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Determining the THz and Infrared Spectral Properties of Single Crystals and Thin Crystalline Films from First Principles.

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***Abstract*—We present recent developments to the software packaged PDielec that can be used to post-process solid-state DFT calculations to determine the THz spectra of single crystals and thin crystalline films, including effects of crystalline orientation, beam incidence angle and beam polarisation, allowing the full interpretation of complex THz spectra. We use the explosive Cyclotrimethylenetrinitramine (RDX) as a previously well studied example.**

I. Introduction 10pt small caps

CYCLOTRIMETHYLENETRINITRAMINE or RDX is a powerful explosive that is well studied in the THz spectral region. It exists in a range of polymorphic forms and has been characterised as a powder [1-4], a crystalline film [5] and as an orientated single crystal [6-8] with a range of calculation methods [2,9,10] used to help interpret the complex THz spectrum. As such it makes an excellent testbed when implementing new calculation methodologies.

PDielec [11-12] is a Python package for post-processing solid state QM and MM calculations of infrared spectra. Previous work has concentrated on the interpretation of spectra of powders, combined with an inert non-absorbing material and pressed into pellets. In the most recent release of PDielec (7.1.2) [13] we have implemented a tool which allows the THz and IR spectrum of an orientated single crystal or thin crystalline film to be calculated. Calculation of the single crystal optical properties is performed using a generalized transfer matrix methodology developed by Passler and co-workers [14-15] and available as a Python module, PyGTM [16]. This allows the single crystal dielectric permittivity tensor to be calculated, and from that determine the transmittance, reflectance and absorption for a single crystal with a specific morphology. In this case absorption is defined as the fraction of radiation which is not reflected and not transmitted.

The measurement can be visualized as seen in Fig. 1. The information required for the calculation is the angle of incidence of the incoming beam (θ) and the orientation of the crystal (in particular the face of the crystal the beam is incident on) and the azimuthal angle (γ) between the plane of the incident beam and the crystalline axis. In the majority of transmission and reflection measurements the incident beam will be at normal incidence to the crystal face (along the z-axis in Fig 1) meaning that $\theta = 0^{\circ}$.

Two methods of optical property calculation have been implemented within PDielec. In the thin film approximation you can input the crystal thickness along with the refractive index of the material before and after the crystal (air by default). This can be used to interpret transmission measurements of single crystals but also allows the calculation of the optical properties of a thin film grown on a known substrate. A second method, the thick slab, assumes a thick crystal where total absorption will take place within the crystal without any internal reflection. This method is useful for interpretation of reflectance measurements.

DFT Calculations of α-RDX were performed using the academic release of CASTEP 19.1 [17] using the Perdew-Burke-Ernzerhof (PBE) functional [18] and D3-BJ dispersion correction [19,20]. The CASTEP 19.1 norm-conserving pseudo-potentials were taken from the 'on-the-fly' pseudo-potentials built using the NCP19 keyword as input to the 'SPECIES_POT' directive. The cutoff energy used was 1000 eV with a Monkhorst-Pack grid of 1,1,1.

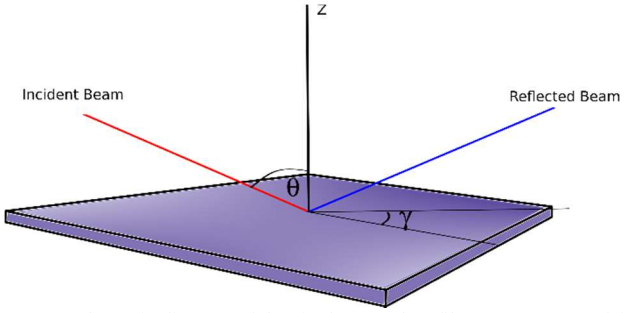

Fig. 1. a schematic diagram of the single crystal or film measurement. θ is the angle of incidence and is 0° at normal incidence (along the z-axis). γ is the azimuthal angle between the plane of the incident beam and the crystalline axis.

II. Results

Fig. 2 and 3 show calculations of the optical properties of RDX using the thin film approximation with an assumed crystal thickness of 1 μm and assuming normal incidence. Fig. 2 shows the absorption spectrum of α-RDX with a beam incident on a number of different faces for both p- and s-polarisations of the incident beam. The crystal faces were chosen to represent the crystals measured by a number of groups previously [6-8]. Calculations that are identical use dotted, rather than solid, lines to show the overlaping spectra. Fig. 4 shows calculations for the (001) face calculations with p-polarisation as the azimuthal angle (γ) is changed from 0° to 90°.

