Vibrational Spectra of β-Lactams. I. 2-Azetidinone and Its Isotopic Compounds

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The infrared and Raman spectra of 2-azetidinone and its 1-*d*, 3,3-d_2, and 1,3,3-d_3 and their ^{15}N compounds have been recorded, and the observed bands have been assigned on the basis of the isotope effects and the normal coordinate analysis. The refined force constants have reproduced the observed frequencies satisfactorily. The C–N stretching mode is strongly coupled with the N–H bending vibration to give a band near 1380 cm^{-1}. However, this coupling does not give rise to any bands corresponding to the amide II and III bands. The concentration dependence of the infrared spectrum suggests the presence of an equilibrium of monomer ⇌ cyclic dimer in carbon tetrachloride solution. The solvent effects on the N–H and C=O stretching bands have also been examined.

2-Azetidinone (2-AZ) is the simplest four-membered lactam. For penicillins and cephalosporins known as β-lactam antibiotics, the relationship between their biological activities and lactam C=O stretching frequencies has been reported in the literature.[1,2] This correlation arises from the fact that the amide resonance affects both the lactam C=O stretching frequency and the ease of hydrolysis of the lactam amide bond.[1–3] Therefore, it is interesting to compare the C=O stretching force constants (or C=O frequencies) or the C–N stretching force constants with the ease of hydrolysis for simple β-lactams. The present paper deals with the vibrational analysis of 2-azetidinone and its seven isotopic compounds.

Experimental

Materials. 2-Azetidinone (2-AZ) was prepared from β-alanine by using Mukaiyama's reagent.[4] β-Alanine (0.89 g) was suspended in 1 L of acetonitrile, and 3.15 g of triphenylphosphine and 2.64 g of di-2-pyridyl disulfide were added with stirring. After the reaction mixture was refluxed for 5 h, the solvent was distilled off and the residue was subjected to sublimation under reduced pressure. The sublimate (0.44 g) was collected and recrystallized three times from hexane–chloroform; mp 77 °C. Its purity was checked by elemental analysis.

2-AZ-^{15}N was prepared from β-alanine-^{15}N, which was obtained by the same method as described in the literature[5] except that an anion exchange resin (Amberlite IRA-45) was used for the isolation of free β-alanine (an isotopic purity of starting material, ammonium-^{15}N sulfate, 99.9%, SHOKO Co., Ltd., Japan); mp 77 °C.

The α-position(to the carbonyl group)-deuterated compounds (2-AZ-3,3-d_2 and 2-AZ-3,3-d_2-^{15}N) were prepared from β-alanine-α,α-d_2 and β-alanine-α,α-d_2-^{15}N, respectively, which were obtained by the following methods. β-Alanine was dissolved in an excess of deuterium oxide, and the solvent was distilled away *in vacuo*. The β-alanine-*N*,*N*,*O*-d_3 thus obtained was dried over phosphorus pentaoxide and heated in an excess of 19.9% hydrochloric acid-*d* (CEA, France, an isotopic purity of 99.5%) under reflux for 80 h,[6] and the solution was evaporated *in vacuo* to dryness. The aqueous solution was passed through an Amberlite IRA-45 column and the water was distilled away *in vacuo*. The β-alanine-α,α-d_2 obtained was purified by recrystallization from aqueous ethanol. β-Alanine-α,α-d_2-^{15}N was obtained by hydrolysis of methyl 3-(phthalimido-^{15}N)-propionate, which was the intermediate product in the preparation of β-alanine-^{15}N, in an excess of 19.9% hydrochloric acid-*d* under reflux for 55 h, and then by treatment with Amberlite IRA-45. The crude azetidinones were recrystallized from hexane–chloroform; mp 77.5 °C for both 2-AZ-3,3-d_2 and 2-AZ-3,3-d_2-^{15}N. Their deuteration degree was checked by NMR spectroscopy and mass spectrometry and estimated to be over 95%. The N-deuterated compounds were obtained by the exchange reaction with deuterium oxide.

Spectra. The infrared spectra of the solids were recorded in KBr disks and Nujol or hexachlorobutadiene mulls on a JASCO DS-403G grating infrared spectrophotometer. The infrared spectra of carbon tetrachloride, chloroform, and benzene solutions were measured. Carbon tetrachloride and benzene were of spectrophotometric grade. Chloroform was purified by a usual method. Raman spectra in the solid state were recorded on a JEOL S-1 laser Raman spectrometer equipped with an argon ion laser (excitation line: 488.0 or 514.5 nm).

The infrared and Raman spectra are shown in Figs. 1—4, and the observed frequencies are listed in Tables 1—4 together with the calculated values.

