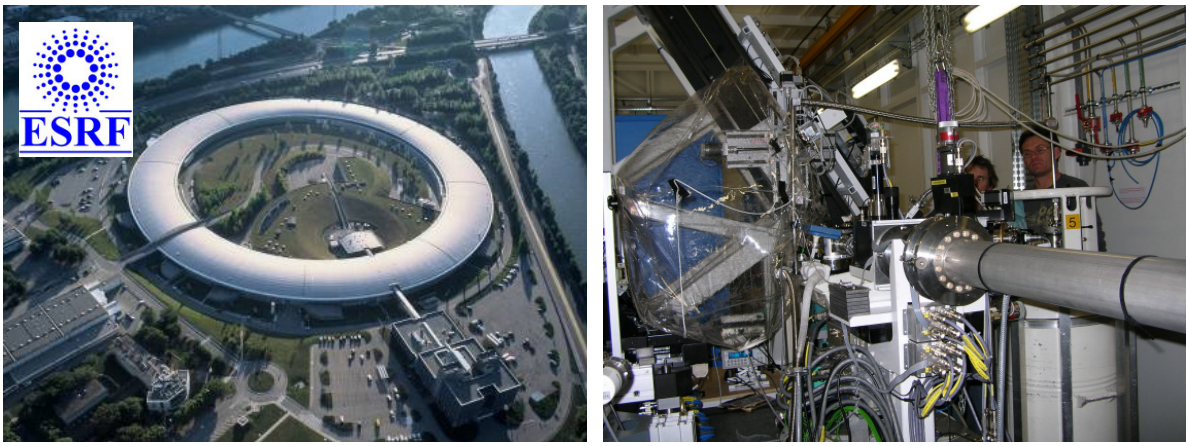
High-resolution time-resolved XAS/XES on high-valent metal sites in H_2O, O_2, and H_2 activating enzymes



XAS/XES spectrometer at beamline ID26 (right) of the ESRF (left).

Summary:

Combining high-resolution and time-resolved X-ray absorption (XAS) and emission (XES) spectroscopy techniques offers exciting perspectives to gain novel information on molecular structure, electronic configuration, and dynamics of metal centers in biological enzymes and synthetic coordination compounds, to unravel the catalytic mechanism. Currently, a worldwide strive for new catalysts is ongoing, aiming at solar-driven hydrogen (H_2) production using electrons from water cleavage into protons and dioxygen (O_2), as a sustainable energy source for the future.

In this project, we study three different systems of high relevance in this context, which catalyze water oxidation, oxygen activation, and hydrogen formation, namely the manganese complex of photosynthesis, manganese-iron and iron-iron centers in ribonucleotide reductases, and nickel-iron and iron-iron centers in hydrogenases. The catalytic centers feature different coordination environments of the metal ions (i.e. covalent and ionic ligands) and show different degrees of sensitivity towards X-ray induced modifications (metal ion reduction). We will focus on the development and application of resonant inelastic scattering (RIXS) techniques at the K-alpha and K-beta emission lines, measurements of valence-to-core transitions (K-beta satellite lines), and their combination with time resolved approaches, to follow changes in molecular and electronic structure and, e.g. metal-substrate interactions during state transitions of the metal centers in the enzymes. State transitions will be induced using laser flash excitation of enzymes in the X-ray beam and by (electro)chemical approaches. Changes in the XAS and XES spectra during the state transitions will be followed with microsecond resolution in timescan and pump-probe experiments.

Measurements are carried out at beamline ID26, where a new XAS/XES spectrometer is available. During the project, the spectrometer will be improved particularly for measurements on ultra-dilute protein samples. Novel X-ray techniques will be developed and applied for use in a large scientific community also on other systems. We expect that unprecedented information on the structure and dynamics of small molecule (H_2O, O_2, H_2) activation at biological and synthetic metal centers will become available, which provides new insights into the mechanisms of catalysis.