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Probing How Dynamics, Disorder and Temperature Influence the Vibrational Spectra of Molecular Crystals.

Andrew D. Burnett[1], Calum N. Towler[1], John Kendrick[1]
[1]School of Chemistry, University of Leeds, Leeds, West Yorks, LS2 9JT, UK

***Abstract*—It has long been known that THz spectra of molecular crystals is very sensitive to the long-range structure of these materials. Here using a combination of measurement and calculations based on Density Functional Theory we explore how spectra of these materials are influenced by temperature, molecular dynamics and disorder within the crystalline environment, and in many cases, how these effects are crucial to spectral interpretation.**

I. INTRODUCTION

THE THz spectra of molecular crystalline materials have long been shown to be sensitive to long-range order with a sensitivity to differences in polymorphs [1] that can rival X-ray based techniques [2]. This sensitivity comes in part because the THz measurement is influenced by the molecular dynamics in the crystalline environment. The majority of methods to calculate THz spectra of crystalline materials from first principles [3] use Density Functional Theory (DFT) that include no influence of temperature (in essence look to perform a calculation based on the crystalline material stable at 0 K), assuming both the harmonic approximation and relying on a perfect crystalline system. It is likely that many of these assumptions are incorrect, but the influence of each is difficult to unpick and can be material dependent. Here we look at two crystalline systems, α-lactose monohydrate and L-Cysteine. α-lactose monohydrate is now a commonly used THz standard, in particular because it has a sharp peak at 0.53 THz [4], which does not show any temperature dependence in either position, width or intensity while other modes in the spectra shift by 100s of GHz as the temperature of the material is altered. L-Cysteine is known to show significant disorder [5] in the crystalline structure because of the low energy barrier of torsional rotation between two stable configurations with the level of disorder decreasing with temperature. These two systems make excellent models to un-pick the influence of temperature, molecular dynamics and crystalline disorder on the resultant THz spectra.

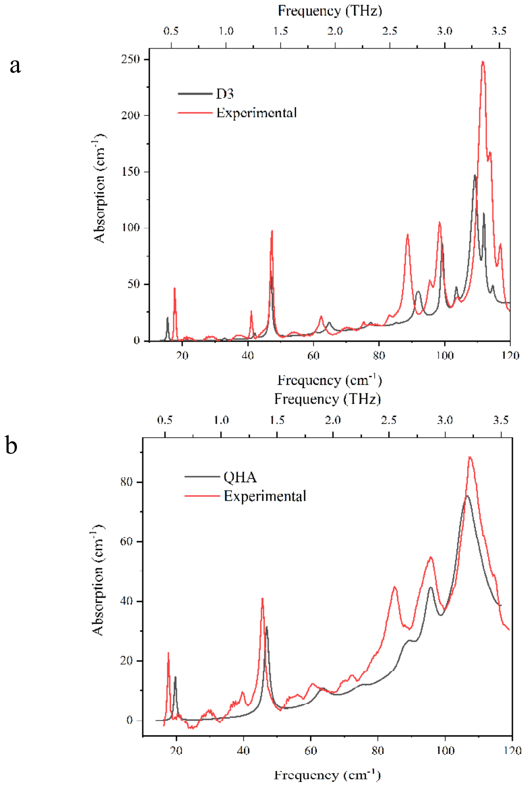

Fig. 1. Shows the THz experimental spectra of α-lactose monohydrate measured at (a) 4 K compared to a static DFT calculation assuming the harmonic approximation and (b) 293 K compared to a QHA generated spectra which takes into account the influence of thermal expansion of the crystalline lattice onto the calculated spectra.

Static DFT calculations were performed with the VASP package [6] using the Perdew-Burke-Ernzerhof (PBE) functional [7] and the Projector Augmented Wave (PAW) pseudo-potentials [8] distributed with VASP 5.4.1. Dispersion corrections (GD3/BJ) [9,10] are included in all calculations and are crucial to determining both the correct electronic and force convergence required to obtain sensible phonon frequencies that correlate with experiment. Both plane-wave cutoff and reciprocal space k-point resolution were determined for each material using convergence testing methods before any calculations were performed and convergence criteria chosen based on our previous work [11,12]. VASP was used for calculation of the Phonon frequencies for small unit cells while for larger cells Phonopy [13] was used (with VASP as the computational engine) to increase the efficiency and practicality of the calculations. Born charges and the high frequency permittivity of the cells were calculated using VASP. Phonopy was used to perform the Quasi-harmonic Approximation (QHA) calculations shown in Fig. 1b.

