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A valence force field for the amide group

J. Jakeš* and S. Krimm
Harrison M. Randall Laboratory of Physics, University of Michigan
Ann Arbor, Michigan

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Abstract—A valence force field is presented for the grouping R—CO—NH—R′ where *R* and R′ are CH_2 or CH_3, derived from the frequencies of N–methylacetanide, nylons, and some of the deuteroderivatives. By refining all experimental data simultaneously, the overall agreement between the experimental and calculated frequencies is good.

INTRODUCTION

During the last decade extensive experimental data have been collected on infrared spectra of molecules with the amide group [1–14]. An assignment of characteristic frequencies of the amide group was soon established [2] and later work led to an understanding of the origin of other bands in N-methylacetamide [11, 12] and in polyamides made from ω-aminoacids [9]. Along with the assignment of spectra, normal coordinate calculations for these molecules were being performed. The first of these was that for N-methylacetamide [2] in which methyl groups were taken as mass points and a Urey–Bradley force field was used. This calculation was later refined to the complete molecular model of N-methylacetamide [12, 15] using, in addition, experimental frequencies of molecules with deuterated methyl groups. A calculation of the out-of-plane vibrations of polyamides in the planar form was done with a valence force field neglecting torsion coordinates and the amide VII vibration [16]. A similar attempt with in-plane vibrations [17], using a Urey–Bradley force field for the amide group, was not

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* Permanent address: Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.

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successful due to a very poor computer used in this calculation (Russian Ural 2). However, it showed the probable necessity of using a valence force field for the amide group. With the Urey–Bradley force field, reproduction of the fine structure of the CH_2 wagging vibrations in the region 1150–1300 cm^{-1} (see [9]) was not possible. Recently, a calculation was done for the dimer of polyglycine ($CH_3NHCOCH_2NHCOCH_3$) and was used for an estimation of the rotation angles of the central CO—CH_2 and CH_2—NH bonds [14]. A calculation on nylon 6, in which methylene groups were taken as mass points [13], showed that such a calculation may serve as a good tool in understanding far infrared spectra below 600 cm^{-1}, where there is no essential contribution from hydrogen atom motions.

In this paper we present a valence force field for the grouping R—CO—NH—R′, where R and R′ are CH_2 or CH_3, which was derived from the frequencies of N-methylacetamide, nylons, and some of their deuteroderivatives. In the nylons, n-paraffin force constants were used for the $(CH_2)_{n-1}$ chain (with the exception of some constants for the first and last methylene groups). The force constants of the amide group were assumed to be transferable between nylons and N-methylacetamide. In out-of-plane blocks, torsion coordinates were included. In deriving this force field, we started from NEEDHAM's force field [12] and refined it using experimental frequencies of polyamides. When the refined force field was applied back to the N-methylacetamide, some frequencies were about 100 cm^{-1} off their experimental values. Therefore, it was necessary to refine all experimental data simultaneously. After doing this, the overall agreement between experimental and calculated frequencies was good, and most of the frequencies were reproduced to within 7 cm^{-1}, although some greater deviations do occur (e.g. in the C—C stretching region in nylon 3). If this force field is applied to similar molecules [18], the agreement goes down only slightly; one frequency which seems to be systematically off about 15 cm^{-1} is the CH_2 wagging mode in the CH_3—CH_2—CO— group.

THE FORCE FIELD

In view of the bad experience in the past with the Urey–Bradley force field for the amide group [17], we decided to introduce a valence force field instead. However, a unique result for this kind of force field cannot be expected, since the problem is expected to be ill-conditioned because of the large number of force constants. Therefore, measures must be taken to ensure the convergence of the refinement. These measures should express mathematically the physical requirements on the force constants, viz., that cross terms between remote coordinates should be small and that similar force constants should be close, and also the requirement that in each refinement cycle the differences between the initial and refined force constants should be small.

In our belief, the best way to do this is to add to the sum of the squares of frequency errors, i.e.

$$\sum_i P_i[\omega_i(\text{calc}) - \omega_i(\text{exp})]^2$$

the sum of squares of all linear combinations of force constants which we wish to keep close to zero, properly weighted according to the accuracy with which we wish to do

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so. Thus, if the force constant f_i should lie between -0.2 and 0.2, we add $(f_i/0.2)^2$; if the constants f_i and f_j should be close to each other with an accuracy of 0.1, we add $[(f_i - f_j)/0.1]^2$. In our refinement program, we have introduced three types of such requirements: that a force constant be close to a predefined value, that the difference between two force constants be close to a predefined value (usually zero), and that the difference between a force constant before and after refinement in each cycle be close to zero. In addition, we permitted the corrections to any two chosen force constants to be kept exactly equal in each cycle. This was done to facilitate introducing more transferability among force constants than was assumed during the original coding of the F matrices (otherwise it is necessary to recode the F matrices).

The final values of the force constants are listed in Table 1. Of the 99 force constants in the polyamides (76 for the in-plane block and 23 for the out-of-plane block), 22 were transferred from n-paraffins, two torsion force constants were transferred from SHIMANOUCHI [22], and the force constant for the N—H stretching vibration was estimated to be 5.98 in order to lead to the value of about 3300 cm^{-1} for the N—H stretching frequency. Twelve more force constants are required for N-methylacetamide, of which 2 constants for C—H stretching were transferred from n-paraffins. The remaining 84 force constants, 60 for the in-plane block, 14 for the out-of-plane block, and 10 new constants for N-methylacetamide, were refined by least squares. The cross terms involving coordinates C—C(—CO)—H, C—C—C(=O), H—C—C(=O), N—C—H, N—C(=H_2)—C, and H—C(—N)—C not shown in Table 1 were also transferred from n-paraffins, neglecting the difference between C(=O), N, and C(=H_2) atoms in these cross terms. Moreover, in the in-plane block 10 of the force constants were forced to the values of the similar force constants in n-paraffins with an accuracy of 0.1, and 6 with an accuracy of 0.2, as shown in Table 1. At first sight, the values of the force constants seem to be reasonable, although the value of the cross term between C—C(=O) and C=O may seem to be too high. But we must keep in mind that this set of force constants certainly is not unique, and we are convinced that other sets, in which some of the force constants may differ by as much as 0.5 from those in Table 1, may reproduce the experimental data equally well.

