Molecules in Motion
Ultrafast Dynamics of Liquid Water

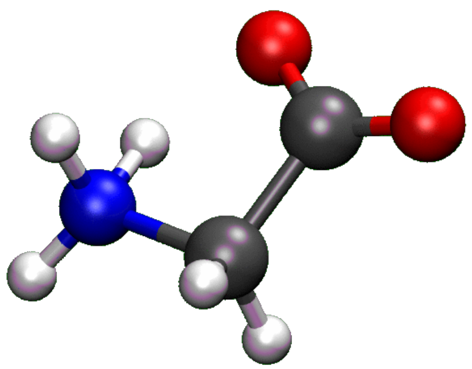
Caroline Arnold

CFEL-DESY Theory Group

DESY Science Day

02.12.2020

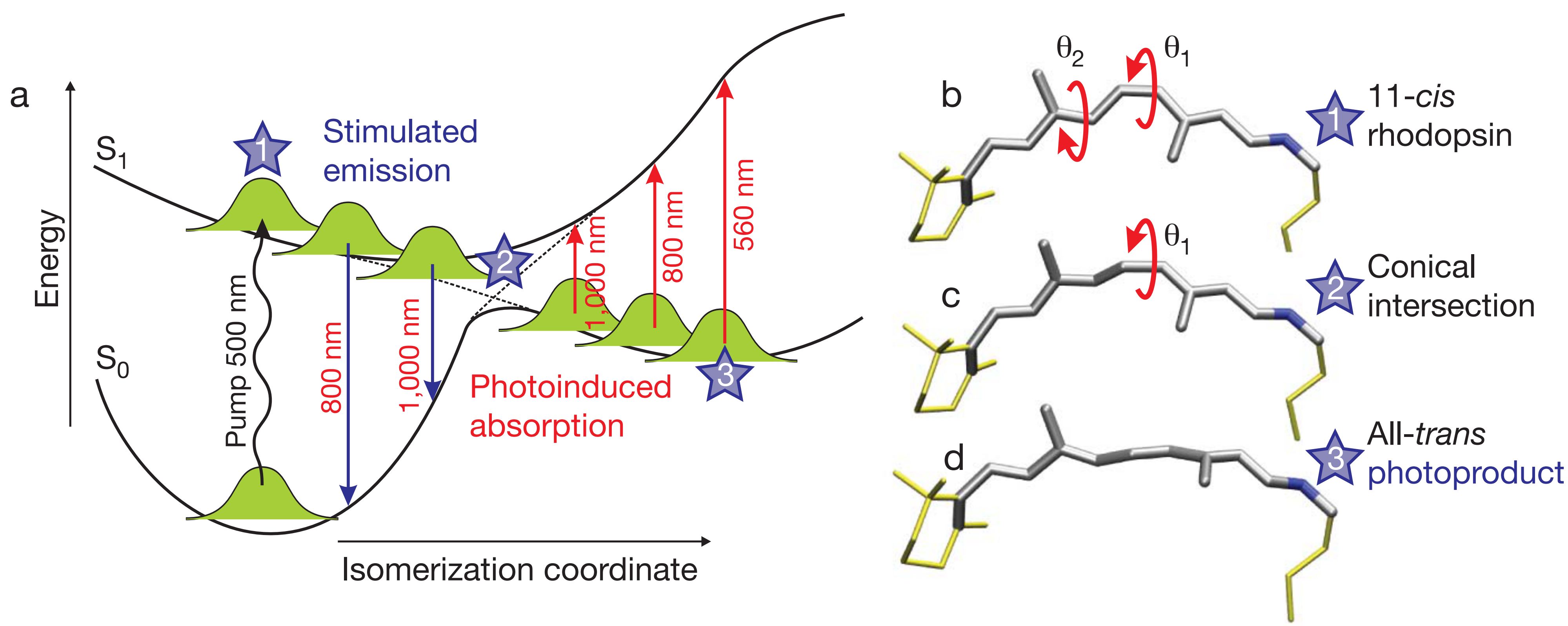
What is ultrafast motion?



femtosecond

$1\ \text{fs} = 0.000000000000001\ \text{s} = 10^{-15}\ \text{s}$

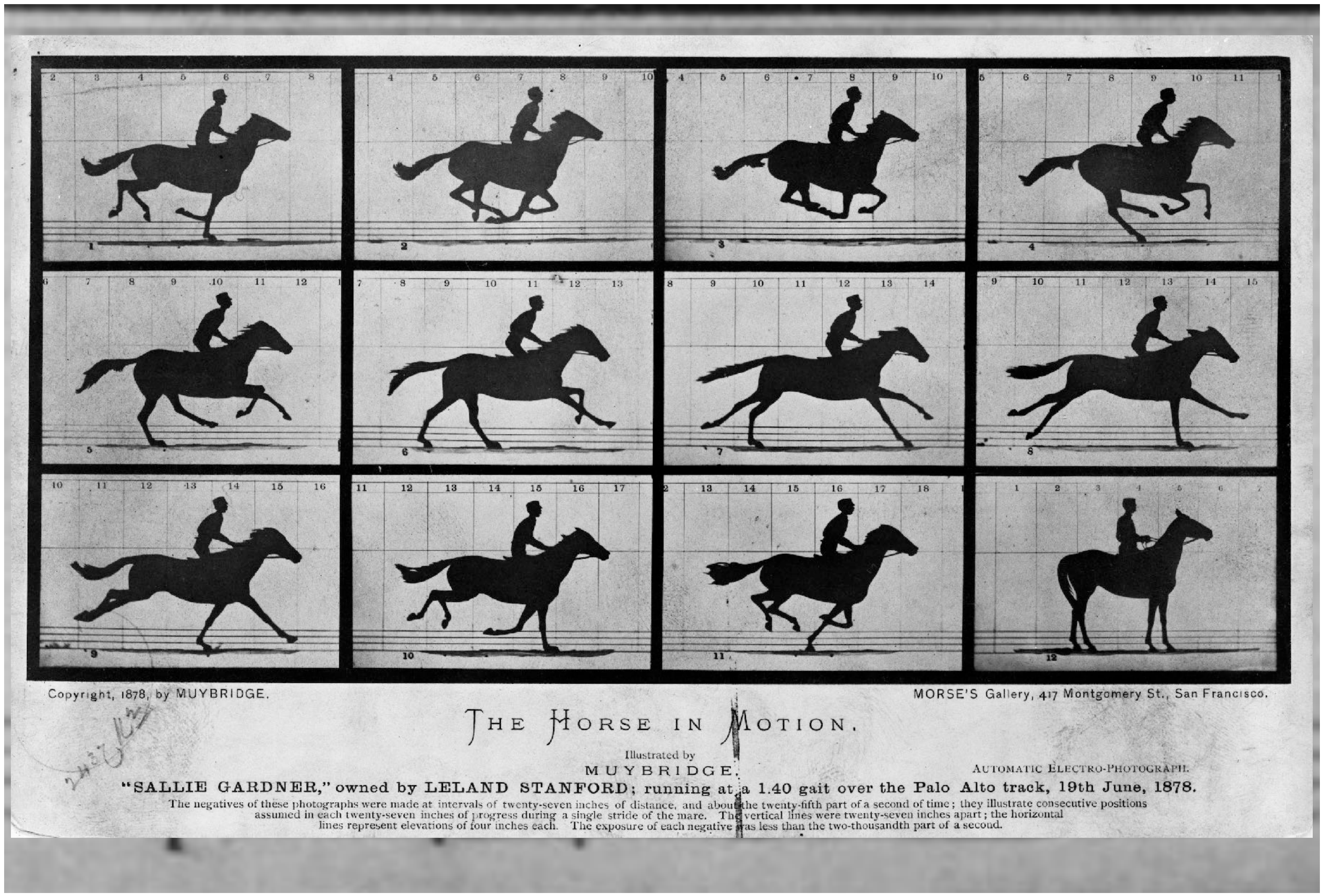
- Elementary processes in chemistry and biology
- Time-resolved observation of molecular dynamics



Polli *et al*, Nature **467**, 440 (2010)

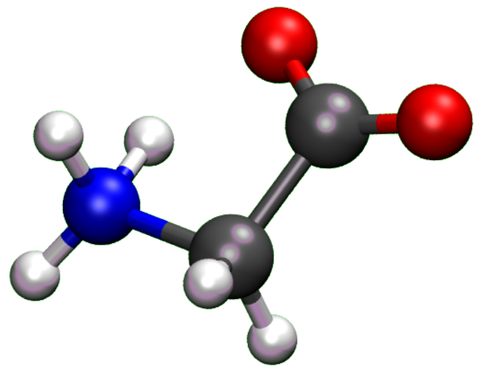
The First Ultrafast Movie

Does a galloping horse ever lift all its legs off the ground?

