Ultrafast Phenomena: Part 2

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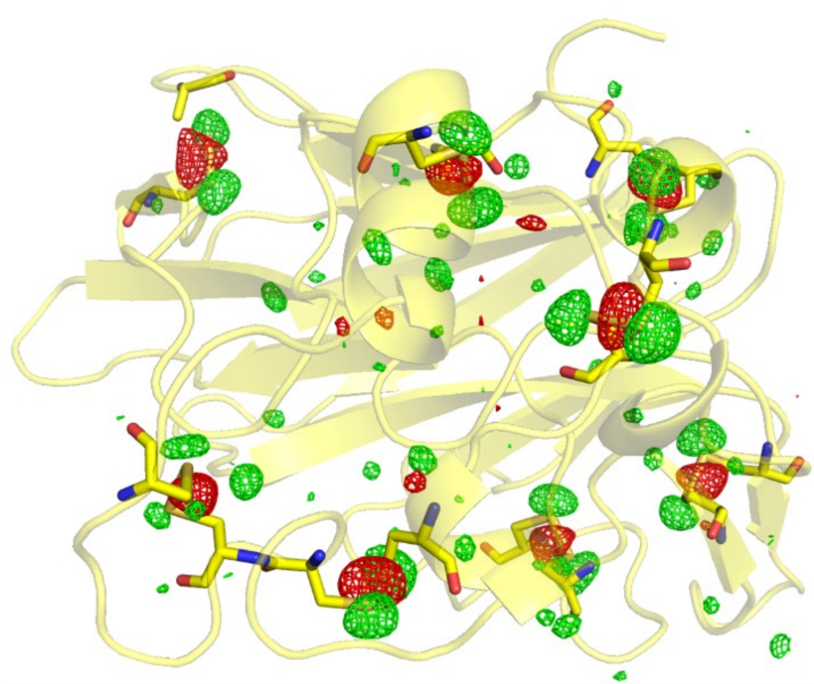
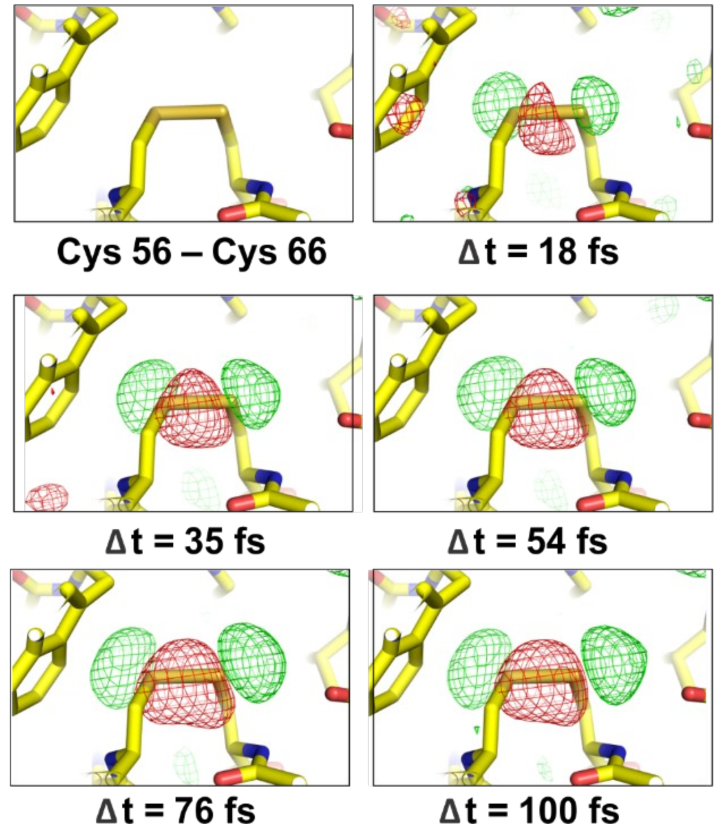
X-ray pump / x-ray probe SFX study of thaumatin

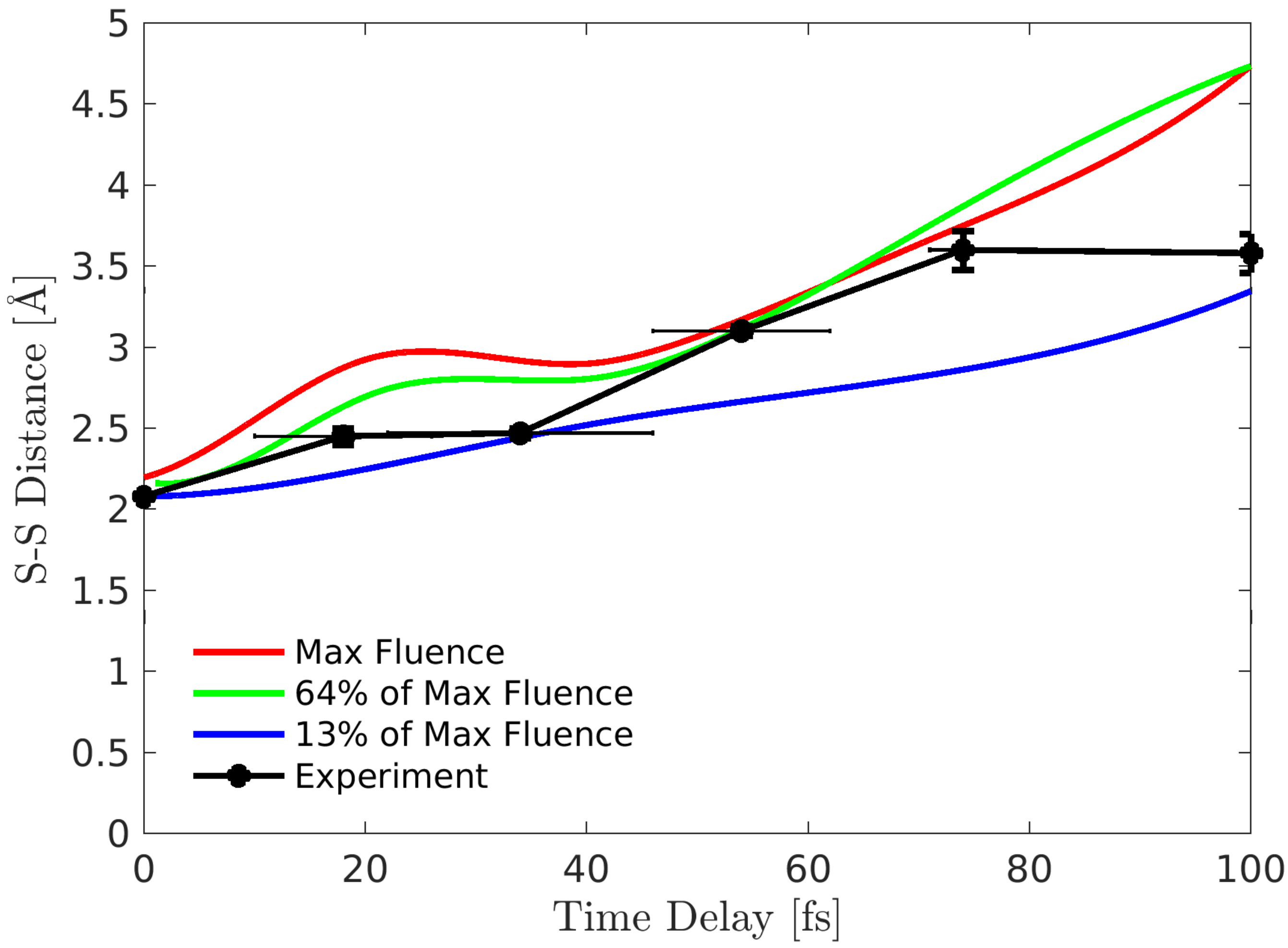
Collaboration with **Ilme Schlichting** et al.
Experiment carried out at LCLS





