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The Vibrational Spectra of Bactericide molecules: Terahertz Spectroscopy and Density Functional Theory Calculations

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Abstract. In the room temperature and nitrogen conditions, we presented well-resolved absorption spectra and indexes of refraction of bactericide molecules in the far infrared radiation (FIR) spectral region recorded by terahertz time-domain spectroscopy (THz-TDS). As illustrative examples we discussed the absorption spectra of captan and folpet in THz region. The absorption coefficient and index of refraction of them were obtained. Meanwhile, density functional theory (DFT) with software package Gaussian 03 using B3LYP theory was employed for optimization and vibration analysis. With the help of Gaussian View 3.09, the distinct absorption peaks of those molecules were assigned with reliable accuracy. They were caused by intermolecular hydrogen-bonding, molecular torsion or vibration modes, absorption of water molecules, etc. As the absorption spectra are highly sensitive to the overall structure and configuration of the molecules, the THz-TDS procedure can provide a direct fingerprint of the molecular structure or conformational state of a compound.

1. Introduction
Pesticides, which are defined by the UN Food and Agricultural Organization (FAO) as substances or mixtures that are used to prevent, destroy, repel or mitigate any pest, including insects, rodents and weeds, have been used in crude forms since antiquity [1]. The expenditure around the world on pesticides totaled more than $32.5 billion in 2000 and nearly $32.0 billion in 2001, and the amount of pesticide used around the world exceeded 5.0 billion pounds in 2000 and 2001 [2]. Food safety is becoming more and more concerned, especially pesticide residual threats today due to the mass use of pesticides in agriculture [3]. Conventionally, HPLC [4], Gas chromatography-mass [5], HPLC-MSMS [6], enzymatic inhibition method [7] are employed for pesticide detection, which are labor intensive and sample and time consuming.

Terahertz time-domain spectroscopy (THz-TDS) is a technique for measuring the complex refractive index of materials over a wide range of frequencies, usually spanning from a few tens of
GHz to several THz. Terahertz spectroscopy causes little damage to the target material due to its low photon energy, can provide rich intermolecular and low-frequency intra-molecular modes of the chemicals, is less sensitive to the thermal background radiation and the scattering effect in the sample, has a stable radiation source, and more especially, can give the amplitude and phase information of the sample simultaneously, proving to be a promising tool for qualitative analyses with the signal-to-noise ratio (SNR) up to 80 dB [8,9]. Due to its uniqueness, this technique has been used in many fields, e.g. chemistry, biology, medical science, homeland security, information and community technology [10-13], etc. In the field of food safety control, especially pesticide detection, Y. Zhang et al. qualitatively studied acephate based on both first principles calculations and experimental investigations [14]; Khan et al. investigated the dielectric property, as well as its relationship to the density of bacillus thuringiensis, along with other household powders [15]. Few papers have been found concerning the analysis of bactericide pesticide as of yet, which will be a meaningful progress.

In this paper, solid-form pesticides were analyzed. We studied two bactericide molecules of captan and folpet, which are similar molecular structure and chemical properties. We tried to obtain the THz temporal waveforms of bactericides from the experiment and acquire their absorbance coefficient and index of refraction. Moreover, we obtained their theory spectra by density functional theory (DFT) calculations, and with the help of Gaussian View 3.09 [16], we account for their different distinctive absorption peaks.

2. Experimental methods and materials

2.1. Sample preparation

The standard folpet and captan were obtained from AccuStandard, Inc., New Haven, USA, with the purity of 97.5% and 99%, respectively. And the polyethylene was bought from the Sigma-Aldrich Company, St.Louis, MO. All the powder-form samples were used without further purification, and were dried at 423 K for at least 1 hour to remove water. The molecular structure of folpet and captan is shown in figure 1(a) and figure 1(b), respectively.

![Figure 1(a). Molecular structure of folpet.](image1)

![Figure 1(b). Molecular structure of captan.](image2)

We prepared material and polyethylene mixtures with the material weight ratio of about 50%. All the mixtures were carefully mixed and ground using a pestle and mortar, and then were pressed into
1-2-mm-thick disks with a aerostatic press under the pressure of approximately 30 MPa.

