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Температурные корреляции терагерцовых спектров *L*-аспарагина и *L*-тирозина

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Методом терагерцовой спектроскопии во временной области измерены температурные зависимости аминокислот алифатической *L*-аспарагин и ароматической *L*-тирозин в условиях низких температур. Наличие низкочастотных (0,1–2 ТГц) максимумов поглощения этих аминокислот при комнатной температуре подтверждено методами инфракрасной фурье-спектроскопии и рамановскими спектрами. Результаты свидетельствуют о том, что терагерцовые спектры алифатических и ароматических аминокислот различным образом меняются с изменением температуры. При понижении температуры максимумы поглощения аминокислот сдвигаются в коротковолновую область, и у некоторых из них появляются дополнительные пики поглощения. Вместе с тем изменения ширины пиков поглощения у них различны. Методами теории функционала плотности выполнены расчеты колебательных мод *L*-аспарагина и *L*-тирозина. Сделан вывод о том, что их колебательные моды формируются межмолекулярными силами.

Ключевые слова: терагерц, спектроскопия, температура, максимумы поглощения

Research on the terahertz temperature correlation of *L*-asparagine and *L*-tyrosine

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In this paper, the temperature characteristics of aliphatic *L*-asparagine and aromatic *L*-tyrosine amino acids at low temperature were measured by terahertz time domain spectroscopy. The low frequency (0.1–2 THz) absorption peaks of these two amino acids at room temperature were verified by Fourier transform infrared spectroscopy and Raman spectra. The results show that the terahertz spectra of aliphatic and aromatic amino acids have different responses to temperature. With the decrease of temperature, the absorption peaks of the two amino acids shifted blue, and some amino acids appeared new absorption peaks. However, the change of absorption peak width is slightly different. In this paper, the vibrational modes of *L*-asparagine and *L*-tyrosine are calculated by density functional theory. It is concluded that the vibrational modes of *L*-asparagine and *L*-tyrosine are formed by intermolecular forces.

Keyword: terahertz, spectroscopy, temperature, characteristics, absorption peak.

OCIS codes: 300.0300, 040.2235, 010.1030

1. INTRODUCTION

Terahertz wave is a kind of electromagnetic wave between microwave and infrared. The frequency range is between 0.1–10 THz. Terahertz spectroscopy is widely used in biomedicine, environmental detection, safety inspection, communication and astronomy [1–4]. Because the metal detection method, resonance method, neutron method and X-ray method, which are often used in the field of security inspection, can cause some harm to human body, therefore, these methods can only be used in the detection of goods and luggage. The low energy of terahertz pulse does not cause photoionization of biomolecules, which makes it an effective non-destructive testing method and has been gradually used in the field of biomolecules.

Fei Wu *et al.* [5] used terahertz time domain spectroscopy (THz-TDS) to measure and analyze 20 kinds of amino acids at room temperature and obtained the characteristic fingerprint spectra of amino acids in the wide spectrum range of 0–6 THz. Williams *et al.* [6] reported the experimental and calculated terahertz spectra of polycrystalline valine samples. The absorption peak of *L*-valine was measured by THz-TDS at room temperature and low temperature (78 K). It was found that the absorption peak red shifted with the increase of temperature. Michael *et al.* [7] used THz-TDS to measure *DL*-leucine and *DL*-valine respectively. When the temperature decreased from room temperature to 80 K, the three absorption peaks of *DL*-leucine shifted from 1.37, 1.87, and 2.25 THz to 1.47, 1.97, and 2.54 THz respectively, and the absorption peak of *DL*-valine shifted from 1.70 to 1.73 THz. When the temperature decreased from room temperature to 80 K, the three absorption peaks of leucine shifted from 1.37, 1.87, and 1.54 THz to 1.47, 1.97, and 2.54 THz respectively. At the same time, the linewidth of the absorption peak narrows with the decrease of temperature. The above studies show that amino acids have a strong temperature correlation in terahertz band, but the previous studies are limited to the comparison of the results of two temperatures, and the selected amino acids belong to aliphatic amino acids. Therefore, in this paper, a number of temperature nodes will be selected to analyze the correlation between terahertz spectra and temperature of aliphatic amino acids and aromatic amino acids, and the single molecule

and unit cell structure will be calculated theoretically.

