Attosecond molecular physics with FEL pulses

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Attosecond Campaign collaboration at LCLS, Collaboration between DESY and Imperial at FLASH

Workshop "Fundamental Research and Applications with the EuPRAXIA Facility at LNF"

(4-6 December 2024)

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EPSRC Pioneering research and skills

MBI

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Acknowledgements

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Dr. Erik Isele

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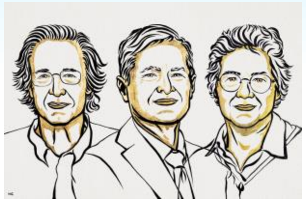
Dr. Tim Laarmann

Dr. David Schwickert

Attosecond many-electron quantum dynamics in matter



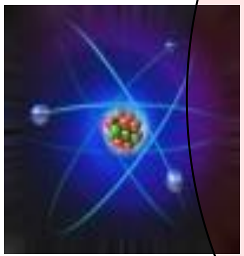
Agostini, Krausz & L'Huillier
Nobel Physics 2023

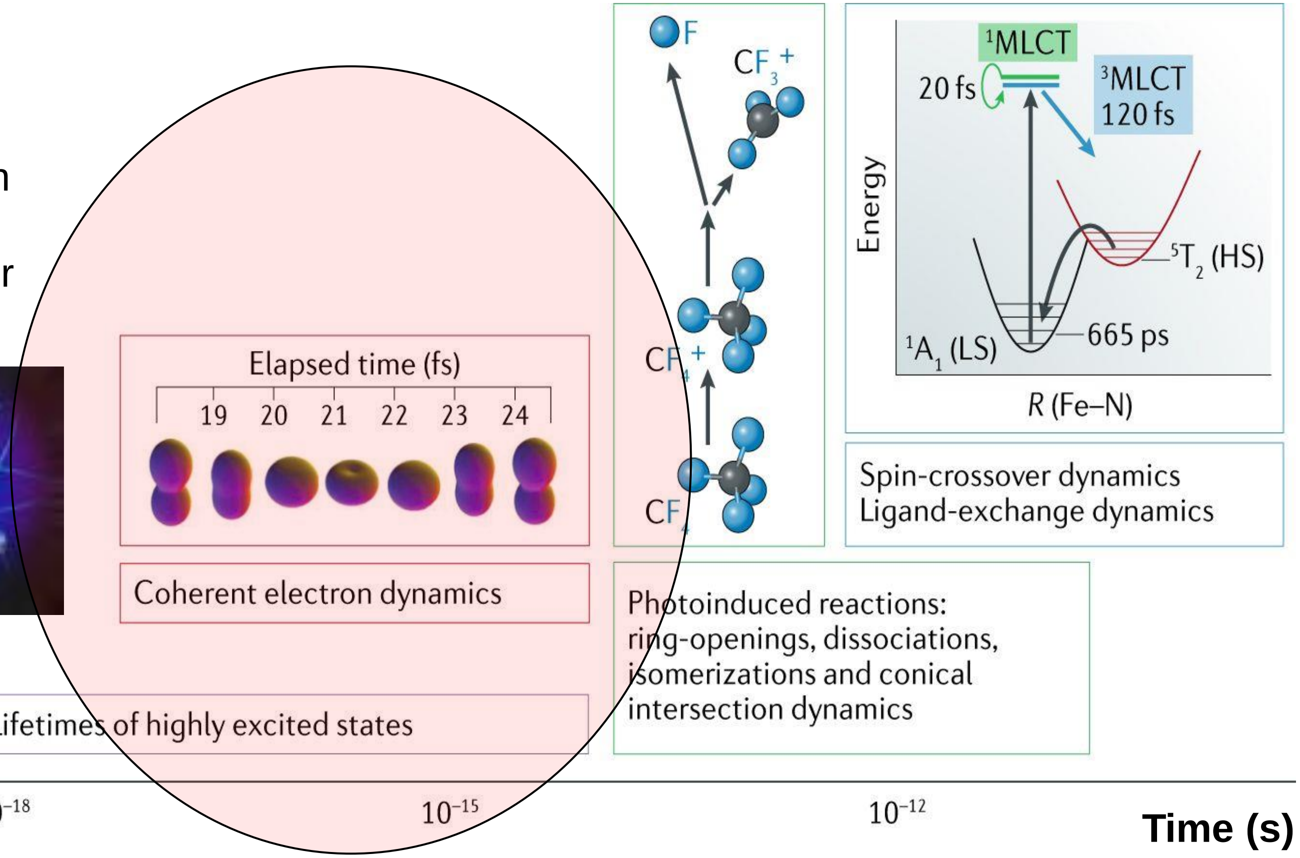
Attosecond science

Access electron dynamics on their natural timescales

Electron Orbit in Bohr Model

$T_{orbit} \approx 150$ *as* for H ground state





Many-electron motion timescale 0.1 – tens of femtoseconds

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

- Photo-excitation/ionisation primary event for key processes such as charge migration/transfer and energy transfer.

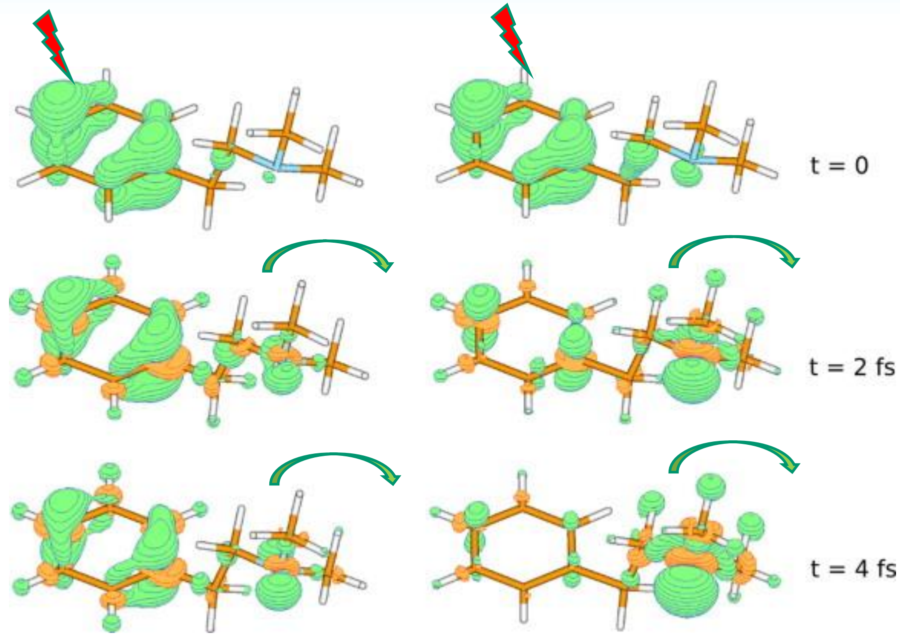
- Coherent superpositions of electronic states to drive new chemistry? ….."*Attochemistry*" ?

- Experimental test-bed for quantum information in open multi-partite quantum systems.

- Ultrafast creation and manipulation of microscopic currents in solid-state materials. Test ultimate physical speed limits of electron-based metrology, optical charge manipulation and signal processing in opto-electronic devices.

Most notorious example: ultrafast charge migration upon molecular photoionization

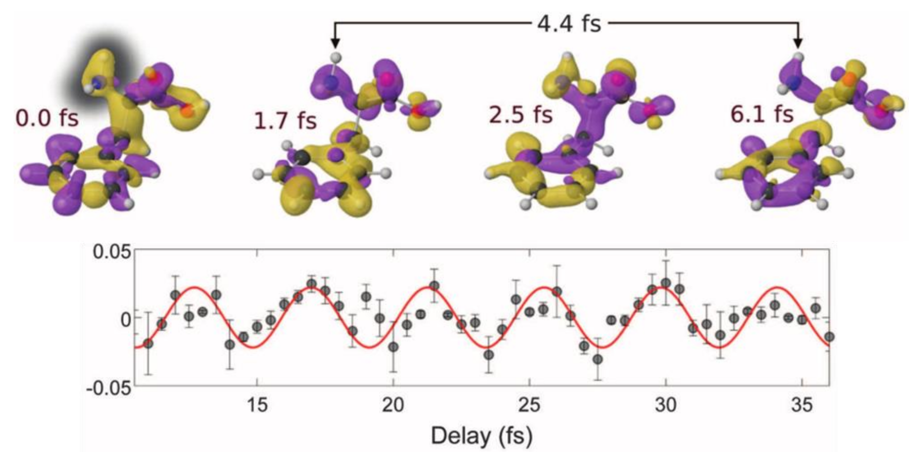
- Photoionization creates non-stationary state of molecular ion
- **Charge migration**: the hole charge oscillates across the molecule on attosecond timescales
- Nuclear motion – hole localization and new paradigm of **“charge-directed” reactivity**” important to photochemistry, biological radiation damage, etc.,



[Lünnemann, Kuleff & Cederbaum, Chem. Phys. Lett. **450**, 232 (2008)]

First attempts of time-resolved observation

Attosecond XUV pump – IR probe spectroscopy on phenylalanine, monitoring ion-fragment yield [Science **346**, 336 (2014)]

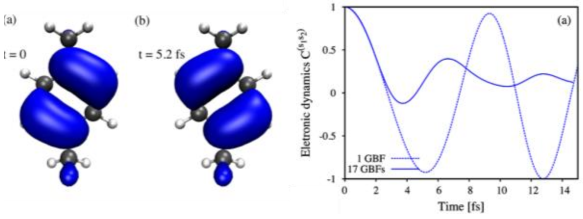


Open Questions

- **Can we prepare and control electronic coherence in molecules?**
  - Does purely-electronic coherent dynamics exist ?
  - How long does it survive for?
  - How does electronic coherence evolve into longer-lived vibronic coherence?