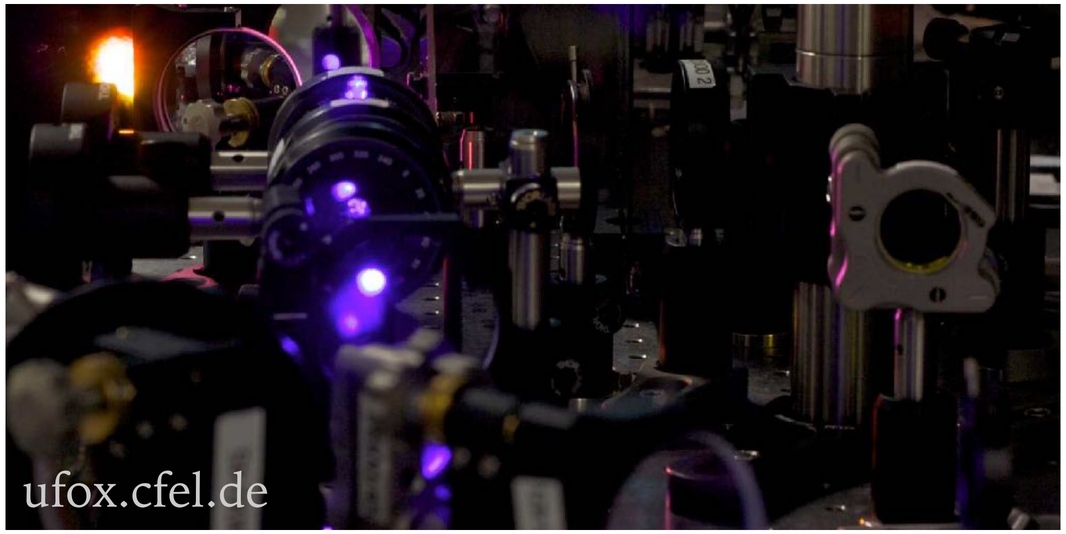


The Horse in Motion, Stanford 1878

Time resolution: imaging with light pulses



lab-based light sources
- ~ VUV wave length
- sub-femtosecond pulses



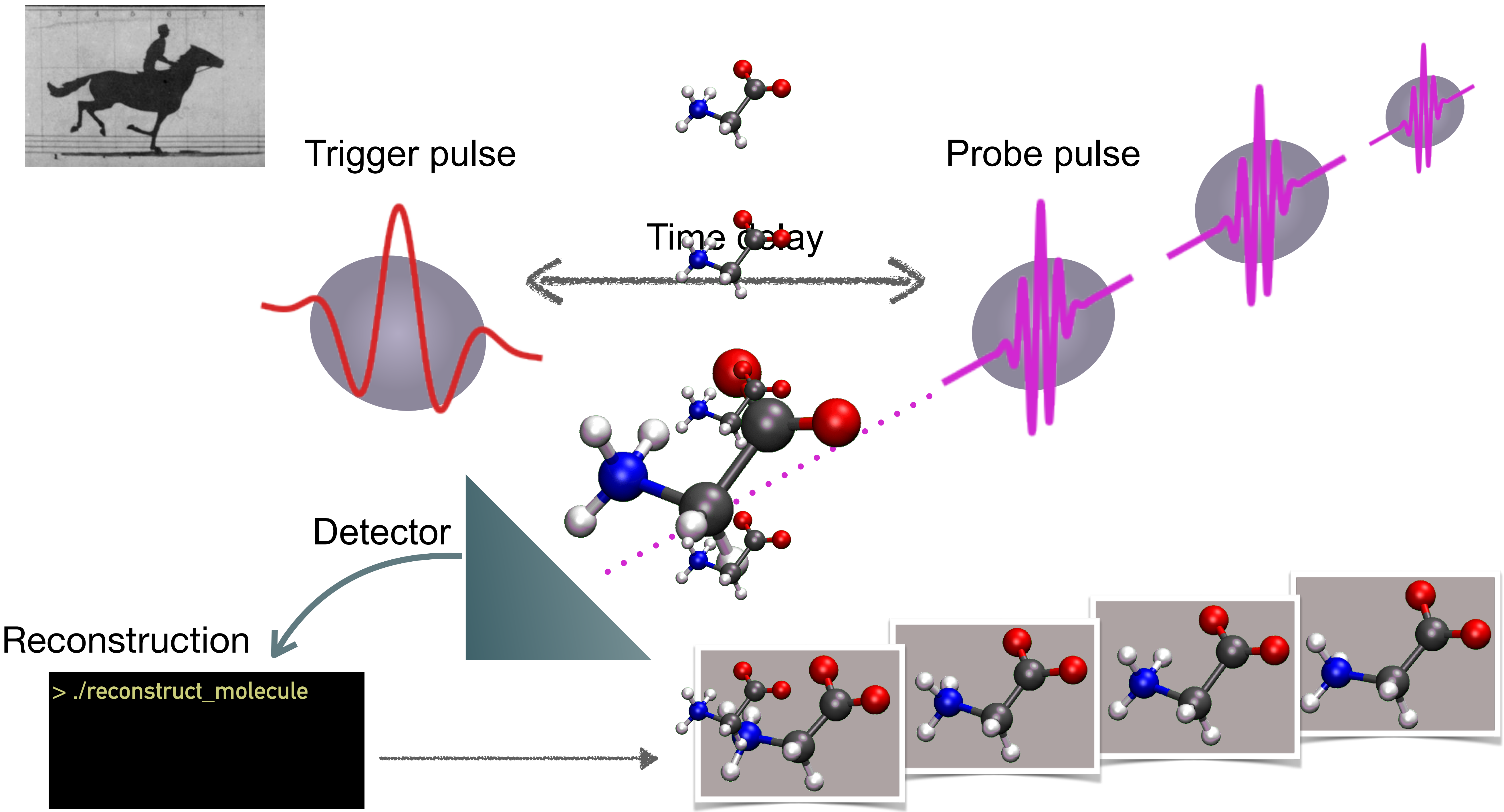
(x-ray) free-electron lasers
- x-ray wave length
- few-femtosecond pulses
- high brilliance

