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Vibrational Spectra of Propionamide and Its C- and N-Deuterated Compounds

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The infrared and Raman spectra of $CH_3CH_2CONH_2$, $CH_3CD_2CONH_2$ and their *N*-deuterated compounds in the solid state have been measured. The normal coordinate analysis has been made by assuming the molecular symmetry of C_s. A Urey-Bradley force field was used for the in-plane vibrations and a valence force field for the out-of-plane vibrations of the amide group. The ethyl group was treated by a Urey-Bradley type force field as well as a valence type force field. The assignments of the fundamental frequencies have been made by referring to the infrared and Raman intensities, isotopic frequency shift and the calculated frequencies by using the force constants which were taken from *n*-paraffins and acetamide. The agreement between the observed and the calculated frequencies in the initial calculation was good for the CH_3 and the amide group vibrations but was not good enough for some vibrations involving the α-carbon atom. Only the force constants related to these vibrations were refined by the least squares method in order to obtain the best fit. The calculated frequencies in this way fit to the observed satisfactorily.

Recently, we reported the infrared spectra of *n*-fatty acid amides, $CH_3(CH_2)_nCONH_2$ (n=1—16), and discussed the effect of the end amide group on the band progression frequencies arising from vibrations of the alkyl chain.[1] By assuming the invariance of the force field of the chain part, the shifts of band progressions on going from *n*-paraffins to amides were elucidated satisfactorily to arise from the change in the fashion of the vibrational coupling between the alkyl chain and the end groups. The force constants related to the α-methylene group are expected, however, to differ more or less from those of the *n*-paraffins, reflecting the change in the electronic structure induced by the polar end group. The present work has been undertaken to see if such difference in the force con-

1) K. Machida, S. Kojima and T. Uno, *Spectrochim. Acta*, **28**, 235 (1972).

stants between amides and *n*-paraffins can be estimated from the vibrational analysis of propionamide.

Besides our previous work,[1] the infrared and Raman spectra of propionamide have been reported by several investigators,[2-6] but there have remained many fundamental frequencies yet unassigned. In order to discuss the vibrational spectra of propionamide more precisely and to examine the transferability of force constants, we synthesized $CH_3CD_2CONH_2$ and $CH_3CD_2COND_2$, and measured the infrared and Raman spectra of these compounds together with those of usual species, $CH_3CH_2CONH_2$ and $CH_3CH_2COND_2$. The infrared spectrum of the 50 per cent *N*-deuterated sample of propionamide was also recorded for comparison. The normal coordinate analysis based on the GF matrix method[7] has been made by using the force constants transferred from acetamide[8-9] and *n*-paraffins.[10] By comparing the observed spectra with the result of the initial calculation, reasonable assignments have been given to all the fundamental frequencies of four isotopic species of propionamide. The agreement between the observed and the initially calculated frequencies was not good enough for some vibrations of the joint part of the ethyl and amide groups, but an appreciable improvement of frequency fits was attained soon by the least squares refinement of the related force constants.

Experimental

Materials. Methylmalonic acid was prepared by the saponification of commercially available diethyl methylmalonate,[11] and was submitted to the exchange reaction with D_2O in a sealed tube twice. After the removal of the excess D_2O, methylmalonic-d_1-acid-d_2 was thermally decomposed at 140—150°C and the product was distilled at the same time.[12] Thus obtained propionic-α,α-d_2 acid-*d* (CH_3CD_2COOD) was purified by distillation under reduced pressure. The deuterium content at the α-position of this acid was estimated to be about 92 per cent by the NMR spectrum. Propionyl-α,α-d_2 chloride (CH_3CD_2COCl) was prepared from propionic-α,α-d_2 acid-*d* and benzoyl chloride,[13] and was converted into propion-α,α-d_2 amide ($CH_3CD_2CONH_2$) by the reaction with NH_3 gas in ether at about −15°C. Similarly, propionamide ($CH_3CH_2CONH_2$) was synthesized from commercially available propionyl chloride. The amides were purified by the recrystallization from benzene. The NH_2 compounds were converted into the corresponding ND_2 compounds by the exchange reaction with

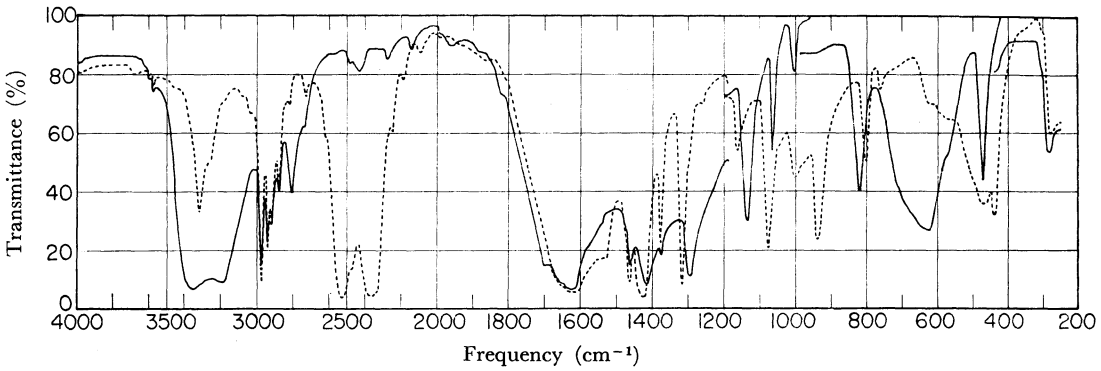

Fig. 1. Infrared spectra of $CH_3CH_2CONH_2$ (——) and $CH_3CH_2COND_2$ (----) in the region between 4000 and 250 cm^{-1}.

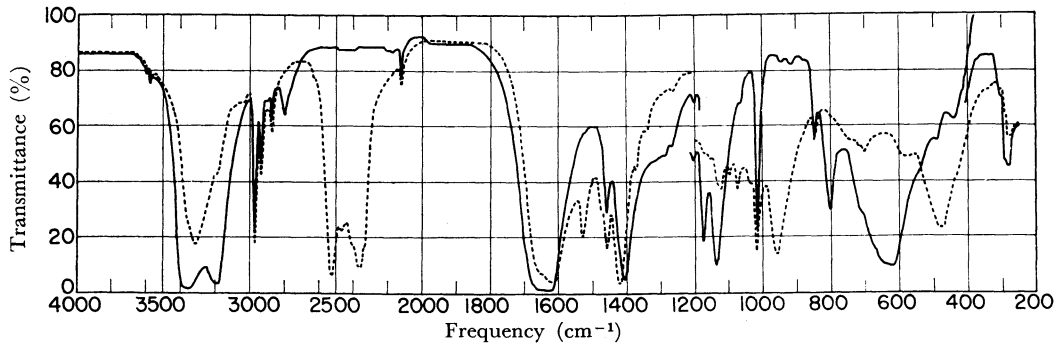

Fig. 2. Infrared spectra of $CH_3CD_2CONH_2$ (——) and $CH_3CD_2COND_2$ (----) in the region between 4000 and 250 cm^{-1}.

2) J. E. Katon, W. R. Feairheller, Jr., and J. V. Pustinger, Jr. *Anal. Chem.*, **36**, 2126 (1964).
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12) P. Hölemann and K. Clusius, *Ber.*, **70**, 819 (1937).
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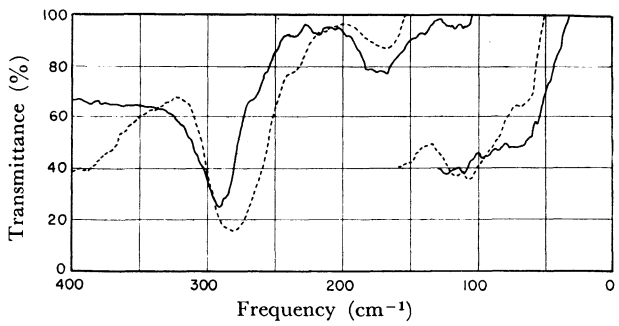

Fig. 3. Infrared spectra of $CH_3CH_2CONH_2$ (——) and $CH_3CH_2COND_2$ (----) in the region between 400 and 33 cm^{-1}.

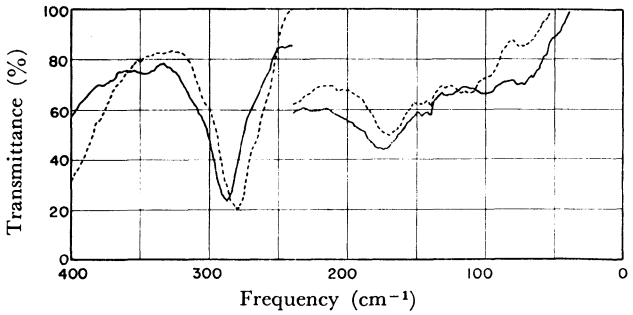

Fig. 4. Infrared spectra of $CH_3CD_2CONH_2$ (——) and $CH_3CD_2COND_2$ (----) in the region between 400 and 33 cm^{-1}.

