

# STUDY OF APPLICATION OF THZ TIME DOMAIN SPECTROSCOPY IN FOOD SAFETY

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**Abstract:** In this paper, a new spectroscopy technology named terahertz time-domain spectroscopy (THz-TDS) is introduced, which is used in food safety. We describe a coherent subpicosecond THz spectroscopy system based on non-resonant optical rectification for the generation of THz radiation. As an example, we measured absorption spectrum of water vapor by THz-TDS in frequency from 0.5 to 2.5 THz. The experiment demonstrated that the spectroscopy resolution of system was up to 0.0001THz, which can be measured vegetable pesticide residual, for it neither need sample pretreatment nor cause pollution.

## 1. INTRODUCTION

In recent years, food quality safe has attracted more and more attention. According to statistics, there are 15 billion of diarrhea cases a year in the whole world, which makes more than 3 million children death. And 70 percent of these result from food and water polluted by many kinds of pathogenic microorganism. There are approximately 76 million food-borne disease cases every year in the US, bringing on 325 thousand persons hospitalization treatment and 5000 deaths, which directly or indirectly causes tens billions dollars loss every year. In particular, the frequently breaking out of International food security incidents, O17 (Japan, 1996), bse (Britain, 2000), Swine streptococcus (China, 2006) and so on, has attacked

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the alarm bell to the common people again. In order to avoid the occurrence of these accidents, the first thing we should do is to carry on the safe examination to the food, which is the base of reducing the food-borne disease. Whether one product has the unsafe factor and what is the unsafe degree both rely on the examination. Therefore, the examination is the most essential method of guaranteeing food safety. In agricultural production, the pesticide which is one kind of organic mixtures has been universally using in pest control. Because of toxic and high residual, while promoting socio-economic development, the pesticide can cause the harm to the human health and the ecological environment either. Presently, the environmental pollution created by the pesticide residue has already aroused widespread social attention. Therefore, it has important meaning to carry on the high sensitive detection aiming at the pesticide residue.

How to detect pesticide residue in food quickly and efficiently is a key problem in food safety controlling system. The conventional methods need complicated sample pretreatment, consume biochemical reagents and last a long measuring period. So we attempt to achieve the pesticide residual measurement by optical method. This paper is concentrated on the methodology study for direct measurement on vegetable pesticide residue based on terahertz time domain spectroscopy, for it neither needs sample pretreatment nor causes pollution.

## **2. THZ TIME DOMAIN SPECTROSCOPY**

THz time domain spectroscopy (A. Rice, 1994) has recently emerged as an extremely useful and powerful probe of charging transport in materials, owing to the fact that it provides a probe of the complex conductivity over a wide frequency range, with sub-picosecond time resolution. As such, it has many advantages over conventional techniques such as resistivity and hall measurements: it is an all-optical technique (and therefore contactless) and it allows the study of non-doped (pristine) samples. Moreover, the experiments are ideally suited for pump-probe experiments that can access charge dynamics such as recombination and trapping. Inorganic and organic semiconductors and non-polar liquids are some of the materials to which THz spectroscopy has been successfully applied. At AMOLF we are currently looking at charge transport in novel materials such as semi-conducting polymers and quantum dots. These materials have important technological applications in solar cells and other electronic devices (D. Dragoman, 2004).

THz generation via optical rectification can be accomplished in two different configurations characterized by slight and tight focusing of femtosecond laser beams. Slight focusing means that the beam size in the

emitter is much larger than the extension of the pulse in the longitudinal direction while for tight focusing they are comparable. When the laser beam is slightly focused on the velocity mismatch, it reduces the effective thickness of the emitter contributing to THz generation. In this situation the THz radiation originates from two thin layers near the front and the back surfaces of the emitter. In the case of tight focusing, the smaller beam waist of the pump thus the increased intensity results in high conversion efficiency of THz radiation.

