BIOPOLYMERS VOL. 11, 1817–1839 (1972)

Normal Vibrations of Crystalline Polyglycine I

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Synopsis

A valence force field has been refined for crystalline polyglycine I using its known antiparallel chain pleated-sheet structure and without replacing the CH_2 group by a point mass. Polyglycine I and four of its isotopic derivatives were used in the refinement. The calculated frequencies are in good agreement with the observed, except for the amide I modes. It is shown that this is a consequence of the fact that no reasonable force field predicts a large D_{10} term of the Miyazawa perturbation treatment. The amide I splittings can, however, be satisfactorily accounted for by introducing a direct interaction force constant between adjacent C=O groups in neighboring chains. This can reasonably arise from transition dipole coupling and corresponds to the heretofore neglected D_{11} term.

INTRODUCTION

There have been many studies of the vibrational spectra of polyglycine, $-\!\!\left(NHCH_2CO\right)\!\!-_n$, the simplest member of the polypeptides, $-\!\!\left(NHCHRCO\right)\!\!-_n$, and of the polyamides $-\!\!\left(NH[CH_2]_mCO\right)\!\!-_n$ as well. The existence of two rotational-isomeric structures in the crystalline state was first suggested by Elliott and Malcolm from their infrared study.[1] They named one form, which is obtained by casting from haloacetic acid solutions, polyglycine I (PG I) and the other, obtained by precipitation from an aqueous solution saturated with LiBr, polyglycine II (PG II). The dichroism of the infrared bands of PG I, of which oriented samples are readily obtainable, was also measured by them. The far infrared region was studied by Miyazawa,[2] who found large spectral differences between PG I and PG II. The most comprehensive infrared data on various isotopic molecules such as —$NHCH_2CO$—, —$N^{15}HCH_2CO$—, —$NDCH_2CO$—, —$NHCD_2CO$—, and —$NDCD_2CO$— were reported by Suzuki et al.[3] Krimm and Kuroiwa analyzed low-temperature infrared spectra in relation to N—H---O=C′ and C—H---O=C′ hydrogen bonding.[4] Raman data were reported recently by Smith et al.[5] and by Small et al.[6] Inelastic neutron scattering has been measured by Gupta et al.[7,8] Infrared and Raman studies on oligomers and model compounds have been undertaken by several workers.[5,9–11]

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Theoretical calculations of normal vibrations of polyglycines have also been carried out. However, most of these calculations are incomplete, in the sense that they were done on only one or two isotopic molecules and/or approximate structures. In addition, limited Urey-Bradley force fields were employed in the calculations. When compared with the abundance of experimental data mentioned above, a more refined calculation is clearly justifiable. As an extension of the recent study on the valence force field of the amide group,[12,13] we have recalculated the normal vibrations of various isotopic molecules of crystalline PG I and of the PG II single chain, and have determined their valence force fields using the actual structures. The results on PG I are reported here and those on PG II in the following paper.

The normal vibrations of the PG I single chain were first treated by Fukushima et al.[14,15] and then by Gupta et al.[7] Fukushima and Miyazawa also treated the PG I crystal consisting of antiparallel chains.[15,16] In all of these calculations the CH_2 group was approximated by a single mass and the chain conformation was assumed to be planar. The present calculations were done on the actual conformation determined by X-ray diffraction studies, and without replacing the CH_2 group by a single mass.

EXPERIMENTAL

Far infrared spectra of PG I in the 500–200 cm^{-1} region were obtained using Beckman IR 12 and Perkin-Elmer 180 spectrometers. The sample, from Sigma Chemical Company (molecular weight $\cong$6,000), was purified by precipitating from a 1% solution of saturared aqueous LiBr. It was then dissolved in dichloroacetic acid or trifluoroacetic acid and cast on polyethylene film. The film was folded over and pressed under ca 18,000 psi. Three bands were found at 321 (very weak), 270 (broad and weak), and at 217 cm^{-1} (medium). The band at 413 cm^{-1} reported by Gupta et al.[7] was found in the unpurified sample, but disappeared upon purification.

CALCULATION OF NORMAL VIBRATIONS

The following normal coordinate treatment was carried out using the GF-matrix method[17] modified for crystals and polymeric chains.[18] The computations were done using PDP-10 and IBM 360 computers.

Crystal Structure

According to X-ray diffraction studies,[19,20] the unit cell of PG I contains pleated sheet antiparallel chains and consists of four asymmetric units (peptide groups). The crystal structure and the dimensions adopted in the present calculations are shown in Figure 1. The structural parameters[21] are listed in Table I. The translation along the chain axis was taken as 3.45 Å per peptide group, which corresponds to bond rotation angles of φ(N–C) = $-140.15°$ and ψ(C–C′) = 135.88°. The distance between the two neighboring chain axes in a sheet was taken as 4.70 Å.

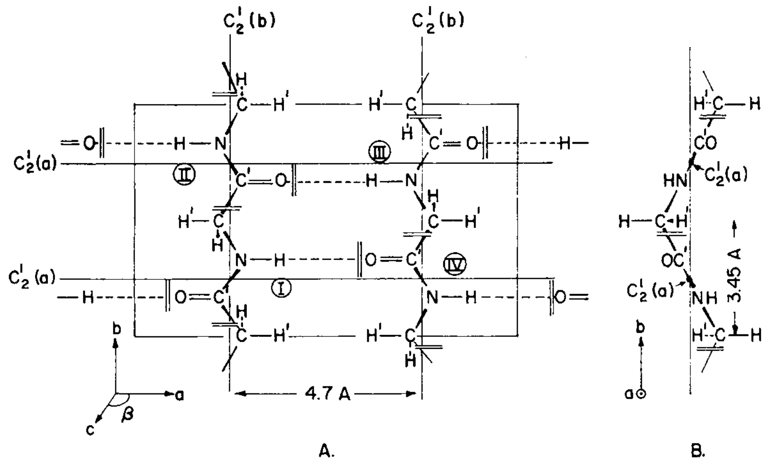


Fig. 1. Structure of crystalline polyglycine I: (A) projected on the *ab* plane, (B) projected along the *a* axis.

TABLE I

Structural Parameters for Polyglycine[21]

Bond lengths (in Å)	
$r(C—C') = 1.53$	$r(C'=O) = 1.24$
$r(C'—N) = 1.32$	$r(C—H) = 1.07$
$r(N—C) = 1.47$	$r(N—H) = 1.00$
Bond angles	
$\angle C—C'—N = 114°$	$\angle C—C'=O = 121°$
$\angle C'—N—C = 123°$	$\angle C'—N—H = 123°$
$\angle N—C—C'$ = tetrahedral	$\angle N—C—H = C'—C—H$ = tetrahedral

The only interchain interaction considered in the calculations was the N—H---O=C′ hydrogen bond. Accordingly, the distance between neighboring sheets, that is the dimension along the *c* axis, and the magnitude of the angle β of the monoclinic unit cell are of no importance. It was assumed that a given peptide group and the peptide group to which it is hydrogen bonded lie in the same plane together with the hydrogen bonds. In other words, the *b* and *c* coordinates of the methylene carbon of unit I are assumed to be the same as those of unit III in Figure 1. For this structure the angles C′=O---H and N—H---O are 175.5° and 176.0°, respectively, C′=O---H—N being almost linear.

