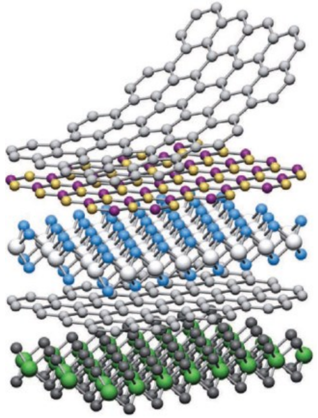
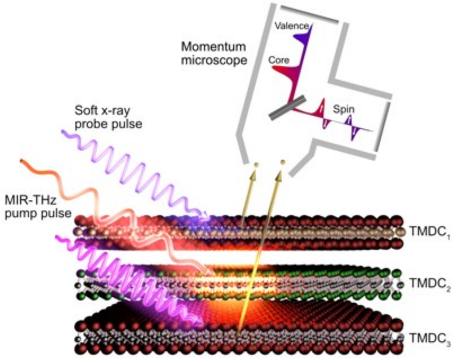
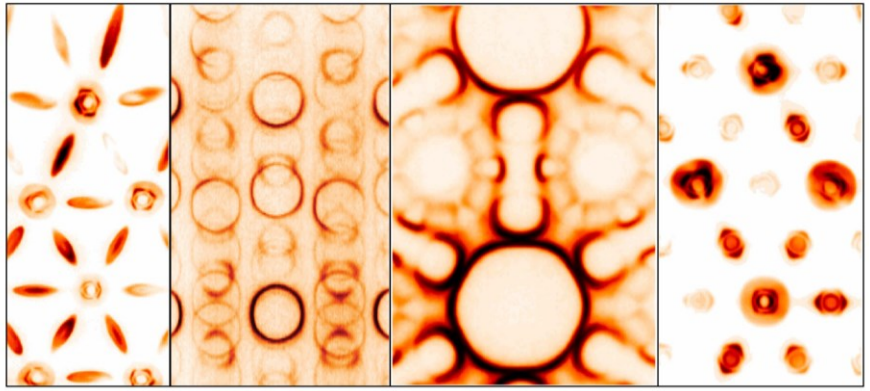
Exploring Quantum Materials with X-ray Spectroscopy, Part 2







Markus Scholz
Hamburg, 4th August 2025

HELMHOLTZ

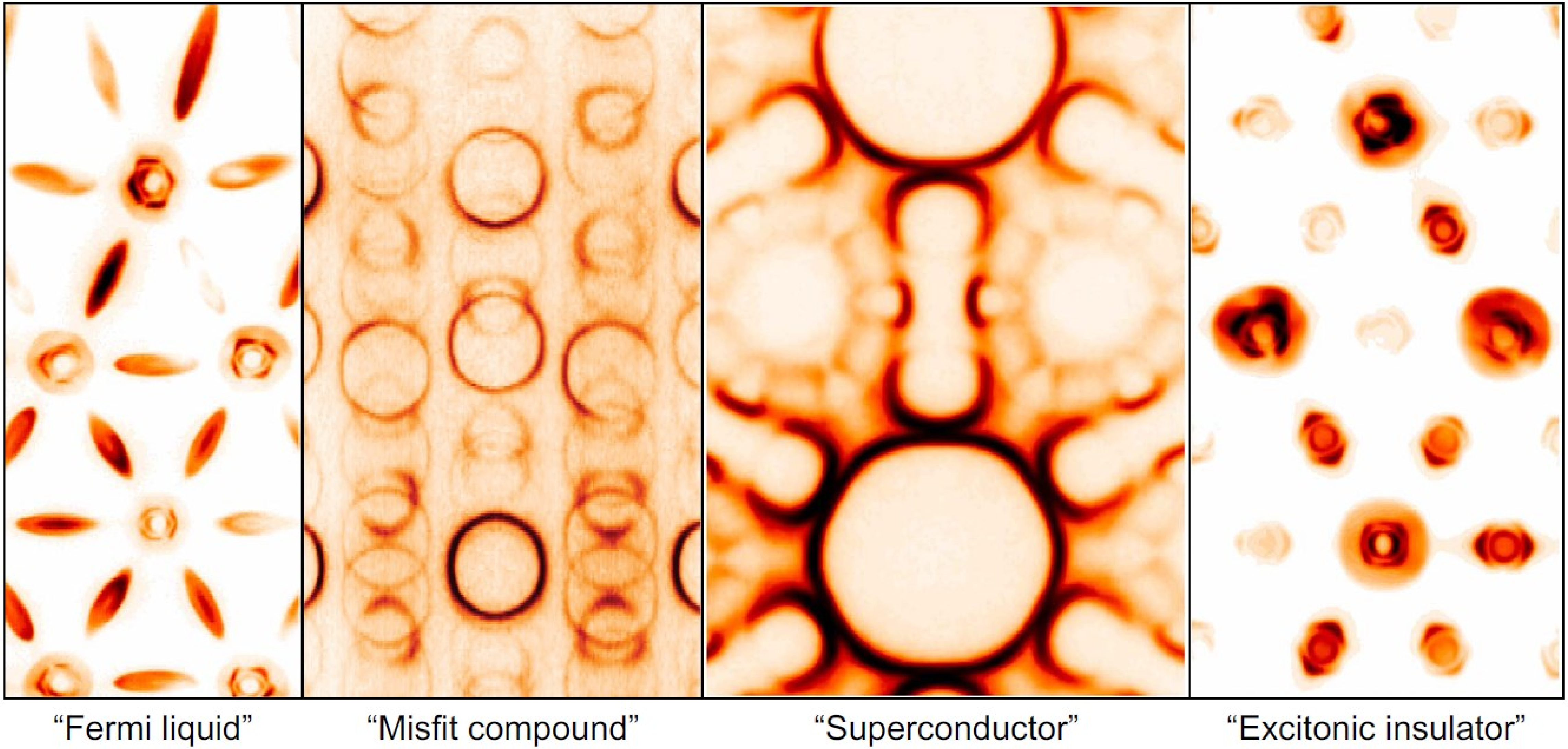
DESY.

Photoemission (“ARPES”) and metals

toutestquantique.fr

Momentum (“velocity”) maps

Imaging of “exotic” electronic structures

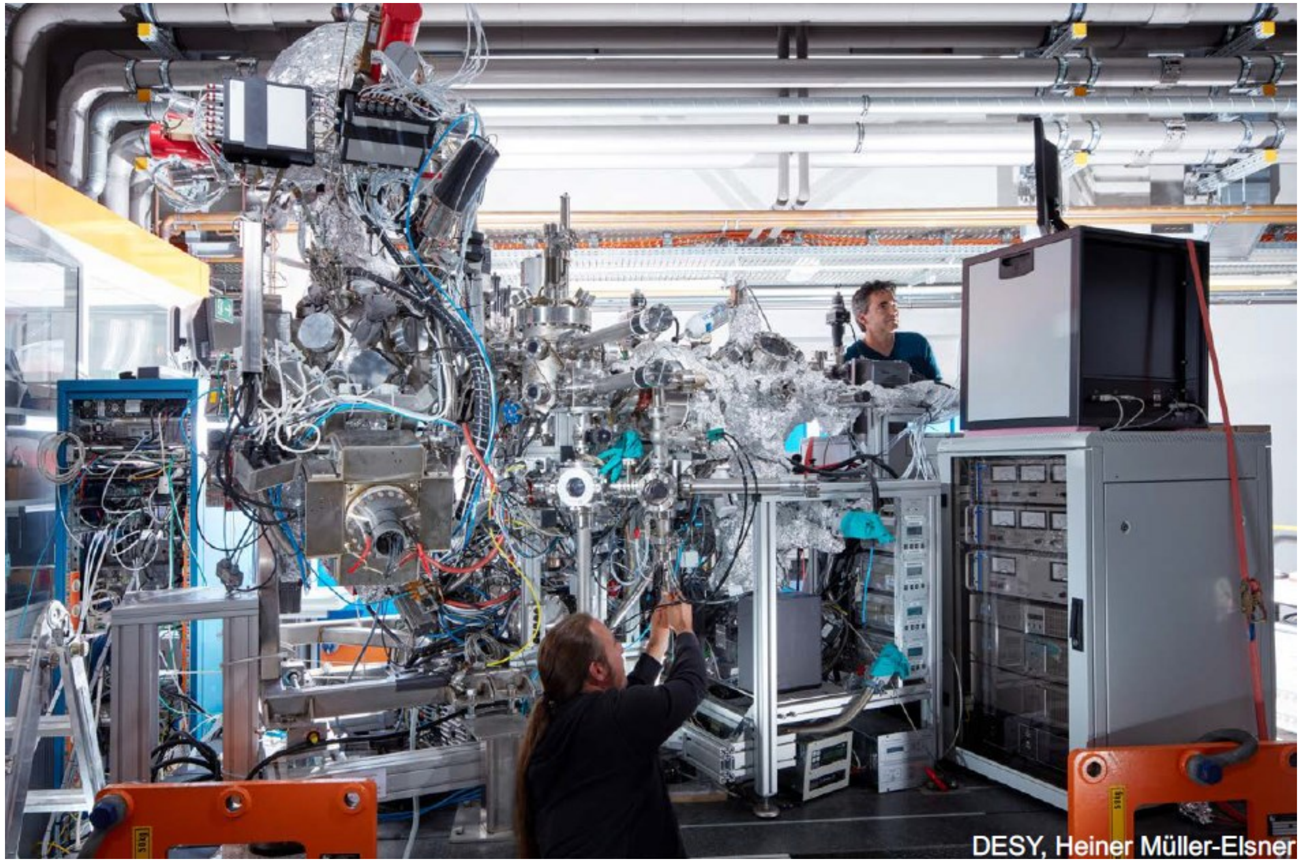


Soft x-rays @ DESY (EuXFEL)

For nanoscopic & femtostroboscopic electronic structure imaging

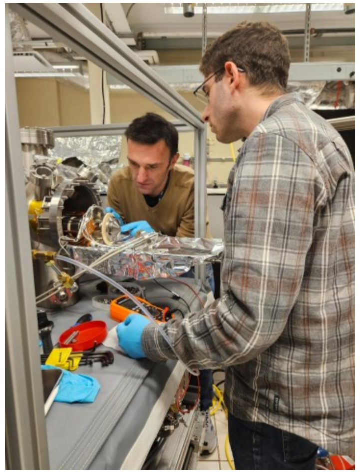
ARPES at PETRA III, DESY

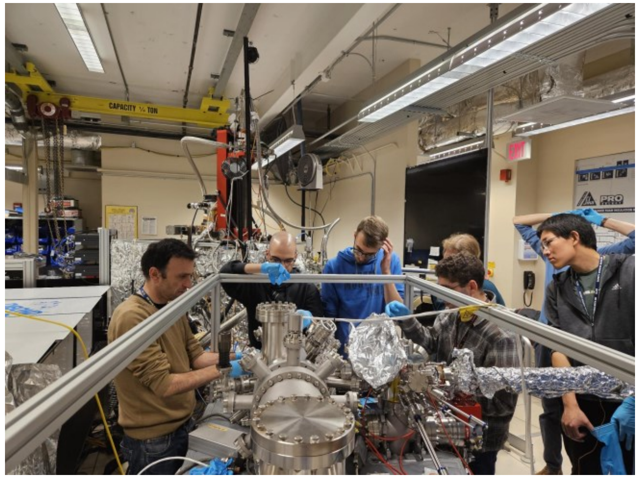
Hemispherical Analyzer



Experiment at LCLS-II, Stanford

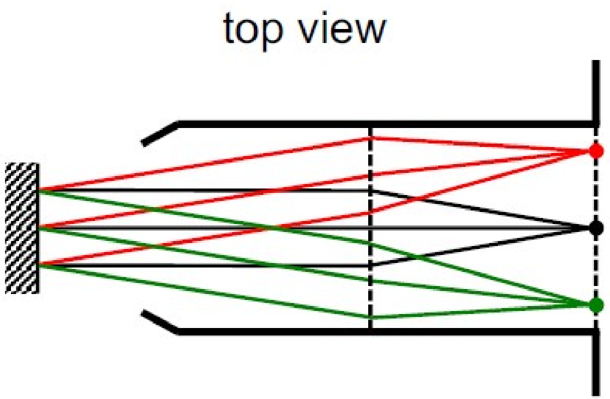
Time-of-flight Analyzer

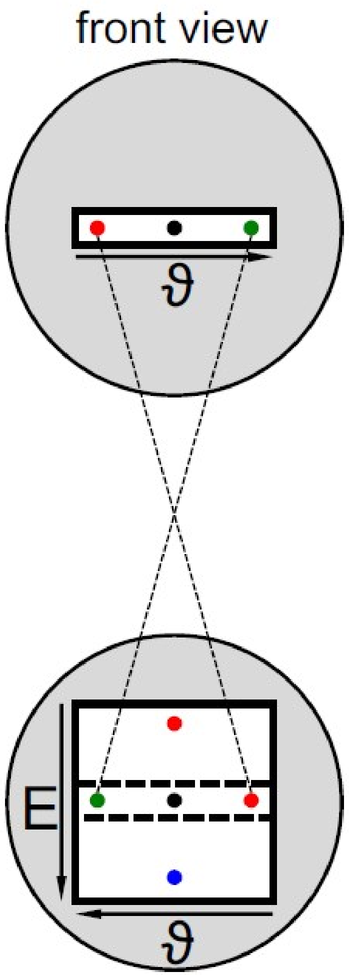


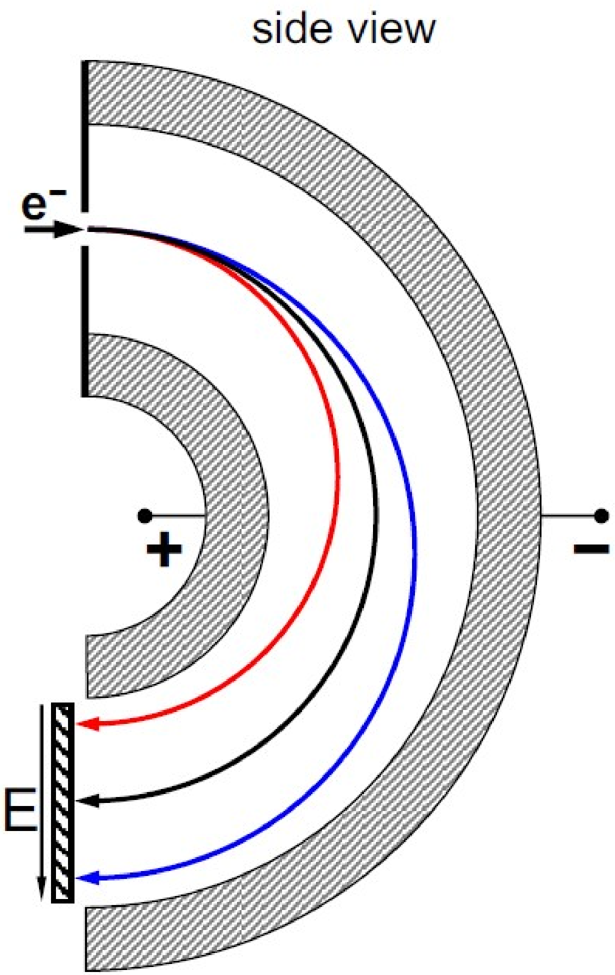


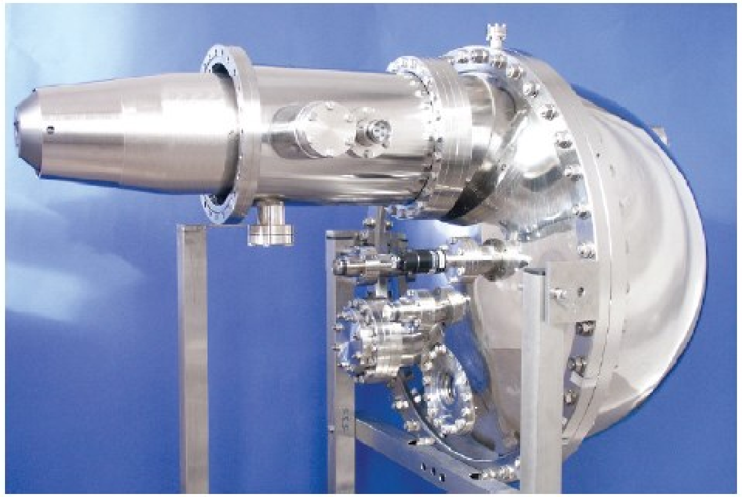
Angle-resolving hemispherical deflection analyzer

