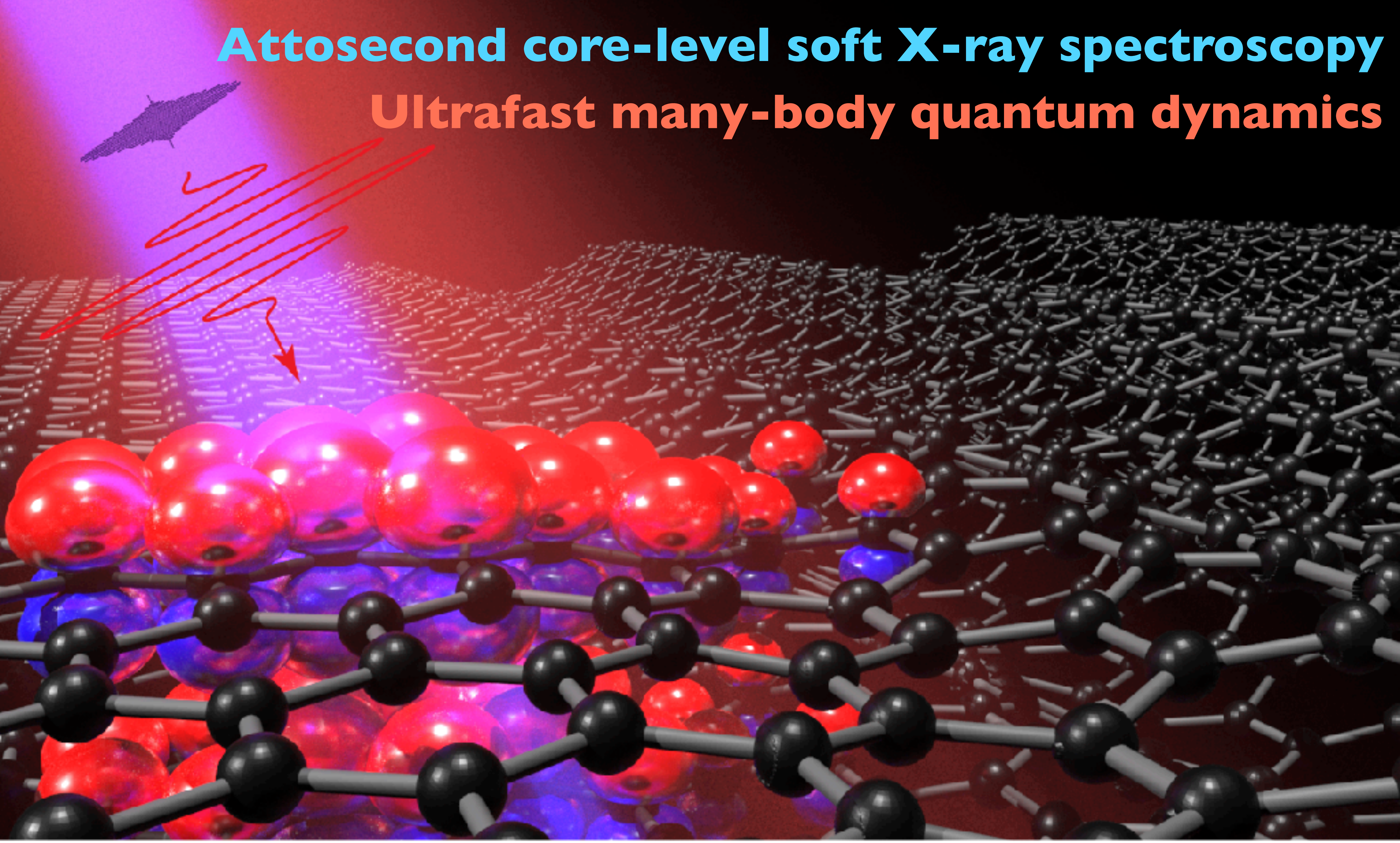
Attosecond core-level soft X-ray spectroscopy

Ultrafast many-body quantum dynamics

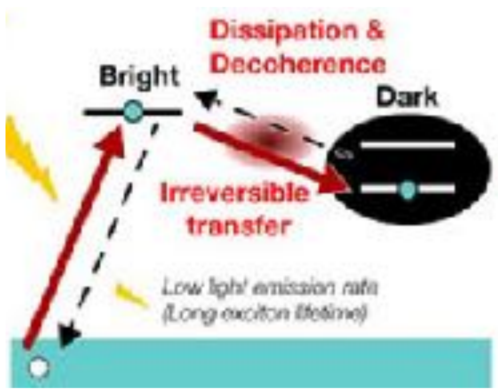


Jens Biegert

ICFO ICREA

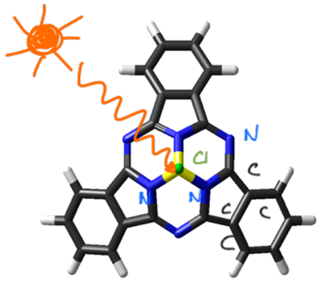
erc Advanced Grant TRANSFORMER

Energy Harvesting

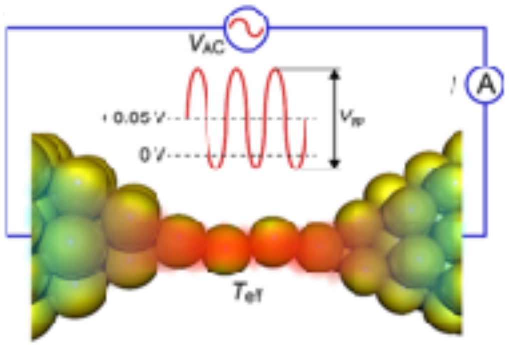


Yamada University of Tokyo

Efficiencies <18%
exciton trapping?



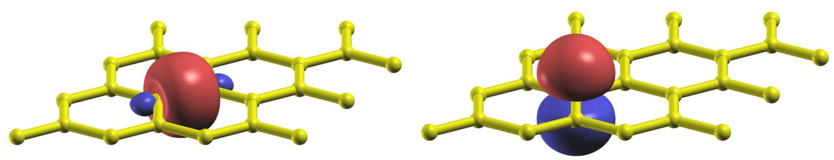
Electronic Transport



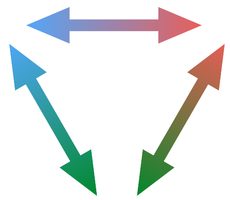
20% of global energy in 2030
dissipation, scattering

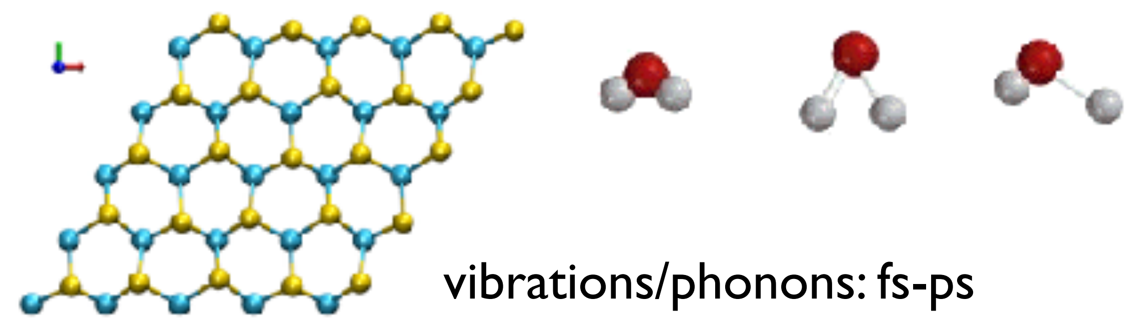
M. Tsutsui et al. Sci. Rep. 9, 18677 (2019)

Existing characterisation methods struggle to provide an overarching view over the actors of many-body physics

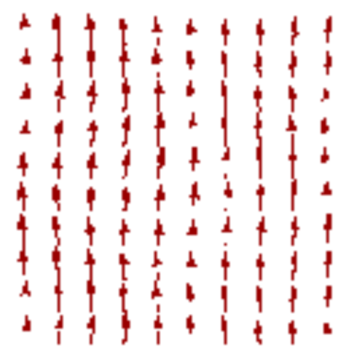


electrons, holes, excitons: as-fs





vibrations/phonons: fs-ps

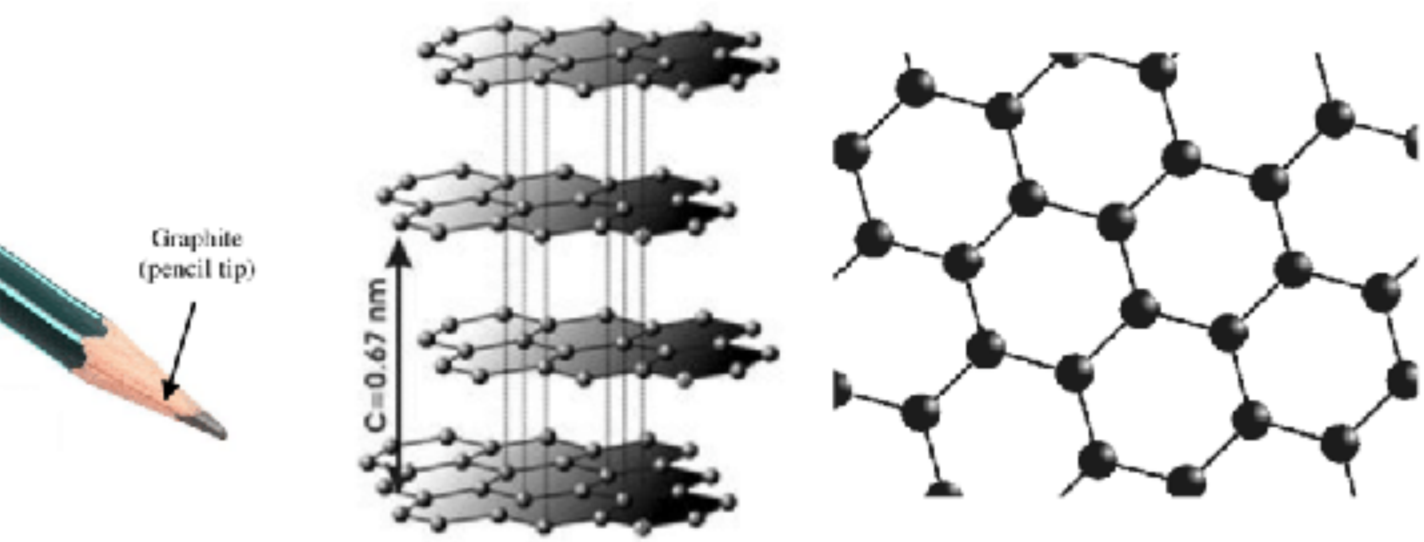


spins/magnons: fs-ms

Non-adiabatic dynamics, charge motion/transfer, Mott physics, phase transitions …

Challenges:
- **Time-overlapping dynamics**
- **Carrier and Nuclear dynamics not separable**
- **Multi-modal measurements under identical conditions**

An example with long-standing open questions: Graphite



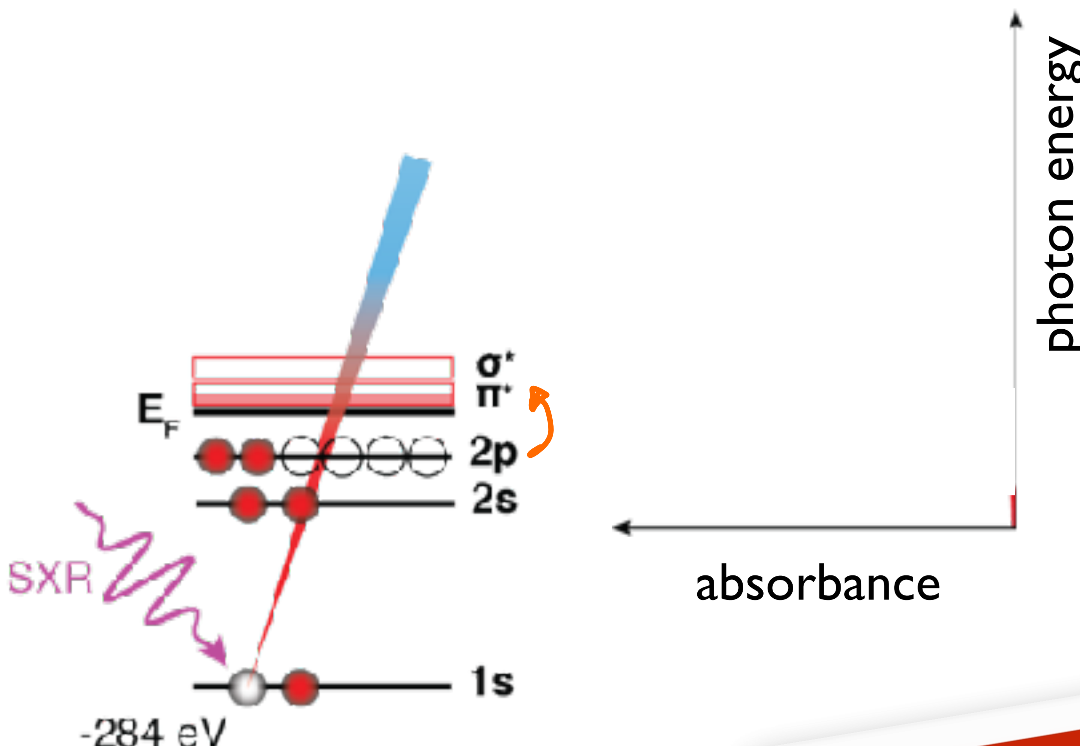
Graphite is a prototypical semi-metal

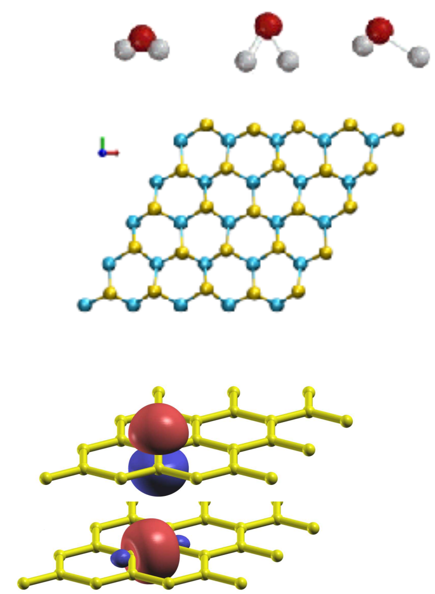
- ❖ Anisotropic properties much alike graphene
- ❖ High carrier mobility
- ❖ Dynamics on all time scales
- ❖ Together with SiC in future high density batteries, etc…
- ❖ Electrode in Lithium Ion Batteries, intercalation problem, carrier scattering