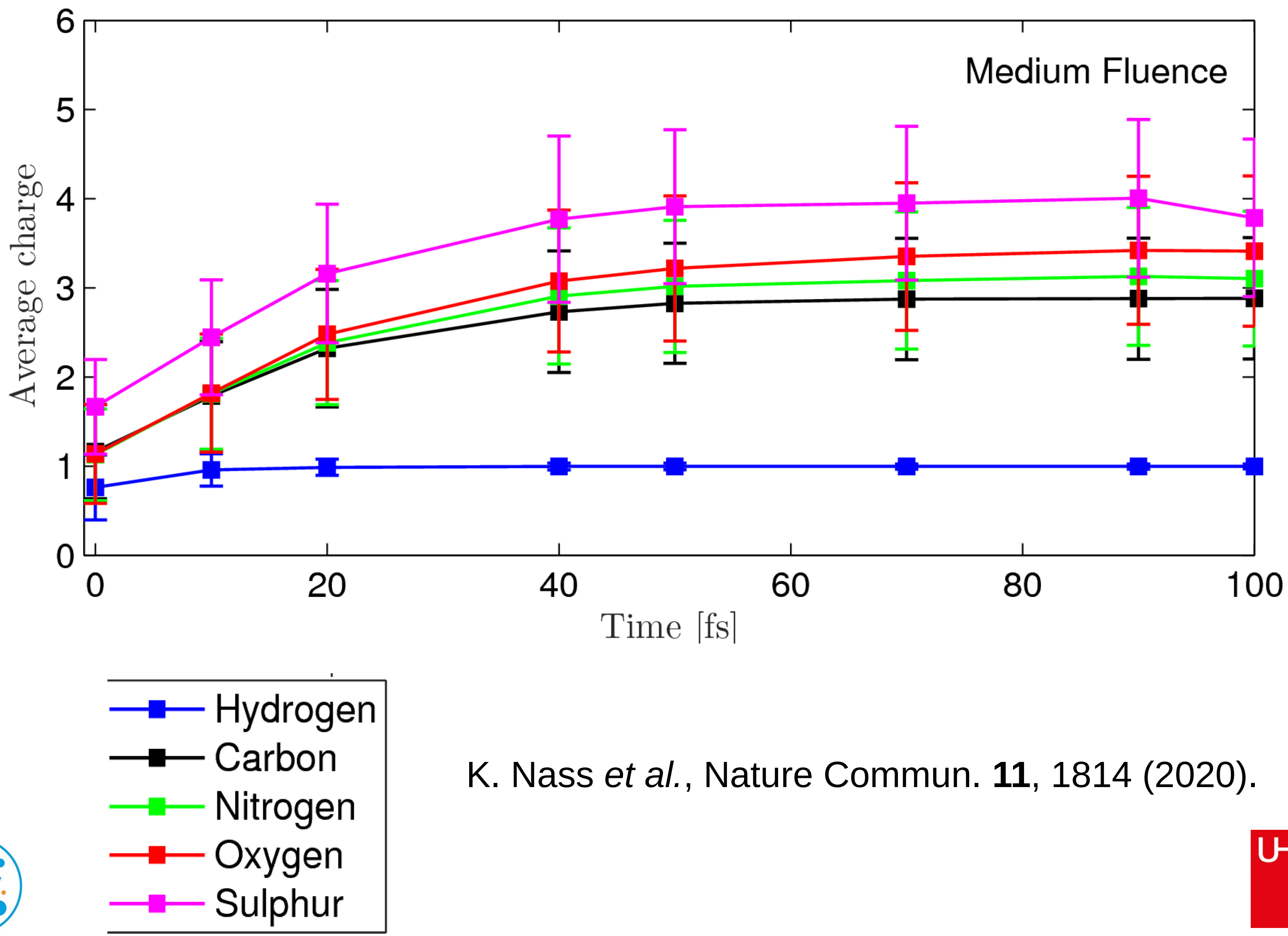
Photon energy: 7.1 keV
Pump (probe) pulse duration: 15 fs (15 fs)
Combined pulse energy: 1 mJ, shared 50%/50% (pump/probe)
Intensity in the focus: 3 x 10^{19} W/cm^2

Disulfide bond length in thaumatin



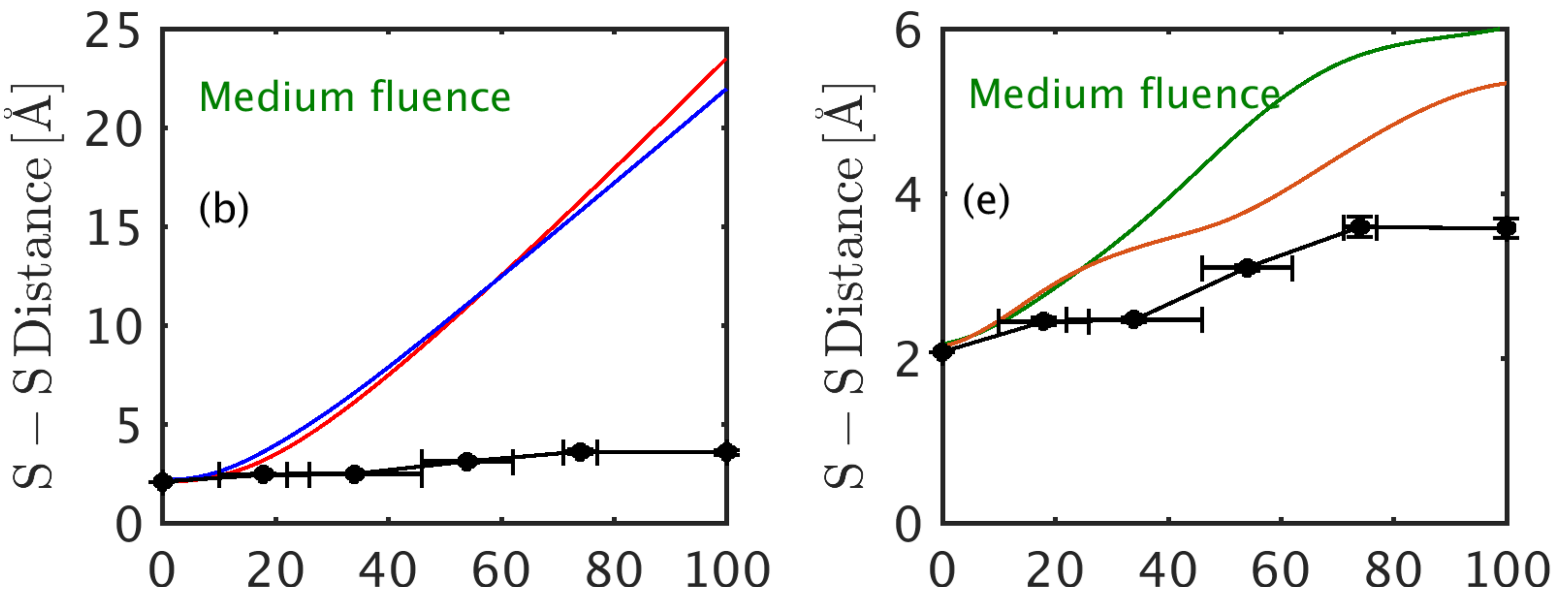
K. Nass *et al.*, Nature Commun. **11**, 1814 (2020).

