Atomic and Molecular Physics with XFELs II

Jon Marangos

Director, Blackett Laboratory Extreme Light Consortium

Imperial College London

Contents

EPSRC Pioneering research and skills

SLAC

European Research Council Executive Agency erc

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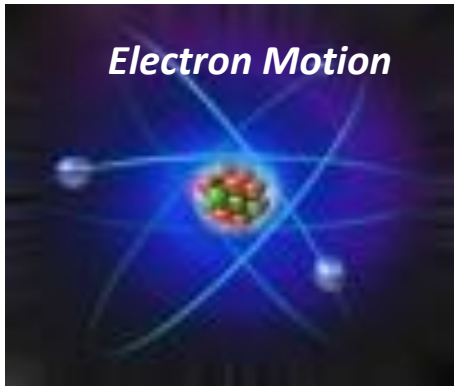
3. Attosecond science and quantum coherence

Period of <r(t)> in a 1s – 2p superposition of the H atom is ~400 as



In most matter electrons are in close proximity to one another and couple to nuclear degrees of freedom. Both electronic correlation and fast electron-nuclear coupling play a vital role in the electron dynamics

Attosecond Science = study and ultimately control of attosecond time-scale electron dynamics in matter.

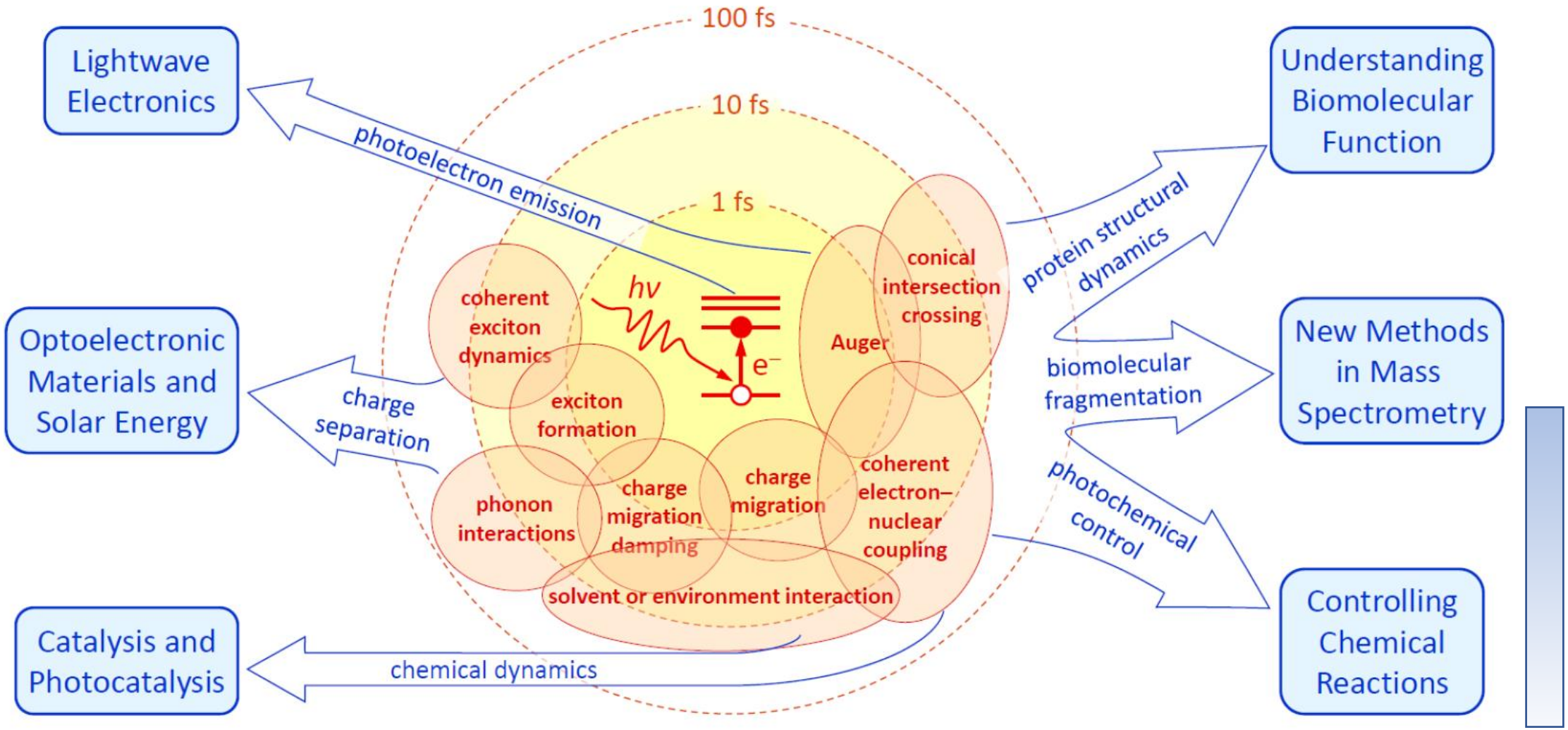
3. Ultrafast electronic and structural dynamics

- **Attosecond electronic coherence in photoexcitation (e.g. charge migration, coherence/decoherence, correlation)**
- **Few-femtosecond electron – nuclear coupling beyond Born-Oppenheimer in photochemistry, (e.g. evolution at conical intersections, formation and decay of vibronic coherences, chemical quantum control)**
- **Few-femtosecond exciton dynamics in photovoltaics (e.g. formation, recombination, delocalisation, charge separation)**

- **Other ultrafast processes where ultrafast X-ray probing will have impact:**
  - **Charge transport and energy transfer**
  - **Formation and decay of polarons, phonons**

etc.

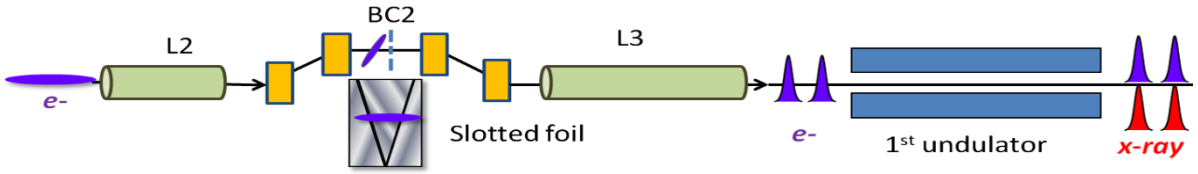
  - **Radiation damage in materials/ biomolecules**
  - **Catalysis and photocatalysis**
  - **Ultra-high speed electronics**
  - **Ultra-fast chiral dynamics**


100 fs
10 fs
1 fs
Lightwave Electronics
photoelectron emission
Understanding Biomolecular Function
protein structural dynamics
Optoelectronic Materials and Solar Energy
charge separation
New Methods in Mass Spectrometry
biomolecular fragmentation
photochemical control
Controlling Chemical Reactions
Catalysis and Photocatalysis
chemical dynamics
hν
e⁻
coherent exciton dynamics
exciton formation
phonon interactions
charge migration damping
charge migration
Auger
conical intersection crossing
coherent electron–nuclear coupling
solvent or environment interaction
Electronic coherence

3. Using short pulses from an X-ray FEL to resolve few-femtosecond dynamics

Several options are currently used for few-fs resolved all X-ray pump – probe e.g.

- **X-ray split and delay**
- **Two-pulse generation at single frequency**
- **Two-pulse / two-colour generation ("fresh slice" mode)**
- **Current temporal resolution to < 1 fs**



Ding et al PRL, 102 254801 (2009)
Ding et al PRL, 109, 258802 (2012)
Marinelli et al, Nat.Comm., 6, 6369 (2015)
Lutmann et al, Nat.Phot. 10, 745 (2016)
Huang et al, PRL, 119, 154801 (2017)

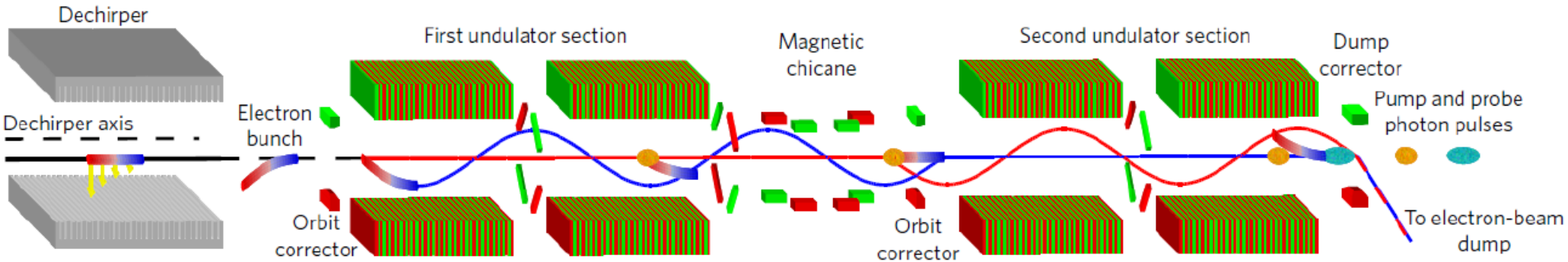
- Example from LCLS, similar modes operating at FLASH, FERMI, Eu XFEL etc.

Or laser pump – X-ray probe measurements:

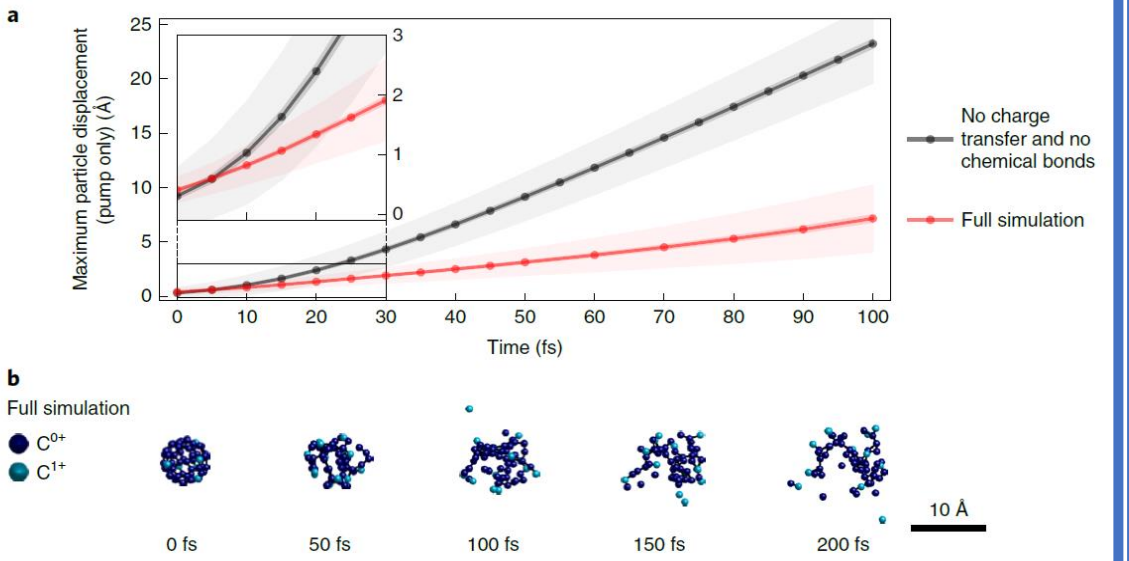
- **Few-cycle laser pulses Vis-IR-MIR give < 10 fs pulses (maybe can be extended into UV/DUV)**
- **"Time-tools" including attoclock streaking based can in principle register laser-X-ray synchronisation to sub-fs accuracy**
- **Current temporal resolution > 10 fs**

3. Fresh slice mode at LCLS

ARTICLES NATURE PHOTONICS DOI: 10.1038/NPHOTON.2016.201



"Fresh slice mode" was used to generate ~ 6 fs pump and probe pulses at the required photon energies with delay variable from -10 to +25 fs

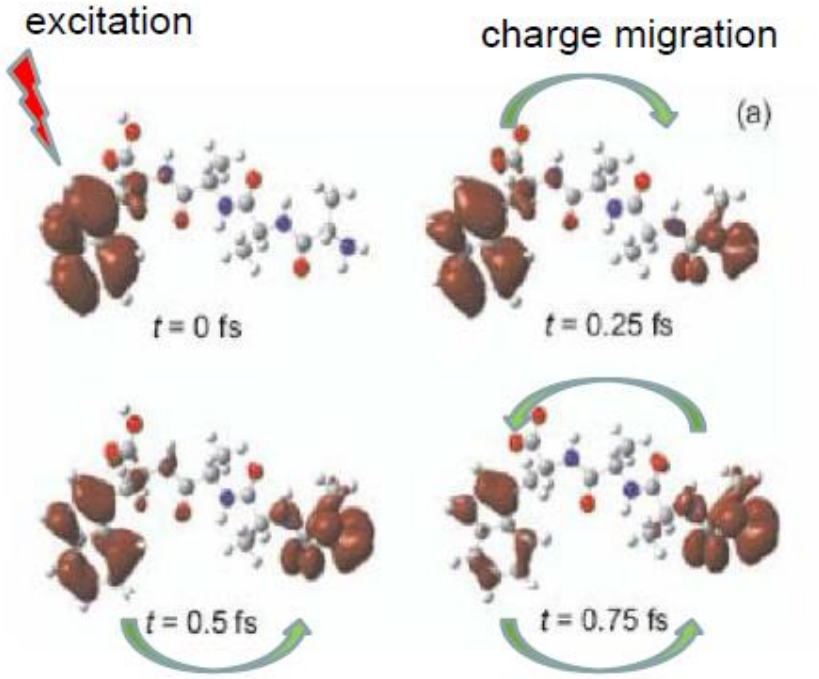


nature physics
ARTICLES
https://doi.org/10.1038/s41567-019-0665-7

Femtosecond-resolved observation of the fragmentation of buckminsterfullerene following X-ray multiphoton ionization

N. Berrah[1*], A. Sanchez-Gonzalez[2], Z. Jurek[3], R. Obaid[1], H. Xiong[1], R. J. Squibb[4], T. Osipov[5], A. Lutman[5], L. Fang[6], T. Barillot[2], J. D. Bozek[7], J. Cryan[8], T. J. A. Wolf[8], D. Rolles[9], R. Coffee[5], K. Schnorr[10], S. Augustin[9], H. Fukuzawa[11], K. Motomura[11], N. Niebuhr[12], L. J. Frasinski[2], R. Feifel[4], C. P. Schulz[13], K. Toyota[3], S.-K. Son[3], K. Ueda[11], T. Pfeifer[10], J. P. Marangos[2] and R. Santra[3,14]

3. X-ray pump-probe experiments of charge migration with XFELs



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)

Note: Coherence time ~ 1.1 fs of Sunlight equivalent to a large coherent bandwidth of ~ 0.5 eV (Ricketti et al, Sci.Rep 12, 5438 (2021))

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.

