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Temperature dependent terahertz properties of energetic materials

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ABSTRACT

Reliable detection of energetic materials is still a formidable challenge which requires further investigation. The remote standoff detection of explosives using molecular fingerprints in the terahertz spectral range has been an evolving research area for the past two decades. Despite many efforts, identification of a particular explosive remains difficult as the spectral fingerprints often shift due to the working conditions of the sample such as temperature, crystal orientation, presence of binders, etc. In this work, we investigate the vibrational spectrum of energetic materials including RDX, PETN, AN, and 1,3-DNB diluted in a low loss PTFE host medium using terahertz time domain spectroscopy (THz-TDS) at cryogenic temperatures. The measured absorptions of these materials show spectral shifts of their characteristic peaks while changing their operating temperature from 300 to 7.5 K. We have developed a theoretical model based on first-principles methods, which is able to predict most of the measured modes in 1, 3-DNB between 0.3 to 2.50 THz. These findings may further improve the security screening of explosives.

Keywords: Terahertz spectroscopy, Explosives, Energetic materials

1. INTRODUCTION

Terahertz represents a special band of the electromagnetic spectrum between microwave and visible wavelengths, covering a spectral range from 0.3 THz to 10 THz (10 cm^{-1} – 330 cm^{-1}). Owing to low photon energy and transparent to many common optically opaque materials, THz has been employed as a spectroscopic tool to reveal fundamental physical mechanisms in condensed matters, non-destructive evaluation of optically opaque materials, and security and sensing applications. Many energetic materials such as RDX, HMX, PETN, and TNT have unique spectral signatures in the $<100\text{ cm}^{-1}$ range [1-10]. At visible wavelengths, many of these explosives look remarkably similar to common baking ingredients such as sugar or salt but have unique spectral signatures in the THz range. X-rays does not offer enough contrasts for the imaging of explosives either. The THz spectral signatures in these explosives are arisen from the intramolecular and intermolecular vibrational modes or phonon modes. Being transparent to many optically opaque packing materials such as clothing, paper, and plastics, terahertz has the ability to identify unknown substances inside the packages without opening these — a trait highly useful for security applications [11-13]. The coherent terahertz time domain spectroscopy (THz-TDS) can measure both transmission amplitude and the phase simultaneously, therefore, can measure complex dielectric constants without Kramers-Kronig analysis [14]. These dielectric properties may be used for positive identification of energetic materials during imaging and standoff detection.

In this paper, we discuss terahertz spectral signatures of a few common energetic materials and mock materials that have resemblance with explosives. We measure refractive indices and absorptions as a function of crystal orientations and temperatures for the single crystal explosives. The measured absorptions of RDX-crystals are highly dependent on the orientation of the THz polarization with respect to their crystallographic axes. In contrast, the absorptions and refractive

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indices of PETN single crystal are almost independent of the crystallographic orientations. We measured the absorption and the refractive index of dinitro-benzene (DNB) and ammonium nitrate (AN) powdered samples. The DNB sample reveals characteristic absorption peaks within our measured spectral window and these absorption peaks exhibit blue-shifting while the sample temperature is reduced from 295 K to 7.5 K. The AN sample shows very different absorption spectra at 295 K and 7.5 K, indicating a temperature induced phase transition.

2. SINGLE CRYSTAL RDX

In this section, we discuss our findings on terahertz spectroscopic measurements of single crystal RDX. The spectrum of RDX below 100 cm^{-1} ($< 3.0\text{ THz}$) was not well understood before [15-17]. Measurements on powdered RDX give an absorption spectrum that is averaged over many randomly oriented crystals, and often the manufacturing process adds additional effects on the convoluted spectrum as well. Absorption spectra measured on RDX from different manufacturers show significant variations [18, 19]. Assignment of absorptions to the vibrational modes of the crystal structure is difficult when using powders because the high density of absorptions make distinguishing each individual peak difficult and each absorption cannot be assigned to a given crystal orientation.

Developing models that can correctly characterize the complex absorption patterns of RDX in the $<100\text{ cm}^{-1}$ region is critically important. This phonon-rich region of the spectrum contains information relevant to the validation of equation of state parameters used to model the detonation process. Accurate modeling would help clarify the role these phonon modes play in shock-initiation of explosives. It has been postulated that energy is funneled from the shock into individual molecules through multiphonon up-pumping via delocalized low-frequency ($<6\text{ THz}$) phonons [20-23], but little experimental data on these phonon modes exist.