2D angle-energy imaging



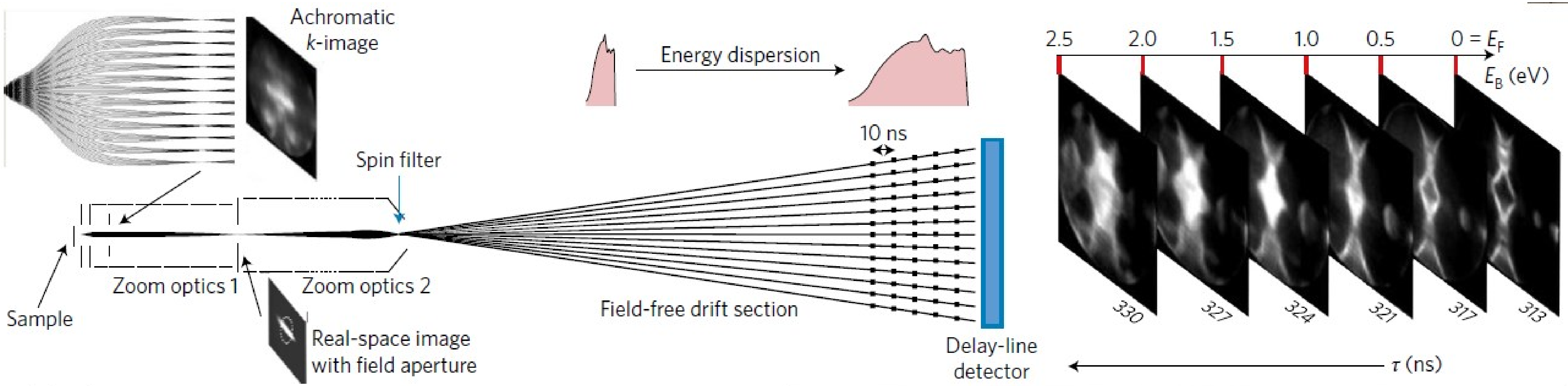


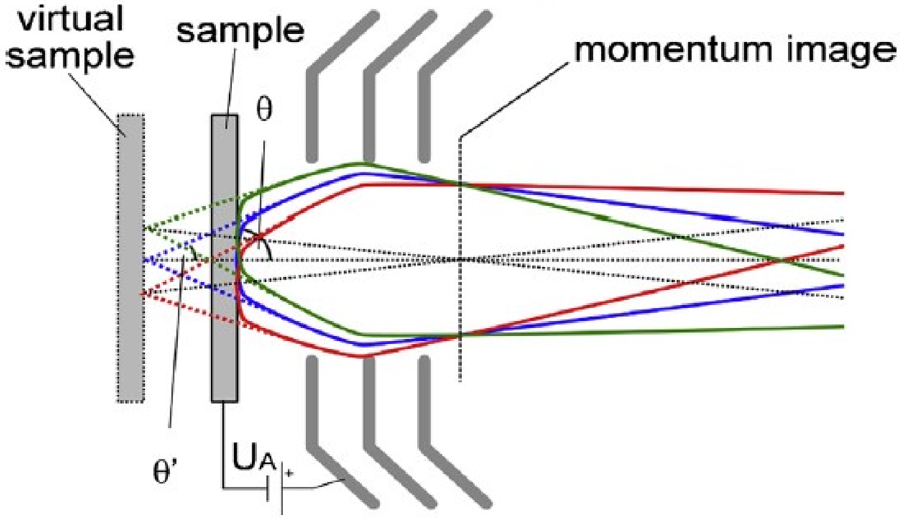


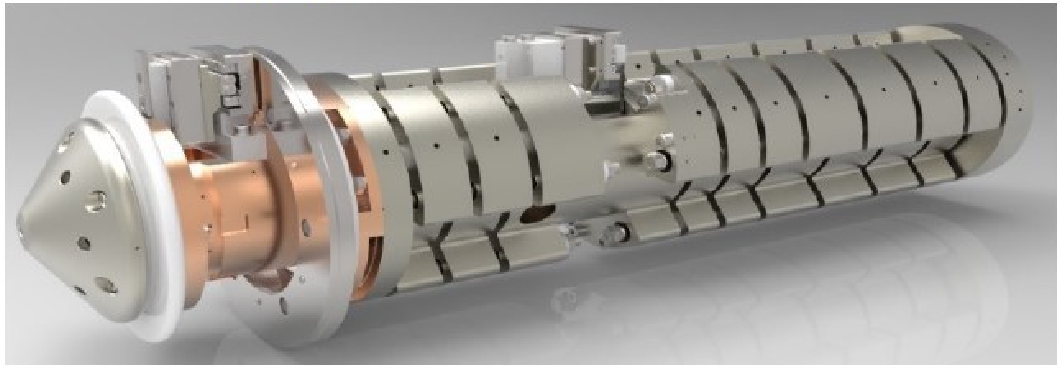


Time-of-flight momentum microscope

3D momentum-energy imaging



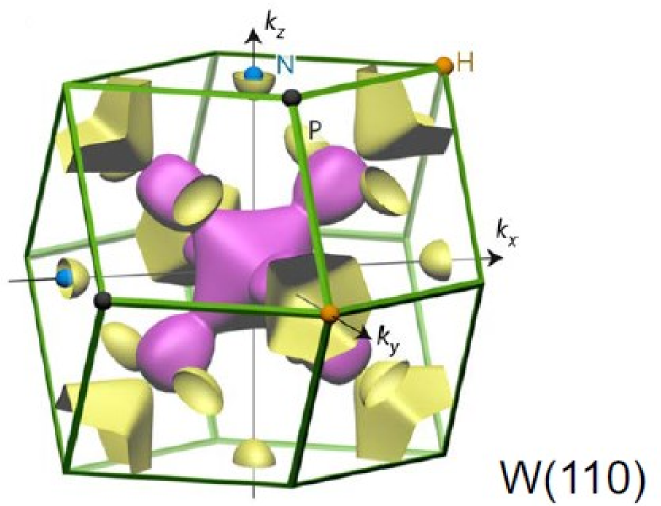


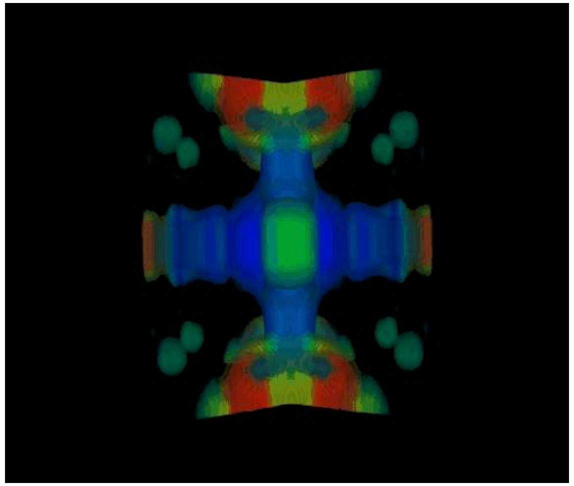


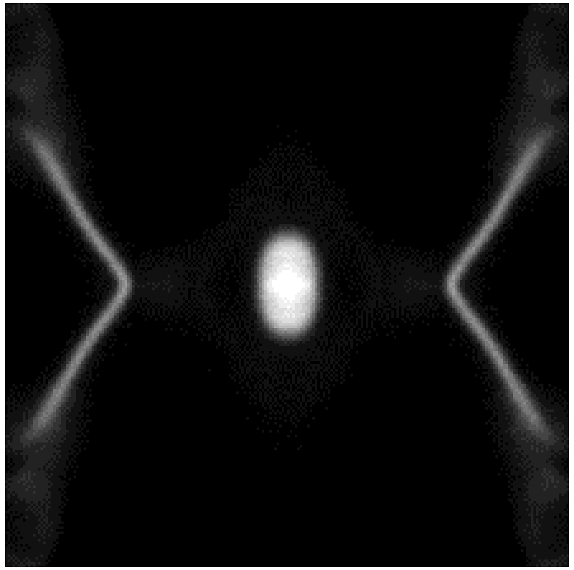
Medjanik *et al*., Nat. Mater. **16**, 615 (2017)
Kotsugi *et al*., Rev. Sci. Instrum. **74**, 2754 (2003)
Tusche *et al*., Ultramicroscopy **159**, 520 (2015)

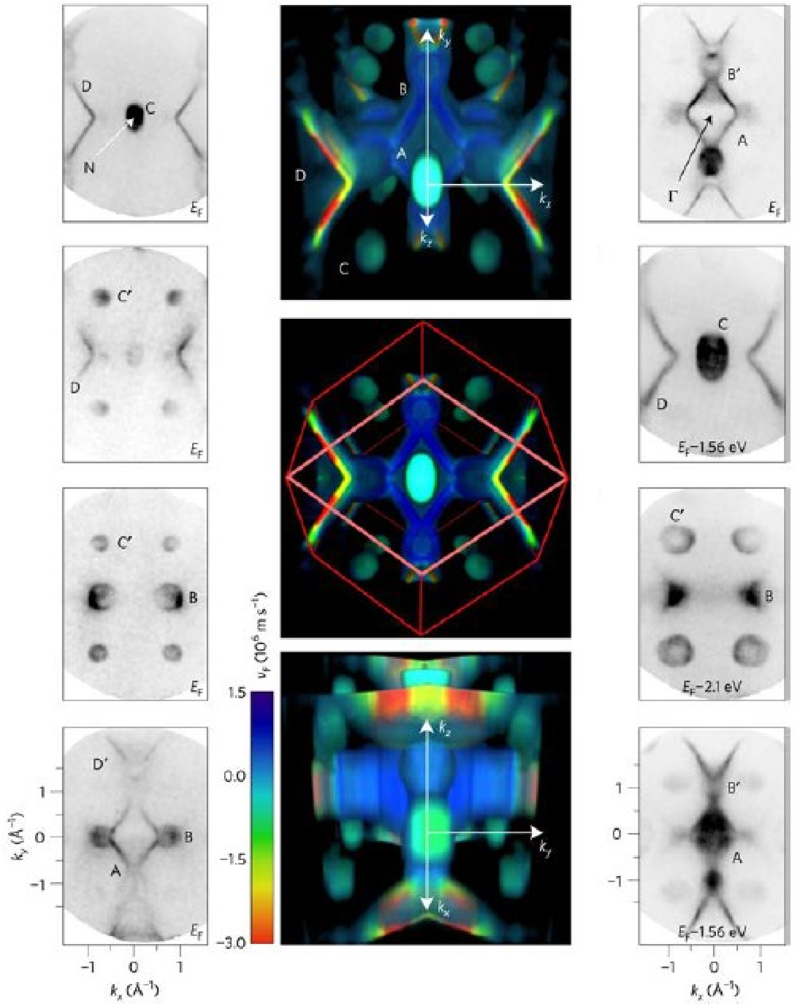
Soft x-ray time-of-flight momentum microscopy

4D momentum-energy imaging







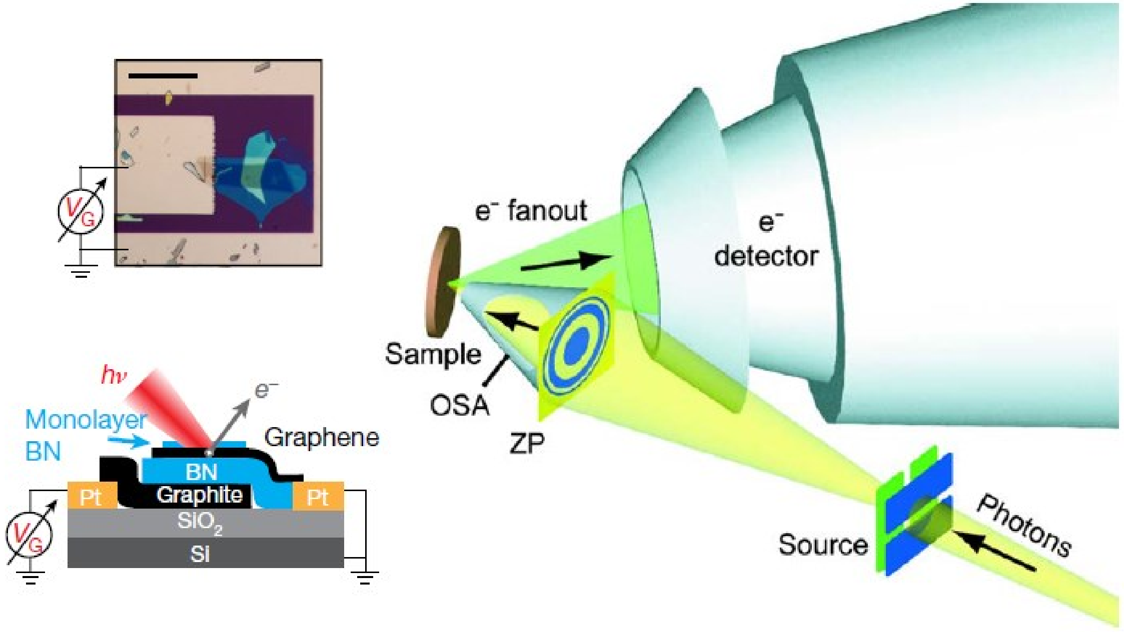


Medjanik *et al.*, Nat. Mater. **16**, 615 (2017)

Advanced photoelectron spectroscopy

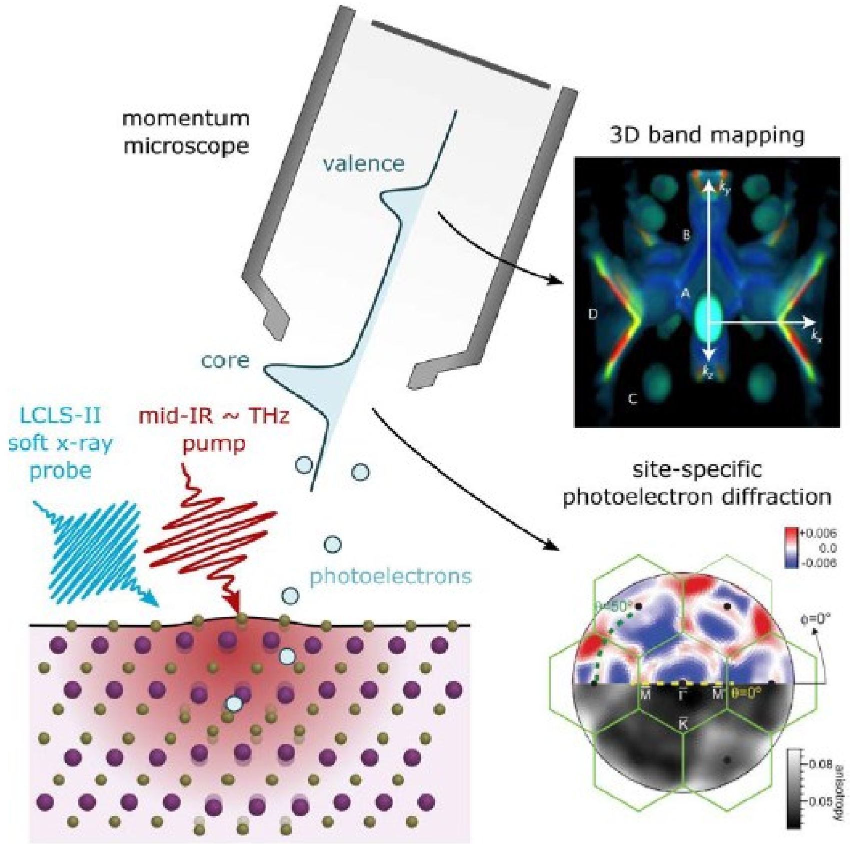
Probing nonequilibrium electronic structure at nanometer & femtosecond scales

In operando **nano/micro**-ARPES



Nguyen *et al.*, Nature **572**, 220 (2019)
Rotenberg & Bostwick, J. Synchrotron Rad. **21**, 1048 (2014)

