# Ultrafast and site selective X-ray pump/ X-ray probe photoemission experiment on CO

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X-ray Free Electron Lasers (XFELs) are a new generation of x-ray sources, offering highly coherent, intense x-ray pulses with pulse lengths down to a few femtoseconds. Recently, XFELs proved the ability to produce two intense femtosecond x-ray pulses with controlled time delay and color. This opened the possibility of carrying out time-resolved studies of complex x-ray induced phenomena with x-ray pump / x-ray probe schemes. The combination of this unique capability with X-ray photoelectron spectroscopy (XPS), enables time-resolved XPS experiments with chemical or even site specificity and femtosecond time resolution. This allows us to observe electronic and nuclear dynamics out of equilibrium and to see how a local excitation “travels” over molecule in real time.

We will present first x-ray pump / x-ray probe XPS experiments aimed at studying energy flow and relaxation dynamics in CO, i.e., small heteronuclear molecules, in the gas phase. We used two x-ray pulses to first excited a core-electron resonantly at the oxygen K-edge and then probed the molecular response with photoemission from the carbon core levels with a second x-ray pulse. The data gives a glimpse of electronic and nuclear relaxation pathways proceeding on time scales <40 fs.

The experimental efforts are accompanied by theoretical work developing a model for the time-resolved core-level photoemission based on the time-dependent Schrödinger equation. This model takes into account the full quantum-mechanical nuclear propagation, as well as Auger decay in the first few femtoseconds. With that a prediction of the core-level shifts for x-ray excited and fragmenting molecule can be calculated for the first 50 fs. These experiments lay the ground for further time resolved photoelectron spectroscopy following energy and charge transfer process upon photoexcitation in more complex molecules.