UK XFEL and Frontiers of Ultrafast Science

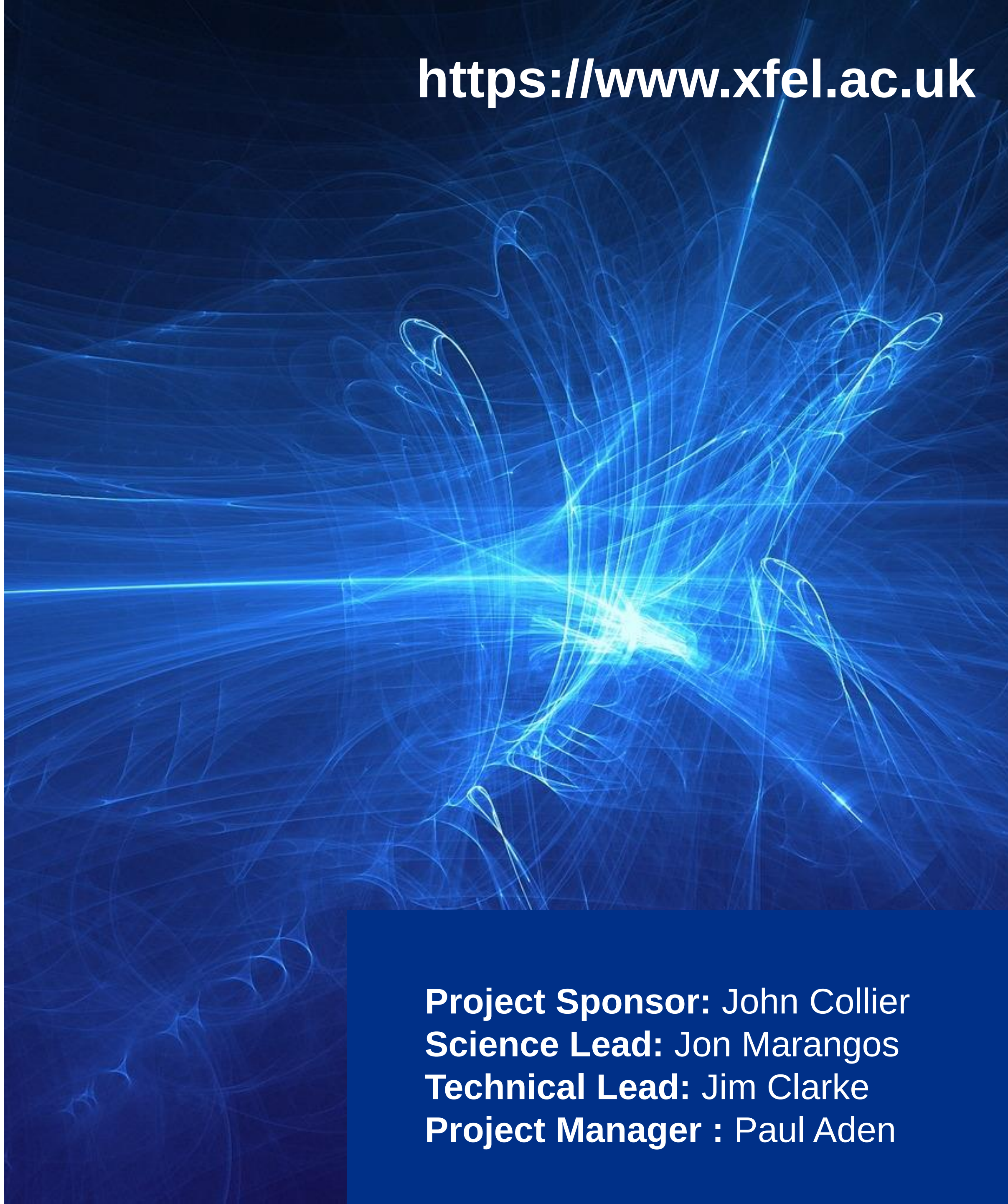
https://www.xfel.ac.uk

1. Overview of UK XFEL Science Case and Project Definition

2. Ultrafast photophysics and photochemistry probed with x-rays

3. Attosecond x-ray non-linear interactions

4. Summary



Project Sponsor: John Collier
Science Lead: Jon Marangos
Technical Lead: Jim Clarke
Project Manager : Paul Aden

Science and
Technology
Facilities Council

1. The Science Case for UK XFEL 2019 -2020

UK RI Science and Technology Facilities Council

UK XFEL Science Case

https://www.xfel.ac.uk/

In the last decade XFELs have had an impressive scientific impact, but there is clearly scope to do much more.

Taking a long view we looked at what kind of science we will do with an advanced XFEL operating from mid 2030’s. Extrapolating current technology advances to frame what will be possible.

Objectives:

- To demonstrate scientific need
- To define a next generation XFEL capability
- To inform the technology that must be developed

Now gathering material for an updated Science & Technology case for 2025

1. Authored by an expert science team

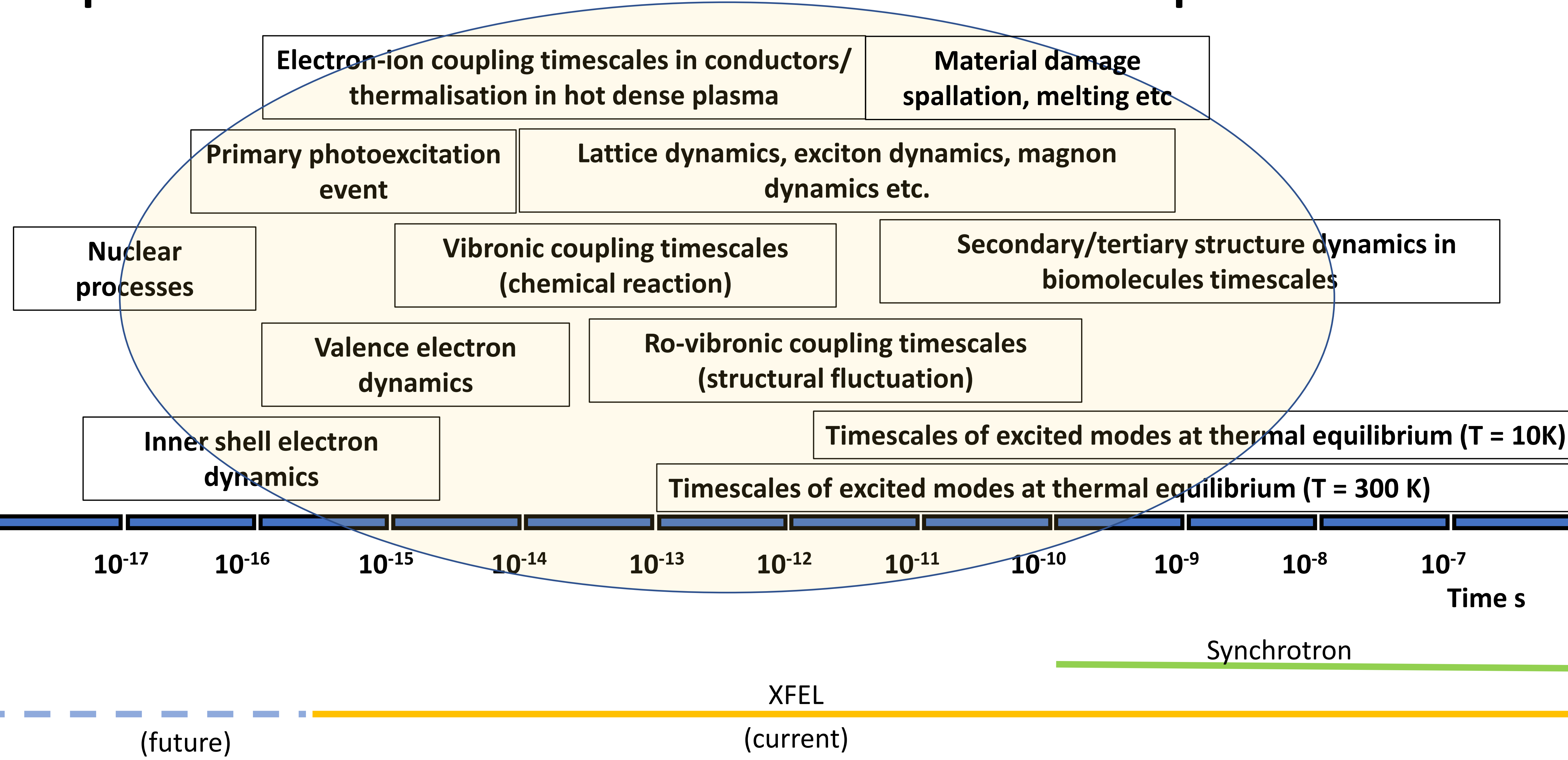
- **Matter in extreme conditions**: *Andy Higginbotham (York), Andy Comley (AWE), Sam Vinko (Ox), Marco Borghesi (QUB), Malcolm McMahon (Edinburgh), Justin Wark (Ox)*
- **Nano/Quantum materials**: *Anna Regoutz (UCL), Marcus Newton (Soton), Ian Robinson (UCL/Brookhaven), Mark Dean (Brookhaven), Simon Wall (ICFO)*
- **Engineering/Materials/Applications** : *David Rugg (RR), Sven Schroeder (Leeds), David Dye (IC)*
- **Life sciences**: *Allen Orville (DLS), Jasper van Thor (IC), Xiaodong Zhang (IC)*
- **Chemical sciences**: *Julia Weinstein (Sheffield), Russell Minns (Soton), Sofia Diaz-Moreno (DLS), Andrew Burnett (Leeds), Tom Penfold (Newcastle)*
- **Physical sciences**: *Amelle Zair (KCL), Adam Kirrander (Edinburgh), Jason Greenwood (QUB), Jon Marangos (IC and Science Lead)*

**** + around 100 additional experts from around the world contributing to Science Case***

Team significantly expanded in 2022 to also include:

Emma McBride (QUB), Shakil Awan (Plymouth), Paolo Raedelli (Oxford), Rebecca Ingle (UCL), Dan Eakins (Oxford), Mark Brouard (Oxford), Claire Vallance (Oxford), Elaine Seddon (Cockcroft), Sarnjeet Dhesi (Diamond), Adrian Mancuso (Diamond), Tian Geng (Heptares), Mike Fitzpatrick (Coventry), David McGonegle (AWE)

Science driver for XFELs is real-time access to the characteristic processes and fluctuations in matter down to the quantum scale



Electron-ion coupling timescales in conductors/ thermalisation in hot dense plasma

Material damage spallation, melting etc

Primary photoexcitation event

Lattice dynamics, exciton dynamics, magnon dynamics etc.

Nuclear processes

Vibronic coupling timescales (chemical reaction)

Secondary/tertiary structure dynamics in biomolecules timescales

Valence electron dynamics

Ro-vibronic coupling timescales (structural fluctuation)

Timescales of excited modes at thermal equilibrium (T = 10K)

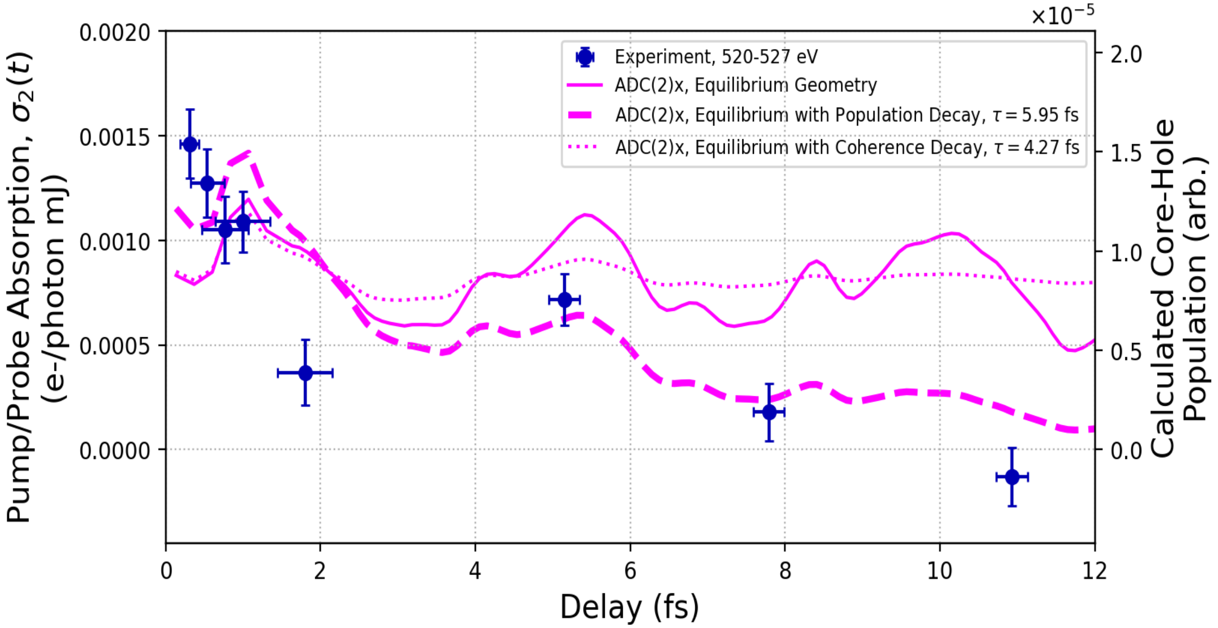
Inner shell electron dynamics

Timescales of excited modes at thermal equilibrium (T = 300 K)

