Infrared Spectra and Normal Vibrations of Acetamide and its Deuterated Analogues

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It has been shown in previous papers[1,2] that normal coordinate analyses of formamide and *N*-methylformamide molecules can be made satisfactorily by employing the Urey-Bradley force field and that the force constants determined for formamide can be used without any significant alternations in value in the normal coordinate treatment of *N*-methylformamide. As a continuation of this research, the acetamide molecule is treated in the present paper.

Only a limited number of spectroscopic investigations of acetamide have been reported[3-5], and the main interests of these authors have been focused rather on the protonated systems of the molecule than on acetamide itself. The vibrational assignments for this molecule are very uncertain. Therefore, infrared measurements have been made not only of CH_3CONH_2, but also of three deuterated species of acetamides, CH_3COND_2, CD_3CONH_2 and $CD_3CO\cdot ND_2$. From the combined results of these measurements and of the calculation of normal vibrations, the nature of the observed frequencies is discussed in detail in the present paper. The Urey-Bradley force constants obtained in the present work are compared with those in formamide and in *N*-methylformamide, and the values of some constants are discussed.

Experimental

Materials.—*Acetamide* CH_3CONH_2. — Acetamide was obtained from a commercial source and was purified by the method of ether precipitation from

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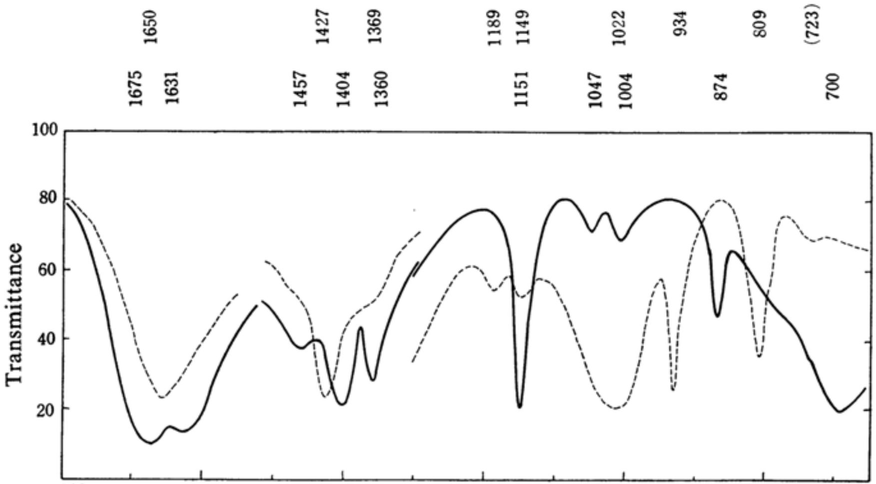
[1] I. Suzuki, This Bulletin, 33, 1359 (1960).

[2] I. Suzuki, ibid., 35, 540 (1962).

[3] M. Davies and H. E. Hallam, *Trans. Faraday Soc.*, 47, 1170 (1951).

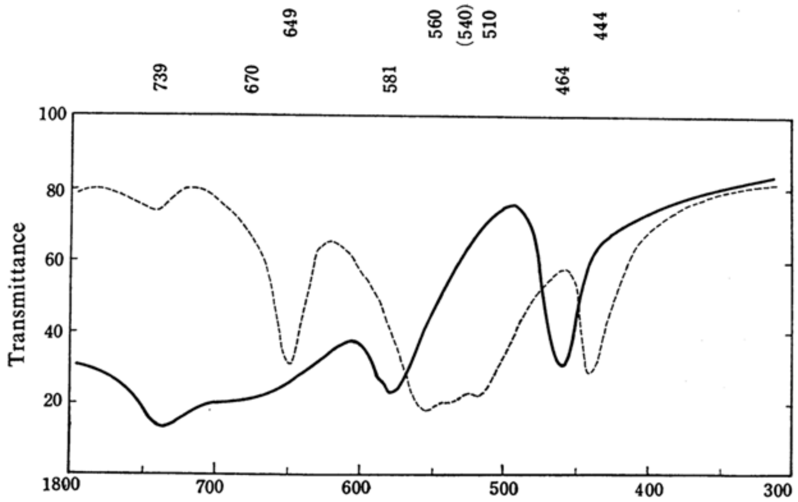
[4] N. Albert and R. M. Badger, *J. Chem. Phys.*, 29, 1193 (1958).

