Measurement of Ultrafast Electronic Dynamics with X-rays

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LR25 collaboration, Attosecond Campaign collaboration, DESY collaboration at FLASH

Contents

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SLAC

1. Why do the ultrafast dynamics of electronically excited systems matter to us ?

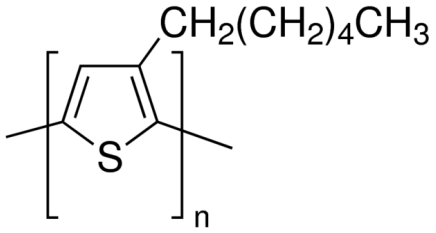
Life-on earth, and increasingly our sustainable technologies, are powered by solar driven electronic excitation.

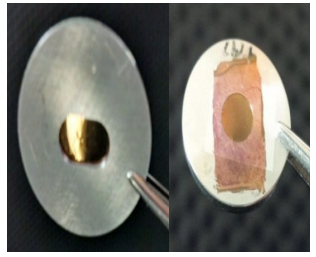
This provides a timely impetus for the science.

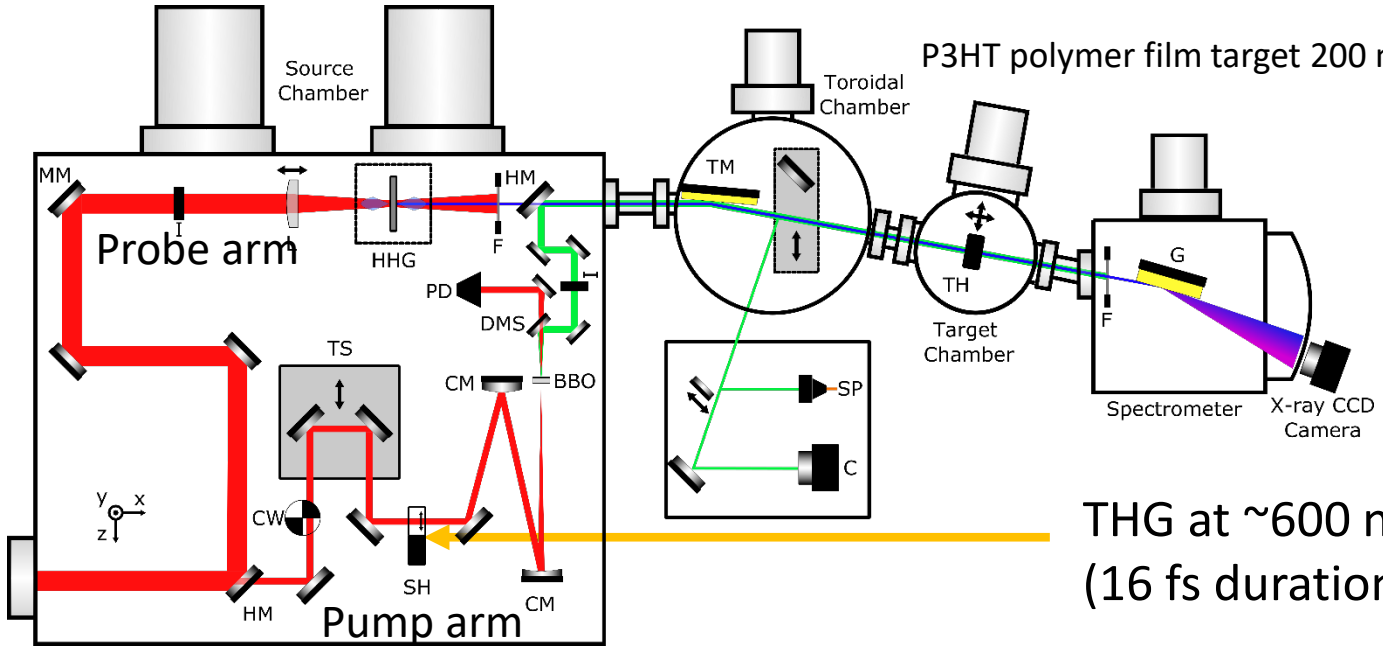
Ultrafast X-rays give us access to the < 10^{-10} m s*patial* and < 10^{-15} s *temporal* scales needed to fully track the electronic excitation driven dynamics in matter

