

## Normal coordinate analyses of molecules with the amide group

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**Abstract**—Normal coordinate analyses have been performed on molecules with the amide group using force constants transferred from N-methylacetamides and polyamides. The molecules involved were hexamethylenedipropionamide, N,N'-dihexyladipamide, N,N'-dihexylsebacamide, some N-alkylamides, and some C-deuterated derivatives of nylon 66. In some molecules the dependence of frequencies on torsion angles about C—C(=O) or N—C(=H<sub>2</sub>) was studied. Dispersion curves were obtained for nylon 6 and nylon 66. The agreement between observed and calculated frequencies is good in most cases, and a complete or nearly complete assignment of infrared frequencies has been established.

### INTRODUCTION

IN the preceding paper [1], a force field for the amide group was derived. The goal of this paper is to apply this force field to other molecules with the amide group which were not part of the previous refinement. For these we have selected N-alkylamides and diamides, whose infrared spectra were measured by KESSLER [2], two C-deuterated nylon 66 with data from HEIDEMANN [3], and the  $\gamma$  form of nylon 6. In some molecules the dependence of frequencies on torsion angles was studied, and dispersion curves for nylon 6 and 66 were obtained. The agreement between calculated and experimental frequencies is generally good, although some features in the spectra still remained unexplained.

### STRUCTURE OF MOLECULES

While the structure of nylons has been thoroughly studied and well established by X-ray diffraction, for example by BUNN *et al.* [4], KINOSHITA [5], and BRADBURY and ELLIOT [6], in the other molecules with the amide group studied here we were able to find the complete X-ray structure in the literature only for hexamethylenedipropionamide [7]. This determination shows the backbone to be nearly planar with only a very small deviation from planarity. In the other molecules we must rely on the infrared spectra for a structure determination. In view of the presence of a strong 1420 cm<sup>-1</sup> band in the spectra of N,N'-dihexyladipamide and N,N'-dihexylsebacamide, we assumed their structures to be planar or nearly planar like that of hexamethylenedipropionamide. We do not know anything about the structures of N-ethylacetamide,

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[2] H. B. KESSLER, Ph.D. Thesis, University of Michigan (1952).

[3] G. HEIDEMANN and H. ZAHN, *Makromol. Chem.* **62**, 123 (1963).

[4] D. R. HOLMES, C. W. BUNN and D. J. SMITH, *J. Polymer Sci.* **17**, 159 (1955).

[5] Y. KINOSHITA, *Makromol. Chem.* **33**, 1 (1959); **33**, 21 (1959).

[6] E. M. BRADBURY, L. BROWN, A. ELLIOTT and D. A. D. PARRY, *Polymer* **6**, 465 (1965).

[7] L. H. JENSEN, S. KRIMM, R. G. PARRISH and D. L. WOOD, *Acta Cryst.* **10**, 528 (1957).

N-propylacetamide, and N-butylacetamide. Therefore we performed frequency calculations for these molecules as a function of the torsion angle about the NH—CH<sub>2</sub> bond. This dependence turned out to be very small in the region above 700 cm<sup>-1</sup>, where the only data are available, and therefore the calculations were of little help for structure determinations. Some hints showing the probability of the presence of more than one conformation were found in the region below 1000 cm<sup>-1</sup>. In the N-alkylpropionamides, the absence of a 1420 cm<sup>-1</sup> band shows that the torsion angle about the CH<sub>2</sub>—CO bond should differ from the *trans* angle. We calculated the complete dependence of frequencies on this angle for N-methylpropionamide. For N-ethylpropionamide, N-propylpropionamide and N-butylpropionamide, we used the values (0°, 0°), (45°, -45°), (60°, -60°), (45°, 45°) and (60°, 60°) for the torsion angles about the CH<sub>2</sub>—CO and NH—CH<sub>2</sub> bonds. The first pair of angles corresponds to the planar form and the next two to a structure similar to that of the  $\gamma$ -form of nylon 6 (the actual torsion angle should lie between 45° and 60°). The last two were added in order to learn something about the interaction between the two torsions. The same values of the torsion angles, omitting the last two, were used in N-nonylcapramide and in the  $\gamma$ -form of nylon 6.

The rotations about the CO—CH<sub>2</sub> and NH—CH<sub>2</sub> bonds introduces the problem of the dependence of cross force constants between the A—B—C and B—C—D angle coordinates on the torsion angle about the B—C bond. We felt that it was not worth while assigning an independent value of this cross term to each torsional angle, and instead we used for this term an interpolation formula,  $f_{ij} = a + b \cos \phi$ . Instead of introducing the constants  $a$  and  $b$ , we introduced the values of  $f_{ij}$  for 60° and 180° (if the conformation in the planar form was *trans* or *gauche*) or for 0° and 120° (in the case of *cis* or skew conformations). For the interaction between the X—C—C angle and the CO out-of-plane bend we used the formula  $c \sin \phi$ , where  $\phi$  is the X—C—C—N dihedral angle; a similar relation was used for the interaction between the X—C—N, angle and the NH out-of-plane bend. This introduces a total of 10 new force constants five for each rotated bond. Four of these were determined from N-methylacetamide (e.g. *cis* HCC with CCO). We do not have any information about the values of the remaining six constants, and these were assigned zero values. This leads to some uncertainty in the calculated frequencies for nonplanar forms, and probably some discrepancies between calculated and experimental frequencies may be explained in such terms.

## RESULTS AND DISCUSSION

### $\gamma$ -form of nylon 6

The  $\gamma$ -form of nylon 6 may be obtained from the planar form by rotation about the CO—CH<sub>2</sub> and NH—CH<sub>2</sub> bonds by the same angle but in opposite directions [5, 6]. The value of the angle is a bit below 60°, and we chose for the calculation the values 45° and 60° in order to see how sensitive the calculated frequencies are to small changes of this angle. The polymer chain is generated from the repeating unit by the operation  $C_{2s}$ , the unit cell contains two repeating units, and the factor group of the chain is  $C_2$ . Therefore, each mode of the monomer unit is split into two infrared active modes, one of species  $A$ , polarized parallel to the chain axis, and the other of

Table 1. Experimental and calculated frequencies of  $\gamma$ -nylon 6, normal and N-deuterated, as a function of  $\text{CH}_2\text{—CO}$  and  $\text{NH—CH}_2$  torsion angles

Exp. [8, 9]	$\gamma$ -nylon 6 Calc.				Assignment
	$\phi = 45^\circ$		$\phi = 60^\circ$		
	A	B	A	B	
1643	1653	1653	1657	1657	Amide I
1567	1555	1555	1555	1555	Amide II
1463	1477	1478	1477	1477	$B_5$
	1473	1474	1473	1473	$B_4$
	1461	1459	1460	1459	$B_3$
1439	1441	1442	1439	1440	$B_2$
	1420	1420	1420	1420	$B_1$
	1382	1385	1383	1384	$W_5$
1369	1369	1374	1370	1375	$W_4$
	1365	1348	1364	1348	Amide III
	1307	1302	1308	1302	$T_3$
1300	1305	1305	1305	1304	$T_1$
	1296	1320	1296	1321	$W_3$
	1280	1279	1271	1278	$T_2$
1266	1271	1251	1280	1253	$W_2$
1235	1234	1235	1231	1235	$T_4$
1216	1204	1217	1205	1218	$W_1$
1170	1180	1176	1186	1176	$T_5$
1120	1134	1126	1136	1132	$S_1$
1078	1088	1081	1082	1078	$R_5$
	1071	1086	1067	1082	$S_2$
	1064	1064	1064	1064	$S_5$
1000	1046	1025	1046	1025	$S_4$
	1002	1013	998	1007	$S_3$
	976	961	937	963	924
914	925	969	922	971	$\text{CH}_2\text{—CO stretch}$
	838	840	830	839	$R_3$
	777	765	776	764	782
730	744	735	752	738	Amide IV
	722	725	721	724	$R_1$
	711	695	693	692	691
623	619	605	630	617	Amide VI
519	516	511	514	508	Skeletal bend and torsion
439	449	434	446	438	
	377	336	384	338	
	307	284	309	296	
	248	259	268	269	
	133	194	137	198	
	123	154	123	148	
	89	124	94	123	
	66	100	71	101	
	46	65	45	62	
	38	61	38	60	
	21	39	21	38	

Exp. [9]	N-deuterated $\gamma$ -nylon 6 Calc.				Assignment
	$\phi = 45^\circ$		$\phi = 60^\circ$		
	A	B	A	B	
1636	1639	1639	1643	1643	Amide I
1476	1488	1490	1489	1491	Amide II
	1476	1476	1475	1475	$B_5$
1467	1471	1470	1472	1469	$B_4$
	1458	1459	1456	1459	$B_3$
	1436	1440	1438	1438	$B_2$
1373	1420	1420	1420	1420	$B_1$
	1376	1376	1376	1376	$W_5$
	1368	1372	1369	1372	$W_4$

Table 1 (cont.)

Exp. [9]	N-deuterated $\gamma$ -nylon 6 (cont.)				Assignment
	Calc.		Calc.		
	$\phi = 45^\circ$		$\phi = 60^\circ$		
	A	B	A	B	
	1339	1335	1338	1336	$W_2$
1302	{ 1305	1305	1305	1305	$T_1$
	{ 1303	1302	1302	1302	$T_2$
	{ 1282	1283	1284	1282	$W_2$
1284	{ 1279	1275	1278	1274	$T_3$
1237	1233	1239	1230	1241	$T_4$
1220	1218	1216	1217	1217	$W_1$
1171	1184	1175	1193	1177	$T_5$
1133	1133	1140	1135	1143	$S_1$
1079	{ 1091	1087	1085	1083	$S_2$
	{ 1080	1081	1073	1076	$R_5$
	1064	1064	1064	1064	$S_3$
	1053	1033	1053	1032	$S_4$
1000	997	1012	995	1006	$S_5$
974	984	992	983	993	Amide III
	956	959	957	961	$R_4$
913	920	929	917	917	$\text{CH}_2$ -CO stretch
					$R_3$
831	835	836	828	837	$R_2$
771	759	767	759	769	$R_1$
	734	727	738	730	Amide IV
733	721	723	720	723	$R_1$
633	639		648		Amide VI
611		624		633	
527	522	512	524	513	Amide V
	493	498	488	496	
441	445	433	444	437	Skeletal bend and torsion
	375	336	383	338	
	306	281	309	293	
	248	257	267	266	
	133	193	136	198	
	123	153	123	147	
	88	124	93	123	
	65	100	71	101	
	46	65	45	62	
	38	60	38	60	
	21	38	21	37	

species  $B$ , polarized perpendicular to the chain axis. The calculated and experimental [8, 9] frequencies of ordinary and N-deuterated nylon 6 are listed in Table 1 together with assignments made on the basis of eigenvectors. These assignments may become ambiguous for individual modes which are interacting strongly, but in any case each frequency contains a large contribution from the mode to which it was assigned. The symbols  $B$ ,  $W$ ,  $T$ ,  $R$  and  $S$  refer to the  $\text{CH}_2$  bending, wagging, twisting, rocking and C—C stretching modes in the polymethylene chain, respectively, and each bears the sequence index of the chain progression. From this table the frequency of the amide V band is seen to be almost  $20 \text{ cm}^{-1}$  off its calculated value. This frequency is sensitive to some of the force constants which were neglected (see above), and moreover it may be influenced by interaction with the amide IV mode, whose position in polyamides is uncertain. The calculated frequency at  $1420 \text{ cm}^{-1}$  is seen to be quite insensitive to the rotation angle. This is in contrast with its absence or shift to  $1440 \text{ cm}^{-1}$  in the spectrum of the  $\gamma$ -form. Since another frequency

[8] B. SCHNEIDER, P. SCHMIDT and O. WICHTERLE, *Coll. Czech. Chem. Commun.* **27**, 1749 (1962).