D_2O. The partially *N*-deuterated samples were prepared by using mixtures of H_2O and D_2O.

Measurement. The infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer (4000—250 cm^{-1}, Figs. 1 and 2) and on a Hitachi FIS-3 grating spectrophotometer (400—33 cm^{-1}, Figs. 3 and 4). The samples were measured as mulls with Nujol or hexachlorobutadiene. The wave number was calibrated by the standard absorptions of polystyrene, indene and ammonia. The Raman spectra were measured for the crystalline samples obtained from the melt sealed in a capillary tube on a SPEX RAMALOG laser Raman spectrophotometer (Figs. 5 and 6). The exciting line (4880 Å) was generated by an argon ion laser at an approximate output power of 200 mW. The observed frequencies are listed in Table 1 together with the relative intensities and assignments.

Normal Coordinate Analysis

The molecular symmetry of propionamide adopted in the present calculation is that of the point group C_s with the C_α-C_β bond at the *trans* position of the C–N bond (hereafter, the alkyl carbon atoms are specified by greek subscripts if necessary). Although the structure determination by the X-ray analysis has not yet been made for propionamide, the assumption of the C_s structure may be justified from the crystallographic data for a number of long chain *n*-fatty acid amides.[14-17] It has been shown that the cell di-

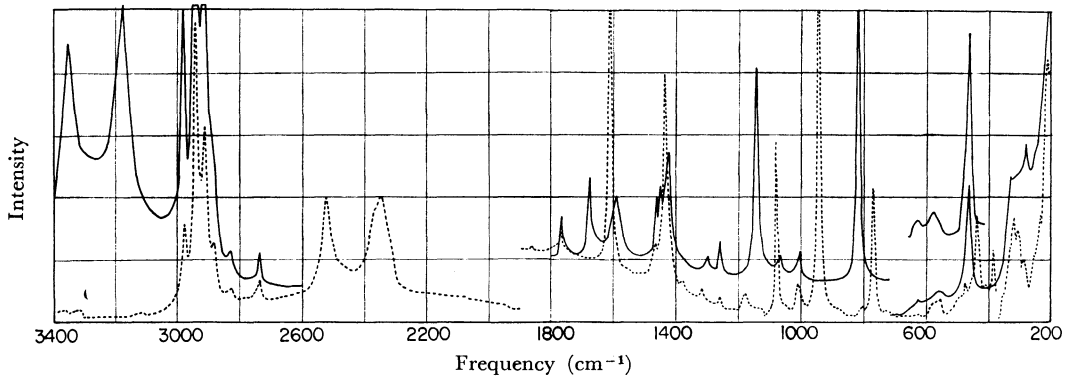

Fig. 5. Raman spectra of $CH_3CH_2CONH_2$ (——) and $CH_3CH_2COND_2$ (----) in the region between 3400 and 200 cm^{-1}.

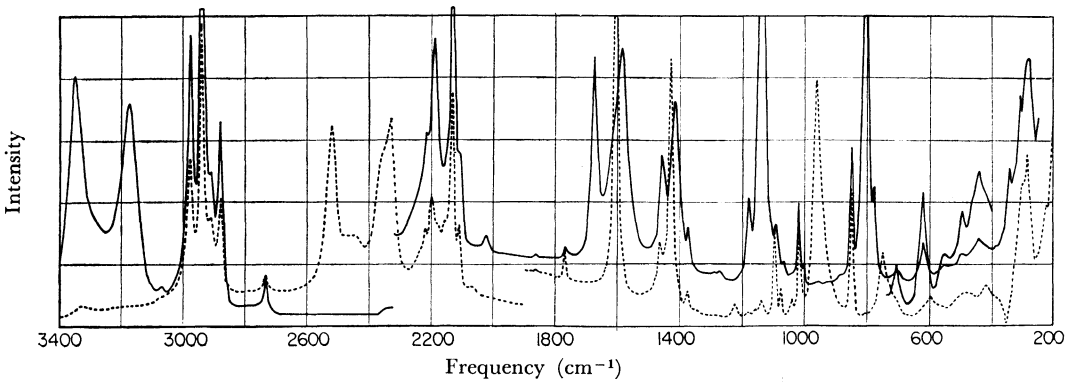

Fig. 6. Raman spectra of $CH_3CD_2CONH_2$ (——) and $CH_3CD_2COND_2$ (----) in the region between 3400 and 200 cm^{-1}.

14) J. D. Turner and E. C. Lingafelter, *Acta Crystallogr.*, **8**, 551 (1955).
15) J. R. Brathovde and E. C. Lingafelter, *ibid.*, **11**, 729 (1958).
16) S. Kurokawa, This Bulletin, **28**, 660 (1955).
17) J. D. Turner and E. C. Lingafelter, *Acta Crystallogr.*, **8**, 549 (1955).

TABLE 1. INFRARED AND RAMAN FREQUENCIES OF $CH_3CH_2CONH_2$, $CH_3CH_2COND_2$, $CH_3CD_2CONH_2$, AND $CH_3CD_2COND_2$ IN cm^{-1}

$CH_3CH_2CONH_2$		$CH_3CH_2COND_2$		$CH_3CD_2CONH_2$		$CH_3CD_2COND_2$	
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman
3350 vs	3350 vs			3350 vs	3350 vs		
3190 vs	3175 vs			3190 vs	3172 vs		
2980 m	2978 vs	2980 m	2978 m	2970 m	2978 vs	2970 m	2974 s
2940 w	2942 vs	2940 w	2942 vs	2935 w	2940 vs	2935 w	2940 vs
2920 sh	2912 vs	2920 vw	2912 vs				
2880 w		2880 w	2884 w	2870 w	2880 s	2870 w	2877 s
2820 sh	2825 vw	2820 vw	2825 vw				
2805 m				2795 w			
2740 sh	2733 w	2730 w	2733 vw		2733 w		2733 w
2435 w		2530 vs	2525 s			2520 vs	2525 vs
		2370 vs	2350 s			2360 vs	2335 vs
2280 vw		2250 vw					
		2190 vw		2180 vw	2190 vs	2180 vw	2190 vs
2150 w		2100 vw		2120 w	2130 vs	2120 w	2130 vs
1960 w					2023 w		2110 sh
	1762 w		1762 w		1765 vw		1765 w
1665 vs	1674 s			1665 vs	1674 vs		
1625 vs	1590 s	1630 vs	1610 vs	1625 vs	1585 vs	1630 vs	1605 vs
1465 m	1460 sh	1466 m	1462 sh	1462 w	1457 s	1462 w	1460 sh
	1450 sh						
1418 vs	1422 s	1425 vs	1435 vs	1409 vs	1416 vs	1425 vs	1428 vs
1382 vw		1382 m	1380 vw	1378 sh	1372 w	1377 vw	1376 w
1296 vs	1300 vw	1318 vs	1327 vw				
	1260 w		1260 vw				
		1165 m	1180 w	1174 m	1179 m		1224 w
1142 s	1148 vs			1136 s	1143 vs	1152 sh	1138 vw
						1120 w	
1068 m	1070 w	1078 s	1078 vs	1093 sh	1095 w	1096 vw	1095 m
				1070 sh	1073 sh	1070 w	1073 w
1004 w	1009 w	1006 w	1009 m			1036 sh	1040 vw
				1016 s	1020 m	1014 s	1018 m
		942 s	945 vs	948 w	1000 sh	956 s	960 vs
				918 w			
				850 w	850 s	845 vw	850 s
821 m	820 vs	808 m	806 vw	803 m	807 vs		
		765 w	769 s		780 sh	740 sh	750 m
				710 sh	703 vw	700 vw	
680 sh				670 sh			
640 vs	630 vw	625 sh		625 vs	618 m	575 sh	600 w
570 sh	570 vw	580 sh	570 vw	550 sh	550 vw	525 sh	
		475 m	470 vw	495 vw	492 vw	470 s	480 w
472 m	470 s	443 m	438 m	442 vw	440 w	420 sh	420 w
			380 w		342 sh		
	320 m		318 m		310 sh		
			308 m				
292 m	285 w	281 m	282 vw	288 m	280 s	280 w	280 s
175 w		170 w		175 w		170 w	
120 vw		117 vw					
110 vw		107 vw					
70 vw		70 vw		70 vw		70 vw	

mension c_0 increases but a_0 and b_0 remain almost constant on going from $CH_3CH_2CONH_2$ to $CH_3(CH_2)_{14}CONH_2$, and that the N, C, C_α and C_β atoms of $CH_3(CH_2)_nCONH_2$ (n=8 and 12) are nearly coplanar.