European XFEL

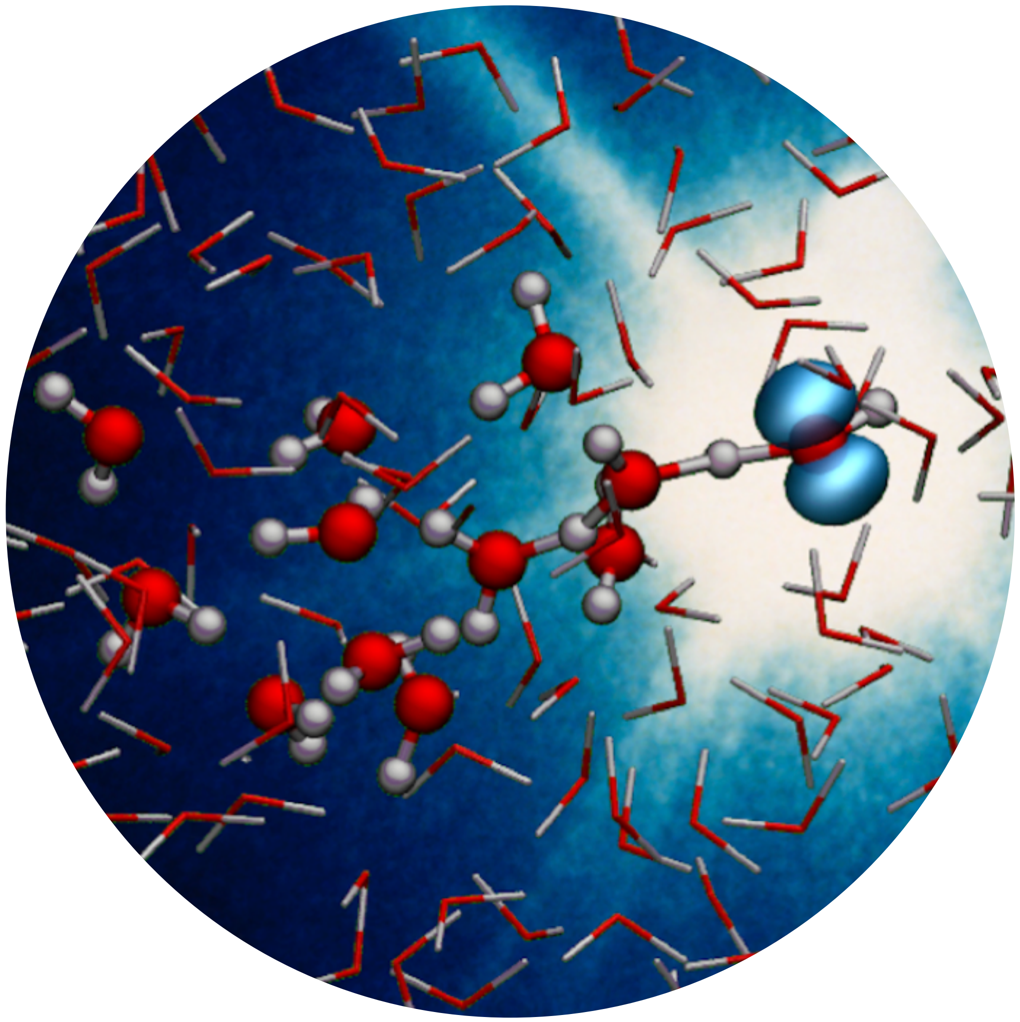
LCLS

Previous talk by Roland Mainz

Molecular Movie



(Photo)Ionisation of liquid water

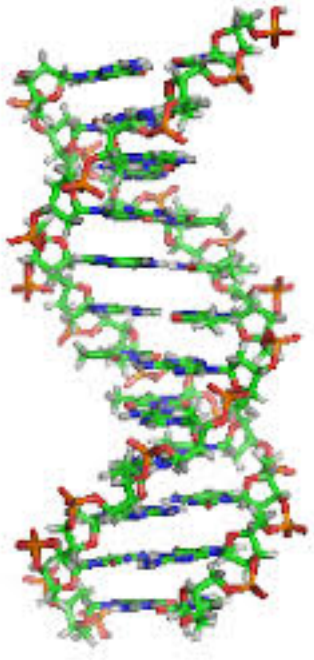


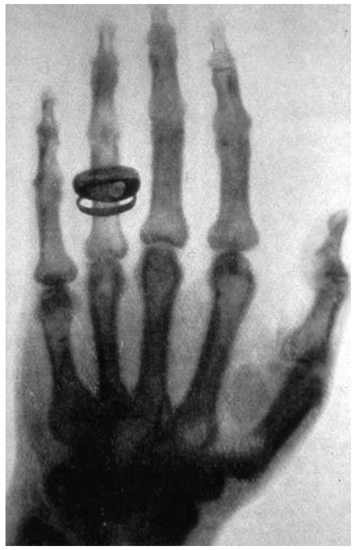
Ionisation removes a valence electron

- by radiation
- by charged particles

Triggers ultrafast molecular dynamics

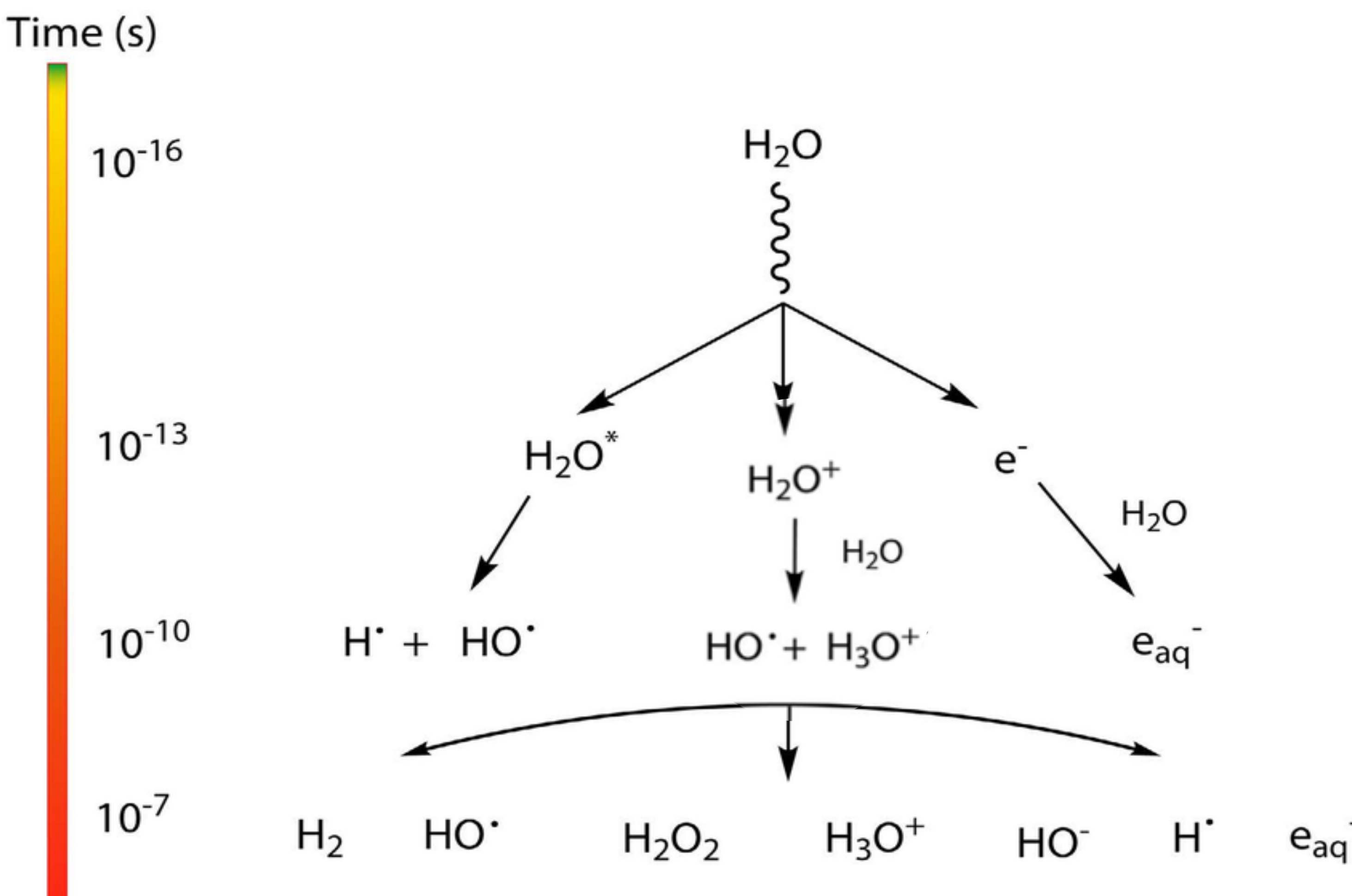
- creates highly reactive free radicals
- radiation damage in biomolecules





Can we observe the first processes after ionisation directly?

