# MS35 Simulation of dynamics in molecular compounds

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## MS35-O1 Lattice Vibrations in Molecular Crystals: Polymorphism and Phase Transitions

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It is possible to predict how molecules will crystallise by performing an exhaustive search of all possible molecular packing alternatives and identifying the most energetically favourable crystal structures. The development of methods for Crystal Structure Prediction (CSP) is a rapidly growing field within computational chemistry. The most common methods rely on computing the cohesive energy between the molecules, while ignoring effects due to temperature and pressure. Lattice vibrational calculations can be used to account for thermal contributions to the lattice free energy and hence have the potential of improving the outcome of crystal structure predictions and may reveal the temperature-dependence of the stabilities of alternative crystal forms, such as polymorphs, cocrystals and solvates, see Figure 1.

We have implemented computationally very efficient methods that facilitate large scale application of harmonic and quasi-harmonic lattice dynamics to hundreds of polymorph pairs or to entire landscapes of predicted crystal structures. A benchmarked and highly accurate anisotropic force field is used to perform rigid-molecule vibrational calculations to obtain Gibbs lattice free energies of molecular crystals. Special care is taken in dealing with phonon dispersion in a way rarely affordable with electronic structure methods. Methods that dramatically improve the sampling of the first Brillouin zone will be presented.

I will also present results demonstrating that polymorphs of organic molecular crystals tend to have very similar thermochemical properties, which has important consequences for the prediction and development of molecular materials.

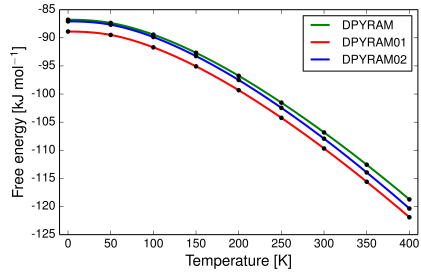


**Figure 1.** Lattice free energy curves of three polymorphs of 2,2'-dipyridylamine (CSD ref. DPYRAM) calculated with quasi-harmonic lattice dynamics in a highly accurate anisotropic force field.

**Keywords:** lattice dynamics, polymorphism, crystal structure prediction, phase transition, Brillouin zone integration