}$$

where **G** is the inverse kinetic energy matrix, **F** the potential energy matrix, **E** the unit matrix, and λ is equal to $4\pi^2c^2\nu^2$, c being the light velocity, N the Avogadro number, and ν the vibrational wave number. As the basis of the **G** and **F** matrices, we choose a set of symmetry coordinates S defined in our previous paper on the five isotopic species of methylamine.[2] The set of normal coordinates $\mathbf{Q}$ is given as

$$\mathbf{S} = \mathbf{L}_{\mathbf{S}}\mathbf{Q} \tag{2}$$

In our treatment we chose the local symmetry force field.[3] The values of force constants, *i.e.* the **F** matrix elements are assumed as shown in Table 1, for all of the four molecules, CH_2DNH_2 (*trans*), CH_2DNH_2 (*gauche*), CH_2DND_2 (*trans*), and CH_2DND_2 (*gauche*). This set of force constants explains reasonably well the vibrational spectra of CH_3NH_2, CH_3ND_2, CD_3NH_2, CD_3ND_2, and $CH_3{}^{15}NH_2$,[2] and we did not attempt any further adjustment of the force constant values this time. The calculation was made by a HITAC 5020E at the Computer Centre of the University of Tokyo, by the use of programs written by Professor T. Shimanouchi and his collaborators.[4] The calculated fre-

TABLE 1. ASSUMED VALUES[a] OF THE **F**-MATRIX ELEMENTS

	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
S_1 NH_2 sym. str.	6.444								
S_2 Methyl sym.str.	0	4.616							
S_3 Methyl deg. str. (A′)[b]	0	0	4.739						
S_4 CN str.	0.443	0.826	0	5.123					
S_5 NH_2 scissor.	0.076	0	0	−0.230	0.661				
S_6 NH_2 wag.	0.289	0	0	0.304	−0.197	0.566			
S_7 Methyl deg. def. (A′)[b]	0	0	−0.093	0	0.030	0	0.567		
S_8 Methyl sym. def.	0	0.093	0	0.499	−0.023	−0.037	0	0.642	
S_9 Methyl rock (A′)[b]	0	0	0.317	0	0.030	−0.024	−0.057	0	0.789

	S_{10}	S_{11}	S_{12}	S_{23}	S_{14}	S_{15}
S_{10} NH_2 antisym. str.	6.385					
S_{11} Methyl deg. str. (A″)[b]	0	4.739				
S_{12} NH_2 twist.	0.192	0	1.101			
S_{13} Methyl deg. def. (A″)[b]	0	−0.093	0.074	0.567		
S_{14} Methyl rock. (A″)[b]	0	0.317	−0.185	−0.057	0.789	
S_{15} Torsion	0	0	0	0	0	0.048

a) Unit: mdyn/Å for stretch-stretch elements, mdyn/rad for stretch-deform elements, and mdyn·Å/rad² for deform-deform elements.

b) A′ and A″ mean the vibrational modes which would be symmetric and antisymmetric, respectively, with respect to the symmetry plane of the molecule if CH_2D group were ordinary CH_3 group.

quencies are given in Table 2 with approximate statements of the vibrational modes which were derived from the calculated $\mathbf{L}_S$ matrix elements and potential energy distribution.

Ferquency Differences of the *trans* and *gauche* Forms

Some of the observed frequencies assignable to the calculated frequencies are listed also in Table 2.

Table 2. Calculated and observed frequencies (in cm^{-1}) of CH_2DNH_2 and CH_2DND_2 in their gaseous states

Mode	Calculated *trans*	Calculated *gauche*	Observed
CH_2DNH_2			
NH_2 antisym. str.	3427	3427	3395
NH_2 sym. str.	3361	3361	3355
CH_2 antisym. str.	2961	2961	2967, 2927
CH_2 sym. str.	2873	2872	2873, 2868
CD str.	2126	2128	2143, 2118
NH_2 scissor.	1624	1624	1623
CH_2 scissor.	1461	1460	1469
NH_2 tiwst.	1423	1423	——
CH_2 wag.	1333	1336	1319, 1313
CH_2 twist	1278	1279	1227
CN str.	1059	1046	1073, 1042
CH_2 rock. (out-of-pl.)[a]	1055	1088	1187, 1087
CD in-pl. def.	938	879	921, 849
NH_2 wag.	744	779	768, 756
torsion	256	255	~250
CH_2DND_2			
CH_2 antisym. str.	2961	2961	2960, 2943
CH_2 sym. str.	2873	2873	2860, 2855
ND_2antisym. str.	2526	2526	2575, 2557
ND_2 sym. str.	2423	2424	2478, 2469
CD str.	2125	2126	2124, 2119.5
CH_2 scissor.	1460	1459	1471
CH_2 wag.	1335	1338	1340
CH_2 twist.	1279	1279	1213
ND_2 scissor.	1219	1230	1230, 1223
ND_2 twist.	1059	1054	——
CH_2 rock. (out-of-pl.)[a]	1049	1079	——
CN str.	1025	999	1038, 979.5
CD in-pl. def.	900	870	903, 901
ND_2 wag.	585	601	622, 610
torsion	207	207	——