- ❖ Open questions on carrier-scattering dynamics
- ❖ Ongoing debates on phonon (de)excitation pathways

X-ray Absorption Spectroscopy

- **core-level spectroscopy**
- **element- and state-specific**
- **typically in user facilities**
- **insufficient time resolution**
- **synchronization**
- **bandwidth**





nuclear/lattice position, vibrations
structural phase-transition

electronic structure, excitation,
bonding, oxidation, spin state

Demonstrated atto SXR and simultaneous measurement of carriers + lattice

D. E. Sayers et al. Phys. Rev. Lett. 27, 1204 (1971)
A. Bianconi, Appl. Surf. Sci. 6, 392 (1980)
J. Stöhr et al. Phys. Rev. Lett. 53, 1684 (1984)

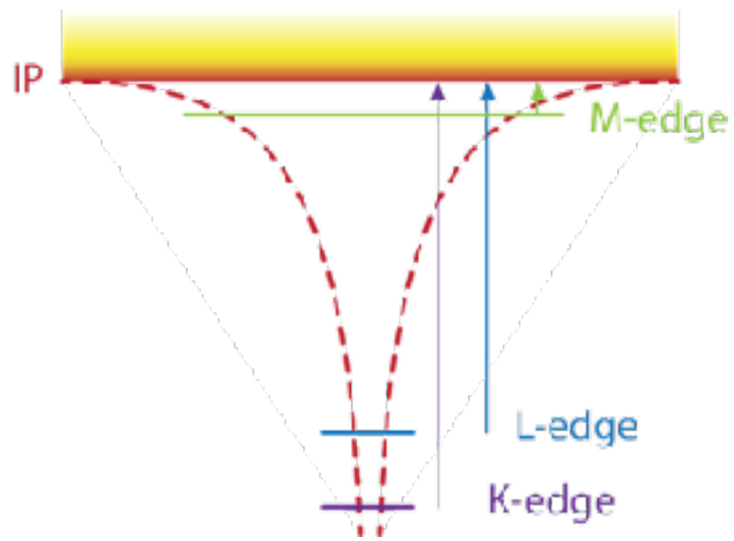
Discussions with J. Rehr and others
S. L. Cousin et al. Opt. Lett. 39, 5383 (2014)
B. Buades et al. Optica 5, 502 (2018)

We measure photons to know about carriers!

Issues with semi-core or valence states:

- **Parasitic ionisation at low photon energy** $\sigma \propto Z^5 \omega^{-9/2}$
- **Multiplet effects: spectral shape and branching ratios**

F. de Groot Coord. Chem. Rev. 249, 31 (2015)



e.g. a 3p "semi-core" hole ($3p^5$ $3d^{N+1}$) would lead to
45 final states that determine the absorption edge spectral shape

Challenge for time-resolved measurements:

- **Time-dependent screening complicates the interpretation**

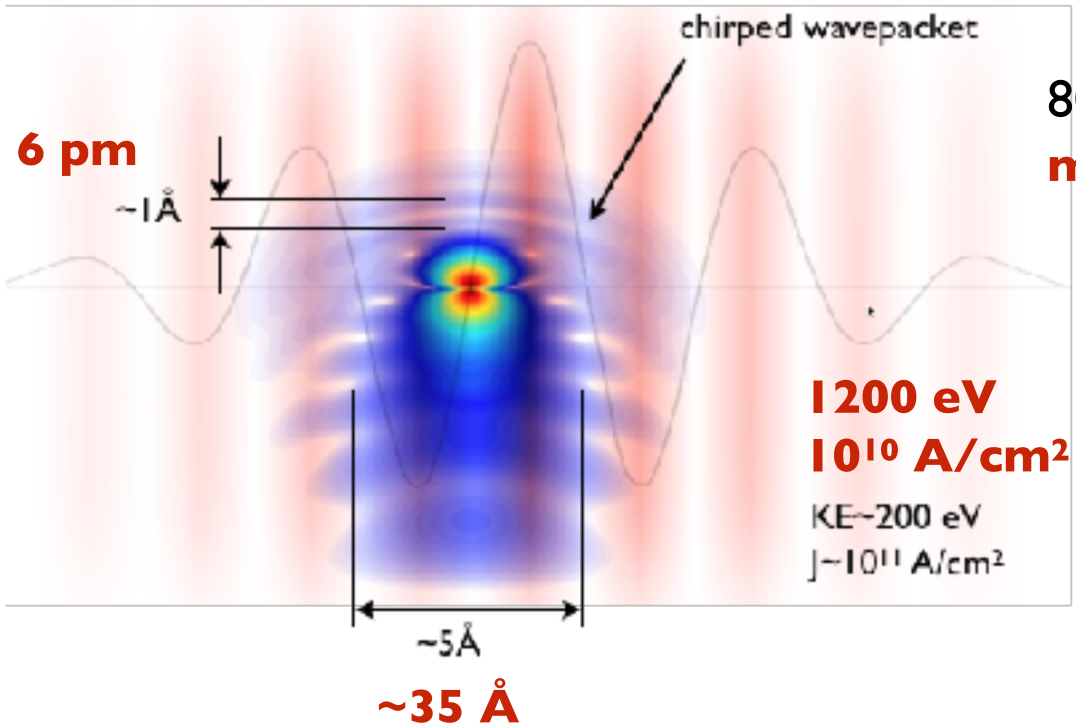
Theoretical descriptions with e-h correlations, BSE

Pump-probe descriptions, 4 particle Greens formalism (??), etc…

Enabled by coherent mid-IR light science

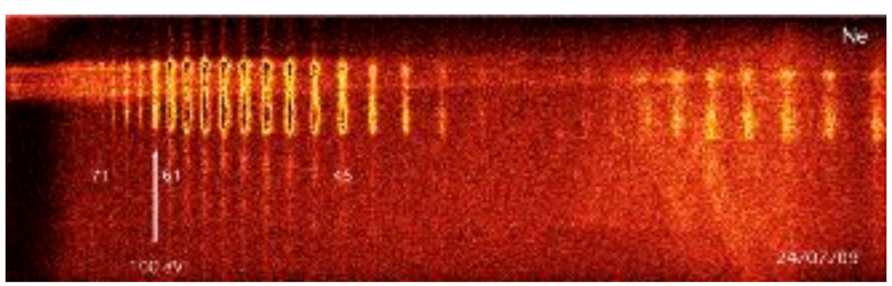
Superb quantum control over light-matter interaction:

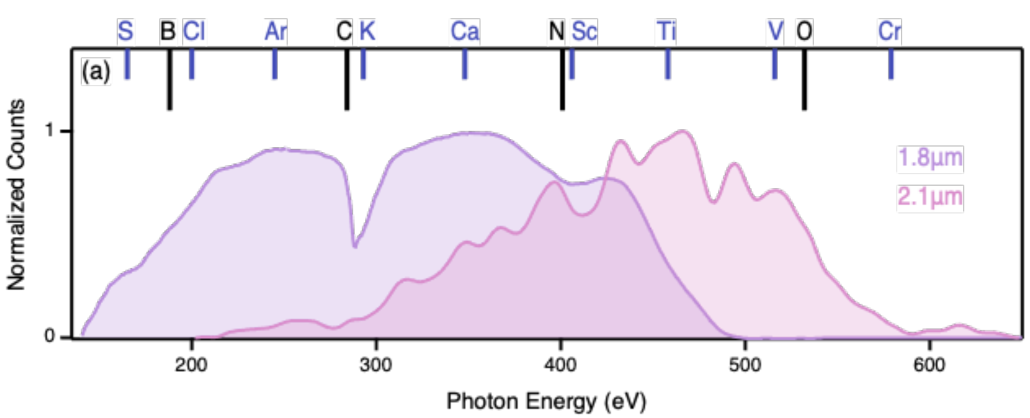
… manipulating radiating electron wavefunction



- ❖ Full spatio-temporal coherence
- ❖ as-fs electron and photon pulses
- ❖ Polarization control
- ❖ 12 octave supercontinua / isolated peaks
- ❖ Fully optically synchronized for pump/probe

from XUV to SXR



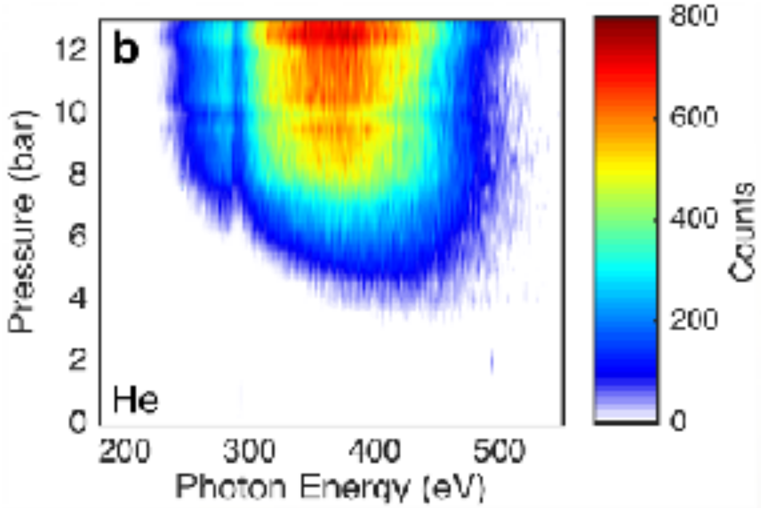


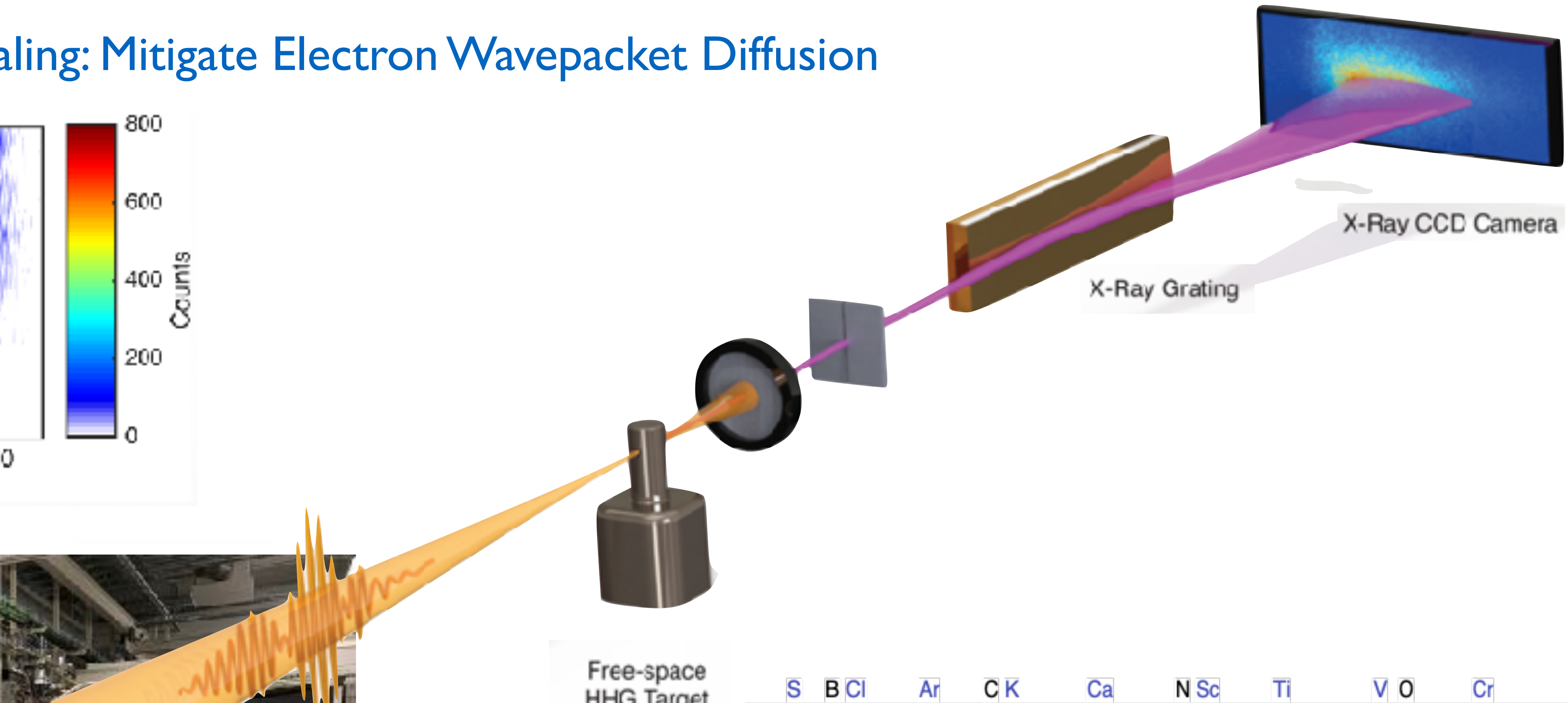
S. L. Cousin et al. Opt. Lett. 39, 5383 (2014)
S. Teichmann et al. Nature Commun. 7, 11493 (2016)
F. Silva et al. Nature Commun. 6, 6611 (2015)
S. Cousin et al. Phys. Rev. X 7, 041030 (2017)
Ultrafast Science 3, 4 (2023)
Science 336, 1287 (2012)