Average charge as a function of pump-probe delay



K. Nass *et al.*, Nature Commun. **11**, 1814 (2020).

Ion caging and plasma screening

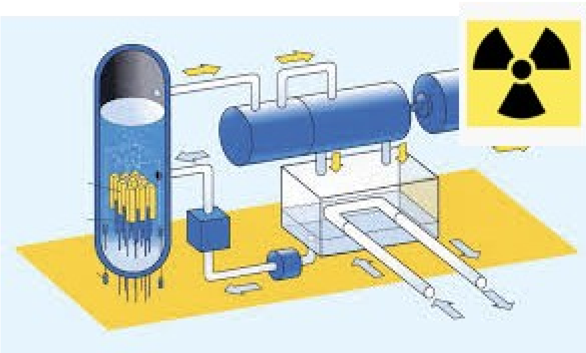


Red: Isolated S-S pair in vacuum
Blue: Isolated S-S pair using charges in crystal environment

Brown: No Coulomb interaction between S atoms and plasma electrons
Green: No Coulomb interaction between S atoms and non-S atoms

K. Nass *et al.*, Nature Commun. **11**, 1814 (2020).

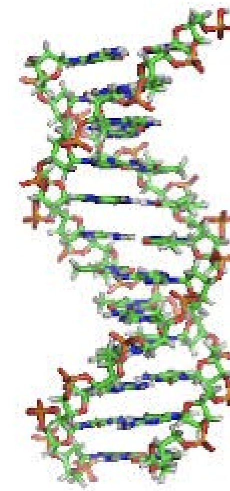
Effects of radiation



Corrosion in nuclear power plants

Medical x-ray imaging

Air travel and spaceflight

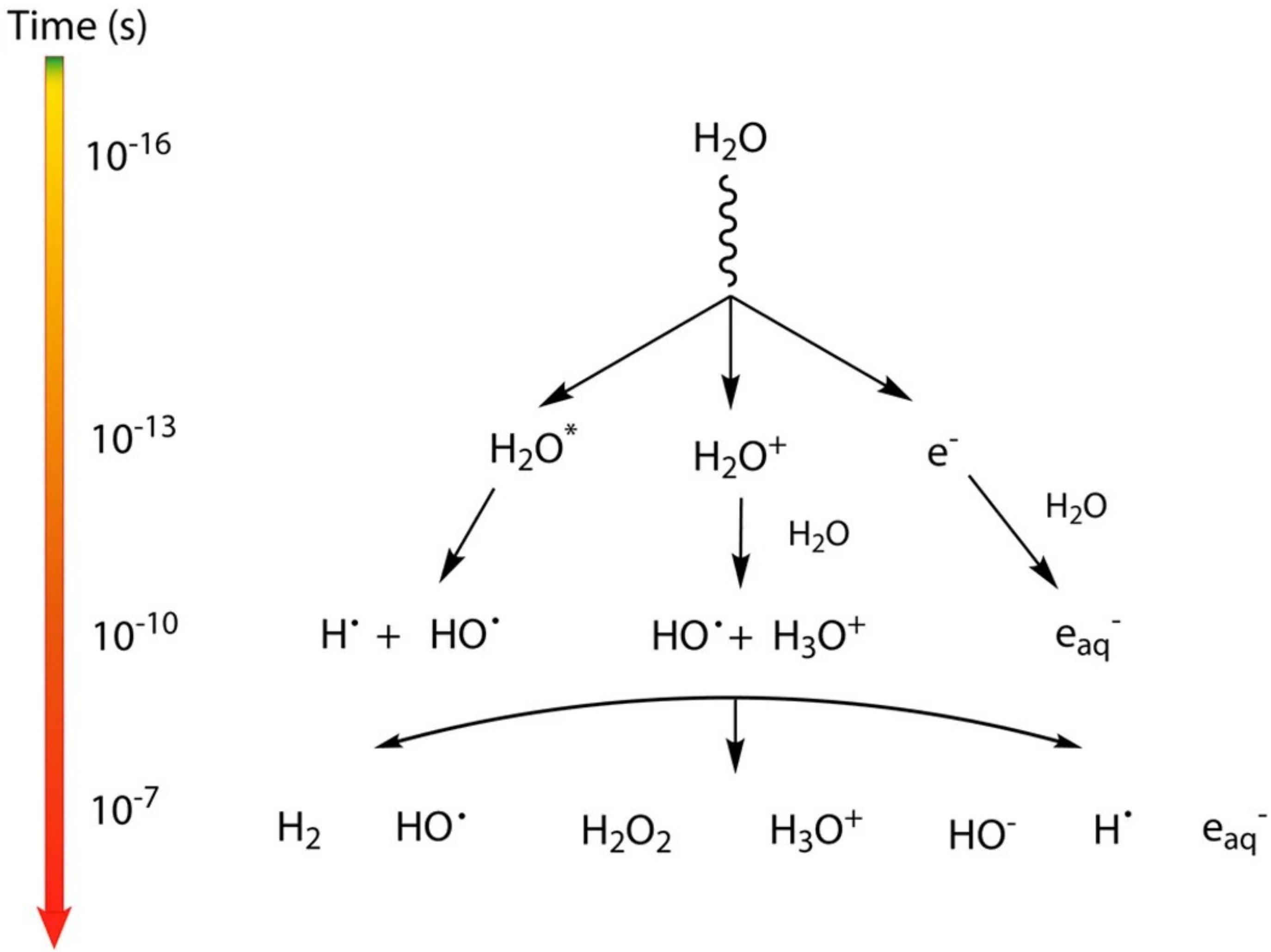


Radiotherapy

What happens microscopically?

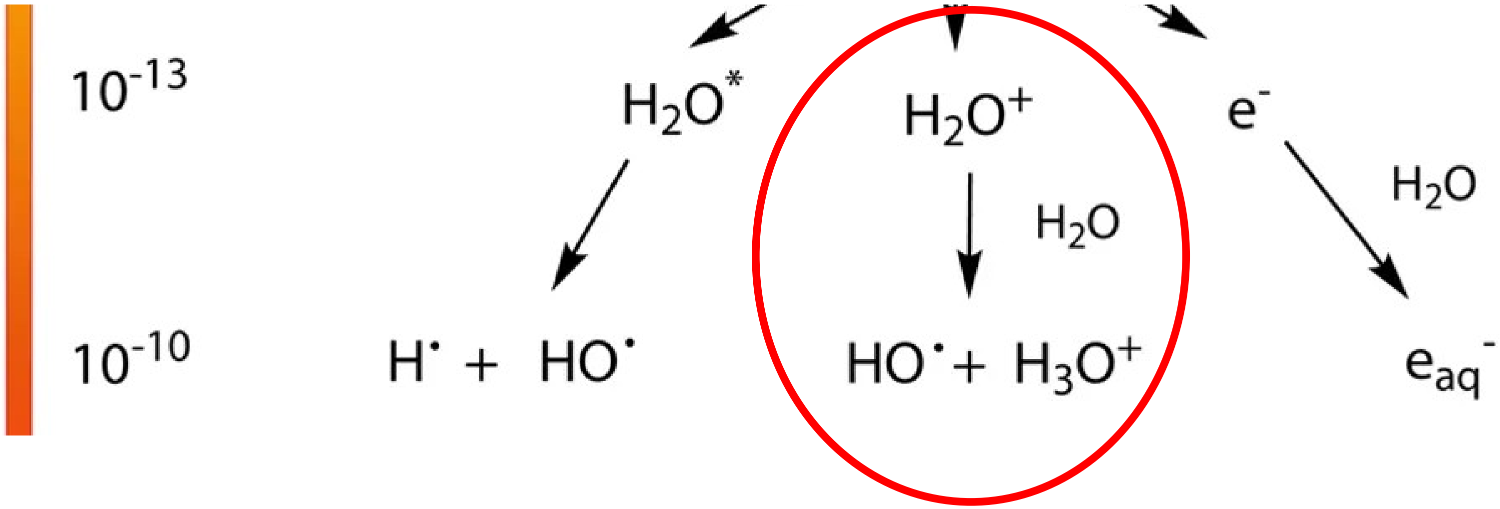
Ionizing radiation (x rays, γ rays, charged particles) gives rise to the **formation of highly reactive radicals**. Particularly, through the **ionization of water**, highly reactive **hydroxyl (OH) radicals** are formed.

How does ionization of water produce OH?



