

Normal Vibrations of Polyglycine II

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Synopsis

A valence force field has been refined for single-chain polyglycine II using the known structure and four isotopic derivatives. The calculated frequencies are in good agreement with the observed. The force field is compared with that derived from polyglycine I and for the nylons.

INTRODUCTION

Normal coordinate calculations of polyglycine II (PG II) have been carried out by Miyazawa and Tsuchida,^{1,2} Small, Fanconi, and Peticolas,³ and Singh and Gupta.⁴ In these calculations, however, only one or two isotopic molecules were treated and/or the CH₂ group was replaced by a single mass.

We have recalculated the normal vibrations of five isotopic species of the PG II chain in the crystal without replacing the CH₂ group by a single mass, and have determined a valence force field in a manner similar to that for the polyglycine I (PG I) crystal in the preceding paper.⁵ The results are presented herein.

CALCULATION OF NORMAL VIBRATIONS

Structure. The X-ray study of Crick and Rich⁶ indicated that PG II is a threefold helical chain which is hydrogen bonded via N—H···O=C' bonds to adjacent chains in the crystal. A small modification regarding the packing of chains was subsequently proposed by Ramachandran, Sasisekharan, and Ramakrishnan.⁷ In this modified structure one third of the C'=O groups are also involved in a C—H···O=C' hydrogen bond. Evidence for such hydrogen bonds was presented in the infrared studies of Krimm, Kuroiwa, and Rebane.^{8,9} It was also noted¹⁰ that antiparallel chain arrangements must exist in the crystal. This requirement was subsequently incorporated into a revised crystal structure.¹¹

The present calculations were done for the parallel-chain structure. The unit cell in this case contains one chain, and thus a single-chain treat-

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ment was adopted. The results are probably very similar for antiparallel chain arrangements. The same structural parameters as given in Table I of the preceding paper⁵ were used. The repeat of the helix is 9.30 Å, which corresponds to bond rotation angles of $\varphi(\text{N}-\text{C}) = -76.89^\circ$ and $\psi(\text{C}-\text{C}') = 145.32^\circ$.

Coordinates and Selection Rules. The internal coordinates and the local symmetry coordinates were defined in the same way as in Tables II and III of the preceding paper,⁵ except for the interchain coordinates which were not considered here.

The optically active symmetry coordinates are classified into two species, A and E, and are given by

$$S(\text{A}) = C \sum_i (\mathbf{S}_I^i + \mathbf{S}_{II}^i + \mathbf{S}_{III}^i) \text{ for the A species } (\delta = 0),$$

$$S^c(\text{E}) = C' \sum_i (2 \cdot \mathbf{S}_I^i - \mathbf{S}_{II}^i - \mathbf{S}_{III}^i), \quad \text{and}$$

$$S^s(\text{E}) = C'' \sum_i (\mathbf{S}_{II}^i - \mathbf{S}_{III}^i) \text{ for the E species } (\delta = \pm 2/3\pi),$$

where \mathbf{S}_I^i , \mathbf{S}_{II}^i , and \mathbf{S}_{III}^i are the vectors consisting of the local symmetry coordinates for the three repeating units, as designated by I, II, and III in Figure 1, of the i th unit cell, δ is the phase angle between neighboring units along a helix, and the C 's are normalization coefficients. The sums are taken over unit cells along a helix. $S^c(\text{E})$ and $S^s(\text{E})$ are a pair of *real* symmetry coordinates for the degenerate species with $\delta = \pm 2/3\pi$, by use of which all numerical calculations can be carried out using real numbers.¹² There are nineteen A species modes and twenty E species modes, all of these being both Raman- and infrared-active.

Valence Force Field. The valence force field of PG II was defined in the same way as for PG I. Since calculations were made for a single chain, seventy-two intrachain force constants out of the seventy-eight constants listed in Table V of the preceding paper were considered here.

The observed frequencies used for adjusting the force constants are considered not to involve the effects of $\text{CH} \cdots \text{O}=\text{C}'$ hydrogen bonding. All chains, however, are assumed to be involved in $\text{N}-\text{H} \cdots \text{O}=\text{C}'$ hydrogen bonding. Therefore, the effects of the latter type of hydrogen bonding are included in the seventy-two intrachain force constants. Although such hydrogen bonding effects depend on temperature,⁹ the force constants determined in the present work correspond to those at room temperature.