Some attention should also be paid to the transferring of force constants from n-paraffins. We calculated frequencies of some longer n-paraffins and observed that a few of the C—C stretching frequencies and several C—C—C bending frequencies were over 10 cm^{-1} off their calculated values. Deviations of up to 7 cm^{-1} were also observed in the CH_2 wagging frequencies, and here they were determined almost exclusively by phase differences associated with the corresponding modes. This dependence was also observed in the C—C stretching and C—C—C bending regions, although the interaction of both branches of the dispersion curves interferes somewhat with this. Such errors are expected to be transferred to the amide force constants. That is, by keeping the n-paraffin force constants fixed during refinement, other constants which are being refined are forced to change so as to compensate for the errors caused by the fixed force constants. This compensation should probably work best for molecules with about five methylene groups, from which most of the data in the refinement were used. On this basis, we can explain some large errors in the C—C stretching frequencies in nylon 3 and in the CH_2 wagging frequency of the CH_3CH_2CO group. The application of this force field to other similar molecules with

Table 1. Force constants for the CH$_2$CONHCH$_2$ group

(a) Force constants involving coordinates symmetric to the skeletal plane

	C—C(CO)	C—C—C(O)	C—C(O)	C—C=O	C=O	C—C(O)—N	C(O)—N	C—N—C	H—N—C(H$_2$)	N—C(H$_2$)	N—C(H$_2$)—C	(N)C(H$_2$)—C
C—C(CO)	4.532††											
C—C—C(O)	0.3155*	1.5985										
C—C(O)	0.0890*	0.3134†	5.1744									
C—C=O	0	−0.0314‡	0.2584	2.8251								
C=O	0	0	0.7637	−0.1167	8.7802							
C—C(O)—N	0	−0.2082‡‡	0.0207	1.4945	−0.4954	2.5393						
C(O)—N	0	0	0.6382	−0.0838	0.2304	0.4377	6.1175					
C—N—C	0	0	0	−0.0121	0	−0.1291	−0.4826	2.3231				
H—N—C(H$_2$)	0	0	0	0.1808	0	−0.0318	−0.3746	0.8481	1.1542			
N—C(H$_2$)	0	0	0	0	0	0	0.3522	0.6152	0.3241	5.2782		
N—C(H$_2$)—C	0	0	0	0	0	0	0	0.0150‡‡	−0.1433‡	0.3118†	1.5625	
(N)C(H$_2$)—C	0	0	0	0	0	0	0	0	0	0.0930*	0.3247*	4.532††

$K_{NH} = 5.98$**.

(b) Force constants involving antisymmetric and/or unsymmetric coordinates

	C—C(CO)—H	H—C—C(O)	CO o.p. bend	C(O)—N tors.	NH o.p. bend	N—C—H	H—C(N)—C
C—C(CO)—H	1.1582						
C—C(CO)—H′	0.5161						
H—C—C(O)	0.4747	1.0665$_5$					
H′—C—C(O)	0.5168	0.4707$_5$					
CO o.p. bend	0	0.0346	0.5797				
C(O)—N tors.	0	0	0.1400	0.6706			
NH o.p. bend	0	0	0.0256	0.0297	0.0800		
N—C—H	0	0	0	0	−0.0009	1.2175	
N—C—H′	0	0	0	0	0.0009	0.3780	
H—C(N)—C	0	0	0	0	0	0.4894$_5$	1.1975
H′—C(N)—C	0	0	0	0	0	0.3819$_5$	0.5177

$\tau_{C-C(O)} = 0.037$,** $\tau_{N-C(H_2)} = 0.037$.**

Table 1 (*cont.*)

(c) Cross terms between symmetric and unsymmetric coordinates

	C—C(CO)	C—C—C(O)	C—C(O)	C—C—O		C—C(O)—N	
				skew	*cis*	*gauche*	*trans*
C—C(CO)—H	0.174††	0.5232*	−0.0730*	0	0	0	0
H—C—C(O)	−0.0923*	0.4920†	0.2074†	0.1317	−0.1936§	−0.0229	0.0278§

	C—N—C		H—N—C(H_2)		N—C(H_2)	N—C(H_2)—C	(N)C(H_2)—C
	gauche	*trans*	skew	*cis*			
N—C—H	−0.0099	−0.0938§	0.0560	−0.0083§	0.3655†	0.4895†	−0.1415*
H—C(N)—C	0	0	0	0	−0.1086*	0.4991*	0.174††

(d) Methyl group force constants in N-methylacetamide

	H_α	H_β	F_β
CH_3(CO)	0.5355	0.5972	−0.0182
CH_3(NH)	0.5277	0.7962	−0.0461

(e) Symmetrized force constants

	H—C—C(O)	H—C(CO)—C	n-paraffin	H—C(N)—C	H—C—N	
						$f_\gamma^g + f_\gamma^t = 0.015$
$H_\gamma + F_\gamma + 2H_\delta$	1.5373	1.6743	1.710	1.7152	1.5955	$f_\gamma^g - f_\gamma^t = -0.131$
$H_\gamma - F_\gamma$	0.5958	0.6421	0.682	0.6798	0.8395	$f_\gamma'^g + f_\gamma'^t = -0.013$
$F_\gamma' + 2H_\delta$	0.9915		1.087	0.8714		$f_\gamma'^g - f_\gamma'^t = 0.005$
F_γ'	−0.0421		0.021	0.1075		$f_\gamma''^g + f_\gamma''^t = 0.022$
						$f_\gamma''^g - f_\gamma''^t = 0.002$

* Kept close to the corresponding force constant in the polymethylene chain with an accuracy of 0.01.
† As in *, with an accuracy of 0.02.
‡ *cis*.
§ From N-methylacetamide (this calculation).
** Assumed (no refinement).
†† Transferred from n-paraffins [21].
‡‡ *trans*.

