

## Wideband terahertz spectroscopy of explosives

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### Abstract

Time-domain terahertz spectroscopy (TDTS) has been shown to be a promising tool in detection of explosives and explosive related compounds. To date, TDTS for many explosives has been limited to spectral regions <3 THz. With recent improvements in emitters and sensors of THz radiation, we report the THz absorption spectra over an extended frequency band from 0.5 to 6 THz for four explosives: RDX (1,3,5-trinitroperhydro-1,3,5-triazine), HMX (1,3,5,7-tetranitroperhydro-1,3,5,7-tetrazocine), PETN (pentaerythritol tetranitrate), and TNT (2,4,6-trinitrotoluene). New distinctive spectral features are shown in these materials between 3 and 6 THz. These data may aid in the spectral identification of these explosives.

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### 1. Introduction

In the past decade, terahertz (THz) spectroscopy has been employed to investigate a variety of materials from solids to gases. The use of this technology as a tool to study materials has been aided by the improvements in THz emitters and sensors [1–11]. With the improvements in organic nonlinear optical polymers made in the last five years, we now have the ability to routinely produce wide-bandwidth gap-free spectra from 0.5 to 10 THz [11].

To date, a host of materials have been studied for their properties in the far-IR using time-domain THz spectroscopy (TDTS) methods, including gases such as ammonia [12] and methyl chloride [13] vapors and solid explosives such as DNT [14] and RDX [15,16]. The use of TDTS can also be applied to imaging and has been used to investigate component analysis of chemical mixtures [17], component spatial pattern analysis of chemicals [18], and

non-destructive imaging of illicit drugs using spectral fingerprints [19].

The THz region of the spectrum is of particular interest to detect and identify [20] explosives because the molecular infrared absorptions in this region can be used to characterize the individual molecules. These ‘skeletal’ motions in the THz region typically involve *every* atom in the molecule, not just the atoms of one functional group, e.g., a C–H stretch. Consequently, these spectra provide a unique signature by which the molecule can be identified.

The explosives we investigated are RDX, HMX, TNT, and PETN. These four explosives were examined through THz spectroscopy by both Fitch and co-workers [21–24] and Tribe and co-workers [16,25]. RDX was studied by Huang, et al. [15], both experimentally (TDTS and FTIR) and theoretically using density functional theory. A recent numerical study of solid-phase HMX by Allis and co-workers [26] using density functional theory has found reasonable agreement between the experimental THz spectra and calculated spectra using periodic boundary conditions with the crystal unit cell assembled from the molecular configuration as resolved by X-ray experiments. Although multiple groups have investigated these chemicals, experimental data for TDTS at frequencies greater than 3 THz have not been reported. We have employed the strength

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of our wide-bandwidth THz system and have obtained the THz spectra of these materials to 6 THz.

## 2. Methods

The experimental apparatus for time-domain THz spectroscopy has been described previously [27], with four off-axis parabolic mirrors forming an intermediate focus of the THz beam where the sample is placed. We use two stacked 75  $\mu\text{m}$  LAPC polymer film emitters and a 75  $\mu\text{m}$  LAPC polymer film sensor [8,9,11]. The explosive chemicals were purchased in solution (Accustandard), and were of the highest purity available. After crystallization by solvent evaporation, the crystals were dried, weighed, ground, and pressed into pellets with a polyethylene (PE) binder (Micro Powders, Inc., 3.5–4.5  $\mu\text{m}$  mean particle size). The reference is a blank pellet of pure PE. The material absorption,  $\alpha$ , can be calculated by comparing the signal and reference frequency-domain waveforms,

$$\alpha = -\frac{2}{d} \ln \left[ \frac{E_{\text{signal}}(\nu)}{E_{\text{reference}}(\nu)} \right],$$

with  $d$  the thickness of the pellet.

The TDTS apparatus is enclosed in a chamber that is purged by dry air. With no sample, the useful experimental bandwidth is from 0.5 THz to near 7 THz. The blank PE pellets show a slight loss of bandwidth, to  $\sim 6$  THz. Fig. 1 shows the system performance with the PE pellet blank inserted at the focus of the THz beam in comparison to the empty spectrometer (without a sample present in the THz beam).