Adjustment of Force Constants. The force constants were adjusted so that they give the best fit with the infrared spectra of $-\text{NHCH}_2\text{CO}-$, $-\text{N}^{15}\text{HCH}_2\text{CO}-$, $-\text{NDCH}_2\text{CO}-$, $-\text{NHCD}_2\text{CO}-$, and $-\text{NDCD}_2\text{CO}-$ reported by Suzuki, Iwashita, Shimanouchi, and Tsuboi¹³ and the Raman bands reported by Small et al.³

The assignments of the observed bands adopted here are almost the same as those of previous workers.^{1,3,4,13} Minor modifications were made

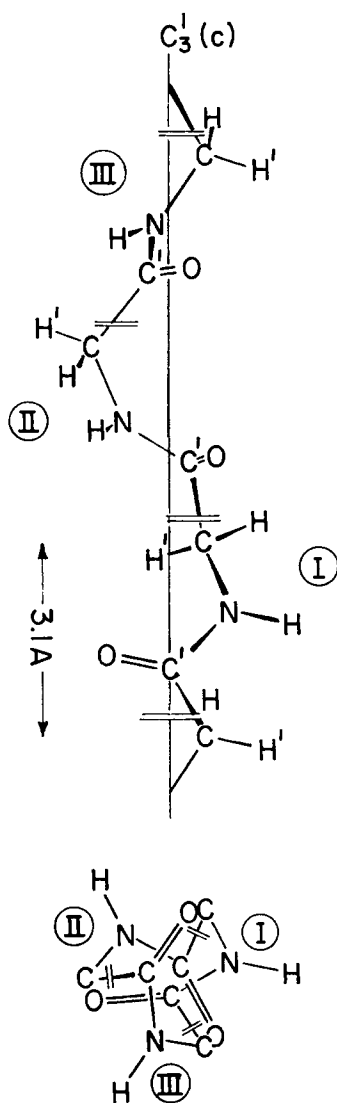


Fig. 1. Structure of the polyglycine II chain.

according to preliminary calculations. For example, the infrared band at 901 cm^{-1} and the Raman band at 884 cm^{-1} of $\text{—NHCH}_2\text{CO—}$, which had been assigned to the CH_2 rocking vibrations, were reassigned to the symmetric stretching vibration of the $\text{N}=\text{C}=\text{O}$ skeleton. This assignment is consistent with the fact that the 884 cm^{-1} Raman band is very strong. The assignment of each band to either the A or the E species was made in such a way that all the assignments were consistent for all the isotopic molecules.