[9] P. SCHMIDT and B. SCHNEIDER, *Coll. Czech. Chem. Commun.* **28**, 2685 (1963).

is calculated at  $1440\text{ cm}^{-1}$ , we cannot decide if this frequency is greatly reduced in intensity and hidden on the side of the  $1440\text{ cm}^{-1}$  band, or is simply shifted to  $1440\text{ cm}^{-1}$ . The fact that the corresponding eigenvector is also quite insensitive to the rotation angle does not seem to support the hypothesis of great reduction of intensity after rotation. All other features of the spectra except the two mentioned above are explained quite well by the calculation, and the calculated and experimental frequencies are very close.

To follow the dependence of frequencies on rotation angle more closely, we calculated the complete dependence of the frequencies of ordinary (nondeuterated) nylon 6 on the angles about the  $\text{CO}-\text{CH}_2$  and  $\text{NH}-\text{CH}_2$  bonds. We let these angles change from the standard all-*trans* values by the same amount in opposite directions in the interval from  $0^\circ$  to  $180^\circ$  in steps of  $15^\circ$ , and also in the same direction in steps of  $30^\circ$  (a change of sign in both angles does not affect the frequencies) to get some information about interaction of these two rotations. With these rotation angles, frequencies were calculated for phase differences of  $0^\circ$  and  $180^\circ$  in the polymer (note that for rotation in the same direction the  $180^\circ$  modes are not unit cell modes). The plots of the dependence of each frequency on the rotation angles are shown in Fig. 1.

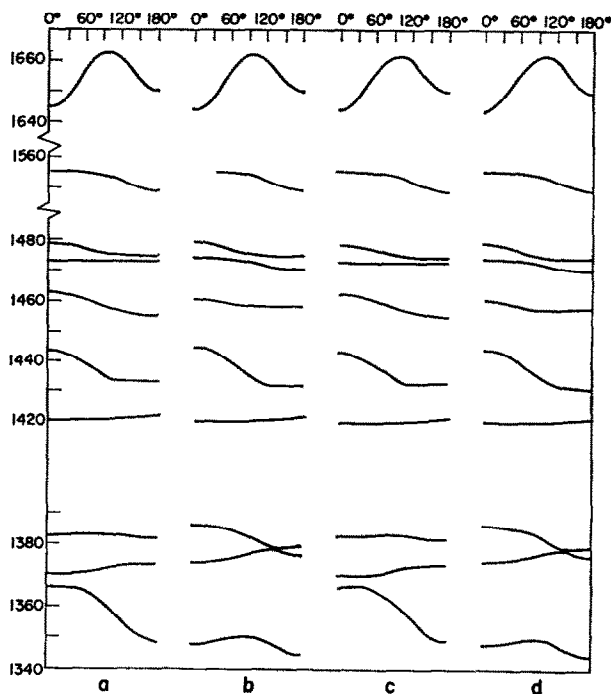


Fig. 1(a)

Fig. 1. The dependence of the frequencies of nylon 6 on the torsion angles around the  $\text{CO}-\text{CH}_2$  and  $\text{CH}_2-\text{NH}$  bonds. Both torsion angles are changed by the same value, either in the same direction, or in opposite directions. The dependence is shown for phase differences between adjacent monomer units of  $\phi = 0^\circ$  and  $180^\circ$ . (a) rotation in opposite direction,  $\phi = 0^\circ$ ; (b) rotation in opposite direction,  $\phi = 180^\circ$ ; (c) rotation in the same direction,  $\phi = 0^\circ$ ; (d) rotation in the same direction,  $\phi = 180^\circ$ .

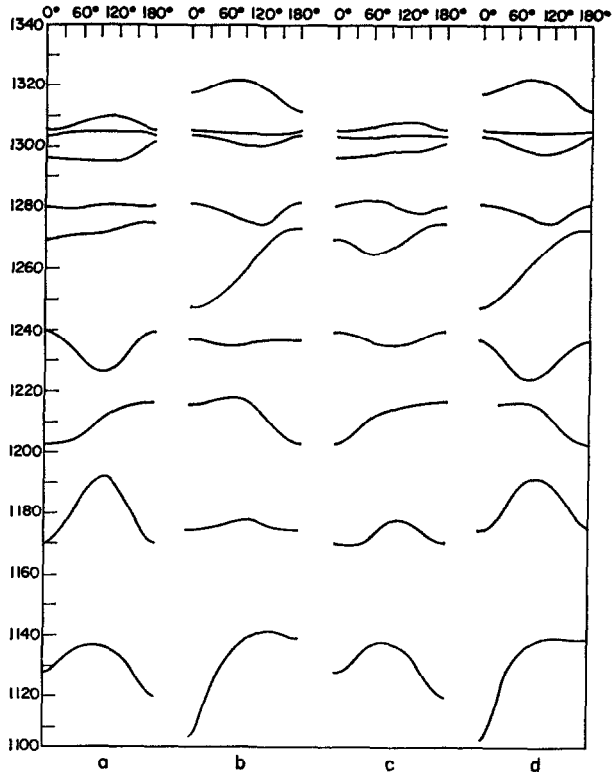


Fig. 1(b)

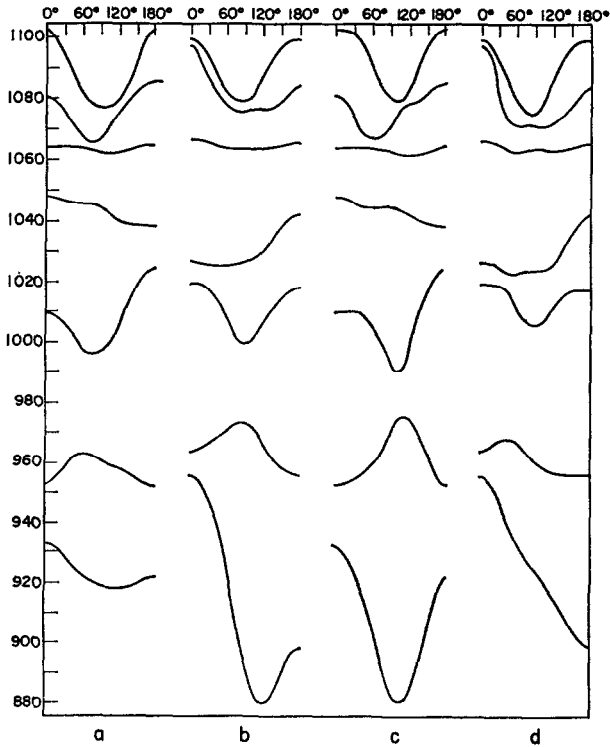


Fig. 1(c)

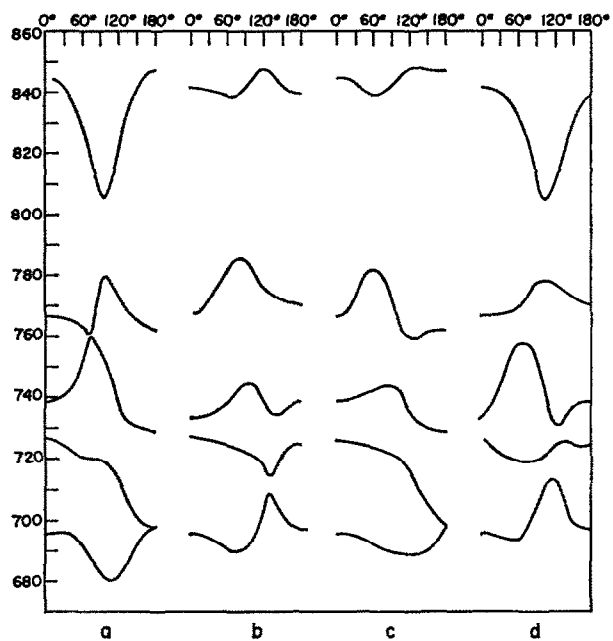


Fig. 1(d)

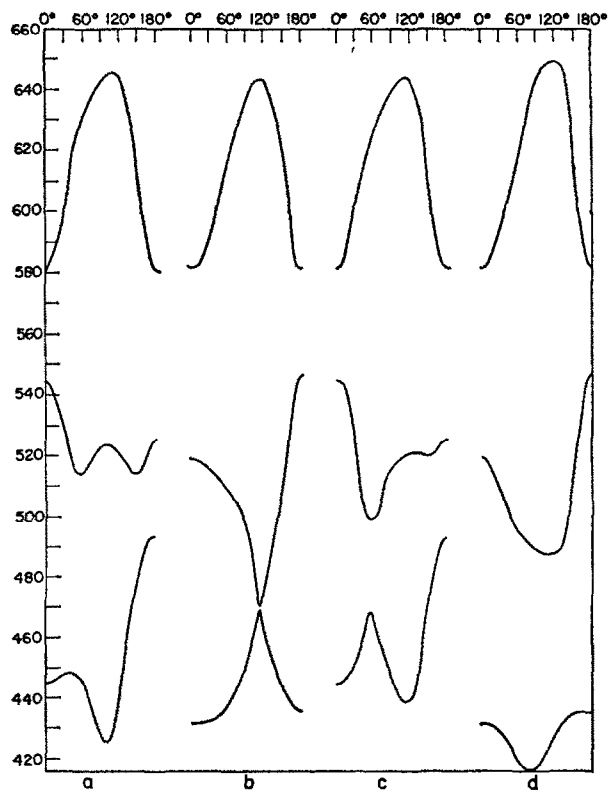


Fig. 1(e)

