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Raman study of L-Asparagine and L-Glutamine molecules adsorbed on aluminum films in a wide frequency range

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Abstract. Using micro-Raman spectroscopy, a detailed study of vibrational spectra of L-Asparagine and L-Glutamine amino acids adsorbed on aluminum foils were carried out within the frequency range 80…3500 cm^{-1} under different excitation wavelengths. On the basis of detailed analysis of Raman spectra of the mentioned above amino acids and data of DFT-calculations of normal modes and isotopic substitution for these analytes available in literature, interpretation of amino acids vibrational bands were performed. The polarized Raman spectra of studied amino acids indicate different ordering of polycrystalline structure in distinct spots on the sample. The most significant variations of ratios between polarized bands are principally observed for deformation vibrations of NH_2, COO^- and CH_2 groups within entire "fingerprint" range and valence vibrations of CC and CN bonds within the range 1000…1100 cm^{-1}.

Keywords: amino acid, L-Asparagine, L-Glutamine, vibrational spectroscopy.

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1. Introduction

In the recent two decades, a quantity of investigations of basic organics compounds forming proteins, components of cell cytoplasm and organelles became one of the most numerical studies in cell biology. It is particularly due to needs of developing new medical methods (targeted drug delivery, nanoparticles treatment, installation of functional implants, *etc*.). Optical methods for direct biological molecule detection have been explored, and vibrational spectroscopies show great promise among them. The vibrational spectroscopic methods of Raman and Fourier-transform infrared (FTIR) spectroscopy applied to study both structural and conformational information of biological systems, including amino acids, proteins and lipids. Detailed understanding the vibrational structure of amino acids is thus helpful in studying intra- and intermolecular interactions. However, implementation of these spectroscopic methods is not an easy task. Recently, Zhu G. *et al*. [1] give an overview of measured Raman spectra of solid amino acids and their aqueous solutions, but today, a database, which would include the vibrational spectra of all amino acids, measured under the same, well-defined and reproducible experimental conditions is not exist.

In the solid state and polar media, both the amino acids L-Asparagine (L-Asn, 2-amino-4-amidosuccinic acid (NH_3^+–$CH(CO_2^-)$–CH_2–$CONH_2$) and L-Glutamine (L-Gln, 2-Amino-4-carbamoylbutanoic acid (NH_3^+–$CH(CO_2^-)$–$(CH_2)_2$–$CONH_2$) form a zwitterionic structure. These are amino acids with polar neutral charged groups and are the single ones that contain carboxamide functional group, which plays a significant role in formation of Van der Waals interactions and hydrogen bonds. Asparagine is necessary for functioning of the brain and plays an important role in formation and functioning of proteins [2]. Glutamine, unlike to Asparagine, is conditionally essential amino acid and plays a more significant role in synthesis of lipids, regulation of kidneys functionality, purines synthesis and safe circulation of ammonia in a human circulatory system [3]. L-Asn and L-Gln side chains can form

hydrogen bonds with water molecules, peptide backbones or other functional groups of biological molecules that plays an important role in formation of the secondary structure in proteins and conformational transitions. Spectroscopic study of these amino acids is an important way to obtain information about molecular conformations and the nature of hydrogen bonding in biological substances.

The only few published infrared and Raman studies of amino acids can be found. In the experiment performed by M. Wolpert *et al.* [4], infrared vibrational spectra and band assignments for all typical amino acids in aqueous solutions within 500…1800 cm^{-1} spectral range were carried out. Implementation of Raman spectroscopy for the solid Glutamine analysis was investigated only in few previous studies [3, 5, 6]. A detailed Raman study of Asparagine monohydrate crystal was carried out by Moreno *et al*. in [7, 8]. By use of IR, Raman, inelastic neutron scattering measurements and DFT calculation, the normal modes of vibrational spectra of pure L-glutamine in the solid state were determined and described [9]. The polarized Raman spectra from the microcrystalline powder of L-glutamine were used to general assignment of the vibrational fundamentals on the basis of the intensity changes observed in some vibrational bands [3]. There are few works published in the journals concerning investigation of fundamental vibrations and molecular structure properties of Asparagine in the solid state [2, 5, 9-12]. It should also be noted that the vibrational spectra of amino acids obtained by different research groups, perhaps measured under slightly different conditions, might be quite dissimilar.

In the literature, only the most significant and characteristic Raman bands are often discussed for each amino acid. Also, low-frequency vibrations assignments performed by different authors are distinguishing by their origin – some of the bands below 200 cm^{-1} are described as lattice vibrations, while the others are attributed to H-bonds formed between the analyte molecules.