Internal Coordinates and Local Symmetry Coordinates

Internal coordinates for a peptide group of crystalline PG I are given in Table II. In this table, Δr and $\Delta\theta$ are increases in bond length and bond angle, respectively; $\Delta\gamma_{\parallel}$ and $\Delta\gamma_{\perp}$ are a pair of bending coordinates per-

TABLE II
Internal Coordinates for One Peptide Group of Crystalline Polyglycine I

$R_1 = \Delta r(\mathrm{C{-}C'})$
$R_2 = \Delta r(\mathrm{C'{-}N})$
$R_3 = \Delta r(\mathrm{N{-}C})$
$R_4 = \Delta r(\mathrm{C'{=}O})$
$R_5 = \Delta r(\mathrm{N{-}H})$
$R_6 = \Delta r(\mathrm{C{-}H})$
$R_7 = \Delta r(\mathrm{C{-}H'})$
$R_8 = \Delta r(\mathrm{H\cdots O})$
$R_9 = \Delta\theta(\mathrm{C{-}C'{-}N})$
$R_{10} = \Delta\theta(\mathrm{C'{-}N{-}C})$
$R_{11} = \Delta\theta(\mathrm{N{-}C{-}C'})$
$R_{12} = \Delta\theta(\mathrm{C{-}C'{=}O})$
$R_{13} = \Delta\theta(\mathrm{N{-}C'{=}O})$
$R_{14} = \Delta\theta(\mathrm{C'{-}N{-}H})$
$R_{15} = \Delta\theta(\mathrm{C{-}N{-}H})$
$R_{16} = \Delta\theta(\mathrm{N{-}C{-}H})$
$R_{17} = \Delta\theta(\mathrm{N{-}C{-}H'})$
$R_{18} = \Delta\theta(\mathrm{C'{-}C{-}H})$
$R_{19} = \Delta\theta(\mathrm{C'{-}C{-}H'})$
$R_{20} = \Delta\theta(\mathrm{H{-}C{-}H'})$
$R_{21} = \Delta\gamma_{\parallel}(\mathrm{C'{=}O\cdots H})$
$R_{22} = \Delta\gamma_{\perp}(\mathrm{C'{=}O\cdots H})$
$R_{23} = \Delta\gamma_{\parallel}(\mathrm{N{-}H\cdots O})$
$R_{24} = \Delta\gamma_{\perp}(\mathrm{N{-}H\cdots O})$
$R_{25} = \Delta\omega\left(\mathrm{O{=}C'}\begin{smallmatrix}\diagup\mathrm{N}\\ \diagdown\mathrm{C}\end{smallmatrix}\right)$
$R_{26} = \Delta\omega\left(\mathrm{H{-}N}\begin{smallmatrix}\diagup\mathrm{C'}\\ \diagdown\mathrm{C}\end{smallmatrix}\right)$
$R_{27} = \Delta t(\mathrm{C{-}C'})$
$R_{28} = \Delta t(\mathrm{C'{-}N})$
$R_{29} = \Delta t(\mathrm{N{-}C})$

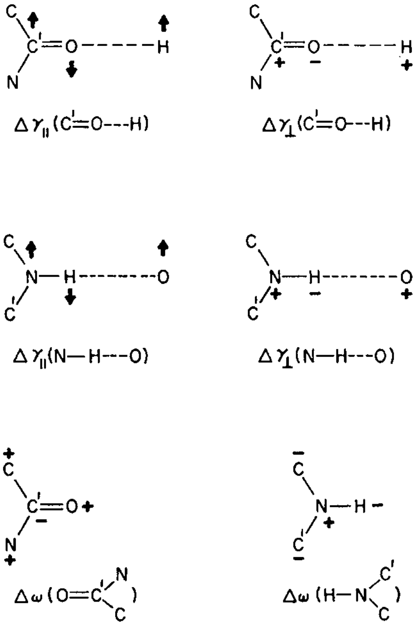


Fig. 2. Definitions of positive directions for some internal coordinates.

pendicular to each other for a linear group such as N–H– – –O;[22] $\Delta\omega$ is an out-of-plane bending coordinate for a trigonal planar group $\mathrm{B{-}A}\begin{smallmatrix}\diagup\mathrm{C}\\ \diagdown\mathrm{D}\end{smallmatrix}$, defined by $\Delta\omega = \Delta\alpha_{\mathrm{B}} \sin(\angle\mathrm{C{-}A{-}D})$ where $\Delta\alpha_{\mathrm{B}}$ is a displacement of the bond B–A from the plane C–A–D; and Δt is the sum of all torsional coordinates associated with a bond divided by the number of terms in the sum[23] (e.g., $\Delta t = (\Delta\tau_{\mathrm{CC'NC}} + \Delta\tau_{\mathrm{CC'NH}} + \Delta\tau_{\mathrm{OC'NC}} + \Delta\tau_{\mathrm{OC'NH}})/4$ for the C′–N bond, $\Delta\tau_{\mathrm{ABCD}}$ being the increase in the torsional angle for AB—CD

TABLE III

Local Symmetry Coordinates[a] for One Peptide Group of Crystalline Polyglycine I

$S_1 = R_3$	N—C stretch
$S_2 = R_1$	C—C′ stretch
$S_3 = R_2$	C′—N stretch
$S_4 = R_4$	C′=O stretch
$S_5 = R_5$	N—H stretch
$S_6 = (R_6 + R_7)/2^{1/2}$	CH_2 sym. stretch
$S_7 = (R_6 - R_7)12^{1/2}$	CH_2 asym. stretch
$S_8 = (2 \cdot R_{10} - R_{14} - R_{15})/6^{1/2}$	C′NC deform.
$S_9 = (5 \cdot R_{11} - R_{16} - R_{17} - R_{18} - R_{19} - R_{20})/30^{1/2}$	NCC′ deform.
$S_{10} = (2 \cdot R_9 - R_{12} - R_{13})/6^{1/2}$	CC′N deform.
$S_{11} = (R_{12} - R_{13})/2^{1/2}$	C′=O ip bend
$S_{12} = (R_{14} - R_{15})/2^{1/2}$	N—H ip bend
$S_{13} = (4 \cdot R_{20} - R_{16} - R_{17} - R_{18} - R_{19})/20^{1/2}$	CH_2 bend
$S_{14} = (R_{16} + R_{17} - R_{18} - R_{19})/2$	CH_2 wag
$S_{15} = (R_{16} - R_{17} - R_{18} + R_{19})/2$	CH_2 twist
$S_{16} = (R_{16} - R_{17} + R_{18} - R_{19})/2$	CH_2 rock
$S_{17} = R_{25}$	C′=O op bend
$S_{18} = R_{26}$	N—H op bend
$S_{19} = R_{29}$	N—C torsion
$S_{20} = R_{27}$	C—C′ torsion
$S_{21} = R_{28}$	C′—N torsion
$S_{22} = R_8$	H· · ·O stretch
$S_{23} = R_{21}$	C′=O· · ·H ip bend
$S_{24} = R_{22}$	C′=O· · ·H op bend
$S_{25} = R_{23}$	N—H· · ·O ip bend
$S_{26} = R_{24}$	N—H· · ·O op bend

[a] Here ip denotes vibrations in the plane of the amide group and op denotes those perpendicular to this plane.

measured in the clockwise direction). Positive directions for the linear bending and the out-of-plane bending coordinates were defined as shown in Figure 2. Local symmetry coordinates for one peptide group, which are constructed from the internal coordinates defined above, are given in Table III.

Optically Active Symmetry Coordinates and Selection Rules

The optically active symmetry coordinates for the whole crystal are classified into four symmetry species, A, B_1, B_2, and B_3. These are shown in Table IV, which was taken from Ref. 15. The symmetry coordinates for each species are given by

$$\begin{aligned} S(A) &= c \sum_i (S_I^i + S_{II}^i + S_{III}^i + S_{IV}^i) \\ S(B_1) &= c \sum_i (S_I^i + S_{II}^i - S_{III}^i - S_{IV}^i) \\ S(B_2) &= c \sum_i (S_I^i - S_{II}^i - S_{III}^i + S_{IV}^i) \\ S(B_3) &= c \sum_i (S_I^i - S_{II}^i - S_{III}^i - S_{IV}^i) \end{aligned} \qquad (1)$$

TABLE IV

Symmetry Species and Selection Rules for Crystalline Polyglycine I[15]

Species	Phase differences[a]	Symmetry[b] C_2^1(a)	Symmetry[b] C_2^1(b)	Number of modes	Selection rules Raman	Selection rules Infrared[c]
A	(0,0)	+	+	21	active	inactive
B_1	$(0,\pi)$	−	+	20	active	active (‖)
B_2	$(\pi,0)$	+	−	20	active	active (⊥)
B_3	(π,π)	−	−	20	active	active (⊥)

[a] The first and the second variables are the phase angles between intrachain and interchain peptide group motions, respectively.