1. Time-resolved HHG based XANES in P3HT

Dougie Garratt, David Wood, Lukas Miseikis, Esben Larsen, Mary Matthews et al

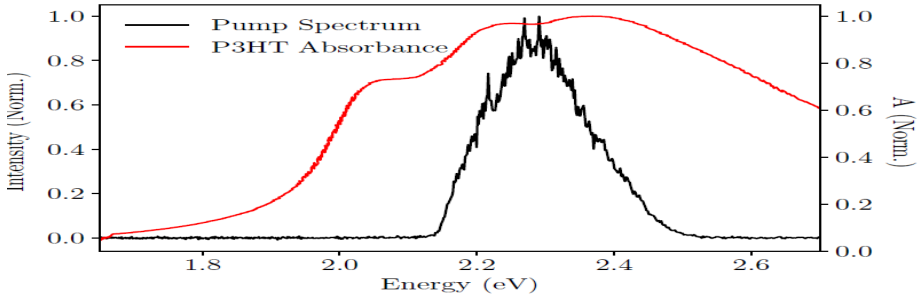


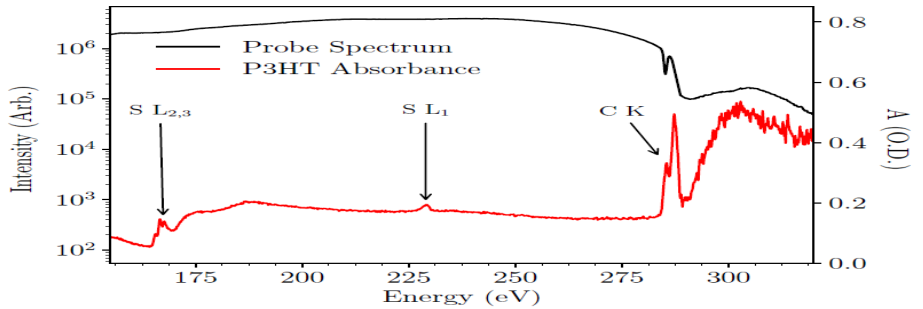




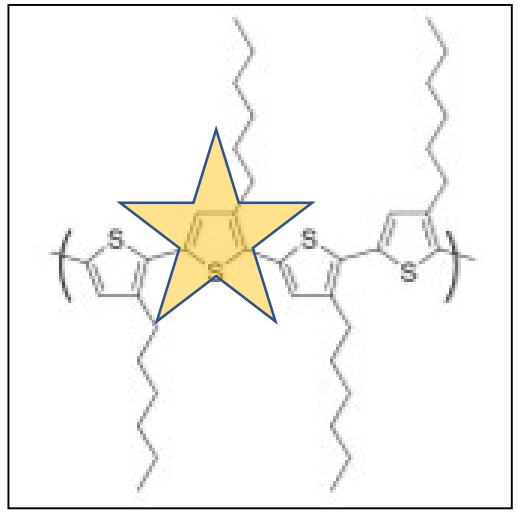
P3HT polymer film target 200 nm thick

THG at ~600 nm to pump exciton
(16 fs duration measured with SH-FROG)





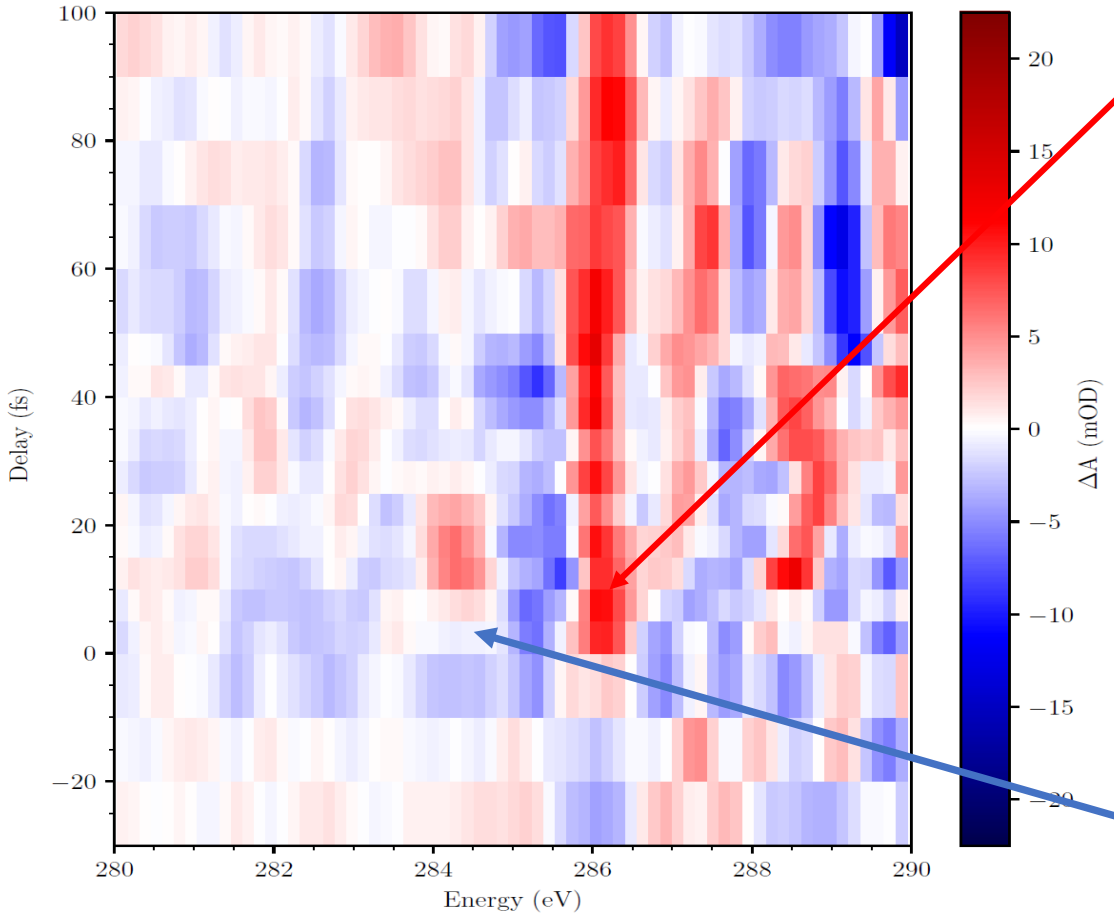
XFEL time-resolved XPS studies recently reported for charge separation in another organic light harvesting system https://doi.org/10.1038/s41467-021-21454-3
but at much lower temporal resolution than in our work



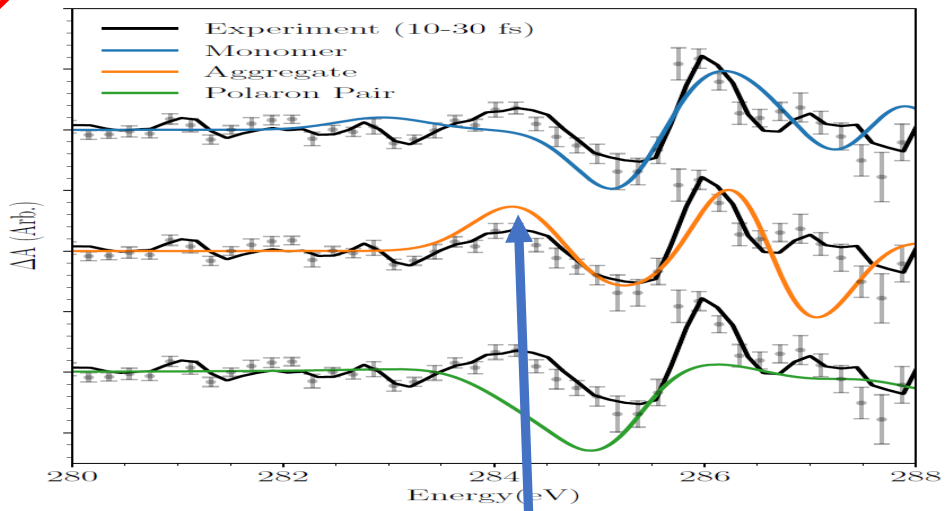
Exciton in polymer ~ 700 – 500 nm

1. New evidence of ultrafast hole delocalisation

X-ray transient absorption signal provides a direct probe of the initial localisation and cooling of the hot exciton formed by the pump