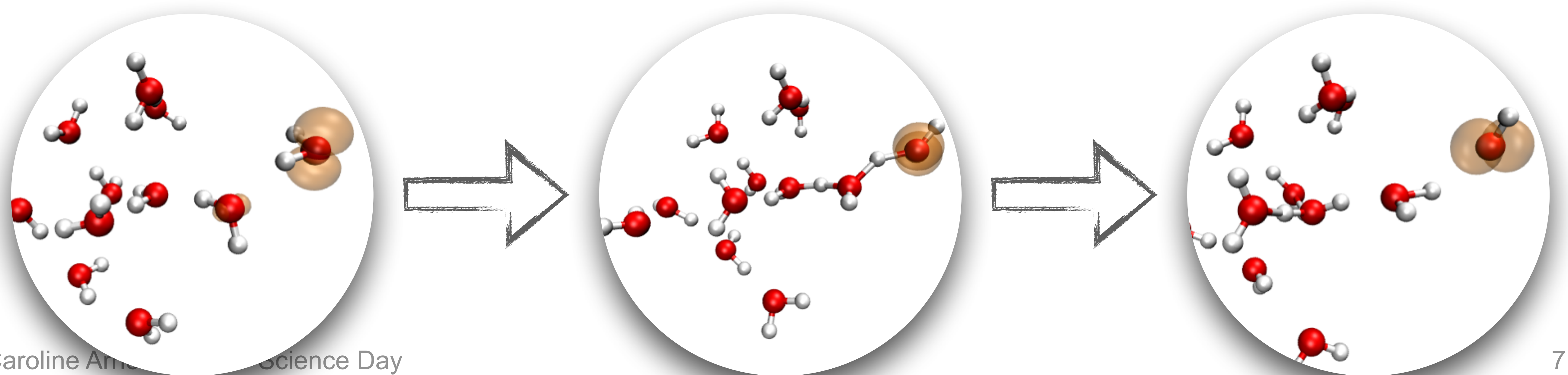
The proton transfer reaction



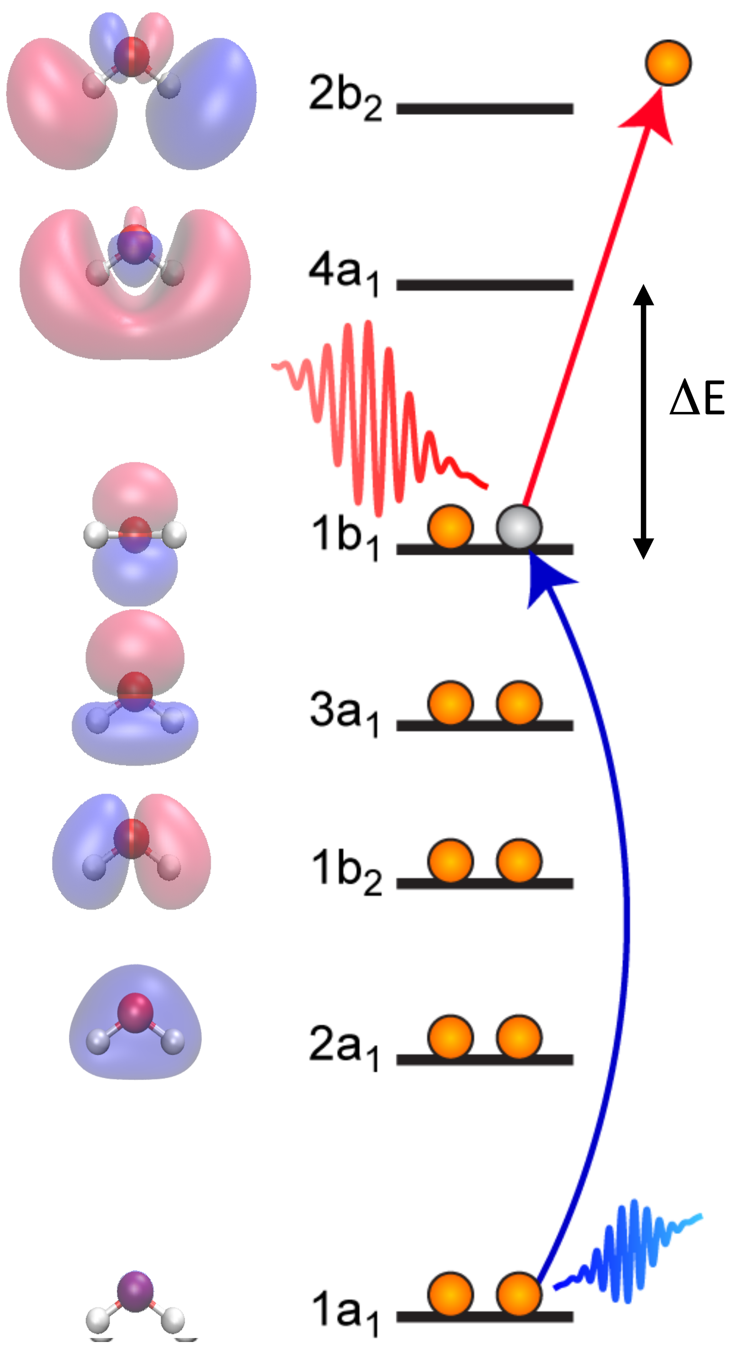
Lousada *et al.* Sci Rep 6 (2015).

- Less than 100 femtoseconds
- Challenging observation
- Dynamics relate to valence hole

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$



Experimental Scheme



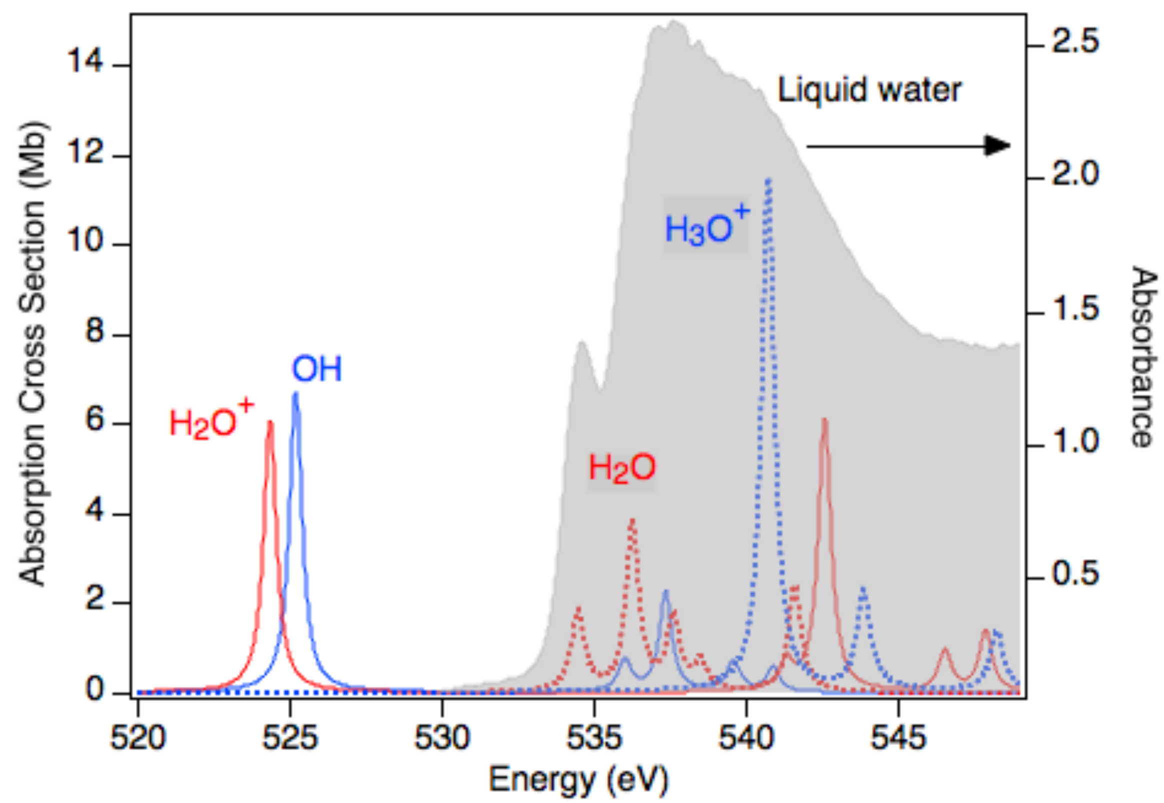
Pump pulse

- Strong-field ionisation removes valence hole

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

Probe pulse

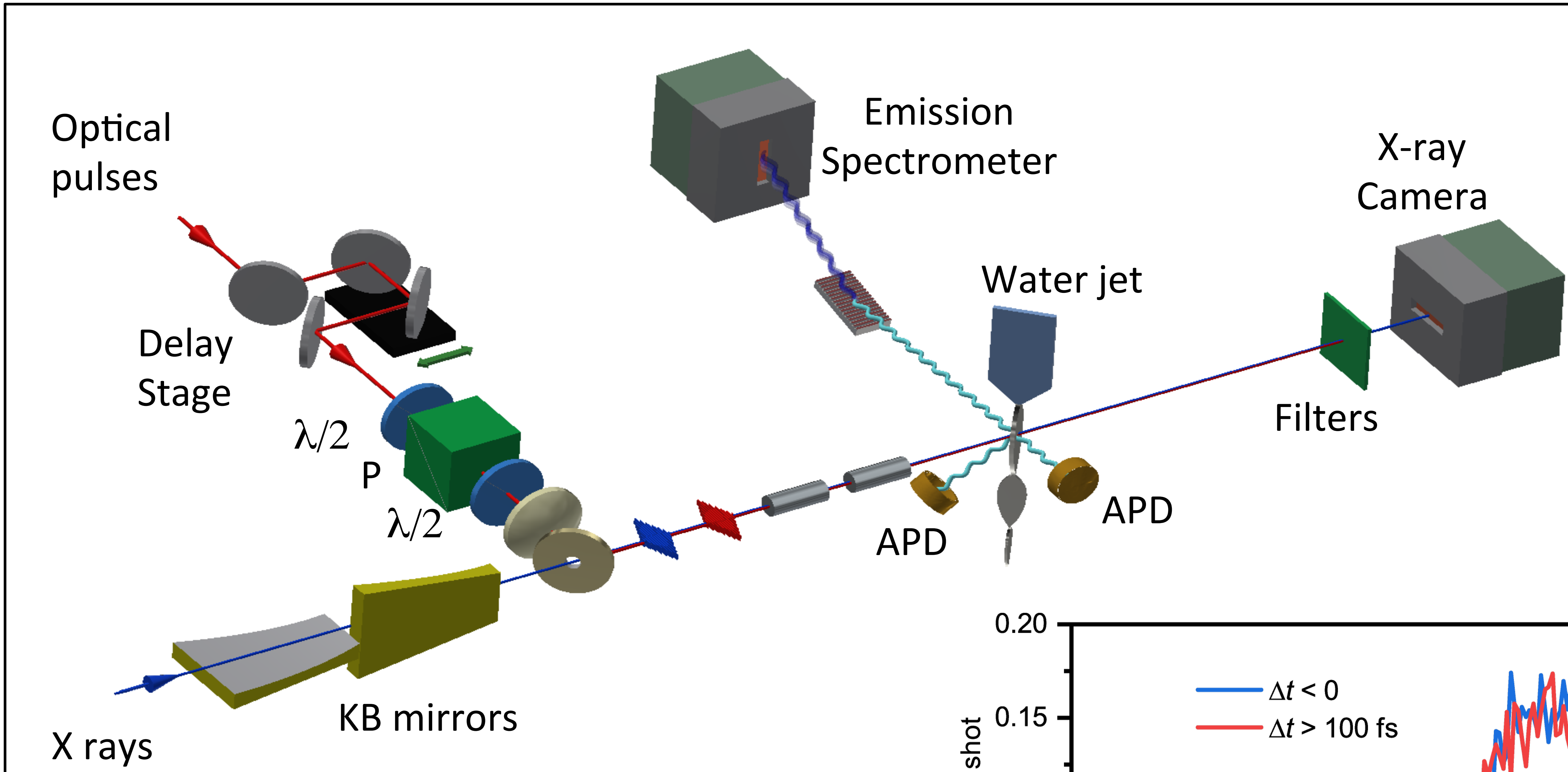
- Resonant x-ray absorption to the valence hole
- Spectrum relates to chemical environment