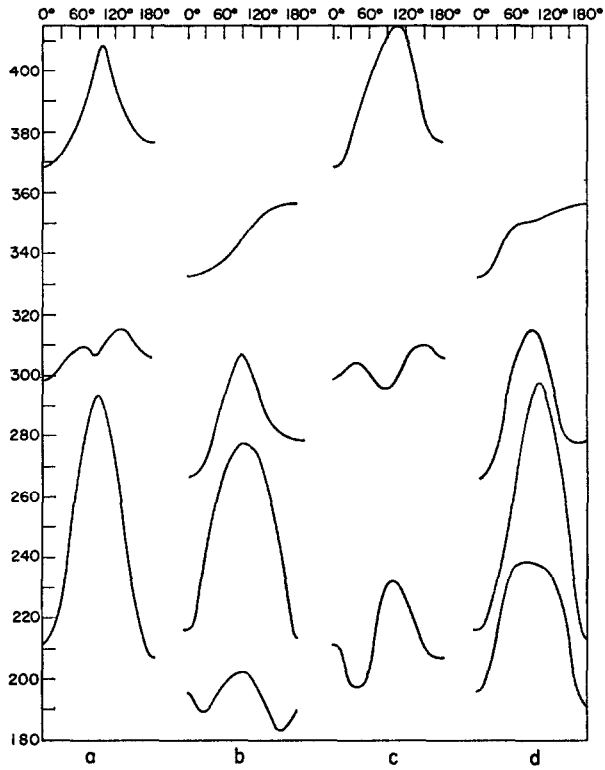


Fig. 1(f)

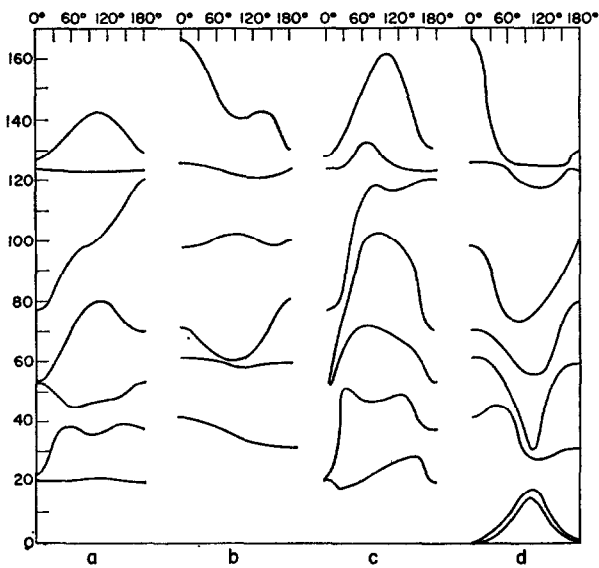


Fig. 1(g)



## Diamides

Spectra of three of the diamides, namely hexamethylenedipropionamide,  $N,N'$ -dihexyladipamide, and  $N,N'$ -dihexylsebacamide, were measured by KESSLER [2]. Our calculated infrared active frequencies for these molecules are compared with the experimental values in Table 2. For the first molecule the structure is well established by X-ray analysis [7]. For the last two, no such structure analysis is available; however, polarized spectra of long, thin single crystals have been obtained [2]. An examination of the dichroism of bands in these spectra shows that out-of-plane modes ( $A_u$ ) are predominantly perpendicular to the plane of cleavage (which is parallel to the long dimension of the crystal and perpendicular to the surface planes which define the thin dimension), while in-plane modes can be parallel or perpendicular to this plane.

Table 2. Experimental and calculated frequencies of some diamides

Hexamethylenedipropionamide				$N,N'$ -dihexyladipamide			
Exp. [2]	$B_u$	$A_u$	Assignment	Exp. [2]	$B_u$	$A_u$	Assignment
1623	1644		Amide I	1634			Amide I
1534	1556		Amide II	1610	1645		
1479	1478		$B_2$	1560			Amide II
1464	1474		$B_4$	1530	1556		
	1461	1458	$CH_2$ as bend	1477	1479		$B_2(NH)$
1443	1445		$B_2$	1474			$B_2(NH)$
1418	1427		$CH_2(CO)$ bend	1472			$B_2(CO)$
	1374		$W_2$	1471			$B_2(NH)$
	1371		$CH_2$ sym bend	1460	1458		$CH_2$ as bend
1362	1362		Amide III	1452			$B_2(NH)$
	1332		$W_2$	1442			$B_2(NH)$
	1305		$T_2$	1414			$B_2(CO)$
1272	1269		$CH_2(CO)$ twist	1385			$W_2(NH)$
1259	1260		$T_4$	1370			Amide III
1244	1261		$CH_2(CO)$ wag	1373			$CH_2$ sym bend
1215	1217		$W_1$	1366			$W_4(NH)$
1176		1178	$T_2$	1340			$W_2(NH)$
1103	1111		$S_2$				$T_1(NH)$
		1073	$R_2(CO)$	1302			$T_1(NH)$
1064	1067		$S_2$				$T_1(CO)$
1047	1058		$CH_2$ rock	1294	1296		$W_2(NH)$
1029	1038		$S_2$	1287		1285	$T_2(NH)$
996		993	$R_2$	1271		1278	$W_2(CO)$
984	990		$CH_2-CH_2$ stretch	1253		1248	$T_2(NH)$
898	897		$CH_2-CO$ stretch	1233		1231	$W_1(NH)$
811		808	$R_2(CO)$	1200		1201	$T_2(NH)$
796		797	$R_2$	1193		1200	$W_1(CO)$
735		721	$R_1$	1156		1158	$R_2(NH)$
687		697	Amide V	1138		1134	$S_1(NH)$
			Amide IV	1133		1144	$T_1(CO)$
		590	Amide VI	1086		1102	$S_2(NH)$
	536		Skeletal bend	1065		1067	$S_2(NH)$
	391			1052		1056	$S_2(NH)$
	320					1051	$S_2(NH)$
	275			1028		1031	$S_2(CO)$
		224	Amide VII			999	$S_2(NH)$
		187	$CH_2$ torsion	991		995	$R_2(NH)$
				936		944	C—CO stretch
		126		907		904	$R_2(CO)$
		84	Skeletal bend and torsion			891	$CH_2$ rock
		50				890	$R_4(NH)$
29		28			800		798
		12		749		749	Amide IV
						742	$R_2(NH)$

Table 2 (cont.)

<i>N,N'</i> -dihexyladipamide (cont.)				<i>N,N'</i> -dihexylsebacamide (cont.)						
Exp. [2]	Calc.		Assignment	Exp. [2]	Calc.		Assignment			
	$B_u$	$A_u$			$B_u$	$A_u$				
742		741	$R_1(\text{CO})$			1257	$T_5(\text{CO})$			
726 $\perp$		721	$R_1(\text{NH})$	1245 $\perp$		1248	$T_4(\text{NH})$			
683 $\perp$		695	Amide V	1239 $\parallel$	1251		$W_3(\text{CO})$			
		582	Amide VI	1225 $\perp$	1229		$W_1(\text{NH})$			
	524	}	Skeletal bend	1200 $\parallel$		1201	$T_5(\text{NH})$			
	441				1190 $\perp$	1191		$W_1(\text{CO})$		
	420				1159 $\parallel$		1158	$R_5(\text{NH})$		
	363				1135 $\perp$	1134		$S_7(\text{NH})$		
	292				1119		1120	$T_5(\text{CO})$		
	218				1093			$S_5(\text{NH})$		
		215	Amide VII	1065 $\parallel$	1104		$S_5(\text{CO})$			
		211	$\text{CH}_3$ torsion		1069		$S_6(\text{NH})$			
	166	}	Skeletal bend and torsion		1066		$S_5(\text{NH})$			
				128		1054 $\parallel$	1056		$S_5(\text{NH})$	
				117		1032 $\parallel$	1051		$S_4(\text{CO})$	
				108		1006 $\parallel$	1037		$S_4(\text{CO})$	
	73	}	Skeletal bend and torsion		1013		$S_4(\text{NH})$			
				69			1001		$R_7(\text{CO})$	
				54		992 $\perp$		997	$R_5(\text{NH})$	
				32		940 $\parallel$	947	995	C—CO stretch	
		24		890	892		$\text{CH}_3$ rock			
	15	}		854 $\perp$		890	$R_4(\text{NH})$			
				6		800 $\perp$		853	$R_5(\text{CO})$	
				755 $\perp$		798	$R_5(\text{NH})$			
				746 $\perp$		759	$R_5(\text{CO})$			
						742	$R_5(\text{NH})$			
					731		Amide IV			
				726 $\perp$		721	$R_1(\text{NH})$			
				722		720	$R_1(\text{CO})$			
				680 $\perp$		696	Amide V			
						581	Amide VI			
1631 $\parallel$	}	1644	Amide I			550	}			
1608 $\parallel$				1468	1458	$\text{CH}_3$ as bend				481
1534								1556	Amide II	
	1479	$B_5(\text{NH})$							402	
	1476	$B_6(\text{CO})$							336	
	1474	$B_4(\text{NH})$							298	
	1472	$B_8(\text{CO})$								
	1471	$B_3(\text{NH})$								
	1460									
	1456	$B_4(\text{CO})$			215	Amide VII				
1451	1452	$B_3(\text{NH})$			211	$\text{CH}_3$ torsion				
1437 $\parallel$	1442	$B_1(\text{NH})$		199						
1418 $\parallel$	1420	$B_2(\text{CO})$		189						
	1385	Amide III			139					
1374 $\perp$	1380	$W_5(\text{NH})$		126						
1370 $\perp$	1373	$\text{CH}_3$ sym bend			125					
	1370	$W_4(\text{NH})$			114					
1359 $\perp$	1358	$W_7(\text{CO})$			102	}				
1339 $\parallel$	1342	$W_5(\text{NH})$			78		Skeletal bend and torsion			
1311 $\perp$		1308	$T_2(\text{CO})$		56					
		1305	$T_1(\text{NH})$							
		1304	$T_3(\text{NH})$	53		46				
		1302	$T_4(\text{CO})$			25				
	1302	$W_5(\text{CO})$				17				
1287 $\perp$	1288	$W_2(\text{NH})$		11						
		1285	$T_3(\text{NH})$			4				

$\parallel$ : polarized parallel to cleavage plane.

$\perp$ : polarized perpendicular to cleavage plane.

While this does not fully define the structure, the overall pattern of polarizations suggests that the chain axes are essentially perpendicular to the plane of the thin crystal, with the  $\text{C}=\text{O} \cdots \text{H}-\text{N}$  bonds being oriented predominantly parallel to the long dimension of the crystal.

