International School and Workshop IMPACT 2024, Cargese, 19 - 31 Aug 2024

Ultrafast Dynamics of Elementary Excitations probed in Momentum and Real Space

Martin Wolf

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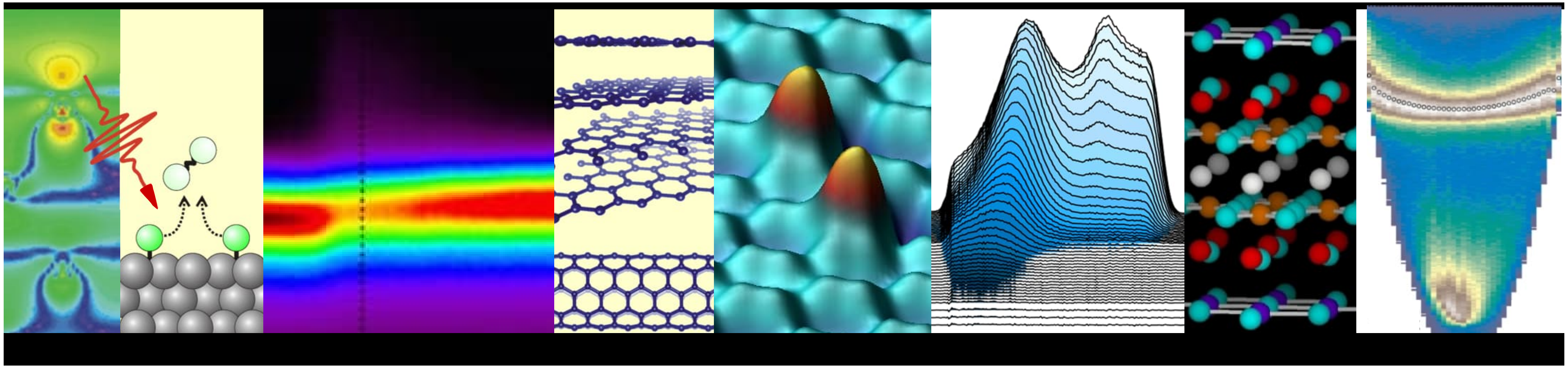
MAX-PLANCK-GESELLSCHAFT



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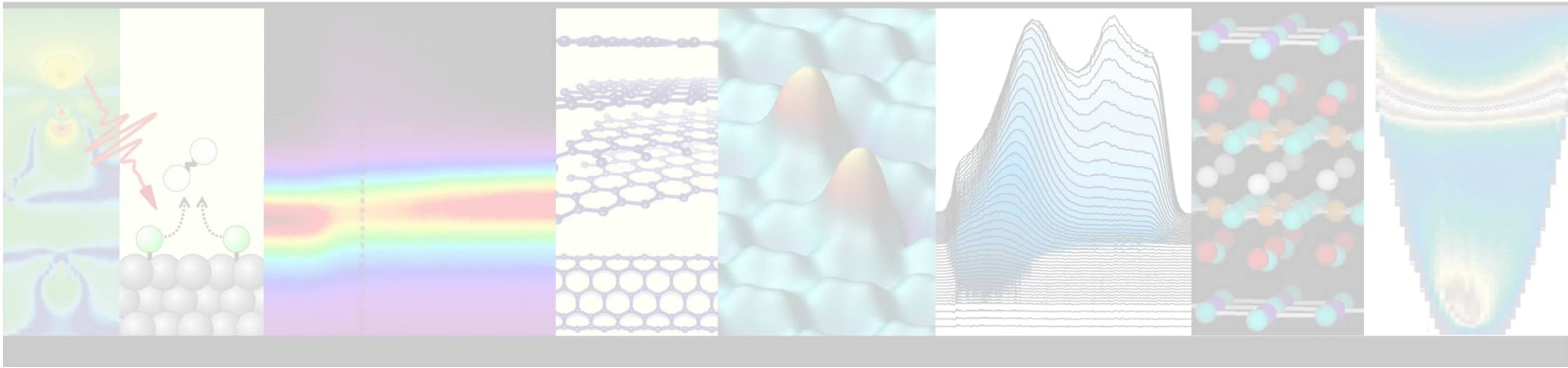
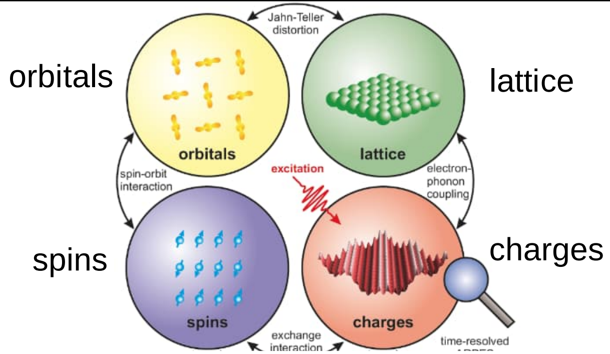
"Transformations of Correlated Electronic States by Electric or Optical Impacts"

International research school and workshop IMPACT – 2024

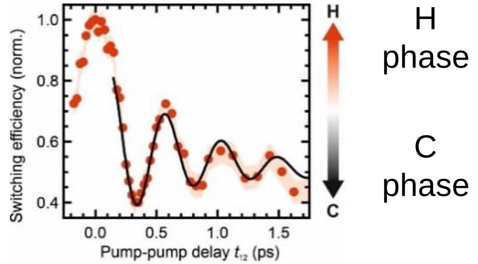


Outline

- **Motivation and general introduction:**
  Material properties, fundamental excitations,
  phase transitions & dynamics

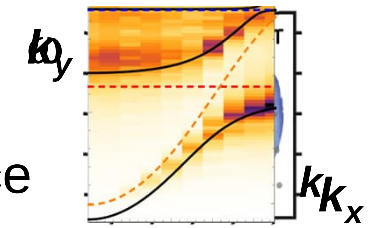


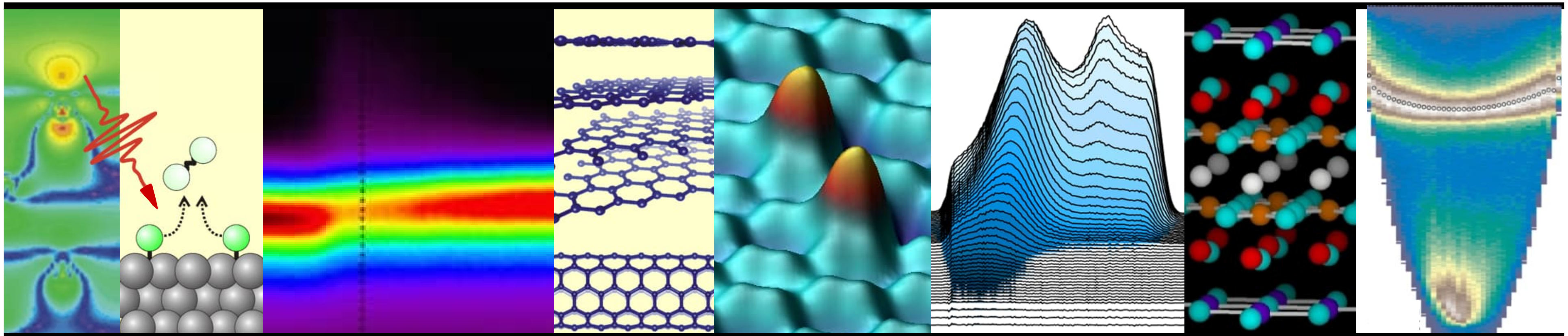
- **Charge density wave dynamics** in TaS_2 :
  - Transition to metastable H phase probed by ARPES
  - Local CDW dynamics probed by THz- STM



- **Exciton dynamics** in momentum space:
  - Mechanism of singlet exciton fission in pentacene

- **Coupling between light and matter**:
  - Phonon polaritons and strong coupling on SiC metasurface

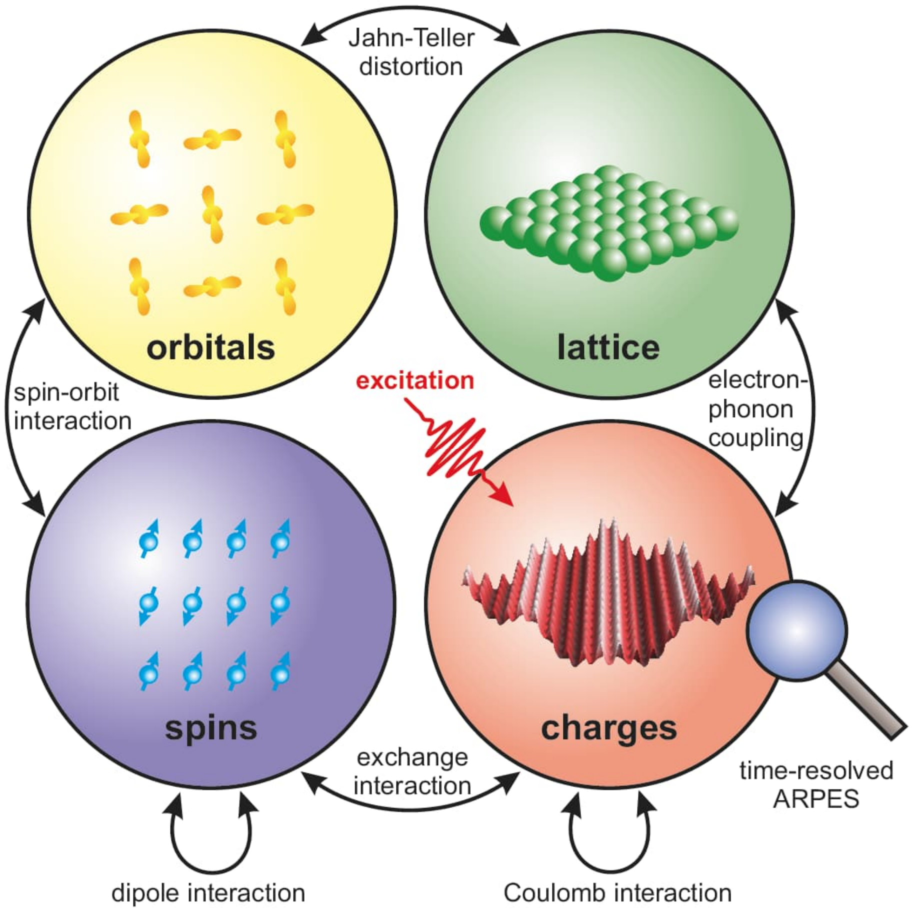




Physical properties of solids

► General questions:

What are the constituents of materials and which processes govern their properties and function?



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► Key physical & chemical properties defined by the **static structure**

- *frequently used concept: periodic crystal structure leading to Bloch states & electronic band structure in k-space*

- *but, also defects play a key role: e.g. in doping of semicondutors or quantum materials*

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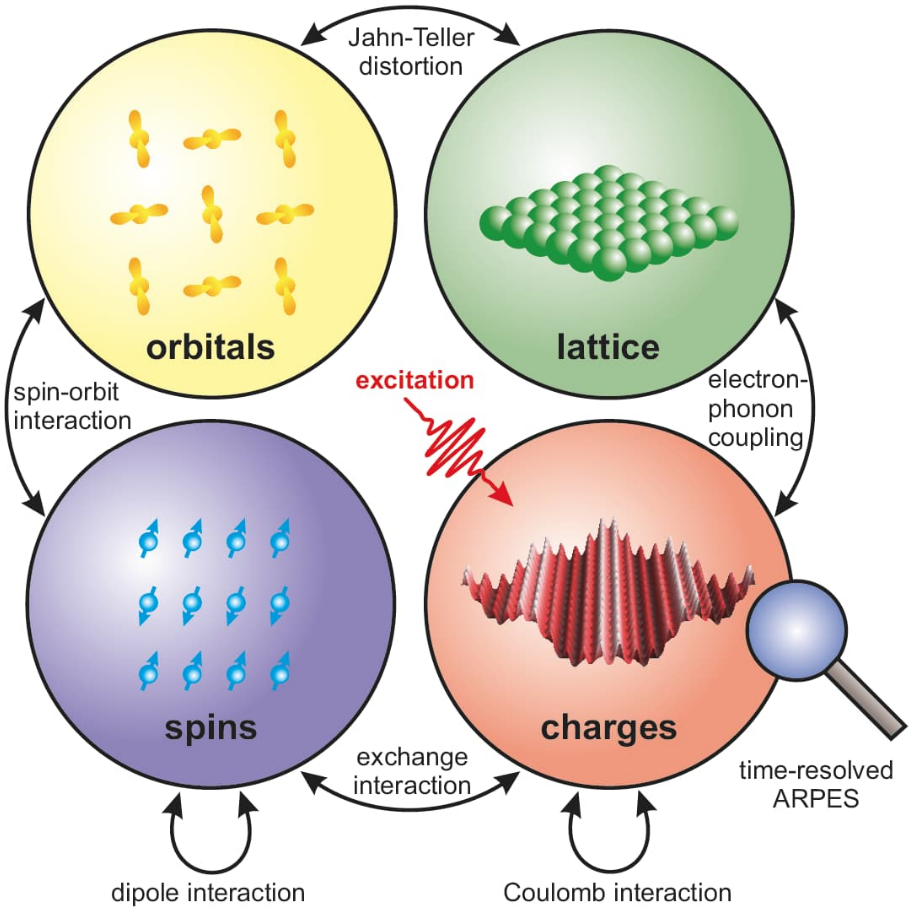

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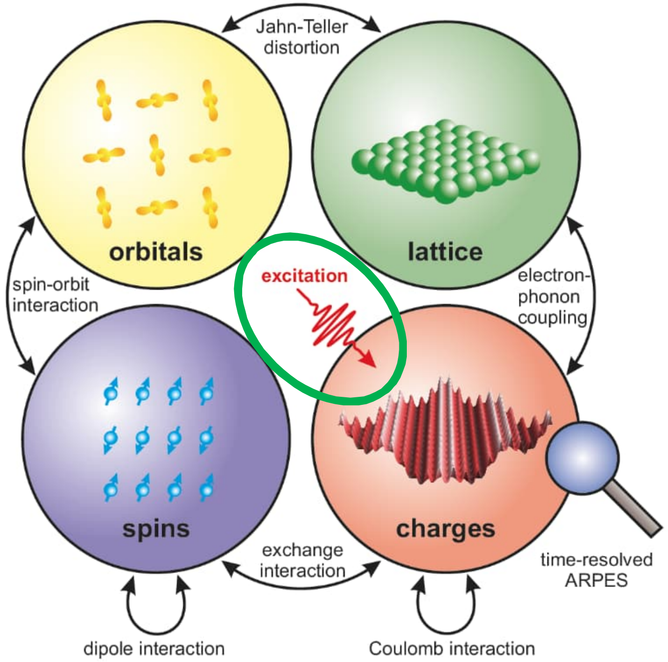
► On the other hand **function of materials** arises often from **non-equilibrium processes**

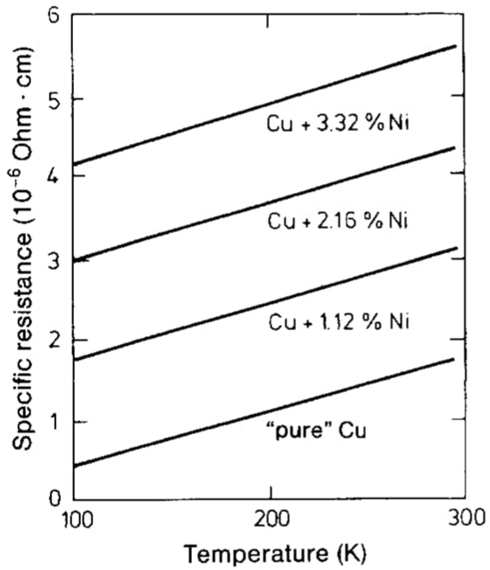
- *optical or thermal excitation, currents, charge transfer,…*
- *electronic devices, optical detectors...*

Elementary excitations of solids



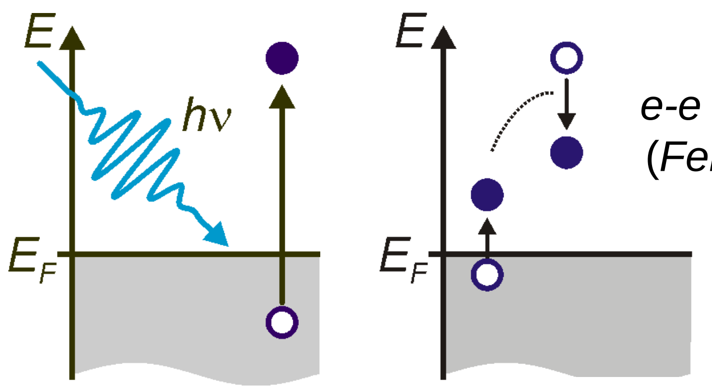
- Thermal excitations:

  Example electrical resistivity of Cu:
  e-ph coupling & defect scattering



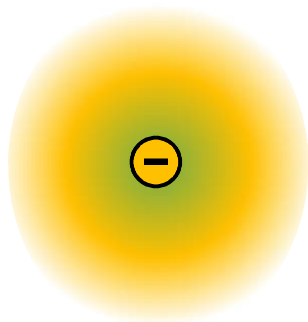
- Optical excitations

Metals (screened Coulomb interaction)



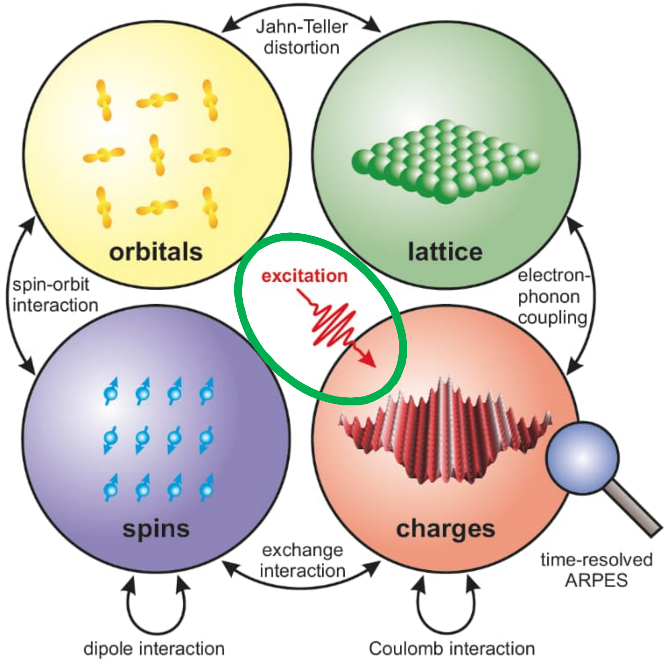
e-e scattering
(*Fermi liquid*)