a) "In-pl." means symmetric with respect to the symmetry plane of the CH_2D group, and "out-of-pl." means antisymmetric with respect to this plane.

For each of the CH_2 wagging, CN stretching, NCD bending (along the direction parallel to the symmetry plane of the CH_2D group), and NH_2 wagging vibrations a sharp Q-branch peak is expected both for *trans* and *gauche* forms (see Fig. 1). The calculation indicates that the frequencies of *trans* and *gauche* forms should be appreciably different for each of these vibrations. In fact for each of these vibrations two sharp Q-branch peaks are observed, one of which may be assigned to the *trans* form and the other to the *gauche* form. Likewise, for each of the ND_2 scissoring, C–N stretching, NCD bending, and ND_2 wagging vibrations of CH_2DND_2, two bands are observed as are expected from the normal coordinate treatment.

Two bands are also observed for each of the CH_2 antisymmetric stretching, CH_2 symmetric stretching and CD stretching vibrations of both of the CH_2DNH_2 and CH_2DND_2. In our present calculation, the frequency of each of these vibrations does not come out to be different in the *trans* form from that in the *gauche* form. Obviously this is because the assumed values of **F**-matrix elements are not proper. Thus, an equal value was assigned to the diagonal elements $F(S_3, S_3)$ and $F(S_{11}, S_{11})$, and the off-diagonal element $F(S_2, S_3)$ was arbitrarily set at zero. The CH stretching frequencies depend almost only upon the **F**-matrix elements $F(S_2, S_2)$, $F(S_3, S_3)$, $F(S_{11}, S_{11})$ and $F(S_2, S_3)$. The normal methylamine CH_3NH_2 molecule gives only three observed CH frequencies (CH_3 symmetric stretching, and two CH_3 "degenerate" stretching frequencies), and therefore it has not been possible so far to fix the values of the four **F**-matrix elements.[2] While, CH_2DNH_2 molecule gives four CH frequencies (*i.e.*, CH_2 symmetric stretching frequencies of *trans* and *gauche* forms and CH_2 antisymmetric stretching frequencies of *trans* and *gauche* forms). Therefore, if the assignments of these observed frequencies to the *trans* and *gauche* forms are fixed (by an analysis of the rotational-structures, for example), then the four **F**-matrix elements should be almost uniquely determined. This should lead us to an interesting piece of information on how one of the CH bonds in methylamine molecule is chemically different from the other two.

Microwave Spectrum

Microwave absorption spectrum of CH_2DNH_2 in its gaseous state was observed by the use of an instrument constructed by Professor Y. Morino, Professor E. Hirota, and their collaborators in the Department of Chemistry, Faculty of Science, here in the University, through their kindness. Assingments of rotational transitions to the observed lines were made by examining the Stark effect and also by some double-resonance experiments. On the basis of the molecular parameters of the so-called r_0-structures (effective structures at vibrational ground state and at $J=0$ and $K=0$) of CH_3NH_2

Table 3. Rotational constants of CH_2DNH_2 (in cm^{-1})

		Calculated[a]	Observed[b]
trans	A	2.86332	2.871396
	B	0.685775	0.685339
	C	0.684532	0.682969
gauche	A	2.885705	2.890871
	B	0.708859	0.708660
	C	0.663108	0.664078

a) On the basis of the r_0-structure of CH_3NH_2 determined by Takagi and Kojima.[5]

b) See text.

and CH_3ND_2 molecules determined by Takagi and Kojima,[5] the rotational constants A, B, and C are calculated for *trans* and *gauche* forms as shown in Table 3. Absorption lines of the *trans* and *gauche* forms are actually found nearly at the frequencies predicted from these values of the rotational constants. They are 34 Q-branch lines ($\Delta J=0$) and 26 P- and R-branch lines ($\Delta J=\pm 1$) of the *trans* form, and 72 Q-branch lines and 68 P- and R-branch lines of the *gauche* forms. All of the *trans*-form lines are explained by considering that every transition expected for a rigid-rotor splits into two components because of the inversion. On the other hand, all of the *gauche*-form lines are explained by considering that every transition expected for a rigid-rotor splits into four components because of the inversion and internal-rotation. After taking an average of the frequencies of these split lines the rotational constants of the *trans*- and *gauche*-form molecules are derived as given in the last column of Table 3.