The structure parameters used in the calculation are shown in Table 2, where the bond lengths and angles concerned with hydrogen atoms are assumed values. The other parameters were taken from the results of X-ray analysis of related molecules.[18-19] In the C_s

Table 2. Structure parameters used for the calculation

Bond length in Å		Bond angles	
r(C=O)	1.260[a]	ϕ(CCN)	117°12'[a]
r(C-N)	1.334[a]	ϕ(CCO)	119°36'[a]
r(C-C=O)	1.527[b]	ϕ(NCO)	123°12'[a]
r(C-CH_2)	1.546[b]	ϕ(CCH)	109°28'
r(C-H)	1.08	ϕ(HCH)	109°28'
r(N-H)	1.02	ϕ(CNH)	120°
		ϕ(HNH)	120°
		ϕ(CCC)	109°28'

a) Taken from Ref. 18.
b) Taken from Ref. 19.

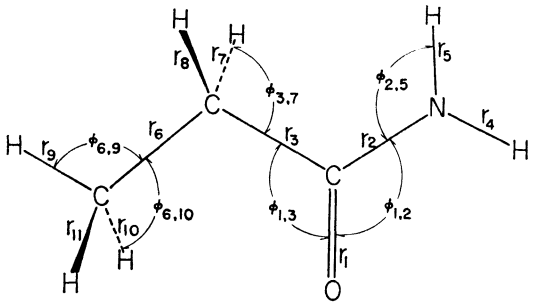

Fig. 7. Molecular structure and internal coordinates.

Table 3. Symmetry coordinates for propionamide

Symmetry coordinates[a]	Description of modes (Abbr.)
(a) In-plane vibrations (a')	
$S_1 = \Delta r_1$	C=O str. (νC=O)
$S_2 = (2\Delta\phi_{4,5} - \Delta\phi_{2,4} - \Delta\phi_{2,5})/\sqrt{6}$	NH_2 bend. (βNH_2)
$S_3 = (\Delta\phi_{2,4} - \Delta\phi_{2,5})/\sqrt{2}$	NH_2 rock. (ρNH_2)
$S_4 = \Delta r_2$	CN str. (νCN)
$S_5 = (\Delta\phi_{1,3} - \Delta\phi_{1,2})/\sqrt{2}$	C=O def. (δC=O)
$S_6 = (2\Delta\phi_{2,3} - \Delta\phi_{1,3} - \Delta\phi_{1,2})/\sqrt{6}$	CCN def. (δCCN)
$S_7 = (\Delta r_4 - \Delta r_5)/\sqrt{2}$	NH_2 asym. str. ($\nu_{as}NH_2$)
$S_8 = (\Delta r_4 + \Delta r_5)/\sqrt{2}$	NH_2 sym. str. ($\nu_s NH_2$)
$S_9 = \Delta r_3$	C-C=O str. (νCC_α)
$S_{10} = \Delta r_6$	C-C str. ($\nu C_\alpha C_\beta$)
$S_{11} = (2\Delta\phi_{10,11} - \Delta\phi_{9,10} - \Delta\phi_{9,11})/\sqrt{6}$	CH_3 asym. def. ($\delta_{as}CH_3$)
$S_{12} = (\Delta\phi_{9,10} + \Delta\phi_{9,11} + \Delta\phi_{10,11} - \Delta\phi_{6,9} - \Delta\phi_{6,10} - \Delta\phi_{6,11})/\sqrt{6}$	CH_3 sym. def. ($\delta_s CH_3$)
$S_{13} = (2\Delta\phi_{6,9} - \Delta\phi_{6,10} - \Delta\phi_{6,11})/\sqrt{6}$	CH_3 rock. (ρCH_3)
$S_{14} = (\Delta\phi_{3,7} + \Delta\phi_{3,8} - \Delta\phi_{6,7} - \Delta\phi_{6,8})/2$	CH_2 wag. (ωCH_2)
$S_{15} = (4\Delta\phi_{7,8} - \Delta\phi_{3,7} - \Delta\phi_{3,8} - \Delta\phi_{6,7} - \Delta\phi_{6,8})/\sqrt{20}$	CH_2 bend. (βCH_2)
$S_{16} = (5\Delta\phi_{3,6} - \Delta\phi_{3,7} - \Delta\phi_{3,8} - \Delta\phi_{6,7} - \Delta\phi_{6,8} - \Delta\phi_{7,8})/\sqrt{30}$	CCC def. (δCCC)
$S_{17} = (2\Delta r_9 - \Delta r_{10} - \Delta r_{11})/\sqrt{6}$	CH_3 asym. str. ($\nu_{as}CH_3$)
$S_{18} = (\Delta r_9 + \Delta r_{10} + \Delta r_{11})/\sqrt{3}$	CH_3 sym. str. ($\nu_s CH_3$)
$S_{19} = (\Delta r_7 + \Delta r_8)/\sqrt{2}$	CH_2 sym. str. ($\nu_s CH_2$)
(b) Out-of-plane vibration (a'')	
$S_{20} = (\Delta\phi_{6,10} - \Delta\phi_{6,11})/\sqrt{2}$	CH_3 rock. (ρCH_3)
$S_{21} = (\Delta\phi_{9,10} - \Delta\phi_{9,11})/\sqrt{2}$	CH_3 asym. def. ($\delta_{as}CH_3$)
$S_{22} = (\Delta\phi_{3,8} - \Delta\phi_{3,7} - \Delta\phi_{6,7} - \Delta\phi_{6,8})/2$	CH_2 rock. (ρCH_2)
$S_{23} = (\Delta\phi_{3,8} - \Delta\phi_{3,7} + \Delta\phi_{6,7} - \Delta\phi_{6,8})/2$	CH_2 twist. ($t CH_2$)
$S_{24} = (\Delta r_{10} - \Delta r_{11})/\sqrt{2}$	CH_3 asym. str. ($\nu_{as}CH_3$)
$S_{25} = (\Delta r_7 - \Delta r_8)/\sqrt{2}$	CH_2 asym. str. ($\nu_{as}CH_2$)
$S_{26} = (\Delta\tau_{3,6,9} + \Delta\tau_{3,6,10} + \Delta\tau_{3,6,11} + \Delta\tau_{7,6,9} + \Delta\tau_{7,6,10} + \Delta\tau_{7,6,11} + \Delta\tau_{8,6,9} + \Delta\tau_{8,6,10} + \Delta\tau_{8,6,11})/3$	CH_3 torsion (τCH_3)
$S_{27} = (\Delta\tau_{1,2,4} + \Delta\tau_{1,2,5} + \Delta\tau_{3,2,4} + \Delta\tau_{3,2,5})/2$	NH_2 torsion (τNH_2)
$S_{28} = (\Delta\tau_{1,2,4} + \Delta\tau_{1,2,5} - \Delta\tau_{3,2,4} - \Delta\tau_{3,2,5})/2$	C=O def. (πC=O)
$S_{29} = (-\Delta\tau_{1,2,4} + \Delta\tau_{1,2,5} - \Delta\tau_{3,2,4} + \Delta\tau_{3,2,5})/2$	NH_2 wag. (ωNH_2)
$S_{30} = (\Delta\tau_{1,3,7} + \Delta\tau_{1,3,8} + \Delta\tau_{1,3,6} + \Delta\tau_{2,3,7} + \Delta\tau_{2,3,8} + \Delta\tau_{2,3,6})/\sqrt{6}$	C-C=O torsion (τCC_α)

a) $\phi_{i,j}$ means the angle formed by the bonds r_i and r_j.
$\tau_{i,j,k}$ means the dihedral angle formed by the planes $r_i - r_j$ and $r_j - r_k$.

18) W. C. Hamilton, *ibid.*, **18**, 866 (1965).
19) T. Uechi, T. Watanabé, and K. Osaki, *Sci. Rep. (Osaka Univ.)*, **15**, 1 (1966).

