Spectrum characteristics of nitrofen by terahertz time-domain spectroscopy

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Abstract. This paper firstly presents the preliminary research on nitrofen with terahertz time-domain spectroscopy (THz-TDS). Different weight ratios of nitrofen in nitrofen-polyethylene combinations were measured. We employed linear fit between not only absorption coefficient but also average refractive index and the concentration of nitrofen. In the frequency region from 0.4 THz to 2.2 THz, seven characteristic absorption peaks of pure sample had been observed, four of which were assigned by using density function theory. Our study demonstrates that THz-TDS is an effective tool to distinguish nitrofen.

1. Introduction
Pesticide residue is one of the prominent factors on influencing the food safety, which has increasingly been paid attention by consumers. The existing detection methods of pesticide residues can be roughly classified into spectrometry, enzyme inhibition and chromatography etc. Spectrometry is generally acted as a qualitative method because of low sensitivity. The sensitivity and reproducibility of enzyme inhibition is poor due to the instability of the sources and types of enzymes. It is difficult to intuitively detect the pesticide residues using chromatography owing to the complex preparation technique of samples, expensive equipments and professional staff [1-2]. Nitrofen, as a kind of selective contact ether herbicides, is widely used on various kinds of vegetables. Research shows that nitrofen will cause hemolytic anemia, toxic hepatitis or various dermatitis while act on the human body [3]. Therefore, it is greatly significant in developing a kind of easy-to-use, quick and sensitive detection method.

This paper achieved the study on the nitrofen molecule by using a relatively novel detection technology of far-infrared spectral -terahertz time-domain spectroscopy technology. Terahertz (THz) wave is the electromagnetic wave of 0.1 ~ 10 THz (1THz = 10^{12} Hz) range, corresponding to a wavelength of 3000 ~ 30 μ m. Terahertz radiation lies between the microwave and infrared regions of the electromagnetic spectrum, and THz spectrums of
substances contain considerable physical and chemical information [4]. In recent years, many scholars at home and abroad have made investigation on considerable substances based on THz - TDS system. For instance, Mittleman D M et al studied polar gases and made identification and detection for gas mixtures [5]. Hua Y F et al quantitatively detected cyfluthrin content in n-hexane solvent by utilizing THz-TDS [6]. THz spectrum of Polycrystalline RDX was acquired by Allis D G et al [7]. Yan Z G et al studied on vibration mode of the organophosphate pesticide acephate in the THz range [8]. The nitrofen detection by utilizing THz-TDS technique has not yet found at home.

We reported the response characteristics and transmission mechanism of nitrofen in the terahertz range by using THz-TDS technology at the room temperature and nitrogen environment. Varieties of nitrofen-polyethylene combinations with differing nitrofen contents were measured to obtain absorption and refractive index spectra. We employed linear fit between not only absorption coefficient but also average refractive index and the concentration. Basing on the experiment, simulation calculation of quantum chemistry software Gaussian 03 was used to analyze experiment data.

2. Experimental methods

2.1. Sample preparation and experimental apparatus

Nitrofen with the purity of 99% was purchased from J&K SCIENTIFIC LTD, Shanghai city, China and was used without further purification or treatment. Firstly, the sample and polyethylene (PE) powder were dried at 310 K for 2 hours. Secondly, they were mixed well with several different concentrations, as shown in table 1, and grinded with a agate mortar to reduce baseline offsets. Furthermore, laboratory tablet press was employed to compress the circular discs with diameter of 13 mm and thickness ranged from 1 to 2 mm at 30 MPa pressure.

| No. | date | thickness(d) / mm | approx weight percentage of sample / % | upper limit THz |
|-----|------|------------------|--------------------------------------|----------------|
| 1   | 1st  | 1.52             | 66%                                  | 1.5            |
| 2   | 1st  | 1.20             | 75%                                  | 2.2            |
| 3   | 2nd  | 1.16             | 100%                                 | 2.4            |
| 4   | 2nd  | 1.60             | 50%                                  | 1.5            |
| 5   | 2nd  | 1.57             | 33%                                  | 1.5            |

THz-TDS spectroscopy experiment setup refers to literature [8]. Experiment was carried out at room temperature (about 294 K), with the optical path of THz Filled with nitrogen and the relative humidity of about 3.0%.

2.2. Data acquisition

The real refractive index \( n(\omega) \) and absorption coefficient \( \alpha(\omega) \) respectively describing the dispersion and absorption characters of substance are generally used to represent macroscopic...
optical properties of substance, and calculated as follows:

\[
 n(\omega) = \frac{\phi(\omega) c}{\omega d} + 1 
\]  

(1)

\[
 \alpha(\omega) = \frac{2\kappa(\omega) \omega}{c} = \frac{2}{d} \ln \frac{4n(\omega)}{A(\omega)(n(\omega) + 1)} 
\]  

(2)

Where \( c \) represents the light velocity, \( d \) is the sample thickness, \( A(\omega) \) is the amplitude ratio of the sample to reference signal, and \( \phi(\omega) \) is the relative phase difference between sample and reference signal. The above are based on the processing model proposed by Dorney T D et al [9] and Duvillaret L et al [10-11].

3. Result and discussion

Molecular formula of nitrofen is \( \text{C}_{12}\text{H}_7\text{Cl}_2\text{NO}_3 \). The molecular structure is shown in Fig. 1, the hydrogen bonds and hydrogen atoms had been omitted. The structure includes a nitrobenzophenone and a 2,4-dichlorophenyl, which are related to vibration modes.