Quasi-particle
(*including interactions*)



single (dressed) particle

Elementary excitations of solids



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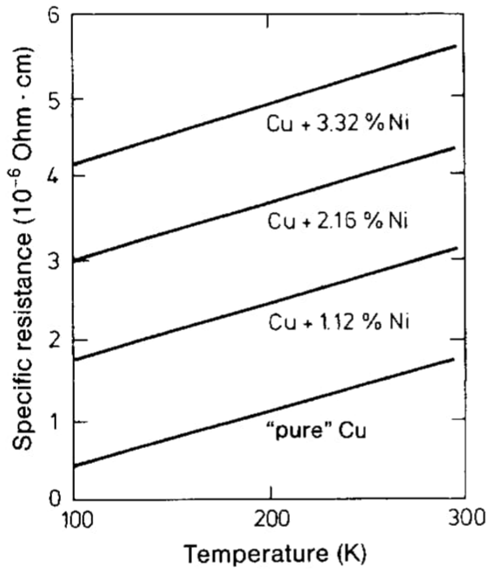
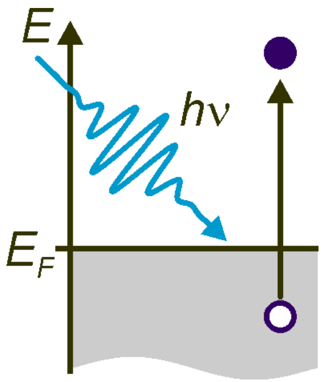
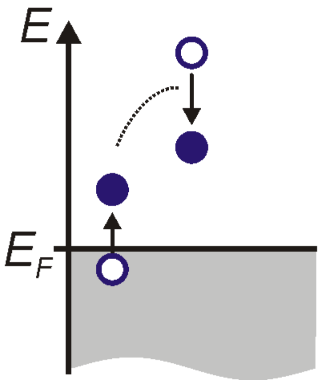


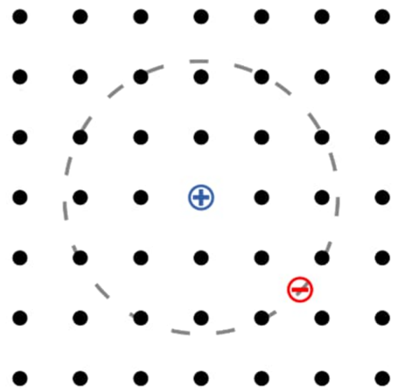
- Optical excitations in metals and semiconductors:

Metals





Semiconductors (Coulomb interaction)

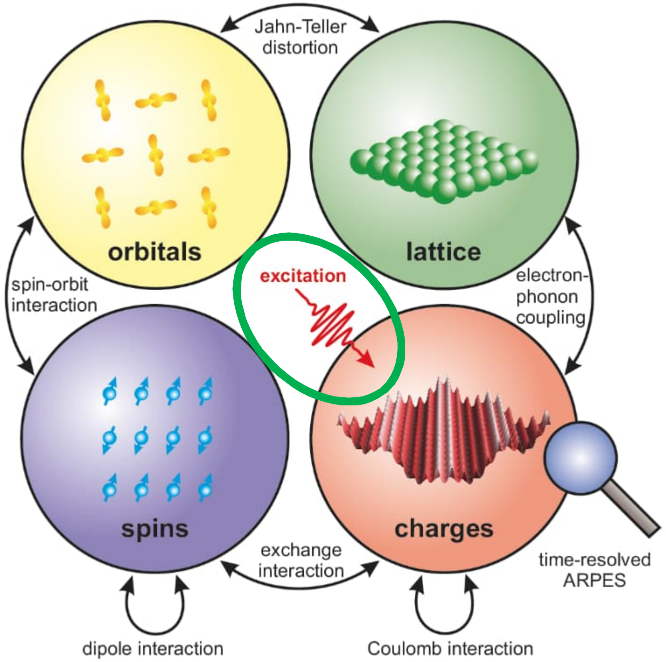


Exciton formation:
- Frenkel exciton
- Wannier (localized)
- Charge transfer

„two-particle excitation“

...weak perturbation

Elementary excitations of solids



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  Example electrical resistivity of Cu:
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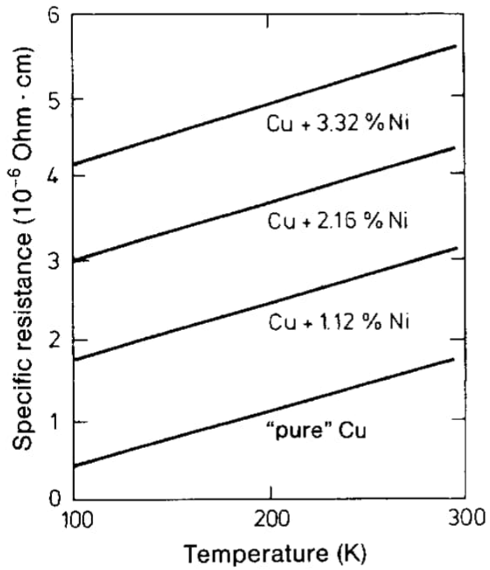
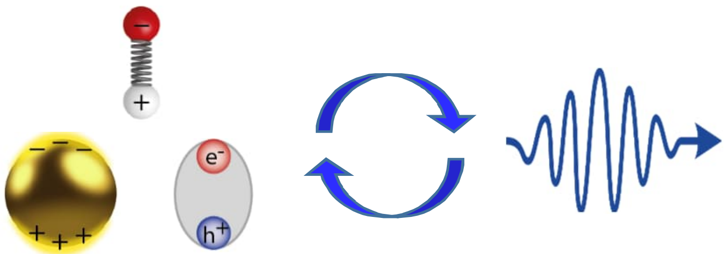
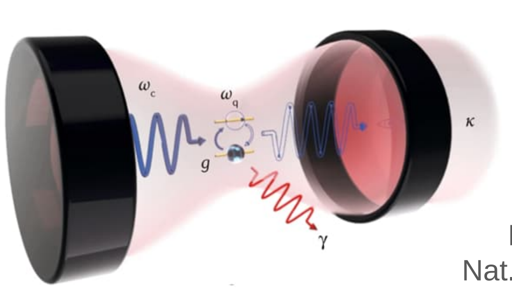


- Optical excitations:
  coupling of light and matter

Mixed light-matter states (molecules, nanoparticles, …)



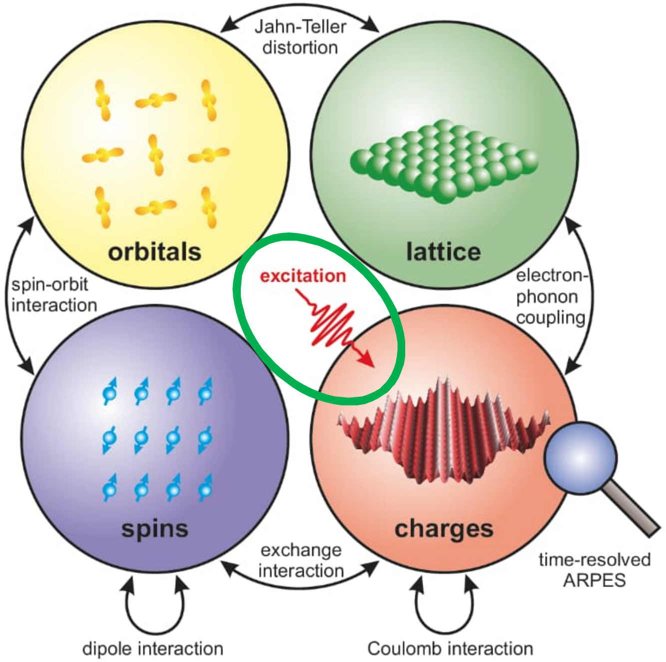
Cavities:



„strong coupling"

Kockum et al.
Nat. Rev. Phys. 2019

Elementary excitations of solids



- ► Thermal excitations:

  Example electrical resistivity of Cu:
  e-ph coupling &
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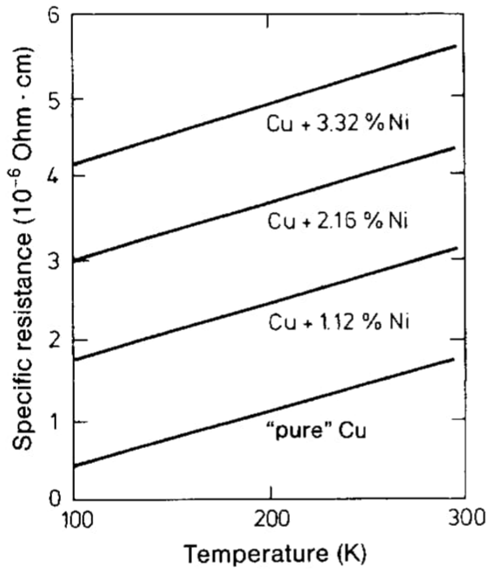
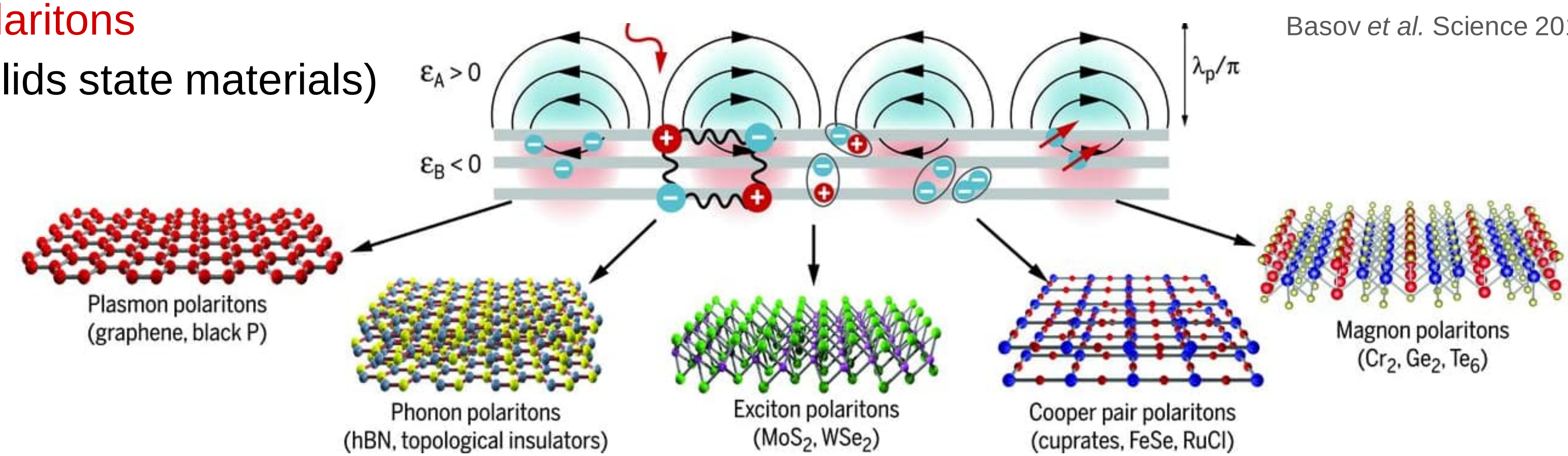


- ► Optical excitations:
  coupling of light and matter

Polaritons
(solids state materials)

Basov *et al.* Science 2016

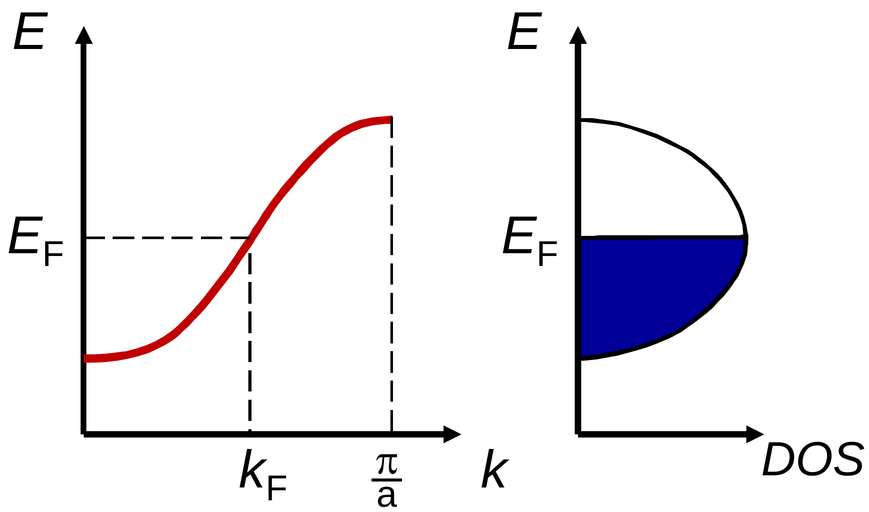


…basic questions in solid state physics

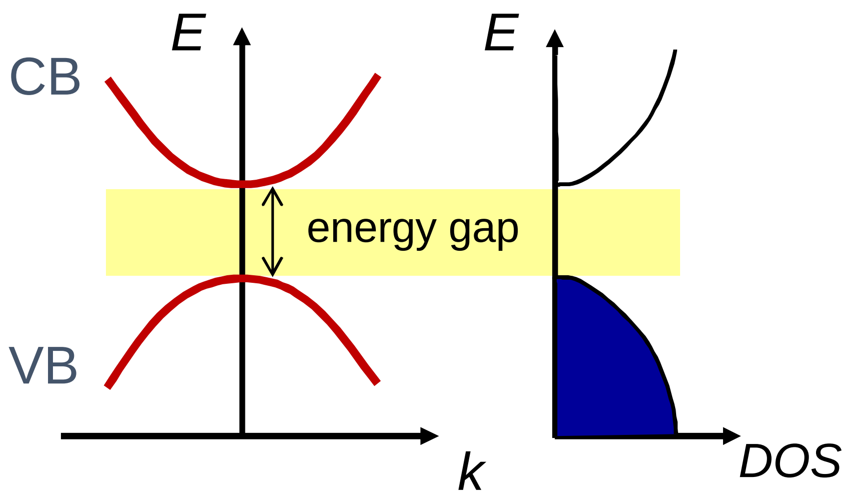
What is the origin of metallic, semiconducting and insulating behaviour?

► Use single-particle band theory

simple metal



insulator, semiconductor



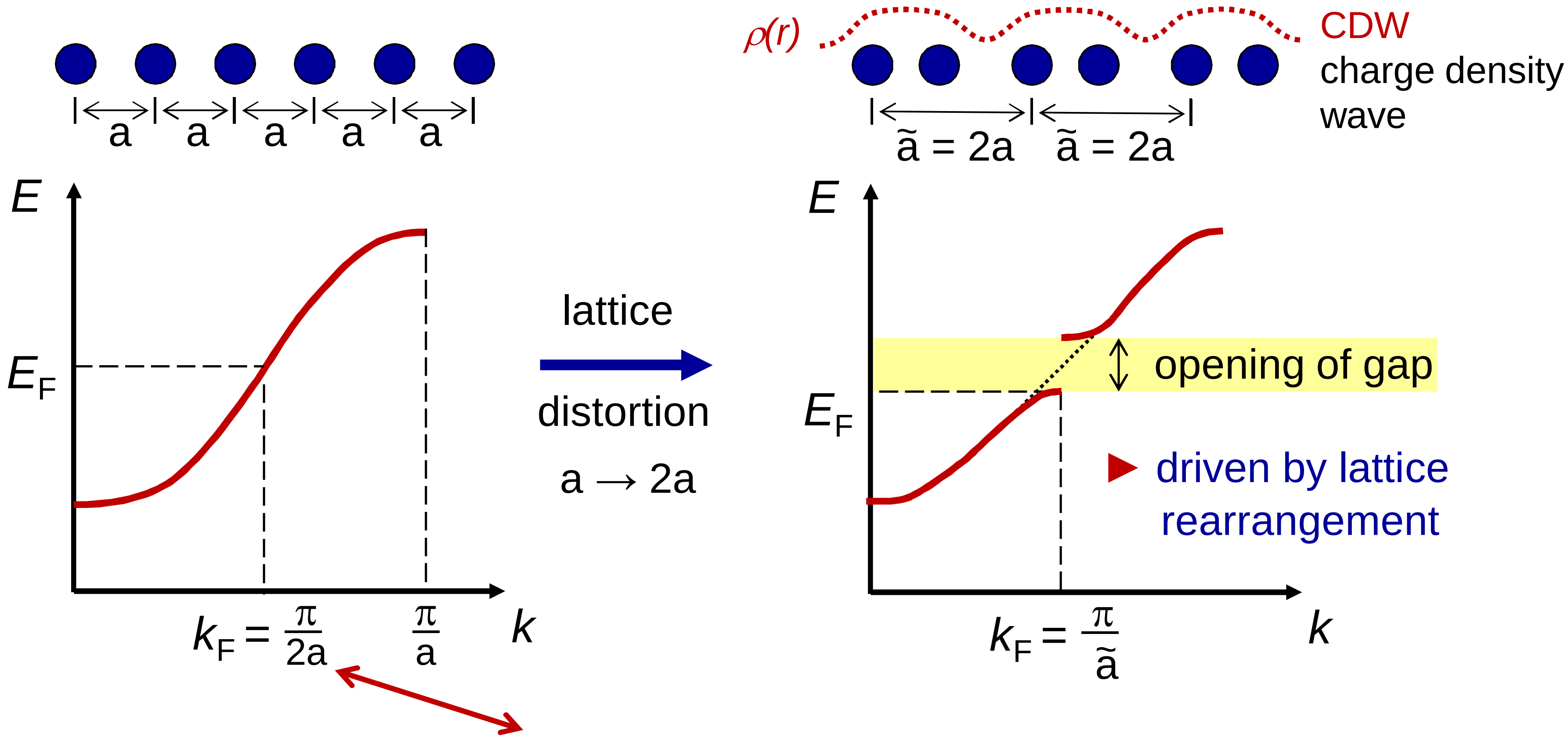
► half filled band ⇔ metal

► filled valence band ⇔ insulator or semiconductor

…basic questions - Peierls instability

Are materials with a half filled valence band always metals?