[5] E. Spinner, *Spectrochim. Acta*, 15, 95 (1959).



Wave number, cm^{-1}

Fig. 1. Infrared spectra of CH_3CONH_2 (solid line) and CH_3COND_2 (broken line) in the solid state in the region from 1800 to 650 cm^{-1}.



Wave number, cm^{-1}

Fig. 2. Infrared spectra of CH_3CONH_2 (solid line) and CH_3COND_2 (broken line) in the solid state in the region from 800 to 300 cm^{-1}.

an alcohol solution[6]. The acetamide precipitated was collected, dried in vacuum, and used in the measurements; m. p., 80°C.

C-Deuterated Acetamide CD_3CONH_2.—First, $CD_3\cdot COOD$ was prepared by the thermal decomposition of $CD_2(COOD)_2$, which was obtained from the exchange reaction of $CH_2(COOH)_2$ with D_2O[7]. Then, CD_3COOD was reacted with liquid ammonia. The ammonium acetate obtained was heated at about 200°C for four hours in a sealed tube, and the CD_3COND_2 (containing CD_3CONHD) thus formed was distilled out in vacuum. It was purified by the method described above.

The exchange reaction with D_2O was employed to replace the amide hydrogen atoms by deuterium.

Infrared Spectra.—The measurements of the infrared spectra were made in the region from 4000 to 650 cm^{-1} with a Hitachi EPI spectrophotometer equipped with sodium chloride optics, and in the region from 800 to 300 cm^{-1} with a Nippon Bunko grating spectrophotometer equipped with a cesium bromide foreprism. The infrared spectra of $CH_3\cdot CONH_2$ and CH_3COND_2 were measured in the solid and liquid states and in solutions. The solid state

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[6] E. C. Wagner, *J. Chem. Educ.*, **7**, 1135 (1930).

[7] J. O. Halford and L. C. Anderson, *J. Am. Chem. Soc.*, **58**, 736 (1936).

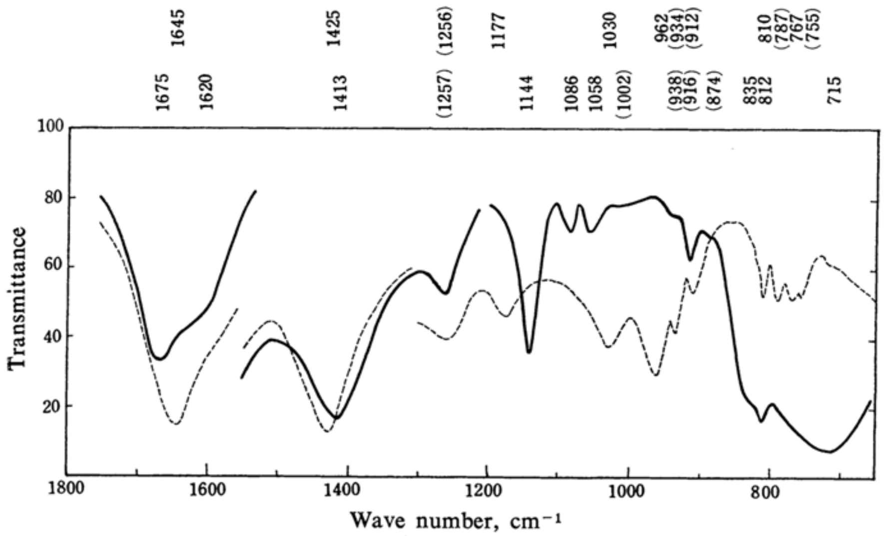

Fig. 3. Infrared spectra of CD_3CONH_2 (solid line) and CD_3COND_2 (broken line) in the solid state in the region from 1800 to 650 cm^{-1}.

