Vibrational Spectroscopy in Metalloproteins

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In principle, vibrational spectroscopy can be used to probe the structure and dynamics of active sites in metalloenzymes, but the high density of protein vibrations (from parts of the molecule away from the active site), and the difficulty of interpreting the low frequency modes that are associated with metals have inhibited many applications. The large number of modes can be dealt with by using resonance Raman or nuclear resonance vibrational spectroscopy (NRVS) to selectively enhance modes at active sites. We have found that straightforward (albeit expensive) density functional (DFT) calculations can provide accurate enough results to be of real help in assignment and interpretation.

In my talk, I will give an overview of our collaborative studies with Steve Cramer (Univ. of California, Davis) to understand NRVS spectra in iron-containing proteins, including ferredoxins, nitrogenase, and an iron-only hydrogenase. NRVS is the vibrational analogue of Mossbauer spectroscopy, and it is notable that both frequencies and intensities of iron-related vibrations can (in favorable cases) be computed by DFT and used to interpret experimental results and to construct molecular mechanics force fields for use in molecular dynamics simulations. I will discuss the general nature of vibrations in iron-sulfur clusters [1], the expected effects of a central atom in the MoFe active site of nitrogenase [2], and the identification of Fe-H stretch and bend modes in iron-hydride complexes like those found in hydrogenases [3].

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[2]. Y. Xiao, K. Fisher, M.C. Smith, W.E. Newton, D.A. Case, S.J. George, H.Wang, W. Sturhahn, E.E. Alp, J. Zhao, Y. Yoda and S.P. Cramer. How nitrogenase shakes: Initial information about P-cluster and FeMo-cofactor normal modes from nuclear resonance vibrational spectroscopy (NRVS). J. Am. Chem. Soc. 128, 7608-7612 (2006).

[3]. Y. Guo, H. Wang, Y. Xiao, S. Vogt, R.K. Thauer, S. Shima, P.I. Volkers, T.B. Rauchfuss, V. Pelmentschikov, D.A. Case, E.E. Alp, W. Sturhahn, Y. Yoda, and S.P. Cramer. Characterization of the Fe Site in Methanothermobacter marburgensis Hydrogenase (mHmd) and a Model Compound via Nuclear Resonance Vibrational Spectroscopy (NRVS). Inorg. Chem. 47, 3969-3977 (2008).