TABLE I
 Force Constants of PGII, PGI, and Nylons

	PGII	PGI ^a	Nylons ¹⁴
1. $f(\text{N}-\text{C})^b$	4.855(0.109) ^c	5.025	5.278
2. $f(\text{C}-\text{C}')$	4.513(0.216)	4.419	5.174
3. $f(\text{C}'-\text{N})$	6.741(0.330)	6.304	6.117
4. $f(\text{C}'=\text{O})$	9.167(0.184)	9.496	8.780
5. $f(\text{N}-\text{H})$	5.992(0.023)	5.998	5.98
6. $f(\text{C}-\text{H})$	4.569(0.012)	4.564	4.545
7. $f(\text{C}'\text{NC})$	0.806(0.160)	1.050	1.475
8. $f(\text{NCC}')$	1.00	1.00	1.028 ^{*d}
9. $f(\text{CC}'\text{N})$	1.40†	1.40	1.045
10. $f(\text{CC}'=\text{O})$	} 1.218(0.111)	1.269	1.331
11. $f(\text{NC}'=\text{O})$			1.495
12. $f(\text{C}'\text{NH})$	} 0.575(0.010)	0.496	0.848
13. $f(\text{CNH})$			0.306
14. $f(\text{NCH})$	0.810(0.039)	0.699	0.728 [*]
15. $f(\text{C}'\text{CH})$	0.693(0.034)	0.673	0.694 [*]
16. $f(\text{HCH})$	0.533(0.014)	0.588	0.553 [*]
17. $f(\text{C}'=\text{O op})$	0.562(0.036)	0.614	0.70
18. $f(\text{N}-\text{H op})$	0.206(0.024)	0.191	0.114
19. $f(\text{N}-\text{C tor})$	0.037	0.037	0.037
20. $f(\text{C}-\text{C}' tor)$	0.037	0.037	0.037
21. $f(\text{C}'-\text{N tor})$	0.604(0.061)	0.598	0.671
22. $f(\text{N}-\text{C}, \text{C}-\text{C}')$	0.3	0.3	0.091
23. $f(\text{C}-\text{C}', \text{C}'-\text{N})$	0.3	0.3	0.638
24. $f(\text{C}'-\text{N}, \text{N}-\text{C})$	0.3	0.3	0.352
25. $f(\text{C}-\text{C}', \text{C}'=\text{O})$	0.5	0.5	0.764
26. $f(\text{C}'-\text{N}, \text{C}'=\text{O})$	0.5	0.5	0.230
27. $f(\text{C}'-\text{N}, \text{C}'\text{NC})$	0.3	0.3	-0.108
28. $f(\text{N}-\text{C}, \text{C}'\text{NC})$	0.3	0.3	0.615
29. $f(\text{N}-\text{C}, \text{NCC}')$	0.3	0.3	0.312
30. $f(\text{C}-\text{C}', \text{NCC}')$	0.3	0.3	0.325
31. $f(\text{C}-\text{C}', \text{CC}'\text{N})$	0.3	0.3	0.021
32. $f(\text{C}'-\text{N}, \text{CC}'\text{N})$	0.3	0.3	0.521
33. $f(\text{C}-\text{C}', \text{CC}'=\text{O})$	0.2	0.2	0.258
34. $f(\text{C}'-\text{N}, \text{NC}'=\text{O})$	0.2	0.2	0.084
35. $f(\text{C}'=\text{O}, \text{CC}'=\text{O})$	0.45	0.45	0.379
36. $f(\text{C}'=\text{O}, \text{NC}'=\text{O})$	0.45	0.45	0.495
37. $f(\text{C}'-\text{N}, \text{C}'\text{NH})$	} 0.232(0.036)	0.298	0.375
38. $f(\text{N}-\text{C}, \text{CNH})$			0.324
39. $f(\text{N}-\text{C}, \text{NCH})$	0.401(0.046)	0.520	0.365
40. $f(\text{N}-\text{C}, \text{C}'\text{CH})$	} 0.005(0.039)	0.044	-0.109
41. $f(\text{C}-\text{C}', \text{NCH})$			-0.073
42. $f(\text{C}-\text{C}', \text{C}'\text{CH})$	0.205(0.062)	0.225	0.207
43. $f(\text{C}'\text{NC}, \text{NCC}')$	0.0	0.0	— ^e
44. $f(\text{NCC}', \text{CC}'\text{N})$	0.0	0.0	—
45. $f(\text{CC}'\text{N}, \text{C}'\text{NC})$	0.0	0.0	0.095
46. $f(\text{NCC}', \text{CC}'=\text{O})$	0.0	0.0	—
47. $f(\text{C}'\text{NC}, \text{NC}'=\text{O})$	0.0	0.0	0.193
48. $f(\text{CC}'\text{N}, \text{C}'\text{NH})$	0.2	0.2	0.213
49. $f(\text{NCC}', \text{CNH})$	-0.1†	-0.1	—

TABLE I (continued)

	PGII	PGI ^a	Nylons ¹⁴
50. $f(\text{C}'\text{NC}, \text{NCH})$	0.0	0.0	-0.010
51. $f(\text{C}'\text{NC}, \text{NCH}')$	0.0	0.0	-0.010
52. $f(\text{CC}'\text{N}, \text{C}'\text{CH})$	0.0	0.0	-0.023
53. $f(\text{CC}'\text{N}, \text{C}'\text{CH}')$	0.0	0.0	-0.023
54. $f(\text{NCH}, \text{NCH}')$	-0.037(0.030)	0.018	-0.013*
55. $f(\text{C}'\text{CH}, \text{C}'\text{CH}')$	0.047(0.033)	-0.022	0.056*
56. $f(\text{NCH}, \text{C}'\text{CH})$	0.093(0.025)	0.022	0.033*
57. $f(\text{NCH}, \text{HCH})$	0.05	0.05	0.046*
58. $f(\text{C}'\text{CH}, \text{HCH})$	0.05	0.05	0.051*
59. $f(\text{NC}'=\text{O}, \text{C}'\text{NH})$	0.140(0.046)	0.238	0.181
60. $f(\text{CC}'=\text{O}, \text{C}'\text{CH})$	0.1†	0.1	0.132
61. $f(\text{CC}'=\text{O}, \text{C}'\text{CH}')$	0.0	0.0	0.132
62. $f(\text{CNH}, \text{NCH})$	0.077(0.030)	0.076	0.056
63. $f(\text{CNH}, \text{NCH}')$	0.002(0.028)	0.068	0.056
64. $f(\text{C}'=\text{O op}, \text{NCC}')$	-0.05†	-0.05	—
65. $f(\text{C}'=\text{O op}, \text{C}'\text{CH})$	0.1†	0.1	0.04
66. $f(\text{C}'=\text{O op}, \text{C}'\text{CH}')$	0.0	0.0	0.04
67. $f(\text{N—H op}, \text{NCC}')$	0.0	0.0	—
68. $f(\text{N—H op}, \text{NCH})$	0.0	0.0	0.00
69. $f(\text{N—H op}, \text{NCH}')$	0.1†	0.1	0.00
70. $f(\text{C}'=\text{O op}, \text{N—H op})$	-0.06†	-0.06	-0.034
71. $f(\text{C}'=\text{O op}, \text{C}'\text{—N tor})$	0.07†	0.07	0.162
72. $f(\text{N—H op}, \text{C}'\text{—N tor})$	-0.08†	-0.08	-0.034