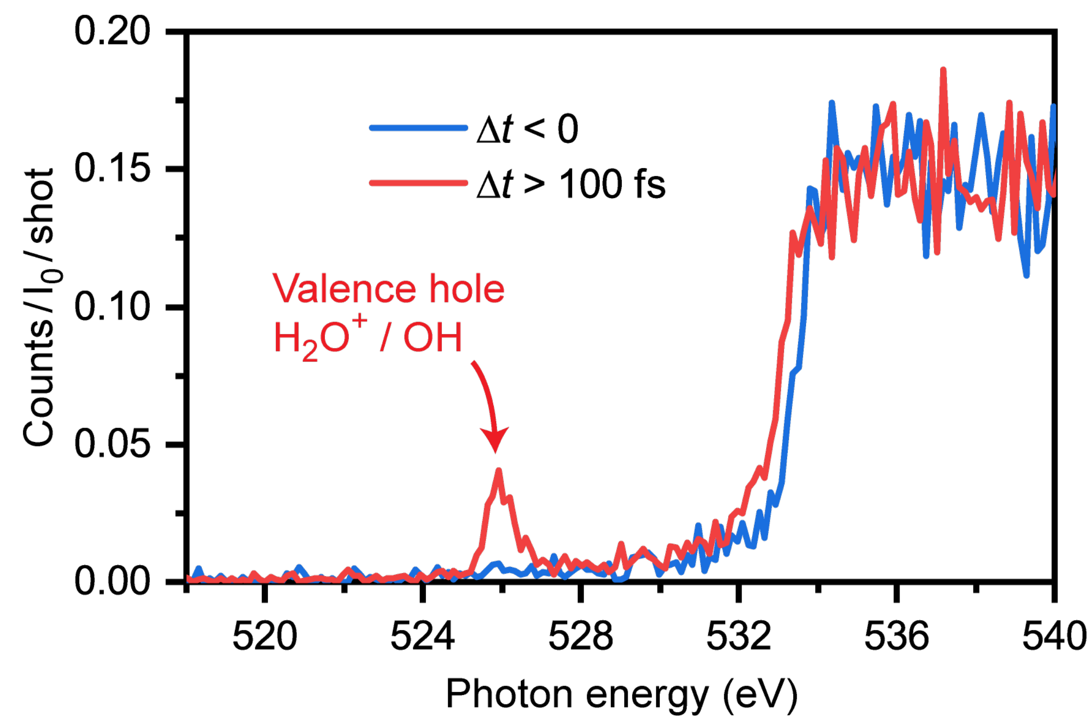


Loh, Doumy, CA, et al, Science 367, 179 (2020)