Results and Discussion

CH_2 Group Vibrations. Assignment of some CH_2 vibrations is straightforwardly made by comparison between Figs. 1 and 2 and between Figs. 3 and 4. In Fig. 3 the two bands at 3003 and 2956 cm^{-1} are attributed to the α-CH_2 stretching vibrations, since they clearly disappear on α-C-deuteration. However, three bands of medium to strong intensity are observed in the CD_2 stretching region of the Raman spectra. The corresponding infrared absorptions are observed as weak bands at the same frequencies. The third band can be explained in terms of Fermi resonance. The highest frequency band at 2255 cm^{-1} which does not shift on N-deuteration is assigned to the CD_2 antisymmetric stretching vibration. Fermi resonance occurs probably between the CD_2 symmet-

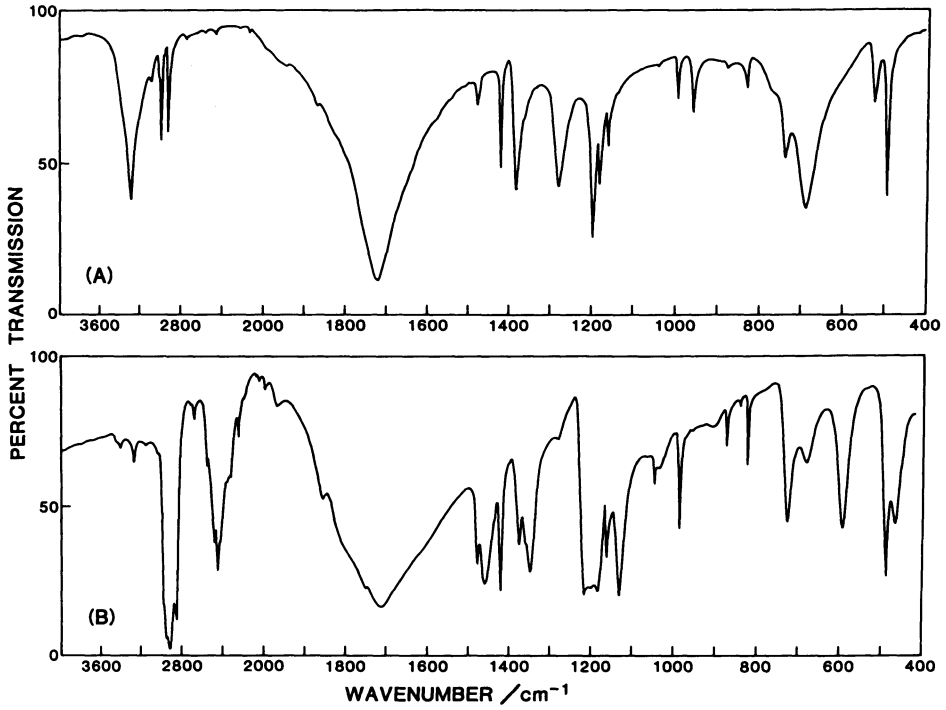


Fig. 1. (A) Infrared spectrum of 2-azetidinone (in a KBr disk); (B) infrared spectrum of 2-azetidinone-1-*d* (in a Nujol mull).

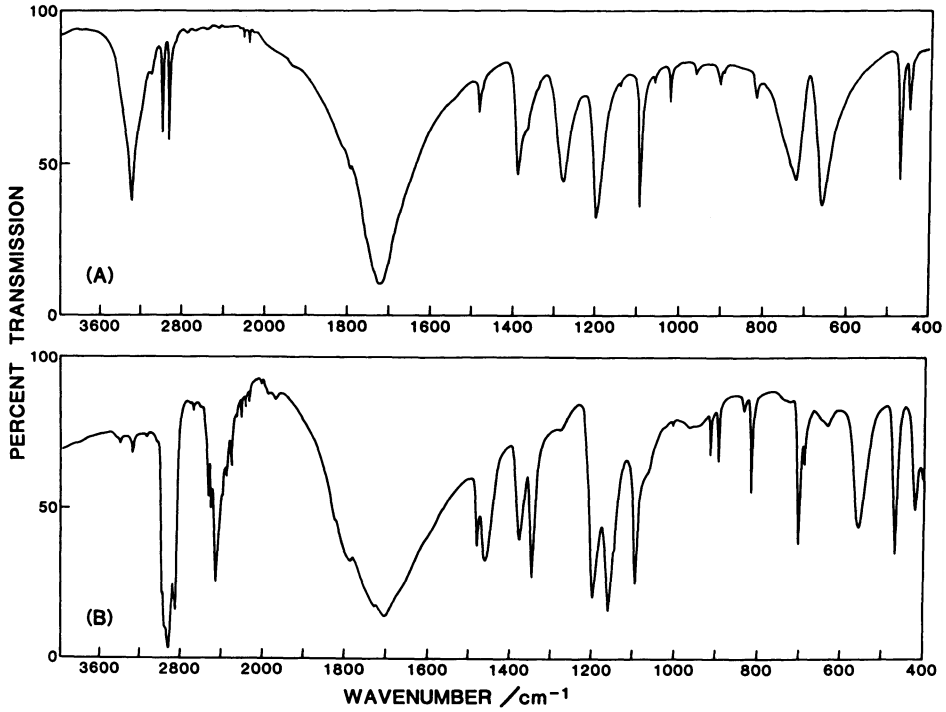


Fig. 2. (A) Infrared spectrum of 2-azetidinone-3,3-d_2 (in a KBr disk); (B) infrared spectrum of 2-azetidinone-1,3,3-d_3 (in a Nujol mull).

ric stretching vibration and the first overtone of the CD_2 bending vibration (1098 cm^{-1}) and gives rise to the two Raman bands at 2209 and 2156 cm^{-1} in 2-AZ-3,3-d_2. From the ^{15}N-isotopic shift, however, it seems that the resonance in 2-AZ-1,3,3-d_3 occurs between the CD_2 symmetric stretching and a combination of the 1350 and 815 cm^{-1} vibrations. A correction for Fermi resonance[7] has revealed that the intrinsic CD_2 symmetric stretching frequencies are 2177 cm^{-1} in 2-AZ-3,3-d_2 and 2175 cm^{-1} in 2-AZ-1,3,3-d_3.

