The Normal Vibrations of Polyglycine I

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The molecular structure and vibrational spectra of polyglycine I, $(\text{-}CH_2CONH\text{-})_n$, are closely related to those of polypeptides and proteins. According to X-ray analyses,1) it has been concluded that the chain conformation of polyglycine I is in the β-conformation. On the basis of this conformation, measurements and partial assignments of the infrared absorption bands of polyglycine I in the spectral region between 2 and 30 μ have been made by Shimanouchi et al. using a sample prepared by them.2)

We are interested in the relationship between the chain conformation of polypeptides and their normal frequencies, especially the characteristic amide frequencies and skeletal frequencies. We have calculated the normal vibrations of polyglycine I and its *N*-deuterated species in order to elucidate the nature of the normal vibrations characteristic of β-chain polypeptides, in which the molecular chain is in the all-trans zig-zag conformation.

Internal Co-ordinates

According to X-ray investigations,1) the molecule of polyglycine I belongs to the factor group C_{2v}. Therefore, the twenty-six normal vibrations (characteristic amide vibrations and skeletal vibrations) of the polyglycine I molecule are grouped into nine A_1, nine B_1, four A_2 and four B_2 vibrations. Of these, only the infrared active in-plane vibrations, A_1 and B_1 will be treated in the present study.

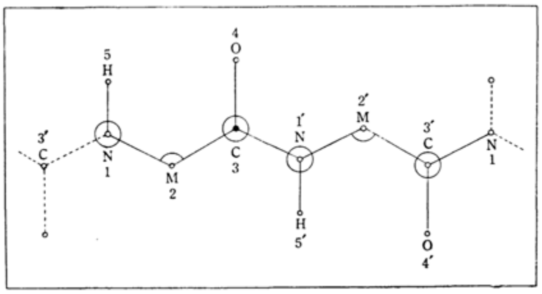

Fig. 1. Numbering of the atoms of the polyglycine I molecule.

The calculations were carried out according to Wilson's ***GF*** matrix method3); the methylene groups were treated as mass points, as the aim of these calculations was the analysis of only skeletal vibrations and characteristic amide vibrations. The molecular model is presented in Fig. 1; the internal co-ordinate vectors belonging to the *m*-th unit of the infinite molecular chain of the polyglycine I molecule will be denoted as $R^{(m)}$ and $R'^{(m)}$. The internal co-ordinates used are;

$R_1^{(m)}$ $\Delta r_{NH}=\Delta r_{15}$

$R_2^{(m)}$ $\Delta \gamma_{NH}=(1/\sqrt{2})\Delta(\alpha_{513'}-\alpha_{215})$

$R_3^{(m)}$ $\Delta \beta_{NH}=(1/\sqrt{6})\Delta(2\alpha_{3'12}-\alpha_{513'}-\alpha_{215})$

$R_4^{(m)}$ $\Delta r_{NM}=\Delta r_{12}$

$R_5^{(m)}$ $\Delta \alpha_{NMC}=\Delta \alpha_{321}$

$R_6^{(m)}$ $\Delta r_{MC}=\Delta r_{23}$

$R_7^{(m)}$ $\Delta r_{CO}=\Delta r_{34}$

$R_8^{(m)}$ $\Delta \gamma_{CO}=(1/\sqrt{2})\Delta(\alpha_{432}-\alpha_{1'34})$

$R_9^{(m)}$ $\Delta \beta_{CO}=(1/\sqrt{6})\Delta(2\alpha_{231'}-\alpha_{1'34}-\alpha_{432})$

$R_{10}^{(m)}$ $\Delta r_{CN}=\Delta r_{31'}$

$R'^{(m)}_1$ $\Delta r'_{NH}=\Delta r_{1'5'}$

$R'^{(m)}_2$ $\Delta \gamma'_{NH}=(1/\sqrt{2})\Delta(\alpha_{31'5'}-\alpha_{5'1'2'})$

$R'^{(m)}_3$ $\Delta \beta'_{NH}=(1/\sqrt{6})\Delta(2\alpha_{2'1'3}-\alpha_{31'5'}$
$-\alpha_{5'1'2'})$