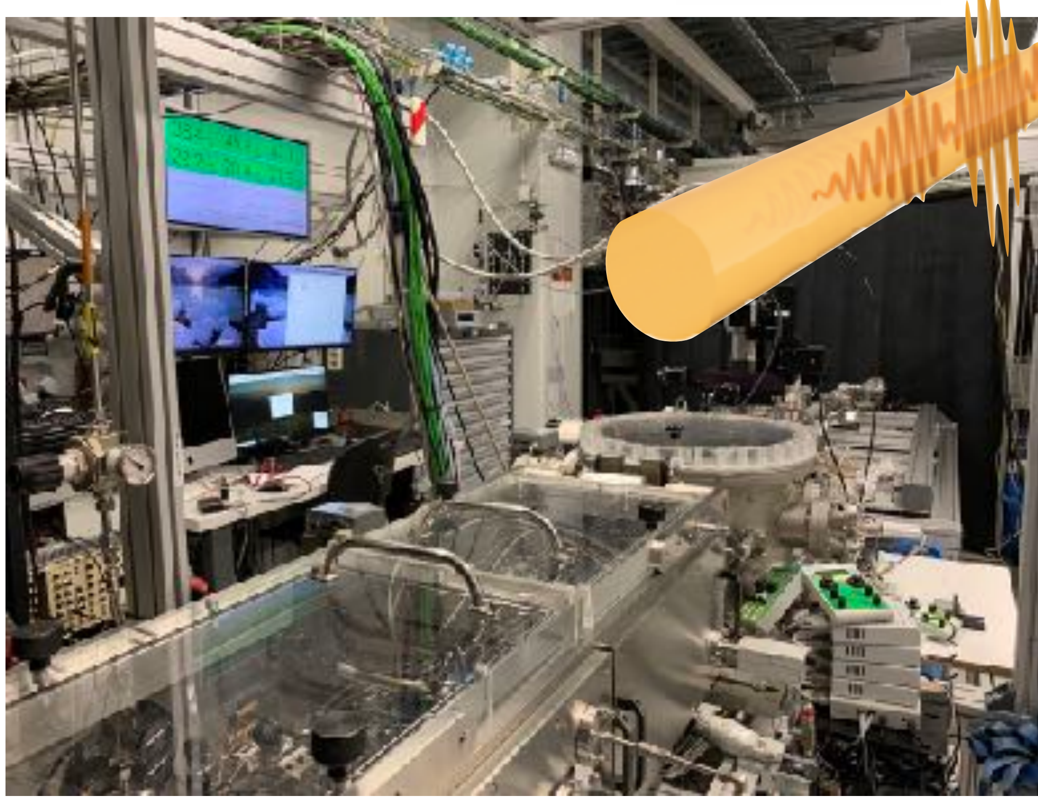
First attosecond soft X-ray Source

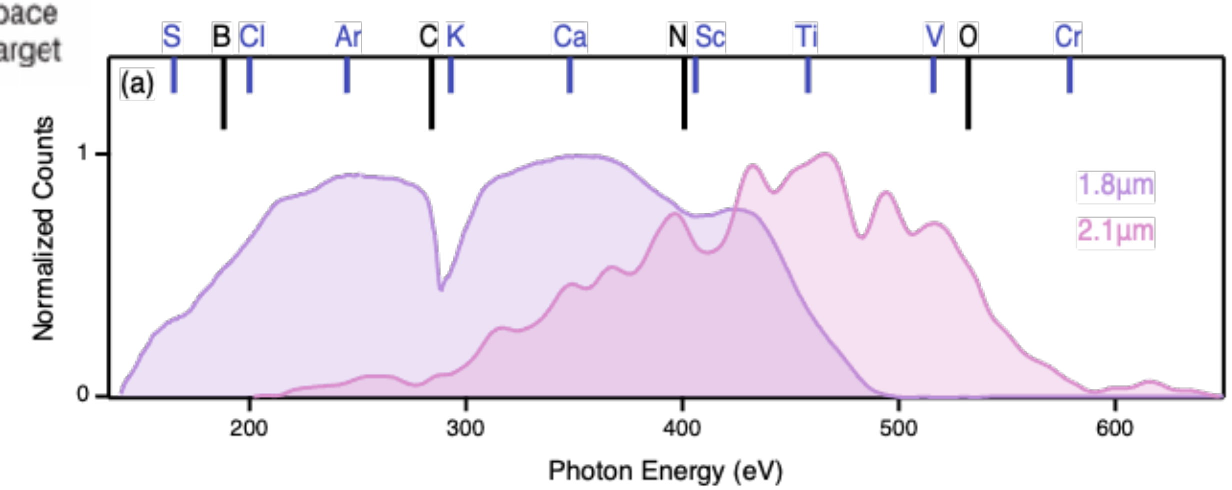
Attosecond SXR technology

- ❖ (Few-cycle, CEP-stable) long wavelength sources
- ❖ Ponderomotive Scaling: Mitigate Electron Wavepacket Diffusion





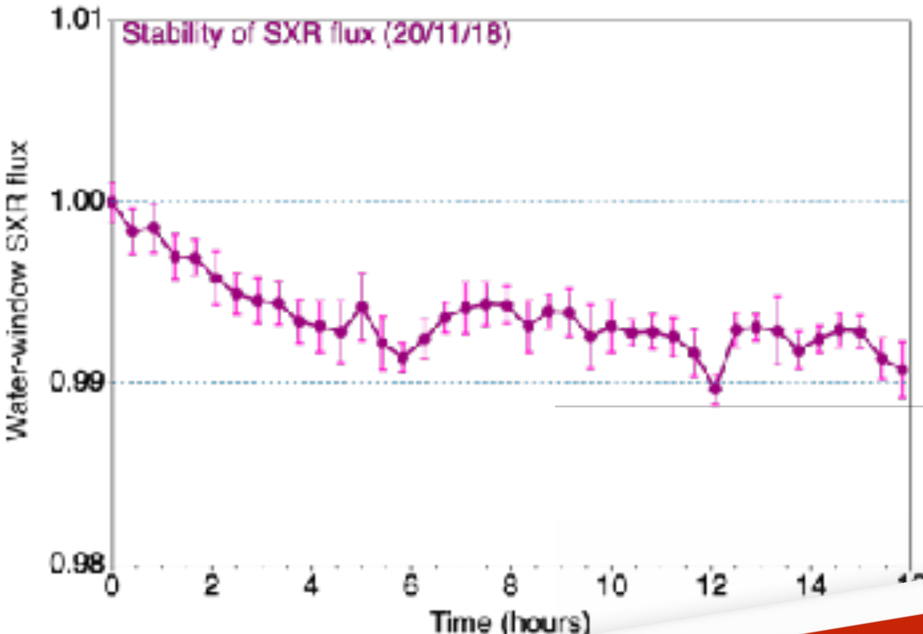


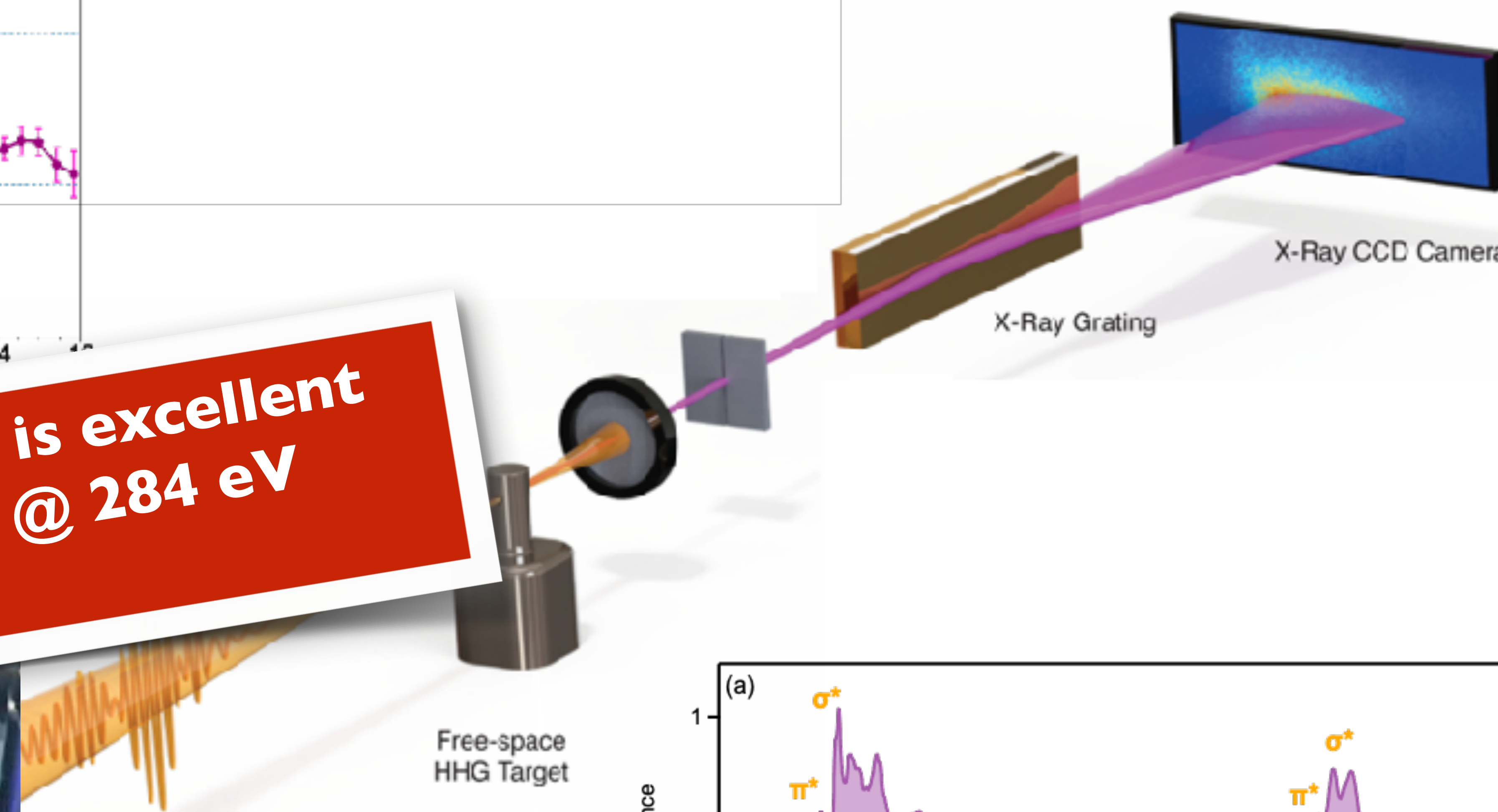


S. Cousin et al. Phys. Rev. X 7, 041030 (2017)

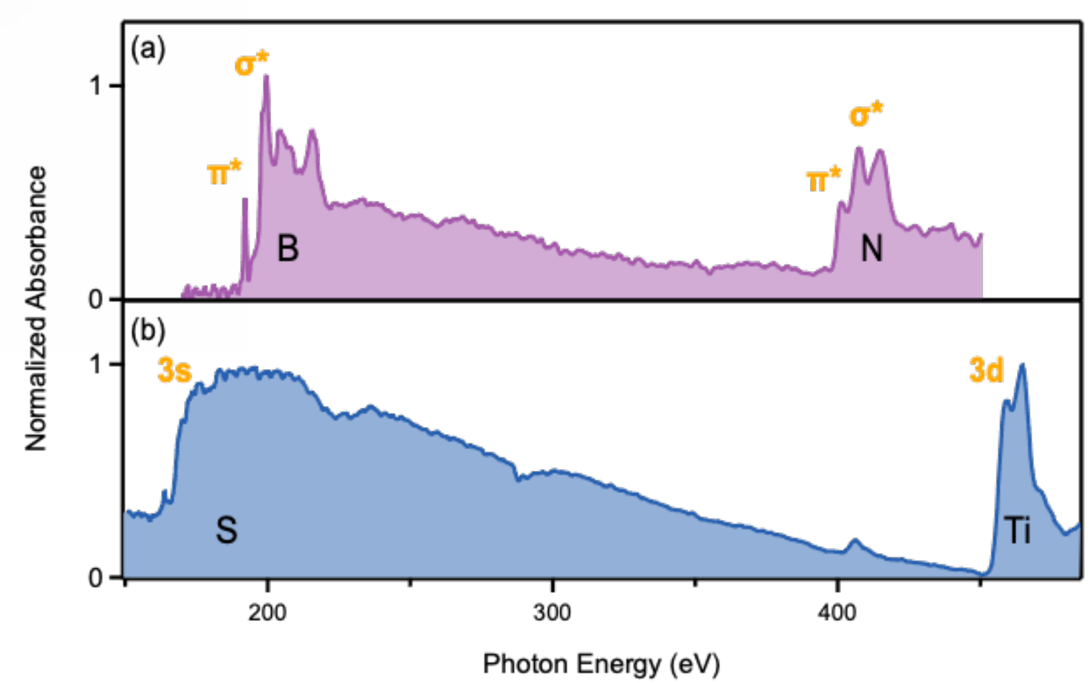
F. Silva et al. Nature Commun. 6, 6611 (2015) S. Teichmann et al. Nature Commun. 7, 11493 (2016) A. Summers et al. Ultraf. Sci 3, 4 (2023)