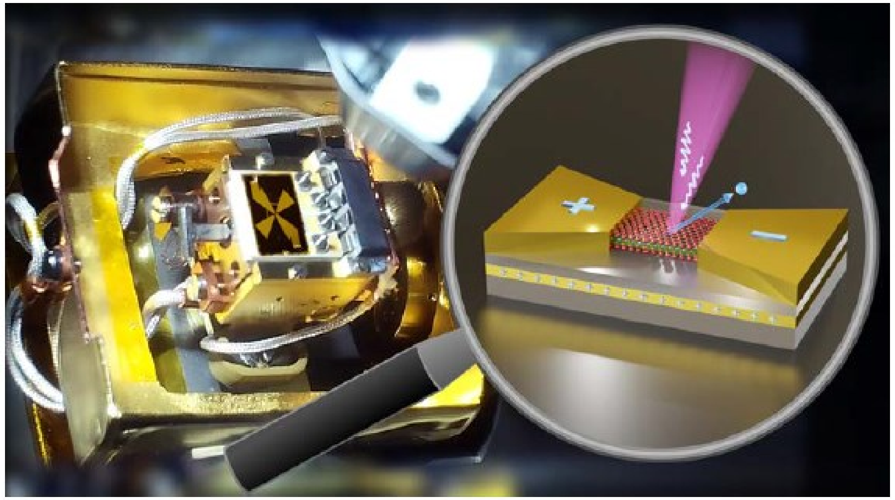
Femto-stroboscopic momentum microscopy

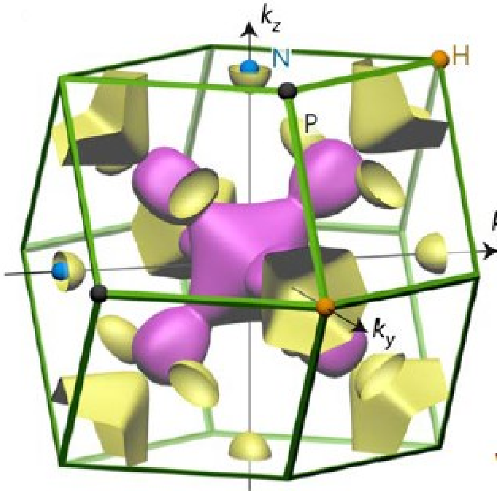


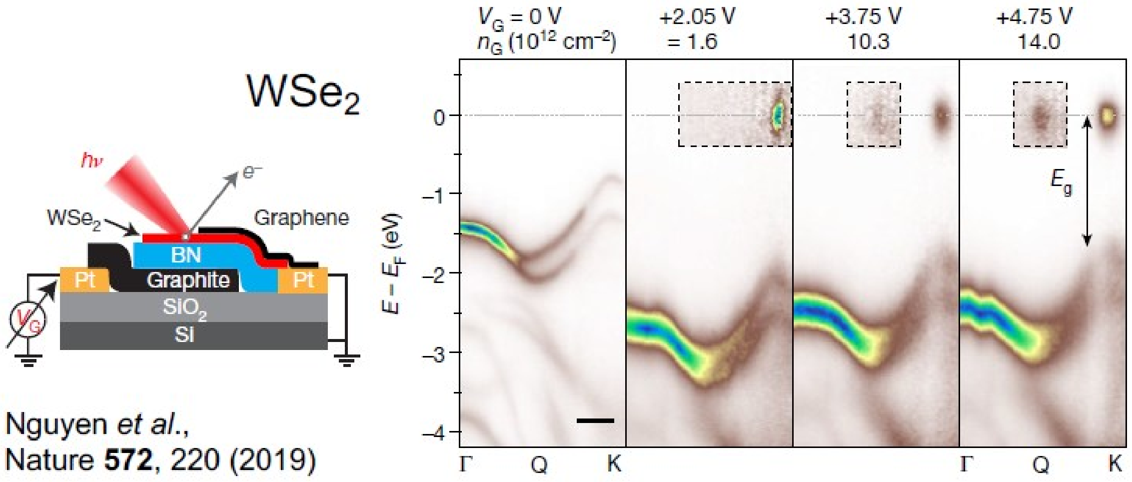
© Jonathan Sobota (Stanford)

In operando ARPES

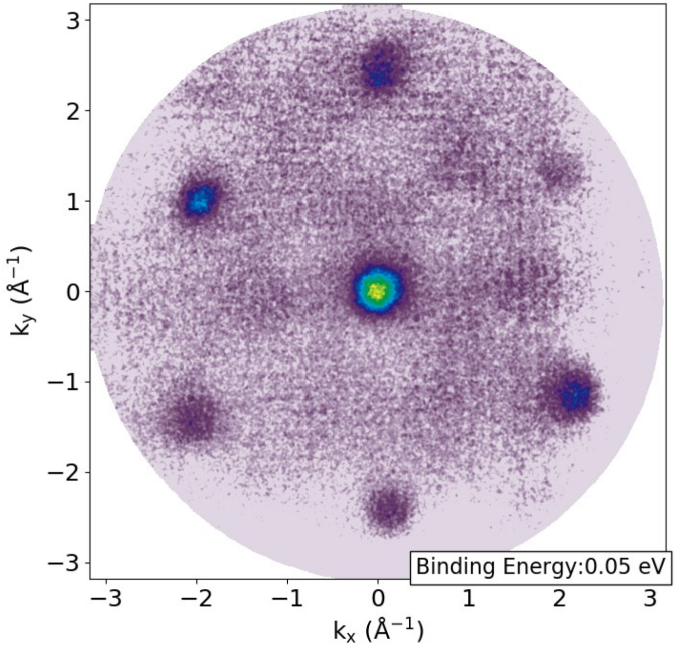
Electronic structure in devices under bias





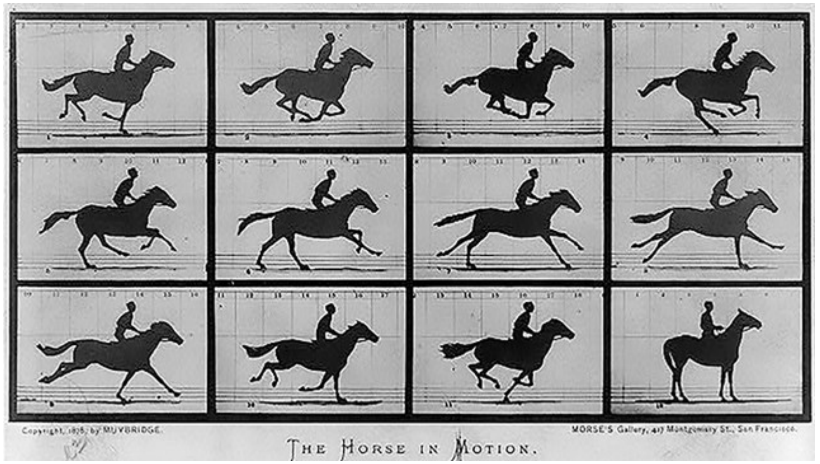


Nguyen *et al.*,
Nature **572**, 220 (2019)



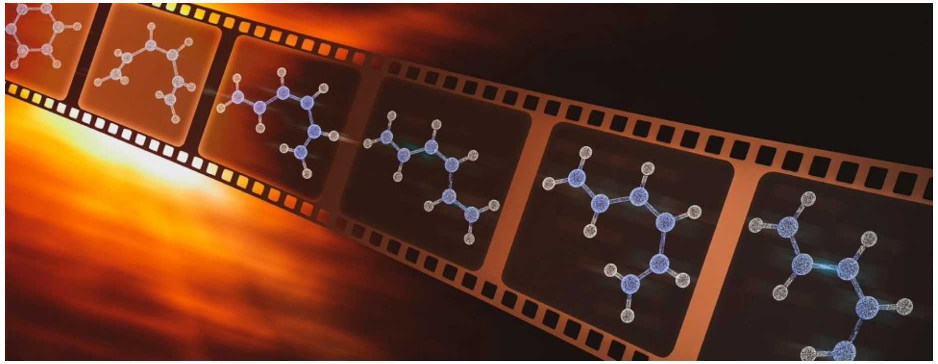
Making a Electron and Molecular Movie

$10^{-3}\ s$
milliseconds

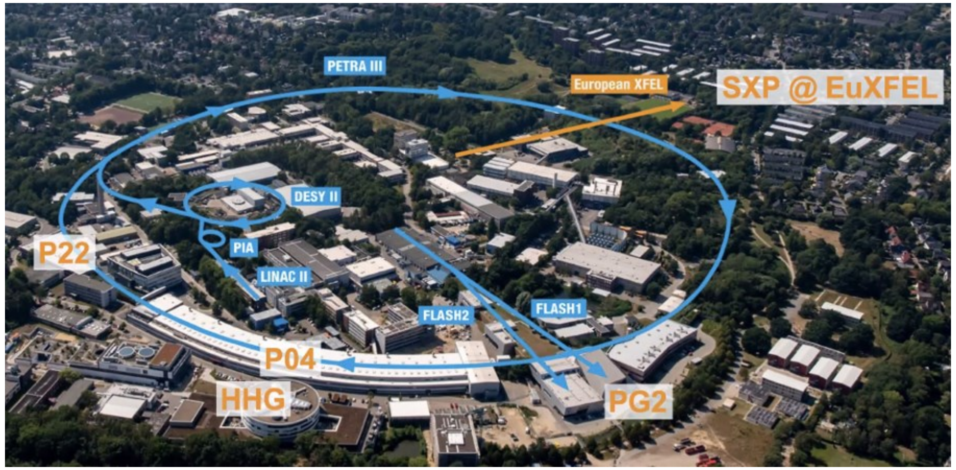


„snapshot photography"
E. Muybridge, 1878

$10^{-18}\ s$
Attoseconds



Today. (Image taken from SLAC webpage)

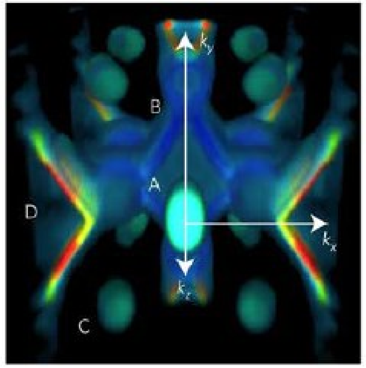


DESY, Hamburg

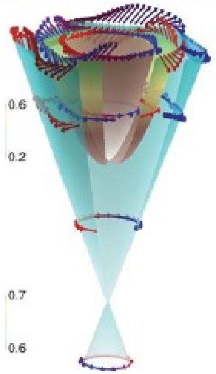
New functionality at interfaces

What are the relevant time scales?

Band structure



Spin structure



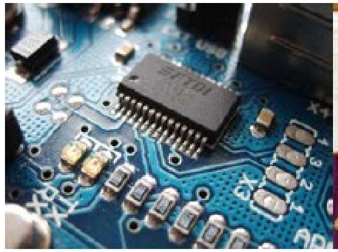
Electron hopping

$$\tau_{\mathrm{e}} = \frac{h}{W} = \mathcal{O}\left(\frac{h}{1\,\mathrm{eV}}\right) = \mathcal{O}(4\,\mathrm{fs})$$

Exchange interaction

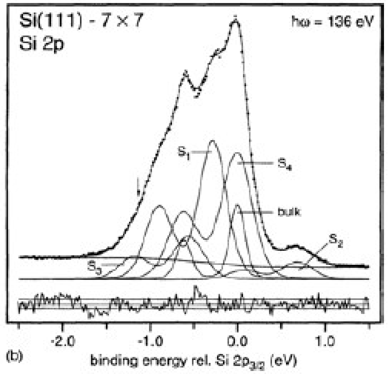
$$\tau_{\mathrm{spin}} = \frac{h}{J_{\mathrm{ex}}} = \mathcal{O}\left(\frac{h}{100\,\mathrm{meV}}\right) = \mathcal{O}(40\,\mathrm{fs})$$

Electronics

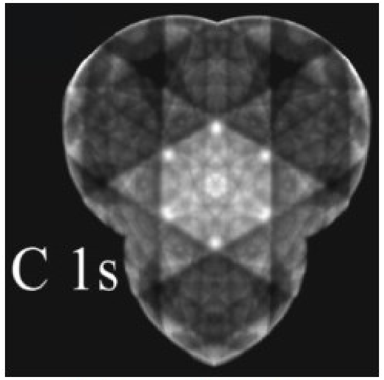


Spintronics

STRUCTURE — DYNAMICS (Electrons at interfaces!) — FUNCTION



Chemical structure



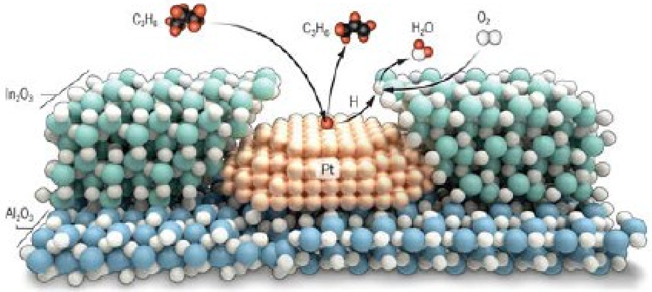
Lattice structure

Charge transfer

$$\tau_{\mathrm{CT}} = \mathcal{O}(\tau_{\mathrm{e}}) = \mathcal{O}(\tau_{\mathrm{core}}) = \mathcal{O}(4\,\mathrm{fs})$$

Lattice vibration

$$\tau_{\mathrm{ph}} = \frac{h}{E_{\mathrm{ph}}} = \mathcal{O}\left(\frac{h}{10\,\mathrm{meV}}\right) = \mathcal{O}(400\,\mathrm{fs})$$