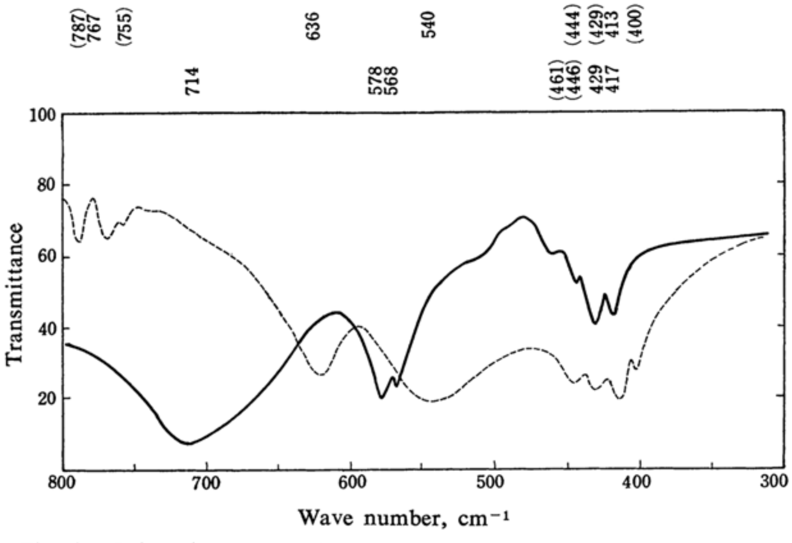

Fig. 4. Infrared spectra of CD_3CONH_2 (solid line) and CD_3COND_2 (broken line) in the solid state in the region from 800 to 300 cm^{-1}.

spectra were taken in Nujol or hexachlorobutadiene mulls and are shown in Figs. 1 and 2. A small heating cell was used to obtain the spectra in the liquid state. The observed frequencies are summarized in Table I. The spectra of CD_3CONH_2 and CD_3COND_2 in the solid state are shown in Figs. 3 and 4. As may be seen from these figures, the spectra of both CD_3CONH_2 and CD_3COND_2 are complicated, particularly in the region below 1000 cm^{-1}. This is due to the presence of bands arising from the CHD_2-species which are contained in the samples. Therefore, the assignments of those vibration bands which are mainly associated with the CD_3 rocking and CC′ in-plane deformation vibrations are uncertain. When the values of the force constants were refined, they were not used as frequency data.

Normal Coordinate Treatment

The calculation of normal vibrations was made as a nine-body problem by Wilson's method[8]. The planar model (C_s), except for two hydrogen atoms attached to the methyl carbon atom (C′)[*1], was adopted (see Fig. 5).

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8) E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1930); **9**, 96 (1941).

[*1] C and C′ denote the carbonyl and methyl carbon atoms respectively.

TAELE I. OBSERVED FREQUENCIES (IN cm^{-1}) OF ACETAMIDE

(a) CH_3CONH_2			(b) CH_3COND_2		
Solid	Liquid	$CHCl_3$ soln.	Solid	Liquid	$CHCl_3$ soln.
3340	3355	3520(3360)	2920	2937	(2980)
3163	3165	3403(3161)	2505	2555	2537
2820	2815		2395	2405	(2460)
			2315		2372
1675	1660?	1680	1650	1634?	1668
1632	1600	1594		(1468)	
1457	1458	1440?	1427	1405	1390
1404	1388	1378	1369	1360	1355
1360	1345	1336	1189	1174	
1152	1138	1118	1150		
1047	1048	1041	1022	1035	(1035)
1005	998	981	934	921	
874	865	872	809	801	
(739)			649		613*
667		527*	560		538*
581		557*	560		518*
464		443*	516		400*
			444		433*

