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Calculating the Complex Permittivity of Powdered Crystalline Materials

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Abstract — **Solid-state density functional theory calculations including periodic boundary conditions have become well established for calculating the THz spectra of crystalline materials. Here we compare a range of DFT programs and calculation parameters including a number of van der Waals' dispersive corrections in combination with our post-processing tool, PDielec, to calculate the complex permittivity of a range of powdered crystalline materials.**

I. INTRODUCTION

THE calculation of the THz spectra of a crystalline material using solid-state density functional theory (DFT) in combination with periodic boundary conditions is established [1] as a reliable and robust method for understanding the origins of the vibrational modes in these, often quite complex, spectra. Here we explore a range of DFT programs, calculation parameters and experimental parameters to improve the correlation between experimental and calculated spectra.

II. RESULTS

Fig. 1 shows the results for the calculated spectra for sodium persulfate ($Na_2S_2O_8$) with DFT calculations performed using VASP [2] with a PBE functional [3] and the PAW psuedopotentials included with the VASP distribution. The spectra calculated using PDielec [1]. We explore the effect of introducing various van der Waals' dispersion corrections including D2 [4] two forms of D3 [5-6] and the TS [7] corrections. In many respects, the observations drawn from the VASP example can be seen when using other DFT programs.

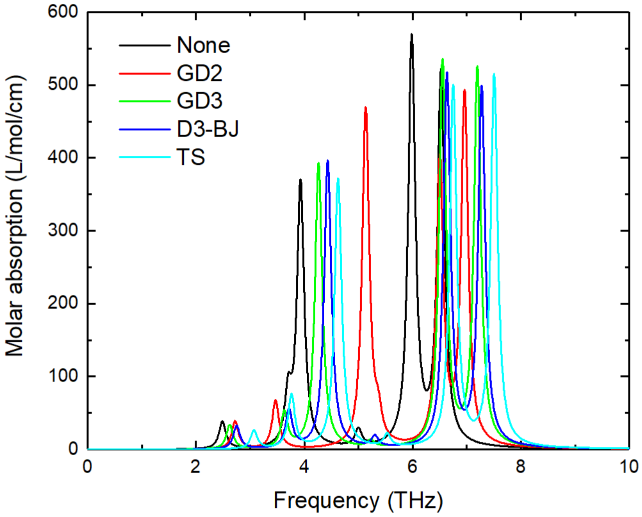

Fig. 1. Dispersion corrected spectra using Maxwell-Garnett effective medium theory for sodium persulfate. Spectra all calculated using VASP with various dispersion corrections.

There tends to be a small shift to higher frequencies when dispersion corrections are included in the mid-IR while the intensities are not affected. However, in the THz region shown in Fig. 1, although the qualitative pattern of absorption is similar, there are significant shifts in the frequency of absorption owing to the inclusion of a dispersion correction. The shift of absorption to higher frequency on the inclusion of dispersion is consistent with the decreased volume of the unit-cell, relative to the non-corrected volume.

As well as exploring a range of calculation parameters and determining suitable choices for molecular crystals we also began to explore the effect of experimental sampling environment on the THz spectra. Most molecular crystals are highly absorbing, and in order to measure their spectra, are often embedded in a non-absorbing medium (such as PTFE or PE) or an Attenuated Total Reflection (ATR) technique could also be used. Thus, the effective permittivity of a mixture, rather than a pure material, is nearly always measured.

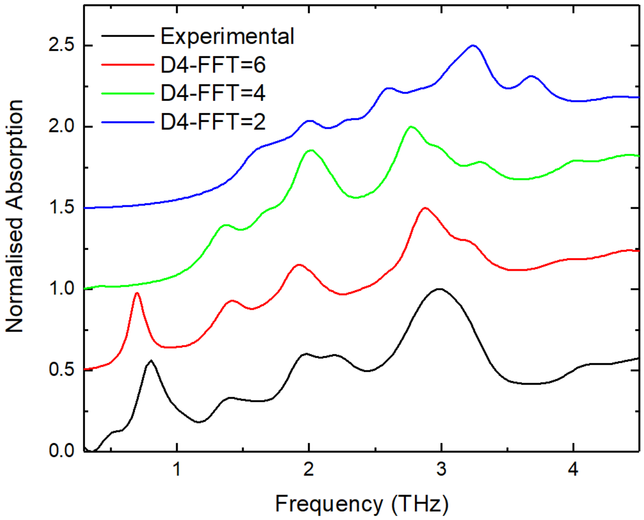

Fig. 2. Shows the experimental (black) and calculated THz spectra of RDX. Spectra were calculated using CASTEP and a D4 Dispersion correction while varying the size of the fine FFT grid used in the calculation.