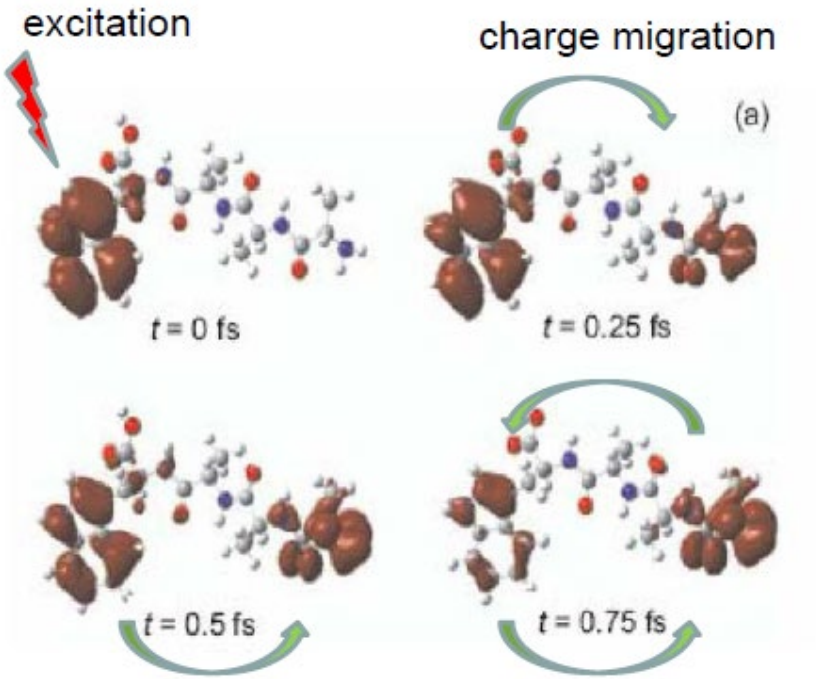
B. Edge shift following exciton creation



Extending model to a pair of tetrathiophene oligomers 0.4 nm apart. Captures the transient feature indicating the role of exciton delocalisation

A. Transient feature – formation of hole state associated with exciton

2. Sudden photo-ionisation of a molecule: The first 10 femtoseconds



Charge (hole) migration in the peptide Trp-Ala-Ala-Ala (Remacle & Levine)

Charge Migration

Sudden electron removal can form a localised hole state that is a coherent superposition of the eigenstates of the molecular ion and so undergoes rapid evolution. This results in large amplitude charge oscillation across the molecule on an attosecond timescale.

Important to photochemistry and biological radiation damage, as well as to the fundamentals of time-dependent behaviour of many electron systems.

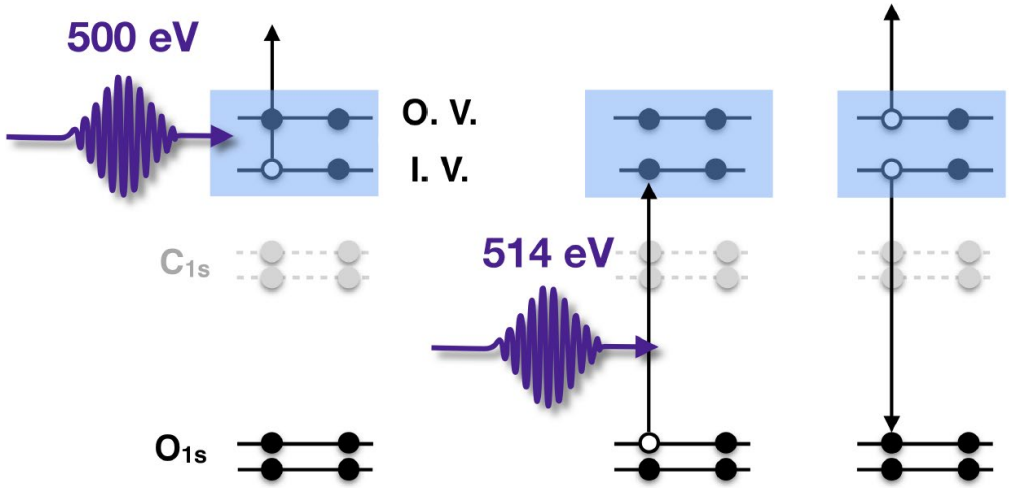
New paradigm in "charge directed" reactivity but:

How long does electronic coherence survive?
Can we control it?
How does electronic coherence evolve into longer lived vibronic coherence?

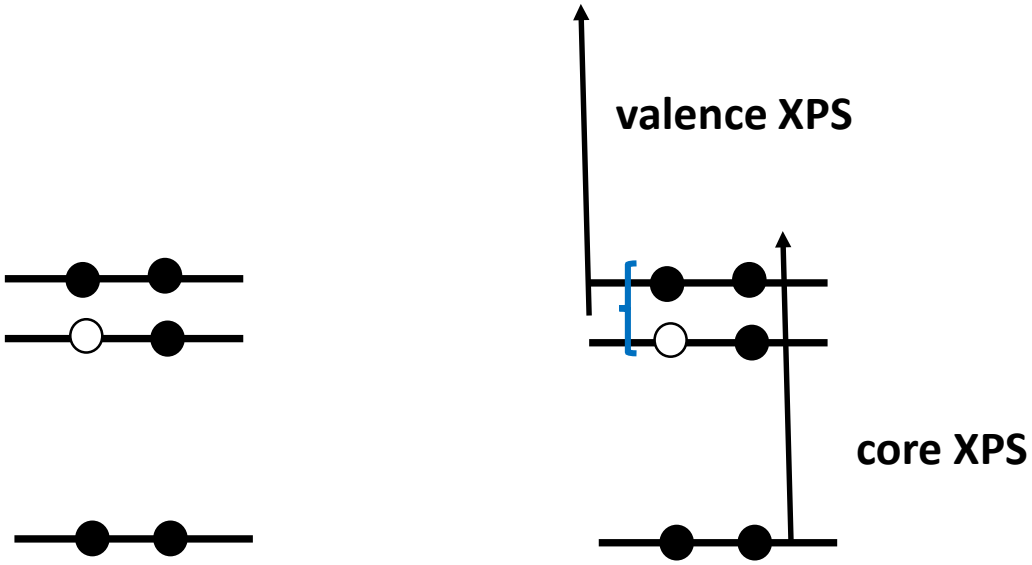
2. Measurement strategy: X-ray pump - X-ray probe