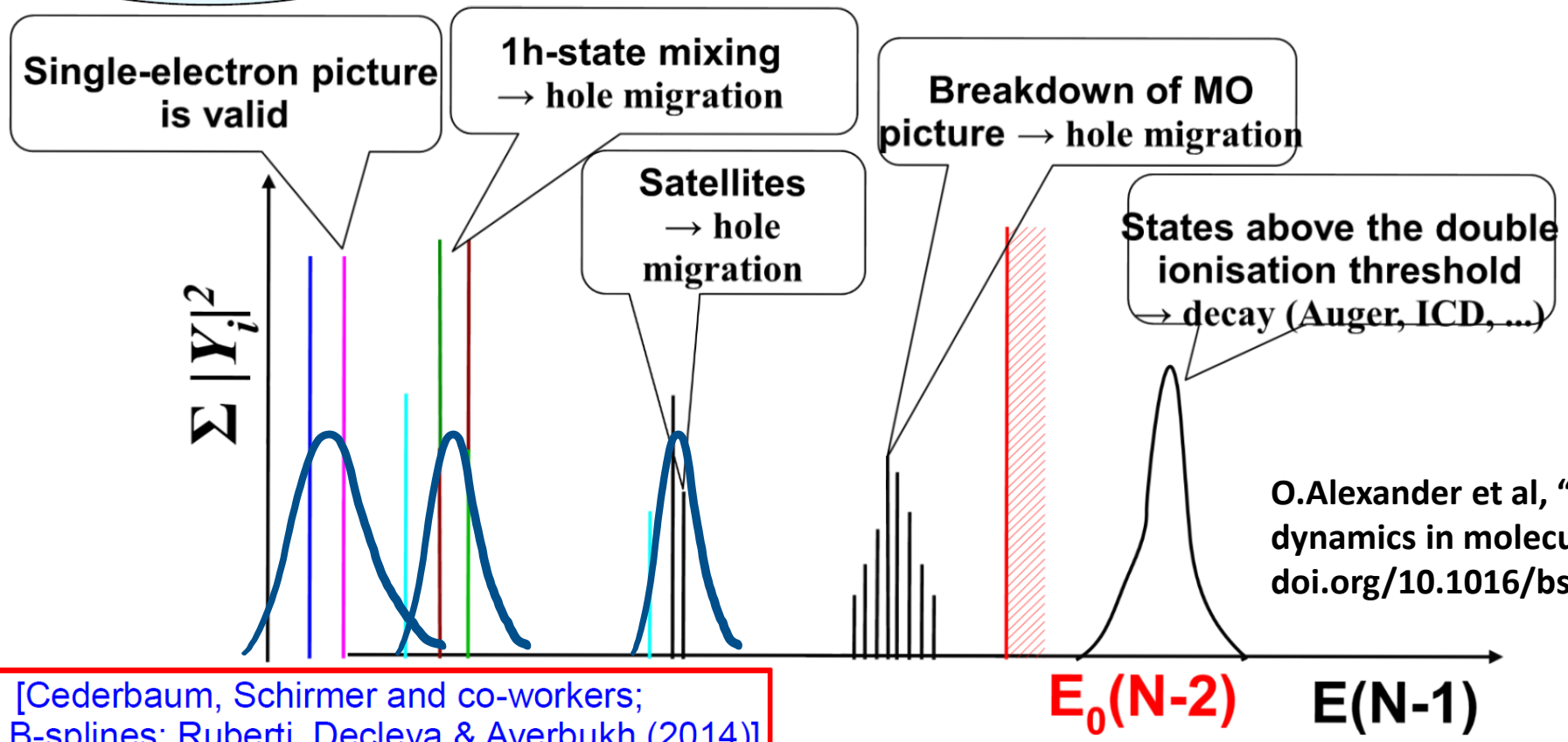
Important to photochemistry and biological radiation damage, as well as to the fundamentals of time-dependent behaviour of many electron systems.

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

Highly excited states of molecular cations: Outer and inner valence hole state superpositions

$$|\tilde{\Psi}^N_{\mu,n}\rangle = \hat{c}^\dagger_\mu \, |\Psi^{N-1}_n\rangle$$

$$\Psi^{(N-1)} = \underbrace{\sum Y_i \Psi_i}_{\text{1h}} + \underbrace{\sum Y_{ij}^{\ a} \Psi_{ij}^{\ a}}_{\text{2h1p}} + \underbrace{\sum Y_{ijk}^{\ ab} \Psi_{ijk}^{\ ab}}_{\text{3h2p}} + \ldots$$



O.Alexander et al, "Attosecond electron dynamics in molecular systems" doi.org/10.1016/bs.aamop.2023.05.001

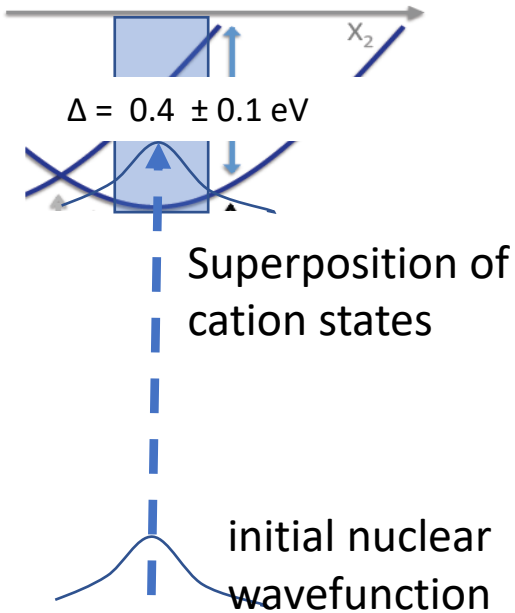
Courtesy of Marco Ruberti

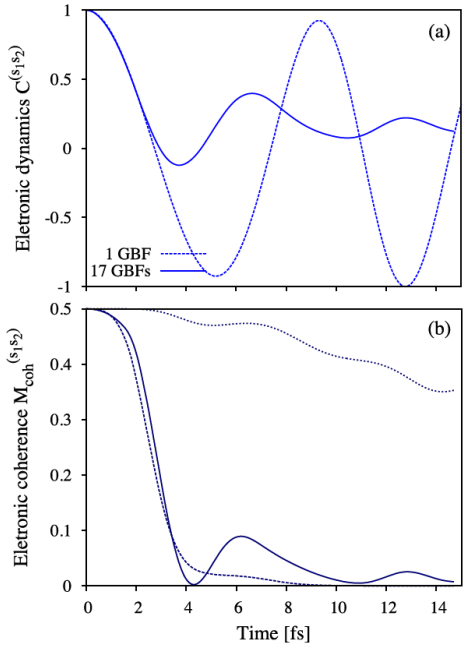
[Cederbaum, Schirmer and co-workers; Using B-splines: Ruberti, Decleva & Averbukh (2014)]

Attosecond dynamics intrinsically involve electron-nuclear coupling: Damping of electronic coherence in charge migration

Initial quantum nuclear zero point state geometry spread - couples to a significant dispersion in electronic timescales and consequently dephasing

Vacher et al PRA 92, 040502(R) (2015)





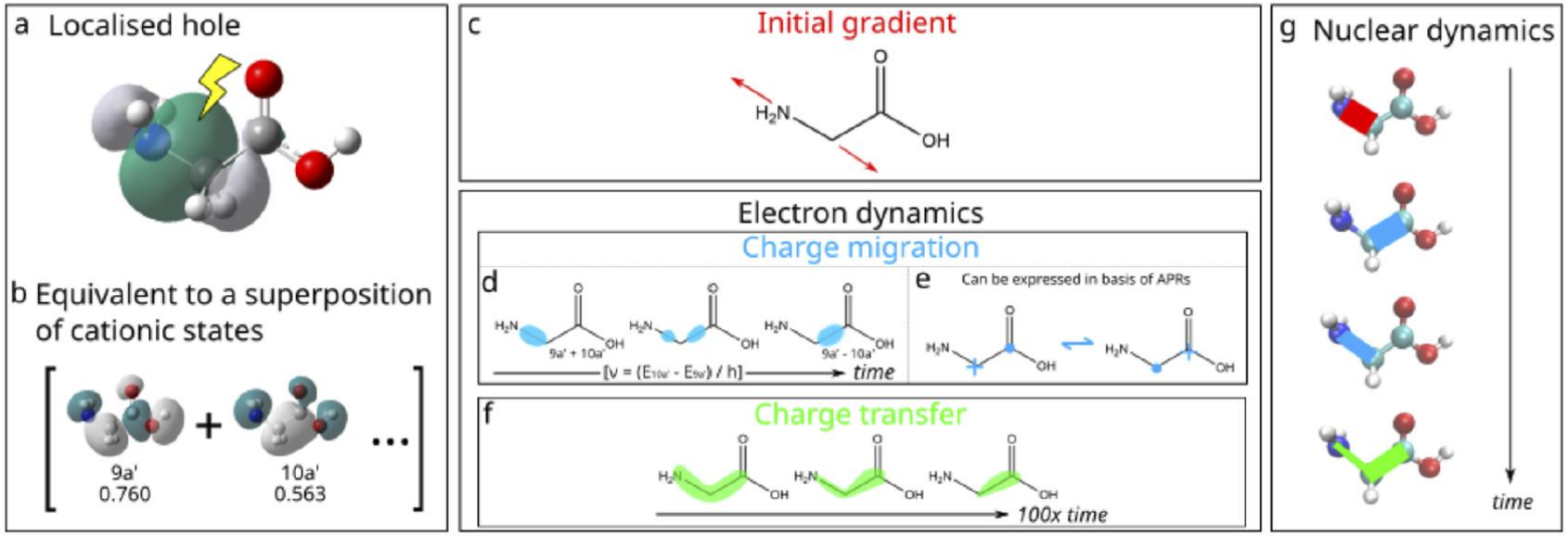
PRL 118, 083001 (2017)

Dephasing timescales and the strength of revivals vary between systems – but typically most electronic coherence is lost in 10's fs

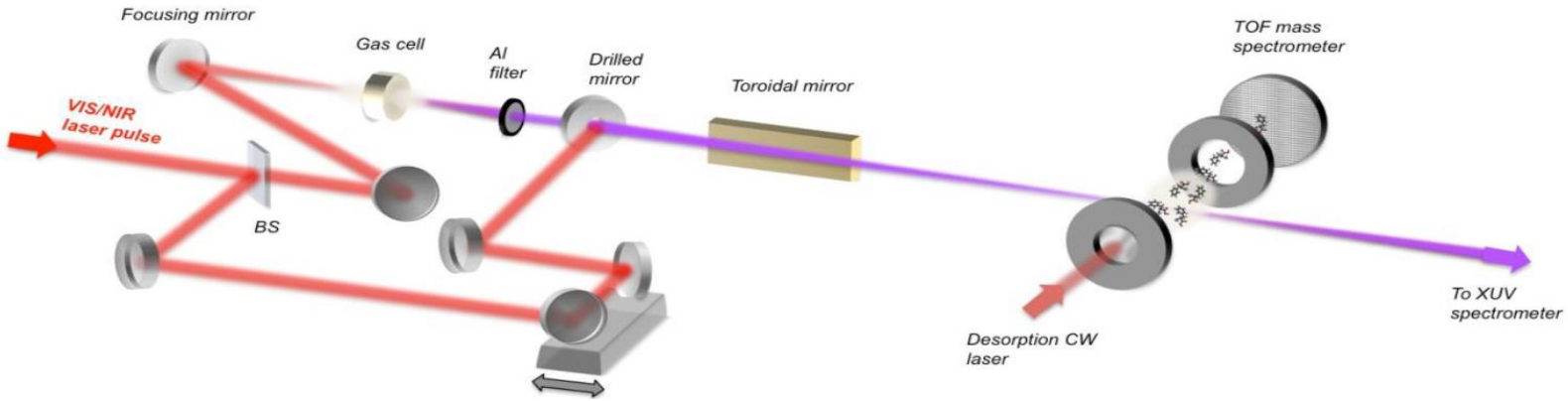
Rapid nuclear motion initiated by excitation – can change evolution of electronic amplitudes in a few fs

Morgane Vacher, Mike Robb and Mike Bearpark **see *J Chem Phys*, 139, 044110 (2013),** Danilov et al, ***J. Chem. Phys.* 156 244114** (2022)

O.Alexander et al, "Attosecond electron dynamics in molecular systems" doi.org/10.1016/bs.aamop.2023.05.001

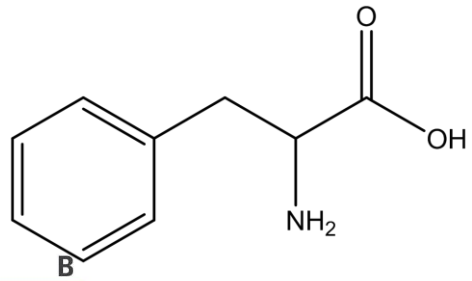


Measurement Strategy: Attosecond XUV pump - optical probe of phenylalinine monitoring ion fragment delay dependence

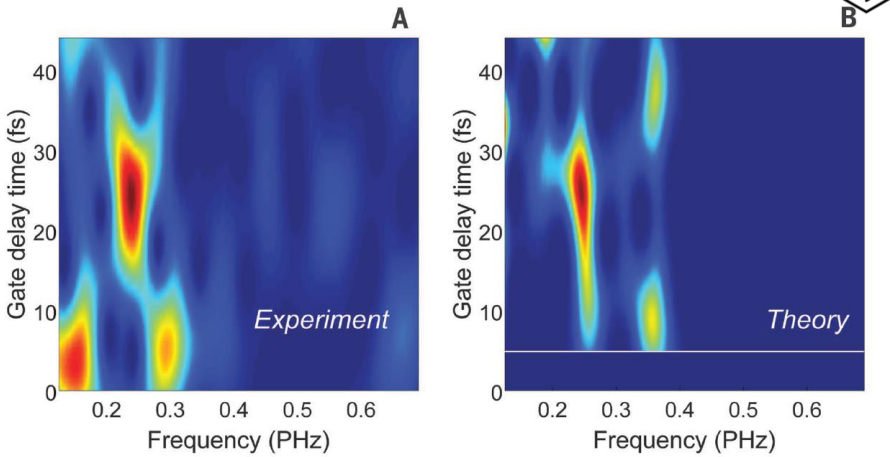


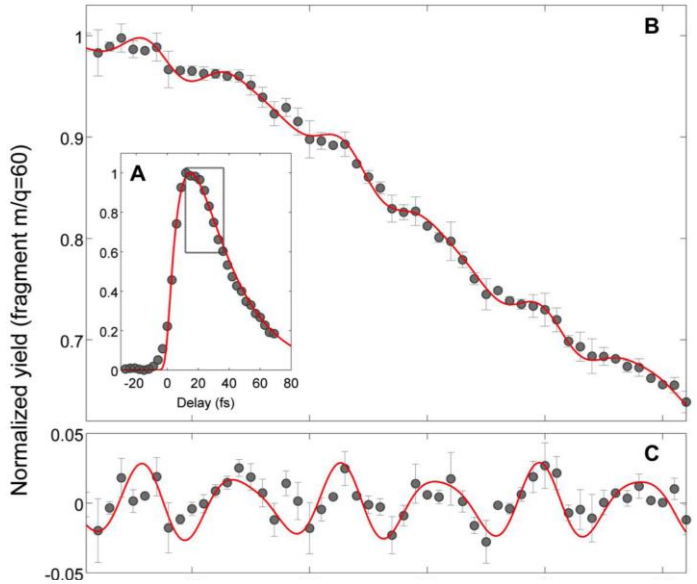
Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses

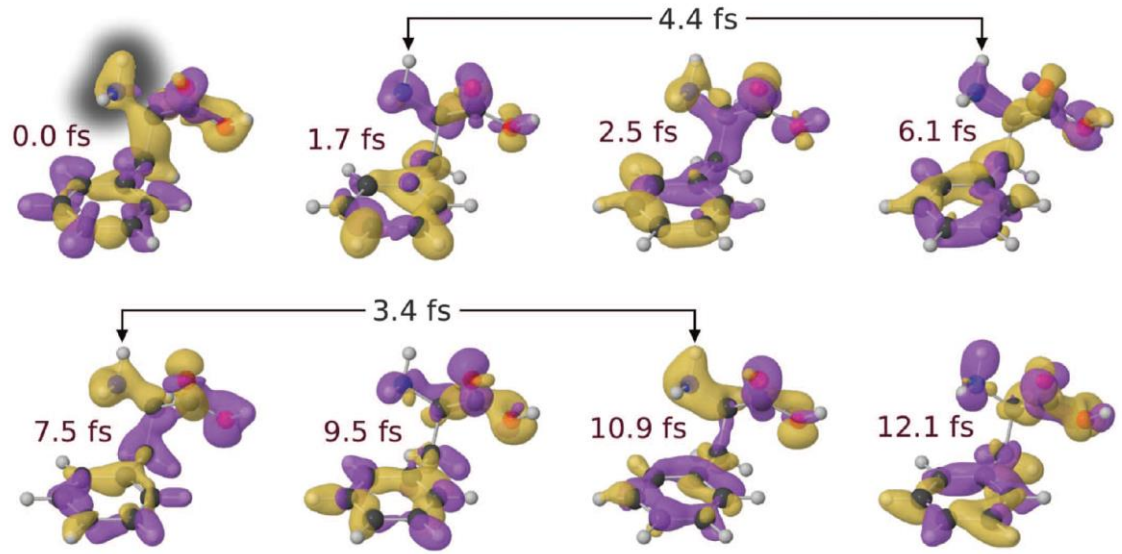
F. Calegari *et al.*
Science **346**, 336 (2014);
DOI: 10.1126/science.1254061



B

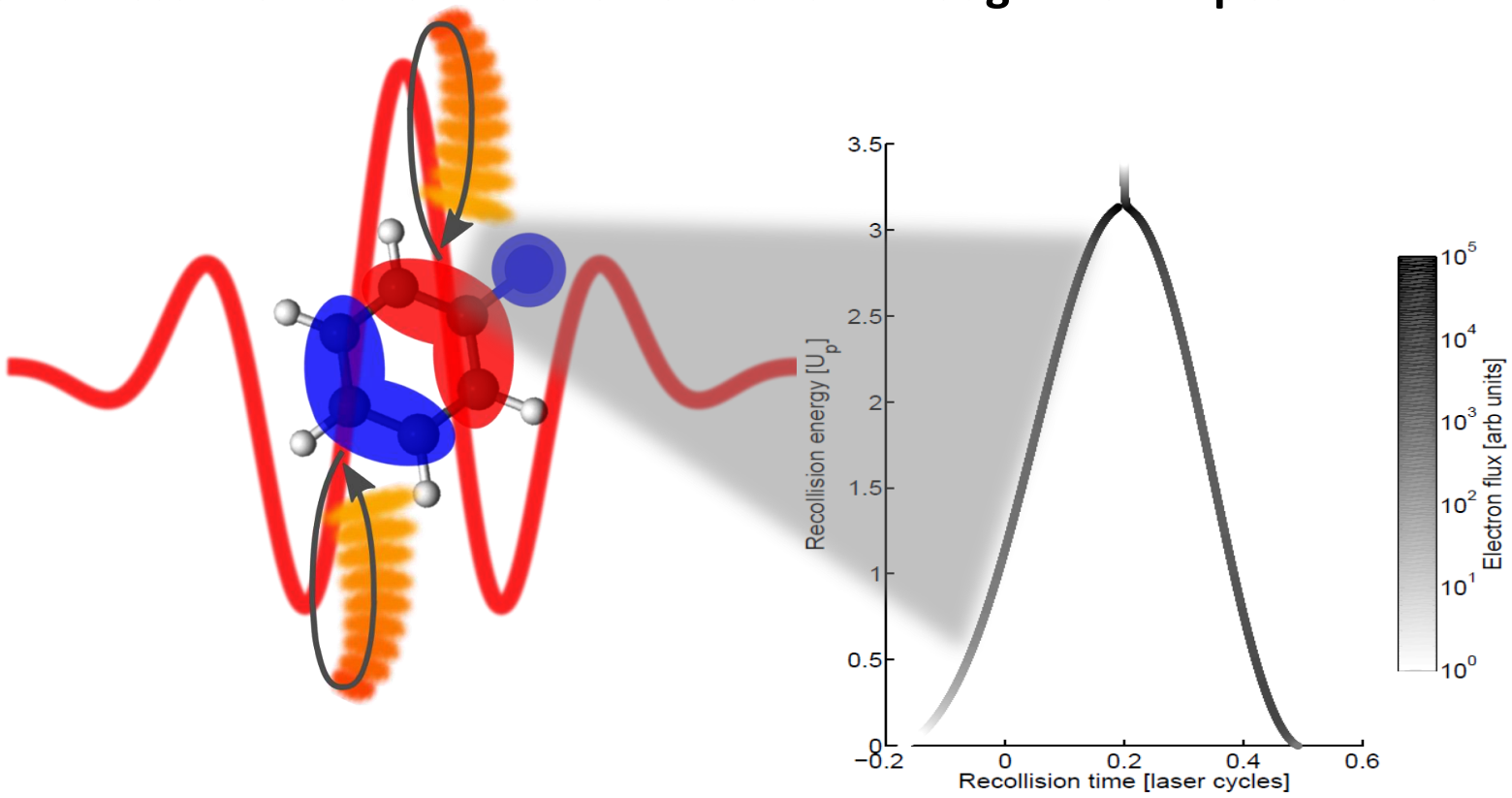


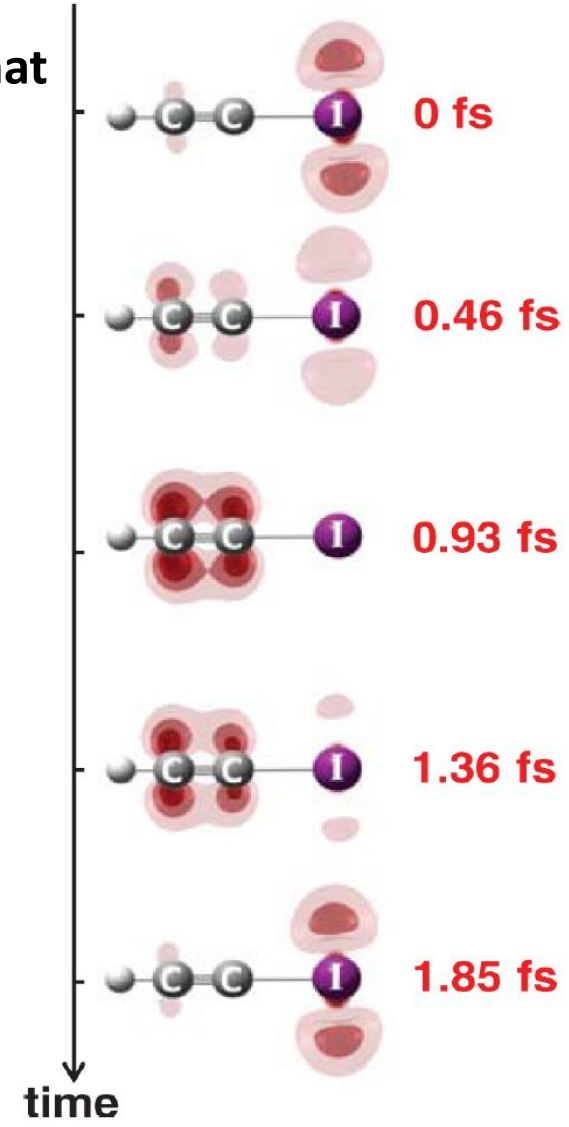




Measurement Strategy: HHG spectroscopy of iodoacetylene

HHG provides an attosecond probe of the response of a molecule to a strong field that can access the first few-fs after ionisation through the chirped harmonic emission





S. Baker *et al.*, **Science 312**, 424 (2006)
J.Marangos **J.Phys.B** (2016)
D.R.Austin *et al,* **Scientific Reports 11,** 2485, (2021)

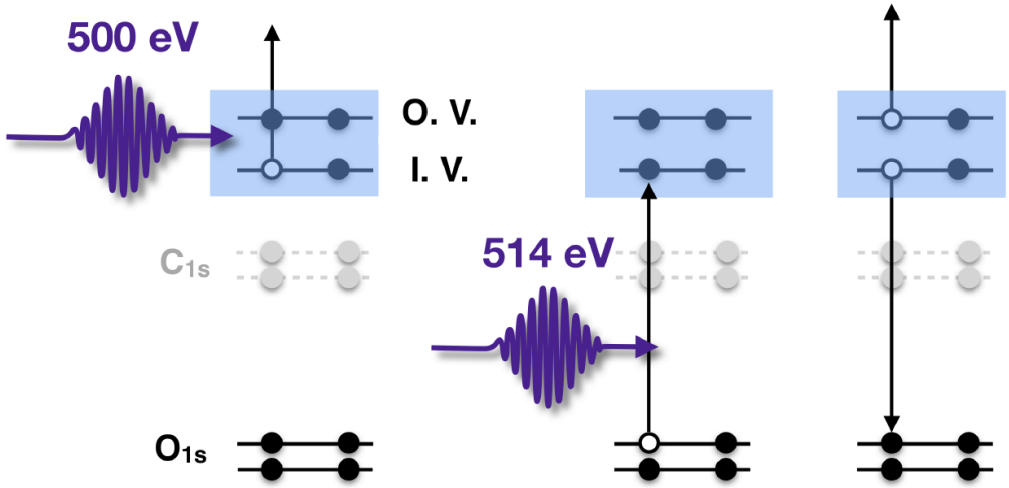
O. Smirnova *et al.*, **Nature** 460 (2009)
J.Leeuwenburgh et al, **PRL** 111, 123002 (2013)

P.M.Kraus et al **Science 350 ,** 790 (2015)

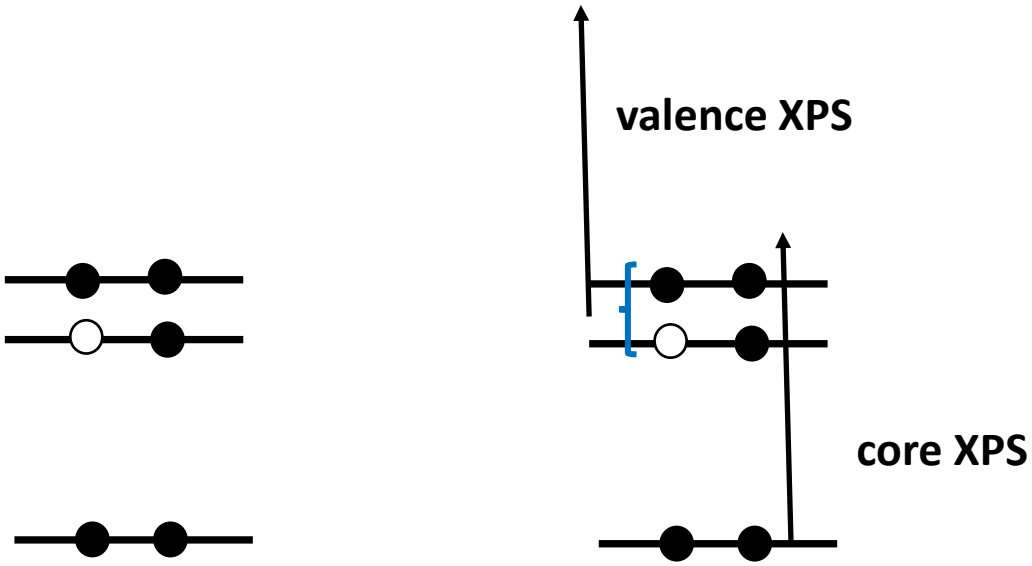
Measurement strategy: X-ray pump - X-ray probe

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

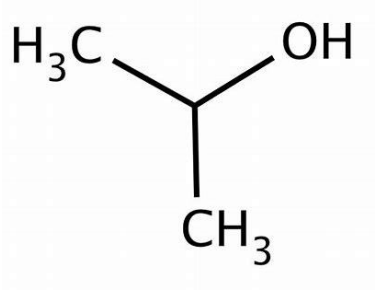


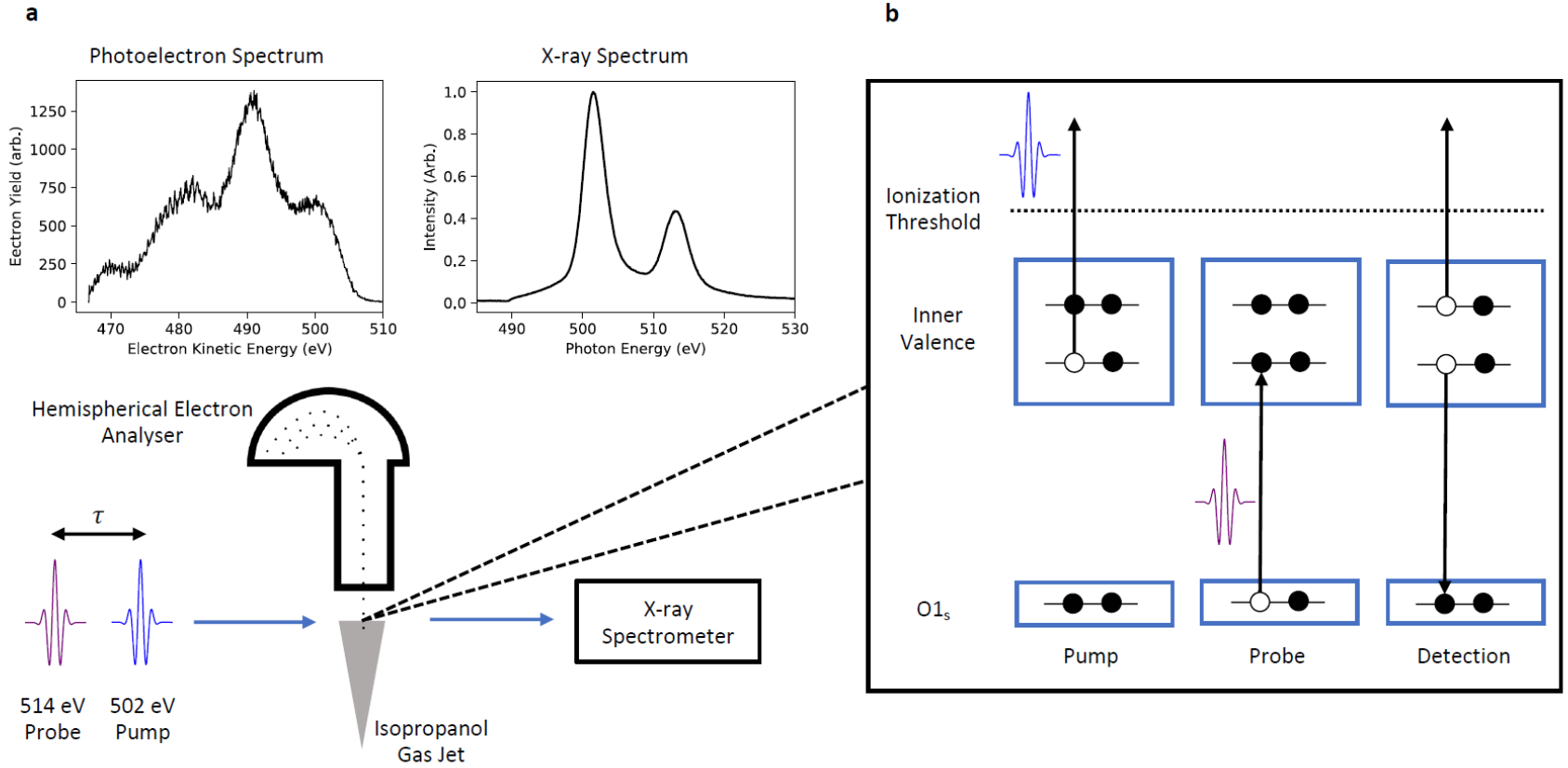
Measurement Strategy: Need for state specific measurements with non-disruptive probing field