For the calculation of the effective permittivity PDielec assumes that the material is a powdered crystal dispersed in a supporting matrix and that the composite material has an effective complex permittivity, calculated using an effective medium theory such as Maxwell-Garnett. This effective permittivity is determined from the calculated permittivity of the material, the shape of the crystal and the permittivity of the supporting matrix. In addition, using PDielec, it is possible to incorporate the effects of scattering during the absorption process using the Mie method for spherical particles or calculate the effective permittivity of a sample when an ATR prism is used.

In Fig. 1–3, the spectra are calculated using a Maxwell-Garnett effective medium approximation assuming spherical particles embedded in a matrix of PTFE with an appropriate mass ratio for the sample. Fig. 2 also assumes that 10% of the volume is air and that these air voids cause Mie scattering and this is used to match the rising background seen experimentally.

Fig. 2 (black line) shows the THz spectra of a sample of RDX, an explosive, embedded in a matrix of PTFE with a 20% mass ratio of sample. The three theoretical spectra in Fig. 2 were all calculated using CASTEP [8] with a PBE functional, on-the-fly generated norm-conserving pseudopotentials (generated using the NCP19 keyword) and the D4 dispersion correction [9]. The only difference between the three calculations is the increase in fine FFT grid from 2 through to 6. While it is well known that a well converged calculation using a very fine FFT grid is required to obtain accurate acoustic mode frequencies, it is often the case that a larger grid is used to reduce computational requirements. This is then corrected by imposing translational invariance which generally has a minimal effect on the frequency of optical modes. As can be seen in Fig. 2 this is not the case for these CASTEP calculations with frequency shifts of more than 1 THz. CASTEP seems to be particularly sensitive to FFT grid size. Therefore, it is important to check the convergence of phonon frequencies with FFT grid size, particularly as the lattice energies of all three unit cells are similar and none of the calculations show any imaginary frequencies. It's clear from Fig. 2 that when an appropriate FFT grid size is used then correlation between experiment and calculation is excellent. It should be noted that the inclusion of dispersion correction in this calculation is crucial and correlation between experiment and calculation is poor (not shown) if this is not the case.

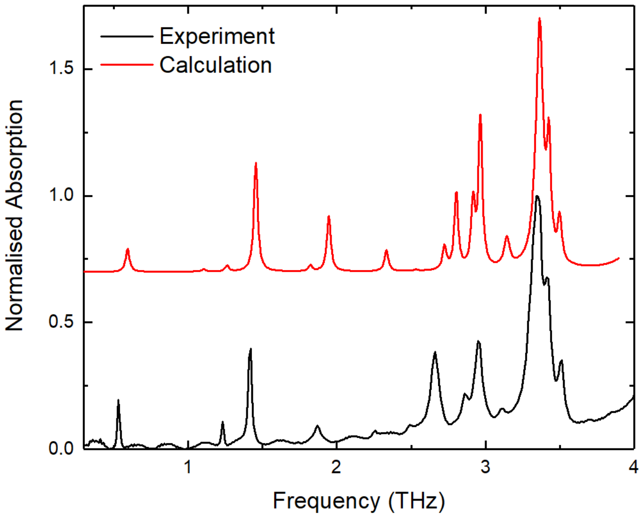

Fig. 3. Shows the experimental (black) and calculated THz spectra (red) of α-Lactose Monohydrate. Spectra were calculated using VASP and Phonopy.

Fig. 3 shows the experimental and calculated spectra of α-Lactose Monohydrate. The sample of α-Lactose Monohydrate is embedded in a matrix of PTFE with a 10% mass ratio of sample and cooled to 4 K using an Oxford Instruments Microstat-He fitted with two TPX windows. Here the geometry optimisation was performed using VASP [2] with the PBE [3] functional in combination with D3-BJ [6] dispersion correction and the PAW pseudopotentials included with the VASP distribution. Phonon frequencies were calculated using Phonopy [10] in combination with VASP with Born charges calculated separately within VASP by enabling the LEPSILON keyword. PDielec then combines these outputs to calculate the spectra shown in Fig. 3. The advantage of this method is that Phonopy can be used to calculate the phonon frequencies of very large systems very quickly while also having the advantage that the addition of the use of the quasi-harmonic approximation [11] to include temperature effects or the calculation of phonon lifetimes [12] to understand the experimental spectral widths is straightforward to implement in the future.

Fig. 3 shows excellent correlation between calculation and experiment. It's again important to note that the inclusion of the dispersion correction in this calculation, particularly for the lowest frequency modes which can shift by several hundred GHz when dispersion correction is not included.

III. SUMMARY

In summary, we explore various DFT programs, calculation parameters and sample environments to calculate the effective permittivity of a range of molecular crystals. In particular we show that while dispersion correction methods can cause a significant change to a calculated spectra the choice of a suitable correction method can significantly enhance the correlation between experimental and calculated spectra, and allow a full interpretation of the origin of all the spectral features in these complex spectra.

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