TABLE 4. FORCE CONSTANTS

(a) Calculation A[a)]

No.	Force constant		No.	Force constant		No.	Force constant	
1	K(NH)	5.728	17	$f_{30,30}$	0.0069	33	$F(CC_\alpha C_\beta)$	0.324
2	H(HNH)	0.375	18	$f_{27,28}$	−0.0160	34	$F(CC_\alpha H)$	0.548
3	H(CNH)	0.406	19	$f_{27,29}$	−0.0061	35	$F(HC_\alpha H)$	0.046
4	H(NCO)	0.521	20	$f_{28,29}$	0.0235	36	$F(C_\beta C_\alpha H)$	0.548
5	$H(C_\alpha CN)$	0.625	21	K(CO)	7.233 (7.438)[b)]	37	$F(C_\alpha C_\beta H)$	0.548
6	$H(C_\alpha CO)$	0.247	22	K(CN)	5.580 (5.525)	38	$F(HC_\beta H)$	0.046
7	F(HNH)	0.0	23	$K(CC_\alpha)$	2.700 (3.187)	39	$f_{4,9}$	−0.2475 (0.000)
8	F(CNH)	0.376	24	$K(C_\alpha C_\beta)$	2.229	40	$\kappa(CH_2)$	−0.016 (0.002)
9	F(NCO)	1.228	25	$K(C_\alpha H)$	4.023	41	$\kappa(CH_3)$	−0.014
10	$F(C_\alpha CN)$	0.137	26	$K(C_\beta H)$	4.425	42	$f_{\beta\omega}{}^t$	0.036
11	$F(C_\alpha CO)$	0.563	27	$H(CC_\alpha C_\beta)$	0.492 (0.290)	43	$f_{\beta\omega}{}^g$	−0.004
12	P(NH-NH)	−0.149	28	$H(CC_\alpha H)$	0.217 (0.195)	44	$f_{\beta\gamma}{}^t$	0.087
13	$f_{26,26}$	0.0069	29	$H(HC_\alpha H)$	0.416 (0.438)	45	$f_{\beta\gamma}{}^g$	−0.009
14	$f_{27,27}$	0.1392	30	$H(C_\beta C_\alpha H)$	0.156 (0.195)	46	$f'_{\beta\gamma}{}^t$	−0.022
15	$f_{28,28}$	0.3825	31	$H(C_\alpha C_\beta H)$	0.191	47	$f'_{\beta\gamma}{}^g$	−0.002
16	$f_{29,29}$	0.0898	32	$H(HC_\beta H)$	0.438	48	$f_{2,14}$	−0.0108 (0.000)

(b) Calculation B[c,d)]

No.	Force constant		No.	Force constant		No.	Force constant	
21	K(CO)	7.376 (7.438)[b)]	31	$F'_{R\gamma}$	−0.004	41	H_ω	1.351 (0.901)
22	K(CN)	5.764 (5.525)	32	$F_{R\omega}$	0.351	42	$f_{\beta\omega}{}^t$	0.072
23	K_r	4.704	33	H_α	0.540	43	$f_{\beta\omega}{}^g$	−0.058
24	F_r	0.039	34	H_δ	0.504 (0.550)	44	$f_{\beta\gamma}{}^t$	0.106
25	K_d	4.546	35	H_β	0.637	45	$f_{\beta\gamma}{}^g$	−0.024
26	F_d	0.016	36	F_β	−0.017	46	$f'_{\beta\gamma}{}^t$	−0.002
27	$K_R{}^I(CC_\alpha)$	3.248 (4.329)	37	H_γ	0.643 (0.666)	47	$f'_{\beta\gamma}{}^g$	0.002
28	$K_R{}^I(C_\alpha C_\beta)$	4.329	38	F_γ	−0.008 (−0.016)	48	$f_{4,9}$	−0.2549 (0.000)
29	F_R	0.064	39	F'_γ	0.001 (0.023)	49	$f_{2,14}$	−0.0276 (0.000)
30	$F_{R\beta}$	0.261	40	$F_{\gamma\omega}$	−0.124			

a) Force constants Nos. 1—12 and Nos. 21—39 in units of mdyn/Å.
Force constants Nos. 13—20 and Nos. 40—48 in units of mdyn·Å/(rad)²
b) ( ): initial value
c) The force constants Nos. 1—20 are the same as those in the Calculation A.
d) The force constants of ethyl group were taken from Calculation V in Ref. 10: Stretching constants in units of mdyn/Å. Stretch-bend interaction constants in units of mdyn/rad. Bending constants in units of mdyn·Å/(rad)².

model, the 30 fundamental vibrations of propionamide are classified into 19 in-plane (a′) and 11 out-of-plane (a″) modes. The internal coordinates and the internal symmetry coordinates are shown in Fig. 7 and Table 3, respectively. In order to avoid missassignments due to any inadequacy of force constants, the calculation was carried out in two ways, in which the CH_3-CH_2-group was treated by a modified Urey-Bradley force field (Calculation A) and by a general valence force field (Calculation B). In both Calculations A and B, the amide group was treated by a simple Urey-Bradley force field for the a′ vibrations and a valence force field for the a″ vibrations. In the initial calculations, the force constants of the amide group were transferred from our earlier results for acetamide.[8-9)] and those of the ethyl group from Schachtschneider and Snyder's work on *n*-paraffins; see Table 4.[10)] Calculations A and B by the transferred force constants gave essentially the same results as each other, reproducing well the observed fundamental frequencies of $CH_3CH_2CONH_2$ and $CH_3CH_2COND_2$ for the vibrations of the CH_3 and the $CONH_2$ ($COND_2$) groups. The initial calculation failed, however, to give satisfactory fits for the C_α–C stretching, the CH_2 bending and the C_β–C_α–C deformation frequencies. By taking account of these results together with the observed infrared and Raman intensities and isotopic frequency shifts, vibrational assignments have been made for the remaining fundamentals of four isotopic species of propionamide.

Vibrational Assignment

There is no question on the assignment of the NH_2 asymmetric and symmetric stretching frequencies (*ca.* 3350 and 3190 cm^{-1}) and their ND_2 counterparts (2530 and 2370 cm^{-1}). They were observed as strong bands in both the infrared and Raman spectra. For the NH_2 and ND_2 symmetric stretching vibrations, we observed an apparent difference by about 20 cm^{-1}

between the infrared and the Raman frequencies. This difference is attributable to the intermolecular interaction by hydrogen bonds in the crystalline state, where the infrared active and the Raman active vibrations may belong to different symmetry species of the factor group. In Figs. 1 and 2, the band at 3310 cm^{-1} and the shoulder at 3200 cm^{-1} are assigned to the NH stretching vibrations of the NHD compounds. In order to distinguish between the bands due to the NHD compounds and those of the ND_2 compounds clearly, the infrared spectra of 50 per cent *N*-deuterated samples were measured and the normal coordinate analysis was also made for the *trans* and the *cis* isomers of CH_3CH_2-CONHD. The observed and the calculated frequencies, the relative intensities and the assignments are summarized in Table 5. The assignments of the CH_3 and CH_2 stretching vibrations are easily made by comparing the infrared and Raman spectra of the CH_2 compounds with those of the CD_2 compounds. Following Nolin and Jones,[20] the strong Raman band at 2940 cm^{-1} observed for each isotope of propionamide may be assigned to the first overtone of the CH_3 asymmetric deformation vibration at about 1460 cm^{-1}, enhanced by the resonance with the CH_3 symmetric stretching vibration. The CD_2 asymmetric and symmetric stretching frequencies were observed, respectively, at about 2180 and 2120 cm^{-1} for $CH_3CD_2CONH_2$ and $CH_3CD_2COND_2$. They are not immediately obvious in the infrared, but are definitely found as sharp strong bands in the Raman spectra.

In the region between 1800 and 1550 cm^{-1}, the infrared spectra of $CH_3CH_2CONH_2$ and CH_3CD_2-$CONH_2$ show two strong and broad bands centered at about 1665 and 1625 cm^{-1} which almost overlap with each other, but the Raman spectra of these compounds show two clearly separated bands at about 1674 and 1590 cm^{-1} (see Figs. 5 and 6). These bands arise certainly from the C=O stretching and the NH_2 bending vibrations. According to the normal coordinate analysis, both S_1 (C=O stretching) and S_2 (NH_2 bending) are important in the potential energy distribution for each of these fundamentals. The infrared band at 1418 cm^{-1} of $CH_3CH_2CONH_2$ shifts to 1425 cm^{-1} on the *N*-deuteration (see Fig. 1). This band is assigned to two fundamentals, *viz.*, the CH_2 bending and the C–N stretching vibrations, the high frequency shift on the *N*-deuteration being associated only with the latter. A distinct evidence for the contribution of the C–N stretching vibration to this band is that CH_3CD_2-$CONH_2$ shows the corresponding band at 1409 cm^{-1}, which shifts also to a high frequency on the *N*-deuteration (Fig. 2). The assignment of the α-CH_2 bending frequency has been established for a number of *n*-acyl compounds.[21]

The infrared band of $CH_3CH_2CONH_2$ observed at 1296 cm^{-1} was assigned previously to the CH_2 wagging mode. The N-deuteration causes an upward shift of this band by about 22 cm^{-1}, in accordance with the removal of the NH_2 bending frequency from its high-frequency side. The corresponding Raman band at 1300 cm^{-1} is very weak, but it is easily assigned to the CH_2 wagging mode since it shifts to a higher frequency on the N-deuteration similar to that of the infrared counterpart. In the Raman spectrum CH_3-CH_2CONH_2 shows a weak band at 1260 cm^{-1} which does not shift on the *N*-deuteration and is assignable to the CH_2 twisting vibration. The corresponding infrared band was not observed. In the region between 1300 and 1200 cm^{-1}, neither the infrared nor the Raman spectrum of $CH_3CD_2CONH_2$ shows noticeable bands, but a weak Raman band is observed at 1224 cm^{-1} for $CH_3CD_2COND_2$. According to the normal coordinate analysis, this band is assigned to the ND_2 bending vibration, which gives rise to the medium infrared band at 1165 cm^{-1} and the weak Raman band at 1180 cm^{-1} for $CH_3CH_2COND_2$.

