X-ray Spectroscopy of Metal Sites in Proteins*

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EXAFS measurements constitute the vast majority of biological x-ray spectroscopy measurements. However, other x-ray techniques are now possible thanks to the continuing increase in flux available from synchrotron radiation sources. Soft x-ray absorption, x-ray magnetic circular dichroism, and high-resolution x-ray fluorescence can all provide information about electronic structure that complements the molecular structures determined from EXAFS. Over the past few years, we have developed instrumentation to enable these measurements on the dilute metals sites found in biological systems.

Sum rules are powerful tools for the interpretation of these x-ray spectra. The integrated intensities of L-edge spectra can be used to quantify the number of d-vacancies on enzyme metal centers. The integrated MCD intensity can be used to characterize the spin and orbital moments on these centers. Finally, the integrated intensity of certain fluorescence features can be used to characterize the filled valence orbitals. This talk will illustrate the application of alternative x-ray spectroscopies with recent results on Ni, Cu, and Mn enzymes.

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