- Strong field perturbs electronic coherence (> 2.7 V/nm & quasi-resonant)
- Probes (mostly) outer valence wavepackets (e.g. SFI or XUV ionisation)
- No state or site specificity
- Temporal resolution/ranges limited (e.g. limited by field cycle time in HHG or pulse duration)

- Use a “weak” X-ray probe
- X-ray tuning permits any hole state to be selectivity probed
- State and atomic site specificity in probe
- Pump-probe arbitrary delay & now reaches sub-fs resolution

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





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

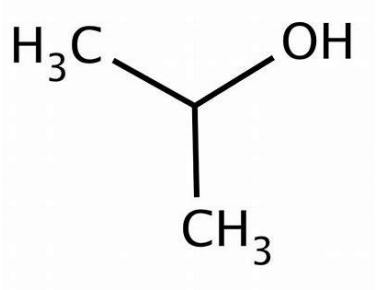
B.Cooper et al Faraday Discussion 171, 93 (2014)

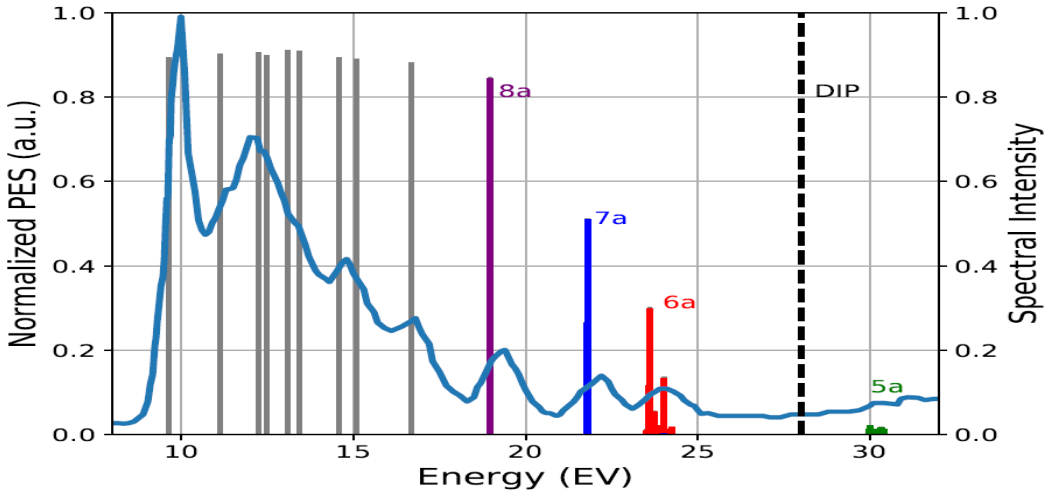
<u>AMO end-station LCLS</u>: Two pulses generated using <u>fresh-slice</u> mode form pump and probe, with chicane controlled delay. Most data was taken with ~ 5 fs pulse durations over a -10 to +25 fs delay range. But a shorter data run with ~ 2.5 fs pulses was also taken.

120 Hz repetition rate, analyzer collection ~ 0.01 so signal limited

Transient inner valence hole states in isopropanol

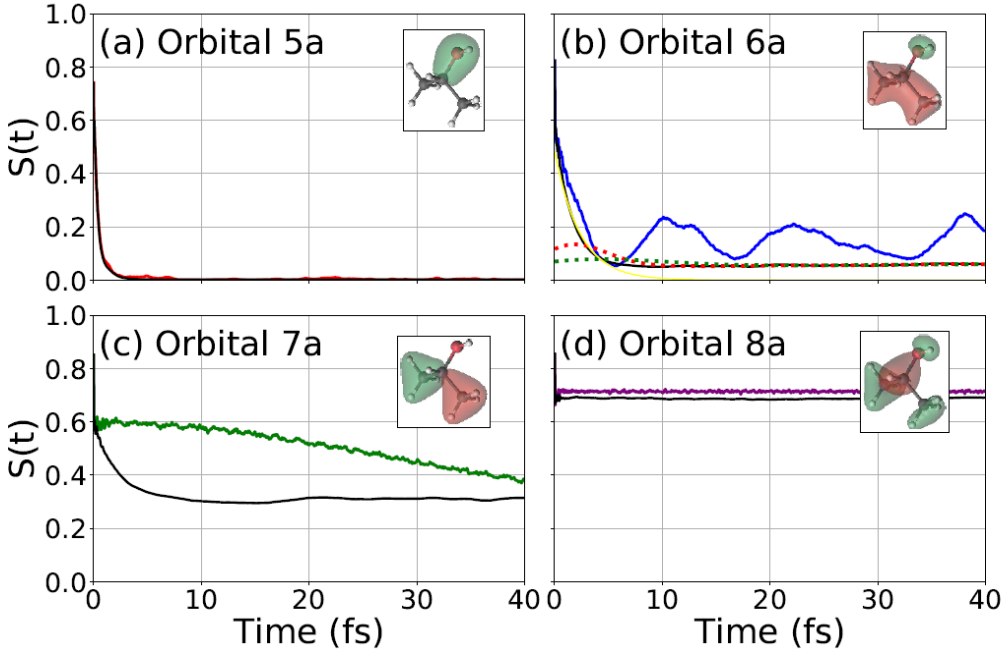
Tom Barillot, Oliver Alexander, Bridgette Cooper, Dougie Garratt, Taran Driver, Siqi Li, James Cryan, LR25 collaboration





Hole survival calculated using ADC(2)x with fixed equilibrium nuclear geometry. Rapid decay and oscillations in 6a driven by frustrated Auger.

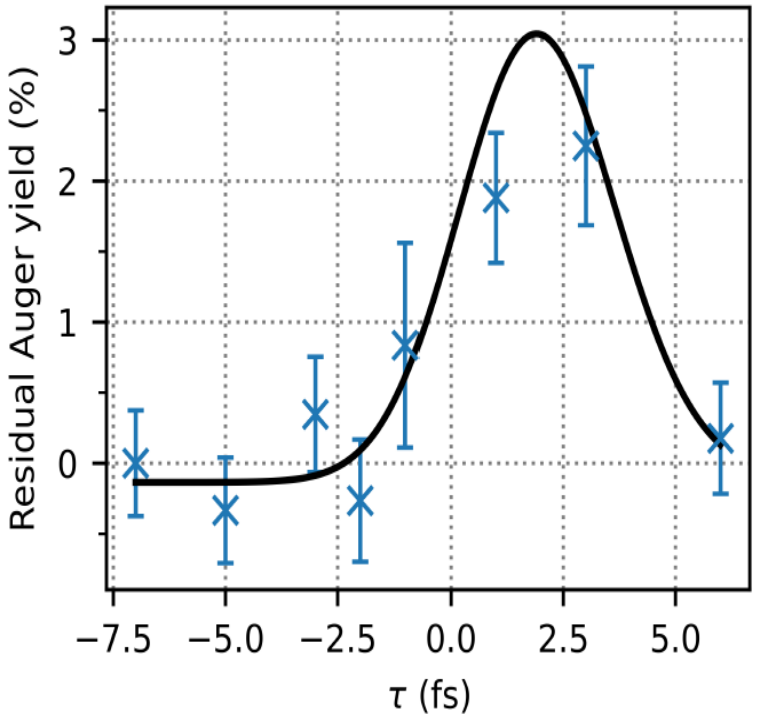
Hole survival calculated using ADC(2)x and averaged over ~500 geometries sampled around equilibrium to incorporate zero point spread

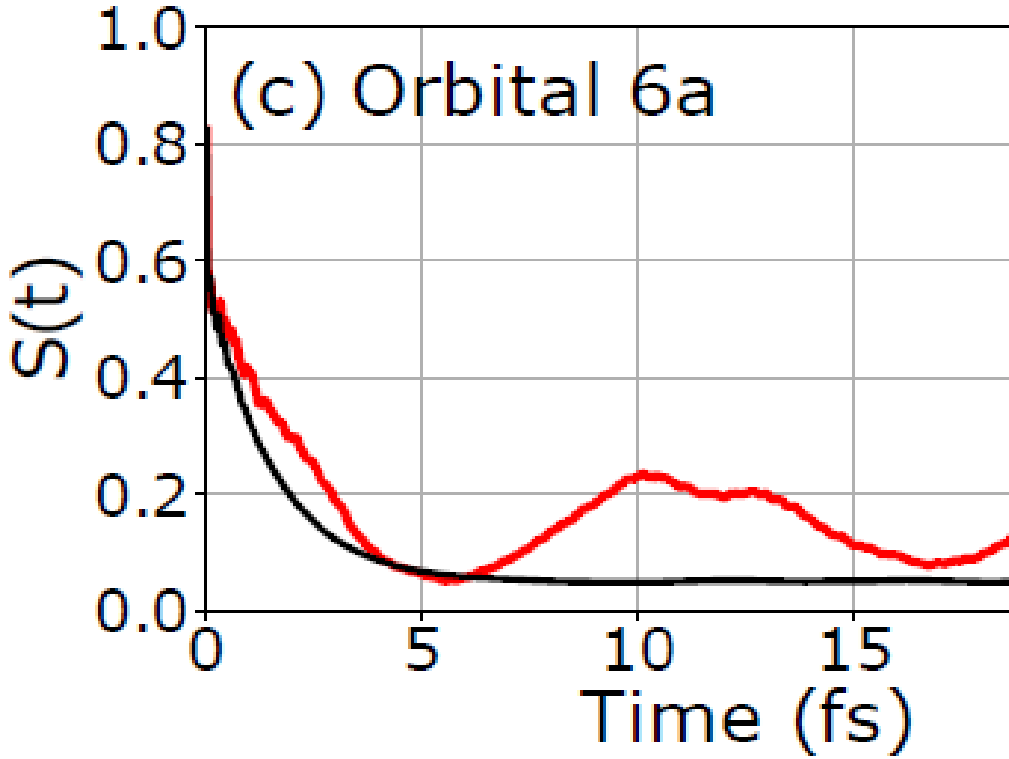


6A state undergoes rapid "breathing dynamics" via coupling of initially localised hole to extended states. Auger decay is energetically forbidden – so "charge migration" via this breathing mode will occur with revivals (return to localised state) damped by nuclear zero-point spread.