In the infrared spectrum between 1200 and 900 cm^{-1} (see Fig. 1), $CH_3CH_2CONH_2$ shows three bands at 1142, 1068, and 1004 cm^{-1}, the first arising from the NH_2 rocking vibration. Its Raman counterpart appears at 1148 cm^{-1} very strongly. The 1068 cm^{-1} band was assigned previously to the C_α–C_β stretching vibration. The normal coordinate analysis in this work indicates that the C_α–C_β stretching and the a′ CH_3 rocking vibrations couple strongly with each other, and give rise to the two bands at 1068 and 1004 cm^{-1}. On the *N*-deuteration the 1068 cm^{-1} band shifts to 1078 cm^{-1} but the 1004 cm^{-1} band remains unshifted. The very strong Raman band at 945 cm^{-1} of $CH_3CH_2COND_2$ is easily assigned to the ND_2 rocking vibration by taking account of the isotope shift and its characteristic intensity. The infrared and Raman spectra of the CD_2 compounds in this region are much more complicated than those of the CH_2 compounds. As shown in Fig. 6, the Raman bands corresponding to the infrared bands at 1136 cm^{-1} of $CH_3CD_2CONH_2$ and at 956 cm^{-1} of $CH_3CD_2COND_2$ are very strong and are easily assigned to the NH_2 and ND_2 rocking vibrations, respectively. The assignments of the other bands have been made by referring to the calculated

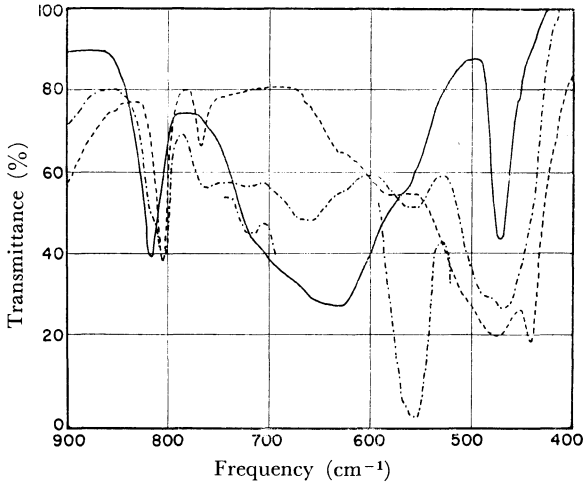

Fig. 8. Infrared spectra of $CH_3CH_2CONH_2$ (——), CH_3-CH_2CONHD (·—·) and $CH_3CH_2COND_2$ (----) in the region between 900 and 400 cm^{-1}.

20) B. Nolin and R. Norman Jones, *J. Amer. Chem. Soc.*, **75**, 5626 (1953).

21) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed. Methuen & Co. Ltd., London, p. 23.

frequencies. According to the normal coordinate analysis, the coupling among the CH_3 rocking, C_α–C_β stretching, $NH_2(ND_2)$ rocking and the CD_2 bending vibrations seems to be considerable.

Three fundamental frequencies are expected for $CH_3CH_2CONH_2$ in the region between 900 and 700 cm^{-1}, *viz.*, the C–C_α stretching, the CH_2 rocking and the NH_2 torsional frequencies, but the infrared spectrum of this compound shows only one medium absorption band at 821 cm^{-1}. We assigned this band to a composite absorption contributed by the above three modes. On the *N*-deuteration, this band is replaced by a medium band at 808 cm^{-1} due certainly to the CH_2 rocking vibration, and a weak band assignable to the C–C_α stretching vibration appears at 765 cm^{-1}. The contribution of the NH_2 torsional

TABLE 5. OBSERVED AND CALCULATED FREQUENCIES OF CH_3CH_2CONHD AND CH_3CD_2CONHD IN cm^{-1}

CH_3CH_2CONHD						CH_3CD_2CONHD					
	Calc. A						Calc. A				
Obs.	*trans*	Δ(%)	*cis*	Δ(%)	Assign.	Obs.	*trans*	Δ(%)	*cis*	Δ(%)	Assign.
(a) In-plane vibrations (a′)											
3310 vs	3291	0.6			νNH	3310 vs	3291	0.6			νNH
3200 sh			3278	2.4	νNH	3200 sh			3278	2.4	νNH
2980 m	2958	0.7	2958	0.7	$\nu_{as}CH_3$	2970 m	2958	0.4	2958	0.4	$\nu_{as}CH_3$
2880 w	2891	0.4	2891	0.4	$\nu_{s}CH_3$	2870 w	2885	0.5	2885	0.5	$\nu_{s}CH_3$
2820 w	2855	1.2	2855	1.2	$\nu_{s}CH_2$	2465 vs			2399	2.7	νND
2465 vs			2399	2.7	νND	2410 vs	2387	0.9			νND
2410 vs	2387	0.9			νND	2120 vw	2078	2.0	2078	2.0	$\nu_{s}CD_2$
1640 vs	1634	0.4	1644	0.2	νC=O	1640 vs	1628	0.7	1640	0.0	νC=O
1528 w	1536	0.5			Amide II	1528 w	1536	0.5			Amide II
1479 sh			1475	0.3	δNH	1474 sh			1472	0.1	δNH
1465 m	1469	0.2	1471	0.4	$\delta_{as}CH_3$	1462 m	1466	0.3	1467	0.3	$\delta_{as}CH_3$
1418 s	1424	0.4	1425	0.5	βCH_2	1409 s			1420	0.7	νCN
1418 s			1417	0.0	νCN	1377 vw	1388	0.8	1387	0.8	$\delta_{s}CH_3$
1382 w	1388	0.4	1388	0.4	$\delta_{s}CH_3$	1346 sh	1334	0.9			Amide III
	1339				Amide III	1166 w			1147	1.6	$\rho CH_3+\omega CD_2$
1318 m			1289	2.2	ωCH_2	1155 w	1138	1.5			$\rho CH_3+\omega CD_2$
1295 m	1281	1.0			ωCH_2	1096 vw	1109	1.2	1112	1.4	$\nu C_\alpha C_\beta$
1078 s	1086	0.8	1086	0.8	$\nu C_\alpha C_\beta+\rho CH_3$	1036 sh	1048	1.2			ρNHD
1045 sh	1048	0.3			ρNHD	1016 s	998	1.8	1000	1.6	βCD_2
1003 m	1010	0.7	1018	1.5	$\nu C_\alpha C_\beta+\rho CH_3$	956 s			954	0.2	ρNHD
948 sh			955	0.7	ρNHD	845 w	860	1.7	860	1.7	ωCD_2
818 sh			839	2.5	νCC_α				827		νCC_α
767 vw	799	4.2			νCC_α		785				νCC_α
			616		δC=O				604		δC=O
565 w	597	5.6			δC=O		587				δC=O
455 sh	452	0.6	441	3.2	δCCN	430 sh	444	3.2	433	0.6	δCCN
285 w	274	4.0	273	4.3	δCCC	281 w	273	3.0	272	3.3	δCCC
(b) Out-of-plane vibrations (a″)											
2980 m	2967	0.4	2967	0.4	$\nu_{as}CH_3$	2970 m	2966	0.1	2966	0.1	$\nu_{as}CH_3$
2920 vw	2900	0.7	2900	0.7	$\nu_{as}CH_2$	2180 vw	2143	1.7	2143	1.7	$\nu_{as}CD_2$
1465 m	1465	0.0	1465	0.0	$\delta_{as}CH_3$	1462 m	1464	0.2	1464	0.2	$\delta_{as}CH_3$
1265 vw	1267	0.1	1267	0.1	tCH_2	1070 w	1091	2.0	1091	2.0	ρCH_3
1066 sh	1083	1.6	1083	1.6	$\rho CH_3+\rho CH_2$		911		911		tCD_2
818 sh	805	1.6	802	1.9	$\rho CH_2+\rho CH_3$				772		τNHD+ωNHD
767 vw			773	0.0	τNHD+ωNHD		735				τNHD+ωNHD
721 vw	721	0.0			τNHD+ωNHD	718 vw			703	2.1	ρCD_2+tCD_2
660 w	636	3.6			πC=O+ωNHD	690 vw	692	0.2			ρCD_2+tCD_2
			599		πC=O	615 vw	597	3.0			$\omega NHD+\rho CD_2$
553 w	521	5.8	519	6.1	ωNHD+πC=O	535 sh			539	0.7	ωNHD+τNHD $+\rho CD_2$
171 w	192	12.4	192	12.7	τCH_3	485 m	486	0.1	507	4.4	πC=O+ρCD_2 +ωNHD
70 w	69	1.4	69	1.4	τCC_α		191		191		τCH_3
							65		65		τCC_α

vibration to the 821 cm^{-1} band of $CH_3CH_2CONH_2$ is suggested from the fact that the infrared spectrum of the 50 per cent *N*-deuterated sample of propionamide shows two weak bands at 767 and 721 cm^{-1} (Fig. 8). These bands may be assigned to the NH out-of-plane deformation vibrations of the NHD compounds.[9] The initially calculated C–C_α stretching frequencies of $CH_3CH_2CONH_2$ and $CH_3CH_2COND_2$ were about 50 cm^{-1} higher than the observed values, but the assignment of these fundamentals was substantiated by the appearance of strong Raman bands at 820 and 769 cm^{-1} for $CH_3CH_2CONH_2$ and $CH_3CH_2COND_2$,