The results of our microwave study on this molecule will be detailed elsewhere. Only an outline of our work on the energy difference ΔE_{TG} between the *trans*- and *gauche*-forms will be reported below.

ΔE_{TG} from Inversion Splitting

By means of the microwave spectroscopy, we can determine the positions of the energy levels of the *trans* form with respect to one another and those of the *gauche* form with respect to one another. It is not usually easy, on the other hand, to determine the positions of the *trans* levels with respect to the *gauche* levels, because there are no transitions allowed between the *trans* and *gauche* levels (unless there is a strong *trans-gauche* mixing). In the present particular case, however, the *trans-gauche* energy difference ΔE_{TG} at $J=0$, $K=0$ can be estimated from the amounts of the inversion splitting of the *trans* levels.

In addition to the internal-rotation, the methylamine molecule experiences another large-scale internal motion, *i.e.*, the inversion of the amino group. Thus, the molecule in question has a two-dimensional six-minimum potential, which is schematically shown in Fig. 4. The inversion splitting of the *trans* form is considered to be caused by a resonance of the energy levels in the two equivalent *trans* valleys in this potential map. If the wavefunction of a vibration-rotation level were completely localized in each of these valleys, however, the amount of the inversion splitting should be negligibly small, because the two *trans* valleys are situated far away from each other (Fig. 4). While, if an appreciable amount of mixing of the *trans* and *gauche* states takes place, an appreciable amount of the inversion splitting of the so-called "*trans*" level (which now involves a small contribution from the *gauche* state) may occur. As has been shown by Itoh,[6] by Kivelson and Lide,[7] and by Tsuboi *et al.*,[8] the inversion splitting of the amino group in the molecule with the rotational quantum number K should be given as

$$E^a - E^s = (-1)^K(E^- - E^+)\int_0^{2\pi}\phi_{\tau K}(x)^*\phi_{\tau K}(x+\pi)\mathrm{d}x, \qquad (3)$$

where $E^- - E^+$ is the hypothetical inversion splitting when the coupling were absent between the inversion and internal-rotation, and $\phi_{\tau K}(x)$ is the internal-rotation eigenfunction for the vibration-rotation state now in question. This $\phi_{\tau K}(x)$ is not a completely localized function but an eigenfunction of a proper internal-rotation Hamiltonian. The subscript τ is for distinguishing three internal-rotation sublevels of the $n=0$ state. The value of the overlap integral in the right side of Eq. (3) for the "*trans*" form should be sensitive to how much mixing takes place of the *trans* and *gauche* states, and hence to the amount of ΔE_{TG}. The integral can be estimated on the basis of a theory of asymmetric internal rotor developed in our previous paper.[1] It comes out as a periodic function of K (rotational quantum number). Therefore, the inversion splitting of the $K+1\leftarrow K$ transition frequency should also be a periodic function of K. In Fig. 5, the amounts of inversion splitting actually observed in the microwave absorption lines of $K+1\leftarrow K$ transitions are plotted against K. The observed values are reproduced by an empirical formula

$$E^a - E^s = 81.85\sin\left[51°41'\times\left(K+\frac{1}{2}\right)\right]\ \text{MHz} \qquad (4)$$

The observed set of values is found to be in a good

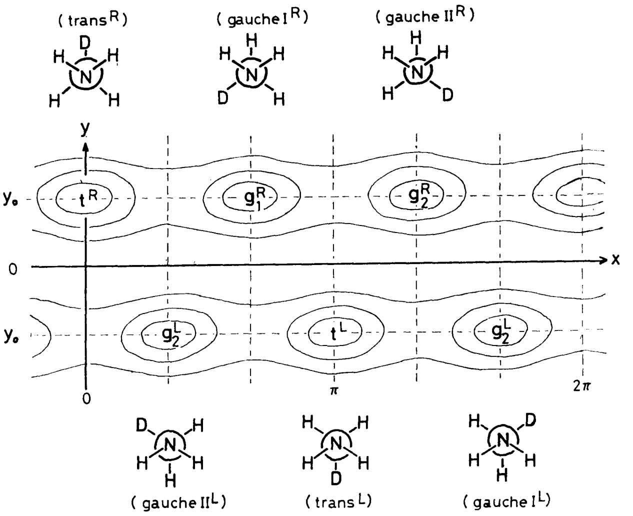

Fig. 4. A schematic drawing of the two-dimensional six-minimum potential function of the CH_2DNH_2 molecule. x: internal rotation. y: inversion.

