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Calculating the Complex Permittivity of Powdered Crystalline Material at Infrared and Terahertz Frequencies.

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Abstract— In this paper we calculate the complex permittivity of a crystalline material supported in a non-absorbing medium. To do this we have developed a software package, PDielec, which post processes solid state quantum mechanical and molecular mechanical calculations of the phonons and dielectric response of the crystalline material. Using an effective medium approximation, the package calculates the internal electric field arising from different particle morphologies and calculates the resulting shift in absorption frequency and intensity arising from the coupling between each phonon mode and the resultant internal field.

I. INTRODUCTION

A common approach to calculate the frequencies and corresponding intensities of infrared (IR) and terahertz (THz) radiation absorption is to assume the harmonic approximation and calculate the mass weighted force constant matrix (for molecules) or the dynamical matrix at the gamma point (for periodic solids). Diagonalisation of the matrix gives the frequencies for absorption and the normal modes (molecules) or phonon displacements (periodic solids). The calculation of the absorption intensity for each mode requires the calculation of the change in dipole moment caused by the displacement of the atoms for that mode. For solids where there is a large separation of charge, there can be a large coupling between each phonon mode and the internal field within a particle resulting from its morphology. We determine the effect of this coupling on the calculation of the complex, frequency dependent permittivity for a finely ground crystalline material dispersed in a low loss dielectric medium, using an effective medium approximation (EMA). This theory has been implemented in a Python software package named PDielec [1]. Currently the package has interfaces to five solid state quantum mechanics codes, namely Abinit, [2] CASTEP, [3] Crystal, [4] Quantum Espresso, [5] and VASP [6]. In addition an interface is available for GULP [7] which is a force field based solid state code. The package includes a number EMAs, including both the Maxwell-Garnett [8] and Bruggeman [8] approximations and can be used to determine how a number of morphological shapes including sphere, ellipse, plate and needle affect the complex, frequency dependent permittivity of the sample.

II. RESULTS

L-aspartic acid is a zwitterion in the solid state and so the shape of the particles used in the measurement of IR and THz spectra maybe important. To determine the THz active phonon modes of L-aspartic acid were calculated using CASTEP [3]. The experimentally determined primitive cell was first optimized using the PBE functional with a plane wave energy cutoff of 1000 eV using norm conserving pseudo-potentials.

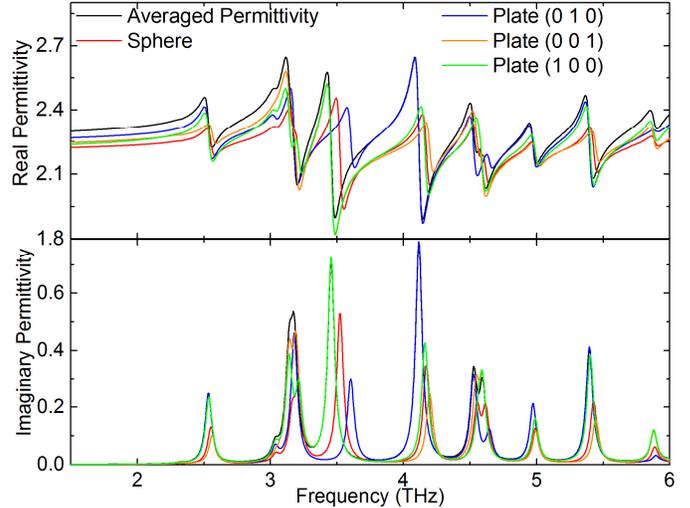


Fig. 1: The effect of particle shape on the complex permittivity of L-aspartic acid calculated using a Maxwell-Garnett EMA and a 10 % volume fraction of L-aspartic acid in PTFE.

The Tkatchenko-Scheffler dispersion correction [10] was also applied. After optimization the phonon spectrum at the gamma point was calculated using density functional perturbation theory.

The calculated complex permittivity of L-aspartic acid shown in Fig. 1 has then been calculated from this phonon spectrum using PDielec. [1,9] A Maxwell-Garnett EMA has been used with a 10 % volume fraction of L-aspartic acid embedded in a polytetrafluoroethylene (PTFE) matrix with a damping factor [9] of 2 cm^{-1} . Spherical and a variety of plate-like inclusions have been calculated in order to demonstrate the effect in both peak position and intensity upon coupling between each phonon mode and the internal field within a particle resulting from its morphology. For comparison an averaged permittivity mixing rule [9] is also used to illustrate the magnitude of the spectral changes owing to particle shape.

