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Analysis of Terahertz absorption spectra characteristic of 1-Naphthaleneacetic acid and 4-Chlorophenoxyacetic acid in Terahertz region

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Abstract—**We firstly study terahertz time-domain spectroscopy (THz-TDS) characterization of two kinds of pesticides 1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid. The absorption spectrum and refractive index of samples were measured. Theoretical investigation of the vibrational spectrum of pesticides was performed based on density function theory (DFT). We observed that experiment spectra are in rough qualitative agreement with these theory spectra. Its chemical composition was successfully identified through spectral analysis of the recorded terahertz waveform. These feature spectra measurements are helpful to form a database of pesticide.**

Keywords- absorption spectrum; 1-naphthaleneacetic acid; 4-chlorophenoxyacetic acid; Terahertz

I. INTRODUCTION

The terahertz (THz) region of the electromagnetic spectrum is typically considered to occupy 300 GHz to 10 THz, bridging the gap between millimeter waves and the infrared. Recent developments have started to address the previous lack of sources and sensitive detectors in this range. THz spectral region was utilized in various applications of materials characterizations during the last decade [1]. Terahertz spectroscopy has some important differences compared with conventional infrared spectroscopy. Whereas the absorption of infrared radiation in solid or liquid is typically due to the excitation of vibration modes of the intra-molecular bonds, terahertz waves are lower in energy and excite longer wavelength vibrations, such as the phonons in a semiconductor crystal or molecular vibrations in an organic material. These molecular vibrations are a unique and distinct signature of a material, and thus terahertz spectroscopy is an important tool in identifying different substances [2].

Consequently, the technological advances have been accompanied by much interest in possible applications of security [3-5], pharmaceutical [6-7], nondestructive testing (NDT) [8-9], drug inspection [10] and biological molecules testing [11-14].

A number of biological and biomedical systems have already been successfully investigated by terahertz spectroscopy [12-13]. The analysis of terahertz spectra yields structural information which is complements for classical infrared spectra. Furthermore, terahertz spectroscopy is well suited to explore the low frequency vibrational modes that define the motions of large scale conformational changes which generally occur along the torsional degrees of freedom.

In the past, high-resolution measurements are sparse and until recently limited to the spectral region covered by FTIR. Most of the published high-resolution data were taken by the FTIR, show weak spectral features that are highly sensitivity to sample size, orientation, and method of preparation. However, quantitative data of their spectral absorption as well as that of pesticide residual materials are only partially documented. Quantitative spectral absorption data of pesticides are relatively sparse. Furthermore, the research of two pesticides 1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid THz spectrum has not reported yet in the references.

In this paper, to measure quantitative data of pesticide absorption spectra in 0.3-1.8 THz, we discuss THz spectra of 1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid through experiment and theory, which is meaningful for applying THz technology in food quality supervision and inspection, and the spectral information is helpful to form a database for detection and identification pesticides.

II. THZ-TDS SYSTEM

A schematic of the pulsed THz-TDS system used is shown in Fig. 1. It is made up of titanium doped sapphire femtosecond laser from Coherent Company and THz system developed by Zomega Company. Femtosecond laser has repeat frequency of 80 MHz and output power of 960 mW, besides the laser pulse has the central wavelength of 800nm and pulse width of below 100 fs. Laser pulse is split into pump beam and probe beam by beam splitter, pump beam is retarded before entering into photoconductive antenna of gallium arsenide (GaAs) crystal to generate the THz pulse. After transmitting through the sample, the THz pulse meets the probe beam at zine telluride (ZnTe) crystal detector. The probe beam carrying sample information is modulated after transmitting through the waveplate and Wollaston prism, finally, the sample information is unscrambled by differential detector and lock-in amplifier.

The whole detection is done in a nitrogen environment, which is to avoid impact from the vapor in the air, because the vapor has strong absorption for THz wave. The effective frequency range of this research is 0.3 – 1.8 THz, because of the strong absorption ability of the pesticide sample for THz wave.

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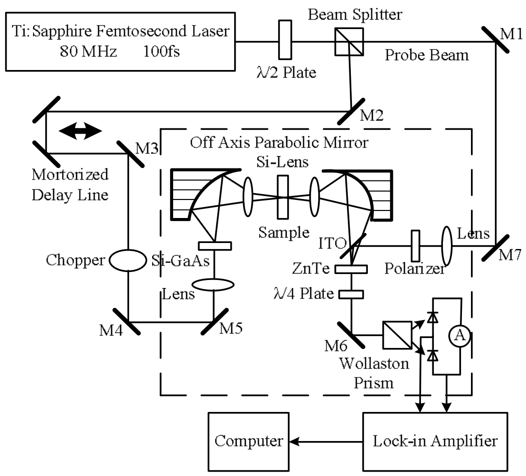

Figure 1. Schematic of a THz-TDS system

1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid are two kinds of herbicide, and their molecular formulas are $C_{12}H_{10}O_2$ and $C_8H_7ClO_3$ respectively. In our experiment, 1-naphthaleneacetic acid is provided by J&K chemical LTD, and 4-chlorophenoxyacetic acid is provided by ALORICH chemistry with the same purity (98%). Two pesticides are mixed with polyethylene sufficiently to prepare samples after being compressed by a pressure of 5 tons, and their purities are 100% (1-naphthaleneacetic acid) and 50% (4-chlorophenoxyacetic acid) respectively. The thickness of the slice is about 1.30 mm and the diameter is 1.43 mm.