![Fig. 1. Nitrofen molecular structure diagram.](image)

THz time-domain waveforms of nitrofen and reference signal are shown in Fig. 2. A certain attenuation of the sample signal relative to the reference signal is due to sample absorption, scattering and other reasons. A certain delay on time is due to the different refractive index of sample and nitrogen.

![Fig. 2. THz time-domain wave of nitrofen.](image)
THz absorption spectra of nitrofen without baselines corrected, shown in Fig. 3(a), are calculated by equation (2). The samples with different thickness have the distinct upper limit THz. That have been assumed to result from different signal-to-noise ratio (SNR). The thinner the sample is, the higher the upper limit THz is. The upper limit THz is shown in Table 1. From Fig. 3(a), we can see that the 3th sample exhibits 7 absorption peaks in the effective frequency range from 0.4 THz to 2.4 THz. The test absorption peaks locates respectively at 0.5412, 0.6592, 0.98145, 1.3330, 1.6260, 1.9775 and 2.2412 THz. With frequency increasing, the baseline of the absorption spectrum has a slowly rising. The phenomenon may be caused by light scattering or sample surface reflection.

The frequencies of the test characteristic absorption peaks $a_1$ and $a_2$ are within effective frequency range of all the samples. The weight content can be regressed linearly against the absorption coefficient at $a_1$ and $a_2$ THz, with correlation coefficients for the linear fit of 0.99049 and 0.99967, respectively. The results of linear fitting are shown in Fig. 4(c) and Fig. 4(a). The solid line is the linear fit. The solid triangles and stars represent the absorption coefficient.

Refractive index spectra of nitrofen shown in Fig. 3(b) are calculated by equation (1). Refractive index decreases with the frequency gradually increasing. In the effective frequency
range, refractive index has a significant change associated with each characteristic absorption peak due to anomalous dispersion. From 0.5 to 1.5 THz, we can learn the average refractive index is 1.43975, 1.48451, 1.50413, 1.53043, 1.62056 with corresponding ascending concentration of nitrofen. We employed linear fit between average refractive index and the concentration of nitrofen and obtained the correlation coefficient 0.9824. In Fig. 4(b), the solid line is the linear fit and the solid square is average refractive index.

We employed linear fit between not only absorption coefficient but also average refractive index and the concentration of nitrofen. In terms of the correlation coefficient, the fit line with absorption coefficient was superior to that with average refractive index. Knowing the fit linear parameters, it is easy to allow a reliable determination of weight content. Nevertheless, the linear fit has been supposed an empiric approximation for the test date. The precision of determining unknown weight content depends on the data used for fitting, while relating to SNR.

The Becke-3-Lee-Yang-Parr (B3LYP) method of DFT at 6-31G (d) basis sets as implemented in Gaussian03 was used to geometrically optimize nitrofen molecules [12]. The frequency calculation results had no imaginary frequency utilizing the same method, indicating that molecular optimization get the minimum energy molecular structure. Four of the characteristic absorption peaks were assigned theoretically, and the intermolecular modes are supposed to dominate the remaining spectrum.

Theoretical simulation results showed that: the four characteristic absorption peaks of nitrofen molecules at this range are corresponding to the different vibration modes of nitrobenzene and 2, 4- dichlorophenyl. With the visual function of Gaussian View 3.09, the vibration modes of characteristic absorption peaks were assigned in Table 2.

| serial number | theory / THz | test / THz | ascription |
|---------------|--------------|------------|-------------|
| 1             | 0.5343       | 0.5412     | swing vibration of nitrobenzophenone and torsional vibration of nitrobenzophenone |
| 2             | 0.9975       | 0.9815     | torsional vibration of nitrobenzophenone and bending vibration of 2,4 – dichlorophenyl |
| 3             | 1.1746       | 1.3330     | torsional vibration of nitrobenzophenone and swing vibration of 2,4 – dichlorophenyl |
| 4             | 2.1220       | 2.2412     | torsional vibration of nitrobenzophenone |

There are some deviations between the experimental frequencies of characteristic absorption peaks and the theoretical values. The reasons causing the difference between the theoretical and experimental values are as follows: Gaussian can calculate the intermolecular and intramolecular chemical properties on the condition of gas or liquid, and the simulative model is a single molecule, while the nitrofen is crystal, involving intramolecular or phonon interactions. Simulation theory often neglects many practical factors and the experimental results are affected by the absorption of system and environment. To sum up, absorption of nitrofen in the terahertz range contains not only the intramolecular interactions, but also the collective-vibration modes or lattice vibrations associated with intermolecular hydrogen.
4. Conclusion

This paper studied on absorption and refractive index spectra of nitrofen based on THz-TDS technology and density functional theory. In the range from 0.4 to 2.4 THz, there are 7 obvious characteristic absorption peaks which respectively locate at 0.5412, 0.6592, 0.98145, 1.3330, 1.6260, 1.9775 and 2.2412 THz, and four of them were assigned theoretically to the different vibration modes of nitrobenzene and 2, 4 - dichlorophenyl. The experimental results were in good agreement with the theory simulation data. Absorption coefficient at $a_1$ and $a_2$ THz and average refractive index raging from 0.5 to 1.5 THz have optimum linear relations with the concentration of nitrofen, with correlation coefficients of 0.99049, 0.99967 and 0.9824, respectively. Knowing the fit linear parameters, it is easy to get a reliable determination of concentration. This study provides qualitative and quantitative analysis technology for pesticide molecular detection by using THz-TDS.

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5. References

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