Applications of Terahertz Spectroscopy

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Abstract — In order to make use of terahertz (THz) spectroscopy technique for homeland security, anti-terrorism, and security inspection, we have examined the applications feasibility of THz spectroscopy to inspect and identify 30 kinds of illicit drugs, 20 kinds of amino acid and 10 kinds of explosives and related compounds (ERCs), respectively. In addition, we also present two reference-free phase feature extraction techniques for identification of ERCs using THz reflection time-domain spectroscopy (RTDS) and transmission TDS, respectively.

I. I. INTRODUCTION

Until now, research has been carried in THz region for several decades. The application of THz spectroscopy is one of the main drive of the rapid development and promotion of THz science and technology. The reasons why people concerned about THz is that there are too rich physical, chemical and biological information in THz region. When THz photos are absorbed or emitted, the rotational, vibrational, bending, even thermal state of the molecules of the materials can be changed, so the THz spectra of the materials can provide the information regarding the physical condition, physical or chemical processes about the molecules of the materials, and the THz spectroscopy technique can get efficiently the finger-print spectra of the materials, and identify them. On the other hand, THz wave almost can penetrate any packing materials, expect metal wrapping. Moreover, there are no ionizing phenomena by using THz spectroscopy technology, because the small photon energy of THz wave.

The spread of terrorism seriously, illicit drugs and ERCs especially are the tools commonly used by terrorists or criminals. In addition, the illicit drugs and ERCs have been smuggled easily resulting in the widely spread of the drugs and explosives. It's because of the absence of nondestructive inspection techniques for illicit drugs and ERCs hidden in envelopes or wrapping materials. At present, several inspection have been used such as police dog inspection, x-ray scanning, trace detection, and developing millimeter wave imaging and infrared imaging techniques. However, each of these techniques has its limitation for the inspection of the illicit drugs and ERCs. Therefore, an effective technique is necessary to make up the limitations of the enlisted techniques for inspection and identification of the drugs and ERCs.

There are several distinctive fingerprints features of illicit drugs, ERCs and amino acid in THz region. We confirm that the THz spectroscopy technique can be quite efficient for homeland security, antiterrorism, security inspection, and nondestructive evaluation (NDE) biological application etc, so we emphasized on investigating the THz spectra of illicit drugs, amino acid and ERCs. We use THz time-domain spectroscopy technique to inspect and identify them. Moreover, we also founded the database of them, respectively. In order to avoid the misplacement phase error in THz-RTDS, we present a feature extraction technique for identification of explosive and biological materials using THz-RTDS without using reference signal, i.e. reference-free phase feature extraction technique. The absorption signatures of the materials are extracted directly from the second-order derivative of the phase of the sample beam with respect to frequency; similarly, we also propose another feature extraction technique to locate the spectral position of an unknown material's absorption lines with reference-free technique by using THz transmission TDS (TTDS). The sample's absorption peaks are extracted from the negative fist-order derivative of the sample signal phase divided by the frequency at each pixel. These two reference-free techniques will greatly benefit the feature development of stand off distance, large-size focal-plane THz sensing and imaging system.

II. SPECTRA OF ILLICIT DRUGS, AMINO ACIDS AND ERCS

Most illicit drugs, amino acids and ERCs have distinctive absorption spectra feature in THz region, which interest in THz spectroscopy. Up to now, we have got the fingerprints of 30 kinds of illicit drugs, 20 kinds of amino acid and 10 kinds of ERCs by using THz-TDS, and found their spectra database, respectively, which can be used to inspect and identify them. While, we also use Gaussian 03 software package[1-2] and Dmol3 software[3], which all based on the density function theory (DFT), to analyze the forming mechanism of those absorption fingerprints of these materials, respectively. For example, we use Gaussian 03 to calculate the single molecule mode of the molecular, and use Dmol3 to deal with the solid-state calculation. In addition, we also take use of Neural networks (NN) such as Back Propagation (BP) [4], self-organizing Map (SOM) [5-6] and multi-layer perceptron (MLP) to identify drugs and ERCs.

The absorption feature of several illicit drugs and ERCs are shown in fig. 1(a) and fig.1 (b) [7]. The fragment of spectra database of amino acids is list in table 1. The identify results of nine illicit drugs by BP NN and nine ERCs by SOM NN are shown in table 2 and table 3, respectively.