Experimental Setup

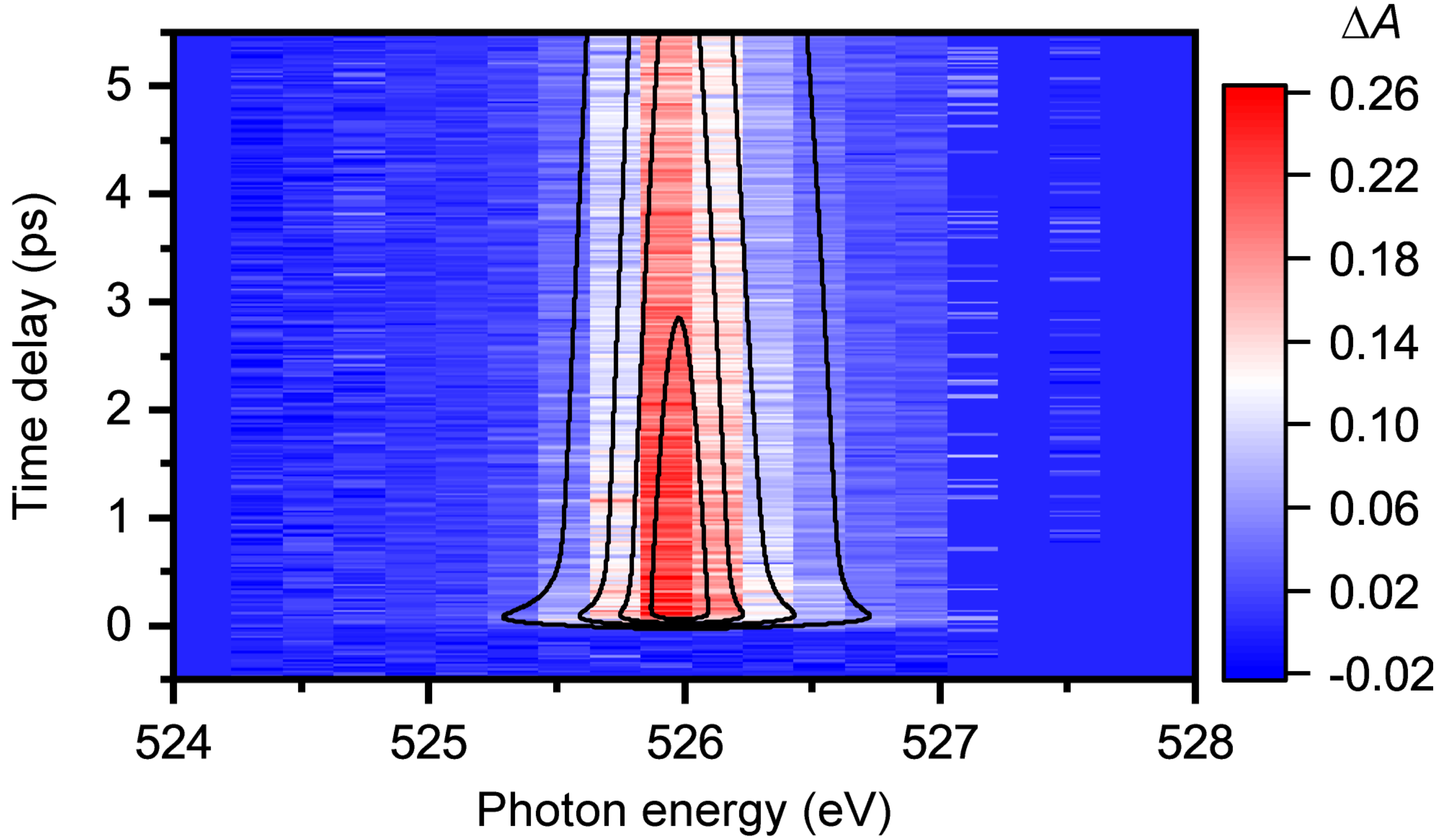
LCLS SXR



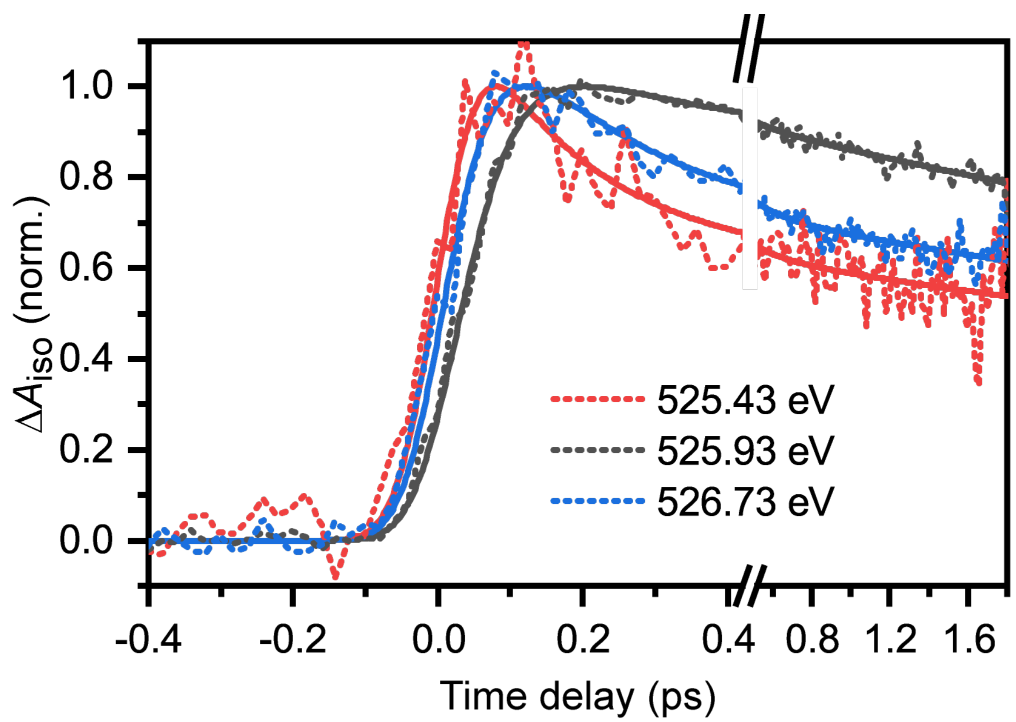


Loh, Doumy, CA, et al, Science 367, 179 (2020)

X-ray Absorption Spectrum (Experiment)



Selected time traces



$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

Sequential kinetics: identify 3 distinct time scales in the x-ray absorption spectrum

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

Interpretation of the spectrum: simulate molecular dynamics

Loh, Doumy, CA, et al, Science 367, 179 (2020)

Ab initio molecular dynamics of ionised liquid water

Large system with non-adiabatic effects

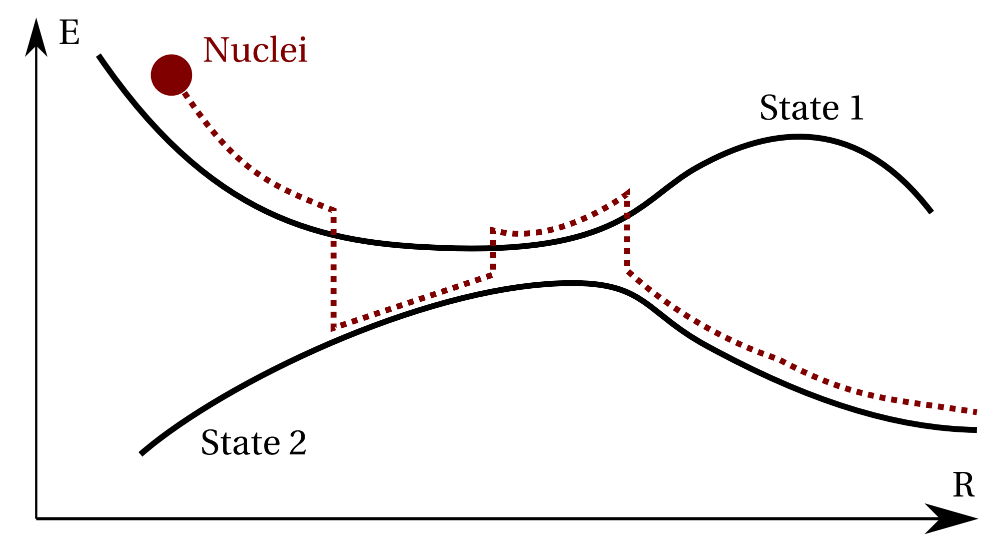
- Computational challenge
- XMOLECULE extension

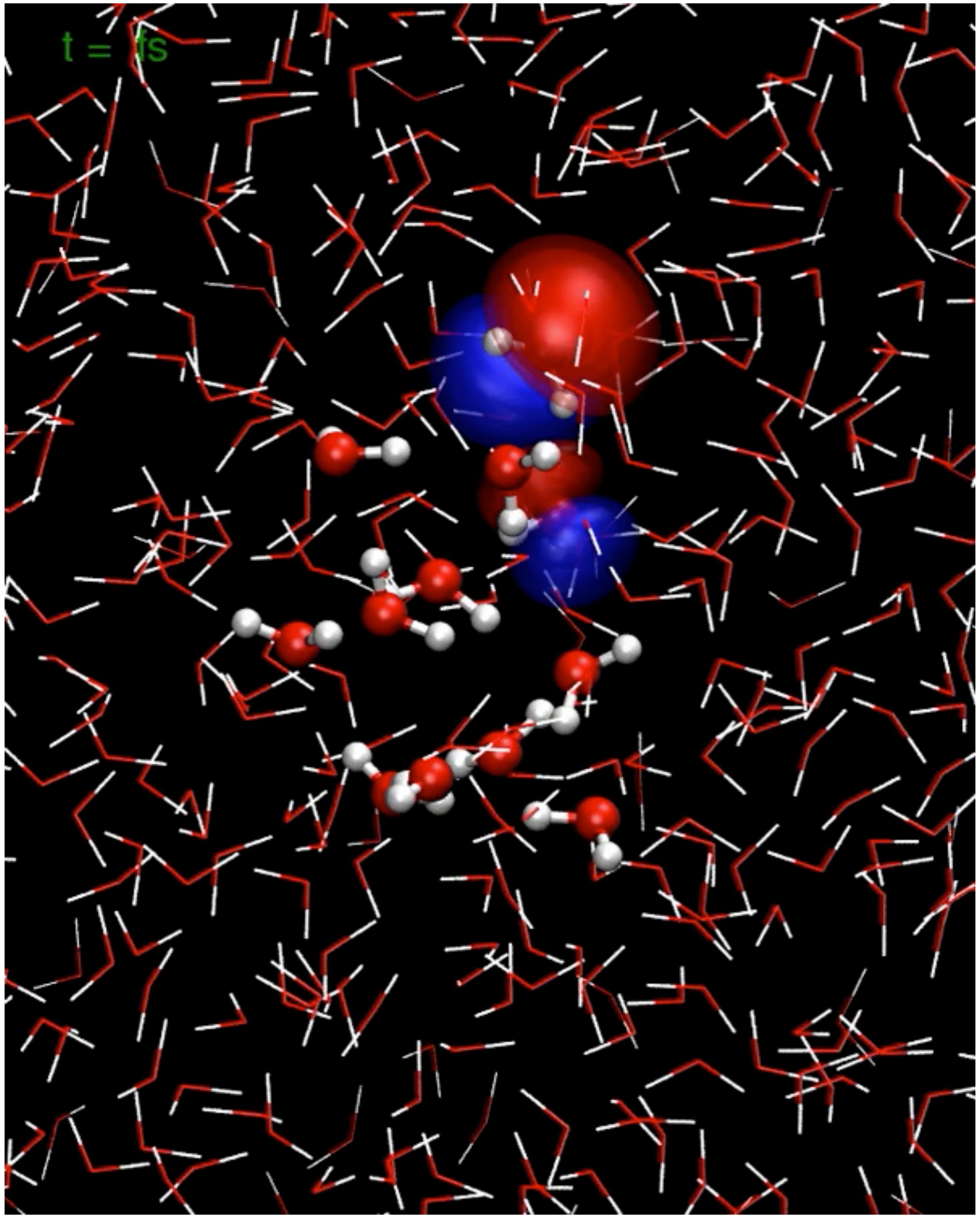
Quantum Electrons

- $(H_2O)_{12}^+$ cluster (QM/MM)
- Hartree-Fock electronic structure + Koopmans' theorem