The results showed that with the decrease of temperature, the absorption peak position of amino acids shifted towards shorter wavelengths, and the absorption peak linewidth of aliphatic amino acids became narrower, while the absorption linewidth and intensity of aromatic amino acids *L*-tyrosine remained unchanged. At the same time, the terahertz spectra of amino acid single molecule and unit cell molecule were calculated by density functional theory. Compared with the experimental results, it was found that there was a strong intermolecular force between the two amino acids, which had a great influence on the terahertz absorption peak.

2. EXPERIMENTAL PART

2.1. Experimental apparatus

The THz-TDS system used in this article is a transmission time-domain spectroscopy detection system, as shown in Fig. 1.

2.1. Sample preparation

The experimental samples were purchased from Sigma Aldrich Chemical Reagent Co., Ltd., with a purity of more than 99% and without further purification. *L*-asparagine is aliphatic amino acid, molecular formula — $C_4H_8N_2O_3$. *L*-tyrosine is aromatic amino acid, molecular formula — $C_9H_{11}NO_3$. All samples were crystalline powder.

The weight of amino acid solid samples varies between 8–10 mg. In order to ensure that the particle size of the sample is much smaller than the terahertz wavelength and reduce the baseline offset caused by non-resonant light scattering at a higher frequency, the sample was prepared by grinding in a mortar [8–9]. In order to reduce the absorption intensity of THz wave by pure sample to an appropriate level, after mixing pure sample with 100 mg polyethylene, the pure sample is pressed into a sheet of about 1.2 mm thickness, and the pressure is 30 MPa, keeping the two surfaces parallel and free of cracks. At the same time, the polyethylene powder of 100 mg was pressed into the same thin sheet as the sample, which was used as the reference background.

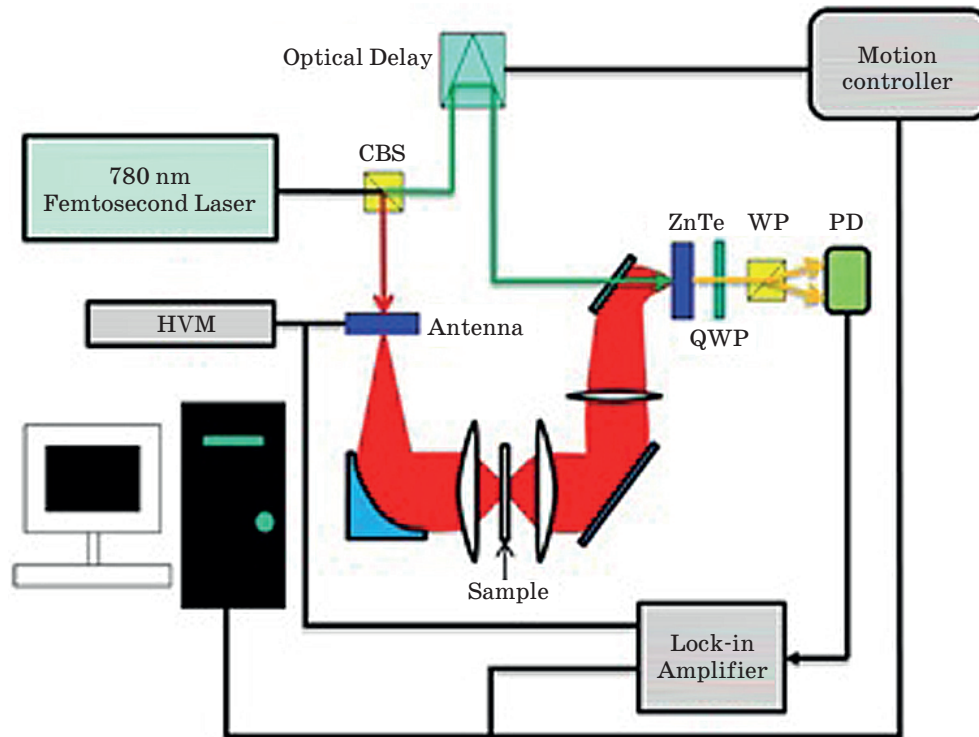


Fig. 1. Transmission time-domain spectroscopy detection system.

