New opportunities in the measurement of electronic and electron-nuclear coupling dynamics with attosecond X-ray pulses

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Time-resolved x-ray spectroscopy provides sensitivity to both the localized electronic excitation and electron-nuclear couplings in matter. We have used ultrafast x-ray pulses from both HHG sources and XFELs to study these dynamics in molecular cations and organic semiconductors. This provides not only an incisive probe of electron dynamics on the timescale of electron coherences (<10 fs) but also the unfolding electron-nuclear coupling to vibrational modes over longer timescales. Using a HHG source to generate water window sub-femtosecond pulses [1] we have probed the exciton dynamics in the organic semiconductor polythiophene (P3HT). We observe the signature of atomically resolved electron density changes following exciton formation, and also a transient pre-edge feature attributed to the initial delocalization of the exciton across neighboring polythiophene chains [2]. Electronic dynamics in inner valence states of molecular cations of isopropanol and glycine are probed using an x-ray pump-probe methodology at LCLS and FLASH using few-fs pulses. In isopropanol we capture breathing mode charge migration dynamics of the excitation formed in a superposition of single hole and 2 hole- 1 particle states [3] which is a signature of frustrated Auger-Meitner decay. In glycine we observe oscillatory signatures of charge migration at early times (to 20 fs) that apparently couple to vibrational motion over longer timescales [4]. We report the use of XLEAP (attosecond) pulses at LCLS to excite electronic impulsive x-ray Raman in liquid water with the Raman signature observed in the transmitted x-ray spectrum.

References

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