The general correlation between these calculations and previously published results is generally good, in particular the peak at 0.82 GHz is reported to change significantly with both morphology and crystal rotation. Direct comparison between these calculations and published experiments remains difficult. This is, in part, because previous publications can omit important details (like beam polarisation) or do not include their definition of azimuthal angle which is often defined to an arbitrary axis. All current experiments also use relatively thick crystals (~500 μm) which can cause peak distortion and saturation effects that are not currently included in either the thin-film or thick slab approximations. However, this new

implementation still provides a useful tool to provide a detailed insight into these common spectral measurements.

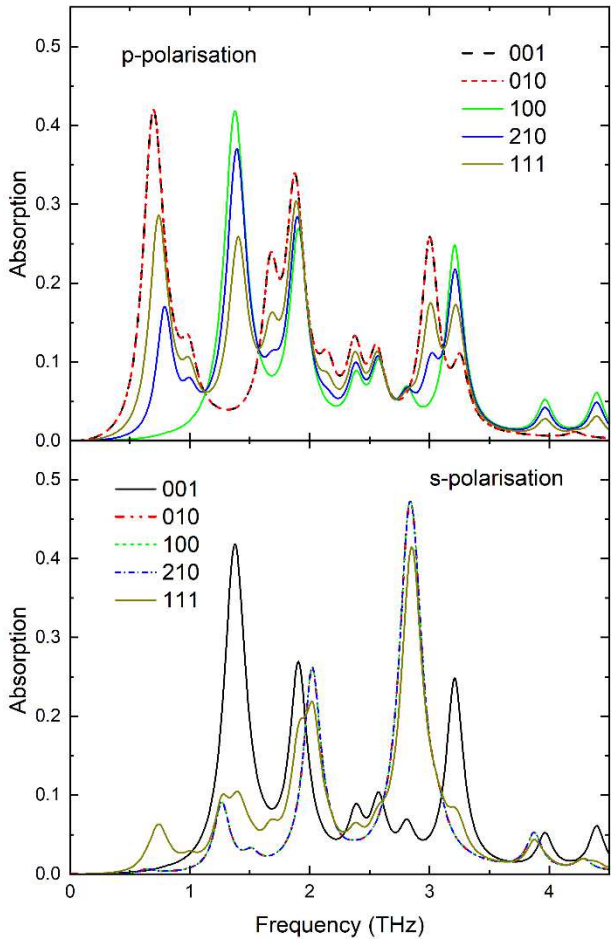

Fig. 2. Shows the calculated THz spectra for α-RDX crystals where the incident beam is incident on a number of different crystalline faces for both p- (top pane) and s-polarisation (bottom pane) incident light. The beam is assumed to be at normal incident to the crystalline face with $\gamma = 0^{\circ}$.

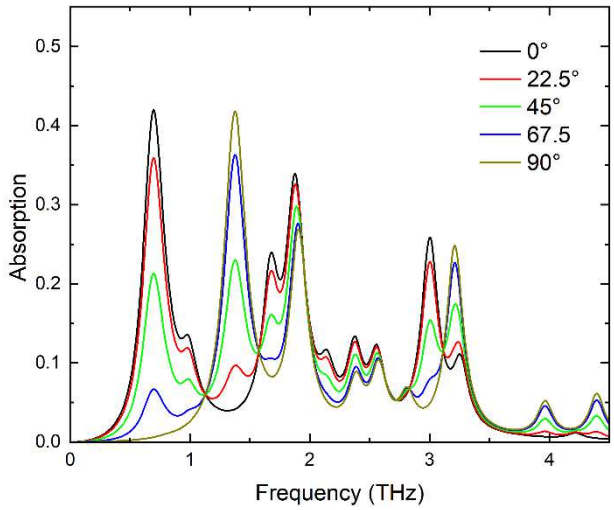

Fig. 3. Shows the calculated THz spectra for an α-RDX crystal (001) with the incident beam (p-polarisation) at normal incidence as the azimuthal angle between the plane of the incident light and the crystalline axis is changed.

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