The observed bands are reproduced quite well by the present normal coordinate analysis. We should, however, note some problems. In hexamethylenedipropionamide the  $\text{CH}_2(\text{CO})$  wagging frequency is off by more than  $15\text{ cm}^{-1}$ , probably due to the fact that no molecule with a  $\text{CH}_3\text{CH}_2\text{CO}$ —group was used in the force field refinement. Several deviations of about  $10\text{ cm}^{-1}$  are also observed in the C—C stretching region. Similar deviations occur in the spectra of the other two molecules. For the latter, the amide V band is completely absent in the parallel polarization, but the  $\text{CH}_2$  rocking bands still possess some intensity in this polarization. This may be due to the fact that the amide group is rotated slightly with respect to the polymethylene chain so that the transition moments of the amide V and  $\text{CH}_2$  rocking modes are not exactly parallel. A serious disagreement with the predicted polarization is the parallel polarization of the  $R_s(\text{NH})$  bands at  $1156$  and  $1159\text{ cm}^{-1}$  in N,N'-dihexyladipamide and N,N'-dihexylsebacamide respectively. A possible explanation for this may be by analogy with the  $1176\text{ cm}^{-1}$   $T_5$  mode of nylon 6, which is known to be strongly enhanced in intensity by rotation to the  $\gamma$  form. If a small rotation occurs, which is probably the case, the  $1156$  and  $1159\text{ cm}^{-1}$  bands may obtain some intensity from weak interaction with in-plane modes having parallel polarization.

A study of the polarized spectra of two sequences of diamides, namely  $(\text{CH}_3(\text{CH}_2)_n\text{CONH}(\text{CH}_2)_m)_2$  and  $(\text{CH}_3(\text{CH}_2)_n\text{NHCO}(\text{CH}_2)_m)_2$  with varying  $m$  and  $n$ , would be of great value in helping to remove the remaining uncertainties in the force field.

### N-alkylamides

The infrared spectra of some N-alkylamides, namely N-methyl, N-ethyl, N-propyl and N-butyl derivatives of acetamide and propionamide, and of N-nonylcappamide, were obtained by KESSLER [2]. We calculated the dependence of vibrational frequencies on the torsion angle about the  $\text{CH}_2$ —NH bond for N-ethyl, N-propyl and N-butyl acetamide, and on the torsion angle about the  $\text{CH}_2$ —CO bond for N-methylpropionamide. The plots of these dependencies are shown in Fig. 2. For other derivatives of propionamide two torsions should be considered. We restricted ourselves to the planar form and to rotations about both bonds by the same angle of  $45^\circ$  and  $60^\circ$  in opposite directions (similar to that in the  $\gamma$  form of nylon 6) and in the same direction. In the N-nonylcappamide we omitted the rotation in the same direction. The experimental frequencies and those calculated for the planar form and for torsion angles of  $45^\circ$  and  $60^\circ$  are listed in Table 3. An examination of this table shows that most of the infrared bands are well understood on the basis of the normal coordinate treatment. The difficulty with the  $\text{CH}_2(\text{CO})$  bending mode met in the  $\gamma$  form of nylon 6 still persists in the propionamide and capramide derivatives, and the same is true of the amide V band in N-nonylcappamide. The main difficulty is in assigning the  $1116$  and  $1119\text{ cm}^{-1}$  bands in N-ethylacetamide and N-ethylpropionamide respectively. Due to this fact, our confidence in the calculated frequencies of the propyl and butyl derivatives in the  $1100\text{ cm}^{-1}$  region should also be lower. The cause for this may be the neglecting of the six force constants in the rotated isomers (see above), or the uncertainty in the force field due to ill-conditioning. In the region below  $1000\text{ cm}^{-1}$  some hints of the possible existence of more than one conformer may be found in the presence of additional observed bands. In the liquid propyl

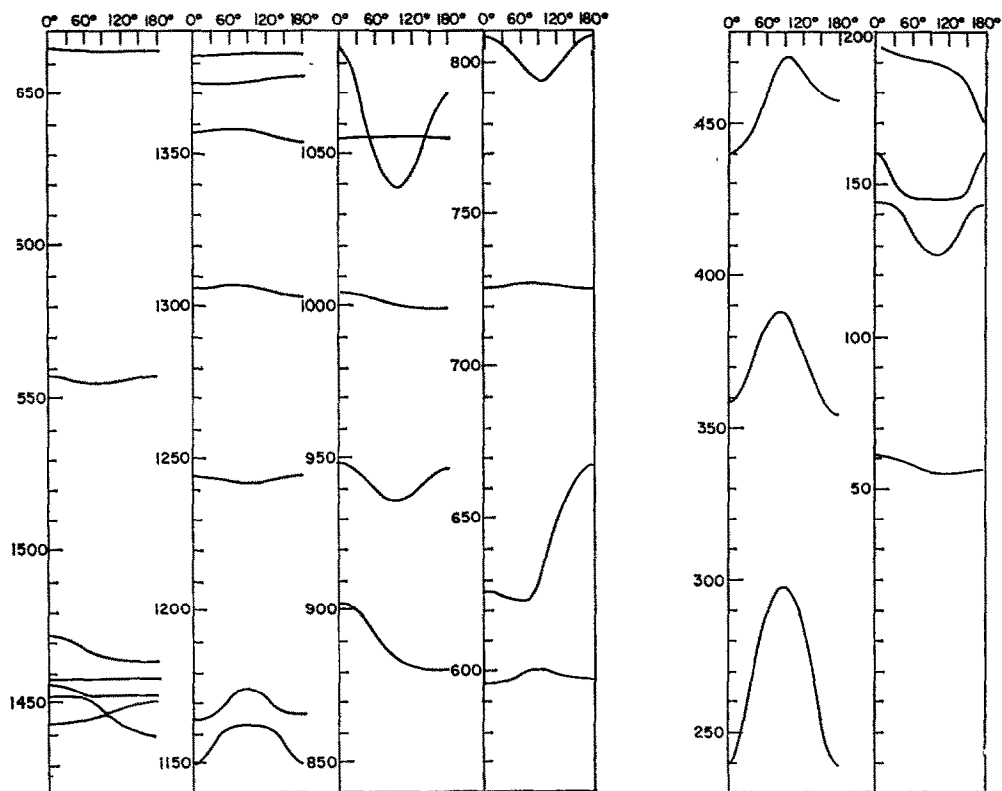


Fig. 2(a)

Fig. 2. The dependence of the frequencies on the torsion angle for N-alkylamides. The dependence on the angle around the  $\text{NH}-\text{CH}_2$  bond is shown in cases (a)–(c) and on the angle around the  $\text{CO}-\text{CH}_2$  bond in case (d). (a) N-ethylacetamide; (b) N-propylacetamide; (c) N-butylacetamide; (d) N-methylpropionamide.

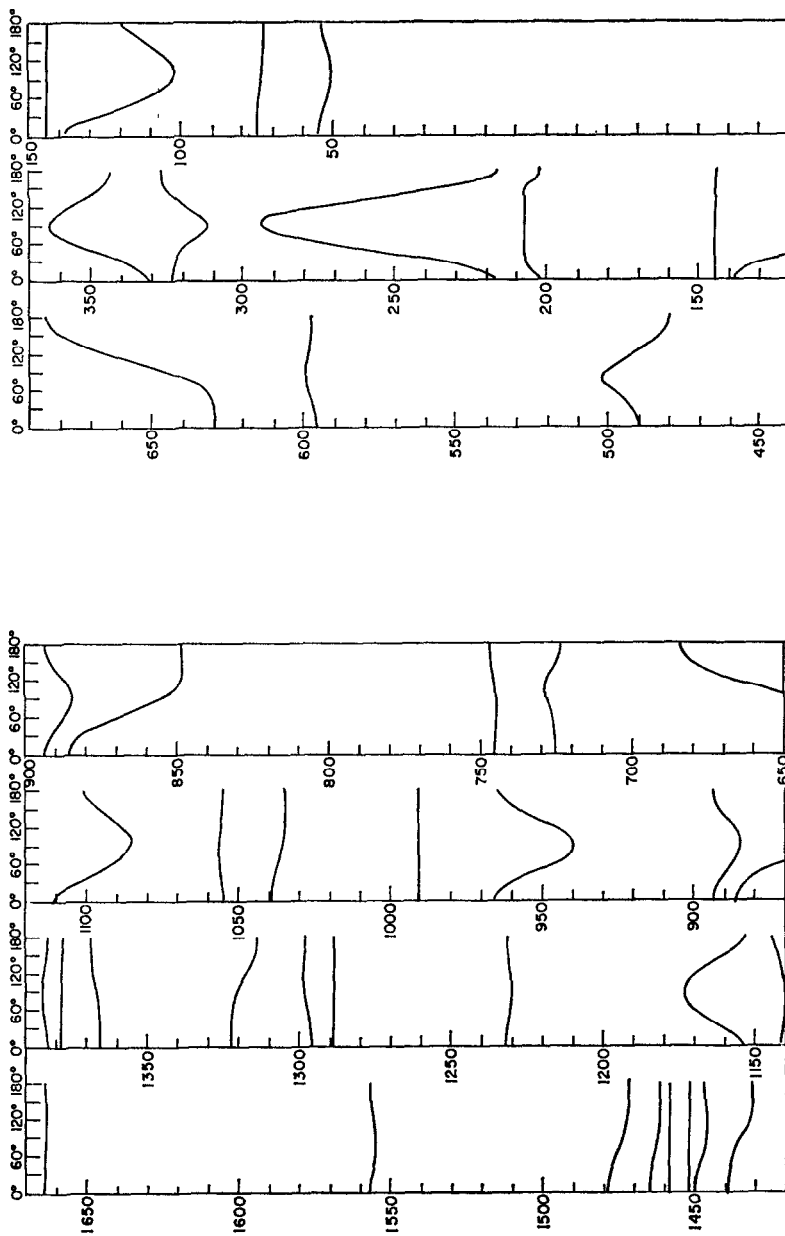


Fig. 2(b)