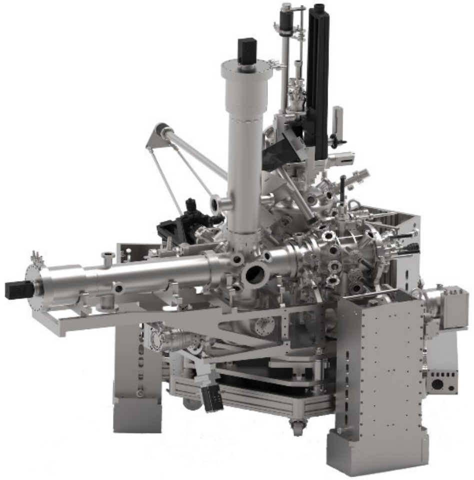


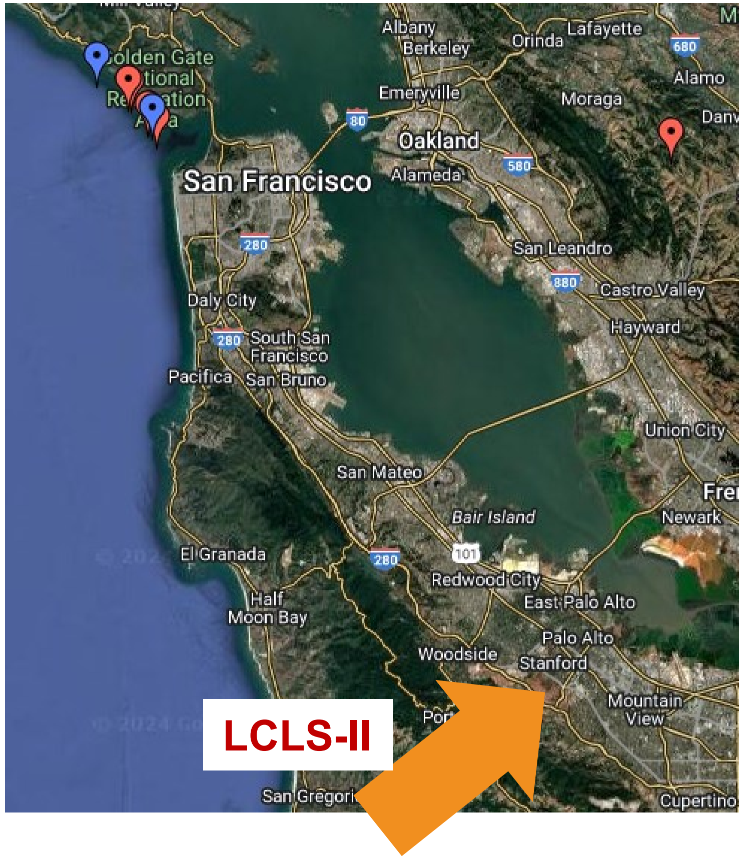
Catalysis

Pump-probe technique

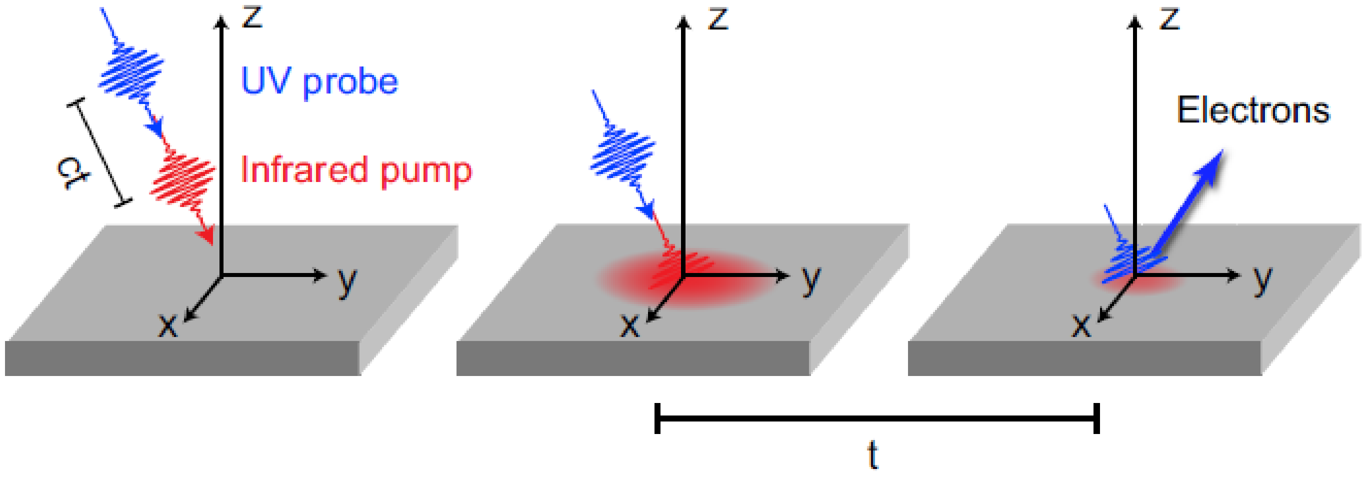
toutestquantique.fr

Synchrotron and FELs at DESY and SLAC





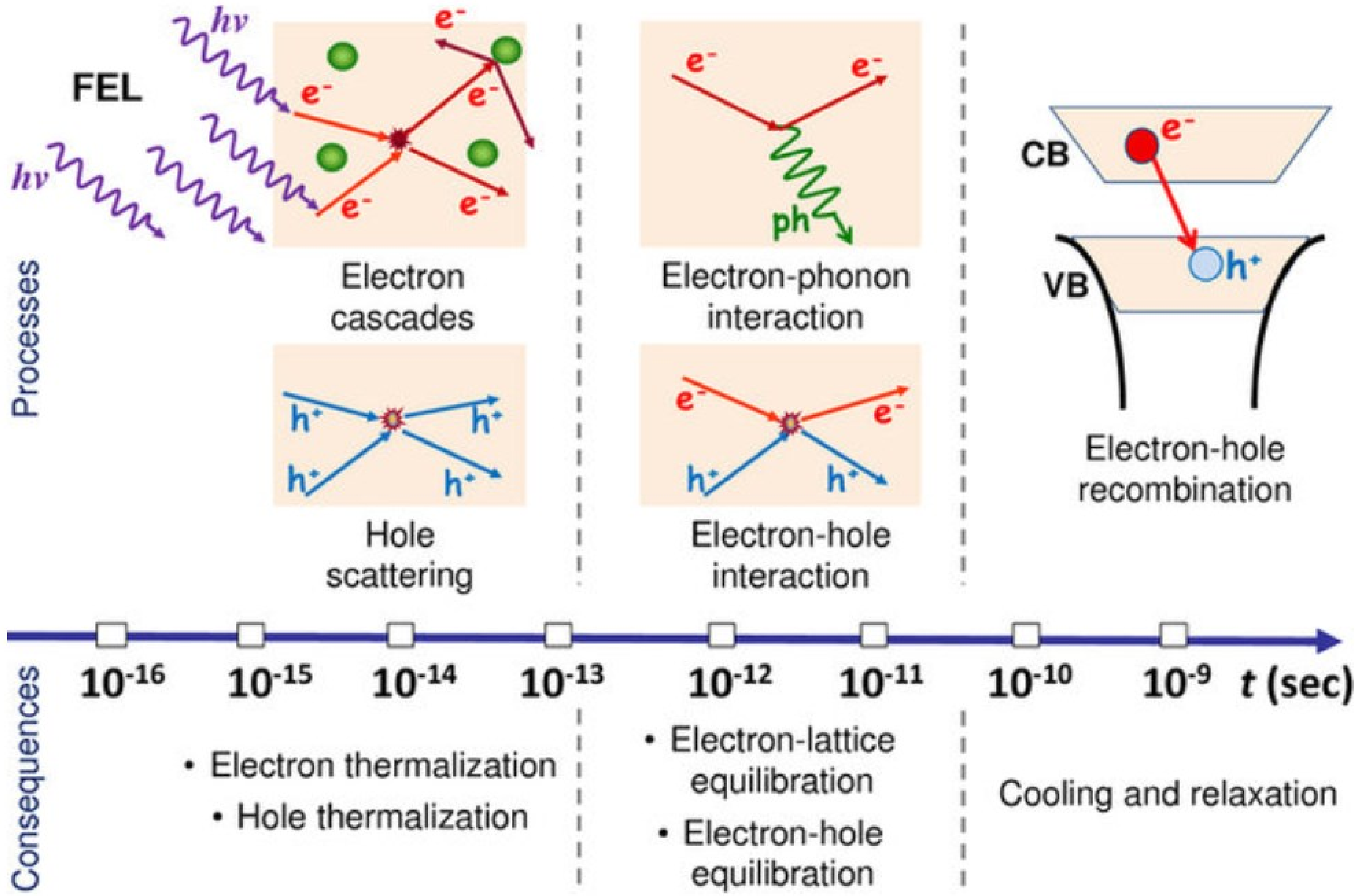
Time-resolved photoelectron spectroscopy



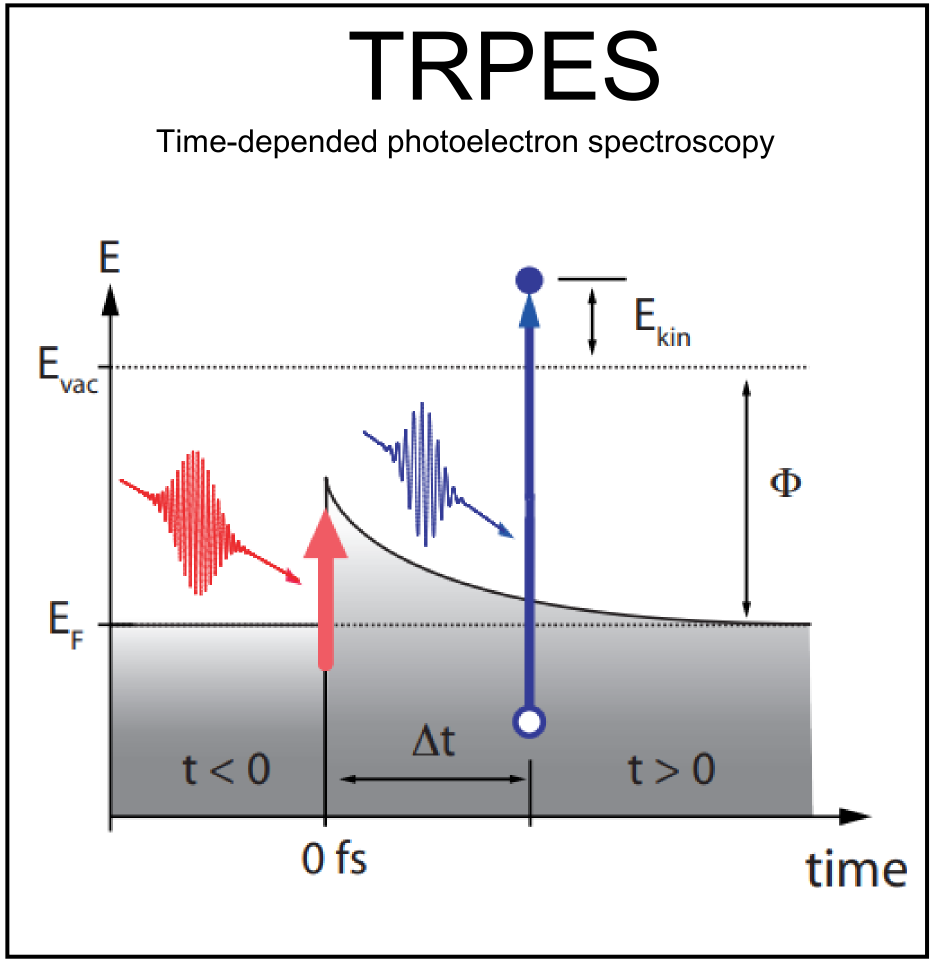
Time-resolved photoemission measurement :

- can offer the real-time study of the dynamics of the electronic state in condensed matter
- used in investigation of the binding energies, dispersion and lifetimes of the electronic state on clean metal surface

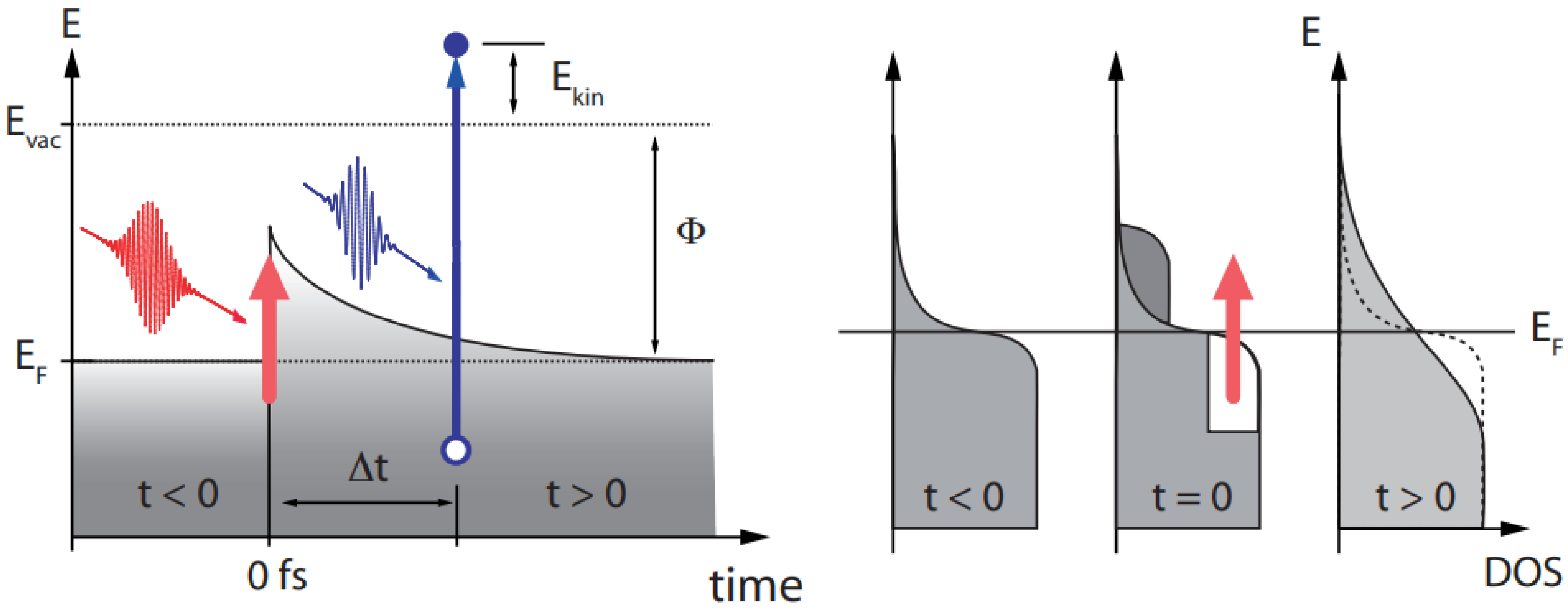
Why time-resolved? Observe and disentangle different processes



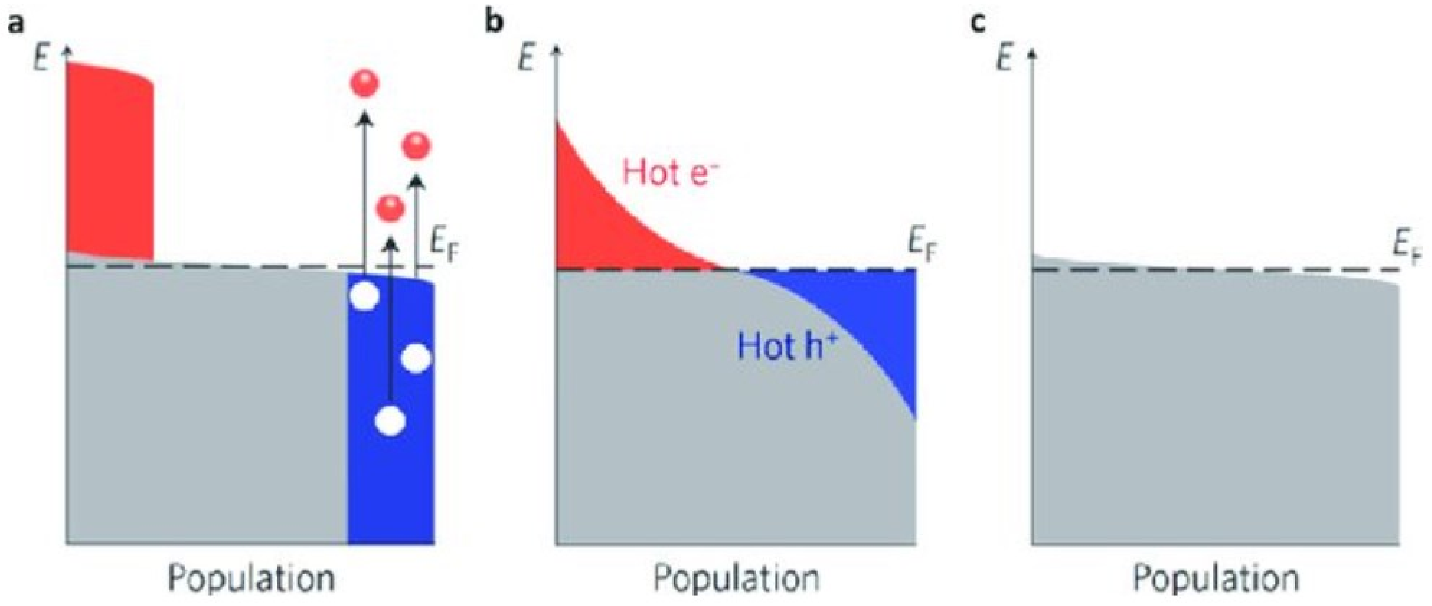
Time-resolved photoelectron spectroscopy



Time-resolved photoelectron spectroscopy



Time-resolved photoelectron spectroscopy



Timeline of thermalization and equilibration

Excitation at the surface and ***ballistic electron motion***. Ballistic electron motion increases effective penetration depth of excitation.

Electrons reform a hotter FD-distribution from e-e scattering, after a finite thermalization time, and begin ***diffusion into the bulk***

On the ps timescale, electrons and phonons scatter, and equilibrate. Standard heat diffusion thereafter.