Table 6. The CH_2 and C–C_α–C_β deformation frequencies of propane and propionamide

	Propane			Propionamide		
	Obs.[a]	Calc. A[a]	Calc. B[b]	Obs.	Calc. A	Calc. B
CH_2 bend.	1449	1452	1449	1418	1457	1469
CH_2 wag.	1332	1347	1333	1296 (1318)[c]	1324 (1330)[c]	1308 (1317)[c]
CH_2 twist.	1278	1282	1275	1260	1279	1279
CH_2 rock.	748	747	729	821	827	819
CCC def.	375	383	383	292	248	251

a) Taken from Ref. 10.
b) Calculated from the force constants of Calc. V in Ref. 10.
c) The frequencies of the ND_2 compound are shown in parentheses.

Table 7. Observed and calculated frequencies of $CH_3CH_2CONH_2$ in cm^{-1}

	Obs.	Calc. A	Δ(%)[a]	Calc. B	Δ(%)[a]	P.E.D.[b] (Calc. A)	Assign.[c]
(a)	In-plane vibrations (a′)						
ν_2	3350	3366	0.5	3366	0.5	$S_7(100)$	$\nu_{as}NH_2$
ν_2	3190	3185	0.2	3185	0.2	$S_8(99)$	ν_sNH_2
ν_3	2980	2958	0.7	2955	0.8	$S_{17}(99)$	$\nu_{as}CH_3$
ν_4	2880	2891	0.4	2877	0.1	$S_{18}(82), S_{19}(16)$	ν_sCH_3
ν_5	2820	2855	1.2	2856	1.3	$S_{18}(17), S_{19}(84)$	ν_sCH_2
ν_6	1665	1662	0.2	1668	0.2	$S_1(24), S_2(53), S_4(25)$	$\nu C{=}O+\beta NH_2$
ν_7	1625	1622	0.2	1626	0.1	$S_1(38), S_2(41)$	$\nu C{=}O+\beta NH_2$
ν_8	1465	1471	0.4	1478	0.9	$S_{11}(79), S_{13}(10)$	$\delta_{as}CH_3$
ν_9	1418	1425	0.5	1421	0.2	$S_9(11), S_{15}(68)$	βCH_2
ν_{10}	1418	1418	0.0	1414	0.3	$S_3(12), S_4(32), S_5(14), S_9(14), S_{15}(26)$	$\nu CN+\beta CH_2$
ν_{11}	1382	1388	0.4	1394	0.9	$S_{12}(104)$	δ_sCH_3
ν_{12}	1296	1289	0.5	1304	0.6	$S_{14}(85)$	ωCH_2
ν_{13}	1136	1148	1.1	1147	0.9	$S_1(19), S_3(63)$	ρNH_2
ν_{14}	1068	1086	1.7	1084	1.5	$S_{10}(56), S_{13}(25), S_{16}(10)$	$\nu C_\alpha C_\beta+\rho CH_3$
ν_{15}	1004	1012	0.8	1001	0.3	$S_{10}(35), S_{13}(34)$	$\nu C_\alpha C_\beta+\rho CH_3$
ν_{16}	821	846	3.0	820	0.1	$S_4(11), S_9(39), S_{13}(18)$	νCC_α
ν_{17}	630	622	1.3	616	2.3	$S_5(59), S_{16}(16)$	$\delta C{=}O$
ν_{18}	472	460	2.5	462	2.2	$S_6(54), S_9(17), S_{10}(11), S_{16}(10)$	δCCN
ν_{19}	292	275	5.8	276	5.3	$S_5(23), S_6(25), S_{16}(54)$	δCCC
(b)	Out-of-plane vibrations (a″)						
ν_{20}	2980	2967	0.4	2963	0.6	$S_{24}(99)$	$\nu_{as}CH_3$
ν_{21}	2920	2900	0.7	2919	0.0	$S_{25}(100)$	$\nu_{as}CH_2$
ν_{22}	1465	1465	0.0	1476	0.8	$S_{21}(89)$	$\delta_{as}CH_3$
ν_{23}	1260	1267	0.6	1271	0.9	$S_{23}(83)$	tCH_2
ν_{24}	1068	1083	1.4	1082	1.3	$S_{20}(49), S_{22}(29), S_{23}(10)$	$\rho CH_3+\rho CH_2$
ν_{25}	821	807	1.7	805	2.0	$S_{20}(31), S_{22}(39), S_{27}(24)$	$\rho CH_3+\rho CH_2$
ν_{26}	821	791	3.8	792	3.7	$S_{22}(10), S_{27}(67), S_{28}(11), S_{29}(11)$	τNH_2
ν_{27}	680	699	2.8	699	2.8	$S_{27}(10), S_{29}(84)$	ωNH_2
ν_{28}	570	580	1.8	581	2.0	$S_{22}(14), S_{28}(70)$	$\pi C{=}O$
ν_{29}	175	193	10.1	193	10.1	$S_{26}(95)$	τCH_3
ν_{30}	70	70	0.0	70	0.0	$S_{30}(98)$	τCC_α

a) $\Delta(\%)=|\nu_{obs.}-\nu_{calc.}|\times 100/\nu_{obs.}$
b) Those less than 10 per cent are omitted.
c) ν: stretching; β: bending; δ: deformation; ω: wagging; ρ:rocking; t: twisting; τ: torsion; π: out-of-plane deformation.

respectively. In the infrared spectrum of $CH_3CD_2CONH_2$, a medium band assignable to the C–C_α stretching and the NH_2 torsional vibrations is observed at 803 cm^{-1}. The corresponding Raman band at 807 cm^{-1} is again very strong and is replaced by a medium band at 750 cm^{-1} on the *N*-deuteration. Besides these bands, $CH_3CD_2CONH_2$ shows a weak band at 850 cm^{-1} which hardly shifts on the *N*-deuteration and is assignable to the CD_2 wagging vibration.

The NH_2 and ND_2 wagging and the skeletal deformation frequencies are expected in the region between 700 and 250 cm^{-1}. For the infrared spectrum of $CH_3CH_2CONH_2$, we assigned previously the very strong and broad band centered near 640 cm^{-1} to the NH_2 wagging vibration, the shoulder band at 570 cm^{-1} to the C=O a'' deformation vibration and the band at 472 cm^{-1} to the C=O a' deformation vibration.[1] The asymmetrical contour of the first of these bands indicates, however, the presence of an implicit absorption with the maximum near 680 cm^{-1}. Furthermore, the 50 per cent *N*-deuterated sample of propionamide shows a weak infrared band at 660 cm^{-1}, which is not observed in the spectrum of $CH_3CH_2COND_2$ (see Fig. 8). If this band is due to a fundamental vibration of *trans* or *cis* CH_3CH_2CONHD, the NH_2 wagging frequency of $CH_3CH_2CONH_2$ should be higher than 660 cm^{-1} in order that the isotopic shifts fulfil the Rayleigh condition.[22] Accordingly we assigned the implicit absorption near 680 cm^{-1} of $CH_3CH_2CONH_2$ to the NH_2 wagging vibration. The strong absorption giving rise to the peak near 640 cm^{-1} was then attributed to the C=O a' deformation vibration by referring to the normal coordinate analysis, which led also to the revised assignment of the band at 472 cm^{-1} to the C_α–C–N deformation vibration. In the Raman spectrum of $CH_3CH_2CONH_2$, there is no noticeable band assignable to the NH_2 wagging vibration, but two weak bands arising from the C=O a' and a'' deformation vibrations are observed at 630 and 570 cm^{-1}, respectively. The shifts of these bands on the C_α- and *N*-deuterations were found to agree well with the initial calculation, and the assignments of the infrared and Raman bands of the CD_2 compounds in this region were made without much difficulty by referring to the calcu-