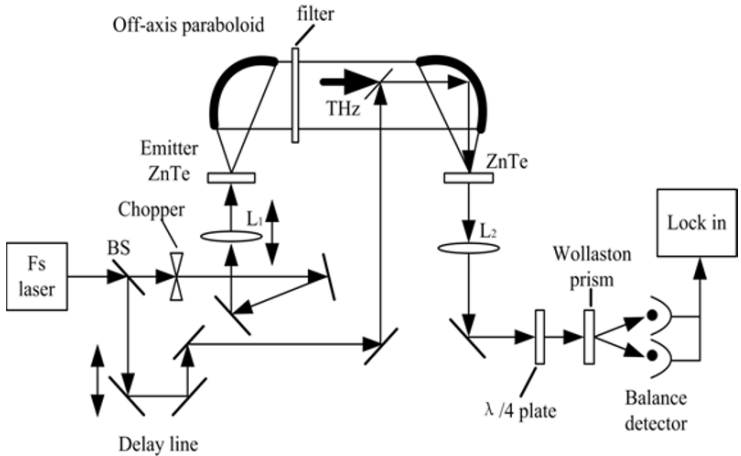


Fig. 1: Schematic drawing of the experimental setup

In a wideband coherent THz radiation system using ZnTe crystals, the generation of THz radiation is based on optical rectification, and THz radiation detection is via electro-optic effects in ZnTe. Optical rectification allows producing much broader THz bands, and the simplicity of the experimental realization is another advantage. Figure 1 schematically illustrates the experimental setup of THz radiation. A homemade self-mode-locked Ti: sapphire laser delivered 40fs pulses with an average power of 300mw at 810nm (Qirong Xing, 1995), repetition rate of 100MHz. The linearly polarized femtosecond laser beam with polarization direction along the table plane was split into two parts, in which 70% was used as the pump beam, and the remains 30% was used as the probe beam. The pump beam chopped into 1050Hz was focused by lens  $L_1$  ( $f=5\text{cm}$ ) on the ZnTe emitter. Lens  $L_1$  was mounted on a translation stage, which was carefully set so that it could be moved along the pump beam direction. Two 1mm thick  $\langle 110 \rangle$  ZnTe crystal was used as the emitter and the detector of the THz radiation respectively. The polarization of both the THz and optical probe beams were aligned parallel to the  $[1, -1, 0]$  direction of the ZnTe detector. The THz radiation was collimated with two off-axis parabolic mirrors and focused on the detector for electro-optic sampling of the THz radiation. A teflon filter, F, was used to remove the residual pump beam. The probe beam modulated by

THz radiation was collimated with lens  $L_2$  and optically biased at a quarter-wave plate, which allows the system to be operated in the linear range. A Wollaston polarizer was used to convert the THz field induced phase retardation of the probe beam into an intensity modulation between the mutually orthogonal linearly polarized beams. A balanced photoelectric detector was used to detect the optical intensity modulation, which wired to give zero current for balanced power. The signal current was sent to a lock-in amplifier for amplifying the signal and filtering noise. The optical delay line worked through a computer-controlled translation stage (Physikinstrumente, M-405.DG) with a resolution of  $0.1\mu\text{m}$ . Via this setup, we succeeded in detecting the spatial profile of a THz radiation. Figure 2 shows the THz temporal signal and the corresponding frequency spectrum (insert) obtained from the emitter ZnTe beyond focus.

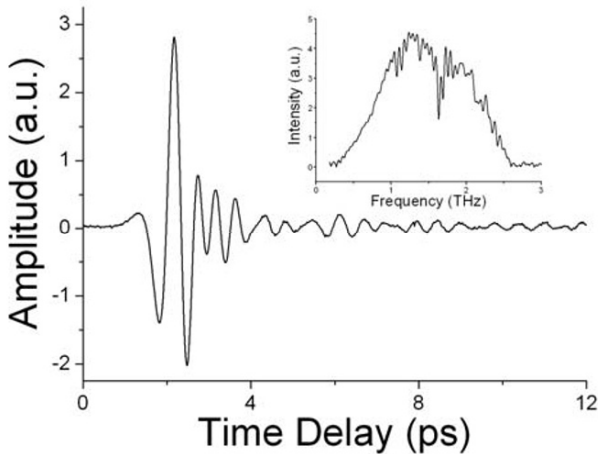


Fig.2: Typical THz waveform and its frequency spectrum

As an application example of our THz system to TDS, we measured the absorption spectrum of water vapor by test THz radiation pulses signal through water vapor. We performed the experiments as follows; firstly, we detected THz radiation pulses as reference background after only propagating through atmosphere in the lab. And then by putting a cup of hot water under the THz radiation beam between two collimating mirrors, we measured THz radiation pulses through water vapor the amplitude absorption spectrum of the atmosphere and water vapor are given from Fourier transform of corresponding to the THz time-domain signals. By subtracting the amplitude absorption spectrum of the atmosphere from that of sample with water vapor the amplitude absorption spectrum of water vapor in frequency range from 0.5 to 2.5 THz shows in Figure 3 with a measurement accuracy as high as reported in the Ref.8. The data in table 1

indicate the comparison of the water vapor spectrum between in Ref (R. A. Cheville, 1999) in our experiment.