In general a CH_2 bending vibration is the most localized mode of CH_2 deformation vibrations. The 1479 and 1422 cm^{-1} infrared bands of 2-AZ are assigned to this mode; the former is due to the β-CH_2

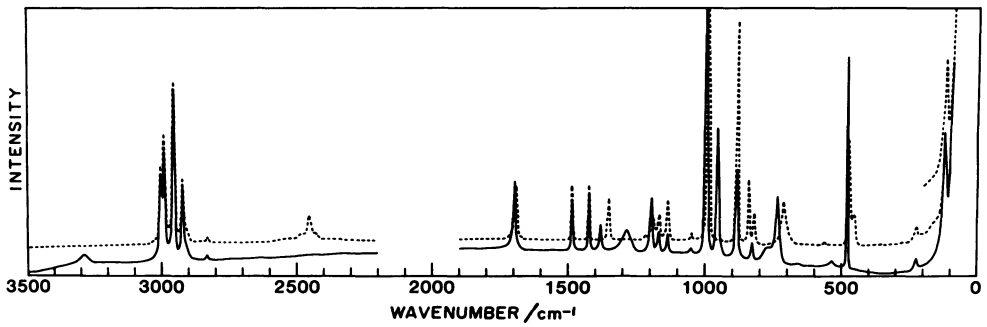


Fig. 3. Raman spectra of 2-azetidinone (solid line) and 2-azetidinone-1-*d* (broken line).

Table 1. Observed and calculated fundamental frequencies (cm^{-1}) for 2-azetidinone

	Obsd			Calcd	$\Delta\nu(^{15}N)$	P. E. D.[b]
	IR	$\Delta\nu(^{15}N)$[a]	Raman			
a'	3282 s	−9	3285 w	3306	−7	1 (100)
	2955 vw	0	2956 s	2971	0	2 (96)
	2921 m	0	2922 m	2918	0	3 (96)
	1723 vs	0	1697 m	1698	−2	4 (74), 11 (15), 13 (10)
	1479 w	0	1486 m	1484	0	7 (86)
	1422 m	0	1423 m	1426	0	6 (77), 8 (11)
	1385 ms	−14	1379 w	1381	−11	11 (28), 5 (25), 9 (19)
	1370 sh	−10	—	1368	−6	5 (62), 9 (10)
	1281 m	−7	1285 w	1246	0	9 (56), 8 (18), 10 (10), 11 (10)
	1182 m	−2	—	1158	−3	8 (58), 14 (30), 11 (14)
	999 w	−7	997 vs	1002	−8	11 (21), 14 (19), 12 (15)
	961 wm	−6	953 ms	957	−5	14 (32), 12 (28), 8 (14)
	880 vw	−7	884 m	897	−11	13 (40), 12 (28), 15 (10)
	741 m	−3	735 m	731	−1	17 (25), 12 (13), 16 (11), 15 (10)
	494 ms	−2	479 vs	477	−3	10 (81), 13 (23), 15 (16), 16 (15)
a''	3002 sh	0	3003 m	3021	0	19 (98)
	2986 m	0	2992 ms	2992	0	20 (98)
	1198 ms	−4	1193 m	1223	0	23 (45), 24 (44)
	1162 w	−1	1167 w	1173	−1	22 (27), 23 (27), 24 (20), 21 (11)
	1048 vw	−1	1051 vw	1019	−1	22 (66), 24 (16), 21 (14)
	832 w	0	828 w	836	0	21 (73), 23 (37)
	690 s	−3	—	671	−5	25 (95), 24 (37), 26 (23)
	527 wm	−1	535 vw	504	0	26 (94), 25 (22), 23 (18)
			119 m	94	0	27 (28), 28 (27), 29 (25), 30 (22)

a) ^{15}N-Isotopic shifts in the infrared spectrum. b) Potential energy distributions, 100 $F_{kk}L_{ki}^2/\lambda_i$, are given in parentheses, where contributions less than 10% have been omitted. The coordinate numbers refer to the following descriptions: 1, NH(ND) stretch; 2, α-$CH_2(CD_2)$ sym stretch; 3, β-CH_2 sym stretch; 4, CO stretch; 5, NH(ND) in-plane bend; 6, α-$CH_2(CD_2)$ bend; 7, β-CH_2 bend; 8, α-$CH_2(CD_2)$ wag; 9, β-CH_2 wag; 10, CO in-plane bend; 11, CN stretch; 12, NC^β stretch; 13, CC^α stretch; 14, $C^\alpha C^\beta$ stretch; 15, CNC^β bend; 16, NCC^α bend; 17, $CC^\alpha C^\beta$ bend; 18, $C^\alpha C^\beta N$ bend; 19, α-$CH_2(CD_2)$ antisym stretch; 20, β-CH_2 antisym stretch; 21, α-$CH_2(CD_2)$ twist; 22, β-CH_2 twist; 23, α-$CH_2(CD_2)$ rock; 24, β-CH_2 rock; 25, NH(ND) out-of-plane bend; 26, CO out-of-plane bend; 27, CN torsion; 28, NC^β torsion; 29, CC^α torsion; 30, $C^\alpha C^\beta$ torsion.

group and the latter to the α-CH_2 group as is evident from the deuteration behavior. The bands at 1281 and 1182 cm^{-1} can be assigned to the wagging vibrations of the β-CH_2 and α-CH_2 groups, respectively. The band at 1198 cm^{-1} which does not disappear on N- and C-deuteration may be ascribed to a CH_2 deformation of the *a″* species.

