

Insights into the Magnetic Coupling of Iron and Heterometal Atoms in FeMo and FeV Cofactor of Nitrogenase Enzyme

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The process of reducing dinitrogen (N_2) to ammonia (NH_3) is essential for producing fertilizers that feed the world's growing population. The cleavage of the N-N bond is achieved industrially in the Haber-Bosch process, while biological N_2 fixation is known to occur at the Fe_7MoS_9C and Fe_7VS_9C active sites of the nitrogenase enzyme (known as FeMo and FeV cofactors). Both processes operate with relatively high efficiency but at different thermodynamic limits: high temperature and pressure (Haber-Bosch) vs. ambient conditions for the biological reduction. These significant differences lead to a large interest in understanding the mechanism of biological nitrogen conversion in order to improve future industrial catalyst and processes.

Last years, X-ray spectroscopy brought new insight into the electronic structure of these enigmatic cofactors. The atomic composition was completed by revealing the central carbon in these clusters using X-ray emission spectroscopy (XES). Recent applications of High Energy Resolution Fluorescence Detected X-ray Absorption Spectroscopy (HERFD XAS) studies provided new insights into the oxidization state assignments of the heterometals in both cofactors as well as iron atoms oxidation state distributions. However, few questions about the electronic structure remained, including the magnetic coupling between iron and heterometal atoms in these cofactors. Both XAS and XES provide information about the average oxidation state (distribution) and/or spin state of the system. However, in order to get more quantitative and also elemental information more sophisticated, spin sensitive X-ray technique like $L_{2,3}$ -edge X-ray Magnetic Circular Dichroism (XMCD) is required. Although this technique was previously widely applied in solid state physics, there are relative few examples of XMCD application to (bio-) inorganic systems.

A systematic study of Fe $L_{2,3}$ -edge XAS and XMCD data on a set of iron molecular complexes of increasing complexity (spanning from mononuclear, through dinuclear complexes to heterometal, tetranuclear structural model complexes of nitrogenase cofactors) will be presented. The influence of oxidation state changes as well as ligation on the shape and energy of $L_{2,3}$ -edge XAS and XMCD spectra will be discussed. The presented results will be extended to data obtained on intact nitrogenase enzymes. Additionally V and Mo $L_{2,3}$ -edge XAS and XMCD data on structural model complexes of nitrogenase as well as intact protein will be shown. The discussed data will provide insights into the magnetic coupling of iron and heterometal atoms in FeMoco and FeVco. The presented study will also show the first experimental evidence of a non-standard spin configuration at both V and Mo atoms in FeMoco and FeVco.

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