^a Set I-3 of Ref. 5.

^b See Ref. 5 for definitions of these internal coordinates.

^c Numbers in parentheses are the uncertainties in the force constants. The values followed by their uncertainties were obtained by least squares, those marked by † were adjusted by trial and error, and the others were transferred from paraffins and amides (see Ref. 5).

^d The values marked by * are the averages of the corresponding values for the $\text{CCH}_2\text{C}'$ and the NCH_2C groups of nylons.

^e — indicates that the force constant cannot be estimated (note there is no $\text{NHC}_2\text{C}'$ group in nylon- p with $p > 2$).

The force constants were determined following the same procedure as in the preceding paper, ie, thirty-four force constants were fixed to the same value as the corresponding ones of PG I, nine constants were adjusted by trial and error, and twenty-nine constants, of which four pairs were set identical with each other, were refined by least squares.

The final values of the force constants are listed in Table I, together with those of PG I⁵ and the nylons¹⁴ obtained by the single-chain treatment. (Some of the definitions of the coordinates and the force constants adopted in Ref. 14 are different from those in the present work. Their values were modified according to the present definitions and are given in Table I.) The frequencies calculated with the final set of force constants, and the potential energy distributions, are given in Table II. The agreement with the observed frequencies is seen to be quite satisfactory.

TABLE II
Observed and Calculated Frequencies of Polyglycine II (in cm^{-1})

Observed		Calculated		Assignment
A	E	A	E	
1. $\text{-(NHCH}_2\text{C}'\text{O)-}_n$				
	3304(-15) ^a	3297(-8)	3297(-8)	NH str.: 5(99) ^b
	2942	2935(0)	2935(0)	CH ₂ asym. str.: 7(99)
	2858	2859(0)	2859(0)	CH ₂ sym. str.: 6(99)
1654		1648(-4)		Amide I: 3(30) 4(64) 10(10)
	1644(-1)		1646(-3)	3(25) 4(69) 10(11)
	1554(-13)	1566(-12)		Amide II: 2(11) 3(14) 12(63)
			1541(-14)	2(11) 3(20) 12(65)
	1420(-1)	1420(0)		CH ₂ bend: 13(100)
			1423(0)	13(95)
		1377(0)		2(22) 12(15) 14(62)
	1380		1374(-1)	CH ₂ wag 2(21) 12(18) 14(55)
1283(-3)		1290(-4)		+ amide 3(14) 12(12) 14(17)
			1313(-3)	III 15(37)
				+ CH ₂ 3(17) 12(14) 14(38)
1249(-4)		1254(-3)		twist: 1(14) 12(11) 14(12)
				15(42)
	1261		1263(-3)	15(74)
1133		1134(-11)		Skel. str. A ^c 1(55) 2(14)
			1065(-6)	+ CH ₂ 1(33) 16(35)
		1039(-3)		rock: 16(64)
	1028		1024(-7)	1(40) 16(30)
884		883(-4)		Skel. str. B ^d : 2 + 3 + 4(58) 9(11)
	901(-1)		893(-6)	2 + 3 + 4(60)
		758(-9)		9(14) 11(12) 18(35)
				Amide V 21(15)
	740		732(-5)	+ Amide 9(10) 18(43) 21(37)
		704(-3)		IV: 11(17) 18(24) 21(55)
	698(-3)		696(-4)	11(21) 18(11) 21(34)
		566(-2)		Amide VI: 11(14) 17(62)
	570(-2)		563(-3)	16(11) 17(54) 18(11)
340		347(-1)		Skel. def. B ^e : 8(37) 10(11) 11(23)
			492(-5)	Skel. def. A ^f : 10(38) 11(12) 17(18)
272		272(-4)		Amide VII 9(21) 17(21) 18(13)
				+ NCC' 21(10)
	363		357(-4)	def: 9(26) 10(11) 11(14)
				21(10)
217		202(-2)		Skel. def. A: 1(15) 8(19) 10(52)
			250(-2)	Skel. def. B: 8(57) 10(12)
		70(0)		NCC' def. 9(24) 18(25) 20(14)
				21(13)
			82(-1)	+ amide 9(26) 18(27) 19(16)
				VII: 21(12)
			42(0)	Torsion: 19(41) 20(53)