$R'^{(m)}_4$ $\Delta r'_{NM}=\Delta r_{1'2'}$

$R'^{(m)}_5$ $\Delta \alpha'_{NMC}=\Delta \alpha_{1'2'3'}$

$R'^{(m)}_6$ $\Delta r'_{MC}=\Delta r_{2'3'}$

$R'^{(m)}_7$ $\Delta r'_{CO}=\Delta r_{3'4'}$

$R'^{(m)}_8$ $\Delta \gamma'_{CO}=(1/\sqrt{2})\Delta(\alpha_{2'3'4'}-\alpha_{4'3'1})$

$R'^{(m)}_9$ $\Delta \beta'_{CO}=(1/\sqrt{6})\Delta(2\alpha_{13'2'}-\alpha_{2'3'4'}$
$-\alpha_{4'3'1})$

$R'^{(m)}_{10}$ $\Delta r'_{CN}=\Delta r_{3'1}$

where r_{ij} and α_{ijk} represent the bond length between atoms, *i* and *j*, and the bond angle formed by atoms, *i*, *j* and *k* respectively.

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1) C. W. Bunn and E. V. Garner, *Proc. Roy. Soc.*, **A189**, 39 (1947); W. T. Astbury, *Nature*, **163**, 722 (1949); C. H. Bamford, L. Brown, E. M. Cant, A. Elliot, E. W. Hanby and B. R. Malcolm, ibid., **176**, 396 (1955).

2) S. Suzuki, Y. Iwashita, T. Shimanouchi and M. Tsuboi, Abstracts of the International Symposium on Molecular Structure and Spectroscopy, Tokyo (1962), A110.

3) E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

$$\begin{array}{c|cccccccc}
 & \cdots & R'^{(m-1)} & R^{(m-1)} & R'^{(m)} & R^{(m)} & R'^{(m+1)} & R^{(m+1)} & \cdots \\
\hline
\vdots & & & & & & & & \\
R'^{(m-1)} & \tilde{B} & A & B & & & & & \\
R^{(m-1)} & & \tilde{B} & A & B & & & & \\
R'^{(m)} & & & \tilde{B} & A & B & & & \\
R^{(m)} & & & & \tilde{B} & A & B & & \\
R'^{(m+1)} & & & & & \tilde{B} & A & B & \\
R^{(m+1)} & & & & & & \tilde{B} & A & B \\
\vdots & & & & & & & &
\end{array}$$

Fig. 2. Form of ***G***, ***F*** matrix of polyglycine I.

TABLE I. FORCE CONSTANTS (mdyn./Å) AND MOLECULAR PARAMETERS

K(N-H)	5.6	H(H-N-C)	0.35	F(H. N. C)	0.50
K(N-C)	5.5	H(C-N-M)	0.30	F(C. N. M)	0.30
K(N-M)	3.4	H(H-N-M)	0.15	F(H. N. M)	0.50
K(M-C)	3.1	H(N-M-C)	0.20	F(N. M. C)	0.30
K(C=O)	8.5	H(O=C-M)	0.30	F(O. C. M)	0.50
		H(M-C-N)	0.30	F(M. C. N)	0.50
		H(O=C-N)	0.35	F(O. C. N)	1.50
		r_{NH}	1.00Å	α_{HNC}, α_{CNM}, α_{MNH},	
		r_{NM}	1.47Å	α_{NMC}, α_{OCM}, α_{MCN},	
		r_{MC}	1.54Å	α_{NCO}............120°	
		r_{CO}	1.21Å		
		r_{CN}	1.32Å		

By the use of these internal co-ordinate vectors, the ***G*** matrix of the polyglycine I molecule was constructed; it is expressed in the form shown in Fig. 2.