Possible mechanisms of electronic decoherence

Nuclear motion



Paraxylene dipeptide
[PRL **118,** 083001 (2017)]

GS quantum nuclear distribution

[PRA **92**, 040502(R) (2015)]

Challenges

- **Can we prepare and control electronic coherence in molecules?**
- Does purely-electronic coherent dynamics exist ?
- How long does it survive for?
- How does electronic coherence evolve into longer-lived vibronic coherence?

C_{EXP} **Need for Attosecond Pump-Probe Spectroscopy & Direct probing:** target electronic degrees of freedom directly

C_{TEO} **Need for advanced first-principles theory** of electronic coherence to **design, guide and interpretation** these complex experiments

Towards attosecond time-resolved experiments

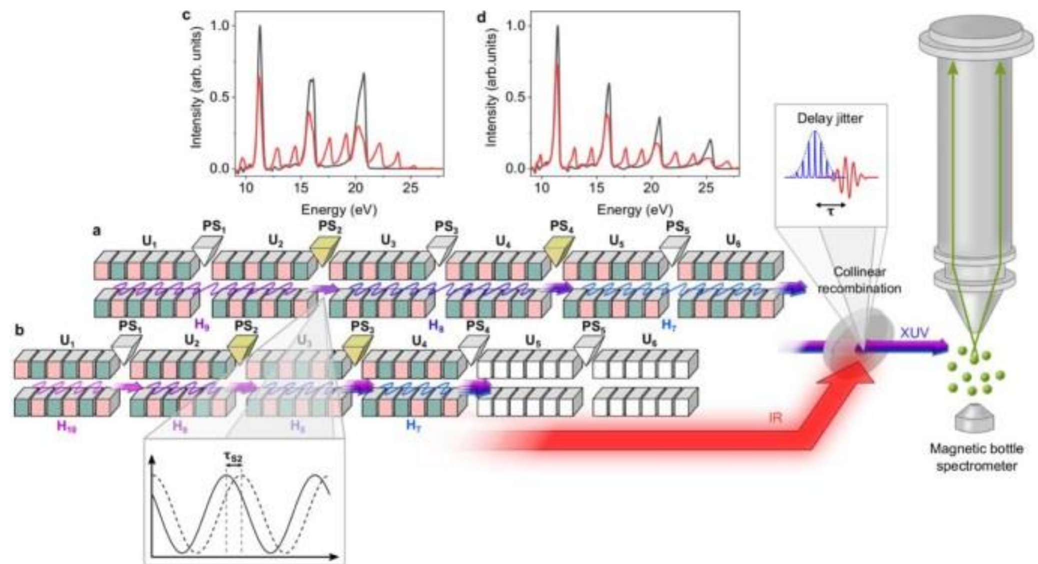
FERMI FEL @ELETTRA (Trieste)

- Seed wavelength: 266 nm
- Wavelength range: 100-4 nm
- Pulse energy: tens of μJ
- Even and odd harmonics

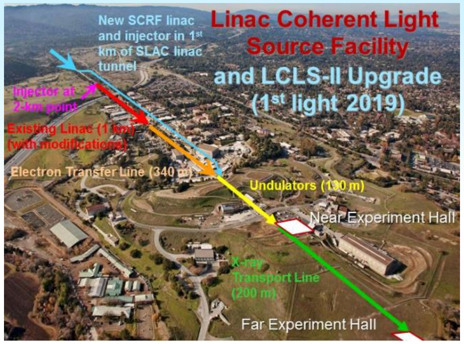
Longitudinal coherence !

- ✓ **Attosecond pulse shaping**
- ✓ **Coherent control**
- ✓ **Attosecond resolution**

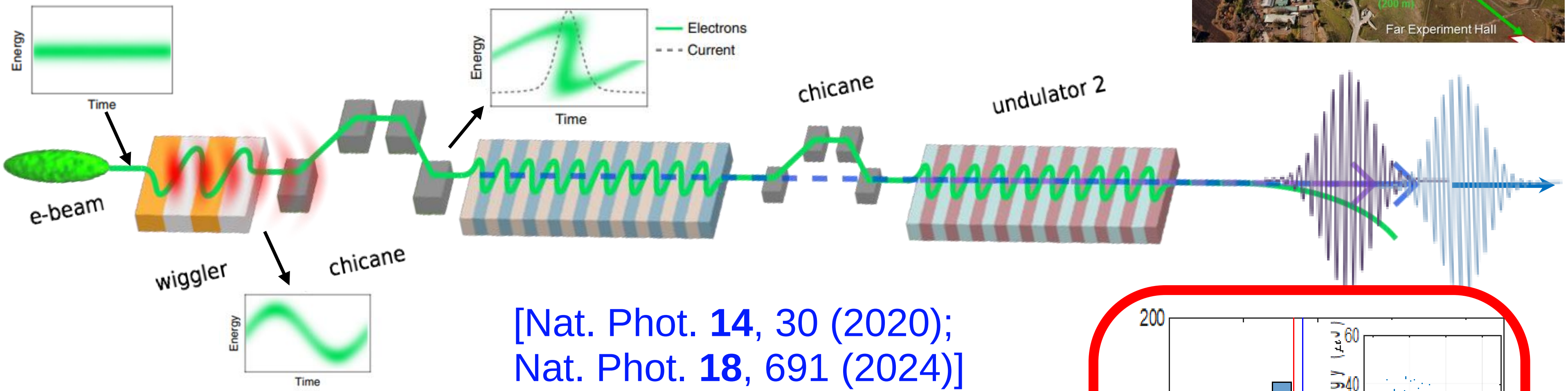
Amplitude & phase manipulation of harmonic components of an attosecond pulse train [Nature **578**, 386 (2020)]



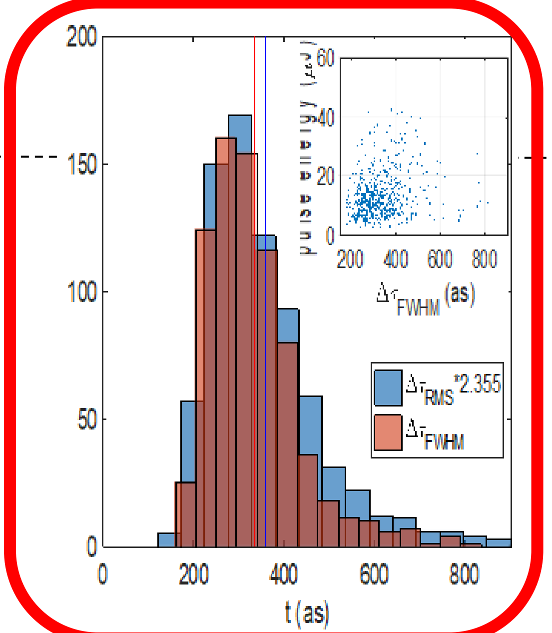
Towards attosecond time-resolved experiments



Soft X-ray: X-LEAP technique at **LCLS-II** (SASE X-ray FEL)