X-ray absorption spectroscopy (XAS) probe measurement – resonant to O 1s to specific inner valence hole state (IVH) to monitor hole amplitude at given delay time

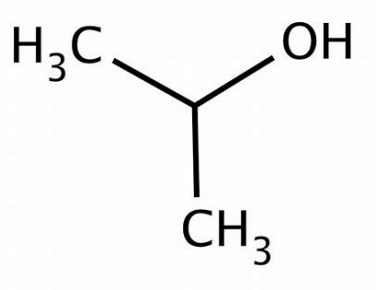
B.Cooper et al Faraday Discussion 171, 93 (2014)

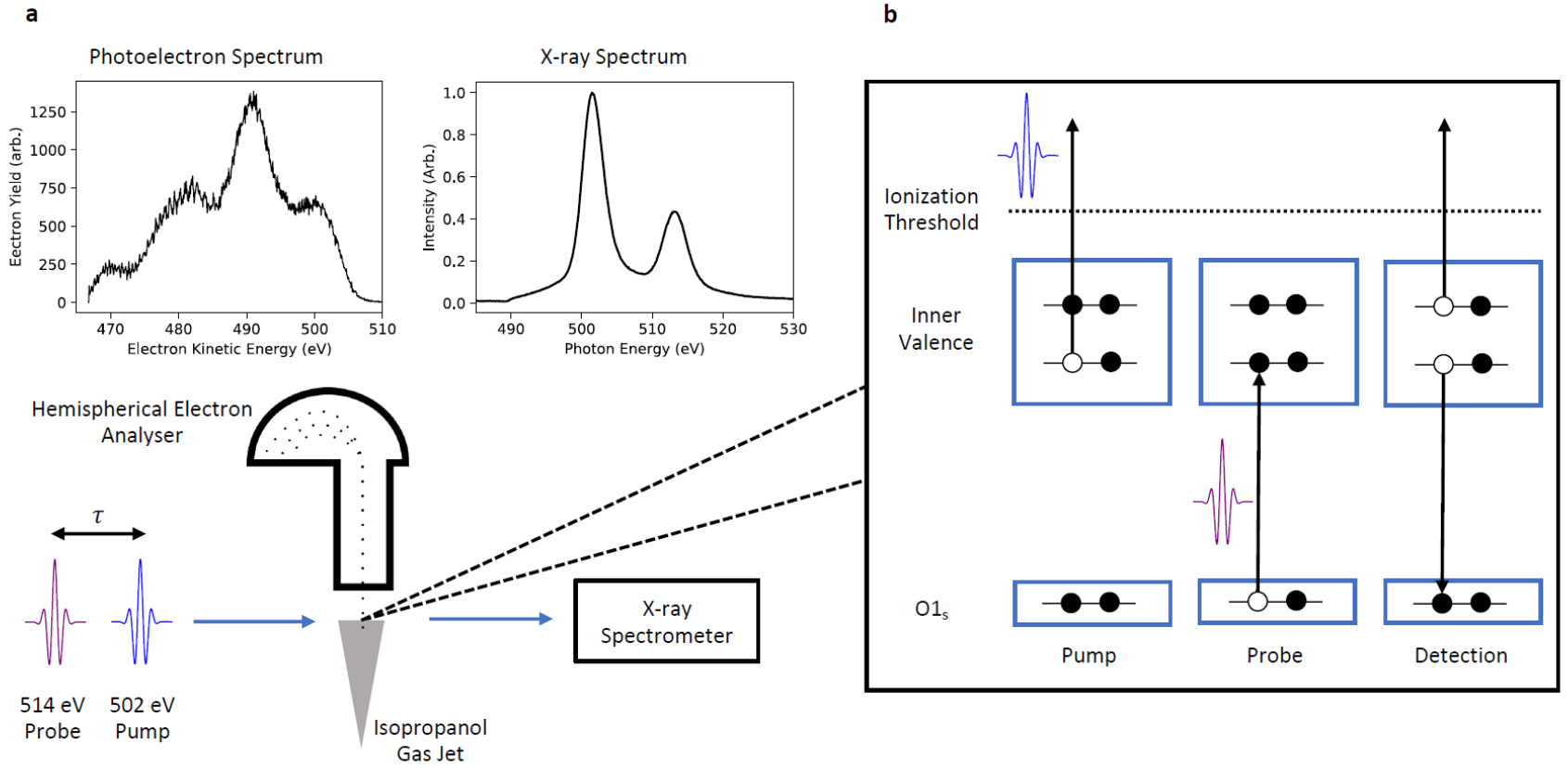


X-ray photoelectron emission spectroscopy (XPS) probe measurement (valence or core shell) – also sensitive to valence state evolution with delay