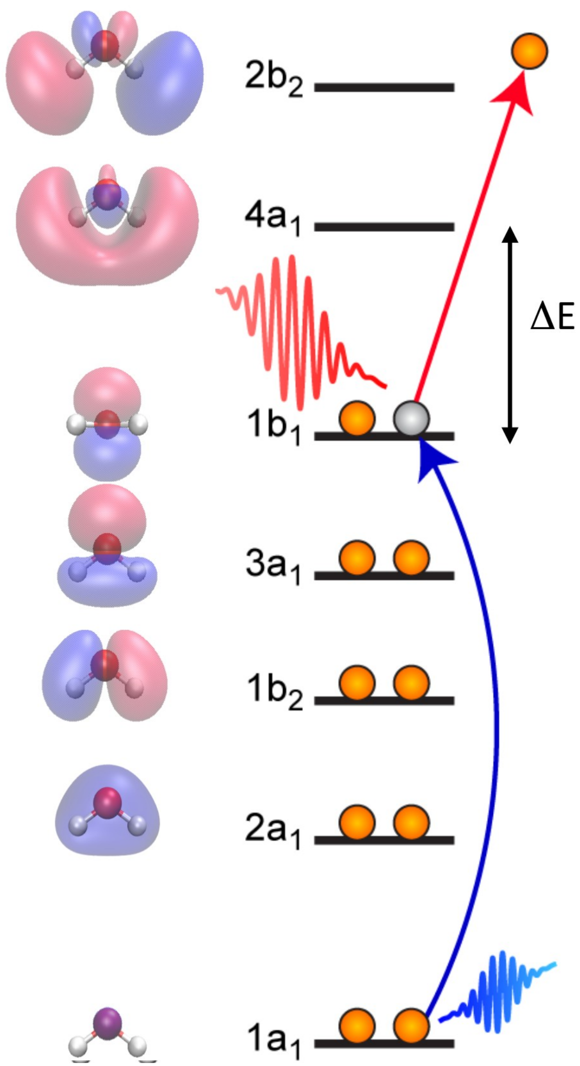
C. M. Lousada *et al.*, Scientific Reports **6**, 24234 (2016).

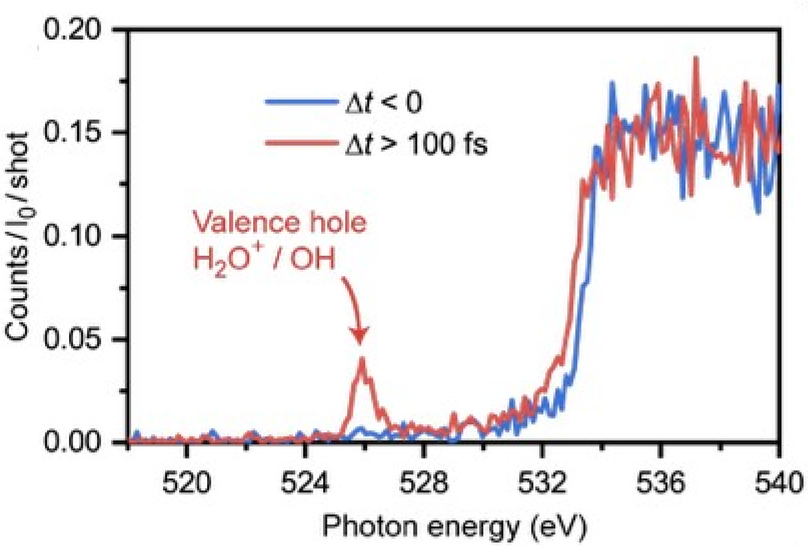
Is it true that the key reaction step takes somewhere between 100 fs and 100 ps?



C. M. Lousada *et al.*, Scientific Reports **6**, 24234 (2016).

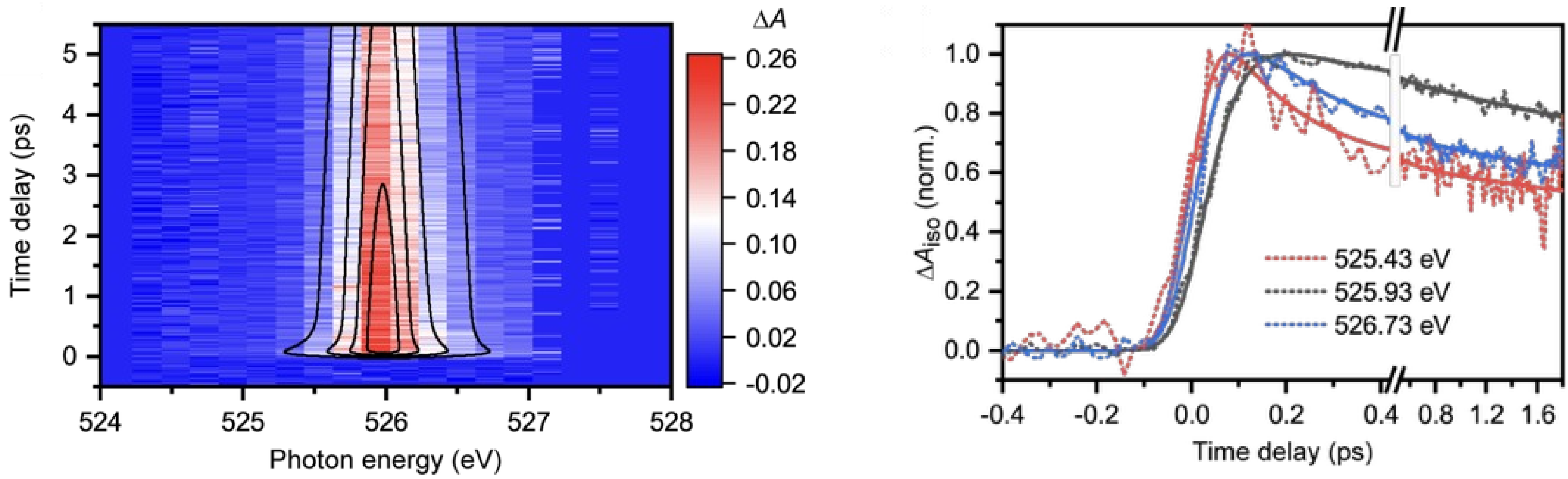
Probing the hole through transient x-ray absorption





Z.-H. Loh *et al.*,
Science **367**, 179 (2020).

Observed delay dependence of x-ray absorption resonance



Sequential kinetics

$$A_0 \xrightarrow{\tau_0} A_1 \xrightarrow{\tau_1} A_2 \xrightarrow{\tau_2} A_3$$

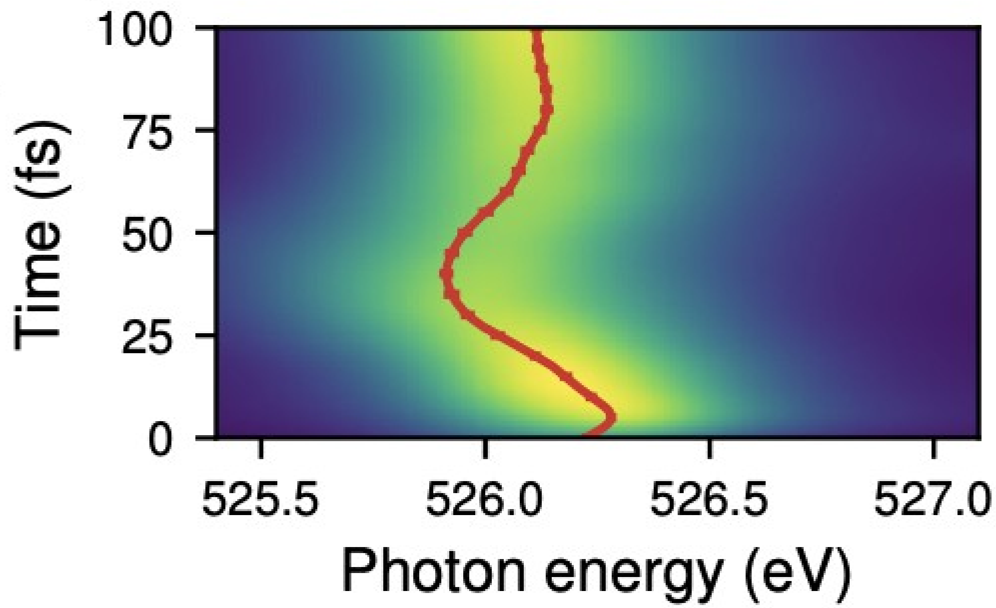
$\tau_0 = 46 \pm 10\,\mathrm{fs}$ — OH formation

$\tau_1 = 180 \pm 20\,\mathrm{fs}$ — Vibrationally hot OH cools

$\tau_2 = 14.2 \pm 0.4\,\mathrm{ps}$ — OH + e recombine

Z.-H. Loh *et al.*, Science **367**, 179 (2020).