RECENT HIGH IMPACT RESULTS – PHYSICS & X-RAY PHOTONICS

Attosecond electron dynamics

Charge migration damping in **aminophenol**



Isolated attosecond pulses ***Nature Photonics*** **14** 30 (2020)

Charge migration and electron-nuclear coupling in glycine

Science Advances **8** eabn6848 (2022)

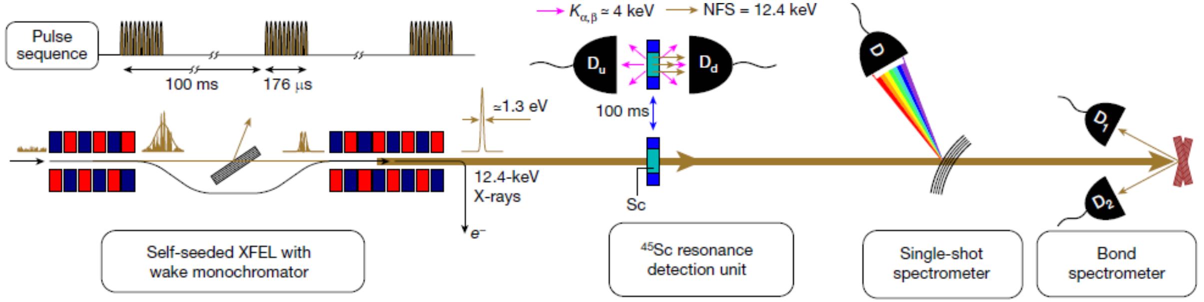
Impulsive stimulated x-ray Raman scattering ***PRL*** **99** 073203 (2020)

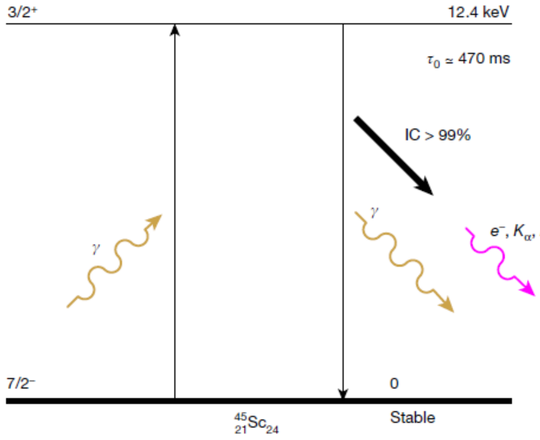
Core electronic wavepacket dynamics ***Science*** **375** 285 (2022)

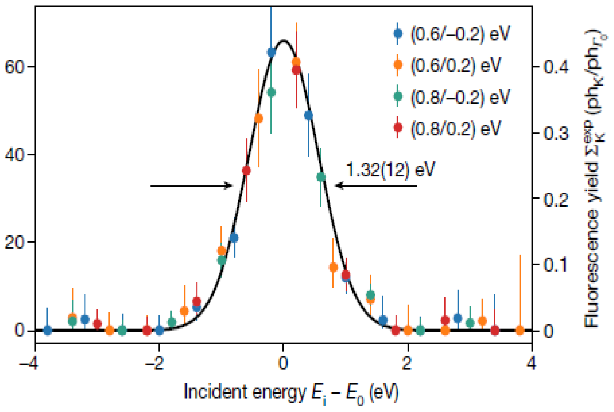
Ionisation physics of water ***Science*** eadn6059 (2024)

New opportunities in physics

Resonant x-ray excitation of nuclear clock isomer ^{45} Sc



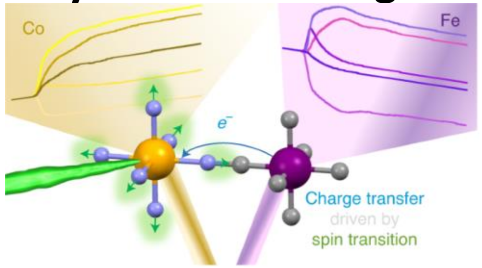




Nature **622** 471 (2023)

RECENT HIGH IMPACT RESULTS – CHEMICAL SCIENCES

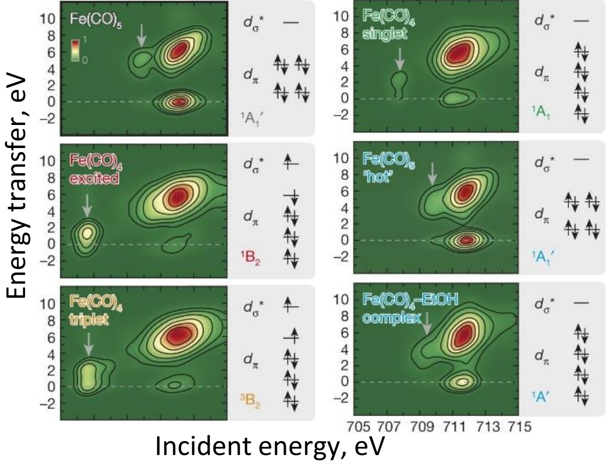
Spin Dynamics & Charge Transfer



Charge transfer driven by ultrafast spin transitions … [*Nature Chem. 13, 10* (2021)]

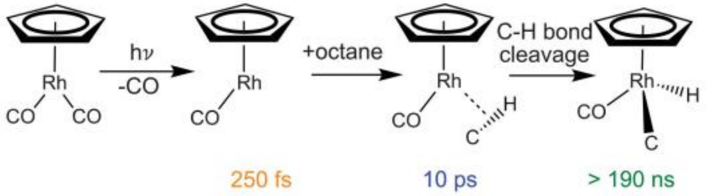
Element- and site-specific probing:

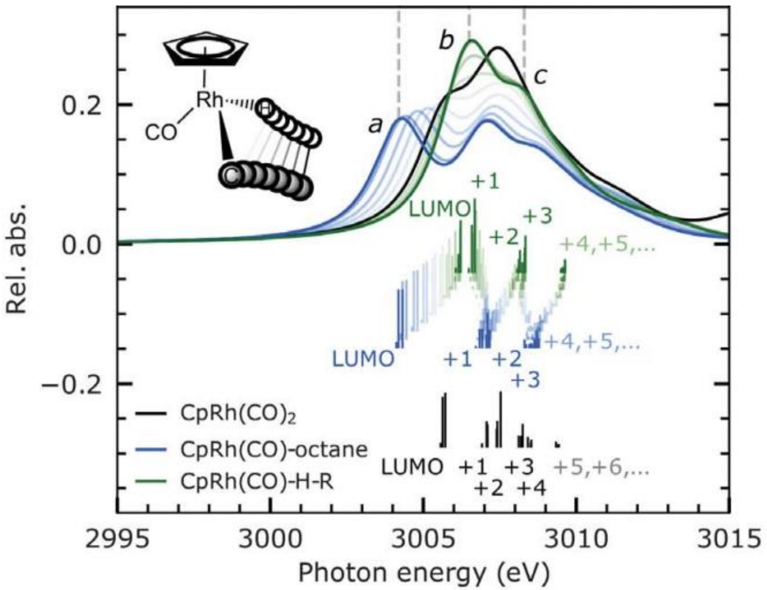
Time-resolved RIXS *at the Fe L_3 edge, $Fe(CO)_5$*



Orbital-specific mapping of the ligand exchange dynamics of $Fe(CO)_5$ in solution [*Nature* 520, **78** (2015)]

Photocatalysis, Enzyme catalysis

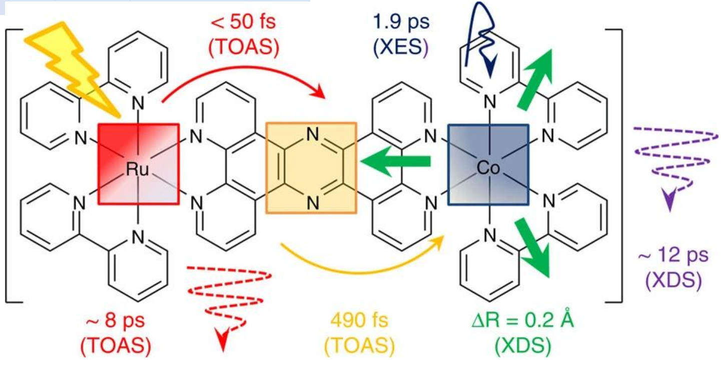




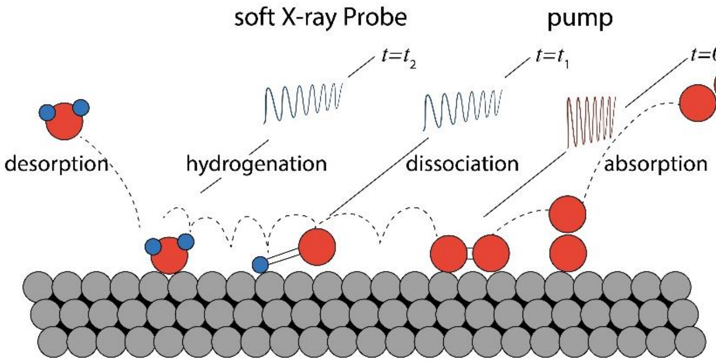
Tracking C–H activation with orbital resolution provides opportunities for manipulating C–H reactivity in transition metals [Science 380, 955 (2023)]

Homogeneous catalysis

UV, IR, THz, e-beam



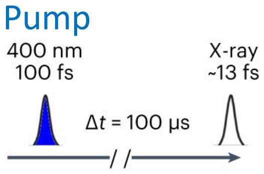
Controlling catalytic reactions with THz excitation

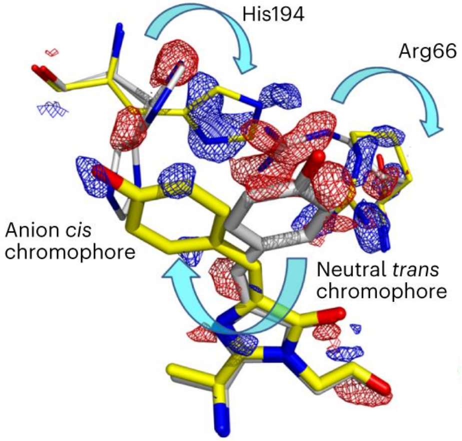


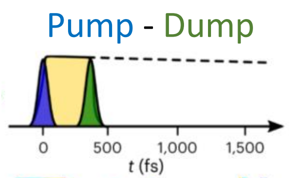
[Chem Phys Lett 675, 145 (2017)]

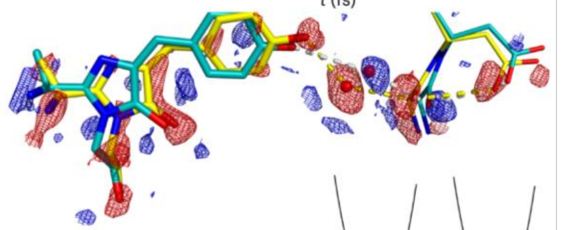
DYNAMIC STRUCTURAL BIOLOGY

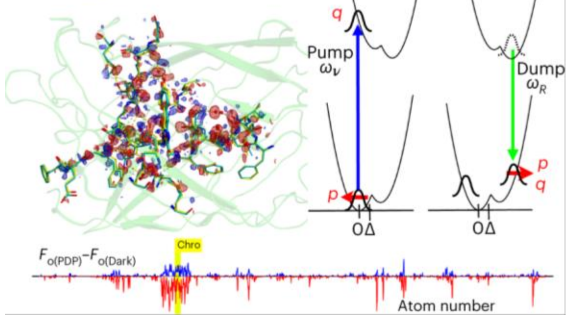
Optical control of ultrafast structural dynamics in a **fluorescent protein**.