Thus, the lack of information and the confusing aspects of the existing published works indicate that a comprehensive study of the vibrational spectra of these molecules as well as their polarized Raman spectra and low-frequency vibrations is necessary.

Here, we report the polarized Raman spectra of L-Asparagine and L-Glutamine amino acids in the solid state within the spectral range 80…3500 cm^{-1}. The special interest of this research was to perform a vibrational study of L-Asn and L-Gln within the frequency range below 400 cm^{-1}. Using the obtained experimental data, we carried out assignments of the observed frequencies of Asparagine and Glutamine in the solid state, which may be used in subsequent works of the spectroscopic analysis of interactions between these amino acids and other molecules of biological importance.

2. Samples and experimental technique

Our samples were prepared by deposition of drops of analytes diluted in distilled water with the concentration 10^{-3} Mol/l on thin films of industrial aluminum foil. Optical images of surface of the films are presented in Fig. 2. Due to hydrophobness of the surface, drops with the volume 8 to 10 µl maintained round shape while evaporating. After it, they formed a concentric spots with a noticeable rim. After next 3 times of deposition, solution was spreading faster and might flow out over the previous rim.

The Raman spectra of amino acids were measured using Jobin Yvon T64000 spectrometer equipped with a thermoelectrically-cooled device CCD detector with a spectral resolution of 0.2 cm^{-1}. 488 and 514.5 nm laser beams (with the power ~1 mW) were focused down to a micrometer sized spot on the sample through the confocal Raman microscope (Olympus BX41 with a 50× objective) equipped with a piezo-scanner. Polarized Raman spectra were obtained using 785.0 nm radiation from a diode-pumped 785 nm near-infrared (NIR) laser excitation operating at ~15 mW (experimental setup briefly described in [13]). The acquisition time of Raman spectra was amounted about 5–10 min for each. All Raman spectra were subjected to processing techniques using a commercial baseline correction process for extracting the data.

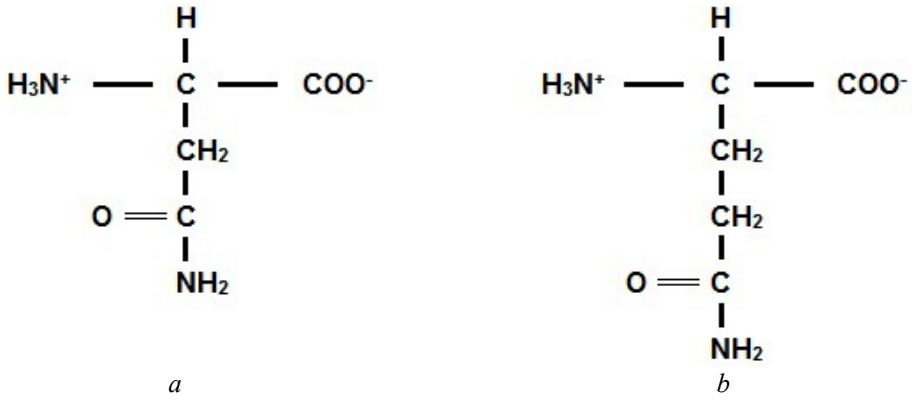

Fig. 1. Schemes of molecular structure of L-Asparagine (a) and L-Glutamine (b).

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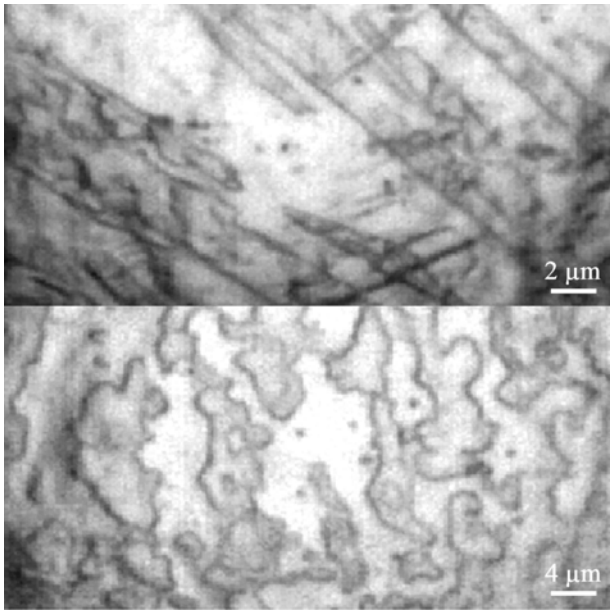


Fig. 2. Optical image of the Glutamine (top) and Asparagine (bottom) aggregates on aluminum foil.