[b] The plus and minus signs indicate that the vibrations are symmetric and antisymmetric, respectively, with respect to the symmetry element.

[c] The ‖ and ⊥ signs indicate parallel and perpendicular dichroism, respectively.

where S_{I}^{i}, S_{II}^{i}, S_{III}^{i}, and S_{IV}^{i} are vectors consisting of the local symmetry coordinates defined by Table III for the peptide groups (I, II, III, and IV as designated in Fig. 1) of the *i*th unit cell. The sums are taken over all unit cells, and *c* is a normalization factor.

Selection rules and the dichroic nature of the infrared bands are also given in Table IV.

Valence Force Field

Force constants corresponding to the following types of potential energy terms were considered in the present calculations (see Fig. 3).

1. Potential energy for each internal coordinate:

$$V(a) = {}^1/_2 f(a)\cdot(\Delta a)^2 \qquad (2)$$

where $\Delta a = \Delta r$, $\Delta\theta$, $\Delta\gamma$, $\Delta\omega$, or Δt given in Table II, and $V(a)$ and $f(a)$ are the relevant potential energy and force constant, respectively. Similar notations are used in the following. (The units of $f(a)$ are mdyn/Å for the stretching coordinate and mdyn-Å for the other coordinates).

2. Interaction energy between the bond stretching coordinates for a pair of bonds which share a common atom:

$$V(r_1, r_2) = f(r_1, r_2)\cdot\Delta r_1\cdot\Delta r_2 \qquad (3)$$

($f(r_1,r_2)$ is in units of mdyn/Å).

3. Interaction energy between the bending coordinate for a bond angle and the stretching coordinate for a bond attached to the apex atom of the angle:

$$V(\Delta r,\Delta\theta) = f(r,\theta)\cdot\Delta r\cdot\Delta\theta \qquad (4)$$

($f(r,\theta)$ is in units of mdyn).

4. Interaction energy between the bending coordinates for a pair of bond angles; between the out-of-plane bending coordinates for a pair of trigonal planar groups; or between the bending coordinate for a bond angle and the

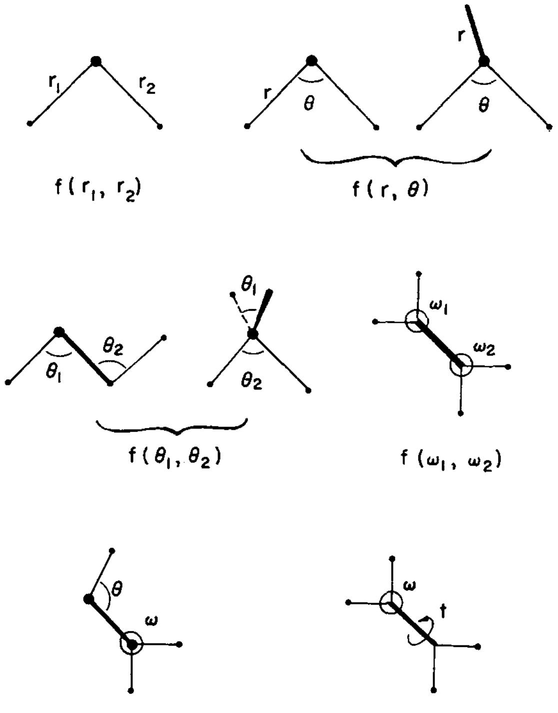


Fig. 3. Definitions of interaction force constants.

out-of-plane bending coordinate for a planar group which share a common bond and/or a common apex atom:

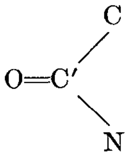
$$V(\theta_1,\theta_2) = f(\theta_1,\theta_2)\Delta\cdot\theta_1\cdot\Delta\theta_2,$$

$$V(\omega_1,\omega_2) = f(\omega_1,\omega_2)\cdot\Delta\omega_1\cdot\Delta\omega_2, \quad \text{or} \tag{5}$$

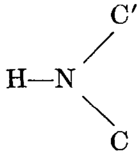
$$V(\theta,\omega) = f(\theta,\omega)\cdot\Delta\theta\cdot\Delta\omega.$$

(the f's in Eq. (5) are in units of mdyn-Å).

5. Interaction energy between the torsional coordinate for a C′–N bond and each of the out-of-plane bending coordinates for the



and

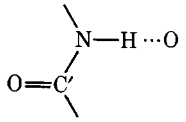


groups attached to the C′–N bond:

$$V(\omega,t) = f(\omega,t)\cdot\Delta\omega\cdot\Delta t \tag{6}$$

($f(\omega,t)$ is in units of mdyn-Å).

No interaction terms were considered for the interchain coordinates except for the one between the C′=O stretching and O---H stretching coordinates in the following part of the structure[15,16]:



The interaction energy between the C–H or N–H stretching coordinate and any other coordinate was also neglected.

Since the angle bending coordinates adopted for the C—C′O—N, C′—NH—C, and N—CH_2—C′ groups are not all independent, the force constants introduced above are not all independent. Instead, only a certain number of linear combinations are independent. The potential energy matrix based on the symmetry coordinates, for which the local redundancies in each of the above three groups are removed, must be expressed in terms of such independent linear combinations only. For example, we do not need the six force constants $f(\mathrm{CC'N})$, $f(\mathrm{CC'{=}O})$, $f(\mathrm{NC'{=}O})$, $f(\mathrm{CC'N,CC'{=}O})$, $f(\mathrm{CC'N,NC'{=}O})$, and $f(\mathrm{CC'{=}O,NC'{=}O})$ for the C—C′O—N group, but only the following three linear combinations:

$$f(\mathrm{CC'N}) - f(\mathrm{CC'N,CC'{=}O}) - f(\mathrm{CC'N,NC'{=}O}) + f(\mathrm{CC'{=}O,NC'{=}O}),$$

$$f(\mathrm{CC'{=}O}) - f(\mathrm{CC'N,CC'{=}O}) + f(\mathrm{CC'N,NC'{=}O}) - f(\mathrm{CC'{=}O,NC'{=}O}),$$

and

$$f(\mathrm{NC'{=}O}) + f(\mathrm{CC'N,CC'{=}O}) - f(\mathrm{CC'N,NC'{=}O}) - f(\mathrm{CC'{=}O,NC'{=}O}).$$

We have taken the above linear combinations as force constants, and represented them by $f(\mathrm{CC'N})$, $f(\mathrm{CC'{=}O})$, and $f(\mathrm{NC'{=}O})$, respectively. That is, the force constants $f(\mathrm{CC'N})$ etc used hereafter include some minor interaction terms such as $f(\mathrm{CC'N,CC'{=}O})$. Similar modifications were made for the force constants of the C′—NH—C and N—CH_2—C′ groups. As a result, the seventy-eight force constants listed in Table V were adopted for the PG I crystal.

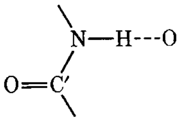
The interdependence of force constants described above comes from geometrical features. Isotopic substitution does not affect it.

Adjustment of Force Constants

The force constants were adjusted by considering (a) the infrared data of —$NHCH_2CO$—, $N^{15}HCH_2CO$—, —$NDCH_2CO$—, —$NHCD_2CO$—, and —$NDCD_2CO$— reported by Suzuki, Iwashita, Shimanouchi, and Tsuboi,[3] (b) the far infrared data on —$NHCH_2CO$— obtained in the present work, and (c) the Raman data on —$NHCH_2CO$— reported by Small, Fanconi, and Peticolas.[6]

Our assignments of observed bands are almost the same as those for a single chain in the previous studies.[3,6,7,14,16] The infrared bands were assigned to B_1 modes, B_2 modes, and/or B_3 out-of-plane modes, since A modes are infrared-inactive and B_3 in-plane modes are expected to be very weak in the infrared spectrum (as pointed out by Fukushima, Ideguchi, and Miyazawa[14]). The infrared dichroism data of Elliott and Malcolm[1] were also considered, and all of the assignments were made consistent for all isotopic molecules. The Raman bands of $—NHCH_2CO—$ were assigned in a similar way.