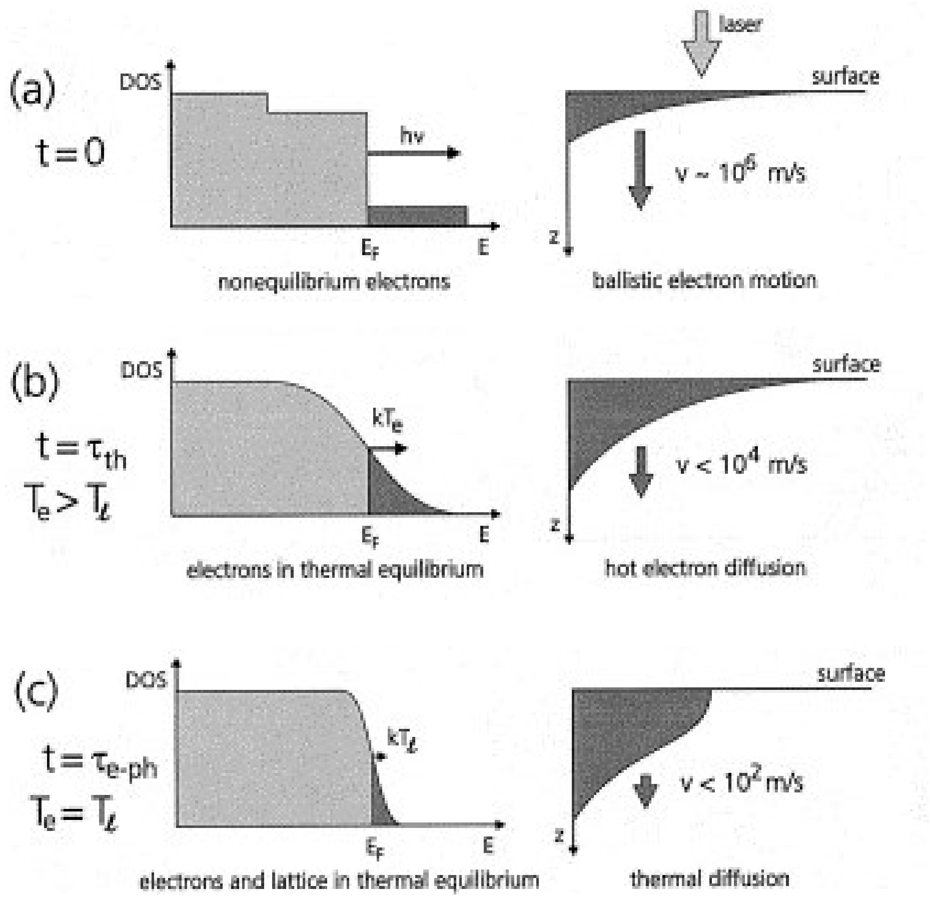
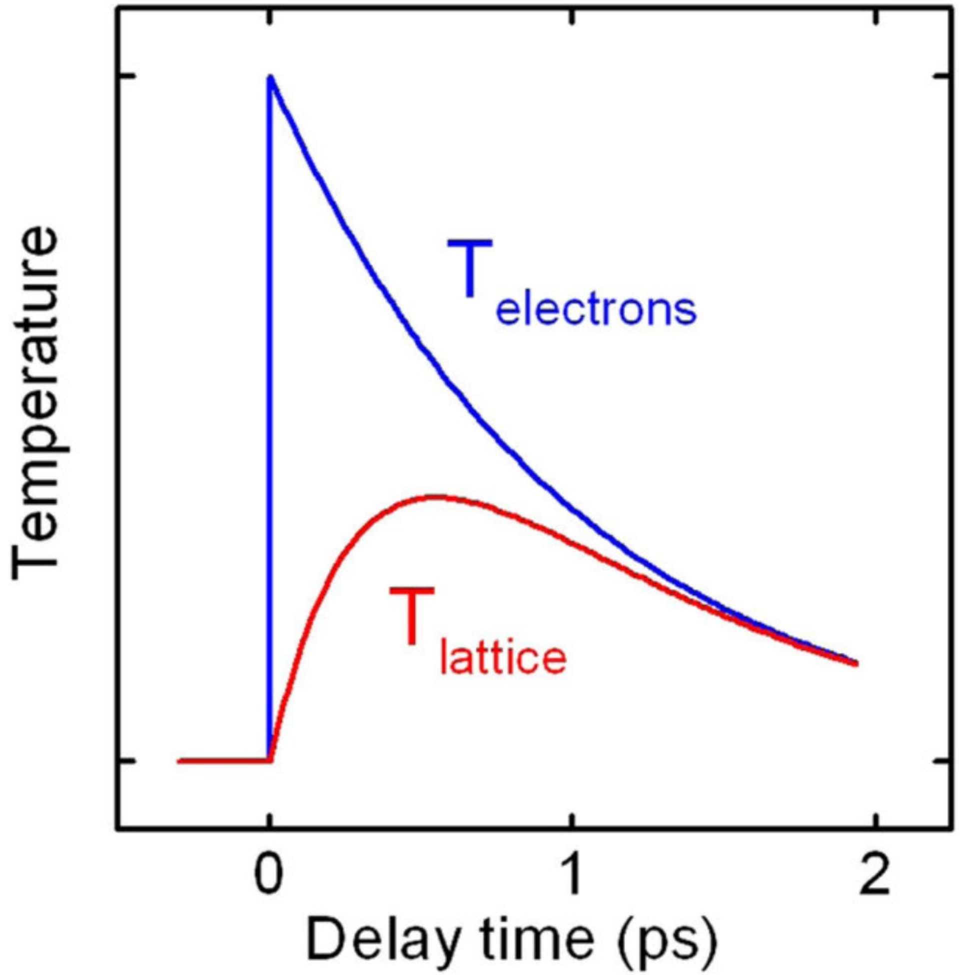
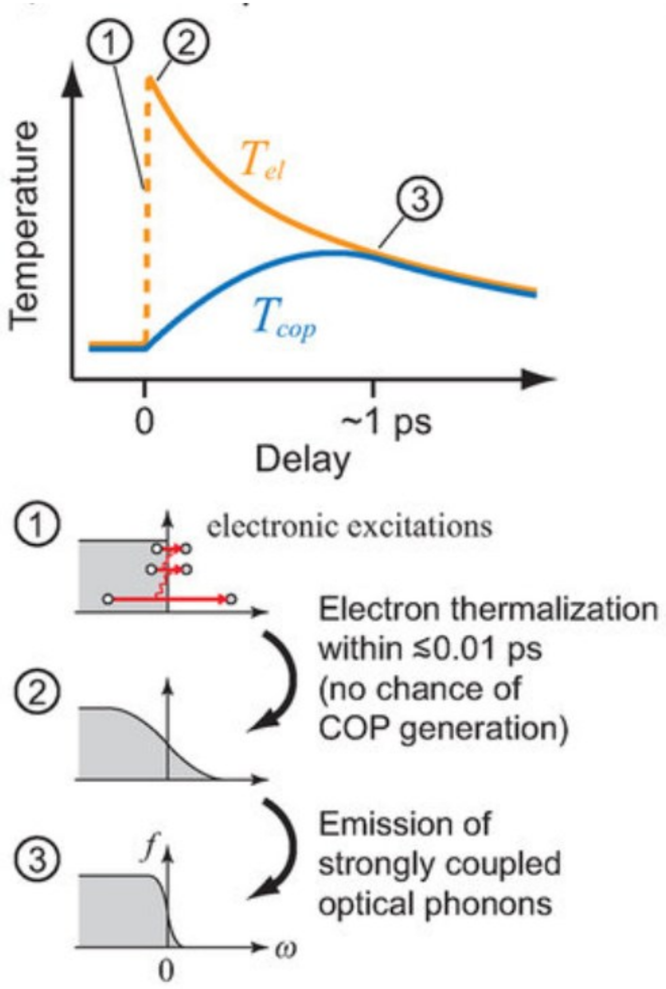


Figure from: J. Hohlfeld et al, Chem Phys. (2000).

Timeline of thermalization and equilibration





Two-temperature model

- We use the two-temperature model to calculate emittance growth due to ultrafast heating in Cu.
  - Electrons and lattice are treated as interacting thermalized subsystems

Electron thermal conduction

Electron-phonon coupling

Laser source term

Electron T_e: $$C_e(T_e)\frac{\partial}{\partial t}T_e = \frac{\partial}{\partial z}\left(K_e(T_e)\frac{\partial}{\partial z}T_e\right) - g(T_e - T_l) + S(t,z)$$

Lattice T_l: $$C_l(T_l)\frac{\partial}{\partial t}T_l = g(T_e - T_l)$$

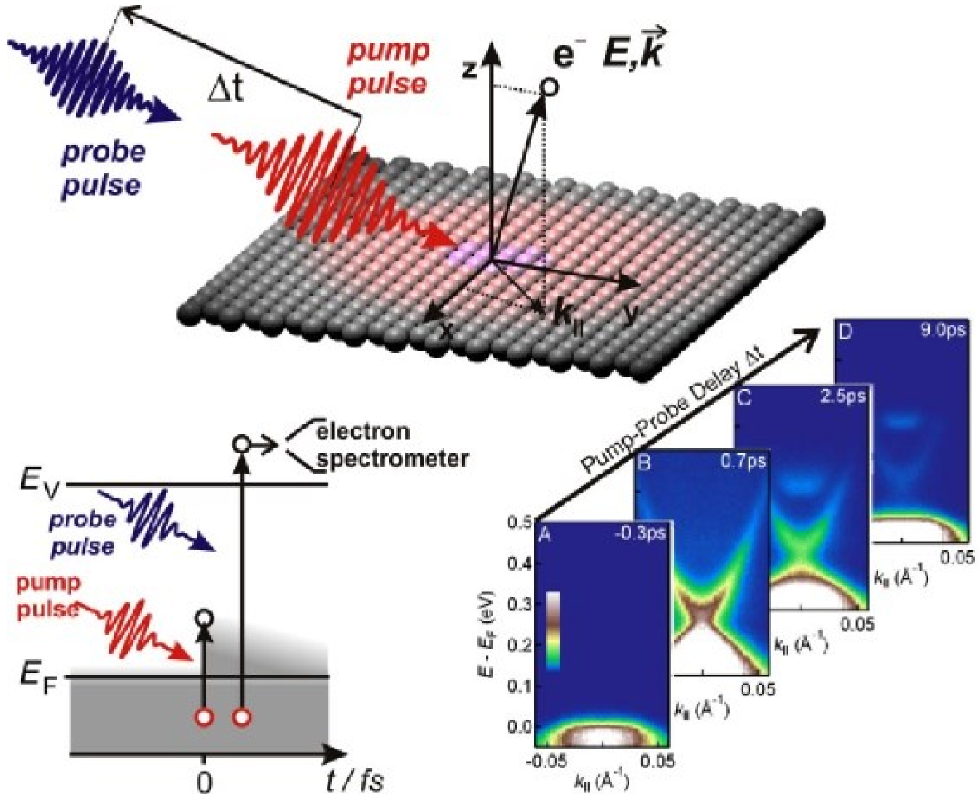
Source term: $$S(t,z) = \frac{(1-R)F_0}{\sqrt{2\pi}\sigma_t d_p}\exp\left[-\frac{(t-t_0)^2}{2\sigma_t^2} - \frac{z}{d_p}\right]$$

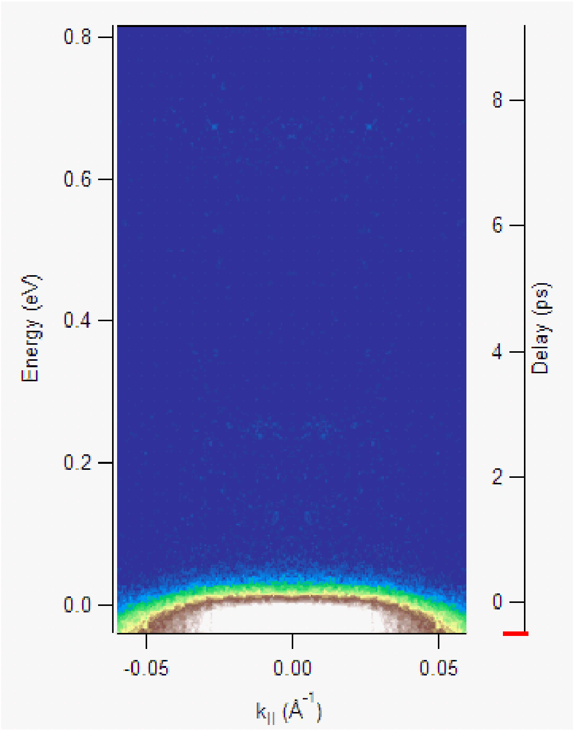
→ Penetration depth

Phenomenological, but…
… it works!

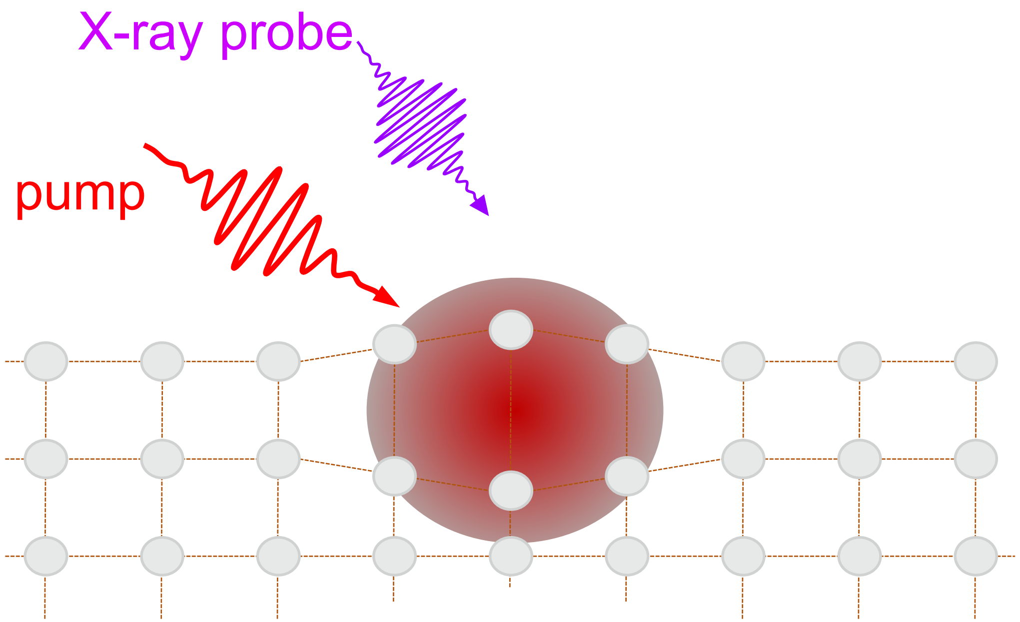
J. Hohlfeld et al, Chem Phys. (2000).

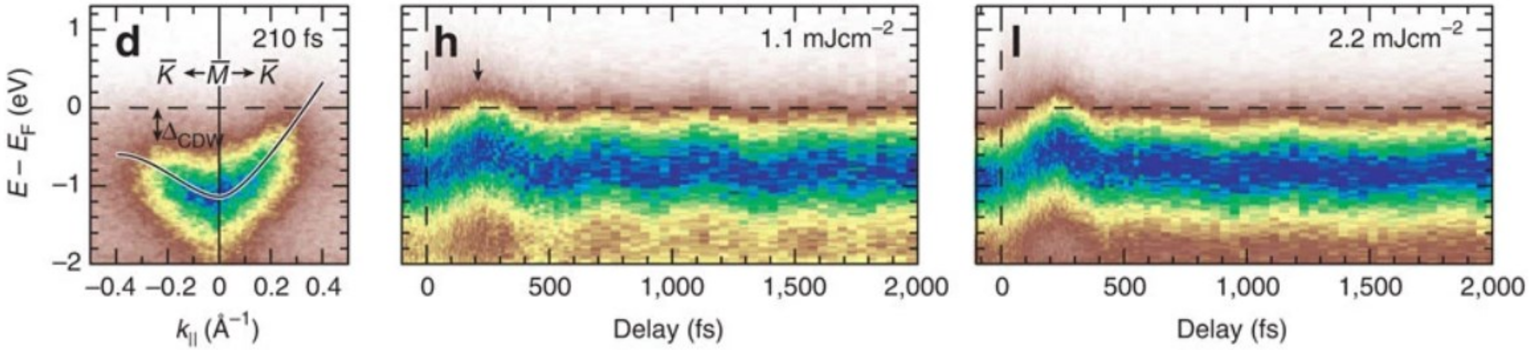
Time-resolved photoelectron spectroscopy





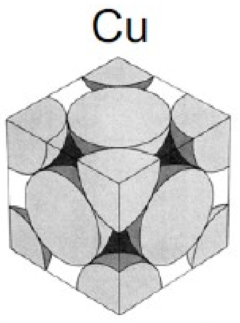
Types of Charge-Density-Wave Insulators





From static properties to dynamic function

What are the relevant time scales?



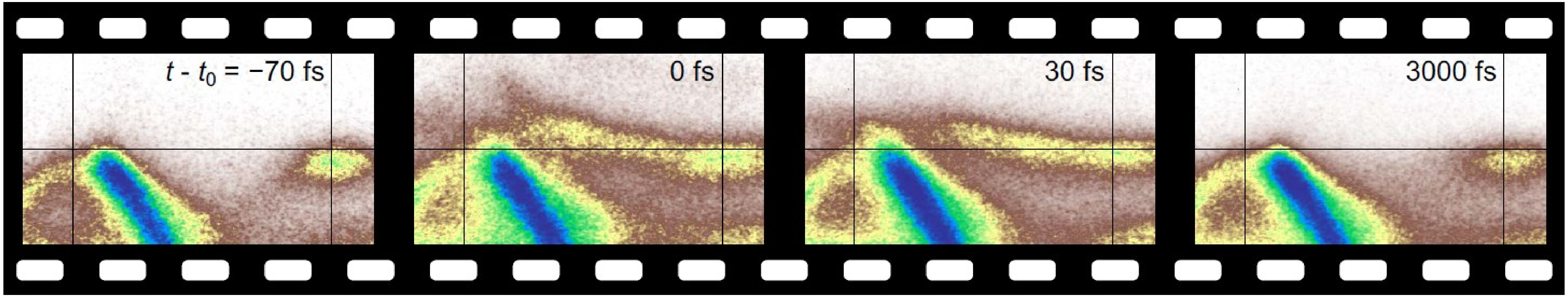
$$a = 3.61\,\text{Å}$$

Electrons (at E_F): $v_e = 1.6 \times 10^6\,\text{m/s} \curvearrowright \frac{a}{v_e} = 0.23\,\text{fs}$

Atomic lattice: $v_s \approx 3.6 \times 10^3\,\text{m/s} \curvearrowright \frac{a}{v_s} \approx 100\,\text{fs}$

$$1\,\text{fs} = 10^{-15}\,\text{s} = 0.000\,000\,000\,000\,001\,\text{s} = \frac{0.3\,\mu\text{m}}{c}$$

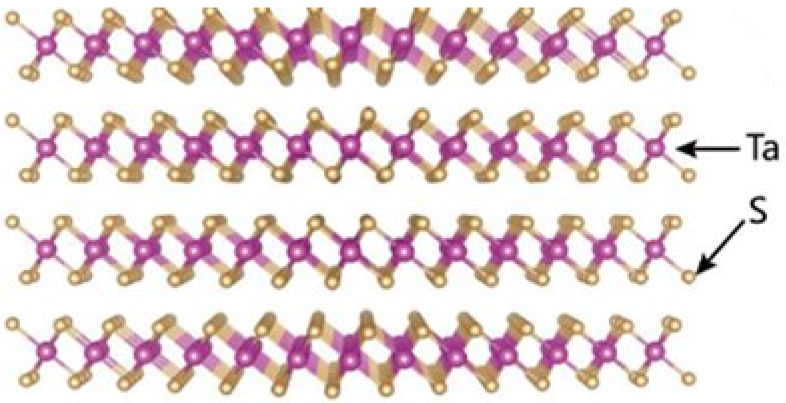
Femtosecond electronic structure snapshots!



