Vibrational Dynamics of Iron in Biological Molecules

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Nuclear resonance vibrational spectroscopy (NRVS) is an emerging synchrotron-based technique that reveals the complete vibrational spectrum of a Moessbauer nucleus, based on ultrahigh-resolution X-ray measurements near the nuclear resonance. I will illustrate novel opportunities that this site-selective method provides for characterizing the vibrational dynamics of ^{57}Fe at the active sites of heme proteins, iron-sulfur proteins, and related model compounds. (1) Quantitative data on the frequency, the amplitude, and in some cases, the direction of all iron vibrations provide a uniquely detailed benchmark for modern quantum chemical vibrational predictions, with which they can be directly compared on an absolute scale. (2) Measurements on oriented single crystals of iron porphyrins reveal low-frequency out-of-plane vibrations that we identify with the long-sought heme doming mode, similar to the motion that takes place on oxygen binding to heme proteins. Moreover, the experimental data provide a direct experimental estimate of the force constant for Fe displacement normal to the heme plane and suggest that this Fe motion is an important element in protein control of biological reaction energetics. (3) Comparison with conventional Moessbauer measurements provides an experimental test for the activation of anharmonic dynamics near 200 K.