To identify the vibrational modes of RDX, single crystals of α -RDX have been studied via THz-TDS. For this measurement we select three orthogonal crystallographic orientations (100), (010), and (001). The samples were mounted on a sample holder with a hole at the center for performing transmission measurements. The azimuthal rotation stage allowed rotation of the sample with respect to the incident terahertz polarization. Transmitted terahertz pulses were recorded at room temperature and at 20 K. Time dependent terahertz pulses were then converted to complex frequency spectra to obtain frequency dependent optical properties. The results of this study enabled new terahertz absorption features that were not observed previously from powders or formulations.

Five different RDX samples were used for these measurements including two (100)-oriented samples, two (010)-oriented samples, and one (001)-oriented sample. The samples were cut from large single crystals, nominally 5 cm on a side. UK-manufactured RDX was dried, purified by Soxhlet extraction in acetone and recrystallized in acetone prior to use [18]. The crystals were grown by slow evaporation of acetone at $32\text{ }^{\circ}\text{C}$, in a 1000 mL, spoutless beaker covered by a Parafilm-coated watch glass. The bottom third of the beaker was immersed in a heating bath and the top was open to air at room temperature. This method allowed for convective mixing and the reflux continuously washed the beaker sides preventing parasitic growth. Seeds were grown from acetone by a similar procedure. The samples were cut using a low-speed diamond impregnated wire saw using a solution of Alconox in deionized water as a lubricant. Samples were measured in an as-cut configuration without further polishing. RDX crystals are extremely fragile, limiting the minimum sample thickness that can be cut without fracture to approximately 1 mm. The (001) and (010) oriented samples were nominally 1 mm thick, the (100) sample was 1.5 mm thick. All samples were approximately $1\text{ cm}\times 1\text{ cm}$ wide.

The samples were measured using photoconductive antenna based terahertz system integrated with a cryostat to control the temperature of the samples [24]. The cryostat and sample mounting structures were specially made to allow sample rotation and cooling under vacuum. Samples were mounted on the front end of the rotating sample holder with a hole at the center, having a diameter larger than the THz beam, through which the focused THz beam propagated. A ring gear was attached to the back of the sample holder and engaged to a pinion gear that was magnetically coupled through the vacuum chamber to a computer-controlled stepper motor. This allowed accurate rotational stepping of the sample orientation under vacuum. The sample holder was thermally connected to the main cryostat cold finger by a flexible copper band. The thermal link was sufficient to reduce the sample temperature to 18 K without interfering with sample rotation. Sample temperatures were monitored by a silicon sensor attached adjacent to the sample. Samples were cooled in a helium cryostat at 0.025 K/s to avoid cracking.

The time dependent terahertz pulses transmitting through the samples were measured for each sample orientation over a 180° rotation around the primary crystallographic axis using angle increments of 9° at 22 K and 22.5° at 295 K. For each data set we recorded a reference terahertz pulse transmitting through the free-space. The ratio of the Fourier-transformed THz-TDS sample data to a reference data set yielded the complex transmission function. Figure 1 shows the results of a typical terahertz reference spectra compared with the transmission spectrum through RDX (010) with the polarization oriented along the c-axis and the noise level.

Figure 1. Electric field amplitude of the THz spectral emission with no sample (black), through (010) RDX with the polarization oriented along the c-axis (red), and the noise level of the detector/lock-in amplifier (green)

Since the samples are homogenous single-crystal specimen with planar faces and known thicknesses, the refractive indices and the absorptions can be extracted using a Beer's law analysis for each orientation without correcting for Fresnel's reflections.