Classical Nuclei

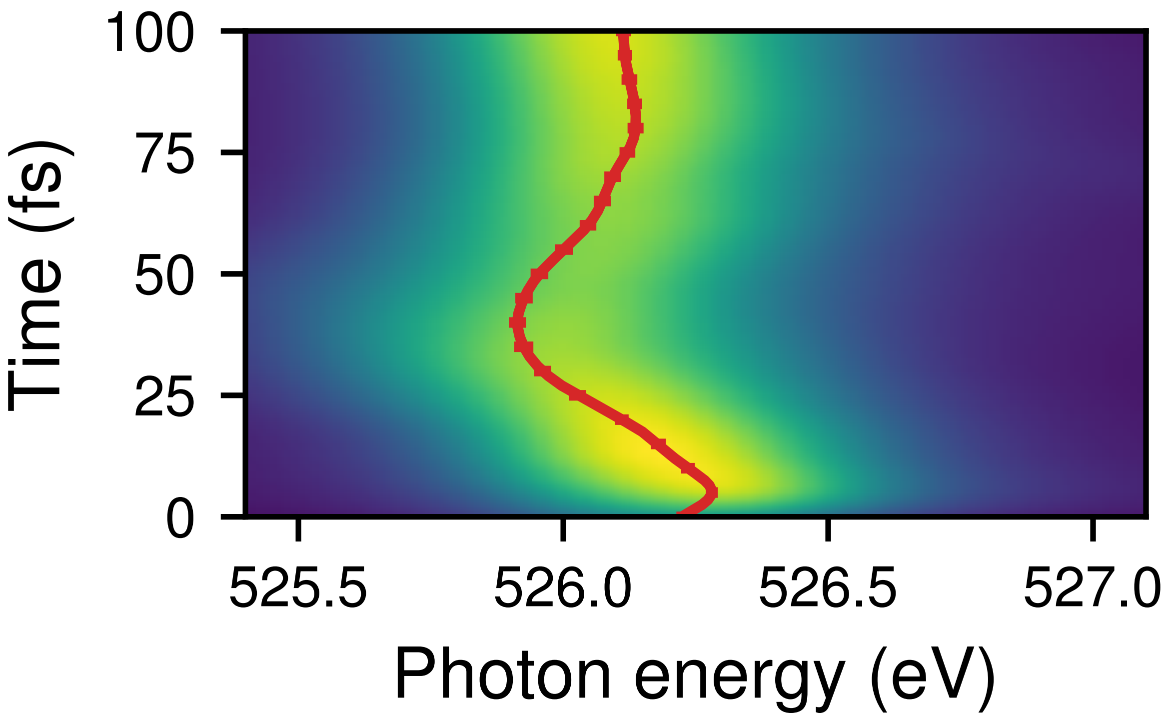
- Fewest-switches surface hopping

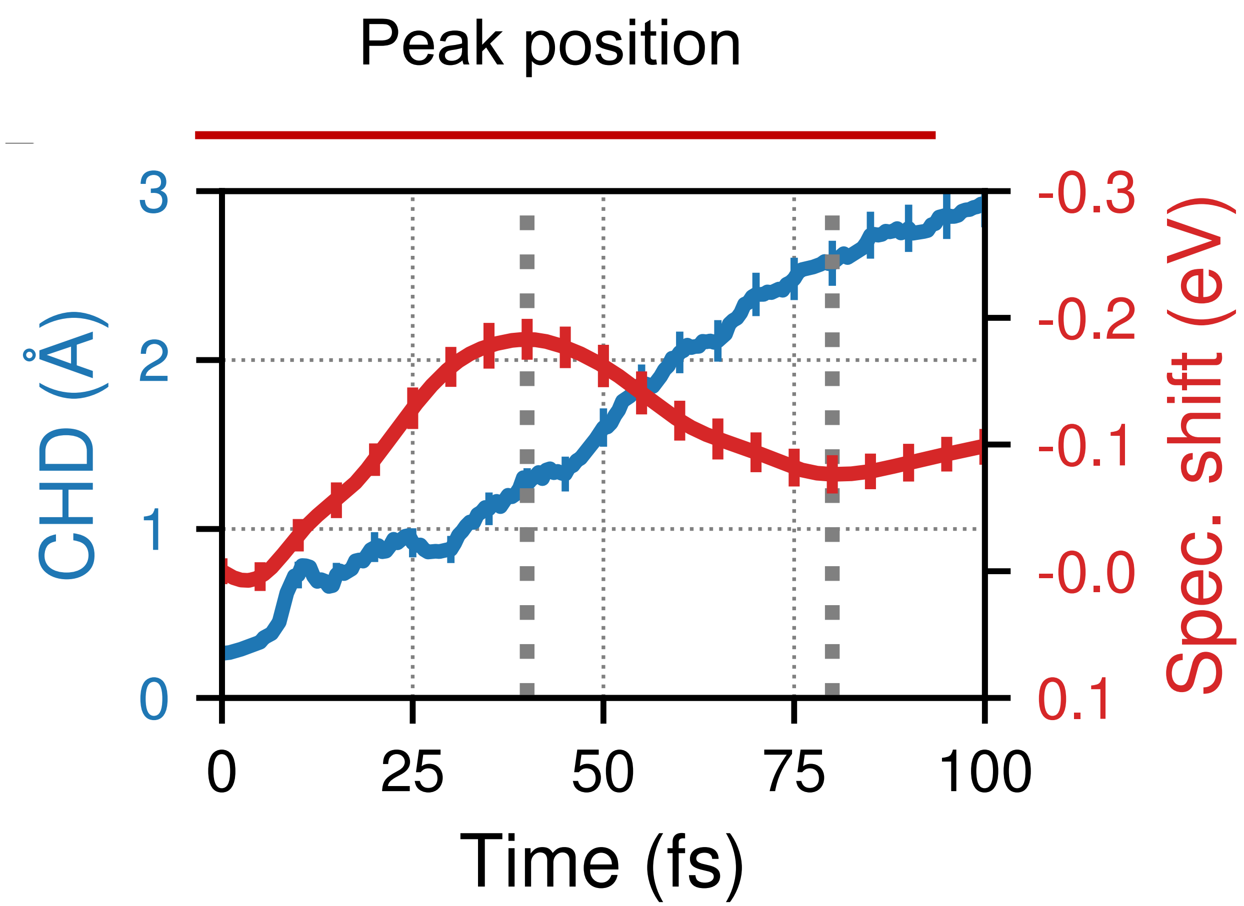




X-ray absorption spectrum and proton transfer

How does the probe signal relate to the ultrafast dynamics?

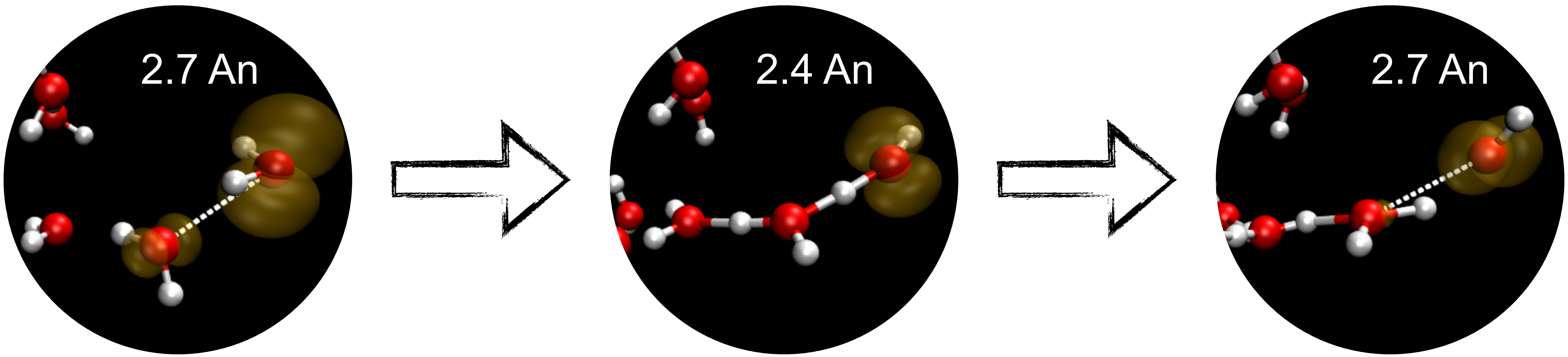




- Charge / hole distance (CHD) = proton transfer completed
- Correlated with spectrum peak shift for 40 femtoseconds
- Something is missing!

