MS35-P3 What happens when thermal motion is frozen? A case study of polymorph stabilities for Gallic Acid Monohydrate

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There is a paramount effort from both theoretical and experimental sides in establishing the structures and properties of all the polymorphs that a system can adopt. However, many theoretical studies, including crystal structure prediction (CSP) methods are typically performed at 0 K and effects of thermal motion are neglected. Because vibrational effects play an important role in assessing the stability of structure, the theoretically predicted structures are often not observed experimentally. A polymorph of gallic acid monohydrate (GAM) was a target of the fifth crystal structure prediction blind test.[1] Of the six targeted systems, GAM was the only one which could not be predicted in the lowest-energy range by any of the 14 contributing groups. Here we show that GAM is a very complex system, and the lack of predictability is due to the neglect of vibrational estimates, combined with the comparison with room-temperature structures. We demonstrate that target polymorph IV is commensurately modulated at 10 K and disordered at higher temperatures. The GAM system is enantiotropic, leading to changes in stability as a function of temperature. Single crystal high resolution X-ray data were collected at four different temperatures (10K, 95K, 123K and 175K). Accurate atomic and anisotropic displacement parameters were derived from aspherical atom refinement. The experimental data were further analysed by refinement of a lattice-dynamical model derived from periodic DFT/B3LYP calculations.[2] This combination of theoretical modelling and experimental data allows us to derive vibrational entropies, and to assess the free energies as a function of temperature. Furthermore, some of the H atoms were disordered, which explains why the predicted hydrogen-bond network was ambiguous. This disorder further helps stabilizing the structure by enhancing the entropy of the system. Therefore, comparing CSP determined at 0K with experimentally structures based on room temperature measurement can often be misleading and structures determined at lowest available temperature is vital for such studies.

References:

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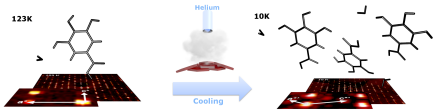

Figure 1. Gallic acid monohydrate form IV transformation under cooling. Three molecules are present in the assymetric unit at 10 K

Keywords: lattice-dynamic, vaibrational entropy