2.2. Data processing

To analyze the optical properties of matter, it is necessary to extract optical physical quantities such as real refractive index and extinction coefficient. Because of the fingerprint spectral characteristics of terahertz wave, the optical constant in this band can be easily extracted by terahertz time domain spectroscopy. Considering that the response function of the THz-TDS system is independent of time, it is necessary to ensure that the structure of the two surfaces of the sample is smooth, parallel and uniform when measuring the sample. The complex refractive index $n_i = n - jk$ can be used to describe the macroscopic properties of the samples. Where n is the refractive index, indicating the dispersion of the sample, k is the extinction coefficient, corresponding to the absorption properties of the sample. The relationship between absorption coefficient and extinction coefficient such as

$$\alpha = \frac{2\omega k}{c}. \quad (1)$$

The frequency domain signals $R(\omega)$ and $S(\omega)$ can be obtained by Fourier transform of the background signal and the time domain signal

of the sample at the same time. The amplitude $\rho(\omega)$ and phase $\varphi(\omega)$ of the sample can be obtained from

$$\frac{S(\omega)}{\rho(\omega)} = \exp(-j\varphi(\omega)). \quad (2)$$

Refractive index

$$n_s(\omega) = \varphi(\omega) \frac{c}{\omega d} + 1. \quad (3)$$

Absorption coefficient

$$a_s(\omega) = \frac{2}{d} \ln \left(\frac{4n_s(\omega)}{\rho(\omega)(n_s(\omega) + 1)} \right). \quad (4)$$

3. RESULTS AND DISCUSSION

3.1. Terahertz absorption spectrum

In this paper, the terahertz spectra of two kinds of amino acids at different temperatures were measured by THz-TDS. Figure 2 shows the absorption spectra of 10 mg *L*-asparagine mixed with 100 mg polyethylene during cooling and heating (the experimental results in the figure

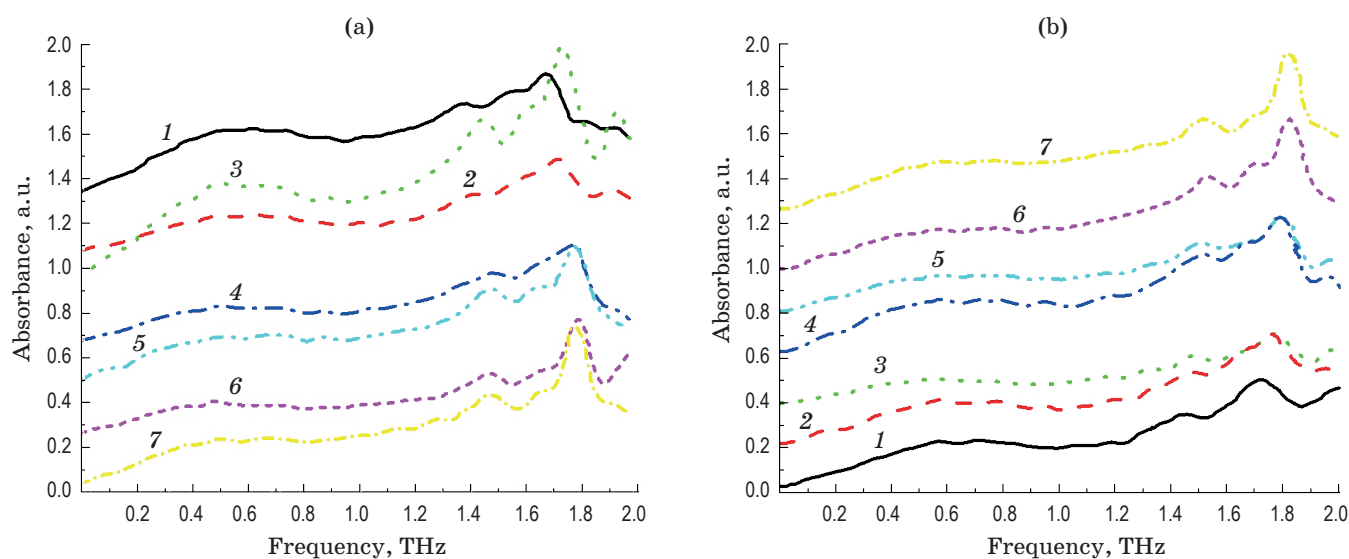


Fig. 2. Terahertz absorption spectra of *L*-asparagine. (a) Temperature dropping process, (b) temperature rising process. 1 — room temperature, 2 — 250 K, 3 — 200 K, 4 — 150 K, 5 — 100 K, 6 — 50 K, 7 — 5 K.

