Ultrafast Structural Changes in Chiral Molecules Measured with Free-Electron Lasers

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Synopsis (X-ray) free-electron lasers are employed to site specifically interrogate atomic fragments during ultrafast photolysis of chiral molecules via time-resolved photoelectron circular dichroism.

The method of photoelectron circular dichroism (PECD) has been shown to be a powerful tool for chiral recognition over the last two decades[1, 2]. It provides up to orders of magnitude stronger effects than normal CD. The observable forward-backward asymmetry in the angular distribution of photoelectrons emitted from a chiral system is very sensitive to the electron energy and also to (ultrafast) changes of the underlying charge distribution. This has been demonstrated for vibrational excitations[3], multiphoton interactions[4] and ultrafast structural changes[5]. Such exceptional sensitivity of PECD opens unique perspectives for addressing nonlinear and ultrafast phenomena with VUV and X-ray free-electron lasers that can uniquely enable site selective interrogation of an observing (e.g. dissociating) atomic site. However, such pump-probe experiments on chiral systems are challenging in terms of their technical, physical and (stereo-)chemical complexity.

In the presented work, we show first approaches from the free-electron lasers LCLS (USA) and FLASH (Germany) to measure the time-resolved (TR-)PECD in chiral model systems, i.e. trifluoromethyloxirane ($C_3H_3F_3O$)[6] and iodomethylbutane($C_5H_{11}I$), respectively.

To measure the TR-PECD of these prototypical chiral molecules during (UV) laser or X-ray triggered fragmentation (pump), highly intense, circularly polarized XUV free-electron laser pulses were used as probe. The presentation will primarily focus on a recent experiment at FLASH (10/2018), where we employed a two-sided velocity map imaging spectrometer in order to obtain electron-ion correlations from a dissociating chiral system. In this case, atomic iodine is ejected from enantiomeric iodomethylbutane, serving as dynamic observer site for monitoring the evolving chirality of the residual molecule on a femtosecond timescale.

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