Picosecond and sub-picosecond structural dynamics of a photoexcited organic chromophore in solution investigated using time-resolved X-ray scattering

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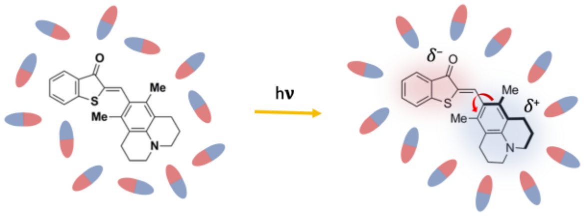
Photoinduced electron transfer and changes in molecular geometries are involved in many fundamental biological processes, such as vision and photosynthesis, and are also relevant for applications within e.g. optoelectronics, phototherapy, and solar energy conversion.[1] Novel molecular systems based around hemithioindigos compounds with electron-donor substituents have recently attracted significant attention for their versatile functions, which have been demonstrated to depend on the molecular environment: photoswitching through photoisomerization in apolar solvents, and electron transfer/internal molecular rotation in polar solvents.[2,3] To disentangle the influences from intramolecular and solvation shell dynamics coupled to intramolecular charge transfer, we investigated a hemithioindigo with a structurally rigid and strong electron-donor julolidine group (HTI-J) in the highly polar solvent acetonitrile. We measured the femto- to picosecond structural response of HTI-J in acetonitrile in an optical laser pump, X-ray probe experiment at an X-ray Free Electron Laser (XFEL). Unlike previous ultrafast X-ray solution scattering experiments, the investigated system does not contain heavy, highly scattering elements. In this poster contribution, I will explain our experimental method, show the data obtained in the beamtime and the results of our preliminary data analysis. This analysis aided by DFT calculations and molecular dynamics simulations reveals the rearrangement of the solvation shell triggered by photoinduced charge transfer in the HTI-J organic chromophore.



Scheme 1: Schematic of the charge redistribution of HTI-J in a polar solvent following photoexcitation. Open questions include the single bond rotation, the charge redistribution in the intramolecular charge transfer state and the time scales of the photoreaction steps.

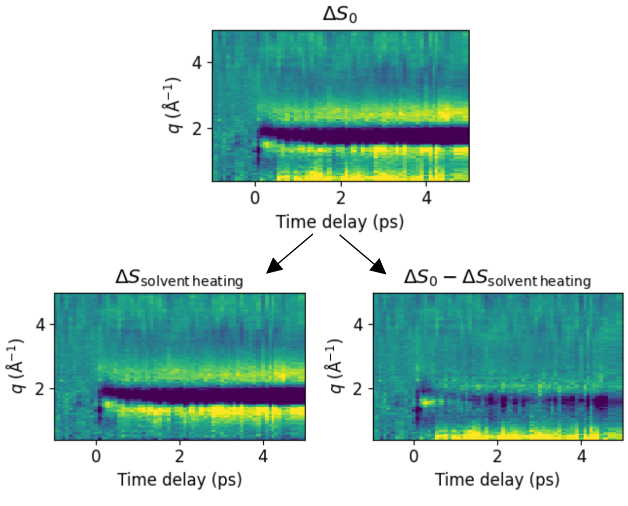


Figure 1: Isotropic difference scattering signal as a function of the scattering vector *q* and the time delay of HTI-J in acetonitrile obtained at the Alvra Endstation at SwissFEL. Removing the solvent heating reveals underlying signal contributions.

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