Dynamic DFT calculations were performed with CP2K package [14]. All calculations used the PBE exchange-correlation functional [7] along with the GD3/BJ dispersion correction [9,10]. The Molopt double zeta valence plus polarisation basis sets [15] were used with the GTH PBE pseudopotentials. [16]. Initial Molecular dynamics (MD) calculations to determine equilibration structures were performed using the Nose thermostat (to constrain temperature) and Nose-Hoover-Chain (to constrain pressure) with a time constant of 100 fs for both (time step = 0.5 fs). After equilibration the average cell dimensions were determined from a simulation of at least 3 ps which were then used in the NVT ensemble simulations. NVT equilibration was at least 2 ps before a production run of at least 30 ps. These MD simulations were then used to determine the calculated spectra of the material by calculation of the autocorrelation function of the cell dipole moment [17]. Previous MD based calculations have

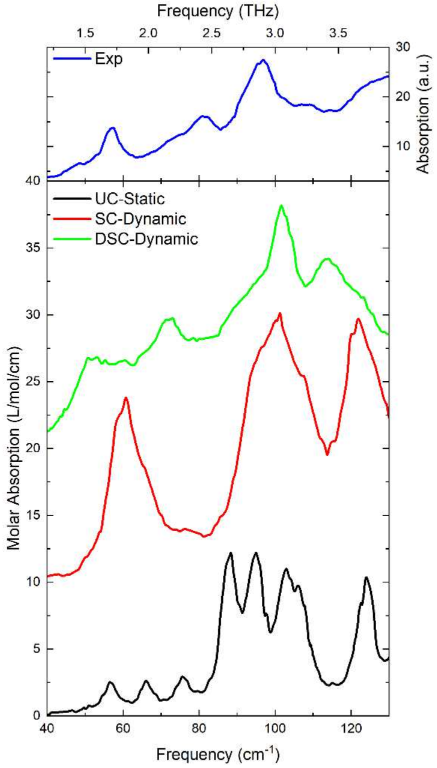

Fig. 2. Shows the calculated spectra for L-Cysteine for various dynamic and disordered models compared to experiment.

used the Travis code [18] to determine the THz spectra. This calculates the molecular dipole moment fluctuations by partitioning the electron-density using the Vornoi algorithm which leads to it ignoring interactions which are crucial to calculating a reasonable spectral response below 400 cm^{-1}.

II. RESULTS

Fig. 1a shows the measured spectra of α-lactose monohydrate recorded at 4 K compared to a static DFT calculation. Correlation between experiment and calculation is good, particularly below 2 THz with larger discrepancies at higher frequencies which tend to be the modes which show a larger temperature dependence. Fig. 1b shows the experimental spectra at room temperature compared to a second calculation using QHA. Here a series of static DFT calculations are performed at fixed volumes and used to determine the thermal properties of the material and in particular the thermal expansion of the crystalline lattice. From here a phonon spectra assuming harmonic motion but taking into account thermal expansion can be determined at any temperature with the spectra calculated at 300 K shown in Fig. 1b. While correlation is good, interestingly the low frequency modes have shifted too high in frequency suggesting a complex interplay between thermal expansion and other anharmonic effects are at play. The experimental mode at ~2.5 THz stands out as correlating poorly with either calculation and requires further investigation.

Fig. 2 shows the experimental spectra of L-Cysteine recorded at 83 K [19] compared to calculated spectra from; a static DFT calculation of the unit cell (UC-Static); a Dynamic calculation of a non-disordered supercell (8-molecules – SC-Dynamic) at 88 K; and a Dynamic calculation of a disorder supercell (32-molecules – DSC-Dynamic) at 88 K. There is very little correlation between the static calculation and experiment, even though at these temperatures there should be very little disorder. Including dynamics significantly improves correlation with experiment which is further improved by including crystalline disorder. Note that at higher frequencies all three simulations produce almost identical results.

ACKNOWLEDGMENTS

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DATA AVAILABILITY

Computational simulations for L-Cysteine are available from [20], other data available on reasonable request.

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