- One-dimensional metallic system with a half filled band can be unstable against lattice distortion → Peierls instability

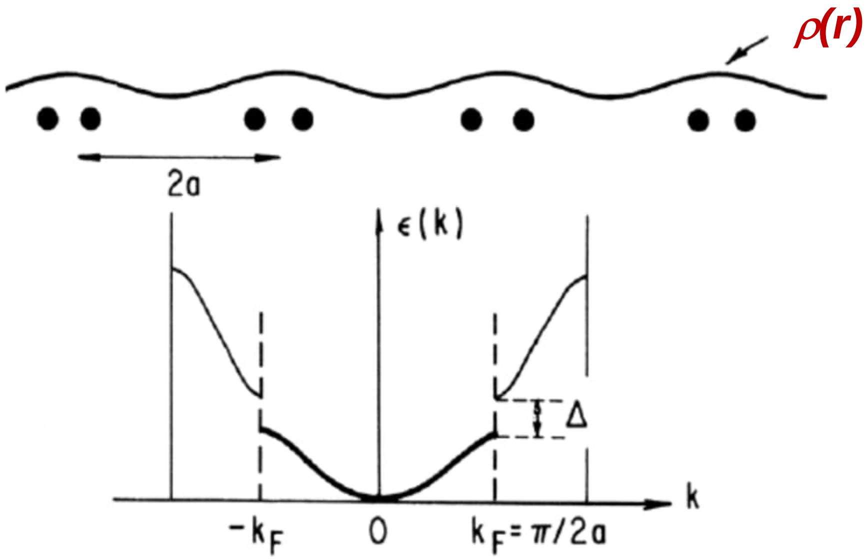


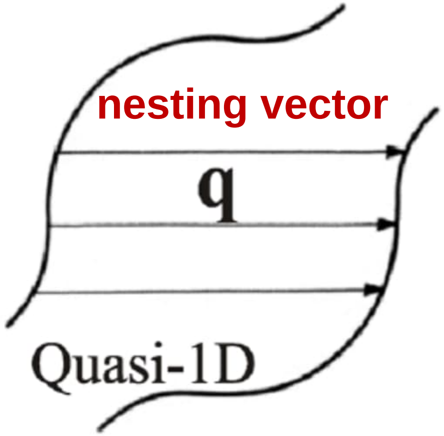
- Note: wave vector $2k_F = \frac{\pi}{a}$ fulfills Bragg reflection ("nesting") condition

Charge Density Waves…

- **C**harge **D**ensity **W**ave (CDW) formation in quasi-1D systems

→ Fermi vector nesting leads to (partial) collapse of Fermi surface





- New ground state if electronic energy δE gain exceeds deformation δU

"energy cost"

$$\delta E + \delta U = -\,|\,V_{2k_F}\,|^2\, N\chi^\circ(2k_F) + \frac{c}{2}u_{2k_F}^2 \; < 0$$

electronic susceptibility at $2k_F$

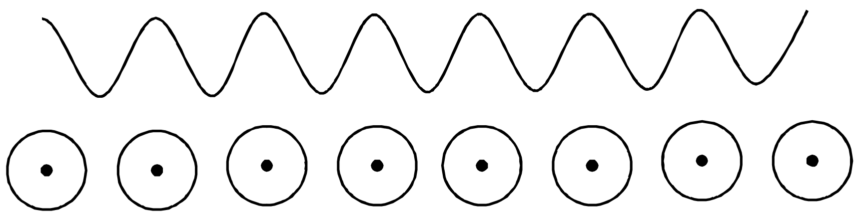
⇨ Governed by electronic band structure around E_F

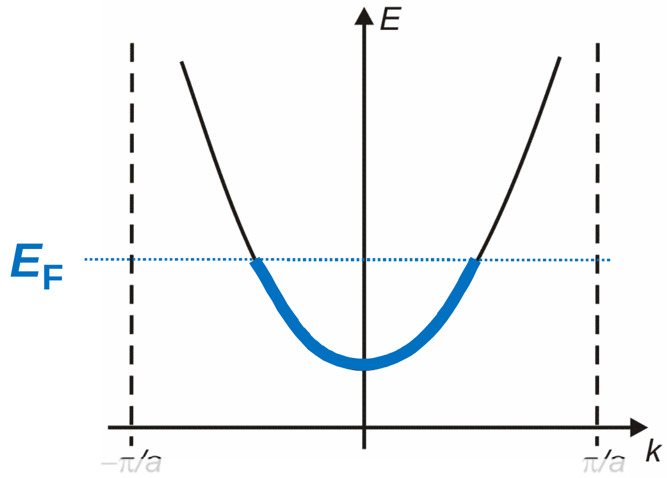
..basic questions – Hubbard Model

Are materials with a half filled valence band always metals?

Quasi-free electrons: Atomic chain

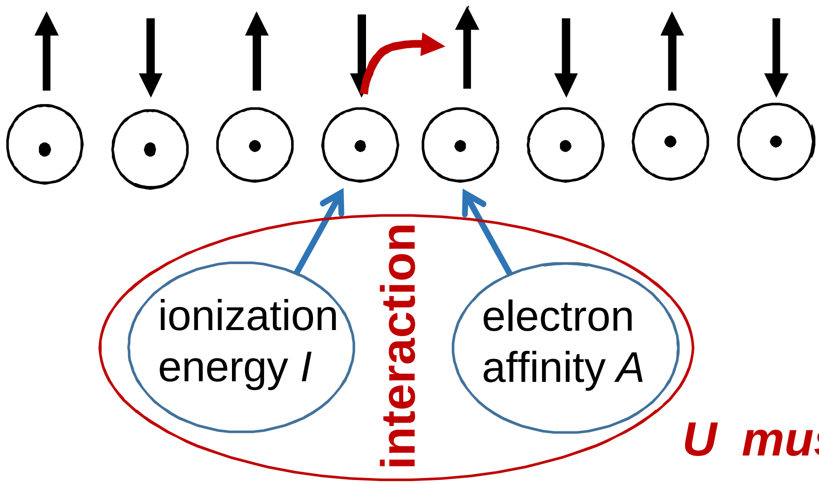
Single particle band theory:
1 partially occupied band → Metal

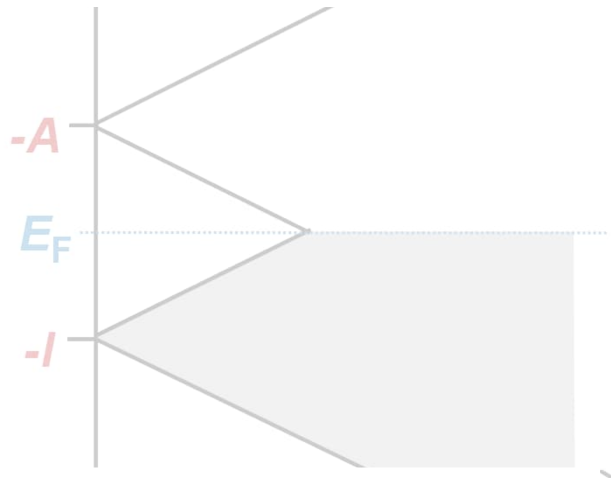




Let's consider Coulomb interaction, but on a 'frozen' lattice

→ on-site Coulomb repulsion *U*

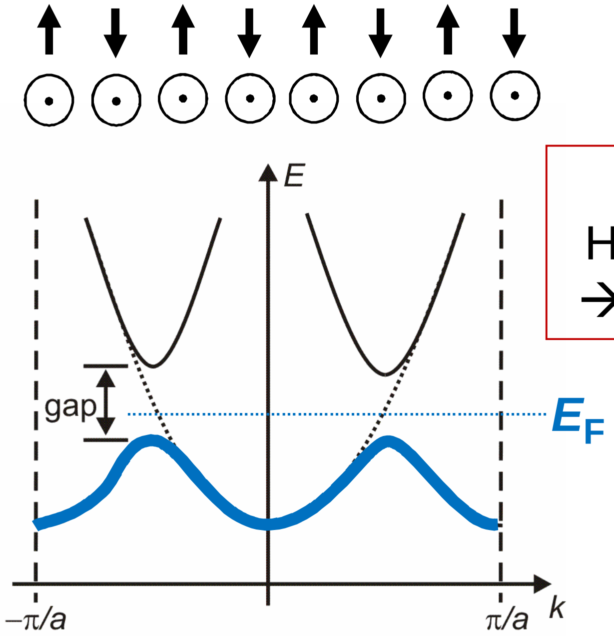




U* must be compared with band width *W

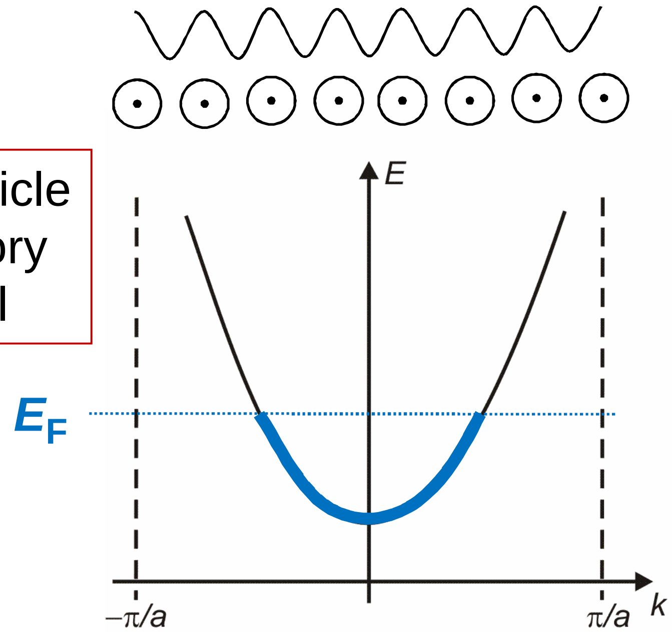
…basic questions – Hubbard Model

W < U



Mott-
Hubbard U
→ Insulator

W > U



Single particle
band theory
→ Metal

Hubbard Model

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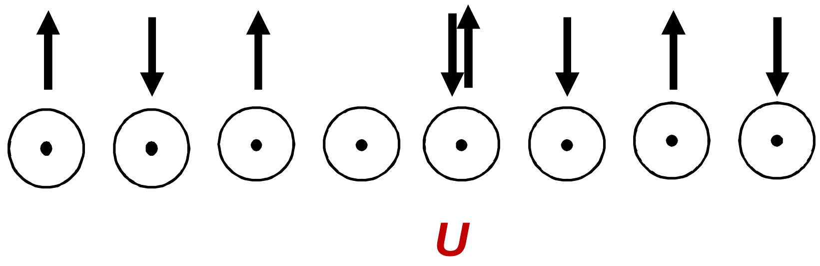
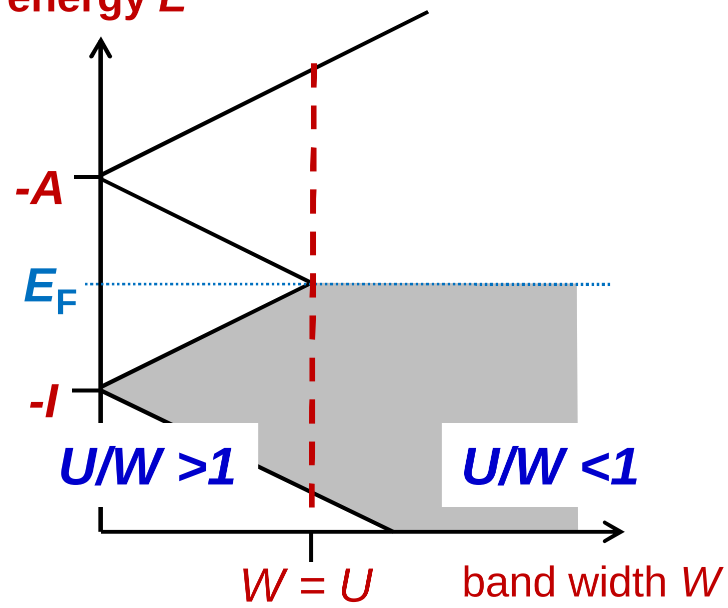
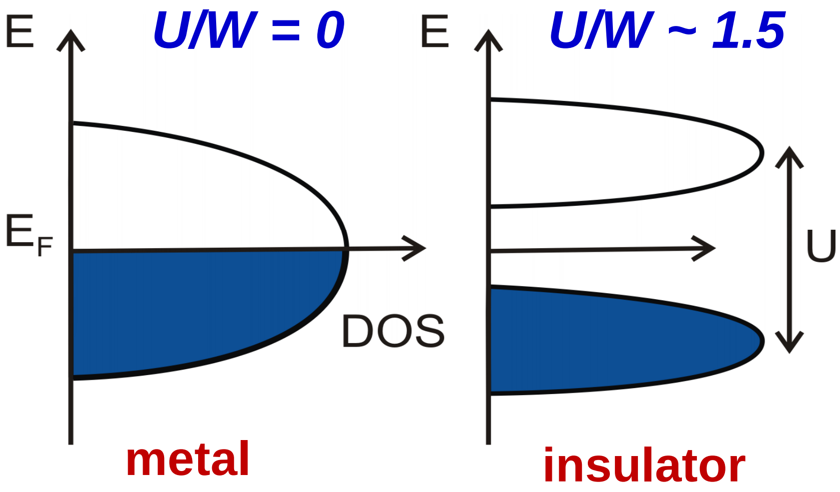
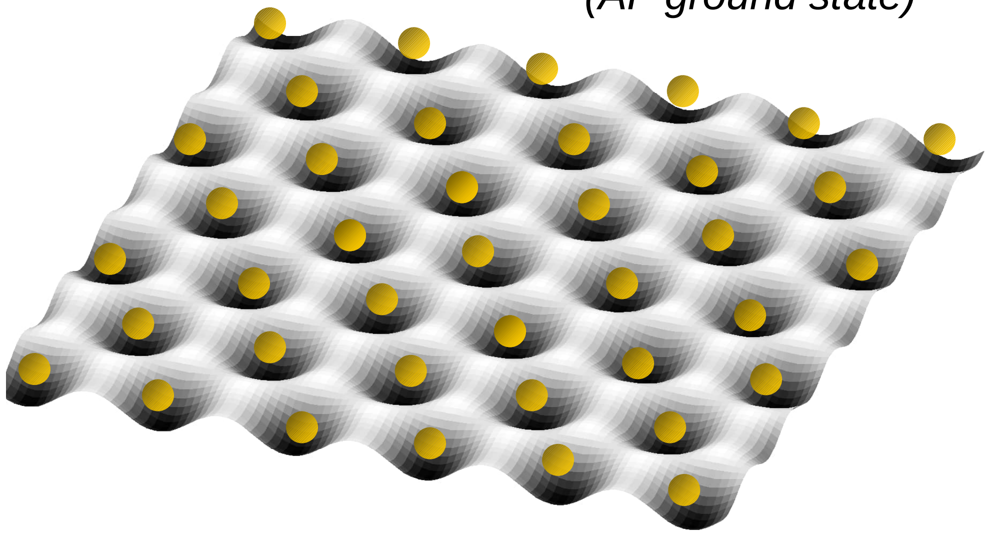




Mott insulator…

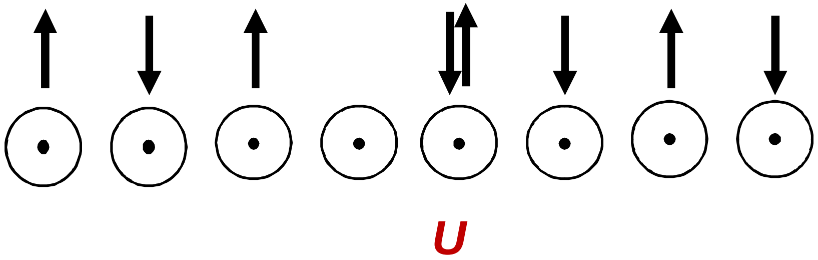


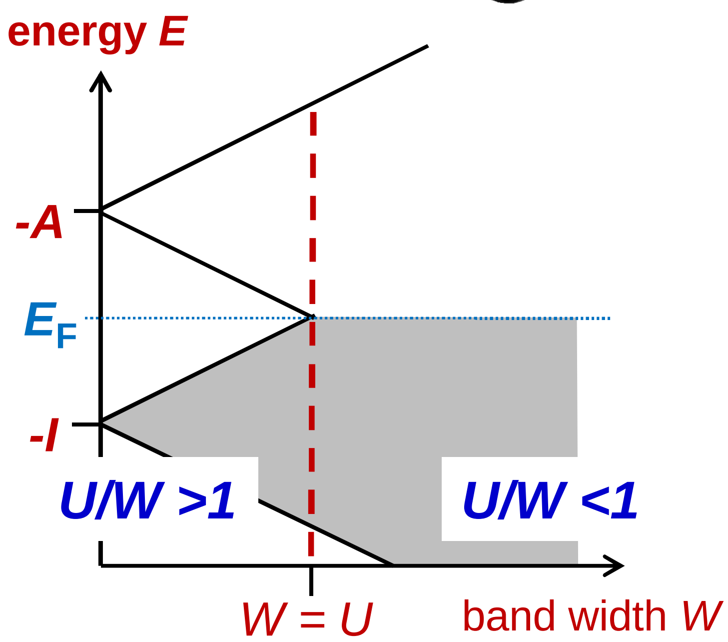
Mott insulator:
(AF ground state)