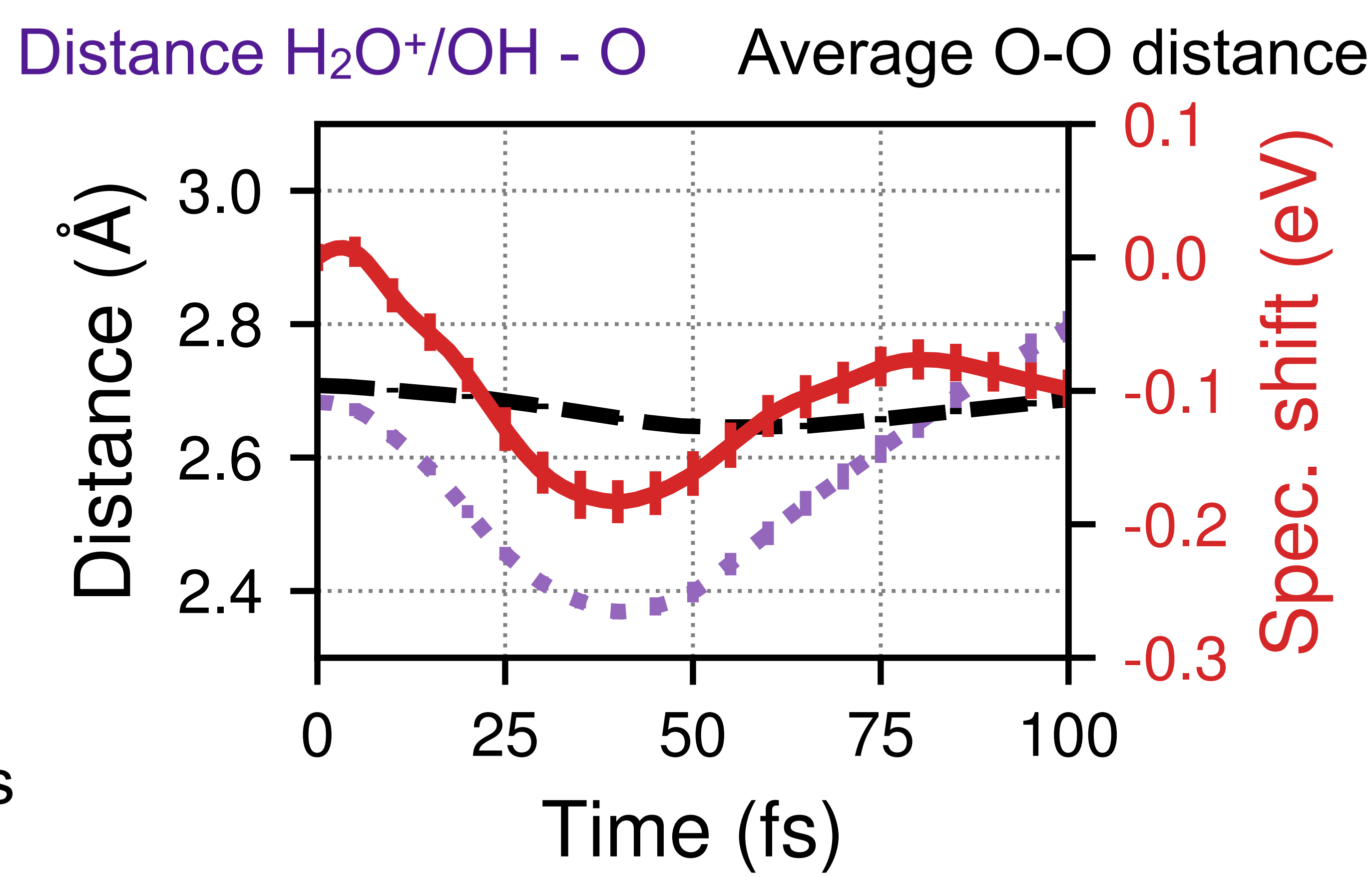
$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$

H_2O^+/OH chemical environment



- Coulomb: O atoms move towards H_2O^+
- Changes chemical environment of hole
- Proton transfer separates hole and charge

- ☑ Correlation with spectral shift
- ☑ Indirect sensitivity to proton transfer
- ☑ Matches experimental $\tau_0 = 46 \pm 10$ fs

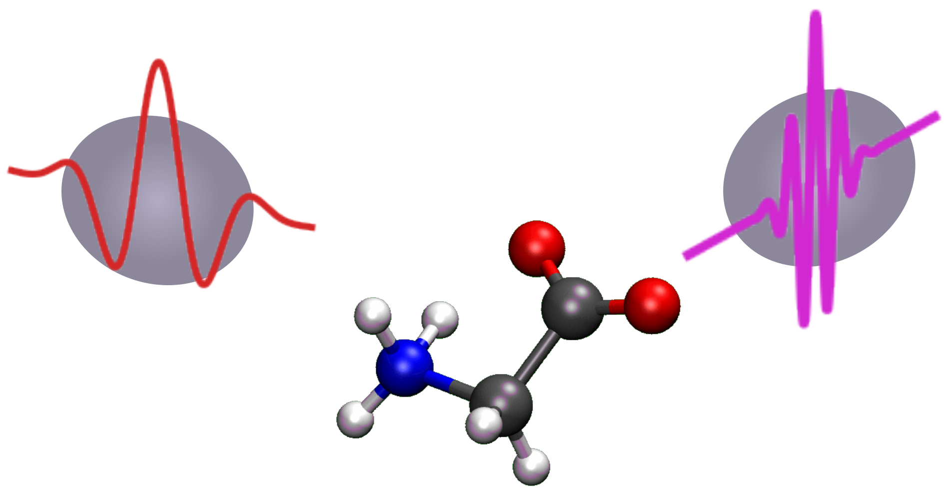


Loh, Doumy, CA, et al, Science 367, 179 (2020)

Conclusion and outlook

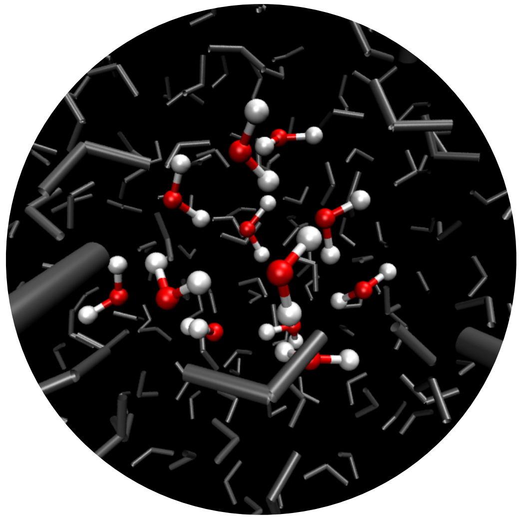
Molecules move within femtoseconds

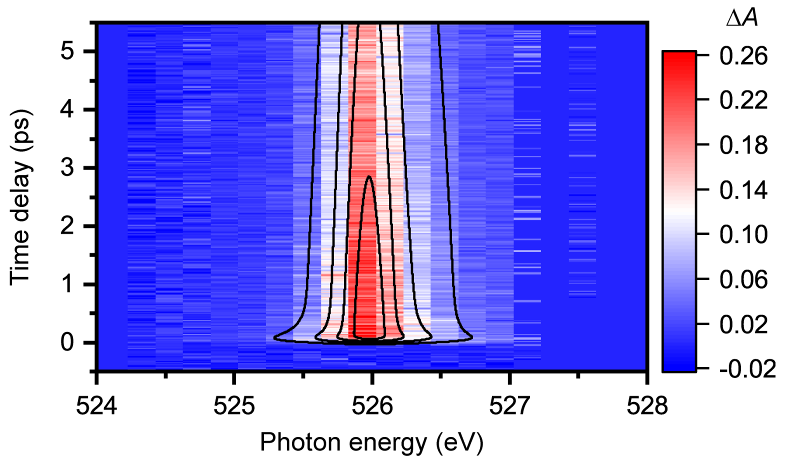
- Imaging with light pulses
- Pump-probe experiment



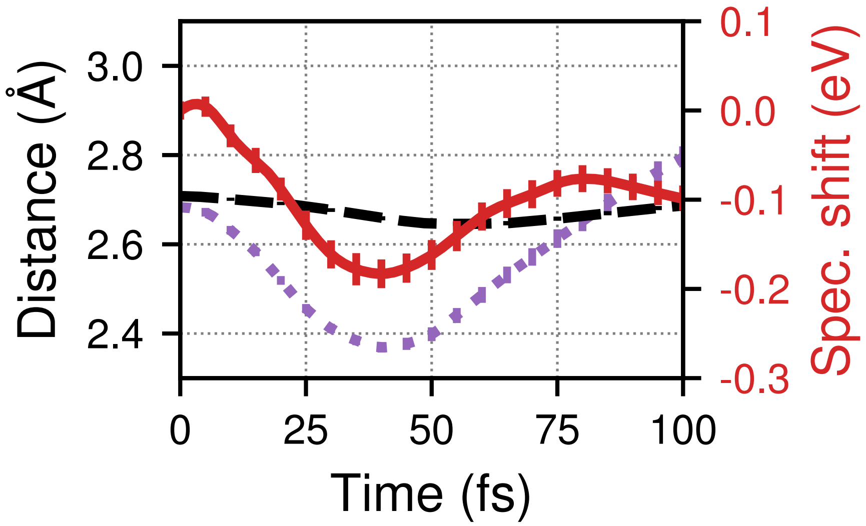
Ionised liquid water

- X-ray absorption spectroscopy
- Reflect OH formation
- Indirect sensitivity to proton transfer





Better time resolution with lab-based light sources?



Publication

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

Thank you for your attention

CFEL-DESY Theory Division

Robin Santra
Ralph Welsch
Ludger Inhester
Khadijeh Khalili

LCLS — W. F. Schlotter

Nanyang Technological University Singapore — Zhi-Heng Loh

Uppsala Universitet — J.-E. Rubensson

Argonne National Laboratory — Linda Young

UCLA — Anna Krylov

CUI The Hamburg Centre for Ultrafast Imaging

Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

DESY.