2.2. Terahertz time-domain spectroscopy (THz-TDS)
A THz-TDS system is employed, which is a THz wave generation and detection setup as illustrated in figure 2. The heart of our setup is a femtosecond titanium sapphire laser. It produces less 100 fs laser pulses with a repetition rate of 80 MHz, and the power of nearly 960 mW is split into the pump beam (I) and probe beam (II) at the splitter for terahertz generation and detection, respectively. After transmitting through the delay line, the pump beam elicits the terahertz beam at the emitter, the photoconductive dipole antenna under the 17-kHz sinusoidal voltage bias. The generated terahertz beam is focused onto the sample by a pair of gold-coated parabolic mirrors, carries sample characteristics, and meets the probe beam at the ZnTe crystal detector, where the probe beam is modulated by the terahertz radiation through the electro-optic effect in which a birefringence is induced in the ZnTe crystal and the polarization of the probe beam is rotated by the terahertz beam. After transmitting through the $\lambda/4$ wave plate and the Wollaston prism, the modulated probe beam is then detected by a set of balanced photodiodes, and the generated photocurrent via a lock-in amplifier is collected by a computer through a Labview program. To avoid moisture absorption in the air, the whole setup is enclosed in a nitrogen-purged box. For further details see reference [17]. The effective frequency range of this research is $20 \sim 80 \text{ cm}^{-1}$ ($0.6 \sim 2.4 \text{ THz}$), with the measurable maximum frequency greatly reduced because of the strong absorption of the pesticide sample.

![Figure 2. Experimental set-up for transmission THz-TDS.](image)

2.3. Data analysis method
In the last decade several authors presented material parameter extraction algorithms to determine the complex refractive indexes of nearly homogenous solid samples with THz-TDS [18,19]. Commonly, for material parameter extraction, a THz pulse which has propagated through a sample is compared to the other THz pulse without the sample in its propagation path. This is achieved by tracing the temporal shape of the electric field with sample $E_{\text{sam}}(t)$ and without sample $E_{\text{ref}}(t)$, where $t$ is the optical delay time. These two pulses are transformed into the frequency domain using fast Fourier
transform (FFT). The frequency-domain reference and sample spectrum denoted as \(E_{\text{ref}}(v)\) and \(E_{\text{sam}}(v)\), respectively. The ratio of these fields are related to the absorption coefficient \(\alpha(v)\) and index of refraction \(n(v)\) of the sample as follows

\[
\frac{E_{\text{sam}}(v)}{E_{\text{ref}}(v)} = 4n(1+n)^{-2} \exp\left[-jvdc^{-1}(n-1)\right] = A(v)\exp[-j\phi(v)]
\]

where \(v\) represents the frequency, \(c\) is the speed of light in vacuum, \(d\) is the sample thickness, \(A(v)\) is the amplitude ratio between the sample and reference spectrum, and \(\phi(v)\) is the relative phase difference. Thus, we can obtain

\[
n(v) = 1 + \left(2\pi vd\right)^{-1} c\phi(v)
\]

\[
\alpha(v) = -2d^{-1}\ln\left[\left(4n(v)\right)^{-1} A(v)\left[1+n(v)\right]^{-2}\right]
\]

3. Results and discussion

As shown in figure 3, the time-domain waveforms of captan and folpet are obtained, respectively. Where solid line represents reference and dashed line represents sample. The reduction in amplitude is attributed to the reflective loss at both surfaces and the absorption during passage through the sample. And the delay in time derives from the different refractive index of the different samples relative to the nitrogen. Meanwhile, owing to the different thickness of captan and folpet, the delay time is different.

![Figure 3](image-url)

**Figure 3.** The THz time-domain waveform of reference (solid curves) and samples (dashed curves).

Figure 4 depicts the frequency-domain waveform of reference and samples (captan and folpet). Below 20 cm\(^{-1}\) oscillatory feature occur due to multiple reflection, and above 80 cm\(^{-1}\) the noise increases significantly and excessive attenuation of the thick sample. Therefore, our reliable data of captan and folpet are from 20 cm\(^{-1}\) to 60 cm\(^{-1}\) and from 20 cm\(^{-1}\) to 80 cm\(^{-1}\), respectively.