Hubbard Model

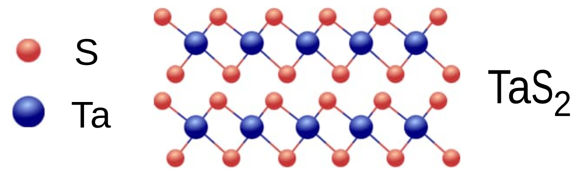
→ on-site Coulomb repulsion U

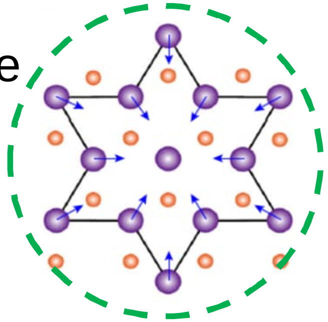


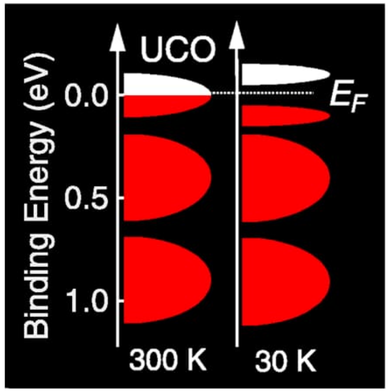


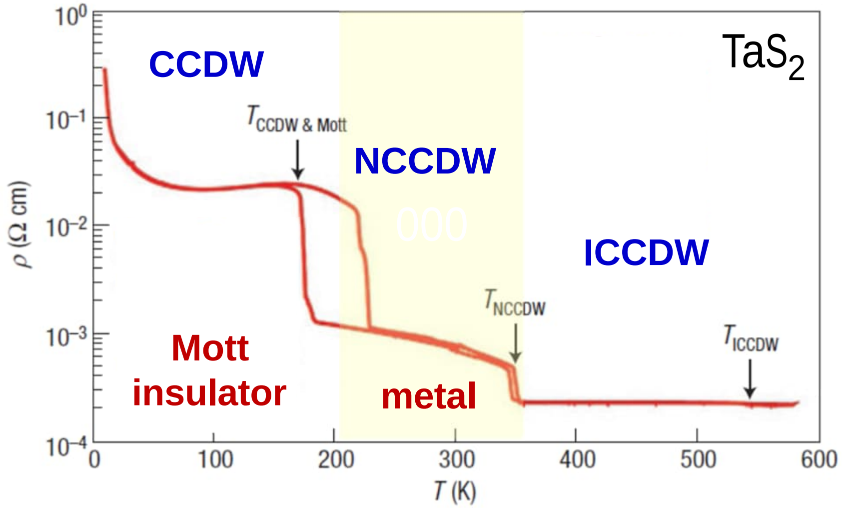
Example: CDW versus Mott physics in TaS_2

- Layered material TaS_2 shows **multiple CDW phases**
- Commensurate CDW phase ($T < T_{CCDW}$) consists of **„Star-of-David“ clusters** (with 13 Ta atoms).
- **Scenario**: Rearrangement of electronic structure due to CDW leads to change in band width W.
- At low T the upper cluster orbital (UCO) splits with **gap** attributed to a **Mott transition** ($W < U$)









Sipos *et al*, Nature Mat. **7**, 960 (2008)

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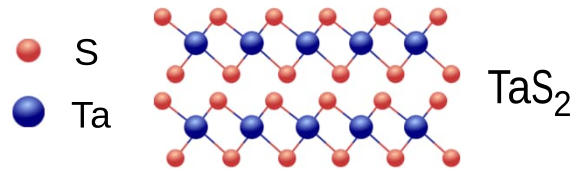

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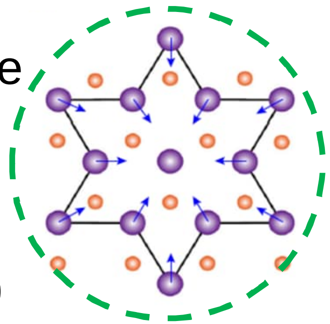
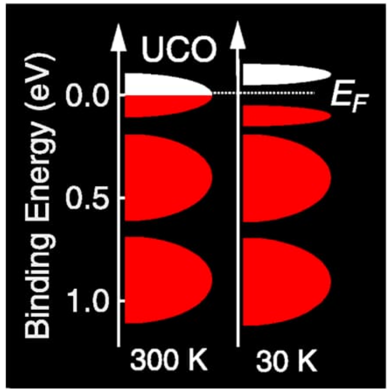


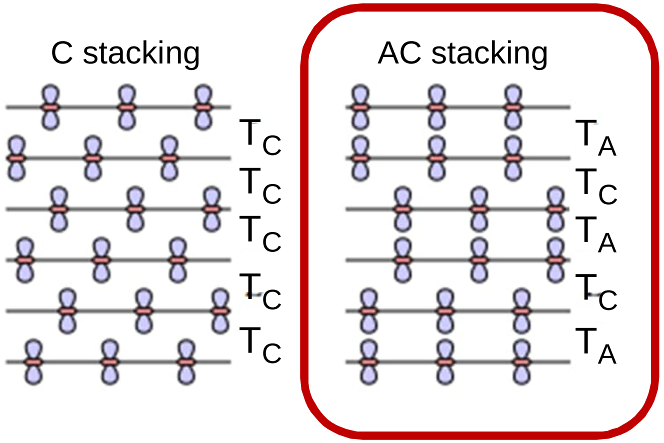


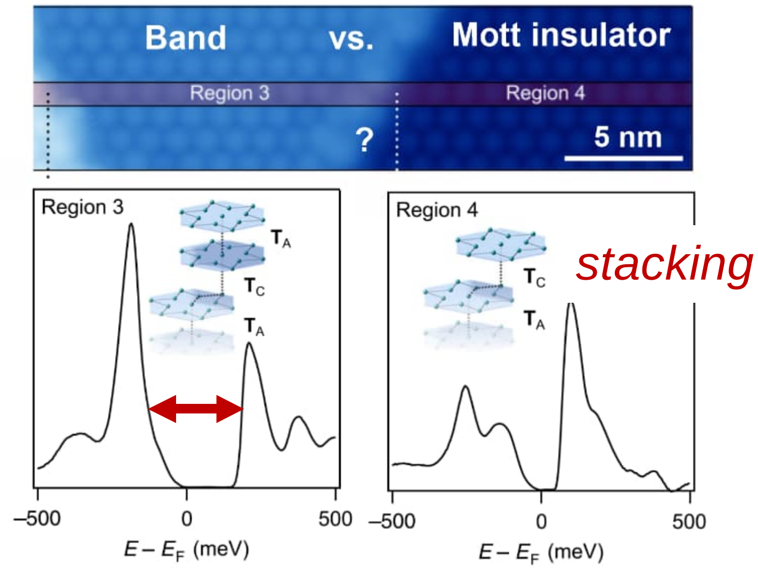
- At low T the upper cluster orbital (UCO) splits with **gap** attributed to a **Mott transition** ($W < U$)

➢ *Note, Mott vs band insulator is debated !*
(see e.g. Nature Comm. 11, 2477 (2020))

Gap opening may result from Peierls scenario along k_z

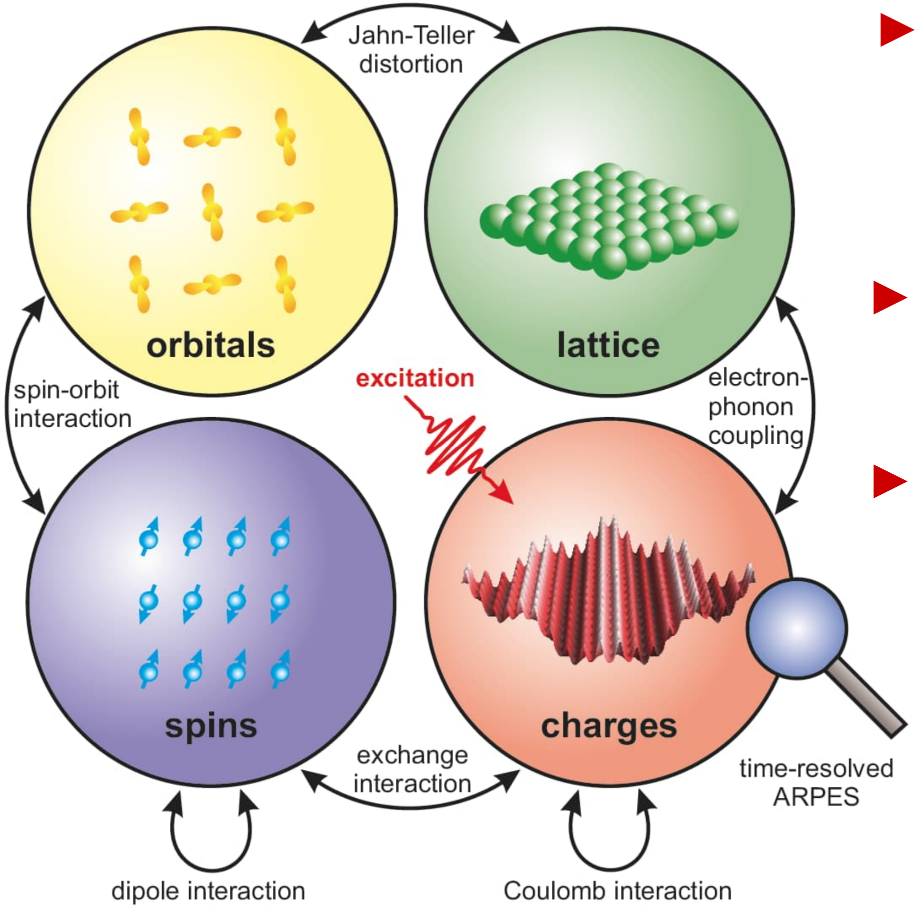
Lee et.al, PRL **122**, 106404 (2020)





Ultrafast dynamics in solids

► General goal: Understanding material properties based on elementary interactions and the coupling between the various degrees of freedom



► **Dynamics** of elementary processes: occurs **on ultrafast timescales**

⇨ Time-resolved spectroscopy

► Electronic structure plays **key role** and governs **ultrafast structural dynamics**

► Requirements to watch such dynamics:
- specific probe of excited states
- momentum resolution
- ultrafast dynamics

Movie of transient electronic structure

Outline

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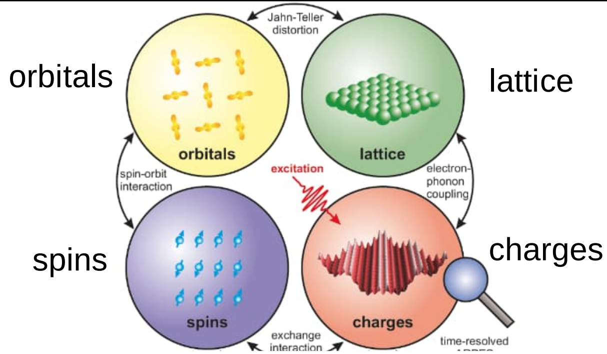
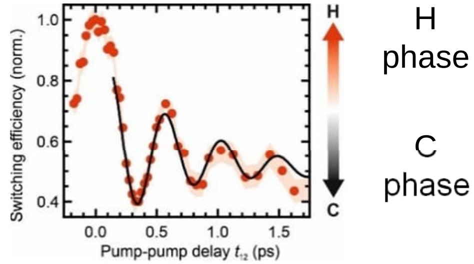


- **Charge density wave dynamics** in TaS_2 :
  - Transition to metastable H phase probed by ARPES
  - Local CDW dynamics probed by THz- STM



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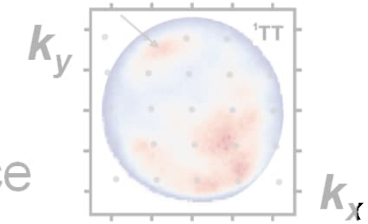
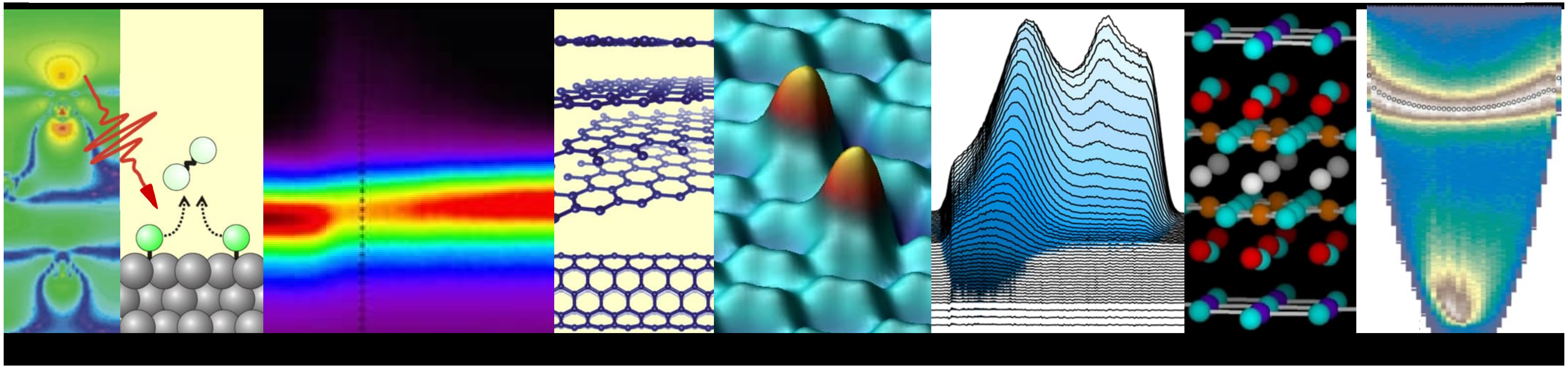
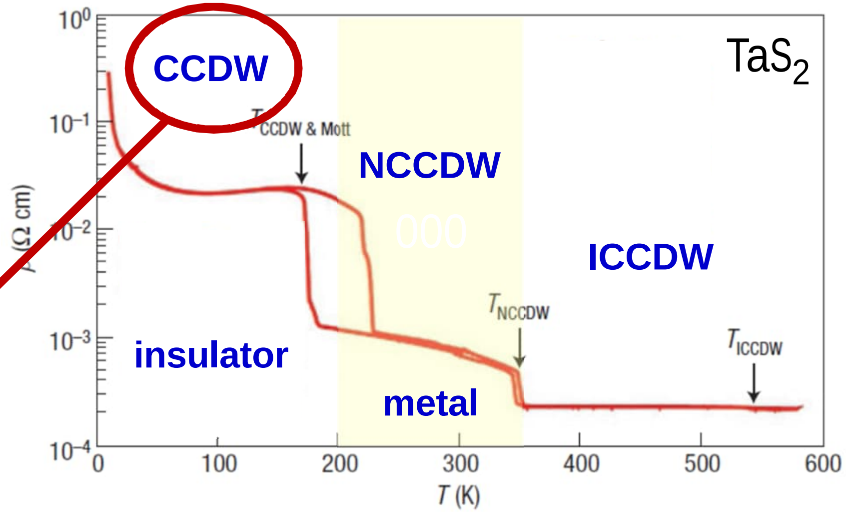


- **Coupling between light and matter**:
  - Phonon polaritons and strong coupling on SiC metasurface

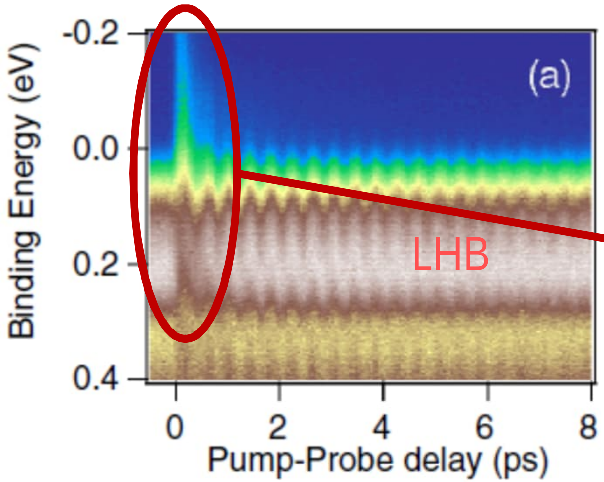


The charge density wave system: TaS_2

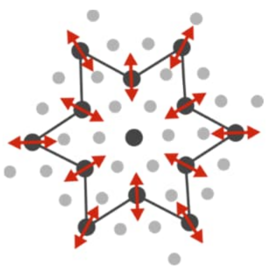
- Charge density wave (CDW) formation as a prototypical case of *e-ph* coupling
- **TaS_2 as model system** with a rich phase diagram
  - Photoexcitation of CCDW phase:



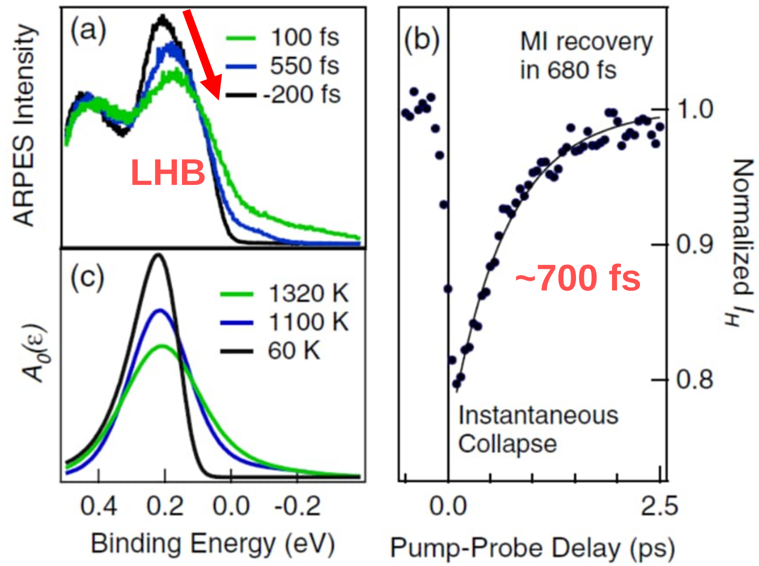
Perfetti *et al*, PRL **97**, 067402 (2006)