Amide Group Vibrations. The N-H stretching band occurs at 3282 cm^{-1} and is at a higher frequency than those of 2-pyrrolidinone (γ-butyrolactam) and 2-piperidinone (δ-valerolactam), which are observed at 3252[8,9] and 3226 cm^{-1},[9,10] respectively. The infrared C=O stretching band is observed at 1723 cm^{-1} higher in frequency than those of 2-pyrrolidinone (1690 cm^{-1})[8,9] and 2-piperidinone (1664 cm^{-1}).[9,10]

There is noncoincidence of frequencies in many bands, particularly the C=O band, between the infrared and Raman spectra. This fact suggests that the two molecules of 2-AZ form a cyclic dimer which has the center of symmetry. In this case the C=O vibration which is symmetric with respect to the center of symmetry is observed at 1697 cm^{-1} in the Raman spectrum and the asymmetric stretching mode

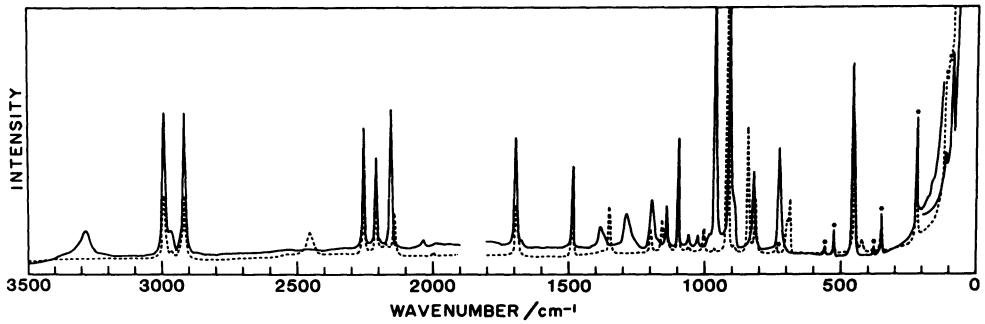


Fig. 4. Raman spectra of 2-azetidinone-3,3-d_2 (solid line) and 2-azetidinone-1,3,3-d_3 (broken line).
* The emission lines of an Ar^+ laser. At 220 cm^{-1} a weak Raman band is overlapped.

TABLE 2. OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES (cm^{-1}) FOR 2-AZETIDINONE-1-*d*

	Obsd			Calcd	$\Delta\nu(^{15}N)$	P. E. D.[b]
	IR	$\Delta\nu(^{15}N)$[a]	Raman			
a′	2956 w	−1	2956 s	2971	0	2(96)
	2921 m	−1	2921 m	2918	0	3(96)
	2450 s	−17	2452 w	2416	−11	1(100)
	1712 vs	−2	1690 m	1690	−1	4(78), 11(15), 13(10)
	1481 wm	−1	1486 m	1484	0	7(87)
	1422 m	0	1422 m	1426	0	6(78), 8(11)
	1350 ms	−12	1349 m	1370	−7	9(31), 11(29), 10(13), 7(10), 14(10)
	1214 s	−4	1215 vw	1246	−1	9(53), 8(19), 11(12)
	1182 s	−3	1188 w	1154	−1	5(45), 12(15), 4(10)
	1129 s	−14	1134 m	1157	−20	8(51), 11(24), 14(22)
	986 m	−4	987 vs	982	−1	14(50), 8(18)
	875 w	−6	881 vs	894	−10	12(57), 13(26)
	842 vw	0	839 m	857	−2	5(31), 13(15), 11(11), 18(11)
	726 ms	−1	715 m	715	−1	17(21), 5(13), 16(12)
	486 s	−2	472 ms	472	−2	10(81), 13(22), 15(16), 16(15)
a″	3003 w	−1	3003 m	3021	0	19(98)
	2987 m	−2	2990 ms	2992	0	20(98)
	1199 s	−4	1188 w	1215	0	23(54), 24(37)
	1162 m	−1	1167 w	1169	−1	22(32), 24(27), 23(18)
	1046 w	−1	1048 vw	1006	−1	22(63), 24(25), 21(18)
	824 m	0	819 wm	832	0	21(69), 23(36), 24(11)
	592 ms	−4	566 vw	601	−5	26(65), 25(54), 24(13), 23(12)
	465 ms	−3	454 w	452	−1	25(66), 26(51), 24(17), 23(10)
			117 m	90	0	27(28), 28(26), 29(25), 30(22)

a) ^{15}N-Isotopic shifts in the infrared spectrum. b) See footnote b in Table 1.