Figure 2. Comparison of the absorption index κ of RDX(100), RDX (010), and RDX(001) in Figs (a), (c), and (e), respectively, over the 7–100 cm^{-1} range at $T=20$ K. Comparison of the index of refraction n of RDX(100), RDX (010), and RDX(001) in Figs (b), (d), and (f), respectively. The dashed circles correspond to 20 cm^{-1} wavenumber intervals. Crystallographic axes are shown as the labeled solid lines

Figure 2 show the angular dependence of absorption index κ - and index of refraction n for samples of RDX (100), (010), and (001) taken at 20 K. The data are presented as radial contour plots with the THz absorption spectrum extending radially outward from the center to a maximum of 100 cm^{-1} . Dashed circles indicate 20 cm^{-1} increments. The values of κ - and n - are plotted as a function of rotation about the sample. RDX has C_2 symmetry so data from 0–180° should be identical to 180–360°. All three orientations of RDX in Fig. 2 show a complex, feature-rich absorption structure. Significant absorption features extend from as low as 12 cm^{-1} to 100 cm^{-1} . Below $\sim 80 \text{ cm}^{-1}$, RDX has a number of rotationally dependent absorptions strongly correlated to its crystallographic orientation with respect to the THz polarization and above $\sim 80 \text{ cm}^{-1}$ absorptions are generally rotationally invariant.

Broad absorption features below 80 cm^{-1} are found along the primary crystallographic axes. The b-axis has a broad absorption from 27–42 cm^{-1} in (001)-oriented RDX and from 48–60 cm^{-1} in (100)-oriented RDX. The a-axis has a broad absorption from 55 cm^{-1} to 59 cm^{-1} seen in both the RDX (010) and RDX (001) orientations. The c-axis has a broad absorption from 25 – 40 cm^{-1} in the (100) orientation, although there is no corresponding c-axis absorption in the (010)-oriented material. In addition, there are two broad low-frequency absorptions located at 45° between in-plane axes. RDX (100) shows an absorption at 18 cm^{-1} located between the b- and c- axes, and RDX (001) shows an absorption at 12 cm^{-1} located between the a- and b-axes. Narrow, rotationally invariant absorptions with 1 cm^{-1} FWHM are found at 40 cm^{-1} in RDX (100), 55 cm^{-1} in RDX (010), and at 25 cm^{-1} in RDX (001). Narrow, orientation-dependent absorptions associated with the c-axis are seen in the (100) and (010) orientations at 27 cm^{-1} . Other narrow absorptions are roughly located equally between the primary in-plane axes at 24 cm^{-1} , 48 cm^{-1} , 67 cm^{-1} in RDX (001) and 40 cm^{-1} and 45 cm^{-1} in RDX (010).

The index of refraction of RDX varies between 1.6 and 3 over the frequency range of 7–100 cm^{-1} . Our measurements also show the birefringing nature of RDX in the terahertz regime which agrees with the birefringent nature of this material shown in optical wavelength. Symmetry points in the angular variation of the index of refraction correspond identically with the primary in-plane axes.

An averaged absorption spectrum of all the angular contributions can be compared to powder spectra if we assume that the powder spectrum is composed of an equally weighted contribution from all possible crystal orientations.

To generate the equivalent of a powder absorption coefficient, we first calculate the average measured light intensity as a function of the various angles measured from all three crystal orientations:

$$\left\langle \frac{I}{I_0} \right\rangle = \frac{\sum_{\theta}^N \text{Exp}(-\alpha_{\theta} t)}{N} \quad (1)$$

where α_{θ} is the absorption coefficient from a given angular contribution, t is the thickness of the sample, N is the number of angular contributions measured, and absorption $\alpha = 4\pi\kappa/\lambda$. Once we have the average measured light intensity from an equal distribution of angles, then we can calculate an average absorption coefficient by solving Beer's law, as,

$$\langle \alpha \rangle = -\ln \left[\left\langle \frac{I}{I_0} \right\rangle \right] / t \quad (2)$$

Figure 3 shows the average absorption calculated from a single crystal RDX by considering that all the contribution from every crystal orientation are identical. Strong absorptions are found at 27, 40, 51–53, 75, 83, and 96 cm^{-1} . Allis et al.[25] and Burnett et al. [26] measured the spectrum of powdered RDX at 5 K. There are similarities between our calculated powdered spectrum and the measured spectrum; however, they are not identical. Perhaps the measured powder spectrum is not a true representation of all crystal orientation. Crystal morphology may cause the crystals to pack along given orientations.

Figure 3. Average spectrum of single crystal RDX at 20 K composed of an equally weighted average of all the angular contributions.