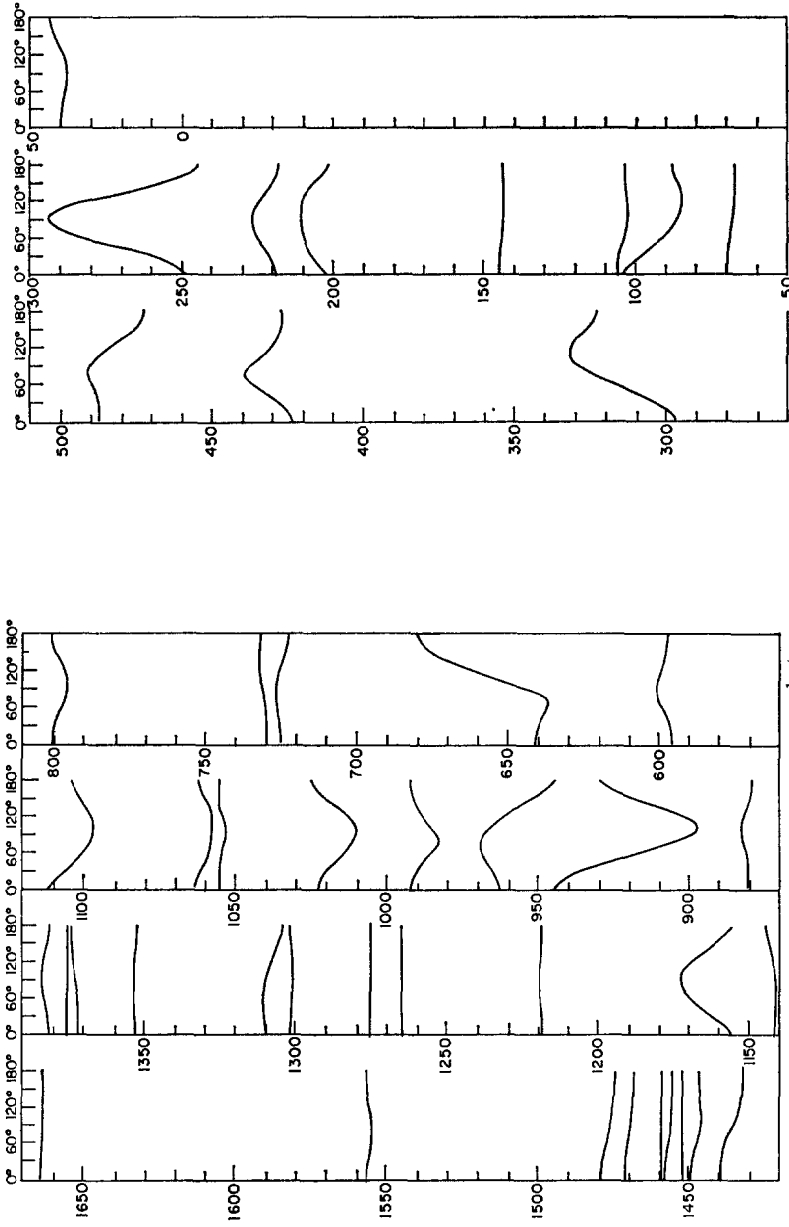


Fig. 2(c)

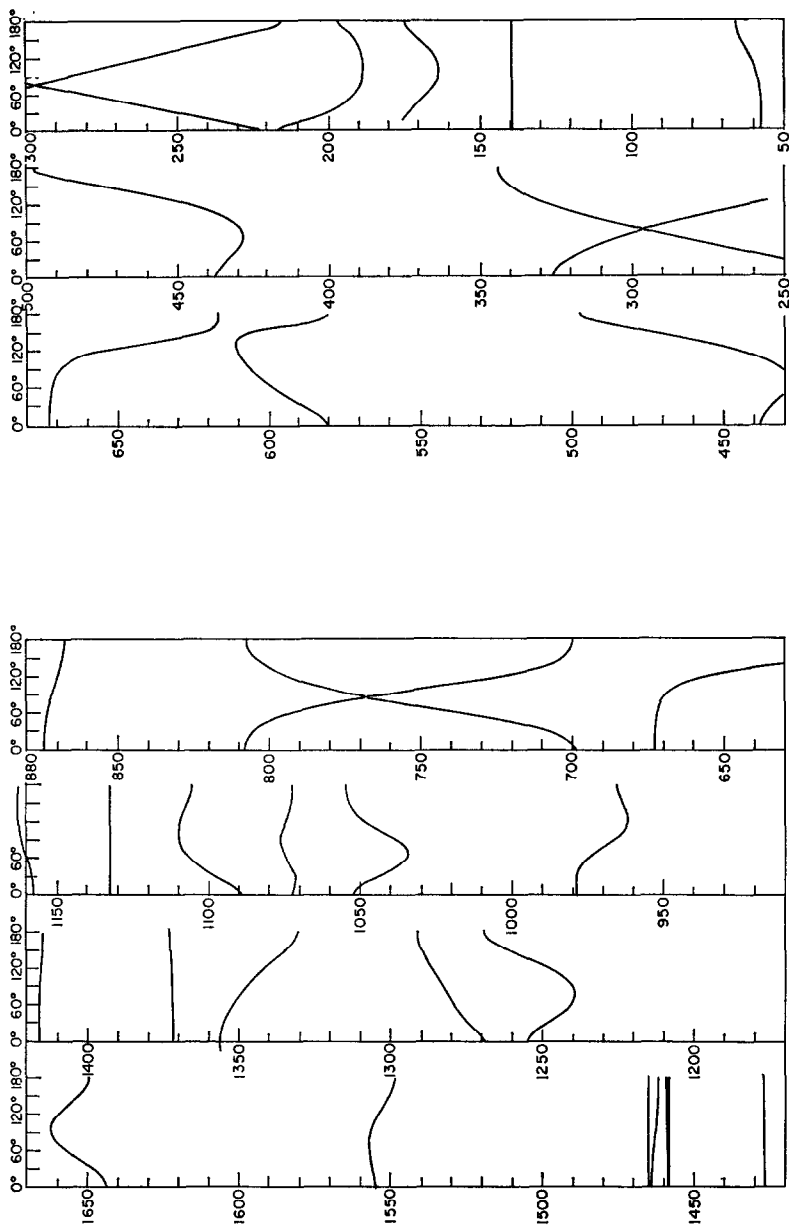


Fig. 2(d)

Table 3. Experimental and calculated frequencies of some N-alkylamides

N-ethylacetamide					
Exp. [2]	Calc.				Assignment
	$A'$ $\phi = 0^\circ$	$A''$	$\phi = 45^\circ$	$\phi = 60^\circ$	
1653	1664		1664	1663	Amide I
1555	1557		1555	1555	Amide II
1480	1472		1469	1467	CH <sub>3</sub> bend
1460	1456	1458	1458	1458	CH <sub>3</sub> (—CH <sub>3</sub> ) as bend op*
			1454	1453	CH <sub>3</sub> (—CH <sub>3</sub> ) as bend ip*
1439	1443	1452	1452	1452	CH <sub>3</sub> (—CO) as bend op
			1444	1444	CH <sub>3</sub> (—CO) as bend ip
1368	1382		1382	1383	CH <sub>3</sub> (—CO) sym bend
		1373	1373	1373	CH <sub>3</sub> (—CH <sub>3</sub> ) sym bend
1351	1357		1357	1358	CH <sub>3</sub> wag
1292	1305		1306	1306	Amide III
1151	1164	1244	1243	1242	CH <sub>3</sub> twist
			1159	1161	N—CH <sub>2</sub> stretch
1116		1149	1168	1171	R <sub>2</sub>
1073	1085		1061	1050	CH <sub>3</sub> —CH <sub>2</sub> stretch
1041		1055	1055	1056	CH <sub>3</sub> (—CO) rock op
1002	1004		1003	1002	CH <sub>3</sub> (—CO) rock ip
947					
935	948		942	939	CH <sub>3</sub> —CO stretch
892	902		896	892	CH <sub>3</sub> (—CH <sub>3</sub> ) rock ip
800		808	803	799	R <sub>1</sub>
775					
720		725	726	727	Amide V
620	626		623	622	Amide IV
		596	597	599	Amide VI
475	440		451	459	Skeletal bend
427					
	359		374	382	
		240	192	192	CH <sub>3</sub> —CH <sub>2</sub> torsion
	195		274	287	Skeletal bend
		161	140	134	Amide VII
		144	147	145	CH <sub>3</sub> —CO torsion
		61	59	58	N—CH <sub>2</sub> torsion

N-propylacetamide					
Exp. [2]	Calc.				Assignment
	$A'$ $\phi = 0^\circ$	$A''$	$\phi = 60^\circ$		
1656	1664			1663	Amide I
1555	1557			1555	Amide II
	1479			1475	B <sub>2</sub>
1460	1465	1458		1463	CH <sub>3</sub> (—CH <sub>3</sub> ) as bend ip
			1452	1458	1458
1437	1450			1452	CH <sub>3</sub> (—CO) as bend op
		1439		1447	B <sub>1</sub>
1366	1383			1437	CH <sub>3</sub> (—CO) as bend ip
		1378		1384	CH <sub>3</sub> (—CO) sym bend
	1366			1379	CH <sub>3</sub> (—CH <sub>3</sub> ) sym bend
	1322			1366	W <sub>2</sub>
	1295			1322	W <sub>1</sub>
1289				1297	Amide III
1250		1289		1289	T <sub>1</sub>
		1232		1231	T <sub>2</sub>
		1153		1170	R <sub>2</sub>
1148	1141			1140	N—CH <sub>2</sub> stretch
1111	1111				
1096				1091	CH <sub>3</sub> —CH <sub>2</sub> stretch
1080					
1038		1055		1056	CH <sub>3</sub> (—CO) rock op



Table 3 (cont.)

N-propylacetamide (cont.)				
Calc.				
Exp. [2]	$A'$ $\phi = 0^\circ$	$A''$	$\phi = 60^\circ$	Assignment
1024	1039		1037	$\text{CH}_2\text{—CH}_2$ stretch
980	991		991	$\text{CH}_2\text{(—CO)}$ rock ip
947	965		945	$\text{CH}_2\text{(—CH}_2\text{)}$ rock ip
			872	$R_2$
889	885	894	887	$\text{CH}_2\text{—CO}$ stretch
870				
847				
775				
763				
743		745	745	$R_1$
727		725	727	Amide V
	629		631	Amide IV
		596	598	Amide VI
	489		498	Skeletal bend
	331		355	
	323		318	
		217	207	$\text{CH}_2\text{—CH}_2$ torsion
		202	111	Amide VII
		144	144	$\text{CH}_2\text{—CO}$ torsion
	138		271	Skeletal bend
		75	74	$\text{CH}_2\text{—CH}_2$ torsion
		55	52	$\text{N—CH}_2$ torsion

N-butylacetamide				
Calc.				
Exp. [2]	$A'$ $\phi = 0^\circ$	$A''$	$\phi = 60^\circ$	Assignment
1653	1664		1663	Amide I
1555	1557		1555	Amide II
	1479		1477	$B_2$
	1471		1470	$B_2$
1464	1458	1458	1458	$\text{CH}_2\text{(—CH}_2\text{)}$ as bend op
	1458		1456	$\text{CH}_2\text{(—CH}_2\text{)}$ as bend ip
	1450	1452	1452	$\text{CH}_2\text{(—CO)}$ as bend op
1439	1439		1447	$B_1$
	1439		1438	$\text{CH}_2\text{(—CO)}$ as bend ip
1366	1381		1383	$\text{CH}_2\text{(—CO)}$ sym bend
	1376		1376	$\text{CH}_2\text{(—CH}_2\text{)}$ sym bend
	1371		1372	$W_2$
	1353		1354	$W_2$
1292	1309		1310	Amide III
		1302	1301	$T_1$
		1275	1275	$T_2$
1259	1264		1265	$W_1$
1225		1218	1219	$T_1$
1148		1156	1170	$R_4$
1133	1142		1141	$S_1$
1117	1112		1099	$S_2$
1096				
	1063		1059	$S_2$
1038		1055	1054	$\text{CH}_2\text{(—CO)}$ rock op
			1014	$S_2$
998	1022		985	$\text{CH}_2\text{(—CO)}$ rock ip
984	962		916	$\text{CH}_2\text{—CO}$ stretch
961		944	968	$R_2$

Table 3 (cont.)