Table 8. Observed and calculated frequencies of $CH_3CH_2COND_2$ in cm^{-1}

	Obs.	Calc. A	Δ(%)	Calc. B	Δ(%)	P.E.D. (Calc. A)	Assign.
(a)	In-plane vibrations (a')						
ν_1	2980	2958	0.7	2955	0.8	$S_{17}(99)$	$\nu_{as}CH_3$
ν_2	2880	2891	0.4	2877	0.1	$S_{18}(82), S_{19}(16)$	ν_sCH_3
ν_3	2820	2855	1.2	2856	1.3	$S_{18}(17), S_{19}(84)$	ν_sCH_2
ν_4	2530	2498	1.3	2498	1.3	$S_7(100)$	$\nu_{as}ND_2$
ν_5	2370	2303	2.8	2303	2.8	$S_8(98)$	ν_sND_2
ν_6	1635	1626	0.5	1636	0.0	$S_1(63), S_4(24), S_6(14)$	$\nu C{=}O$
ν_7	1466	1470	0.3	1478	0.8	$S_{11}(80), S_{13}(10)$	$\delta_{as}CH_3$
ν_8	1425	1426	0.0	1420	0.4	$S_4(33), S_5(10), S_9(24), S_{15}(20)$	$\nu CN+\nu C_\alpha C_\beta+\beta CH_2$
ν_9	1418	1423	0.3	1413	0.4	$S_4(12), S_{15}(74)$	βCH_2
ν_{10}	1382	1388	0.4	1394	0.9	$S_{12}(104)$	δ_sCH_3
ν_{11}	1318	1299	1.5	1327	0.7	$S_{14}(83)$	ωCH_2
ν_{12}	1165	1182	1.5	1173	0.7	$S_2(73)$	βND_2
ν_{13}	1078	1086	0.7	1084	0.6	$S_{10}(55), S_{13}(24), S_{16}(10)$	$\nu C_\alpha C_\beta+\rho CH_3$
ν_{14}	1006	1010	0.4	1000	0.4	$S_{10}(33), S_{13}(40)$	$\nu C_\alpha C_\beta+\rho CH_3$
ν_{15}	942	946	0.4	948	0.6	$S_1(18), S_3(48), S_4(10)$	ρND_2
ν_{16}	765	795	3.9	764	0.2	$S_3(22), S_9(44), S_{13}(15)$	$\nu CC_\alpha+\rho ND_2$
ν_{17}	580	593	2.3	593	2.3	$S_5(59), S_{16}(14)$	$\delta C{=}O$
ν_{18}	443	435	1.9	436	1.5	$S_6(50), S_9(16), S_{16}(11)$	δCCN
ν_{19}	281	271	3.5	272	3.1	$S_5(21), S_6(29), S_{16}(53)$	δCCC
(b)	Out-of-plane vibrations (a'')						
ν_{20}	2980	2967	0.4	2963	0.6	$S_{24}(99)$	$\nu_{as}CH_3$
ν_{21}	2920	2900	0.7	2919	0.0	$S_{25}(100)$	$\nu_{as}CH_2$
ν_{22}	1465	1465	0.0	1476	0.8	$S_{21}(89)$	$\delta_{as}CH_3$
ν_{23}	1260	1267	0.6	1271	0.9	$S_{23}(82)$	tCH_2
ν_{24}	1078	1082	0.4	1082	0.4	$S_{20}(49), S_{22}(29), S_{23}(10)$	$\rho CH_3+\rho CH_2$
ν_{25}	808	802	0.7	801	0.9	$S_{20}(36), S_{22}(53), S_{28}(16)$	$\rho CH_3+\rho CH_2$
ν_{26}	625	636	1.7	636	1.7	$S_{22}(13), S_{27}(15), S_{28}(53), S_{29}(28)$	$\pi C{=}O+\omega ND_2$
ν_{27}	580	554	4.5	555	4.5	$S_{27}(84)$	τND_2
ν_{28}	475	505	6.3	505	6.3	$S_{28}(19), S_{29}(69)$	$\omega ND_2+\pi C{=}O$
ν_{29}	170	192	13.0	192	13.0	$S_{26}(95)$	τCH_3
ν_{30}	70	68	2.9	68	2.9	$S_{30}(97)$	τCC_α

22) D. Steele, E. R. Lippincott, and J. Xavier, *J. Chem. Phys.*, **33**, 1242 (1960).

lated frequencies. For the $C-C_\alpha-C_\beta$ deformation frequency of $CH_3CH_2CONH_2$, the initially calculated values are about 40 cm^{-1} lower than the observed frequency of the infrared band (292 cm^{-1}), but we are quite confident on the assignment of this fundamental from the previous analysis of the band progression of *n*-fatty acid amides as well as the intensity of the Raman counterpart.

In the region below 200 cm^{-1}, $CH_3CH_2CONH_2$ and its *N*- and C_α-deuterated compounds show several infrared bands assignable to the torsional vibrations about the $C-C_\alpha-C_\beta$ skeleton, but unambiguous assignments of these fundamentals are difficult since the bands due to lattice vibrations may overlap with them. According to the normal coordinate analysis, the $C_\alpha-C_\beta$ and $C-C_\alpha$ torsional vibrations of the CH_2 compounds are thought to contribute to the bands at about 170 and 70 cm^{-1}, respectively. No appreciable shifts of these bands were observed on the C_α-deuteration.

Refinement of Force Constants

There are two factors which may affect the shifts of the CH_2 group frequescies on going from propane to propionamide, *viz.*, the change in the fashion of mechanical couplings with the rest of molecules and the change in the force constants within the CH_2 group. How these two factors participate in the observed shifts may be estimated from a comparison of the experimental results with the initially calculated frequencies, since the force constants for the CH_3CH_2-group used in the initial calculation have been known to reproduce the observed frequencies of *n*-paraffins very well.[10] Table 6 shows the observed and the calculated values of the CH_2 group frequencies of propane and propionamide; the results for the $C-C_\alpha-C_\beta$ deformation frequency are also listed. From the failure of the calculation to reproduce the observed difference in the CH_2 bending frequency between propane and propionamide, it is seen that the observed shift stems from the change of the force constants related to this frequency. Contrarily, the agreement between the calculated and the observed shifts of the CH_2 rocking frequency suggests that the nature of the shift is essentially mechanical. The calculated shift of the $C-C_\alpha-C_\beta$ deformation frequency is too large and the mechanical effect on this shift should be cancelled partly by the change in appropriate force constants. For the