3. SINGLE CRYSTAL PETN

PETN is generally found as a white powdery substance similar in color and texture to sugar or table salt. However, sugar and PETN have different and unique absorption signatures in the 7-100 cm^{-1} region of the electromagnetic spectrum. Powder measurements of PETN below 100 cm^{-1} show two broad distinct peaks at 67 and 96 cm^{-1} [7, 17, 27, 28]. The lower frequency peak often shows a shoulder at 72 cm^{-1} . Raman experiments on PETN powder [29] and molecular dynamics calculations [30-32] suggest a number of additional absorptions should exist in the 30-100 cm^{-1} region. To get a clear understanding of orientation dependence of the THz absorption in PETN, here we present the terahertz absorption measurements of single crystal PETN oriented along the [001], $\langle 10(a/c)^2 \rangle$, and $\langle 110 \rangle$ crystallographic directions.

The PETN samples were prepared with parallel faces normal to the [001], $\langle 10(a/c)^2 \rangle$, and $\langle 110 \rangle$. The samples were cut from large single crystals, nominally 4-6 cm on a side. PETN powder used for crystal growth was obtained from the Dupont, dissolved in ethyl acetate, filtered, recrystallized, and dried. The crystals were grown by controlled evaporation of saturated solutions of PETN dissolved in ethyl acetate. Contact goniometry was used to locate planes in PETN by redundant reference to crystal facets. The samples were cut using a low-speed diamond impregnated wire saw using a solution of Alconox in deionized water as a lubricant. Terahertz spectra were measured in the as-cut crystal without further polishing. The final dimension of the samples were approximately 1 cm $\times$ 1 cm with thickness of 1 mm [33].

To measure the crystal orientation dependent terahertz absorptions, the sample was rotated about its normal, which was either the [001], $\langle 10(a/c)^2 \rangle$, and $\langle 110 \rangle$ crystallographic direction. The sample was rotated 9° after every time-domain spectrum at 20 K, and 22.5° at 300 K. To cool the samples to 20 K without cracking them, we used a cooling rate of 0.025 K/s.

Crystallographic orientation dependent absorption coefficients are shown in Figure 4. Again, the data are presented as radial contour plots with the THz frequency extending radially outward from the center to a maximum of 100 cm^{-1} . Dashed circles are at 20 cm^{-1} increments. The figure represents the measured absorption coefficients of PETN as the polarization is rotated a full 360° about a fixed crystallographic direction. Since PETN shows C_2 symmetry, the spectral changes with crystal rotation were only measured over 180°, and then reproduced over the 180-360° range to make the radial contour plots shown in Figure 4.

For all three orientations of PETN crystals, our measurements exhibit two very strong and broad absorption peaks, one centered around 72 cm^{-1} , and the other peak centered at frequency higher than 90 cm^{-1} . Both of these absorptions were strong enough to block the entire incident THz radiation, which saturated the measured absorption coefficients. For all three samples,

there were no significant dependencies of the absorption on the incident polarization angles. This is in distinct contrast to RDX, whose measured THz spectra were strongly dependent on the orientation of the crystal with respect to the polarization [18].

Figure 4. Absorption spectrum of (a) [001], (b) $\langle 10(a/c)^2 \rangle$, and (c) $\langle 110 \rangle$ oriented PETN at 20 K as a function incident polarization angle. The in-plane crystallographic axis is shown on the [001] oriented sample. Purple represents transparent regions, red represents strong absorption regions. The dotted circles move outward in 20 cm^{-1} increments to a maximum of 100 cm^{-1} .

Since there are little rotational dependencies to the measured THz spectrum of the three orientations of PETN, we average all spectra collected for one sample orientation to produce a representative spectrum for that orientation. Figure 5 shows a comparison of these averaged spectra for the three measured orientations of PETN taken at 20 K. All three orientations exhibit a similar spectrum with a few minor differences. All show the strong absorption at $\sim 72 \text{ cm}^{-1}$ and a shoulder at $\sim 75 \text{ cm}^{-1}$. The $\langle 110 \rangle$ orientation shows a shoulder on the low energy side at $\sim 65 \text{ cm}^{-1}$, suggesting multiple components to this absorption. The strong absorption at $\sim 90 \text{ cm}^{-1}$ is present in all three samples with both [010] and $\langle 110 \rangle$ orientations exhibiting a shoulder at $\sim 87 \text{ cm}^{-1}$. Weaker absorptions are found at 80 cm^{-1} in $\langle 10(a/c)^2 \rangle$ and $\langle 110 \rangle$ and 82 cm^{-1} in [001] and 83 cm^{-1} in $\langle 110 \rangle$. A few weak absorptions at 36 and 55 cm^{-1} are primarily associated with the [001] orientation.