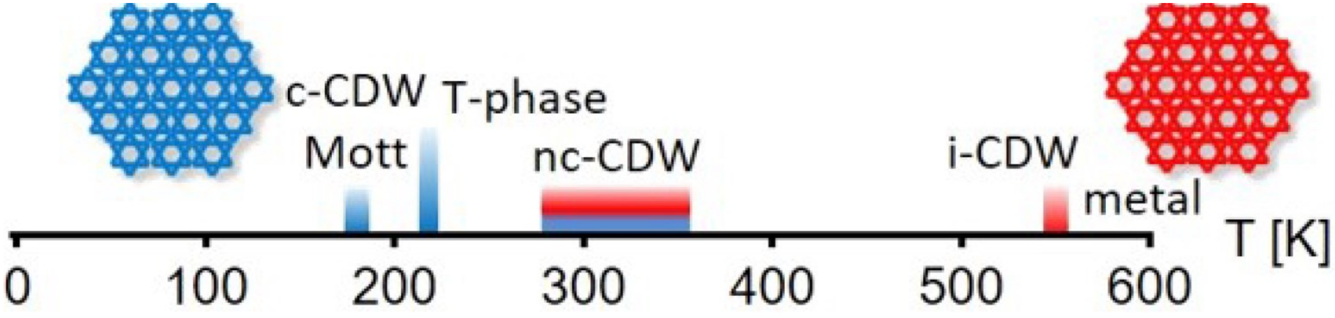
1-*T* TaS_2

A system with multiple “exotic” properties

[1]



[2]

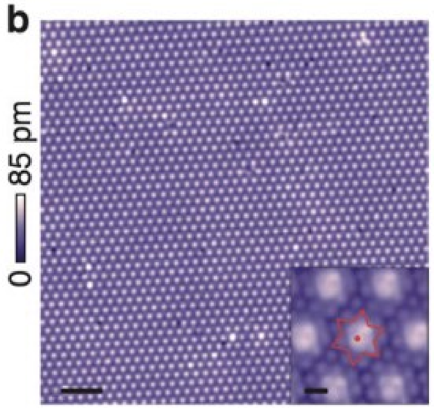


[1] D. Shao et al., *Phys. Rev B.*, **94**, 125126, (2016)
[2] I. Avigo et al., *Appl. Sci.*, **9**, 44, (2019)

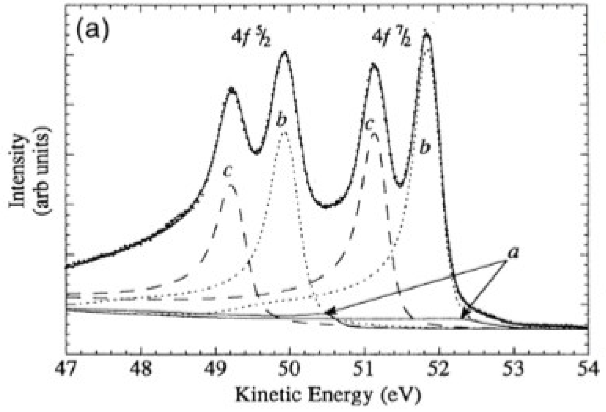
What is a charge-density wave (CDW)?

1*T*-TaS_2

Charge-density modulation

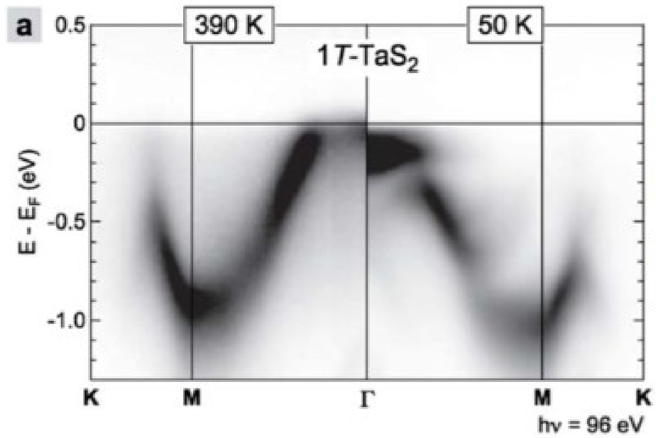


Ma *et al.*, Nat. Commun. **7**, 10956 (2016)



Hughes & Scarfe, Phys. Rev. Lett. **74**, 3069 (1995)

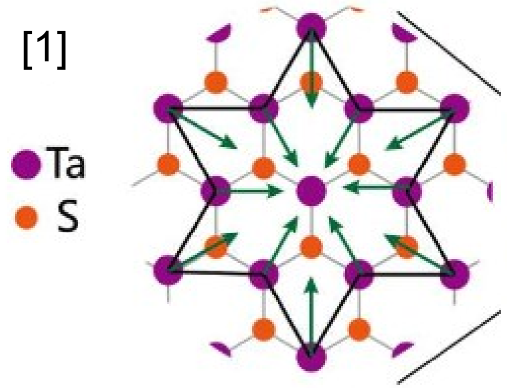
Energy gap(s)



J. Phys.: Condens. Matter **23**, 213001 (2011)

Periodic lattice distortion

[1]



David Star

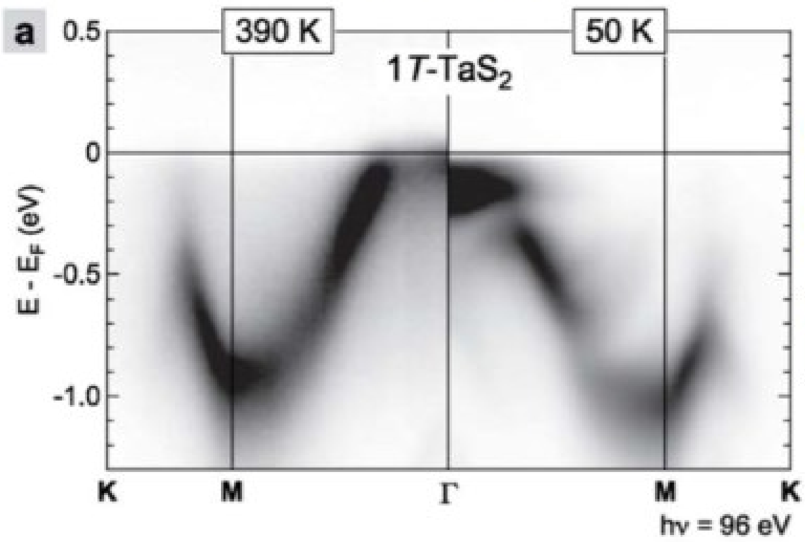
[1] D. Shao et al., *Phys. Rev B.*, **94**, 125126, (2016)

Mott insulation

1-*T* TaS_2

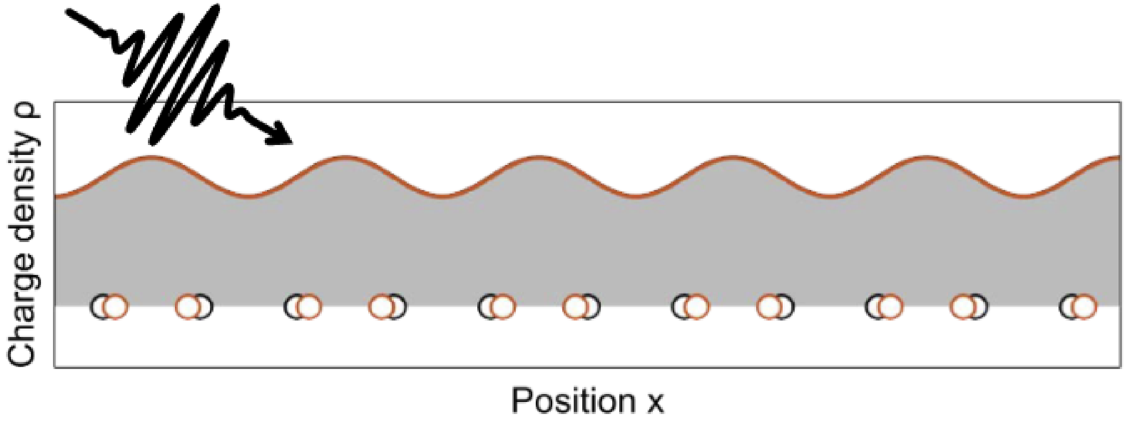
- Fulfill all criteria for conductors, i.e. should be metallic but experiments show an insulator
- Large CDW unit cell leads to flat bands
- Strong electron-electron interaction leads to localization of electrons
- Splitting into lower and upper Hubbard band

Energy gap(s)



J. Phys.: Condens. Matter **23**, 213001 (2011)

[1] S. Hellmann et al., *Nature Comm.*, **3**, 1069, (2012)

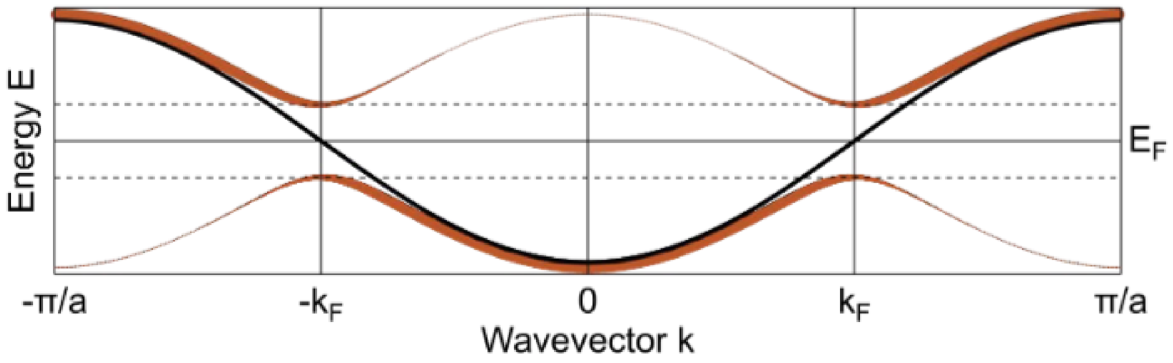


Charge-density wave

$$\tau_\mathrm{e} = \frac{h}{W} = \mathcal{O}\left(\frac{h}{1\,\mathrm{eV}}\right) = \mathcal{O}(4\,\mathrm{fs})$$

Periodic lattice distortion

$$\tau_\mathrm{lat} = \frac{h}{E_\mathrm{A}} = \mathcal{O}\left(\frac{h}{10\,\mathrm{meV}}\right) = \mathcal{O}(400\,\mathrm{fs})$$



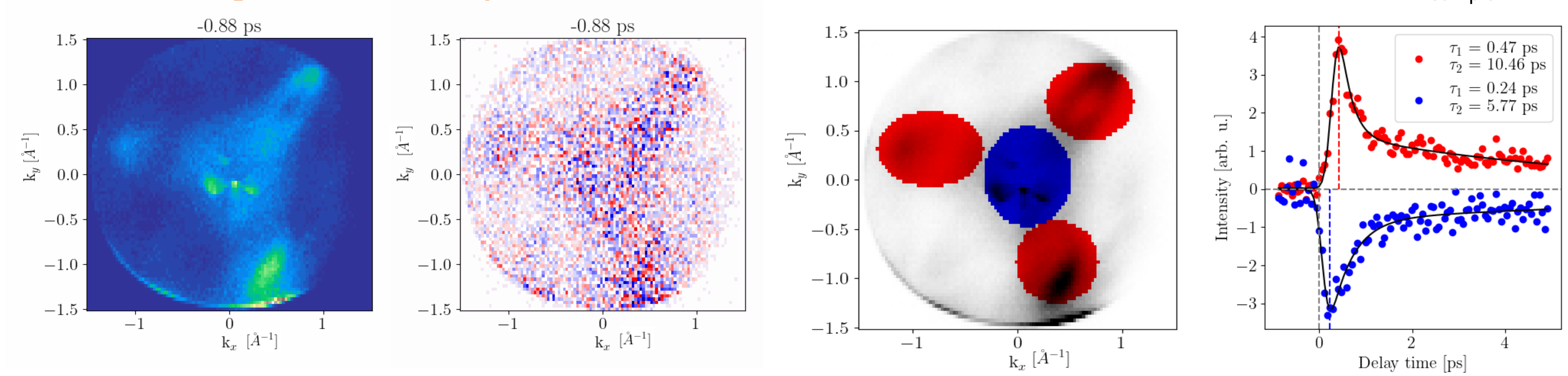
Energy gap

$$\tau_\Delta = \frac{h}{2\Delta} = \mathcal{O}\left(\frac{h}{200\,\mathrm{meV}}\right) = \mathcal{O}(20\,\mathrm{fs})$$

FEL-based time-resolved conduction PES

$h\nu_{\text{probe}} =$ 82.8 eV
$h\nu_{\text{pump}} =$ 1.2 eV
T_{sample} < 100 K

Valence band dynamics in TaS_2

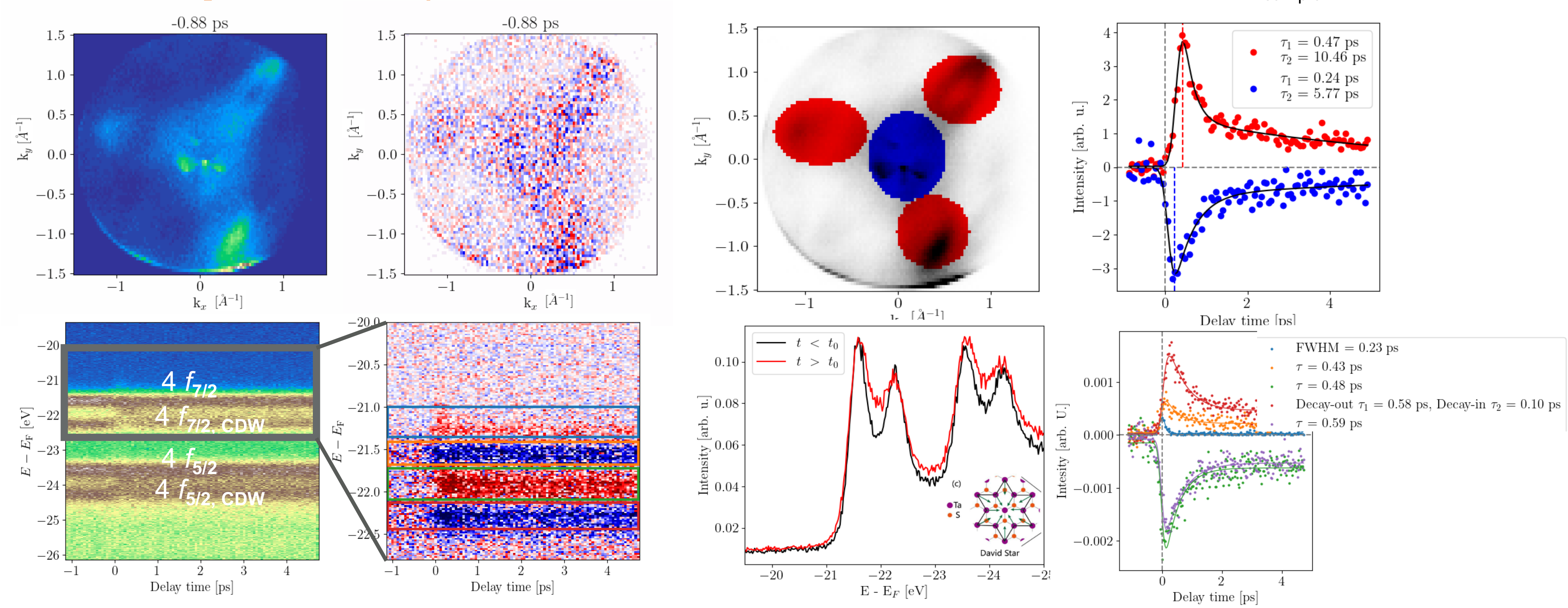


- Increase of intensity at *M*-points only after 0.17 ps
=> phonon driven process
- Loss of intensity at $\Gamma-$point right at t_0
=> electron driven process