Potential Energy

The Urey-Bradley potential energy⁴⁾ of the polyglycine I molecule is expressed as:

$$\begin{aligned}V=&\sum_{m,i,j}K'_{ij}r^{(m)}_{ij}[\varDelta r^{(m)}_{ij}]+(1/2)K_{ij}[\varDelta r^{(m)}_{ij}]^2\\&+\sum_{m,i,j,k}H'_{ijk}r^{(m)}_{ij}r^{(m)}_{jk}[\varDelta\alpha^{(m)}_{ijk}]\\&+(1/2)H_{ijk}r^{(m)}_{ij}r^{(m)}_{jk}[\varDelta\alpha^{(m)}_{ijk}]^2\\&+\sum_{m,i,j,k}F'_{ik}q^{(m)}_{ik}[\varDelta q^{(m)}_{ik}]+(1/2)F_{ik}[\varDelta q^{(m)}_{ik}]^2\end{aligned}$$

For the term containing F'_{ik} and F_{ik}, the summation is taken for all i and k combinations which correspond to the index i and k in α_{ijk}. In the above formula, m is the index for chain units, while $r^{(m)}_{ij}$, $r^{(m)}_{jk}$ and $q^{(m)}_{ik}$ represent the equilibrium value of the interatomic distance.

The Reduction of the Secular Equation

For a long chain molecule such as polyglycine I, only the vibrations in which all units in the molecular chain vibrate in phase are optically active.⁵⁾ Since the polyglycine I molecule has a plane of symmetry as well as a two-fold screw axis (fiber axis), the optically-active vibrations are classified into four species, A_1, B_1, A_2 and B_2. The A_1 and B_1 vibrations are symmetric with respect to the molecular plane, whereas the A_2 and B_2 vibrations are antisymmetric with respect to this plane. From the ***G*** and ***F*** matrices of infinite order shown in Fig. 2, the ***G*** and ***F*** matrices for the optically-active A_1 and B_1 vibrations were constructed by the symmetry co-ordinates shown below:

$$S_i=(1/\sqrt{N})\sum_m(R^{(m)}_i+R'^{(m)}_i)\quad\text{for }A_1\text{ species}\tag{2}$$

$$S'_i=(1/\sqrt{N})\sum_m(R^{(m)}_i-R'^{(m)}_i)\quad\text{for }B_1\text{ species}\tag{3}$$

In these equations, N is the total number of chain units in the polyglycine I molecular chain.

The secular equations (10th order) for the A_1 and B_1 vibrations

$$|\boldsymbol{G}_{A}\boldsymbol{F}_{A_1}-\lambda E|=0\tag{4}$$

$$|\boldsymbol{G}_{B_1}\boldsymbol{F}_{B_1}-\lambda E|=0\tag{5}$$

were solved by an NEAC model 2101 electronic computer. The force constants and the molecular parameters used in this calculation are listed in Table I. The calculated normal frequencies and the diagonal terms of potential

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4) T. Shimanouchi, *J. Chem. Phys.*, **17**, 243, 734, 848 (1949).

5) S. E. Whitcomb, H. H. Nielsen and L. H. Thomas, *J. Chem. Phys.*, **8**, 143 (1940).

TABLE II. OBSERVED AND CALCULATED FREQUENCIES OF POLYGLYCINE I AND *N*-DEUTERATED POLYGLYCINE I AND CALCULATED ^{15}N ISOTOPE SHIFTS OF FREQUENCIES*

	Polyglycine I			*N*-Deuterated polyglycine I		
	ν_o	ν_c	^{15}N Shift	ν_o	ν_c	^{15}N Shift
A_1		176	−1		173	−2
		223	−2		221	−1
	628(IV)	589	−2		587	−2
	987	991	−13	935(III′)	963	−3
	1112	1101	−11		984	−9
	1235(III)	1305	−3		1153	−10
	1524(II)	1518	−17	1475(II′)	1425	−19
	1685(I)	1652	−2		1642	−2
B_1		278	−1		278	−1
		541	−6		518	−5
	773(IV)	741	−3		737	−3
		874	−9		863	−7
	1015	1001	−16		984	−13
	1215(III)	1295	−3		1037	−4
	1524(II)	1512	−17	1475(II′)	1425	−19
	1630(I)	1647	−1		1632	−1
A_1, B_1	3300(νNH)	3340	−7	2500(νND)	2438	−11

