Vibrational signatures in the THz spectrum of 1,3-DNB: A first-principles and experimental study

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Abstract – Understanding the fundamental processes of light-matter interaction is important for detection of explosives and other energetic materials, which are active in the infrared and terahertz (THz) region. We report a comprehensive study on electronic and vibrational lattice properties of structurally similar 1,3-dinitrobenzene (1,3-DNB) crystals through first-principles electronic structure calculations and THz spectroscopy measurements on polycrystalline samples. Starting from reported x-ray crystal structures, we use density-functional theory (DFT) with periodic boundary conditions to optimize the structures and perform linear response calculations of the vibrational properties at zero phonon momentum. The theoretically identified normal modes agree qualitatively with those obtained experimentally in a frequency range up to 2.5 THz and quantitatively at much higher frequencies. The latter frequencies are set by intra-molecular forces. Our results suggest that van der Waals dispersion forces need to be included to improve the agreement between theory and experiment in the THz region, which is dominated by intermolecular modes and sensitive to details in the DFT calculation. An improved comparison is needed to assess and distinguish between intra- and intermolecular vibrational modes characteristic of energetic materials.

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Introduction. – The challenging problem of reliable detection of energetic materials and explosives is an evolving and active research field. A particularly interesting aspect is the remote stand-off detection using the molecular fingerprint in the THz region. We report a comprehensive study on electronic and vibrational lattice properties of structurally similar 1,3-dinitrobenzene (1,3-DNB) crystals through first-principles electronic structure calculations and THz spectroscopy measurements on polycrystalline samples. Starting from reported x-ray crystal structures, we use density-functional theory (DFT) with periodic boundary conditions to optimize the structures and perform linear response calculations of the vibrational properties at zero phonon momentum. The theoretically identified normal modes agree qualitatively with those obtained experimentally in a frequency range up to 2.5 THz and quantitatively at much higher frequencies. The latter frequencies are set by intra-molecular forces. Our results suggest that van der Waals dispersion forces need to be included to improve the agreement between theory and experiment in the THz region, which is dominated by intermolecular modes and sensitive to details in the DFT calculation. An improved comparison is needed to assess and distinguish between intra- and intermolecular vibrational modes characteristic of energetic materials.

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structural properties with explosives such as a backbone benzene ring, NO$_2$ antenna groups, intermolecular hydrogen bonds, and planar packing. Here we investigate the vibrational spectrum of the 1,3-DNB molecular crystal using periodic DFT and THz-TDS methods. Our DFT calculations on a model 1,3-DNB single molecule with periodic boundary conditions identify most of the normal modes, which were measured accurately by our THz-TDS technique on the more complicated molecular crystal within the frequency between 0.5 and 2.5 THz. Interestingly, the prediction also reproduces, for the first time, the experimentally identified low-energy modes at $\approx$ 1.05 and 1.28 THz by subtracting three translational and three rotational modes of the 1,3-DNB single molecule, which is also in good agreement with earlier work by Fischer et al. [5]. We also find that these modes are associated with torsional motion of the NO$_2$ group attached with the ring. Our work demonstrates that DFT can provide a theoretical underpinning for an accurate detection of 1,3-DNB and similar explosive materials. The experimental validation of DFT predictions should drastically improve once van der Waals dispersion forces are included to deal with intermolecular interactions. Finally, this suggests that such theoretical capability should also enable the identification of intrinsic THz modes from high-order harmonics of GHz modes, which can originate from intermolecular interactions.

**Methods.** — All calculations were performed by using the plane-wave pseudo-potential method of DFT with periodic boundary conditions, as implemented in the VASP [6] code. The crystal structure of the 1,3-DNB solid, as shown in fig. 1(b), is orthorhombic (space group Pna2$_1$ or No. 33) [7–11]. Each unit cell contains four 1,3-DNB molecules and at 130 K has the reported linear dimension of 0.6 × 0.6 × 0.6 nm$^3$. The linear dimension of 1,3-DNB solid with experimental lattice parameters at 130 K after ref. [7].

