Quantitative THz Spectroscopy of Explosive Materials

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Abstract: Quantitative terahertz absorption spectra of the commonly encountered high explosives pentaerythritoltetranitrate and cyclotrimethylenetrinitramine are presented. Different matrix materials were investigated and data analysis methods for extraction of the complex index of refraction are discussed.
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1. Introduction and significance

Through-container explosive sensing represents a promising application of THz technology. Because of the relative safety of low-power THz radiation when compared to other methods such as X-Ray imaging and neutron scattering, THz radiation is of particular interest for the task of screening explosives concealed on personnel. The first step for the development of a THz explosives sensor is the identification of features in the THz spectra of the targeted explosives.

   Explosives are typically deployed in a powdered polycrystalline form and dispersed in a binder material. The basis for the THz spectral signatures of the explosives is associated with phonon bands that are a product of their crystalline nature. Initial measurements of high explosive compounds identifying the presence of spectral signatures have been previously presented by us and others [1-3]. However, further work was necessary to generate more quantitative data. Here we present quantitative spectra of several high explosive compounds and describe in detail the methods used to acquire these spectra.

   In our earlier report [1], we presented spectra of explosives pressed into polyethylene (PE) pellets. However, these data were influenced by scattering losses in the pellets, which partially obscured the resonances and complicated quantitative analysis of the absorption spectra of the explosives. Quantitative analysis of these data were further complicated by difficulties in the mixing process associated with electrostatic interactions of the PE powder and the explosive compounds leading to inexact mixing. Therefore, alternative sampling methods for the powdered explosives samples were desired. To this end, we reported the spectra of several candidate matrix materials [1]. The goal of this previous investigation was to find a viscous substance that does not appreciably flow at room temperature and which does not dissolve the explosive compounds. Because the spectral signatures are thought to be associated with phonon bands, the lack of solubility in the matrix material is necessary if meaningful spectra are to be acquired. We identified Type M Apiezon hydrocarbon vacuum grease as an excellent candidate matrix material for the spectroscopy of the high explosives based on the transparency of the material at THz frequencies and the chemical similarity to the waxy materials often used as binders for high explosive formulations.

2. Experimental methods

Samples of high explosives and commonly employed oxidizing agents such as ammonium nitrate were obtained from ATK Thiokol. Measured quantities of these samples were thoroughly mixed with Type M Apiezon vacuum grease at room temperature and the mass of the mixture was then recorded. Sample holders were fabricated from a 4 mm thick block of Teflon with a shallow hole, 15 mm diameter and 2 mm deep bored into the face of the block. This hole is then filled with the pre-mixed sample; care is taken to avoid air inclusions as the sample holder is filled. Once the sample holder is filled, the front surface is made flat by scraping excess mixture away with a straight edge. The quantity of explosive in the sample holder is then determined from the known mixing ratio of vacuum grease to explosive and the measured mass of the sample in the sample holder.

   The polyethylene pellet samples were purchased from an explosives vendor (Accurate Energetics) where they were prepared in the following manner: A known mass of explosive sample is mixed with a known mass of

powdered polyethylene that will be used for the pellet formation. The mixture is placed in a die and pressed between two pistons with a hydraulic press. The mass, thickness, and diameter of the resulting pellet are then recorded.

The THz spectra of the samples are acquired using PSI's time domain THz spectrometer, which has been described elsewhere [4]. However, further improvements have been made for the data reported here. A rapid sample switcher has been employed that allows the rapid acquisition of time domain THz scans in the presence and absence of the sample. Typically, 100 sample/reference pairs of data sets are acquired. THz spectra are then calculated for each data pair and the average spectrum is determined. Acquisition of data in this manner helps reduce $1/f$ noise in the system, and therefore permits better cancellation of etalons not associated with the sample itself.

3. Data analysis

Truncation of the time domain data before the appearance of the first reflected etalon pulse can eliminate the sample induced etalons from the measured spectra. However, the sample must be sufficiently thick so as to generate a round trip optical delay that leads to acceptable resolution when the data are truncated. The pellets used to generate the data reported here were approximately 9 mm thick. The data were truncated at least 25 ps after the primary THz pulse, leading to a Fourier transform limited resolution of 40 GHz. Although truncation was also used to remove etalons from the previously reported absorbance data [3], we have developed a straightforward method for extraction of index of refraction data when etalon truncation is appropriate. Previous efforts at extraction of both the real index and absorption spectra from time domain THz data have focused on numerically finding the roots of Eq. 1, which describes the transmission through a slab of material of thickness, z [5,6].

$$\tilde{E}(\omega,z) = \tilde{T}_{12}(\omega) e^{-i\frac{\omega}{c}\tilde{n}(\omega)z} \tilde{T}_{23}(\omega) \left\{ \sum_{j=0}^{k} \left[\tilde{R}_{23}(\omega) e^{-i\frac{\omega}{c}\tilde{n}(\omega)z} \tilde{R}_{21}(\omega) \right] \right\} \tilde{E}(\omega,0). \tag{1}$$

If the sample is a transparent dielectric, the Fresnel transmission coefficients are real and there is no change in phase associated with transmission through the air/sample interfaces. In practice, the imaginary components of the Fresnel transmission coefficients are only relevant in strongly absorbing media. The phase shift associated with transmission through a simple air-material interface is often negligible in dielectric media suitable for transmission measurements. Therefore, if the etalons are truncated, the summation in Eq. (1) is no longer relevant and the real index can be obtained from solving Eq. (2) for $\mathrm{Re}(\tilde{n})$.

$$\frac{-\tilde{E}(\omega,z)}{\tilde{E}(\omega,0)} \approx i\frac{\omega}{c}\tilde{n}(\omega)z - \ln\left[T_{12}(\omega)\, T_{23}(\omega)\right]. \tag{2}$$

This approach leads to an analytical solution for n, which can be then used to extract the internal absorbance. Once the real index is determined, the internal transmittance can be determined through calculation of the interface losses from the Fresnel transmission coefficients. Using this strategy, a robust analytical inversion of the data is possible and numerical root finding methods are not necessary.