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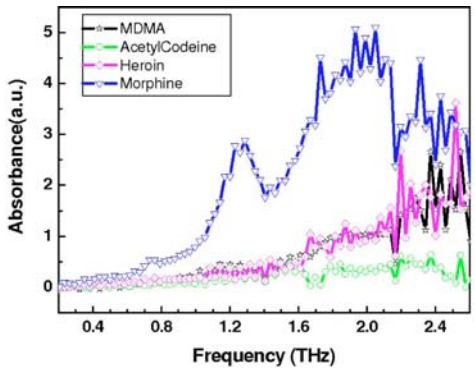
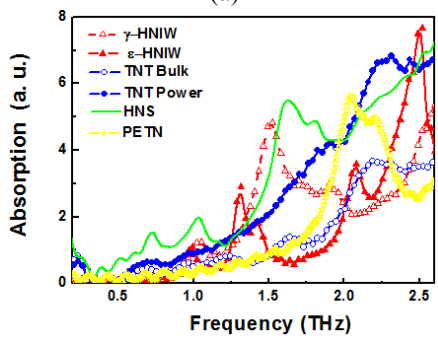


(a)



(b)

Fig. 1.(a) Absorption spectra of MDMA, acetylcodeine, heroin, and morphine. (b) Absorption spectra of HNIW, TNT, HNS, PETN, to attention, we can identify the isomer, such as γ-HNIW and ε-HNIW, by using THz spectroscopy technique.

Table 1 Fragment of spectra database of amino acids

Amino acids	**Features(THz)**
Lysine	1.26,1.79,2.25,2.60
Glycine	2.30,2.53
Alanine	2.23,2.56,2.73
Tyrosine	0.97,1.90,2.08,2.70
Threonine	1.11,1.41,2.14,2.58
Serine	2.01,2.40,2.71
Asparagine	1.64,2.26
…	…

Table 2 Identifying results of nine illicit drugs

Object vector (T) / Sample vector (P)	1	2	3	4	5	6	7	8	9	Expected output	Actual output
1 Caffeine	1									1	1
2 Heroin		1								2	9
3 Ketamine			1							3	3
4 MA				1						4	4
5 MDA					1					5	5
6 MDMA						1				6	6
7 O^3-monoacetylomorphine							1			7	7
8 O^6-monoacetylomrphine								1		8	8
9 Acetylocdeine									1	9	9

Table 3 Identifying results of nine ERCs

Input	Output	Training times	The times of correct output	accuracy
RDX	RDX	20	20	100%
HMX	HMX	20	19	95%
PETN	PETN	20	20	100%
8701	RDX	8	8	100%
R791	RDX	8	8	100%
R852	RDX	8	8	100%
PW0	RDX	8	8	100%
Plastic explosive	RDX	8	8	100%
8702	HMX	8	8	100%

The identifying results indicated that it is feasible to apply the BP NN and SOM NN on the identification of illicit drugs or ERCs, and providing an effective method in the secure inspection and identification for these drugs and ERCs by using THz-TDS technique.

III. Reference-fee technique

Conventionally, THz spectroscopic measurements both reflection geometry and transmission geometry measurement all need a sample signal and a reference signal. However, these two methods have their limitations, respectively. For example, in reflection TDS, the retrieval of phase shift caused by absorption has been a bottleneck, because the misplacement phases error between sample signal and reference signal is hard to correct. Otherwise, most methods need a large amount of human intervention and computation. For transmission TDS, the feature extraction is limited by the beam quality and signal to noise ratio (SNR), it's hard to apply in standoff and large size focal-plane imaging system. So, we propose two reference-free feature extraction techniques for THz-RTDS and THz-TTDS, respectively.

Unlike common spectroscopy measurement, in these two methods, the amplitude spectrum of the THz signal is not considered at all. Instead, the absorption features are extracted only from the phase information by taking use of the almost-linear phase spectrum of THz pulses and the correlation between dispersion and absorption, in an ideal case ignoring the atmospheric absorption. It is noted the spectral phase of the THz pulse can be determined with far greater accuracy than the amplitude, which makes this method even more favorable.

The spectral phase, derived form a typical time-domain THz waveform by Fourier transform, is essentially linear. For the reflection geometry [8], the THz pulses are reflected by the target surface after traveling for a path length of L in the air, its phase φ_s is governed by:

$$\varphi_s(\omega) = \varphi_0 + \omega n_{air} L / c, \quad (1)$$

where φ_0 is the phase change caused by the material absorption, ω is the angular frequency, n_{air} is the refractive index of the air, and the c is the speed of light. n_{air} is generally regarded as a constant at low humidity level. It has been demonstrated elsewhere that for a weakly polarized organic compound, the extinction coefficient κ can be determined directly from φ_0 by

the following approximation:

$$\varphi_0 = \tan^{-1}\left(\frac{2\kappa}{n^2+\kappa^2-1}\right) \sim \tan^{-1}\left(\frac{2\kappa}{n_\infty^2-1}\right) \quad (2)$$