Every H atom lies on the upper side of the skeletal plane and every H′ atom on the lower side. The positive direction of the CO and NH out-of-plane (o.p.) bending coordinates corresponds to the situation in which the CO or NH bond enters the upper side of the skeletal plane. The positive direction of a torsion coordinate corresponds to the situation in which the outer skeletal atoms (i.e. C or N) involved in this coordinate enter the upper side of the skeletal plane.

All zero values of force constants were assumed.

the amide group showed the force field to be a powerful means of understanding and assigning their spectra [18]. But it also showed clearly that a further refinement of this force field to remove some of the uncertainty caused by ill-conditioning would be possible and desirable if new experimental data, and/or a more refined set of n-paraffin force constants, were available.

ASSUMED STRUCTURES AND COORDINATES

In the calculations we used the following bond lengths [19]: $d_{\mathrm{CH}} = 1.093$ Å, $d_{\mathrm{CC}} = 1.54$ Å, $d_{\mathrm{NH}} = 1.01$ Å, $d_{\mathrm{CO}} = 1.23$ Å, $d_{\mathrm{C(=O)-N}} = 1.34$ Å, $d_{\mathrm{C(-H)-N}} = 1.47$ Å. All angles in the methylene and methyl groups were assumed tetrahedral, and angles in the C—CO—NH—C group were assumed trigonal (120°). Mass values used were $m_{\mathrm{H}} = 1.007825$, $m_{\mathrm{C}} = 12$, $m_{\mathrm{N}} = 14.00307$, $m_{\mathrm{O}} = 15.99491$, and $m_{\mathrm{D}} = 2.01410$. For the velocity of light and Avogadro's number we used the values 2.997925×10^{10} cm/sec and 6.02257×10^{23} mol^{-1} respectively.

The internal coordinates were bond lengths, bond angles, out-of-plane bend angles, and torsion angles. The first two kinds were used in the usual way: a $+1$ value of the coordinate means an increase by 1 Å, or 1 rad., respectively. For defining the next two types, let us call one side of the carbon skeleton the upper side and the other the lower side. The value $+1$ for the coordinate C═O (or N—H) out-of-plane bend means the C═O (N—H) bond is rotated by 1 rad. perpendicular to the C—C—N (C—N—C) plane and moves into the upper side of this plane. In the internal torsion coordinates we follow the FUKUSHIMA convention [20]: if atom X has m adjacent atoms and atom Y has n adjacent atoms, $(n-1)(m-1)$ dihedral angles about the X—Y bond may be defined. For the torsion coordinate about this bond we take the sum of the changes of all of these dihedral angles divided by $(m-1)(n-1)$. The plus sign for a dihedral angle is chosen in a direction such that the change of the skeletal dihedral angle (i.e. the angle involving the C and N atoms only) moves both outer skeletal atoms into the upper side of the skeletal plane. This convention has the disadvantage that it changes the direction of the torsion coordinate about adjacent skeletal bonds from clockwise to counterclockwise; on the other hand, we found it very convenient for setting up the B matrix elements. If the rotation angles in the molecule differ from those of the standard all-*trans* for the skeleton (e.g. the γ form of nylon 6), we first rotate it to the standard conformation for determining the positive direction of the out-of-plane bending and torsion coordinates.

We decided to remove the local redundancy in each methylene group by omitting the H—C—H bending coordinate and in the amide group by omitting the H—N—C(═O) and O═C—N coordinates. The omission of the H—C—H bending coordinate leads to an increase by the value of H_{δ} of all diagonal and cross terms between the remaining five angle coordinates around this carbon atom. This change is included in Table 1, where final refined values of force constants are listed. In the actual coding of the F matrices, we further changed our force constant set in the case of the CCH

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bending, NCH bending, and CH stretching coordinates to some sums and differences of force constants yielding in-plane and out-of-plane blocks in polyamides which are mutually independent. Even in the case where complete independence is not obtained, it is worth doing so since the conditioning of the in-plane and out-of-plane blocks may be different, requiring a different approach to ensuring convergence. This is difficult to do without having separated the force constants influencing the individual blocks. For the convenience of those who would wish to follow this approach, we also include the symmetrized combinations of force constants in Table 1. Note only that in forming out-of-plane coordinates, the internal coordinate containing the hydrogen atom on the *upper* side of the skeletal plane always enters with a + sign.

All calculations were performed on an IBM 360 computer using a computer program written by one of us (J. J.). In coding this program, care was taken to save computer time and storage space in handling large matrices. The method of calculation was essentially the same as in the previous work [15, 16].