N-butylacetamide (cont.)					
Exp. [2]	Calc. $\phi = 0^\circ$		$\phi = 60^\circ$		Assignment
	A'	A''			
886	880		881		CH <sub>3</sub> (—CH <sub>2</sub> ) rock ip
		800	797		R <sub>2</sub>
736		729	730		R <sub>1</sub>
725		725	726		Amide V
620	641		637		Amide IV
		596	599		Amide VII
515					
500	487		489		Skeletal bend
450	423		436		
	297		318		
	249		282		
		218	210		CH <sub>3</sub> —CH <sub>2</sub> torsion
		202	91		Amide VII
		145	144		CH <sub>3</sub> —CO torsion
		106	104		CH <sub>2</sub> —CH <sub>2</sub> torsion
	104		225		Skeletal bend
		70	69		CH <sub>3</sub> —CH <sub>2</sub> torsion
		40	38		CH <sub>2</sub> —N torsion

N-methylpropionamide					
Exp. [2]	Calc. $\phi = 0^\circ$		$\phi = 45^\circ$	$\phi = 60^\circ$	Assignment
	A'	A''			
1653	1644		1652	1657	Amide I
1560	1555		1557	1557	Amide II
		1465	1465	1465	CH <sub>3</sub> (—NH) as bend op
1464	1464		1464	1463	CH <sub>3</sub> (—NH) as bend ip
		1458	1458	1458	CH <sub>3</sub> (—CH <sub>2</sub> ) as bend op
	1458		1458	1459	CH <sub>3</sub> (—CH <sub>2</sub> ) as bend ip
	1427		1427	1427	CH <sub>2</sub> bend
1410	1416		1416	1416	CH <sub>3</sub> (—NH) sym bend
1368	1371		1372	1372	CH <sub>3</sub> (—CH <sub>2</sub> ) sym bend
	1356		1354	1352	Amide III
1272		1269	1277	1279	CH <sub>2</sub> twist
1236	1255		1243	1240	CH <sub>2</sub> wag
1160	1158		1159	1160	CH <sub>3</sub> (—NH) rock ip
1109		1133	1133	1133	CH <sub>3</sub> (—NH) rock op
	1089		1103	1107	CH <sub>2</sub> —NH stretch
1088		1072	1073	1074	R <sub>2</sub>
1045	1052		1038	1034	CH <sub>3</sub> (—CH <sub>2</sub> ) rock ip
971	979		977	975	CH <sub>3</sub> —CH <sub>2</sub> stretch
867	874		874	873	CH <sub>2</sub> —CO stretch
805		808	800	792	R <sub>1</sub>
699		699	722	672	Amide V
	673		672	738	Amide IV
		581	594	599	Amide VI
	438		431	429	Skeletal bend
	326		315	307	
	223		266	281	
		217	194	191	
		177	171	168	Amide VII
		139	139	139	CH <sub>3</sub> —NH torsion
		58	58	58	CH <sub>2</sub> —CO torsion

Table 3 (cont.)

N-ethylpropionamide							
Calc.							
Exp. [2]	$\phi = 0^\circ$		Opposite direction		Same direction		Assignment
	$A'$	$A''$	$\phi = 45^\circ$	$60^\circ$	$\phi = 45^\circ$	$60^\circ$	
1650	1644		1653	1657	1653	1657	Amide I
1550	1556		1555	1555	1555	1557	Amide II
1462	1472	1458	1469	1467	1469	1467	$\text{CH}_2(\text{NH})$ bend
	1460		1460	1460	1460	$\text{CH}_2(\text{CH}_2\text{CO})$ as bend ip	
			1458	1458	1458	1458	$\text{CH}_2(\text{CH}_2\text{CO})$ as bend op
			1458	1458	1458	1458	$\text{CH}_2(\text{CH}_2\text{NH})$ as bend op
1447	1454		1453	1451	1453	1451	$\text{CH}_2(\text{CH}_2\text{NH})$ as bend ip
	1427		1426	1426	1426	1426	$\text{CH}_2(\text{CO})$ bend
1372	1374		1373	1373	1373	1373	$\text{CH}_2(\text{CH}_2\text{NH})$ sym bend
	1371		1372	1372	1372	1372	$\text{CH}_2(\text{CH}_2\text{CO})$ sym bend
1346	1369		1369	1368	1370	1369	Amide III
	1345		1346	1347	1346	1346	$\text{CH}_2(\text{NH})$ wag
1272	1260	1269	1248	1247	1249	1247	$\text{CH}_2(\text{CO})$ twist
			1280	1282	1279	1281	$\text{CH}_2(\text{CO})$ wag
1236		1244	1239	1237	1240	1237	$\text{CH}_2(\text{NH})$ twist
1152	1152	1149	1149	1153	1152	1156	N— $\text{CH}_2$ stretch
1119			1168	1172	1168	1171	$R_2(\text{NH})$
1080	1081		1046	1041	1063	1054	$\text{CH}_2$ — $\text{CH}_2(\text{NH})$ stretch
1070		1072	1071	1058	1047	1041	$R_2(\text{CO})$
1053	1060		1067	1072	1071	1072	$\text{CH}_2(\text{CH}_2\text{CO})$ rock ip
1001	1001		1000	999	1001	1000	$\text{CH}_2$ — $\text{CH}_2(\text{CO})$ stretch
902	908		904	903	903	901	$\text{CH}_2(\text{CH}_2\text{NH})$ rock ip
	903		900	896	899	896	$\text{CH}_2$ —CO stretch
801		806	806	803	806	803	$R_1(\text{NH})$
775		810	793	788	789	782	$R_1(\text{CO})$
695	682	698	701	702	702	702	Amide V
			708	723	721	737	Amide IV
		580	609	606	603	603	Amide VI
	435		447	456	439	449	Skeletal bend
	355		373	384	369	378	
	279		280	290	315	312	
		243	179	199	178	181	
		201	200	181	207	202	$\text{CH}_2$ — $\text{CH}_2(\text{NH})$ torsion
	161		273	275	238	260	$\text{CH}_2$ — $\text{CH}_2(\text{CO})$ torsion
		154	118	110	128	116	Skeletal bend
		73	71	69	69	67	Amide VII
		44	44	44	44	46	N— $\text{CH}_2$ torsion
							$\text{CH}_2$ —CO torsion

N-propylpropionamide								
Calc.								
Exp. [2]	$\phi = 0^\circ$		Opposite direction		Same direction		Assignment	
	$A'$	$A''$	$\phi = 45^\circ$	$60^\circ$	$\phi = 45^\circ$	$60^\circ$		
1653	1644		1653	1657	1653	1657	Amide I	
1555	1556		1555	1555	1555	1555	Amide II	
	1478		1476	1475	1476	1475	$B_2$	
1464	1465	1458	1464	1463	1464	1463	$\text{CH}_2(\text{CH}_2\text{CH}_2)$ as bend ip	
	1460		1460	1460	1460	$\text{CH}_2(\text{CH}_2\text{CO})$ as bend ip		
			1458	1458	1458	1458	1458	$\text{CH}_2(\text{CH}_2\text{CH}_2)$ as bend op
			1458	1458	1458	1458	1458	$\text{CH}_2(\text{CH}_2\text{CO})$ as bend op
1439	1443		1441	1439	1441	1439	$B_1$	
	1427		1426	1426	1426	1426	$\text{CH}_2(\text{CO})$ bend	
1376	1381		1381	1382	1381	1382	$W_1$	
	1371		1372	1372	1372	1372	$\text{CH}_2(\text{CH}_2\text{CO})$ sym bend	
1344	1368		1369	1369	1369	1369	$\text{CH}_2(\text{CH}_2\text{CH}_2)$ sym bend	
	1358		1357	1356	1357	1356	Amide III	

Table 3 (cont.)

Exp. [2]	N-propylpropionamide (cont.)						Assignment
	Calc.						
	$\phi = 0^\circ$		Opposite direction		Same direction		
$A'$	$A''$	$\phi = 45^\circ$	$60^\circ$	$\phi = 45^\circ$	$60^\circ$		
	1310		1312 1312		1311 1312	$W_1$	
1280		1289	1289 1290		1289 1290	$T_1$	
1271		1269	1245 1242		1245 1242	$CH_3(CO)$ twist	
1250	1257		1277 1279		1277 1279	$CH_3(CO)$ wag	
1236		1232	1229 1228		1230 1229	$T_3$	
1152		1153	1165 1169		1166 1169	$R_2(NH)$	
1116	1132		1132 1135		1134 1137	$S_2$	
1083	1104		1098 1092		1096 1092	$S_3$	
		1072	1055 1050		1053 1048	$R_3(CO)$	
1062	1063		1070 1072		1070 1071	$CH_3(CH_2CO)$ rock ip	
1027	1033		1029 1028		1030 1029	$S_4$	
1015							
972	995		991 988		991 988	$CH_3-CH_2(CO)$ stretch	
931	945		936 887		936 886	$CH_3(CH_2CH_2)$ rock ip	
925		894	890 932		889 932	$R_2(NH)$	
885			864 861		863 859	$CH_3-CO$ stretch	
867	868						
840		808	795 790		792 785	$R_1(CO)$	
802							
776		745	746 748		745 746	$R_1(NH)$	
744		697	707 702		701 702	Amide V	
700			701 722		718 734	Amide IV	
	677		611 610		611 616	Amide VI	
		580	500 501		490 488	Skeletal bend	
	498		354 366		341 352		
	341		314 314		317 319		
	308		267 277		307 309		
	257		95 87		113 101		
		225	208 208		203 207	Amide VII	
		209	188 189		194 191	$CH_3-CH_2(CH_2)$ torsion	
		184	253 261		219 237	$CH_3-CH_2(CO)$ torsion	
	116		73 73		72 71	Skeletal bend	
		74	39 39		40 41	$CH_3-CH_2$ torsion	
		71	68 67		63 61	$NH-CH_2$ torsion	
		38				$CH_3-CO$ torsion	

Exp. [2]	N-butylpropionamide						Assignment
	Calc.						
	$\phi = 0^\circ$		Opposite direction		Same direction		
$A'$	$A''$	$\phi = 45^\circ$	$60^\circ$	$\phi = 45^\circ$	$60^\circ$		
1647	1644		1653 1657		1653 1657	Amide I	
1548	1556		1555 1555		1555 1555	Amide II	
	1479		1477 1477		1477 1477	$B_3$	
	1471		1470 1470		1470 1470	$B_2$	
1458	1462		1461 1461		1461 1461	$CH_3(CH_2CO)$ as bend ip	
		1458	1458 1458		1458 1458	$CH_3(CH_2CH_2)$ as bend op	
		1458	1458 1458		1458 1458	$CH_3(CH_2CO)$ as bend op	
	1456		1456 1456		1456 1456	$CH_3(CH_2CH_2)$ as bend ip	
1435	1444		1442 1440		1442 1440	$B_1$	
	1427		1426 1426		1426 1426	$CH_2(CO)$ bend	

Table 3 (cont.)