0.5 keV attosecond continua





Spectral stability is excellent
$2x10^7$ phot/s/1% @ 284 eV
165 as duration



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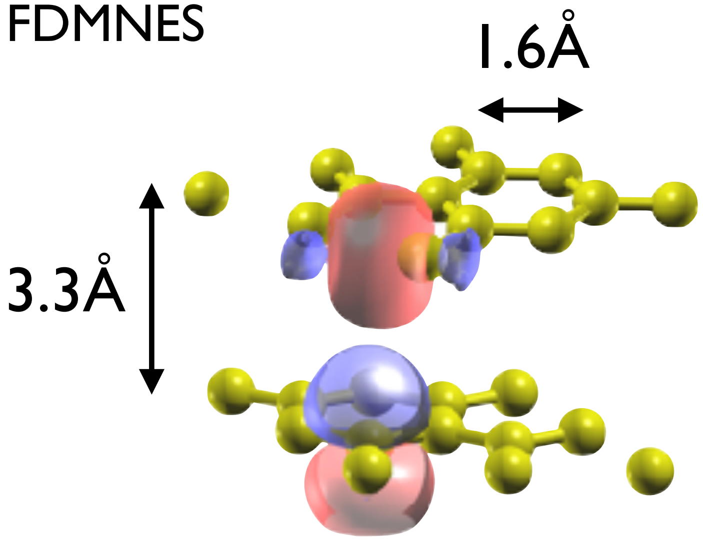
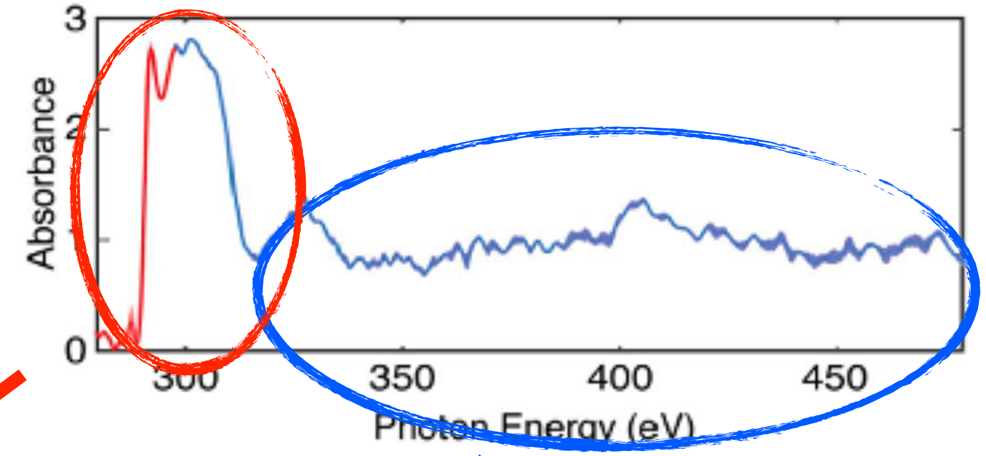
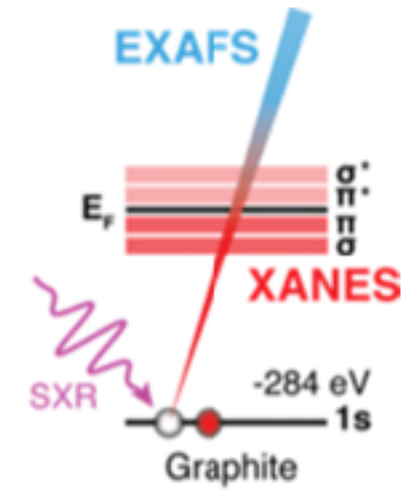
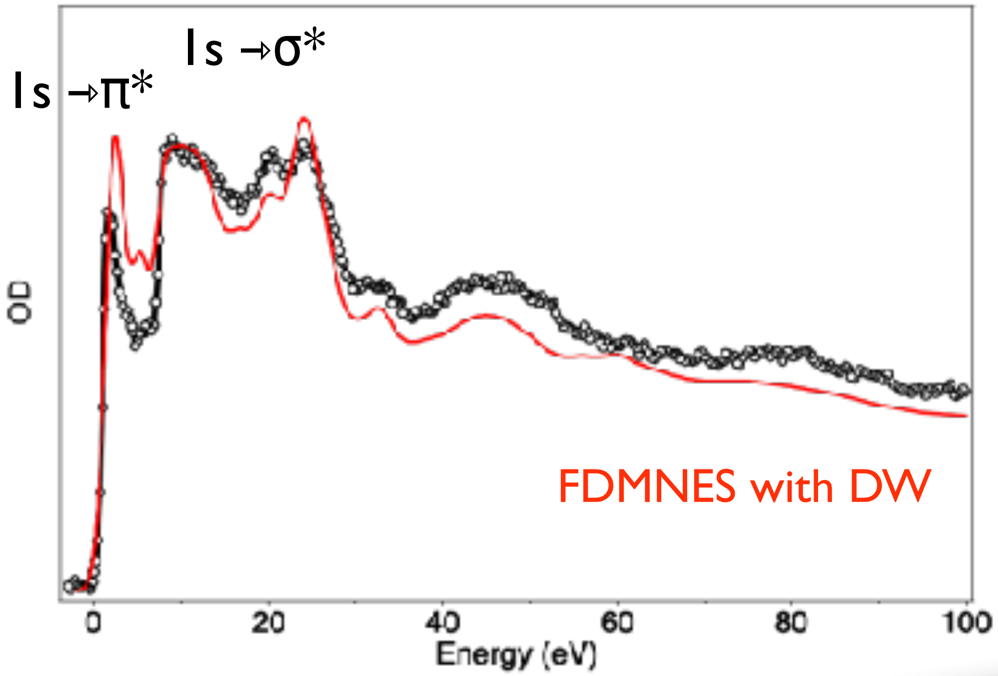
Graphite: static electronic and lattice structure

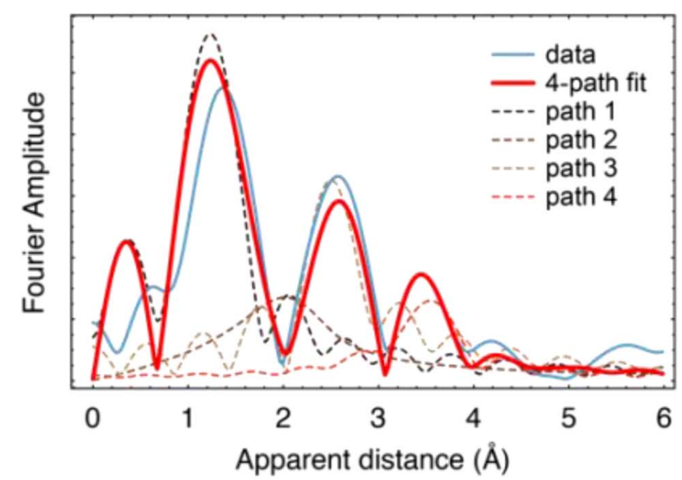
Y. Joly (NEEL-CNRS)
FDMNES

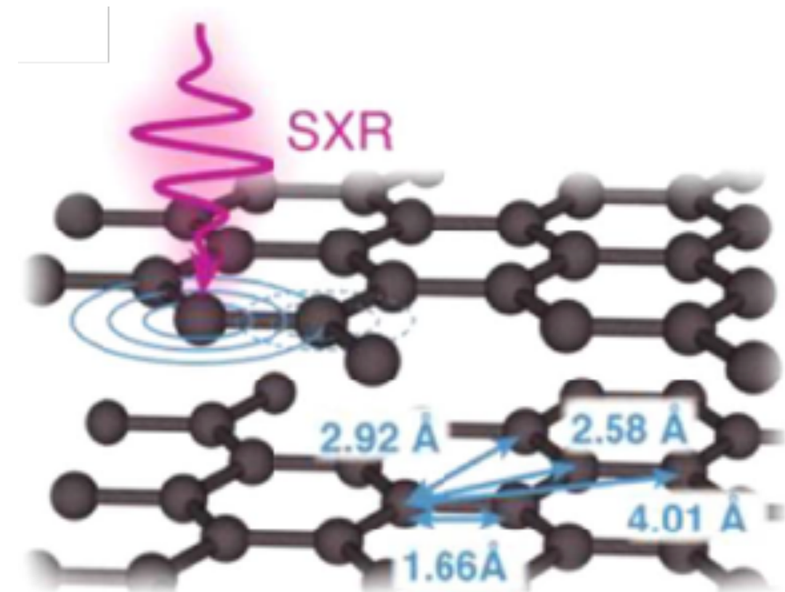








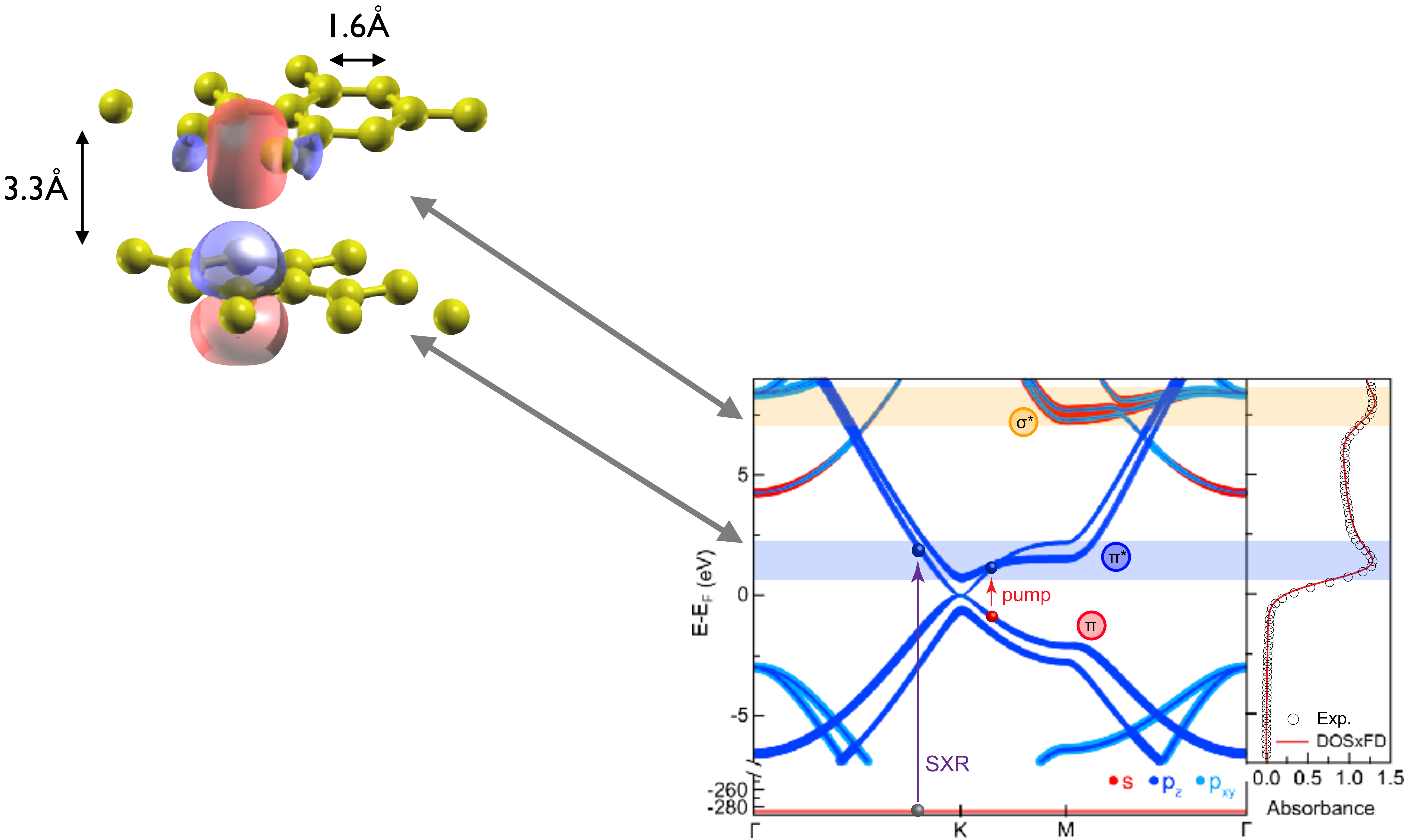




Simultaneous electronic and nuclear information!

B. Buades et al. Optica 5, 502 (2018)

Real-time electron and lattice dynamics in graphite



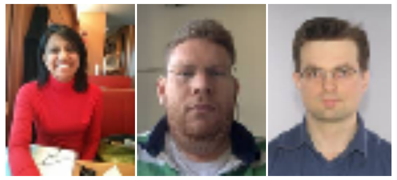
T.P.H. Sidiropoulos et al. Phys. Rev. X 11, 041060 (2021)

Real-time electron and lattice dynamics in graphite

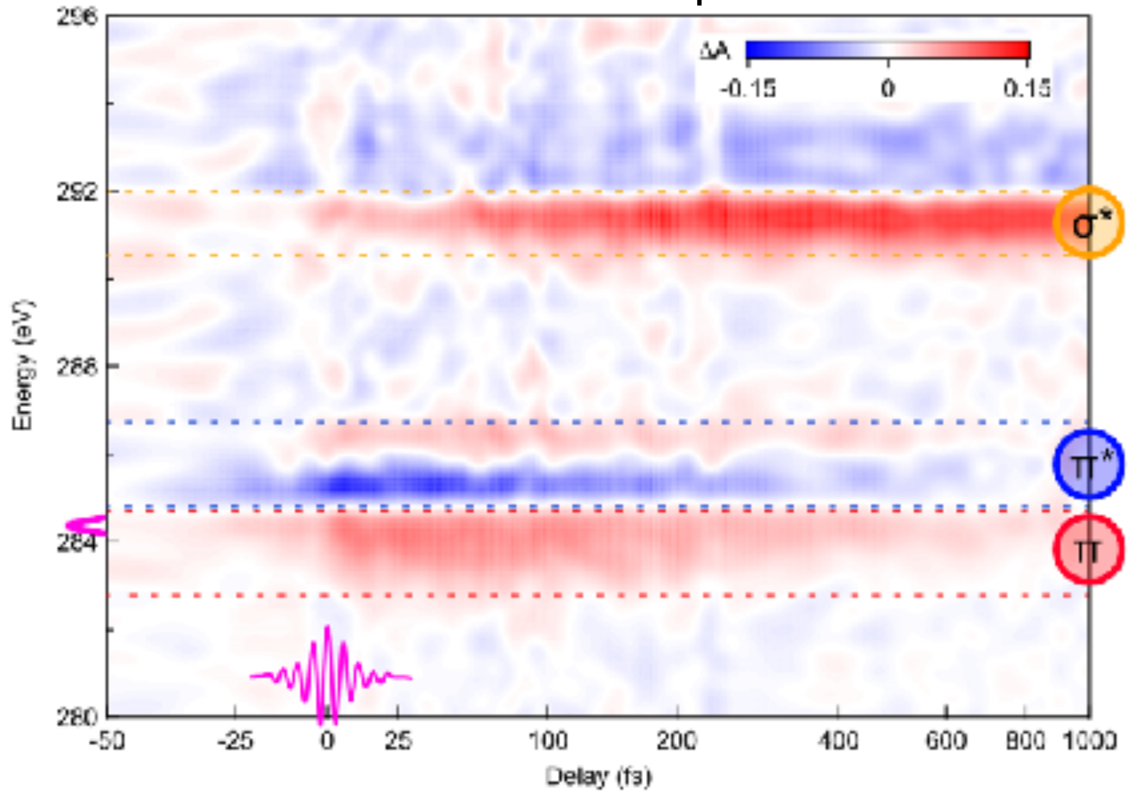
Pump: 0.7-eV, 1.8-cycle
0.07 - 0.33 V/Å

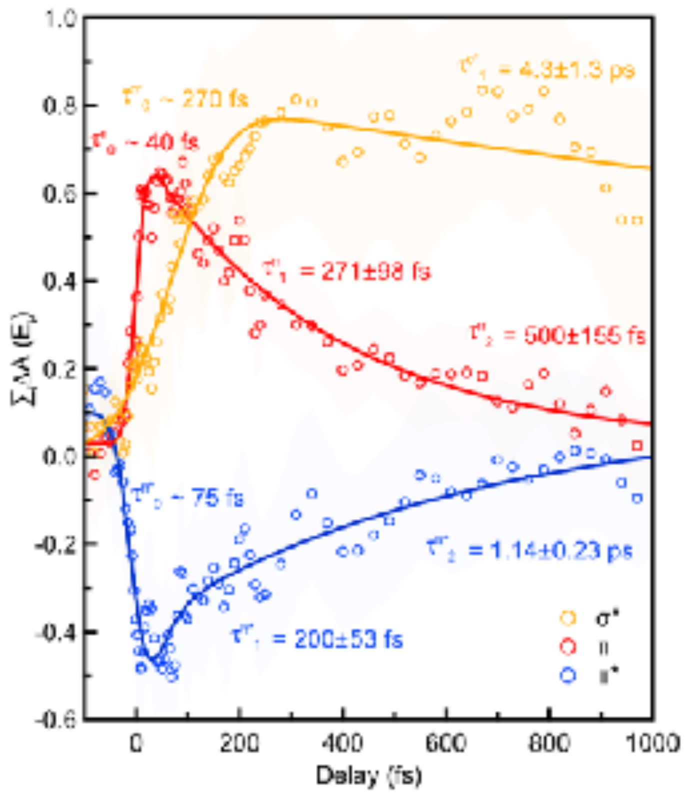
Probe: 200-500 eV, 165 as

S. Sharma (MBI)
ELK RT-TDDFT



Differential absorption





❖ $\pi - \pi^*$ due to optical pumping

❖ σ^* due to el-nuclear coupling

(here we only include E_{2g} (bec unit cell))

