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The Normal Coordinate Analysis of α-Aminoisobutyric Acid Anhydride (3,3,6,6-Tetramethyl-2,5-Piperazinedione)

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Abstract The infrared spectra of α-aminoisobutyric acid anhydride and its *N*-deuterated compound in the solid state have been observed in the frequency region from 4000 to 250 cm^{-1}. The normal coordinate analysis has been made by assuming the molecular symmetry of C_{2h} and by treating the methyl groups as mass points. A simple Urey-Bradley force field has been employed and the normal frequencies have been calculated by using the force constants of glycine anhydride. The assignments of the fundamental frequencies have been made by referring to isotopic frequency shifts, calculated frequencies, and potential energy distributions.

Introduction

The infrared spectroscopic study of amino acid anhydrides (2,5-piperazinediones) has been mostly done on glycine anhydride, which is the simple unsubstituted 2,5-piperazinedione, by many authors. On the other hand, the infrared absorption bands of the substituted 2,5-piperazinediones (*e.g.*, 3,3,6,6-tetramethyl-2,5-piperazinedione) have not been studied in detail. In the preceding paper[1] the authors reported the normal coordinate analysis of glycine anhydride as a complete fourteen-body problem with C_{2h} symmetry. Therefore in the present work, the normal coordinate analysis of the A_u and B_u fundamental vibrations of α-aminoisobutyric acid anhydride and its *N*-deuterated compound has been attempted by applying the information on the force constants of glycine anhydride, and the analysis has also been made in an attempt to confirm the empirical vibration assignments of those compounds in our previous study[2].

Results and Discussion

The infrafed spectra were recorded on a Nipponbunkô DS-301 infrared spectrophotometer equipped with sodium chloride prism in the 4000 - 650 cm^{-1} region and on a Hitachi EPI-L grating infrared spectrophotometer in the 700 - 250 cm^{-1} region. The samples were measured as mulls with Nujol and hexachlorobutadiene. The absorption

Table 1. Observed infrared frequencies (cm^{-1}) for α-aminoisobutyric acid anhydride and its N-deuterated compound and their assignments

$[C(CH_3)_2CONH]_2$	$[C(CH_3)_2COND]_2$	Assignment
3370 w		N—H stretching (free)
	3300 vw	2336+(964)[a]
3244 s 3068 s		N—H stretching (hydrogen bonded) 1682+(1474)[a], (1726)[a]+1430 [Fermi resonance]
3010 w 2988 w	3005 w 2980 m	CH_3 asymmetric stretching
2947 vw	2940 w	CH_3 asymmetric stretching
2910 w	2877 vw	CH_3 symmetric stretching
	2435 w	N—D stretching (free)
	2393 vw 2336 s 2294 w 2270 vw 2238 vw	N—D stretching (hydrogen bonded)
	2120 vw	
1682 vs	1653 vs	C=O stretching
1496 s	1472 s	CH_3 asymmetric deformation
1463 sh		N—H in-plane bending, ring skeletal stretching, C=O in-plane bending
1453 s		CH_3 asymmetric deformation
	1442 s	CH_3 asymmetric deformation and ring skeletal stretching (overlapped)
1430 w		ring skeletal stretching, N—H in-plane bending, C=O stretching
1379 vw 1370 w	1380 vw 1369 w	CH_3 symmetric deformation
	1289 w	ring skeletal stretching, $C(CH_3)_2$ symmetric stretching, $C(CH_3)_2$ scissoring, N—D in-plane bending
	1262 vw	
1237 s		$C(CH_3)_2$ symmetric stretching, ring skeletal stretching, $C(CH_3)_2$ scissoring
1205 s	1225 s	$C(CH_3)_2$ antisymmetric stretching
1173 m	1170 m	CH_3 rocking
	1137 m	N—D in-plane bending, $C(CH_3)_2$ symmetric stretching
1012 w	(1013 vw)[b]	ring skeletal stretching
	955 m	ring skeletal stretching
	940 w	CH_3 rocking
939 m		CH_3 rocking and ring skeletal stretching, ring skeletal in-plane deformation (overlapped)
	913 m	N—D in-plane bending, ring skeletal stretching
864 s	(863 vw)[b]	N—H out-of-plane bending
813 w	(806 vw)[b]	$C(CH_3)_2$ symmetric stretching, ring skeletal in-plane deformation

Table 1. (continued)

	787 w	$C(CH_3)_2$ symmetric stretching, ring skeletal in-plane deformation
	770 m	N—D out-of-plane bending, $C(CH_3)_2$ twisting, C=O out-of-plane bending
745 vw	690 m	$C(CH_3)_2$ scissoring, ring skeletal in-plane deformation
700 m		$C(CH_3)_2$ rocking, C=O out-of-plane bending
	631 s	$C(CH_3)_2$ rocking, N—D out-of-plane bending, C=O out-of-plane bending
449 vs		C=O in-plane bending and $C(CH_3)_2$ rocking, $C(CH_3)_2$ twisting, N—H out-of-plane bending (overlapped)
	444 vs	C=O in-plane bending and $C(CH_3)_2$ twisting, N—D out-of-plane bending, $C(CH_3)_2$ rocking (overlapped)
339 w	337 w	$C(CH_3)_2$ wagging
314 w	312 w	$C(CH_3)_2$ twisting, C=O out-of-plane bending

a) Frequencies estimated for infrared inactive bands from combination bands.
b) Assigned to undeuterated species.