3. Results and discussion

The vibrational spectrum of microcrystalline acids exhibits two distinct ranges: the low frequency range associated to lattice vibrations; the medium and high frequency range associated with molecular vibrations.

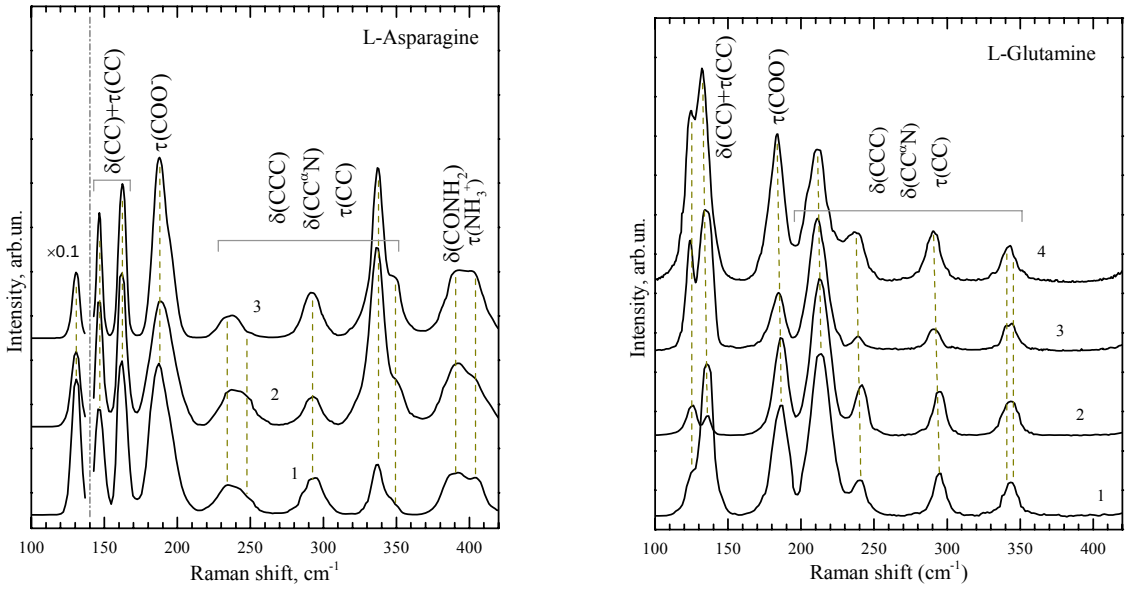
Despite the similar structure of L-Asparagine and L-Glutamine molecules, the number of normal modes in their spectra considerably varies as the additional $–CH_2–$ section of Glutamine provides opportunities for different skeletal and complex vibrations of the molecule.

Raman spectra of studied amino acids obtained with VIS and NIR excitation are shown in Figs. 3 to 5. The analysis of their origin can be performed within the low-wavenumber range (below 400 cm^{-1}), medium-wavenumber range (400…1800 cm^{-1}) and high-wavenumber range (over 2700 cm^{-1}). The polarized Raman spectra in Fig. 5 were obtained using the Wollastone polarizing prism. Marking z(x, x)ž(||,||) denotes that both polarizer and analyzer have the same direction, whereas z(y, x)ž(⊥,||) indicates that the analyzer has perpendicular orientation.

Low-wavenumber range 100…400 cm^{-1}

Spectroscopic studies of Raman scattering in the aforementioned amino acids showed the impact of rotational spectra of Oxygen and Nitrogen molecules to the final ones. Thus, comparing the spectra of amino acids and clear aluminum substrate, we excluded them as well as edge-filter artifacts.

Raman peaks that appeared within the low-frequency range of amino acids shown in Fig. 3 and enlisted in Table 1 include the bands attributed to lattice vibrations and molecular vibrations involving the COO^- torsion, NH_3 torsion and $CC^{\alpha}N$ deformation ones [6-9, 14-16]. They are specific for each type of molecules. The Raman bands of amino acids within the lattice vibrational range below 150 cm^{-1} arise as a result of the rotational and translational vibrations of the molecules or their parts in crystal, however Pawlukojc *et al*. [9] assigned the L-Glutamine bands detected within this range as torsion vibrations of CO_2^- unit and molecule backbone. Different types of intermolecular interactions caused by the forces between hydrocarbon molecules are generally weak, and therefore do not contribute significantly to the spectrum.



a *b*

Fig. 3. Low frequency Raman spectra of L-Asparagine (a) and L-Glutamine (b) amino acids adsorbed on aluminum films at T = 293 K and excitation wavelengths: 785 nm (⊥,||) (*1*) and (||,||) (*2*), 488 nm (*3*) and 514 nm (*4*).