Table 3. Observed and calculated fundamental frequencies (cm^{-1}) for 2-azetidinone-3,3-d_2

	Obsd			Calcd	$\Delta\nu(^{15}N)$	P. E. D.[b]
	IR	$\Delta\nu(^{15}N)$[a]	Raman			
a'	3281 s	−9	3282 m	3306	−7	1(100)
	2918 m	0	2917 s	2920	0	3(99)
	2208 vw, 2156 vw [c] (2179)	−1, −1	2209 ms, 2156 s [c] (2177)	2153	0	2(99)
	1720 vs	0	1695 ms	1698	−3	4(74), 11(15), 13(10)
	1482 w	−1	1484 ms	1484	−1	7(88)
	1389 m	−12	1383 wm	1380	−12	5(33), 11(27), 9(18)
	1370 sh	−9	1375 sh	1367	−5	5(54), 9(14)
	1277 m	−8	1289 m	1228	−2	9(62), 11(22), 10(14)
	1095 ms	0	1098 ms	1102	−2	6(55), 14(18)
	1061 vw	0	1059 w	1069	0	14(52), 8(42)
	963 w	−7	962 vs	974	−14	12(45), 11(21), 6(10)
	906 w	−3	909 vs	866	−9	13(34), 12(25), 6(11)
	819 w	−4	821 m	798	−1	8(59), 14(13), 6(12)
	723 ms	−1	726 ms	711	−1	17(26), 6(13), 16(11)
	472 ms	−1	458 s	459	−2	10(78), 13(23), 15(15), 16(15)
a''	2985 m	0	2992 s	2993	0	20(101)
	2252 vw	0	2255 s	2237	0	19(102)
	1198 ms	−4	1193 m	1197	0	24(66), 22(15)
	1025 w	0	1024 w	1049	−2	22(74), 23(15), 24(14)
	896 vw	0	898 sh	888	0	23(63), 21(14)
	658 ms	−2	—	673	−3	25(46), 26(32), 24(31), 21(12)
	—	—	—	645	−1	25(55), 21(51), 23(14), 24(11)
	452 wm	0	453 sh	471	0	26(81), 21(33), 23(26), 25(13)
			114 w	91	−1	27(28), 28(27), 29(25), 30(22)

a) ^{15}N-Isotopic shifts in the infrared spectrum. b) See footnote b in Table 1. c) Splittings due to Fermi resonance. The values in parentheses are frequencies corrected for it.

at 1723 cm^{-1} in the infrared spectrum. 2-Pyrrolidinone and 2-piperidinone also form such dimers and show similar frequency differences[8,10] as given in Table 9.

The C-N stretching vibration is expected to be coupled with other ring stretchings or deformations to give complicated modes. However, it is possible to assign the band to which the C-N stretching vibration contributes considerably. The ^{15}N isotopic compounds are useful for this purpose. The infrared band at 1385 cm^{-1} shows a ^{15}N shift of 14 cm^{-1} to a lower frequency as given in Table 1 and can be assigned to this vibration. For 2-AZ-3,3-d_2 the corresponding band is observed at 1389 cm^{-1} with a ^{15}N shift of 12 cm^{-1}. The N-H bending bands in 2-AZ and 2-AZ-3,3-d_2 occur at 1370 cm^{-1} and show ^{15}N shifts of about 10 cm^{-1}. Although these bands are observed as poorly-characterized shoulders, the corresponding vibration of 2-AZ-3,3-d_2-^{15}N appears at 1361 cm^{-1} as a clear-cut band. 2-AZ does not show any band in the 1550 cm^{-1} region; the amide II band, which is very characteristic of *trans* secondary amides, is absent from the spectra of small ring lactams.[9] The infrared bands at 690 and 527 cm^{-1} are ascribed to the N-H and C=O out-of-plane modes, respectively, or their coupled modes.

Skeletal Vibrations. For 2-AZ the three infrared bands (999, 961, and 880 cm^{-1}), which have the strong Raman counterparts, are observed in the 1000—800 cm^{-1} region and exhibit ^{15}N-isotopic shifts of about 7 cm^{-1}. Therefore, these bands are assigned to the skeletal vibrations, although an appreciable contribution of other vibrations must be considered as can be seen from the deuteration behavior.

Combination and Overtone Bands. In addition to the bands due to the fundamentals, a number of weak bands are observed and assignable to combinations or overtones. They are listed for 2-AZ and 2-AZ-3,3-d_2 in Table 5.

The origin of a weak band around 3100 cm^{-1} was discussed for *cis* secondary amides by Miyazawa[11a,b] and explained in terms of the combination of the C=O stretching and N-H in-plane bending vibrations. In the present study this conclusion was confirmed by the ^{15}N shift; the ^{15}N substitution shifts the frequency by 16 cm^{-1} depending upon the shift of the N-H bending frequency, whereas the α-C-deuteration does not affect it.