For the 1,3-DNB molecular crystal, as shown in fig. 1(b), we used the VASP-5.3.1 package [6] 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 [13,14] PBE pseudo-potentials, provided by VASP, are 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 testing the reliability of the optimized volume. For both the single-molecule and the molecular-crystal case, the density functional perturbation theory (DFPT) was used to obtain in the linear response the vibrational dispersion at the center of the lattice Brillouin zone (phonon momentum $\mathbf{q} = 0$). For the latter case we also used the Phonopy package [15] for cross-checking the results, and confirmed that the calculated mode frequencies obtained from both approaches agreed well with each other.

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 [16]. During measurements, the sample is attached to one hole, while the other clear hole is used as a reference. We employed a ZnTe-based THz-TDS spectrometer for sample measurements [17]. 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 the 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. To mitigate the THz absorption by the ambient water vapor, the enclosed THz system is continuously purged with dry air. The sample holder is attached to a liquid-helium-cooled cryostat, allowing precise control of the sample temperature. The measured time-dependent THz pulses transmitting through the sample and reference are converted to complex frequency spectra using numerical fast Fourier transform. Because of the finite thickness of the sample pellets, the THz pulse through the sample is usually accompanied by multiple reflected pulses. However,
clear time separation between main and reflected pulses enables the truncation of the sample THz pulses just before the arrival of the first reflection, alleviating multi-reflection–induced oscillations in spectra, but also limiting the low-frequency resolution. Earlier measurements [5] have employed photoconductive antenna-based terahertz time-domain spectroscopy to characterize the absorption properties of 1,3-DNB at room and cryogenic (13 K) temperature. The dynamic range of such THz system limits, to some extent, the accuracy of measurements below 2.0 THz at room temperature. However, the dynamical range of the terahertz system used in our work was able to detect absorption peaks for the vibrational modes at 2.4 THz, allowing us to measure five distinct low-frequency modes, providing a further confirmation of earlier measurements. Additionally, the cryogenic system allowed us to cool our sample down to 7.5 K.

Results and discussions. – Our calculations for the 1,3-DNB single molecule with periodic boundaries gives all normal modes with physically real frequencies, except for the three translational and three rotational modes. For the 1,3-DNB molecular crystal, the calculations yield imaginary vibrational modes, irrespectively of using the reported x-ray crystal structure or the relaxed atomic structure obtained with fixed experimental lattice parameters [7] at 130 K, suggesting the structure is dynamically unstable toward small perturbations. Therefore, we performed total energy calculations for a sequence of volumes. For each of them the internal atomic positions were fully optimized. Figure 2 shows the volume dependence of the total energy calculated with an energy cutoff of 500 eV and 700 eV. A rigid shift in total energy can collapse both curves, demonstrating good convergence for finding the optimized volume, since they are cutoff independent. The importance of selecting a sufficiently large energy cutoff, due to its size dependence of the basis set, has also been discussed for organic explosives [18,19]. The theoretically optimized unit cell has the linear dimension $a_{\text{opt}} = sa$, $b_{\text{opt}} = sb$, and $c_{\text{opt}} = sc$, where uniform relaxation of the lattice parameters with scaling factor $s = 1.064$ was assumed. This scaling amounts to a theoretical unit volume of 825 Å$^3$, which is noticeably bigger than that of the experimental volume of 685 Å$^3$ [7] (marked by a vertical dashed line in fig. 2). The overestimation of the volume could be due to the PBE exchange-correlational functional, which routinely underestimates the binding strength of molecular crystals. Similar discrepancies have been reported in the literature for other molecular crystals [20,21]. This behavior is indicative of the importance of the van der Waals dispersion forces, which are absent in our DFT calculation. Noteworthy, we found that the calculations with the theoretically optimized volume give all normal vibrational modes.

After fast-Fourier-transforming our measured THz-TDS spectra, we fit the complex spectra to the following relation between the electric field of the sample and the

$$E_{\text{sample}}(\omega) = E_{\text{ref}}(\omega) e^{i(k-\omega)d/2}$$

(1)

to obtain the complex refractive index $n = n_r + i\kappa$ and the absorption coefficient $\alpha = 4\pi\kappa/\lambda$. Here $k_0 = 2\pi/\lambda$ is the free-space wave vector, $\omega = \hbar c$ with speed of light $c$, $k = 2\pi n_r/\lambda$ is the wave vector inside the sample, $d$ is the sample thickness, and $t_{12}(\omega)$ and $t_{21}(\omega)$ are the frequency-dependent Fresnel transmission coefficients from the front- and back-side of the sample. With the extracted complex refractive index and absorption coefficient, the complex dielectric function is given by the relation

$$\epsilon(\omega) = n_r + i\kappa = (n_r + i\kappa)^2$$

(2)

That is, $\epsilon_r = n_r^2 - (\alpha\lambda/4\pi)^2$ and $\kappa = \alpha\lambda/2\pi$.