* ν_o Observed frequency, cited from Ref. 2 ν_c Calculated frequency

energy distributions are shown in Tables II and III respectively. The $\boldsymbol{L}^x$ matrix, which is used for the transformation from the normal co-ordinate vector, Q, into the cartesian co-ordinate vector fixed to the molecule, X, was calculated by the following formulae ;[6]

$$X = \boldsymbol{L}^x Q \qquad (6)$$

$$\boldsymbol{L}^x = M^{-1}\tilde{\boldsymbol{B}}\boldsymbol{F}\boldsymbol{L}\Lambda^{-1} \qquad (7)$$

The schematic representations of the atomic displacements thus calculated are shown in Figs. 3 and 4. The ^{15}N isotope shifts of the normal frequencies of the polyglycine I molecule were calculated by the following equation :[7]

$$\lambda_a = (1/m'_n - 1/m_n)(m_n)^2 \times [(\boldsymbol{L}^x_{na})^2 + (\boldsymbol{L}^y_{na})^2 + (\boldsymbol{L}^z_{na})^2] \qquad (8)$$

λ_a : The isotope shift of the a-th frequency parameter
m_n : The mass of the n-th atom
m'_n : The mass of the isotope atom
$(\boldsymbol{L}^x)_{na}$: The vector associated with the n-th atom in the a-th normal vibration

$$(\boldsymbol{L}^x)_{na} = \begin{pmatrix} \boldsymbol{L}^x_{na} \\ \boldsymbol{L}^y_{na} \\ \boldsymbol{L}^z_{na} \end{pmatrix}$$

The calculated isotope shifts of the normal frequencies are shown in Table II.

Discussion

Polyglycine I is in the antiparallel chain-pleated sheet structure in the crystalline state.[1] Therefore, the assignment of the infrared absorption bands has to be made according to this structure, which contains interchain hydrogen bonds. Each of the internal vibrations of the polyglycine I molecule splits into two normal vibrations in the case of the polyglycine I crystal as follows :[8]

Molecule	Crystal	Selection rule
A_1	→ (0, 0)	IR inactive
	→ (0, π)	IR active
B_1	→ (π, 0)	IR active
	→ (π, π)	IR active
A_2	→ (0, 0)	IR inactive
	→ (0, π)	IR inactive
B_1	→ (π, 0)	IR active
	→ (π, π)	IR active

In principle, all the infrared active vibrations of the polyglycine I crystal are expected to appear in the infrared absorption. However, except for the amide I, II and III vibrations the frequency difference of each pair of splitted

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[6] B. L. Crawford, Jr., and W. H. Fletcher, ibid., **19**, 141 (1951).

[7] T. Miyazawa, Abstracts of the 15th Annual Meeting of the Chemical Society of Japan, Kyoto (1962), p. 20211.

[8] T. Miyazawa, *J. Chem. Phys.*, **32**, 1647 (1960).

TABLE III. THE DIAGONAL TERMS OF POTENTIAL ENERGY DISTRIBUTIONS OF POLYGLYCINE I MOLECULE AND *N*-DEUTERATED SPECIES

Polyglycine I molecule, A_1 vibration

ν_c	S_i									
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
3340	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1652	0.0	0.0	0.1	0.0	0.0	0.0	0.8	0.1	0.0	0.1
1518	0.0	0.0	0.7	0.1	0.0	0.0	0.0	0.0	0.1	0.4
1304	0.0	0.0	0.3	0.0	0.0	0.3	0.1	0.0	0.1	0.3
1101	0.0	0.0	0.0	0.7	0.0	0.2	0.0	0.1	0.0	0.0
991	0.0	0.2	0.0	0.0	0.1	0.2	0.2	0.1	0.1	0.1
589	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.7	0.0
223	0.0	0.3	0.0	0.0	0.1	0.0	0.0	0.6	0.0	0.0
176	0.0	0.4	0.0	0.0	0.5	0.0	0.0	0.0	0.1	0.0

