Spectroscopic studies of intermediates in biological dinitrogen reduction

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The conversion of dinitrogen to ammonia is a challenging, energy intensive process, which is enabled biologically by the nitrogenase family of enzymes. The Mo-dependent nitrogenases contain two cofactors, the 8Fe-8S P-cluster and the Mo-7Fe-9S-C iron-molybdenum cofactor, known as “FeMoco”, which is the active site for dintirogen reduction. FeMoco has long been, and continues to be, an enigmatic cluster. Over 8 years ago the presence of a carbide in the cluster was first revealed. However, the role of the carbide, the role of the Mo heterometal, and the changes which occur at the seven iron sites during the course of catalysis all remain open questions. Herein, we present studies of selenium incorporated FeMoco. High-energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD XAS) at the Se K-edge is utilized to obtain selective information about the electronic structure of FeMoco. These studies reveal a significant asymmetry in the electron distribution within FeMoco, suggesting a much more localized electronic structure than typically assumed for iron sulfur clusters. Further XAS studies of both natively reduced and cryoreduced MoFe protein will be presented. These studies are essential for establishing the nature of the first redox event in the catalytic cycle of nitrogenase. The beamline instrumentation advances that are needed to further our understanding of biological nitrogen reduction will be highlighted.

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