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The effect of conformational freedom of side chain on low-frequency motions of amino acids in solid-state

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ABSTRACT

A comparison of low frequency motions of two amino acids, namely L-threonine and L-valine are made by employing terahertz spectrometer and DFT calculations. Quantitative analyses of the composition of their low-frequency motions are performed. The results suggest that the distortions of dihedral angles of L-threonine dominate intramolecular motions over distortions of bond angles, while the difference between the degrees of distortions of dihedral angles and bond angles of L-valine is much smaller. These observations can be interpreted from the view of conformational freedom of their side chains.

1. Introduction

Low-frequency motions in biological system play significant roles in ligand-protein interaction [1], solvation of protein in aqueous phase [2,3], intercalation of drug in DNA [4] and other processes [5–7]. Understanding the nature and properties of low-frequency motions of biomolecules is important for the elucidation of functions of proteins and drugs in biological processes. However, clarifying the mechanism of low-frequency motions of large biomolecules is always challenging due to structure-less spectra and high computational costs. As unit block of protein, amino acids have been intensively measured and modeled in their solid-state forms [8–14]. Nevertheless, only a few investigations [8,10,14] were carried out for revealing the relationship between low-frequency motion and molecular structures. From our point of view, to comprehensively understand low-frequency motions of amino acids, efforts are essentially required to figure out how different structures of amino acids affect their low-frequency motions. It has been shown that the conformational freedom of side chain has great impacts on bindings of peptides to membrane system [15] and hydrations of amino acids in aqueous phase [16]. Therefore, it is an important factor of governing functionality of amino acids or peptides. In this work, we aim at studying how the conformational freedom of side chain of amino acids affects their low-frequency motions.

L-threonine, which is a polar amino acid with α-hydroxyethyl group as its side-chain (Fig. 1a), is essential to human beings. L-valine is also an essential and branched-chain amino acid. It is hydrophobic as it possesses a side chain of isopropyl group (Fig. 1b). Those two molecules have similar sizes. Furthermore, as Table 1 shows, their unit cell volumes are roughly close. In both crystals, adjacent molecules are connected with each other via hydrogen bonds (Fig. 2). It should be noted that compared with the side chain of L-threonine, that of L-valine does not form any hydrogen bond with others, resulting in a larger degree of freedom. We are interested in examining how this difference affects their low-frequency motions. We employed time-domain terahertz spectrometer to probe their low-frequency motions. And we carried out solid-state DFT calculations to obtain vibrational modes. To analyze atomic displacement vectors in each vibrational mode, we employed the approach proposed by Schmuttenmaer and his coworkers [8]. It can produce colorful figures which quantitatively project collective

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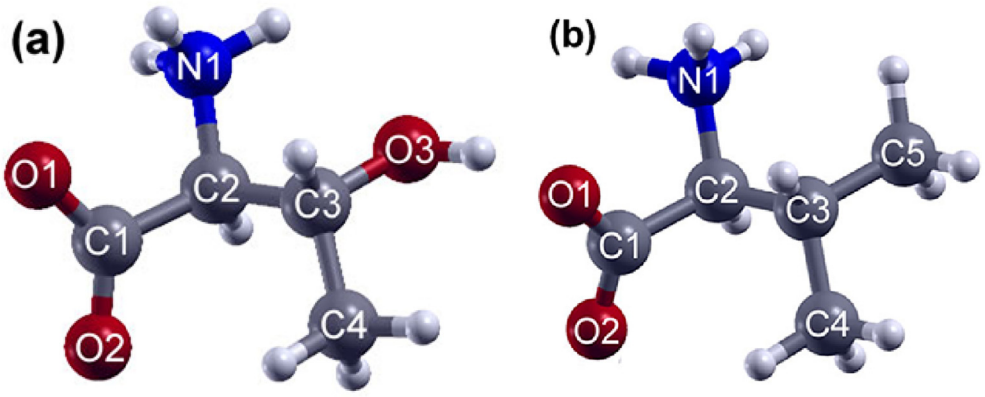

Fig. 1. Molecular structures of L-threonine (a) and L-valine (b). Heavy atoms including carbon, nitrogen and oxygen are marked with symbols and numbers.

Table 1
Crystallographic unit cell dimensions of L-threonine and L-valine. Data are obtained from Ref. [17] and Ref. [18], respectively.