III. Model of Parameter Extraction

To validate that THz technology is capable of detecting different pesticides, we first measured the spectrum of various common pesticides in transmission. This was performed using a commercial THz-TDS system. In transmission, the THz field is modified by dispersion and the absorption of the media under examination [3]. The ratio of the electric field strength before $E_r(\omega)$ and after transmission $E_s(\omega)$, is given by

$$\frac{E_s(\omega)}{E_r(\omega)} = t(\omega)\exp\left(-\frac{\alpha(\omega)}{2} + \frac{-j\omega d(n(\omega)-1)}{c}\right) \tag{1}$$

$$t_n(\omega) = \frac{4n(\omega)}{(1+n(\omega))^2} \tag{2}$$

In (1) and (2), where d is the thickness of the sample, ω is the frequency of the radiation, c is the speed of light, and $t_n(\omega)$ is the reflection loss at the sample surface as defined above. Hence, in transmission spectroscopy, both the refractive index $n(\omega)$ and the absorption coefficient $\alpha(\omega)$ can be determined from the measured amplitude and phase information by

$$\alpha(\omega) = \frac{2}{d}[-\ln(\mathrm{Re}(\frac{E_s(\omega)}{E_r(\omega)})) + \ln\frac{4n(\omega)}{(n(\omega)+1)^2}] \tag{3}$$

$$n(\omega) = 1 + \frac{c}{\omega d}\ln(\mathrm{Im}(\frac{E_s(\omega)}{E_r(\omega)})) \tag{4}$$

IV. THz Spectra Results and Discussion

A. Experimental Results

The temporal waveforms of two pesticides are shown in Fig. 2. It presents transmitted terahertz pulses of reference and samples respectively.

High-resolution THz spectra were obtained using THz-TDS. The spectral absorbance of 1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid are presented in Fig. 3(a-b). Distinct phenomena are observed: (1) Typical spectral features of 1-naphthaleneacetic acid include two main peaks, while 4-chlorophenoxyacetic acid has only one main peak. (2) There are differences between the absorbance spectra of two solid samples. Lower and overlapping frequency THz spectra 0.3- 1.8 THz are obtained.

Fig. 3 presents the measured absorption spectra and refractive index of 1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid, from the Fig. 3, a conclusion is drawn that there are clear and unique spectral features corresponding to each pesticide.

For 1-naphthaleneacetic acid, it has two absorption spectra peaks at 1.52THz, 1.68THz, and they have different amplitudes. For 4-chlorophenoxyacetic acid, it has one peak at 1.31THz. These feature spectra are a clear demonstration that terahertz spectroscopy can help identify an unknown pesticide by recording its absorption spectrum.

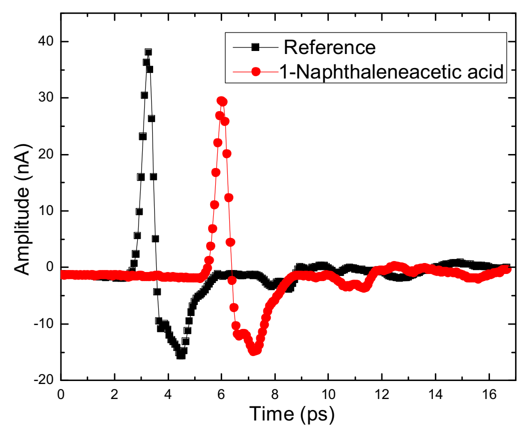

Figure 2(a). Terahertz pulses as transmitted through 1-naphthaleneacetic acid and reference

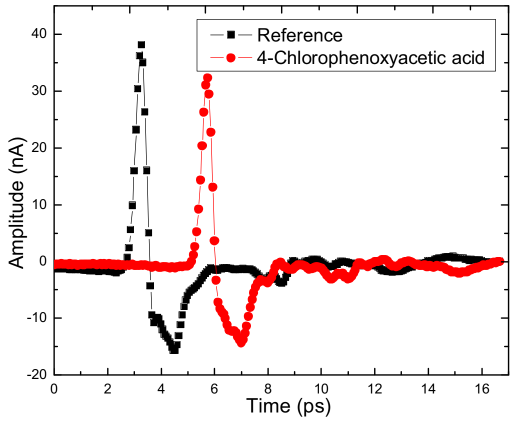

Figure 2(b). Terahertz pulses as transmitted through 4-chlorophenoxyacetic acid and reference