Table 1. Changes of absorption peak position of *L*-asparagine during cooling and heating

| Temperature dropping process | | | Temperature rising process | | | | |
|------------------------------|-----------------------|------|----------------------------|-----------------------|------|------|------|
| Temperature, K | Absorption peaks, THz | | Temperature, K | Absorption peaks, THz | | | |
| room | 0.92 | 1.63 | 1.86 | 5 | 0.95 | 1.70 | 1.95 |
| 250 | 0.93 | 1.65 | 1.87 | 50 | 0.94 | 1.69 | 1.95 |
| 200 | 0.93 | 1.66 | 1.89 | 100 | 0.94 | 1.68 | 1.93 |
| 150 | 0.93 | 1.68 | 1.91 | 150 | 0.93 | 1.67 | 1.90 |
| 100 | 0.94 | 1.69 | 1.92 | 200 | 0.93 | 1.65 | 1.89 |
| 50 | 0.94 | 1.69 | 1.94 | 250 | 0.92 | 1.65 | 1.88 |
| 5 | 0.95 | 1.70 | 1.95 | room | 0.92 | 1.63 | 1.86 |

are translated upward with the change of temperature on the basis of the original longitudinal coordinates in order to distinguish the results many times). It can be seen from Fig. 2, that *L*-asparagine has three strong absorption peaks at room temperature: 0.92, 1.63, and 1.86 THz. With the change of temperature, the position of the absorption peak changes as shown in Table 1.

By observing the data in Table 1, it can be concluded that when the temperature decreases from room temperature to 5 K, the absorption peaks at 0.92, 1.63, and 1.86 THz shift to 0.95, 1.70, and 1.95 THz respectively, and when the temperature increases from 5 K to room temperature, the corresponding absorption peaks shift

from 0.95, 1.70, and 1.95 THz to 0.92, 1.64, and 1.86 THz respectively. With the increase of temperature, the position of the absorption peak shifts around 0.1 THz. Because the resolution of the instrument is 10 GHz, the shortwave shift is not caused by the equipment error. At the same time, it can be observed from Fig. 1 that the linewidth of the absorption peak is the narrowest at 5 K. Compared with the same temperature in the process of heating and cooling, it is found that the change of the position of the absorption peak is also in the error range, which is not affected by the temperature, indicating that the biological characteristics of amino acids have not changed in the process of temperature change.