* CH_3CN solution

TABLE II. SYMMETRY COORDINATES

S_i	$S=UR$	Vibrational mode	Abbr.
S_1	Δr_{14}	CN stretching	$\nu(CN)$
S_2	Δr_{45}	CC′ stretching	$\nu(CC')$
S_3	Δr_{46}	CO stretching	$\nu(CO)$
S_4	$(2\Delta\alpha_{23}-\Delta\alpha_{42}-\Delta\alpha_{34})/\sqrt{6}$	NH_2 bending	$b(NH_2)$
S_5	$(\Delta\alpha_{42}-\Delta\alpha_{34})/\sqrt{2}$	NH_2 rocking	$r(NH_2)$
S_6	$(2\Delta\alpha_{61}-\Delta\alpha_{15}-\Delta\alpha_{56})/\sqrt{6}$	NCO deformation	$\delta(NCO)$
S_7	$(\Delta\alpha_{15}-\Delta\alpha_{56})/\sqrt{2}$	CC′ deformation	$\delta(CC')$
S_8	$(2\Delta\alpha_{89}-\Delta\alpha_{78}-\Delta\alpha_{79})/\sqrt{6}$	CH_3 asym. deformation	$\delta_a(CH_3)$
S_9	$(\Delta\alpha_{47}+\Delta\alpha_{48}+\Delta\alpha_{49}-\Delta\alpha_{78}-\Delta_{79}-\Delta\alpha_{89})/\sqrt{6}$	CH_3 sym. deformation	$\delta_s(CH_3)$
S_{10}	$(2\Delta\alpha_{47}-\Delta\alpha_{48}-\Delta\alpha_{49})/\sqrt{6}$	CH_3 rocking	$r(CH_3)$

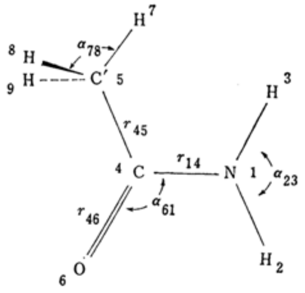

Fig. 5. Molecular structure and internal coordinates of acetamide.

The normal vibrations are classified into 14 in-plane (A′) and 7 out-of-plane (A″) vibrations, of which the in-plane vibrations are treated. The structural parameters used in the present work are as follows: the bond lengths of $r(C=O)=1.28$ Å, $r(C-N)=1.38$ Å, $r(C-C')=1.51$ Å, $r(N-H)=1.02$ Å and $r(C'-H)=1.09$ Å⁹⁾ and the bond angles of 120° for those around the N and C atoms and of 109°47′ for those around the C′ atom. To simplify the calculation, lower frequencies are separated from four higher frequencies which are mainly associated with the CH and NH(D) stretching vibrations⁸⁾. The symmetry coordinates used are given in Table II (see also Fig. 5 for definitions of the internal coordinates).

Force Constants.—As has already been mentioned, the potential function used in the calculation is of the Urey-Bradley type¹⁰⁾:

$$2V=\sum_i K_i(\Delta r_i)^2+\sum_{i\neq j}H_{ij}r_i^0r_j^0(\Delta\alpha_{ij})+\sum_{i\neq j}F_{ij}(\Delta q_{ij})^2+\text{Linear terms}$$

The same notations as in the preceding papers¹,²⁾ are used. In addition, the intramolecular tension, κ, is introduced in the elements of the $\boldsymbol{F}$-matrix when the linear terms are eliminated by a redundancy condition¹⁰⁾.

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9) F. Senti and D. Harker, *J. Am. Chem. Soc.*, 62, 2008 (1940).

10) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

TABLE III. FORCE CONSTANTS IN md./A*

A	K_{CN}	5.75 (6.15)	H_{HNH}	0.40 (0.40)	$F_{H(N)H}$	**0** (0)
	K_{CO}	8.50 (8.80)	H_{HNC}	0.32 (0.32)	$F_{H \cdots C}$	0.46 (0.46)
			H_{NCO}	0.34 (0.34)	$F_{N \cdots O}$	1.50 (1.50)
B	K_{CC}	2.40	H_{CCN}	0.30	$F_{C \cdots N}$	0.70
			H_{CCO}	0.32	$F_{C \cdots O}$	0.72
C	κ	**−0.05** (md·A)	H_{HCH}	**0.43**	$F_{H(C)H}$	**0.03**
			H_{HCC}	0.25	$F_{H(C)C}$	0.47

* Initial set of values for the force constants in group A are given in parenthesis.