EXPERIMENTAL DATA

Extensive experimental data on infrared frequencies of molecules with the amide group were collected in Prague in the early sixties [4, 5, 9, 11]. These data were used in the present refinement, complemented by some data in the region below 400 cm^{-1} [10, 13]. Although other data are available in the literature [1, 7, 8], there is an advantage in using experimental data from a single source, since systematic errors in a given region of the spectrum are then the same for all the frequencies. This is important for a successful simultaneous refinement of a transferable set of force constants, since accurate frequency shifts are much more relevant than accurate frequencies. This is so because such a refinement is in reality an extrapolation from frequency shifts to unknown eigenvectors, and in some cases changes in such frequency shifts of as little as 3 to 5 cm^{-1} can lead to drastic changes in eigenvectors.

The experimental frequencies are listed in Table 2 together with their statistical weights and calculated values. In our coding, 1273/3 means that the contribution to the sum of error squares was $((\omega_{calc} - 1273)/3)^2$; i.e. rather than statistical weights P_i, the values $P_i^{-\frac{1}{2}}$ are listed. Because of the small difference between the starting and refined set of force constants in the last refinement cycle, we did not repeat the frequency calculations with the final set in Table 1 for all molecules. Only the frequencies of nylon 6 and nylon 66 listed in Table 2 are those obtained with the set of force constants in Table 1; the other calculated frequencies are those obtained with the next-to-last set of force constants.

In Table 2, B, W, T, R, and S mean CH_2 bending, wagging, twisting, rocking, and C—C stretching modes respectively. Where the assignment is shown between two lines, it relates to both of them (in the case of splitting of the monomer unit modes). The indices in the B, W, T, R, and S modes are sequence indices of the progression and are related to the phase differences in the polymethylene portion of the chain [23, 24]. Compared to the previous assignment [9], we now denote one band in the CH_2 wagging progression as amide III, although the selection of the proper one is

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Table 2. Experimental and calculated frequencies of nylons and N-methylacetamides

Nylon 3

Exp.	Calc.		Assignment
[9, 10]	A'	A''	
1646/6	1643		Amide I
1537/6	1553		Amide II
1467/4	1454		CH_2(—NH) bend
1428/4	1421		CH_2(—CO) bend
1373/3	1374		Amide III
1358/3	1363		W_2
1291/2		1285	T_1
1224/2	1227		W_1
1203/3		1201	T_2
1116/2	1118		S_1
		1064	R_2
1050/4	1070		S_2
976/4	995		C—CO stretch
792/3		806	R_1
	722		Amide IV
697/3		695	Amide V
580/3		582	Amide VI
456/4	459		Skeletal bend
343/4	333		
230/3		225	Amide VII
		92	Skeletal torsion

Nylon 4

Exp.		Calc.		Assignment
[9, 10]	A_1	B_2	B_1	
1641/6	1645		1645	Amide I
1550/6	1558		1554	Amide II
1474/3	1477		1477	B_3
1451/3	1452		1455	B_2
	1419			
1418/2			1419	B_1
			1382	Amide III
	1379		1371	W_3
1351/6	1354			Amide III
1312/2	1314			W_2
		1302		T_1
1274/3			1278	W_2
1263/3		1266		T_2
1231/3			1239	W_1
1212/2	1213			
1190/2		1192		T_3
1126/2	1123			S_1
1105/3			1104	
		1081		R_2
			1081	
1070/4	1068			S_2
	1021		1062	S_3
951/4	958		949	C—CO stretch
870/2		875		R_2
755/2		756		R_1
	777		690	Amide IV
692/3		695		Amide V
574/3		580		Amide VI
	545			Skeletal bend
454/3			455	
	384		372	
214/3		202		Amide VII
	104		338	Skeletal bend and torsion
		107		
	98		242	
		93		
		49		

Nylon 6

Exp.		Calc.		Assignment
[9, 13]	A_1	B_2	B_1	
1647/6	1644		1645	Amide I
1551/6	1556		1556	Amide II
1480/2			1479	
1479/2	1479			B_5
1466/3			1474	
	1473			B_4
1455/3	1462			
			1460	B_3
			1444	
1439/2	1443			B_2
1420/2	1420		1420	B_1
	1382		1386	Amide III
	1369		1374	W_5
	1365		1346	W_4
			1318	W_3
1305/3		1305		T_2
		1304		T_1
1295/2	1296			W_2
1282/3		1281		T_3
1270/2	1270			
1244/4			1247	W_2
1244/3		1237		T_4
1217/2			1216	
1205/2	1203			W_1
1173/2		1175		T_5
1128/2	1128			
1115/2			1106	S_1
		1099		R_5
			1097	
1078/4	1081			S_2
	1064		1067	S_5
1043/2	1048			
1032/2			1026	S_4
	1010		1019	S_3
964/2			964	C—CO stretch
955/2		955		R_4
931/2	933			C—CO stretch
838/2		842		R_3
		767		R_2
	738		733	Amide IV
734/2		727		R_1
692/3		696		Amide V
579/3		581		Amide VI
	544			
524/2			519	Skeletal bend
445/2	445			
429/2			431	
370/2	368			
345/6			332	
295/2	299			
			266	
220/3		217		Amide VII
195/2			196	Skeletal bend and torsion
170/2			166	
		126		
		98		
		71		
		62		
	54			
	53			
		41		

Table 2 (*cont.*)

