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Investigation of aging characteristics in explosive using terahertz time-domain spectroscopy

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The terahertz absorption spectrum of the five aging explosive samples (PETN, RDX, HMX, LLM-105 and TATB) was measured and calculated by Terahertz time-domain spectroscopy system (THz-TDS) and air-biased coherent detection system (ZAP-ABCD), respectively. In this paper, compared with the unaging explosive, each aging explosive sample's terahertz time-domain spectra were obtained and the terahertz absorption spectra were calculated by using Fourier transform and Lambert's law. The results show that there are several terahertz absorption peaks which were called "fingerprint spectra" for different aging explosive samples in the range of 0.3–6.0 THz spectrum. Meanwhile, the results also show that the locations of the characteristic absorption peaks are not the same. Moreover, the unaging and aging explosive samples have obviously different terahertz absorption spectra.

Keywords: Aging explosive; characteristic absorption spectrum; Terahertz time-domain spectroscopy; Terahertz.

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1. Introduction

Since it was first produced by Nobel in the 1860s, explosive has played a very important role in the field of aerospace, military, national infrastructure and other social development. With the development of explosive technology, the demand and consumption of explosive has increased dramatically. Up to now, almost every country will store a large amount of explosive weapons in peacetime for the reason that they can defend the national security in the emergency war. However, the explosive is a kind of energetic material which can be easily oxidized and relatively unstable. Its physical and chemical properties will change with the influence of temperature,

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humidity and corrosive gas during the long period of storage.[1–3] This phenomenon will seriously affect the reliability and stability of explosive, so it is extremely important to utilize new spectral technology to detect materials with its low energy and penetration. Meanwhile, the aging process of explosive is mainly influenced by the change of molecular structure and crystal structures in the long period of external environment stimulation, which changes the physical and chemical properties of explosive.

The existing methods of explosive aging detection[4,5] (such as Raman spectroscopy, scanning microscopy, atomic force microscopy, etc.) can neither effectively distinguish the aging characteristics of explosive nor make a more accurate identification of the change in the molecular structure of aging explosive. Especially in the previous work, some works although wide-spectrum Terahertz time-domain spectroscopy (THz-TDS) technology has been used to detect explosives, the aging characteristics of explosive have not been considered and some works have studied the aging characteristic of explosive, but the frequency spectrum width is extremely narrow.[6–10] Therefore, in this paper, the wide-spectrum THz-TDS technology is used to study the aging characteristics of explosives, which is helpful to understand the sensitivity and reaction mechanism of explosive to the external environment.

Terahertz wave (Terahertz, THz), the terahertz band used in this paper is 0.3–6.0 THz, the wavelength range is 1000–50 μm, and the corresponding wavenumber range is 10–200 cm^{-1}, located between microwave and infrared bands, has photon energy equivalent to the vibrational and rotational levels of the most organic molecules and molecular groups. Therefore, the special "fingerprint spectra" can be formed for weak intermolecular interactions (such as hydrogen bonds), skeleton vibration of macromolecules, rotation and vibration transition of dipoles, and low-frequency vibration absorption of lattices in crystals.[11–14]

2. Experimental Setup

The experiment uses THz-TDS system: (1) self-constructed transmission THz-TDS (spectrum range: 0.3–2.5 THz, THz wave generation mode: LT-GaAs photoconductive antenna), the laser used was Spectra-Physics MaiTai femtosecond laser with a center wavelength of 800 nm, a repetition rate of 80 MHz,a pulse width of 70 fs and an average power of 1 W; (2) Zomega corporation researches and develops air-biased coherent detection (ZAP-ABCD) system (spectrum range: 0.5–6.0 THz, THz wave generation mode: air plasma), using a laser of femtosecond laser amplifier, a center wavelength of 800 nm, a repetition rate of 1 kHz, a pulse width of less than 100 fs and an average power of 5 W. The terahertz optical path is sealed with a Plexiglas box, so that the relative humidity inside the box is kept at 0%, the experimental temperature is about 21°C, and the signal-to-noise ratio can reach 10^3 orders of magnitude. The structure schematic diagram of the THz-TDS system and ZAP-ABCD system used in the experiment is shown in Fig. 1.