❖ Real real-time electron **and** hole dynamics

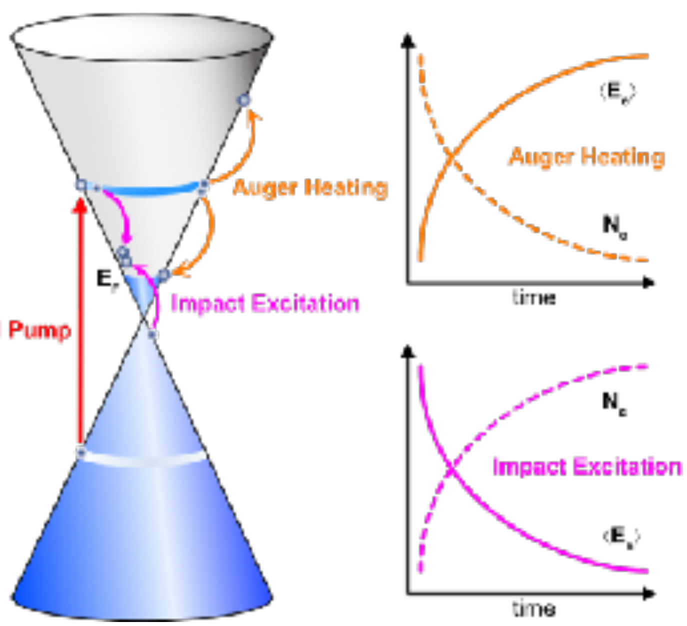
❖ Chemical potential: 200 meV n-doping

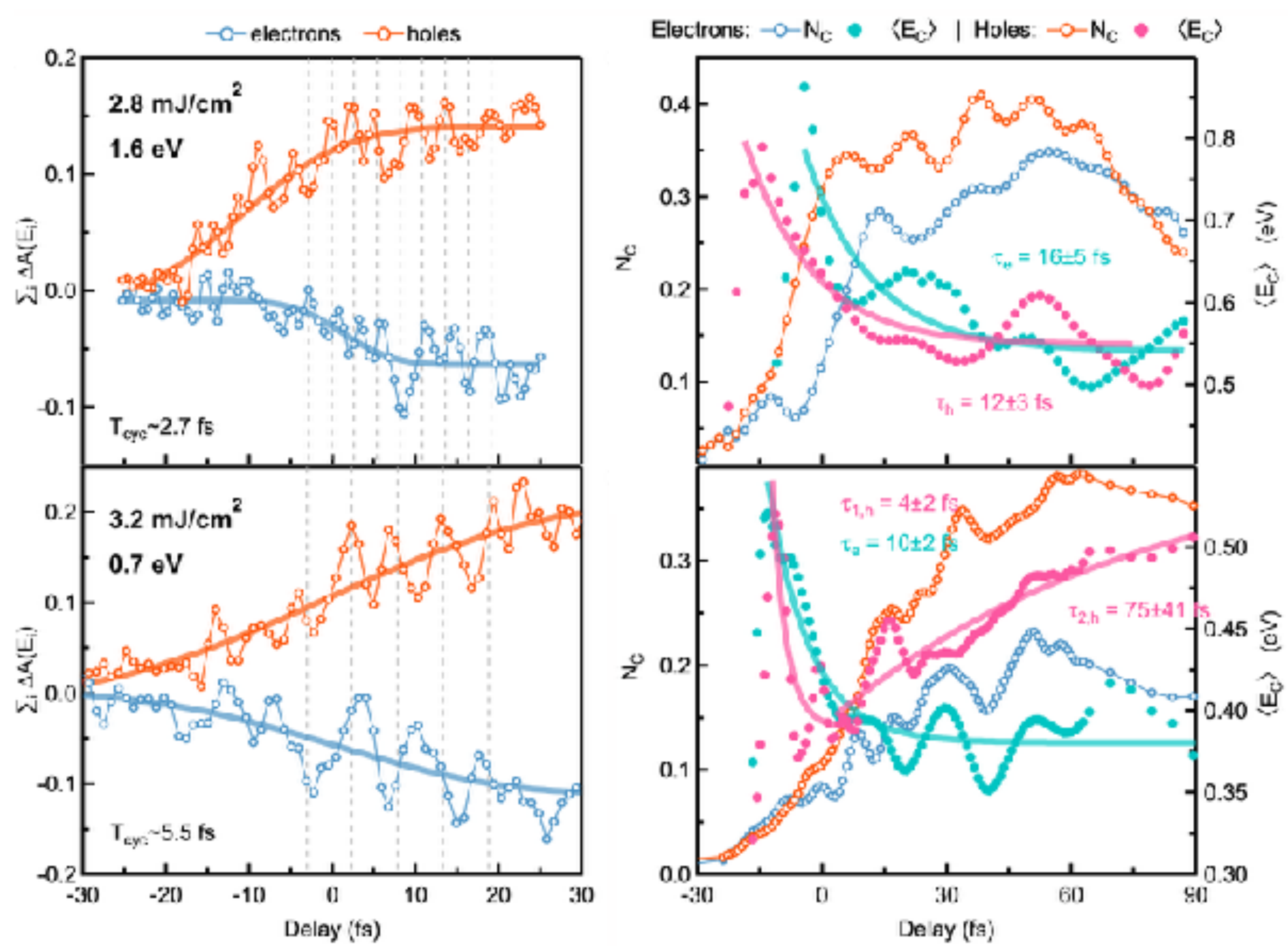
❖ Carrier concentration up to $5x10^{22}$ cm^{-3}

❖ Different e-h dynamics important for carrier recombination (think light harvesting)

Carrier scattering mechanism

Carrier scattering and multiplication:



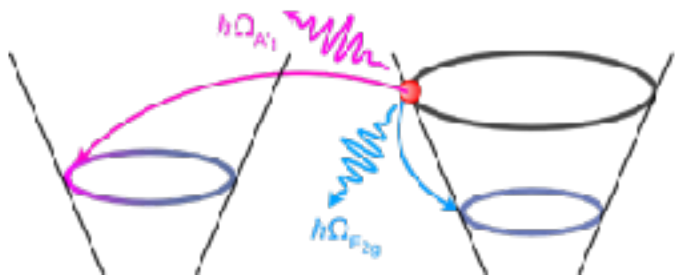


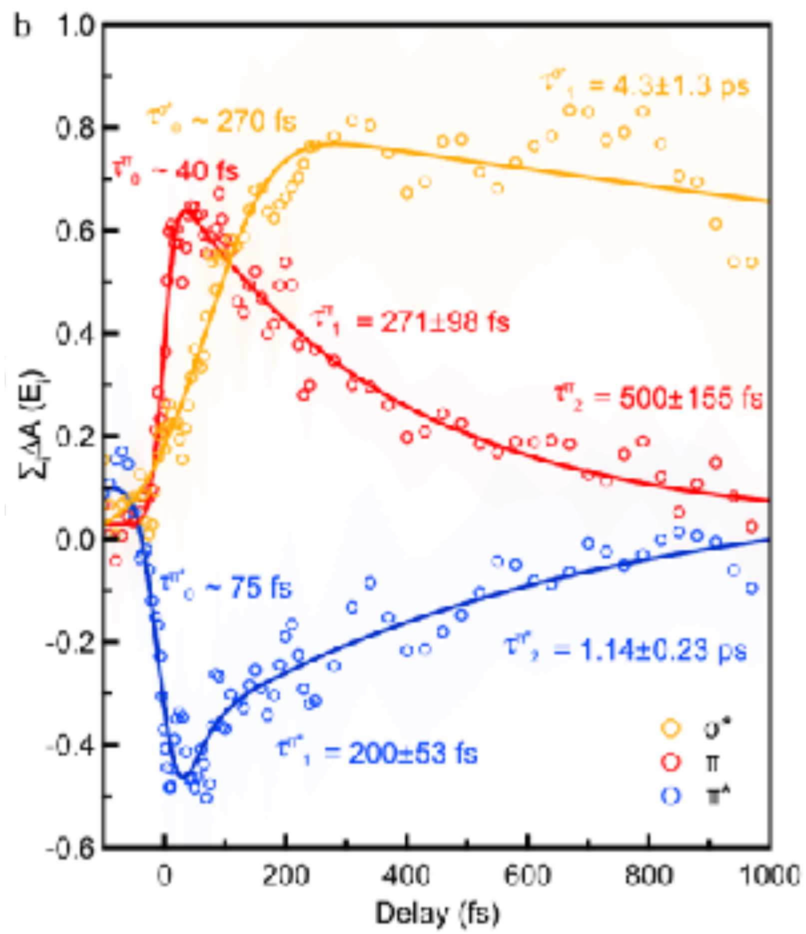
- ❖ Carrier motion directly with ω_{pump}
- ❖ IE dominates for e and h at 1.5 eV
- ❖ At 0.7 eV, IE for e but not for h
- ❖ Asymmetric scattering phase-space for h / e

T.P.H. Sidiropoulos et al. Phys. Rev. X 11, 041060 (2021)

STFT analysis of the coherent σ^* signal

Displacive (K) Raman active (G)





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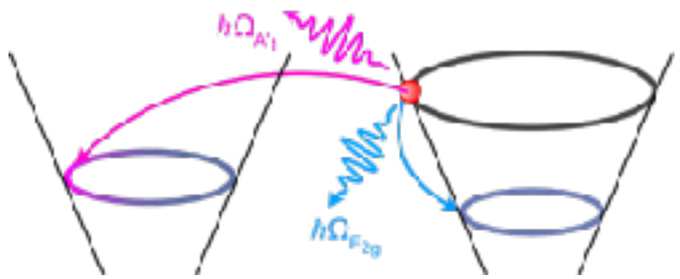
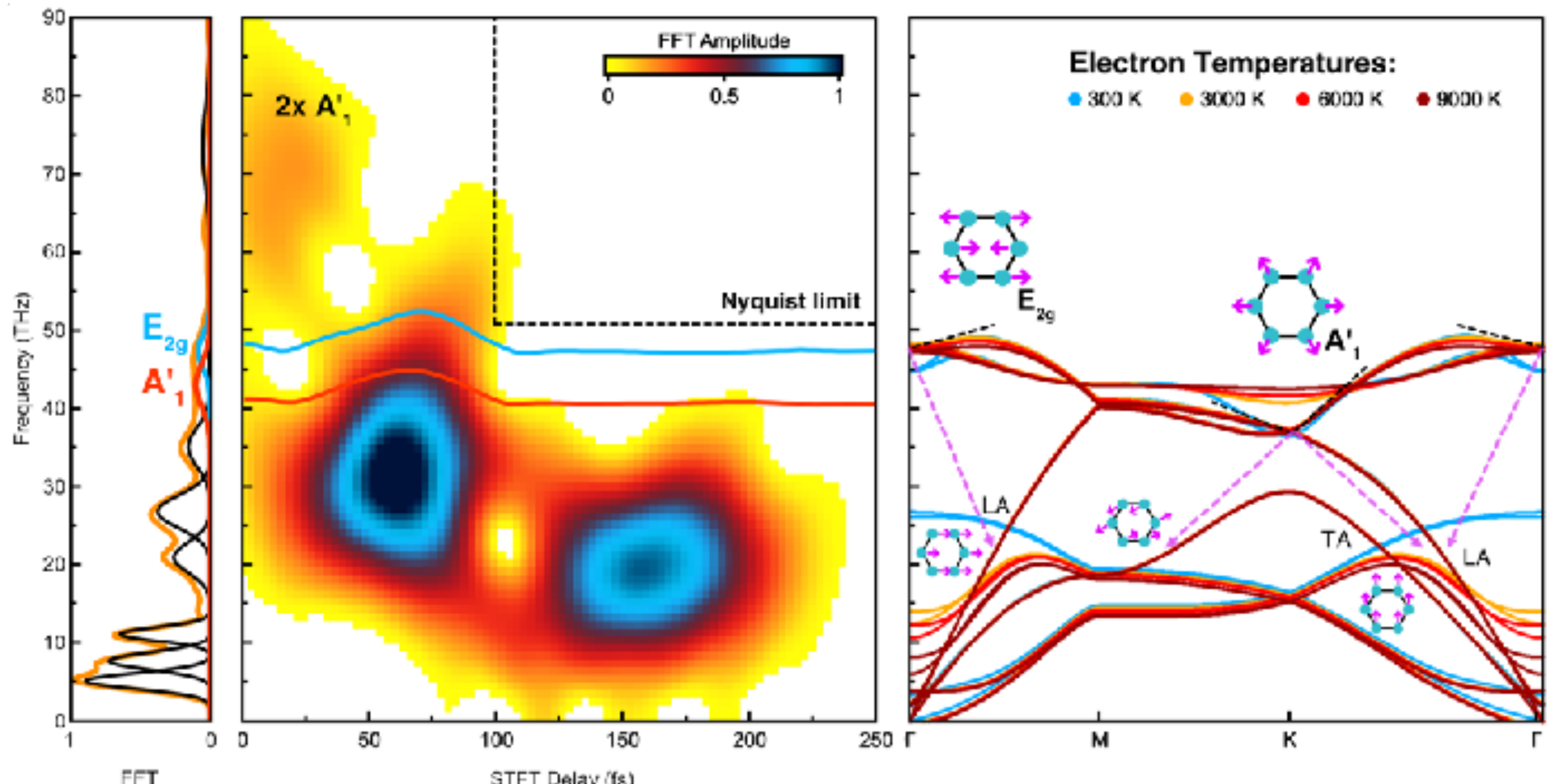
STFT analysis of the coherent σ^* signal

Displacive (K)   Raman active (G)



46.4 ± 2.7 THz

42.7 ± 1.1 THz



calculated with EPW

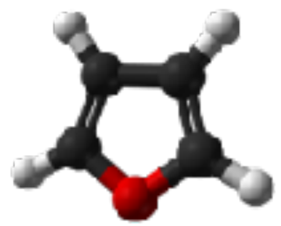
- ❖ $\bar{G} - E_{2g}$ and $\bar{K} - A_1'$ appear already after ~20 fs
- ❖ Both maximize ~67 fs; already 30 fs *after* the pump pulse
- ❖ A_1' is not Raman active!

