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# Understanding the influence of morphology on the terahertz spectra of a powdered ionic crystalline system.

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**Abstract**—We show that the terahertz (THz) frequency spectra of powdered ionic crystalline systems are not described by their infrared active phonon modes alone. Instead, it is necessary to include the coupling of the phonon modes with the macroscopic electric field generated by the collective displacement of the vibrating ions.

## I. INTRODUCTION AND BACKGROUND

TERAHERTZ (THz) frequency spectroscopy has developed into a valuable technique for probing the vibrational properties of crystalline materials. [1] Solid state density functional theory (DFT) [2, 3] has shown that the spectra can be represented well by transverse optical (TO) phonon modes, which can be broken down into contributions from translatory, rotary and vibrational motion. In this paper we compare and contrast the experimentally-measured THz spectra of tetramethylammonium bromide (TMAB) with simulations of the spectra obtained using density functional perturbation theory. We show that for ionic crystals it is necessary to include contributions arising from the macroscopic electric field in the simulations.

## II. RESULTS

Fig. 1 shows the experimentally measured spectra for TMAB recorded at 293 K (black line) and 4 K (red line), for a pellet diluted to a 5 % w/w concentration with PTFE. The spectrum at 293 K shows a peak centered at 2.25 THz with a broad shoulder centered at 3.12 THz. Upon cooling to 4 K, the spectrum shows only small shifts in spectral features, something we have noted previously for another ionic salt, cocaine hydrochloride [4]. Specifically, the main peak increases in intensity and shifts to 2.27 THz, whilst the shoulder splits into two features at 3.02 and 3.31 THz. The calculated TO modes (using Castep) are shown as vertical red lines (Fig. 2); there are two pairs of degenerate modes at 2.41 and 3.53 THz, with the first pair being strong translatory modes, and the second very weak rotary modes which makes virtually no contribution to the spectrum. There is also a singlet mode at 2.78 THz, which can be assigned to a translatory lattice mode. The THz spectrum is therefore dominated by three translatory modes involving anti-symmetric movement of the four ions along each of the three

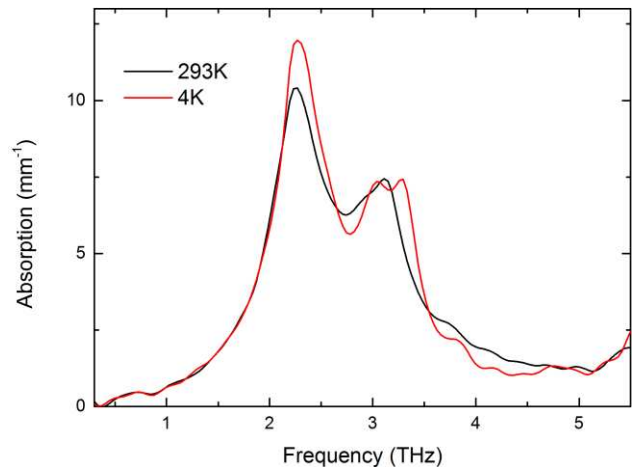


Figure 1 The experimentally observed spectra for TMAB recorded at 293 K (black line) and 4 K (red line)

crystal axis directions. An approximate predicted spectral shape can be created by adding Lorentzian curves with a FWHM of  $35 \text{ cm}^{-1}$  to the TO modes and is shown as the red curve in Fig. 2. The predicted spectrum, although comprised of three normal modes, shows only one spectral feature, centered at 2.49 THz. The reason for the discrepancy between the experimental and calculated spectra is that the theoretical description of absorption ignores any contribution arising from the macroscopic electric field generated in a crystal by the collective displacement of ions. This is the so-called non-analytical term in the expression for absorption intensity, which gives rise to an intensity contribution from shifted longitudinal optical (LO) modes. Because of the strongly ionic nature of salts, it is expected that the absorption intensities and frequencies will be heavily influenced by particle shape and the nature of the surfaces, which may dominate for any particular morphology. By using an effective medium theory for dielectric particles embedded in a low dielectric constant medium [5], the effective frequency-dependent dielectric constant can be calculated from a combination of the electric field arising from the infrared radiation in the surrounding low dielectric constant medium and the complex frequency dependent permittivity tensor of the crystal. For ionic materials, the presence of surface charge modifies the crystal's internal electric field by a depolarization field, which in turn