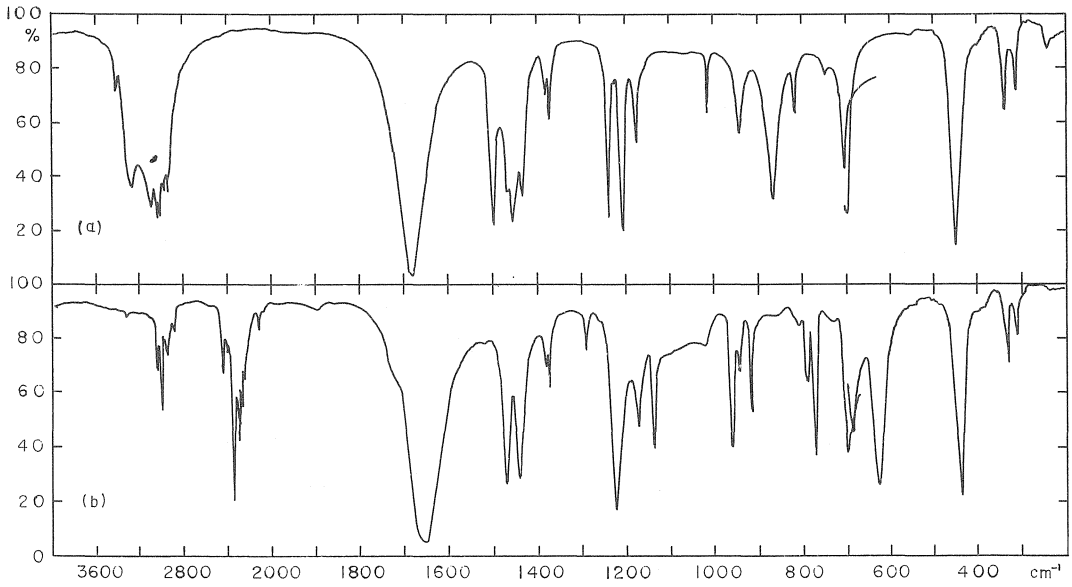


Fig. 1. Infrared spectra of α-aminoisobutyric acid anhydride (a) and its *N*-deuterated compound (b) in the region between 4000 and 250cm^{-1}.

frequencies are listed in Table 1 together with their assignments and the actual spectra are given in Fig. 1.

Spectral assignment

With the aid of the spectral change on deuteration, the frequency calculation, and the potential energy distributions, the infrared absorption bands observed for α-aminoisobutyric acid anhydride and its *N*-deuterated compound may be assigned as shown in Table 1. The present assignment agrees with the empirical assignment in the previous paper[2] except for several bands.

The 4000-2000 cm^{-1} *region.* α-Aminoisobutyric acid anhydride shows a series of bands between 3400-2800 cm^{-1}. Deuteration shifts the bands from the 3400-3050 cm^{-1} region to the 2500-2200 cm^{-1} region as expected. These deuteration sensitive bands are obviously due to the stretching vibrations of the NH group. Among these bands, the weak band at the highest frequency 3370 cm^{-1} may be assigned to the free N-H stretching vibration, as in the case of glycine anhydride[1]. The corresponding N-D stretching band also appears at 2435 cm^{-1} in the deuterated compound. The unshifted bands in the 3050-2800 cm^{-1} region are easily assigned to the C-H stretching vibrations of the CH_3 group. However, it is noteworthy that the shift on deuteration is about 30 cm^{-1} in the CH_3 symmetric stretching band.

The 2000-900 cm^{-1} *region.* The very strong bands at about 1670 cm^{-1} in both isotopic species are readily attributable to the C=O stretching vibrations. The two bands at 1496 and 1453 cm^{-1}, the two bands at 1379 and 1370 cm^{-1}, and the two bands at 1173 and 939 cm^{-1}—all these six bands show no marked frequency shift on deuteration (1472, 1442 cm^{-1}; 1380, 1369 cm^{-1}; 1170, 940 cm^{-1})—can be assigned to the CH_3 asymmetric deformation vibrations, CH_3 symmetric deformation vibrations, and CH_3 rocking vibrations, respectively, as usually seen many compounds[3]. The band at 1430 cm^{-1} which disappears on deuteration may not be assigned simply to the N-H in-plane bending vibration. By the normal coordinate analysis, in the normal species, the two bands at 1463 and 1430 cm^{-1} are attributable to the mixed contributions of the N-H in-plane bending vibration, ring skeletal stretching vibration, *etc.* The 1463 cm^{-1} band is observed as a weak shoulder by the stronger 1453 cm^{-1} band. In the deuterated species, the highest frequency band mainly due to the ring skeletal stretching vibration may well be expected near 1445 cm^{-1}. In the actual spectrum the corresponding band does not appear there. Thus the missing band may be overlapped by the adjacent 1442 cm^{-1} band which is assigned to the CH_3 asymmetric deformation vibration.