Figure 5. Comparison of averaged absorptions of PETN for different orientation [001] (black), $\langle 10(a/c)^2 \rangle$ (red), and $\langle 110 \rangle$ (green) at 20 K

Figure 6 shows the comparison of absorption spectra of three different orientations measured at 20 and 300 K. Similar to the 20 K spectra, the 300 K spectra have no dependence on the in-plane crystallographic axes, so we only present the average spectral data here for the three measured crystal orientations. All three orientations show phenomenologically the same temperature dependence. As the sample is cooled, the peaks become narrower and shift to higher frequency, similar to the behavior reported by Barber et al. on single crystals⁸ and by Fan et al. on powders [7]. The weak absorptions between 80-83 cm^{-1} cannot be resolved at 300 K due to the temperature-dependent spectral shift and broadening of features. The weak absorptions at 36 and 55 cm^{-1} were not resolved at 300 K either. Otherwise, the 300 K spectrum is a good representation of the spectrum measured at 20 K.

Figure 6. Absorption spectrum of (a) [001], (b) $\langle 10(a/c)^2 \rangle$, and (c) $\langle 110 \rangle$ oriented PETN at 300 K (solid line) and 20 K (dotted line)

Finally, we present a comparison of our normalized single crystal spectra taken at 20 and 300 K with normalized powder data taken at 4 K in Figure 7. To produce this figure, we assume that the powder spectrum represents equal contributions from all possible crystal orientations. The averaged single-crystal spectrum presented in Figure 7 shows similarities with the powdered spectrum measured at 4 K by Fan et al [7]. Both show strong absorptions in the 65-75 cm^{-1} range and strong absorption at frequencies greater than 90 cm^{-1} .

Figure 7. Comparison of single crystal spectra at 20 K (solid) and 300 K (dotted) averaged over all orientations (solid) with the powder spectrum from Fan et al. taken at 4 K (dashed) [7].

4. THZ SIGNNATURES OF 1, 3 DNB: A FIRST PRINCIPLES

In this section, we present our experimental and theoretical studies of the spectroscopic signatures of 1,3-dinitrobenzene (1,3-DNB) at terahertz wavelengths. As mentioned earlier in this article that most of the explosives and energetic materials show spectral signatures due to their low frequency vibrational modes at terahertz frequencies. However, predicting and identifying the vibrational modes of energetic materials from the first principles density functional theory (DFT) calculation in the terahertz regime remains a daunting challenge [34]. Therefore, a success in overcoming this challenge will have huge technological implications. In particular, knowing the vibrational modes of a dielectric insulator will allow us to understand the origin of the electromagnetic signature of the molecular crystal for fingerprinting its response in the THz regime of these materials. In this work, we use DFT with periodic boundary conditions to optimize the structures and perform linear response calculations of the vibrational properties at zero phonon momentum in 1,3 DNB crystals. The theoretically predicted modes were compared with the measured spectra, showing qualitative agreements between theory and experiments.

The 1,3-DNB molecular crystal is an inert material, yet an ideal substitute for explosives due to its similarity in chemical composition, molecular structure, and physical and dielectric properties. It also shares many common structural properties with explosives such as a backbone benzene ring, NO₂ antenna groups, intermolecular hydrogen bonds, and planar packing.

The sample was prepared from commercially available 1,3-DNB powder and hand-pressed at 4000 psi using a 2-ton Carver press to 6 mm diameter by 1 mm thick pellets. A metallic sample holder containing two identical apertures of diameter 3.5 mm is used for sample measurements. During measurements, the sample is attached to one hole, while the other identical clear hole is used as the reference. We employed a ZnTe-based THz-TDS spectrometer for sample measurements [35]. A Titanium:Sapphire amplified pulsed laser system, operating at $\lambda=800$ nm with 50 fs laser pulses, is used for THz generation and detection via nonlinear electro-optic effect in ZnTe crystals. Generated THz pulses are collected, collimated through the sample, and finally detected on the THz detector by two pairs of parabolic mirrors. The THz beam centered through the sample holder's aperture has a frequency independent diameter of 3.5 mm. The sample holder is attached to a liquid helium cooled cryostat, allowing precise control of sample temperature. The time domain THz pulses then converted to the complex spectra through numerical FFT. The transmitted terahertz spectrum through the sample is compared to the reference spectrum to obtain frequency dependent refractive index and absorbance.