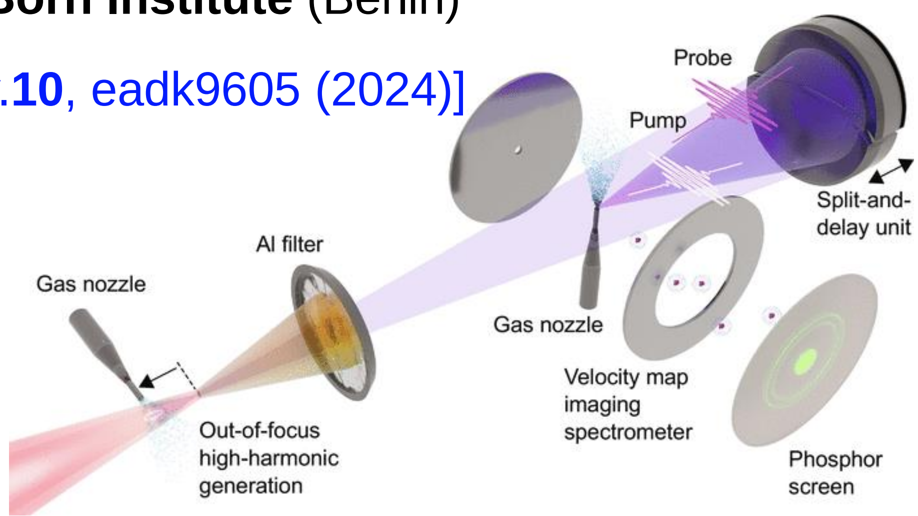
[Nat. Phot. **14**, 30 (2020);
Nat. Phot. **18**, 691 (2024)]



Attosecond duration

XUV: High order Harmonic Generation sources at **Max Born Institute** (Berlin)

[Sci. Adv.**10**, eadk9605 (2024)]

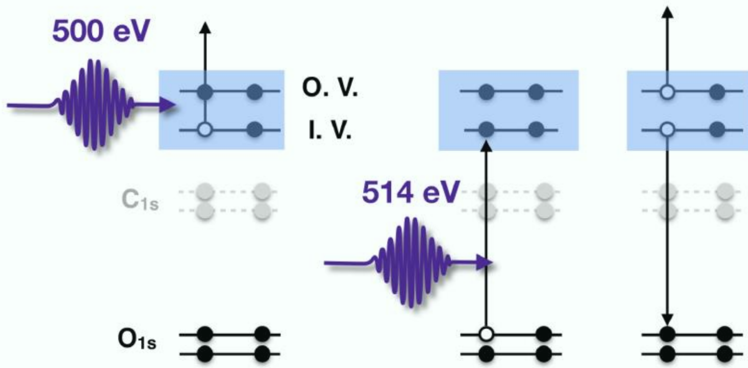


Advantage of attosecond X-ray pump-probe

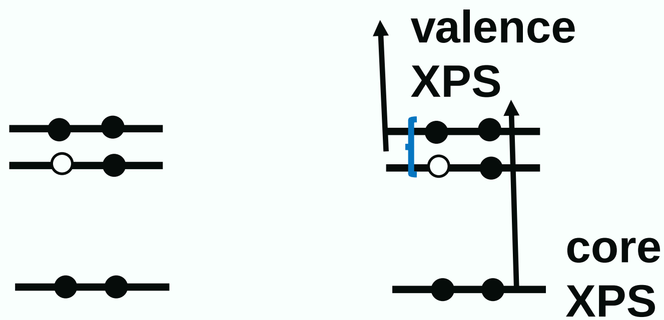
Access to < 10^{-10} m *spatial* and < 10^{-15} s *temporal* scales
to fully track the dynamics driven by electronic ionization and excitation

- ✓ Electronic state & atomic site specificity in probe – C, N, O K-edges (**Water Window**)
- ✓ Pump-probe arbitrary delay & now reaches sub-fs resolution
- ✓ "Weak" non-disruptive X-ray probe field

X-ray absorption spectroscopy (XAS) resonant core shell - specific inner valence hole state (IVH) to monitor hole amplitude at given delay time

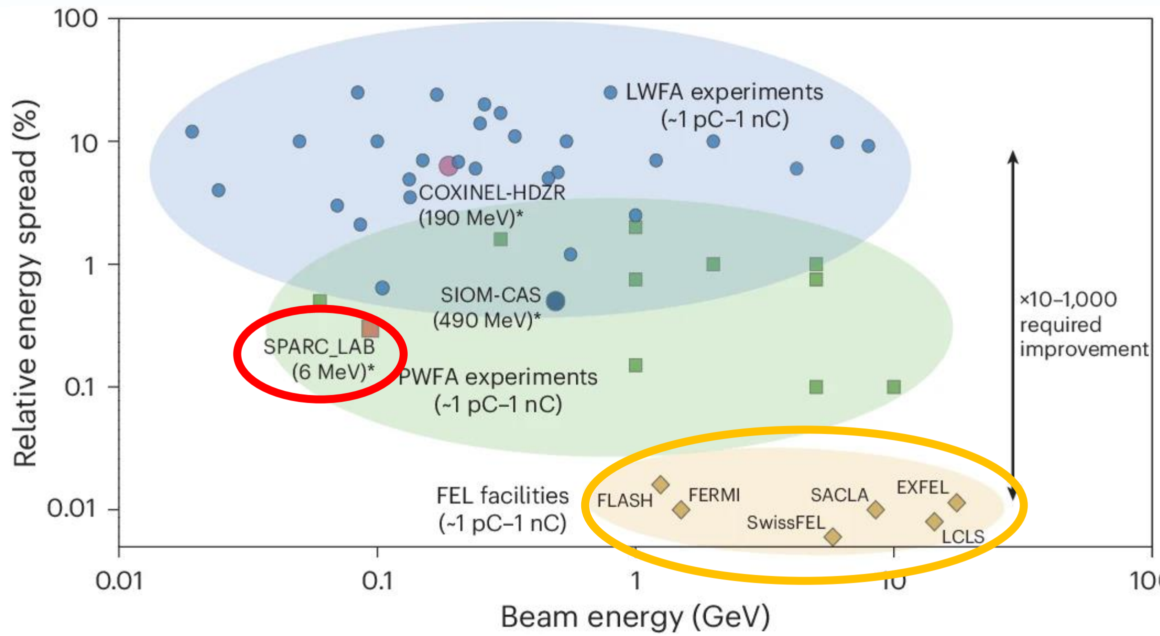


X-ray photoelectron emission spectroscopy (XPS) (valence or core shell) – also sensitive to valence state evolution with delay



Compact laser-plasma-accelerators - driven FELs

Beam- & Laser- driven wakefield acceleration FELs [Nat. Phot. **18**, 780 (2024)]



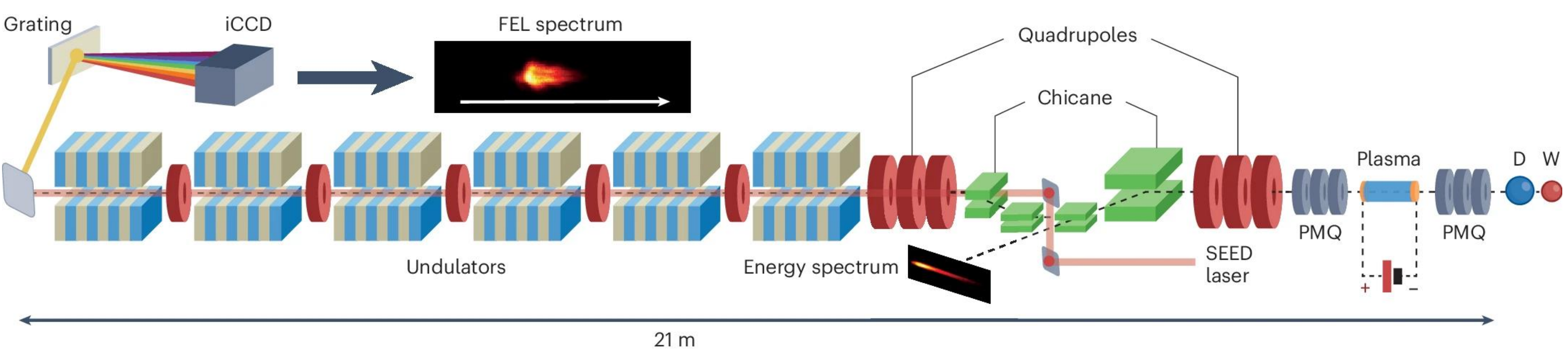
Grand Challenge:

FEL radiation

from vacuum UV to soft X-ray

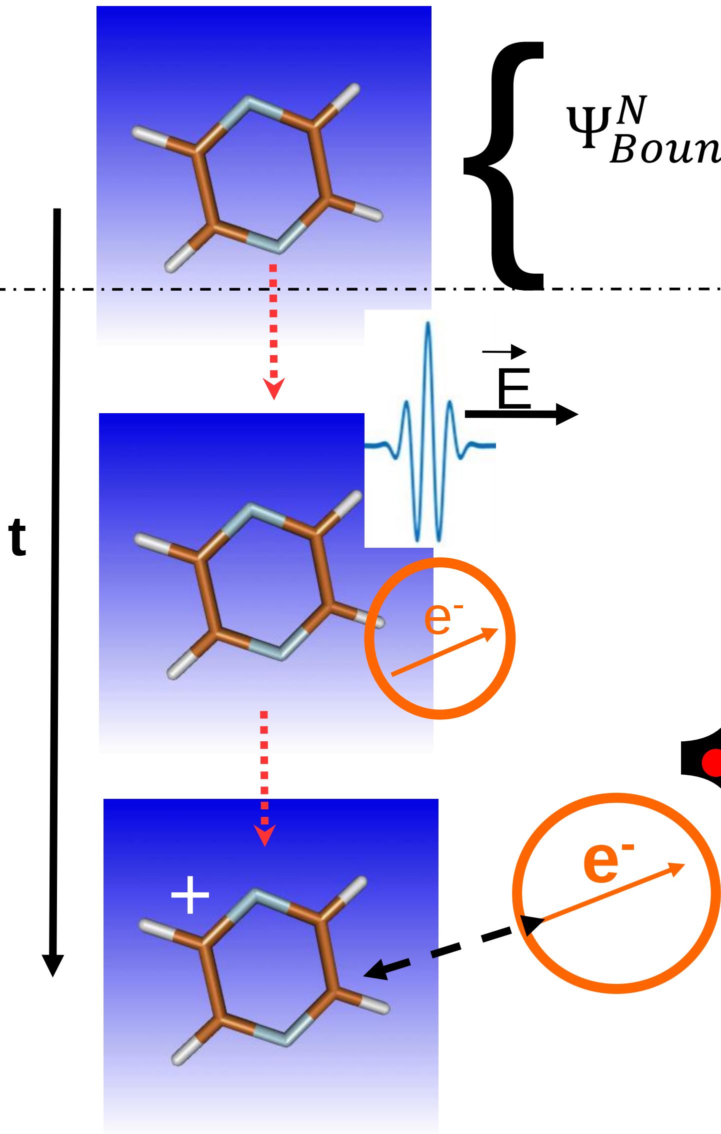
at **EuPRAXIA@SPARC_LAB**

Experimental set-up of **SASE** and **seeded** PWFA-based **FEL** at **SPARC_LAB**



[Nature **605**, 659 (2022); PRL **129**, 234801 (2022)]

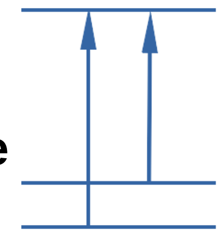
Fundamental theoretical understanding:
quantum coherence upon photoionization?



$$\Psi^{N}_{Bound}(1,\ldots,N)$$

What is the final state upon ultrafast molecular photoionization?

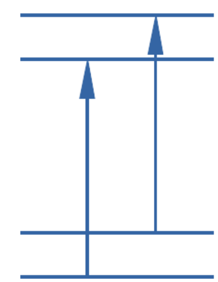
Molecular ion in a pure quantum state



$$\approx A\left[\left(\sum_{m} c_m\,\Phi_m^{N-1}(1,\ldots,N-1)\right)\times\varphi^{e^-}(N)\right]$$

?

Ion-photoelectron entanglement

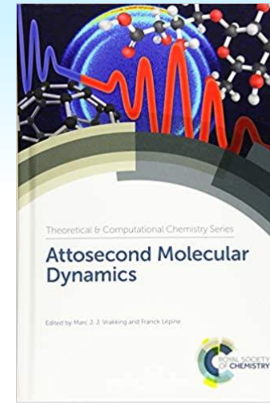


$$\approx A\left[\sum_{m} c_m\,\Phi_m^{N-1}(1,\ldots,N-1)\,\times\varphi_m^{e^-}(N)\right]$$

[M. Ruberti *et al*, PCCP **24**, 19673 (2022)]

CTEO

First-principles theory:
Time-dependent B-spline RCS-ADC method



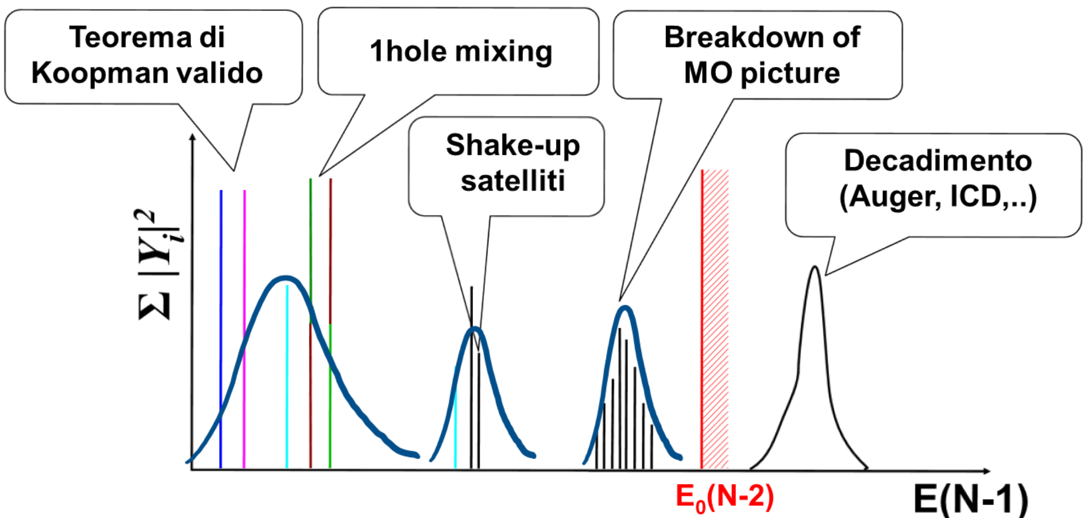
State-of-the-art *ab initio* method: time-dependent (TD) multicentre- **B-spline** restricted correlation space **(RCS) –** algebraic diagrammatic construction **ADC**

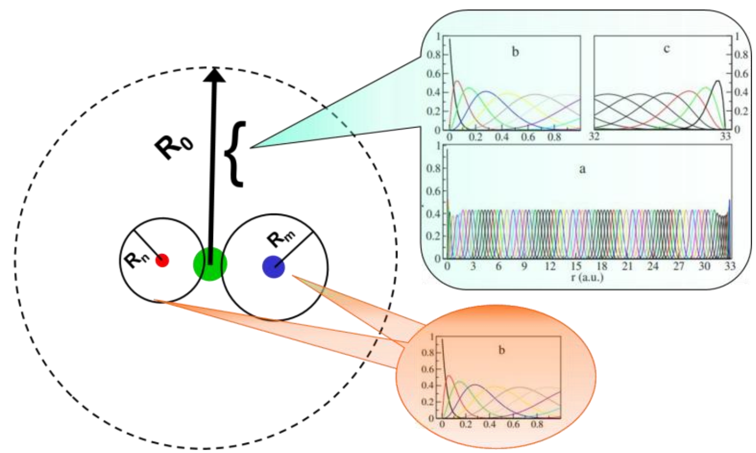
$$i\hbar\frac{\partial}{\partial t}|\Psi^N(t)\rangle = \hat{H}^N(t)|\Psi^N(t)\rangle \qquad |\Psi^N_{m\mu}\rangle = \hat{c}^\dagger_\mu |\Phi^{N-1}_m\rangle$$

Quantum Chemistry ground and excited states + **Photoelectron description**

$$\Psi^{(N-1)} = \sum Y_i \Psi_i + \sum Y_{ij}^{a} \Psi_{ij}^{a} + \sum Y_{ijk}^{ab} \Psi_{ijk}^{ab} + \dots$$