Therefore, eighteen force constants are necessary to calculate normal vibrations of the acetamide molecule. As may be seen from Table III, these force constants are classified into three groups, A, B and C, and their values were first determined by the following method: The constants in group A were directly transferred from the formamide molecule[1]. The constants in group B are associated with the "joint" of the CH_3 and amide groups, and $K_{CC}=3.00$ md./A, $H_{CCN}=0.23$ md./A, $H_{CCO}=0.31$ md./A, and $F_{C \cdots N}=F_{C \cdots O}=0.50$ md./A were first assumed[*2]. Those belonging to group C are associated with the methyl group. In our laboratory, a number of compounds containing methyl groups have been studied, and it has been found that one set of constants, $H_{HCH}=0.43$ md./A, $F_{H \cdots H}=0.03$ md./A and $\kappa=-0.05$ md·A, always gives a good frequency fit with the observed data. These values have also been adopted in the present work; they are not varied in the course of refinements. As for other constants, $H_{HCC}=0.25$ md./A and $F_{H \cdots C}=0.45$ md./A were used.

The normal vibrations were calculated from these force constants, and they give fairly good agreement with the observed frequencies. Then the values of the constants were refined as indicated by the Jacobian matrix[12] to obtain a better frequency fit. At the first step of the refinements, only the frequencies of CH_3CONH_2 and CH_3COND_2 were used. Then at the final step those of CD_3CONH_2 and CD_3COND_2 above 1000 cm^{-1} were also taken into account. However, the frequencies of the latter two molecules found below 1000 cm^{-1}[*3] were not used for the reason indicated in the preceding section. At first the force constants in group B were subjected to refinements, since their values were less certain than those in groups A and C.

Although only five constnats were refined, the frequency fit between the observed and the calculated was improved remarkably. In fact, the agreements were so good that refinement was practically unnecessary for the constants in groups A and C, except for two stretching constants, K_{CN} and K_{CO}. The final set of force constants is listed in Table III.

Results and Discussion

Assignments of Vibration Bands. — The frequencies calculated from the force constants given in Table III are compared with the observed frequencies in Tables IV(a)—(d) for each isotopic species of acetamide. In Tables IV(a)—(d), the potential energy distribution among the symmetry coordinates is also given for each normal mode. This represents the quantitative assignment.

In CH_3CONH_2, each normal vibration takes place along one or two symmetry coordinates and is easily identified. As expected, the band at 1676 cm^{-1} of acetamide is associated with the ν(CO) mode. However, the ν(CN) and $b(NH_2)$ vibrations also contribute to this band. The bands at 1632 and 1152 cm^{-1} are mainly associated with the $b(NH_2)$ and $r(NH_2)$ vibrations respectively, and the fact that they move to lower frequencies in a $CHCl_3$ solution is consistent with the above assignments. The bands at 1457, 1360 and 1005 cm^{-1} are associated with the methyl deformation vibrations and are assigned, respectively, to the $\delta_a(CH_3)$, $\delta_s(CH_3)$ and $r(CH_3)$ vibrations. The nature of the 1404 cm^{-1} band is a little complicated. This band can be called the ν(CN) band, although there are considerable contributions from the $\nu(CC')$, $r(NH_2)$, δ(NCO) and $\delta_s(CH_3)$ vibrations. The band at 864 cm^{-1} is associated with the $\nu(CC')$ vibrations, while the bands at 581 cm^{-1} and 464 cm^{-1} are associated with δ(NCO) and $\delta(CC')$ vibrations respectively.