2. X-ray absorption spectroscopy: X-ray pump/X-ray probe of correlation driven hole dynamics in isopropanol



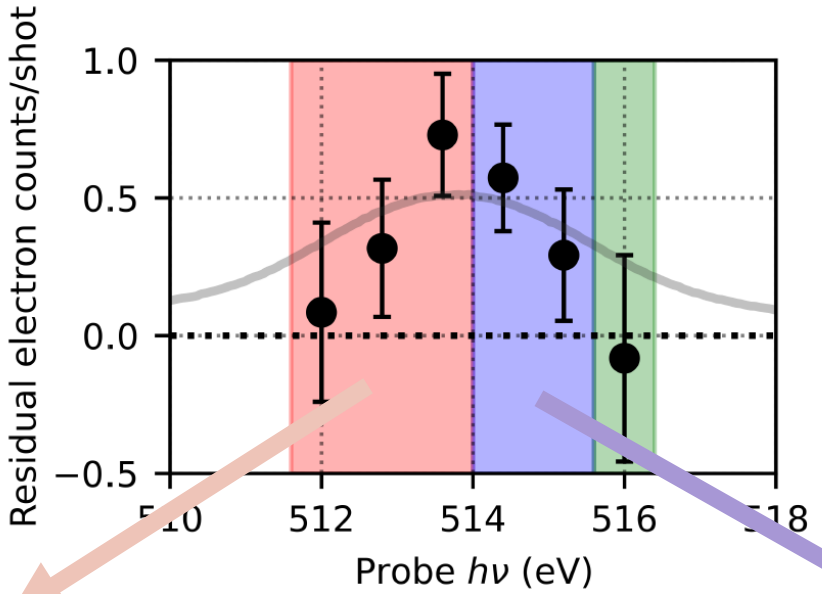


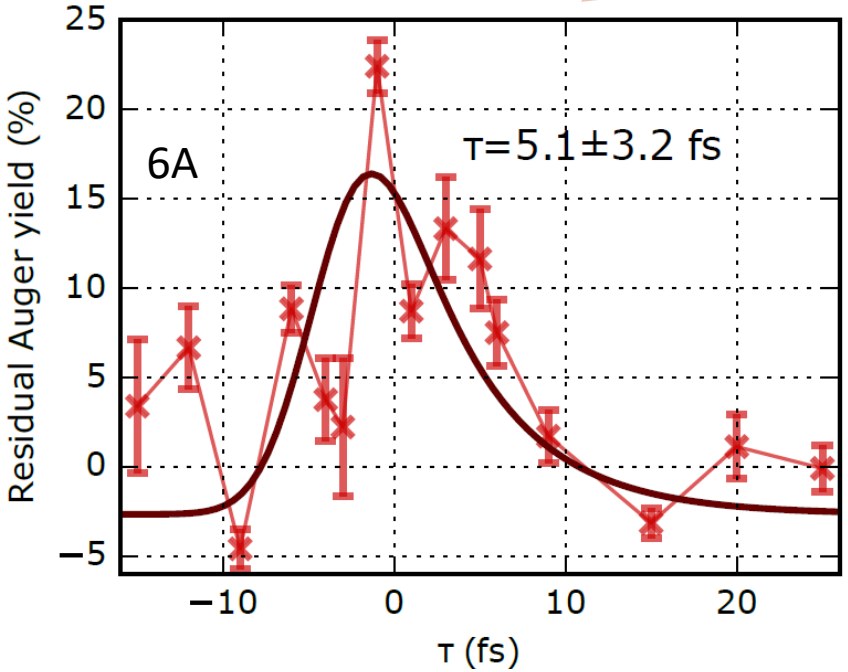
Transient hole states – but Auger decay energetically forbidden so can't use streaking probes

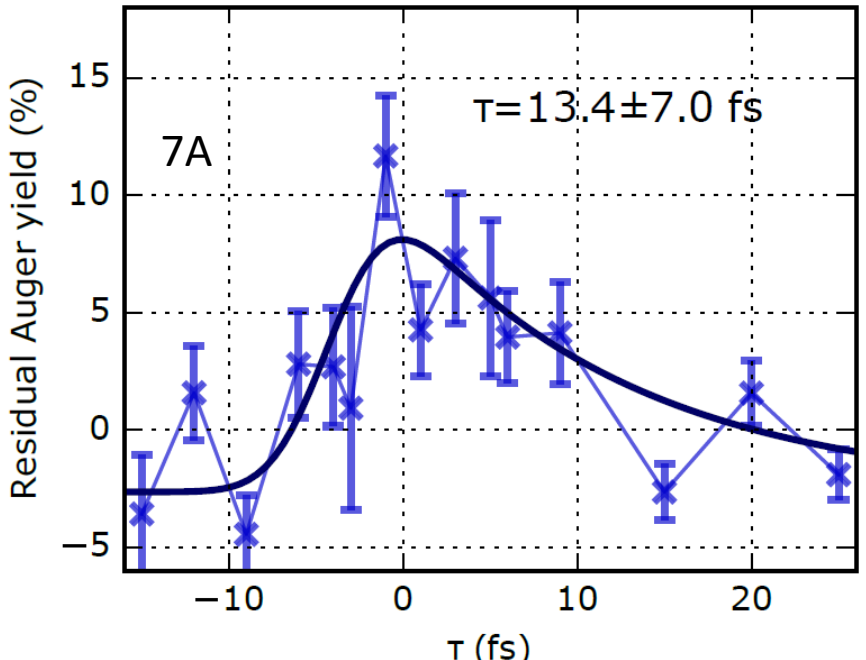
<u>AMO end-station LCLS</u>: Two pulses generated using <u>fresh-slice</u> mode form pump and probe, with chicane controlled delay. Most data was taken with ~ 5 fs pulse durations over a -10 to +25 fs delay range. But a shorter data run with ~ 2.5 fs pulses was also taken.

Extensive data reduction and analysis is required to establish the signal from background and to sort shots against intrinsic fluctuations in X-ray properties

