Nuclear Resonance Vibrational Spectroscopy of Hemes—New Results for NO and CO Species

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Nuclear resonance vibrational spectroscopy (NRVS) is an emerging site-specific probe of active site vibrational dynamics in hemes and metalloproteins. NRVS is a synchrotron-based technique that uniquely targets the vibrations of a Mössbauer nucleus, such as ^{57}Fe, without interference from vibrations of other atoms, revealing not only the frequency, but also the amplitude, of all vibrations of the probe nucleus along the direction of the incident X-ray beam. We have applied NRVS, metal-based isotope-labeling Raman spectroscopy, and DFT calculations to further characterize the vibrational dynamics of iron in six-coordinate nitric oxide and carbonyl hemes. These studies have clarified the nature of the axial ligand vibrational assignments and character that appears to be a particularly difficult issue in six-coordinate species. Supported by: NIH GM-38401, GM52002, NSF 0240955, and DOE Contract No. W-31-109-Eng-38.