First principles investigation of L-alanine in terahertz region

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Abstract Terahertz absorption spectrum (0.5–4.0 THz) of L-alanine in the solid phase was measured by terahertz time-domain spectroscopy at room temperature. Simulations utilizing gaseous-state and solid-state theory were performed to determine the origins of the observed vibrational features. Our calculations showed that the measured features in solid-state materials could be well understood by considering the crystal packing interactions in a solid-state density functional theory calculation. Furthermore, intermolecular vibrations of L-alanine are found to be the dominating contributions to these measured spectral features in the range of 0.5–4.0 THz, except that located at 3.11 THz.

Keywords THz-TDS · L-alanine · Solid-state theory

1 Introduction

Terahertz (THz) radiation, the frequency of which is between those of infrared and microwave, is of critical importance in the spectroscopy of many molecular systems [1, 2]. Studies of THz waves were hindered for many years due to the lack of convenient and suitable radiation sources and detectors. However, advances over the last decade in lasers and semiconductors have opened up tremendous opportunities in this region. In recent years, THz time-domain spectroscopy (THz-TDS) based on femtosecond laser technology has been considered as a competitive tool for medical diagnosis [3–5], pharmaceutical characterization [6–8], and security applications [9, 11] because THz-TDS is strikingly sensitive not only to the biological molecule itself but also to its surrounding environment.

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For example, the spectrum of glucose in polycrystalline form measured by THz-TDS is totally different from the spectrum measured in amorphous form, which can be considered as an easy way to identify materials in different states [12]; the spectra among all-trans, 9-cis, and 13-cis retinal are also distinctly different, making the characterization of isomeric crystals efficient [13].

As important biological materials, amino acids have received extensive attention due to their THz absorption spectra [14–18]. Among amino acids, of particular interest is L-alanine due to its simple molecular structure. Much work has been carried out on the spectral properties of L-alanine, including Raman scattering ($25\text{--}175\text{ cm}^{-1}$) [19], far-infrared absorption spectra ($20\text{--}600\text{ cm}^{-1}$) [20], and THz absorption spectra [21–25]. Up to now, some work dealt with the THz spectrum of L-alanine only in terms of experiment [21–23]. Others, using a combination of experiment and simulation, only focused on the spectral range in $0.5\text{--}3.1\text{ THz}$ [24] or calculated the THz spectrum in a single molecular mode [25]. Through these previous researches, we find that the origins of the measured spectral peaks of L-alanine in the range of $0.5\text{--}4.0\text{ THz}$ are still not clearly explained, especially the peaks located at 3.11 and 3.33 THz .

Thus, in this paper, we investigated the spectrum of L-alanine ranging from 0.5 to 4.0 THz experimentally and theoretically. Specifically the THz spectrum of L-alanine at room temperature (RT) was measured by THz-TDS. The absorption spectra of isolated molecule and crystal cell were calculated by the theory of linear combination of atomic orbital (LCAO) and plane-wave pseudopotentials (PWP), respectively. Based on the calculated results, the structure of the L-alanine monomer has been theoretically analyzed and the measured spectral peaks in the range of $0.5\text{--}4.0\text{ THz}$ have been clearly assigned.

2 Experimental and theoretical methods

The THz-TDS setup used in our experiment has been described previously [26]. In brief, a Ti:sapphire laser provides ultrafast pulses of 15-fs duration at a center wavelength of 790 nm with a repetition rate of 76 MHz . The output beam is split into a pump beam and a probe beam by a beam splitter. The photoconductive emitter is used to generate THz radiation, which is detected effectively by electro-optic sampling (EOS) [27] with a bandwidth between 0.1 and 4.5 THz . Four off-axis parabolic mirrors are used to collect and collimate THz radiation. The output signals from the balanced photodiodes are monitored by a lock-in amplifier and a computer. The sample pellet is mounted in an aluminium sample holder fixed in position with a Teflon securing ring for the measurements at room temperature.

