Electron Transfer Energies and Electron Binding Energies of Redox-Active Metal Sites in Biology

Dennis L. Lichtenberger and Nadine E. Gruhn.

Center for Gas-Phase Electron Spectroscopy, Department of Chemistry, The University of Arizona, Tucson, AZ, 85721

The functions of metals in the active sites of many biological species depend on electron transfer rates and electron binding energies associated with oxidations and reductions of chemical substrates. These functions are linked to the availability of various metal oxidation states, the specific metal electronic configurations, the bonding interactions of the metal with surrounding ligands, the delocalization of metal electron density, the electronic perturbations created by the active site environment, and other factors of electronic structure. Recently, we have been developing photoelectron spectroscopy to provide experimental *energy* measures of the electronic structure factors of biologically relevant metal sites. When applied to model complexes in the gas phase, the method provides well-defined and precise measures of electron binding energies that serve as excellent benchmarks for "gas-phase" electronic structure calculations. In addition, the method provides direct information on electron configurations, bonding influences, and electron delocalizations, as well as a unique energy measure of the parameters that control electron transfer rates in Marcus theory without the complications of solvent reorganization. Applications of the technique to study of the electronic factors of metalloporhyrins, molybdoenzymes, hydrogenases, and related molecules will be presented.