Poster Presentation

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Redox modulation of Low-Volume (100 µL) Solutions for XAFS measurements

S. Best[1], M. Islam[1,2], C. Chantler[2], J. Bourke[1]

[1]University of Melbourne, School of Chemistry, Melbourne, Australia, [2]University of Melbourne, School of Physics, Melbourne, Australia

A key to the understanding of transition metal catalysis is a detailed knowledge of the changes in coordination environment that accompany a change in redox state. The capacity of a given metal complex to support the high rates of electron transfer needed for effective catalysis is strongly dependent on the magnitude of structural reorganization coupled to the redox step. The ability of the ligand to control the dynamics of electron transfer is beautifully illustrated by copper redox proteins such as plastocyanin.[1] The polypeptide-imposed constraints on the environment at the coordination site of the metal minimize the structural change attendant on interconversion between the CuI and CuII redox states of the metal, facilitating fast electron transfer. Further, unravelling the molecular details of enzyme catalysis often hinges on knowledge of the structural changes attendant on oxidation or reduction. XAFS can provide the key structural information for reactive or unstable redox states of biological and abiological molecules. Our research has mostly centred on the use of a combination of spectroscopic and computational techniques to reveal the chemistry associated with dihydrogen activation in diiron compounds related to [FeFe]-hydrogenases [2], where a combination of XAFS, IR spectroscopy and theory can provide reliable structural information. Sampling of such species can provide a comparable challenge to spectral analysis – an issue made more difficult in cases where the quantity of sample is limited. We have developed low-volume electrosynthesis cells suitable for the study of electrogenerated species where the total volume of solution required for XAS data collection is of order 100 µL [3]. The design and operation of cells designed to allow freeze quenching and tow-temperature spectral collection or RT on-line measurement will be described.

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