Table 1. Vibrational frequencies and band assignment for the low-frequency Raman spectra of the L-Asparagine and L-Glutamine amino acids recorded at different excitation wavelengths and polarization geometry (here and after, we use the following abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder, sc = scissoring, r = rocking, wag = wagging, tw = twisting, ν = stretching, δ = bending, γ = out-of-plane bending, τ = torsion, s = symmetric, a = antisymmetric).

L-Asparagine			L-Glutamine				Assignment
488 nm	785 nm (∥,∥)	785 nm (⊥,∥)	488 nm	514 nm	785 nm (∥,∥)	785 nm (⊥,∥)	
			124 m	124 m	126 w	126 w	Lattice vibrations
131 m	131 m	131 m	133 m	135 m	136 w	136 m	
147 m	147 m	147 m					δ(CC) + τ(CC)
162 m	162 m	162 m					
187 m	189 m	187 m	184 m	185 m	185 m	186 m	$\tau(COO^-)$
			211 m	211 m	213 m	213 m	δ(CCC); $\delta(CC^{\alpha}N)$; τ(CC)
237 w	237 w	235 w	238 m	239 w	240 m	242 w	
292 w	293 w	293 w	291 m	291 w	294 m	294 m	
338 m	337 m	337 w					
350 m	351 w	350 vw	343 m	343 w	343 m	343 m	
392 m	392 w	392 w					$\delta(CONH_2)$
402 m	403 w	404 w					$\tau(NH_3^+)$

The bands at 147 and 162 cm^{-1} of L-Asn were attributed to bending vibrations of skeletal structure, a band at 188 cm^{-1} originates from COO^- torsion vibrations. The mode at 131 cm^{-1} in Asparagine as well as modes at 125 and 135 cm^{-1} in Glutamine can be assigned to molecular associated vibrations in amino acid in the solid state [3]. These bands belong to B-symmetry modes and should be both Raman and IR active [7]. The medium intensity Raman band of L-Gln located at about 185 cm^{-1} was attributed to a COO^- torsion vibration; the medium bands at 212, 240, 293 and 343 cm^{-1} were attributed to skeletal vibrations of torsion and bending nature. Similar features are represented by L-Asn at 236, 293, 337 and 350 cm^{-1}. Also, bending and torsion vibrations of Asparagine functional groups were identified at 382 and 403 cm^{-1}.

Medium-wavenumber range 400 – 1700 cm^{-1}

From Figs. 4 and 5 one can see that Raman spectra of L-Asn and L-Gln within this range have a large number of bands corresponding to bending vibrations of the NH_3^+ and stretching vibrations of the CO_2 and C=O groups, symmetric and antisymmetric vibrations of molecular backbone and side-groups. Vibrational frequencies obtained from the measured micro-Raman spectra and proposed assignments for the observed bands are summarized in Table 2. Most assignments are based on the works [3, 7], while other sources were usually indicated in text.

The spectra of studied amino acids may be conditionally separated into several ranges, where the significant types of vibrations are observed. Within the range 450…700 cm^{-1}, one can find the complex vibrations involving massive parts of the molecule. It should be noted that symmetrical stretching vibrations of CO_2^- group in both amino acids have a similar value in Raman spectra (566 cm^{-1} for Asparagine and 563 cm^{-1} for Glutamine). Meanwhile, the NH_3^+ torsion mode appears in Glutamine at 478 cm^{-1} and at 496 cm^{-1} in Asparagine. This assignment was made using the previous reports for Alanine (NH_3^+ torsion mode found at 477 cm^{-1} in [17, 18]) and cysteine (at 498 cm^{-1} in [19]). The NH_2 torsion vibration gives rise to the band at 537 cm^{-1} [11], as compared to the bands at ~520 cm^{-1} (Asparagine) and ~544 cm^{-1} (Glutamine) observed in our work (Fig. 4).

