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Force Spectroscopy of Iron in Nitrosylated Hemes J.T. SAGE, A. BARABANSCHIKOV, W. ZENG, Northeastern University, N.J. SILVERNAIL, W.R. SCHEIDT, Notre Dame University — Nitric oxide (NO) regulates important physiological processes by interacting with the Fe atom in heme proteins. We investigate the effect of NO binding on the local structure and dynamics of ^{57}Fe by determining its vibrational density of states (VDOS), both experimentally, using nuclear resonance vibrational spectroscopy (NRVS) and computationally, using density functional theory (DFT). All Fe-ligand modes contribute to the VDOS, which provides uniquely quantitative information on the frequency, amplitude, and direction of the Fe motion. The VDOS also yields an experimental value for the stiffness, an effective force constant that probes nearest-neighbor interactions by measuring the force required to displace the Fe with the surrounding atoms fixed. Although vibrational mixing between Fe-NO stretching and FeNO bending character complicates structural interpretations of FeNO vibrations observed near 450 and 560 cm^{-1}, we find that the former mode contributes more strongly to the stiffness, indicating its sensitivity to the strength of the Fe-N bond. Comparison with DFT predictions identifies a feature observed near 130 cm^{-1} in the VDOS of nitrosylated myoglobin as a vibration of the covalent link to the protein. We find that NO binding alters the interaction of the heme Fe with its local environment, and may facilitate NO recognition by heme proteins.

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