TaS_2
'Star-of-David'
breathing mode
ν = 2.4 THz



- Ultrafast LHB dynamics

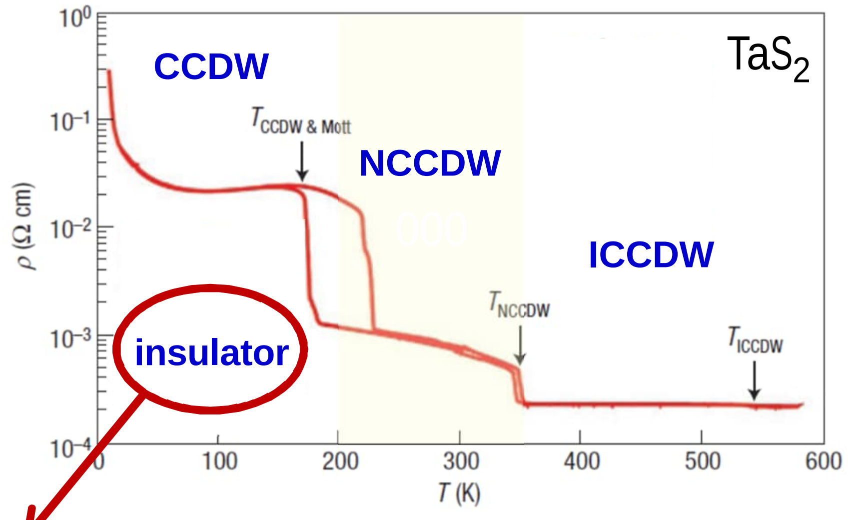


‚Hidden State‘ in the CDW system TaS_2

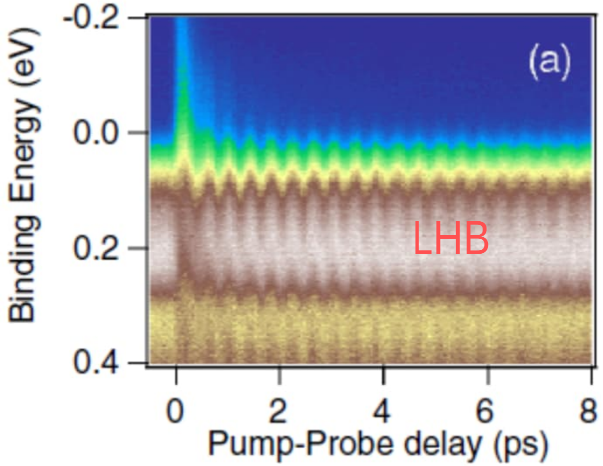
➢ Charge density wave (CDW) formation as a prototypical case of *e-ph* coupling

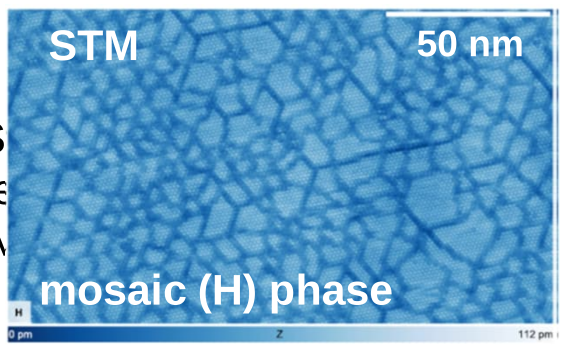
➢ **TaS_2 as model system** with a rich phase diagram

- Photoexcitation of CCDW phase:



PRL **97**, 067402 (2006)



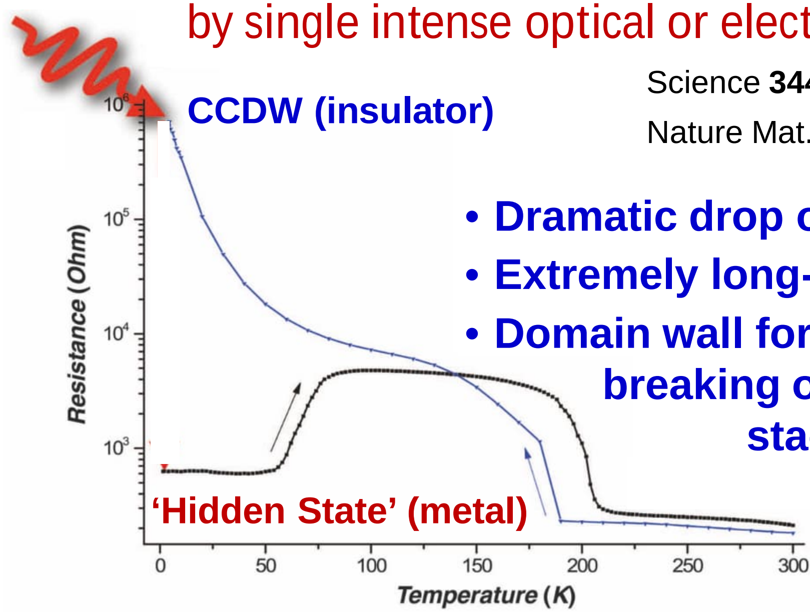


➢ **Transition to <u>metallic mosaic phase</u> of TaS_2**

by single intense optical or electrical pulse

Science **344**, 6180 (2014)

Nature Mat. **18**, 1078 (2019)



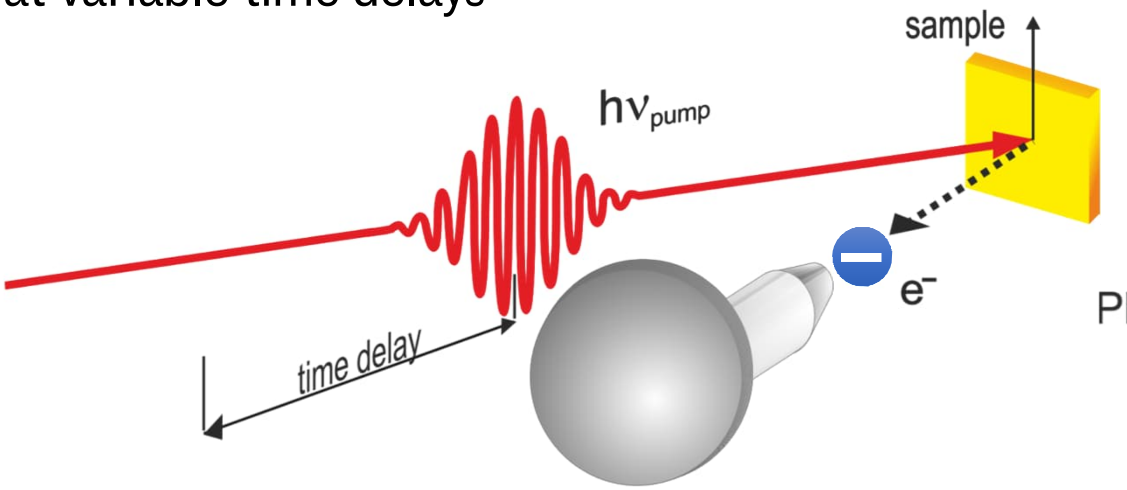
- **Dramatic drop of resistivity**
- **Extremely long-lived phase**
- **Domain wall formation & breaking of interlayer stacking order**

Time- and angle-resolved photoemission

Pump pulse: creates non-equilibrium state

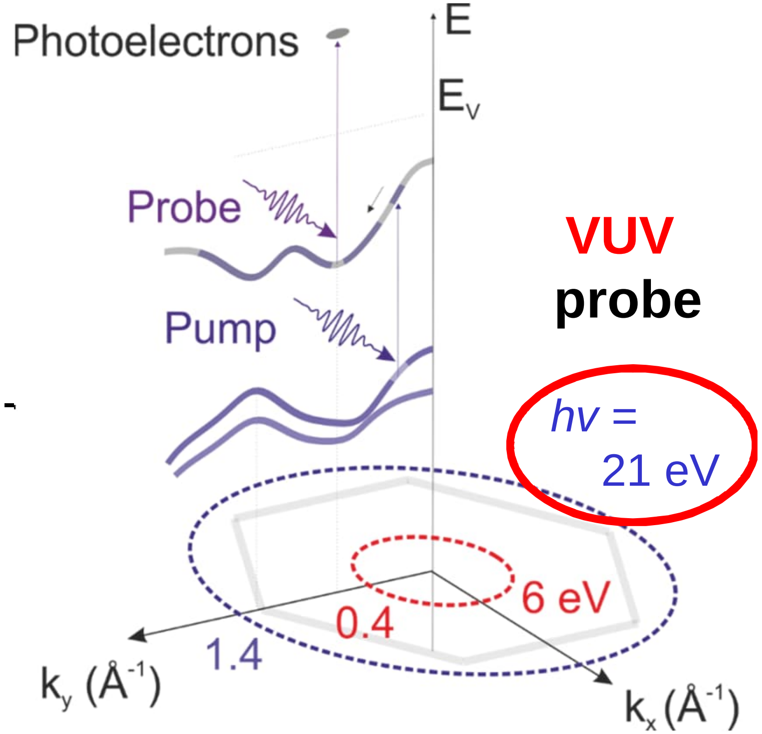
Probe pulse: monitors photoinduced dynamics at variable time delays

ARPES from a laser excited sample



Accessible momentum space is limited by E_{kin}

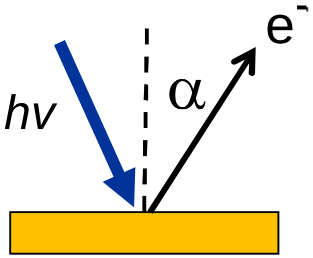
VUV probe



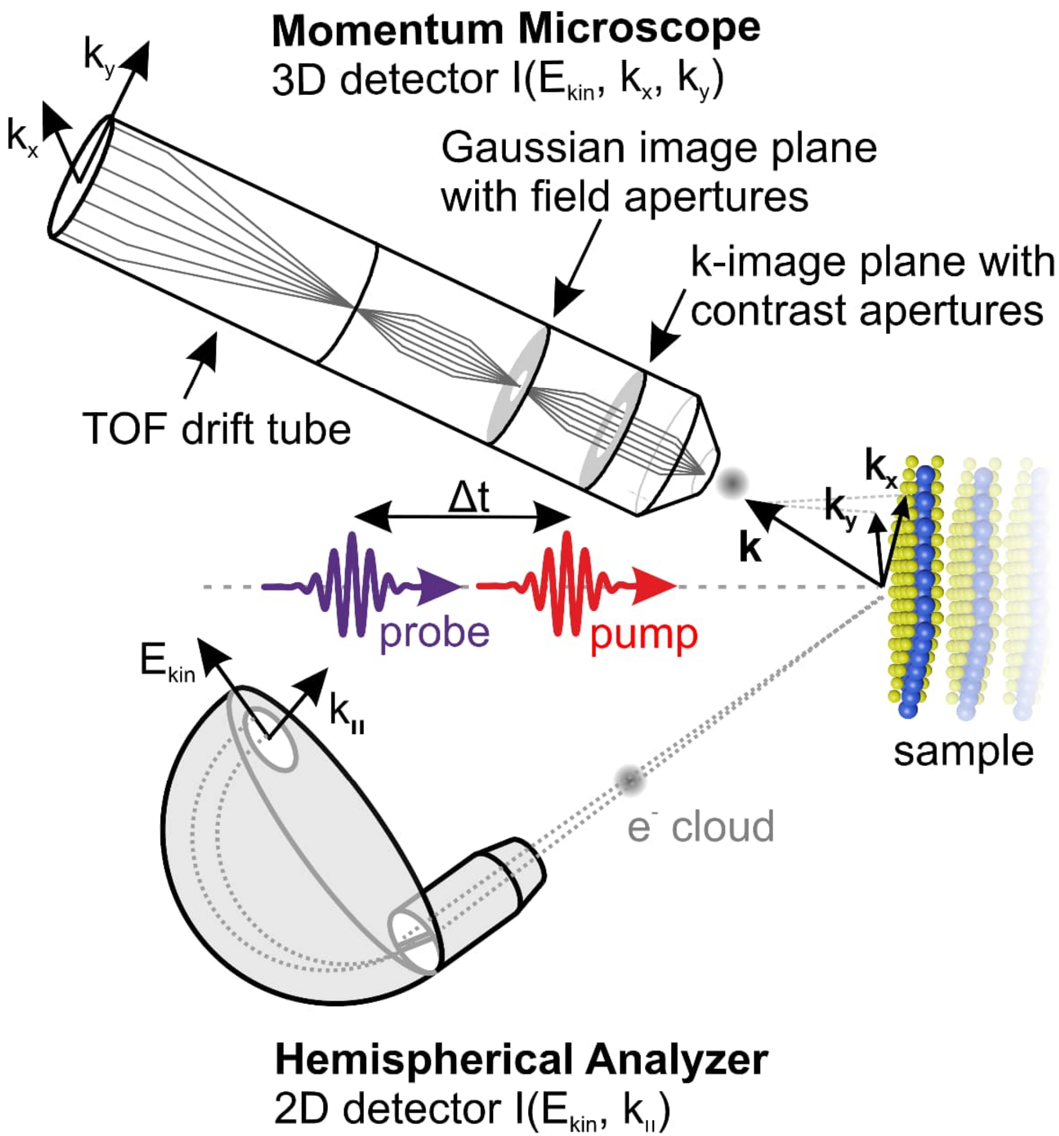
Energy and momentum resolution:

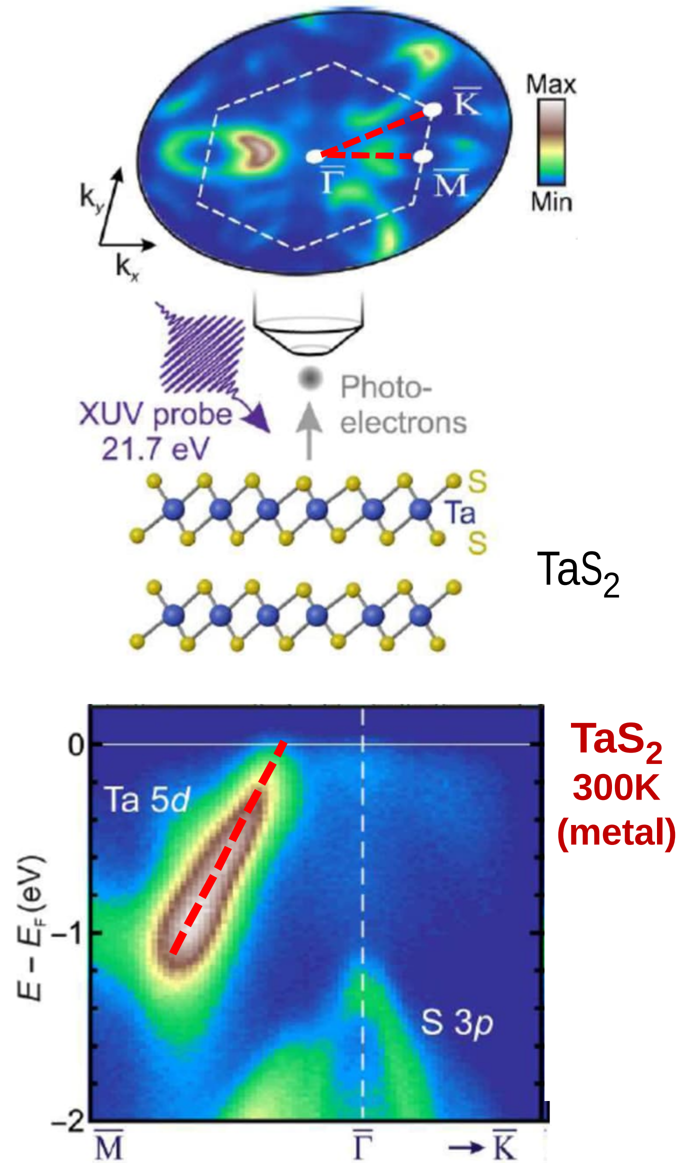
$$E_{kin} = \hbar\omega - E_b - \Phi$$

$$\hbar k_{||} = \sqrt{2m_e E_{kin}} \cdot sin\alpha$$



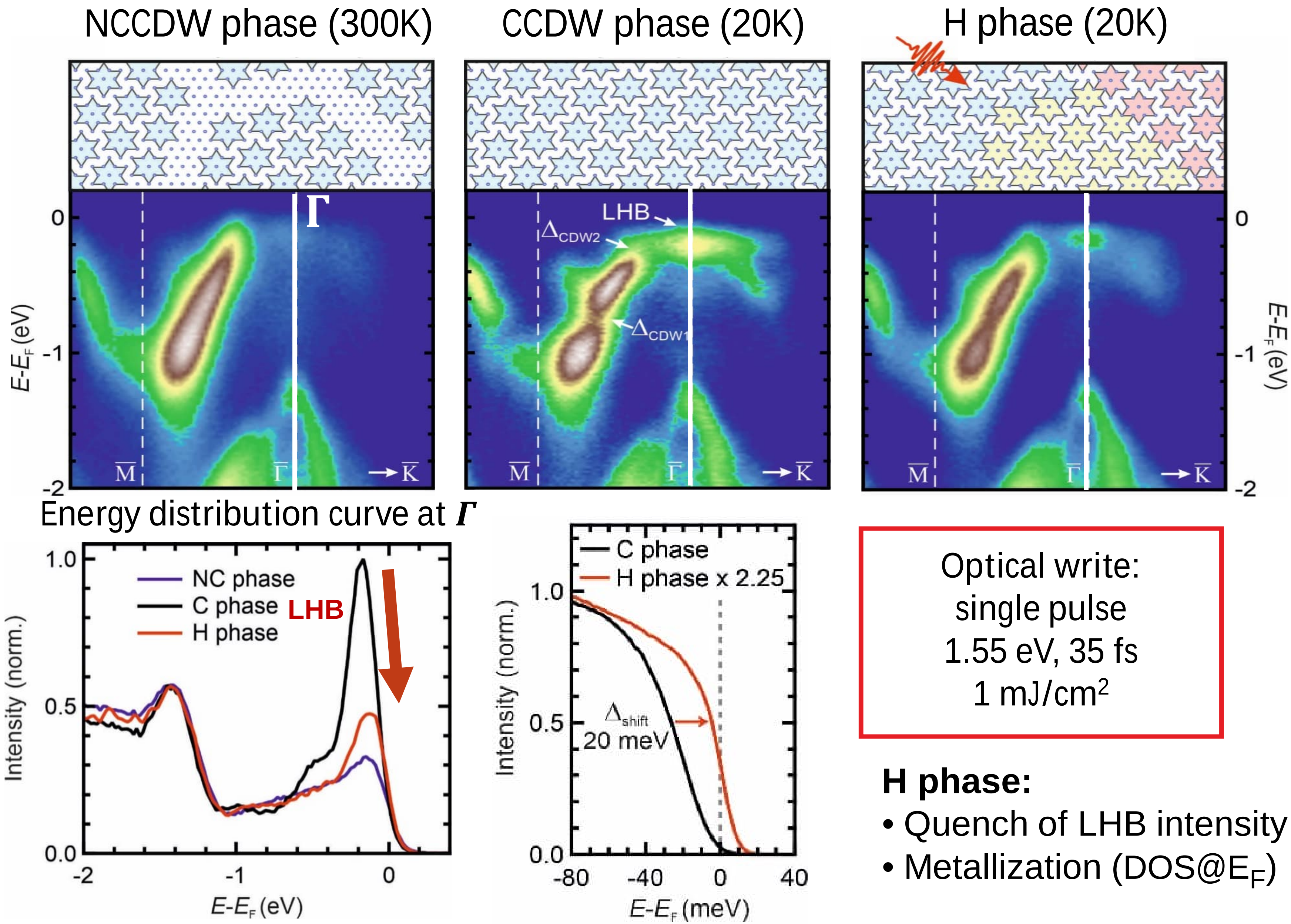
trARPES from TaS_2





J. Makler *et al.*, Science Advances **9**, eadi4661 (2023)

Band structure of H phase in TaS_2

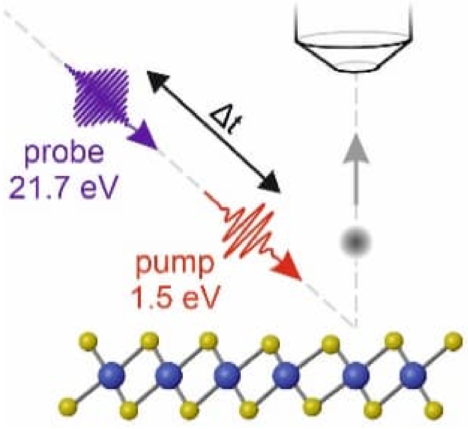


Optical write:
single pulse
1.55 eV, 35 fs
1 mJ/cm^2

H phase:

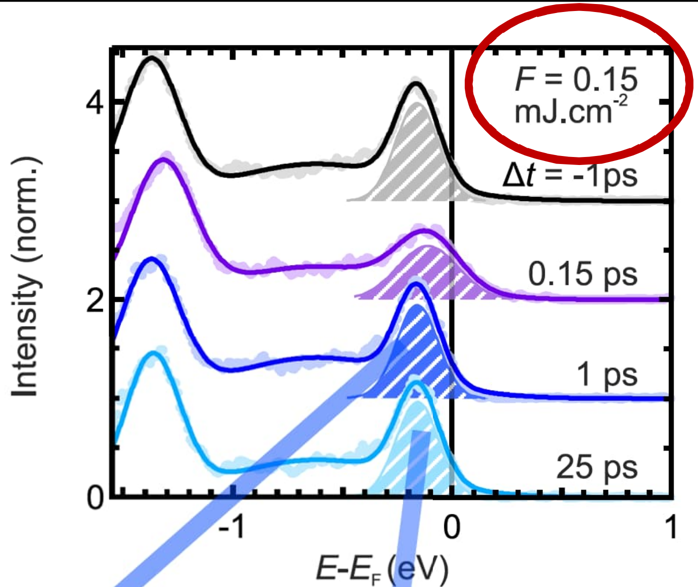
- Quench of LHB intensity
- Metallization (DOS@E_F)

Excitation of amplitude mode of CCDW phase

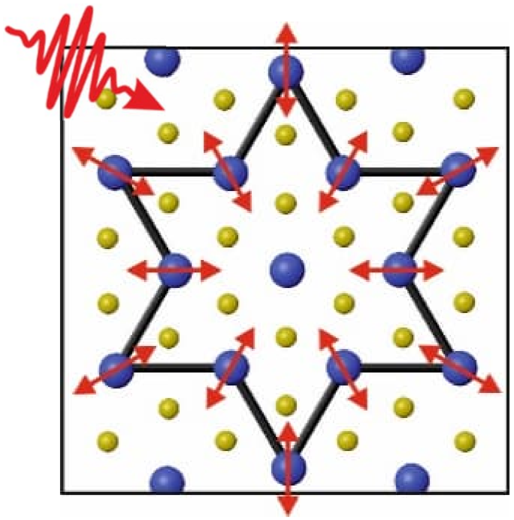


→ Lifetime of H phase decreases with T

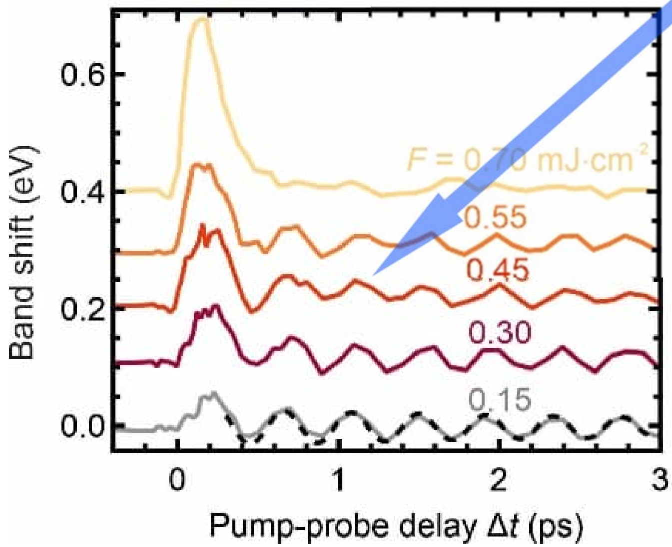
- 4 K ~ 10^8 s (extrapolated)
- 50 K ~ 10 s
- 160 K ~ 100 μs



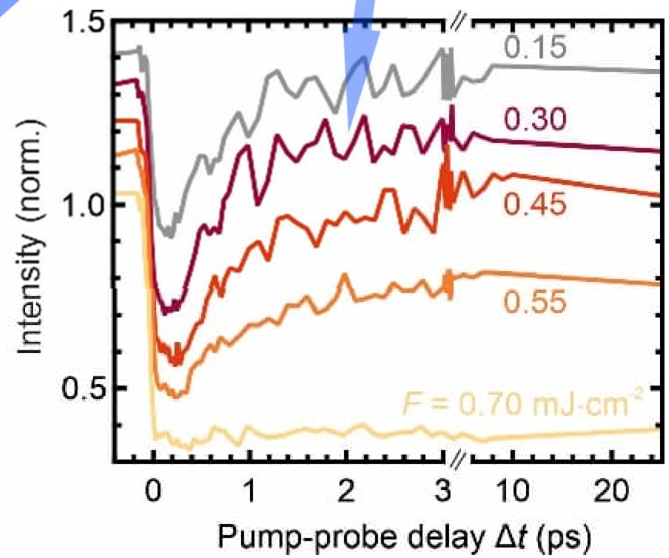
In weak-response regime:
CDW amplitude mode @ 2.4 THz



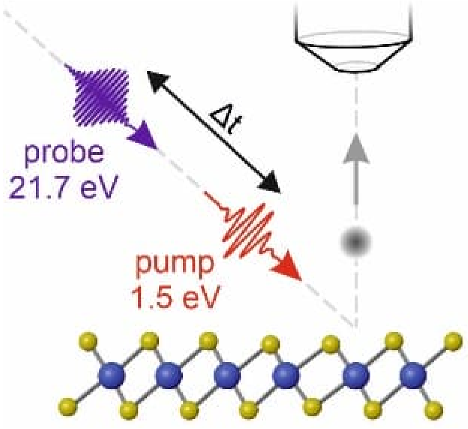
Band **shift**



Band intensity



Switching from CCDW to hidden phase



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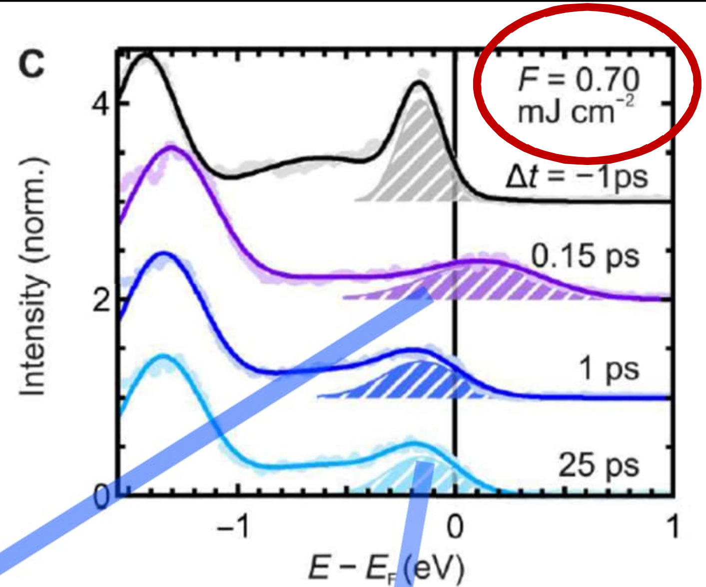
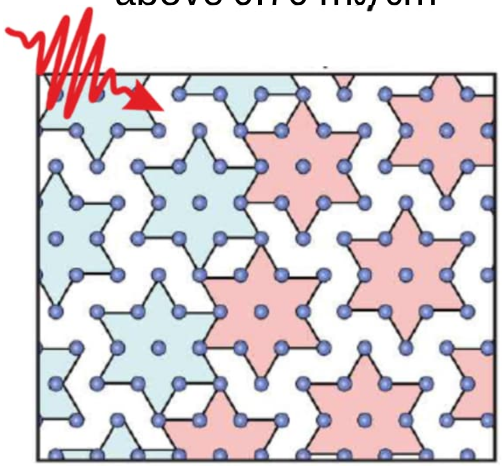
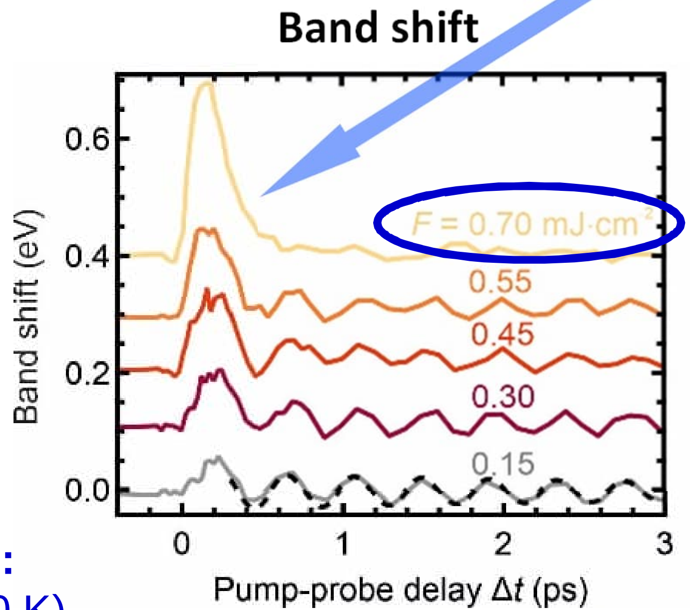
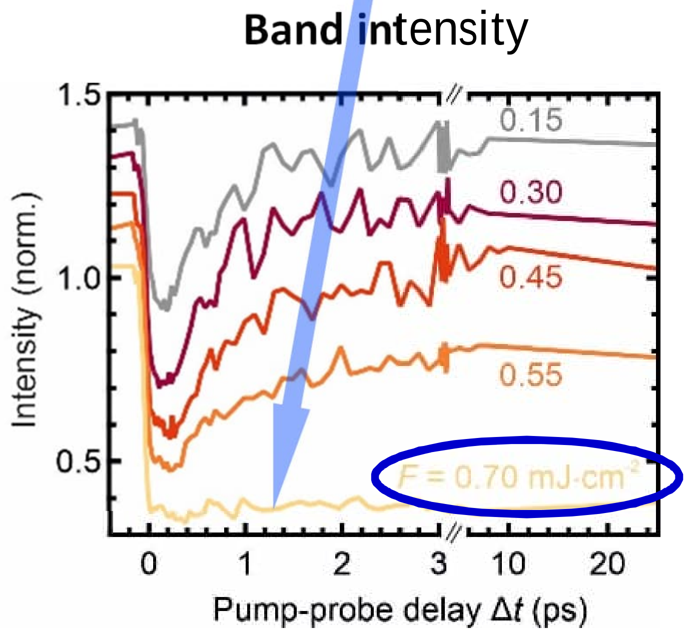


Switching to H phase: above 0.70 mJ/cm^2



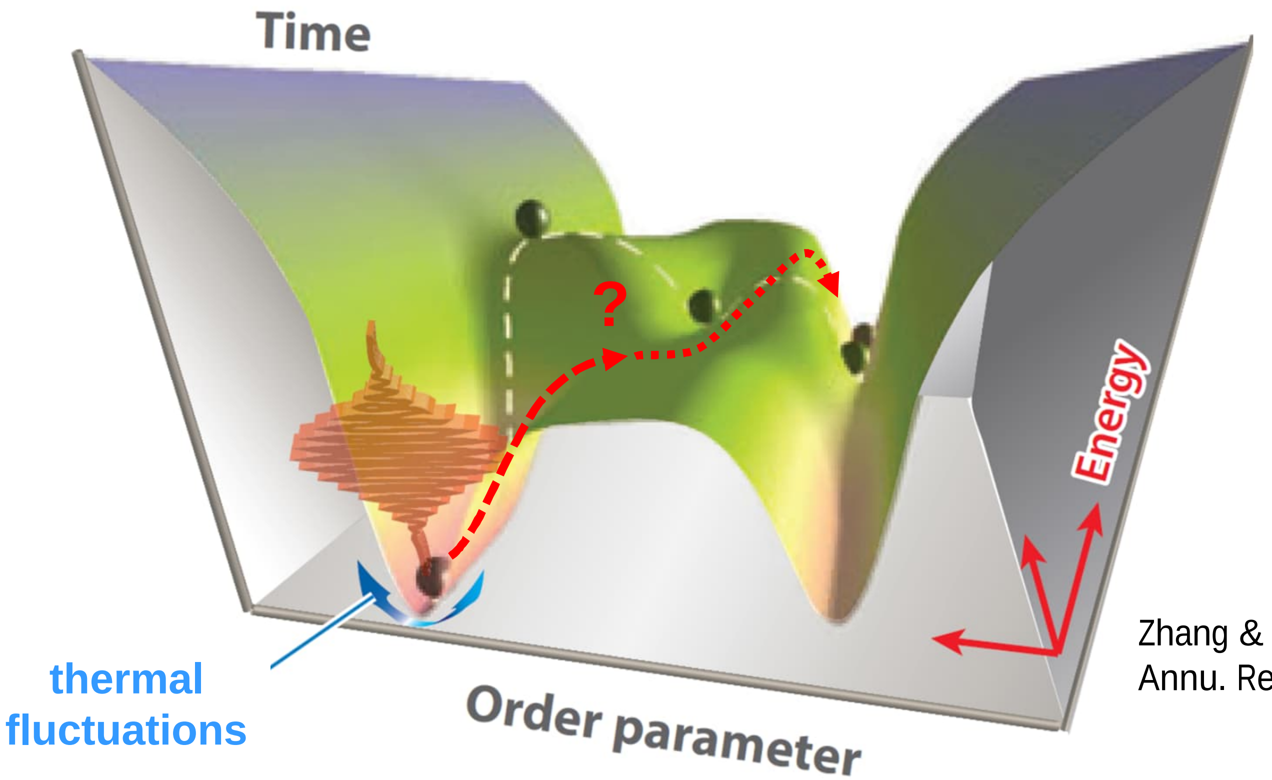




- **Collapse of Mott gap**
- **Reach long-lived state:** (recovery ~100μs at 160 K)

Control of trajectory into the hidden phase?

► How can we access states not realized in equilibrium phase diagram?

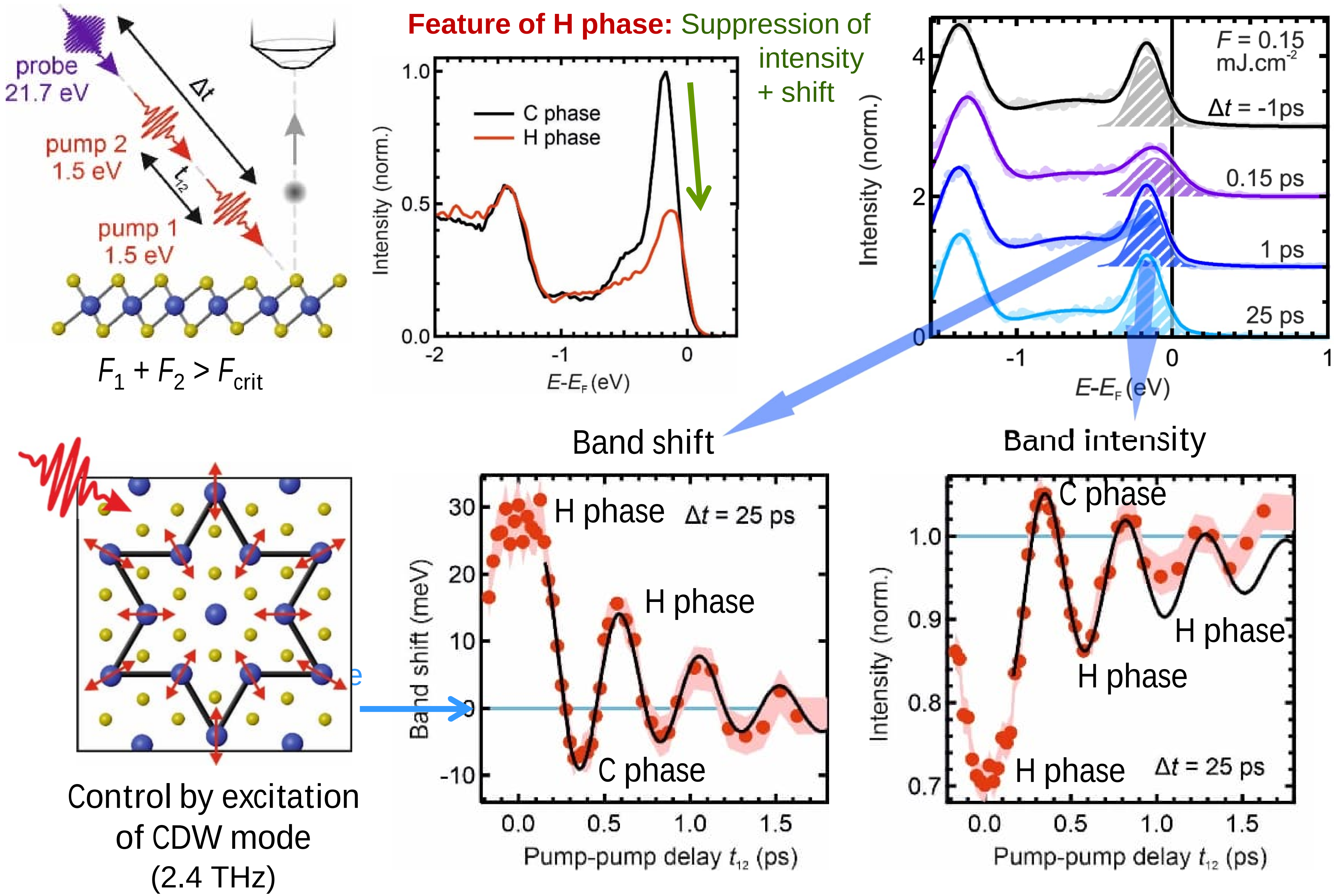


Zhang & Averitt
Annu. Rev. Mater. Res. (2014)

► Is there a non-thermal, vibrational coherent pathway to the H phase ?