This approach was successfully used for analysis of the PE pellet data. However, the situation with the samples in the Apiezon matrix is complicated by the geometry of the Teflon sample holder. Eq. (1) must be modified to take into account the additional etalons generated by the presence of the back window and numerical root finding methods must be used if the complex index of refraction is to be extracted. This work is ongoing. In the absence of the etalon free data extraction methods, the absorbance spectrum can nonetheless be extracted without explicit consideration of the surface reflections. However the absorption spectrum is contaminated with the etalon signals from the sample and window.

Because of the difficulties encountered in quantitative spectroscopy using the PE pellet method, the data from the PE pellets are presented as base e extinction coefficients, i.e., $(-1/l)\ln(I/I_0)$, where l is the thickness of the pellet. On the other hand, the quantitative mixing of explosives with the Apiezon and the relatively low scattering losses, permit quantitative spectroscopy. Therefore, these data are presented as mass-weighted cross sections where the measured extinction, $-\ln(I/I_0)$, is divided by the column density in g/cm^2.

4. Results

The polyethylene pellet data for pentaerythritoltetranitrate (PETN) and cyclotrimethylenetrinitramine (RDX) is presented in Figures 1 and 2 respectively. Note that the absorption signatures are clearly accompanied with changes in the measured index of refraction as is expected by the Kramer's-Kronig relationships. However, the quantitative value of the measured indices of refraction is representative of the mixture composing the pellet, and not the intrinsic index of the pure explosive compound. Furthermore, the measured indices of refraction are lower than one

would expect for a PE matrix. The measured density of a pure PE pellet made under similar conditions was 0.7955 g/cm^3, which is 84% of the maximum density We postulate that microscopic voids in the pellets associated with this lack of density are the cause of the observed scattering losses, and also the reduced indices of refraction. Since the pellets are not approaching their theoretical density, we can anticipate pellet to pellet discrepancies in index and scattering losses. This makes it difficult to precisely separate the matrix effects, which vary from pellet to pellet, from the intrinsic spectra of the high explosives.
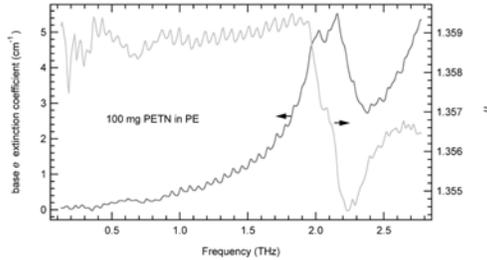

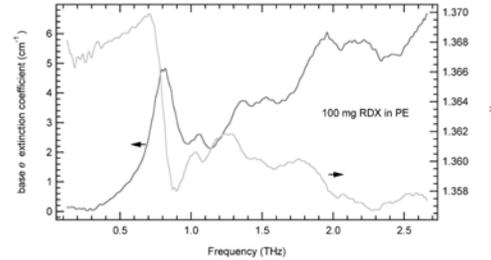Fig. 1. The spectral extinction coefficient (base *e*) and refractive index of PETN (100 mg in polyethylene).

Fig. 2. The spectral extinction coefficient (base *e*) and refractive index of RDX (100 mg in polyethylene).

The Apiezon matrix spectra of PETN and RDX are presented in Figures 3 and 4 respectively. For each compound, multiple dilutions were measured. When the data are plotted as an absorption cross section, the overlapping results from the multiple dilutions provide confidence that the intrinsic absorption of the explosives is indeed being measured.
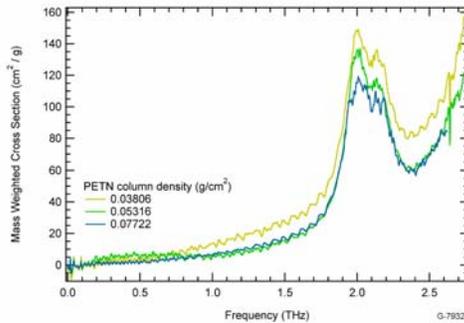

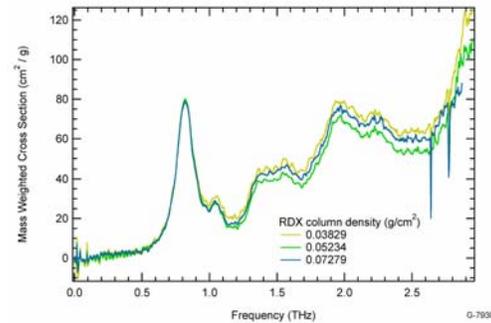Fig. 3. THz spectra of PETN in Apiezon vacuum grease.

Fig. 4. THz spectra of RDX in Apiezon vacuum grease.

5. Conclusions

Methods for acquiring quantitative THz absorption spectra of polycrystalline materials insoluble in a hydrocarbon vacuum grease have been presented. Furthermore, quantitative spectra of PETN and TNT have been presented and the previously reported resonances in these high explosives have been reproduced.

6. References

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