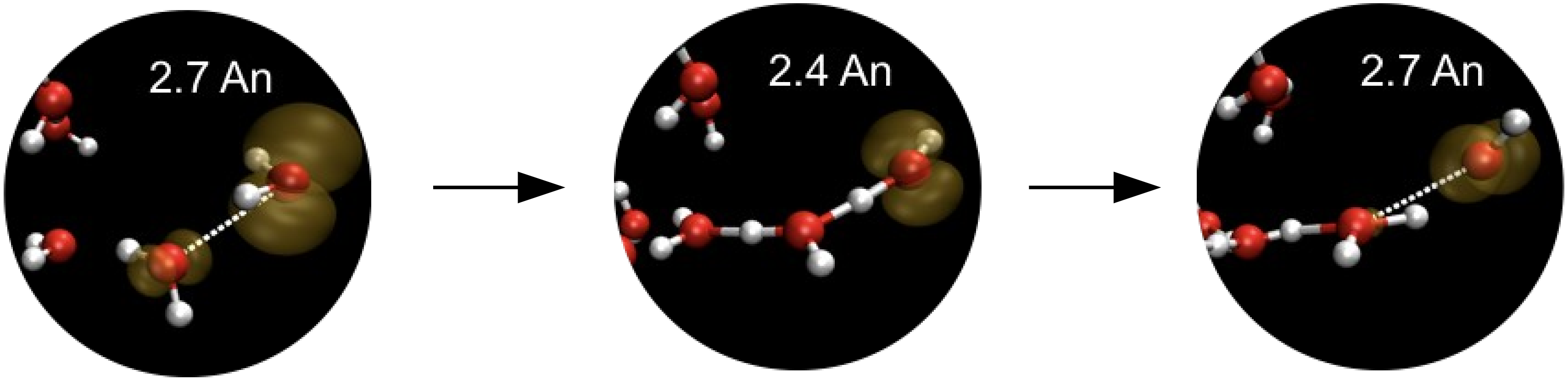
XMOLECULE simulation

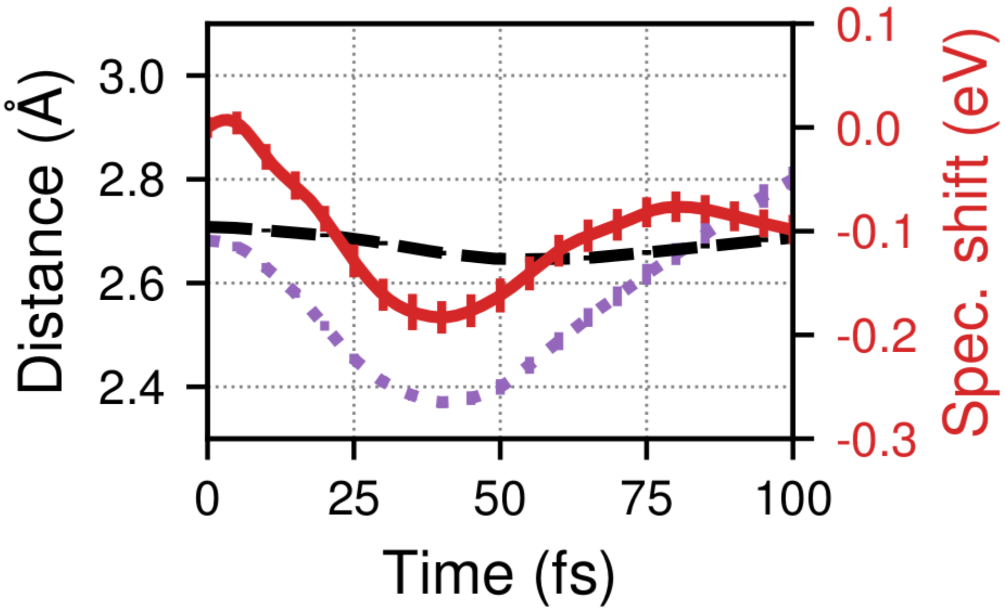


How are these spectral dynamics connected to the decay of H_2O^+ and the formation of OH?

Z.-H. Loh *et al.*, Science **367**, 179 (2020).

Impact of chemical environment of H_2O^+/OH





Z.-H. Loh *et al.*, Science **367**, 179 (2020).

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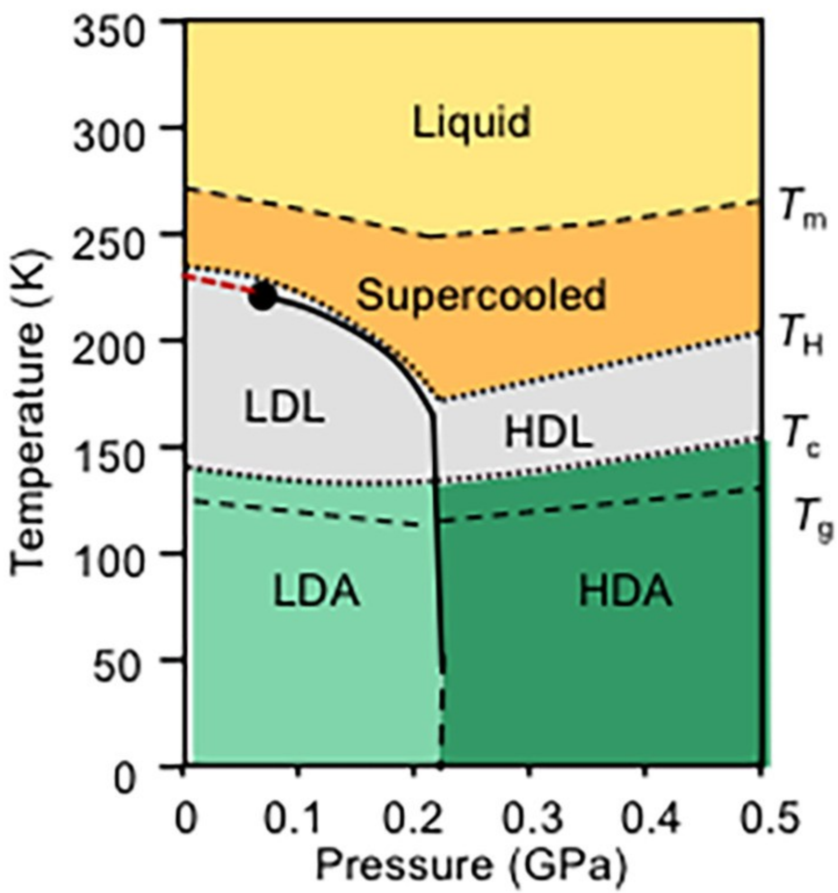
- Nanyang Technological University: **Z.-H. Loh**, M. S. Bin Mohd Yusof, T. Debnath
- Uppsala University: L. Kjellsson, J.-E. Rubensson
- Sorbonne Université and CNRS: M. Simon
- University of Southern California: K. Nanda, A. I. Krylov
- SLAC National Accelerator Laboratory: S. Moeller, G. Coslovich, J. Koralek, M. P. Minitti, W. F. Schlotter