The strong band at 1237 cm^{-1} in the normal species has been assigned to the ring skeletal stretching vibration in the previous paper[2], but now from the potential energy distributions, this band may be attributable to the CH_3-C-CH_3 symmetric stretching vibration as mixed with the ring skeletal stretching vibration, *etc.* In the previous assignment, both the 1205 cm^{-1} band in the normal species and the 1225 cm^{-1} band in the deuterated species were ascribed tentatively to the overlap of the bands caused by the symmetric and antisymmetric stretching vibrations of the $C(CH_3)_2$ structure. However, the results of the normal coordinate analysis show only the contribution of the

CH_3-C-CH_3 antisymmetric stretching mode to those bands.

The band observed at 939 cm^{-1} in the normal species appears as two separate bands at 940 and 913 cm^{-1} on deuteration. This suggests an overlapping of two bands at 939 cm^{-1}. The missing band in the normal species is probably overlapped by the 939 cm^{-1} band assigned to the CH_3 rocking vibration. Thus the band at 1012 cm^{-1} and the missing one at 939 cm^{-1} in α-aminoisobutyric acid anhydride are replaced by the bands at 955 and 913 cm^{-1} on deuteration, as seen in Fig. 1 and Table 1. These four bands may all be attributed to the ring skeletal stretching vibrations. The new band of medium intensity which appears at 1137 cm^{-1} on deuteration may be assigned undoubtedly to the N-D in-plane bending vibration. According to the potential energy distributions, the other new band at 1289 cm^{-1} in the deuterated species is ascribed to a complicated vibration concerned with the ring skeletal stretching, CH_3-C-CH_3 symmetric stretching, $C(CH_3)_2$ scissoring, and N-D in-plane bending modes.

The 900 - 250 cm^{-1} *region.* The strong band at 864 cm^{-1} which disappears on deuteration can be assigned to the N-H out-of-plane bending vibration. The 813 cm^{-1} band in the normal species and the 787 cm^{-1} band in the deuterated species were assigned together to the ring skeletal in-plane deformation vibrations in the previous paper[2]. However, the potential energy distributions reveal that the contribution of the CH_3-C-CH_3 symmetric stretching vibration to those bands is larger rather than that of the ring skeletal in-plane deformation vibration. The four bands at 745, 700, 339, and 314 cm^{-1} in the normal species which do not appear in the spectrum of glycine anhydride may be assigned to the $C(CH_3)_2$ scissoring, rocking, wagging, and twisting vibrations, respectively, by referring to the calculated frequencies. These bands are replaced by the bands at 690, 631, 337, and 312 cm^{-1} on deuteration. As for the above 745 and 700 cm^{-1} bands, however, the former has been assigned to the $C(CH_3)_2$ rocking mode in the previous paper and the latter to the $C(CH_3)_2$ scissoring mode. From the potential energy distributions, it is clear that the contributions of the $C(CH_3)_2$ scissoring and ring skeletal in-plane deformation vibrations are mixed on the above 745 and 690 cm^{-1} bands. The above 631 cm^{-1} band has been assigned to the coupling between the N-D out-of-plane bending and $C(CH_3)_2$ rocking vibrations in the previous study. However, this band is now assigned to the $C(CH_3)_2$ rocking vibration as mixed with the N-D out-of-plane bending vibration, *etc.*, according to the normal coordinate analysis. Similarly, the 770 cm^{-1} band in the deuterated species, which was formerly assigned to the coupling between the $C(CH_3)_2$ rocking and N-D out-of-plane bending modes, is now assigned to the N-D out-of-plane bending mode as mixed somewhat with the $C(CH_3)_2$ twisting mode, C=O out-of-plane bending mode, *etc.*

In the previous paper, the very strong band at about 445 cm^{-1} in each isotopic species was ascribed to the overlap of the C=O in-plane and out-of-plane bending bands. However, the potential energy distributions elucidate that the C=O in-plane bending mode contributes to the 445 cm^{-1} band, but that the C=O out-of-plane bending mode does not affect the band. Accordingly, the 445 cm^{-1} band is now assigned to the overlap

of the two bands caused by the C=O in-plane bending vibration and a complicated vibration involving the $C(CH_3)_2$ rocking and twisting, and N-H (or N-D) out-of-plane bending vibrations. From the normal coordinate analysis, it can be seen that the C=O out-of-plane bending vibration in each isotopic species contributes more or less to all bands in the region below 900 cm^{-1}. Therefore the band mainly due to the C=O out-of-plane bending mode cannot be identified. It is also shown that the two ring skeletal out-of-plane deformation bands lie in the region below 250 cm^{-1}. The two bands due to the internal rotations of the CH_3 group were unobserved, so it is likely that these bands lie in the region below 250 cm^{-1} or their intensity is very weak.

