Pseudoscalar lattice modes in the amino acid crystals and DNA

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Abstract. Intense sharp lines corresponding to the librational modes were found in the low-frequency Raman scattering spectra of the glycine, lysine, asparagine and tyrosine aminoacids as well as in the dry DNA crystal lattices. According to the group-theoretical analysis such modes were assigned to the pseudoscalar type of symmetry.

1. Introduction
The effective methods for studying the vibrational spectra of molecules and crystals are infrared (IR) spectroscopy and Raman spectroscopy (RS). The vibrational spectra of amino acids were researched in many works using IR spectroscopy [1-2] and Raman spectroscopy [3-4]. In this paper we have carried out the group-theoretic analysis of the normal vibrations of such crystals as glycine, lysine, asparagine and tyrosine and registered the Raman spectra of the corresponding amino acids and dry DNA.

2. Experimental results and discussion
The schematic of the experimental setup for the Raman spectra registration is shown in Figure 1. The argon laser (1) with the wavelength of 514.5 nm and the power of 10 mW was used as the source of pumping radiation. Having passed through the semitransparent mirror (2) the laser radiation was focused into 10 micron spot by the collecting lens (3) on the sample (4) (polycrystalline amino acid or dry DNA of the calf). The scattered radiation was collected on the entrance slit of the triple monochromator Horiba Jobin Yvon T64000 (5). The spectra were detected by the CCD-matrix,

Figure 1. The experimental setup for the Raman spectra registration: 1 - laser; 2 – mirrors; 3 - lenses; 4 - sample; 5 - monochromator; 6 - computer
the data being transmitted and accumulated in the computer (6). The spectral resolution was less than 1 cm\(^{-1}\).

Glycine (H\(_2\)NCH\(_2\)COOH) is the simplest aliphatic amino acid which has no optical isomers (Figure 2a). L-lysine (figure 2b), D-asparagine (figure 2c) and tyrosine (figure 2d) have more complex structural formulas.

![Figure 2. Structural formulas of glycine (a), L-lysine (b), D-asparagine (c) and tyrosine (d)](image)

The \(\alpha\)-glycine crystal is monoclinic; the space group of this crystal symmetry is \(C_{2h}^{5}\) (the structural class is \(P2_1/n\) [5,6]; the primitive cell contains 4 molecules (figure 3a). The \(\alpha\)-glycine unit cell has the following parameters at room temperature: \(a = 5.1020 \pm 0.0005\) Å, \(b = 11.9709 \pm 0.0010\) Å and \(c = 5.4575 \pm 0.0009\) Å; the volume of the unit cell is equal to 333.3 Å\(^3\).

![Figure 3. Primitive cells of \(\alpha\)-glycine (a), \(\beta\)-glycine, L-lysine and D-asparagine (b). The molecules within the cell are presented by circles: the black circles are in the XY plane, the white circles are shifted along the Z-axis by half-period](image)

In the case of \(\beta\)-glycine the structural class is \(P2_1\) (space group \(C_{2h}^{2}\)) [7]; the primitive cell contains two molecules (Figure 3b). L-lysine [8] and D-asparagine [7] crystals belong to the same structural class.

Another example of the amino acid is tyrosine, for which the amino-acid residue is of the form \(R=(CH_2)\text{--}(C_6H_5)\text{--}OH\). The amino acid molecules in the protein are formed as zwitterions \((NH_3)^+\text{--}(CH--R)\text{--}(COO)^-\). Tyrosine \((C_9H_11NO_3)\) is aromatic amino acid which exists in two optically isomeric forms - L and D as well as in the form of the racemate DL.

The crystal structure of L-tyrosine is orthorhombic with the space group \(D_2^1\) \((P2_12_12_1)\) [9, 10]; the primitive cell contains 4 molecules (Figure 4a). At room temperature the unit cell parameters have the following values: \(a = 6.913\) Å, \(b = 21.116\) Å and \(c = 5.829\) Å; the volume of the unit cell is equal to 850.9 Å\(^3\).
The DL-tyrosine has a space group $C_{2v}^9$ (the structural class $Pna2_1$) [7], the primitive cell contains 4 molecules and is presented in Figure 4b.