Powder X-ray diffraction experiments were performed at the Analytical Research Facility of Northwestern University. The X-ray diffraction (XRD) pattern was recorded using a D/MAX-3C X-ray powder diffractometer. Data were collected in 2-theta ranges from 10 to 50° using Cu K α radiation.

L-alanine was purchased from WOLSEN Co., LTD. (China) in the purest form ($>99.5\%$) and used without further purification. The L-alanine was mixed with high-density polyethylene (HDPE) powder in a mass ratio of $1:15$ (sample: PE). The mixture was then compressed into a 2.40-mm -thickness pellet with a pressure of 600 kg/cm^2 . The experiment was performed with the reference of HDPE at room temperature.

Calculations on the isolated molecule were carried out using the gaseous-state theory within the LCAO method. The Hartree-Fock (HF) function together with the 6-311++G(d, p)

Fig. 1 Arrangement and interactions of L-alanine molecules in the solid-state

basis set was carried out with the program option ‘tight’ convergence criteria. Simulation of the unit cell was performed using the solid-state theory based on the PWP density functional method within the generalized gradient approximation of Perdew-Wang 91 (PW91) function [28]. The total energy was converted to 10^{-8} eV/atom and the atomic coordinates were optimized until the maximum forces between atoms was less than 10^{-5} eV/Å. Brillouin zone integrations use only the Γ point because the electronic energy levels are non-dispersive. The crystal structure of L-alanine is taken from ref. [29]. The unit cell is orthorhombic with space group $P2_12_12_1$ and contains four L-alanine molecules. The available unit cell parameters at room temperature are $a = 6.032$ Å, $b = 12.343$ Å, $c = 5.784$ Å, $\alpha, \beta, \gamma = 90.0^\circ$, and volume $V = 429.4$ Å³. However, it is worth noting that the solid-state calculation is performed with the fixed unit cell. The structure of L-alanine in polycrystalline state is shown in Fig. 1. The dashed lines indicate the hydrogen bonds between molecules in the unit cell. The isolated molecule of L-alanine has 13 atoms and does not possess any symmetry. All the 33 intra-molecular modes are IR active. The coupling of 52 atoms of four zwitterions in the unit cell leads to 153 optical modes. However, owing to the D_2 space group symmetry, there are 132 internal and 15 intermolecular modes which are IR active.

3 Results and discussion

Prior to the THz-TDS experiment, the purity of the L-alanine powder was verified by powder X-ray diffraction, as shown in Fig. 2. As expected, L-alanine has $P2_12_12_1$ crystal symmetry. The inset (b) in Fig. 2 provides expected 2-theta positions and relative peak intensities for previous published structure [29]. The XRD pattern is in good agreement with previous structural data.

THz spectra of L-alanine have been published previously [20–22] and are summarized in Table 1 together with our experimental results. It is evident that our experimental results show good agreement with these previous works measured at room temperature. From the

Fig. 2 Powder XRD patterns of L-alanine (**a**). The line patterns represent previously published XRD (**b**)

data in ref. [20], it can be observed that all absorption features shift to higher frequency as the temperature is decreased from 300 K to 6 K, especially the two peaks at 3.33 THz and 3.81 THz, which show the typical shift of about 5 cm^{-1} and 13 cm^{-1} at 6 K, respectively. This pronounced shift suggests that THz spectrum of L-alanine is highly sensitive to its surrounding temperature.