- ❖ Direct real-time measurement of the non-Raman-active A_1' phonon
- ❖ DFT-MD shows strong EPC is the mechanism; no displacive excitation
- ❖ 90% contribution from A_1', despite impulsive excitation of E_{2g}

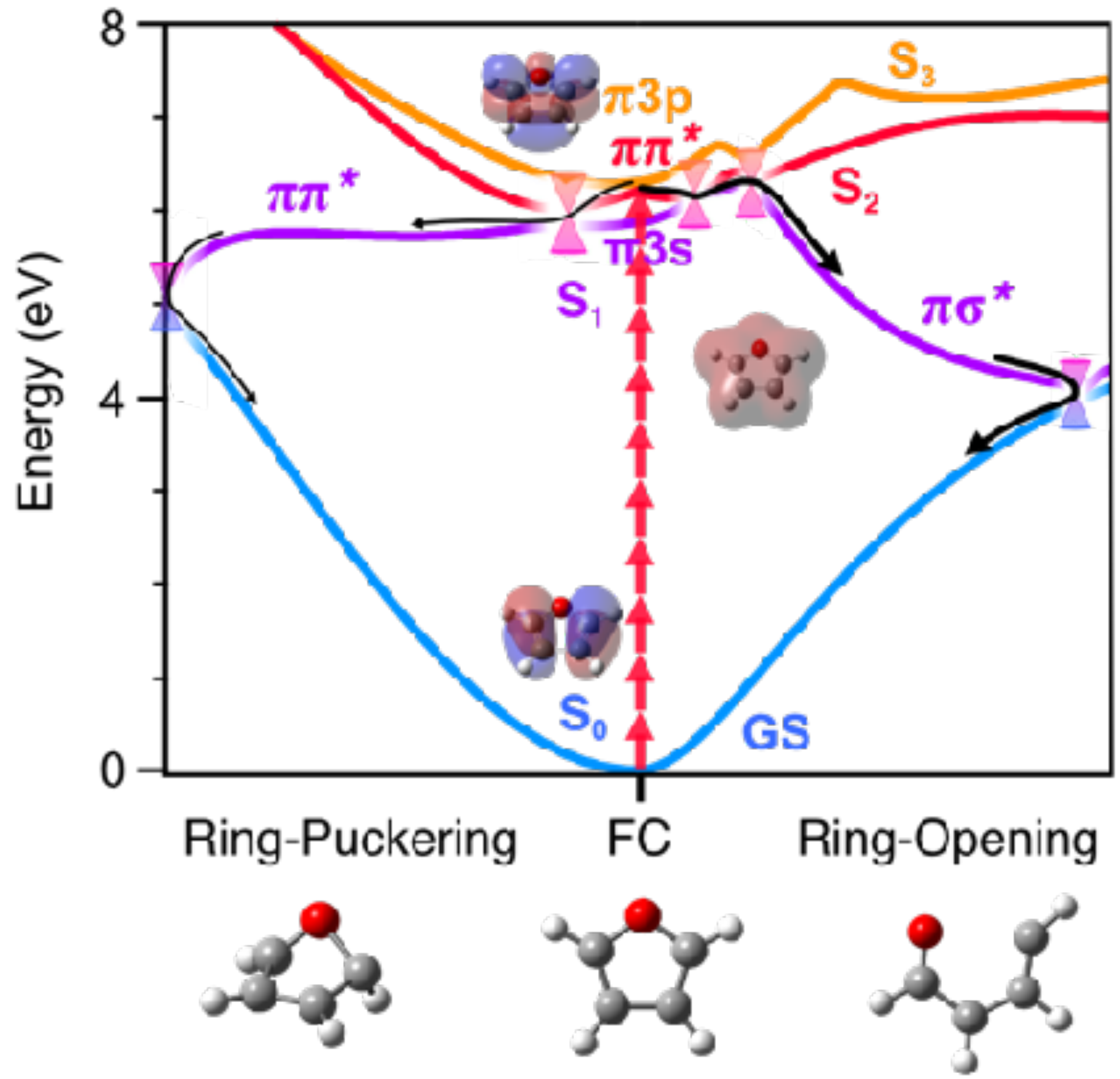
T.P.H. Sidiropoulos et al. Phys. Rev. X 11, 041060 (2021)

Reaction pathways / conical intersection / non-adiabatic dynamics

Ultrafast correlated many-body dynamics



Aromat: Furan [planar]



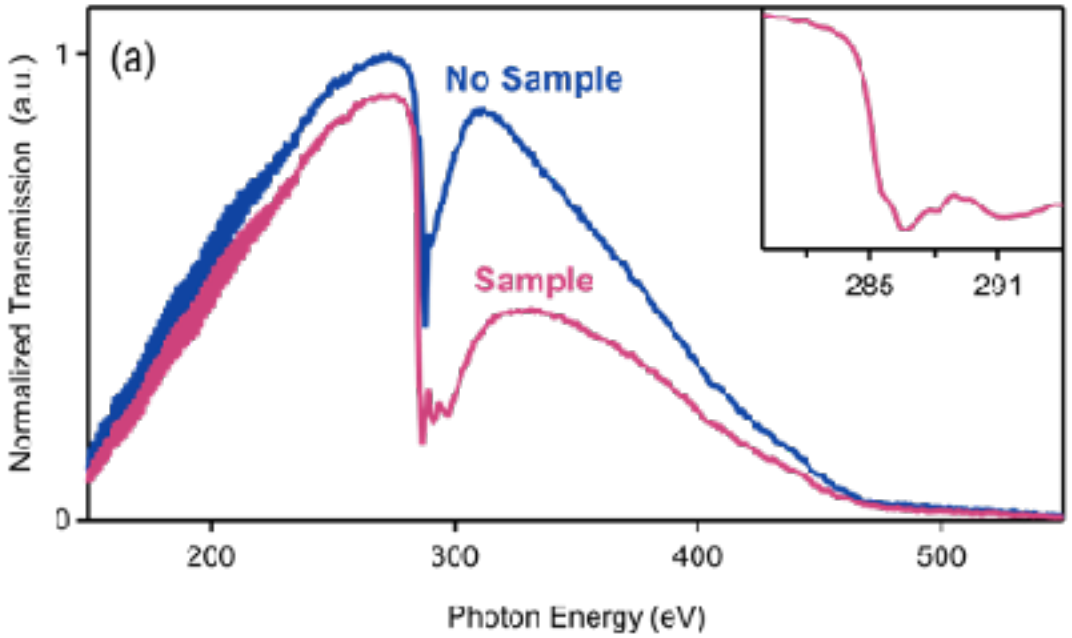
- Some transition states are optically dark
- Involves multiple conical intersections - couplings
- Dynamics is too fast to resolve and to energetically identify with existing methods

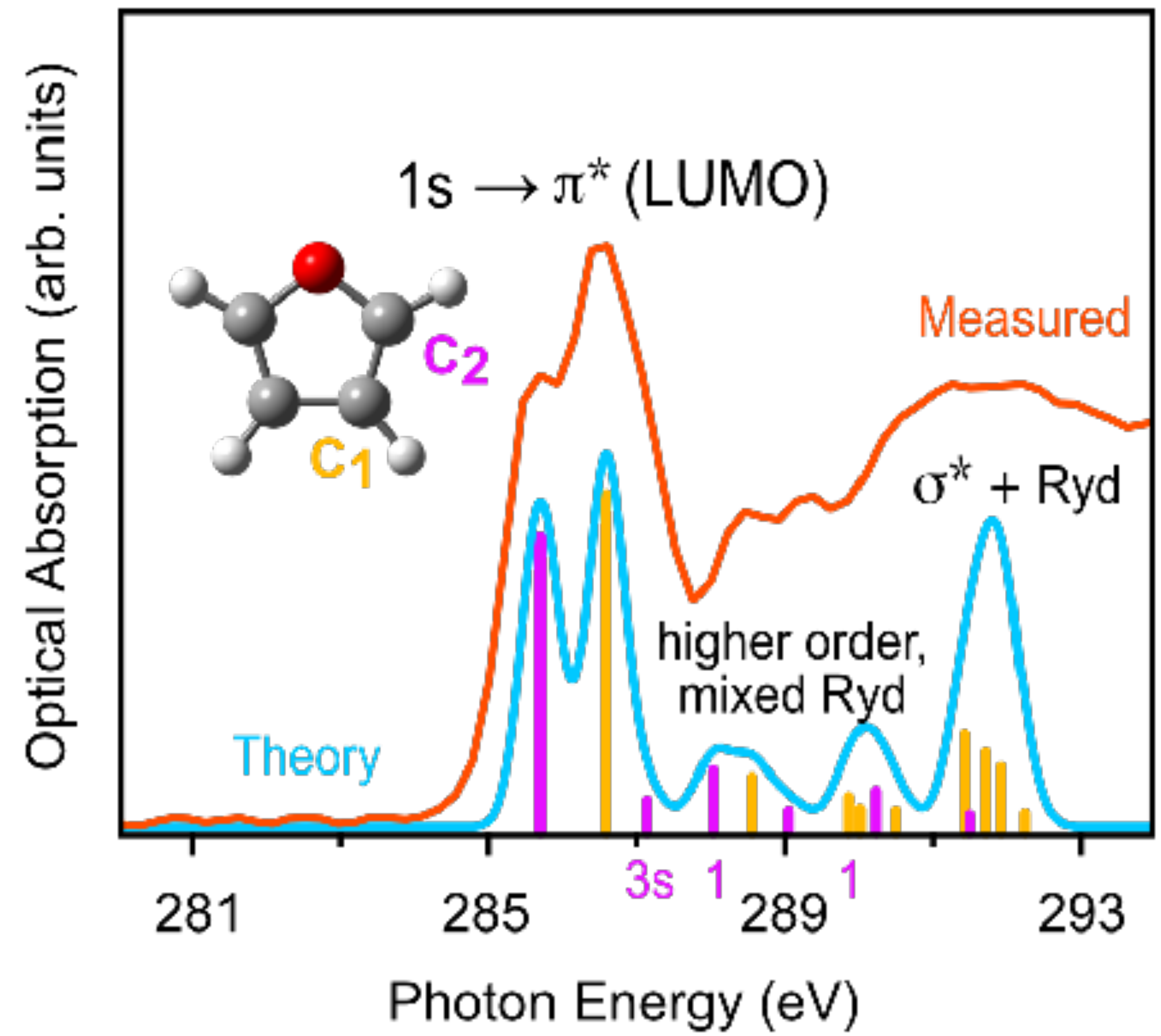
S. Cousin .. JB, Opt. Lett. 39, 5383 (2014) F. Silva .. JB, Nature Commun. 6, 6611 (2015)

Y. Pertot et al. Science 355, 6322 (2017) N. Saito et al. Optica 6, 1542 (2019) S. Severino et al. arXiv:2209.04330

attoXANES: Furan

Theory: K.M. Ziems, S. Gräfe (Jena)





OD = -ln(p/up)

0.7 eV, 17 fs, 4.7×10¹³ W/cm²

(TI/MPI negligible 2.5%)