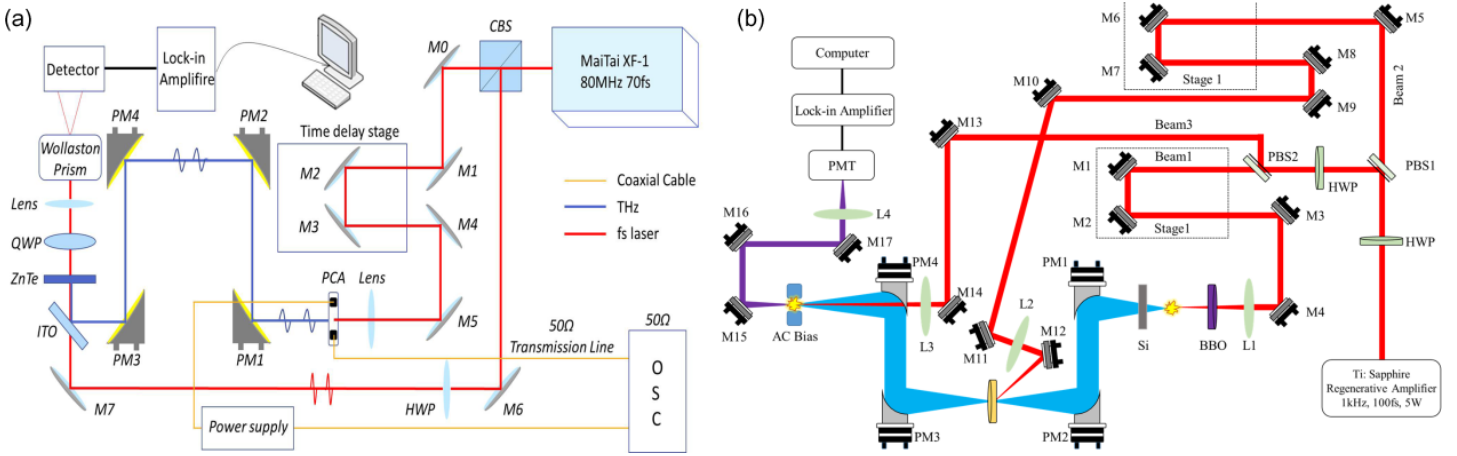

Fig. 1. (Color online) The structural schematic diagram of (a) THz-TDS system and (b) ZAP-ABCD system.

The five kinds of explosive used in the experiment were Pentaerythritol tetranitrate (PETN), Cyclotrimethylenetrinitramine (RDX), Cyclotetramethylene tetranitramine (HMX), 2,6-Diamino-3,5-dinitropyrazine 1-oxide (LLM-105) and 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB).[8,15] The samples were divided into aging and unaging groups, the aging of explosive group needs to be aging treatment. The process is to place the explosive power in a constant temperature and humidity box at a controlled temperature of 71°C, a relative humidity of 95% and accelerated aging for 14 days. Then, the explosive power was dried for 3 h by a drying box with a temperature of 60°C, in order to remove a large amount of water in the explosive power and reduce the influence of water molecules in the experimental measurement results, because the drying process is to reduce the influence of water vapor absorption, but does not lead to the molecular and crystal structures of explosives which have been further changed. Finally, the explosive powder and the polyethylene powder are uniformly mixed at a mass ratio of 1:10 in order to reduce the risk of explosive samples exploding during grinding and the strong absorption of terahertz waves in explosive samples. Compared with the 1:1 mass ratio of explosive samples, its terahertz time-domain spectrum signal noise is higher and the noise has less effect on the absorption spectrum of explosives. So, the sample with the mass ratio of explosive to PE powder of 1:10 was selected as the main test sample in the experiment.