Instead of the 1632 cm^{-1} band, a band appears at 1189 cm^{-1} in CH_3COND_2; this is assigned to an almost pure $b(ND_2)$ vibration. The ν(CO) band is lowered, probably by the decoupling of the $b(NH_2)$ vibrations, while the ν(CN) band moves to a higher frequency and appears at 1427 cm^{-1}. The $b(ND_2)$ vibration

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[*2] Miyazawa et al., obtained a good frequency agreement for the skeletal deformation vibrations of N-methylacetamide[11] from the values of $H_{CH_3 \cdot C \text{-} N}=H_{CH_3 \cdot C=O}=0.30$ md./A and $F_{CH_3 \cdots N}=F_{CH_3 \cdots O}=0.50$ md./A, although they treated the methyl group as a dynamic unit.

[*3] Those frequencies are given in parentheses in the first column of Tables IV (c) and (d).

TABLE IV. OBSERVED AND CALCULATED FREQUENCIES, AND POTENTIAL ENERGY DISTRIBUTIONS AMONG SYMMETRY COORDINATES; $(F_{ii}L_{is}^2/\lambda_s)\times 100$

(a) CH_3CONH_2

					P. E. D.									
Q_i	ν_{obs}	ν_{calcd}	$\varDelta\nu$	$\varDelta$	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Q_1	1676	1678	−2	0.1	**28**	1	**59**	**16**	4	1	7	1	0	4
Q_2	1632	1630	+2	0.1	1	1	**17**	**80**	2	1	1	0	0	1
Q_3	1457	1462	−5	0.4	1	1	3	0	1	1	0	**82**	0	9
Q_4	1404	1396	−8	0.6	**48**	**13**	2	4	**10**	**14**	2	5	**12**	0
Q_5	1360	1366	−6	0.5	6	**20**	1	0	2	2	0	0	**92**	0
Q_6	1152	1133	+19	1.7	7	1	**16**	6	**70**	1	1	0	0	0
Q_7	1005	1002	+3	0.3	5	0	2	0	1	0	3	**11**	0	**81**
Q_8	874	892	−18	2.1	**10**	**61**	4	1	7	8	0	0	0	0
Q_9	581	580	+1	0.2	0	10	0	0	3	**74**	5	0	0	0
Q_{10}	464	465	+1	0.2	1	0	1	0	2	5	**82**	2	0	5

(b) CH_3COND_2

					P. E. D.									
Q_i	ν_{obs}	ν_{calcd}	$\varDelta\nu$	$\varDelta$	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Q_1	1650	1666	−16	1.0	**24**	2	**75**	1	3	1	9	1	0	6
Q_2	(1455)	1461	—	—	1	1	4	0	0	1	0	**81**	0	8
Q_3	1427	1419	+8	0.5	**56**	**13**	7	**13**	3	**12**	1	5	7	0
Q_4	1369	1367	+2	0.1	4	**16**	1	1	0	1	0	0	**98**	0
Q_5	1189	1191	−2	0.2	1	**14**	0	**72**	3	8	2	1	0	2
Q_6	1022	1006	+16	1.6	1	3	9	0	5	2	3	**10**	0	**70**
Q_7	934	936	−2	0.2	**13**	5	7	**10**	**36**	6	0	1	0	**10**
Q_8	809	818	−9	1.1	6	**50**	0	3	**35**	0	0	0	0	0
Q_9	560	556	+4	0.8	0	6	1	0	7	**64**	**15**	0	0	1
Q_{10}	444	442	+2	0.5	1	0	0	0	8	**12**	**70**	0	0	4

(c) CD_3CONH_2

					P. E. D.									
Q_i	ν_{obs}	ν_{calcd}	$\varDelta\nu$	$\varDelta$	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Q_1	1675	1672	+3	0.2	**29**	1	**57**	**21**	4	1	7	0	0	2
Q_2	1620	1629	−9	0.6	0	2	**22**	**75**	2	1	2	0	0	1
Q_3	1413	1394	+19	1.4	**56**	**27**	3	4	**12**	**17**	2	0	0	1
Q_4	1144	1133	+11	0.9	7	0	**16**	0	**70**	1	1	0	0	0
Q_5	1086	1092	−6	0.6	1	**30**	0	0	2	0	0	0	**86**	0
Q_6	1058	1048	+10	0.9	0	0	0	0	0	0	1	**91**	0	5
Q_7	(835)	842	−7	0.9	**11**	**14**	0	0	2	8	6	3	6	**45**
Q_8	(812)	839	−27	3.3	1	**23**	5	0	5	9	3	3	9	**35**
Q_9	(578)	553	−25	4.3	0	**13**	0	0	2	**68**	3	0	4	1
Q_{10}	(429)	429	0	0	1	0	0	0	1	3	**78**	4	0	**12**

