Study on the THz spectra of four kinds of Nipagin esters

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The transmission spectra of methylparaben, ethylparaben, propylparaben, and butylparaben in the range of 0.2–2.5 THz are measured using terahertz time-domain spectroscopy (THz-TDS). Their refractive index and absorption spectra are obtained at room temperature in nitrogen atmosphere. The results show that the four kinds of Nipagin esters have obvious absorption peaks at 1.54 and 1.83 THz for methylparaben, 1.98 THz for ethylparaben, 1.37 and 1.61 THz for propylparaben, and 0.76 and 1.68 THz for butylparaben. Their anomalous dispersion of the refractive index appears at the corresponding position. Based on the density functional theory (DFT), the vibration absorption spectra of their single molecule are simulated. The numerical simulation and experimental results generally agree with each other. Then the reasons for their minor differences are analyzed. Overall, the spectral properties of Nipagin esters are found to have great significance for the detection of preservatives and for food safety.

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Food preservation is an enduring topic. With continuous scientific and technological progress, the preservatives in synthetic food have been found to threaten human health. With the improvement of living and consumption levels, people have thus proposed higher requirements on food safety and health. Therefore, food safety testing is very important. Food components can be analyzed by Terahertz Time-Domain Spectroscopy (THz-TDS). It has practical significance for the study of molecular structure and preservative functions. The molecular formula of methylparaben is $C_8H_8O_3$. It is mainly used in organic synthesis, food, cosmetics, and preservatives. The molecular formula of ethylparaben is $C_9H_{10}O_3$. It is mainly utilized in the production of soy sauce and beer and is also used in other aspects of corrosion. The molecular formula of propylparaben is $C_{10}H_{12}O_3$. It is used in food, cosmetics, medicines, and biocides. The molecular formula of butylparaben is $C_{11}H_{14}O_3$. It is used in medicines, food, and cosmetics preservatives. To date, the methods used for the analysis of Nipagin esters are high performance liquid chromatography (HPLC)[1], capillary column gas chromatography[2], gas chromatography[3], infrared spectroscopy[4], and liquid chromatography[5], etc. The mechanism involved in Nipagin esters in food has been determined. The Fuzhou Product Quality Monitoring Bureau has examined the application of accelerating solvent extraction (ASE) and chromatograph of gel permeation (GPC) techniques for parabens assay[6]. However, there have been no studies to date which employed the terahertz (THz) spectroscopy of Nipagin esters.

THz radiation is a kind of electromagnetic wave located between infrared ray and microwave with a frequency in the range of 0.1–10 THz and a wavelength in the range of 30 μm–3 mm[7]. It belongs to the far-infrared band and the transition region in electronics to photonics. It has important academic value and potential applications. Experimental results are obtained using THz spectrum technology in the domain of preservative food testing. Using fast Fourier transformation (FFT) of time-domain spectroscopy, frequency domain spectra such as amplitude and phase are obtained. A series of optical parameters can then be derived[8] such as refractive index, extinction coefficient, absorption coefficient, and so on. This is followed by the analysis of the THz optical characteristics of the materials. In a previous work, the components of vitamins have been analyzed using THz-TDS measurement[9]. In this letter, the THz transmission spectra of methylparaben, ethylparaben, propylparaben, and butylparaben in the range of 0.2–2.5 THz were measured by THz-TDS. Their refractive index and absorption spectra were measured. Numerical simulations based on the Density Functional Theory (DFT) were also conducted using Gaussian 03 software package. By comparing the calculated results and the experimental measurements, their differences were analyzed. THz-TDS is expected to be used as a method for non-destructive spectral inspection.

The experimental samples are commercially available, with their purity more than 99%. Four samples of methylparaben, ethylparaben, propylparaben, and butylparaben were pressed under the pressure of 4 tons after grinding by a tablet press machine. Their thicknesses are 0.754, 0.800, 0.724, and 0.806 mm, respectively, and their diameter is 13 mm. The surfaces of the samples are smooth and parallel. Using THz-TDS, the THz
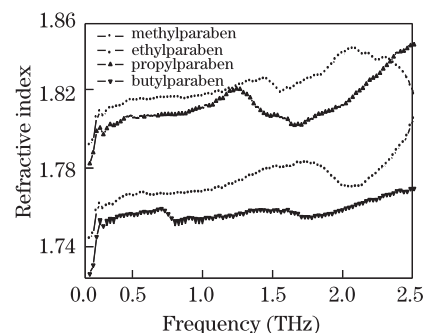

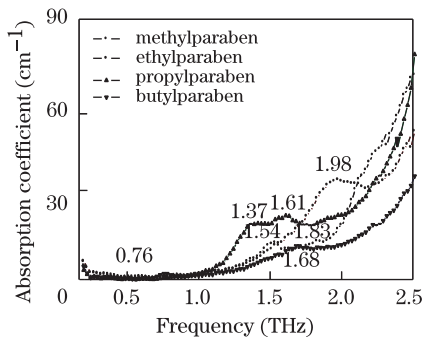Fig. 1. Refractive index spectra of four kinds of Nipagin esters.