2. Transient 6A & 7A hole states probed by X-ray spectroscopy

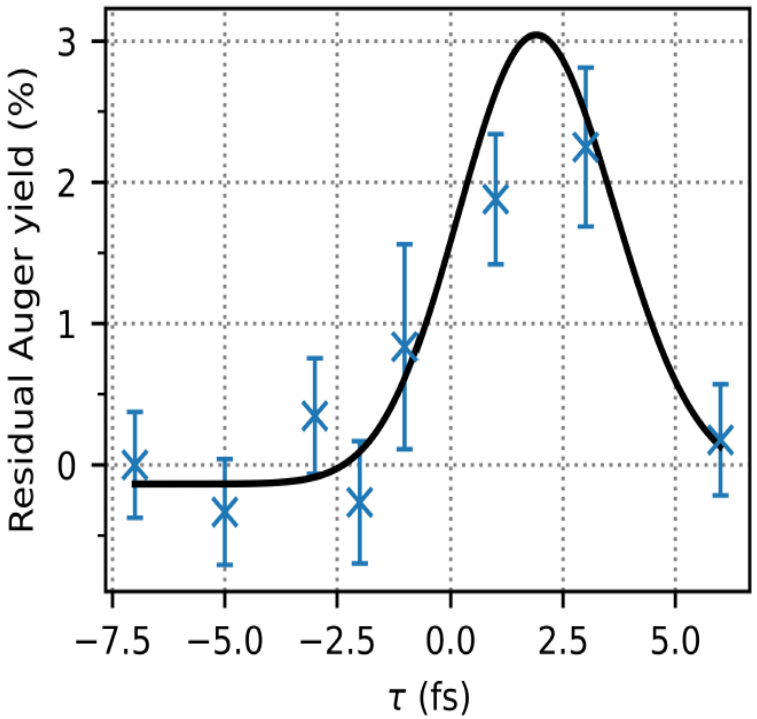


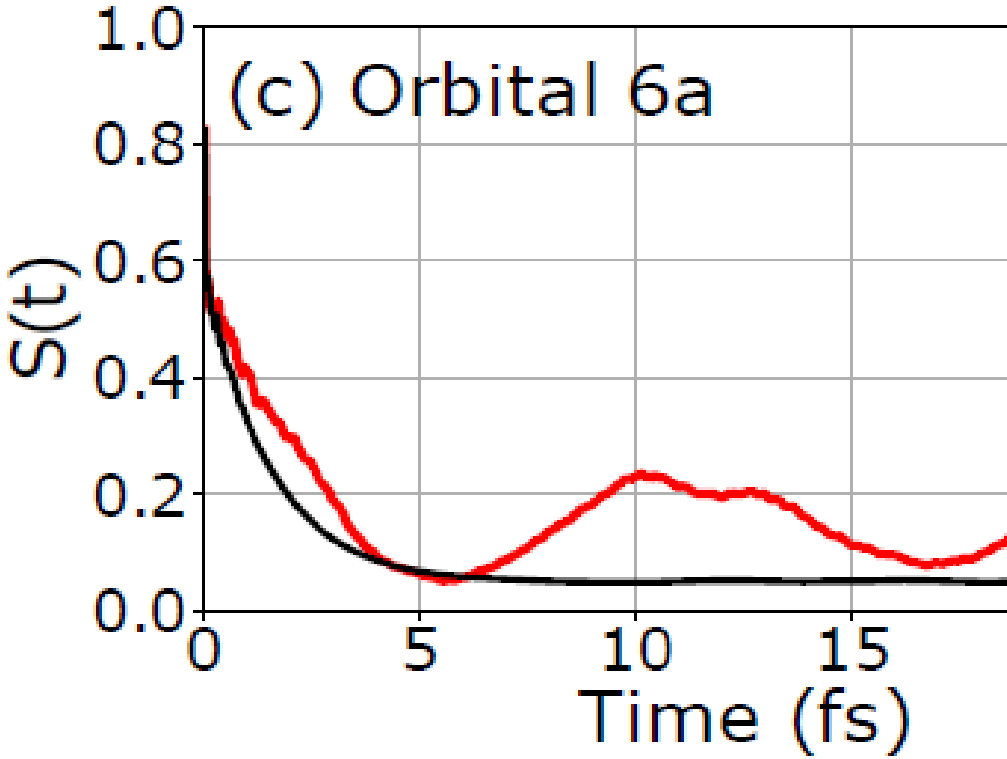




2. Transient 6A hole state probed by X-ray spectroscopy

6A measured with shorter pulses, exponential fit to data gives lifetime 1 +/- 2 fs. Consistent with the ultrafast state decays driven by electron correlation calculated via ADC theory



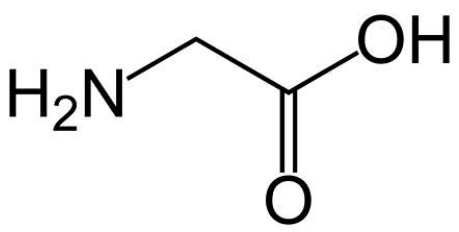


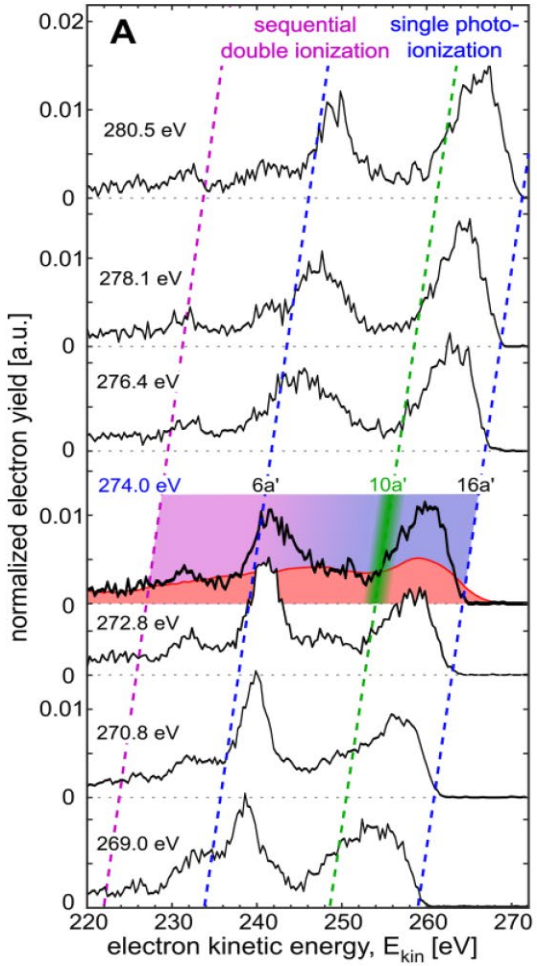
T.Barillot et al, "Correlation Driven Transient Hole Dynamics Resolved in Space and Time in the Isopropanol Molecule", accepted PRX June 2021 (arXiv:2105.06507)