Normal coordinate analysis

The X-ray diffraction study of α-aminoisobutyric acid anhydride has not been carried out. α-Aminoisobutyric acid anhydride can be regarded as the derivative of glycine anhydride, *that is,* the four hydrogen atoms of the methylene groups in the latter are replaced by the four methyl groups in the former. In the preceding paper[1], it was assumed that the glycine anhydride molecule belongs to C_{2h} symmetry by referring to the X-ray diffraction studies[4),5)]. Accordingly, the molecular symmetry of α-aminoisobutyric acid anhydride adopted in the present calculation is that of the point group C_{2h} with the planar diketopiperazine ring, as in the case of glycine anhydride[1]. On the basis of this model simplifying the methyl groups as mass points, we have calculated the normal vibrations of α-aminoisobutyric acid anhydride and its N-deuterated compound as a fourteen-body problem. Excepting the vibrations of the methyl groups which are simplified as mass points, there are thirty-six normal vibrations, and these are classified into twelve A_g, six B_g, eleven B_u, and seven A_u vibrations. The former two species are Raman active, while the latter two species are infrared active.

The Wilson **GF** matrix method[6] was used for the calculation. The numerical calculation was carried out by means of a computer program using a FACOM 230-25/35 electronic computer. The program was made conveniently for our calculation by modifying the programs BGLZ and LSMB written by Shimanouchi *et al.*[7] The inverse kinetic energy matrix, **G**, was constructed by using the structure parameters, internal coordinates, and internal symmetry coordinates. The structure parameters used for α-aminoisobutyric acid anhydride were those employed for glycine anhydride, excepting that the C-CH_3 bond length was assumed to be 1.52 Å. The internal coordinates are the same as those of glycine anhydride, excepting that the C-H bonds of glycine anhydride are replaced by C-CH_3 bonds. The internal symmetry coordinates are also the same as those of glycine anhydride. In the descriptions of the modes, however, the notation CH_2 is replaceable with $C(CH_3)_2$. The masses of atoms used in the calculation of the **G** matrix are naturally identical with those of glycine anhydride, excepting that the methyl groups are treated as mass points. The potential energy matrix, **F**, was a simple Urey-Bradley force field. The potential field took the same form as glycine anhydride. The force constants used in the calculation of the **F** matrix

were transferred from our result of glycine anhydride, excepting that the force constants, which are connected with the methyl group treated as a mass point, were assumed by referring to the force constants of tetramethylmethane[8] in the initial calculation. As usual, F' (linear repulsive force constant) was assumed to be -0.1 F (quadratic repulsive force constant). The force constants are the same set for both isotopic species since the only change between the compounds is that of mass.

The number of the fundamental frequencies observed for each isotopic species is fourteen, except for the frequencies assigned to the vibration modes of the methyl group treated as a mass point in the normal coordinate analysis. On the other hand, the corresponding number of the infrared active normal frequencies for each isotopic species is sixteen except for two ring torsion modes. Then, it may be considered that the two missing bands in each isotopic species are overlapped by the adjacent bands. The number of the force constants used in the calculation is thirty-one. In the refinement process, a number of force constants need to be fixed to the appropriate values, because of the large number of force constants against the small number of observed frequencies. The initial calculation revealed that with respect to the vibrations related to the methyl group which is treated as a mass point, the agreement between the calculated and observed frequencies is not so good as other vibrations. Then, we fix the force constants transferred from glycine anhydride and refine other force constants by the least squares method. The refined force constants are one stretching, three bending, and three repulsion force constants which are related to the C–CH_3 bond or the CH_3 group treated as a mass point. Furthermore, taking into account the result of the initial calculation, we suppose that the missing bands are probably overlapped by other bands at 939 and 449 cm^{-1} in the normal species and at 1442 and 444 cm^{-1} in the deuterated species. As a result of the calculation based on the above views, it may be said that the three repulsion force constants should be fixed to the appropriate values, which are larger than the value (0.33) transferred from tetramethylmethane, rather than be varied. This is because those force constants become the unreasonably large values in the refinement process and because a bending force constant becomes the negative value which does not have any special chemical meaning.

In view of the above fact, we fixed the three repulsion force constants to the assumed values (0.50) indicated in Table 3 and tried various calculations varying the initial values of the four force constants of Table 2 to be adjusted in the

Table 2. Refined force constants (mdyn/Å)

	Set A	Set B
K(C—CH_3)	2.65	4.05
H(CH_3—C—C)	1.11	0.35
H(CH_3—C—CH_3)	0.67	1.27
H(N—C—CH_3)	0.26	0.19

Table 3. Force constants (mdyn/Å) used for α-aminoisobutyric acid anhydride

Stretching and bending		Repulsion, out-of-plane bending, and torsion	
K_1(C—CMe_2)[a]	2.95	F_1(N.C.CMe_2)	0.50
K_2(N—CMe_2)	2.78	F_2(C.CMe_2.N)	0.30
K_3(C—N)	5.52	F_3(CMe_2.N.C)	0.30
K_4(C=O)	8.15	F_4(O.C.N)	1.50
K_5(C—CH_3)	4.05[b]	F_5(CMe_2.C.O)	0.50
K_6(N—H)	5.79	F_6(H.N.CMe_2)	0.44
H_1(N—C—CMe_2)	0.67	F_7(C.N.H)	0.61
H_2(C—CMe_2—N)	0.25	F_8(CH_3.C.C)	0.50
H_3(CMe_2—N—C)	0.15	F_9(CH_3.C.CH_3)	0.50
H_4(O=C—N)	0.32	F_{10}(N.C.CH_3)	0.50
H_5(CMe_2—C=O)	0.71	P_1(C=O)	0.14
H_6(H—N—CMe_2)	0.10	P_2(N—H)	0.25
H_7(C—N—H)	0.26	T_1(C—CMe_2)	0.04_0
H_8(CH_3—C—C)	0.35[b]	T_2(N—CMe_2)	0.03_8
H_9(CH_3—C—CH_3)	1.27[b]	T_3(C—N)	0.06_8
H_{10}(N—C—CH_3)	0.19[b]		

a) CMe_2 shows the carbon atom attached the methyl groups.
b) Refined.