## 3. Results and discussion

The measured THz spectra of the four explosives, RDX, HMX, PETN, and TNT are shown in Fig. 2. The spectrum of RDX below 3 THz agrees with previously published work [15,16,28], as do the spectra of HMX, PETN, and

TNT [16]. The 0.8 THz band in RDX is prominent, and is particularly useful for identification as this band is present in RDX but not in the other explosives. The locations of the spectral features in the THz spectra have been identified using Lorentzian peak fitting algorithms.

In addition to the previously identified spectral features below 3 THz, the RDX spectra show multiple features between 3.5 and 6 THz which have not been previously reported. New features are also reported in the spectra of HMX, PETN, and TNT spectra. In RDX, the strength of the feature nearest to 6 THz is subject to discussion due to the limited dynamic range at high frequencies of the TDTS experiment. The dynamic range of the frequency spectrum is limited by the location of the noise floor for each of our samples. In the case of RDX, the feature near 6 THz exhibits an absorption in which the strength of the frequency-dependent signal falls near the upper limit of the noise floor. Therefore, the location (in frequency) of the absorption feature can be determined while the strength of the feature remains undetermined from the data. Increasing the signal-to-noise ratio will enable more accurate determination of the strength of this absorption feature.

The HMX spectrum exhibits spectral features below 3 THz which concur with previously published work [16] and additionally shows six features between 3 and 5 THz, which have not been reported to date. The features between 3 and 5 THz are distinctly different from those present in RDX, allowing improved spectral identification. The data for our HMX samples in the 5–6 THz range show several spectral features, however their proximity to the noise floor of the frequency data do not allow us to reliably predict their strengths. We have verified the presence of spectral features in the 5–6 THz region using FTIR spectroscopy.

The PETN spectrum exhibits two broad bands between 1.5 and 2.5 THz and between 2.5 and 3.5 THz. These two bands replicate that previously reported [16] by Tribe and co-workers. An additional eight features have been identified between 3 and 6 THz.

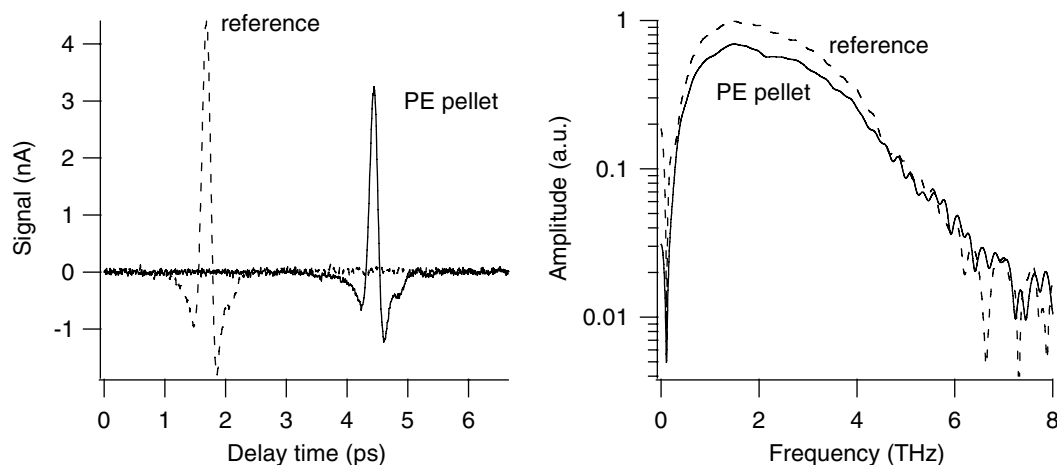


Fig. 1. Time-domain (left) and frequency-domain (right) waveforms for our system without any material present in the path of the THz beam (dotted line) and for a blank PE pellet (solid line) used as the reference sample. Two 75  $\mu\text{m}$  electro-optic polymer films were used as an emitter and one 75  $\mu\text{m}$  electro-optic polymer sensor were used. With the signal-to-noise ratio shown here, the bandwidth of the system is limited to near 6 THz.

