

# Vibrational Spectroscopy and Normal-Mode Analysis of Fe(II) Octaethylporphyrin

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## **Abstract:**

The normal-mode spectrum for the four-coordinated heme compound Fe(II) octaethylporphyrin, Fe(OEP), has been determined by refining force constants to the experimental Fe vibrational density of states measured with nuclear resonance vibrational spectroscopy (NRVS). Convergence of the calculated spectrum to the data was achieved by first imposing  $D_4$  symmetry on the model structure as well as the force constants, progressively including different internal coordinates of motion, then allowing the true  $C_i$  (or  $S_2$ ) point group symmetry of the  $C_i^1$  Fe(OEP) crystal structure. The NRVS-refined normal modes are in good agreement with Raman and IR spectra at high frequencies. Prior density functional theory predictions for a model porphyrin are similar to the core modes computed with the best-fit force field, but significant differences between  $D_4$  and  $C_i$  modes underline the sensitivity of porphyrin Fe normal modes to structural details. Some differences between the  $C_i$  best fit and the NRVS data can be attributed to intermolecular contacts not included in the normal-mode analysis