Figure 3 shows the extracted refractive index, absorbance (absorption coefficient), and the complex dielectric function (real and imaginary parts) from the measured THz spectra on the 1,3-DNB polycrystal at temperatures 295 K and 7.5 K. In our experiment, the absorption spectrum shows multiple signatures of prominent resonant peaks within our measured spectral window between 0.3 and 2.5 THz. As shown in fig. 3(a) and (b), both refractive index and absorbance show weak frequency dependence, yet strong temperature dependence. Their values decrease as the temperature of the sample decreases from room temperature to 7.5 K. The refractive index drops nearly 30%, while the real part of the dielectric
Fig. 3: (Colour online) Frequency dependence of the refractive index (a), absorbance (b), real (c) and imaginary (d) parts of the dielectric function, extracted from the THz-TDS experiments measured on a polycrystalline (compressed powder) pellet 1,3-DNB at 295 K (red) and 7.5 K (blue) curves, respectively.

Fig. 4: (Colour online) 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) of 1,3-DNB. For the crystalline solid, only the phonon frequency modes are calculated, which are identified by the vertical lines.

The function drops roughly 60%. In addition, we observe blue shifts and narrowing of the absorption peaks at cryogenic temperature.

In fig. 4 the first-principles phonon modes for the molecular crystal are shown as vertical solid lines. Comparing our crystalline 1,3-DNB calculation with our THz experiment (solid black curve), we find that the observed modes at 1.05 THz and 1.28 THz are qualitatively identified, while the measured 0.59 THz normal mode is missing from our selective dynamics calculations. On the other hand, in our DFPT phonon calculation for the periodic single molecule of 1,3-DNB (solid green curve, obtained via eq. (3) below), using the VASP package we recover the lowest-frequency modes at 1.15 THz and 1.36 THz by subtracting three translational and three rotational modes by using the 3N − 6 rule. Furthermore, by performing a selective dynamics analysis of only the NO₂ group attached to the benzene ring of 1,3-DNB, we readily identify the torsional modes to be associated with these lowest modes of the 1,3-DNB single molecule. Although one of our calculated rotational modes is very close to 0.5 THz, we cannot rule out that this is in fortuitous agreement with the lowest mode observed in our THz spectra. A crystalline environment is most likely responsible for this mode. Although our calculations for crystalline 1,3-DNB did not reveal any modes at such low energy, we believe that a more accurate yet computationally expensive treatment of the vdW interactions will soften our calculated modes of the 1,3-DNB crystal to reproduce all five low-energy modes observed in our experiment. Two experimentally identified low-energy modes at 1.05 THz and 1.28 THz have been reproduced very accurately in our DFT calculations, which are also in good agreement with earlier experiments [5].

Our calculations also revealed that such modes originate from the normal motion of the NO₂ antenna groups attached to the “1” and “3” positions of the carbon ring. A similar conclusion was drawn from a rigid structure model analysis by Wójcik et al., yet with overestimated frequencies, who assigned these internal torsion modes to 1.89 and 1.92 THz [7].

Furthermore, 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 [22]

\[
\epsilon(\omega) = \epsilon_\infty + \sum_j \frac{f_j \omega_j^2}{\omega_j^2 - \omega^2 - i \Gamma_j \omega}.
\]

Here \(\epsilon_\infty\) is the high-frequency dielectric constant, \(f_j\) is the dimensionless oscillator strength, \(\omega_j\) is the \(j\)-th normal mode, and \(\Gamma_j\) is the damping constant. For simplicity, we assume frequency-independent damping. By fitting the measured \(\epsilon(\omega)\) at 7.5 K to eq. (3), we identify the first five transverse optical (TO) phonon modes, including their oscillator strengths and damping constants, which are listed together with the different theoretical values of low-energy modes in table 1.