Polyglycine I molecule, B_1 vibration

ν_c	S'_i									
	S'_1	S'_2	S'_3	S'_4	S'_5	S'_6	S'_7	S'_8	S'_9	S'_{10}
3340	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1647	0.0	0.0	0.1	0.0	0.0	0.0	0.8	0.1	0.0	0.1
1512	0.0	0.0	0.6	0.1	0.0	0.1	0.0	0.0	0.1	0.4
1294	0.0	0.0	0.3	0.1	0.0	0.2	0.1	0.0	0.1	0.3
1001	0.0	0.1	0.0	0.5	0.0	0.1	0.1	0.0	0.1	0.2
874	0.0	0.0	0.0	0.3	0.0	0.5	0.0	0.0	0.1	0.0
741	0.0	0.3	0.0	0.1	0.1	0.2	0.0	0.0	0.3	0.0
541	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.7	0.1	0.0
278	0.0	0.3	0.0	0.0	0.2	0.0	0.0	0.0	0.4	0.0

N-Deuterated polyglycine I molecule, A_1 vibration

ν_c	S_i									
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
2438	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1642	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.1	0.0	0.2
1425	0.0	0.0	0.2	0.1	0.0	0.2	0.0	0.0	0.1	0.7
1153	0.0	0.0	0.4	0.1	0.0	0.1	0.1	0.0	0.0	0.1
984	0.0	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.0	0.0
963	0.0	0.0	0.2	0.5	0.0	0.4	0.0	0.0	0.1	0.0
587	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.7	0.0
221	0.0	0.3	0.0	0.0	0.1	0.0	0.0	0.6	0.0	0.0
173	0.0	0.4	0.0	0.0	0.5	0.0	0.0	0.0	0.1	0.0

N-Deuterated polyglycine I molecule, B_1 vibration

ν_c	S'_i									
	S'_1	S'_2	S'_3	S'_4	S'_5	S'_6	S'_7	S'_8	S'_9	S'_{10}
2438	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1632	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.1	0.0	0.2
1425	0.0	0.0	0.2	0.1	0.0	0.2	0.0	0.0	0.1	0.6
1037	0.0	0.0	0.7	0.0	0.0	0.1	0.0	0.0	0.1	0.0
984	0.0	0.1	0.0	0.4	0.0	0.1	0.1	0.0	0.1	0.2
863	0.0	0.0	0.0	0.3	0.0	0.4	0.1	0.0	0.0	0.0
737	0.0	0.3	0.0	0.1	0.1	0.2	0.0	0.0	0.3	0.0
518	0.0	0.0	0.1	0.0	0.2	0.0	0.0	0.6	0.1	0.0
278	0.0	0.3	0.0	0.0	0.2	0.0	0.0	0.0	0.4	0.0