Nylon 7			
Exp. [9]	Calc. A'	A''	Assignment
1644/6	1645		Amide I
1550/6	1556		Amide II
1479/2	1479		B_6
1470/2	1474		B_5
	1469		B_4
	1456		B_3
1440/2	1442		B_2
1422/2	1420		B_1
	1386		W_6
	1375		W_5
1360/2	1359		Amide III
1346/2	1341		W_4
1309/3		1307	T_2
1303/3		1305	T_3
1291/3		1296	T_1
1281/2	1278		W_3
1271/3		1269	T_4
1252/2	1258		W_2
1229/3		1230	T_5
1199/2	1199		W_1
1167/2		1166	T_6
1128/2	1129		S_1
		1106	R_6
1081/2	1084		S_2
1066/4	1065		S_6
	1052		S_5
	1030		S_4
1012/4	1021		S_3
978/2		977	R_5
943/2	943		C—CO stretch
879/2		880	R_4
793/3		799	R_3
		747	R_2
	726		Amide IV
727/2		723	R_1
693/3		696	Amide V
581/3		581	Amide VI
513/2	514		Skeletal bend
	469		
437/4	448		
	338		
		214	Amide VII
	153		Skeletal bend
	140		
		134	Skeletal torsion
		125	
		84	
		60	
		53	

Nylon 8				
Exp. [9]	Calc. A_1	B_2	B_1	Assignment
1642/6	1645		1645	Amide I
1549/6	1556		1556	Amide II
1480/2	1479		1479	B_7
1469/3	1474			B_6
1469/2			1474	
	1474		1473	B_5
	1464		1465	B_4

Nylon 8 (*cont.*)				
Exp. [9]	Calc. A_1	B_2	B_1	Assignment
	1452		1451	B_3
	1441		1442	B_2
1419/2	1420		1420	B_1
	1384		1386	W_7
	1380		1377	Amide III
	1372		1365	W_6
			1356	W_5
1343/3	1341			
1325/2	1319			W_4
			1304	
1308/3		1308		T_2
		1306		T_3
		1302		T_1
1287/2		1288		T_4
			1284	W_3
1267/2	1267			
1259/4		1259		T_5
1245/2	1248			W_2
			1233	
1219/2		1219		T_6
1204/3			1205	W_1
1197/2	1196			
1163/2		1167		T_7
1126/2	1129			S_1
			1111	
		1106		R_7
	1087		1105	S_2
	1067		1065	S_7
	1064		1062	S_6
	1042		1059	S_3
	1020		1027	S_5
	1008		987	S_4
1000/2		996		R_6
940/4	952		939	C—CO stretch
908/2		906		R_5
830/2		831		R_4
770/2		772		R_3
		737		R_2
	729		746	Amide IV
726/2		721		R_1
688/3		696		Amide V
582/3		581		Amide VI
550/3			562	Skeletal bend
	509			
	481		471	
	466		386	
	358		342	
	249		258	
	221		215	
		214		Amide VII
		137		Skeletal bend and torsion
		135		
			123	
			112	
		100		
		67		
		49		
		45		
		35		
	33			
	32			

Table 2 (*cont.*)

	Nylon 11		
Exp.	Calc.		
[9]	A'	A''	Assignment
1644/6	1645		Amide I
1549/6	1556		Amide II
1482/2	1479		B_{10}
1470/2	1476		B_9
	1475		B_8
	1473		B_7
	1470		B_6
	1463		B_5
	1454		B_4
	1446		B_3
	1440		B_2
1420/2	1420		B_1
	1386		W_{10}
	1382		W_9
	1376		Amide III
	1372		W_8
1353/3	1348		W_7
1340/2	1334		W_6
		1309	T_3
		1308	T_2
		1305	T_4
		1303	T_1
		1299	T_5
1298/2	1296		W_5
		1284	T_6
1281/2	1282		W_4
1263/3		1263	T_7
1242/2	1246		W_3
		1234	T_8
1226/2	1229		W_2
1199/3		1204	T_9
1191/2	1191		W_1
1162/2		1160	T_{10}
1127/2	1130		S_1
		1109	R_{10}
1090/3	1093		S_2
	1070		S_3
	1068		S_{10}
	1067		S_9
	1062		S_8
	1043		S_7
	1036		S_4
		1024	R_9
999/3	1005		S_6
987/3	980		S_5
968/2		964	R_8
940/2	942		C—CO stretch
900/2		900	R_7
		845	R_6
793/2		796	R_5
		761	R_4
	740		Amide IV
		738	R_3
		724	R_2
723/2		718	R_1
690/3		696	Amide V
584/3		581	Amide VI
544/3	560		Skeletal bend
494/3	504		
444/3	448		
	409		
	370		
	313		
	247		
	223		

	Nylon 11 (*cont.*)		
Exp.	Calc.		
[9]	A'	A''	Assignment
		214	Amide VII
		144	Skeletal bend and torsion
		143	
		119	
		106	
		90	
		82	
	71		
	68		
		59	
		30	
		28	

	Nylon 66				
Exp.	Calc.				
[4]	A_g	B_g	B_u	A_u	Assignment
1640/6			1645		Amide I
	1644				
1551/6			1556		Amide II
	1555				
	1480				B_5(NH)
1480/2			1478		B_6(NH)
1471/2			1474		B_4(NH)
			1472		B_4(CO)
	1462				B_3(NH)
	1460				B_3(CO)
1446/3			1447		B_2(NH)
	1440				B_1(NH)
1423/2			1422		B_2(CO)
	1419				B_1(CO)
	1386				Amide III
1376/6			1378		
	1378				W_6(NH)
			1370		W_5(NH)
	1367				W_4(NH)
			1334		W_3(NH)
	1331				W_4(CO)
		1305			T_1(CO)
		1305			T_1(NH)
				1305	T_2(NH)
				1302	T_2(CO)
		1289			T_3(NH)
1281/2			1282		W_3(CO)
	1282				W_2(NH)
		1264			T_3(CO)
				1260	T_4(NH)
	1243				W_2(CO)
		1226			T_5(NH)
1226/2			1221		W_1(NH)
1201/2			1199		W_1(CO)
1183/2				1178	T_6(NH)
		1150			R_6(NH)
1145/2				1144	T_4(CO)
	1131				Skeletal stretch
			1106		
	1099				
	1069				
		1065			R_4(CO)
	1064				Skeletal stretch
1065/2			1064		
	1049				
1043/2			1043		
1017/3			1019		
	1003				