TABLE 4. OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES (cm^{-1}) FOR 2-AZETIDINONE-1,3,3-d_3

	Obsd			Calcd	$\Delta\nu(^{15}N)$	P. E. D.[b]
	IR	$\Delta\nu(^{15}N)$[a]	Raman			
a'	2919 m	−2	2916 m	2920	0	3(99)
	2454 s	−15	2454 wm	2416	−11	1(100)
	2207 w, 2138 w[c]	−1, −10	2209 m, 2140 m[c]	2153	0	2(99)
	(2177)		(2175)			
	1705 vs	−5	1691 m	1690	−2	4(78), 11(15), 13(11)
	1481 wm	0	1485 m	1484	−1	7(89)
	1349 m	−10	1350 m	1368	−7	9(35), 11(28), 10(12), 7(10), 13(10)
	1197 s	−6	1200 wm	1226	−2	9(59), 11(27), 10(13)
	1158 s	−15	1158 wm	1161	−17	5(47), 12(13), 4(10)
	1092 s	−1	1097 m	1094	−2	6(50), 14(34)
	1063 sh	−1	1059 vw	1060	−2	8(42), 14(36), 6(11)
	914 wm	−4	918 vs	894	−7	12(58), 5(12)
	835 w	0	842 ms	840	−4	13(29), 6(23), 5(18)
	817 m	−5	815 m	788	−1	8(46), 14(11)
	703 ms	−2	697 w	696	−1	17(22), 16(12), 6(12), 5(11)
	467 ms	−2	453 s	455	−2	10(79), 13(22), 15(15), 16(14)
a''	2987 m	0	2991 m	2993	0	20(101)
	2254 vw	0	2256 m	2237	0	19(102)
	1197 s	−6	1200 wm	1185	0	24(65), 22(20)
	1005 vw	−4	1003 wm	1039	−1	22(69), 24(22), 23(19)
	894 wm	0	896 vw	881	−1	23(59), 21(16), 22(10)
	689 wm	−1	688 m	665	−1	21(40), 26(34), 23(17), 24(10)
	556 ms	0	—	565	−4	25(64), 21(37), 26(23), 23(16) 24(12)
	420 m	0	422 w	436	−1	26(58), 25(49), 21(17), 23(16) 24(15)
			112 m	87	−1	27(28), 28(26), 29(25), 30(22)

a) ^{15}N-Isotopic shifts in the infrared spectrum. b) See footnote b in Table 1. c) Splittings due to Fermi resonance. The values in parentheses are frequencies corrected for it.

Normal Coordinate Analysis. The normal coordinate calculations were carried out according to the GF matrix method. A 2-AZ molecule was assumed to have the symmetry plane, *i.e.*, to belong to the point group C_s. This assumption seems to be reasonable from the X-ray studies on 1-substituted 2-azetidinones[12,13] and from the quantum chemical studies on 2-AZ.[14,15] The bond lengths and angles were taken from 1-(4-bromophenyl)-2-azetidinone,[12] 1-(2-bromophenyl)-2-azetidinone[13] and 5-iodomethyl-2-pyrrolidinone.[16] Table 6 gives the structural parameters used in the calculation. The internal symmetry coordinates were constructed in the usual form. A Urey-Bradley force field, to which some constants of valence force type for the *a''* species were added, was used in the calculation. In the initial calculation the force constants were transferred from *N*-acetylglycine methylamide[17] and 2-piperidinone[18] and refined by the least-squares method. The final force constants which give the best fit between the observed and calculated frequencies are given in Table 7. For the two force constants (F(HC$^{\beta}$H) and F(C$^{\alpha}$CO)), the negative values seem to be inevitable in the force field where only a small number of interaction constants are included.

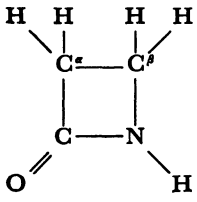
The agreement between the observed and calculated frequencies is satisfactory. Although the observed frequencies of the ^{15}N compounds have not been used in the force constant refinement, the force constants in Table 7 reproduce well the ^{15}N shifts as given in Tables 1—4. It can be seen from the potential energy distributions (P. E. D.) that the vibrations below 1400 cm^{-1} are highly coupled modes as is to be expected.

In *trans* secondary amides, the N-H bending vibration is strongly coupled with the C-N stretching mode to give two bands near 1550 (amide II) and 1270 cm^{-1} (amide III). In 2-AZ the 1385 cm^{-1} band arises from mixing of the C-N stretching and N-H bending vibrations. However, this mixing does not give rise to any bands corresponding to the above characteristic frequencies for *trans* amides. The vibrational modes of *cis* *N*-methylacetamide and 2-piperidinone are interesting in connection with the

Table 5. Combination and overtone bands (cm^{-1})

	IR	Raman	Assignment
2-AZ:	3087		1723+1370=3093
	2855		1479+1385=2864
		2831	2×1422=2844
	2745		1385+1370=2755, 2×1370=2740
	2560		2×1281=2562
	2460		1281+1182=2463
	2232		1182+1048=2230
	2147		1182+961=2143
	1868		1182+690=1872
	1735		999+741=1740
	1138	1135	?
	775	775	?
2-AZ-3,3-d_2:	3086		1720+1370=3090
		2965	2×1484=2968
	2744		1720+1025=2745, 2×1370=2740
	2666		1389+1277=2666
	2559		1370+1198=2568
	2438		1482+963=2445
	2208	2209	2×1095=2190
	2156	2156	(Fermi resonance)
	2116		2×1061=2122
		2034	2×1024=2048
	1793	1794	2×896=1792, 906+896=1802
	1143	1139	?

