

Intermolecular dynamics in crystalline iron octaethylporphyrin (FeOEP)

Valeriia Starovoitova^{†*}, Graeme R. A. Wyllie[#], W. Robert Scheidt[#],
Wolfgang Sturhahn[§], E. Ercan Alp[§], and Stephen M. Durbin^{*}

^{*}Department of Physics, Purdue University, West Lafayette, Indiana 47907

[#]Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556

[§]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

[†] Current address: (Department of Physics, Idaho State University, Pocatello, Idaho 83201)

Abstract

Dynamical properties of the heme compound iron octaethylporphyrin (FeOEP) were previously determined by direct measurement of the Fe vibrational density of states with nuclear resonance vibrational spectroscopy (NRVS). A best-fit set of normal modes was calculated by comparing simulations using classical force fields to the NRVS results. Like all previous calculations of this type, a single isolated molecule was assumed, even though the data were from solid polycrystalline specimens. A complete three-dimensional crystal normal mode calculation reported here reveals that the previously neglected intermolecular couplings lead to a significantly better fit at low frequencies, and certain high frequency artifacts are removed as well. The off-diagonal coupling constants imposed by single molecule calculations prove to be unnecessary, indicating that these had served to simply emulate the missing crystal field effects. Dispersion curves also yield the speed of sound, which could be compared to the independently determined NRVS value to further fine-tune intermolecular force constants.