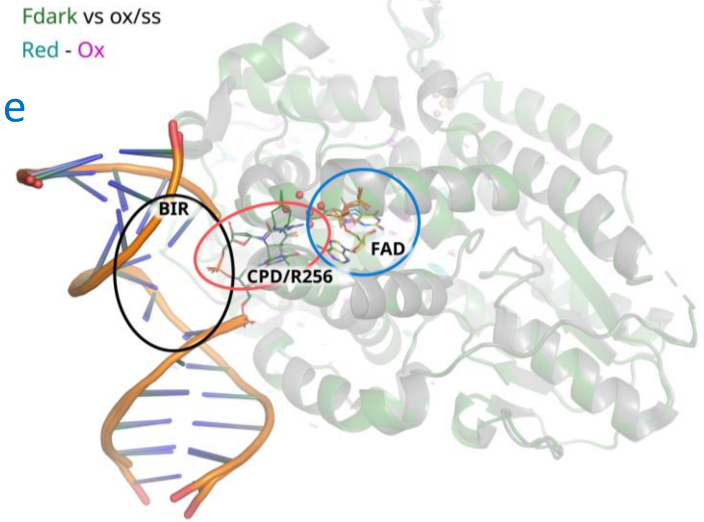


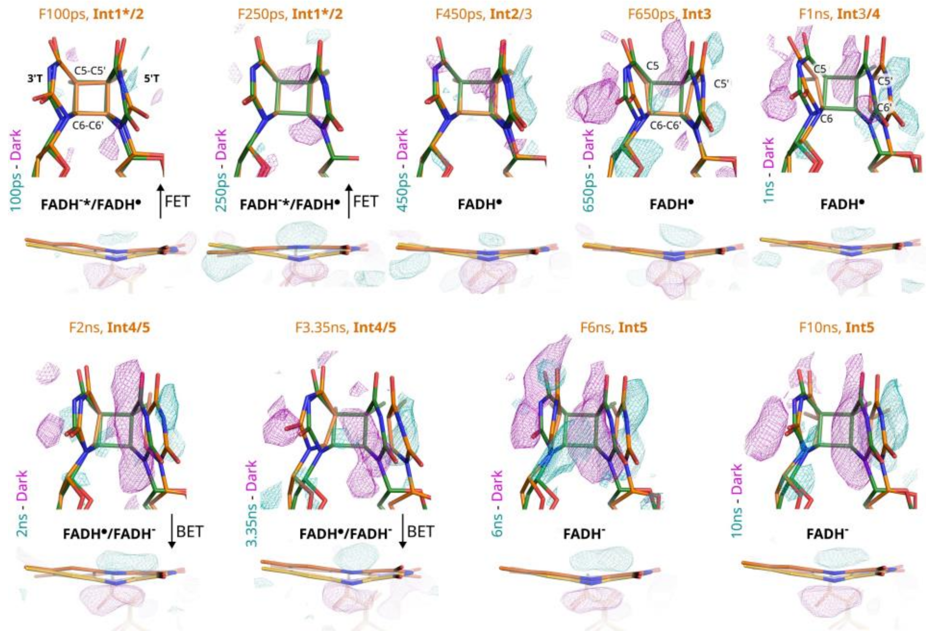




Hutchison *et al* (**2023**)
Nature Chem. 12, 1607

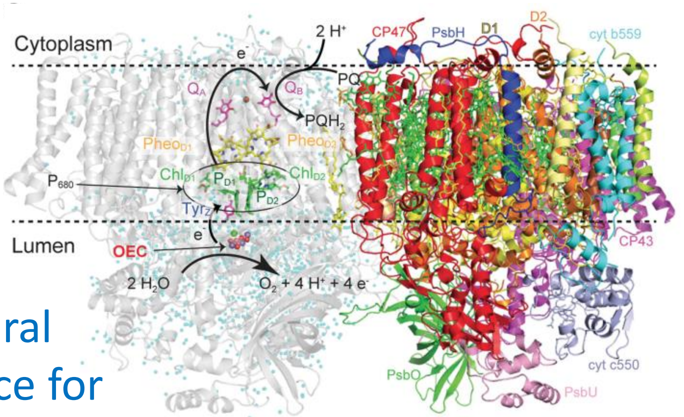
Visualizing the **DNA repair** process at atomic resolution

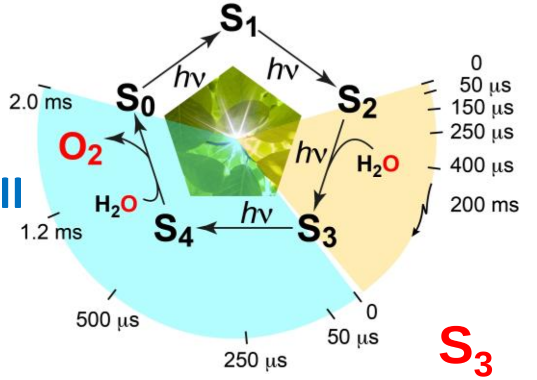




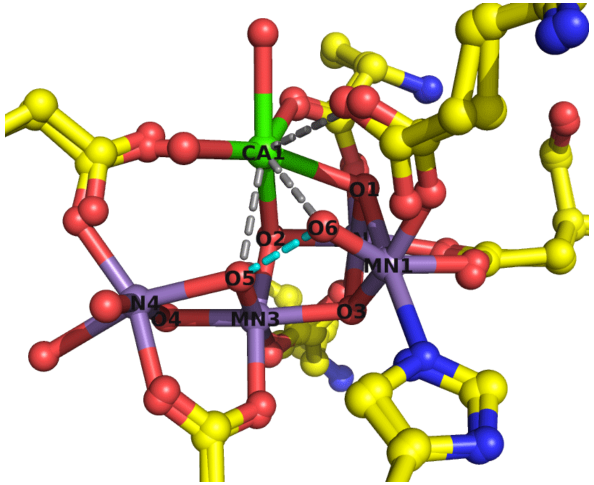
Maestre-Reyna *et al* (**2023**) *Science* **382**, eadd7795

Structural evidence for intermediates during O_2 formation in **photosystem II**





S_3



Kern *et al* (**2018**) *Nature* 563:421
Bhowmick *et al* (**2023**) *Nature* 617:629

UK XFEL: An exciting opportunity for science and innovation

Key next-generation capabilities identified from the UK XFEL Science Case:

- Transform limited operation across entire X-ray range
- High efficiency science facility with a step-change in the parallel operation of multiple end stations
- Evenly spaced high-rep rate pulses to match samples & detectors
- Improved synchronisation/timing data with external lasers to < 1 fs
- Multiple colour X-rays at one end-station
- Full array of synchronised sources: XUV-THz, e-beams, high power & high energy lasers at high rep-rate

Read the UK XFEL Science Case, visit https://www.xfel.ac.uk

Science and Technology Facilities Council

1. Satisfying Future Scientific Research Needs

- **Transform limited operation across entire X-ray range**

Fully resolving dynamics at the combined limits of temporal and energy resolution

- **High efficiency facility with a step-change in the simultaneous operation of multiple end stations**

Expanding access by providing scope for many hundreds of unique experiments every year

- **Evenly spaced, high-rep rate pulses to match samples & detectors**

Enabling the most advanced measurement methodologies whilst supporting high throughput measurements with standard capabilities

- **Improved synchronisation/timing data with external lasers to < 1 fs**

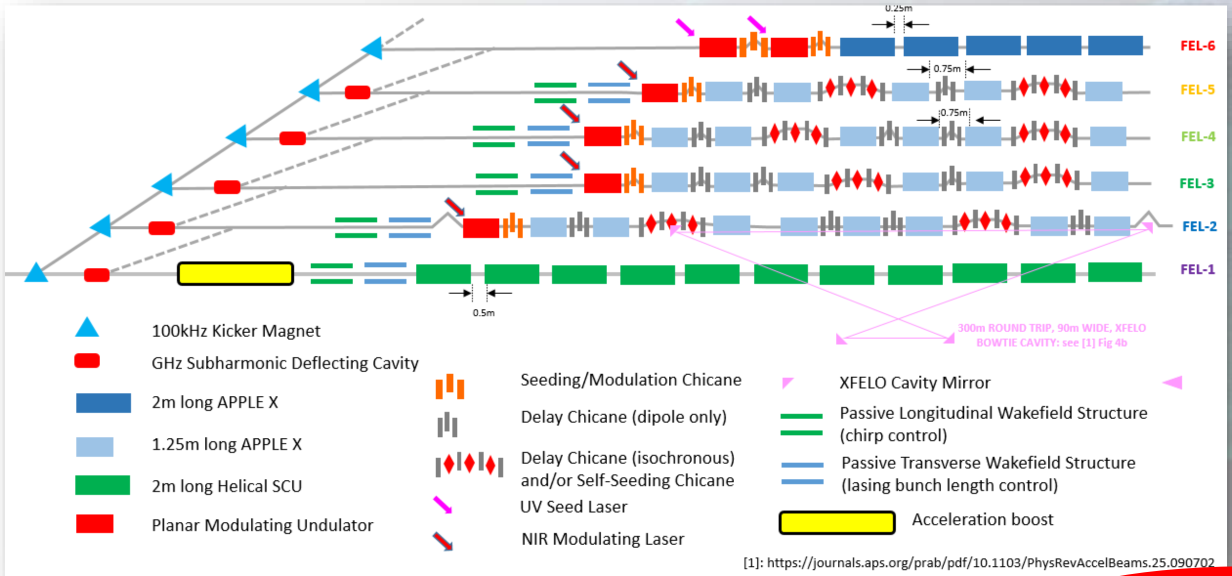
Realising the full temporal resolution to see dynamics unfold across multiple timescales from sub-femtosecond electronic dynamics to nanosecond thermal relaxation and larger scale structural changes

- **Multiple colour X-rays at one end-station and full array of synchronised sources:**

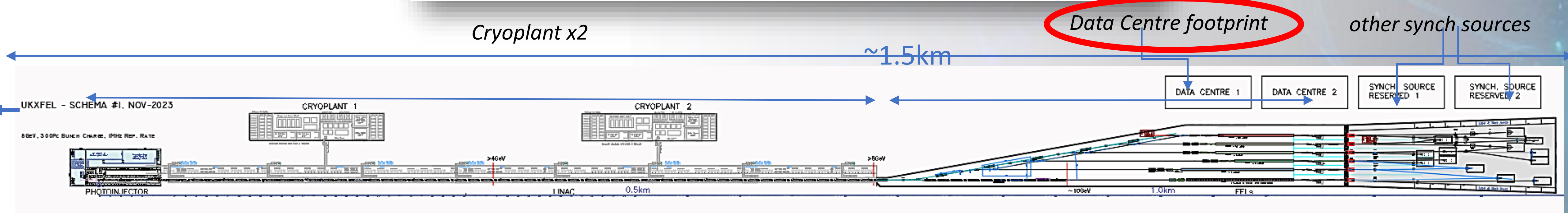
To interrogate specific electronic, vibronic, excitonic etc. modes to completely uncover the complex dynamical pathways and couplings in matter

The Conceptual Design of such a facility is progressing rapidly

Important technical choices are being explored and down selected. Already the basic concept has emerged of multiple FELs lines fed by the MHz pulses using kicker magnets to feed each FEL with upwards of 100 kHz



[1]: https://journals.aps.org/prab/pdf/10.1103/PhysRevAccelBeams.25.090702



LINAC 8GeV ~750m

8GeV can be achieved with x46 TESLA/Fermi type cryomodules

FELs ~350 - 400m

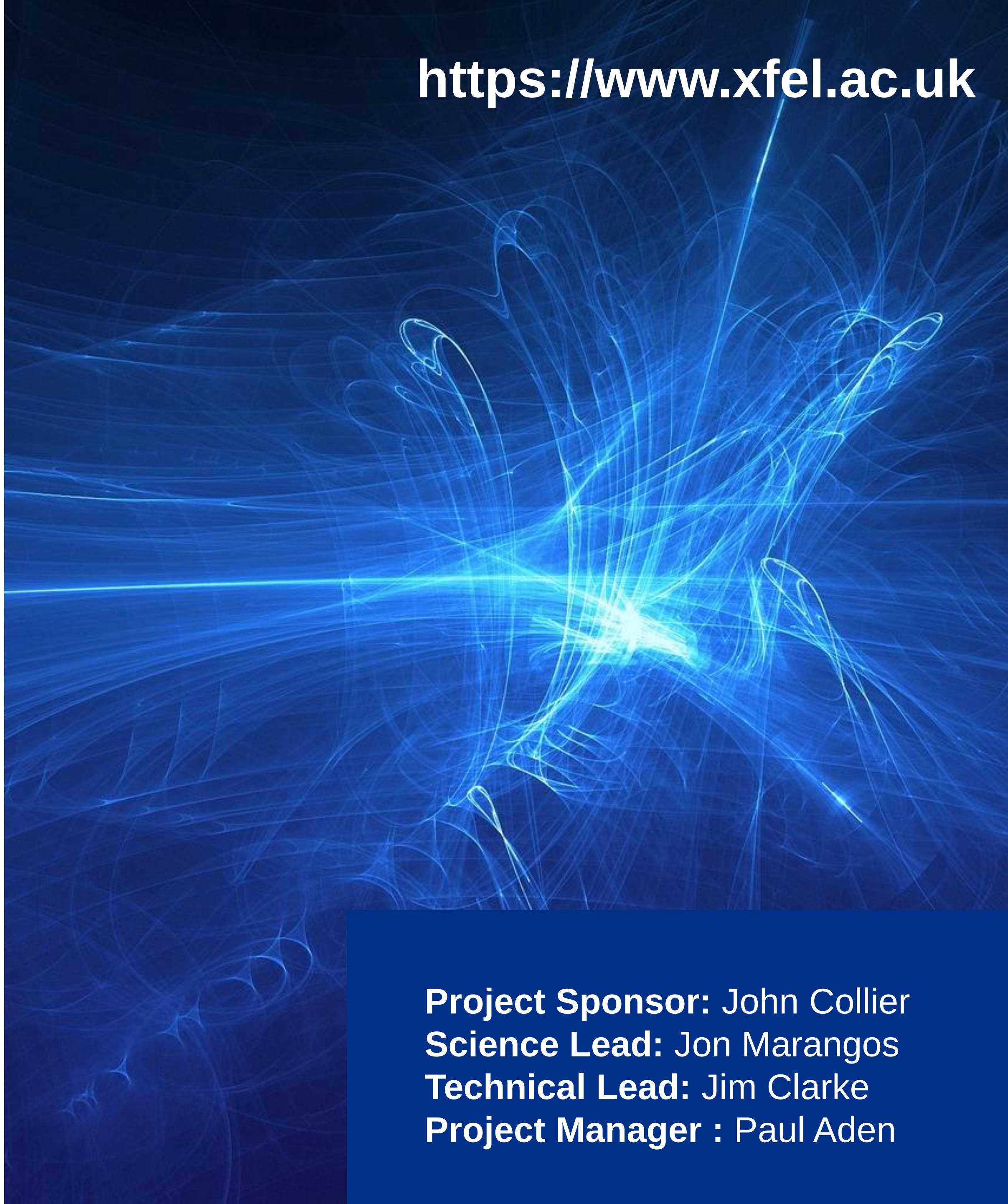
A Next Generation XFEL

Over the next 3 years we will:

- **Map out how best to deliver the advanced XFEL capabilities identified in the Science Case.**
- **Explore a Conceptual Design for a unique new machine that can fulfil all required capabilities and more.**
- **Examine other investment options in existing XFELs**
- **Update Science Case to inform process and future decisions & we will hold Townhall Meetings around UK**

The collaborative effort will be led by a team at STFC Daresbury Laboratory with strong engagement from those looking at the developing science opportunities to inform the design.