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 (e.g., the green curve in fig. 4). We find that the calculated real and imaginary dielectric functions agree reasonably well with our measurements at low temperatures with only a single fit parameter \(\epsilon_\infty\). The direct comparison is shown in fig. 5. For a consistency check we also compare our calculated real and imaginary dielectric functions for the single molecule with those of single crystal experimentally reported by Trzebiatowska-Gusowska et al. [23]. Our calculated complex dielectric function in
Table 1: Experimental and DFPT-calculated THz frequency modes and oscillator strengths of the 1,3-DNB molecular crystal. The oscillator strengths for the single molecule (sm) obtained from VASP using the linear response method.

| Mode | \( \omega_j/2\pi \) (THz) | \( f_j \) (Exp) | \( \Gamma_j/2\pi \) (THz) | \( \omega_j/2\pi \) (DFT sm) | \( f_j \) (DFT sm) | \( \omega_j/2\pi \) (DFT x-tal) | \( f_j \) (Wójcik) |
|------|-----------------|-------------|-----------------|-----------------|-------------|-----------------|-------------|
| 1    | 0.59            | 0.012       | 0.07            | 0.57            | 0.95        | 0.72, 0.84      | 0.57        |
| 2    | 0.86            | 0.031       | 0.15            | 0.95            | 0.97        | 0.93, 0.96      | 1.29        |
| 3    | 1.05            | 0.026       | 0.11            | 1.15            | 1.29        | 1.14            | 1.35        |
| 4    | 1.28            | 0.037       | 0.20            | 1.36            | 1.50        | 1.68            | 1.59        |
| 5    | 2.40            | 0.090       | 0.60            | 1.96            | 1.96        | 1.83            | 2.06        |

Fig. 5: (Colour online) Comparison between interpolated experimental infrared (IR) spectra at 130 K [23] (solid black line) and theoretical (solid red line) single-molecule calculation for 1,3-DNB. The theoretical complex dielectric function used the single fit parameter \( \epsilon_\infty = 1.75 \) to fit the THz spectrum at 7.5 K. Panels (a) and (b) show the Re[\( \epsilon(\omega) \)] and Im[\( \epsilon(\omega) \)] in the infrared region up to 100 THz; (c) and (d) show the low-frequency THz spectra of Re[\( \epsilon(\omega) \)] and Im[\( \epsilon(\omega) \)] for the calculations (solid red line), THz-TDS experiments (solid black line), and Lorentz fit to experimental data (dashed blue line).

The five lowest-frequency vibrational modes, which are observed in our measurements and calculations, are presented in table 1. They compare reasonably well with the infrared and Raman measurements at 0.84, 0.93, 0.96, 1.14, 1.20, 1.68, 1.83, 2.34, 2.37, 4.89 and 5.94 THz reported originally by Bobrov et al. [24] and revisited by Wójcik et al. [7], who used a rigid structure analysis for the normal modes of the single molecule.

Conclusions. – In summary, we performed first-principles DFT electronic-structure and DFPT phonon calculations of the THz spectrum of the dielectric 1,3-DNB molecular crystal to compare with THz-TDS measurements in the 0.3–2.5 THz region. Calculations for the single molecule with periodic boundaries and the molecular
crystal were in overall good agreement except for the low-
frequency THz modes of interest, pointing to subtle dif-
fferences in intermolecular interactions and details in DFT
codes. The relaxed structural crystal properties obtained
from VASP differ noticeably from the experimentally re-
ported volume, leading to a larger unit cell as is often the
case for PBE exchange functionals. However, the VASP-
calculated vibrational modes are in qualitatively good
agreement with measurements from the THz spectroscopy.
We note that our measured low-temperature spectrum it-
self is in overall good agreement with previous reports for
solid 1,3-DNB. Our high-resolution measurements enabled
us to clearly identify a low-frequency mode at 0.59 THz
and another mode at 0.86 THz. Quantitatively, the theo-
retical (VASP) and experimental spectra are overall offset
by about 0.2 THz. While this is of little concern at high
frequencies, it makes a direct first-principles prediction of
low-frequency modes below 2.5 THz challenging for abso-
lute fingerprinting of molecular crystals. Nevertheless, the
DFPT-calculated modes still capture the general trends in
the absorption spectrum of the 1,3-DNB crystal. In the
future, we plan to improve the DFT calculations by in-
corporating van der Waals interactions for the long-range
dispersive forces between molecules to correct for the over-
estimation of the optimized unit cell volume and lowest
normal modes.

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