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### **Far Infrared Spectroscopy of Porphyrin Crystals**

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**Introduction:** Vibrational frequencies are widely used as markers for structural changes in biological molecules. In principle, vibrational frequencies of reactive modes should directly probe the curvature of the chemical reaction surface. However, reactive modes are notoriously difficult to detect and characterize in biological systems, partly because of competing absorption from water and partly because of the inherent weakness of thermal sources in the far infrared region. Using a synchrotron source, we obtained far infrared data on oriented single crystals of the iron porphyrin Fe(TPP)(NO<sub>3</sub>), which serves as a molecular model for the active site of heme proteins.

**Methods and Materials:** Crystals of Fe(TPP)(NO<sub>3</sub>) were mounted on a eucentric goniometer and indexed on a laboratory X-ray diffractometer in advance of synchrotron measurements. The goniometer was mounted on a motorized rotational stage with its axis parallel to the porphyrin planes.

**Results:** The absence of water or polypeptide absorption allows us to detect a number of low frequency vibrations of the porphyrin molecule. Interestingly, the frequencies differ from those observed on the same sample using nuclear resonance vibrational spectroscopy (NRVS), which is only sensitive to vibrational motion involving Fe. As a result, far infrared measurements provide a more complete picture of low frequency vibrations in this molecule. Measurements as a function of crystal orientation, which should be able to distinguish modes having transition dipoles parallel and perpendicular to the plane of the porphyrin molecule, did not follow the expected sine squared dependence below 200 cm<sup>-1</sup>.

**Conclusions:** Further studies will seek to uncover the source of this discrepancy and extend the measurements to a wider range of porphyrins.

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