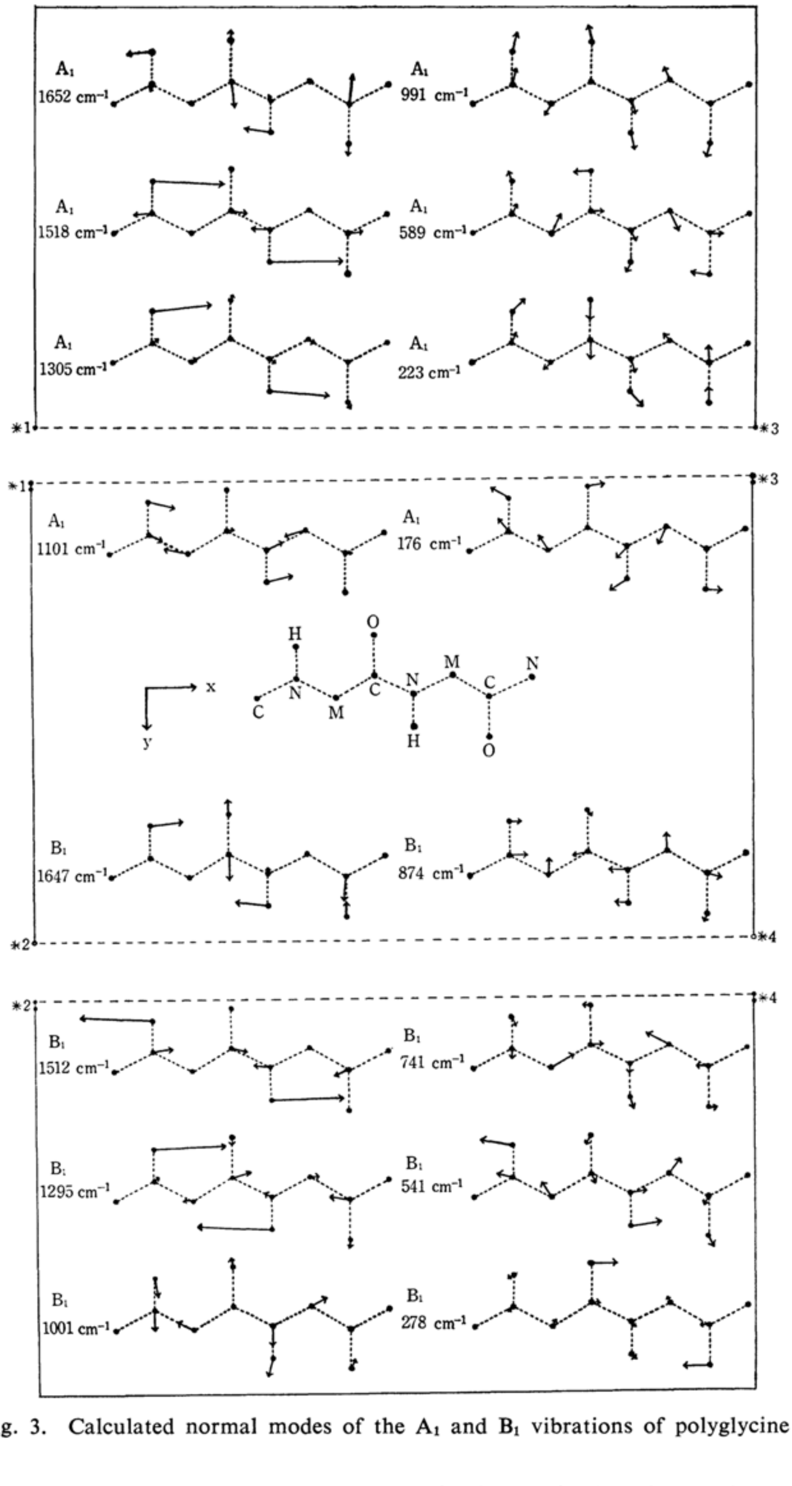

Fig. 3. Calculated normal modes of the A$_1$ and B$_1$ vibrations of polyglycine I.

bands may be very small in the case of in-plane vibrations. Therefore, detailed assignments on the basis of the selection rule for the crystal were made only for the amide I, II and III vibrations; the assignments of the other vibrations were made according to the selection rule based on the molecular symmetry. Accordingly, the bands assigned to the B$_1$ vibrations are considered to be due to the $\nu(\pi, 0)$ and $\nu(\pi, \pi)$ vibrations.

Characteristic Amide Vibrations.—Among the vibrations characteristic of polypeptides, six