Water is anomalous

Image credit: Eloi Omella via Getty Images

Water is anomalous

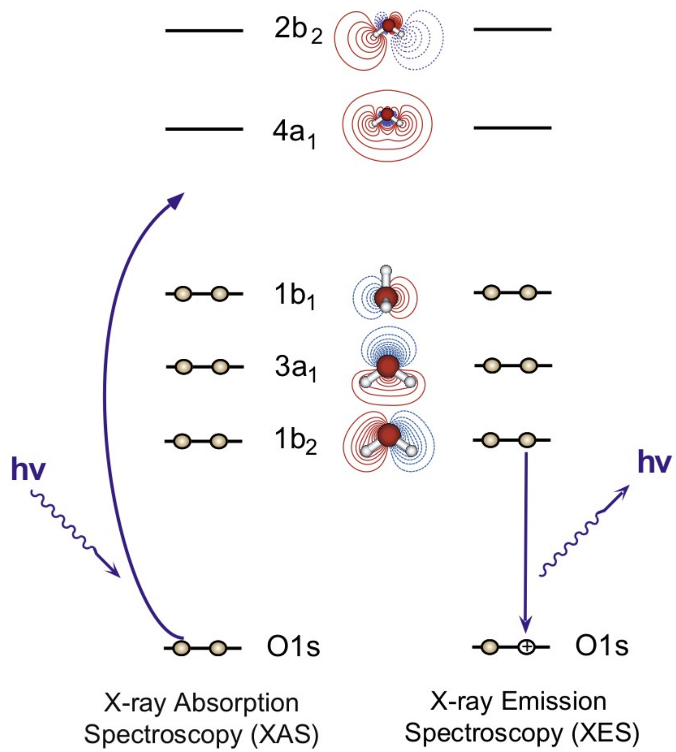


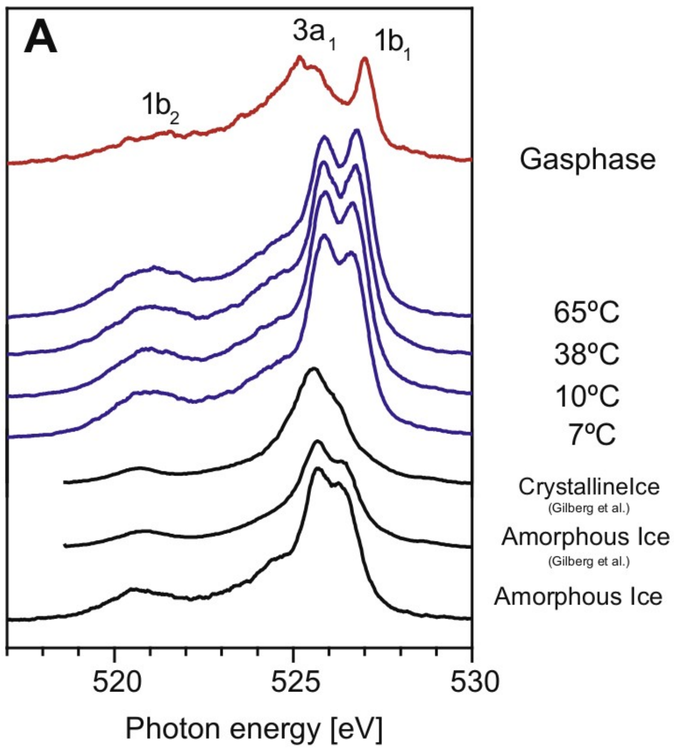
Water phase diagram based on experiments at x-ray free-electron lasers.

A. Nilsson, J. Non-Cryst. Solids X **14**, 100095 (2022).

A long-standing controversy

T. Tokushima *et al.*, Chem. Phys. Lett. **460**, 387 (2008).

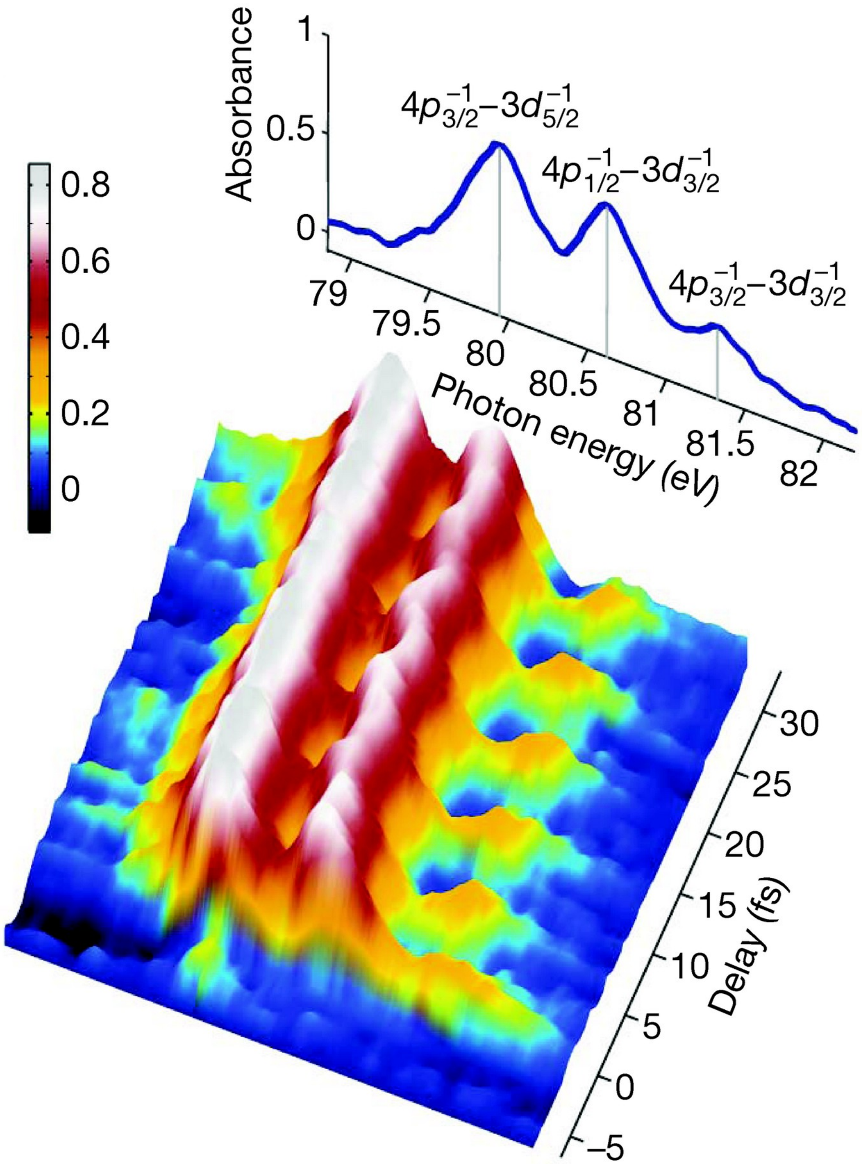




Interpretation: $1b_1$ splitting indicates the presence of two distinct structural motifs in liquid water

Alternative interpretation: $1b_1$ splitting indicates that there is partial dissociation of water in core-excited water, within the lifetime of the core hole [PRL **100**, 027801 (2008); PRB **79**, 144204 (2009)]

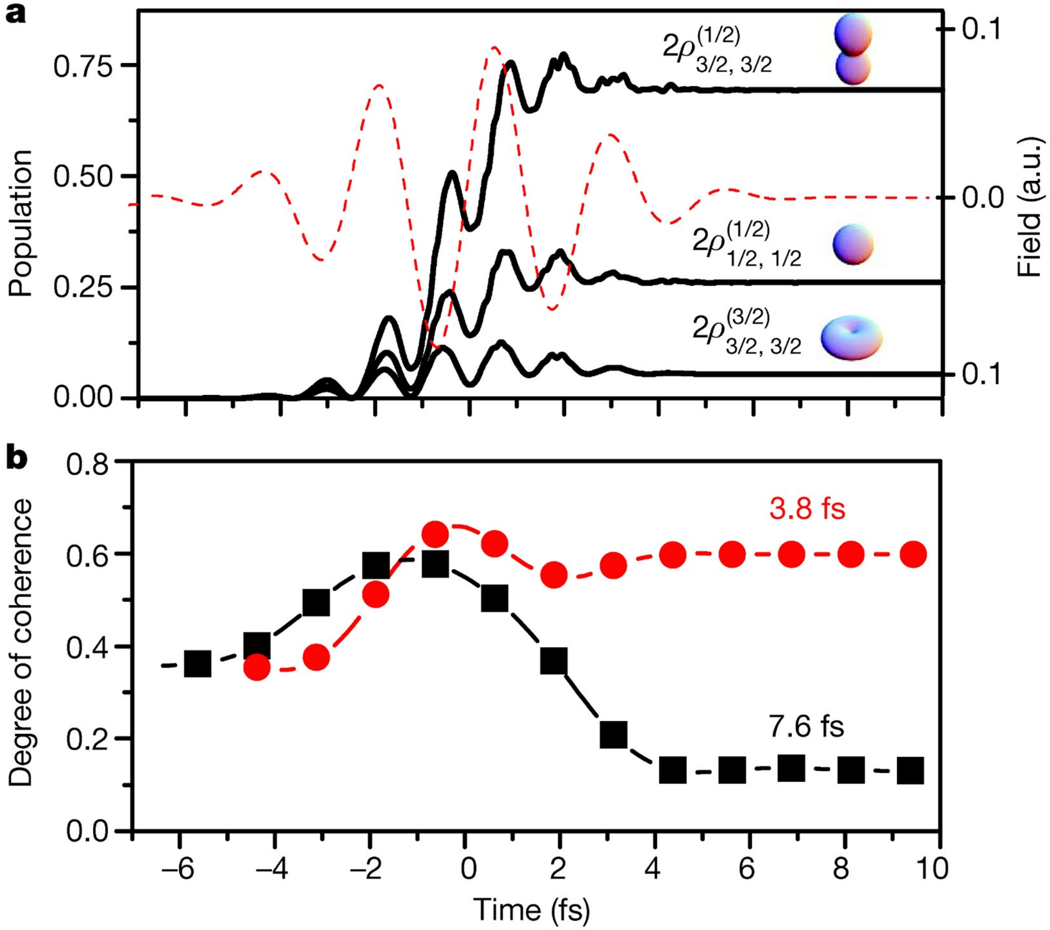
Attosecond transient absorption spectroscopy