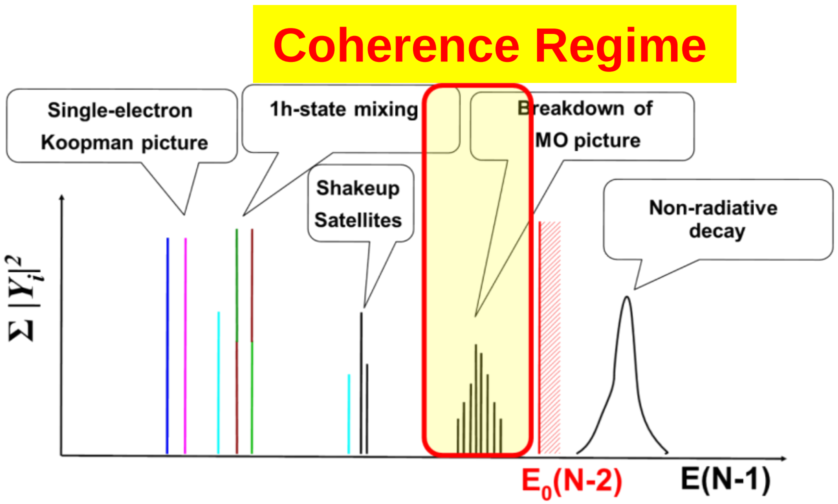
1h **2h1p** **3h2p**

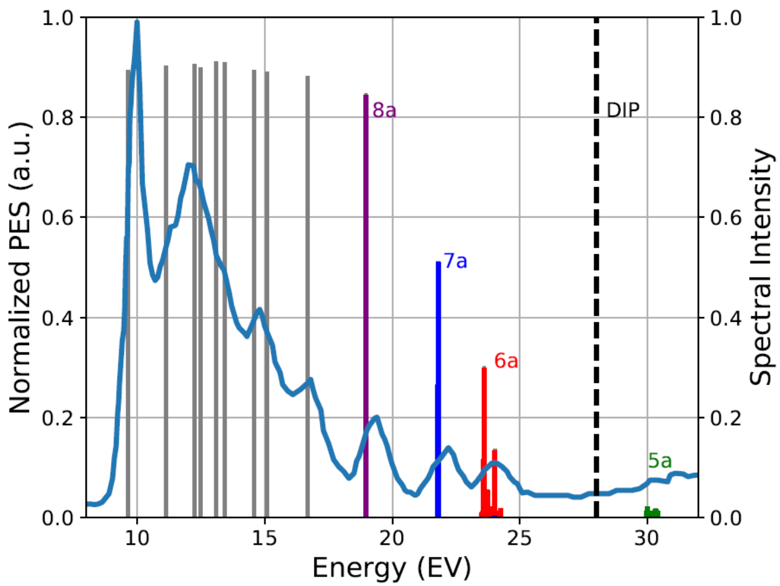




[M. Ruberti, JCTC **14**, 4991 (2019);
M. Ruberti, PCCP **21**, 17584 (2019);
M. Ruberti, Faraday Discuss. **228**, 286 (2021)]

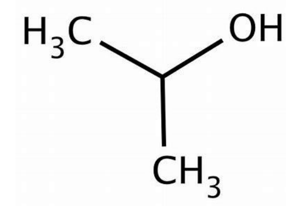
Correlation-Driven Transient Hole Dynamics Resolved in Space and Time in the Isopropanol Molecule



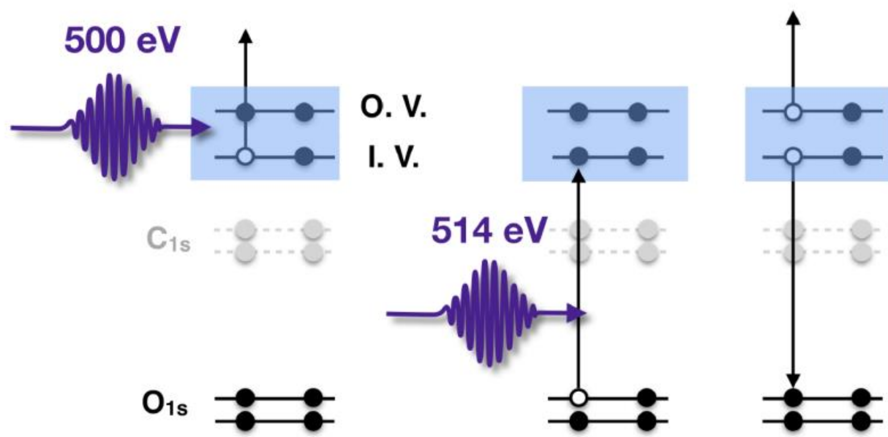


Experiment led by Dr. James Cryan at LCLS

X-ray FEL Pulse duration
~ 3 femtoseconds



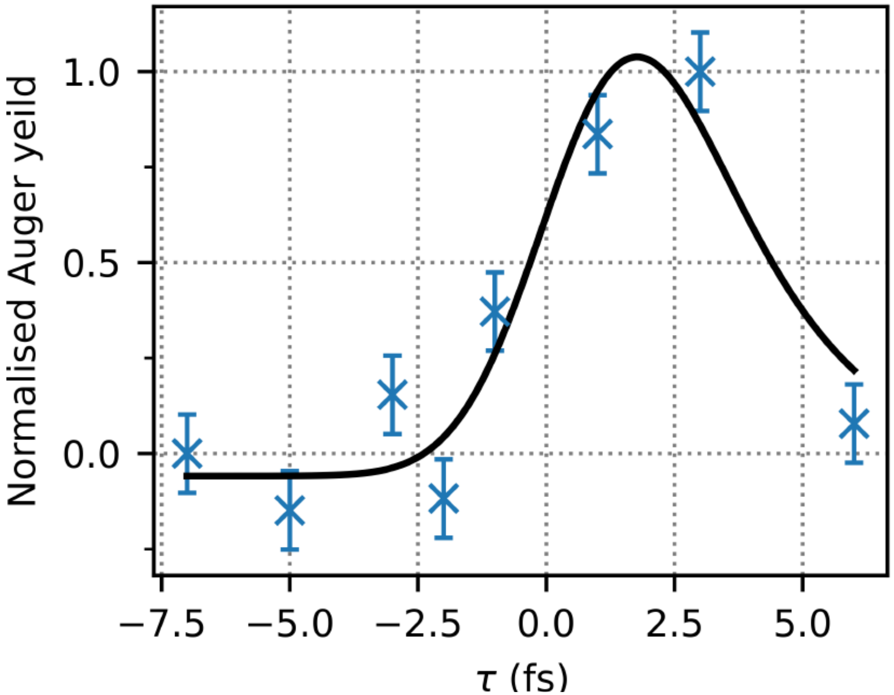
XAS probe scheme



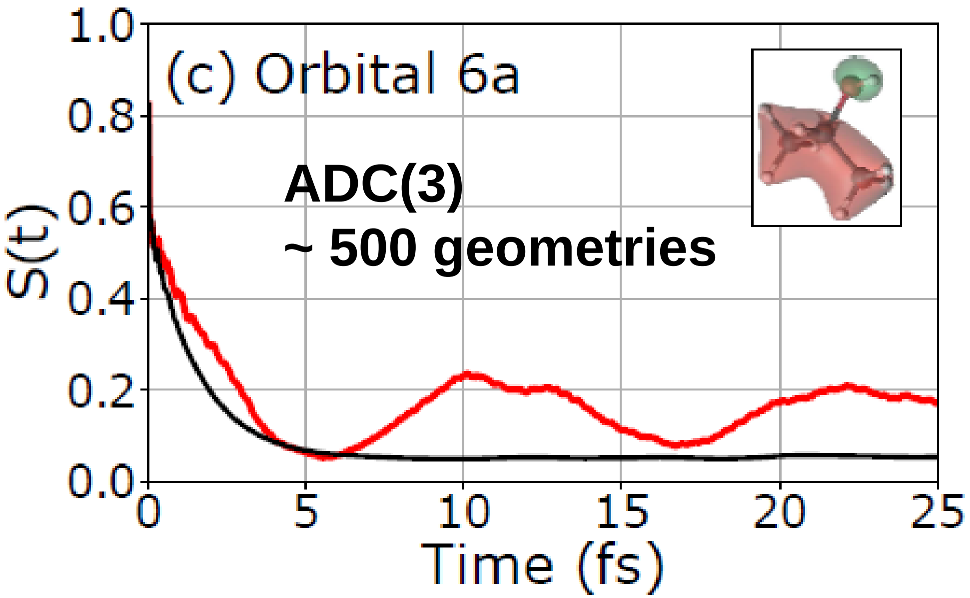
[Phys. Rev. X **11**, 031048 (2021)]

Transient 6A hole states probed by X-ray spectroscopy

"Breathing dynamics" from initially localised hole to extended states.
Revivals damped by nuclear zero-point spread.