Science and
Technology
Facilities Council



https://www.xfel.ac.uk

Project Sponsor: John Collier
Science Lead: Jon Marangos
Technical Lead: Jim Clarke
Project Manager : Paul Aden

Developing Science & Technology Case and Community Engagement

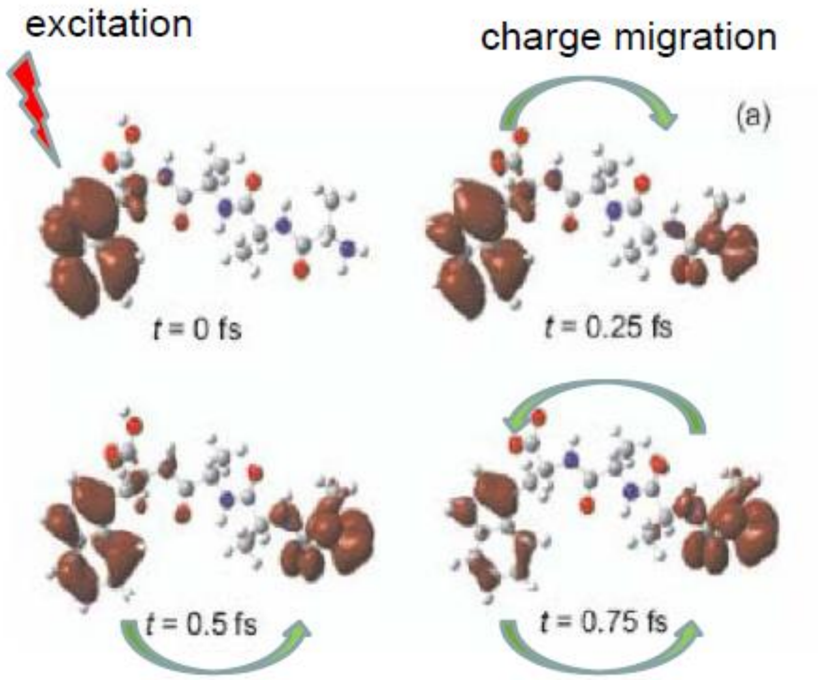
1. Northern Ireland Townhall (hosted by: Queens Belfast) June 20th & 21st 2023 Focus discussion topic: Frontiers of measurement technology	Physics, Life Sciences, Chemistry, Engineering, Quantum Materials
2. Scotland Townhall (hosted in Glasgow at Strathclyde) Oct 2 & 3rd 2023 Focus discussion topic: Materials, chemistry and biology at extreme conditions	Physics, Astrophysics, Materials, Defence, Chemistry, Life Sciences
3. Southwest England Townhall (hosted by Plymouth) 18th & 19th Jan 2024 Focus discussion topic: Fundamental Physics, AI & quantum computing	All areas – an advanced technology& fundamental science focus
4. Sheffield Townhall (hosted by University of Sheffield early 4th& 5th June 2024) Focus discussion topic: Energy, environmental and climate technologies	Chemistry, Quantum Materials, Engineering, Materials, Physics
5. London Townhall (hosted in London, July 29th and 30th 2024) Focus discussion topic: Lifesciences and Biomedicine	Life Sciences, Engineering, Chemistry, Physics and Photonics
6. Manchester Townhall (hosted by Royce Institute, August 8th & 9th 2024) Focus discussion topic: Electronics, photonics and quantum technologies	Quantum Materials, Physics & Photonics, Materials
7. Cardiff Townhall (in Cardiff ~ Late September 2024) Focus discussion topic: Advanced materials and manufacturing	Engineering, Defence, Materials, Physics, Chemistry, Life Sciences

2. Building on the foundations of attosecond physics

We seek to develop:

- **Attosecond x-ray time-resolved spectroscopy using HHG**
- **High brightness attosecond x-rays from XFELs**
- **Applications to photo-physics, photo-chemistry and energy materials**
- **Non-linear and linear attosecond spectroscopy**

2. X-ray pump-probe measurement of charge migration dynamics



Charge (hole) migration in the peptide Trp-Ala-Ala-Ala (Remacle & Levine Z.Phys.Chem. 221, 647 (2007))

F. Calegari et al, Science 346, 336 (2014)
P. Kraus et al, Science, 350, 790 (2015)

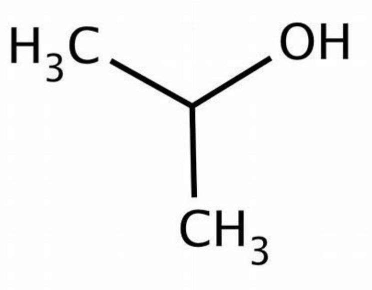
Charge Migration

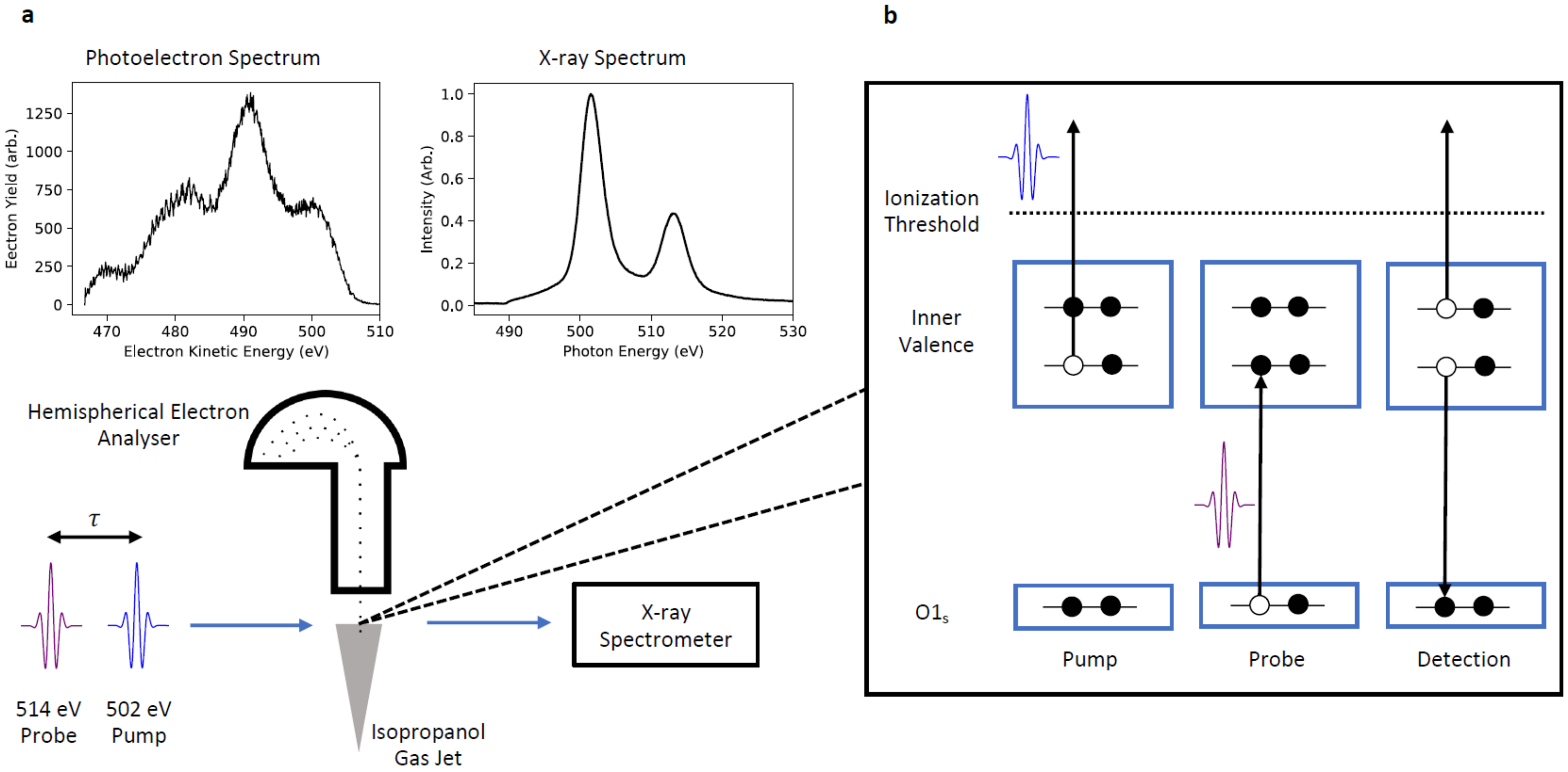
Sudden electron removal can form a localised hole state that is a coherent superposition of the electronic eigenstates of the molecular ion and so undergoes rapid evolution. This results in large amplitude charge oscillation across the molecule on an attosecond timescale.

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

How long does electronic coherence survive?
How does electronic coherence couple into longer lived vibronic coherence?
What are the consequences for "chemical change"?
Can we control it?

2. X-ray absorption spectroscopy: X-ray pump/X-ray probe of inner valence hole dynamics in isopropanol at LCLS





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

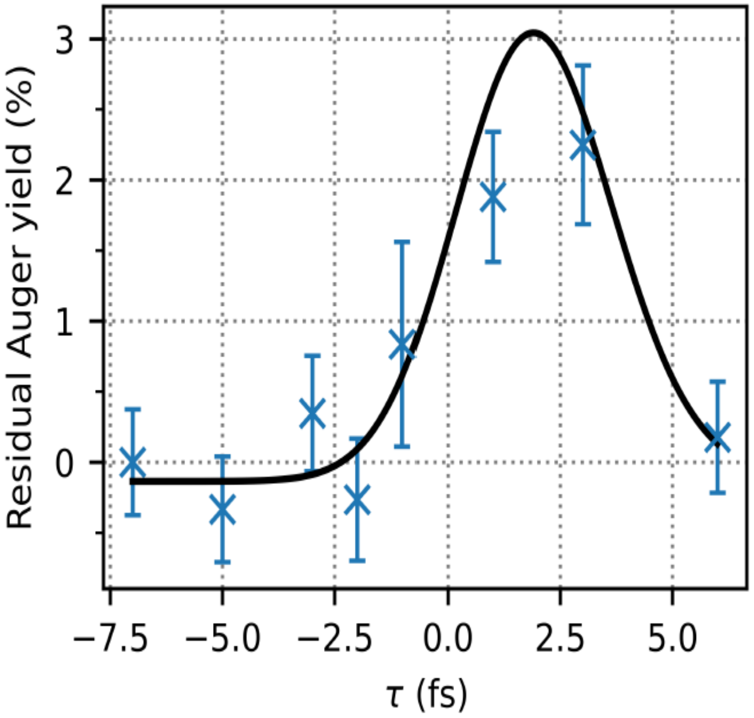
B.Cooper et al Faraday Discussion 171, 93 (2014)

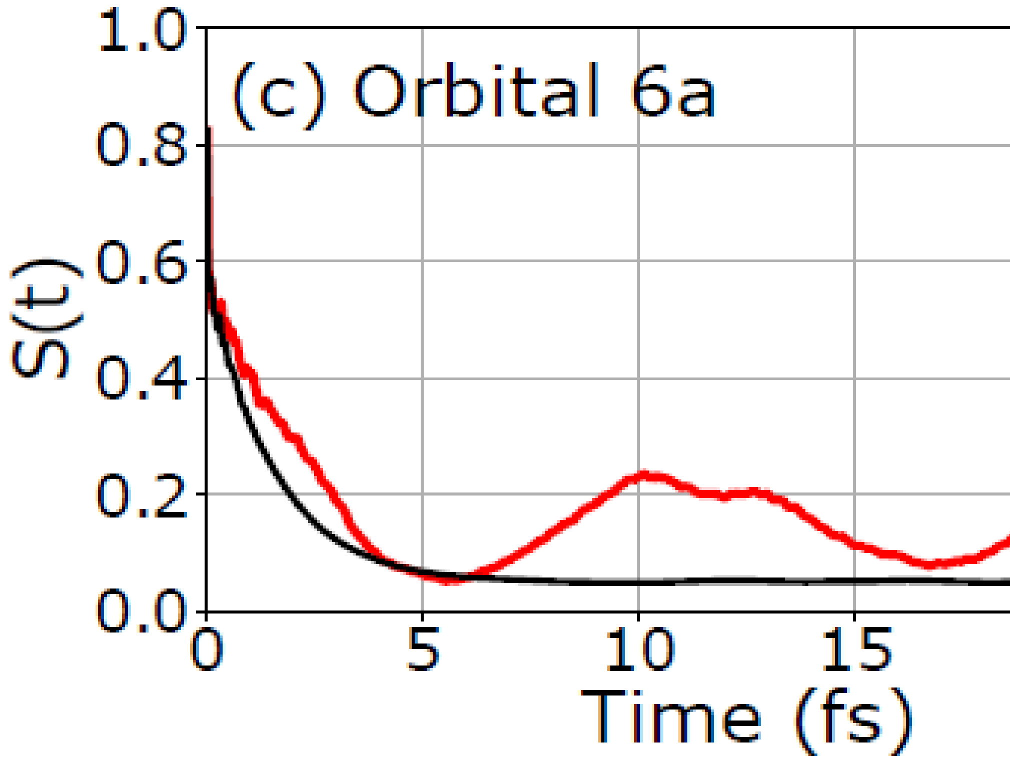
<u>AMO end-station LCLS</u>: Two pulses generated using <u>fresh-slice</u> mode form pump and probe, with chicane controlled delay. Most data was taken with ~ 5 fs pulse durations over a -10 to +25 fs delay range provided evidence of timescale of nuclear dynamics for 7a state. But a shorter data run with ~ 2.5 fs pulses was also taken.