The mixture was placed in an agate mortar and thoroughly ground until it was completely ground, and then the mixture was pressed into a sheet sample having a thickness of about 0.6 mm and a diameter of about 13 mm by a tableting machine as shown in Fig. 2.

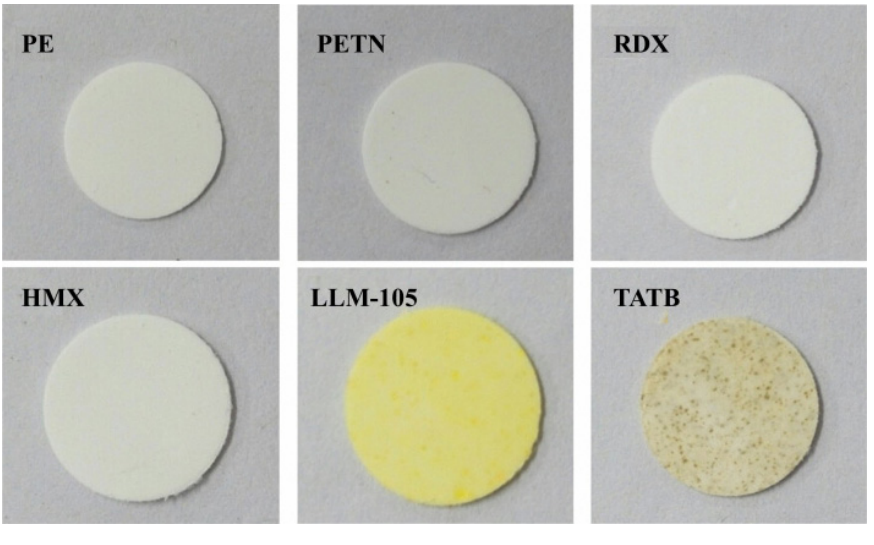

Fig. 2. (Color online) Samples of PE and other explosives.

3. Results and Discussion

The THz-TDS system and the ZAP-ABCD system were used to detect the unaging and aging explosive examples, and finally, their terahertz time-domain waveform and frequency-domain waveform were obtained. Processing data based on the theoretical model of extraction for optical constants of material through terahertz time-domain spectroscopy was proposed by Dorney and Duvillaret. Normally,[16,17] we use the complex refractive index to characterize the optical properties of the material. The complex refractive index is calculated as

$$\tilde{n}(\omega) = n(\omega) - jk(\omega), \tag{1}$$

where ω is the angular frequency, the real part $n(\omega)$ is called the real refractive index and $k(\omega)$ is called the extinction coefficient, which is used to represent the dispersion and absorption characteristics of the material.

The terahertz time-domain spectroscopy system is used to perform and repeat the test three times on the reference sample and the test sample, respectively. On preforming Fourier transform on the two sets of time-domain waveform data to obtain corresponding spectral waveform, the spectrum of the reference signal is set as $R(\omega)$ and the spectrum of the sample signal is set as $S(\omega)$. In the vacuum approximation (in a vacuum environment, the refractive index of the medium around the sample is 1) and the weak absorption approximation ($n \ll \kappa$),

$$\frac{S(\omega)}{R(\omega)} = T(\omega) \cdot e^{-j\phi(\omega)}. \tag{2}$$

Through Eq. (2), we can get $T(\omega)$ and $\phi(\omega)$. According to the following equation:

$$n(\omega) = \frac{c}{\omega d} \cdot \phi(\omega) + 1, \tag{3}$$

$$k(\omega) = \frac{c}{\omega d} \cdot \left[\frac{4n(\omega)}{T(\omega) \cdot (1 + n(\omega))^2} \right]. \tag{4}$$

Thus, the optical constants of the refractive index and the extinction coefficient of the sample in the THz spectrum range are calculated. In Eqs. (3) and (4), d is the thickness of the sample and ω is the angular frequency.