Spectra of the absorption coefficient and the index of refraction of the different samples were obtained in the figure 5. We can see that the both bactericide samples exhibit distinctive absorption peaks, and can be easily discriminated from each other with the peaks positions of captan at 39.3 cm\(^{-1}\).
46.9 cm$^{-1}$ and 58.1 cm$^{-1}$, and folpet at 42.7 cm$^{-1}$, 67.4 cm$^{-1}$ and 72.6 cm$^{-1}$. There are obviously different in position of peaks and absorption intensity.

![Figure 4](image-url)

**Figure 4.** (a) and (b) are the THz frequency-domain waveform of reference (solid curves) and samples (dashed curves).

We can also obtain that the average index of refraction of captan and folpet is 1.49 and 1.43 from figure 5. All absorption peaks are accompanied by a characteristic change of the index of refraction. Comparing the absorption coefficient and index of refraction between captan and folpet, the former is more smooth and distinct than the latter; this is very possibly caused by the unsatisfactory sample and unsuitable thickness.

![Figure 5](image-url)

**Figure 5.** Absorption coefficient and index of refraction of captan (a) and folpet (b).

In order to back up the above conclusions we performed a theory analysis based on density functional theory (DFT) for captan and folpet molecule, performed with the software package Gaussian 03 using B3LYP theory and the 6-31G basis set. In figure 6 we compared the experimental and calculated absorption spectra of captan and folpet in the range 20 – 60 cm$^{-1}$ and 20 – 80 cm$^{-1}$, respectively. The experimental spectrum of captan shows obvious absorption peak at 39.3 cm$^{-1}$, but the peak of calculated spectrum indicates at about 43.0 cm$^{-1}$. And the obvious absorption peaks of folpet at 42.7 cm$^{-1}$ and 67.4 cm$^{-1}$ in the experimental spectrum and at 38.2 cm$^{-1}$ and 61.3 cm$^{-1}$ in the calculated spectrum. We can see that two different bactericide molecules have different positions and absorption
intensity in their distinctive spectra. So these characteristic absorption peaks as fingerprint can be used to detect and identify this substance.

![Graph](image)

**Figure 6.** Comparison between a DFT calculation and experimental determination of absorption spectrum of (a) captan and (b) folpet.

With the help of Gaussian View 3.09, the peak of captan at 39.3 cm⁻¹ and the peak of folpet at 42.7 cm⁻¹ all correspond to the trichloromethyl-sulphur vibration, but the peak of folpet at 67.4 cm⁻¹ corresponds to the phthalimide torsion. While the peaks of captan at 46.9 cm⁻¹, 58.1 cm⁻¹ and folpet at 72.6 cm⁻¹ perhaps correspond to the intermolecular hydrogen-bonding, absorption of water molecules, etc. The concrete reasons for those peaks are yet unknown and will be the subject of further studies.

### 4. Conclusions

In this article we report measurements of the FIR absorption spectra of captan and folpet by THz-TDS. The results show that the similar molecules have obviously absorption peaks and the positions of peaks are totally different. We observe well-resolved absorption features due to collective intermolecular motion and show their strong sensitivity to the molecular structure. We calculate the theory spectra of bactericide molecules based on DFT. And with the help of Gaussian View 3.09, we illustrates reasons of the distinctive absorption peaks. This illustrates how THz-TDS provides a fingerprint of the molecular conformation, and it must be pointed out that THz-TDS is an optical technique that can detect and distinguish the molecular structure and bactericide residues. It not only offers references to the application of other bactericide, but also is significant for the detection of pesticide residues.

### Acknowledgments

This work is supported by the National Quality Supervision and Inspection Public Welfare Project of China under Grant 200910181 and in part by the National Natural Science Foundation of China under Grant 60902095.

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