(d) CD_3COND_2

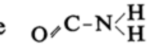
					P. E. D.									
Q_i	ν_{obs}	ν_{calcd}	$\varDelta\nu$	$\varDelta$	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Q_1	1645	1658	−13	0.8	**25**	2	**78**	1	3	1	9	0	0	3
Q_2	1425	1416	+9	0.6	**61**	**22**	**10**	**15**	3	**14**	1	0	0	0
Q_3	1177	1192	−15	1.3	1	**22**	0	**67**	3	8	1	0	6	1
Q_4	—	1089	—	—	3	**16**	1	9	0	1	0	0	**82**	0
Q_5	1030	1049	−19	1.8	0	0	0	0	0	0	1	**91**	0	5
Q_6	(962)	940	−22	2.3	5	1	**13**	5	**48**	9	3	0	3	4
Q_7	(810)	823	−13	1.7	7	0	1	2	2	1	6	5	0	**77**
Q_8	(767)	764	+3	0.4	5	**38**	1	2	**29**	3	0	0	**11**	1
Q_9	(540)	530	+10	1.9	0	9	1	0	7	**64**	8	1	3	2
Q_{10}	(413)	404	+9	2.2	1	0	0	0	5	7	**74**	3	0	8

$\varDelta\nu=\nu_{obs}-\varDelta\nu_{calcd}$, $\varDelta=|\varDelta\nu|/\nu_{obs}$

also contributes to the latter band. The $r(ND_2)$ vibration takes part in both the 934 and 809 cm^{-1} bands. The $\nu(CN)$, $b(ND_2)$ and $r(CH_3)$ vibrations also contribute to the former band, and the $\nu(CC')$ vibration to the latter.

The nature of the 1676, 1632, 1404 and 1152 cm^{-1} bands of CH_3CONH_2 is not much affected by the *C*-deuteration; they are found at 1672, 1620, 1413 and 1144 cm^{-1} in CD_3CONH_2, The 1414 cm^{-1} band is assigned to a composite mode in which the $\nu(CN)$, $\nu(CC')$ $r(NH_2)$ and $\delta(NCO)$ vibrations take place. In $CD_3\cdot COND_2$, it is found at 1425 cm^{-1}, and the $b(ND_2)$ vibration contributes to this band instead of $r(NH_2)$ vibration. The $\delta_a(CD_3)$ vibration occurs at 1058 cm^{-1}, which is lower by 28 cm^{-1} than the $\delta_s(CD_3)$ vibration. The reversal of these two methyl deformation vibrations is often observed in the spectra of compounds containing CD_3 groups[13]. For the CD_3-species of acetamide, the vibrational assignments of the observed bands below 1000 cm^{-1} are very difficult, because of the presence of the bands arising from the CHD_2-species contained in the sample. (The 1257 cm^{-1} band is assigned to the CH bending vibration of the CHD_2-species.) Aside from the bands of the CD_3-species, CD_2 wagging, bending, rocking and twisting vibrations are expected to appear in this region. Therefore, the assignments given in Table IV are tentative. The features of the $\delta(CC')$ vibration region are very interesting; four small peaks are observed around 420 cm^{-1} in the spectra of both CD_3CONH_2 and CD_3COND_2. The present calculations indicate that an interaction takes place between the $\delta(CC')$ and $r(CD_3)$ vibrations. It is also probable the vibrational interaction occurs between the $r(CD_2)$ and $\delta(CC')$ modes. However, the degrees of the interaction depend on the mutual positions of the CHD_2 group to the plane determined by the amide group. Several stable but non-equivalent configurations can be considered as for the positions of the CHD_2 group, and this may be the cause of the complexity of the $\delta(CC')$ bands.