⇨ Study role of collective CDW excitation in “double pump” experiment

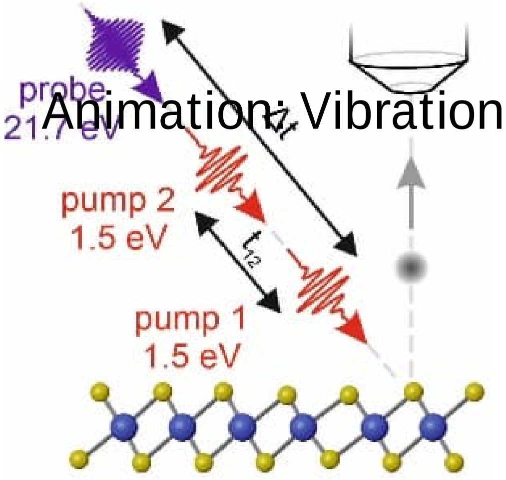
Coherent control of switching to H phase



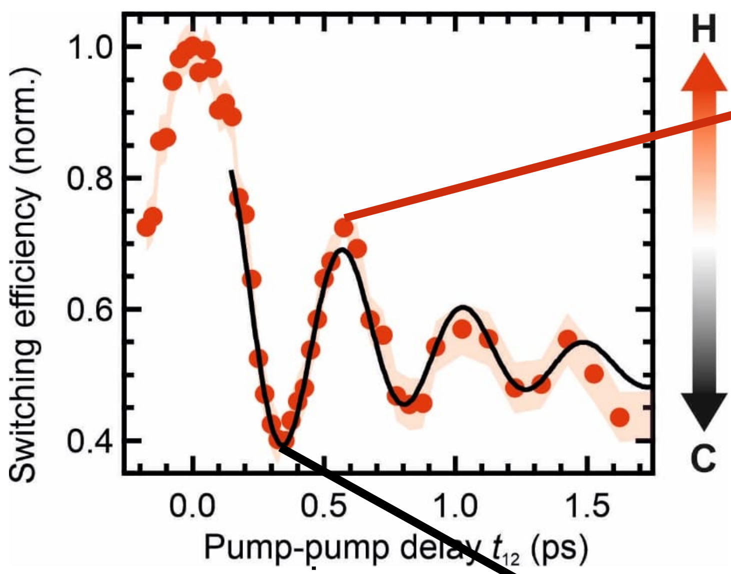
Coherent control of switching to H phase

Animation: Vibrational coherent transition to H phase

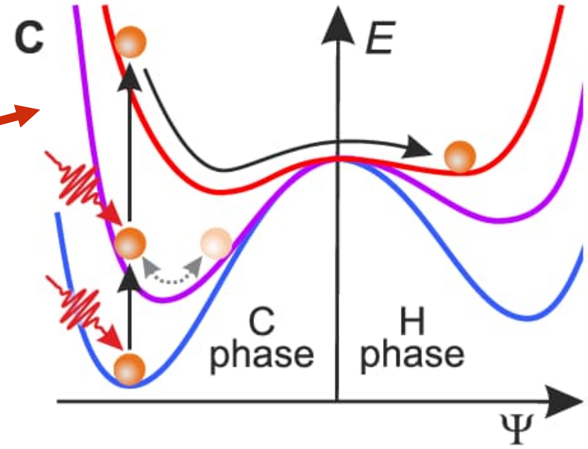
Switching efficiency



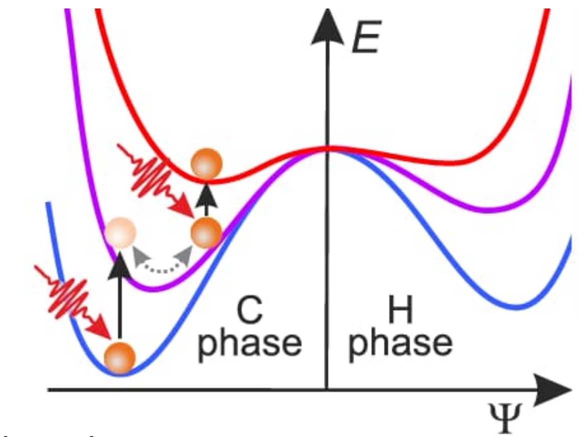
$F_1 + F_2 > F_{crit}$

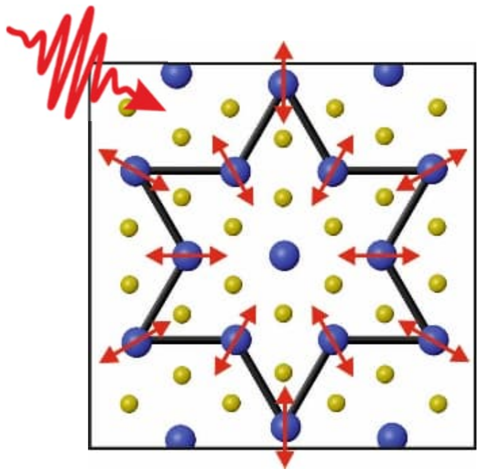


in-phase excitation & overshoot to H phase



out-of-phase excitation





Control via CDW mode excitation

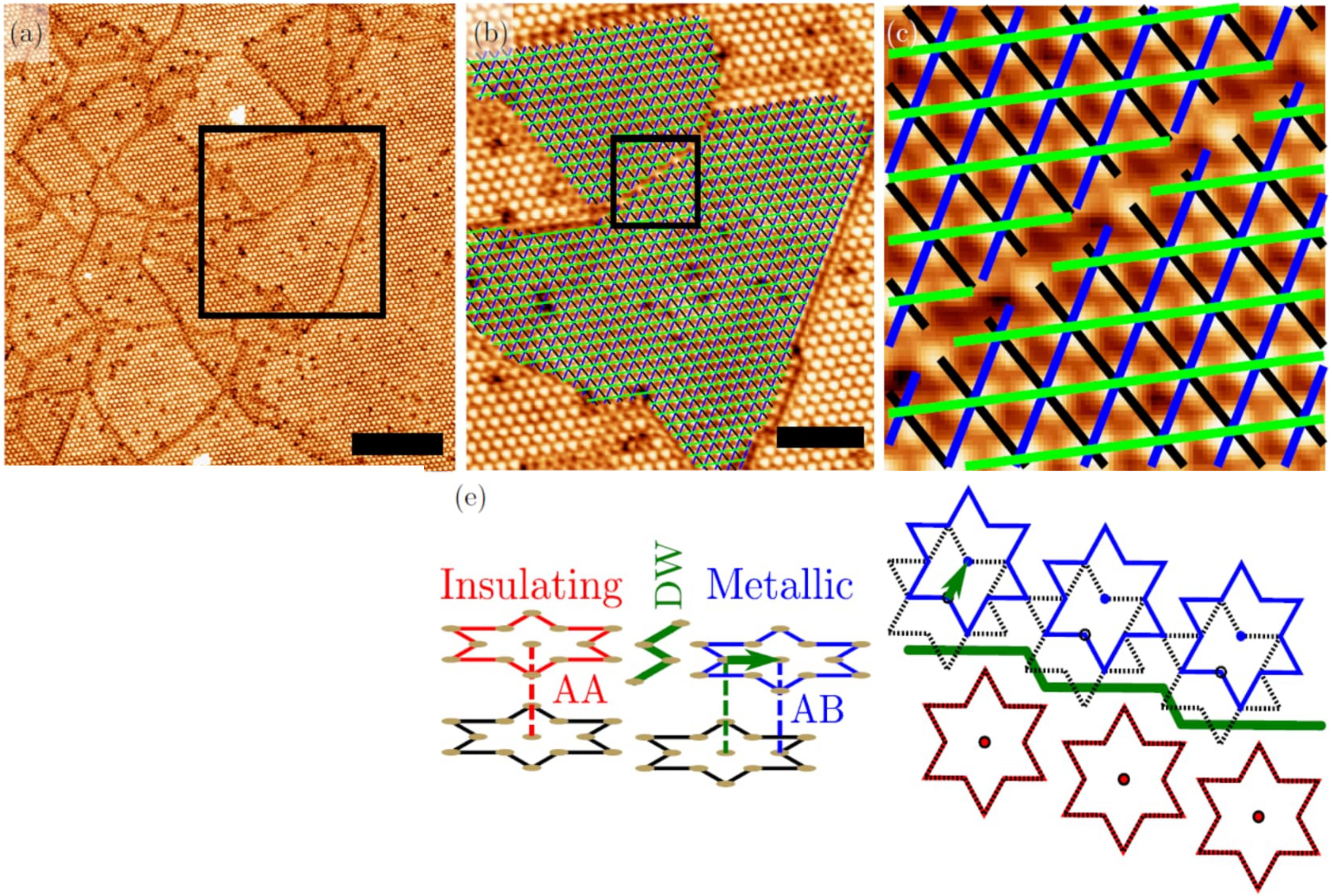
J. Makler *et al.*, Science Advances **9**, eadi4661 (2023)

Domain boundaries & stacking in TaS_2 mosaic phase

PHYSICAL REVIEW MATERIALS **7**, 064005 (2023)

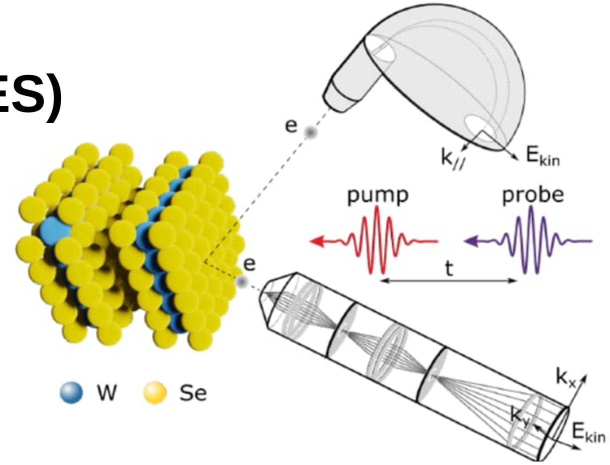
Observation of the metallic mosaic phase in 1*T*-TaS_2 at equilibrium

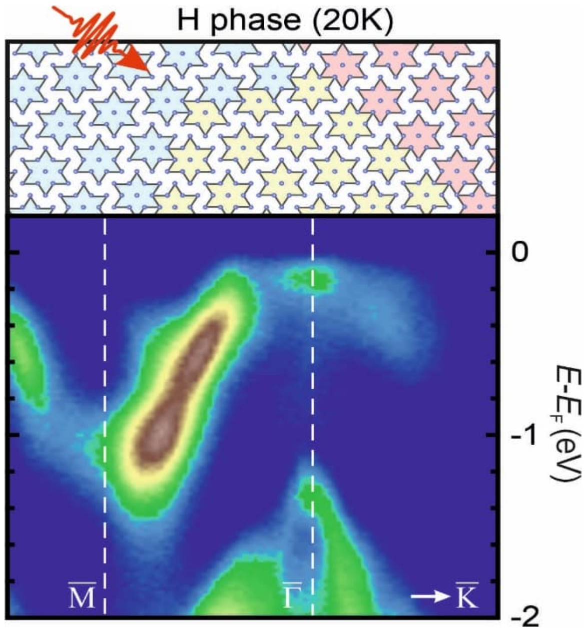
C. Monney & coworkers



Take home…

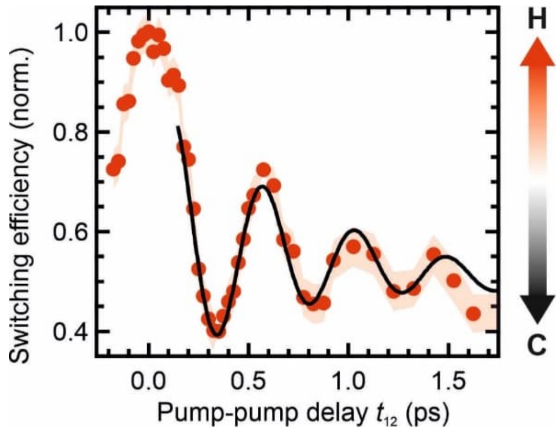
Time- and angle-resolved photoemission (trARPES) as direct probe of electronic structure





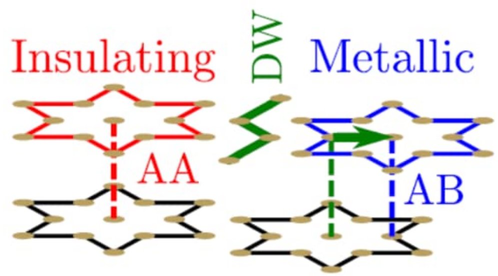
trARPES applicable to transitions to metastable ‘hidden’ states

Science Adv. **9**, eadi4661 (2023)



Vibrational coherent control of reaction coordinate and ultrafast switching speed in TaS_2

Change of interlayer stacking is key for metallicity of H phase

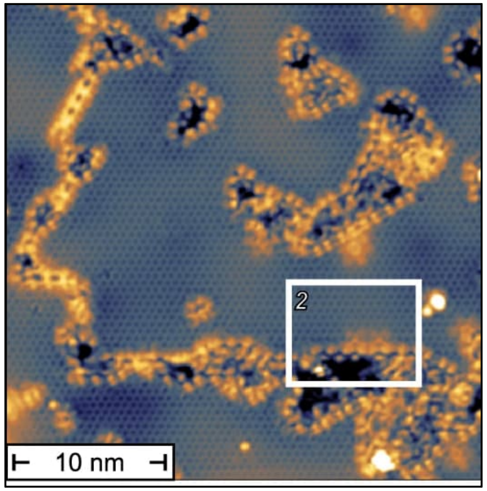


taken from Phys. Rev. Mat. **7**, 064005 (2023)

Global versus local dynamics?

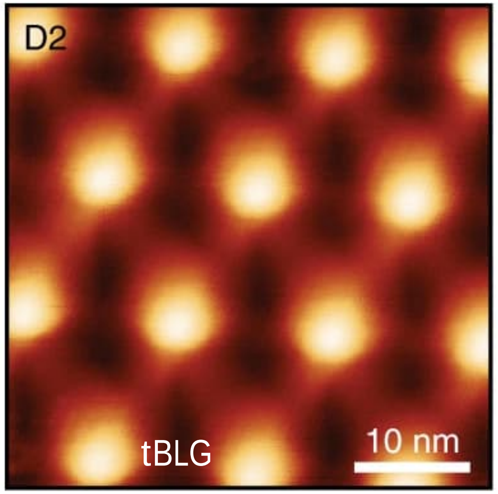
► Quantum materials are often inhomogenious, exhibit phase boundaries, edge states, moire structures ect.

Localized states
e.g. Bismuthene



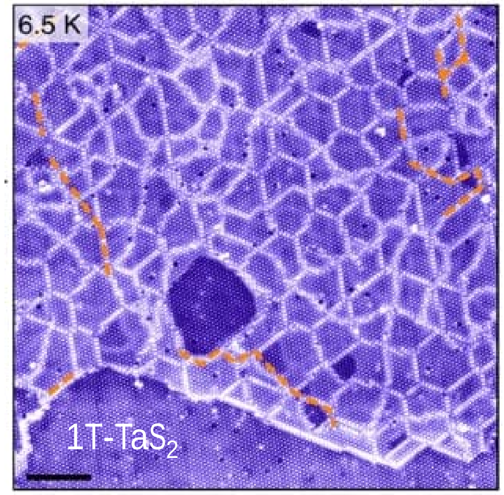
Stühler, Nat. Comm. 13, 3480 (2022)

Moiré potentials
e.g. twisted bilayer graphen



Kerelsky, Nature 572, 95 (2019)

Spatial inhomogenity
e.g. mosaic phase TaS_2



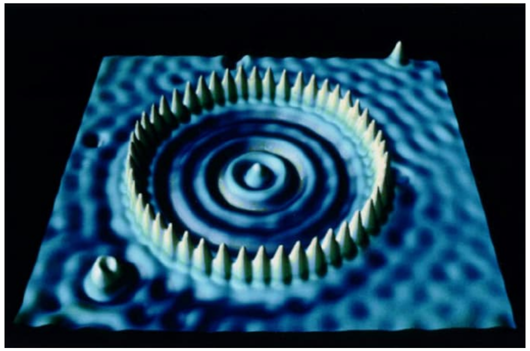
Ma, Nat. Comm. 7, 10956 (2016)

► Is there a local or globally synchronized dynamics ?