TABLE II (continued)

Observed		Calculated		Assignment
A	E	A	E	
2. $\text{-(NDCH}_2\text{C'O)-}_n$				
	2940	2935	2935	CH ₂ asym. str.: 7(99)
	2858	2859	2859	CH ₂ sym. str.: 6(99)
	2466	2426	2426	ND str.: 5(98)
1640	2417	1643		
	1639	1641		Amide I: 3(27) 4(67) 10(10)
		1479		2(27) 3(29) 4(12)
	1473	1467		Amide II: 11(16) 12(15)
				1(11) 2(31) 3(27) 4(10)
				11(15) 12(11)
1420		1420		CH ₂ bend: 13(100)
	1349	1343	1416	13(94)
1277	1262	1263	1344	CH ₂ wag: 14(84)
1131		1133	1258	CH ₂ twist: 15(80)
				1(48) 2(18)
			1117	Skel. str. A 1(17) 2(16) 12(38)
				+ CH ₂ 16(17)
		1050		rock 12(18) 16(50)
	1032	1022		+ amide 1(22) 15(11) 16(46)
995		996		III: 12(51) 16(18)
	987	986		1(31) 12(39)
875		872		Skel. str. B: 2 + 3 + 4(57) 9(11)
	886	883		2 + 3 + 4(61)
734		732		3(10) 8(14) 9(18)
				11(24) 16(10)
	693	701		Amide IV: 8(11) 9(18) 11(28)
				17(10)
		584		2(10) 11(20) 17(40)
	576	577		Amide VI 18(27)
				+ amide 17(36) 18(16) 21(19)
		519		V: 17(23) 18(27)
	520	522		17(29) 18(47) 21(43)
335		345		Skel. def. B: 8(37) 10(11) 11(22)
			479	Skel. def. A: 10(42) 11(12)
		266		Amide VII
				+ NCC' 9(22) 17(20) 21(16)
	356	350		def.: 9(24) 11(14) 21(17)
		200		Skel. def. A: 1(15) 8(19) 10(52)
			246	Skel. def. B: 8(55) 10(12)
		70		9(24) 18(25)
				NCC' def. 20(14) 21(13)
			81	+ amide 9(27) 18(27)
				VII: 19(16) 21(12)
			41	Torsion: 19(41) 20(53)

(continued)

TABLE II (continued)

