

Capturing Elusive Reaction Intermediates with Ultrafast X-ray Spectroscopy

Observing light-induced chemical reactions on the timescales during which they occur has been a long-standing objective since it is an effective route to understand mechanistic details at the molecular scale. This understanding can then inform rational design of new molecules for applications such as, for instance, light harvesting and energy conversion, as well as illuminate new means of controlling reactions to yield more of a desired photoproduct or to inhibit unwanted reactions. Much of chemistry happens in liquids and so the ability to observe reactions in these disordered environments is highly desirable. Time-resolved techniques using ultraviolet, visible, and infrared light have proven to be powerful. Over the last decade or so, time-resolved x-ray spectroscopy has emerged as a valuable complementary technique that can overcome some limitations of the other methods and bring new insight. Around the world, many x-ray facilities providing the requisite high flux and short duration pulses are being upgraded or newly built, making it an exciting time for time-resolved x-ray science. In this talk I will discuss what makes x-rays so powerful for probing photochemical reactions and will highlight two recent experiments carried out by our group and collaborators at the LCLS, the x-ray free electron laser at SLAC in California, and at the Advanced Photon Source, the synchrotron facility outside of Chicago. At the LCLS we tracked, with femtosecond resolution, the early-time dynamics of ionized liquid water [1] and at the APS, characterized on the picosecond timescale the elusive intermediate in the ligand exchange reaction of aqueous ferrocyanide [2].

[1] Z.-H. Loh *et al.*, "Observation of the fastest chemical processes in the radiolysis of water," *Science* **367**, 179 (2020).

[2] A. M. March *et al.*, "Elucidation of the photoaquation reaction mechanism in ferrous hexacyanide using synchrotron x-rays with sub-pulse-duration sensitivity," *J. Chem. Phys.* **151**, 144306 (2019).