Table 2 (*cont.*)

Nylon 66 (*cont.*)

Exp. [4]	Calc. A_g	B_g	B_u	A_u	Assignment
988/2				993	R_5(NH)
	960				C—CO stretch
934/2			935		C—CO stretch
908/2				904	R_3(CO)
		888			R_4(NH)
		803			R_2(CO)
798/2				798	R_3(NH)
			745		Amide IV
		743			R_2(NH)
				741	R_1(CO)
	726				Amide IV
732/3				721	R_1(NH)
		697			Amide V
695/3				695	
583/3				582	Amide VI
		581			
535/2			539		Skeletal bend
	522				
	472				
405/3			394		
358/3			356		
	351				
330/3			318		
	254				
230/3				214	Amide VII
		214			
			183		Skeletal bend and torsion
	178				
		129			
				128	
				112	
		107			
				74	
		72			
		60			
	53				
			51		
				44	
				22	
		19			

N-deuterated nylon 4

Exp. [9]	Calc. A_1	B_2	B_1	Assignment
1629/6	1630		1630	Amide I
1473/4	1490			Amide II
			1481	
1464/4	1471			B_3
			1475	
1448/4	1451			B_2
			1451	
1419/2	1417		1418	B_1
1384/4	1374			W_3
1359/4			1371	
			1346	W_2
1334/4	1331			
		1302		T_1
1263/3		1266		T_2
1251/2	1247			W_1
			1240	
1192/2		1192		T_3
			1132	S_1
1121/2	1118			
1092/4	1087			S_2
1079/2			1078	
		1079		R_3
	1034		1059	S_3
984/4	989		986	Amide III
940/4	939		939	C—CO stretch
869/2		872		R_2
754/2		743		R_1
	770		687	Amide IV
		604		Amide VI
495/3		502		Amide V
	532			Skeletal bend
449/2			450	
	383		366	
			334	
			242	
		202		Amide VII
		107		Skeletal bend and torsion
	103			
	97			
		93		
		48		

N-deuterated nylon 6

Exp. [9, 13]	Calc. A_1	B_2	B_1	Assignment
1637/6	1630		1630	Amide I
	1486		1487	Amide II
	1478		1476	B_5
	1471		1471	B_4
	1459		1460	B_3
	1443		1443	B_2
1419/2	1420		1420	B_1
1371/4			1376	W_5
1381/4	1376			
	1367		1372	W_4
1349/4	1339			
			1330	W_3
1303/3		1305		T_2
1293/3		1304		T_1
1278/2		1281		T_3
	1276		1281	W_2
1243/2		1237		T_4
1227/2	1220			W_1
			1214	
1173/2		1175		T_5
			1127	S_1
1122/2	1125			
	1102			S_2
		1098		R_5
1090/2			1095	S_2
	1064		1067	S_5
	1055		1035	S_3
	1004		1023	S_4
981/4	983		990	Amide III
961/2			945	C—CO stretch
951/2		954		R_4
923/2	926			C—CO stretch
837/2		836		R_3
773/2		762		R_2

Table 2 (*cont.*)

Exp. [9, 13]	Calc. A_1	B_2	B_1	Assignment
N-deuterated nylon 6 (*cont.*)				
	736		730	Amide IV
734/2		723		R_1
		604		Amide VI
496/3		502		Amide V
	541			
512/2			513	Skeletal bend
442/2	440			
429/2			431	
365/2	365			
345/4			332	
294/2	298			
			263	
220/3		217		Amide VII
195/2			195	Skeletal bend and torsion
170/2			165	
		126		
		97		
		71		
		61		
	53			
	53			
		40		

Exp. [9]	Calc. A'	A''	Assignment
N-deuterated nylon 7			
1632/6	1630		Amide I
	1487		Amide II
	1476		B_6
	1474		B_5
	1467		B_4
	1454		B_3
	1442		B_2
1421/2	1420		B_1
1374/2	1380		W_6
	1373		W_5
1355/4	1348		W_4
1323/2	1314		W_3
		1307	T_2
1302/3		1305	T_1
1289/3		1296	T_3
1262/2		1269	T_4
	1260		W_2
1230/2		1229	T_5
1219/2	1213		W_1
1168/2		1166	T_6
1127/2	1125		S_1
1110/4		1105	R_6
1095/4	1105		S_2
1066/3	1065		S_6
	1055		S_5
	1036		S_3
1021/4	1016		S_4
973/2	980		Amide III
973/3		975	R_5
937/2	935		C—CO stretch
878/2		878	R_4
793/2		791	R_3
		744	R_2
728/2		721	R_1

Exp. [9]	Calc. A'	A''	Assignment
N-deuterated nylon 7 (*cont.*)			
	722		Amide IV
		604	Amide VI
493/3		502	Amide V
	508		Skeletal bend
	467		
435/4	443		
	337		
		214	Amide VII
	153		Skeletal bend
	139		
		134	Skeletal torsion
		125	
		83	
		59	
		52	