It is clear from Fig. 1 that although shifts in peak position are relatively minor in the case of L-aspartic acid, the changes in peak intensity of the imaginary permittivity (bottom pane) coupled to the increased changes in real permittivity (top pane) are large — as much as 50 % for different particle shapes. The understanding of this effect is therefore crucial for a full analysis of a THz spectra of any ionic crystalline solid. Similar calculations also show that both the permittivity of the matrix and volume fraction of the mixture have a subtle effect on the resultant spectra and must also be considered.

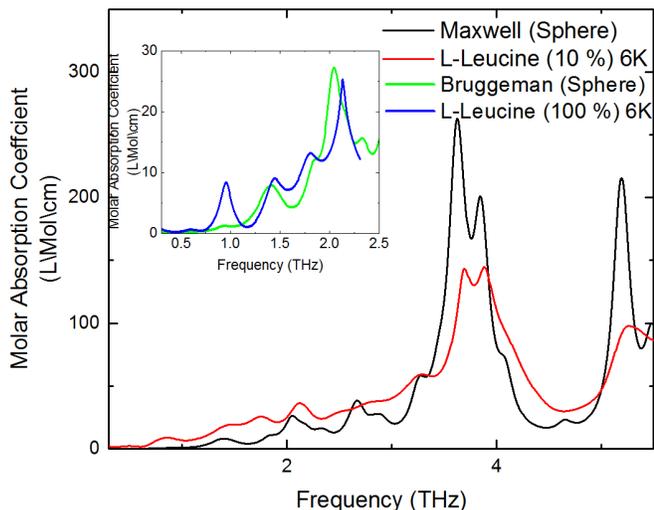


Fig. 2: Shows the calculated spectra of L-Leucine using the Maxwell-Garnett (black line) approximation. This is compared to the diluted (10 %) measured sample recorded at 6 K (red line). The inset to the figure shows the Bruggeman (green line) approximation. This is compared to the pure measured sample recorded at 6 K (blue line). Both calculated spectra were generated using PDielec [1] and assume a spherical particle shape and damping factor of 6 cm^{-1} .

As a second example Fig. 2 shows the THz spectra of L-leucine. Samples were pressed into pellets $\sim 500\text{-}\mu\text{m}$ -thick both as pure samples (100 %) and mixed with PTFE with a mass ratio of 10 %. To determine the THz active phonon modes of L-leucine, the experimentally determined primitive cell was first optimized and the phonon spectrum at the gamma point calculated using CASTEP with the same parameters as L-aspartic acid. [3]

Fig. 2 shows the calculated molar absorption coefficient using the Maxwell-Garnett approximation (black, for the 10 % sample) and the Bruggeman approximation (green, for the 100 % sample) using appropriate mass fractions. This is then compared to the experimental molar absorption coefficients for the spectra of the two samples. In all calculations here a damping factor of 6 cm^{-1} and a spherical particle shape has been assumed. It should be noted that molarity is expressed in terms of the concentration of crystallographic unit cells, not the molecular molarity.

Fig. 2 shows good agreement in both peak position and intensity between experiment and calculation for the majority of spectral features seen in the experimental THz spectra. This is particularly surprising considering the phonon calculation predicts 32 normal modes contributing to the THz spectra of L-leucine between 0 and 5.5 THz. It's clear from Fig. 2 that the method employed within PDielec [1,9] is excellent at estimating the experimental absorption coefficient. There is however one large discrepancy between the experimental and calculated spectra and that is the mode at 0.95 THz which shows seven times the intensity in the experimental spectra compared to calculation — this is emphasised best in the inset to Fig. 2. It is still unclear why this discrepancy exists and we are currently investigating this. There is also a much larger difference between experiment and calculation for the lower concentration sample. This is likely due to natural inhomogeneity of any pelletised mixture combined with spectral effects attributed to clustering in the mixture [8] and scattering due to the difference

in refractive index between the sample and PTFE matrix [11] which are currently not taken into account with PDielec [1].

The results for both amino acids show the sensitivity of the complex permittivity measurements to both particle morphology and diluting matrix and illustrates the complexity of interpreting IR and THz absorption spectra. This is particularly apparent when comparing absolute rather than relative absorption.

The power of the methods implemented within the PDielec python package [1] lie in its ability to calculate the complex permittivity of a material from a range of calculation methodologies and compare these directly with THz time-domain spectroscopy. This in turn will allow us to compare different levels of theory easily, to determine appropriate methods for a chosen sample.

III. SUMMARY

We have developed a method for taking into account the coupling between each phonon mode and the internal field within a particle resulting from its morphology. We have then proceeded to demonstrate the expected effect of changes in particle shape to the complex, frequency dependent permittivity of L-aspartic acid samples embedded in a PTFE matrix and the excellent fit for the calculated and experimental spectra of L-leucine. Although we only discuss our results at THz frequencies it's important to note that these methods are applicable for all IR active modes.

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