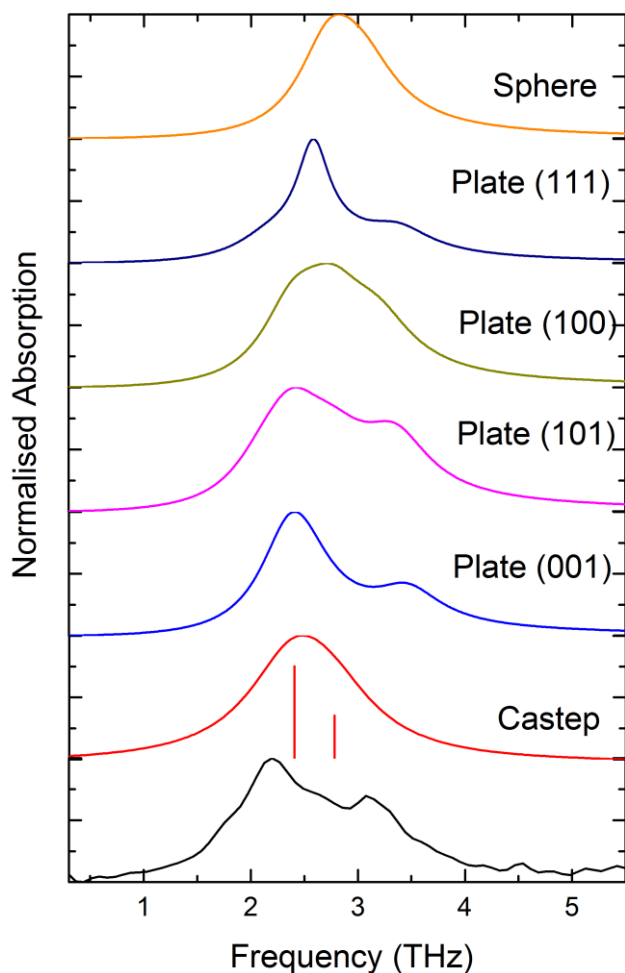


Figure 2 A comparison of the experimental THz spectrum (12.5% w/w sample, black) with the calculated spectra for TMAB calculated using Castep [6] (red, vertical lines show predicted infrared active peak positions) with no particle shape taken into account, four plate shaped crystals (numbers in parentheses show plate orientation), and spherical particles.

influences both the position and intensity of LO absorption modes.

A number of crystal morphologies can grow from any unit cell. To determine which crystal morphologies were most likely to be encountered we calculated growth morphologies using Materials Studio 4.0 [7], with the Dreiding forcefield [8] and charge equilibrated (QEQ) charges [9]. These calculations suggested four families of faces ( $\{001\}$ ,  $\{101\}$ ,  $\{100\}$  and  $\{111\}$ ) to be the most important in the crystal habit of TMAB crystals, on the basis of the calculated attachment energies. SEM images of the powder shows that the sample has a preponderance of flat surfaces, consistent with the material comprising plate-like particles. Although the crystal habit of the powder is unknown, the likelihood is that it is dominated by plate-like particles with the large faces belonging to one of the four families of faces calculated above.

It can be seen in Fig. 2 that particle shape has a dramatic influence on the calculated spectra with some modes shifting to higher frequencies by up to 800 GHz. In contrast to the

results from plate-like faces, the calculated spectrum for spherical particles is similar to that obtained using the transverse optical (TO) frequencies and intensities reported by Castep [6], but with the single broad peak shifted to slightly higher frequencies. All four simulated spectra of TMAB for crystals with a plate morphology show a large peak centered between 2.3 and 2.6 THz with a shoulder at higher frequencies, much like the experimental spectra in Fig. 1, although the ratio of peak heights and widths varies between plates. It is clear that the prediction for a plate like morphology associated with the  $\{101\}$  surfaces most closely resembles the experimentally observed spectra, and it is likely that the majority of particles show this morphology.

The results clearly show that, for compounds with charge separation such as salts, there is a large coupling between the electric field induced by the phonon vibrations and that induced by the radiation. It is, therefore, essential to have a theoretical understanding of the impact of the particle shape on the absorption of radiation to understand the underlying contributions to the experimentally-measured spectrum. In the case where the particle shape can be well characterized [5] it is possible to calculate the spectrum. However, where the particle shape is not fully characterized, as with the TMAB here, it is only possible to use the calculations to estimate the range of shifts in peak positions and intensities that could be observed. In summary, detailed understanding of the nature of the vibrational contributions to the observed spectra is only possible for extremely well characterized particles.

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