Experiment on krypton at a near-IR peak intensity near 10^{14} W/cm^2

E. Goulielmakis *et al.*, Nature **466**, 739 (2010).

Calculated hole populations and degree of coherence



The degree of electronic coherence calculated using the methodology from

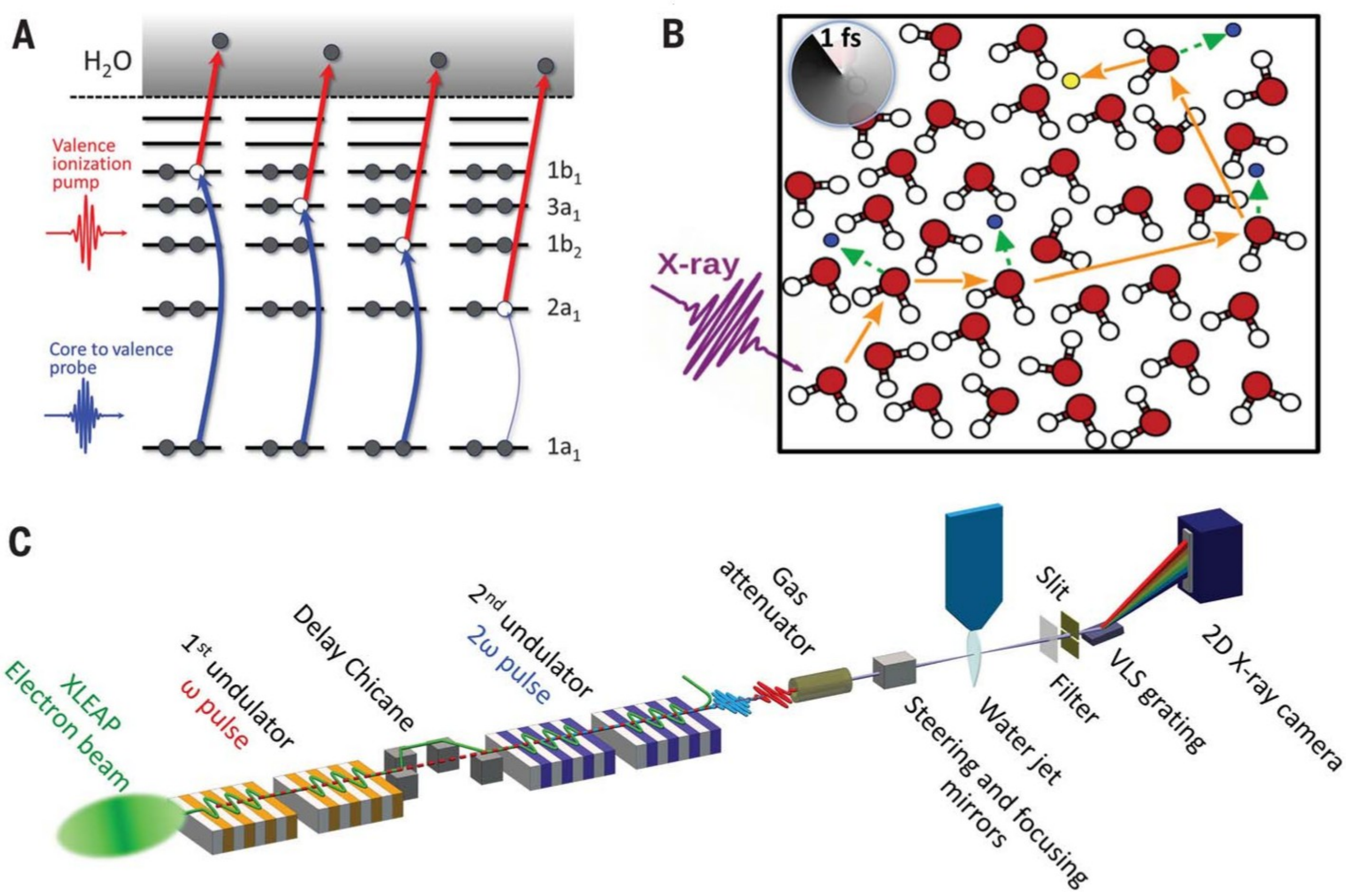
N. Rohringer and R. Santra, Phys. Rev. A **79**, 053402 (2009),

is consistent with the degree of coherence extracted from the experimental transient-absorption data using the methodology from

R. Santra *et al.*, Phys. Rev. A **83**, 033405 (2011).

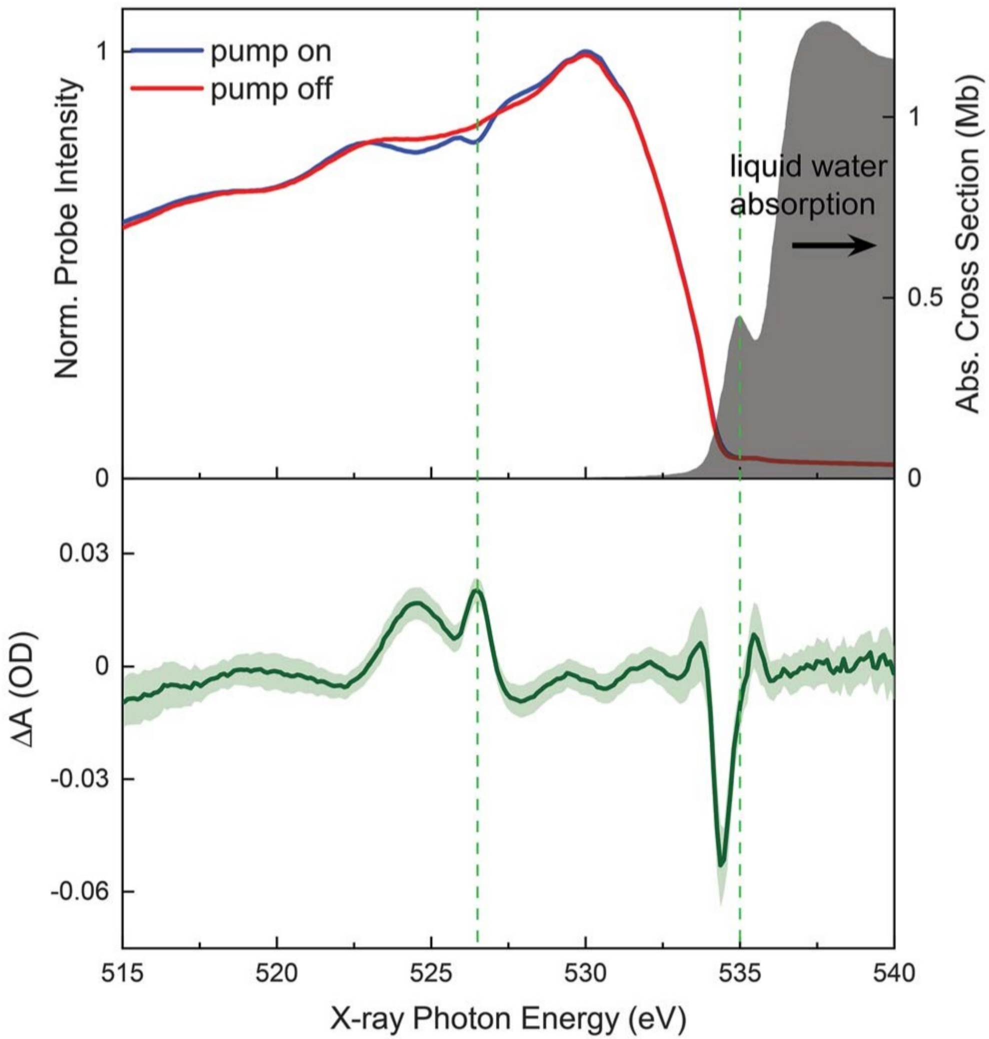
E. Goulielmakis *et al.*, Nature **466**, 739 (2010).

