The possibility to obtain time-resolved information on single molecules with Angstrom spatial and femtosecond temporal resolution (i.e. recording the so-called “molecular movie”) is one of the driving forces for the development of short-pulse VUV and X-ray sources such as Free-Electron Lasers (FELs). While coherent diffractive imaging, even though still facing many challenges, certainly appears to be a promising avenue to study larger (nano-scale) structures, time-resolved photoelectron diffraction is another viable and, in many respects, complementary option. The site-selectivity of the inner-shell photoemission process allows selectively probing the local environment of the emitter, and Angstrom-resolution can already be obtained with photon energies ~100 eV above a given inner-shell threshold. The photoelectron diffraction technique is especially valuable for investigating fundamental chemical reaction dynamics in small to medium-sized organic molecules, which are hard to probe by coherent imaging due to the low target density in a supersonic jet and the small X-ray scattering cross sections for low-Z molecular constituents.

Figure 1: Experimental setup. The molecules, aligned by the YAG laser, are dissociated (or Coulomb exploded) with a femtosecond Ti:Sa laser and then photoionized by the FEL for different delays between Ti:Sa and FEL. Photoelectrons and fragment ions are recorded with a Velocity Map Imaging (VMI) spectrometer.
As the typically random orientation of gas phase molecules averages out most of the intensity variations in the photoelectron angular distribution, we investigated laser-aligned [1] molecules. Static and time-resolved photoelectron angular distributions of adiabatically laser-aligned carbonyl sulfide molecules (OCS) were measured at FLASH. A double-sided velocity map imaging (VMI) spectrometer was installed in the CFEL-ASG MultiPurpose (CAMP) chamber [2] to record sulphur 2p photoelectrons and fragment ions. The molecules were introduced into the chamber as a cold molecular beam produced by a pulsed Evan-Lavie nozzle and were adiabatically laser-aligned (see Figure 2) by a ~10 nanosecond Nd:YAG laser pulse synchronized to the FEL.

Time-resolved photoelectron angular distributions were recorded by dissociating (or Coulomb exploding) the molecules with a femtosecond Ti:Sa laser pulse prior to the FEL ionization. By varying the delay between Ti:Sa pump and FEL probe pulse, a “molecular movie” of the dissociation reaction can be produced. Figure 3 shows the photoelectron distributions of aligned molecules for different time delays between Ti:Sa and FEL. A clear difference is observed for different delays and further data analysis is on-going. Through comparison of the recorded molecular-frame photoelectron distributions with multiple scattering calculations [3], we can relate them to the geometric structure of the molecules. This offers a structure-sensitive method to image molecules “from within”.

Figure 3: Sulphur 2p photoelectron angular distributions for aligned OCS molecules. Left: Ti:Sa hits molecules 1ps before the FEL. Centre: Ti:Sa hits molecules 1ps after FEL. Right: Difference “TiSa 1ps before FEL” minus “Ti:Sa 1ps after FEL”. A time dependent change of the photoline (blue ring) is visible in the difference picture. The signal in the centre of the three images is due to slow electrons from Ti:Sa-induced ATI, YAG post-ionization of FEL excited molecules, and Auger processes.

References