FEL-based time-resolved conduction PES

$h\nu_{probe} =$ 82.8 eV
$h\nu_{pump} =$ 1.2 eV
T_{sample} < 100 K

Valence band dynamics in TaS_2



- Increase of intensity at *M*-points only after 0.17 ps => phonon driven process
- Loss of intensity at Γ– point right at t_0 => electron driven process

Methods: Time-Resolved Orbital Tomography

Easiest approach:

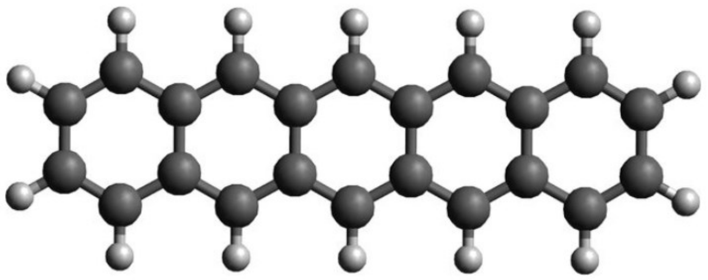
→ final state ≈ plane wave

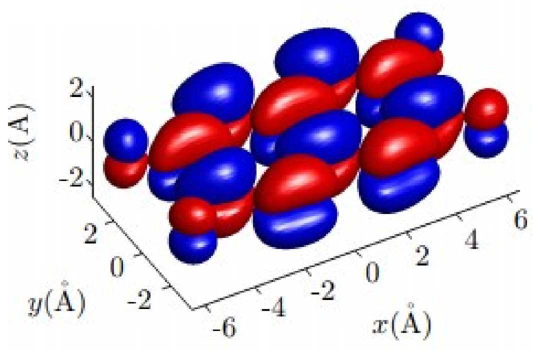
$$I_i(\theta, \phi) \sim |\mathbf{A} \cdot \mathbf{k}|^2 (\widetilde{\psi_i}(\mathbf{k}))^2$$

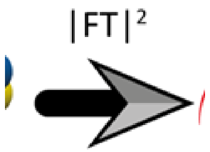
J.W. Gadzuk, PRB **10(12)**, 5030 (1974).

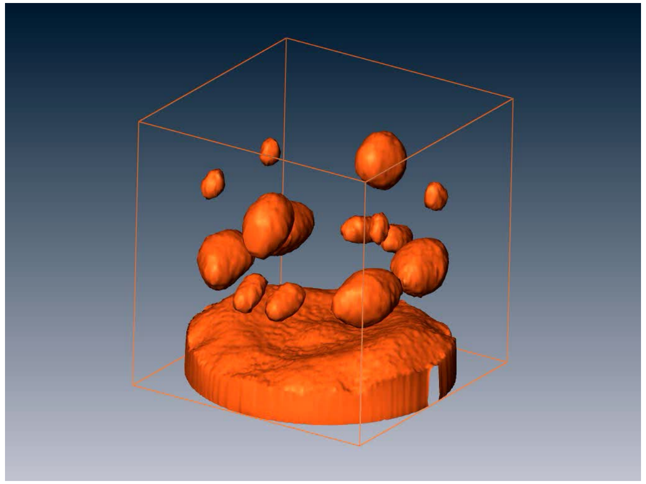
P. Puschnig *et al.*, Science **326**, 702 (2009).

Fourier-Transform of the molecular orbital!



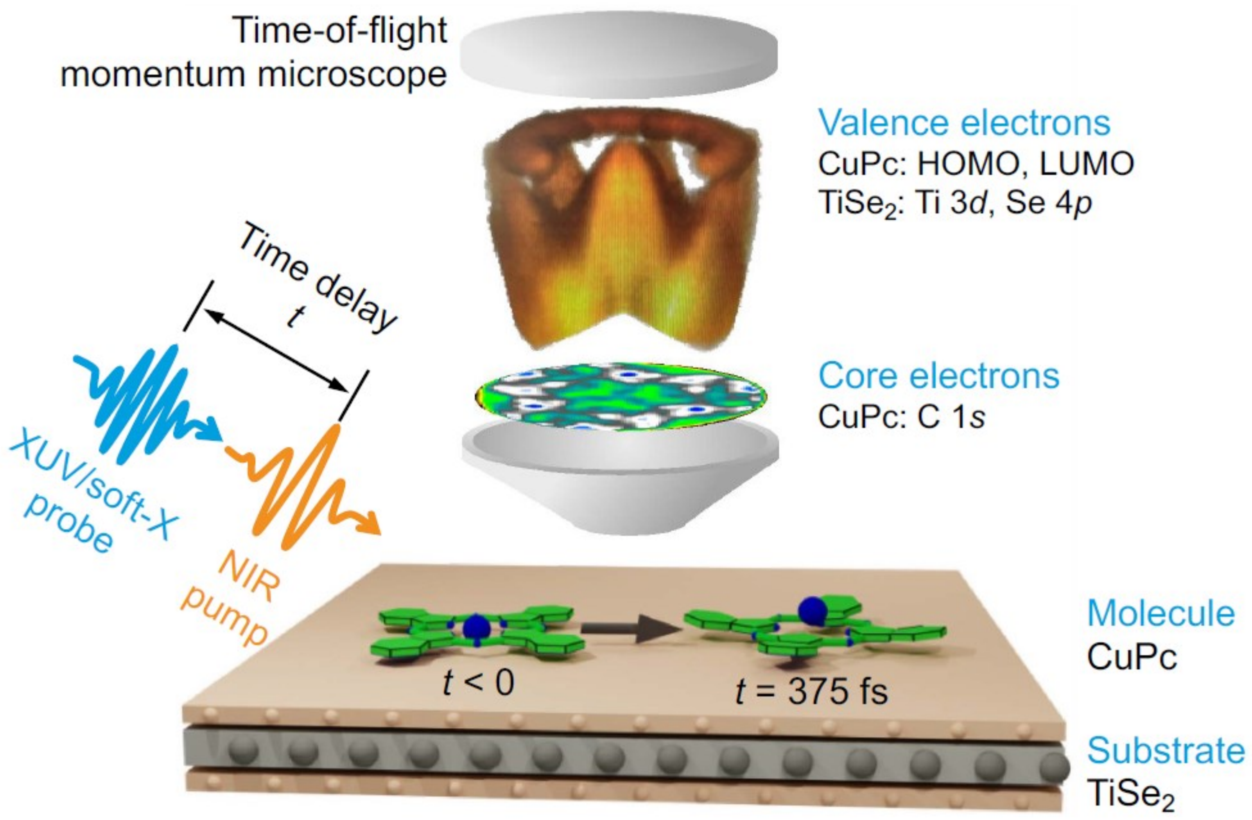


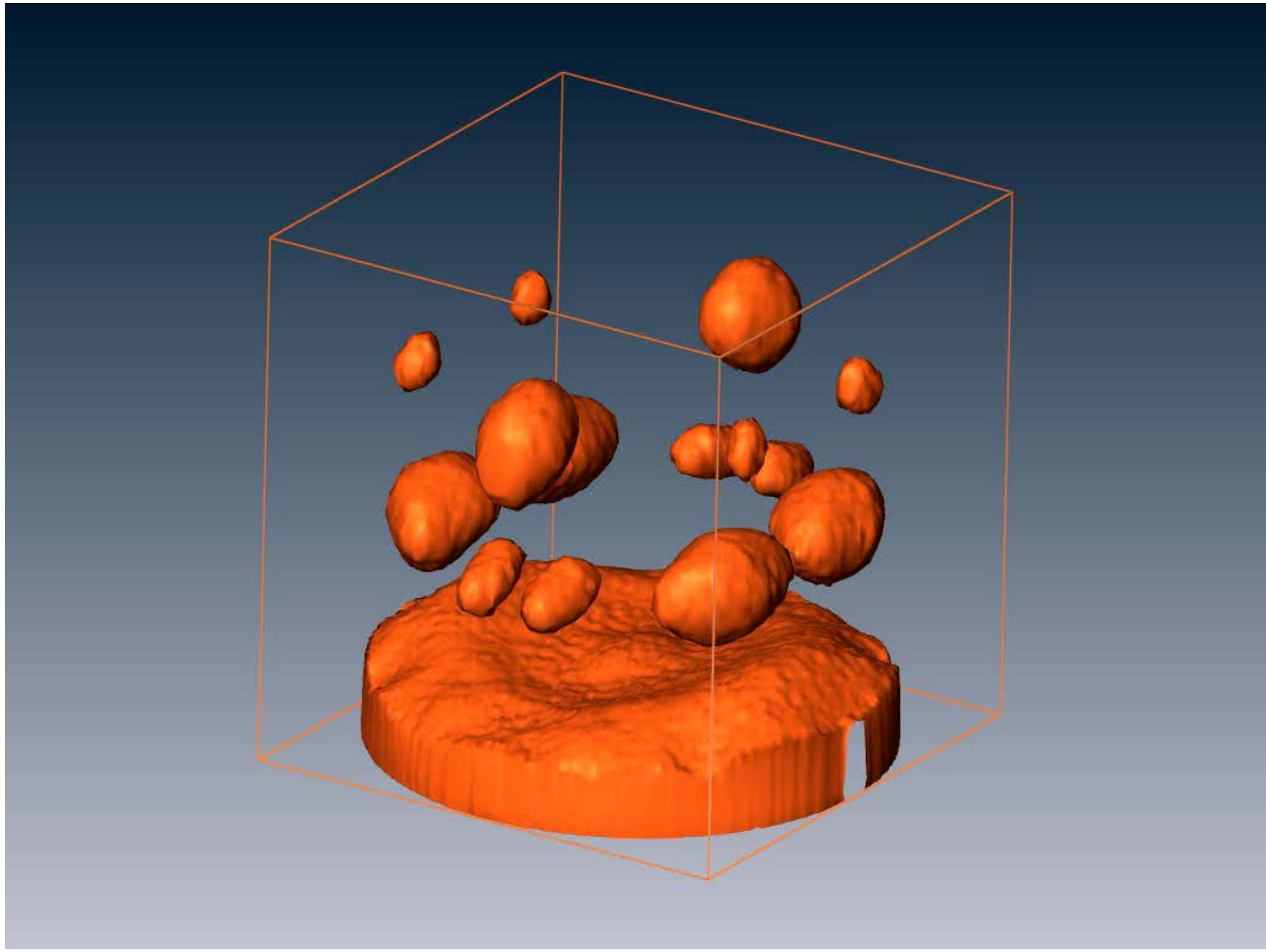




Charge-transfer & structural dynamics in $CuPc/TiSe_2$

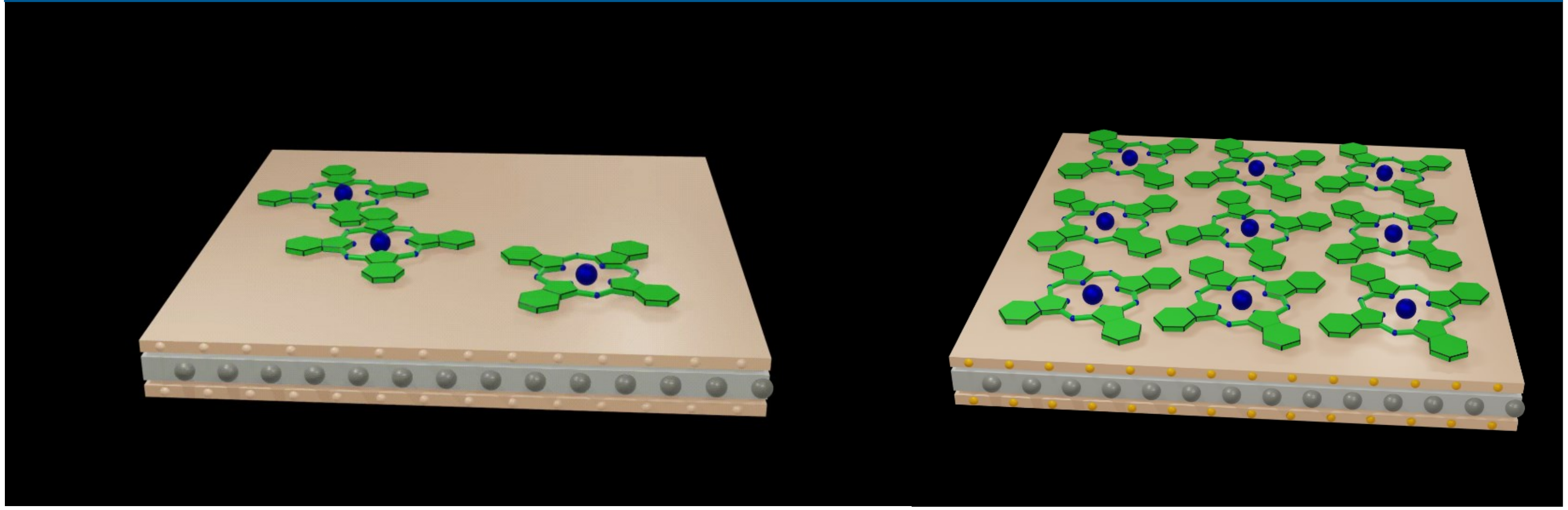
Ultrafast multiplex electron cinema at a molecule/2D material interface