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



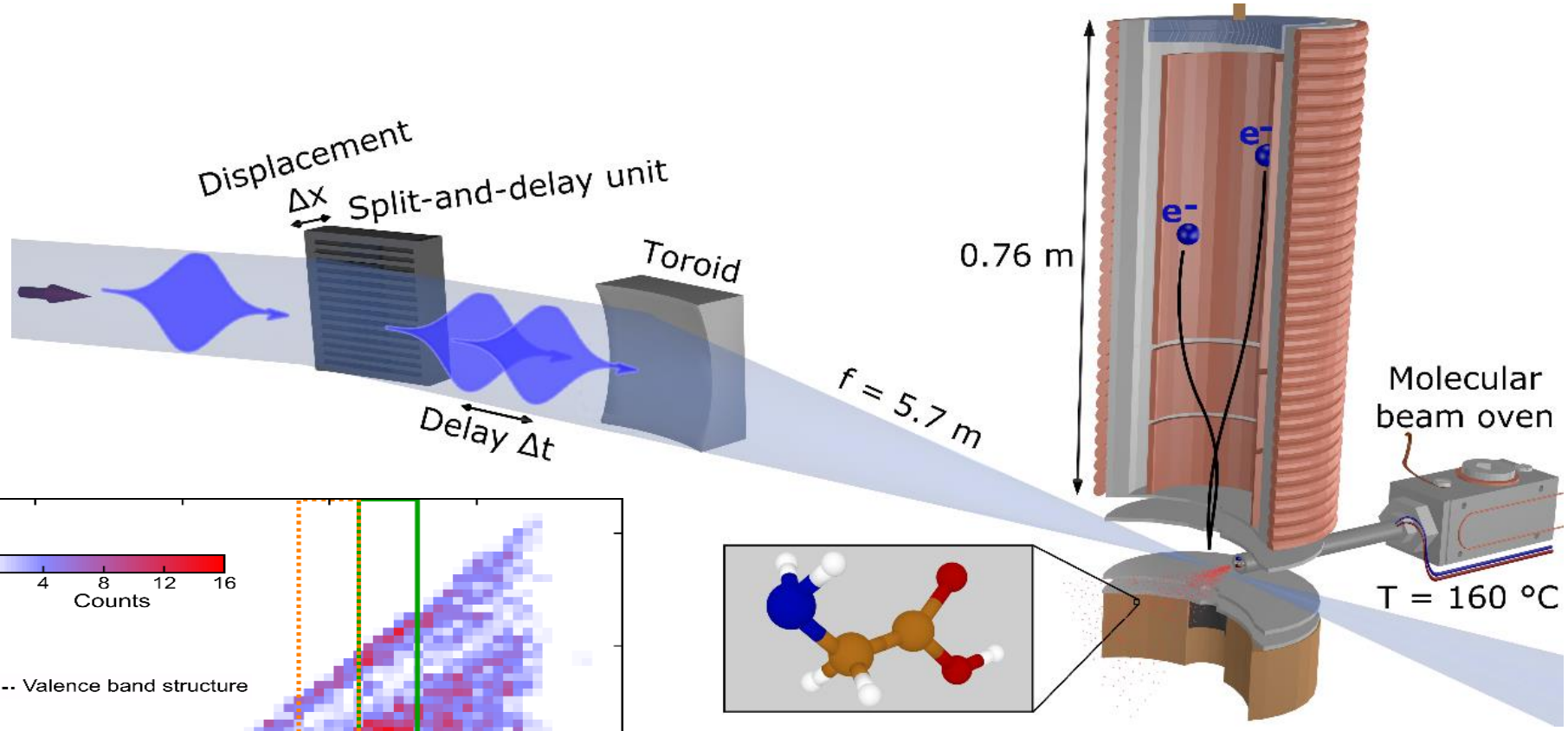


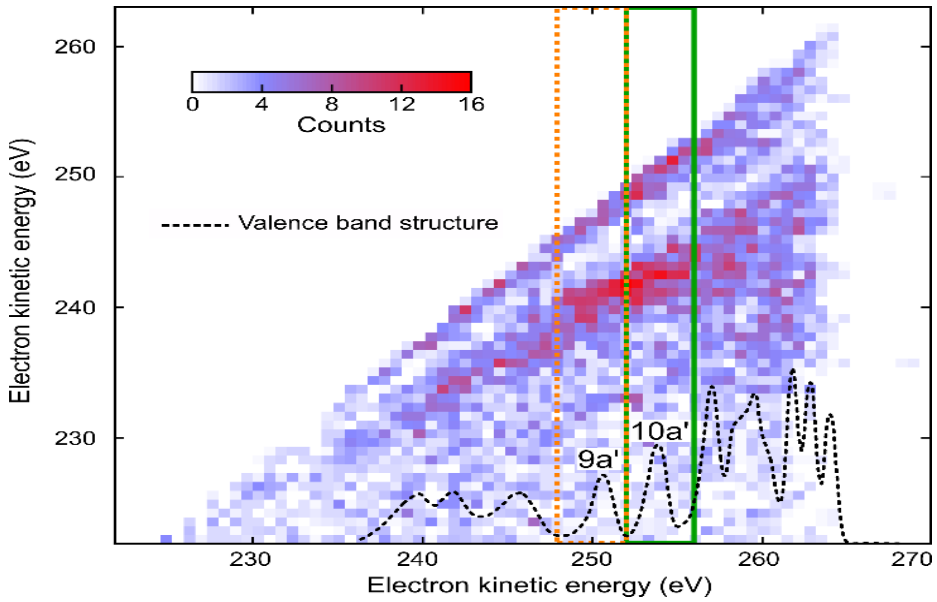
Measurement of a highly transient hole (few-fs lifetime) with decay driven by fast oscillation inherent to superposition of states and the dephasing due to the zero-point geometry spread

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

X-ray absorption spectroscopy of amino acids: X-ray pump/X-ray probe of cation dynamics in glycine at FLASH



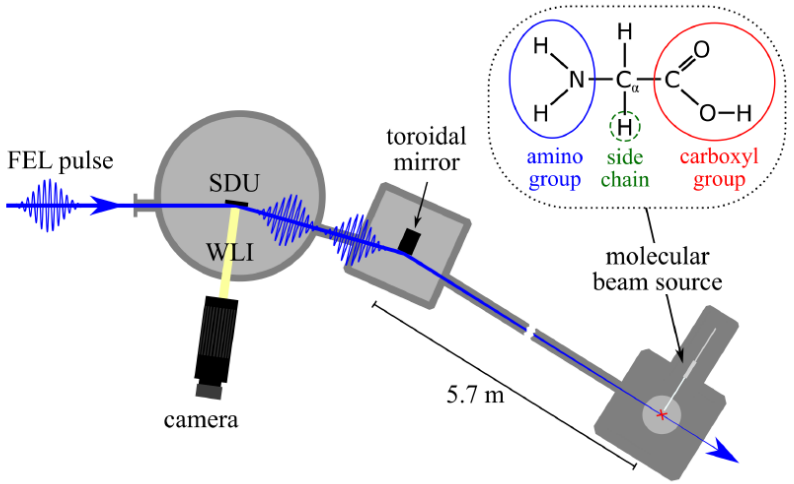


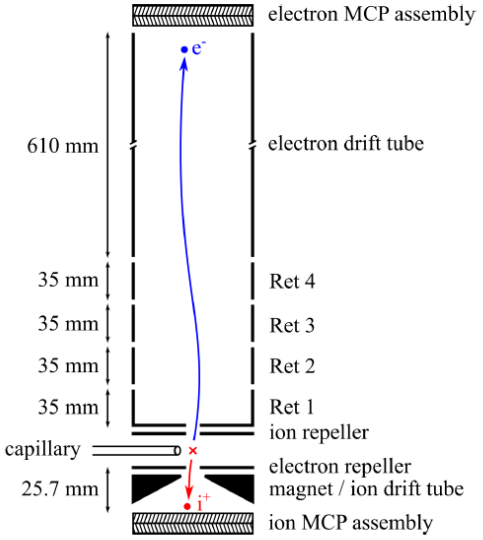
Pulse repetition rate ~ 4000 per second
Magnetic bottle provides high collection efficiency

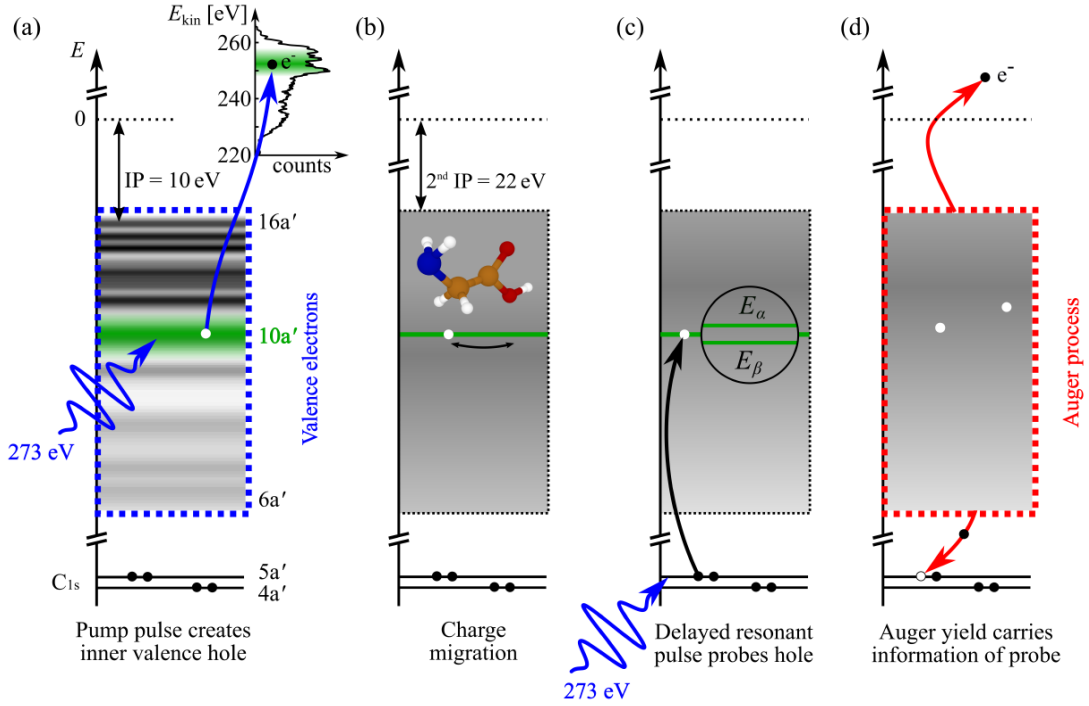
Coherent hole dynamics in glycine

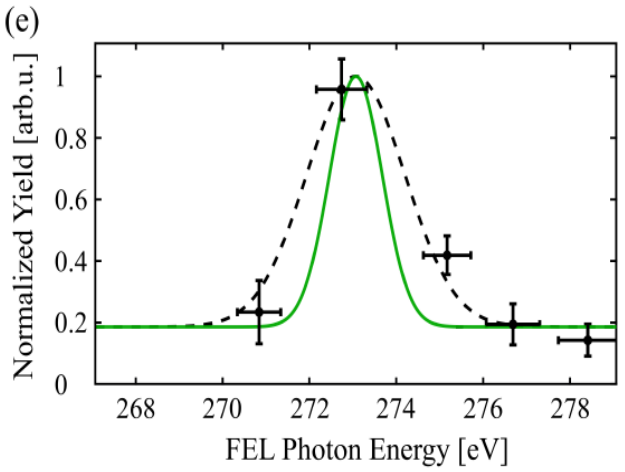
Led by Tim Laarmann, DESY Collaboration at FLASH

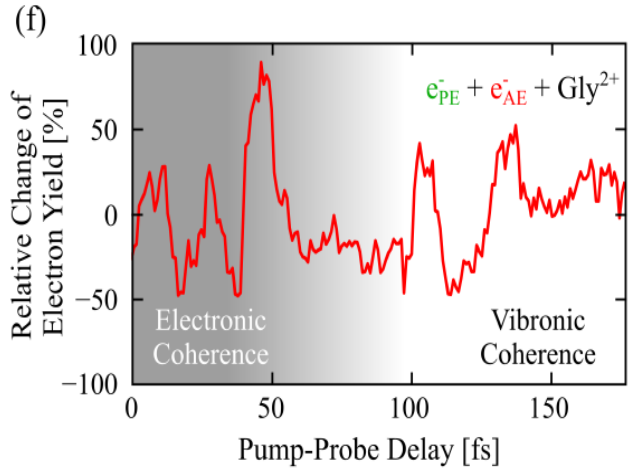
Measurements at FLASH using X-ray split-and-delay with a short pulse for a single colour pump-probe measurement. X-ray photoelectron spectra observable was measured with the pulses ~ 273 eV with a pulse duration < 5 fs delayed between 0 – 25 fs



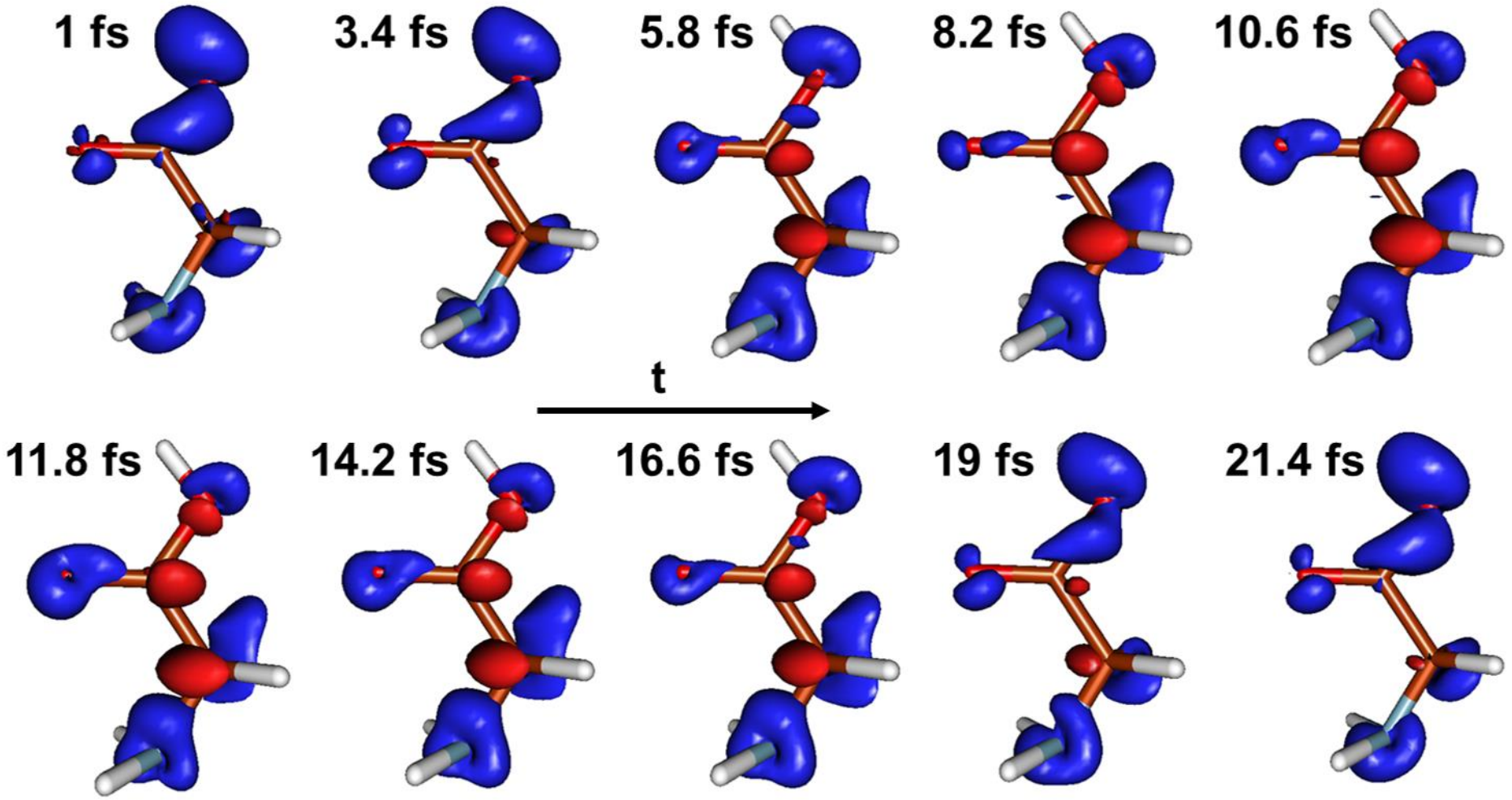








Oscillatory electron dynamics in glycine 10a’ hole dynamics predicted from ADC(2) with a 19 fs period