Finally, based on Lambert's law, also known as Lambert–Beer Law, the relative absorption coefficient of the sample in the THz band can be calculated. The equation is as follows:

$$\alpha(\omega) = -\ln \frac{S(\omega)}{R(\omega)}. \tag{5}$$

The measure THz time-domain spectra and frequency spectra of the five explosives were obtained by experiments. Take the testing results of PETN as an example as shown in Fig. 3. Its total spectrum range is 0.3–6.0 THz, including THz-TDS system: 0.3–2.5 THz and ZAP-ABCD system: 0.5–6.0 THz. Meanwhile, the measurement results show that different explosive samples have different time-domain

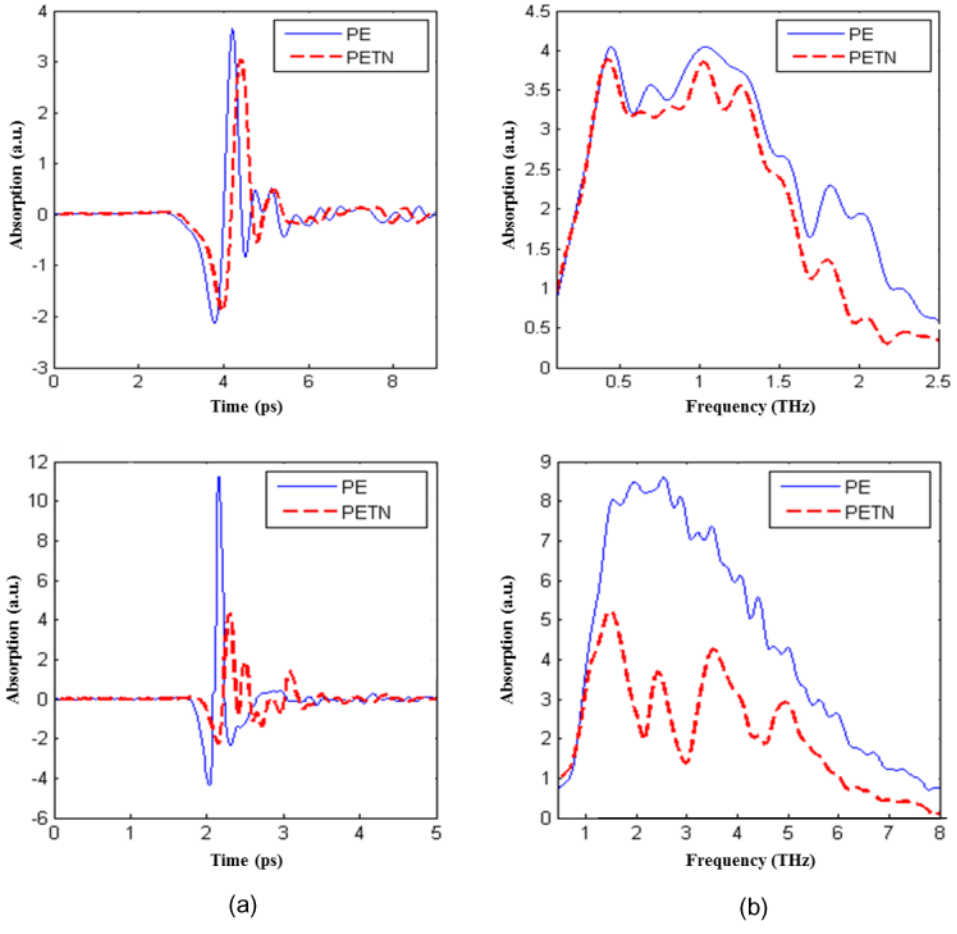

Fig. 3. (Color online) THz waveform of time and frequency domain of PETN: (a) THz-TDS system and (b) ZAP-ABCD system.

spectra in the THz spectrum range. The corresponding frequency spectra are obtained by Fourier transform, and the relative absorption coefficient of THz band is obtained by Lambert–Beer law.