120 Hz rep-rate, analyser had a moderate collection efficiency

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 (breathing mode) driven by electron correlation calculated via ADC theory





Measurement of a highly transient hole (few-fs lifetime) with decay driven by fast oscillation inherent to superposition of inner valence state with a correlation satellite and the dephasing due to the zero-point geometry spread

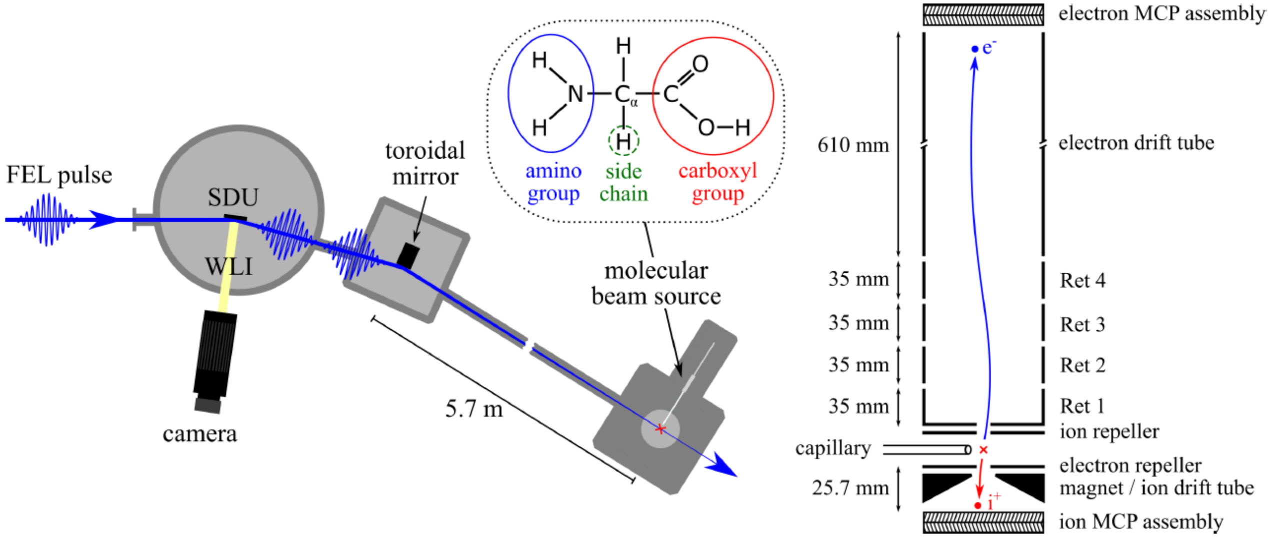
T.Barillot et al, "Correlation Driven Transient Hole Dynamics Resolved in Space and Time in the Isopropanol Molecule", PRX 11, 031048 (2021)

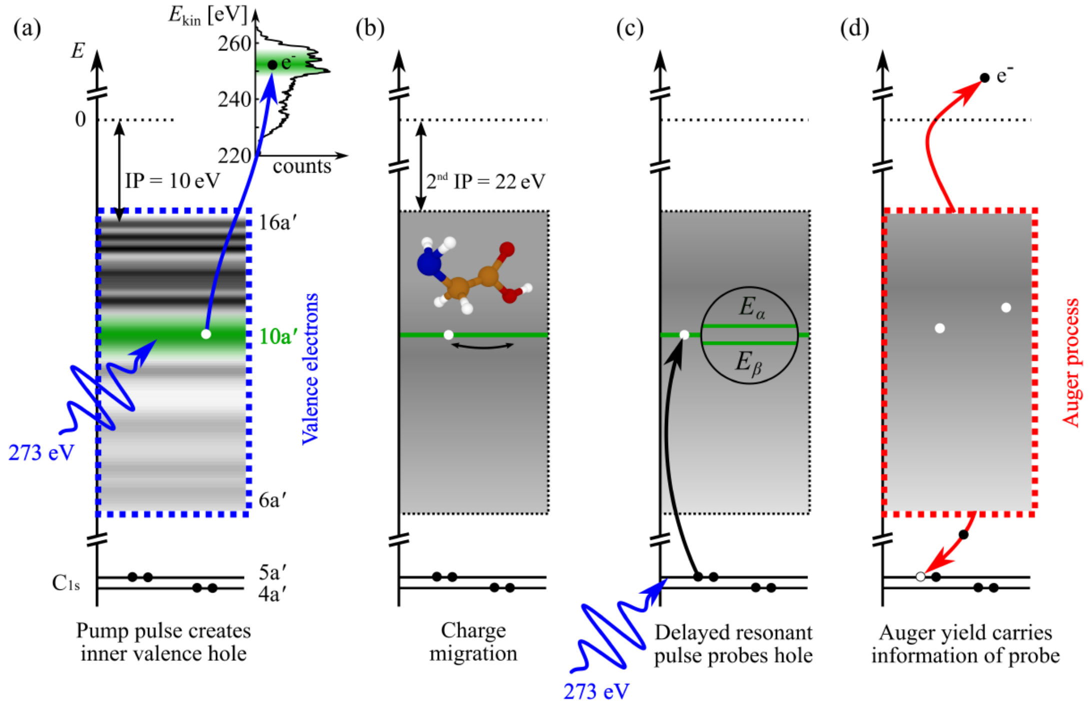
Spectral domain ghost imaging analysis DOI: 10.1039/D0FD00122H *Faraday Discuss.*, 2021

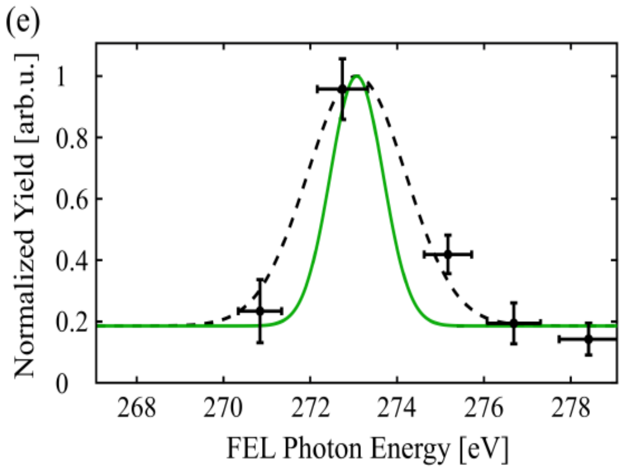
2. Coherent hole dynamics in glycine

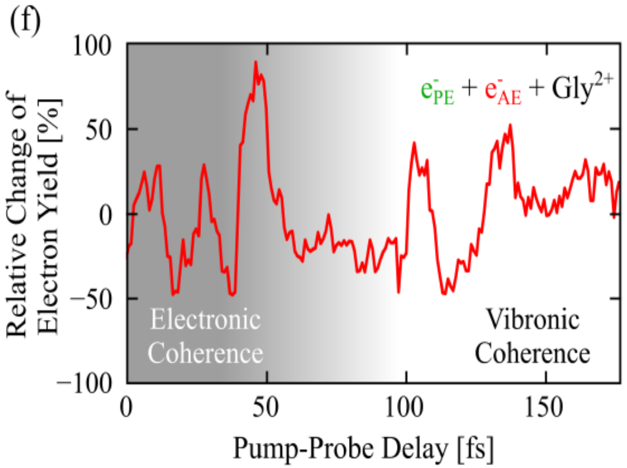
Led by Tim Laarmann, DESY Collaboration at FLASH

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 ~ 273 eV with a pulse duration ~ 3 fs delayed between 0 – 175 fs

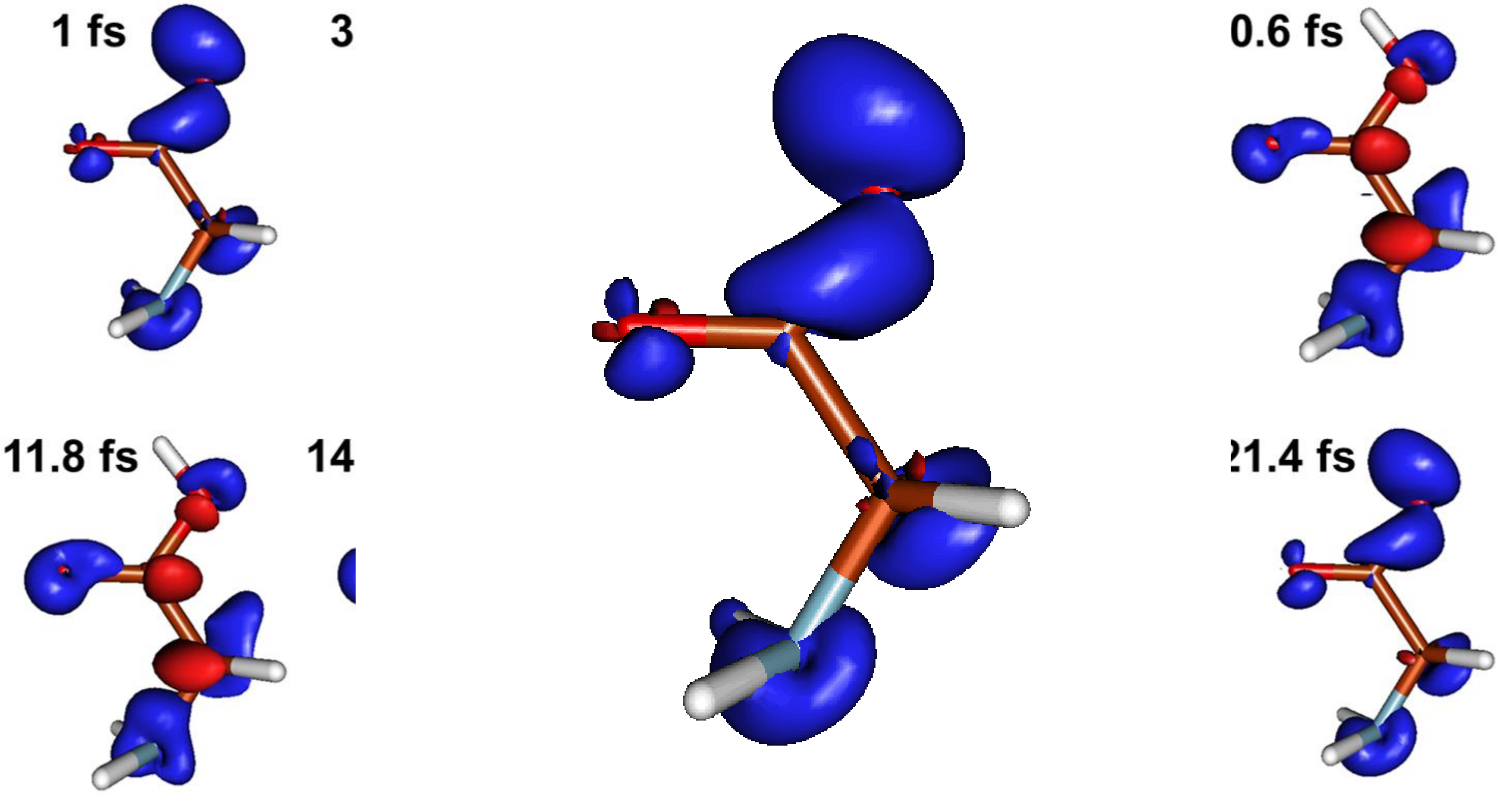








2. Oscillatory electron dynamics in glycine 10a’ hole dynamics predicted from ADC(2) with a 19 fs period



ADC 2 calculations by Marco Ruberti of 10a’ state manifold (hole mixing + shake up satellite)

2. Transient x-ray absorption with 3 fs near transform limited pulses in glycine show initial electronic coherence coupling to vibronic coherence