The modes that include complex full-molecule bending were situated between 600 to 670 cm^{-1} for both – Asparagine and Glutamine [3, 18]. Further, we see the 100 cm^{-1} gap in Raman spectra of both analytes, typical for many organic substances.

From 700 to 1400 cm^{-1}, there is a range of stretching and bending vibrations of C–C bonds as well as out-of plane deformation ones related to NH_2, CO_2^- and CH_2 groups. In between 775…800 cm^{-1} range, we observe rocking and twisting vibrations of side parts; different rocking vibrations of CH_2 group were identified at 886 and 896 cm^{-1} for Asparagine and Glutamine, respectively. The remaining asymmetrical bending vibrations of CH_2, NH_2, and NH_3^+ units are mainly observed around 1200 cm^{-1}.

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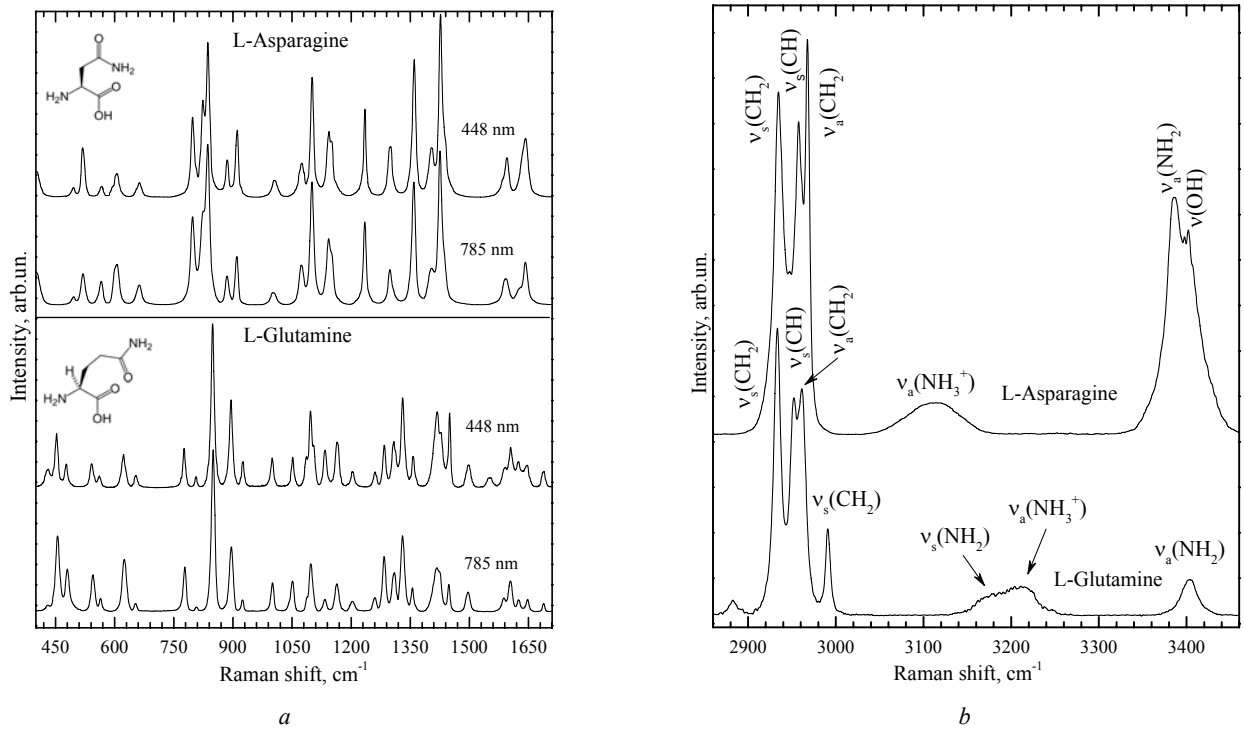

Fig. 4. Raman spectra of L-Glutamine and L-Asparagine in (a) medium-wavenumber ("fingerprint") and (b) high-wavenumber range (λ_{exc} = 488.0 nm). T = 293 K. Within high-wavenumber range, Raman spectra were normalized on the band at 2934 cm^{-1}.

