Measuring Valence Wavepackets with Attosecond XFEL Pulses

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Coherent superpositions of electronic states in molecules, *i.e.* electronic wavepackets, are capable of attosecond dynamics because of their large (>1 eV) coherent energy bandwidth. To differentiate it from charge transfer mediated by nuclear dynamics, this has been referred to as purely electronic charge migration; however, it is now understood that due to coupling between electronic and nuclear degrees of freedom, nuclear motion and the spread of nuclear geometries play a significant role in charge migration. The same electonic-nuclear coupling may lead to different long-term structural outcomes for molecules where an electronic wavepacket is excited and which depend on the initial shape and coherence of the wavepacket.

With attosecond soft X-ray pulses, one- or two-photon interactions can be used to excite and measure electronic wavepackets. Although this is possible with tabletop sources using HHG, excitation fractions are too low for X-ray pump, X-ray probe schemes, and they are typically restricted to cationic wavepackets either created or measured via strong-field ionisation. With this in mind, we have developed techniques for exciting and measuring electronic wavepackets on the attosecond timescale using X-ray free electron laser sources, and used them to probe small molecular systems.

In an all-X-ray transient absorption experiment, a single-photon X-ray interaction ionises, creating a valence hole wavepacket. This valence wavepacket can be probed using a second single-photon interaction resonant with a core-to-valence excitation, creating a core hole which subsequently decays and emits an Auger electron. We have used this Auger emission to probe few-femtosecond transient wavepackets in gas-phase isopropanol and few-hundred to few-femtosecond transient wavepackets in aminophenol, and explored the effects of electronic-nuclear interaction on decoherence.

We have also used stimualated X-ray Raman scattering (SXRS), a two photon X-ray interaction which can excite valence states in neutral molecules. In the impulsive case (ISXRS), this is faster than the electronic response of the system and can be used to excite coherent charge wavepackets. Specifically, we have investigated signatures of ISXRS in micrometre thick liquid water samples through the transmitted X-ray spectrum of 350 attosecond pulses tuned below the oxygen K-edge and found evidence of a nonlinear emission spatially collinear with the XFEL pulses, which we attribute to ISXRS.