Where n_∞ is constant. From Eq. (1), under the assumption of a weakly polarized organic compound, the first-order derivative of the sample beam phase is determined by

$$\frac{d\varphi_0}{d\omega} = \frac{2}{(n_\infty^2-1)[1+4\kappa^2/(n_\infty^2-1)^2]}\frac{d\kappa}{d\omega} \sim \frac{2}{n_\infty^2-1}\frac{d\kappa}{d\omega} \quad (3)$$

As a result

$$\frac{d^2\varphi_s}{d\omega} = \frac{d^2\varphi_0}{d\omega^2} \sim \frac{2}{n_\infty^2-1}\frac{d^2\kappa}{d\omega^2} \quad (4)$$

Because $d^2\kappa/d\omega^2$ has a similar shape with κ (negative), and the water vapor absorption cannot be neglected, Eq. (4) becomes

$$\frac{d^2\varphi_s}{d\omega^2} \sim \frac{2}{(n_\infty^2-1)}\frac{d^2\kappa}{d\omega^2} + \frac{L}{c}\left(2\frac{dn_{air}}{d\omega} + \frac{d^2n_{air}}{d\omega^2}\right) \sim \frac{2}{(n_\infty^2-1)}\frac{d^2\kappa}{d\omega^2} + \frac{2L}{c}\frac{dn_{air}}{d\omega}$$

As a result, a reference beam with phase φ_r has to be applied to remove the second term, so that

$$\frac{d^2(\varphi_r-\varphi_s)}{d\omega^2} \sim \frac{2}{(n_\infty^2-1)}\frac{d^2\kappa}{d\omega^2} + \frac{2\delta L}{c}\frac{dn_{air}}{d\omega} \quad (5)$$

where δL is the ranging difference between the reference surface and sample surface. It is noteworthy that the distortions caused by this term only center around water absorption line. As long as the absorption peak of the target lies between two water lines, this term does not affect the shape of the phase feature. Here, we will show that at a stand-off sensing distance of 5 m, under a high humidity level of 37%, a δL less than 20 mm does not introduce any significant error to the final result, and the reference-free phase spectrum $d^2(\varphi_s-\varphi_r)/d\omega^2$ of RDX plotted in liner scale with arbitrary unit is shown in Fig. 2.

For transmission geometry [9], as the THz pulse move through the sample with thickness *h* after traveling for a path length *L* in the air, its phase is governed by:

$$\varphi_s(\omega) = \omega h n(\omega)/c + \omega n_{air}(L-h)/c \quad (6)$$

This equation includes the small but measurable contribution of refractive index from air at standard pressure and room temperature.

The complex refractive index of a dielectric material can be simulated using the Lorentz oscillator model in dispersion theory. It has been demonstrated that in the situation of weakly polarized organic compound, such as ERCs, which has a moderated absorption compared to dispersion in THz range, the locations of resonance frequencies can be determined not only from the spectrum of absorption coefficient α or extinction coefficient κ but also from $-dn(\omega)/d\omega$, where $n(\omega)$ is the refractive index. From Eq. (6), the negative derivative of phase divided by frequency follows:

$$-d\left(\frac{\varphi_s(\omega)}{\omega}\right)/d\omega = -\frac{h}{c}dn(\omega)/d\omega \quad (7)$$

That means that for a weakly polarized organic compound, the negative derivative of phase of the sample THz signal divided by frequency also contains the absorption features of the material around the resonance frequencies. In order to demonstrate the concept of this technique, the reference-free phase spectrum $-d[\varphi_s(\omega)/\omega]$ of RDX is shown in fig. 3.

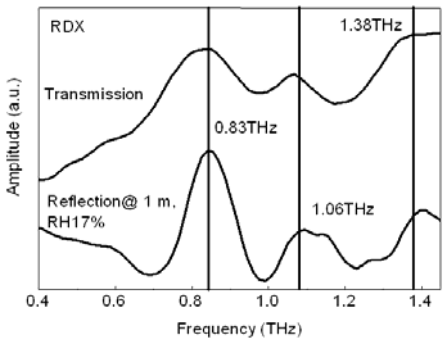
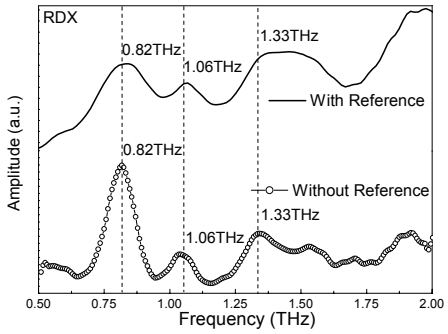


Fig. 2. The absorbance spectrum taken in transmission setup (top) and reference-free feature extraction result (bottom) of RDX



Fi. 3. The absorbance spectrum calculated by using a reference signal (solid curve) and the reference-free phase spectra (dotted curve) of RDX.

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