Table 4. Calculated frequencies and main potential energy distributions of α-aminoisbutyric acid anhydried

No.	Calc.	Obs.	PED(%)[a]	Description[b]
Infrared active vibration				
A_u species				
1	1213	1205	K_5(80); H_8(7), H_{10}(4), F_8(2), F_{10}(2)	$\nu_a C(CH_3)_2$; $\rho C(CH_3)_2$
2	864	864	P_2(72); H_8(3), H_{10}(2), F_8(1), F_{10}(3); P_1(8)	πNH; $t C(CH_3)_2$; πCO
3	618	700	H_8(24), H_{10}(1), F_8(20),F_{10}(3); P_1(22); P_2(10)	$\rho C(CH_3)_2$; πCO; πNH
4	412	449	H_8(1), H_{10}(26), F_8(1), F_{10}(31); P_2(15); T_3(11); T_2(10)	$\rho C(CH_3)_2$, $t C(CH_3)_2$; πNH; τCN; τN-CMe_2
5	247	314	H_8(26), H_{10}(9), F_8(16), F_{10}(10); P_1(28); T_3(9)	$t C(CH_3)_2$; πCO; τCN
6	105		T_3(38); P_1(31); T_2(20); H_8(1), H_{10}(5), F_8(1), F_{10}(5)	τCN; πCO; τN-CMe_2; $\rho C(CH_3)_2$
7	53		T_1(54); T_2(27); H_8(2), H_{10}(2), F_8(1), F_{10}(2); P_1(6); T_3(5)	τC-CMe_2;τN-CMe_2; $\rho C(CH_3)_2$; πCO; τCN
B_u species				
8	3380	3370	K_6(91), F_6(3), F_7(5)	νNH
9	1696	1682	K_4(54); K_3(19); H_1(9)	νCO; νCN; δN-C-CMe_2

Table 4. (continued)

10	1479	1463	$H_6(8)$, $H_7(21)$, $F_6(11)$, $F_7(19)$; $K_1(12)$; $H_4(3)$, $H_5(6)$, $F_4(1)$; $K_3(7)$	βNH; νC-CMe$_2$; βCO; νCN
11	1397	1430	$K_3(32)$; $H_6(5)$, $H_7(7)$, $F_6(4)$, $F_7(2)$; $K_4(14)$; $K_1(11)$; $K_2(8)$	νCN; βNH; νCO; νC-CMe$_2$; νN-CMe$_2$
12	1309	1237	$K_5(27)$; $K_1(3)$; $K_2(9)$; $K_3(4)$; $H_9(25)$	ν_sC(CH$_3$)$_2$; νC-CMe$_2$; νN-CMe$_2$; νCN; σC(CH$_3$)$_2$
13	1097	1012	$K_2(31)$; $K_1(10)$; $H_8(9)$, $H_{10}(5)$, $F_8(2)$, $F_{10}(3)$; $H_4(3)$, $H_5(5)$, $F_4(2)$, $F_5(6)$	νN-CMe$_2$; νC-CMe$_2$; ωC(CH$_3$)$_2$; βCO
14	935	939	$K_1(18)$; $K_3(3)$; $H_1(8)$; $H_4(6)$, $H_5(1)$, $F_4(21)$, $F_5(3)$	νC-CMe$_2$; νCN; δN-C-CMe$_2$; βCO
15	735	813	$K_5(39)$; $H_1(7)$; $H_2(2)$; $H_3(2)$; $H_9(15)$, $F_9(15)$	ν_sC(CH$_3$)$_2$; δN-C-CMe$_2$; δC-CMe$_2$-N; δCMe$_2$-N-C; σC(CH$_3$)$_2$
16	632	745	$H_9(32)$, $F_9(6)$; $H_1(9)$; $H_2(5)$; $H_3(4)$; $H_5(13)$, $F_5(3)$	σC(CH$_3$)$_2$; δN-C-CMe$_2$; δC-CMe$_2$-N; δCMe$_2$- N-C; βCO
17	389	449	$H_4(8)$, $H_5(17)$, $F_4(16)$,$F_5(8)$; $K_2(16)$; $K_1(7)$	βCO; νN-CMe$_2$; νC-CMe$_2$
18	328	339	$H_8(26)$, $H_{10}(15)$, $F_8(22)$, $F_{10}(20)$	ωC(CH$_3$)$_2$