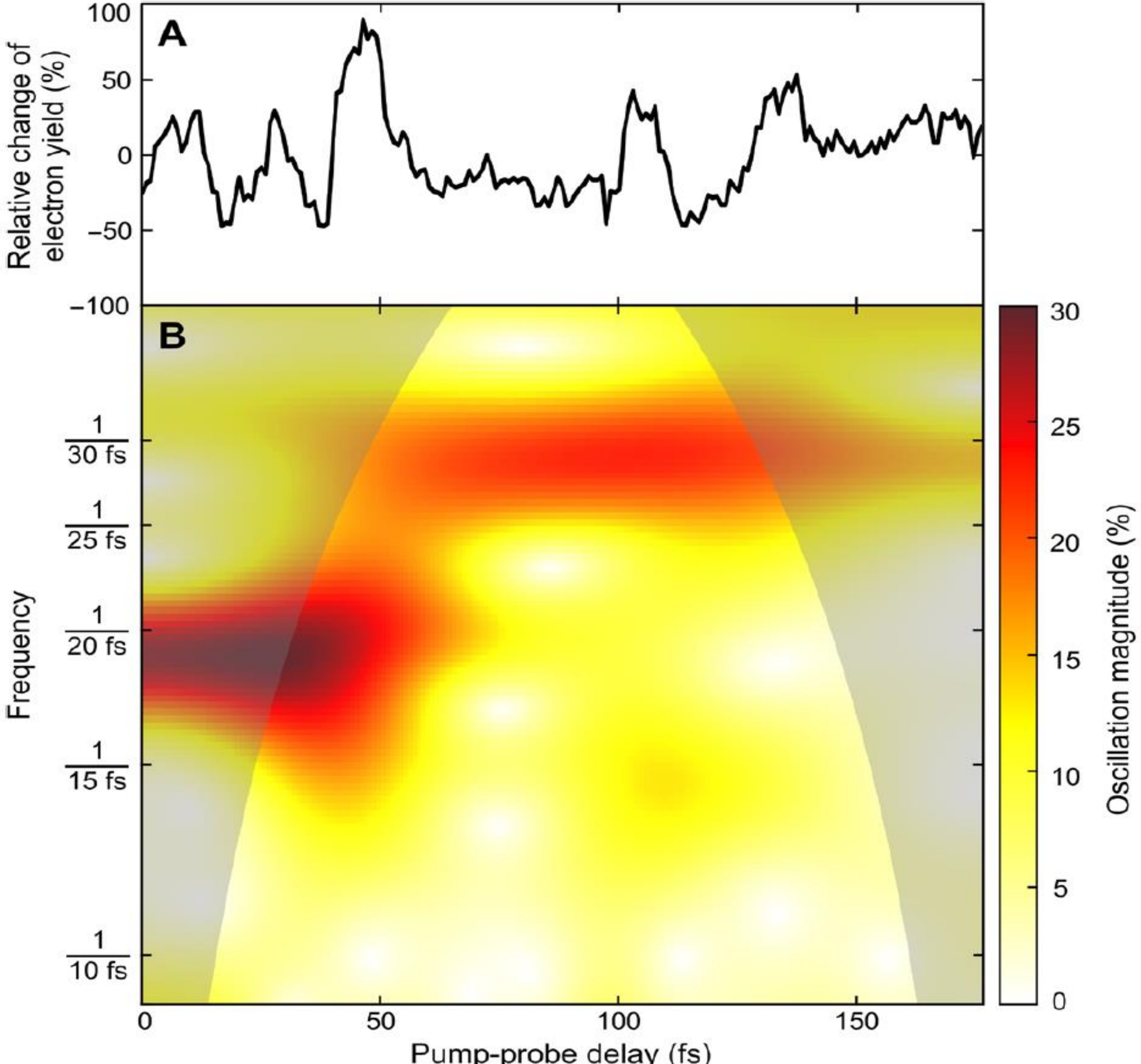
Tim Laarmann (DESY), Marco Ruberti (Imperial) et al measurements @ FLASH

Probing the hole following x-ray ionisation of glycine we observe both oscillatory charge migration and evidence of vibronic coupling. A near transform limited 3 fs pulse enabled the temporal and energy resolution needed for this measurement.

Schwickert et al, **Science Advances,** 1 Jun 2022 Vol 8, Issue 22 DOI: 10.1126/sciadv.abn6848

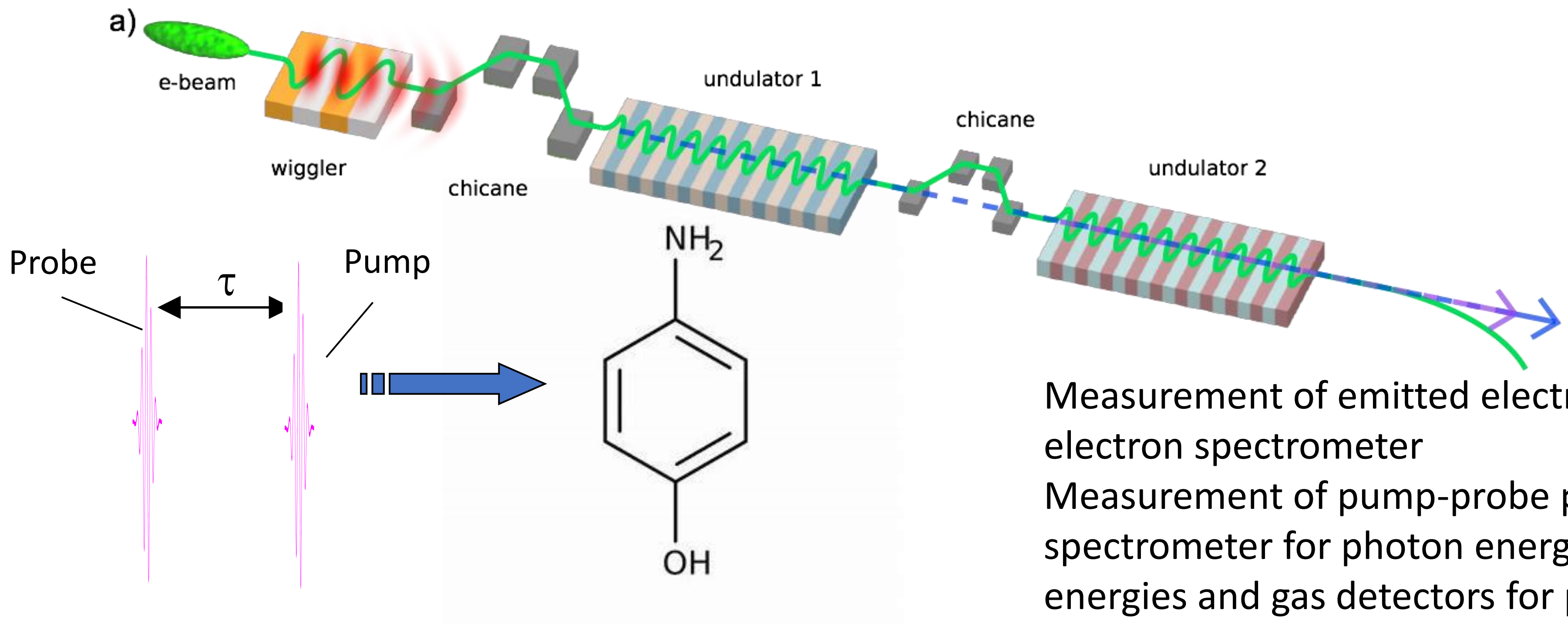
Potential impact on:

- **Fundamentals of chemical dynamics beyond the Born-Oppenheimer approximation**
- **Testing computational quantum chemistry**
- **Understanding radiation damage in materials and biology**
- **Atmospheric- and Astro-chemistry**
- **Ultrafast quantum coherence, entanglement and control of chemical reactions**



2. Attosecond X-ray pump-probe measurements of valence hole wavepacket dynamics in para-aminophenol

Led by James Cryan & Ago Marinelli, Attosecond Campaign Collaboration with Imperial College



Pump ω ~ 250 – 270 eV

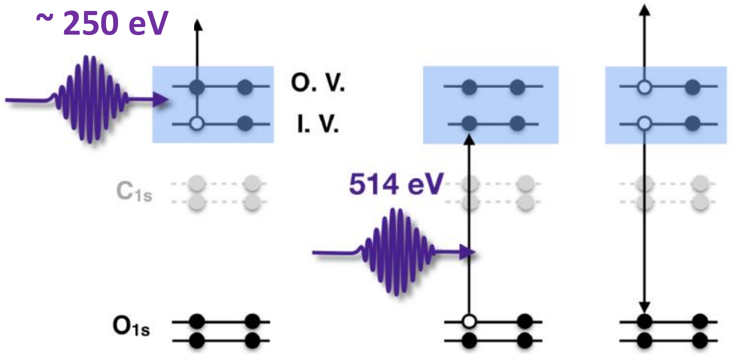
Measurement of emitted electron *spectrum* using electron spectrometer

Measurement of pump-probe pulses using X-ray spectrometer for photon energies and relative pulse energies and gas detectors for pulse energy

Pump-probe delays scanned for 0.3 fs (minimum) to ~ 10 fs

Probe at 2ω (500 – 540 eV) for O 1s XAS

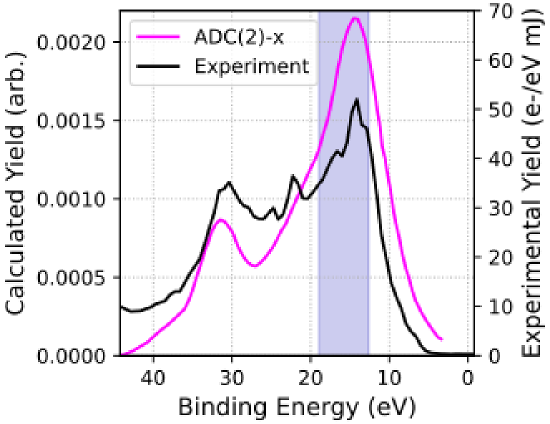
X-ray transient absorption method developed by Imperial College, but now the bandwidth is high enough that ionisation creates a superposition of single-electron hole states

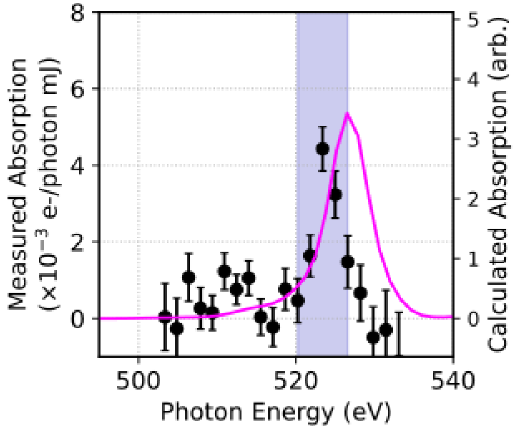


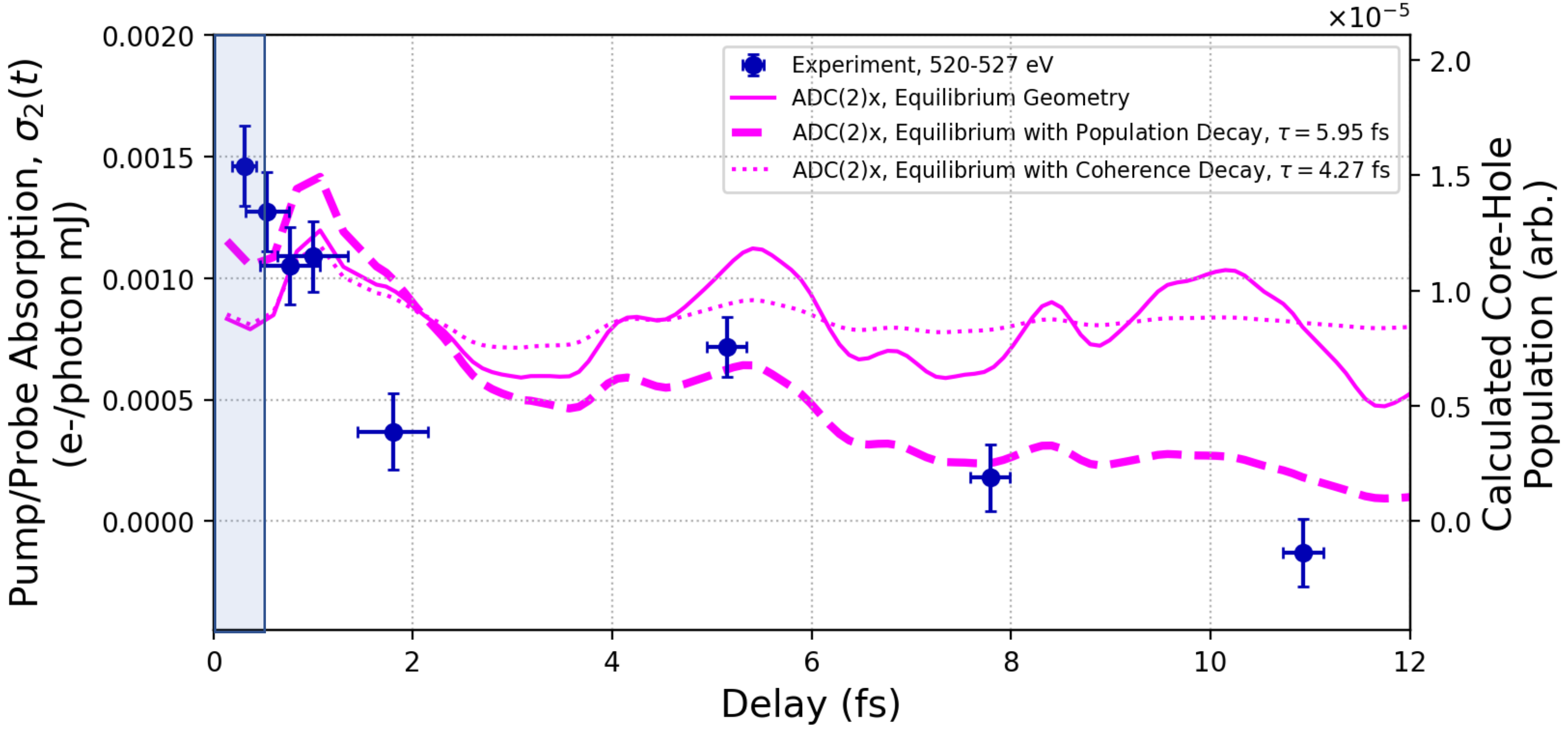
2. Attosecond electron hole dynamics in x-ray ionized aminophenol: Resolving electronic events with ~ 300 attosecond near transform limited pulses

