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Terahertz spectroscopy investigation of preservative molecules

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ABSTRACT

We obtained the terahertz (THz) absorption characteristics of six types of preservatives in the 0.2–2 THz range using THz time-domain spectroscopy (THz-TDS). The structural and vibrational frequencies of the samples were calculated using density functional theory (DFT); the calculated results fit well with the experimental data. Assignments of the observed THz absorptions were proposed, based on the DFT calculations. The results indicate that the measured characteristic frequencies arise from the collective vibration of intramolecular, intermolecular, and phonon modes. This work demonstrates that THz-TDS spectroscopy can be useful for investigating preservatives in food and agriculture products.

1. Introduction

Recently, terahertz (THz) electromagnetic waves with frequencies in the 0.3–10 THz range have attracted interest as important spectroscopic tools for characterizing the properties of materials based on their intramolecular and intermolecular modes. The absorption spectrum, called the fingerprint, of a material significantly depends on the conformation modes of its molecules [1–3]. THz spectroscopy produces spectra that act as unique signatures for identification, and offers an effective method for exploring the structures and spectral features of molecules. Moreover, THz radiation can pass through most nonpolar materials, such as cotton, paper, and plastics. The unique properties of THz radiation make THz technology particularly interesting and it has applications in fields such as security [4], biomedical engineering [5], quality control [6], and the identification of chemical materials [7]. Compared to conventional spectroscopic techniques, such as X-ray, Infrared, and microwave, THz time-domain spectroscopy (THz-TDS) has an extremely high signal-to-noise ratio (SNR) because of pump-probe detection, and can be used to obtain the absorption coefficient and refractive index of a material without using the Kramers–Kronig relation [8]. Therefore, investigation of molecules in the low-frequency THz region is very important for the identification and characterization of materials, security detection, and quality control.

Preservatives including sorbic acid, potassium sorbate, benzoic acid, sodium benzoate, sodium diacetate, and sodium dehydroacetate are commonly used in food, agricultural products, and cosmetics to prevent decomposition by bacteriostatic fragrances and destructive metabolic activity [9,10]. The quality of post-harvest grain has been significantly affected by mildew growth. Mildew causes grain to spoil and is dangerous to human health and mildew losses are particularly high in China. Applying preservatives to grain is necessary to ensure the safety and quality of the product. However, the research and development of special preservatives (formulation and dose) for green, safely stored grain are still in the initial stages. Much information can be gained by analyzing preservatives by THz and infrared spectroscopies. Recently, there have been some reports in the literature concerning the use of THz spectroscopy for preservatives [11,12]; however, only a few have focused on the special preservatives used for stored grain. Thus, this study on the preservatives used for agricultural products will have practical significance.

In this paper, we report the measurement of the THz spectra of six types of preservatives using THz-TDS at room temperature. The absorption characteristics of the six preservatives were obtained and analyzed in the 0.2–2 THz range. In addition, the structural and vibrational frequencies of the samples were calculated using DFT in the far-infrared region. The computational and experimental results were compared, and the observed THz absorption features were assigned based on DFT calculations.

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2. Materials and methods

2.1. Experimental setup

A standard transmission THz-TDS system was used for characterizing the spectral features of the preservatives. The details of the system configuration and data analysis method used are described in recent literature [13,14]. In this system, a mode-locked Ti:sapphire laser with a center wavelength of 800 nm and a repetition rate of 82 MHz provided femtosecond pulses with a duration of 100 fs. The femtosecond laser was split into pump and probe beams by a beam splitter. The pump beam was used to generate THz radiation from a biased GaAs emitter, whereas the probe beam was focused onto a 1-mm-thick ZnTe Electro-optic (EO) crystal to probe the THz pulses. The spectral range of the system was 0–2.5 THz with a resolution of 0.03 THz, and its SNR was 5000:1. The THz light path was purged with nitrogen and maintained at a relative humidity of 2%, thus minimizing the influence of water vapor. Temperature in the THz-TDS system was maintained at 294 K.

The spectral data sets were analyzed, and the absorption coefficients, $\alpha(\omega)$, and refractive indices, $n(\omega)$, of the samples were obtained from the sample and reference spectral data using the following equations:

$$n(\omega) = \frac{\varphi(\omega)}{\omega d}c + 1 \quad (1)$$

$$a(\omega) = \frac{2}{d}\ln\left[\frac{4n(\omega)}{\rho(\omega)(n(\omega)+1)^2}\right] \quad (2)$$

where c is the speed of light, ω is the cyclic frequency, $\rho(\omega)$ and $\phi(\omega)$ are the amplitude ratio and phase difference, respectively of the reference and sample, and d is the sample thickness.

