Phonon Kinetics at the Solid to Liquid Phase Transition

Alex Davie1, Farah Vandevvala2, Yanting Deng1, Deepu George1, Eric Sylvester3, Timothy Korter4, Erik Einarssson2, Jason Benedict3, Andrea Marke1

1Department of Physics, University at Buffalo, Buffalo, New York, United States
2Department of Electrical Engineering, University at Buffalo, Buffalo, New York, United States
3Department of Chemistry, University at Buffalo, Buffalo, New York, United States
4Department of Chemistry, Syracuse University, Syracuse, New York, United States

Abstract— Terahertz time domain spectroscopy is used to measure the melting kinetics of fructose molecular crystals. Combining single crystal anisotropy measurements with density functional calculations we assign the phonon frequencies and interrogate how specific phonons behave with melting. While nearly all the low frequency phonons continuously red shift with heating and melting, the lowest energy phonon polarized along the c-axis blue shifts at the melting temperature, suggesting an initial structural change immediately before melting. We find that the kinetics follow a 3D growth model with large activation energies consistent with previous DSC measurements. The large activation energies indicate multiple H-bonds must break collectively for the transition. The results suggest THz TDS with sub picosecond resolution could be used to measure ultra-fast kinetics.

I. INTRODUCTION

Phase transitions of molecular crystals are important to food production, pharmaceuticals and energetic materials. For pharmaceuticals, crystallization can lead to reduced efficacy, and for energetic materials the melt transition determines the energy release. For molecular crystals, weak hydrogen bonding is responsible for the crystal structure, leading to phonons in the far infrared or THz range. The majority of phonon studies of phase transitions have focused on the amorphous to crystalline transition [1-4] mainly due to the challenge of performing a melting measurement. The most significant challenge being how rapidly melting occurs. However molecular crystal transitions are sufficiently slow that rates can be measured with DSC and fast DSC even when samples are superheated. Recent measurements have suggested that a high number of H bonds are involved in the melting of both glucose and fructose and suggest that there may be structural change at the transition[5]. Here we use terahertz spectroscopy on single crystal fructose to examine how the crystal phonons evolve as through the phase transition.

II. RESULTS

We find phonons polarized along the a and b axes monotonically decrease in frequency as the temperature approaches melting and with melting whereas the lowest frequency phonon with symmetry along the c axis the red shifting halts at the melting temperature and the phonon then blue shifts and diminishes with amplitude with the loss of structure. We analyze the melting using an Avrami-Erofe’ev model where the integrated absorption line of a b-polarized phonon is used to determine the fraction of crystallinity. We find that the model is well fit by a nucleus growth model with n = 3, consistent with the polycrystalline DSC results. Further we find a melting rate $k = .0230 \text{min}^{-1} \pm .0024 \text{min}^{-1}$ which gives kinetic parameters consistent with DSC measurements.

References

[1] S. Engelbrecht, et al., "Monitoring the Isothermal Crystallization Kinetics of PET-A Using THz-TDS," Journal of Infrared Millimeter and Terahertz Waves, vol. 40, pp. 306-313, Mar 2019.
[2] N. R. Rexrode, et al., "Effects of Solvent Stabilization on Pharmaceutical Crystallization: Investigating Conformational Polymorphism of Probucol Using Combined Solid-State Density Functional Theory, Molecular Dynamics, and Terahertz Spectroscopy," Journal of Physical Chemistry A, vol. 123, pp. 6937-6947, Aug 2019.
[3] K. Shportko, et al., "Anharmonicity of the vibrational modes of phase-change materials: A far-infrared, terahertz, and Raman study," Vibrational Spectroscopy, vol. 95, pp. 51-56, Mar 2018.
[4] J. Sibik, et al., "Predicting Crystallization of Amorphous Drugs with Terahertz Spectroscopy," Molecular Pharmaceutics, vol. 12, pp. 3062-3068, Aug 2015.
[5] L. Liavitskaya, et al., "Melting kinetics of superheated crystals of glucose and fructose," Physical Chemistry Chemical Physics, vol. 19, pp. 26056-26064, Oct 2017.