Exp. [2]	N-butylpropionamide (cont.)						Assignment	
	$\phi = 0^\circ$		Calc.					
	A'	A''	Opposite direction		Same direction			
			$\phi = 45^\circ$	$60^\circ$	$\phi = 45^\circ$	$60^\circ$		
1366	{	1376		1376	1376	1376	1376	CH <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> ) sym bend
		1374		1374	1375	1375	1375	W <sub>2</sub>
		1371		1372	1372	1372	1372	CH <sub>2</sub> (CH <sub>2</sub> CO) sym bend
		1364		1363	1362	1363	1362	Amide III
		1346		1347	1347	1347	1347	W <sub>3</sub>
1265 } 1235 }	{		1302	1302	1302	1302	1302	T <sub>1</sub>
		1275		1285	1265	1266	1266	W <sub>1</sub>
			1275	1274	1274	1275	1275	T <sub>2</sub>
			1269	1242	1240	1242	1240	CH <sub>2</sub> (CO) twist
		1250		1284	1286	1283	1285	CH <sub>2</sub> (CO) wag
1148		1218	1217	1217	1218	1217	T <sub>3</sub>	
1127	1134		1166	1169	1166	1169	R <sub>4</sub> (NH)	
1114			1134	1137	1136	1139	S <sub>1</sub>	
1100	1103		1103	1101	1101	1100	S <sub>2</sub>	
1063	{		1072	1047	1042	1046	1041	R <sub>2</sub> (CO)
		1066		1061	1059	1061	1059	S <sub>4</sub>
		1057		1070	1072	1070	1071	CH <sub>2</sub> (CH <sub>2</sub> CO) rock ip
1046								
1033								
1000	1019		1011	1009	1012	1011	S <sub>3</sub>	
		1002		998	993	998	991	CH <sub>2</sub> -CH <sub>2</sub> (CO) stretch
970								
948		944	951	953	949	951	R <sub>2</sub> (NH)	
943								
901	926		874	873	873	873	CH <sub>2</sub> -CO stretch	
877	874		913	906	913	906	CH <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> ) rock ip	
803	{		808	793	789	790	784	R <sub>1</sub> (CO)
			800	801	799	801	799	R <sub>2</sub> (NH)
740								
735		729	730	732	730	728	R <sub>1</sub> (NH)	
701		697	701	702	702	703	Amide V	
	684		709	722	719	737	Amide IV	
			580	616	616	614	617	Amide VI
	500		492	489	485	479		
	423		432	436	431	438		
	297		312	329	313	312		
	278		289	289	296	306	Skeletal bend	
	216		226	206	207	196	200	Amide VII
				258	267	254	271	Skeletal bend
		210	212	211	214	213	CH <sub>2</sub> -CH <sub>2</sub> (CH <sub>2</sub> ) torsion	
		184	188	188	192	191	CH <sub>2</sub> -CH <sub>2</sub> (CO) torsion	
		108	105	104	104	103	CH <sub>2</sub> -CH <sub>2</sub> (CH <sub>2</sub> ) torsion	
88			76	72	93	85	Skeletal bend	
			70	68	67	65	64	CH <sub>2</sub> -CH <sub>2</sub> (NH) torsion
			62	61	60	57	56	CH <sub>2</sub> -CO torsion
			30	30	30	31	32	CH <sub>2</sub> -NH torsion

Table 3 (cont.)

Exp. [2]	N-nonylcapramide				Assignment	
	Calc.		Opposite direction			
	$A'$	$\phi = 0^\circ$	$A''$	$\phi = 45^\circ$	$\phi = 60^\circ$	
1642	1644			1653	1657	Amide I
1563	1556			1555	1555	Amide II
	1479			1478	1477	$B_9(\text{NH})$
	1475			1475	1475	$B_8(\text{NH})$
	1474			1474	1474	$B_6(\text{NH})$
	1474			1474	1474	$B_4(\text{CO})$
1464	1473			1473	1473	$B_7(\text{NH})$
	1471			1471	1471	$B_3(\text{CO})$
	1468			1467	1467	$B_4(\text{NH})$
	1460			1460	1460	$\text{CH}_2(\text{NH})$ as bend ip
	1460			1460	1460	$\text{CH}_2(\text{CO})$ as bend ip
		1458		1458	1458	$\text{CH}_2(\text{NH})$ as bend op
		1458		1458	1458	$\text{CH}_2(\text{CO})$ as bend op
	1454			1454	1453	$B_3(\text{NH})$
	1451			1451	1451	$B_3(\text{CO})$
	1446			1445	1445	$B_3(\text{NH})$
	1441			1439	1438	$B_1(\text{NH})$
1433	1420			1420	1420	$B_1(\text{CO})$
	1385			1385	1385	$W_4(\text{CO})$
	1384			1384	1384	$W_9(\text{NH})$
	1378			1378	1378	$W_7(\text{NH})$
1376	1376			1376	1376	$\text{CH}_2(\text{CO})$ sym bend
	1373			1373	1373	$\text{CH}_2(\text{NH})$ sym bend
	1370			1370	1370	$W_6(\text{NH})$
	1363			1362	1362	Amide III
1350	1351			1352	1352	$W_5(\text{NH})$
1326	1324			1325	1325	$W_4(\text{NH})$
	1315			1316	1317	$W_3(\text{CO})$
		1308		1308	1308	$T_3(\text{NH})$
		1308		1308	1308	$T_2(\text{NH})$
1297		1305		1305	1305	$T_1(\text{CO})$
		1303		1301	1300	$T_3(\text{CO})$
		1302		1302	1302	$T_1(\text{NH})$
		1299		1299	1299	$T_4(\text{NH})$
	1287			1287	1287	$W_3(\text{NH})$
1285		1282		1282	1282	$T_5(\text{NH})$
		1272		1262	1260	$T_2(\text{CO})$
1264	1267			1276	1277	$W_3(\text{CO})$
1258		1256		1255	1255	$T_6(\text{NH})$
1248	1250			1249	1250	$W_9(\text{NH})$
1236		1224		1226	1221	$T_7(\text{NH})$
1222	1219			1220	1227	$W_1(\text{CO})$
1202	1209			1210	1210	$W_1(\text{NH})$
		1206		1202	1201	$T_4(\text{CO})$
1185		1188		1189	1189	$T_8(\text{NH})$
1160		1169		1166	1168	$R_2(\text{NH})$
1127	1135			1137	1139	$S_1(\text{NH})$
1119	1121			1114	1116	$S_1(\text{CO})$
		1104		1083	1077	$R_1(\text{CO})$
	1100			1121	1120	$S_2(\text{NH})$
1071	1079			1065	1062	$S_3(\text{NH})$
	1066			1070	1068	$S_3(\text{NH})$
	1064			1064	1065	$S_3(\text{NH})$
	1062			1062	1063	$S_4(\text{CO})$
	1060			1058	1055	$S_7(\text{NH})$
	1050			1050	1049	$S_3(\text{CO})$

Table 3 (cont.)

Exp. [2]	N-nonylcapramide (cont.)				Assignment
	Calc.				
	$A'$ $\phi = 0^\circ$	$A''$	$\phi = 45^\circ$	$\phi = 60^\circ$	
1022	1031	1027	1030	1030	$S_6(\text{NH})$
1015	1015		1005	999	$R_8(\text{NH})$
	1006		1008	1010	$S_1(\text{NH})$
993	989		991	991	$S_2(\text{CO})$
966		960	966	969	$R_7(\text{NH})$
929		957	953	952	$R_4(\text{CO})$
	951		943	936	$\text{CH}_3\text{—CO stretch}$
	894		896	897	$\text{CH}_3(\text{CO}) \text{ rock ip}$
888	891		891	891	$\text{CH}_3(\text{NH}) \text{ rock ip}$
		888	884	881	$R_6(\text{NH})$
		845	841	837	$R_3(\text{CO})$
820		823	824	824	$R_5(\text{NH})$
		773	775	777	$R_4(\text{NH})$
758		766	767	767	$R_2(\text{CO})$
740		741	744	739	$R_3(\text{NH})$
	733		737	746	Amide IV
		726	722	721	$R_1(\text{CO})$
721		725	725	725	$R_2(\text{NH})$
		718	718	718	$R_1(\text{NH})$
715		696	693	690	Amide V
		581	612	623	Amide VI
	541		531	532	
	490		494	496	
	486		473	466	
	428		431	433	
	398		394	392	
	370		377	379	
	307		319	328	
	272		276	282	
	231		255	267	
		215	112	113	Amide VII
		212	212	212	$\text{CH}_3\text{—CH}_2(\text{NH}) \text{ torsion}$
		211	212	212	$\text{CH}_3\text{—CH}_2(\text{CO}) \text{ torsion}$
	177		233	234	
	142		166	169	Skeletal bend
		141	141	141	
		134	133	134	
		119	119	119	Skeletal torsion
		111	108	108	
	109		160	160	Skeletal bend
		104	98	96	
		86	87	88	
		73	70	68	
	61		62	62	
		52	49	48	
		48	46	45	
		32	32	32	
		25	24	24	Skeletal torsion and bend
	23		21	21	
		9	9	10	

\* op = out-of-plane; ip = in plane.