Observed		Calculated		Assignment
A	E	A	E	
3. $\text{-(NHCD}_2\text{C'O)-}_n$				
	3290	3297	3297	NH str.: 5(99)
	2172	2197	2196	CD ₂ asym. str.: 7(97)
	2117	2094	2095	CD ₂ sym. str.: 6(97)
		1640		Amide I: 3(30) 4(67) 10(10)
	1639		1639	3(25) 4(71) 10(11)
	1551	1564		Amide II: 2(10) 3(15) 12(63)
			1539	3(21) 12(66)
1309		1318	1349	Amide III: 2(32) 3(13) 11(13)
				12(34)
1205		1208		Skel. str. A 1(65) 14(29)
			1134	+ CD ₂ wag: 1(33) 3(11) 14(49)
	1057	1056	1061	CD ₂ bend: 13(73)
		1015		13(25) 15(17) 16(11)
	1016		1010	CD ₂ bend 8(10) 15(20) 16(21)
		925		+ CD ₂ wag 14(49) 15(13)
920		943	954	+ CD ₂ 1(27) 13(17) 14(16)
		901		twist 15(31) 16(27)
				+ CD ₂ 17(19)
	866		873	rock: 15(51) 16(14)
				17(12)
		807		2 + 3 + 4(37)
				15(17) 16(11)
			808	Skel. str. B: 2 + 3 + 4(29)
				14(12) 16(24)
		716		Amide V: 15(11) 18(48) 21(50)
	715		717	20(43) 21(50)
		673		9(10) 11(28) 16(21)
				21(19)
	670		663	Amide IV: 9(13) 11(21) 15(14)
				17(11) 21(17)
		530		2(10) 15(11) 16(12)
				17(52)
	502		511	Amide VI: 10(10) 14(10) 16(15)
				17(41) 18(11)
		323		Skel. def. B: 8(33) 9(14) 10(12)
				11(27)
			466	Skel. def. A: 10(27) 11(16) 17(16)
		254		Amide VII
				+ NCC' 9(14) 17(19) 18(16)
	347		337	def.: 9(28) 10(14) 11(11)
		199		Skel. def. A: 1(14) 8(19) 10(51)
			232	Skel. def. B: 8(61) 10(13)
		69		NCC' def. 9(24) 18(25) 20(14)
				21(13)
			79	+ amide 9(26) 18(27) 19(17)
				VII: 21(11)
			41	Torsion: 19(40) 20(53)

TABLE II (continued)

Observed		Calculated		Assignment
A	E	A	E	
4. $\text{-(NDCD}_2\text{C'O)-}_n$				
	2485			
	2451	2426	2426	ND str.: 5(97)
	2417			
	2173	2196	2196	CD ₂ asym. str.: 7(97)
	2108	2094	2095	CD ₂ sym. str.: 6(97)
	1632	1635	1634	Amide I: 3(27) 4(70) 10(10)
		1471		2(25) 3(33) 11(17)
	1462		1460	Amide II: 12(16)
				1(14) 2(29) 3(33) 11(18)
1222		1233		12(13)
			1171	Skel. str. A 1(57) 2(26) 14(33)
				+ CD ₂ wag: 1(23) 2(23) 12(23)
		1061		14(36)
	1065		1066	CD ₂ bend: 13(68)
		1005		13(57) 14(15)
	1034		1029	12(23) 13(27)
993		990		Amide III 12(38) 13(23) 14(17)
			988	12(46) 14(16) 15(10)
				+ CD ₂ 15(24) 16(17)
917		920		wag 14(43) 15(23)
	935		928	+ CD ₂ 1(25) 12(13)
		895		twist 15(22) 16(30) 17(20)
	866		869	+ CD ₂ 15(50) 16(17) 17(13)
		803		rock 2 + 3 + 4(39)
	794		801	+ skel. 15(20)
				str. B: 2 + 3 + 4(31)
		673		14(12) 16(24)
	667		667	Amide IV: 3(10) 9(12) 11(26)
		554		16(23)
				9(16) 11(24) 15(13)
	534		549	Amide V 11(13) 15(11) 17(18)
		508		18(44) 21(23)
	497		494	+ amide 17(11) 18(30) 21(45)
				VI: 17(36) 21(52)
		320		16(19) 17(43) 18(32)
				21(15)
			456	Skel. def. B: 8(34) 9(12) 10(12)
				11(25)
		249		Skel. def. A: 10(33) 11(13)
	345		330	Amide VII 9(15) 17(19) 18(12)
				+ NCC' 21(14)
				def.: 9(27) 10(12) 13(11)
		197		21(16)
			229	Skel. def. A: 1(14) 8(20) 10(51)
				Skel. def. B: 8(60) 10(13)

(continued)

TABLE II (continued)

Observed		Calculated		Assignment
A	E	A	E	
		68		NCC' def. 9(24) 18(25) 20(14) + 21(12)
			78	Amide VII: 9(26) 18(26) 19(17) 21(12)
			41	Torsion: 19(40) 20(53)

^a $() = \nu(\text{N}^{15}) - \nu(\text{N}^{14})$.