In order to exploit the origins of these measured features, simulation was needed. Before the spectral calculation is performed, two points should be addressed here. The first is that the molecular structure of L-alanine monomer in the zwitterion form $[\text{CH}_3\text{CH}(\text{NH}_3^+)\text{-COO}^-]$ was changed to the neutral form $[\text{CH}_3\text{CH}(\text{NH}_2)\text{-COOH}]$ after geometry optimization by the HF function. The configurations of the L-alanine monomer in the two forms are shown in Fig. 3. According to the structure transformation after geometry optimization, the neutral form of the L-alanine monomer is able to obtain a lower minimum energy than that in the zwitterion form. Meanwhile, a new intra-molecular hydrogen bond has been formed between the hydrogen atom of the carboxy group and the nitrogen of the amine group so as to stabilize the neutral form. However, molecules of L-alanine in the unit cell, which has four molecules, still have the zwitterion structure $[\text{CH}_3\text{CH}(\text{NH}_3^+)\text{-COO}^-]$, even after geometry optimization. Indeed, it is not easy to clearly explain the reason that the zwitterionic structure of L-alanine is so stable, but whether a crystal becomes zwitterionic or non-zwitterionic in the minimum-energy state can be decided by the total energy of the enthalpy of sublimation [20]. Moreover, the calculation on isolated molecule only involves the intra-molecular vibrational modes, while simulation of the unit cell presents both the intra-molecular and intermolecular modes.

In isolated-molecule simulation, an intra-molecular vibrational mode at 1.89 THz (62.46 cm^{-1}) is obtained, but this feature does not appear in our experimental data. The reason may be the differences of the structures presented in the gaseous-state calculation and the solid-state experiment. In fact, the lowest-frequency mode of the calculated spectral

Table 1 Experimental frequencies (THz) for solid-state L-alanine

Our work	Ref. [20]		Ref. [21]	Ref. [22]
	6 K	300 K	RT	RT
2.20	2.26	2.21	2.25	2.25
2.53	2.64	2.58	2.60	2.60
3.11	3.33	2.85 ^a		3.20
3.33	3.81	3.18		3.40
		3.41		

^aThe peak is centered at 3.18 THz and a weak shoulder is around 2.85 THz

Fig. 3 The molecular structures of L-alanine in the zwitterion form before optimization (a) and in the neutral form after optimization (b)

peak was found at 5.70 THz (188 cm^{-1}) utilizing the CASTEP code in a single molecular mode [25] and the lowest-frequency mode in our calculation on a unit cell with four molecules was presented at 2.25 THz. These numerical results suggest calculation on isolated molecules should be interpreted with caution when discussing the vibrational modes of condensed phase materials in the THz region.

Since isolated-molecule mode has no contribution to our region of interest, solid-state theory has to be used for further investigation. The quality of the simulation is first evaluated

Table 2 Comparison of experimental and calculated molecular geometries of L-alanine

	Experiment	Calculation
Bond lengths		
C1-C2	1.531	1.536
C2-C3	1.524	1.506
C2-H2	1.093	1.088
C3-H5	1.082	1.086
C3-H3	1.081	1.088
C3-H7	1.081	1.087
C2-N1	1.487	1.488
N1-H1	1.029	1.042
N1-H4	1.047	1.065
N1-H6	1.031	1.047
C1-O1	1.242	1.160
C1-O2	1.258	1.185
RMSD		0.033
Bond angles		
C1-C2-C3	111.07	110.32
C2-C3-H5	110.57	110.73
C2-C3-H3	110.33	110.50
C2-C3-H7	111.37	110.83
H7-C3-H5	108.36	108.14
H7-C3-H3	108.25	108.31
H3-C3-H5	108.90	108.24
C1-C2-H2	108.55	108.94
C1-C2-N1	110.05	110.98
C2-N1-H1	111.33	110.56
C2-N1-H4	109.40	109.98
C2-N1-H6	109.05	110.26
C2-C1-O1	118.39	118.00
C2-C1-O2	115.97	115.71
RMSD		0.59

Fig. 4 The experimental and calculated THz absorption spectra of L-alanine

by the comparison of experimental and calculated structural parameters of L-alanine. The published crystal structure [29] at room temperature was used as the starting point for geometry optimization. It is worth noting that the calculation is performed with the fixed unit cell and the structural studies of L-alanine with different theories have been reported previously [30–32]. In Table 2, a complete list of tabulated bond lengths and bond angles for L-alanine obtained from the solid-state calculation using PW91 are provided. The structural data from the corresponding crystallographic measurement are also given along with root-mean-square deviation (RMSD) of the calculated bond lengths and angles as compared with the experimental values. RMSD are provided for an overall quantitative measure of the quality of structural reproduction by the theory. From Table 2, it can be seen that solid-state calculation yields a very good agreement with the experimental structures with the maximum RMSD being 0.033 Å for bonds and 0.59° for angles.