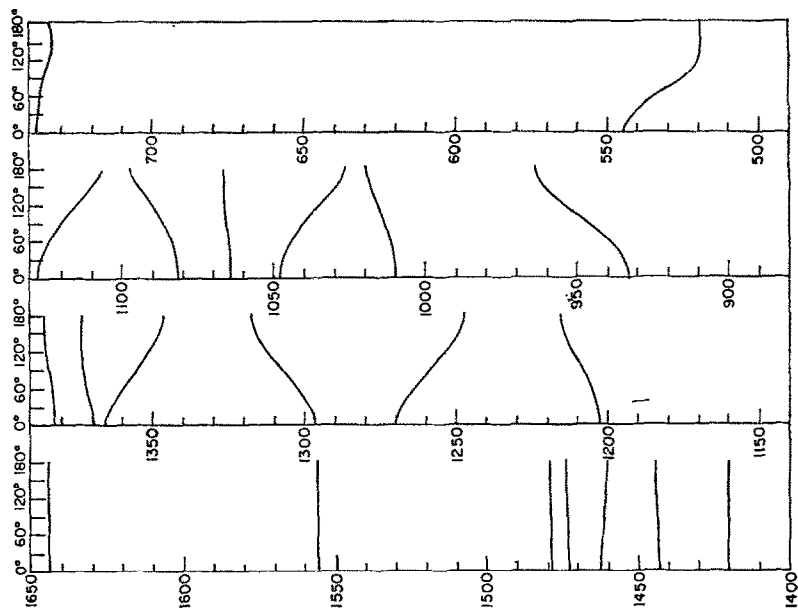
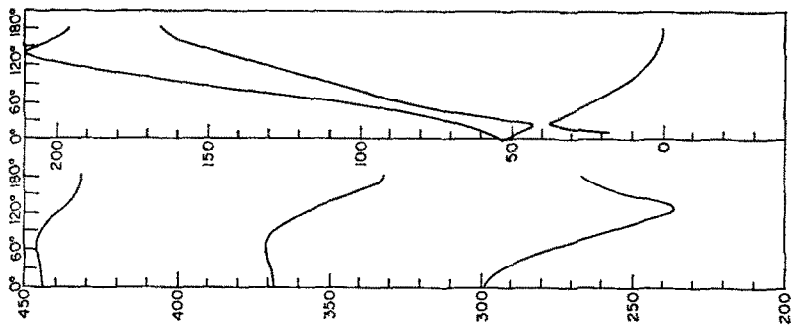


Fig. 3(a)

Fig. 3. Dispersion curves for nylon 6 and nylon 66 (a) nylon 6, in plane; (b) nylon 6, out of plane; (c) nylon 66 in plane; (d) nylon 66, out of plane.

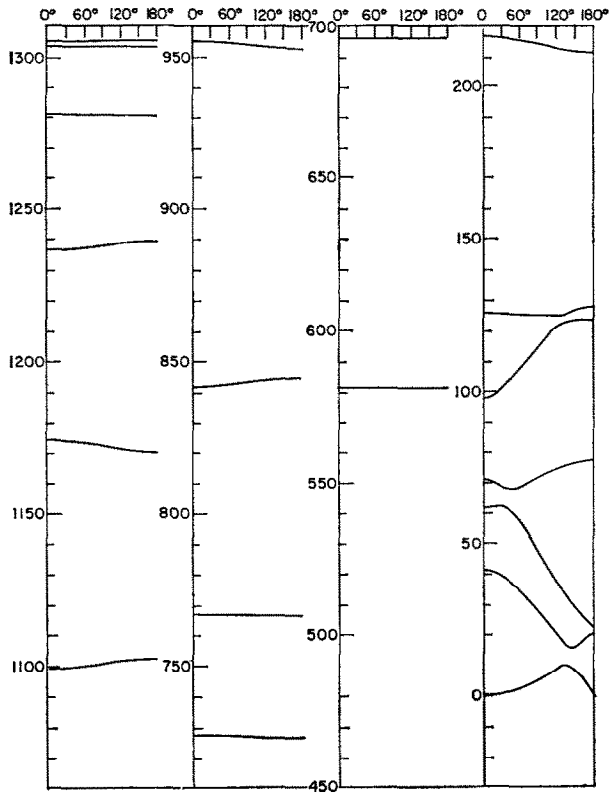


Fig. 3(b)

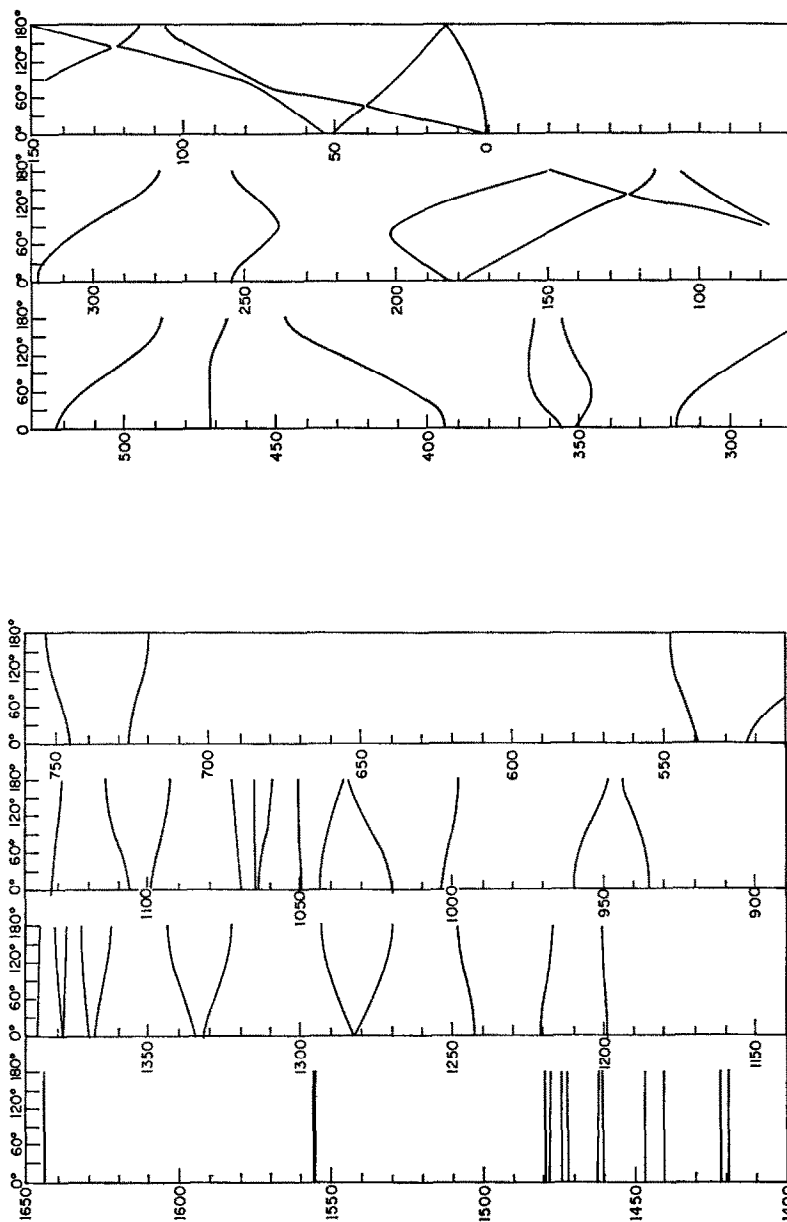


Fig. 3(c)

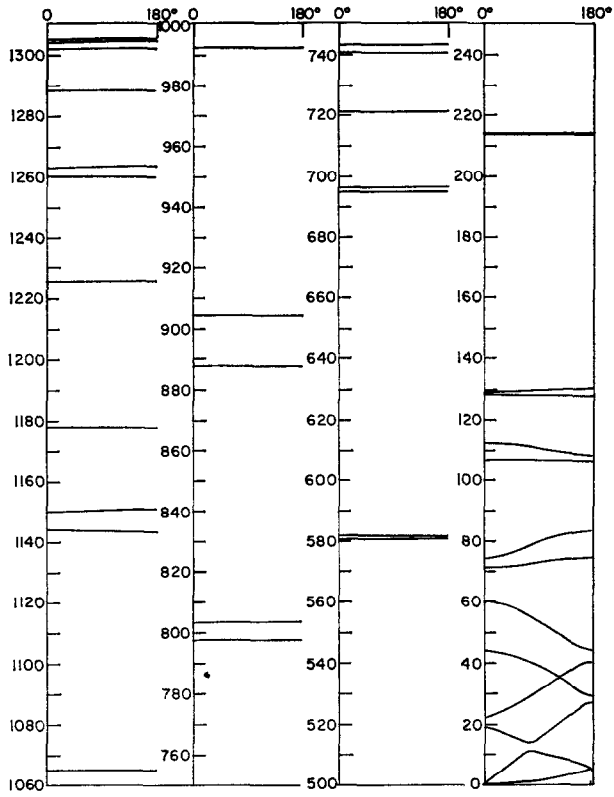


Fig. 3(d)

1238, 1191 and 1144  $\text{cm}^{-1}$  observed bands, no close calculated counterparts can be found, and to assign them 20–30  $\text{cm}^{-1}$  errors would have to be admitted. The situation that introducing  $\text{CD}_2$  groups worsens the agreement between calculated and experimental frequencies is known, e.g. from n-paraffins. In our case, the selective worsening after deuteration on the carbonyl side may indicate that further improvement of the force field on the carbonyl side may be possible provided some new data (e.g. from diamides) are available. This indication is also supported by the previously noted greater deviation in some  $\text{CH}_2(\text{CO})$  wagging frequencies in diamides and in the  $\text{CH}_2(\text{CO})$  bending frequency in the  $\gamma$  form of nylon 6.

#### *Dispersion curves of nylon 6 and nylon 66*

Dispersion curves of the  $\alpha$  forms of nylon 6 and nylon 66 were calculated and are presented in Fig. 3. Above 700  $\text{cm}^{-1}$  no extrema are observed in these curves, and most of them follow the simple  $a + b \cos \phi$  function at least approximately. In the low frequency region the curves appear complicated at first sight. But their course may be easily understood if in first approximation we replace the CO and NH groups by  $\text{CH}_2$  groups. Dispersion curves for polyethylene, with phase difference multiplied by 7 (in nylon 6) or 14 (in nylon 66), then result. The similarity to these curves is striking, and the deviations near  $\phi = 0^\circ$  and  $\phi = 180^\circ$  and where two branches cross should be assigned to the change from the  $\text{CH}_2\text{—CH}_2$  to the CO—NH group.

#### CONCLUSIONS

Normal coordinate analyses of about 15 molecules containing the amide group were performed. Most features of their infrared spectra were explained, and an almost complete assignment of their infrared bands was established. The differences between calculated and experimental frequencies generally lie within 10  $\text{cm}^{-1}$ . Some greater differences occurred especially in the CO vicinal C deuterated nylon 66, and also in some frequencies involving motion of the  $\text{COCH}_2$  group in other molecules. This may indicate the possibility of further improvement of the force field on the carbonyl side provided some new experimental data are available. The polarized infrared and Raman spectra of a more complete set of diamides would be most suited for this purpose.

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