6A measured with ~ 2.5 fs pulses, indicates a few-fs (2-3) decay time



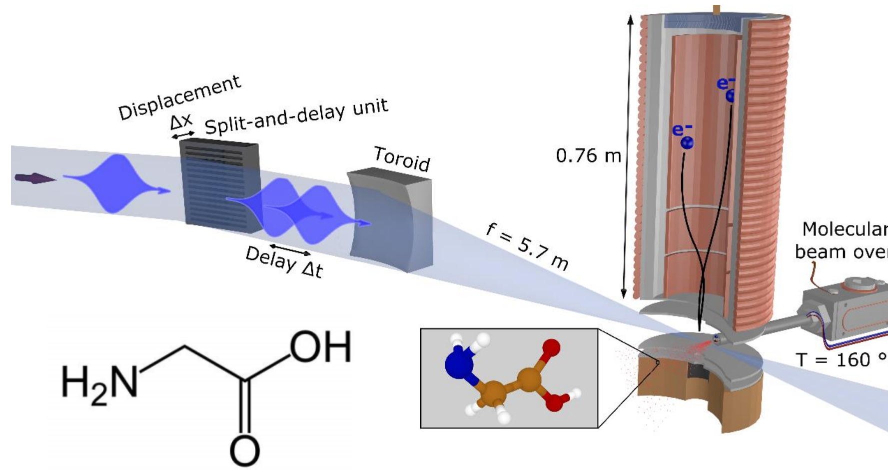
Consistent with the decay driven by electron correlation predicted by ADC theory

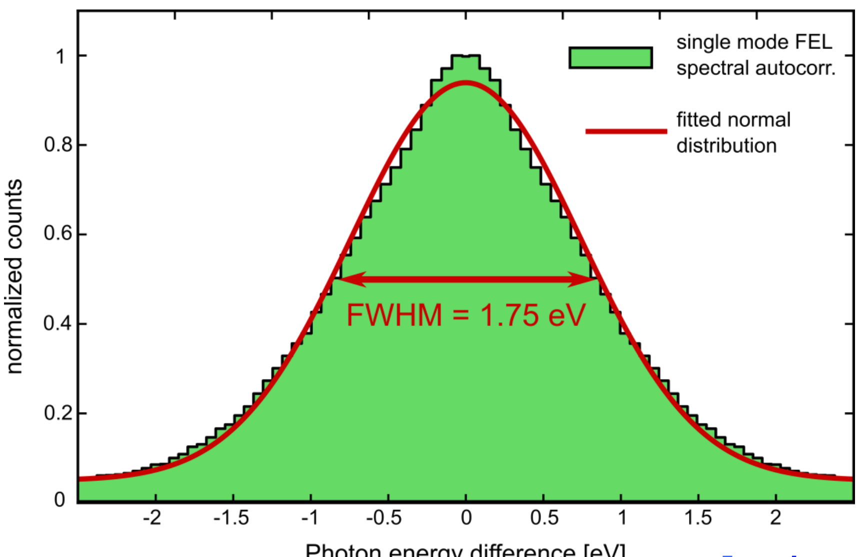
[Phys. Rev. X **11**, 031048 (2021)]

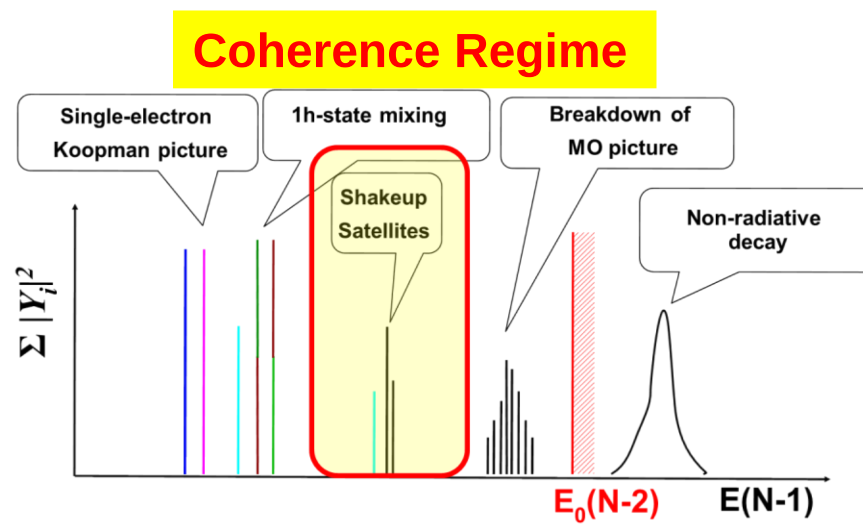
Electronic Quantum Coherence in Glycine Molecules Probed with Ultrashort X-ray Pulses in Real Time

Experiment led by Dr. Tim Laarman at FLASH

X-ray split-and-delay with a short pulse for a single colour pump-probe measurement.



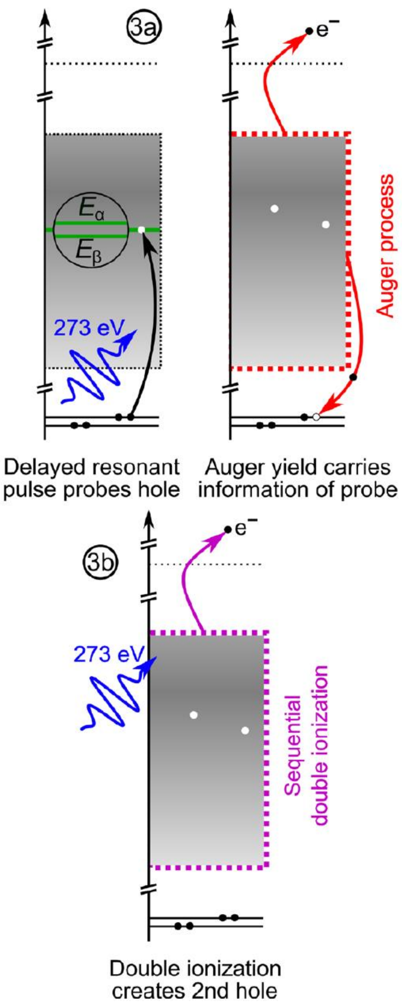




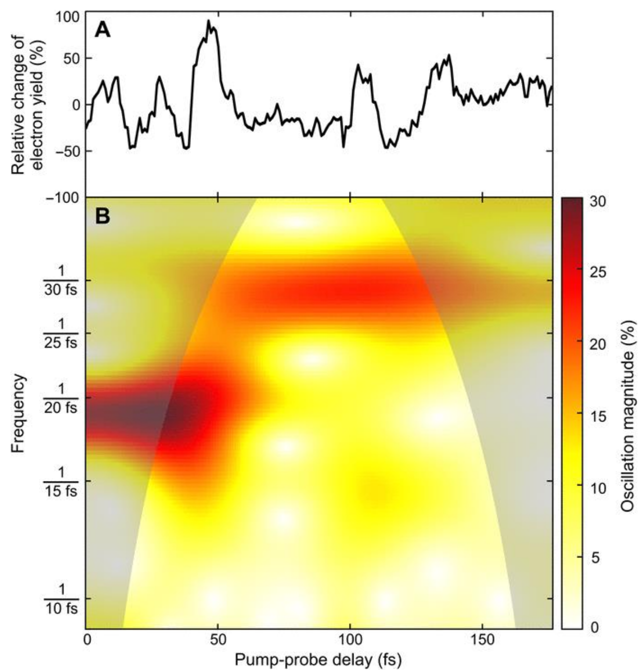
[Sci. Adv. **8**, eabn6848 (2022)]

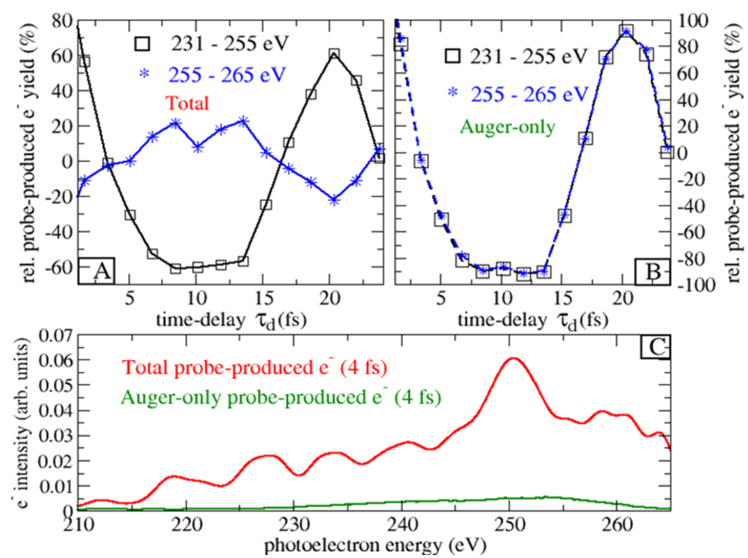
Electronic Quantum Coherence in Glycine Molecules Probed with Ultrashort X-ray Pulses in Real Time

Coincident detection of 1^{st} + 2^{nd} photoelectron + Gly^{2+} fragment



Electronic dynamics consistent with periodicity ~ 20 fs, in excellent agreement with the predictions of B-spline RCS-ADC