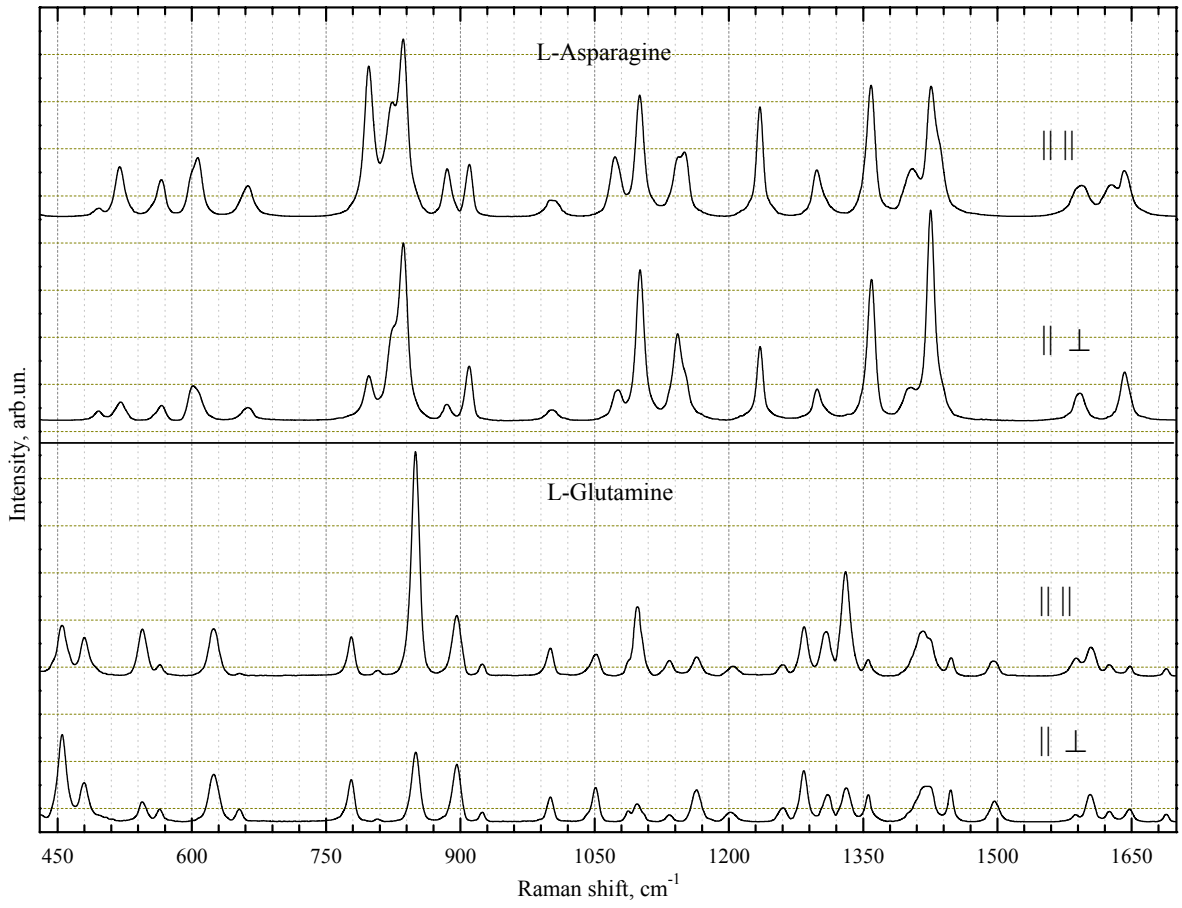

Fig. 5. Polarized Raman spectra of L-Asparagine and L-Glutamine within the wavenumber range 200…1700 cm^{-1} with z(x, x)ž(||,||) and z(y, x)ž(⊥,||) scattering geometries. λ_{exc} = 785 nm. T = 293 K.

Table 2. Vibrational frequencies and bands assignment for the Raman spectra of L-Asparagine and L-Glutamine within the medium-wavenumber spectral range.