^b The first number refers to the symmetry coordinate (see Table III of Ref. 5 for a detailed description of these coordinates), the number in parenthesis to the fractional potential energy in this coordinate (if it is 10 or greater). Qualitatively, the symmetry coordinates are: 1: N-C str.; 2: C-C' str.; 3: C'-N str.; 4: C'=O str.; 5: N-H str.; 6: CH₂ sym. str.; 7: CH₂ asym. str.; 8: C'NC def.; 9: NCC' def.; 10: CC'N def.; 11: C=O ip bend; 12: N-H ip bend; 13: CH₂ bend; 14: CH₂ wag; 15: CH₂ twist; 16: CH₂ rock; 17: C=O op bend; 18: N-H op bend; 19: N-C tor; 20: C-C' tor; 21: C'-N tor.

^c Skeletal stretch A is mainly the N-C stretching vibration.

^d Skeletal stretch B is mainly a symmetric stretching vibration of the C-C'-N skeleton.

^e Skeletal deformation B is mainly the C'NC deformation vibration slightly mixed with the CC'N deformation.

^f Skeletal deformation A is mainly the CC'N deformation vibration slightly mixed with the C'NC deformation.

DISCUSSION

The potential energy distributions of the modes of PG II show that extensive mixing occurs. In particular, it is seen that for $\rightarrow\text{NHCH}_2\text{C}'\text{O}\leftarrow_n$ the CH₂ wagging and twisting vibrations are mixed with the amide III mode to an even greater extent than in the case of PG I. For other isotopic species amide III is relatively pure (cf, $\rightarrow\text{NHCD}_2\text{C}'\text{O}\leftarrow_n$) or even more extensively mixed with other modes (cf, $\rightarrow\text{NDCD}_2\text{C}'\text{O}\leftarrow_n$).

Force constants for the hydrogen-bonded CH₂ group were estimated by Krimm et al.⁸ from an approximate calculation on a CH₂...O system. It was found that the CH₂ stretching frequencies observed at 2980 and 2800 cm⁻¹ for the hydrogen-bonded group could be reproduced by changing the force constant $f(\text{C}-\text{H})$ by +6% for the free C-H and by -6% for the hydrogen-bonded C-H, and that the -14 cm⁻¹ shift of the CH₂ bending vibration could be explained by a 3% decrease in $f(\text{HCH})$. We have repeated this calculation using the entire chain and the complete force field. Again a 6% change in $f(\text{C}-\text{H})$, i.e., $f'(\text{C}-\text{H}) = 4.843$ and $f'(\text{C}-\text{H}_0) = 4.295$ md/Å, gives $\nu'(\text{C}-\text{H}) = 2991$ and $\nu'(\text{C}-\text{H}_0) = 2801$ cm⁻¹, where the primed quantities pertain to the hydrogen-bonded CH₂ group and H₀ is the hydrogen in C-H...O. The shift in the CH₂ bending frequency is given by $\Delta\nu \cong 586 (\Delta f(\text{HCH})/f(\text{HCH}))$. The observed shift of -14 cm⁻¹ corresponds to a 2.4% decrease in $f(\text{HCH})$.

In evaluating the differences in force constants between PG II and PG I, as listed in Table I, the following facts should be kept in mind. First, the force constants were determined using a single-chain treatment, and they therefore include the effects of interchain $\text{N}-\text{H}\cdots\text{O}=\text{C}'$ hydrogen bonding. These effects are probably different for PG II than for PG I. Second, the bond rotation angle $\varphi(\text{N}-\text{C})$ differs from PG II ($\varphi = -77^\circ$) to PG I ($\varphi = -140^\circ$). This can influence the force constants somewhat.¹⁵ Third, some force constants have large uncertainties due to the interdependence of force constants.

The differences in values of $f(\text{C}'\text{NH}) \equiv f(\text{CNH})$, $f(\text{C}'=\text{O op})$, $f(\text{C}'-\text{N}, \text{C}'\text{NH}) \equiv f(\text{NC}, \text{CNH})$, and $f(\text{NC}'=\text{O}, \text{C}'\text{NH})$ between PG I and PG II are probably due to differences in hydrogen bonding, which directly affect these force constants. The difference in $f(\text{C}'\text{NC})$ may be due to the same reason, since the $\text{C}'\text{NC}$ deformation vibration is considerably coupled with the $\text{H}\cdots\text{O}$ stretching vibration, as was seen in the case of PG I.⁵ The difference in $f(\text{NCH})$ and in $f(\text{NC}, \text{NCH})$ between PG I and PG II may be due to the different bond rotation angles $\varphi(\text{N}-\text{C})$. Actually, the diagonal term $f(\text{NCH})$ should itself not be very different, and some other force constants, probably interaction constants between the CH_2 group and the neighboring NH group, perhaps account for the effects of rotation about the $\text{N}-\text{C}$ bond. Unfortunately, not enough experimental data were available, and we had to assume the same values for most of the interaction constants of both PG I and PG II. The force constant $f(\text{HCH})$ of PG II is smaller than that of PG I by $\sim 10\%$. As mentioned above, the effect of hydrogen bonding on $f(\text{HCH})$ accounts for only a 2.4% decrease. The remainder may be due to some difference in the environment of the CH_2 group itself between PG I and PG II, for example, associated with intermolecular interactions.

