O-08   **Session B, Tuesday, 14.06., 12²⁰ - 12⁴⁰**

Fe X-ray Absorption and X-ray Magnetic Circular Dichroism Studies on FeMo cofactor of Nitrogenase and Related Models

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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. Nowadays, the cleavage of the N-N bond is achieved industrially using heterogeneous catalysts in the Haber-Bosch process, while biological N_2 fixation is known to occur at the FeMo cofactor of nitrogenase enzyme found in diazotrophs. Although, both processes operate with relatively high efficiency, they require different thermodynamic limits: high temperature and pressure for the industrial process vs. ambient conditions for biological nitrogen 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.

The active site of nitrogenase is a $MoFe_7S_9C$ cofactor (FeMoco, Figure 1), which has brought out a fair amount efforts in understanding its' geometrical structure [1], however there's still a lack of information to complete the electronic structure of this complex system.
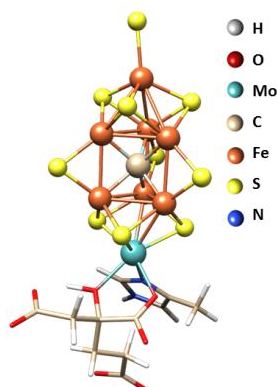

Figure 1. Structure of the FeMo cofactor of nitrogenase.

The current goal is to provide insights into the iron oxidation state distribution and magnetic coupling within this cofactor.

Recently applied X-ray spectroscopic studies revealed the presence of a central carbon in this cluster and also the Mo atom as Mo(III).[2,3] Based on these results, together with the EPR total spin of 3/2, three main oxidation state scenarios have been proposed, that need experimental verification. Therefore, we have utilized high energy resolution fluorescence detected (HERFD) X-ray absorption spectroscopy (XAS) on Fe K-edge to address this question. Although HERFD XAS allows one to obtain spectra with the energy resolution below the Fe 1s core hole lifetime, the presence of 7 iron atoms as well as lack of magnetic information limits the analysis of such spectra (Figure 2). A way to overcome these limitation is to apply L-edge XAS and also X-ray magnetic circular dichroism (XMCD) spectroscopy at the $L_{2,3}$-edge that enabling more quantitative assessment of the obtained data.

Fe K-edge HERFD XAS, L-edge XAS and XMCD data on model compounds and FeMoco will be presented. The observed trends upon oxidation state changes and ligand environment will be explained based on the changes in electronic structure of the studies systems. Moreover, the experimental data will be supported with theoretical calculations indicating possible scenarios of Fe oxidation state distribution in FeMoco.
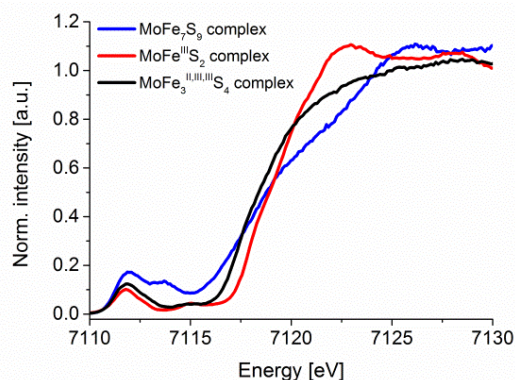

Figure 2. Fe HERFD XAS spectra of monomeric, tetrameric Mo-Fe-S model complexes and FeMoco.

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