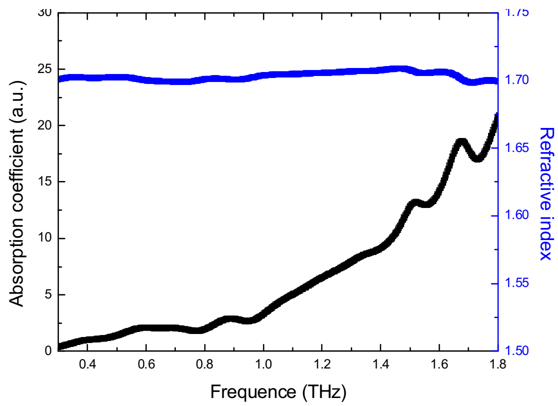

Figure 3(a). 1-naphthaleneacetic acid refractive index and absorption spectra

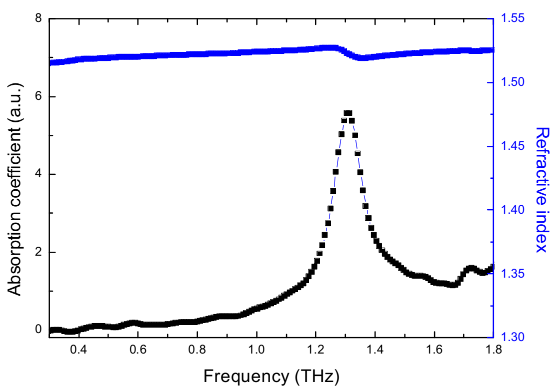

Figure 3(b). 4-chlorophenoxyacetic acid refractive index and absorption spectra

Corresponding to every absorption peak, a characteristic change is shown in the refractive index spectrum, which means that an abnormal dispersion is always accompanied with an obvious absorption. The average refractive index of 1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid samples are 1.70 and 1.53 respectively.

B. Theoretical Spectral Calculations

To better understand and interpretation of absorption spectra through experiment, vibration frequency calculations for each molecule were performed by the Gaussian software package with the Becke-3-Lee-Yang-Parr(B3LYP) functional and 6-311++G* basis set under the Windows 32 operating system environment [15].

Fig. 4 shows the experiment and theory absorption spectra: (a) 1-naphthaleneacetic acid and (b) 4-chlorophenoxyacetic acid.

In the Fig. 4(a), peaks of experiment absorption spectrum are more than theory absorption spectrum because of the influence from intermolecular forces, in addition, there are similar peaks between experiment and theory spectrums, for example, the peak of 1.52THz for 1-naphthaleneacetic acid and the peak of 1.31THz for 4-chlorophenoxyacetic acid, which are caused by the vibration inside the molecule. For 1-naphthaleneacetic acid, the calculation predicts that the absorption peak takes place at the frequencies of 1.68THz caused by intermolecular vibration. This demonstrates that the theory spectrum can interpret and predict the experiment spectrum to a certain extent.

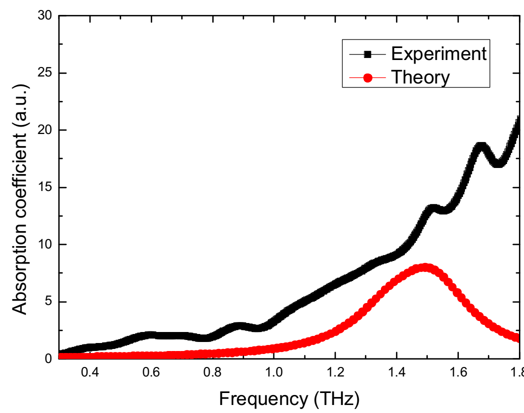

Figure 4(a). The experiment and theory absorption spectrums of 1-naphthaleneacetic acid sample

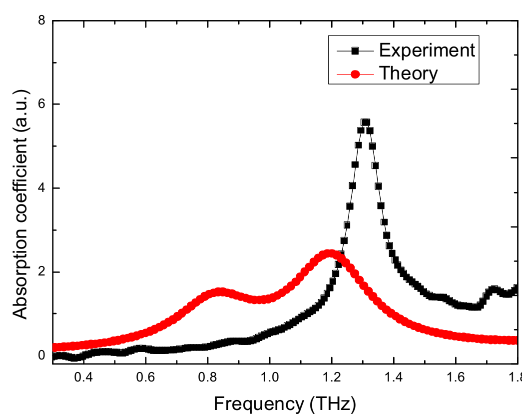

Figure 4(b). The experiment and theory absorption spectrums of 4-chlorophenoxyacetic acid sample

V. Conclusion

In this paper, the THz spectra of solid pesticides have been experimentally obtained and theoretically studied in detail. We have discussed some of the important factors involved in addressing pesticide inspection of THz-TDS. The THz absorption spectra of 1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid have firstly measured at room temperature. Using this apparatus, we have verified spectroscopic detection by 1-naphthaleneacetic acid and 4-chlorophenoxyacetic acid. The THz spectra of this experiment enrich the fingerprint database of pesticide, which is of great importance for pesticides detection using THz-TDS.

The measurements show that each material has typical absorption spectrum which is different from other material. Further experimental investigations of pesticide are going on, as well as the application of solid state density function theory to precisely simulate absorption spectrum.

Acknowledgment

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