ADC 2 calculations by
Marco Ruberti

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

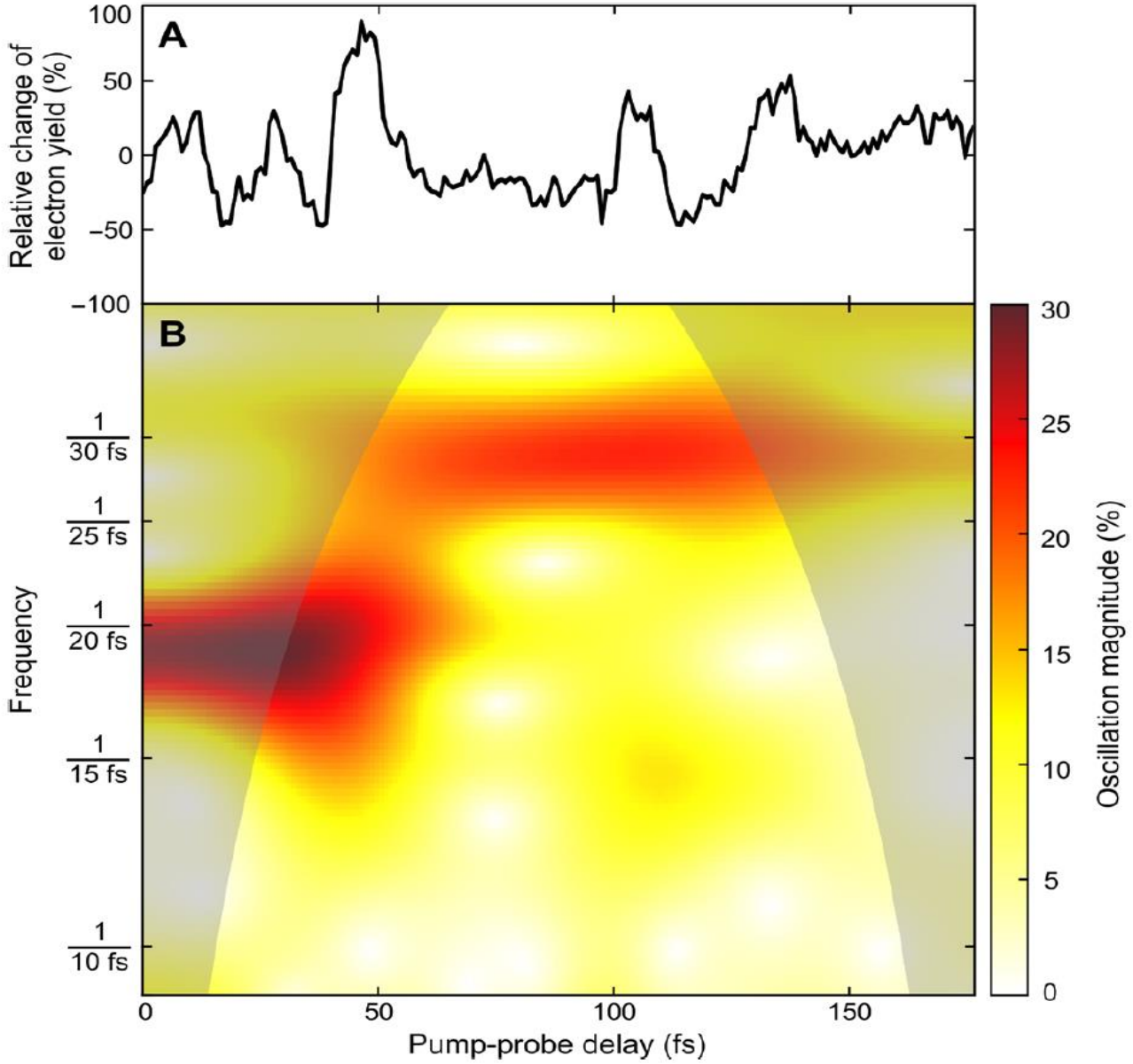
Tim Laarmann (DESY), Marco Ruberti (Imperial) et al measurements @ FLASH

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

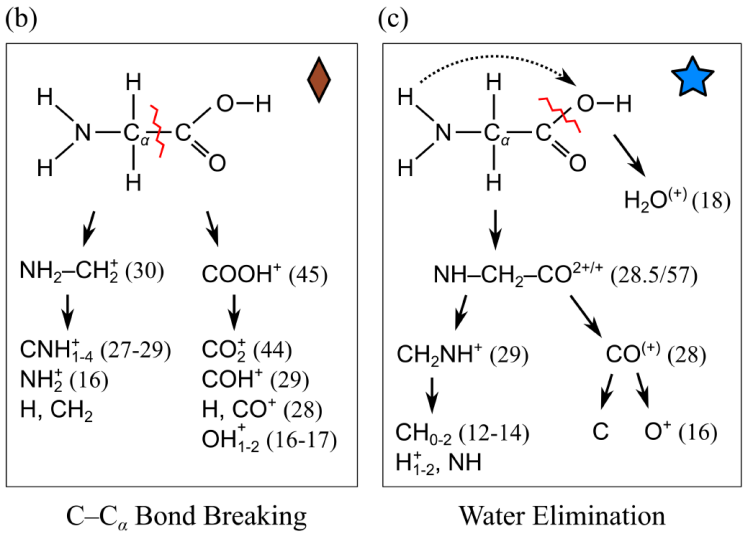
Impacts on:

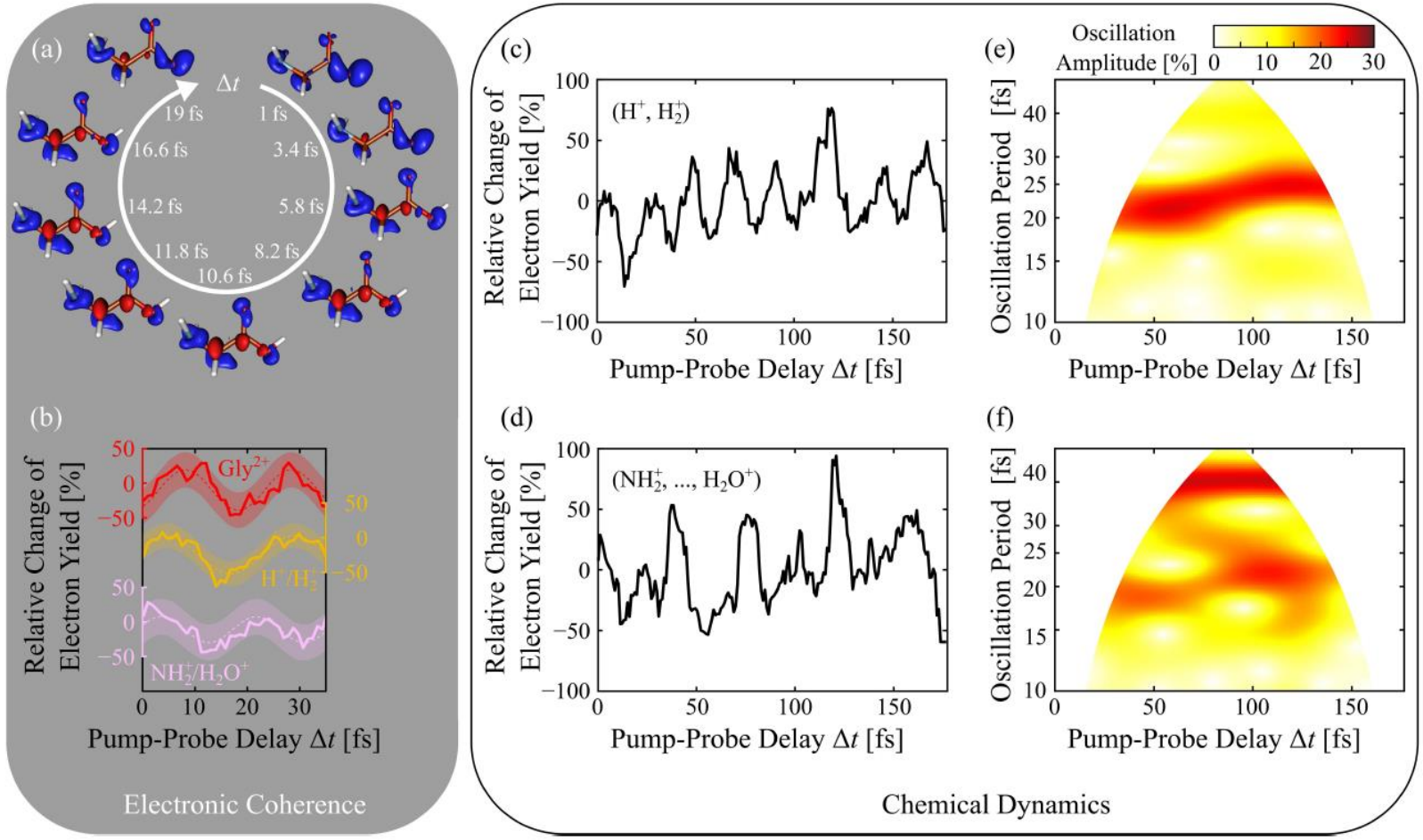
- ***Understanding radiation damage in materials and biology***
- ***Fundamentals of chemical dynamics***
- ***Testing computational quantum chemistry***
- ***Atmospheric- and Astro-chemistry***
- ***Ultrafast quantum coherence and entanglement***



Coherent hole dynamics and other fragmentation channels in glycine

Led by Tim Laarmann, DESY Collaboration at FLASH

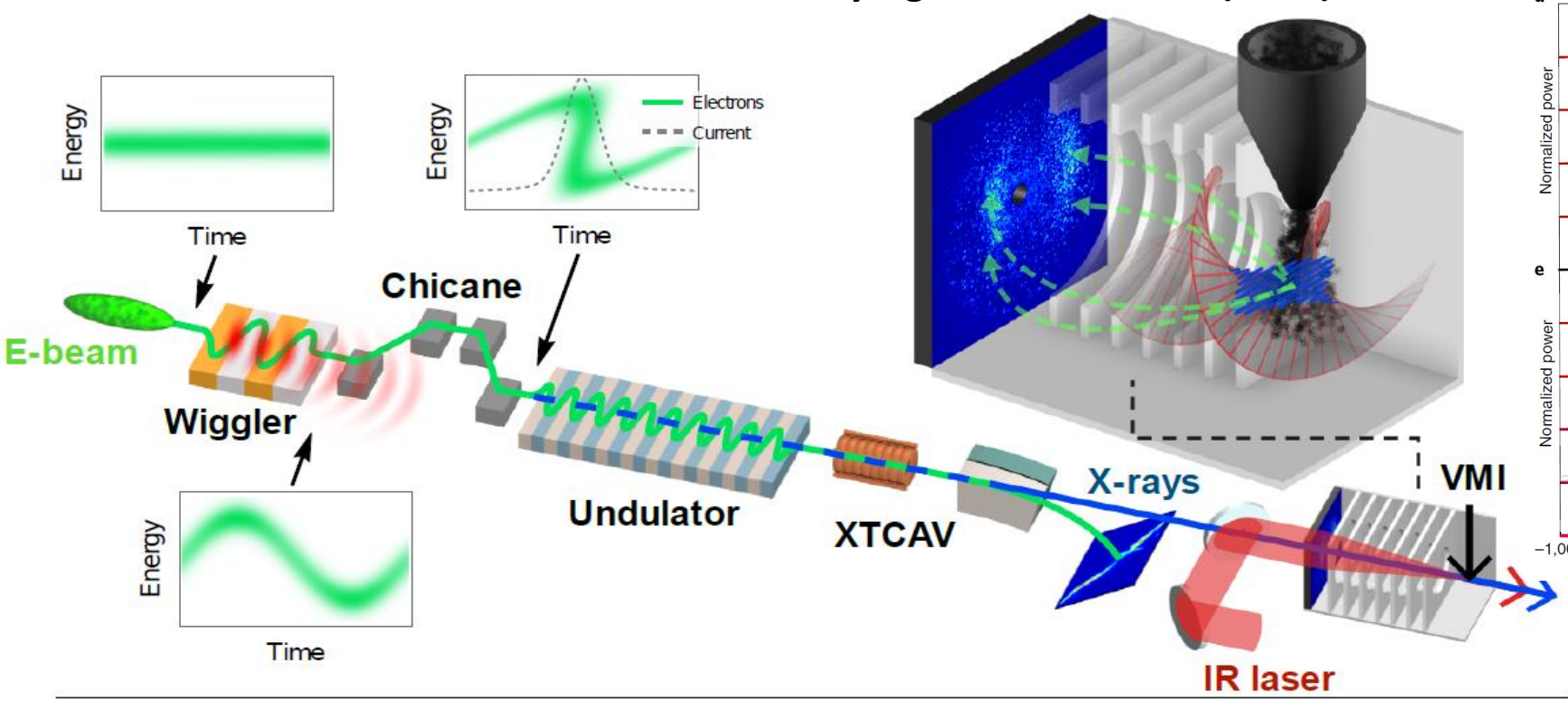


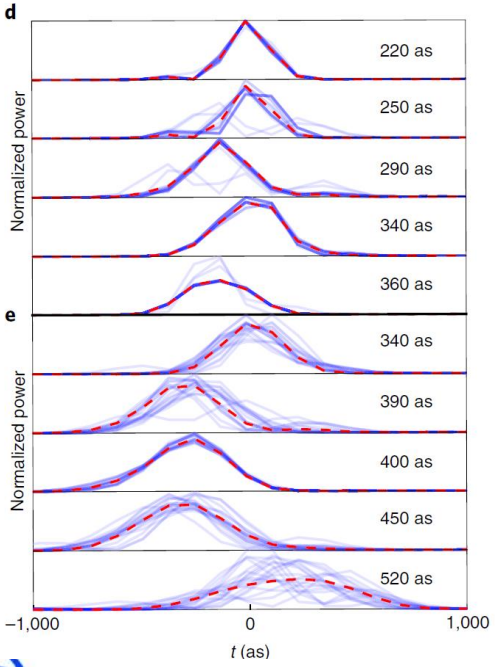


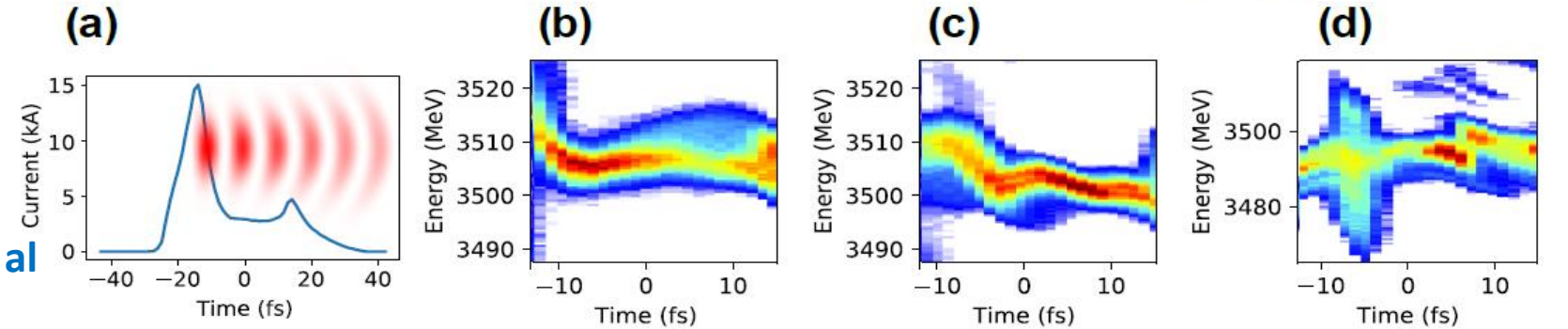
D.Schickert et al, Structural Dynamics (2022), DOI:10.1063/4.0000165

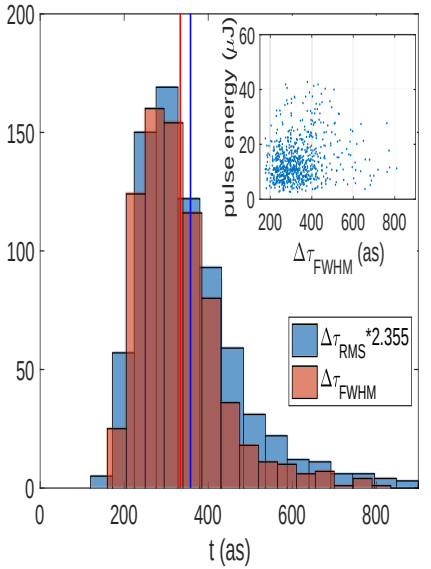
4. Isolated Attosecond X-ray pulses from XFELs