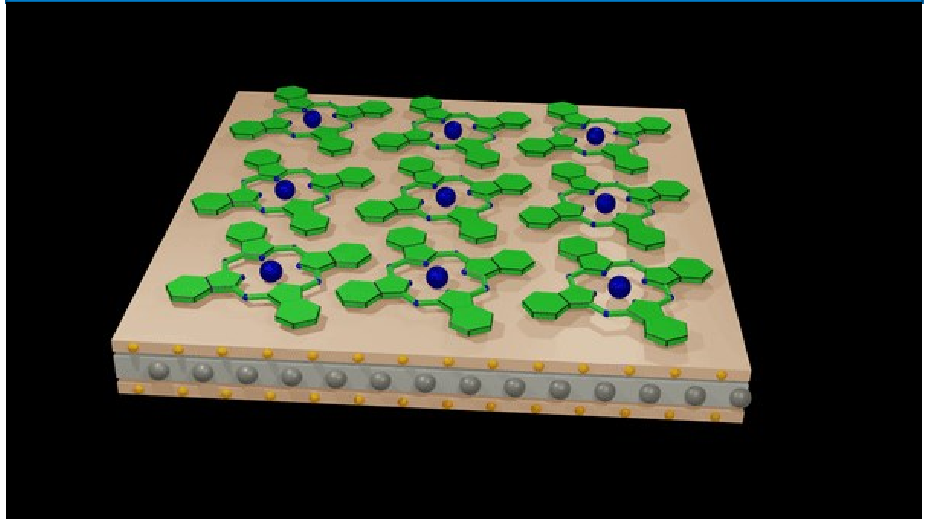


Molecules on 2D material

„static“

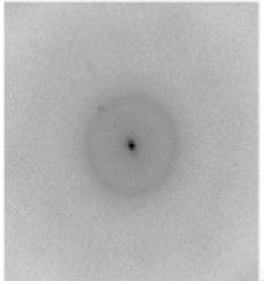


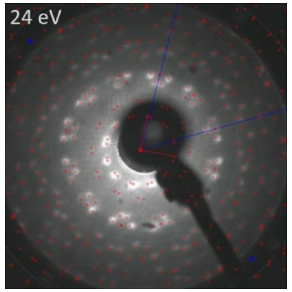
Non-equilibrium

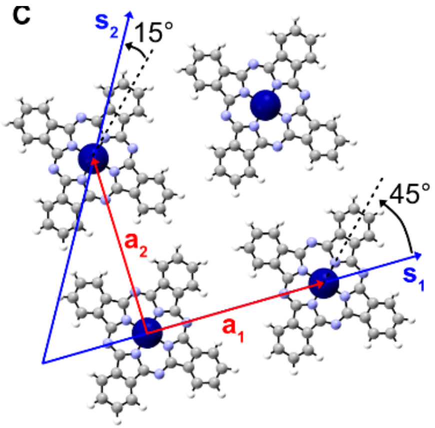


0.1 ML

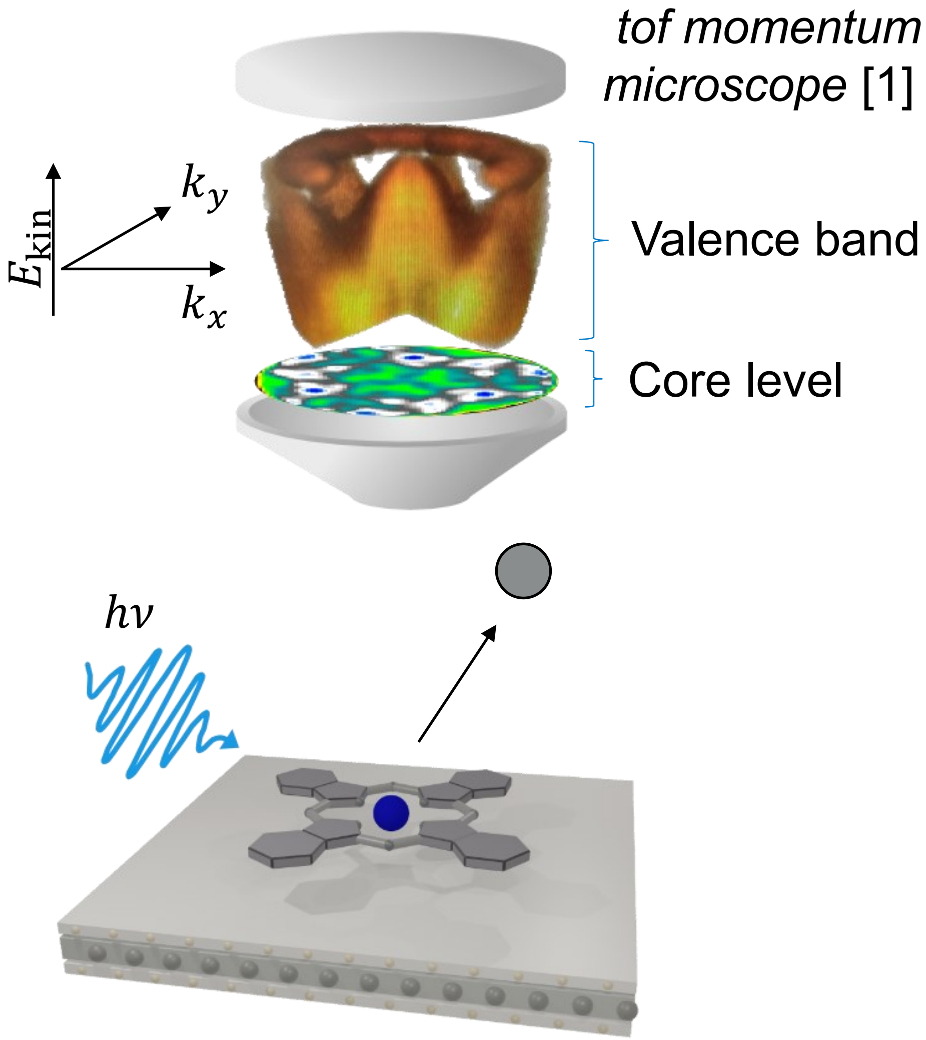
0.9-1 ML





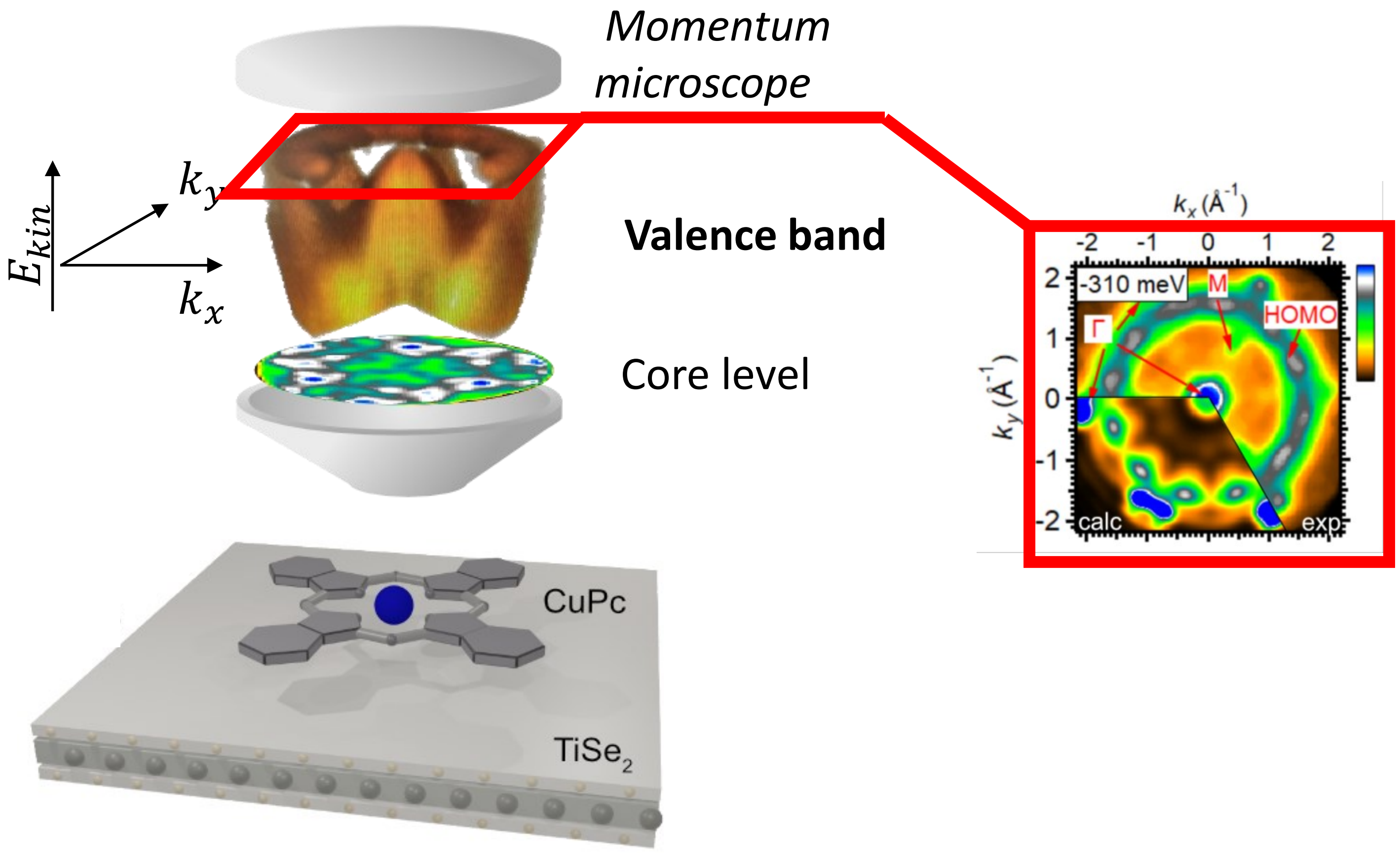


Time-resolved Orbital Tomography

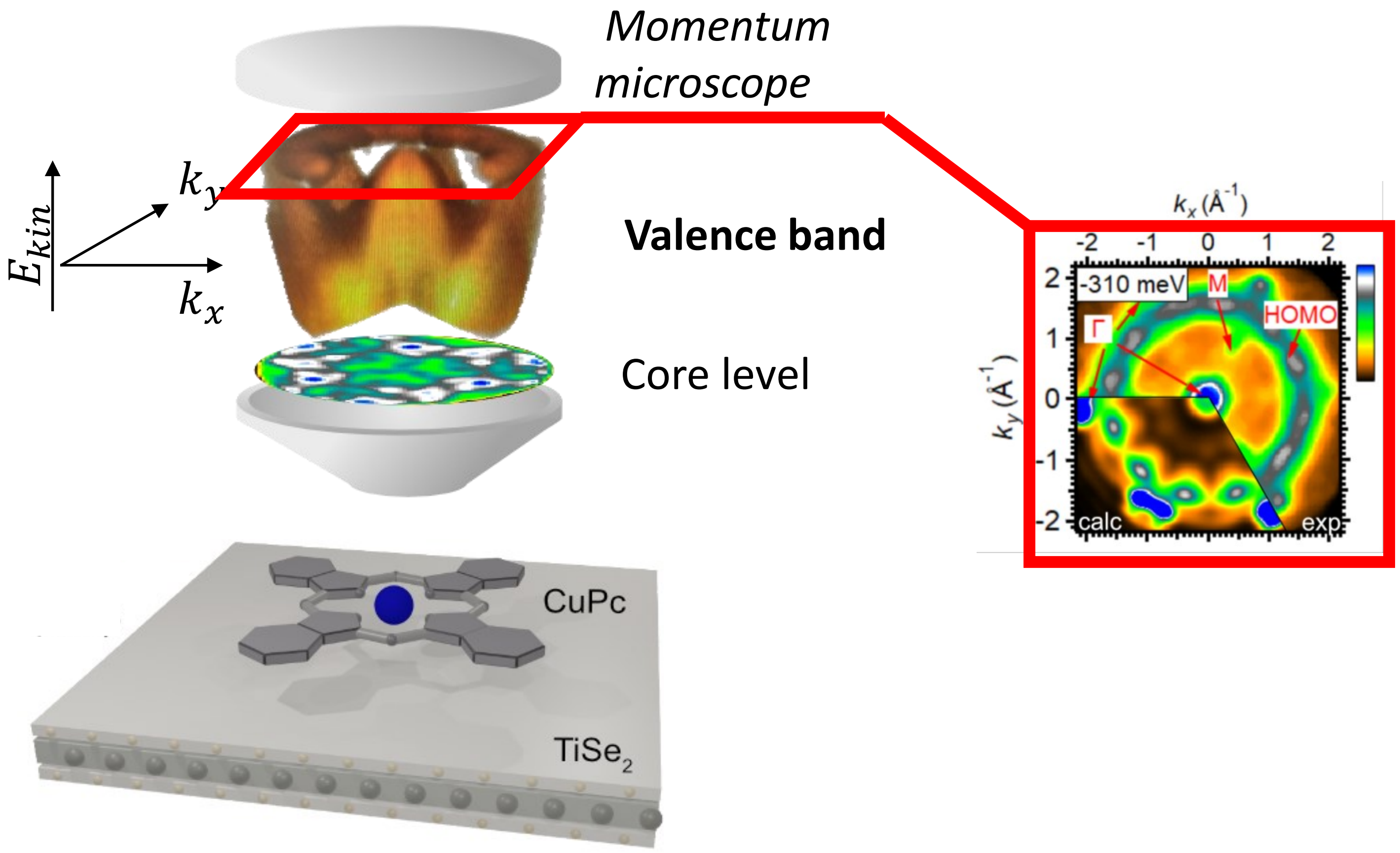


Time-resolved Orbital Tomography

Orbital tomography



Time-resolved Orbital Tomography



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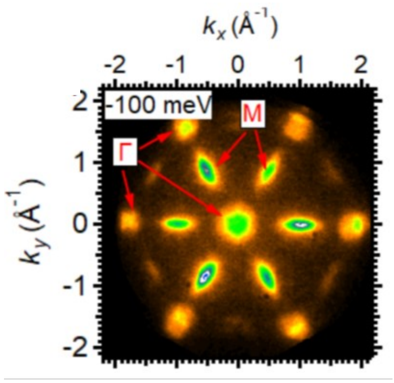
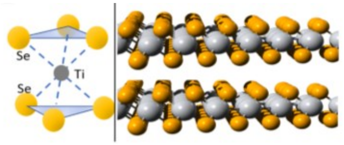
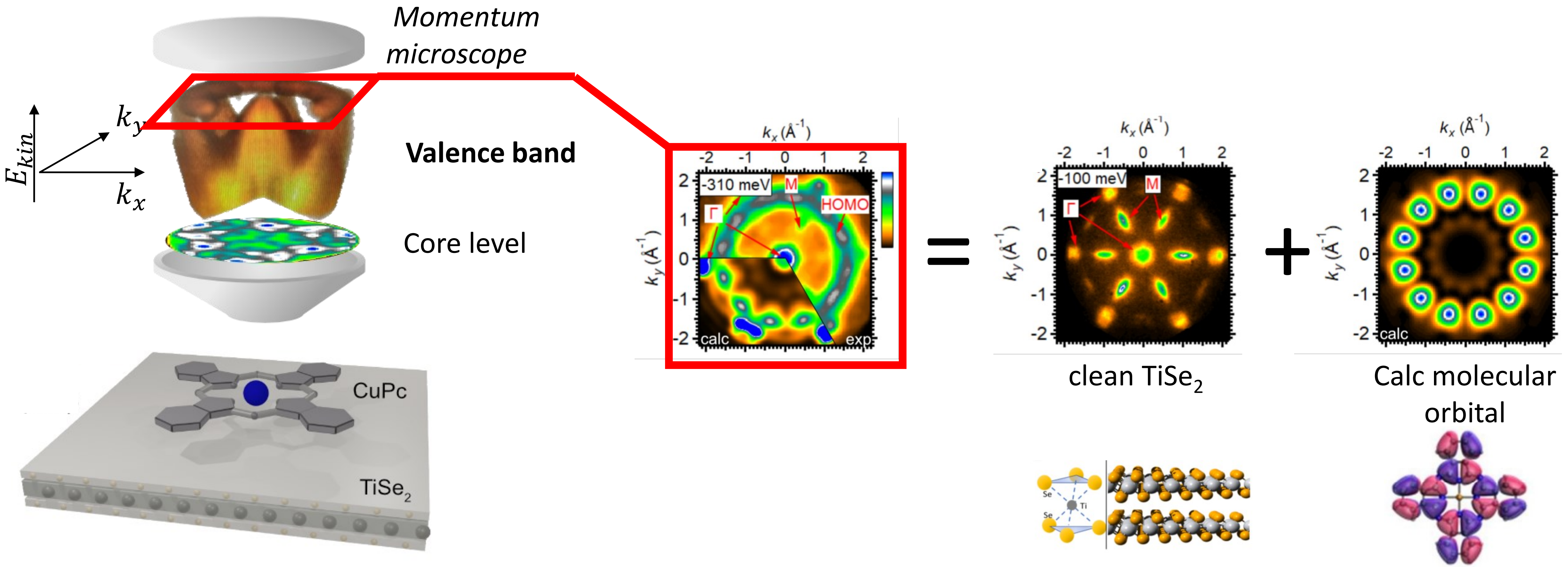
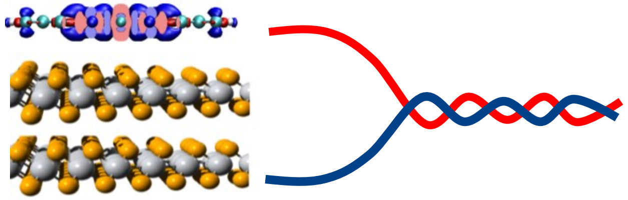


clean $TiSe_2$



Time-resolved Orbital Tomography





„ disentangle" molecular orbitals and substrate dynamics

Photoemission of Quantum Materials at SLAC/Stanford University

SLAC

DESY.

SIMES
Energy solutions through materials science

JOHANNES GUTENBERG UNIVERSITÄT MAINZ

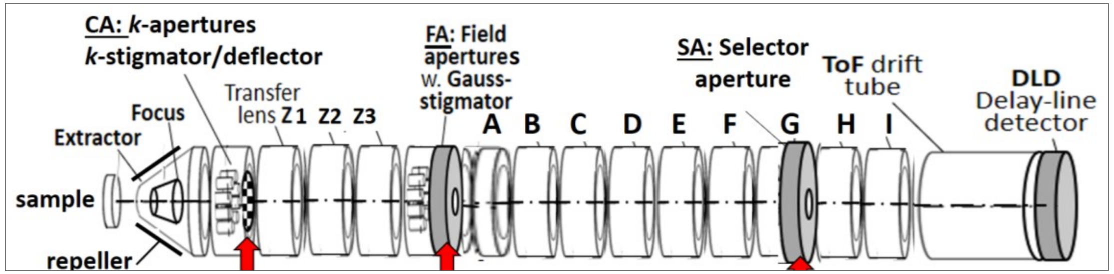
ETH zürich

Stony Brook University

LCLS

Optimum combination: LCLS-II + *k*-mic

Highest repetition rate of soft x-ray pulses + highest efficiency in photoelectron detection



- Several iterations of electron column
- Successful Commissioning P04@PETRA in 2022, 2023
- in-house and user beamtime at P04@PETRA and PG2@FLASH in 2022, 2023, 2024

novel momentum microscope:

- multimode lens and sparce-charge reduction
- machine learning for optimizing lens settings

early science cases: quantum materials, soft- and hard material interfaces, in situ/operando measurements of devices, …

Jakob Dilling

Lukas Bruckmeier

Thank you

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