Infrared inactive vibration

A_g species

19	3380		$K_6(91)$, $F_6(3)$, $F_7(5)$	νNH
20	1709	1726[c)]	$K_4(48)$; $K_3(22)$; $H_1(9)$	νCO; νCN; δN-C-CMe$_2$
21	1462	1474[c)]	$K_1(21)$; $K_3(19)$; $H_4(4)$, $H_5(7)$, $F_4(4)$; $K_4(9)$; $H_6(1)$, $H_7(6)$, $F_6(2)$, $F_7(10)$	νC-CMe$_2$; νCN; βCO; νCO; βNH
22	1432		$H_6(13)$, $H_7(28)$, $F_6(17)$, $F_7(16)$; $K_4(12)$	βNH; νCO
23	1264		$K_5(27)$; $H_9(23)$, $F_9(1)$; $K_3(15)$; $K_2(10)$	ν_sC(CH$_3$)$_2$; σC(CH$_3$)$_2$; νCN; νN-CMe$_2$
24	1177		$K_2(23)$; $K_1(16)$; $K_4(12)$; $H_8(4)$, $H_{10}(2)$, $F_{10}(3)$	νN-CMe$_2$; νC-CMe$_2$; νCO; ωC(CH$_3$)$_2$
25	761		$H_4(11)$, $H_5(23)$, $F_4(22)$, $F_5(6)$; $H_8(8)$, $H_{10}(6)$, $F_8(7)$, $F_{10}(4)$	βCO; ωC(CH$_3$)$_2$
26	735		$K_5(35)$; $H_9(23)$, $F_9(17)$	ν_sC(CH$_3$)$_2$; σC(CH$_3$)$_2$
27	591		$K_1(22)$; $H_9(19)$, $F_9(4)$; $H_1(5)$; $H_2(3)$; $H_3(5)$	νC-CMe$_2$; σC(CH$_3$)$_2$; δN-C-CMe$_2$; δC-CMe$_2$-N; δCMe$_2$-N-C
28	483		$H_1(24)$; $H_3(3)$; $K_2(23)$; $K_4(7)$	δN-C-CMe$_2$; δCMe$_2$-N-C; νN-CMe$_2$; νCO
29	335		$H_8(16)$, $H_{10}(15)$, $F_8(13)$, $F_{10}(21)$; $H_4(3)$, $H_5(11)$, $F_4(5)$, $F_5(5)$	ωC(CH$_3$)$_2$; βCO
30	321		$H_2(25)$; $H_3(9)$; $H_8(11)$, $H_9(6)$, $H_{10}(2)$, $F_8(9)$, $F_{10}(3)$	δC-CMe$_2$-N; δCMe$_2$-N-C; σ(CH$_3$)$_2$

B_g species

31	1257		$K_5(66)$; $H_8(8)$, $H_{10}(4)$, $F_8(2)$, $F_{10}(1)$	ν_aC(CH$_3$)$_2$; ρC(CH$_3$)$_2$

Table 4. (continued)

32	876	$P_2(54)$; $K_5(20)$	πNH;ν_aC(CH_3)$_2$
33	608	$P_2(34)$; $P_1(17)$; $H_8(18)$, $F_8(14)$	πNH; πCO; tC(CH_3)$_2$, ρC(CH_3)$_2$
34	391	$H_8(10)$, $H_{10}(32)$, $F_8(6)$, $F_{10}(36)$; $P_2(7)$	tC(CH_3)$_2$, ρC(CH_3)$_2$; πNH
35	254	$H_8(26)$, $H_{10}(5)$, $F_8(16)$, $F_{10}(6)$; $P_1(40)$	ρC(CH_3)$_2$; πCO
36	112	$P_1(32)$; $T_3(23)$; $T_2(15)$; $T_1(14)$; $H_8(1)$, $H_{10}(7)$, $F_{10}(7)$	πCO; τCN; τN-CMe_2; τC-CMe_2; ρC(CH_3)$_2$

a) PED(%): potential energy distributions (in %) for force constants.
b) ν: stretching: δ: in-plane deformation; β: in-plane bending; π: out-of-plane bending; σ: scissoring; ω: wagging; ρ: rocking; t: twisting; τ: torsion. a: antisymmetric; s: symmetric. CMe_2 shows the carbon atom attached the methyl groups. ν_a and ν_s, or ω, ρ, and t can be distinguished from potential energy distributons for symmetry coordinates.
c) Estimated from combination bands.

Table 5. Calculated frequencies and main potential energy distributions of *N*-deuterated α-aminoisobutyric acid anhydride

