Full Multiple-Scattering Calculations of Cu *K*-edge XANES in Bioinorganic Systems

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The x-ray absorption near-edge structure (XANES) region covers the low-energy part of the XAS spectrum, extending up to 50-150 eV above the rising edge. This region is particularly sensitive to the details of the geometric arrangement of scattering atoms around an absorber, such as symmetry, distances, and bond angles; therefore a recovery of the structural information from experimental spectra can in principle be achieved. A quantitative XANES analysis would greatly complement EXAFS studies on metal sites in biological systems, where the EXAFS signal is not very sensitive to the number of ligands and their chemical nature.

Whereas several codes for XANES calculations at different levels of theory have recently become available, their applications to bioinorganic systems need to be thoroughly tested and validated. We present here a detailed analysis of the Cu *K*-edge XANES spectra of a series of mononuclear copper complexes calculated by using the *ab initio* FEFF8.2 code. FEFF8.2 is based on a real-space, multiple-scattering approach and allows for the structural and electronic interpretation of the XANES peaks. The effect of the cluster size, final-state potential, presence of hydrogen atoms, and structural changes on the line shape of the XANES spectra has been evaluated, and the range of parameters required for an agreement between the experimental and theoretical data has been established. A high sensitivity of the calculated XANES features to small structural changes indicates the feasibility of using the FEFF8.2 code as a tool for elucidating the geometric structure of metal centers in model complexes and enzymes.

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