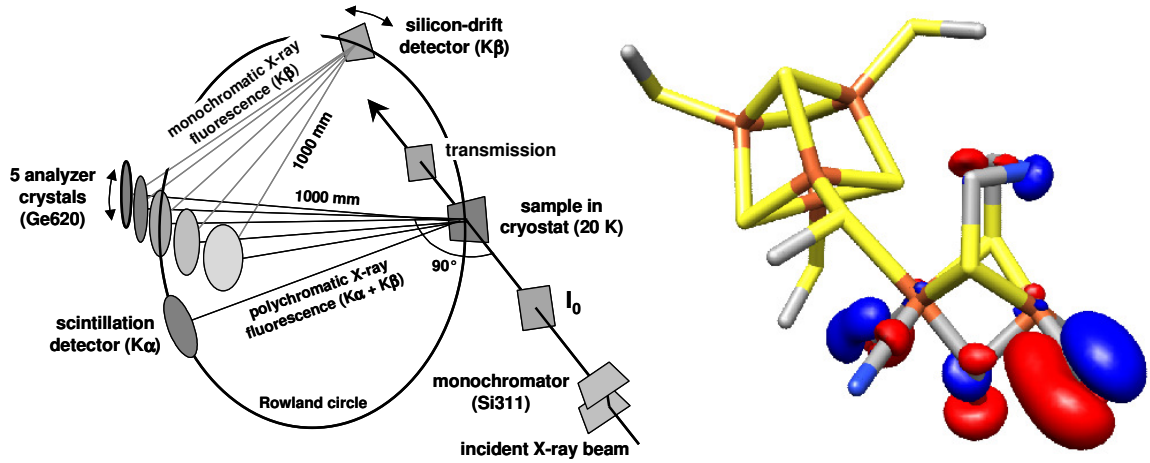
Iron centers in FeFe hydrogenase and biomimetic coordination complexes studied by XAS/XES and DFT: hydrogen catalysis and oxygen inhibition



Setup for high-resolution XAS/XES at ESRF (left) and molecular orbitals from DFT calculations on the H-cluster of [FeFe] hydrogenase (right).

Summary:

Understanding the mechanism of molecular hydrogen (H_2) production at iron centers and inhibition of this reaction by oxygen (O_2) is an important topic in sustainable energy research. [FeFe] hydrogenase proteins are the most efficient biological H_2 catalysts, which contain a six-iron active site ([4Fe4S]-2Fe_H) denoted as H-cluster. Synthetic chemistry has produced coordination complexes, which mimic structural features of the diiron sub-cluster in the enzymes, but often show unsatisfying activity and stability. Mechanistic bottlenecks of the reactions in [FeFe] hydrogenase and diiron model complexes will be studied, employing high-resolution X-ray absorption and emission spectroscopy (XAS/XES) in combination with density functional theory calculations (DFT).

Intermediates in the H_2 cleavage/production and O_2 modification processes are characterized using XAS/XES to determine their molecular structure (metal-ligand bond lengths; metal-metal distances; ligation changes; substrate interactions; reactive oxygen species formation) and electronic configuration (metal oxidation state; spin state; molecular orbitals structure, occupancy, and energy; HOMO-LUMO energy gap). Site-selective XAS/XES methods are developed and applied for the discrimination of individual iron species in the polynuclear complexes. By DFT the spectroscopic results are integrated in geometry-optimized structural models and quantitatively interpreted in terms of the electronic structure, which are related to the H_2 and O_2 reaction pathways.

Comparative investigations on [FeFe] hydrogenase and model complexes will lead to an advanced understanding of the specific prerequisites of H_2 turnover and O_2 inhibition at the molecular level. In addition, the XAS/XES-DFT approach for the study of metal centers in biology and chemistry is further developed. General insights into routes towards more efficient H_2 formation and increased O_2 tolerance will be obtained, which will be tested in genetically engineered hydrogenase and tailored synthetic diiron catalysts.