In this paper, the characteristic absorption peaks of explosive obtained by using THz-TDS system are basically the same as that obtained by domestic and foreign research results. More importantly, the absorption spectrum in the range of 2.5 THz of explosive obtained by using ZAP-ABCD system is in good agreement with the experimental results of THz-TDS system. Therefore, we only choose the experimental results in the range of 0.3–2.5 THz in THz-TDS system and in the range of 1.5–6.0 THz in ZAP-ABCD system as shown in Fig. 4.

As can be seen from Fig. 4, the THz absorption spectra of the unaging PETN, RDX, HMX, LLM-105 and TATB below 6.0 THz are highly consistent with the previously published work, different explosives have different fingerprint characteristic

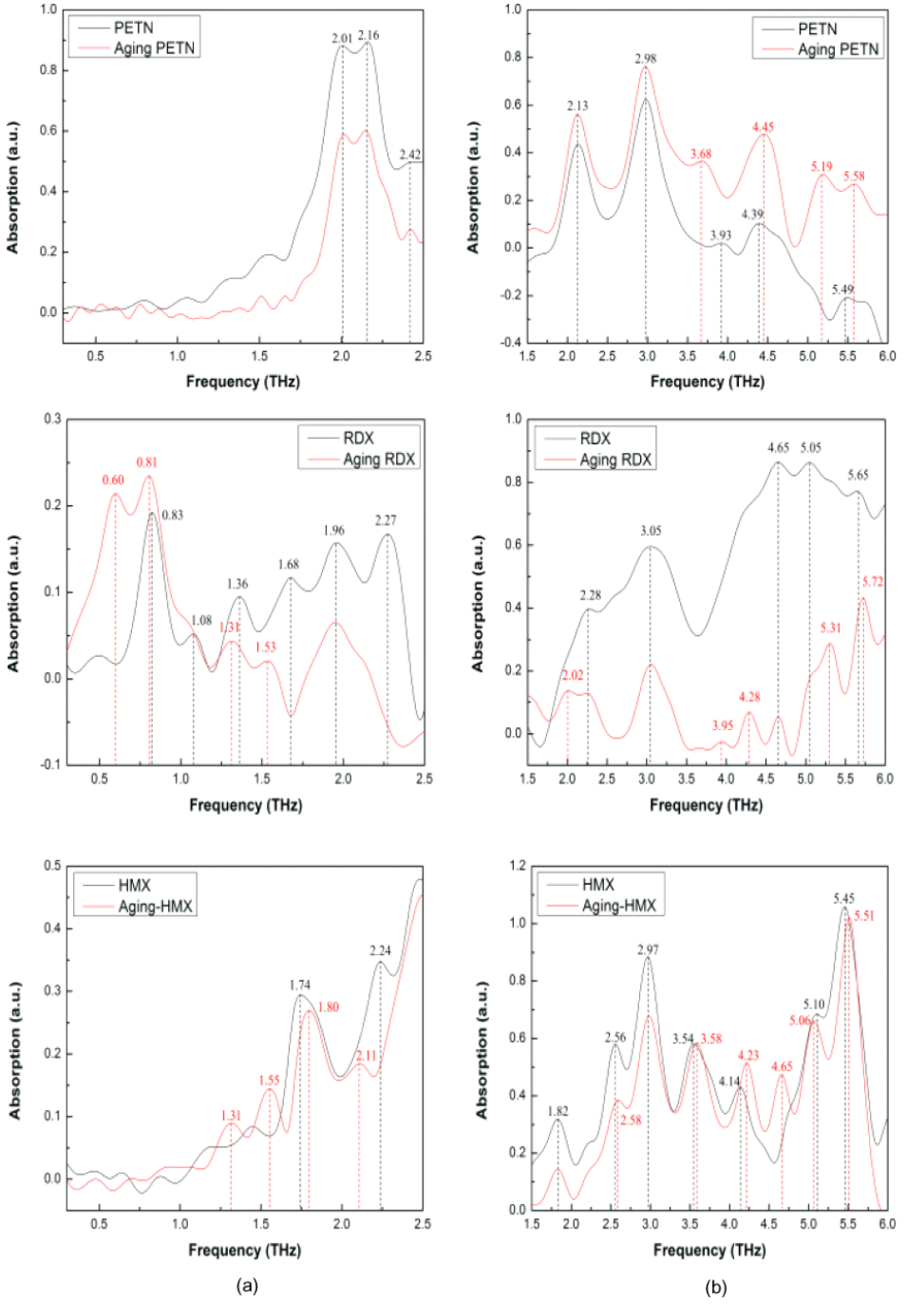

Fig. 4. (Color online) THz absorption spectra of the unaging and aging explosives PETN, RDX, HMX, LLM-105 and TATB: (a) THz-TDS system and (b) ZAP-ABCD system.

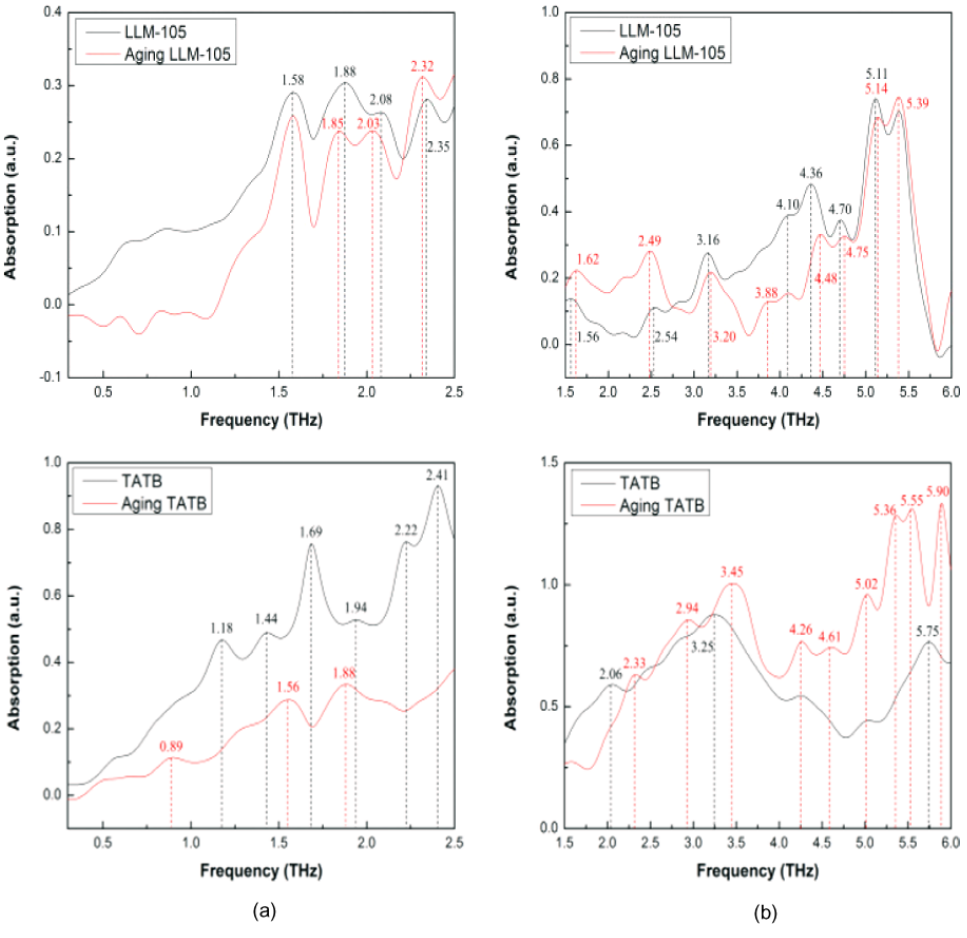

Fig. 4. (*Continued*)

spectra, which can be used to distinguish different types of explosive materials. The aging mechanism of explosives is mainly caused by thermal decomposition, water decomposition and ionizing radiation, the most important reason of aging is pyrolysis reaction of explosive, which results in the change of the molecular structure and crystal structure of the explosive and affects its properties. Therefore, the THz absorption spectra of the aging and unaging explosive samples have very obvious changes.