Values for the interchain force constants were chosen in the following way. A broad band centered at ca 140 cm^{-1} was observed by Krimm and Kuroiwa,[24] and also reported by Gupta, Trevino, and Boutin.[7] Similar bands were observed in the 110 $\sim$ 130 cm^{-1} region for several poly-(-α-amino acids) in the β-form by Itoh, Shimanouchi, and Oya.[25] These bands were assigned to the translational lattice vibration of the B_3 species, which is approximately the O---H stretching vibration. From the observed frequency of ca 140 cm^{-1}, f(O---H str.) = 0.2 mdyn/Å was derived. The bending force constants for the C′═O---H and N—H---O groups were transferred from *N*-methylacetamide studied by Itoh and Shimanouchi.[26] The interaction force constant f(C′═O str., O---H str.) in the structure below was introduced by Fukushima and Miyazawa[16] in



order to reproduce the $\nu(0,\pi) - \nu(\pi,0)$ splitting of the amide I frequencies. (Such an interaction term is probably physically justifiable, since the resonant nature of the peptide group implies that changes in the C′═O bond will influence the electronic distribution in the N—H bond, which in turn will affect the H---O stretching vibration). In the present calculations two values were assumed, 0.0 and 0.45 mdyn/Å, the latter having been used by Fukushima and Miyazawa.

With respect to the seventy-two intrachain force constants, the eigenvalues and eigenvectors of the $\tilde{\mathbf{J}}\,\mathbf{W}\,\mathbf{J}$ matrix (where $\mathbf{J}$ is the Jacobian matrix defined by $J_{ij} = \partial\nu_i/\partial f_j$, $\tilde{\mathbf{J}}$ is the transpose of $\mathbf{J}$, and $\mathbf{W}$ is a diagonal weighting matrix for the frequencies) indicate that more than thirty force constants are badly correlated with other force constants and that most of the former are associated with skeletal vibrations. This is natural because there are thirty-five force constants directly associated with skeletal vibrations while only fifteen observed frequencies serve to determine them (note that the skeletal modes of deuterated molecules are almost the same as those of the normal molecule, and their observed frequencies therefore cannot be considered as independent data for determining the force constants). After several least-squares adjustment trials under various conditions, twenty-nine force constants (of which four pairs were set equal to

TABLE V Force Constants for Polyglycine I

Force constant	Value		
	Set I-1[a]	Set I-2	Set I-3
1. *f*(N—C)[b]	5.043(0.156)[c]	5.078(0.144)	5.025(0.170)
2. *f*(C—C′)	4.509(0.356)	4.520(0.304)	4.419(0.372)
3. *f*(C′—N)	6.299(0.515)	6.111(0.440)	6.304(0.536)
4. *f*(C′=O)	9.549(0.174)	9.436(0.153)	9.496(0.183)
5. *f*(N—H)	5.827(0.032)	5.825(0.028)	5.998(0.034)
6. *f*(C—H)	4.564(0.016)	4.564(0.014)	4.564(0.017)
7. *f*(C′NC)	0.787(0.164)	0.788(0.151)	1.050(0.199)
8. *f*(NCC′)	1.00	***[d]	***
9. *f*(CC′N)	1.40†	***	***
10. *f*(CC′=O)	1.246(0.098)	1.274(0.091)	1.269(0.106)
11. *f*(NC′=O)			
12. *f*(C′NH)	0.463(0.015)	0.466(0.014)	0.496(0.016)
13. *f*(CNH)			
14. *f*(NCH)	0.715(0.032)	0.717(0.028)	0.699(0.033)
15. *f*(C′CH)	0.684(0.029)	0.682(0.025)	0.673(0.032)
16. *f*(HCH)	0.581(0.013)	0.584(0.012)	0.588(0.014)
17. *f*(C′=O op)	0.594(0.045)	0.595(0.039)	0.614(0.046)
18. *f*(N—H op)	0.171(0.018)	0.170(0.016)	0.191(0.038)
19. *f*(N—C tor)	0.037	***	***
20. *f*(C—C′ tor)	0.037	***	***
21. *f*(C′—N tor)	0.579(0.053)	0.580(0.048)	0.598(0.087)
22. *f*(N—C,C—C′)	0.3	***	***
23. *f*(C—C′,C′—N)	0.3	***	***
24. *f*(C′—N,N—C)	0.3	***	***
25. *f*(C—C′,C′=O)	0.5	***	***
26. *f*(C′—N,C′=O)	0.5	***	***
27. *f*(C′—N,C′NC)	0.3	***	***
28. *f*(N—C,C′NC)	0.3	***	***
29. *f*(N—C,NCC′)	0.3	***	***
30. *f*(C—C′,NCC′)	0.3	***	***
31. *f*(C—C′,CC′N)	0.3	***	***
32. *f*(C′—N,CC′N)	0.3	***	***
33. *f*(C—C′,CC′=O)	0.2	***	***
34. *f*(C′—N,NC′=O)	0.2	***	***
35. *f*(C′=O,CC′=O)	0.45	***	***
36. *f*(C′=O,NC′=O)	0.45	***	***
37. *f*(C′—N,C′NH)	0.294(0.061)	0.302(0.057)	0.298(0.067)
38. *f*(N—C,CNH)			
39. *f*(N—C,NCH)	0.517(0.043)	0.532(0.038)	0.520(0.046)
40. *f*(N—C,C′CH)	0.026(0.051)	0.036(0.041)	0.044(0.050)
41. *f*(C—C′,NCH)			
42. *f*(C—C′,C′CH)	0.205(0.068)	0.217(0.058)	0.225(0.073)
43. *f*(C′NC,NCC′)	0.0	***	***
44. *f*(NCC′,CC′N)	0.0	***	***
45. *f*(CC′N,C′NC)	0.0	***	***
46. *f*(NCC′,CC′=O)	0.0	***	***
47. *f*(C′NC,NC′=O)	0.0	***	***
48. *f*(CC′N,C′NH)	0.2	***	***
49. *f*(NCC′,CNH)	−0.1†	***	***
50. *f*(C′NC,NCH)	0.0	***	***
51. *f*(C′NC,NCH′)	0.0	***	***
52. *f*(CC′N,C′CH)	0.0	***	***
53. *f*(CC′N,C′CH′)	0.0	***	***
54. *f*(NCH,NCH′)	0.026(0.028)	0.026(0.026)	0.018(0.030)

TABLE V (*continued*)

Force constant	Value		
	Set I-1[a]	Set I-2	Set I-3
55. f(C′CH,C′CH′)	−0.023(0.027)	−0.027(0.025)	−0.022(0.030)
56. f(NCH,C′CH)	0.033(0.018)	0.030(0.015)	0.022(0.018)
57. f(NCH,HCH)	0.05	***	***
58. f(C′CH,HCH)	0.05	***	***
59. f(NC′=O,C′NH)	0.251(0.072)	0.273(0.071)	0.238(0.081)
60. f(CC′=O,C′CH)	0.1†	***	***
61. f(CC′=O,C′CH′)	0.0	***	***
62. f(CNH,NCH)	0.058(0.034)	0.066(0.031)	0.076(0.034)
63. f(CNH,NCH′)	0.077(0.033)	0.073(0.028)	0.068(0.036)
64. f(C′=O op,NCC′)	−0.05†	***	***
65. f(C′=O op,C′CH)	0.1†	***	***
66. f(C′=O op,C′CH′)	0.0	***	***
67. f(N—H op,NCC′)	0.0	***	***
68. f(N—H op,NCH)	0.0	***	***
69. f(N—H op,NCH′)	0.1†	***	***
70. f(C′=O op,N—H op)	−0.06†	***	***
71. f(C′=O op,C′—N tor)	0.07†	***	***
72. f(N—H op,C′—N tor)	−0.13†	***	−0.08†
73. f(H···O)	0.2	***	0.0
74. f(C′=O···H ip)	0.01	***	0.0
75. f(C′=O···H op)	0.01	***	0.0
76. f(N—H···O ip)	0.03	***	0.0
77. f(N—H···O op)	0.03	***	0.0
78. f(C′=O, H···O)	0.0	0.45	0.0

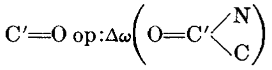
---

[a] Set I-1 was obtained by assuming f(C′=O,H···O) = 0.0, Set I-2 by assuming f(C′=O,H···O) = 0.45, and Set I-3 by the single-chain treatment.