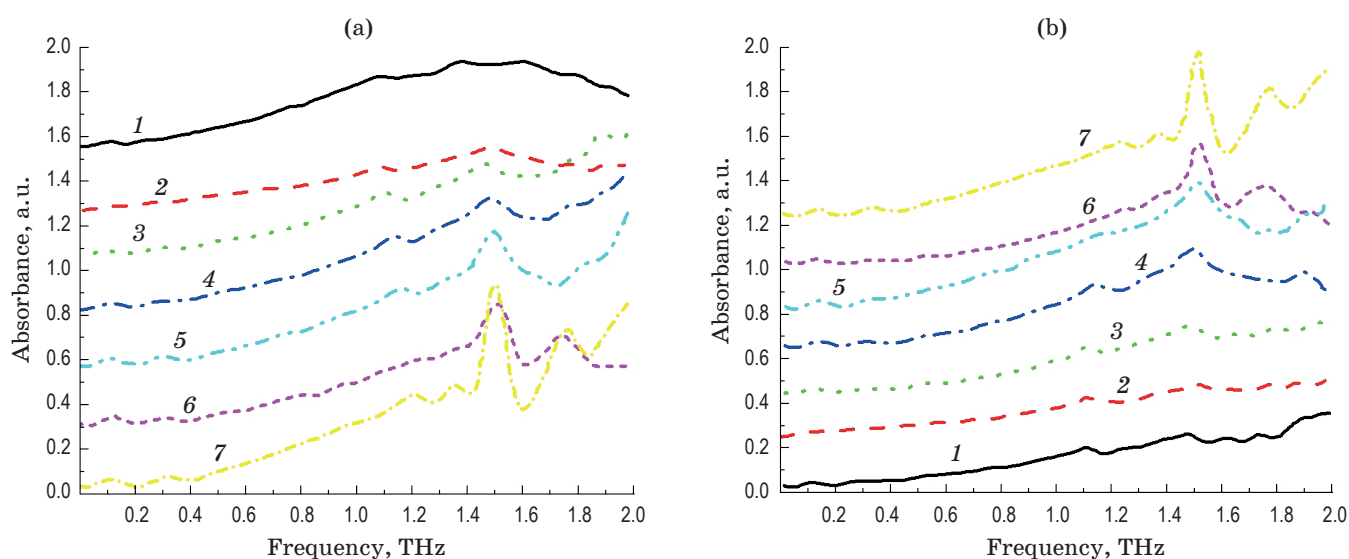


Fig. 3. Terahertz absorption spectra of *L*-tyrosine. (a) Temperature dropping process, (b) temperature rising process. 1 — room temperature, 2 — 250 K, 3 — 200 K, 4 — 150 K, 5 — 100 K, 6 — 50 K, 7 — 5 K.

Table 2. Changes of absorption peak position of *L*-tyrosine during cooling and heating

| Temperature dropping process | | | | | Temperature rising process | | | | |
|------------------------------|-----------------------|------|------|------|----------------------------|-----------------------|------|------|------|
| Temperature, K | Absorption peaks, THz | | | | Temperature, K | Absorption peaks, THz | | | |
| room | 1.17 | 1.26 | 1.48 | 1.75 | 5 | 1.24 | 1.31 | 1.60 | 1.81 |
| 250 | 1.18 | 1.26 | 1.49 | 1.75 | 50 | 1.23 | 1.30 | 1.58 | 1.80 |
| 200 | 1.18 | 1.27 | 1.51 | 1.76 | 100 | 1.22 | 1.29 | 1.55 | 1.79 |
| 150 | 1.19 | 1.28 | 1.55 | 1.77 | 150 | 1.21 | 1.28 | 1.53 | 1.77 |
| 100 | 1.20 | 1.29 | 1.57 | 1.78 | 200 | 1.19 | 1.27 | 1.51 | 1.76 |
| 50 | 1.22 | 1.30 | 1.59 | 1.80 | 250 | 1.18 | 1.27 | 1.49 | 1.76 |
| 5 | 1.24 | 1.31 | 1.60 | 1.81 | room | 1.17 | 1.26 | 1.48 | 1.75 |

Figure 3 shows the absorption spectra of 10 mg *L*-tyrosine mixed with 100 mg polyethylene during cooling and heating. Figure 3 shows that *L*-tyrosine have four strong absorption peaks at room temperature: 1.17, 1.26, 1.48, and 1.75 THz. When the temperature decreased from room temperature to 5 K, the corresponding absorption peaks shifted to 1.24, 1.31, 1.60, and 1.81 THz respectively, and when the temperature increased from 5 K to room temperature, the corresponding absorption peaks shifted from 1.24, 1.31, 1.60, and 1.81 THz to 1.17, 1.26, 1.48, and 1.75 THz. Tables are typed on separate sheets and are not embedded in text.

Respectively, with the change of temperature, the position of the absorption peak chang-

es as shown in Table 2. It can be concluded that with the decrease of temperature, the absorption peak of tyrosine to terahertz spectrum has the law of shortwave shift, but the linewidth and intensity of absorption peak have no obvious change in the process of temperature decrease.

3.2. Comparison of the results of THz-TDS, Fourier-transform infrared and Raman spectra

Figure 4 is the comparison of the test results of THz-TDS, Fourier-transform infrared (FTIR) spectrometer and Raman spectrometer the temperature of the sample is room. The test result of FTIR spectrometer is the combination of 6 μ m Mylar film and 25 μ m Mylar film. The 0.1–2 THz range is measured by 25 μ m Mylar film beam