Table 6. Bond lengths and angles used in the calculation



Bond length (l/Å)		Bond angle (ϕ/°)	
C=O	1.21	NCO	131.9
N-H	1.03	$C^{\alpha}CO$	135.4
C^{α}-H	1.08	$C^{\alpha}CN$	92.7
C^{β}-H	1.09	CNH	132.9
C-N	1.37	$C^{\beta}NH$	132.9
C-C^{α}	1.51	CNC^{β}	94.2
N-C^{β}	1.48	$CC^{\alpha}H$	113.5
C^{α}-C^{β}	1.55	$C^{\beta}C^{\alpha}H$	113.5
		$HC^{\alpha}H$	113.98
		$CC^{\alpha}C^{\beta}$	85.9
		$NC^{\beta}H$	112.5
		$C^{\alpha}C^{\beta}H$	119.0
		$HC^{\beta}H$	105.83
		$C^{\alpha}C^{\beta}N$	87.1

result of this calculation. Miyazawa[11a] calculated the normal vibrations of the *cis* isomer of *N*-methylacetamide and compared them with the infrared frequencies of 2,5-piperazinedione. The potential energy distributions for the former molecule show that the 1445 cm^{-1} vibration consists of the N-H bending (78%) and the C=O stretching (22%), and that the 1386 cm^{-1} vibration consists of the C-N

Table 7. Force constants[a]

K(N-H)	5.391	$F(C^{\alpha}C^{\beta}H)$	0.448
$K(C^{\alpha}$-H)	4.386	$F(NC^{\beta}H)$	0.367
$K(C^{\beta}$-H)	4.379	F(NCO)	1.586
K(C=O)	8.652	$F(C^{\alpha}CO)$	−0.0219
K(C-N)	4.786	$F(CNC^{\beta})$	0.350
$K(N$-$C^{\beta})$	1.872	$F(C^{\alpha}CN)$	0.520
K(C-C^{α})	2.578	$F(CC^{\alpha}C^{\beta})$	0.300
$K(C^{\alpha}$-$C^{\beta})$	2.561	$F(C^{\alpha}C^{\beta}N)$	0.270
H(CNH)	0.393	$\kappa(C^{\alpha})$	0.157
$H(C^{\beta}NH)$	0.0903	$\kappa(C^{\beta})$	0.0822
$H(HC^{\alpha}H)$	0.254	p(C-N, N-C^{β})	0.050
$H(C^{\beta}C^{\alpha}H)$	0.115	p(N-C^{β}, C^{α}-C^{β})	−0.155
$H(CC^{\alpha}H)$	0.230	p(C^{α}-C^{β}, C-C^{α})	−0.172
$H(HC^{\beta}H)$	0.401	p(C-C^{α}, C-N)	0.0262
$H(C^{\alpha}C^{\beta}H)$	0.179	$f_1[\gamma$(N-H)]	0.256
$H(NC^{\beta}H)$	0.367	$f_2[\gamma$(C=O)]	0.635
H(NCO)	0.759	$f_3[\tau$(C-N)]	0.030[b]
$H(C^{\alpha}CO)$	0.106	$f_4[\tau(N$-$C^{\beta})]$	0.030[b]
$H(CNC^{\beta})$	0.538	$f_5[\tau(C^{\alpha}$-$C^{\beta})]$	0.030[b]
$H(C^{\alpha}CN)$	0.170	$f_6[\tau$(C-C^{α})]	0.030[b]
$H(CC^{\alpha}C^{\beta})$	0.618	$f_{1,2}$	0.0096
$H(C^{\alpha}C^{\beta}N)$	0.169	$f_{1,3}$	0.0147
F(CNH)	0.0797	$f_{1,4}$	0.030
$F(C^{\beta}NH)$	0.848	$f_{2,3}$	−0.0554
$F(HC^{\alpha}H)$	0.0611	$f[\delta$(N-H), $\omega(C^{\beta}H_2)]$	0.0603
$F(C^{\beta}C^{\alpha}H)$	0.330	$f[\rho(C^{\alpha}H_2), \gamma$(C=O)]	0.237
$F(CC^{\alpha}H)$	0.631	$f[\rho(C^{\beta}H_2), \gamma$(N-H)]	0.195
$F(HC^{\beta}H)$	−0.0725		

a) K, H, F, p, f_i, $f_{i,j}$, and f in mdyn/Å (10^2 N/m). κ in mdyn Å (10^{-18} N m). In the constants, f_i, $f_{i,j}$, and f, γ, τ, δ, ω, and ρ denote out-of-plane bending, torsion, in-plane bending, wagging, and rocking, respectively. b) Assumed.

stretching (71%) and the C-CH_3 stretching (24%). On the other hand, in 2-piperidinone,[18] the 1425 cm^{-1} band originates in the N-H bending (56%) and the C=O stretching vibration (14%). However, the C-N stretching mode is dispersed in several vibrations, and there are no bands to which it contributes largely. From these results it seems that the *cis* CONH group does not have any characteristic bands similar to those of the *trans* CONH group except for the N-H stretching and C=O stretching bands owing to the coupling of the CONH vibrations with other modes in varying degrees.