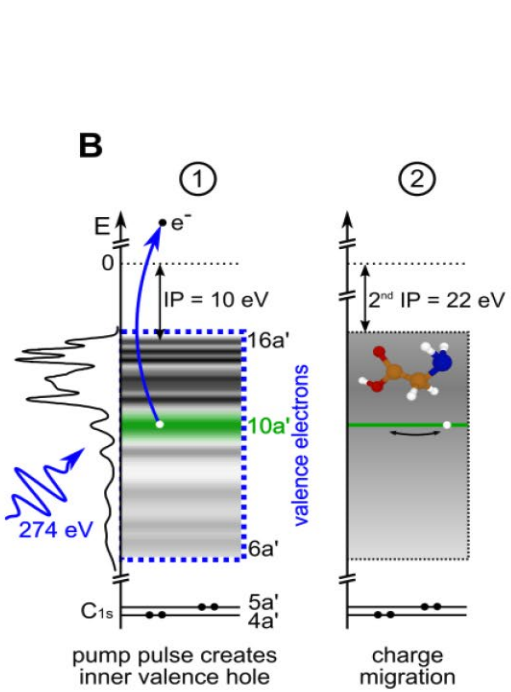
Spectral domain ghost imaging analysis DOI: 10.1039/D0FD00122H (Paper) *Faraday Discuss.*, 2021,

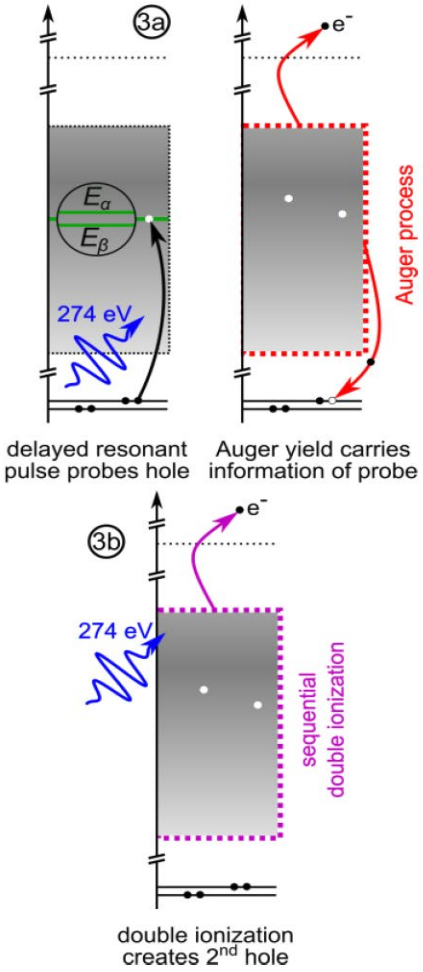
2. Split and delay at FLASH : Coherent hole dynamics in glycine

Led by Tim Laarmann, DESY Collaboration at FLASH





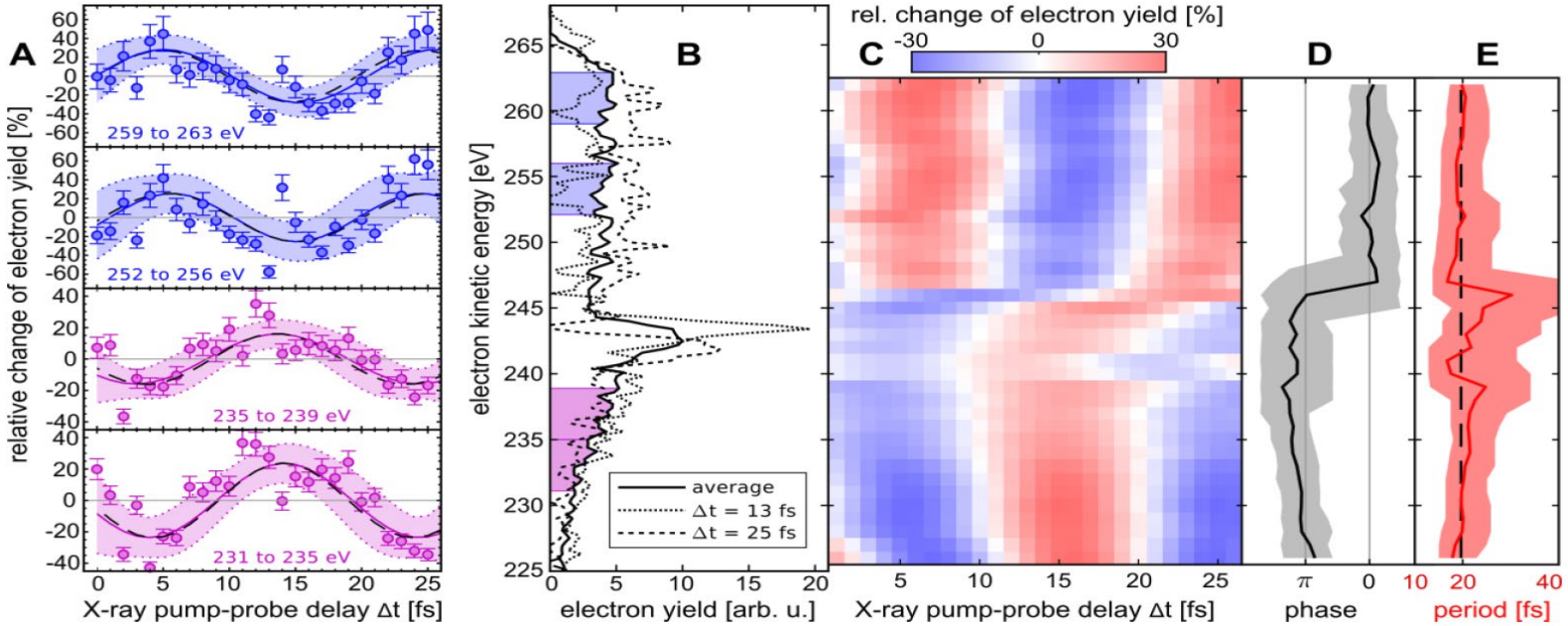




Measurements at FLASH using X-ray split-and-delay with a short pulse for a single colour pump-probe measurement. X-ray photoelectron spectra observable was measured with the pulses ~ 275 eV with a pulse duration < 5 fs delayed between 0 – 25 fs