No.	Calc.	Obs.	PED(%)	Description
Infrared active vibration				
A_u species				
1	1211	1225	$K_5(80)$; $H_8(7)$, $H_{10}(4)$, $F_8(2)$, $F_{10}(2)$	ν_aC(CH_3)$_2$; ρC(CH_3)$_2$
2	783	770	$P_2(50)$; $H_8(6)$, $H_{10}(3)$, $F_8(3)$, $F_{10}(4)$; $P_1(16)$; $T_3(13)$	πND; tC(CH_3)$_2$; πCO; τCN
3	596	631	$H_8(22)$, $H_{10}(4)$, $F_8(19)$, $F_{10}(9)$; $P_2(15)$; $P_1(13)$; $K_5(10)$	ρC(CH_3)$_2$; πND; πCO; ν_aC(CH_3)$_2$
4	348	444	$H_{10}(25)$, $F_{10}(27)$; $P_2(32)$	tC(CH_3)$_2$, ρC(CH_3)$_2$; πND
5	245	312	$H_8(26)$, $H_{10}(7)$, $F_8(16)$, $F_{10}(7)$; $P_1(31)$; $T_3(9)$	tC(CH_3)$_2$; πCO; τCN
6	102		$T_3(40)$; $P_1(29)$; $T_2(20)$; $H_8(1)$, $H_{10}(4)$, $F_{10}(4)$	τCN; πCO; τN-CMe_2; ρC(CH_3)$_2$
7	53		$T_1(53)$; $T_2(28)$; $H_8(2)$, $H_{10}(2)$, $F_8(1)$, $F_{10}(2)$; $P_1(6)$	τC-CMe_2; τN-CMe_2; ρC(CH_3)$_2$; πCO
B_u species				
8	2468	2435	$K_6(92)$, $F_6(2)$, $F_7(5)$	νND
9	1691	1653	$K_4(56)$; $K_3(20)$; $H_1(9)$	νCO; νCN; δN-C-CMe_2
10	1421	1442	$K_1(27)$; $K_3(27)$; $H_4(5)$, $H_5(7)$, $F_4(5)$; $K_4(11)$	νC-CMe_2; νCN;βCO; νCO
11	1345	1289	$K_2(19)$; $K_3(14)$; $K_5(21)$; $H_9(21)$, $F_9(1)$; $H_6(2)$, $H_7(3)$, $F_6(1)$, $F_7(1)$	νN-CMe_2; νCN; ν_sC(CH_3)$_2$; σC(CH_3)$_2$; βND
12	1138	1137	$H_6(5)$, $H_7(21)$, $F_6(5)$, $F_7(14)$; $K_5(11)$; $H_4(4)$, $H_5(1)$, $F_4(9)$	βND; ν_sC(CH_3)$_2$; βCO
13	1084	955	$K_1(15)$; $K_2(23)$; $K_3(3)$; $H_8(9)$, $H_{10}(6)$, $F_8(2)$, $F_{10}(2)$; $K_4(7)$; $H_6(2)$, $H_7(1)$, $F_6(11)$	νC-CMe_2; νN-CMe_2; νCN; ωC(CH_3)$_2$; νCO; βND

Table 5. (continued)