![Figure 4](image-url)

**Figure 4.** Primitive cells of L-tyrosine (a) and DL-tyrosine (b). The molecules within the cell are presented by circles; the black circles are in the XY plane, the white circles are shifted along the Z-axis by half-period.

Based on the carried out group-theoretical analysis [11-13] of the discussed crystals the selection rules were determined in the Raman and IR spectra for the translational (tr) and libration (lib) modes of these crystals (see tables 1-4).

**Table 1.** The results of the group-theoretic analysis of the spatial symmetry group $C_{2h}^5$ ($P2_1/n$) ($\alpha$-glycine crystals); $a_i$, $a_{ij}$ - the components of the vector and symmetric tensor of the second rank respectively; $\chi_V$, $\chi_{\psi}$, $\chi_{tr}$, $\chi_{lib}$ - the characters of the vector, pseudovector, translational and libration representations, respectively.

|        | $E$  | $C_2(z)$ | $\sigma_h$ | $I$  | $a_i$  | $a_{ij}$ |
|--------|------|----------|------------|------|--------|----------|
| $\alpha$ | 0;0;0 | 0;0;1/2 | 1/2;0;0    | 1/2;0;1/2 | 1      | 1        |
| $A_y$   | 1    | 1        | 1          | 1    | $a_{xx}$, $a_{yy}$, $a_{zz}$, $a_{xy}$ |
| $A_u$   | 1    | 1        | -1         | -1   | $a_z$  |
| $B_y$   | 1    | -1       | -1         | 1    | $a_{xz}$, $a_{yz}$ |
| $B_u$   | 1    | -1       | 1          | -1   |        |
| $\chi_V$ | 3    | -1       | 1          | -3   | $T_u = 2A_u + 1B_u$ (IR) |
| $\chi_{\psi}$ | 3    | -1       | -1         | 3    | $T_{lib} = 3A_u + 3B_u$ (IR) |
| $\chi_{tr}$ | 9    | 1        | -1         | 3    | $T_{tr} = 3A_g + 3B_g$ (RS) |
| $\chi_{lib}$ | 12   | 0        | 0          | 0    | $T_{lib} = 3A_g + 3B_g$ (RS) |
| $m_0$   | 4    | 0        | 0          | 0    |        |
Table 2. The results of the group-theoretic analysis of the $\beta$-glycine, D-asparagine and L-lysine crystals with the space group symmetry $C_{2h}^2 (P2_1)$; $a_i, a_{ij}$ – the components of the vector and symmetric tensor of the second rank respectively; $\chi_V, \chi_V', \chi_{tr}, \chi_{lib}$ - the characters of the vector, pseudovector, translational and libration representations, respectively.

|     | E   | C$_2$ | $a_i$                      | $a_{ij}$             |
|-----|-----|-------|---------------------------|----------------------|
| $\alpha$ | 0;0;0 | 0;0; $\frac{1}{2}$ | $a_z$                       | $a_{xx}, a_{yy}, a_{zz}, a_{xy}$ |
| $A_1$ | 1   | 1     | $a_z$                       | $a_{xx}, a_{yy}, a_{zz}, a_{xy}$ |
| $A_2$ | 1   | -1    | $a_x, a_y$                  | $a_{xz}, a_{yz}$      |
| $\chi_V$ | 3   | -1    |                             | $T_t = 2A_1 + 1A_2$ (IR) |
| $\chi_V'$| 3   | -1    |                             | $T_{lib} = 3A_1 + 3A_2$ (IR) |
| $\chi_{tr}$| 3   | 1     |                             | $T_t = 2A_1 + 1A_2$ (RS) |
| $\chi_{lib}$ | 6   | 0     |                             | $T_{lib} = 3A_1 + 3A_2$ (RS) |
| $m_0$ | 2   | 0     |                             |                      |

