

Time-Resolved Photoelectron Diffraction from Laser-Aligned Molecules at FLASH

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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.

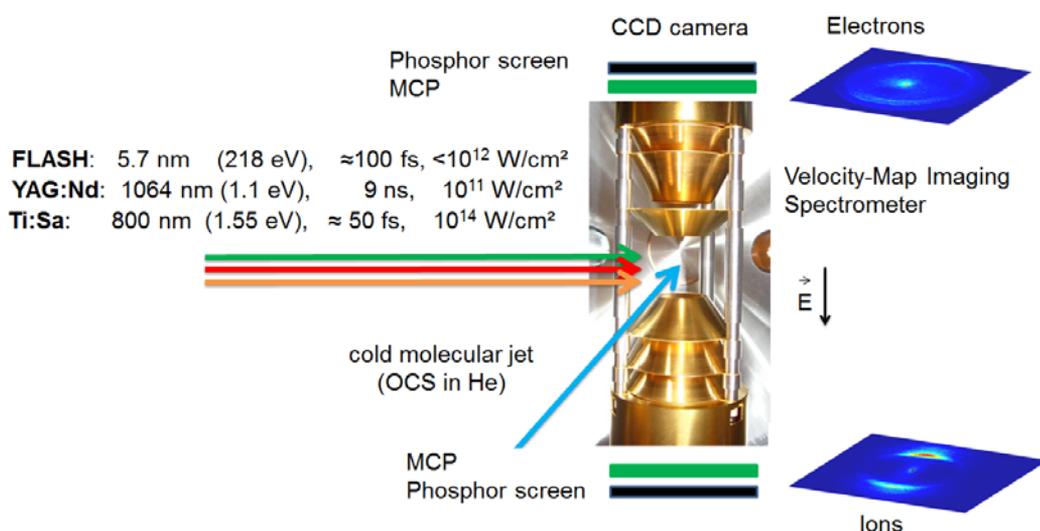


Figure 1: Experimental setup. The molecules, aligned by the YAG laser, are dissociated (or Coulomb exploded) with a femtosecond Ti:Sa laser and then photoionized by the FEL for different delays between Ti:Sa and FEL. Photoelectrons and fragment ions are recorded with a Velocity Map Imaging (VMI) spectrometer.

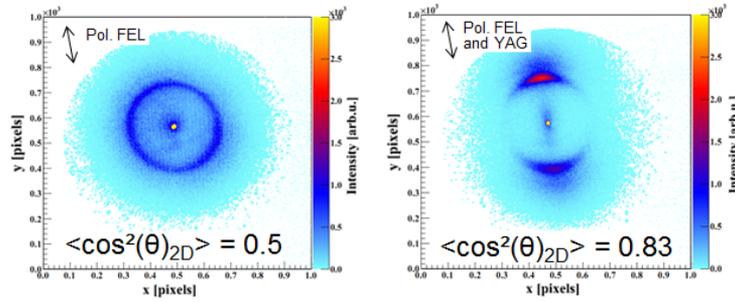


Figure 2: Ion angular distribution of S^+ fragment ions from randomly oriented (left) and aligned (right) carbonyl sulfide molecules (OCS) probed by VUV photons (218 eV, 5.7nm) from FLASH. The molecules in the right image were adiabatically aligned in the electric field of a ~ 10 ns long Nd:YAG pulse. In the centre slow background ions can be seen. The outer ring shows detected S^+ ions. Left: The alignment laser is switched off and the S^+ ions are isotropically distributed. Right: The molecules are aligned along the polarization axis of the Nd:YAG laser.

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”.

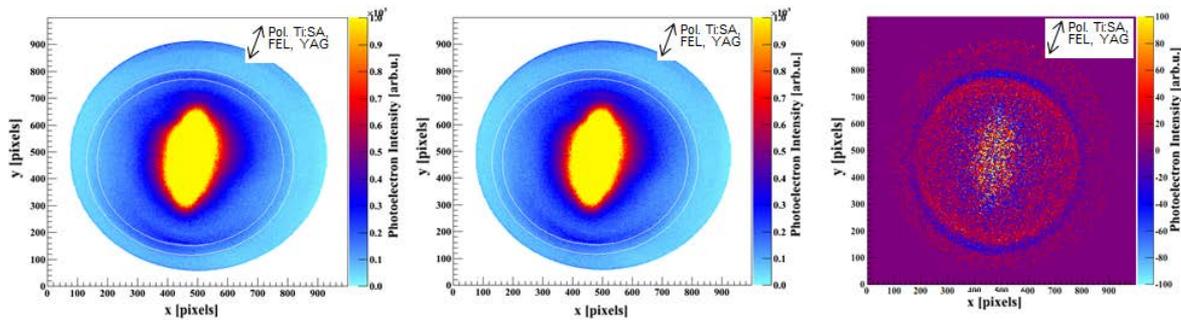


Figure 3: Sulphur 2p photoelectron angular distributions for aligned OCS molecules. Left: Ti:Sa hits molecules 1ps *before* the FEL. Centre: Ti:Sa hits molecules 1ps *after* FEL. Right: Difference “TiSa 1ps before FEL” minus “Ti:Sa 1ps after FEL”. A time dependent change of the photoline (blue ring) 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

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- [2] L. Strüder *et al.*, *Nucl. Instr. and Meth. in Phys. Res. A* **514**, 473 (2011).
- [3] F. J. Garcia de Abajo *et al.*, *Phys. Rev. B* **63**, 075404 (2001).