Vibrational Dynamics of Iron in Proteins

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High-resolution x-ray measurements near the nuclear resonance reveal the complete vibrational spectrum of a Mössbauer nucleus. 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) Comparisons with calculations and with independent Raman isotope shift measurements probes the extent to which active site vibrations couple to global protein motions.

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