All x-ray attosecond transient absorption spectroscopy (AX-ATAS) of liquid water



S. Li *et al.*, Science **383**, 1118 (2024).

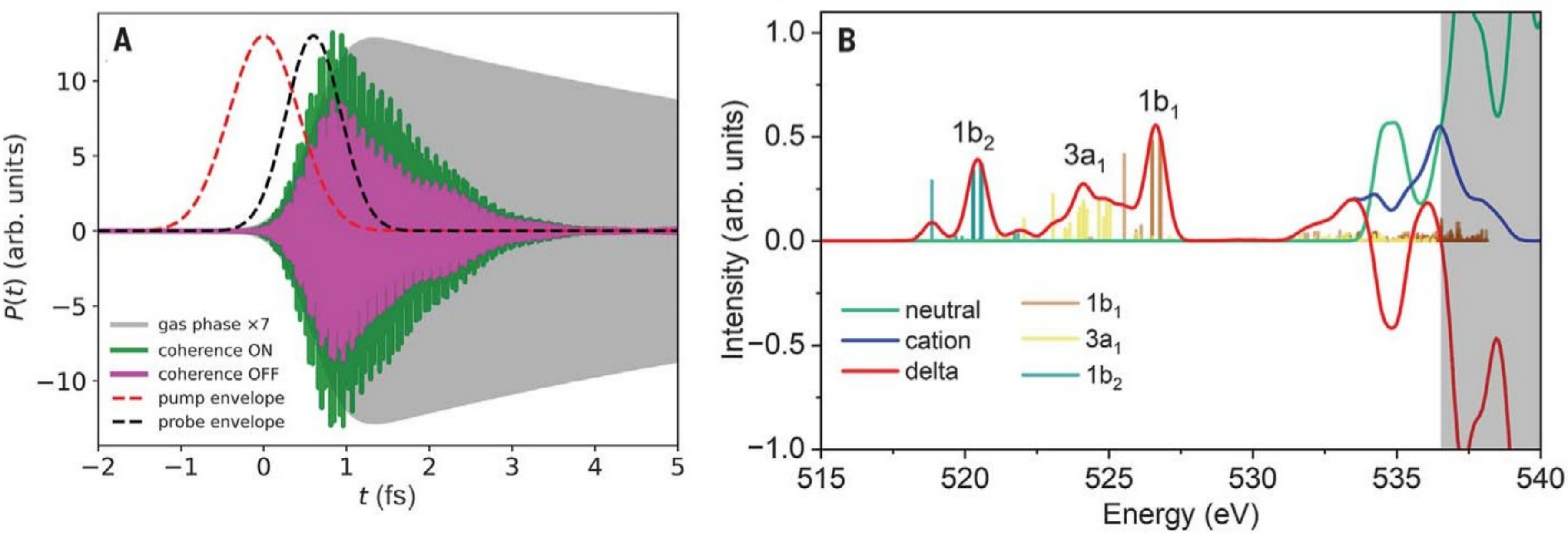
Experimental AX-ATAS spectra of liquid water



S. Li *et al.*, Science **383**, 1118 (2024).

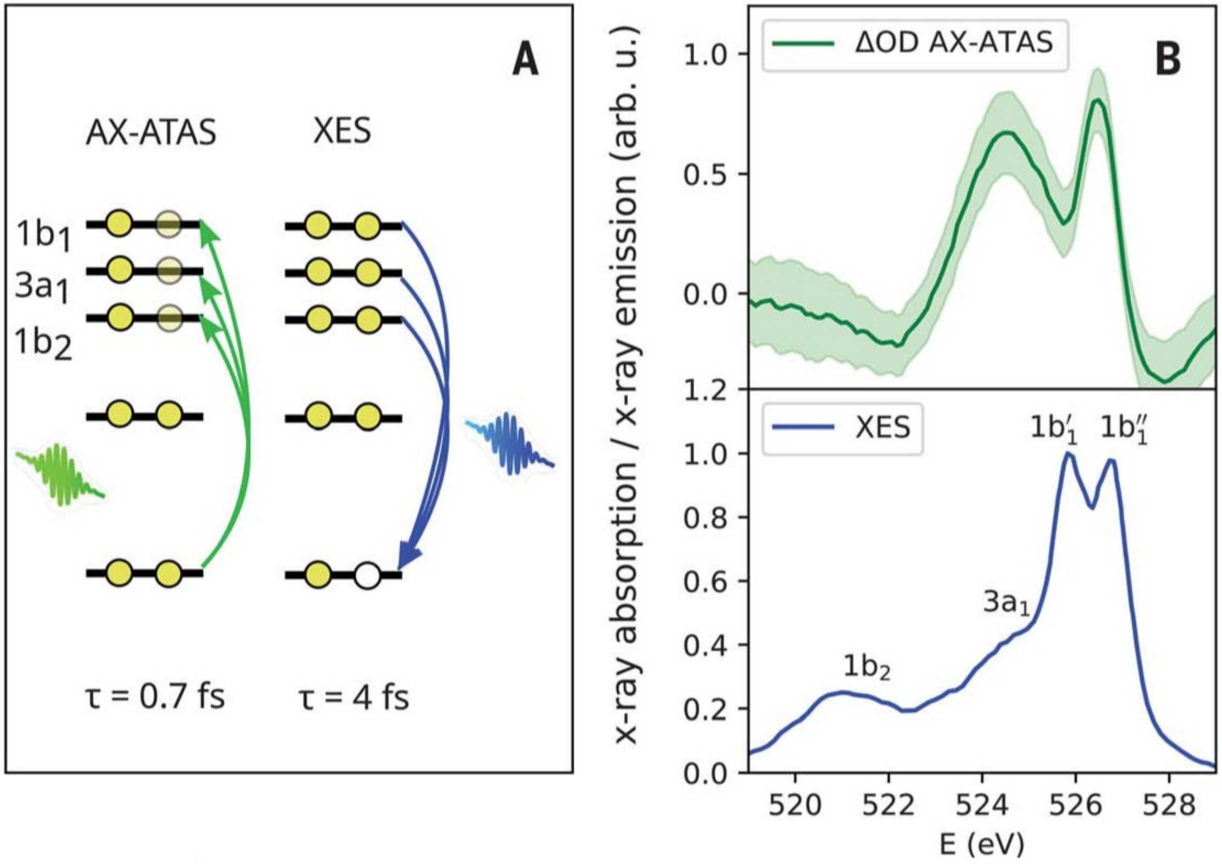
Theoretical modeling of AX-ATAS for liquid water

Theoretical framework for computing the probe-induced polarization based on R. Santra *et al.*, Phys. Rev. A **83**, 033405 (2011).



S. Li *et al.*, Science **383**, 1118 (2024).

Comparison of AX-ATAS and XES



S. Li *et al.*, Science **383**, 1118 (2024).

Acknowledgment

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- University of Washington: L. Lu, X. Li
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Conclusions

> In spatially extended systems, transient plasmas are formed.

> In such plasmas, atomic displacements are smaller than one might naively expect.

> Ultrafast x-ray absorption enabled the first observation of the proton transfer reaction following ionization of liquid water, giving rise to the chemically aggressive OH radical.

Conclusions

- First **x-ray attosecond pump and x-ray attosecond probe measurement** on a condensed-phase sample.
- In **AX-ATAS**, the signal is formed on a time scale that is **much shorter than the O 1s core-hole lifetime**.
- The fact that in **AX-ATAS, the 1b$_1$ peak does not display a doublet structure** is evidence that the lower-energy peak in the 1b$_1$ doublet in XES is caused by hydrogen motion in core-excited water during the O 1s core-hole lifetime.
- **The 1b$_1$ doublet in XES does not represent evidence that in liquid water, there are two distinct structural motifs.**