2 distinct C in ground-state furan due to slightly different binding energy

S. Severino et al. arXiv:2209.04330

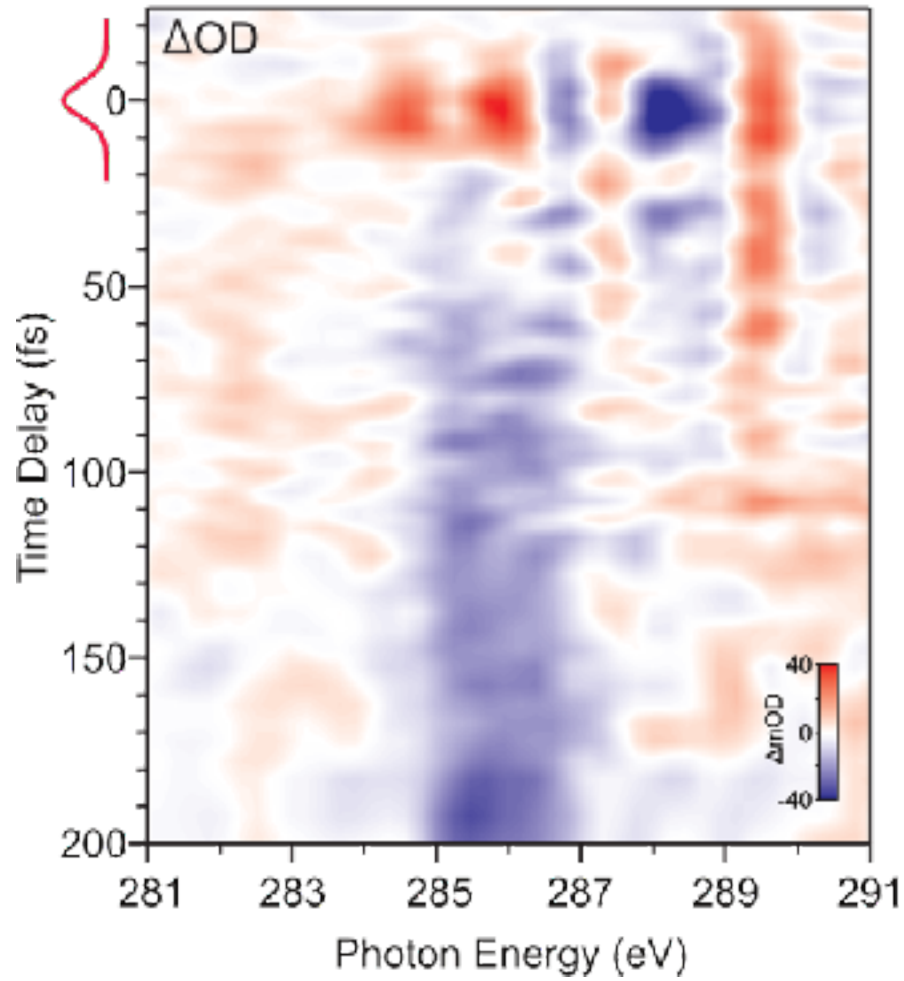
attoXANES: Furan

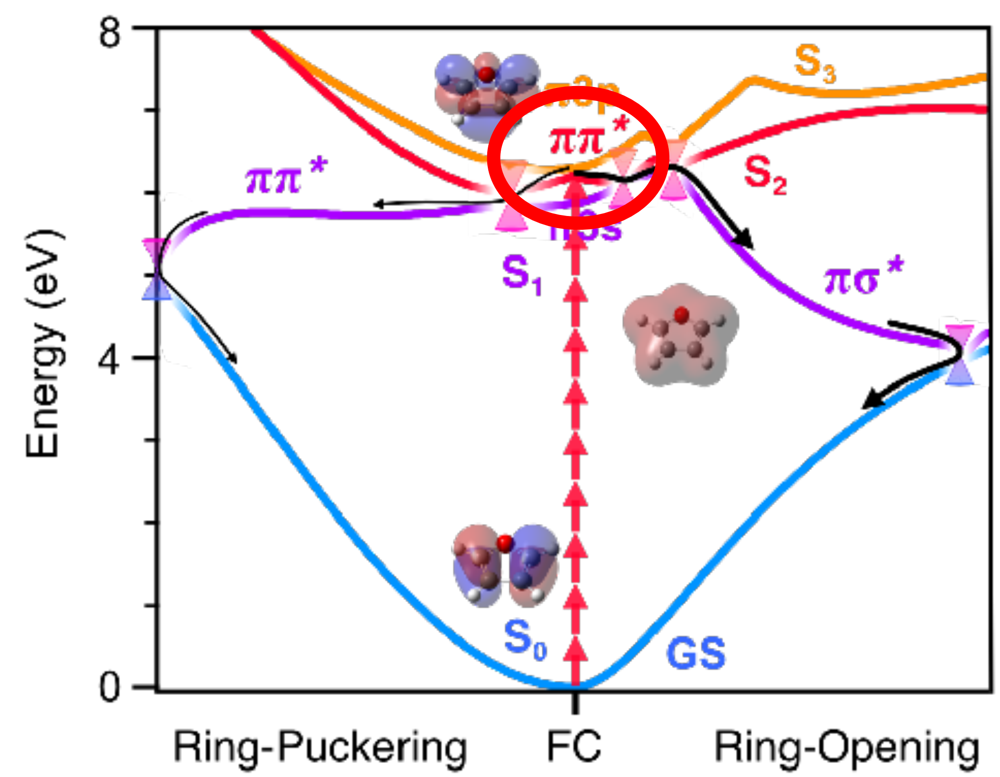
Initial excitation and time evolution

Pump: 0.7-eV, 17-fs
up to 47 TW/cm²

Probe: 200-500 eV, 165 as

Differential absorption (pumped - unpumped)





	Transition	ΔE(eV)	f
S_1	$\pi \rightarrow 3s$	5.87	0.00
S_2	$\pi \rightarrow \pi^*$	6.2	0.17
S_3	$\pi \rightarrow 3p$	6.37	0.03

Excitation π → π* (HOMO → LUMO)

S. Severino et al. arXiv:2209.04330

Initial excitation and time evolution

Pump: 0.7-eV, 17-fs
up to 47 TW/cm²

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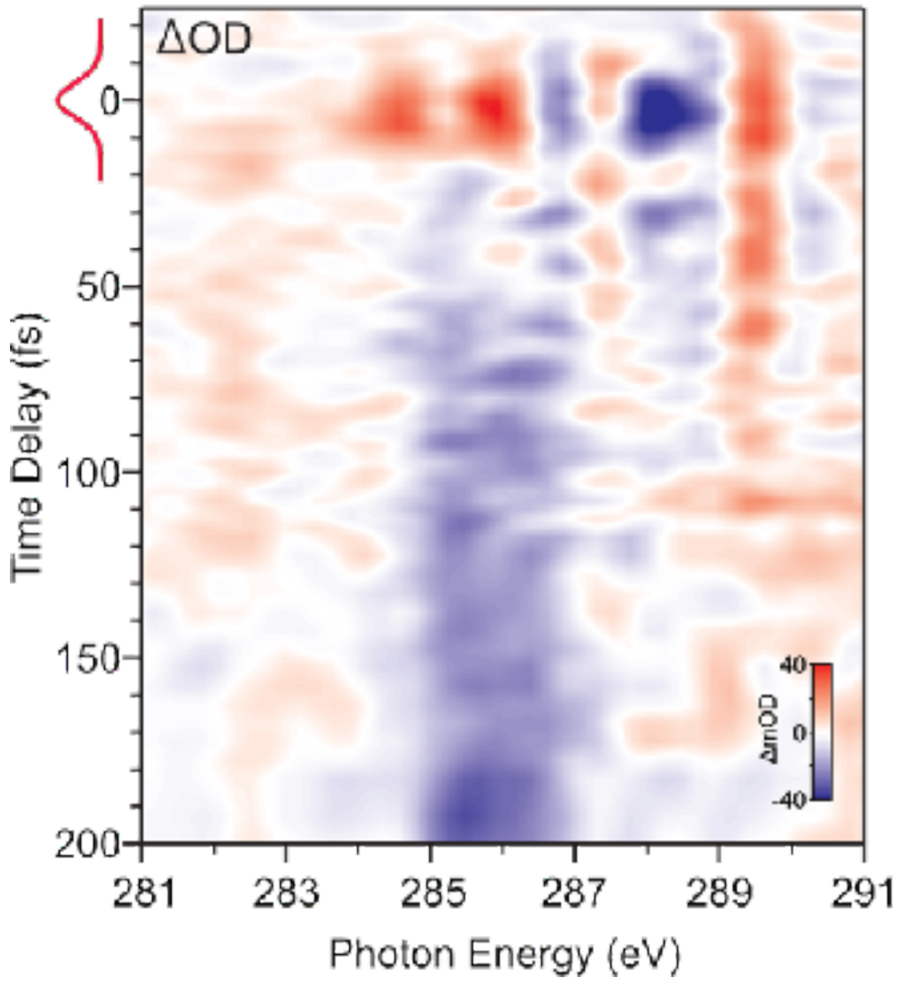
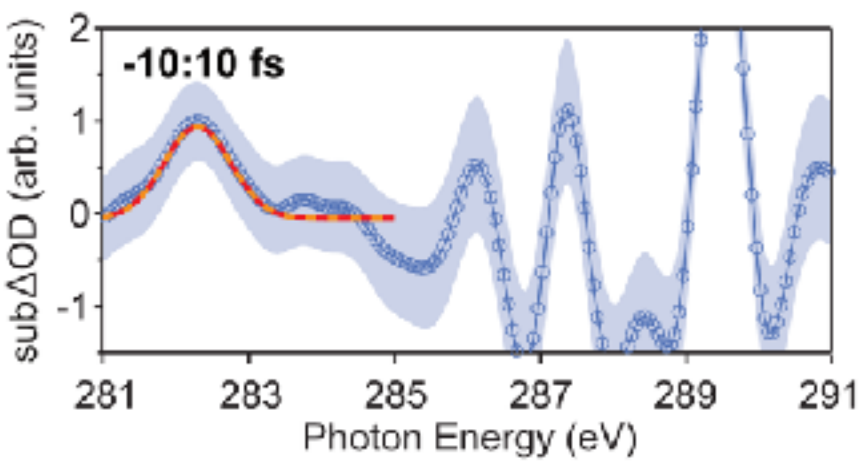
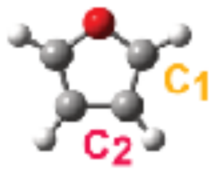




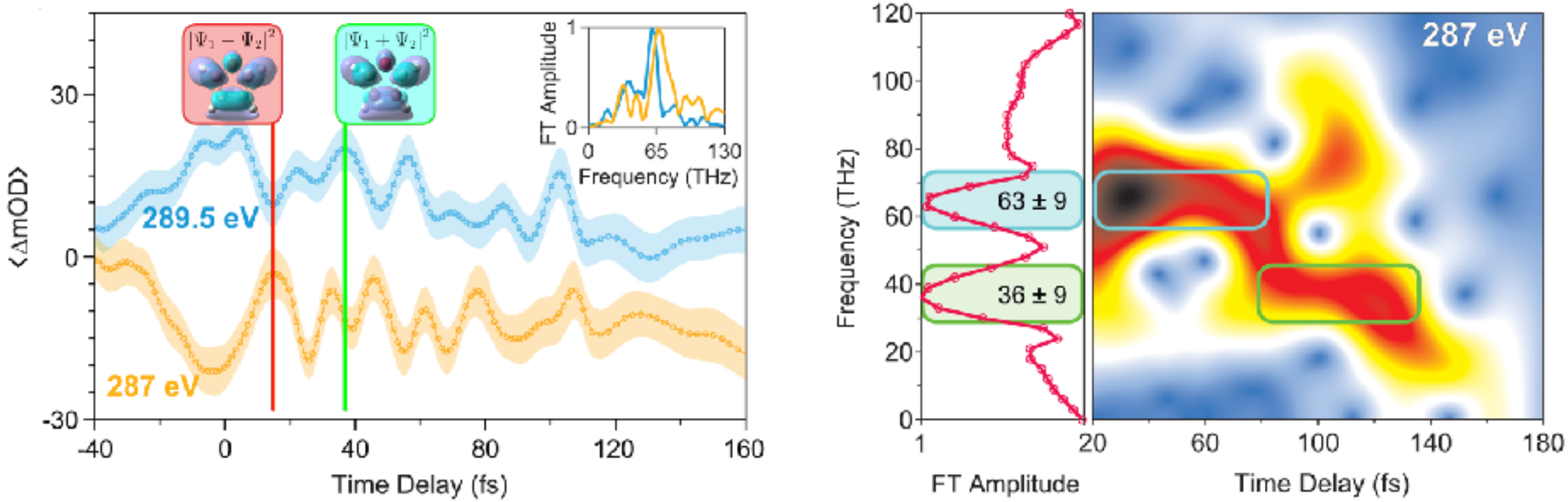


- ❖ SOMO peak due to excitation
- ❖ 2 carbons are (initially) distinct
- ❖ oscillations after 16 fs

… let's look at those oscillations

S. Severino et al. arXiv:2209.04330

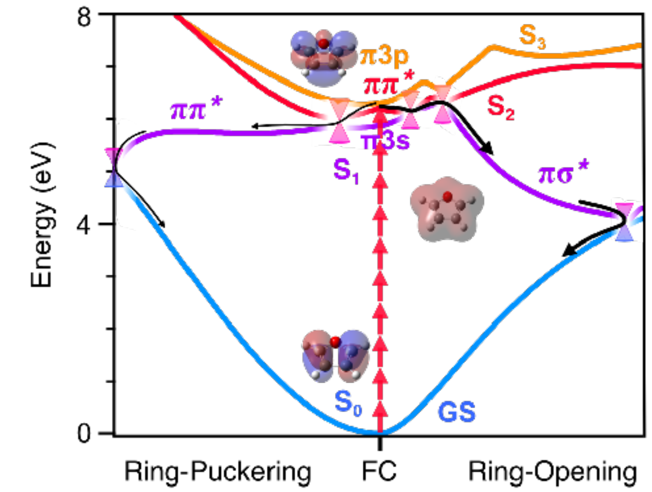
Electronic coherence and loss - quantum beats



❖ quantum beats at 64 THz until ~80 fs, then downshift to 37 THz

❖ phase-shift is explained by coherent superposition at distinct sites

S. Severino et al. arXiv:2209.04330



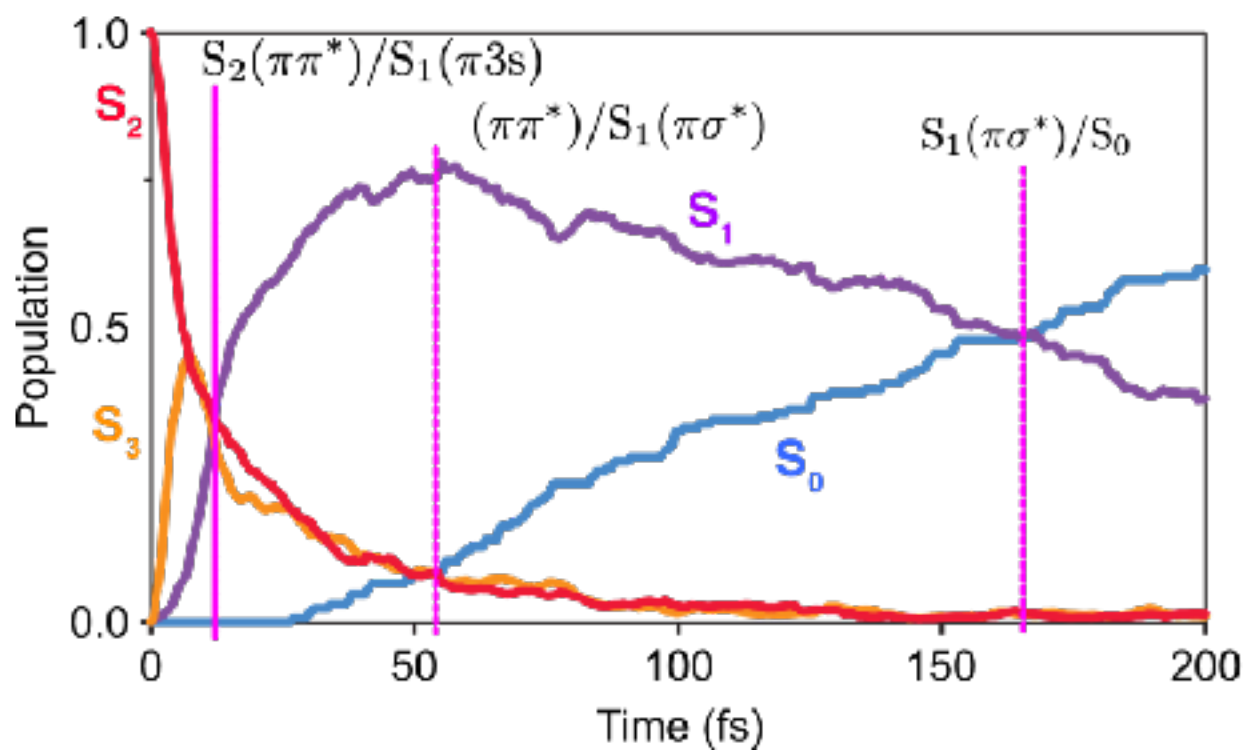
Identification of CI's

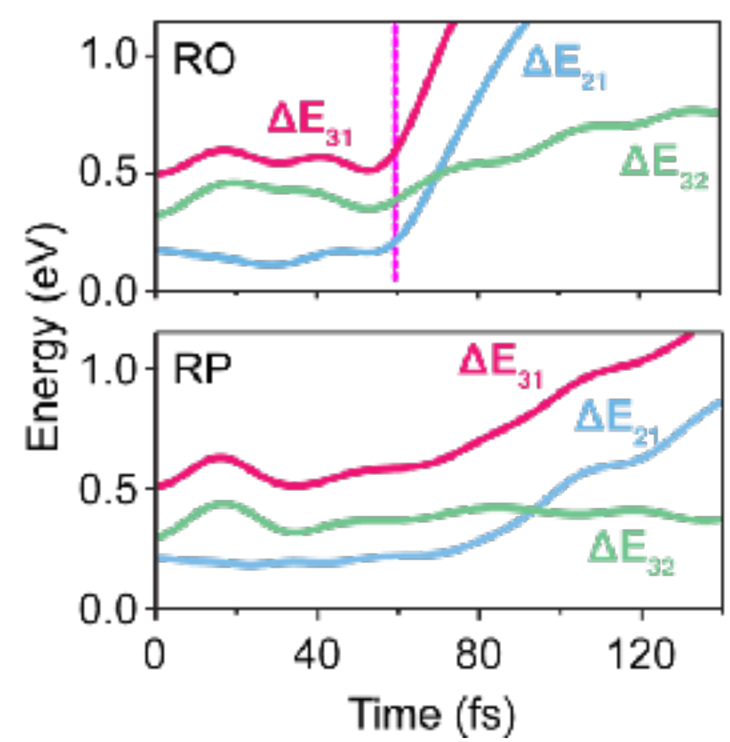
- 12 fs to CI $\pi\pi^*/\pi 3s$ and 60 THz quantum beats