Led by Agostino Marinelli (SLAC)



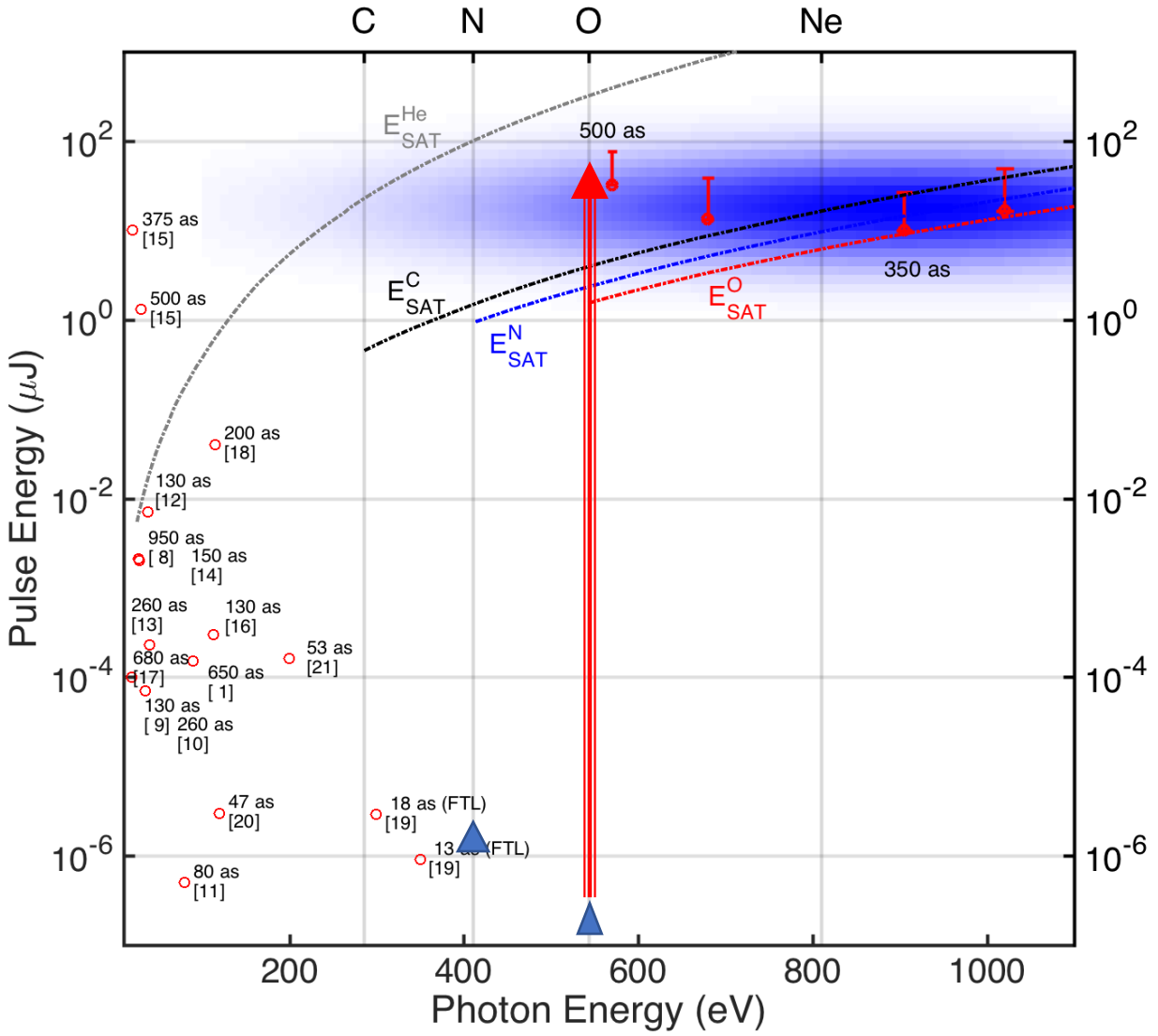






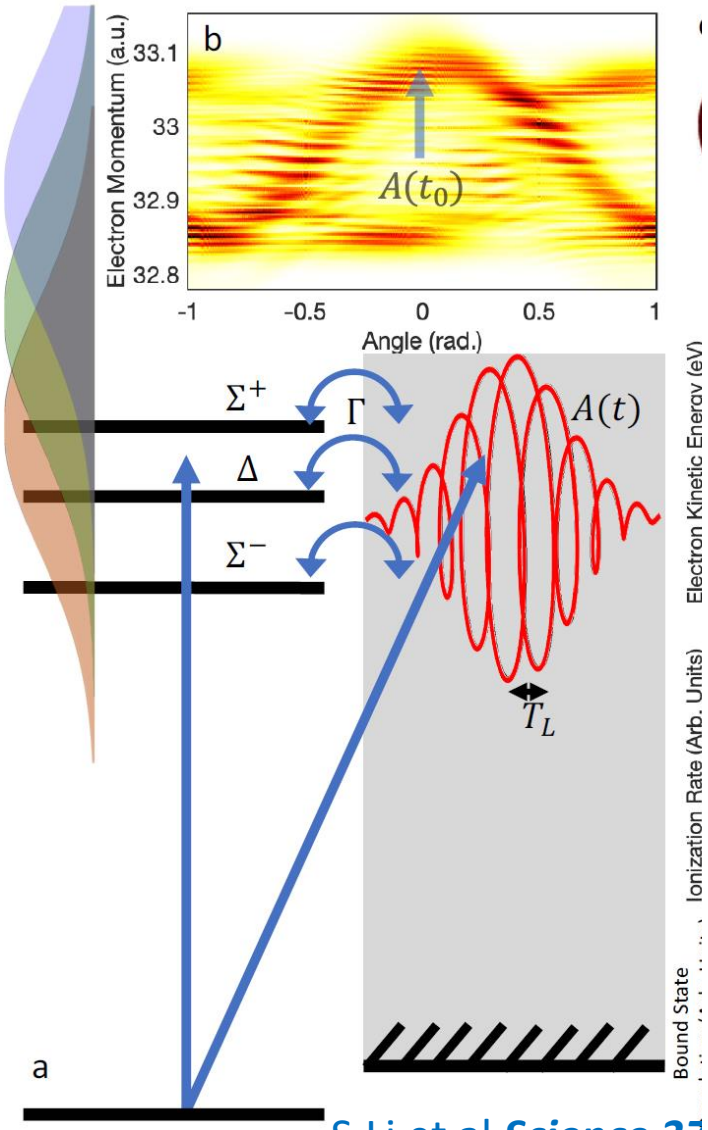
J.Duris et al Nature Photonics 14, 30 (2020)

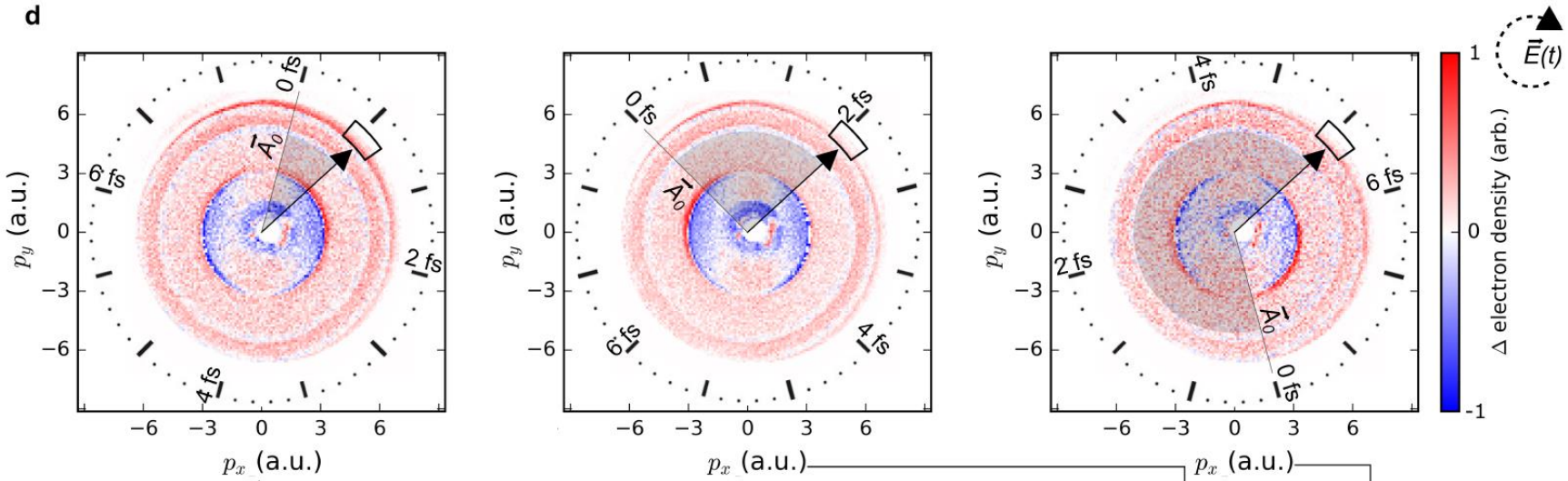
4. XFELs high brightness attosecond X-ray sources

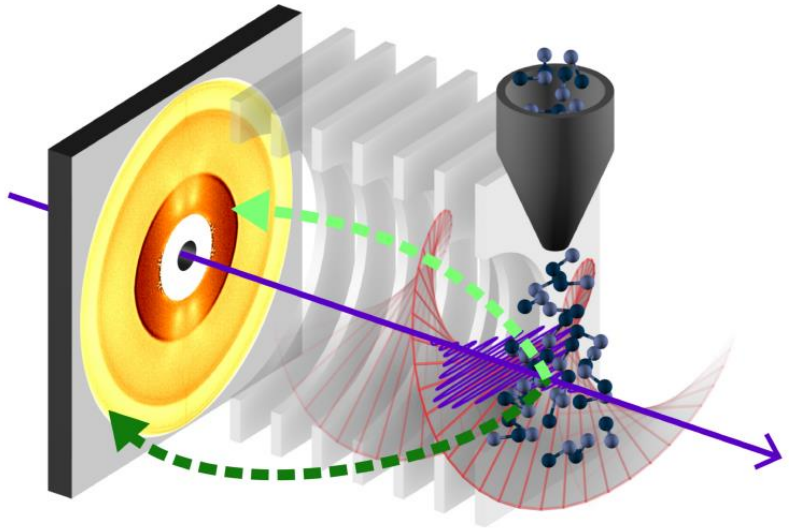


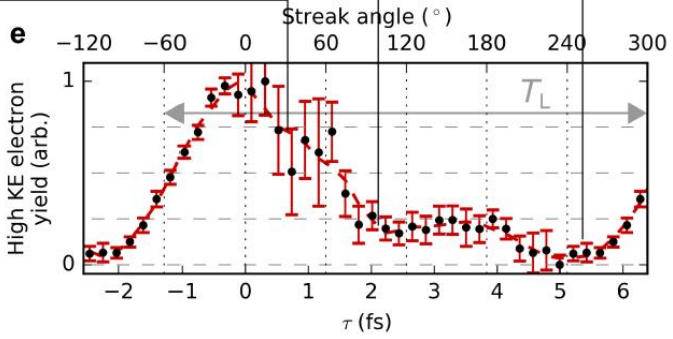
- **Near-transform limited with 5-10 eV coherent bandwidth**
- **8 - 9 orders of magnitude brighter than HHG sources in X-ray range.**
- **Unique source for non-linear (2 or more photon) x-ray interactions and ultrafast measurement:**
  - **x-ray pump-probe measurements**
  - **x-ray photo/Auger electron streaking**
  - **non-linear x-ray interactions (cf impulsive Raman, PRL (2020))**
  - **x-ray multi-dimensional spectroscopy**

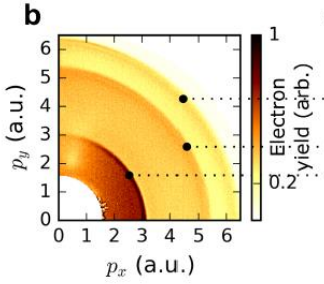
4. Core excited electronic wavepackets in NO – quantum interference in Auger-Meitner decay registered in time-domain