Calculations by Marco Ruberti
ADC(1)/(2)-x measurements @ LCLS
James Cryan, Ago Marinelli, Marco Ruberti, Eric Isele, Taran Driver, Zhaoheng Guo, Oliver Alexander et al
"Attosecond Campaign"

New tools for fundamental understanding of electron-hole dynamics in many-electron systems with applications to the photon-electron coupling in molecules, metals, semiconductors, dielectrics and amorphous systems







2. Not just "attosecond" problems where high level electronic calculations needed – consider the excited state dynamics of uracil……

Only one to agree with recent measurements is XMS-CASPT2 that includes dynamic electron correlations

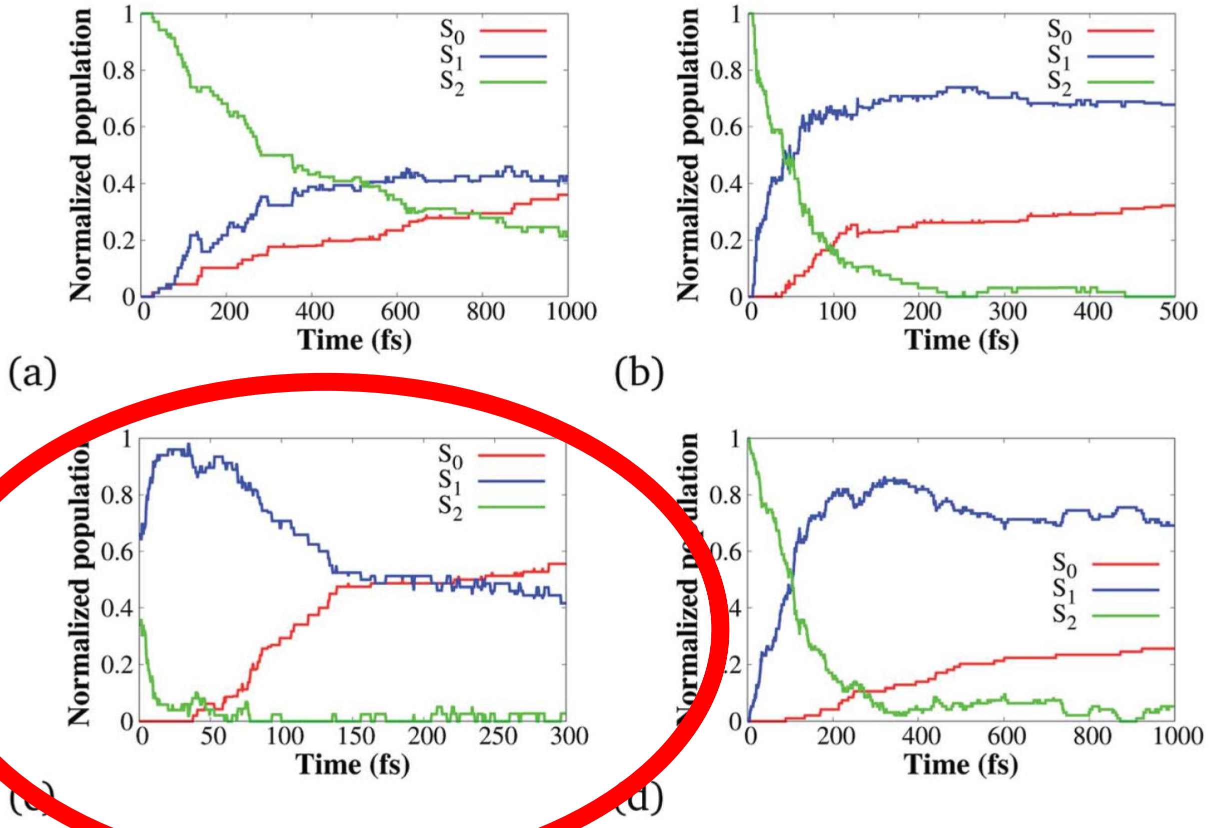


Fig. 5 Normalized population dynamics for the lowest three singlet states (S_2, S_1 and S_0) of uracil at the (a) CASSCF, (b) MRCIS, (c) XMS-CASPT2, and (d) TD-DFT level.

276 | *Faraday Discuss.*, 2021, **228**, 266–285 This journal is © The Royal Society of Chemistry 2021

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

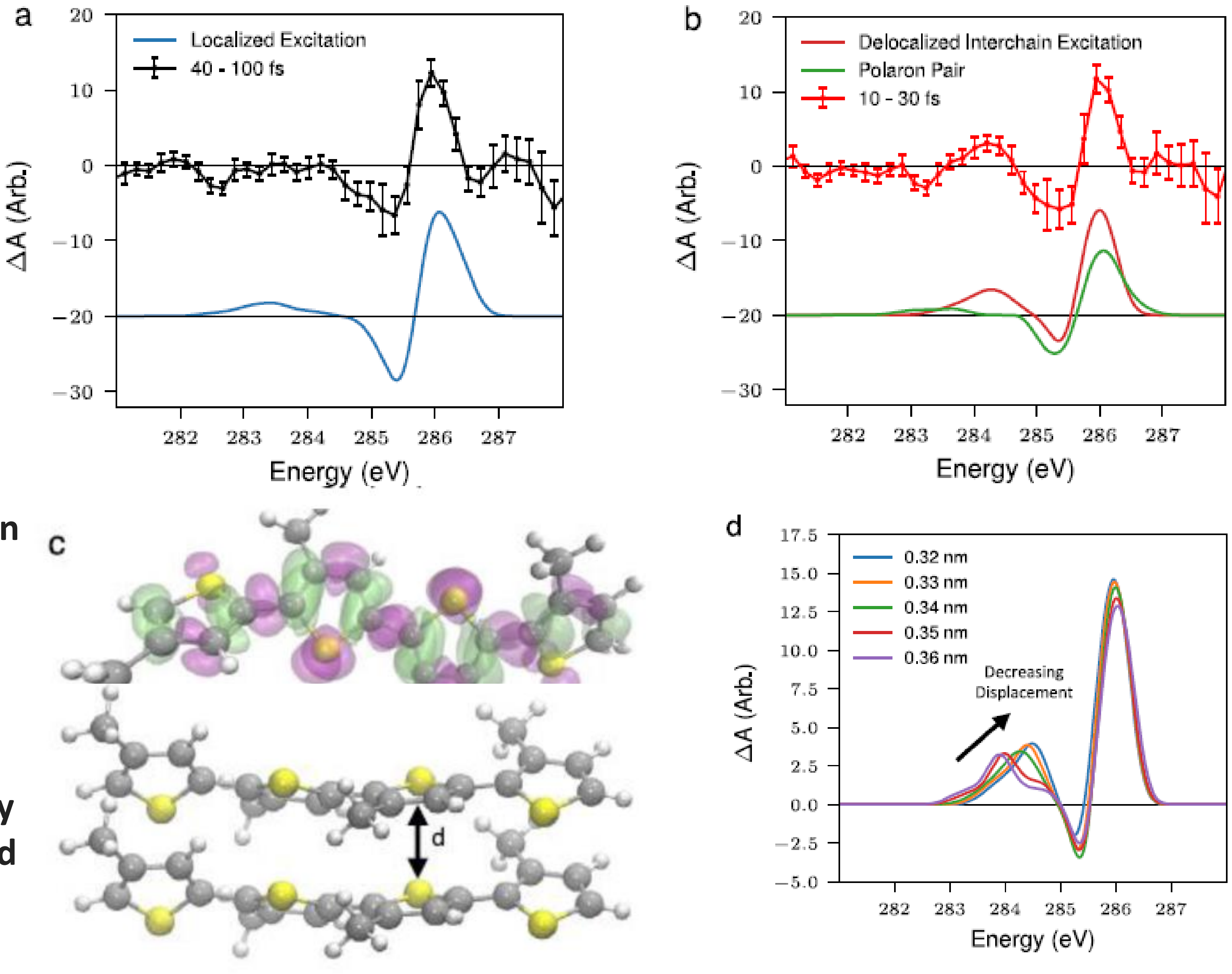
Using HHG beamline at IC
A.Johnson et al *Science Advances* ***4, 3761*** (2018)

XAS spectra simulated with TDDFT by Tom Penfold (Newcastle)

Garratt, D *et al.* ***Nat Commun*** **13,** 3414 (2022).

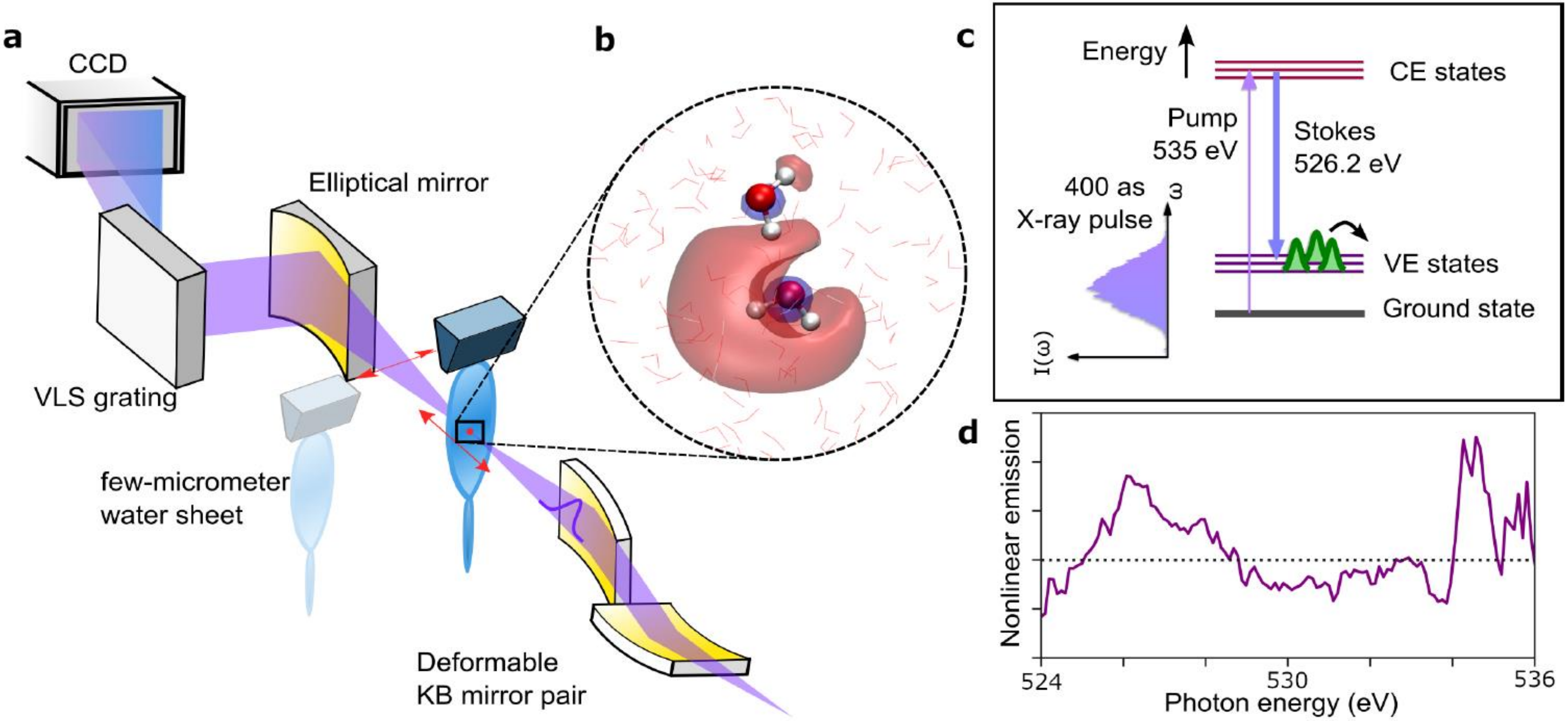
Application of attosecond probing techniques to excitons in organic semiconductors reveals new aspects of the critical early dynamics. Relevant to solar energy

Will need state-of-the-art theory and calculations to be developed hand-in-hand with new measurement techniques



3. Non-linear X-ray optics in liquid water: Impulsive stimulated electronic Raman with high intensity attosecond X-ray pulses