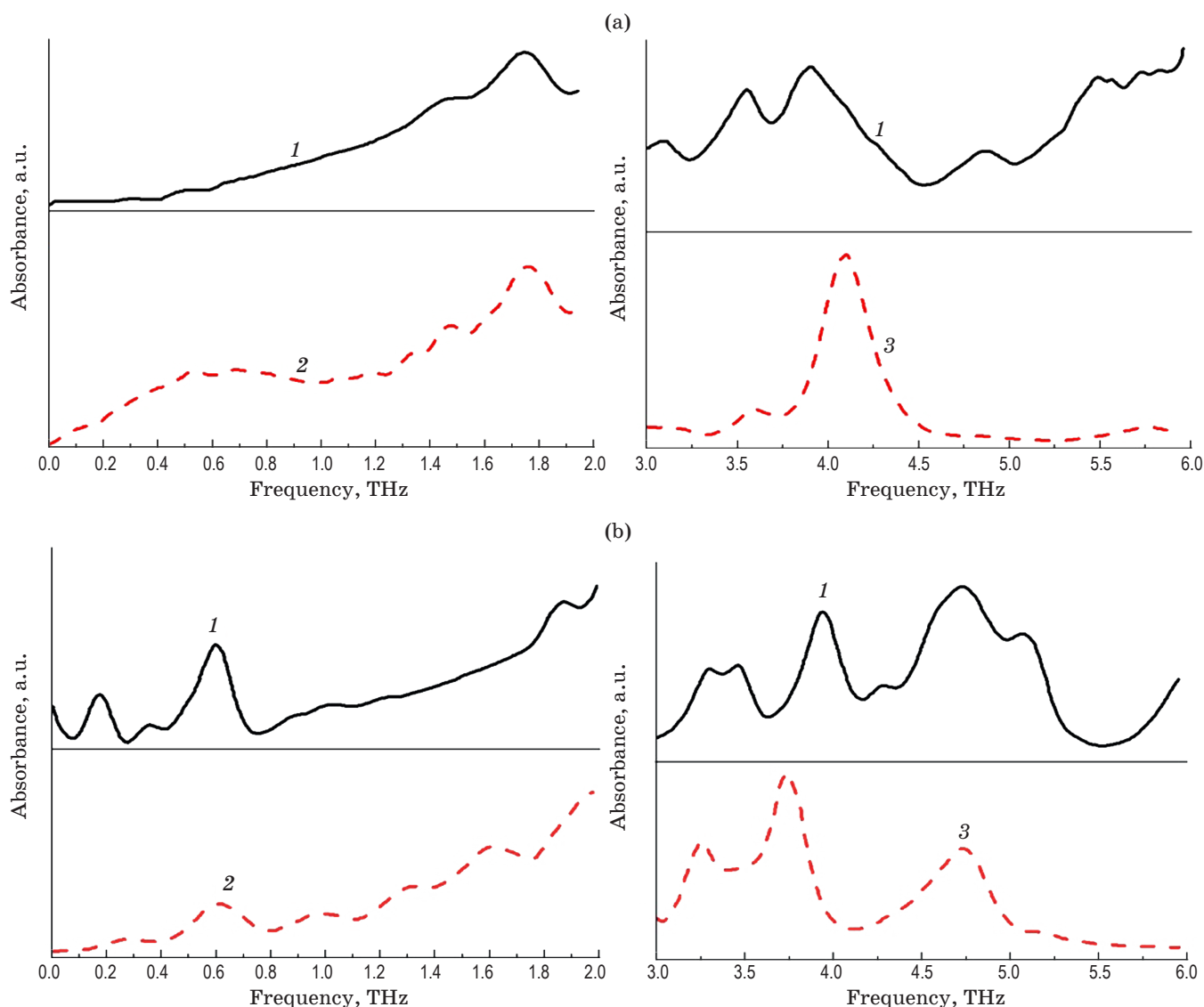


Fig. 4. Comparison of the results of three spectra of *L*-asparagine (a) and three spectra of *L*-tyrosine (b). 1 — FTIR, 2 — THz-TDS, 3 — Raman.

splitter and the 3–6 THz range is measured by 6 μm Mylar film.

It can be found from Fig. 4 that FTIR spectrometer and THz-TDS can detect consistent absorption peaks in the 0.2–2 THz range. Obviously, the THz-TDS measurement results are more accurate and can detect more absorption peaks, especially the degenerate peaks. In the 3–6 THz range, compared with the test results of FTIR spectrometer and Raman spectrometer, it can be found that the frequency of the sample absorption peak corresponds to the Raman intensity, which further verifies the accuracy of the experiment.

4. THEORETICAL ANALYSIS

In this paper, the molecular structures of an aliphatic amino acid *L*-asparagine and an aromatic amino acid *L*-tyrosine were calculated by using quantum chemistry Gaussian 09 Software package [10–12]. The molecular structure comes from the molecular structure of Cambridge crystal structure center (Cambridge crystallographic data Centre). In the process of calculation, the single molecular structure and unit cell of the two amino acids were calculated by density functional theory and B3LYP/6-31G (d) method respectively.