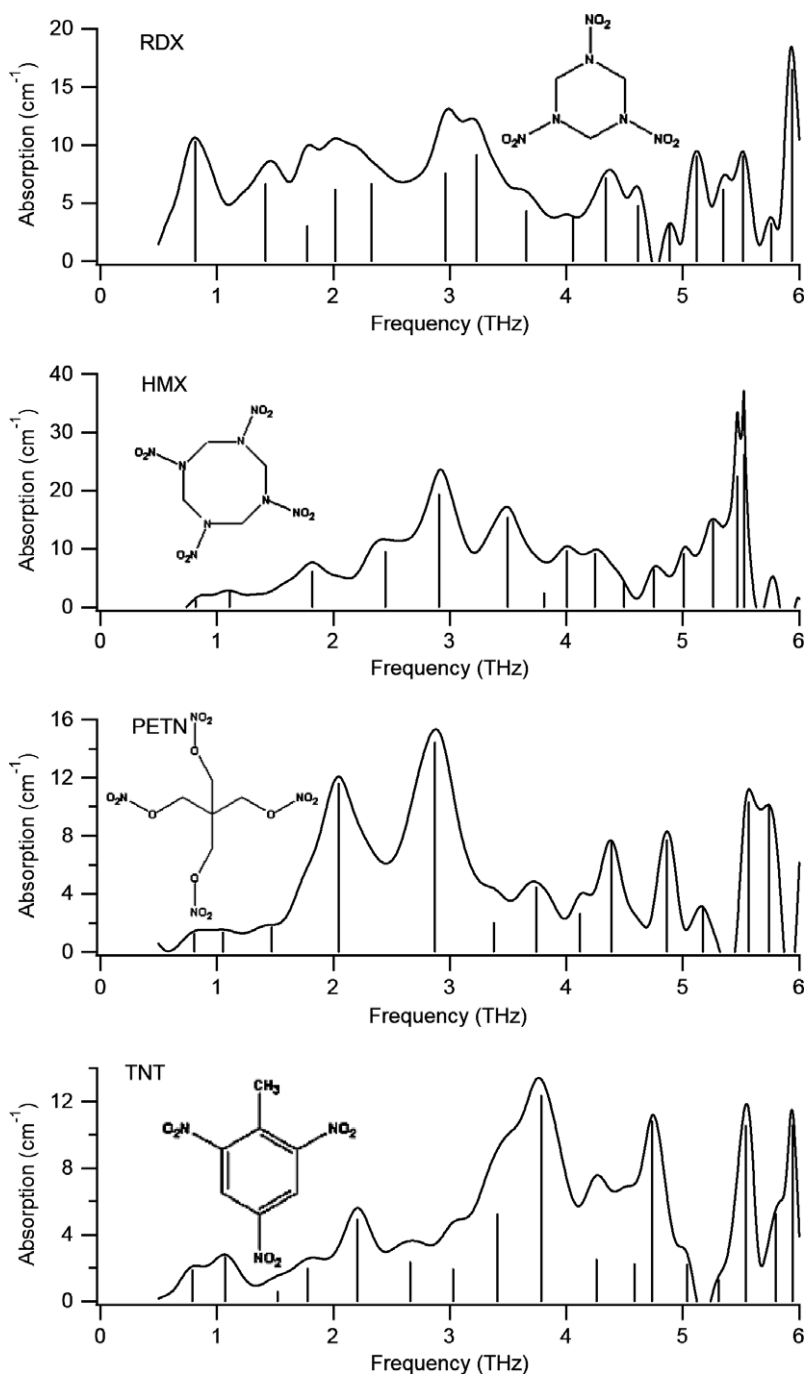


Fig. 2. THz absorption spectra of the explosives RDX, HMX, PETN, and TNT. The chemical structures of the explosives are also shown. Lorentzian line shapes were fitted to the spectra and indicated by lines at the center frequency.

Similarly, the TNT spectrum follows the trend shown by Tribe and his co-workers [16] below 3 THz. Both our spectra and that of Tribe show a feature near 2 THz as well as an increase in absorption with increasing frequency in the 0.5–3 THz range. Above 3 THz, there are several significant features present as well as some additional minor features which have not been previously reported.

Recent work by Allis and co-workers [29–31] has shown the agreement between solid-state modeling spectra of both HMX and PETN and the THz time-domain spectra in the region below 3 THz. In their work with HMX [29], the

authors identify several of the lowest-energy modes of motion in the system. In the region between 1 and 3 THz, there are three optical translations, along the three crystal planes. In addition, there are two ring twisting motions, one which also includes N–NO<sub>2</sub> pendulum motions. Comprehensive numerical studies of the solid-state spectra of a range of explosives in the terahertz region between 0.5 and 6 THz, including those studied in this letter, have yet to be published.