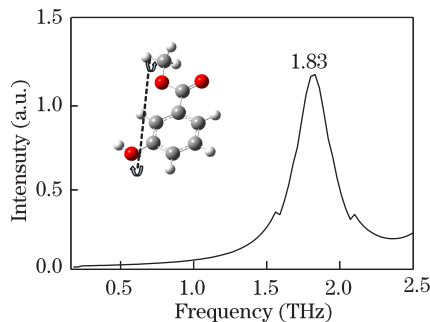Fig. 2. Absorbance of four kinds of Nipagin esters.

Fig. 3. Simulated absorbance of methylparaben at 0.2–2.5 THz. The inset shows the oscillation mode of the methylparaben molecule at 1.83 THz.

time-domain waveforms of the reference and the sample were obtained. The frequency domain spectra of the samples were extracted by FFT. To avoid the influence of water vapor, the THz optical path was sealed by a chamber of organic glass filled with high-purity nitrogen. The relative humidity in the organic glass box was maintained at about 3.6% and the temperature at 295.7 K during the experimental measurement.

Figure 1 shows the refractive index spectra of the four kinds of Nipagin esters. The average refractive indexes of methylparaben, ethylparaben, propylparaben, and butylparaben are 1.78, 1.81, 1.82, and 1.75, respectively. Figure 2 shows the absorption spectra of the four kinds of Nipagin esters. The absorption peak of methylparaben appears at 1.54 and 1.83 THz, that of ethylparaben appears at 1.98 THz, that of propylparaben appears at 1.37 and 1.61 THz, and that of butylparaben appears at 0.76 and 1.68 THz. Evidently, the absorption peaks correspond to the abnormal dispersion in the refractive index spectra.

The molecular structures of four Nipagin esters consist of a benzene ring and hydroxyl. Their main difference is that carboxyl hydrogen is replaced by a different number of hydrocarbon elements. Their vibrations of functional groups are different. These lead to the different vibration absorption peaks of the four samples.

To explain further the mechanism of the THz optical properties of the four samples above, theoretical simulations of the absorption spectra of the four kinds of Nipagin esters are carried out. As is well known, DFT is frequently used in quantum chemistry calculations. It can theoretically simulate the THz absorption spectra

of materials and is an effective method of theoretical calculation for the analysis of the molecular response of low-frequency collective vibration. At present, this method is widely used in the analysis of THz spectral response[10,11].

Using Gaussian 03 software based on DFT, the THz absorption spectra of four kinds of Nipagin esters were calculated based on a 6-31G-based cluster. The theoretical simulations were carried out in absolute zero degree of temperature. Clearly, there is a difference between the simulation and experimental results. In the calculation, an effective frequency range of 0.2–2.5 THz corresponding to the case of our experiments was selected.

Figure 3 shows the absorption spectrum of methylparaben. There is one absorption peak located at 1.83 THz. The inset of Fig. 3 shows the oscillation mode of the methylparaben molecule at 1.83 THz. The carboxyl and benzene rings of methylparaben swing around the intermediate shaft clockwise and counterclockwise, respectively.

Figure 4 shows the THz absorption spectrum of ethylparaben. There are two absorption peaks located at 1.32 and 1.83 THz. The inset of Fig. 4 shows the oscillation mode of the ethylparaben molecule at 1.83 THz. The ethylparaben molecule swings around the axis.

The THz absorption spectrum of propylparaben is shown in Fig. 5. There are three vibration absorption peaks at 0.93, 1.47, and 2.13 THz, respectively. The inset of Fig. 5 shows the oscillation mode of the propylparaben molecule at 1.47 THz. The propylparaben molecule swings around the intermediate shaft clockwise and counterclockwise.
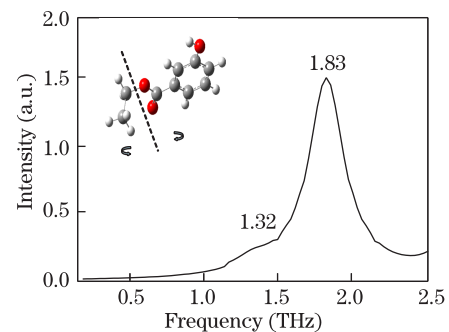

