TRACKING STRUCTURAL SOLVENT REORGANIZATION AND RECOMBINATION DYNAMICS FOLLOWING ELECTRON PHOTOABSTRACTION FROM AQUEOUS HALIDES WITH FEMTOSECOND X-RAY SPECTROSCOPY AND SCATTERING

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We present a sub-picosecond resolved investigation of the structural solvent reorganization and geminate recombination dynamics of photogenerated halogen atoms in aqueous solutions. Nascent iodine radicals were generated via 400 nm 2-photon ionization of the parent iodide, while nascent bromine and chlorine atoms were generated via 1-photon ionization with 200 nm light. Time-resolved X-ray Absorption Near Edge Structure Spectroscopy around the L_1-edge of the photogenerated nascent iodine atoms (I^0) delivered kinetic traces in agreement with a purely diffusion-driven geminate iodine-electron recombination model without the need of a long-lived (I^0:e^-) contact pair [1]. Nonequilibrium classical MD simulations indicate a delayed (ca. 100 fs) response of the caging H_2O solvent shell supported by the structural analysis of the X-ray Solution Scattering data. In-house QM/MM simulations [2] indicate a decreasing cage orientation time in the homologue series from Cl to I, which may be due to a more rigid H bond network around the smaller halogen atom. We will compare the femtosecond photodetachment results on iodide, measured at the LCLS X-ray Free Electron Laser (XFEL), with those on aqueous bromide ions, measured at SACLA XFEL, together with laser-only spectroscopy measurements on the nascent solvated electrons.

[1] P. Vester, K. Kubicek et al., J. Chem. Phys. 157, 224201 (2022); [2] M. Reidelbach et al., J. Phys. Chem. B 127, 1399–1413 (2023)