Consequence of a Defect on the Terahertz Spectra of L-Asparagine Monohydrate

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We measured the terahertz vibrational spectra of a solid solution of L-asparagine and L-aspartic acid monohydrate at 0.5 to 6.0 THz using a GaP Raman THz spectrometer. The absorption peaks at below 2.5 THz clearly showed intensity changes reflecting the change in hydrogen bonding between molecules. The peaks in the higher frequency region were indirectly affected by intermolecular bonding, which resulted in broadening.

The vibrational spectra of weak intermolecular interactions such as hydrogen bonding and van der Waals' force in organic crystals can be detected in the terahertz (THz, 10^{12} Hz) region, and the skeletal vibrations of molecule and phonon modes also lie in this frequency region. Currently, THz spectroscopy is applied to biochemical compounds, human tissue, and other organic materials.

For a perfect crystal without any irregularity, it is possible to simulate and assign the THz vibrations of compounds on the basis of theoretical calculations to some degree. When a lattice or point defect (vacancy, interstitial atom, and substitutions) exists, the THz absorption peak in the THz band should change accordingly.[1] Extremely accurate equipment developed in our laboratory allows us to measure the change in the vibrational spectrum caused by these point defects.[2]

L-Asparagine (L-Asn) crystallized from an aqueous solution forms a monohydrate ($Asn{\cdot}H_2O$). L-Aspartic acid (L-Asp) can dissolve in $Asn{\cdot}H_2O$ crystals while maintaining its $P2_12_12_1$ space group at concentrations <15 mol % because of the similarity in the shapes of the molecules. L-Asp replaces L-Asn, and the hydrogen bonding between the amine and carboxyl groups changes to a repulsive force in the solid solution. The nature of these intermolecular interactions is shown in Figure 1.[3]

Since the first generation of THz waves at a frequency of 12.1 THz from a GaP Raman laser, we have developed tunable terahertz-wave sources and spectrometers.[4] A high-resolution source and spectrometer were first realized with a 1064-nm Nd:YAG laser and optical parametric oscillator.[5] We have also constructed a simpler spectrometer using two Cr:forsterite lasers in the 1.2-µm band as the excitation source.[6] These spectrometers are principally based on difference-frequency generation in GaP crystal based on the Raman effect of the phonon–polariton mode. In this study, we used two GaP Raman THz spectrometers consisting of Cr:forsterite lasers. One had a resolution of 30 GHz and was suitable for conventional measurements. The resolution of the other was 1 GHz, which enabled more precise measurements.[7] Both of these spectrometers can sweep the frequencies in the 0.5–6.2-THz range while tuning the frequency of the Cr:forsterite laser emission.

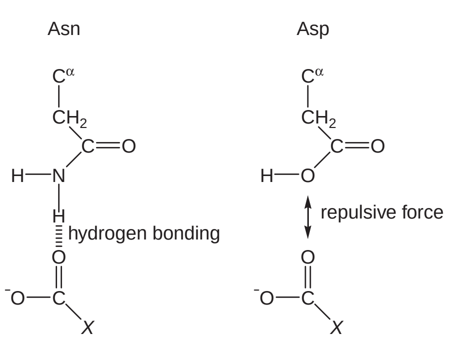

Figure 1. Intermolecular interaction in solid solution of L-Asn–L-Asp.

L-Asn (Sigma, 98%) and L-Asp (TCI, 98%) were dissolved in deionized water in mol fractions of 0, 5, and 15 mol %-L-Asp, and cooled slowly from 80 °C to room temperature to produce colorless crystals <6 mm in size. The actual mole fractions of the solid solution were determined using an amino acid analyzer (HPLC) after crystallization, which were estimated to be 4.6 and 12.3 mol %. The crystals were ground into a powder with a mortar and pestle. The powder samples (7.1 and 18.8 mg) were mixed with polyethylene (300 mg) and pressed into pellets, which were 20 mm in diameter and approximately 1 mm thick, resulting in concentrations of 0.15 and 0.4 M, respectively. Pairs of pellets with different concentrations are necessary for measuring the THz-wave transmission in a suitable range. A pure polyethylene pellet was also prepared as a reference for estimating the transmittance.

The THz spectra at room temperature were measured using a spectrometer with 30-GHz resolution (Figures 2 and 3). Generally, the absorption coefficient is often relatively large in the higher-frequency THz region. In order to measure spectra with a high signal-to-noise (S/N) ratio, the 0.4 M pellets were used for the lower frequency range (Figure 2) and the 0.15 M pellets for the higher frequency range (Figure 3).