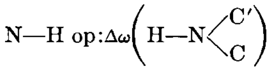
[b] The symbols in the parentheses correspond to the internal coordinates of Table II in the following way:

A—B:Δr(A—B)

ABC:Δθ(A—B—C)



$$\text{C}'\text{=O op}:\Delta\omega\left(\text{O=C}'\begin{smallmatrix}\diagup \text{N}\\ \diagdown \text{C}\end{smallmatrix}\right)$$



$$\text{N—H op}:\Delta\omega\left(\text{H—N}\begin{smallmatrix}\diagup \text{C}'\\ \diagdown \text{C}\end{smallmatrix}\right)$$

A—B tor:Δt(A—B)

A—B···C ip:$\Delta\gamma_{\parallel}$ (A—B···C)

A—B···C op:$\Delta\gamma_{\perp}$(A—B···C).

[c] The values in the parentheses of the last three columns are the uncertainties in the force constants calculated by

$$\text{uncertainty in } f_i = \left[\frac{\sum_i w_i(\nu_i^{\text{obs}} - \nu_i^{\text{calc}})^2}{n_{\text{obs}} - n_{\text{fc}}}(\mathbf{A}^{-1})_{ii}\right]^{1/2}$$

where n_{obs} is the number of observed frequencies, n_{fc} the number of variable force constants, and $w_i = W_{ii}$ and $\mathbf{A} = \tilde{\mathbf{J}}\,\mathbf{W}\,\mathbf{J}$, $\mathbf{W}$ and $\mathbf{J}$ being defined in the text.

The force constants followed by their uncertainties were determined by least squares, those marked by † were adjusted by trial and error, and other force constants were transferred from amides[12] and paraffins.[27]

[d] *** indicates that the value is in the same as in set I-1.

each other) were determined by least squares, nine more constants were adjusted by estimation, and the remaining thirty-four constants were fixed to zero or to rough values estimated from the valence force field of the amide group[12] and that of the paraffins.[27] In carrying out the least-squares adjustment, all observed frequencies were weighted by unity and N^{15} isotope shifts were weighted by five, except for the shifts of amide I and amide II which were weighted by fifty since they only can determine the difference $f(C'{=}O) - f(C'{-}N)$. Only B_1 and B_2 vibrations were taken into account in the adjustment of the intrachain force constants, because only a few experimental data are available for A and B_3 vibrations. Splittings between $A(\nu(0,0))$ and $B_1(\nu(0,\pi))$ frequencies and between $B_2(\nu(\pi,0))$ and $B_3(\nu(\pi,\pi))$ frequencies are small for most intrachain modes, as will be shown later, and this simplified procedure does not produce any significant error. For comparison, values of the force constants based on the single-chain treatment were also derived by setting all interchain force constants equal to zero.

The values of the force constants are listed in Table V. Set I-1 corresponds to taking $f(C'{=}O,H{-}{-}{-}O) = 0.0$, set I-2 to taking $f(C'{=}O, H{-}{-}{-}O) = 0.45$ mdyn/Å, and set I-3 is that for a single chain. The frequencies of crystalline PG I calculated with the force constants of set I-1 are compared with the experimental values in Table VI. Assignments based on the calculated potential energy distributions[28] are also given in the table. While not a perfect description of the normal coordinate, the potential energy distribution is a useful indication of the nature of the normal vibration. The agreement between observed and calculated frequencies is generally good, except for the amide I frequencies which will be discussed in the next section. The frequencies calculated with set I-2 force constants are all within a few cm^{-1} of those calculated with set I-1, except for the amide I modes (A, 1645; B_1, 1686; B_2, 1641; B_3, 1682), the coupled CH_2 rock and skeletal stretch B modes in the A and B_2 species (A, 987 and 931, B_2, 987 and 872), and the H---O stretching lattice vibration (B_3, 138). For purposes of comparison the calculated frequencies, assignments, and potential energy distributions for the single chain case (ie, using force constant set I-3) are given in Table VII.

DISCUSSION

It is of interest to compare the potential energy distributions for the normal modes of a single chain, given in Table VII, with those given by previous calculations.[7,14,15] We find from the present calculation that the CH_2 wagging and rocking modes make a significant contribution to the characteristic amide vibrations. This was of course not apparent in earlier calculations where the CH_2 group was approximated by a point mass. The present calculation also shows that the $C'{=}O$ out-of-plane bending mode (amide VI) and the $C'{=}O$ in-plane bending mode (amide IV) are significantly mixed. This is of course due to the nonplanar chain geometry used in the present calculation as compared to the planar polypeptide chain which was assumed in the earlier calculations. The different assignments of some of the lower frequency amide modes as well as some of the skeletal modes undoubtedly arise from the different force field used in the present work as well as from the factors mentioned above.

With respect to the calculation on crystalline PG I, it will be seen that force constant sets I-1 and I-2 are not very different. Thus, the choice of $f(C'{=}O,H{-}{-}{-}O) = 0.0$ or 0.45 does not affect the other force constants appreciably. However, some force constants, such as f(C'NC), f(N-H op), f(C'—N tor), and f(N-H op,C'-N tor), are considerably different for the crystal than for the single chain. This is because the amide V and the C'NC deformation vibrations are coupled with lattice vibrations of the crystal: amide V is coupled with the N—H---O out-of-plane bending mode and the C'NC vibration is coupled with the H---O stretching mode. This demonstrates the importance of including intermolecular interactions if a valid description of the force field and of the normal modes is to be obtained.

The agreement between observed and calculated frequencies for amide I is not very good. According to the first-order perturbation theory[29,30,31] the frequency of an amide I mode is given by

$$\nu(\delta,\delta') = \nu_0 + \sum_{s,t} D_{st}\cdot\cos(s\delta)\cos(t\delta') \tag{7}$$

where ν_0 is the unperturbed frequency and D_{st} is the constant determining interactions between peptide groups separated by t chains and s groups along the tth neighboring chain. Usually, only D_{s0}'s and D_{0t}'s are considered to be important, and for the antiparallel chain pleated sheet only D_{10} and D_{01}[32] have been used so far. Thus, in this case

$$\nu(\delta,\delta') = \nu_0 + D_{10}\cos\delta + D_{01}\cos\delta' \tag{8}$$

Application of Eq. (8) to the three observed Amide I frequencies of —NHCH$_2$CO—, $\nu(0,0) = 1674$, $\nu(0,\pi) = 1685$, and $\nu(\pi,0) = 1636$ cm^{-1}, yields $\nu_0 = 1660.5$, $D_{10} = 19$, and $D_{01} = -5.5$ cm^{-1}. However, we have found that the large and positive value of D_{10} cannot be reproduced by using any ordinary force field, which is why there is poor agreement between the observed and calculated amide I frequencies shown in Table VI. Although calculations were also done for different repeat lengths, viz, 3.35, 3.55, and 3.62 Å, for crystal structures in which neighboring chains were displaced +0.5 Å and −0.5 Å along the chain direction, with respect to the structure shown in Figure 1, a large and positive D_{10} could never be obtained. Nor have we been able to reproduce the large splittings claimed by Gupta et al.[7] by using their force field. It seems therefore that the only way to explain the splitting of the Amide I frequencies is to introduce direct interaction force constants between amide I vibrations, or roughly speaking, between C'=O stretching vibrations.