2. Split and delay at FLASH : Coherent hole dynamics in glycine

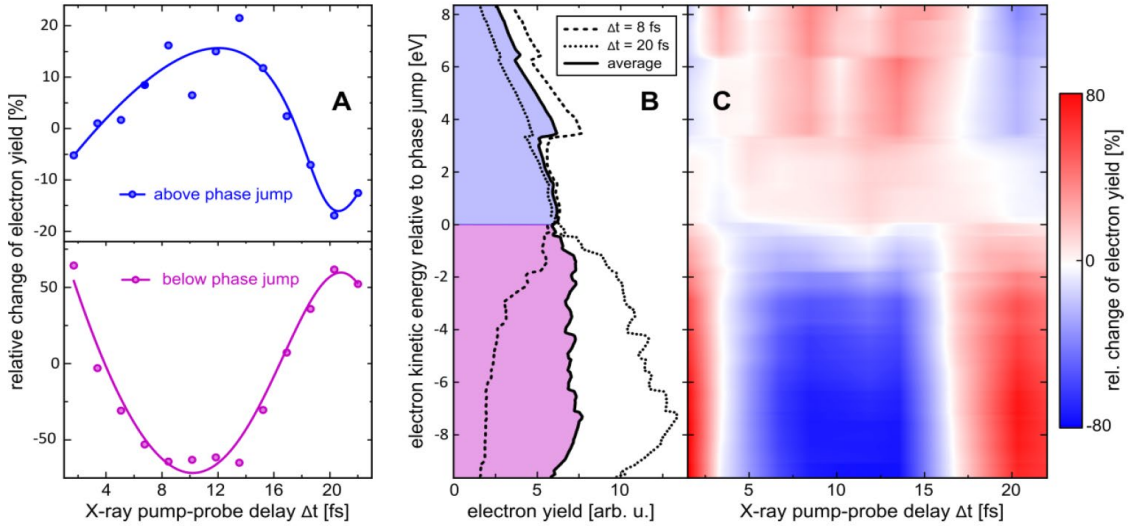
Led by Tim Laarmann



Dominant channel was XPS. This showed time dependent signatures in the photoelectron yield.

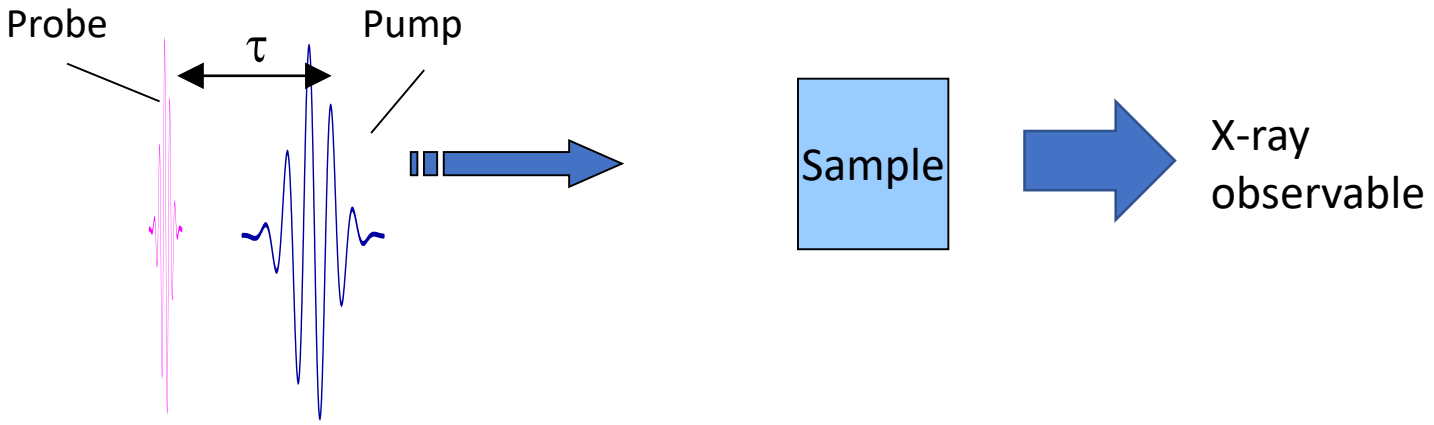
Amplitude interference (due to pump-probe degeneracy) reveals the relative sign in the photoionisation dipole across the photoelectron spectrum

Measurements suggests coherent (oscillatory) hole dynamics with a ~ 20 fs periodicity, in quantitative agreement with predictions for 10a state hole with B spline RCS-ADC theory, also agrees on amplitude and phase of oscillation



D. Schwickert et al, Electronic quantum coherence in glycine probed with femtosecond x-rays (2021), arXiv:2012.04852

3. Probing a wider class of electronic dynamics calls for a wider range of highly synchronized ultrafast pumps



Going beyond X-ray pump to capture first steps in electronic excitation from UV-visible or charge particles

Pump (X-ray to THz) + electron/ion beams – activates the sample:
e.g. Optical & UV electronic excitation, XUV excitation of specific cation channels, excitation by charge particles, simultaneous excitation of vibrational/rotational states

Probe (X-ray) – interrogates the sample after delay time τ by generating a suitable observable:
e.g. X-ray scattering/diffraction, resonant inelastic X-ray scattering (RIXS), X-ray spectroscopy (absorption (XAS) and emission (XES), X-ray photoelectron spectroscopy (XPS) etc.)

3. Future opportunities in ultrafast electron dynamics with XFELs

- To explore electronic coherence in neutral systems requires optical/UV sources (laser or accelerator based) synchronized to XFELs to better than 1fs or sorted with time tools e.g. using “streaking”
- Extension from gas to liquid phase looks promising (e.g. liquid sheet jets suitable for XAS approach) but need photonic as well as electronic detection channels.
- Fast sample scanning and/or measurement before destruction needed for solid phase systems
- Need more access to, and development of, XFEL attosecond modes at other facilities
- Need high rep-rate (X-rays and synchronized sources) matched to samples, detectors and external lasers to measure with sufficient sensitivity in dilute systems in realistic complex environments

4. Conclusions

- **Ultrafast electronic coherence and coupling to nuclear modes is important in future solar driven and quantum control technologies**
- **X-ray FELs are now able to provide unique probes of these dynamics with exquisite precision as demonstrated by recent X-ray pump-probe experiments**
- **Need a broader range of ultrafast capabilities at high repetition rate and with tightly synchronized/timed (to < 1 fs) X-ray and optical fields (from XUV to THz) to fully capture the opportunities for transformative research**

Thank you for your attention

Acknowledgements

Attosecond Campaign Collaboration +++

LR25 Collaboration

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