

Supporting Information for: “Intermolecular Anharmonicity in Molecular Crystals: Interplay between Experimental Low-Frequency Dynamics and Quantum Quasi-Harmonic Simulations of Solid Purine”

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1 Computational Details

A developmental version of the CRYSTAL14 software package was used for all simulations [1]. The all-electron def2-SVP basis set [2] was used and the Perdew-Burke-Ernzerhof (PBE) density functional adopted [3], as corrected for dispersion forces by means of the D3 correction by Grimme [4].

1.1 Structural Relaxation

The simulations were initialised from the experimental atomic coordinates and lattice parameters determined from single crystal X-ray diffraction (SCXRD) structures. A full structural relaxation of both atomic positions and lattice parameters was performed by means of the computational strategy described below. A quasi-Newton scheme for energy minimisation is implemented in the CRYSTAL program [5], which is based on the calculation of analytical energy gradients at each optimisation step [6–9]. The initial guess for the Hessian matrix of energy second derivatives is obtained through a classical force-field model as proposed by Schlegel [10]. During the optimisation, the Hessian is updated from the gradients by means of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [11–14]. At each cycle, a Newton step is evaluated, which, by default, is constrained to lie within the quadratic region of the potential energy hyper-surface by a “trust radius” technique, as proposed by Simons and Nichols [15]. Convergence of the optimisation process is checked on both gradient components and nuclear displacements with convergence thresholds on their root-mean-square set to 0.00001 and 0.00004 a.u., respectively. The optimised lattice parameters are $\mathbf{a} = 15.434 \text{ \AA}$, $\mathbf{b} = 9.184 \text{ \AA}$ and $\mathbf{c} = 3.558 \text{ \AA}$.

1.2 Basis Set

To investigate the effect of a larger basis set on the simulated structure, the triple- ζ 6-311G(2d,2p) basis set [16] was used. The result of this calculation did not significantly reduce the contraction of the unit cell, producing deviations of -0.24%, -1.83%, and -0.87% for the \mathbf{a} , \mathbf{b} , and \mathbf{c} axes, respectively. Given the significantly increased computational cost of the larger basis set, the def2-SVP basis set was used for all simulations.

2 Single Crystal X-ray Diffraction Details

Single crystals of purine were grown via sublimation of the as-received sample. The material was placed into a Sigma-Aldrich sublimation apparatus and evacuated using a standard laboratory vacuum pump. A cold finger was filled with solid carbon dioxide and the sample heated to 450 K under vacuum, and

within a few hours needle-like crystals of purine had formed on the cold finger. SCXRD experiments were performed at three temperatures (100 K, 200 K, and 300 K) on a Bruker KAPPA APEX DUO diffractometer with Mo K_{α} radiation, and full structural determinations were completed. The structures were solved using direct methods using the SHELXTL software,[17] with all non-hydrogen atoms first refined anisotropically followed by identification of the hydrogen atoms and isotropic refinement.

References

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