TABLE VI

Observed and Calculated Frequencies of Crystalline Polyglycine I[a] (in cm^{-1})

Observed	Calculated		Assignment
	1. $-\!(\mathrm{NHCH_2C'O})\!-_n$		
B_1	A	B_1	
3302(−9.5)[b]	3300(−8)	3300(−8)	NH str.: 5(97)[c]
2930	2932(0)	2932(0)	CH_2 asym. str.: 7(99)
2869	2858(0)	2858(0)	CH_2 sym. str.: 6(99)
1674, A 1685(−0.8)	1663(−2)	1666(−2)	Amide I: 3(17) 4(76) 10(12)
1517(−14.4)	1507(−31)	1510(−13)	Amide II: 2(14) 3(32) 11(15) 12(37)
1460	1441(0)	1441(0)	CH_2 bend: 13(99)
1409	1403(−1)	1403(−1)	CH_2 wag: 2(16) 12(20) 14(62)
	1245(−1)		CH_2 twist: 14(10) 15(71)
1255		1254(−1)	15(72)
1214(−4)	1219(−3)	1218(−3)	Amide III: 1(13) 3(14) 12(26) 14(24) 15(20)
1162	1156(−13)	1154(−13)	Skel. str. A[d]: 1(62) 2(14)
	1003(−6)		CH_2 rock: 4(15) 16(39)
1018(−6)		995(−5)	4(14) 16(48)
	944(−5)		2 + 3 + 4(25) 9(12) 16(35) 17(11)
936		938(−6)	Skel. str. B[e]: 2 + 3 + 4(40) 9(14) 16(27) 17(11)
	704(−2)	703(−2)	Amide V: 18(54) 21(59) 26(23)
628(−2)	646(−5)	639(−5)	Amide IV: 11(36) 16(11) 17(17) 21(11)
	572(−2)		Amide VI: 2(12) 11(29) 17(44)
589		572(−2)	2(11) 11(26) 17(49)
321	319(−1)	329(−1)	Skel. def. A[f]: 1(12) 9(15) 10(48)
	226(−3)		Skel. def. B[g]: 8(50) 18(14)
270		257(−2)	8(54) 22(21)
207, A 217	201(−4)		Amide VII: 8(21) 10(11) 18(30)
		207(−5)	8(43)
	131(0)		Torsion + lattice vib: 9(33) 20(11) 22(11)
		137(0)	9(27) 20(10) 21(13)
	41(0)		22(37) 23(15) 26(19)
		75(0)	18(11) 21(16) 24(18) 25(17) 26(36)
	36(0)		24(24) 25(51)
3302(−9.5)	3299(−8)	3299(−8)	NH str.: 5(97)
2930	2932(0)	2932(0)	CH_2 asym. str.: 7(99)
2869	2858(0)	2858(0)	CH_2 sym. str.: 6(99)
1636(−0.9)	1659(−1)	1662(−2)	Amide I: 3(15) 4(76) 10(12)
	1518(−11)	1520(−11)	Amide II: 1(11) 2(20) 3(26) 11(11) 12(37) 14(10)
1432(−1)	1440(0)	1440(0)	CH_2 bend: 13(98)
1340	1344(−5)	1343(−5)	CH_2 wag: 14(76)
	1259(0)		Amide III: 2(13) 11(12) 12(44)
		1257(−1)	2(12) 11(11) 12(40) 15(12)
1236(−1)	1236(−1)		CH_2 twist: 15(79)
		1234(−1)	12(12) 15(76)

TABLE VI (*continued*)

Observed	Calculated		Assignment
1018(−6)	1038(−8)		Skel. str. A: 1(65) 2(10)
		1033(−9)	1(71) 2(12)
	991(−7)		CH_2 rock: 3(14) 16(59)
		975(−6)	3(11) 16(70)
	896(−9)	881(−8)	Skel. str. B: 2 + 3 + 4(67) 16(11)
	768(−4)	766(−4)	Amide IV: 1(20) 2(14) 8(10) 9(18) 11(22)
708	705(−1)		Amide V: 18(35) 21(66) 26(22)
		692(−1)	18(42) 21(67) 26(23)
614(−3)	616(−5)		Amide VI + skel. def. A: 10(38) 17(23) 18(13)
		623(−4)	10(25) 14(11) 17(43) 18(12)
	546(−5)		10(21) 16(11) 17(55) 18(17)
		561(−5)	10(37) 17(39)
	356(−4)	355(−4)	Amide VII: 9(22) 11(12) 18(20) 21(13)
270	267(0)	264(−1)	Skel. def. B: 8(41) 11(31)
	69(−1)		Lattice vib + torsion: 18(13) 19(29) 20(30) 21(11) 26(18)
~140		149(−1)	22(92)
	34(0)		21(12) 24(32) 25(10) 26(28)
		106(−1)	18(22) 20(13) 21(21) 24(20) 26(33)

2. $-\!(NDCH_2C'O)\!-_n$

B_1	A	B_1	
2929	2932	2932	CH_2 asym. str.: 7(99)
2870	2858	2858	CH_2 sym. str.: 6(99)
2462 2419	2424	2424	ND str.: 5(95)
1680	1658	1662	Amide I: 3(17) 4(76) 10(12)
1475	1469	1470	Amide II: 2(29) 3(33) 11(19) 14(12)
	1440	1440	CH_2 bend: 13(99)
	1346		CH_2 wag: 1(16) 3(11) 14(79)
1352		1346	14(80)
1276 1237	1247	1247	CH_2 twist: 15(92)
	1150	1149	Skel. str. A: 1(68) 2(11)
	1028		Skel. str. B 2 + 3 + 4(27) 12(26) 14(10) 16(16)
1015		1024	
	963		+ CH_2 rock 12(14) 16(56) 17(11)
950		963	
	905		+ amide III: 2 + 3 + 4(35) 12(33)
		895	
625	640	636	Amide IV: 11(30) 16(10) 17(24)
572	572	575	Amide VI: 2(14) 11(35) 17(37)
	511	501	Amide V: 18(46) 21(72) 26(23)

(*continued*)

TABLE VI (*continued*)

Observed	Calculated		Assignment
B_1	A	B_1	
	316		Skel. def. A: 1(13) 9(16) 10(46)
		326	1(11) 9(15) 10(51)
	223		Skel. def. B: 8(51) 18(12)
		255	8(54) 22(21)
	197		Amide VII: 8(20) 18(28)
		204	18(37) 21(11)
	129	135	9(34) 20(11) 22(11) 9(28) 20(10) 21(12)
	41		Torsion + lattice vib: 22(36) 23(15) 26(19)
		74	18(11) 21(16) 24(18) 25(17) 26(36)
	36		24(25) 25(50)
B_2, B_3	B_2	B_3	
2929	2932	2932	CH$_2$ asym. str.: 7(99)
2870	2858	2858	CH$_2$ sym. str.: 6(99)
2462 2419	2423	2423	ND str.: 5(95)
1629	1653	1656	Amide I: 3(17) 4(77) 10(11)
	1468	1468	Amide II: 1(11) 2(29) 3(25) 11(14) 13(18)
1432	1433	1433	CH$_2$ bend: 13(82)
	1342	1341	CH$_2$ wag: 14(77)
1276 1237	1236	1235	CH$_2$ twist: 15(88)
	1035		Skel. str. A: 1(49) 2(14) 16(20)
		1027	1(70) 2(14)
1015	1007		CH$_2$ rock + amide III: 1(22) 12(24) 16(25)
		1007	12(39) 16(34)
950	941		12(45) 16(30)
		924	12(37) 16(42)
	889		Skel. str. B: 2 + 3 + 4(67)
		873	2 + 3 + 4(71)
	760	759	Amide IV: 1(18) 2(15) 8(12) 9(16) 11(20)
614	614		Amide VI + skel. def. A: 10(23) 17(41)
		616	10(15) 17(58)
	542		10(34) 17(35)
		553	10(43) 17(27) 18(10)
504	506		Amide V: 18(68) 21(56) 26(24)
		504	18(56) 21(65) 26(24)
	354	353	Amide VII: 9(22) 11(12) 18(15) 21(19)
	266	262	Skel. def. B: 8(41) 11(31)
	67		Lattice vib + torsion: 18(12) 19(30) 20(30) 26(19)
		148	22(92)
	34		21(12) 24(32) 25(10) 26(28)
		104	18(20) 20(13) 21(19) 24(20) 26(34)

TABLE VI (*continued*)