14	838	913	$H_6(7)$, $H_7(12)$, $F_6(13)$, $F_7(10)$; $K_1(11)$; $H_4(4)$, $H_5(1)$, $F_4(13)$, $F_5(1)$; $H_1(5)$	βND; νC–CMe$_2$; βCO; δN–C–CMe$_2$
15	732	787	$K_5(38)$; $H_1(7)$; $H_2(2)$; $H_3(2)$; $H_9(17)$, $F_9(16)$	ν_sC(CH$_3$)$_2$; δN–C–CMe$_2$; δC–CMe$_2$–N; δCMe$_2$–N–C; σC(CH$_3$)$_2$
16	624	690	$H_9(30)$, $F_9(5)$; $H_1(10)$; $H_2(5)$; $H_3(4)$; $H_5(13)$, $F_5(3)$	σC(CH$_3$)$_2$; δN–C–CMe$_2$; δC–CMe$_2$–N; δCMe$_2$–N–C; βCO
17	388	444	$H_4(8)$, $H_5(18)$, $F_4(15)$, $F_5(9)$; $K_2(16)$; $K_1(7)$	βCO; νN–CMe$_2$; νC–CMe$_2$
18	327	337	$H_8(26)$, $H_{10}(15)$, $F_8(22)$, $F_{10}(21)$	ωC(CH$_3$)$_2$
Infrad inactive vibation				
A_g species				
19	2468		$K_6(92)$, $F_6(2)$, $F_7(5)$	νND
20	1705		$K_4(49)$; $K_3(23)$; $H_1(9)$	νCO; νCN; δN–C–CMe$_2$
21	1455		$K_1(23)$; $K_3(19)$; $K_4(17)$; $H_4(4)$, $H_5(6)$, $F_4(5)$	νC–CMe$_2$; νCN; νCO; βCO
22	1270		$K_5(22)$; $K_1(2)$; $K_2(16)$; $K_3(12)$; $H_9(19)$, $F_9(1)$	ν_sC(CH$_3$)$_2$; νC–CMe$_2$; νN–CMe$_2$; νCN; σC(CH$_3$)$_2$
23	1207		$K_1(10)$; $K_2(14)$; $K_3(8)$; $H_6(2)$, $H_7(8)$, $F_6(1)$, $F_7(3)$; $K_4(12)$; $K_5(9)$	νC–CMe$_2$; νN–CMe$_2$; νCN; βND; νCO; ν_sC(CH$_3$)$_2$
24	1057		$H_6(11)$, $H_7(22)$, $F_6(23)$, $F_7(15)$; $H_8(5)$, $H_{10}(3)$, $F_8(1)$, $F_{10}(1)$; $K_1(5)$; $K_2(5)$	βND; ωC(CH$_3$)$_2$; νC–CMe$_2$; νN–CMe$_2$
25	737		$K_5(36)$; $H_9(18)$, $F_9(15)$	ν_sC(CH$_3$)$_2$; σC(CH$_3$)$_2$
26	715		$H_4(10)$, $H_5(17)$, $F_4(17)$, $F_5(5)$; $H_8(8)$, $H_{10}(3)$, $F_8(3)$, $F_{10}(6)$; $H_6(2)$, $H_7(5)$, $F_6(3)$, $F_7(4)$	βCO; ωC(CH$_3$)$_2$; βND
27	578		$K_1(22)$; $K_2(6)$; $H_1(5)$; $H_2(3)$; $H_3(5)$; $H_9(17)$, $F_9(3)$	νC–CMe$_2$; νN–CMe$_2$; δN–C–CMe$_2$; δC–CMe$_2$–N; δCMe$_2$–N–C; σC(CH$_3$)$_2$
28	482		$H_1(25)$; $H_3(3)$; $K_2(23)$; $K_4(7)$	δN–C–CMe$_2$; δCMe$_2$–N–C; νN–CMe$_2$; νCO
29	334		$H_8(17)$, $H_{10}(15)$, $F_8(14)$, $F_{10}(21)$; $H_4(3)$, $H_5(11)$, $F_4(5)$, $F_5(5)$	ωC(CH$_3$)$_2$; βCO
30	320		$H_2(25)$; $H_3(9)$; $H_8(11)$, $H_9(6)$, $H_{10}(2)$, $F_8(9)$, $F_{10}(3)$	δC–CMe$_2$–N; δCMe$_2$–N–C; σC(CH$_3$)$_2$
B_g species				
31	1253		$K_5(68)$; $H_8(8)$, $H_{10}(4)$, $F_8(2)$, $F_{10}(1)$	ν_aC(CH$_3$)$_2$; ρC(CH$_3$)$_2$
32	822		$P_2(32)$; $K_5(21)$; $P_1(12)$	πND; ν_aC(CH$_3$)$_2$; πCO
33	536		$P_2(40)$; $H_8(23)$, $H_{10}(3)$, $F_8(16)$, $F_{10}(2)$; $P_1(12)$	πND; tC(CH$_3$)$_2$; πCO
34	355		$H_8(3)$, $H_{10}(31)$, $F_8(1)$, $F_{10}(35)$; $P_2(22)$	tC(CH$_3$)$_2$, ρC(CH$_3$)$_2$; πND
35	250		$P_1(42)$; $H_8(26)$, $H_{10}(3)$, $F_8(16)$, $F_{10}(4)$	πCO; ρC(CH$_3$)$_2$
36	109		$P_1(31)$; $T_3(24)$; $T_2(15)$; $T_1(15)$; $H_8(1)$, $H_{10}(7)$, $F_{10}(7)$	πCO; τCN; τN–CMe$_2$; τC–CMe$_2$; ρC(CH$_3$)$_2$

refinement process. It can be see from the results of the calculations that the variable force constants are converged to either the values of the set A or those of the set B shown in Table 2, but that the weighted sum of the squared deviations of the calculated frequency parameters from the observed ones in the case of the set B is smaller than that in the case of the set A. Accordingly, the following result of the normal coordinate analysis is described with the case of the set B.

The force constants used in the final calculation are given in Table 3. The calculated frequencies, potential energy distributions, and approximate descriptions obtained from these force constants together with the observed frequencies are listed in Table 4 for α-aminoisobutyric acid anhydride and in Table 5 for its N-deuterated compound. The agreement between the observed and calculated frequencies in each isotopic species is not so good for both of A_u and B_u vibrations. This is mainly found in the vibrations related to the methyl group which is treated as a mass point. The poor agreement may be (1) because the methyl group was treated as a mass point; or (2) because the force constants transferred from glycine anhydride were not refined; or (3) because the assumed structure parameters were not good. Nevertheless, it is confirmed that the empirical assignment in the previous paper[2] is almost correct by referring to the potential energe distributions. However, it should be noted that the contribuion of the C=O out-of-plane bending vibration is dispersed to many A_u vibrations and then that the band mainly due to the C=O out-of-plane bending mode cannot be pointed out. In the previous study, the $C(CH_3)_2$ rocking frequency of species A_u was considered to be higher than the $C(CH_3)_2$ scissoring frequency of species B_u. The result of the normal coordinate analysis is rather inverse in this respect. Although the assignments of those frequencies have been made according to the result in the present work, a detailed examination may be required to account for the small difference between those frequencies. As a result of the refinement of force constants, it was found that the value of the C-CH_3 stretching force constant, K(C-CH_3), became somewhat larger than that of tetramethylmethane (3.44) used in the initial calculation and that the value of the CH_3-C-CH_3 bending force constant, H(CH_3-C-CH_3), became much larger than that of tetramethylmethane (0.20). As to the remaining two refined bending force constants, H(CH_3-C-C) and H(CH_3-C-N), the value of the former became larger, while that of the latter became slightly smaller, than the initial value (0.20) assumed from the value of tetramethylmethane.

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