Table 3. The results of the group-theoretic analysis of the spatial symmetry group $C_{2h}^9$ (Pna21) (DL-tyrosine crystals); $a_i, a_{ij}$ – the components of the vector and symmetric tensor of the second rank respectively; $\chi_V, \chi_V', \chi_{tr}, \chi_{lib}$ - the characters of the vector, pseudovector, translational and libration representations, respectively.

|     | E          | C$_2$(z) | $\sigma(xz)$ | $\sigma(yz)$ | $a_i$                      | $a_{ij}$             |
|-----|------------|-----------|--------------|--------------|---------------------------|----------------------|
| $\alpha$ | 0;0;0      | $\frac{1}{2}$; $\frac{1}{2}$; $\frac{1}{2}$ | $\frac{1}{2}$;0;0 | $\frac{1}{2}$; $\frac{1}{2}$ | $a_z$                       | $a_{xx}, a_{yy}, a_{zz}$ |
| $A_1$ | 1          | 1         | 1            | 1            | $a_z$                       | $a_{xx}, a_{yy}, a_{zz}$ |
| $A_2$ | 1          | 1         | -1           | -1           | $a_x$                       | $a_{xy}$             |
| $B_1$ | 1          | -1        | 1            | -1           | $a_y$                       | $a_{xz}$             |
| $B_2$ | 1          | -1        | -1           | 1            | $a_z$                       | $a_{yz}$             |
| $\chi_V$ | 3          | -1        | 1            | 1            | $T_t = 3A_1 + 2B_1 + 2B_2$ (IR) |
| $\chi_V'$| 3          | -1        | -1           | -1           | $T_{lib} = 3A_1 + 3B_1 + 3B_2$ (IR) |
| $\chi_{tr}$| 9          | 1         | 1            | 1            | $T_t = 3A_1 + 2A_2 + 2B_1 + 2B_2$ (RS) |
| $\chi_{lib}$ | 12         | 0         | 0            | 0            | $T_{lib} = 3A_1 + 3A_2 + 3B_1 + 3B_2$ (RS) |
| $m_0$ | 4          | 0         | 0            | 0            |                           |                      |
Table 4. The results of the group-theoretic analysis of the spatial symmetry group $D_2^4$ ($P2_12_12_1$) (L-tyrosine crystals); $a_i$, $a_{ij}$ – the components of the vector and symmetric tensor of the second rank respectively; $\chi_V$, $\chi_V'$, $\chi_{tr}$, $\chi_{lib}$ – the characters of the vector, pseudovector, translational and libration representations, respectively.

| E  | C2(z) | C2(y) | C2(x) | $a_i$ | $a_{ij}$ |
|----|-------|-------|-------|--------|---------|
| $\bar{a}$ | 0;0;0 | $\frac{1}{2}$; $\frac{1}{2}$;0 | $\frac{1}{2}$; $\frac{1}{2}$;0 | 1; 1 | $a_{xx}$, $a_{yy}$, $a_{zz}$ |
| $A$ | 1; 1; 0 | 1; 0; 1 | 0; 0; 1 | $a_z$ | $a_{xy}$ |
| $B_l$ | 1; 0; 1 | 1; 0; 1 | 0; 0; 1 | $a_y$ | $a_{xz}$ |
| $B_2$ | 1; 0; 1 | 1; 0; 1 | 0; 0; 1 | $a_y$ | $a_{xz}$ |
| $B_3$ | 1; 0; 1 | 1; 0; 1 | 0; 0; 1 | $a_y$ | $a_{xz}$ |
| $\chi_V$ | $\frac{1}{2}$; $\frac{1}{2}$;0 | $\frac{1}{2}$; $\frac{1}{2}$;0 | 1; 0; 1 | $T_{ir} = B_1 + 3B_2 + 3B_3$ (IR) |
| $\chi_V'$ | $\frac{1}{2}$; $\frac{1}{2}$;0 | $\frac{1}{2}$; $\frac{1}{2}$;0 | 1; 0; 1 | $T_{lib} = 2B_1 + 4B_2 + 4B_3$ (IR) |
| $\chi_{tr}$ | $\frac{1}{2}$; $\frac{1}{2}$;0 | $\frac{1}{2}$; $\frac{1}{2}$;0 | 1; 0; 1 | $T_{tr} = 2A + 1B_1 + 3B_2 + 3B_3$ (RS) |
| $\chi_{lib}$ | 1; 0; 1 | 1; 0; 1 | 0; 0; 1 | $T_{lib} = 2A + 2B_1 + 4B_2 + 4B_3$ (RS) |
| $\alpha_0$ | 4; 4; 0 | 4; 4; 0 | 0; 0; 0 | 0; 0; 0 |

