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The first few femtoseconds: using attosecond spectroscopy to understand how electronic excitation leads to photochemistry

Laboratory scale setups driven by ultrafast lasers are now capable of generating coherent valence-electronic excitations spanning approx. 1 eV in biomolecules, and probing the resulting dynamics with synchronized pulses in optical or soft x-ray wavelengths. The hope of such experiments is to answer long-standing questions of how these excitations influence nuclear motion and further relaxation pathways of the molecule. However, their interpretation is complicated by limitations in the pump and probe steps. A prominent example is the few-fs temporal beating in the laser-assisted fragmentation distribution of a biomolecule after ionization by a sub-fs XUV pulse. The large number of accessible cationic states combined with the complexity of the fragmentation process poses significant theoretical challenges. In the first part of my talk I will discuss how further development of lab-scale setups will allow more controlled excitation and more direct probing in biomolecules, and speculate on the future state-of-the-art in laser-based attosecond photochemistry experiments in the coming decade.

The second part of my talk will examine possibilities offered by LCLS-II for these kinds of experiments. Provided sufficient soft x-ray bandwidth is available, transient absorption spectroscopy may be possible at much higher repetition rates, and the increased flux raises the possibility of inelastic Raman x-ray emission. The possibility of hard x-ray scattering for probing nuclear positions would be a powerful complement to laser-based approaches. Regardless of the probing method, synchronized, tunable pumping of valence excitations will remain essential. Whilst approaches involving core excitations such as stimulated x-ray Raman spectroscopy have great promise, optical/UV pumping with synchronized lasers poses fewer FEL challenges and more directly addresses questions of photochemical dynamics, and will be highly beneficial in connecting LCLS-II to setups based on ultrafast lasers.