Remarkable peaks were detected at 1.6 and 2.3 THz (Figure 2), which were dependent on the concentration. The intensity of the peak at 1.6 THz decreased gradually as the Asp concentration increased. This implies that the 1.6-THz peak corresponded to vibrations involving each Asn molecule, like molecular skeletal vibrations or intermolecular interactions, and not to lattice vibrations, such as phonons. Conversely, the peak at 2.3 THz decreased rapidly when the Asp concentration exceeded 4.6 mol %. Therefore, the 2.3-THz peak likely originated from phonons rather than skeletal or local vibration in each molecule.

Hangyo reported the 1.6-THz absorption peak of $Asn{\cdot}H_2O$ using THz time-domain spectroscopy and revealed that this peak decreased gradually with dehydration at 70 °C. After 3 h of annealing, the substance became an anhydrous crystal and the peak essentially disappeared.[8]

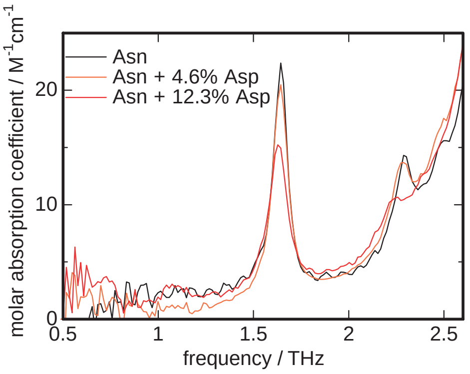

Figure 2. Terahertz transmission spectra of L-Asn and solid solutions L-Asn–L-Asp monohydrate in range of 0.5–2.6 THz.

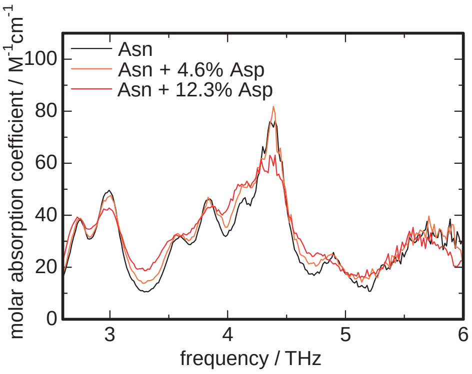

Figure 3. Terahertz transmission spectra of L-Asn and solid solutions L-Asn–L-Asp monohydrate in range of 2.6–6.0 THz.

Table 1. Temperature dependence of peak frequency of 1.6- and 2.3-THz bands of L-Asn

Absorption band	Peak frequency/THz		Peak shift /GHz
	4 K	298 K	
1.6-THz band	1.695	1.640	55
2.3-THz band	2.407	2.304	103

Their finding that the intensity of the 1.6-THz peak decreased with the progress of dehydration supports our hypothesis that this absorption band at 1.6 THz corresponds to molecular-scale vibration, such as skeletal vibration or intermolecular hydrogen bonds between Asn and water molecules, and not to phonons.

The precise dependence of the peak frequency and intensity on temperature enabled us to assign each peak. The peak frequencies of the absorption lines of the 1.6- and 2.3-THz bands of L-Asn measured at 4 and 298 K using a high-resolution THz spectrometer with 1-GHz resolution are summarized in Table 1. The S/N ratio around absorption peak is more than 4 at worst. The peak shift of the 2.3-THz band was about twice that of the 1.6-THz band. A large peak shift is one of the distinguishing characteristics of lattice vibration mode.[9]

The absorption lines at frequencies higher than 2.5 THz seen in Figure 3 become less clear as the Asp fraction increases. This is likely because the lattice defect indirectly affects the intramolecular vibration of each molecule, and the absorption peaks of the Asn molecule are lower and broader.

One can regard an L-Asp molecule in an L-Asn$\cdot H_2O$ crystal as a typical model of a point defect in a molecular crystal. Our result clearly showed that THz spectroscopy is an effective tool for detecting point defects in a molecular crystal. The absorption peak of the phonon mode is most sensitive to point defects. The peak of the intermolecular interaction related to a defective site is also a sign distinguishing defect incorporation. This also indicates that THz spectroscopy is a promising tool for detecting point defects in functional materials and biological systems, like proteins and genes.

In summary, we investigated a solid solution of L-Asn and L-Asp monohydrate using a GaP Raman THz spectrometer, and determined peaks thought to involve lattice vibration, local vibration, and skeletal vibration. Furthermore, we measured the temperature dependence of the peak frequency at high resolution using a newly developed spectrometer.

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