Imperial College + Stanford, LCLS + Autonoma Madrid



3. Non-linear X-ray optics in liquid water: Impulsive electronic Raman with high intensity attosecond X-ray pulses

Imperial College + Stanford, LCLS + Autonoma Madrid

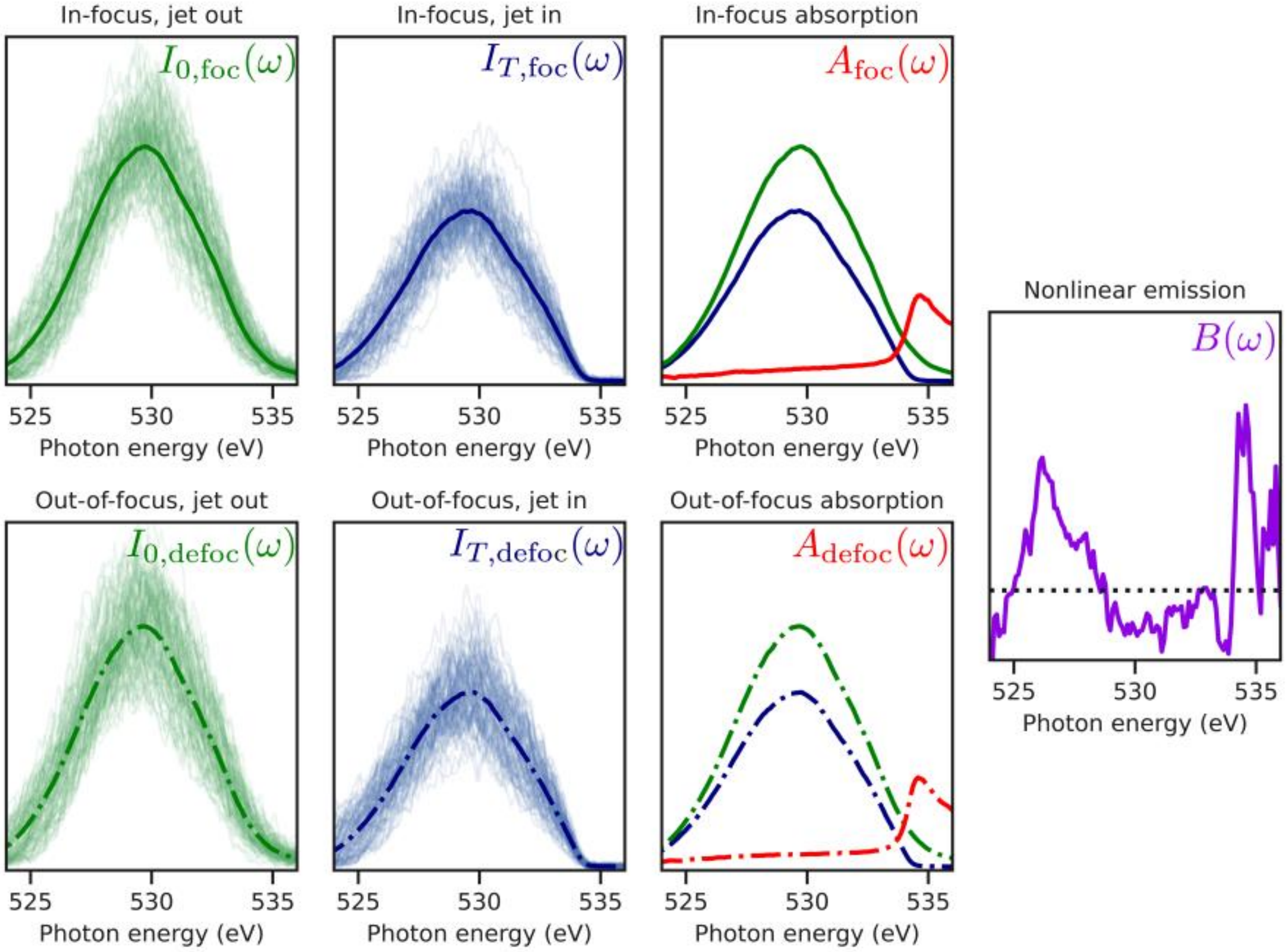
We measure the change in the transmitted spectrum when moving to the nonlinear regime

$$\log\frac{I_{0,f}}{I_{T,f}} - \log\frac{I_{0,df}}{I_{T,df}}$$

We observe an emission feature consistent with expected Stokes sideband emission populating the $1b_1^{-1}4a_1$ LUMO state of wate (c.f. earlier RIXS measurements Pietzsch, A., al. *PRL, 114*(8) (2015))

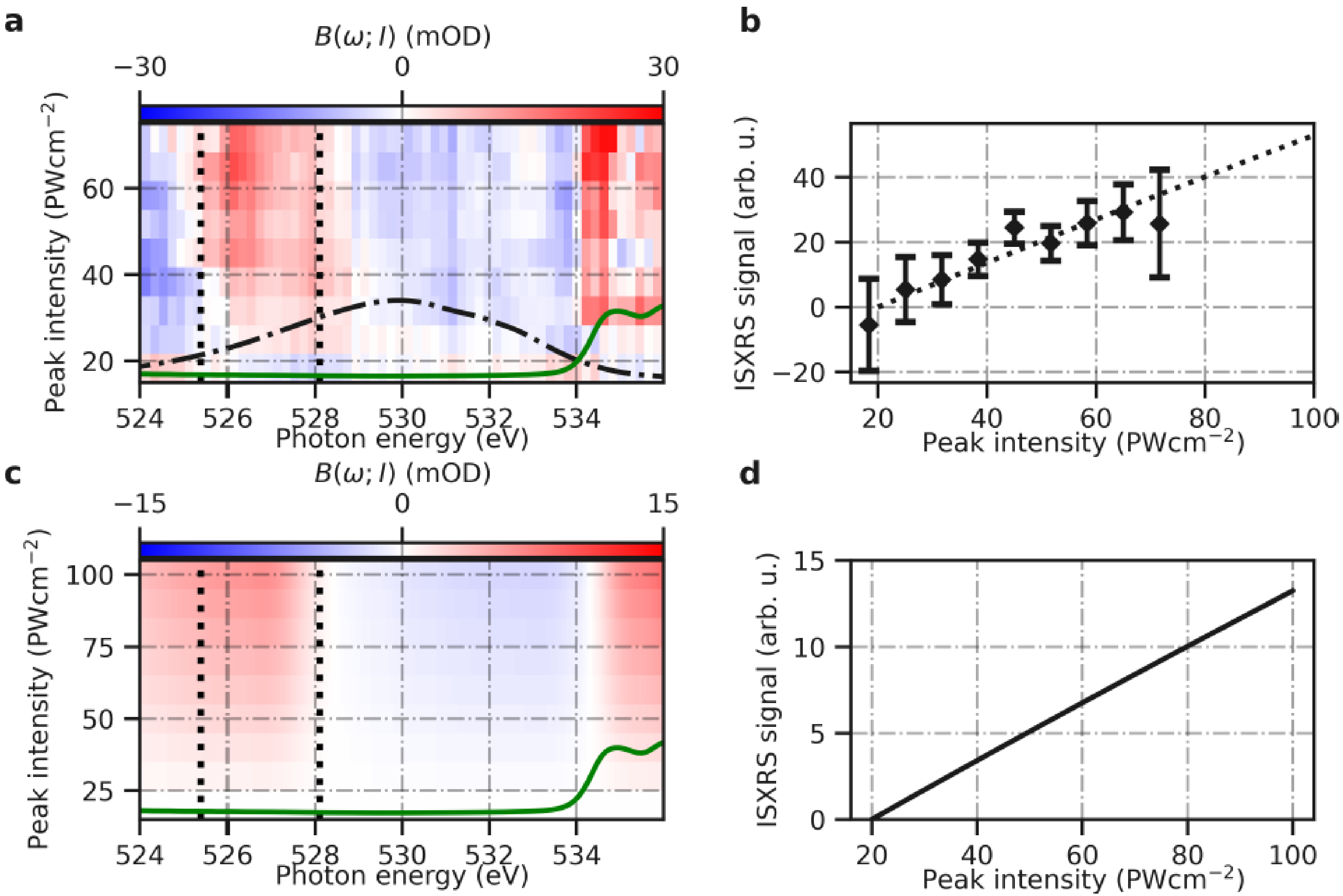
526 eV, ~1 eV bandwidth

Grows in the intensity range 20 – 80 PW cm

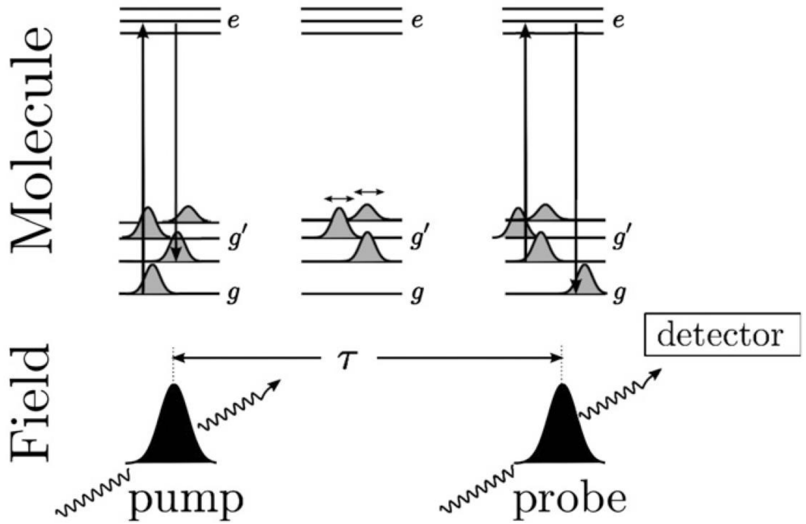


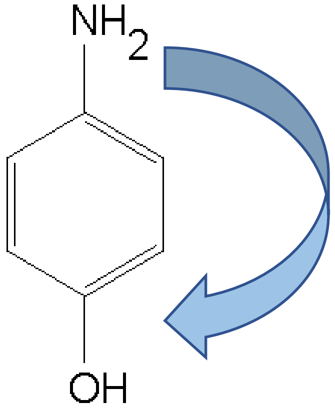
3. Non-linear X-ray optics in liquid water: Impulsive electronic Raman with high intensity attosecond X-ray pulses

Imperial College + Stanford, LCLS + Autonoma Madrid

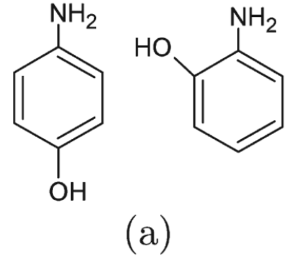


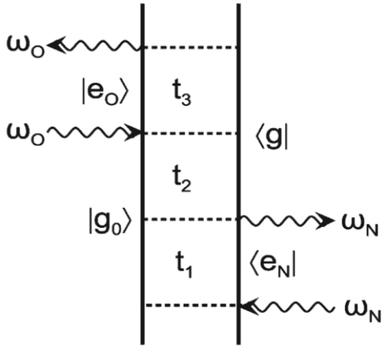
3. Impulsive X-ray stimulated Raman Scattering: A New Tool to Study Evolution of Localised Electronic Excitation in Neutral Matter



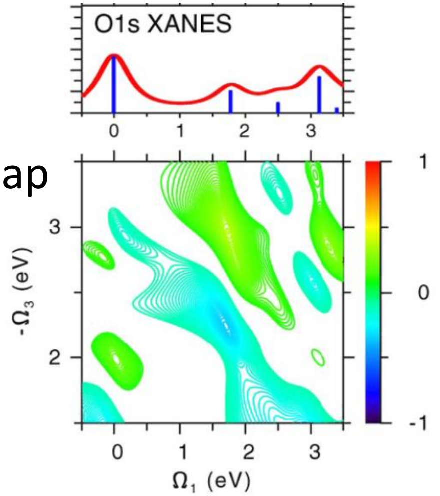


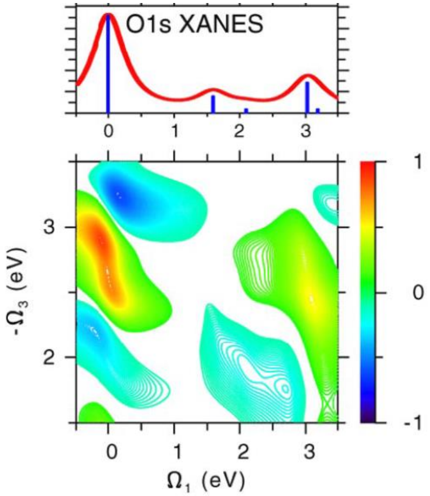
I.V. Schweigert and S. Mukamel, *PRL* **99**, 163001 (2007)
J.D.Briggs et al, Energy transfer in metalloporphyrin heterodimers using stimulated X-ray Raman spectroscopy PNAS, 110, 11597 (2013)



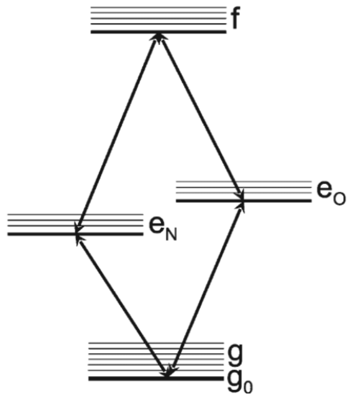


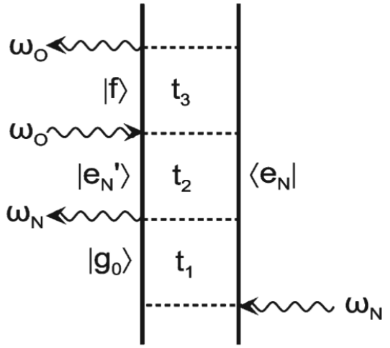
para-ap





ortho-ap





4. Advanced theory and computation are essential for progress in understanding ultrafast dynamics

- **Measurements can now benchmark theoretical calculations of attosecond dynamics – but these calculations remain challenging**

- **Approaches are needed that accurately capture BOTH electronic and the coupled nuclear dynamics**

- **Even for “slower” timescales the higher accuracy approaches that treat adequately electron correlation are often essential**

- **Future non-linear/multidimensional x-ray measurements will also need to be simulated for exploring new applications and interpreting data from measurements**

- **Future facilities will be high throughput – to match the science output accompanying calculations will also need to be high throughput (i.e. “good” approximate approaches that work in a given class of problem will need to be identified)**

Thank You For Your Attention