Amino acid	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	V(Å^3)
L-threonine	13.628	7.618	5.110	90.00	90.00	90.00	530.511
L-valine	9.682	5.247	11.930	90.00	90.57	90.00	606.031

motions into a given number of sub-motions. With its assistance, we can gain deep insights into the character of low-frequency motions.

2. Experimental and theoretical methods

2.1. Materials

L-threonine (purity: ≥98%), L-valine (purity: ≥98%) and polyethylene (particle size: 40–48 μm) were all purchased from Sigma–Aldrich Co. LLC, and used without further purification.

2.2. Experimental method

Sample pellets of compound were made via sufficient mixing of desired amount of amino acids with polyethylene then following a pressing of 20 MPa. The thickness of pellet is about 0.2–0.3 mm.

Time-domain THz spectrometer (THz-TDS1008, BATOP system from Germany) was employed to record THz absorption spectra. In order to avert the influence of humidity, dry nitrogen gas was continuously purged into the sample compartment prior to any measurement. THz signals of blank and sample were obtained in the absence and presence of sample pellet, respectively. All the measurements were performed in transmission configuration at room temperature. The delay time for each measurement is about 70 ps, corresponding to a resolution of 14.3 GHz in frequency-domain. The recorded time-domain signals were converted into frequency-domain absorption spectra with fast Fourier transform (FFT) algorithm.

2.3. Computational method

Variable-cell geometry optimizations were carried out using PWscf code within Quantum Espresso code package [19]. Ultrasoft pseudopotentials generated with PBE and BLYP functionals were used to describe electron–ionic core interactions. The van der Waals correction option "grimme-d2" [20] was switched on when optimizing geometries. Monkhorst-Pack *k*-point samplings were

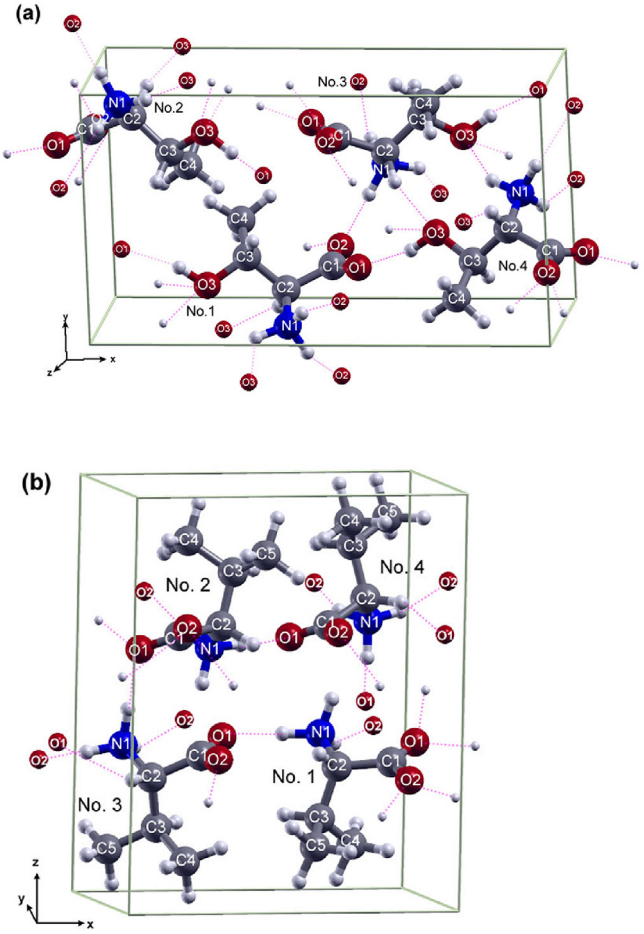

Fig. 2. Drawings of unit cell of L-threonine crystal (a) and L-valine crystal (b). Hydrogen bonds are indicated in purple. The atoms which do not belong to the presenting unit cell are drawn as small spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

generated with a $2 \times 3 \times 4$ grid for L-threonine and a $2 \times 4 \times 2$ grid for L-valine, respectively. The maximum planewave cutoff energy was set at 60 Ry. Kinetic energy cutoff (Ry) for charge density and potential was set to 600 Ry. The convergence criterion of geometry optimization for total energy and force were set at 1.0×10^{-5} Ry and 5.0×10^{-6} Ry/atom, respectively. A convergence threshold of 1.0×10^{-10} Ry was used in the iteration cycles of the self-consistent