Table 9. Observed and calculated frequencies of $CH_3CD_2CONH_2$ in cm^{-1}

	Obs.	Calc. A	Δ(%)	Calc. B	Δ(%)	P.E.D. (Calc. A)	Assign.
(a)	In-plane vibrations (a′)						
ν_1	3350	3366	0.5	3366	0.5	$S_7(100)$	$\nu_{as}NH_2$
ν_2	3190	3185	0.2	3185	0.2	$S_8(99)$	ν_sNH_2
ν_3	2970	2958	0.4	2955	0.5	$S_{17}(100)$	$\nu_{as}CH_3$
ν_4	2870	2885	0.5	2877	0.3	$S_{18}(99)$	ν_sCH_3
ν_5	2120	2078	2.0	2092	1.3	$S_{19}(99)$	ν_sCD_2
ν_6	1665	1661	0.3	1666	0.1	$S_1(21), S_2(58), S_4(24)$	$\nu C{=}O+\beta NH_2$
ν_7	1625	1617	0.5	1617	0.5	$S_1(42), S_2(36), S_6(10)$	$\nu C{=}O+\beta NH_2$
ν_8	1462	1468	0.4	1477	1.0	$S_{11}(84)$	$\delta_{as}CH_3$
ν_9	1409	1420	0.8	1418	0.7	$S_3(16), S_4(41), S_5(17), S_9(24)$	$\nu CN+\nu CC_\alpha$
ν_{10}	1378	1387	0.7	1394	1.1	$S_{12}(106)$	δ_sCH_3
ν_{11}	1174	1165	0.8	1179	0.4	$S_3(39), S_9(15), S_{13}(20), S_{14}(15)$	$\rho NH_2+\rho CH_3$
ν_{12}	1136	1128	0.7	1133	0.3	$S_1(19), S_3(19), S_{13}(22), S_{15}(11)$	$\rho NH_2+\rho CH_3$
ν_{13}	1093	1107	1.3	1086	0.6	$S_{10}(64), S_{14}(19), S_{15}(22)$	$\nu C_\alpha C_\beta+\beta CD_2$
ν_{14}	1016	998	1.8	1005	1.1	$S_{10}(15), S_{13}(17), S_{15}(60)$	βCD_2
ν_{15}	850	861	1.2	845	0.6	$S_{10}(12), S_{13}(15), S_{14}(61)$	ωCD_2
ν_{16}	803	836	4.1	812	1.1	$S_4(11), S_9(36), S_{13}(13)$	νCC_α
ν_{17}	618	608	1.6	603	2.4	$S_5(57), S_{16}(17)$	$\delta C{=}O$
ν_{18}	442	452	2.2	453	2.5	$S_6(53), S_9(17), S_{16}(10)$	δCCN
ν_{19}	288	274	4.8	276	4.3	$S_5(23), S_6(25), S_{16}(55)$	δCCC
(b)	Out-of-plane vibrations (a″)						
ν_{20}	2970	2966	0.1	2963	0.2	$S_{24}(100)$	$\nu_{as}CH_3$
ν_{21}	2180	2143	1.7	2180	0.0	$S_{25}(102)$	$\nu_{as}CD_2$
ν_{22}	1462	1464	0.2	1475	0.9	$S_{21}(90)$	$\delta_{as}CH_3$
ν_{23}	1070	1091	2.0	1110	3.8	$S_{20}(68)$	ρCH_3
ν_{24}	918	912	0.7	887	3.4	$S_{22}(14), S_{23}(62), S_{28}(18)$	tCD_2
ν_{25}	803	795	1.1	794	1.1	$S_{27}(92)$	τNH_2
ν_{26}	710	721	1.5	722	1.6	$S_{20}(12), S_{22}(12), S_{23}(21), S_{28}(23), S_{29}(47)$	$\omega NH_2+\pi C{=}O+tCD_2+\rho CD_2$
ν_{27}	670	671	0.2	673	0.4	$S_{22}(26), S_{29}(47)$	$\omega NH_2+\rho CD_2$
ν_{28}	495	517	4.4	517	4.4	$S_{22}(42), S_{28}(50)$	$\pi C{=}O+\rho CD_2$
ν_{29}	175	191	9.3	191	9.3	$S_{26}(96)$	τCH_3
ν_{30}	70	65	7.7	65	7.7	$S_{30}(98)$	τCC_α

TABLE 10. OBSERVED AND CALCULATED FREQUENCIES OF $CH_3CD_2COND_2$ IN cm^{-1}

	Obs.	Calc. A	Δ(%)	Calc. B	Δ(%)	P.E.D. (Calc. A)	Assign.
(a)	In-plane vibrations (a')						
ν_1	2970	2958	0.4	2955	0.5	$S_{17}(100)$	$\nu_{as}CH_3$
ν_2	2870	2885	0.5	2877	0.3	$S_{18}(99)$	ν_sCH_3
ν_3	2520	2498	0.9	2498	0.9	$S_7(100)$	$\nu_{as}ND_2$
ν_4	2360	2303	2.4	2303	2.4	$S_8(98)$	ν_sND_2
ν_5	2120	2078	2.0	2092	1.3	$S_{19}(99)$	ν_sCD_2
ν_6	1630	1621	0.6	1628	0.1	$S_1(64), S_4(25), S_6(14)$	$\nu C{=}O$
ν_7	1462	1468	0.4	1477	1.0	$S_{11}(83), S_{13}(10)$	$\delta_{as}CH_3$
ν_8	1425	1425	0.0	1417	0.6	$S_2(10), S_4(43), S_5(14), S_9(26)$	$\nu CN+\nu CC_\alpha$
ν_9	1377	1387	0.8	1394	1.2	$S_{12}(106)$	δ_sCH_3
ν_{10}	1224	1205	1.5	1221	0.2	$S_2(61), S_9(15), S_{14}(11)$	βND_2
ν_{11}	1120	1129	0.8	1135	1.4	$S_2(12), S_{13}(37), S_{14}(10), S_{15}(14)$	ρCH_3
ν_{12}	1096	1107	1.0	1087	0.8	$S_{10}(61), S_{14}(20), S_{15}(21)$	$\nu C_\alpha C_\beta$
ν_{13}	1014	998	1.6	1004	1.0	$S_{10}(14), S_{13}(16), S_{15}(61)$	βCD_2
ν_{14}	956	946	1.1	948	0.8	$S_1(18), S_3(46), S_4(10)$	ρND_2
ν_{15}	845	859	1.7	843	0.2	$S_{10}(12), S_{13}(20), S_{14}(63)$	ωCD_2
ν_{16}	740	779	5.3	750	1.3	$S_3(25), S_9(41)$	$\nu CC_\alpha+\rho ND_2$
ν_{17}	577	585	1.7	585	1.7	$S_5(59), S_{16}(15)$	$\delta C{=}O$
ν_{18}	420	427	1.6	428	1.9	$S_6(48), S_9(16), S_{16}(11)$	δCCN
ν_{19}	280	270	3.5	271	3.2	$S_5(21), S_6(29), S_{16}(53)$	δCCC
(b)	Out-of-plane vibrations (a'')						
ν_{20}	2970	2966	0.1	2963	0.2	$S_{24}(100)$	$\nu_{as}CH_3$
ν_{21}	2180	2143	1.7	2180	0.0	$S_{25}(102)$	$\nu_{as}CD_2$
ν_{22}	1462	1464	0.2	1475	0.9	$S_{21}(90)$	$\delta_{as}CH_3$
ν_{23}	1070	1091	2.0	1110	3.8	$S_{20}(68)$	ρCH_3
ν_{24}	918	911	0.8	886	3.5	$S_{22}(14), S_{23}(62), S_{28}(18)$	tCD_2
ν_{25}	700	705	0.6	707	0.9	$S_{20}(20), S_{22}(30), S_{23}(30), S_{28}(33)$	$\rho CD_2+tCD_2+\pi C{=}O$
ν_{26}	575	602	4.7	601	4.5	$S_{22}(17), S_{27}(47), S_{28}(13), S_{29}(25)$	$\tau ND_2+\omega ND_2$
ν_{27}	525	535	1.9	536	2.0	$S_{22}(12), S_{27}(52), S_{29}(38)$	$\tau ND_2+\omega ND_2$
ν_{28}	470	482	2.6	483	2.7	$S_{22}(21), S_{28}(34), S_{29}(32)$	$\pi C{=}O+\omega ND_2$
ν_{29}	170	191	12.3	191	12.3	$S_{26}(96)$	τCH_3
ν_{30}	70	64	9.4	64	9.4	$S_{30}(98)$	τCC_α

CH_2 wagging frequency, Calculation B gave a much better result than Calculation A, but both the calculations failed to give sufficient shift of this frequency on the *N*-deuteration of propionamide.

Taking account of these results as well as the discrepancies in the C–C_α stretching frequencies, we tried to improve the force field of propionamide by the least squares refinement of the deformation constants related to the valence angles around the C_α atom and the C–C_α, C=O, and C-N stretching constants. In addition to the adjustment of the last two constants, the introduction of an interaction constant $f_{4,9}$ was found necessary to suppress the influence of the C–C_α stretching constant on the C=O and the C–N stretching frequencies. Another interaction constant, $f_{2,14}$ was introduced to amplify the calculated shift of the CH_2 wagging frequency on the *N*-deuteration. The other force constants were fixed to the transferred values. In the course of the refinement in Calculation A, the C–C_α stretching constant, $K(CC_\alpha)$, became smaller than the fixed C_α–C_β stretching constant, $K(C_\alpha C_\beta)$. This result is physically unacceptable, since the bond order of the C–C bond adjoining a double bond is expected to be higher than that of an isolated C–C bond. Accordingly, we fixed $K(CC_\alpha)$ to the mean value of those of acetamide (3.187)[8] and *n*-paraffins (2.229)[10], and refined the remaining constants until they converged. A similar diminishing of the C–C_α stretching constant, $K_R^I(CC_\alpha)$, occurred also in Calculation B. In this case the diagonal *F* matrix element for the C–C_α stretching coordinate is contributed not only from $K_R^I(CC_\alpha)$ but also from the Urey-Bradley type repulsion constants of the amide group, $F(C_\alpha CO)$ and $F(C_\alpha CN)$, and it is difficult to correlate the force constants to the bond order directly. Accordingly, the refinement was carried through with no restriction on $K_R^I(CC_\alpha)$.

The final sets of force constants are given in Table 4, and the results obtained from these constants are summarized together with the observed frequencies in Tables 7—10. The discrepancies between the observed and the calculated values of the C–C_α stretching frequencies in Calculation A are larger than those in Calculation B, because of fixing $K(CC_\alpha)$ to a value which perhaps is not optimum. In other respects, the results of Calculations A and B are not much different

from each other, the fits between the observed and the calculated frequencies being fairly good.

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