L-Asparagine			L-Glutamine				Assignments
488	785 (∥,∥)	785 (⊥,∥)	488	514	785(∥,∥)	785 (⊥,∥)	
			430	430	430	430	δ(skel)
			452	454	455	455	
496	494	496	477	477	480	480	$\tau(NH_3^+)$
519	520	520	541	543	545	545	$\tau(NH_2)$
567	566	566	561	561	564	564	$\delta_s(CO_2^-)$
603	603	602	623	623	625	625	$\delta(NH_3^+) + \delta_s(CONH_2)$
663	663	663	654	654	653	653	$\gamma(CCN)$ [2] / $\delta_a(CONH_2)$ [7] / $\delta_a(COO^-)$ [14]
798	798	798	777	778	778	778	$\delta_r(CH_2)$ [3, 15, 16] / $\delta_{tw}(NH_2)$ [9]
824	824	826	807	807	808		$\gamma(CO_2^-)$
837	837	836					$\gamma(NH_2)$
			848	849	850	850	ν(CC)
885	886	886	896	896	896	896	$\delta_r(CH_2)$
911	910	910	925	925	925	925	ν_s(CC)
1006	1004	1004	1001	1001	1001	1001	ν(CC) [3, 9]
			1052	1053	1051	1051	
			1086	1087	1089	1088	
1075	1074	1076	1097	1097	1098	1098	ν(CN) [3]
1101	1101	1101	1105	1105	1103	1105	$\delta_r(NH_2)$
1144	1143	1143	1134	1135	1133	1133	$\delta_r(NH_3^+)$
1151	1151	1151	1164	1167	1164	1164	$\delta_r(NH_3^+)$ [3] / $\delta_r(NH_2)$ [7]
1235	1235	1235	1204	1204	1205	1203	$\delta_{tw}(CH_2)$ [3] / $\delta_{wag}(CH_2)$ [9]
			1261	1261	1261	1261	$\delta_{tw}(CH_2)$ [3] / $\delta_r(CH_2)$ [9]
			1284	1286	1283	1283	$\delta_{wag}(CH_2)$
1300	1299	1299	1309	1309	1308	1310	$\delta_{wag}(NH_2)$
			1331	1332	1331	1331	δ(CH)
1360	1359	1359	1358	1359	1356	1356	δ_s(CH)
1399	1398	1397					$\delta_s(CH_2)$
1404	1404	1402	1418	1418	1417	1418	δ(CN) A_{III}
1426	1426	1425	1428	1428	1425	1425	$\delta_s(CO_2^-)$ [3] / $\delta_{sc}(CH_2)$ [9]
1439	1437	1437	1450	1451	1449	1449	$\delta_{sc}(CH_2)$
			1498	1498	1496	1497	$\delta_s(NH_3)$ [3, 9]
			1552	1552			overtone (2×776) [9]
			1591	1588	1588	1588	$\nu(NH_2)$ A_{II}
1595	1594	1592	1605	1606	1605	1604	$\delta_a(NH_3)$ [3, 9] / H_2O [7]
1632	1628		1624	1624	1624	1625	$\nu_a(CO_2^-)$ [3, 9] / $\delta(NH_2)$ [7]
1642	1642	1642	1646	1648	1648	1648	ν(C=O) [7] / $\delta_a(NH_3)$ [3, 9]
			1688	1690	1689	1689	ν(C=O) A_I [3, 9]

The range 1050–1100 cm^{-1} contains C–C stretching modes of Glutamine backbone, which are absent in Asparagine. The characteristic Amide III features of Asparagine and Glutamine were identified at 1075 and 1098 cm^{-1}, respectively. A much lower frequency position of this band in the spectrum of Asparagine may be related to distinctive allocation of functional groups and, therefore, their different relative dispositions to backbone.

Within the range after 1400 cm^{-1}, the spectra mainly contain the asymmetrical stretching and bending vibrations of functional and sidechain groups. They also contain scissoring CH_2 vibrations (1426 and 1438 cm^{-1} for Asparagine, and 1427 and 1450 cm^{-1} for Glutamine). Unlike to Glutamine, Asparagine spectrum demonstrates no features between 1450 to 1550 cm^{-1}.

A comparison between vertically and perpendicularly polarized spectrum components that have been recorded simultaneously was performed for Raman spectra normalized on bands at 910 cm^{-1} (for Asparagine) and 92cm^{-1} (for Glutamine). There is only one band in Asparagine spectra at 1628 cm^{-1} that was absent at perpendicular polarization. Many other modes show insignificant deviation in intensity levels between differently polarized components. The bands at 337, 520, 798, 886, 1073 and 1235 cm^{-1} are much larger in case of parallel polarization, while the intensity of bands at 1001, 1143, 1359 and 1426 cm^{-1} in perpendicularly polarized spectrum prevail over their equivalents with lesser values.