Figure 8. (a) Comparison of measured frequency dependent refractive index of 1, 3 DNB at 7.5 K (blue) and 295 K (red). (b) Comparison of measured frequency dependent absorbance at 7.5 K (blue) and 295 K (red).

Figure 8 (a) shows the measured refractive index of the 1,3 DNB sample at two different temperatures 295 K (red) and 7.5 K (blue), and corresponding absorptions are shown in Figure 8(b). Both refractive index and absorption reveal the presence of multiple phonon modes within our measured spectral windows. The values of refractive index and absorbance were found to decrease while the temperature of the sample was reduced to 7.5 K. In additionally, the linewidth of the phonon modes became sharper and moved to the higher frequency at 7.5 K compared to their values at

room temperature. With the extracted complex refractive index and absorption coefficient, one can calculate the complex dielectric constants using the following relations,

$$\varepsilon(\omega) = \varepsilon_r + i\varepsilon_i = (n + i\kappa)^2 = (n + i\alpha\lambda/4\pi)^2 \quad (3)$$

Which gives, $\varepsilon_r = n^2 - (\alpha\lambda/4\pi)^2$ and $\varepsilon_i = \alpha\lambda/2\pi$. Figure 9 shows the extracted real part (Fig. 9 a) and imaginary part (Fig. 9 b) of the dielectric constants at room temperature (red curve) and at 7.5 K (blue curve). Both real and imaginary parts of the dielectric constant show temperature dependence, and their values decrease at cryogenic temperature. The low frequency resonant features are clearly visible in the imaginary part of the dielectric constant.

Figure 9. (a) Comparison of measured frequency dependent real dielectric constant of 1, 3 DNB at 7.5 K (blue) and 295 K (red). (b) Comparison of measured frequency dependent imaginary dielectric constant at 7.5 K (blue) and 295 K (red).

In the absence of a contribution from conduction electrons, which is the case for the dielectric 1,3-DNB molecular solid, the total complex dielectric function can be described by the Lorentz model [36]

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_j \frac{f_j \omega_j^2}{\omega_j^2 - \omega^2 - i\Gamma_j \omega} \quad (4)$$

Where ε_∞ is the high-frequency dielectric constant, f_j is the dimensionless oscillator strength, ω_j is the j -th normal mode, and Γ_j is the damping constant. By fitting the measured $\varepsilon(\omega)$ at 7.5 K to the above equation, we identify the first five transverse optical (TO) phonons, including their oscillator strengths and damping constants, which are listed together with the different theoretical values of low-energy modes in Table 1.

To compare with our experimental measurements, we calculate the dielectric properties using first principle DFT calculations. All calculations were performed by using the plane-wave pseudo-potential method of DFT with periodic boundary conditions, as implemented in VASP [37] and Quantum Espresso (QE) [38] codes. The crystal structure of the 1,3-DNB solid is orthorhombic (space group Pna21 or #33) [39-41]. Each unit cell contains four 1,3-DNB molecules and at 130 K has the reported linear dimension of $a=14.040$ Å, $b=13.208$ Å, $c=3.6940$ Å [42]. We used the x-ray refined atomic structure provided in the Crystallography Open Database as the starting basis for our studies. We considered vibrational properties for both an isolated 1,3-DNB single molecule by introducing an enlarged periodic supercell of

dimension ($a \times b \times 4c$) and the molecular crystal study on electronic and vibrational lattice properties of structurally similar 1,3-dinitrobenzene (1,3-DNB) crystals through first-principles electronic structure calculations.

Table 1. Comparison of fitting parameters obtained from the measured dielectric constants and theoretical calculations.