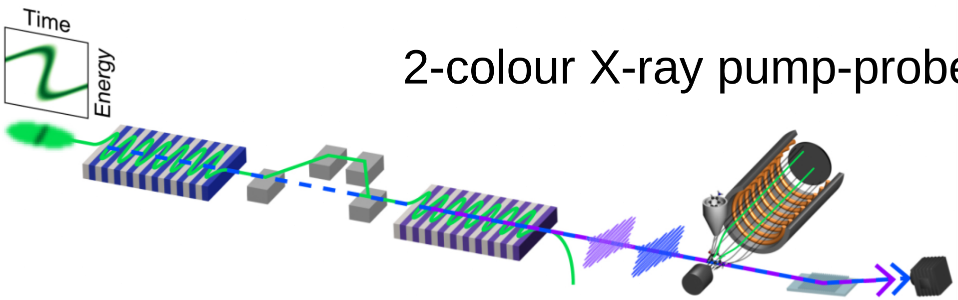


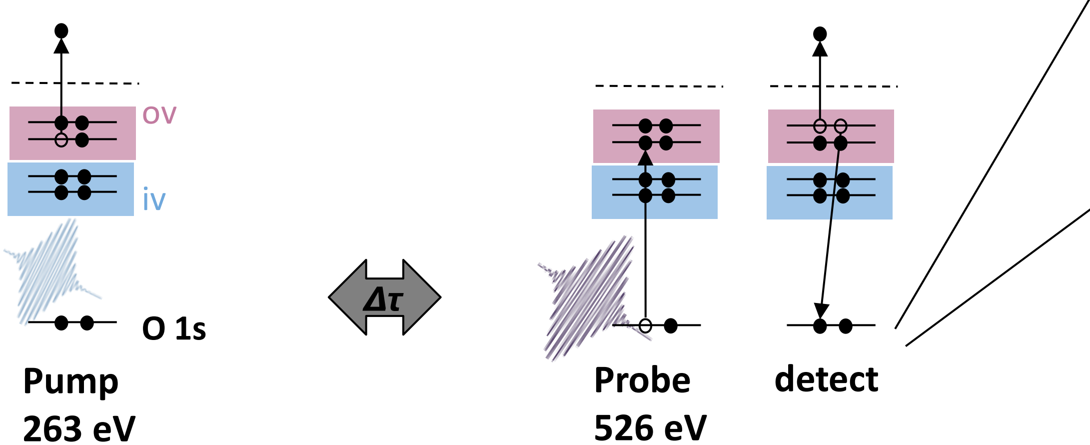
[Sci. Adv. **8**, eabn6848 (2022);
Structural Dynamics **9**, 064301 (2022)]

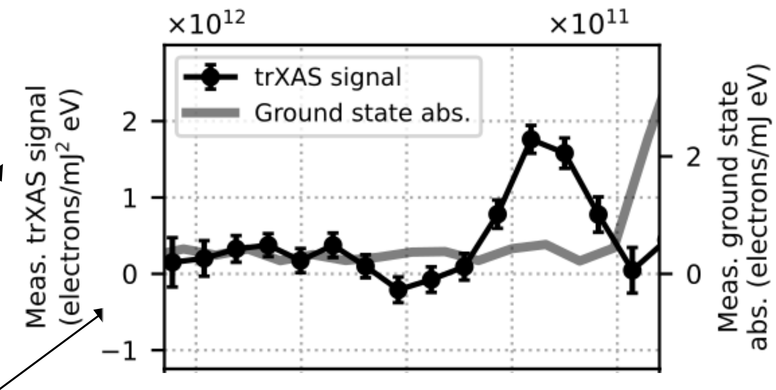
Attosecond Campaign @ LCLS: *Real-time Observation of Ultrafast Electron Motion Using Attosecond XFELs*

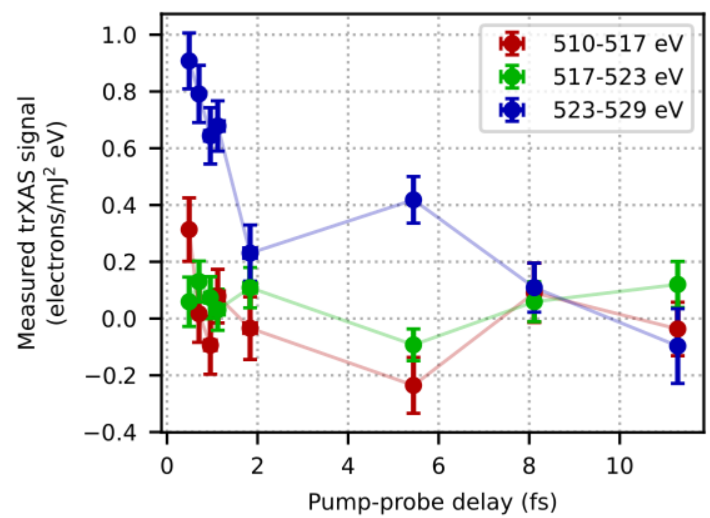
Led by James Cryan, Agostino Marinelli, Peter Walter (SLAC)

2-colour X-ray pump-probe experiment at LCLS-II









X-ray probe absorption at O K-edge maps to transient valence electron density at oxygen site

[T. Driver et al., arXiv:2411.01700 **[physics.chem-ph]**]

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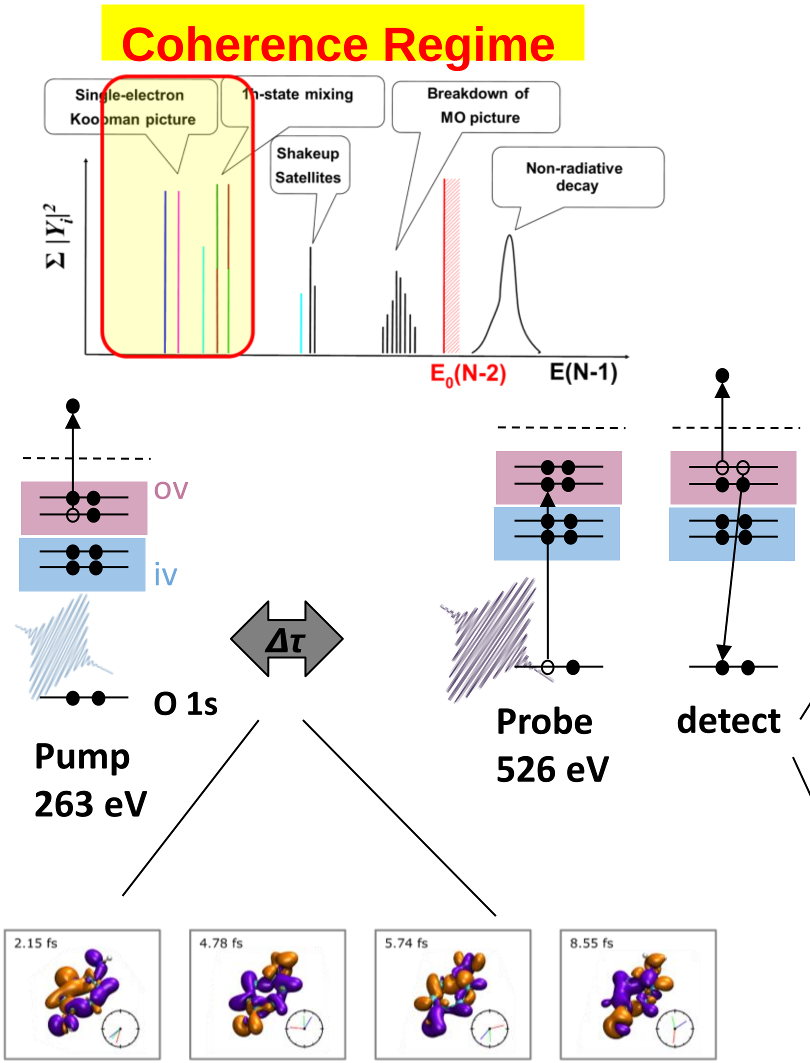
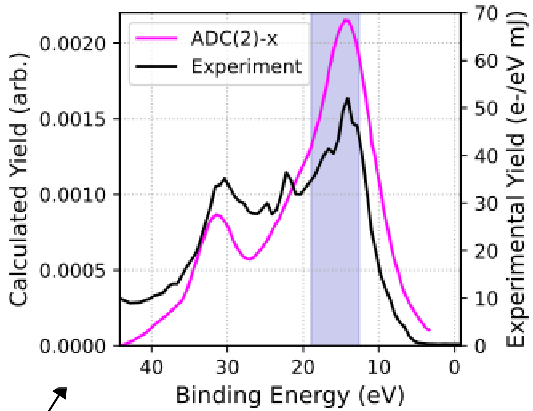
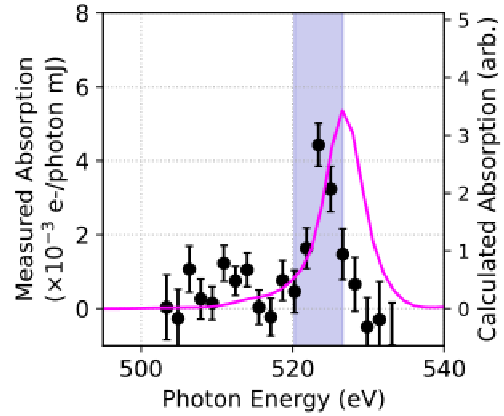
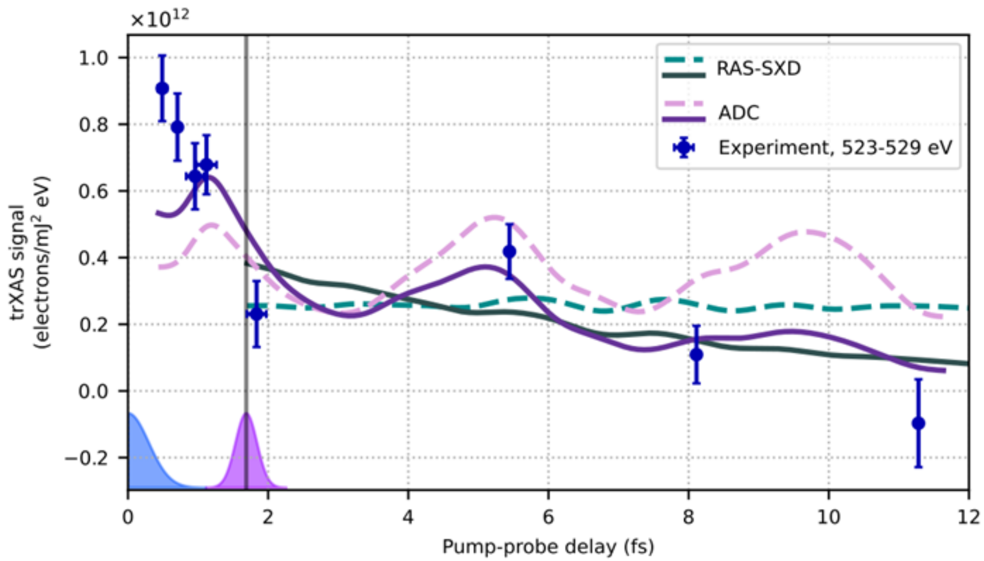


