

# Ultrafast hole dynamics in liquid water detected by x-ray transient absorption spectroscopy

C Arnold<sup>1,2,3\*</sup>, L Inhester<sup>1,3</sup>, R Welsch<sup>1,3</sup>, L Young<sup>4,5</sup>, and R Santra<sup>1,2,3</sup>

<sup>1</sup>Deutsches Elektronen-Synchrotron DESY, 22607 Hamburg, Germany

<sup>2</sup>Universität Hamburg, 22761 Hamburg, Germany

<sup>3</sup>Centre for Ultrafast Imaging, 22761 Hamburg, Germany

<sup>4</sup>Argonne National Laboratory, Lemont, IL 60439, USA

<sup>5</sup>University of Chicago, IL 60637, USA

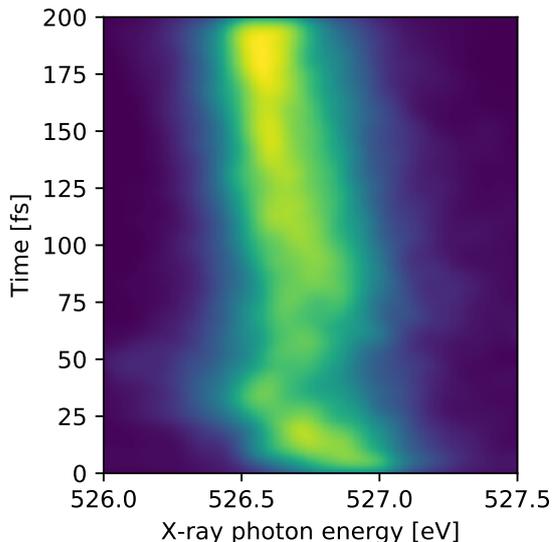
**Synopsis** Electron-hole dynamics can be triggered in liquid water through photoionization from a valence orbital. The hole dynamics can be tracked by resonant x-ray absorption spectroscopy at the oxygen K-edge with femtosecond time resolution. We present a theoretical, *ab initio* description of the hole dynamics in ionized water and the resulting x-ray absorption spectra. To this end, we perform excited-state molecular dynamics simulations of liquid water following valence ionization by employing a quantum-classical, QM/MM scheme which includes non-adiabatic transitions.

The elementary dynamics following photoionization of liquid water are of interest as the primary events in radiation chemistry. Valence photoionization creates a hydrated electron and a residual cation. While the dynamics of the hydrated electron following strong-field ionization have been studied extensively [1], the dynamics of the residual cation remains elusive. Current XFEL sources allow to detect the hole by resonant x-ray absorption spectroscopy at the oxygen K-edge with femtosecond time resolution and excellent spatial selectivity.

We theoretically describe the initial hole dynamics following the creation of a valence hole through strong-field ionization in liquid water. To this end, we treat excited-state molecular dynamics *ab initio* in a quantum-classical scheme, where non-adiabatic transitions are included through surface hopping. A QM/MM approach and the use of Hartree-Fock electronic structure theory in combination with Koopmans' theorem allows for the efficient treatment of large water clusters [2]. X-ray absorption cross sections are calculated using an extended version of our in-house software XMOLECULE [3].

We here present first results on time-resolved x-ray absorption spectra in the first 200 femtoseconds following photoionization and discuss their use as a probe for hole dynamics (Fig. 1). Dynamical events in the trajectories are correlated with characteristic signatures in the absorption spectrum. This provides a path to-

wards resolving ultrafast electron-hole dynamics in strong-field ionized liquid water on its natural time scale.



**Figure 1.** Calculated x-ray absorption spectrum following valence photoionization of liquid water, taking into account resonant transitions from oxygen core orbitals to the valence hole. Cross sections are convolved with 10 fs and 0.1 eV FWHM in time and energy, respectively.

## References

- [1] Li J *et al* 2013 *J. Phys. Chem. Lett.* **21** 3698
- [2] Arnold C *et al* 2019 *J. Chem. Phys.* **150** 2019
- [3] Khalili K, Inhester L, Arnold C *et al* 2019, *in preparation*.

\*E-mail: [caroline.arnold@cfel.de](mailto:caroline.arnold@cfel.de)