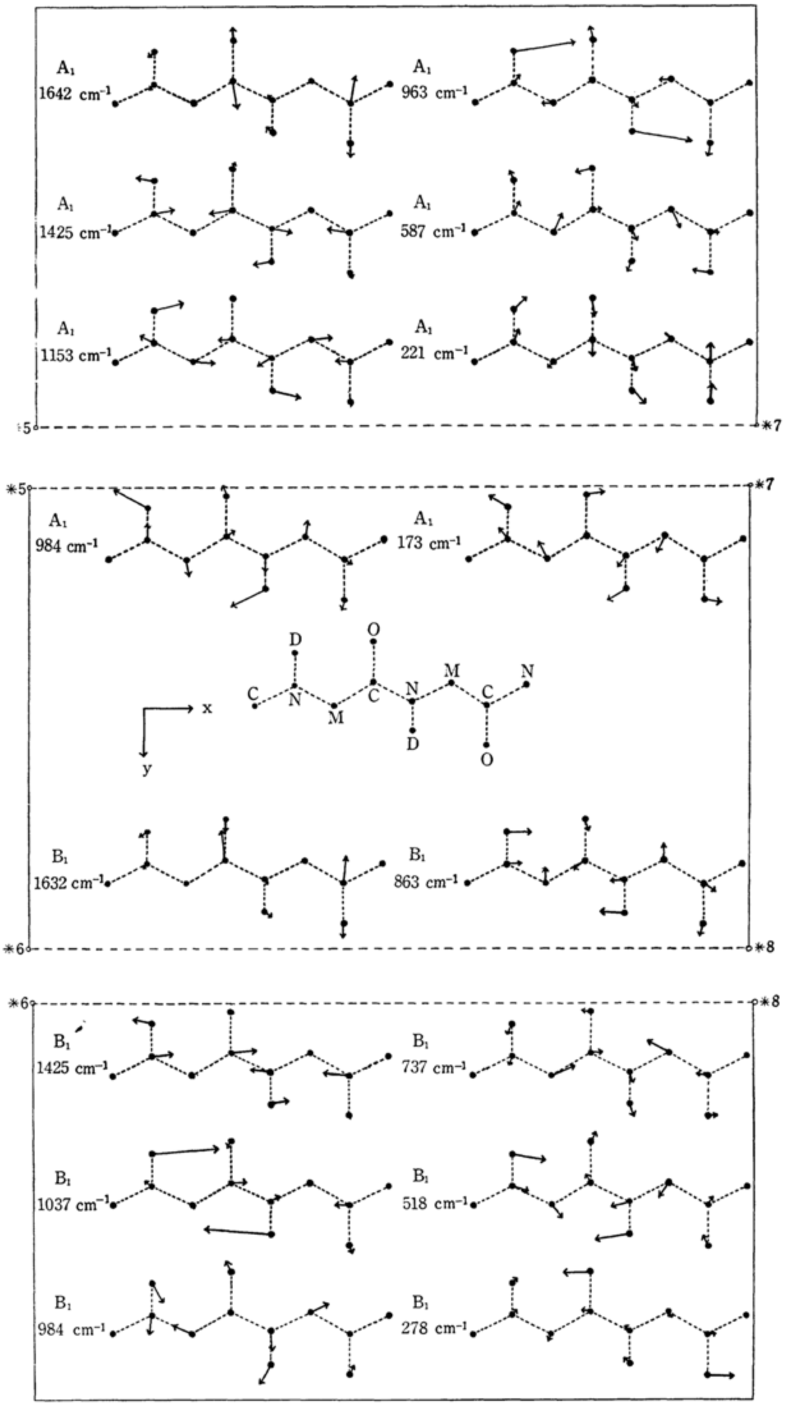

Fig. 4. Calculated normal modes of the A_1 and B_1 vibrations of *N*-deuterated polyglycine I.

vibrations (amide I, amide II, amide III, amide IV, amide II′ and amide III′) are treated as the in-plane vibrations of polyglycine I and its *N*-deuterated compound. The nature of these vibrations will now be discussed.

Amide I Vibration.—As Table III shows, this vibration is the antisymmetric stretching vibration of the O=C–N skeleton, in which the ratios of the energy associated to the C=O and C–N bonds are 0.78 : 0.14 for the A_1 vibration and 0.78 : 0.10 for the B_1 vibration. There are three types of amide I vibrations, $\nu(0, \pi)$,

$\nu(\pi, 0)$ and $\nu(\pi, \pi)$. The frequency of the $\nu(0, \pi)$ vibration is higher than those of $\nu(\pi, 0)$ and $\nu(\pi, \pi)$. These vibrations have been observed at 1688 cm^{-1} ($\nu(0, \pi)$) and 1630 cm^{-1} ($\nu(\pi, 0)$). The direction of the transition moment associated with the $\nu(0, \pi)$ vibration is parallel to the fiber axis. Since the C=O bonds are nearly perpendicular to the chain axis, the C=O bond transition moments are largely canceled in the $\nu(0, \pi)$ vibration. Therefore, this vibration is expected to be weak in intensity. For the $\nu(\pi, 0)$ vibration, in which the direction of the transition moment is perpendicular to the fiber axis, the contribution of the C=O bond moment change is great. Therefore, the intensity of this vibration is expected to be strong. The assignments of the 1685 cm^{-1} band to $\nu(0, \pi)$ and the 1630 cm^{-1} band to $\nu(\pi, 0)$ reasonably follow from a consideration of their intensities.