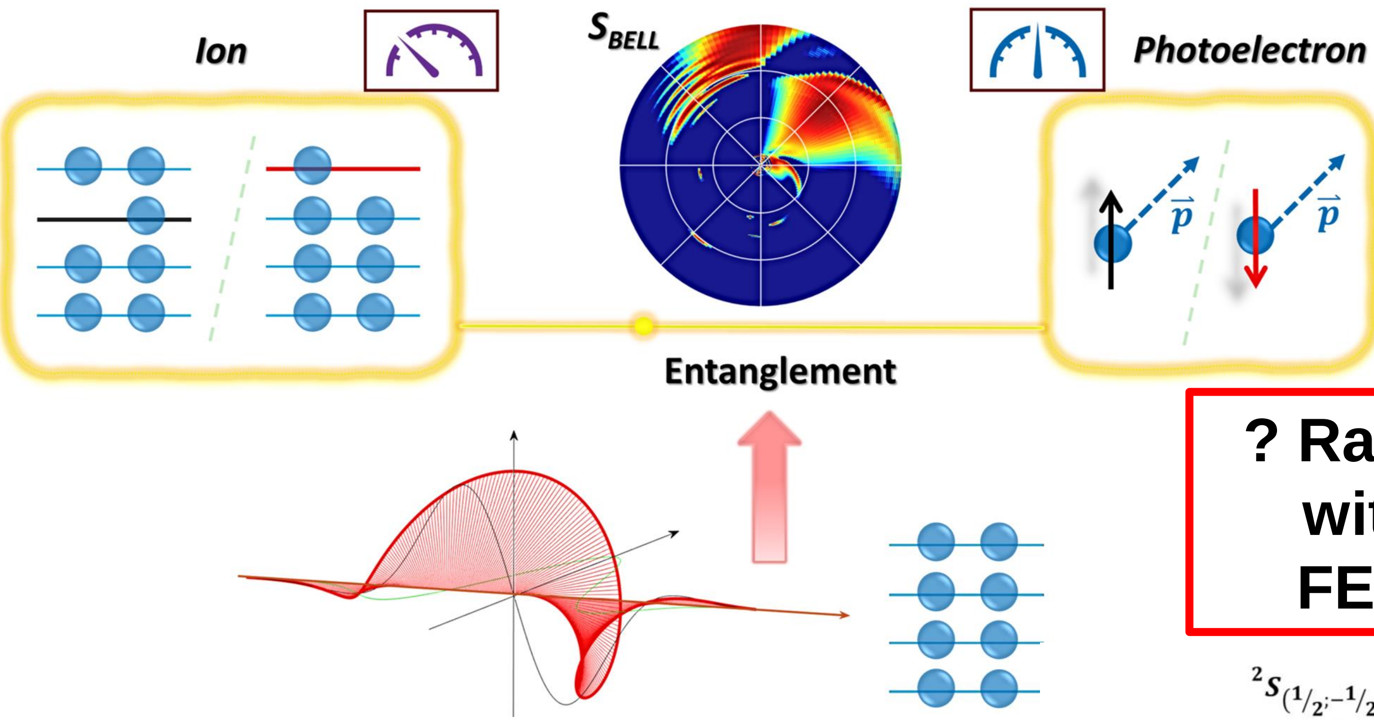




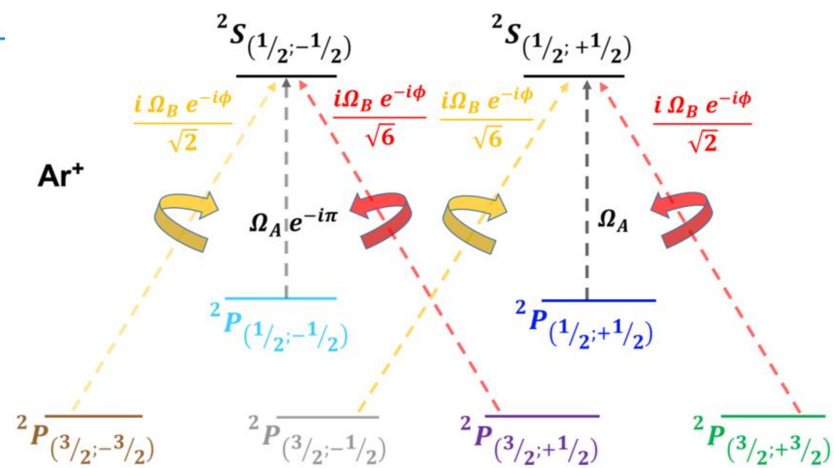


[T. Driver et al., arXiv:2411.01700 [physics.chem-ph]]

Bell Test of Quantum Entanglement in Attosecond Photoionisation



? Rabi dynamics with UV-XUV FEL pulses ?



[M. Ruberti, V. Averbukh, F. Mintert, Physical Review X **14**, 041042 (2024)]

Outlook

☺ **Attosecond pump-probe experiments with X-ray FELs** provide **unique powerful schemes** to access attosecond quantum-coherent electron dynamics with **unprecedented time resolution.**

☺ **Description and interpretation of these novel experiments in polyatomic molecules** requires state-of-the-art ab initio methods such as **Time-dependent B-spline RCS-ADC.**

☺ Quantum electronic **coherence & entanglement** can be calculated **from first-principles in photoionized many-electron systems**.

[M. Ruberti, V. Averbukh, WIREs Comput. Mol. Sci. **13**, e1673 (2023);
O. Alexander, J. Marangos, M. Ruberti, M. Vacher, *Attosecond electron dynamics in molecular systems* in "*Advances in Atomic, Molecular and Optical Physics*", **72**, Elsevier, 183 (2023)]

☼ We need **compact plasma-based FELs for university-based facilities** – Complements HHG-based sources & **Essential in the water window for studying biomolecules.**

☼ End-stations: detection of photons & electrons; coincidence detection with COLTRIMS.

Thank you for your attention!

EPSRC
Pioneering research and skills

MBI

Imperial College London