Several bands can be assigned to the out-of-plane vibrations. In the NH_2-species, a broad band is found around 700 cm^{-1} and is assigned to the NH_2 wagging vibration. The NH_2 twisting band may overlap with this band. The corresponding bands are found around 500 cm^{-1} in the ND_2-species. A strong band found at about 640 cm^{-1} in the ND_2-species may be associated with the CC′ out-of-plane vibration[*4]. but the ND_2 twisting and wagging vibrations may also contribute to this band.

Force Constants. — The force constants in group A are associated with the  $O{=}C{-}N\langle^{H}_{H}$ part of the molecule and are transferred form formamide[1]. As may be seen from the process of determining their values, they can be used without significant alternations in value. This is the second example of showing a fine transferability of the constants determined in the formamide molecule[2]. A stretching force constant, *K*, has often been used as a measure of the bond order or character of the corresponding bond. In the series of amides, the K_{CO} and K_{CN} values are always found, respectively, around 8.50 and 6.00 md./A and are considered to indicate the partial single and double bond characters of the respective C=O and C–N bonds. In urea, however, the K_{CO} value falls to 6.47 md./A[14]. The lowering of the K_{CO} value may partly be accounted for by the presence in urea of two C–N bonds adjacent to the C=O bond[*5]. In the Urey-Bradley force field, the value of a given stretching constant is closely correlated with those of the repulsive constants around the bond. It is often odserved for a molecule which contains conjugated systems that some repulsion constants become very large[17]. In such a molecule, the resonance term $k_{ab}(\Delta r_a)(\Delta r_b)$[*6], which is neglected in the Urey-Bradley field, is of considerable magnitude and affects the corresponding force constant $F_{a\cdots b}$. In the present case, the $F_{N\cdots O}$ value is found to be as large as 1.50 md./A. The lowering of the K_{CO} value in urea as compared with that in acetamide can be explained by the superposed effect of $F_{N\cdots O}$ from two adjacent C–N bonds. It should be noted that the direct comparison of stretching constants sometimes leads to an incorrect conclusion, especially when some repulsive force constants are considerably large.

The force constants in group B are primarily

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[11] T. Miyazawa, T. Shimanouchi and S. Mizushima, ibid., **29**, 611 (1958).

[12] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 1132 (1955).

[13] For example, H. C. McMurry and V. Thornton, *J. Chem. Phys.*, **19**, 1014 (1951).

[14] A. Yamaguchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 1319, 1467 (1957).

[*4] In the NH_2-species, the corresponding band can not be found; it is probable that the band is overlapped with that of the $\delta(NCO)$ vibration at about 560 cm^{-1}.

[*5] However, the reported value of 1.26 Å for the C=O bond in urea[15] is not much different from that of 1.255 Å in formamide[16] and only a little shorter than that of 1.28 Å in acetamide[9].

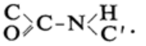
[15] A. Yamaguchi, T. Miyazawa, T. Shimanouchi and S. Mizushima, *Spectrochim. Acta*, **17**, 719 (1961).

[16] J. Landall and B. Post, *Acta Cryst.*, **7**, 559 (1954).

[17] T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 381 (1956).

[*6] r_a and r_b denote the bonds resonated with each other, and k_{ab} is a force constant. In fact, Scherer and Overend include the analogous term in the normal vibration calculation of the benzene molecule[18].

[18] J. R. Scherer and J. Overend, *Spectrochim. Acta*, **17**, 719 (1961).

concerned with the C–C bond of the molecule. The present results, if combined with those of *N*-methylformamide, give the reliable set of force constants necessary to describe the peptide skeletals:  $\begin{smallmatrix}C\\O\end{smallmatrix}\!\!>\!C{-}N\!<\!\begin{smallmatrix}H\\C'\end{smallmatrix}$. The force constants in group C are concerned with the CH_3 group, and it is shown that the values of the force constants recommended in our laboratory can also be used in this molecule.

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