For Glutamine, we carried out more detailed polarization study. The spectra were obtained from 6 different spots and then averaged. It was found for modes at 480, 925, 1088, 1204, 1261, 1425, 1497, 1605 and 1624 cm^{-1} minimal difference in their intensities under different polarizations of incident laser beam. The intensities of modes at 185, 213, 343, 625, 778, 1001, 1284 and 1404 cm^{-1} in the averaged spectra are comparable, but may slightly deviate within 20…50% range for each separate measurement. Meanwhile, some bands of Glutamine spectrum are regularly polarized. The polarization ratio between the parallel and perpendicular components of the mode at 545 cm^{-1}, which corresponds to the torsion bending of NH_2 group, typically is ½. Similar ratios were found for the bands at 850, 1098, 1331 and 1418 cm^{-1} (⅓, ⅓, ¼ and ¾, respectively). The modes at 1098 and 1418 cm^{-1} are related to C–N bond stretching and bending vibrations and, therefore, reveal distinct polarization ratio.

In the spectra of Glutamine, we also observed the inversely polarized modes. The band at 241 cm^{-1} related to complex backbone bending was usually absent in parallel polarized spectrum. The symmetrical bending and asymmetrical stretching feature of CO^- unit located at 564 cm^{-1} were regularly polarized with the ratio 4/3. The intensity of perpendicularly polarized component of 653 cm^{-1} mode was very weak or up to 4 times smaller. Similar behavior was found for the band at 1588 cm^{-1} that corresponds to Amide II stretching vibration. The polarization ratio of asymmetrical bending mode at 1449 cm^{-1} was found to be 2/1. The band corresponding to the Amide mode at 1689 cm^{-1} was weakly distinguishable, so that its polarization ratio remains uncertain.

The only difference between the experimental spots, where the Raman spectra were obtained, was aluminum film morphological variability and random nature of amino acids recrystallization in solution. Taking these factors into account, we can state, that the microaggregates of Asparagine and Glutamine obtained from water solutions reveal complex disposition on the surface that affects their optical properties.

High-wavenumber range 2700…3500 cm^{-1}

Within this range, the vibrations associated with C–H, N–H and O–H stretching modes are expected to appear (Fig. 4b). Its assignments were identified according to the references [2, 3, 7-9, [11], 20]. The Raman spectrum of microcrystalline L-Asp shows three bands occurring at the highest frequencies, which are associated with the modes involved in hydrogen bonds formation: asymmetric amino group stretching vibrations $\nu_a(NH_2)$ (at 3386 cm^{-1}), asymmetric ammonium group stretching $\nu_a(NH_3)$ (at about 3113 cm^{-1}) and the weak band at 3402 cm^{-1}, often associated with OH symmetric stretching vibration of water ν_s(OH) [2, 20], however, it may be related to some OH vibration of the coupled oxygen and hydrogen from carboxyl and ammonium group of the same molecule, because of a reasonably large difference between experimental and DFT-calculation data [2]. In the Raman spectrum of L-Gln, we assigned the bands at 3404 and 3175 cm^{-1} to the asymmetric and symmetric stretching of the amino group [3, 9]. The band at 3212 cm^{-1} corresponds to the asymmetric stretching mode of NH_3^+ unit.

Within the high-wavenumber range, the spectrum of L-Glutamine reveals more intensive bands of CH modes that are related with the presence of one additional –CH_2– segment in this amino acid. It is noticeable not only for the enhanced intensity of CH_2 symmetric and asymmetric stretching, but also for appearance of CH mode at 2991 cm^{-1}. The study of Dhanelincourt *et al.* [3] states that the significant difference in intensity of polarized spectra of Glutamine is mostly observed for the band at 2950 cm^{-1} (which we found at 2952 cm^{-1}) for its in-plane attaching to NH_2 group. The significant decrease in the polarized spectrum intensity was also found for the bands corresponding to both symmetrical and asymmetrical stretching modes of amino groups. In the work of Moreno *et al.* [7], polarized electric field mostly affects the intensity of bands at about 3113 and 3402 cm^{-1}, which is consistent with our assumption about the nature of L-Asparagine stretching mode at 3402 cm^{-1}.

4. Conclusions

This study shows a significant difference in the Raman spectra of similar polar uncharged amino acids L-Asparagine and L-Glutamine, molecular structures of which distinguish only by the backbone methyl group. This difference influences the CH-vibrations frequency range as well as the fingerprint range due to spatial reorganization of functional groups. The dissimilar crystalline structure also affects their polarization features, which, we believe, depends on crystallization of aggregates. It could be seen from experiments that the intensity levels of vibrational bands, which correspond to normal modes of functional molecular groups, discriminate mostly.

The results presented in this report clearly show that the technique involving a micro-Raman spectroscopy provides good quality, reproducible vibrational spectra of amino acids in solid state. The spectra can be used to identify an amino acid or to elucidate the nature of adsorption of the molecules upon metallic surfaces.

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