Observed	Calculated		Assignment
	3. $\text{-(}\mathrm{NHCD_2C'O}\text{)-}_n$		
B_1	A	B_1	
3297	3300	3300	NH str.: 5(97)
2165	2191	2191	CD_2 asym. str.: 7(97)
2118	2096	2096	CD_2 sym. str.: 6(96)
1684	1657	1661	Amide I: 3(17) 4(77) 10(12)
1498	1505	1508	Amide II: 2(13) 3(32) 11(14) 12(39)
1297	1317	1315	Amide III: 2(31) 12(42) 14(14)
1189	1186	1186	Skel. str. A: 1(71) 14(20)
	1071		2 + 3 + 4(20) 13(51)
		1066	CD_2 bend 2 + 3 + 4(15) 13(65)
	1030		+ skel. str. B 2 + 3 + 4(13) 13(44) 14(15)
1015		1023	+ CD_2 twist 2 + 3 + 4(16) 13(30) 14(19)
928	934	934	+ CD_2 14(13) 15(52) 17(11)
866	871	867	wag: 2 + 3 + 4(18) 14(33) 16(15)
	819	818	CD_2 rock: 15(33) 16(32) 17(16)
	698	696	Amide V: 18(52) 21(63) 26(24)
610	612	610	Amide IV: 2(12) 11(51) 16(13)
	520		Amide VI: 11(11) 16(26) 17(46)
534		520	16(27) 17(46)
	300		Skel. def. A: 1(12) 9(20) 10(48)
		314	9(17) 10(51) 22(11)
	217		Skel. def. B: 8(48) 18(16)
		244	8(55) 11(11) 22(18)
	198		Amide VII: 8(24) 10(10) 18(27)
		205	18(42)
	122		Torsion + lattice vib.: 9(31) 20(12)
		129	9(24) 20(11) 21(15)
	40		22(36) 23(16) 25(10) 26(19)
		71	18(12) 21(14) 24(17) 25(18) 26(33)
	35		24(26) 25(49)
B_2,B_3	B_2	B_3	
3297	3299	3299	NH str.: 5(97)
2165	2193	2191	CD_2 asym. str.: 7(97)
2118	2095	2095	CD_2 sym. str.: 6(96)
1627	1653	1656	Amide I: 3(14) 4(79) 10(12)
	1508	1511	Amide II: 1(13) 2(18) 3(32) 11(13) 12(39)
	1256	1253	Amide III: 2(15) 11(11) 12(52)
1099	1107	1107	CD_2 wag: 2(16) 13(13) 14(52)
1073	1071	1070	CD_2 bend + 1(26) 13(56) 14(21)
1015	1016	1011	skel. str. A: 1(36) 13(22)
928	937		1(12) 2 + 3 + 4(29) 11(12) 15(16)

(*continued*)

TABLE VI (*continued*)

Observed	Calculated		Assignment	
B_2, B_2	B_2	B_3		
		930	Skel. str. B	1(14) 2 + 3 + 4(24) 11(12) 15(24)
866	876		+ CD_2 twist	2 + 3 + 4(15) 15(50) 16(13)
		861	+ CD_2 rock:	2 + 3 + 4(23) 15(49) 16(11)
	806	796		2 + 3 + 4(19) 10(13) 16(42)
	719		Amide IV:	1(13) 2(11) 9(20) 11(15) 17(12)
		718		1(14) 9(15) 11(14) 17(11) 21(12)
700	695		Amide V:	18(37) 21(60) 26(22)
		679		15(10) 16(18) 18(36) 21(48) 26(18)
564	561		Amide VI + skel. def. A:	10(37) 14(22) 17(11)
		566		10(18) 14(25) 17(35) 18(12)
	515			10(10) 16(19) 17(53) 18(24)
		534		10(33) 17(29)
	327	325	Amide VII:	9(23) 11(25) 18(11)
	243	244	Skel. def. B:	8(39) 11(18)
	68		Lattice vib + torsion:	18(12) 19(30) 20(30) 21(11) 26(17)
		145		22(90)
	33			21(13) 24(32) 25(10) 26(28)
		105		18(21) 20(13) 21(22) 24(20) 26(33)
		4. $-\!(\!-NDCD_2C'O-\!)\!-_n$		
B_1	A	B_1		
2464 2416	2424	2424	ND str.:	5(95)
2161	2191	2191	CD_2 asym. str.:	7(97)
2109	2095	2095	CD_2 sym. str.:	6(96)
1681	1652	1656	Amide I:	3(17) 4(77) 10(11)
1460	1456	1457	Amide II:	2(26) 3(41) 11(21)
	1228	1228	Skel. str. A + CD_2 bend + skel. str. B:	1(52) 2 + 3 + 4(29) 12(12) 14(35)
	1097	1093		1(25) 13(38)
	1027			13(61)
1015		1024		13(56)
950	942		CD_2 twist:	12(22) 14(22) 15(28)
		941		12(17) 14(23) 15(31)
923	916	912	Amide III:	3(10) 12(42) 15(25)
866	869	864	CD_2 wag:	2 + 3 + 4(19) 14(32) 16(17)
	813	813	CD_2 rock:	15(37) 16(32) 17(16)

TABLE VI (*continued*)

Observed	Calculated		Assignment
605	606	603	Amide IV: 2 + 3 + 4(20) 11(48) 16(13)
	528	532	Amide V: 11(12) 16(12) 17(29) 18(28) 21(12)
	505	494	Amide VI: 16(14) 17(17) 18(26) 21(60) 26(16)
	297		Skel. def. A: 1(12) 9(19) 10(48)
		310	9(16) 10(51) 22(11)
	215		Skel. def. B: 8(50) 18(13)
		242	8(55) 11(10) 22(18)
	195		Amide VII: 8(22) 18(25)
		201	18(37) 21(11)
	120		9(31) 20(12)
		128	9(24) 20(10) 21(15)
	40		Torsion + lattice vib: 22(35) 23(16) 25(11) 26(19)
		71	18(12) 21(13) 24(17) 25(18) 26(34)
	35		24(26) 25(49)
B$_2$, B$_3$	B$_2$	B$_3$	
2464 2416	2423	2423	ND str: 5(95)
2161	2192	2191	CD$_2$ asym. str.: 7(97)
2109	2095	2095	CD$_2$ sym. str.: 6(96)
1630	1646	1649	Amide I: 3(16) 4(80) 10(11)
	1455	1456	Amide II: 1(17) 2(29) 3(37) 11(20) 12(11)
1101	1105	1105	CD$_2$ wag: 2(17) 13(15) 14(53)
1075	1069	1068	CD$_2$ bend + skel. str. A: 1(25) 13(57) 14(22)
1015	1005	1000	1(42) 13(21)
	983	982	Amide III: 11(13) 12(62)
901	912		CD$_2$ twist + skel. str. B + CD$_2$ rock: 2 + 3 + 4(24) 12(11) 15(24)
		906	2 + 3 + 4(18) 12(10) 15(38)
866	871		2 + 3 + 4(21) 15(39) 16(15)
		853	2 + 3 + 4(33) 15(34) 16(11)
	793		2 + 3 + 4(15) 15(12) 16(47)
		780	2 + 3 + 4(17) 10(11) 16(54)
	710		Amide IV: 1(12) 2(13) 9(18) 11(14) 17(11)
		706	1(12) 9(18) 11(12) 17(15)
554	571		10(19) 14(12) 17(23) 21(18)

(*continued*)

TABLE VI (*continued*)

Observed	Calculated		Assignment	
B_2, B_3	B_2	B_3		
		570	Amide VI + skel. def. A: + amide V:	10(11) 17(43) 21(11)
	515			10(29) 17(25) 21(16)
		529		10(30) 17(24) 18(24)
493	496			14(11) 16(11) 17(18) 18(72) 21(36) 26(20)
		497		10(11) 18(47) 21(58) 26(21)
	325	322	Amide VII:	9(23) 11(25) 21(12)
	243	244	Skel. def. B:	8(39) 11(17)
	66			18(11) 19(31) 20(30) 26(18)
		144	Lattice vib + torsion:	22(90)
	33			21(13) 24(32) 25(10) 26(29)
		104		18(20) 20(13) 21(19) 24(20) 26(34)

[a] Calculated with Set I-1 force constants.