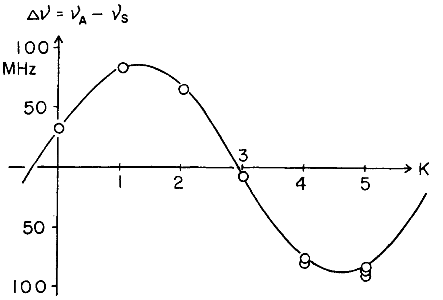

Fig. 5. The amount of inversion splitting, $\nu_a-\nu_s$, of the absorption lines of the $K+1\leftarrow K$ transitions plotted against K. o: observed. ——: calculated by equation (4).

agreement with the calculated set (on Eq. (3)) if ΔE_{TG} is assumed to be 6.7 cm^{-1}. The ambiguity of this value is $\pm$0.4 cm^{-1} here.

ΔE_{TG} from a *trans-gauche* Accidental Degeneracy

The ΔE_{TG} value (6.7 cm^{-1}) just estimated happens to be close to the value (6.6 cm^{-1}) of $3[A-(B+C)/2]$ of this molecule. Therefore, the $K=1$ levels of the *trans* form should be situated close to the $K=2$ levels of the *gauche* form (see Fig. 6), and an interaction may be expected between one of such *trans* levels and a *gauche* level with the same J-value. In fact, an anomaly in the observed frequency of the *trans* form has been found for $K=1\leftarrow0$ and $J=10\leftarrow10$ transition (see Fig. 7). This fact is interpreted by considering that the ($K=1$, $J=10$) level of the *trans* form is accidentally coincident with the ($K=2$, $J=10$) level of the *gauche* form. On the basis of this interpretation the difference (ΔE_{TG}) between the ($K=0$, $J=0$) levels of the *trans* and *gauche* forms is determined to be 7.06$\pm$0.03 cm^{-1}. This is probably the first example of the energy difference precisely determined of rotational isomers caused by an isotopic substitution.

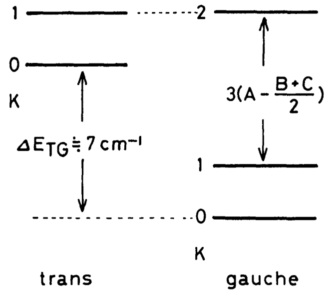

Fig. 6. Accidental degeneracy of the *trans* ($K=1$) and *gauche* ($K=2$) levels.

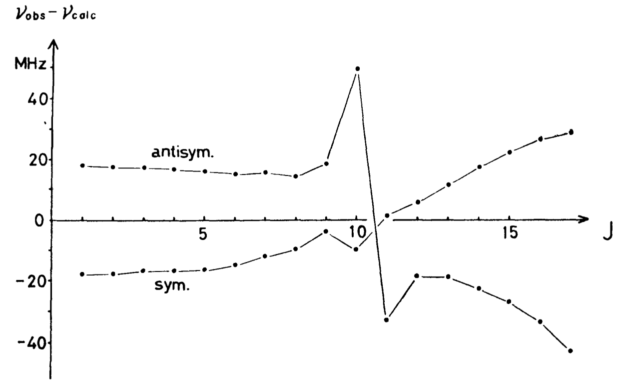

Fig. 7. $\nu_{obs}-\nu_{calc}$ plotted against J. Here ν_{obs} are the observed frequencies (MHz) of the Q-branch lines ($J_{1,J-1}\leftarrow J_{0,J}$) of the trans form. ν_{calc} are the frequencies calculated on the assumption that the molecule is a rigid rotor with the ratotional constants given in Table 3. For every ($K=1\leftarrow0$, $J=J\leftarrow J$) transition two absorption lines are observed, and they are considered to be caused by the inversion of the amino group.

We wish to express our deep appreciation to Professor Yonezo Morino, Professor Eiji Hirota, and Professor Takehiko Tanaka for their kindness in allowing us to use their microwave instrument, for their kind instruction and valuable discussions.

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