Mode	$\omega_j/2\pi$ (THz) (Exp)	f_j (Exp)	$\Gamma/2\pi$ (THz) (Exp)	$\omega_j/2\pi$ (THz) (DFT sm)	f_j (DFT sm)	$\omega_j/2\pi$ (THz) (DFT x-tal)	$\omega_j/2\pi$ (THz) (Wójcik)
1	0.59	0.012	0.07	0.45	0.175		0.57
2	0.86	0.031	0.15			0.95	0.72, 0.84
3	1.03	0.026	0.11	1.00	0.044	0.97	0.93, 0.96
4	1.28	0.037	0.20	1.30	0.043	1.29	1.14
						1.35	1.20
						1.50	1.68
						1.59	
5	2.40	0.090	0.60	1.90	0.010	1.96	1.83
				2.14	0.003	2.06	2.34
						2.12	2.37
						2.16	
						2.20	
						2.29	
						2.54	

For the single-molecule case, the calculations were performed by using the QE 5.0.1 package with the provided ultra-soft PBE [43] pseudo-potentials [44]. The first Brillouin zone is sampled with $8 \times 8 \times 8$ k-points. The energy cutoffs of 40 and 160 Rydberg (Ry) were taken for wave function and charge density, respectively. With the fixed linear dimension of the supercell, the internal atomic structure was relaxed and optimized with the self-consistency resolution of 10^{-14} Ry for total energies and 0.4 mRy/Å for mean atomic forces per atom.

For the 1,3-DNB molecular crystal, we used the VASP-5.3.1 package to calculate the total energy as a function of volume and optimized the internal atomic positions at each volume. For all atoms, the ultra-soft [44, 45] PBE pseudo-potentials, provided by VASP, is used and the first Brillouin zone is sampled with a mesh of $6 \times 6 \times 6$ k-points. The energy and force convergence criteria are 10^{-6} eV and 10^{-4} eV/Å per atom, respectively. Various values of the energy cutoff parameter, 500 eV and 700 eV, were taken for the reliability of the optimized volume. For both single molecule and molecular crystal case, the density functional perturbation theory (DFPT) was used to obtain in linear response the vibrational dispersion at the center of the lattice Brillouin zone (phonon momentum $q = 0$). For the latter case we also used the Phonopy package [46] for crosschecking the results, and confirmed that the calculated mode frequencies obtained from both approaches agreed well with each other.

Figure 10. Comparison between experimental and theoretical THz absorbance spectra: measurements (solid black lines) were performed at 7.5 K. Calculations are shown for both single molecule (solid green), and crystalline solid (vertical blue)

By setting the damping coefficient to a constant for all modes (a reasonable physical value is 0.2 THz), we can calculate the dielectric function and in turn the absorption coefficient for the single molecule as shown in Fig. 10. The green curve is the calculated absorbance for single molecule and black curve is our measured data. The vertical blue lines show the frequency of various phonon modes obtained from our theoretical calculation of crystalline solid of 1, 3 DNB. We find that the calculated absorption qualitatively reproduces most of the phonon modes within our measured THz window.

In Fig. 11 we compare the calculated dielectric constants of our single-molecule calculations with the experimental results of pressed pellet sample. A Lorentzian fit of the dielectric constants was obtained from experimentally determined Lorentz parameters shown in the table 1. The magnitude of the distinct peak-like feature present in our calculation at 0.45 THz is stronger than the experimental peak intensity at 0.59 THz. This peak suppression may be due to the surrounding environment of intermolecular forces in the crystal, which constrains the motion of the NO₂ antenna group present in the individual molecules of the solid. Our measured peak at 0.86 THz was not captured in the DFT calculation of the single molecule, while it agrees with the lowest mode at 0.95 THz in the crystal. It is feasible that incorporation of van der Waals interactions lowers the symmetry of the crystal and generates additional low frequency modes missed currently.

Figure 11. (a) Comparison of real part of the dielectric constants obtained from the calculations (solid red), experiments (solid black), and Lorentz fit to experimental data (dashed blue). (b) Comparison of imaginary part of the dielectric constants obtained from the calculations (solid red), experiments (solid black), and Lorentz fit to experimental data (dashed blue).

5. PHASE TRANSITION OF AMMONIUM NITRATE (AN)

Finally, we present our terahertz spectroscopic measurements on ammonium nitrate (NH₄NO₃ or AN). Detection of AN is of particular interest because of its wide availability as a fertilizer, however, its strong oxidizing properties are often used in improvised explosive devices. AN is classified as a weak group II explosive for which the critical diameter increases with the initial density. Understanding the low frequency vibrational modes, and their dependence on the ambient temperature and the adjacent binders are very important for positive detection of AN. The dielectric functions of thin layer AN deposited on top of metal layer was found to be affected by the presence of different metals [47].