[b] ( ) = $\nu(N^{15}) - \nu(N^{14})$.

[c] The first number refers to the symmetry coordinate in Table III (S_5 in this case), the number in parenthesis to the fractional potential energy in this coordinate (if it is 10 or greater). Where one designation is given it signifies that both species have the same potential energy distribution.

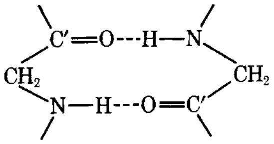
[d] Skeletal stretch A is mainly the N–C stretching vibration.

[e] Skeletal stretch B is mainly a symmetric stretching vibration of the $C{-}\overset{\overset{O}{\|}}{C'}{-}N$ skeleton.

[f] Skeletal deformation A is mainly the CC′N deformation vibration mixed with the C′NC deformation.

[g] Skeletal deformation B is mainly the C′NC deformation vibration slightly mixed with the CC′N deformation.

If direct interaction force constants are introduced between C′=O stretching vibrations, the one in the following structure



that is between the groups II and IV in Figure 1, seems to be the most natural. This is because the distance between the centers of the above two C′=O bonds is shorter than for any other pair. This interaction corresponds to the D_{11} term of Eq. (7). As we have suggested,[33] the D_{11} term is probably generally important in interpreting the splittings of the amide I frequencies of the antiparallel chain pleated sheet structure. Thus, we expect that a more valid approximation of Equation (7) is

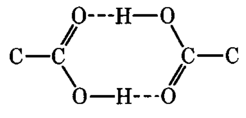
$$\nu(\delta,\delta') = \nu_0 + D_{10}\cos\delta + D_{01}\cos\delta' + D_{11}\cos\delta\cos\delta' \qquad (9)$$

TABLE VII
Calculated Frequencies of Single-Chain Polyglycine I[a]

Calculated frequency		
$\delta = 0$[b]	$\delta = \pi$	Assignment
1666	1660	Amide I: 3(16) 4(74) 10(13)[c]
1508		Amide II: 2(13) 3(33) 11(15) 12(40)
	1519	1(11) 2(19) 3(27) 11(12) 12(40) 14(10)
1439	1439	CH_2 bend: 13(99)
1404		CH_2 wag: 2(16) 12(20) 14(60)
	1342	14(72)
1253	1239	CH_2 twist: 15(80)
1218		Amide III: 1(18) 3(14) 12(29) 14(29) 15(12)
	1249	2(13) 11(11) 12(50)
1151		Skel. str. A[d]: 1(56) 2(15)
	1039	1(65) 2(12)
998		CH_2 rock: 4(18) 8(11) 16(34)
	987	3(13) 8(10) 16(61)
937		Skel. str. B[d]: 2 + 3 + 4(22) 9(12) 16(40) 17(13)
	884	2 + 3 + 4(63) 16(11)
712		Amide V: 18(59) 21(55)
	699	18(45) 21(68)
639		Amide IV: 11(35) 16(11) 17(11) 21(16)
	778	1(22) 2(18) 8(11) 9(15) 11(18)
572		Amide VI: 2(12) 11(27) 16(10) 17(45)
	549	10(27) 16(10) 17(48) 18(11)
318		Skel. def. A[d]: 1(13) 9(17) 10(45)
	621	10(32) 14(11) 17(32) 18(14)
239		Skel. def. B[d]: 8(58) 10(14)
	273	8(41) 11(34)
200		Amide VII: 18(32) 21(18)
	350	9(23) 11(11) 18(19) 21(18)
119		Torsion: 9(43) 18(11) 19(10) 20(13)
	59	19(50) 20(42)

[a] Calculated with Set I-3 force constants.
[b] Modes with phase differences of 0 or π between peptide group motions.
[c] Convention for potential energy distribution same as for Table VI.
[d] See Table VI for descriptions of modes.

If we apply Eq. (9) to the three observed amide I frequencies of PG I, and assume that $D_{10} = 5$ cm^{-1}, which is the largest value given by any of our trial calculations so far, we get $\nu_0 = 1674.5$, $D_{01} = -19.5$, and $D_{11} = 14$ cm^{-1}. It should be mentioned that large splittings have also been observed for the C=O stretching frequencies of dimers of carboxylic acids[34] which have the structure



and the existence of some sort of direct interaction between the C=O stretching vibrations was also suggested in this case.[35] In the latter case the interaction term corresponding to D_{11} was found to be -20 to -40 cm^{-1}.

The D_{11} term could have its physical origin in the interactions between the transition dipoles of the C=O stretching vibrations, which would be given by

$$f(\mathrm{C{=}O_1,C{=}O_2}) = 0.1 \times \left(\frac{\partial\mu^2}{\partial r_{\mathrm{C=O}}}\right)^2 \cdot \frac{\cos\alpha - 3\cos\beta\cdot\cos\gamma}{|\mathbf{R}|^3} \tag{10}$$

where $f(\mathrm{C{=}O_1,C{=}O_2})$ is the interaction force constant between the two C=O stretching vibrations, $\mathbf{R}$ is the vector connecting the centers of $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, $\cos\alpha = \boldsymbol{\mu}_1\cdot\boldsymbol{\mu}_2/|\boldsymbol{\mu}_1||\boldsymbol{\mu}_2|$, $\cos\beta = \boldsymbol{\mu}_1\cdot\mathbf{R}/|\boldsymbol{\mu}_1||\mathbf{R}|$, and $\cos\gamma = \boldsymbol{\mu}_2\cdot\mathbf{R}/|\boldsymbol{\mu}_2||\mathbf{R}|$, $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ being the two transition dipoles ($|\boldsymbol{\mu}_2| = |\boldsymbol{\mu}_2| = |(\partial\mu/\partial r_{\mathrm{C=O}})|$). $|\mathbf{R}|$ is given in Å, $(\partial\mu/\partial r_{\mathrm{C=O}})$ in Debye/Å, and $f(\mathrm{C{=}O_1,C{=}O_2})$ in mdyn/Å. If we assume that the center of the transition dipole of the amide I vibration is on the C′=O bond located 0.6 Å from the C′ atom, that the dipole is tilted by 20° from the C′=O bond toward the N → C direction,[36] and that $(\partial\mu/\partial r_{\mathrm{C=O}}) = 8$ D/Å, we get

$$f(\mathrm{C'{=}O_I,C'{=}O_{II}}) = f(\mathrm{C'{=}O,C'{=}O})_{10} = -0.03$$

$$f(\mathrm{C'{=}O_{II},C'{=}O_{III}}) = f(\mathrm{C'{=}O,C'{=}O})_{01} = -0.12$$

$$f(\mathrm{C'{=}O_{II},C'{=}O_{IV}}) = f(\mathrm{C'{=}O,C'{=}O})_{11} = 0.26$$

where I, II, III and IV denote the four groups shown in Figure 1 and 10, 01, and 11 correspond to the subscripts in Eq. (9). Readjusting the force constants $f(\mathrm{C'{=}O})$ and $f(\mathrm{C'{=}O,H{-}{-}{-}O})$ to 9.71 and 0.35 md/A, respectively, we calculate the four amide I frequencies of PG I at $\nu(0,0) = 1674$, $\nu(0,\pi) = 1688$, $\nu(\pi,0) = 1639$, and $\nu(\pi,\pi) = 1721$ cm^{-1}, in good agreement with experiment. It should be noted that the application of Eq. (10) to dimers of carboxylic acids always yields negative interaction terms (of magnitude -15 to -30 cm^{-1}), as found by experiment. The direct interaction between C′=O transition dipoles thus seems to be a reasonable and probably necessary mechanism for accounting for the Amide I splittings in polypeptides and proteins.

We thank Dr. T. Miyazawa of Osaka University and Dr. K. Fukushima of Shizuoka University for supplying us with the details of their calculations. This work was supported by grants GP-10922 and GB-15682 from the National Science Foundation. A postdoctoral fellowship from the Macromolecular Research Center at the University of Michigan to one of us (Y.A.) is gratefully acknowledged.

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Received March 18, 1972