  Exp: Quantum beats after ~16 fs and beats at 63 ± 9 THz

- 58 fs to CI $\pi\pi^*/\pi\sigma^*$ and 37 THz mode

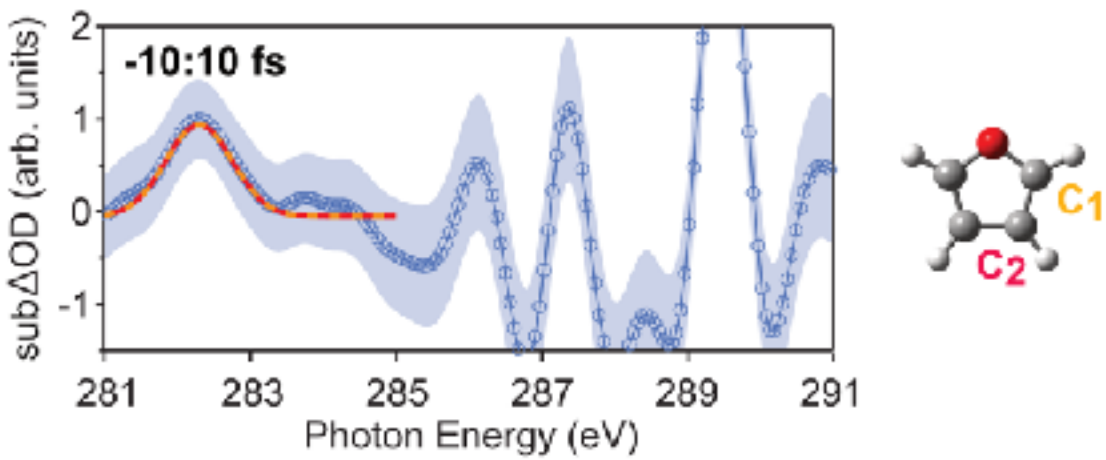
  Exp: Quantum beats shift after 80 fs to 36 ± 9 THz and decay after ~140 fs

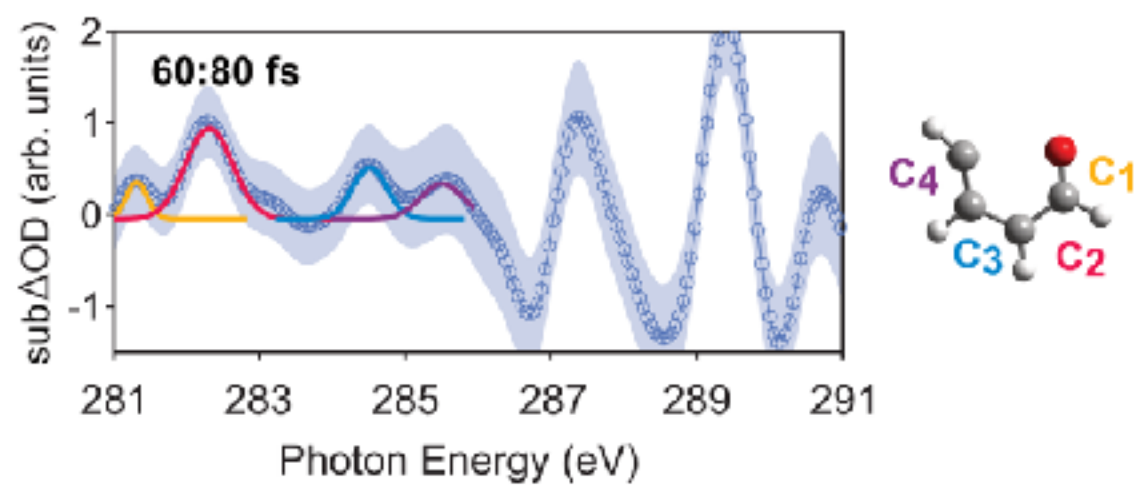




S. Severino et al. arXiv:2209.04330

RO as dominant pathway is also confirmed by symmetry change

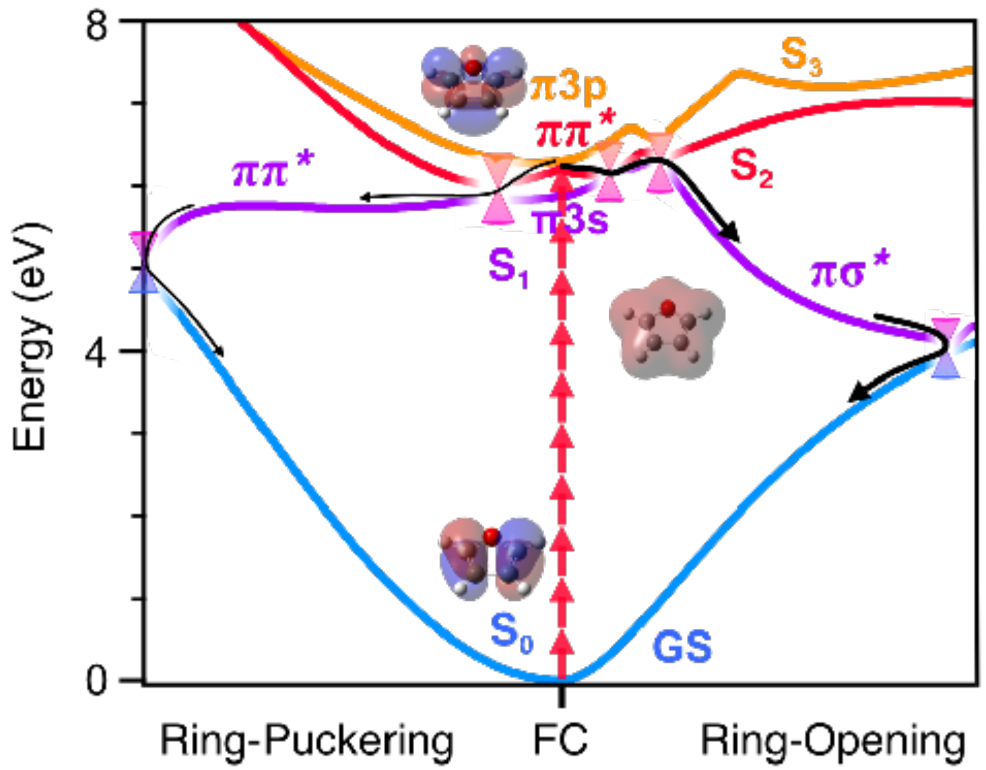


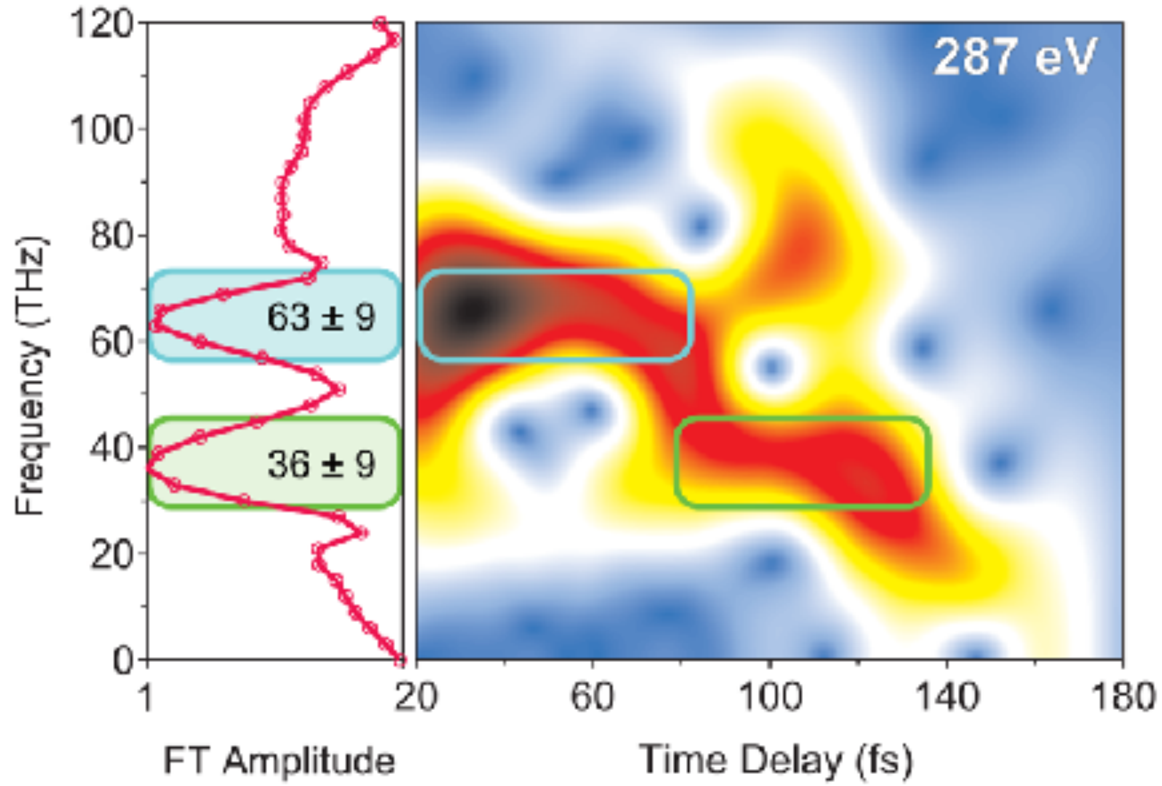


- ❖ splitting of SOMO peak for RO since the 4 C are distinct
- ❖ breakup occurs after about 60-80 fs

S. Severino et al. arXiv:2209.04330

Decay of coherence indicates new RO ground state





- ❖ vibronic coherence decays after ~140 fs
- ❖ theory predicts passage through RO CI $\pi\sigma^*/S_0$ after 158 fs
- ❖ 76% of trajectories are RO

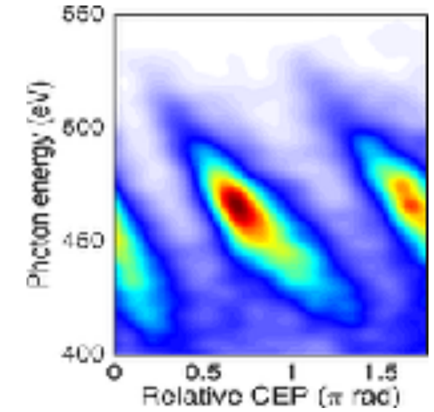
S. Severino et al. arXiv:2209.04330

Summary

❖ Attosecond soft X-rays / fully coherent SXR radiation

- Table-top attosecond soft X-ray pulses

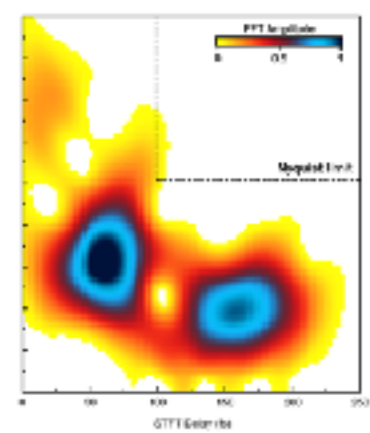
Nat. Commun. 6, 6611 (2015) Nat. Commun. 7, 11493 (2016)
Phys. Rev. X 7, 041030 (2017) Ultrafast Science 3, 4 (2023)

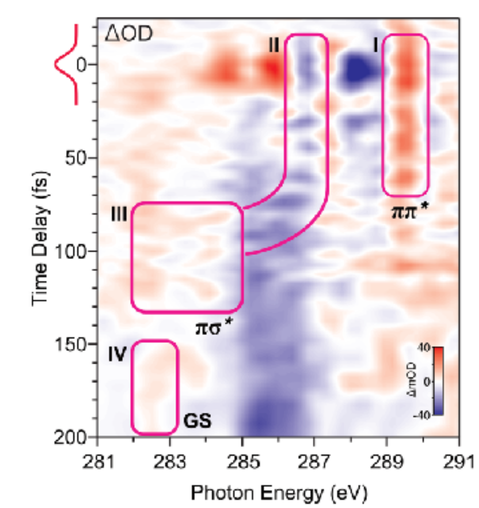


❖ Real-time electronic and nuclear dynamics in molecules / solids

- Attosecond core-level spectroscopy
- Real-time many-body interactions

Opt. Lett. 39, 5383 (2014) Optica 5, 502 (2018)
Appl. Phys. Rev. 8, 011408 (2021) Phys. Rev. X 11, 041060 (2021)
S. Severino et al. arXiv:2209.04330





Lots of exciting opportunities for time-resolved X-ray spectroscopies. HHG (XAS) and FELs (XAS, RIXS, etc)

Attoscience and Ultrafast Optics

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European Research Council
Generalitat de Catalunya
Laserlab Europe
European Commission
Fundació Privada CELLEX
Agència de Gestió d'Ajuts Universitaris i de Recerca AGAUR
Unterstützt von / Supported by Alexander von Humboldt Stiftung/Foundation
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