2.2. Sample preparation

The six preservatives, sorbic acid, potassium sorbate, benzoic acid, sodium benzoate, sodium diacetate, and sodium dehydroacetate, studied in our experiment were purchased from Tianjin Dongda Chemical Co., Ltd (purity 99%) and used without further purification. The molar mass and appearance of the six types of preservatives are shown in Table 1. The samples were prepared by weighing 80–100 mg of each solid, then grinding each into a fine powder using a mortar and pestle. Next, the six samples were compressed into 13-mm-diameter pellets under a pressure of 5 ton for 5 min. The sample thickness was about 1.2 mm, and samples were labeled “Sample 01,” “Sample 02,” . . . “Sample 06.”

Table 1
The molar mass and appearance of the six types of preservatives.

Preservative name	Molecular formula	Molar mass	Appearance
Sorbic acid	$C_6H_8O_2$	112.13	Crystalline powder
Potassium sorbate	$C_6H_7KO_2$	150.21	White crystals
Benzoic acid	$C_7H_6O_2$	122.12	Colorless crystalline solid
Sodium benzoate	$C_7H_5NaO_2$	144.10	White or colorless crystalline powder
Sodium diacetate	$C_4H_7NaO_4$	142.09	Crystalline solid
Sodium dehydroacetate	$C_8H_7NaO_4$	190.13	Crystalline powder

2.3. Theoretical methods

In recent years, quantum chemical methods have made low-frequency molecular calculations feasible [15–17]. DFT has proven to be a reliable method for the investigation of molecular geometries, vibration frequencies, energies of chemical reactions, and thermodynamic properties [18–20]. Theoretical calculations potentially offer a molecular level description of vibrations in molecular crystals. Quantum chemical calculations with full geometry optimization and frequency analysis were performed using DFT with the Becke-3-Lee-Yang-Parr (B3LYP) functional and 6-311++G (d, p) basis set for isolated molecules. The DFT calculations were carried out using the Gaussian 09 program package, one of the most popular quantum-chemical program packages [21].

3. Results and discussion

3.1. THz spectra of preservatives

The electric field of a THz pulse transmitted through a sample is modified by the absorption and dispersion of the sample. The time-domain waveforms of the THz signals both with and without (reference) the sample are shown in Fig. 1. The measured sample pulse is delayed, indicating that the refractive index of the sample is different from that of the reference. The amplitude of the measured sample pulse is decreased relative to the reference because of absorption by the preservative molecules. The absorption coefficients and refractive indices of the six preservatives are presented in Fig. 2(a–f).

The six preservatives exhibit unique absorption characteristics. The THz spectra of these preservatives are obviously different; thus, the THz absorption spectra can be used as characteristic fingerprints. Even minor changes in structure can bring about distinctive differences in absorption peak values. In addition, it is notable that the refractive index varies with every absorption peak, which shows that an abnormal dispersion is associated with a characteristic peak.

The absorption peaks and refractive indices corresponding to frequencies in the 0.2–2 THz range are listed in Table 2. Among these spectral features, it is obvious that the strongest absorption intensity is located at 1.85 THz; the others can be regarded as weak-intensity or medium-intensity absorption features. However, no distinct absorption features are observed in the lower frequency range of 0.1–1 THz for sodium dehydroacetate and sodium diacetate. The average refractive indices of the six preservative samples are 1.62, 1.81, 1.69, 1.77, 2.03, and 1.75 respectively. The characteristic resonances originating from the inter- or intramolecular modes in the lower frequency range suggest that THz-TDS is sensitive to the presence of preservatives molecules; therefore, it can be a powerful tool for the qualitative analysis of preservatives.

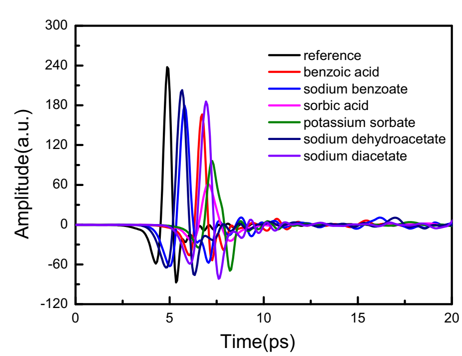

Fig. 1. THz time-domain spectra of preservatives.