Fig. 4. Simulated absorbance of ethylparaben at 0.2–2.5 THz. The inset shows the oscillation mode of the ethylparaben molecule at 1.83 THz.
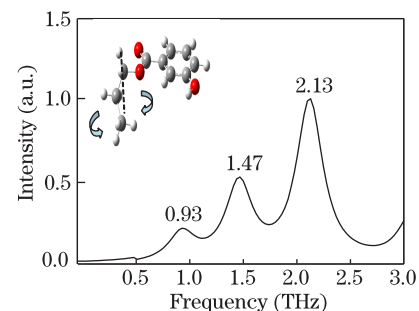

Fig. 5. Simulated absorbance of propylparaben at 0.2–2.5 THz. The inset shows the oscillation mode of the propylparaben molecule at 1.47 THz.
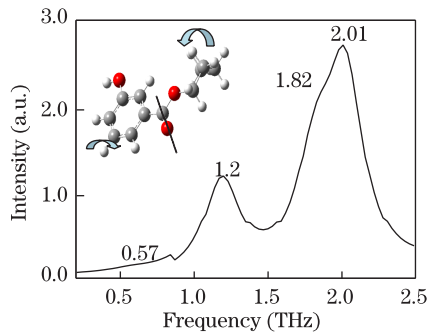
Fig. 6. Simulated absorbance of butylparaben at 0.2–2.5 THz. The inset shows the oscillation mode of the butylparaben molecule at 2.01 THz.

Figure 6 shows the THz absorption spectrum of butylparaben. There are four absorption peaks located at 0.57, 1.2, 1.82, and 2.01 THz, respectively. However, the absorption peaks located at 0.57 and 1.82 THz are not obvious. The inset of Fig. 6 shows the oscillation mode of the butylparaben molecule at 2.01 THz. There is an axis consisting of a carbon-oxygen double bond. Benzene ring swings around this axis. The functional groups of the butylparaben molecule at the right side of the axis twist around it.

By comparing the experimental and simulated results, we find that the absorption peak of methylparaben at 1.83 THz in the experimental results agrees with the simulation results. However, the absorption peak is not obvious in the experimental results. The absorption peak located at 1.54 THz in the experimental results is not obtained in the simulation. This indicates that this absorption peak corresponds to the collective vibration between molecules. The case is the same for other Nipagin esters.

The simulated absorption peak of propylparaben at 1.47 THz is higher than 1.37 THz in the experiment. The simulation result is obtained at absolute zero degree of temperature, whereas the experimental result is measured at room temperature. The low temperature makes the absorption peak move to a higher frequency, that is, the blue shift. Another absorption peak of propylparaben located at 1.61 THz in the experiment does not appear in the simulation. However, the simulation shows that two absorption peaks caused by the intra-molecule interaction are not observed in the experiment. Similarly, for the THz absorbance of methylparaben, ethylparaben, and butylparaben, there are some extra absorption peaks in the simulation and experiment which do not agree with each other. There are absorption peaks that appear in the simulation but not in the experiment. This is mainly due to the sample pressed into thin pill and measured at room temperature. This may cause the nonlinear broadening of the absorption spectrum so that the absorption peaks are superposed into one another. On the other hand, some absorption peaks appear in the experiment but not in the simulation. This is because the model used in the theoretical calculations is a single molecule, whereas that in the experimental samples is of a multi-molecular structure. The interactions between the molecules and the lattice vibration are not included in the simulation. For the solid materials without heavy atoms, the vibration modes in the far-infrared band include not only molecular vibration but also the interaction between the molecules such as lattice vibration, which is caused by the relative translation, twist, or swing of the molecules. In the experiment, the absorption peak of methylparaben appears at 1.83 THz because of carboxyl and benzene swing. The absorption peak of ethylparaben appears at 1.98 THz because the three hydrogen atoms on the benzene and functional groups swing. As the two hydrogen atoms on the benzene and functional groups swing, the absorption peak of propylparaben appears at 1.37 THz. Meanwhile, the absorption peak of butylparaben appears at 1.68 THz because the functional groups twist clockwise. The different axes of vibration, directions, and modes lead to the different numbers and positions of the absorption peaks. Therefore, the four Nipagin esters are distinguished from their THz spectra. Overall, THz-TDS may serve as an effective tool to identify food additives in safety testing.

In conclusion, the THz spectra of four kinds of Nipagin esters are measured by THz-TDS. The esters are found to have different fingerprint absorption spectra. The simulation based on Gaussian 03 software using DFT partly reveals the origin of the absorption peaks wherein the experimental results generally agree with the simulation ones. Significant differences in the four Nipagin esters can be seen in the comparison of refractive indexes and absorption spectra. Therefore, THz-TDS can serve as a new method for the non-destructive inspection of the four kinds of Nipagin esters.

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