Exp. [9]	Calc. A_1	B_2	B_1	Assignment
N-deuterated nylon 8				
1637/6	1630		1630	Amide I
	1486		1486	Amide II
	1478		1477	B_7
	1474		1474	B_6
	1471		1471	B_5
	1463		1463	B_4
	1451		1451	B_3
	1441		1441	B_2
1420/2	1420		1420	B_1
	1381		1382	W_7
	1372		1374	W_6
	1366		1360	W_5
	1328		1335	W_4
1307/3		1308		T_2
		1306		T_3
		1302		T_1
	1294		1290	W_3
1288/2		1288		T_4
1253/2		1259		T_5
	1249		1253	W_2
1219/3		1219		T_6
1211/2	1208			W_1
			1204	
1164/2		1167		T_6
			1128	S_1
1124/2	1126			
1096/3	1109		1104	S_2
		1105		R_7
	1068		1066	S_7
	1064		1064	S_6
	1036		1059	S_3
			1036	S_5
1022/3	1032			
	1009		993	S_4
999/2		995		R_6
978/3	980			Amide III
978/2			974	
934/2	940		931	C—CO stretch
911/3		903		R_5
828/2		828		R_4
770/2		766		R_3

Table 2 (*cont.*)

N-deuterated nylon 8 (*cont.*)

Exp. [9]	Calc. A_1	B_2	B_1	Assignment
	725		742	Amide IV
		735		R_2
726/2		719		R_1
		604		Amide VI
494/3		502		Amide V
543/3			555	Skeletal bend
	501			
	479		469	
	466		383	
	355		340	
	249		258	
	220		214	
		213		Amide VII
		137		Skeletal bend and torsion
		135		
			122	
			111	
		100		
		67		
		49		
		44		
		34		
	33			
	32			

N-deuterated nylon 11

Exp. [9]	Calc. A'	A''	Assignment
1632/6	1630		Amide I
	1486		Amide II
	1478		B_{10}
	1476		B_9
	1474		B_8
	1473		B_7
	1469		B_6
	1462		B_5
	1453		B_4
	1445		B_3
	1440		B_2
1420/2	1420		B_1
	1384		W_{10}
	1379		W_9
	1372		W_8
	1366		W_7
	1340		W_6
	1318		W_5
		1309	T_3
		1308	T_2
		1305	T_4
		1303	T_1
		1299	T_5
	1286		W_4
1288/2		1284	T_6
1256/3		1263	T_7
	1261		W_3
1233/2		1234	T_8
	1229		W_2
1199/2		1204	T_9
	1198		W_1

N-deuterated nylon 11 (*cont.*)

Exp. [11]	Calc. A'	A''	Assignment
1162/2		1160	T_{10}
1129/2	1127		S_1
	1115		S_2
		1109	R_{10}
	1070		S_3
	1068		Skeletal stretch
	1064		
	1062		
	1048		
	1035		
		1024	R_9
	1012		Skeletal stretch
	968		
975/2	972		Amide III
968/2		963	R_8
934/2	933		C—CO stretch
		898	R_7
848/2		843	R_6
792/2		792	R_5
764/4		759	R_4
741/2		735	R_3
	736		Amide IV
		723	R_2
723/2		718	R_1
		604	Amide VI
486/3		502	Amide V
541/3	554		Skeletal bend
498/3	502		
441/3	445		
	408		
	370		
	311		
	246		
	222		
		214	Amide VII
		144	Skeletal bend and torsion
		143	
		119	
		105	
		90	
		82	
	70		
	68		
		58	
		30	
		28	

$CH_3CONHCH_3$

Exp. [11]	Calc. A'	A''	Assignment
1660/6	1662		Amide I
1569/6	1557		Amide II
1471/4	1462		
1451/6		1465	CH_3(NH) as bend
1458/6	1446		CH_3(CO) as bend
1441/6		1452	
1414/2	1415		CH_3(NH) sym bend
1374/2	1378		CH_3(CO) sym bend
1300/2	1302		Amide III

Table 2 (*cont.*)

$CH_3CONHCH_3$ (*cont.*)

Exp. [11]	Calc. A'	A''	Assignment
1161/3	1163		CH_3(NH) rock
		1134	
1096/6	1105		N—CH_3 stretch
1044/3		1054	CH_3(CO) rock
991/2	987		C—C stretch
883/2	884		CH_3(CO) rock
725/3		726	Amide V
628/2	634		Amide IV
600/3		597	Amide VI
439/3	442		Skeletal bend
289/3	295		
192/3		195	Amide VII
		147	CH_3 torsion
		136	

$CH_3CONDCH_3$

Exp. [11]	Calc. A'	A''	Assignment
1647/6	1648		Amide I
1485/6	1496		Amide II
1471/4	1459		CH_3(ND) as bend
		1465	
1440/6		1452	CH_3(CO) as bend
1446/4	1439		
1406/2	1408		CH_3(ND) sym bend
1372/2	1365		CH_3(CO) sym bend
1185/3	1186		CH_3(ND) rock
		1134	
1123/3	1114		N—CH_3 stretch
1045/3		1052	CH_3(CO) rock
1000/2	993		
965/3	967		Amide III
872/2	872		C—C stretch
		635	Amide VI
628/2	628		Amide IV
510/3		504	Amide V
439/3	439		Skeletal bend
292/3	294		
189/3		195	Amide VII
		147	CH_3 torsion
		136	

$CD_3CONHCH_3$

Exp [11]	Calc. A'	A''	Assignment
1647/6	1651		Amide I
1567/6	1550		Amide II
1462/2	1460		CH_3 as bend
1446/6		1465	
1416/2	1415		CH_3 sym bend
1326/2	1320		Amide III
1161/3	1165		CH_3 rock
		1133	
1120/3	1121		N—CH_3 stretch
	1048	1046	CD_3 as bend
	1039		CD_3 sym bend
871/4	865		C—C stretch
907/3		908	CD_3 rock
800/3	803		

$CD_3CONHCH_3$ (*cont.*)

Exp. [11]	Calc. A'	A''	Assignment
715/3		699	Amide V
592/3	587		Amide IV
537/3		536	Amide VI
407/3	404		Skeletal bend
288/3	282		
182/3		189	Amide VII
		140	CH_3 torsion
		104	CD_3 torsion