Solution Spectra. Figure 5 shows the infrared spectra of 2-AZ in carbon tetrachloride over the concentration range from 0.06 to 0.001 M. The relative intensities of the free N-H stretching band at 3435 cm^{-1} and the hydrogen-bonded N-H band at 3236 cm^{-1} change with concentration in the expected manner, but their frequencies remain invariant within experimental deviation over the whole concentration range. Furthermore, the shape of the 3236 cm^{-1} band remains symmetric in different con-

centrations; this band does not seem to be overlapped with other bands. These findings suggest that the two species are predominantly present in carbon tetrachloride solution, namely an equilibrium of monomer $\rightleftharpoons$ dimer occurs in this solution as in 2-pyrrolidinone[8,9] and 2-piperidinone.[9,19] Possibly this associated species is the same cyclic dimer as in the crystal. The weak band at 3113 cm^{-1} is ascribed to a combination of the C=O stretching and N-H in-plane bending vibrations. The C=O stretching bands also exhibit the behavior corresponding to the above spectra. The free and hydrogen-bonded C=O stretchings occur at 1781 and 1769 cm^{-1}, respectively. The band at 1756 cm^{-1}, which is observed as a shoulder, may be ascribed to an overtone or combination.

TABLE 8. EFFECT OF SOLVENTS ON THE INFRARED N-H AND C=O STRETCHING FREQUENCIES (cm^{-1}) OF 2-AZETIDINONE

		Crystal (KBr disk)	CCl_4[a] (0.06 −0.001M)	$CHCl_3$[a] (0.1 −0.01M)	Benzene[a] (0.1 −0.01M)
ν_{N-H}	free	—	3435	3429	3408
	bonded	3282	3236	3260[b]	3245
$\nu_{C=O}$	free	—	1781	1767	1776
	bonded	1723	1769	—	1755[c]
			1756[c]	1753[c,d]	

a) 1 M = 1 mol dm^{-3}. b) Very weak even in 0.1 M. c) Shoulder bands. d) The intensity does not vary with concentration.

Table 8 gives the infrared N-H and C=O stretching frequencies in a few solvents. The solvent dependence of the spectra of the free molecule can be explained as follows. In chloroform solution the lactam C=O associates weakly with chloroform to give the 1767 cm^{-1} band, which is at a lower frequency by 14 cm^{-1} than the C=O band in carbon tetrachloride. On the other hand, benzene appears to interact with the lactam hydrogen to a considerable extent, since the free N-H frequency is lowest in benzene; it is observed at 3408 cm^{-1}, which is lower by 27 cm^{-1} than that in carbon tetra-

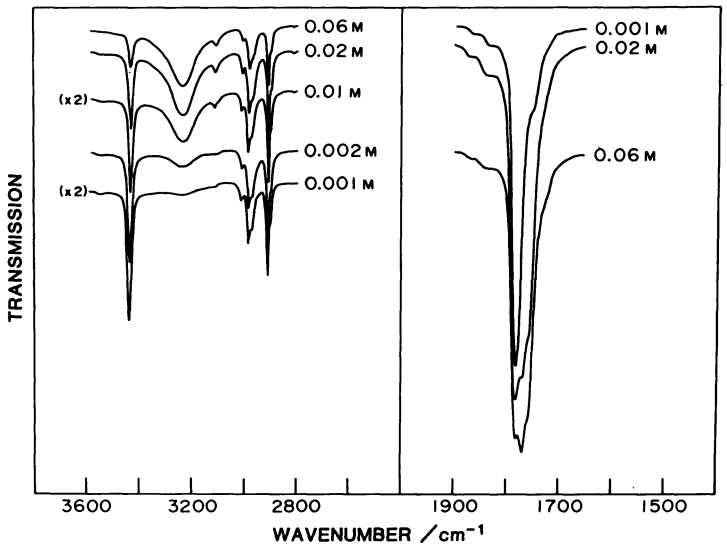


Fig. 5. Infrared spectra of 2-azetidinone in CCl_4.

TABLE 9. N-H AND C=O STRETCHING FREQUENCIES (cm^{-1}) OF LACTAMS[a]

$(CH_2)_{n-2}$ C=O, N-H	n = 4 2-Azetidinone[b]	5 2-Pyrrolidinone[c,d]	6 2-Piperidinone[d,e]	7 ε-Caprolactam[f]
Crystal(C) or Liquid(L)				
ν_{N-H}	3282(C)	3252(L)	3226(L)	3211(C)
$\nu_{C=O}$ IR	1723(C)	1690(L)	1664(L)	1664(C)
$\nu_{C=O}$ Raman	1697(C)	1658(L)	1627(L)	
CCl_4 solution				
ν_{N-H} free	3435	3453	3416	3428
ν_{N-H} bonded	3236	3204	3203	3216
$\nu_{C=O}$ free	1781	1717	1677	1676
$\nu_{C=O}$ bonded	1769	1700	1672	1672

a) Infrared frequencies unless otherwise noted. b) This work. c) Ref. 8. d) For the solution spectra, Ref. 9. e) Ref. 10. f) Ref. 9.

chloride. Other amides and lactams also exhibit this effect.[8,20,21]

Comparison with γ-, δ-, and ε-Lactams. The C=O frequencies of alicyclic ketones depend on the ring size.[22] Table 9 gives the N-H and C=O stretching frequencies of 2-AZ compared with those of five-, six-, and seven-membered lactams reported in the literature.[8,9,10] In the crystalline or liquid states, the N-H stretching and C=O stretching frequencies decrease with increase of the ring size. However, in carbon tetrachloride solution both the associated and free N-H stretching frequencies do not change regularly with the ring size, whereas the C=O stretching frequencies decrease in the expected manner. An explanation for the former behavior cannot be given, but there is a possibility that the steric effect of the CH_2 group adjacent to the N-H is responsible for it.

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