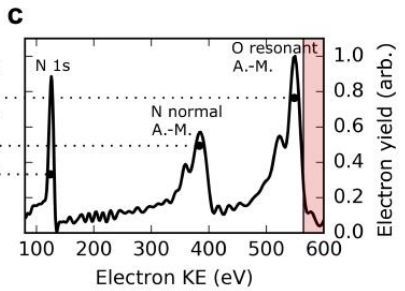








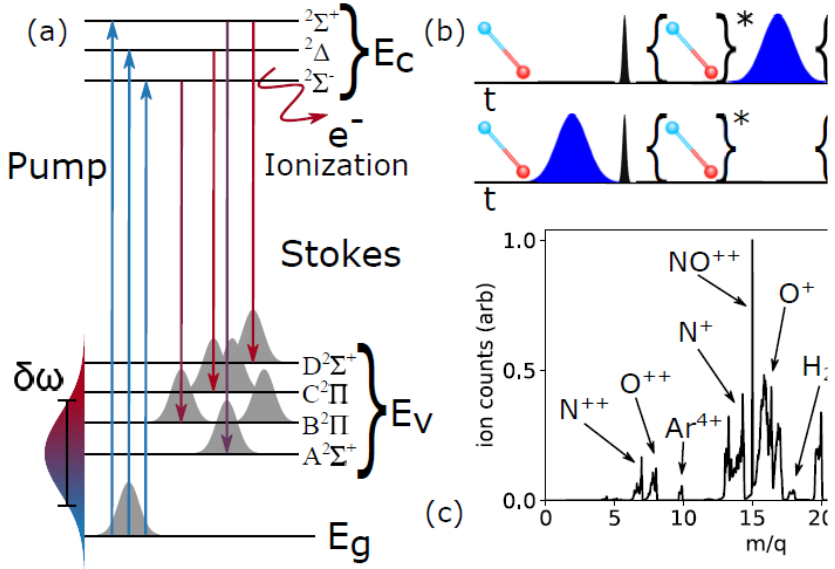


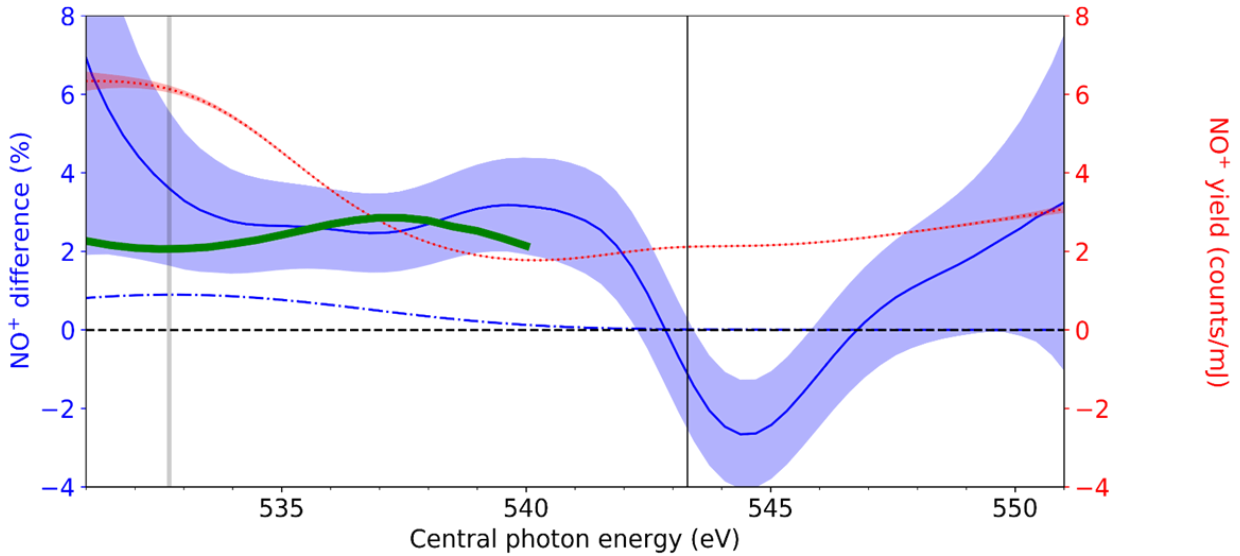


S.Li et al ***Science 37***

4. Non-linear X-ray interactions with attosecond pulses: Impulsive X-ray Raman

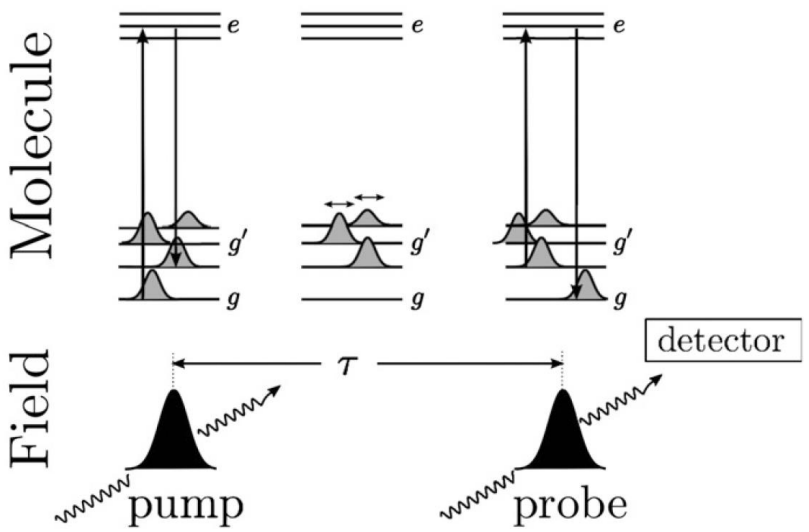
collaboration led by James Cryan SLAC

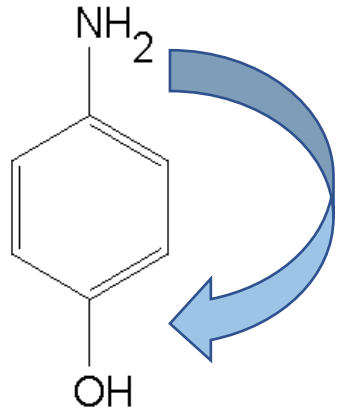




First evidence of impulsive electronic X-ray Raman utilising > 5 eV coherent bandwidth – excited electronic state population in NO detected using ions produced from a following (ns delayed) UV laser pulse, in good agreement with calculations (Antonio). J.T.O'Neal et al, PRL, 125, 073203 (2020)

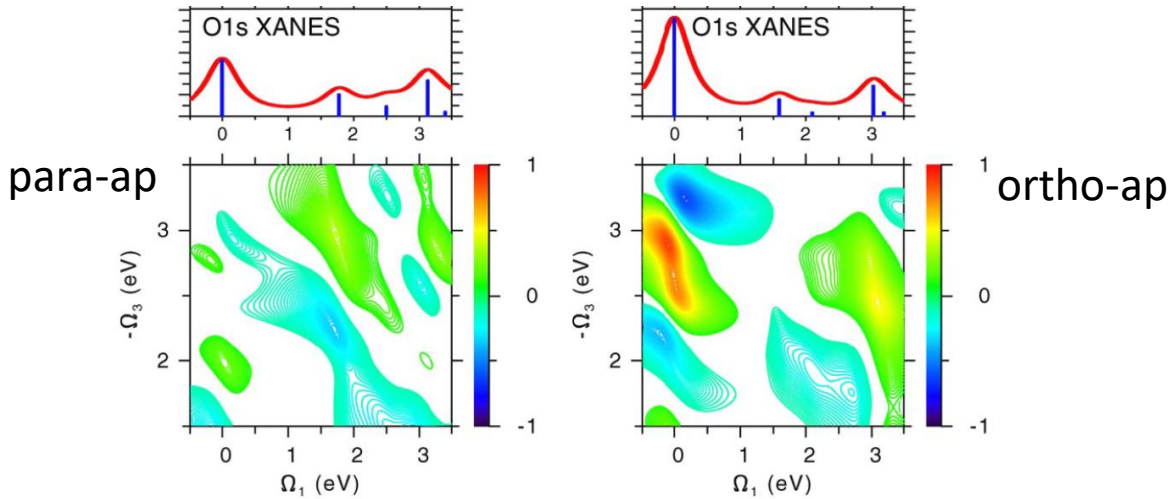
4. Impulsive X-ray stimulated Raman Scattering: A New Tool to Study Evolution of Localised Electronic Excitation in Neutral Matter

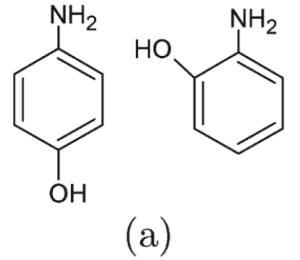


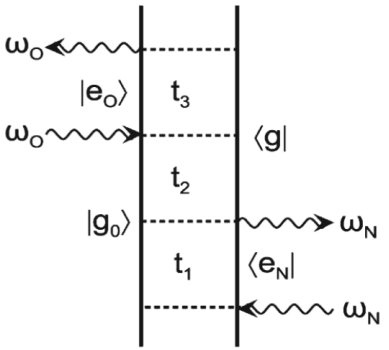


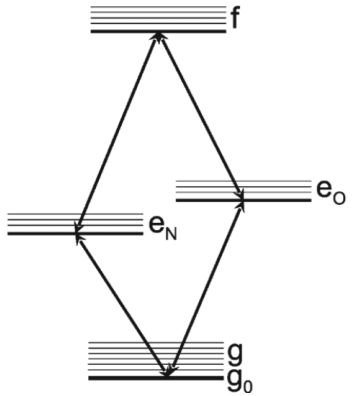
I.V. Schweigert and S. Mukamel, *PRL* **99**, 163001 (2007)

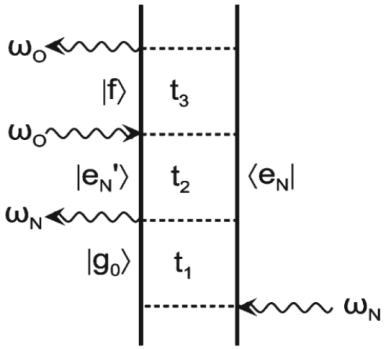
J.D.Briggs et al, Energy transfer in metalloporphyrin heterodimers using stimulated X-ray Raman spectroscopy PNAS, 110, 11597 (2013)









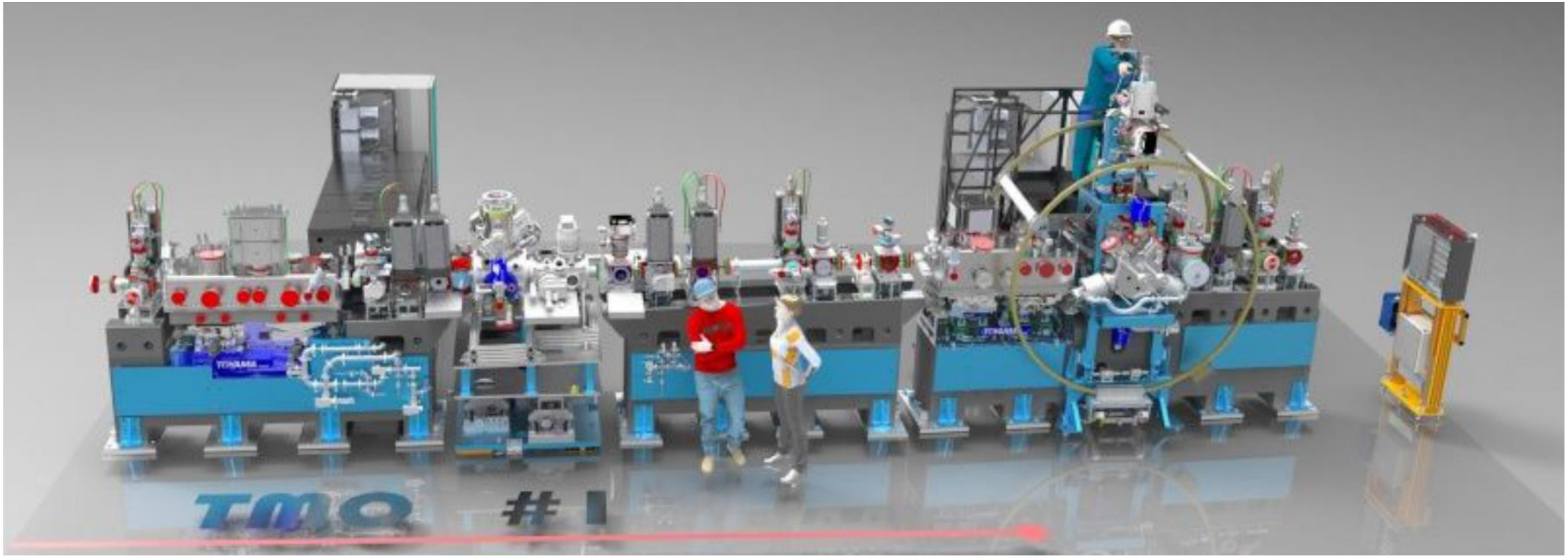


4. Upgraded end-stations are being built for high rep-rate attosecond capability at LCLS – operational late 2023

Variable Kirkpatrick-Baez focus mirrors to achieve high intensity

High resolution electron spectrometers, ion velocity mapping VMI, and coaxial electron VMI + single shot spectral monitor

COLTRIMS – Momentum microscope for coincidence detection



4. Conclusions & Outlook

- **X-ray FELS offer X-ray pump-probe capabilities with few-fs temporal resolution, and now sub-fs modes, to probe fundamental electronic and electron-nuclear coupling dynamics in molecules and clusters**

- **HHG sources and XFELs can be used for high quality time-resolved X-ray spectroscopy applicable to condensed phase materials and gives new insights, e.g. in understanding early evolution of exciton dynamics in molecules and polymers**

- **Attosecond XFELs now reach an intensity to permit new measurement methodologies – attosecond pump probe, attosecond streaking, non-linear x-ray Raman**

Thank you for your attention

Jon Marangos
j.marangos@imperial.ac.uk

Thank you for your attention

Acknowledgements: EPSRC, SLAC, ERC (£, $, €)

LR25 Collaboration (Transient hole dynamics in isopropanol)

T. Barillot,[1] O. Alexander,[1] B. Cooper,[1,2] T. Driver,[1,3,4,*] D. Garratt,[1] S. Li,[5] A. Al Haddad,[6,7] A. Sanchez-Gonzalez,[1] M. Agåker,[8,9] C. Arrell,[7] M. Bearpark,[10] N. Berrah,[11] C. Bostedt,[6,7,12] J. Bozek,[13] C. Brahms,[1] P. H. Bucksbaum,[3] A. Clark,[14] G. Doumy,[6] R. Feifel,[15] L.J. Frasinski,[1] S. Jarosch,[1] A. S. Johnson,[1] L. Kjellsson,[8] P. Kolorenč,[16] Y. Kumagai,[6] E. W. Larsen,[1] P. Matia-Hernando,[1] M. Robb,[10] J.-E. Rubensson,[8] M. Ruberti,[1] C. Sathe,[9] R. J. Squibb,[15] A. Tan,[1] J. W. G. Tisch,[1] M. Vacher,[10,17] D. J. Walke,[1] T. J. A. Wolf,[3] D. Wood,[1] V. Zhaunerchyk,[15] P. Walter,[4] T. Osipov,[4] A. Marinelli,[5] T. Maxwell,[5] R. Coffee,[4] A. A. Lutman,[5] V. Averbukh,[1] K. Ueda,[18] J. P. Cryan,[3,4] and J. P. Marangos[1]

DESY-FLASH-IC Collaboration (Glycine)

David Schwickert[1], Marco Ruberti[2], Přemysl Kolorenč[3], Sergey Usenko[1,4,†], Andreas Przystawik[1], Karolin Baev[1], Ivan Baev[4], Markus Braune[1], Lars Bocklage[1,5], Marie Kristin Czwalinna[1], Sascha Deinert[1], Stefan Düsterer[1], Andreas Hans[6], Gregor Hartmann[6], Christian Haunhorst[7], Marion Kuhlmann[1], Steffen Palutke[1], Ralf Röhlsberger[1,5], Juliane Rönsch-Schulenburg[1], Philipp Schmidt[6], Sven Toleikis[1], Jens Viefhaus[8], Michael Martins[4], André Knie[6], Detlef Kip[7], Vitali Averbukh[2], Jon P. Marangos[2], Tim Laarmann[1,5*]

Attosecond Campaign @ LCLS

PIs
James Cryan
Agostino Marinelli
Peter Walter

Imperial College
Vitali Averbukh
Oliver Alexander
Douglas Garratt
Jon Marangos
Marco Ruberti

UAM
Gilbert Grell
Solene Oberli
Fernando Martin
Antonio Picon
Alicia Palacios

SLAC
Taran Driver
Philip Bucksbaum
Ryan Coffee
Thomas Wolf
Jordan O'Neil
Zhaoheng Guo
Siqi Li
Paris Franz
David Cesar
Joe Duris
Nick Sudar
Zhen Zhang
Anna Wang
Razib Obaid
River Robles
Alberto Lutman

OSU
Lou Dimauro
Greg McCracken
Daniel Tuthill

LBNL
Oliver Gessner
Daniel Slaughter
Thorsten Weber

Argonne NL
Gilles Doumy
Linda Young

Univ. Conn.
Nora Berrah

KSU
Daniel Rolles
Artem Rudenko

LMU
Matthias Kling
Philipp Rosenberger

LSU
Ken Lopata

Tohoku Univ.
Kiyoshi Ueda

PSI
Christoph Bostedt
Andre Al-Haddad

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