Table 3 Experimental and calculated frequencies (THz) of L-alanine

Experiment	Calculation	
RT	Crystal	Description ^b
2.20	2.25 (7.33) ^a	ET along crystal a axis
	2.50 (1.35)	ET along crystal a axis
2.53	2.63 (1.75)	ET along crystal c axis
	2.65 (8.13)	ER along crystal b axis
3.11	3.02 (35.6)	–CH ₃ bending
	3.12 (9.48)	C2 and C3 bending
	3.17 (0.16)	ET along crystal c axis
	3.29 (2.93)	ER along crystal c axis
3.33	3.74 (18.75)	ER along crystal b axis

^aInfrared intensities (KM/mol) are shown in parentheses

^bET, external translation; ER, external rotation

In Fig. 4, we present the comparison of the THz spectra of L-alanine between experiment and solid-state calculation. An empirical 3 cm^{-1} full-width half-maximum Lorentzian line shape has been convolved with the theoretical data for visual comparison. It can be seen that the THz spectrum from solid-state calculation provides a reasonable agreement with the experimental data.

Based on the solid-state calculation, four experimental spectral features observed at low frequency consist of nine IR-active vibrational modes. However, because four calculated modes located at 2.50, 2.63, 3.17, and 3.29 THz have weak intensities, the four measured features can be mainly interpreted by the remaining five predicted modes. Specifically, it is clear that the calculated mode at 2.25 THz contributes to the lowest energy feature observed at 2.20 THz in the experiment, and the calculated mode at 2.65 THz corresponds to the experimental feature at 2.53 THz. The feature at 3.11 THz in the experimental spectrum is primarily assigned to the calculated modes at 3.02 and 3.12 THz. The absorption at 3.33 THz could be assigned to the calculated mode at 3.74 THz. Nevertheless, the limitation of solid-state calculation still exists. It is clear that the last calculated mode shifts significantly to high frequency. A possible explanation may be due to the overestimation the energies of the mode at 3.74 THz. It is worth noting that the same phenomenon can be found in many solid-state calculations [8, 33–35].

To fully interpret the vibrational modes of L-alanine, assignments of these vibrational modes are described in Table 3. Descriptions of each mode were made by visual inspection of the atomic displacements and are based on the most significant contributions to the vibrational mode character. Since the normal modes have been assigned to the specific modes of molecules in the unit cell, the natural origins of these measured spectral features can be determined as follows: two measured experimental peaks at 2.20 THz and 2.53 THz may originate from the inter-molecular vibrations. This conclusion is consistent with the experimental result obtained in ref. [21]. Also, the experimental feature at 3.11 THz is theoretically assumed to be an intra-molecular mode, in addition to the last feature at 3.33 THz caused by inter-molecular vibration. The conclusions of the last two features are supported by the observation in [22] that only one absorption feature of DL-alanine has been obtained in the neighborhood of 3.15 THz in the region of 2.0–5.0 THz.

4 Conclusions

In conclusion, we have investigated experimentally and theoretically the THz spectra of L-alanine. The structural change of the isolated L-alanine after optimization implies that the L-alanine monomer in the neutral form is more stable than that in the zwitterion form. The numerical result suggests that cautious interpretation of the THz spectrum in solid-state material is necessary when calculation is performed on isolated molecule. Meanwhile, simulation using the solid-state theory has produced a nearly realistic description of the low-THz spectrum, implying that solid-state DFT is an excellent method for THz spectrum reproduction. Through our theoretical analyses, intermolecular vibrations are found to be the dominating contributions to these measured spectral peaks of L-alanine in the range of 0.5–4.0 THz, except for the peak located at 3.11 THz.

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