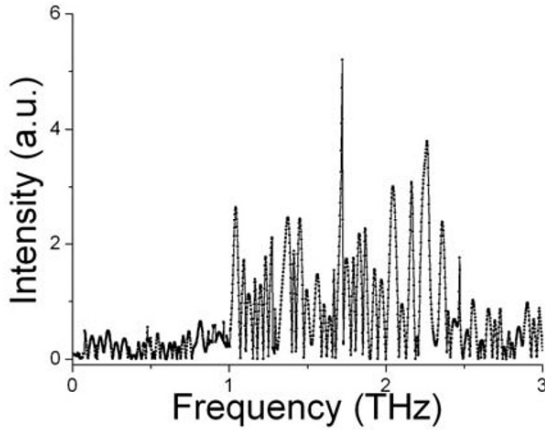


Fig.3: the water vapor absorption spectrum

Table .1 Water vapor spectrum

D1	1.09922	1.1156964	1.16257	1.20938	1.23055	1.41094	1.60323	1.67109
D2	1.09367	1.1256175	1.16686	1.20078	1.23272	1.41312	1.60480	1.66869
D1	1.71808	1.79766	1.87031	1.91965	2.04147	2.16563	2.19860	2.25703
D2	1.72131	1.79272	1.86788	1.92801	2.04452	2.16479	2.19861	2.26251

\*  $D_1$ -the water vapor spectrum of in Ref (R. A. Cheville, 1999),  $D_2$ -the spectrum of water vapor in our experiment. Units: THz

As an application example of our system to TDS, we measured the amplitude absorption spectrum of water vapor in frequency range from 0.5 to 2.5 THz. The measured spectrum data show that our system possesses a measured accuracy as high as reported in the literature.

### 3. ANALYSIS OF MEASURED THEORY

Taking into account these important advantages it was believed that TDS will surmount in many ways the conventional spectroscopic method used in the THz range of frequencies, i.e. the Fourier-transform infrared (FTIR) spectroscopy. The FTIR spectrometer has as a source of radiation an incoherent lamp and is based on the two-beam interferometry principle. Contrast to TDS, the output signal of the FTIR spectrometer is proportional to the intensity of the FIR field.

However, recent results have demonstrated that the SNR of TDS is better than that of FTIR for frequencies in the range 10GHz-4THz. In this range the field amplitude SNR of THz TDS is 104 while that of FTIR is about 300.

Beyond this frequency range (the FTIR method is able to work from FIR up to visible spectral range), the SNR of FTIR is better. The SNR of TDS is drastically decreased when its bandwidth is increased up to 40 THz. Both methods show a similar spectral resolution  $\approx 0.1 \text{ cm}^{-1}$ .

Thus, TDS is an extremely powerful method of spectroscopy, working at room temperature with an impressive sensitivity. TDS is performed in two steps. Firstly, a reference signal  $E_r(t)$  is detected in the absence of the sample. Then, a signal in the presence of the sample,  $E_s(t)$ , is detected. The transmission function of the TDS is given by (L. Xu, 1992)

$$T(\omega) = E_s(\omega) / E_r(\omega) = |T(\omega)| e^{i\varphi(\omega)} \quad (1)$$

The index of refraction of the sample  $N = n + iK$  is related to the transmission function through the equation:

$$T(\omega) = 4N \exp[i\omega(N-1)d/c] \sum_{i=0}^P \{[(N-1)/(N+1)] \exp(i\omega Nd/c)\}^{2i} \quad (2)$$

Where  $d$  is the thickness of the sample, Expression (2) is the transfer function resulting from the passage of the THz field through the sample, the THz field being reflected  $P$  times inside the sample. These repeated reflections inside the sample, which can be modeled as a Fabry-Perot-like effect, are seen in the time domain as distinct pulses accompanying the main time domain response. Thus,  $P$  is easily determined at least in the case of thick samples.

When  $p=0$ , Eq. (2) allows a simple determination of the real and imaginary parts of the refractive index of the material as:

$$|T(\omega)| = 2(n^2 + k^2)^{-\frac{1}{2}} \exp(-\omega kd/c) / [(n+1)^2 + k^2] \quad (3)$$

$$\varphi(\omega) = \omega(n-1)d/c + \arctan\left\{-k(n^2 + k^2 - 1) / [n(n+1)^2 + k^2(n+1)]\right\} \quad (4)$$

Solving the system formed by the last two equations we can extract the real and imaginary part of the index of refraction from the known amplitude and phase of the transmission function at a certain frequency. The procedure is repeated for any frequency with the bandwidth of the TDS system. Thus only two time-domain measurements are necessary to determine  $T(\omega)$ , from which the frequency behavior of the complex index of refraction of the material is determined. Both analytical methods and numerical algorithms are used to determine simultaneously.

The index of refraction and the thickness of the sample, a procedure useful mainly for thin samples, is difficult to estimate the sample thickness.

#### **4. CONCLUSION**

In this paper, a coherent subpicosecond THz spectroscopy system is introduced based on non-resonant optical rectification for the generation of THz radiation. As an example, we measured absorption spectrum of water vapor by THz-TDS in frequency from 0.5 to 2.5 THz. The experiment demonstrated that the spectroscopy resolution of system was up to 0.0001 THz. With the installation of the system continuously improving, it will certainly have the widespread application prospect.

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