The PETN THz absorption spectrum has spectral features in the 0.3–6.0 THz spectral range. Especially, in the range of 0.3–6.0 THz spectrum, the position of characteristic absorption peaks at 2.01 THz and 2.16 THz was not different between the aging and unaging PETN, but obvious characteristic absorption peaks appeared at 2.42 THz after aging process. In the range of 0.3–6.0 THz spectrum, the position of characteristic absorption peaks at 2.13 THz and 2.98 THz did not change of the

Table 1. THz absorption peak of explosive samples in different THz spectrum range.

	Unaging explosive		Aging explosive	
Abbr.	0.3–2.5 THz	1.5–6.0 THz	0.3–2.5 THz	1.5–6.0 THz
PETN	2.01, 2.16	2.13, 2.98, 3.93, 4.39, 5.49	2.01, 2.16, 2.42	2.13, 2.98, 3.68, 4.45, 5.19, 5.58
RDX	0.83, 1.08, 1.36, 1.68, 1.96, 2.27	2.28, 3.05, 4.65, 5.65	0.60, 0.81, 1.31, 1.53, 1.96	2.02, 2.28, 3.05, 3.95, 4.28, 4.65, 5.31, 5.72
HMX	1.74, 2.24	1.82, 2.56, 2.97, 3.54, 4.14, 5.10, 5.45	1.31, 1.55, 180, 2.11	1.82, 2.58, 2.97, 3.58, 4.23, 4.65, 5.06, 5.51
LLM-105	1.58, 1.88, 2.08, 2.35	1.56, 2.54, 3.16, 4.10, 4.36, 4.70, 5.11, 5.39	1.58, 1.85, 2.03, 2.32	1.62, 2.49, 3.20, 3.88, 4.10, 4.48, 4.75, 5.14, 5.39
TATB	1.18, 1.44, 1.69, 1.94, 2.22, 2.41	2.06, 3.25, 4.26, 5.02, 5.75	0.89, 1.56, 1.88	2.33, 2.94, 3.45, 4.26, 4.61, 5.02, 5.36, 5.55, 5.90

aging and unaging PETN. Among them, the 2.13 THz characteristic absorption peaks in the ZAP-ABCD system correspond to 2.16 THz characteristic absorption peaks in the THz-TDS system, which ensures the consistency of the two system tests. After aging treatment, the molecular structure of PETN changed because of thermal decomposition reaction. The blueshift occurred at the characteristic absorption peak of 4.39 THz. The characteristic absorption peak of 3.93 THz and 5.49 THz disappeared, and the new characteristic absorption peak of 3.68 THz, 5.19 THz and 5.58 THz were generated. These new characteristic absorption peaks were more obvious, which could be used as a good basis for judging the aging degree of PETN. Finally, RDX, HMX, LLM-105 and TATB were treated in the same way. The variation of their characteristic absorption peaks was shown in Table 1.

4. Conclusion

In conclusion, it is effective to detect the aging characteristics of explosive by THz-TDS technology. Compared with the unaging explosive samples, the aging explosive samples have special fingerprint spectrum which can be used to distinguish whether the explosive is aging or not. The experimental results show that the explosive is prone to thermal decomposition at high-temperature, which results in the change of the group in the aging explosive molecules. For instance, the N–NO_2 bond of Nitrosamine explosive and the C–ONO_2 bond of Nitrate explosive will break at high-temperature, which will change the molecular structure, and then lead to the disappearance and generation of some characteristic absorption peaks of aging explosive. Therefore, THz-TDS technology can accurately reflect the changes of the molecular structure of explosive in the field of the aging explosive detection. Based on the discussion above, it can be seen that the aging detection of explosive has broad practical prospects and profound research value.

Acknowledgments

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