Amide II Vibration. — This is the coupled vibration of the N–H in-plane bending and the amide C–N stretching vibrations. The degree of the coupling of these two vibrations is nearly the same for the A_1 and B_1 vibrations. These vibrations are observed at 1524 cm^{-1}.

Amide II′ Vibration. — This is the coupled vibration of the C–N stretching, the N–D in-plane bending and the C–M stretching vibrations.

Amide III Vibration.—To this vibration, the contributions of the N–H in-plane bending, the C–M stretching and the N–C stretching modes are important. The couplings of these modes are different for the A_1 and B_1 vibrations, as Table IV shows. The frequency of the A_1 vibration is higher than that of the B_1 vibration. The $\nu(0, \pi)$ (A_1) vibration appears at 1236 cm^{-1} and the $\nu(\pi, 0)$ and $\nu(\pi, \pi)$ (B_1) vibrations at 1214 cm^{-1}.

Amide III′ Vibration.—To this vibration, the N–D in-plane bending mode contributes mainly; however, the contributions of skeletal stretching modes are also important.

Amide IV Vibration. — In this vibration, the frequency difference between the A_1 and B_1 vibrations is large. The calculated A_1 frequency is 589 cm^{-1} while the calculated B_1 frequency is 741 cm^{-1}. The A_1 vibration is an almost pure C=O in-plane bending vibration with a small contribution by the C–M stretching mode, whereas the B_1 vibration is a coupled vibration of the C=O in-plane bending, C–N–M skeletal deformation and C–M stretching modes. In the A_1 vibration, all the C=O bonds displace in phase, with a resultant strong transition moment along the molecular chain, so the intensity of this vibration may be expected to be very strong. Therefore, the strong band at 628 cm^{-1} is assigned to this vibration. In the B_1 vibration the bond moment change associated with the C=O in-plane bending mode will not contribute much to the total dipole moment change, and the transition moment of this B_1 vibration is possibly due to the dipole moment change of the C–N–M skeletal mode. Since the intensity of this B_1 vibration is considered to be weak, the weak band at 773 cm^{-1} is assigned to this vibration.

Nature of the Skeletal Vibrations. — The skeletal vibrations of polyglycine I are important in studying the changes in the polypeptide chain conformation. From the results of the calculations, the nature of the skeletal vibrations of the β-type polypeptide chain with no side chains has been made clear.

Skeletal Stretching Vibrations.—There are four skeletal stretching vibrations in the polyglycine I molecule, two belonging to the A_1 species and the other two belonging to the B_1 species. As Table II shows, the A_1 vibration calculated at 1101 cm^{-1} is the antisymmetric stretching vibration of the N–M–C skeleton. The band at 1112 cm^{-1} is assigned to this vibration. The other A_1 vibration, calculated at 991 cm^{-1}, is the C–M stretching vibration coupled with the M–C–N and C–N–M skeletal deformation modes. The band at 987 cm^{-1} is assigned to the A_1 vibration. For the B_1 species, the vibration calculated at 1001 cm^{-1} is the antisymmetric stretching vibration of the C–N–M skeleton coupled with the C–N–M skeletal deformation mode. The band at 1015 cm^{-1} is assigned to this vibration. The other B_1 vibration calculated at 874 cm^{-1} is the symmetric stretching vibration of the N–M–C skeleton. The band due to this vibration has not yet been identified.

Skeletal Deformation Vibrations. — There are four skeletal deformation vibrations, two belonging to the A_1 species and two belonging to the B_1 species. The A_1 vibrations include the antisymmetric skeletal deformation vibration of the M–C–N–M skeleton calculated at 223 cm^{-1} and the antisymmetric skeletal deformation vibration of the C–N–M–C skeleton calculated at 176 cm^{-1}. The two skeletal deformation frequencies of the B_1 species are very different from those of the A_1 species. The B_1 vibrations include the symmetric deformation vibration of the C–N–M–C skeleton, coupled with the amide IV vibration calculated at 278 cm^{-1}, and the symmetric deformation vibration of the N–M–C–N skeleton (calculated frequency at 541 cm^{-1}).

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