AN exhibits rich polymorphism at ambient pressure, showing five stable polymorphic forms from cryogenic to its melting temperature at 442 K. These phases are defined as I, II, III, IV, and V and strongly depend on the sample temperature [48]. Phase IV is stable in a temperature range of 255-305 K, and below 255 K AN changes the phase to phase V. At room temperature, the THz absorption spectrum shows a featureless absorption which is non-ideal for detection [3]. An extant demonstration shows the characteristic change in the absorption spectrum while reducing the

temperature of the AN sample from room to cryogenic temperature due to the temperature induced phase transition [49]. In this study, we want to investigate the dependence of the terahertz absorption as a function of sample temperature.

The AN sample used in this study was mixed with a powdered polytetrafluoroethylene (PTFE, Teflon) matrix to dilute the AN concentrations, allowing terahertz transmission measurements. The pressed pellet AN sample were prepared using a hand-pressed at 4000 psi with a 2-ton Carver press, forming 6 mm diameter pellets with 1 mm thickness. The sample was attached to a metallic sample holder thermally connected to a cryogenic cooler. The transmitted terahertz spectra through the sample at different temperature are shown in Figure 12.

Figure 12. (a) Transmitted terahertz spectrum through AN sample at various temperature. (b) Extracted refractive index at 300 K (black) and 7 K (red).

At room temperature the transmitted spectrum is featureless which agrees well with the previous measurements [49], manifestation of polymorphic phase IV. As the temperature of the sample was reduced to 250 K, a kink in the absorption spectrum was appeared around 2.0 THz. Further reduction of the temperatures opened multiple transparency windows in the transmission spectrum around 0.6 THz and around 1.5 THz, indicating the polymorphic phase transition from phase IV to phase V. Despite a significant change in the transmission spectrum as a function of sample temperature, the index of refraction of the material remain almost identical as shown in Fig. 12 (b).

Figure 13. (a) Measured absorption at various temperature. (b) Temperature dependent shift of the first two resonant frequencies: the 1st peak around 1.25 THz (red curve) and the 2nd peak around 2 THz (blue curve).

To understand the nature of the absorption as a function of sample temperature, we extracted the effective absorption coefficient of the AN sample at various temperature and plotted them in Fig. 13 (a). At room temperature, the absorption shows a monotonic increases with frequency without the presence of any distinct feature. As the sample was cooled below 250 K, we observed emergence of multiple characteristic features within our measured terahertz windows. There are two distinct absorption peaks, the first peak is ~ 1.25 THz and the second peak is ~ 2.0 THz. These absorption peaks were arisen because of the presence of phonon modes in polymorphic phase V. The absorptions at both peaks increased when the as the sample temperature was reduced and the peak frequencies showed temperature dependent shifting.

To reveal the temperature dependent frequency shifts of resonant modes, we plot the peak frequencies of 1st and 2nd mode as a function of temperature which is shown in Fig. 13 (b). The second peak (blue curve) shows a blue shifting when the sample was cooled from room temperature to 7 K, which is similar to frequency shift in other material such as 1,3 DNB and PETN. However, the frequency of the first peak (red curve) does not show any blue-shifting with decreasing sample temperature. In contrast to the second peak, the first peak shows slight red-shifting. This anomalous behavior of the frequency shifting of first phonon mode requires further investigations.

6. CONCLUSIONS

In this paper, we have shown terahertz transmission measurements through single crystal RDX and PETN sample. Our measurements reveal strong dependence of the incident THz polarization with the crystallographic axes of RDX crystal. The terahertz absorption spectrum in a single crystal RDX showed the presence of multiple phonon modes below 100 cm^{-1} . The strength of absorption and the refractive index strongly depend on the crystal orientation. In contrast, PETN single crystal samples show almost polarization independent absorption. We have observed multiple absorption bands due to the low frequency phonon modes within our measured spectral window. The measured phonon modes of both crystals exhibits spectral blue shifting while the sample temperatures was reduced to cryogenic temperature. We employed the first principal DFT calculation to obtain theoretical dielectric properties of 1, 3 DNB samples in terahertz frequencies. These dielectric parameters were compared with measured values of 1, 3 DNB pressed pellet sample, which showed qualitative agreement. Finally, we measured AN sample at various temperature which exhibited characteristic spectral modes at low temperature but a broad un-featured absorption at room temperature, demonstrating temperature induced crystallographic phase change.

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