$CD_3CONDCH_3$

Exp. [11]	Calc. A'	A''	Assignment
1647/6	1634		Amide I
1480/6	1488		Amide II
1452/6		1465	CH_3 as bend
	1451		
1408/2	1407		CH_3 sym bend
1198/4	1200		CH_3 rock
		1133	
1125/4	1126		N—CH_3 stretch
	1047	1045	CD_3 as bend
	1044		CD_3 sym bend
976/4	968		Amide III
910/3		899	CD_3 rock
861/3	857		C—C stretch
795/4	798		CD_3 rock
588/3	583		Amide IV
		559	Amide VI
505/3		498	Amide V
402/3	402		Skeletal bend
280/3	281		
173/3		189	Amide VII
		140	CH_3 torsion
		103	CD_3 torsion

$CH_3CONHCD_3$

Exp. [11]	Calc. A′	A″	Assignment
1647/6	1662		Amide I
1564/6	1549		Amide II
1447/3	1446		CH_3 as bend
1437/6		1452	
1373/2	1380		CH_3 sym bend
1302/2	1304		Amide III
1145/3	1144		N—CH_3 stretch
	1051	1059	CH_3 rock
	1030	1044	CD_3 as bend
	1019		CD_3 sym bend
968/4	967		C—C stretch
890/4		884	CD_3 rock
	781		
725/3		724	Amide V
606/4	610		Amide IV
600/3		595	Amide VI

Table 2 (*cont.*)

$CH_3CONHCD_3$ (*cont.*)

Exp.	Calc.		
[11]	A'	A''	Assignment
430/3	430		Skeletal bend
	275		
		181	Amide VII
		144	CH_3 torsion
		101	CD_3 torsion

$CH_3CONDCD_3$

Exp.	Calc.		
[11]	A'	A''	Assignment
1640/6	1647		Amide I
1480/6	1484		Amide II
1432/4	1440		CH_3 as bend
1473/6		1452	CH_3 as bend
1367/2	1365		CH_3 sym bend
1160/3	1167		N—CH_3 stretch
	1065		Amide III
		1056	CH_3 rock
	1045		CD_3 as bend
1041/3		1044	
	1009		CD_3 sym bend
966/4	982		CH_3 rock
	937		C—C stretch
773/3	777		CD_3 rock
890/4		884	
		632	Amide VI
606/3	605		Amide IV
516/4		503	Amide V
428/3	428		Skeletal bend
	274		
		181	Amide VII
		144	CH_3 torsion
		101	CD_3 torsion

$CD_3CONHCD_3$

Exp.	Calc.		
[11]	A'	A''	Assignment
1645/6	1650		Amide I
1555/6	1540		Amide II
1326/2	1323		Amide III
1147/3	1149		N—CH_3 stretch
1098/4	1091		CD_3(CO) sym bend
	1046		C—C stretch
		1048	CD_3(NH) as bend
	1046	1045	CD_3(CO) as bend

$CD_3CONHCD_3$ (*cont.*)

Exp.	Calc.		
[11]	A'	A''	Assignment
1027/3	1015		CD_3(NH) as bend
979/3	969		CD_3(NH) sym bend
911/3		916	CD_3(CO) rock
821/6	826		
		874	CD_3(NH) rock
750/6	746		
716/3		698	Amide V
574/3	570		Amide IV
526/3		534	Amide VI
394/3	392		Skeletal bend
266/3	264		
		175	Amide VII
		109	CD_3 torsion
		96	

$CD_3CONDCD_3$

Exp.	Calc.		
[11]	A'	A''	Assignment
1635/6	1633		Amide I
1473/2	1468		Amide II
1174/6	1184		N—CH_3 stretch
1110/6	1097		CD_3 bend, C—C stretch, and Amide III (strongly mixed)
		1048	
	1047		
	1046		
		1045	
1010/4	1022		
980/4	991		
950/4	931		
912/3		910	CD_3(CO) rock
815/4	825		
		873	CD_3(ND) rock
746/4	741		
573/3	566		Amide IV
		556	Amide VI
506/3		498	Amide V
396/3	390		Skeletal bend
268/3	263		
		175	Amide VII
		109	CD_3 torsion
		96	

quite ambiguous since amide III contributes significantly to several bands in the CH_2 wagging region. On the other hand, the previous notation, where we included the amide III band with the wagging sequence, was rather confusing. Further, we now denote the band at about 940 cm^{-1} as C—C(=O) stretch instead of its previous inclusion with the *S* progression.

There are some frequencies which were not experimentally observed. Of greatest significance is the amide IV in polyamides, whose absence has for a long time been discussed by those studying the infrared spectra of polyamides. The present calculations show the somewhat surprising fact that this mode should lie in the 700 cm^{-1}

region, rather than in the 600 cm^{-1} region where it was expected. In the former region it is masked by the strong amide V band, and in the deuterated molecules an ambiguity occurs as to whether some unpronounced shoulders in the vicinity of R_1 may belong to the remnants of nondeuterated molecules or to a weak amide IV′ band. No amide VI′ band was observed; calculation places it at 604 cm^{-1} in nylons and at 628 cm^{-1} in N-methylacetamide. The bands R_{n-1} in nylons are masked by C—C stretching bands and could not be located with certainty. The dependence of these frequencies on force constants is somewhat similar to that of the 1045 cm^{-1} band of nylon 66, and since the latter is well assigned, we can have some confidence in the calculated values of the former frequencies. No data for skeletal torsions (with the exception of amide VII), and for skeletal bends below 150 cm^{-1}, are available.

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