The Raman spectra of some amino acids were reported in [14-16]. These spectra were registered in the middle (above 400 cm$^{-1}$) and high wave numbers range [14]. In [15] the Raman spectrum of L-lysine is shown in the 600-1700 cm$^{-1}$ range. In [16] the Raman spectrum of D-asparagine is reported in the 200-3500 cm$^{-1}$ range.

Figure 5 shows the Raman spectrum of the D-asparagine polycrystalline amino acid registered in the wide (10-3700 cm$^{-1}$) wave numbers range at room temperature.

![Figure 5](image_url)

Figure 5: The Raman spectrum of the D-asparagine polycrystalline amino acid in the wide spectral range at room temperature.
Figure 6 shows the Raman spectrum of the polycrystalline L-lysine amino acid registered in the wide (10-3700 cm\(^{-1}\)) wave numbers range at room temperature.

![Raman spectrum of L-lysine polycrystalline amino acid](image)

**Figure 6.** The Raman spectrum of the L-lysine polycrystalline amino acid in the wide spectral range at room temperature.

Figure 7 shows the Raman spectrum of the calf dried DNA registered in the wide (10-3700 cm\(^{-1}\)) wave numbers range at room temperature.

![Raman spectrum of calf dried DNA](image)

**Figure 7.** The Raman spectrum of the calf dried DNA in the wide spectral range at room temperature.
Figure 8 shows the low-frequency Raman spectra of the polycrystalline amino acids: α-glycine (a), L-tyrosine (b), DL-tyrosine (c), D-asparagine (d) and L-lysine (e) at room temperature. Figure 8(f) shows the comparison between the low-frequency Raman spectra of the polycrystalline L-lysine amino acid (1) and the dried DNA of the calf (2).

**Figure 8.** The Raman spectra of the polycrystalline amino acids: α-glycine (a), L-tyrosine (b), DL-tyrosine (c), D-asparagine (d) and L-lysine (e) in the low-frequency region at room temperature, (f) the low-frequency Raman spectra of the polycrystalline L-lysine amino acid (1) and dried DNA of the calf (2)
The low-frequency spectra of the polycrystalline amino acids D-asparagine and L-lysine (figures 8d,e) consist of several Raman lines, the most narrow and intense of which falls (figure 8f) into the region of the low-frequency component of the DNA bands.

According to the properties of the lattice modes in the Raman spectra the most intense peaks of the spectra in Figures 5,6,7 should be attributed to the pseudoscalar libration modes corresponding to the turning antiphase motions of two L-lysine or D-asparagine molecules present in the primitive cell of the corresponding crystal and similar to the motions of the nucleobases in DNA. The corresponding peaks in the glycine and tyrosine vibration spectra were also attributed to the pseudoscalar modes [17].

3. Conclusions
Thus, it has been established that at the low-frequency region of the Raman spectra of the α-glycine, L- and DL-tyrosine, D-asparagine and L-lysine amino acids there are very intensive and sharp lines. Such lines were attributed to the pseudoscalar libration modes of the amino acid crystalline lattice. The spectral positions of such libration modes are close to the low-frequency intensive band of the dry DNA molecule that may result in the strong resonant interaction between the amino acids and the DNA molecules in biostructures.

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