Some differences in the force constants between PG I or PG II and the nylons may arise from the same reasons as given above. In this case, the correlation of force constants also enters in. For example, for the nylons $f(\text{C}'\text{NH}) = 0.848$ and $f(\text{CNH}) = 0.306$, the average of which is 0.572 and is very close to the value for PG II.

Two problems may bear further examination. One concerns the assignment of amide III of $(-\text{NHCH}_2\text{C}'\text{O})_n$. Three possible assignments for the three bands observed at 1283, 1261, and 1247 cm^{-1} suggest themselves, as shown in Table III. Assignment 1 is the one used in the present calculation. The force constants were also determined for assignments 2 and 3. For assignment 2 $f(\text{C}'\text{N}) = 6.949$, $f(\text{C}'\text{NH}) \equiv f(\text{CNH}) = 0.557$, and $f(\text{C}'\text{N}, \text{C}'\text{NH}) \equiv f(\text{NC}, \text{CNH}) = 0.251$ were obtained, and for assignment 3 these constants were 6.597, 0.573, and 0.211, respectively. There are reasons to believe that the first assignment is the most probable one. First, in the infrared spectra of the model compounds $\text{CH}_3\text{CO}(\text{NHCH}_2\text{CO})_n\text{NHCH}_3$ and $\text{CH}_3\text{CO}(\text{NHCH}_2\text{CO})_n\text{NHC}_2\text{H}_5$,^{16,17} two amide III bands are observed at ca 1305 and 1285 cm^{-1} . In most cases the amide III frequency of the A species is calculated at a lower value than

TABLE III
Possible Assignments^a for Amide III of $\text{-(NHCH}_2\text{C}'\text{O)-}_n$

	A	E
<i>Assignment 1</i>		
Amide III	$\left\{ \begin{array}{l} 1283(\text{IR}) \\ 1283(\text{R}) \\ 1249(\text{IR}) \\ 1244(\text{R}) \end{array} \right.$?
CH ₂ twist.		1261(R)
<i>Assignment 2</i>		
Amide III	$\left\{ \begin{array}{l} 1261(\text{R}) \\ 1249(\text{IR}) \\ 1244(\text{R}) \end{array} \right.$	$\left\{ \begin{array}{l} 1283(\text{IR}) \\ 1283(\text{R}) \\ 1249(\text{IR}) \\ 1244(\text{R}) \end{array} \right.$
CH ₂ twist.		
<i>Assignment 3</i>		
Amide III	$\left\{ \begin{array}{l} 1283(\text{IR}) \\ 1283(\text{R}) \\ 1249(\text{IR}) \\ 1244(\text{R}) \end{array} \right.$	$\left\{ \begin{array}{l} 1283(\text{IR}) \\ 1283(\text{R}) \\ 1261(\text{R}) \end{array} \right.$
CH ₂ twist.		

^a IR, observed infrared bands; R, observed Raman bands.

that of the E species. Accordingly, the 1283 cm⁻¹ band of PG II should be assigned to the A species rather than the E species. Secondly the calculated frequencies using the force constants based on assignments 2 or 3 are not in as good agreement with the observed values as for assignment 1. While we therefore favor it, more experimental evidence may still be needed in order to establish this assignment conclusively.

The second problem is that we could not determine many of the force constants for the skeletal vibrations, and we had to assume approximate values for these. This problem is not particular to polyglycine, but rather is common to all molecules of relatively large size. Experimental data on frequency shifts due to isotopic substitution of skeletal atoms is required in order to solve the problem, since isotopic substitution of the pendant atoms does not yield observably different skeletal frequencies.

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