Gas-phase calculated spectra of many organic molecules including the explosive TNT [22] and one of its degradation

byproducts, 2,4-dinitrotoluene [14] have been calculated; however, single-molecule gas-phase calculations routinely fail to predict the solid-phase spectra of these and many other compounds in the terahertz region. The recent work by Allis and his co-workers [29–31] asserts that the level of theory needed to accurately reproduce the terahertz spectra of most compounds is solid-state density functional theory. These calculations are intensive in computer time because the modes of oscillation must be solved accurately for a unit cell containing many molecules and hundreds of atoms. There is a clear need for an efficient, accurate numerical tool to predict the solid-phase THz spectra of organic compounds, especially for THz sensing of explosives, chemical warfare agents, and toxic industrial chemicals. Large-scale brute-force modeling using density functional theory is at present the best available tool.

#### 4. Conclusions

We report the THz absorption spectra of four explosives between 0.5 and 6 THz. Previously, THz absorption data for these explosives has been reported only to 3 THz. We identify additional unique spectral features in several of the explosives which may aid in their spectral identification. Continued improvement of the signal-to-noise ratio as well as improved sample preparation will allow us to continue to investigate the THz absorption spectra of explosives for more detailed spectral identification capabilities. In addition, the use of amorphous polymers as both emitters and sensors of THz radiation allows wideband gap-free spectra to be obtained.

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#### References

- [1] M. Rochat et al., *Appl. Phys. Lett.* 81 (2002) 1381.
- [2] K.A. McIntosh et al., *Appl. Phys. Lett.* 67 (1995) 3844.
- [3] G.L. Carr et al., *Phys. Med. Biol.* 47 (2002) 3761.
- [4] R. Huber et al., *Appl. Phys. Lett.* 76 (2000) 3191.
- [5] Q. Wu, X.-C. Zhang, *Appl. Phys. Lett.* 70 (1997) 1784.
- [6] K. Liu et al., *Appl. Phys. Lett.* 85 (2004) 863.
- [7] A.M. Sinyukov, L.M. Hayden, *Opt. Lett.* 27 (2002) 55.
- [8] L.M. Hayden et al., *J. Polym. Sci.: Part B: Polym. Phys.* 41 (2003) 2492.
- [9] A.M. Sinyukov, L.M. Hayden, *J. Phys. Chem. B* 108 (2004) 8515.
- [10] A.M. Sinyukov et al., *Appl. Phys. Lett.* 85 (2004) 5827.
- [11] X. Zheng et al., *Appl. Phys. Lett.* 87 (2005) 081115.
- [12] H. Liu et al., *Proc. SPIE* 5268 (2004) 43.
- [13] S.A. Harmon, R.A. Cheville, *Appl. Phys. Lett.* 85 (2004) 2128.
- [14] Y. Chen et al., *Chem. Phys. Lett.* 400 (2004) 357.
- [15] F. Huang et al., *Appl. Phys. Lett.* 85 (2004) 5535.
- [16] W.R. Tribe et al., *Proc. SPIE* 5354 (2004) 168.
- [17] Y. Watanabe et al., *Opt. Commun.* 234 (2004) 125.
- [18] Y. Watanabe et al., *Appl. Phys. Lett.* 83 (2003) 800.
- [19] K. Kawase et al., *Opt. Express* 11 (2003) 2549.
- [20] X.-C. Zhang, *Phys. Med. Biol.* 47 (2002) 3667.
- [21] M.J. Fitch et al., *Proc. SPIE* 5411 (2004) 84.
- [22] M.J. Fitch et al., *Proc. SPIE* 5354 (2004) 45.
- [23] Y. Chen et al., *Proc. SPIE* 5411 (2004) 1.
- [24] Y. Chen et al., *Proc. SPIE* 5790 (2005) 19.
- [25] Y.C. Shen et al., *Appl. Phys. Lett.* 86 (2005) 241116-1.
- [26] D.G. Allis et al., *J. Phys. Chem.* 110 (2006) 1951.
- [27] T.R. Tsai et al., *Appl. Optics* 42 (2003) 2372.
- [28] Y.C. Shen et al., *Appl. Phys. Lett.* 86 (2005) 241116.
- [29] D.G. Allis et al., *J. Phys. Chem. A* 110 (2006) 1951.
- [30] D.G. Allis et al., *Proc. SPIE* 6212 (2006) 62120F-1.
- [31] D.G. Allis, T.M. Korter, *Int. J. High Speed Electron. Syst.* in press.