Figure 5 shows that the calculated results of the single molecular structure and unit cell

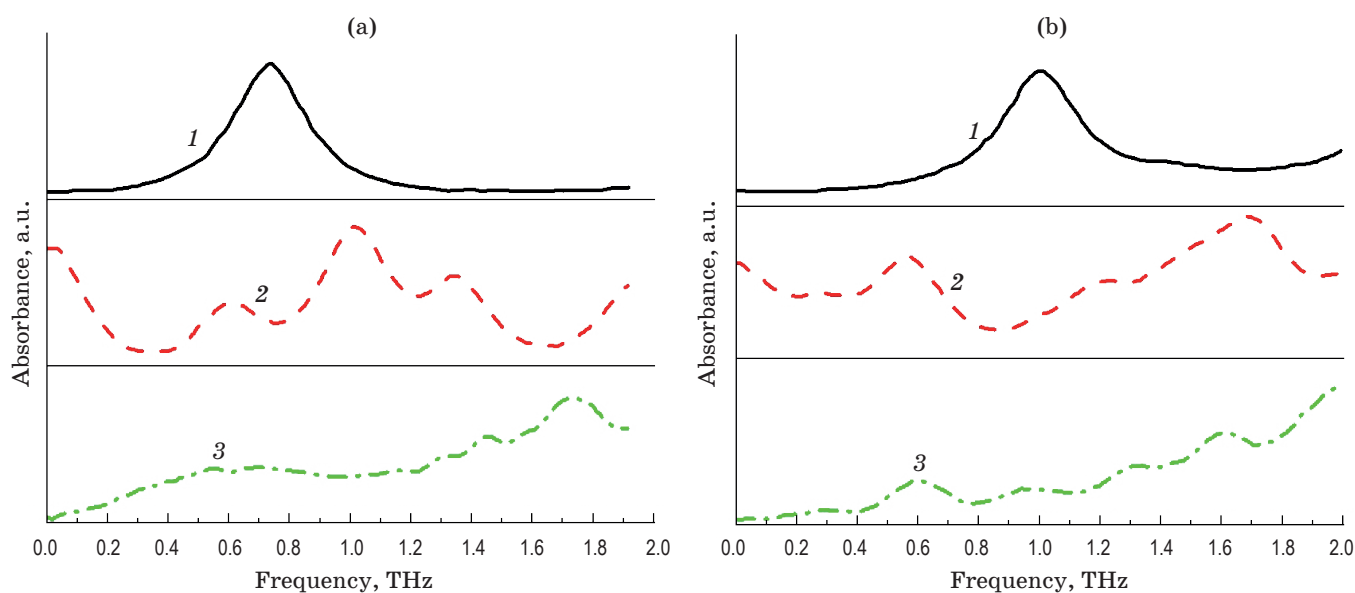


Fig. 5. Calculation results of single molecular structure and unit cell structure of *L*-asparagine (a) and *L*-tyrosine (b) at room temperature. 1 — molecule, 2 — unit, 3 — THz-TDS.

structure of *L*-asparagine and *L*-tyrosine are compared with the experimental results. Figure 5 shows that the calculated results of the crystal cell structure are basically consistent with the absorption peak position obtained from the experiment, which further verifies the accuracy of the experiment. At the same time, it shows that the vibration mode of the single molecule is mainly determined by the intramolecular force. The vibration mode of the unit cell is determined by the intramolecular force and the intermolecular force, which is more consistent with the experimental environment.

5. CONCLUSION

The correlation between spectral characteristics and temperature of two aliphatic amino acids *L*-asparagine and aromatic amino acid *L*-tyrosine in 0.2–2 THz frequency band was studied by using terahertz time domain spectrometer. Combined with Fourier transform infrared spectroscopy, the frequency measurement range is expanded, the accuracy of terahertz time domain spectroscopy is verified, and the measurement results of terahertz time domain spectroscopy at room temperature are further verified by Raman spectroscopy. It is found that the absorption peaks of aliphatic *L*-aspara-

gine are shortwave shifted with the decrease of temperature, and the absorption peak linewidth is narrower, the intensity is stronger and easier to distinguish at low temperature. When the temperature is reduced to 40 K, it is found that the absorption intensity and linewidth of *L*-tyrosine do not change. The crystal cell structures of *L*-asparagine and *L*-tyrosine molecules were calculated by Gaussian Software, and the absorption peaks consistent with the measurements were obtained. It is predicted that the interaction between molecules has a great influence on the terahertz spectral absorption of amino acid molecules.

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