⇨ Need a local probe with ultrafast time resolution

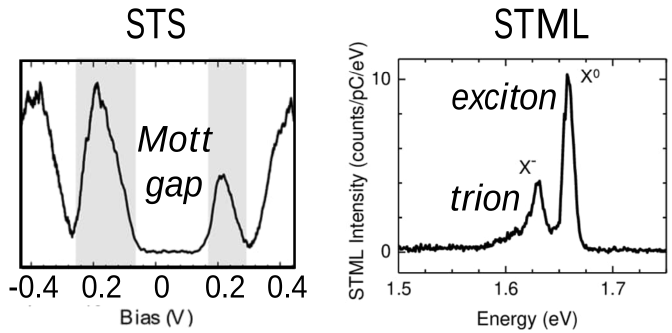
Light coupling to STM junctions

Å spatial resolution

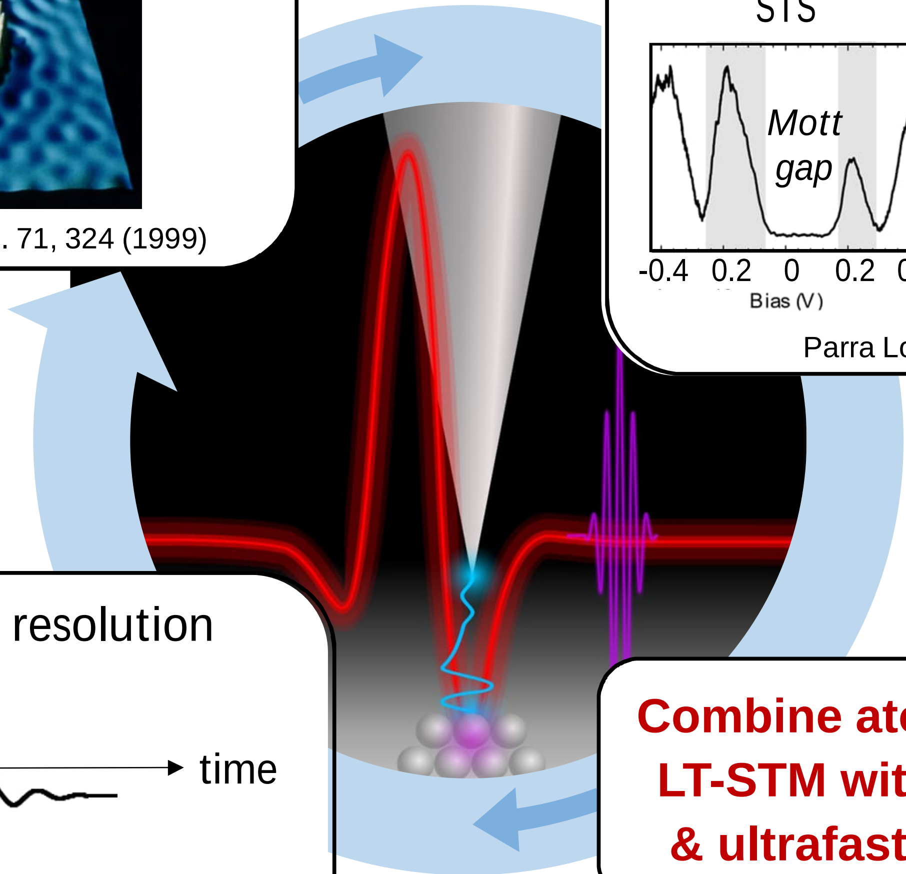


Binning, Rohrer, Rev. Mod. Phys. 71, 324 (1999)

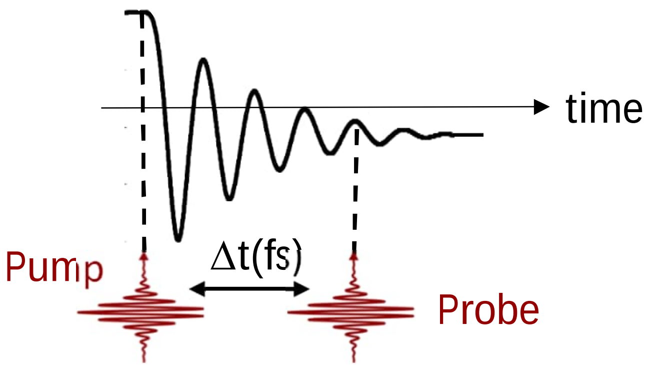
meV energy resolution



Parra Lopéz, Nat. Mat. 22 (2023)



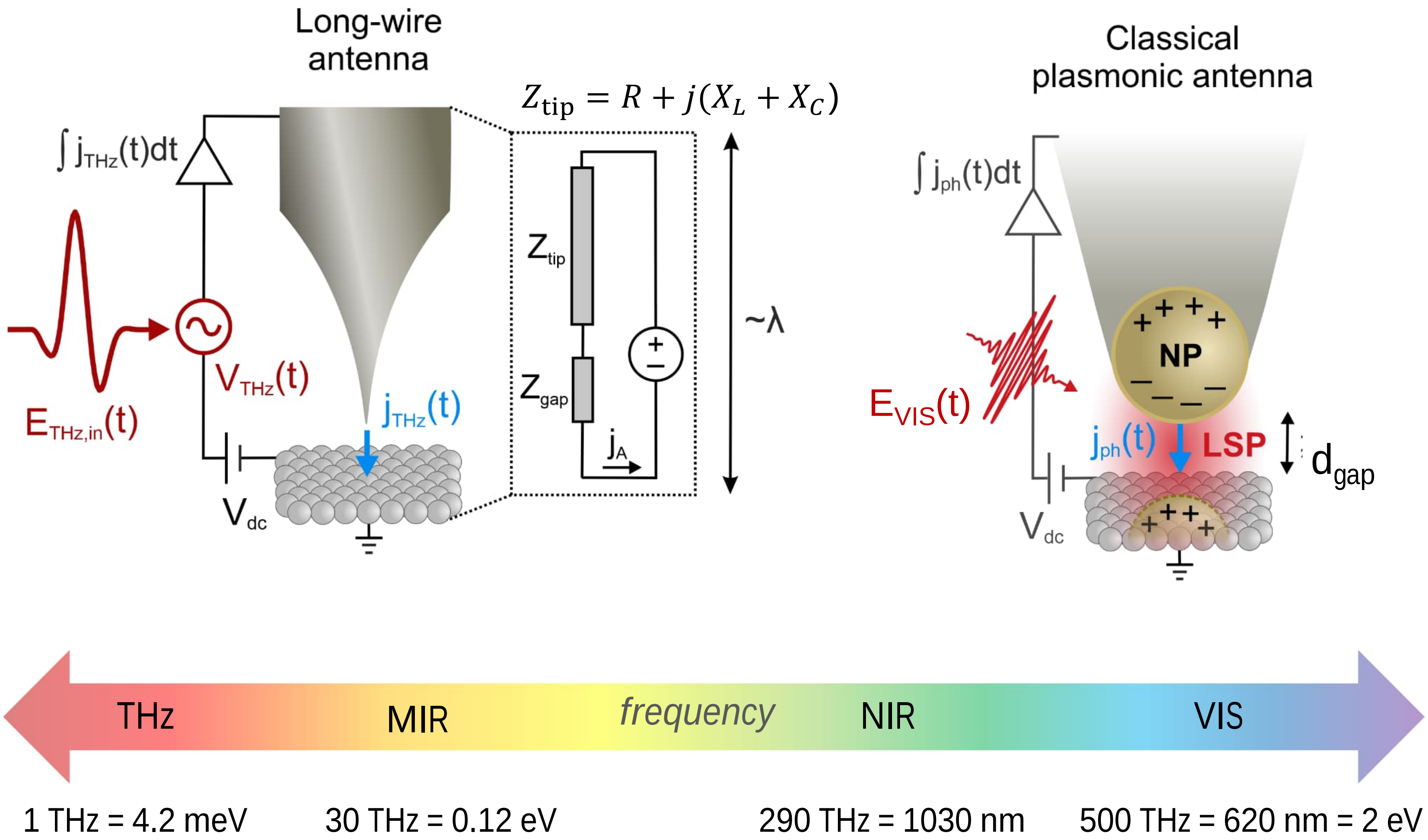
ultrafast time resolution



Combine atomistic control of LT-STM with near-field light & ultrafast time-resolution

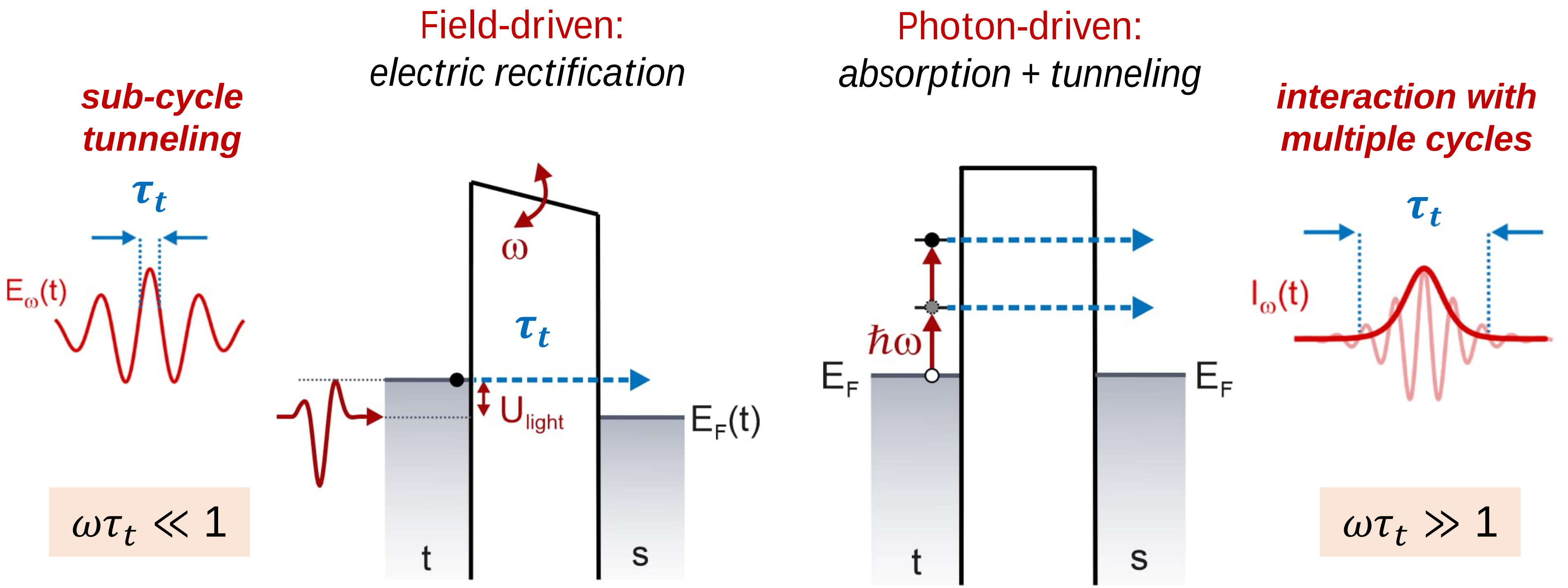
Light coupling to STM junctions

STM tips can act as broadband antennas from THz to VIS regime



Light coupling to STM junctions

Field-driven versus photon-driven electron tunneling



τ_t: traversal time for tunneling (“barrier interaction time”)

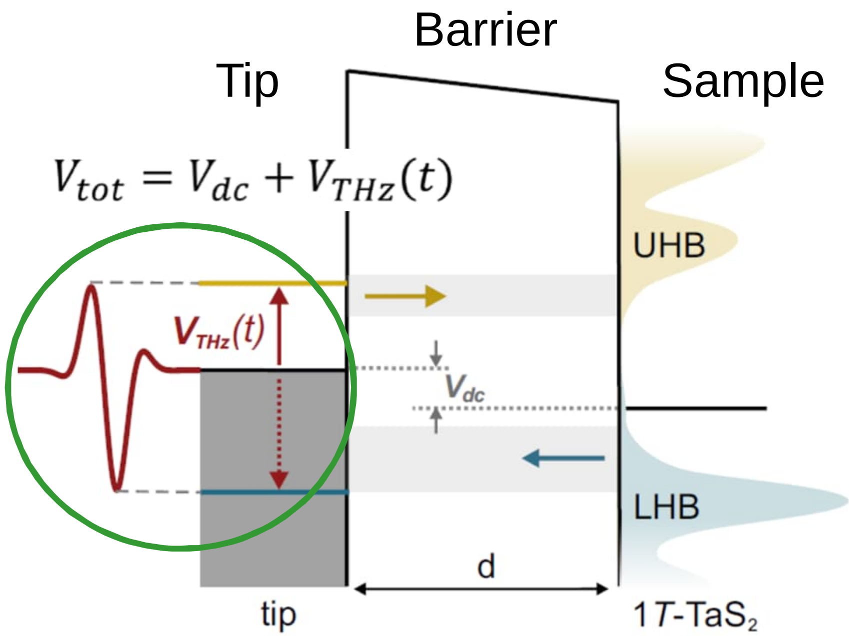
JETP. 20, 5 (1965) &
PRL 49, 1739 (1982)

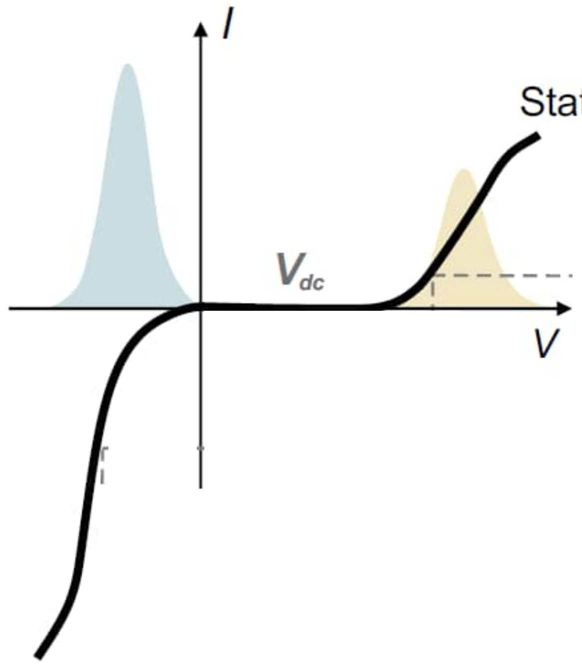
Keldysh parameter: $\gamma = \sqrt{\frac{\Phi}{2U_p}} = \omega\tau_{t,K}$

M. Müller, Prog. Surf. Sci. (2023)

THz light-wave driven STM

Concept: **Single-cycle THz field acts as ultrafast bias voltage**





- Sample DOS structure implies nonlinear current-voltage response of STM junction
- THz field induces instantaneous AC current *I(t)*
- Non-zero rectified DC current

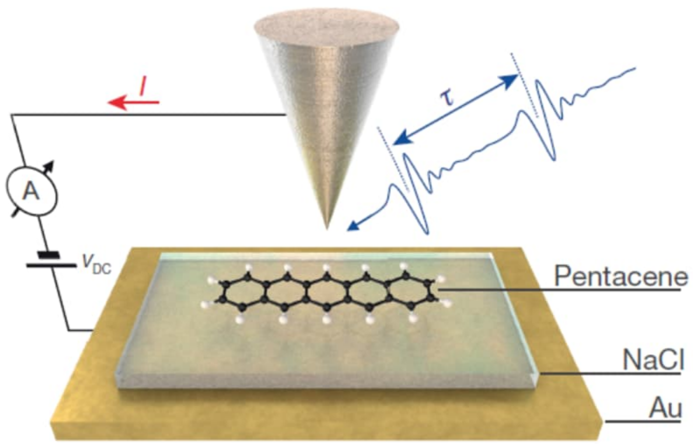
Charge per pulse:

$$Q_e = \frac{I_{THz}}{f_{rep}} = \int I_{pulse}(t)dt \neq 0$$

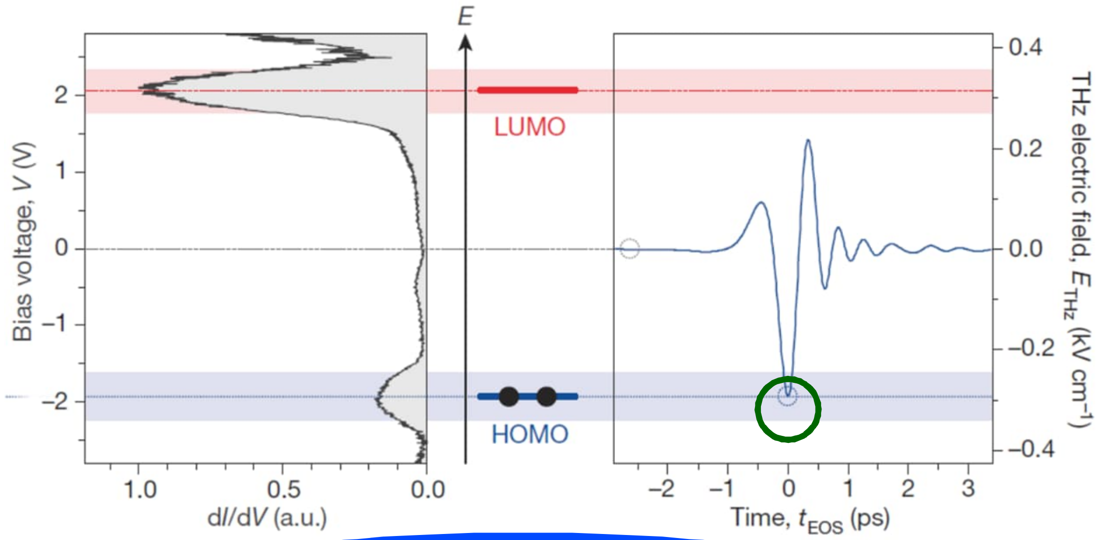
Review: Cocker, Nature Phot. **15**, 558 (2021)

Ultrafast THz STM

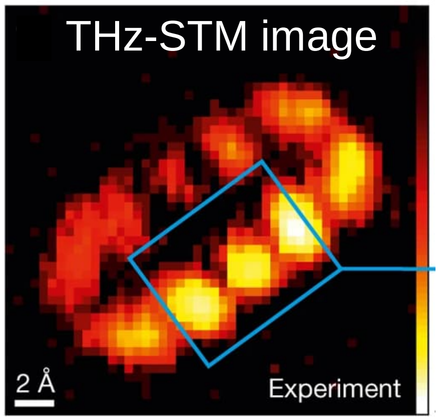
► Ultrafast THz-STM: J. Repp & R. Huber et al., Nature **539**, 263 (2016)

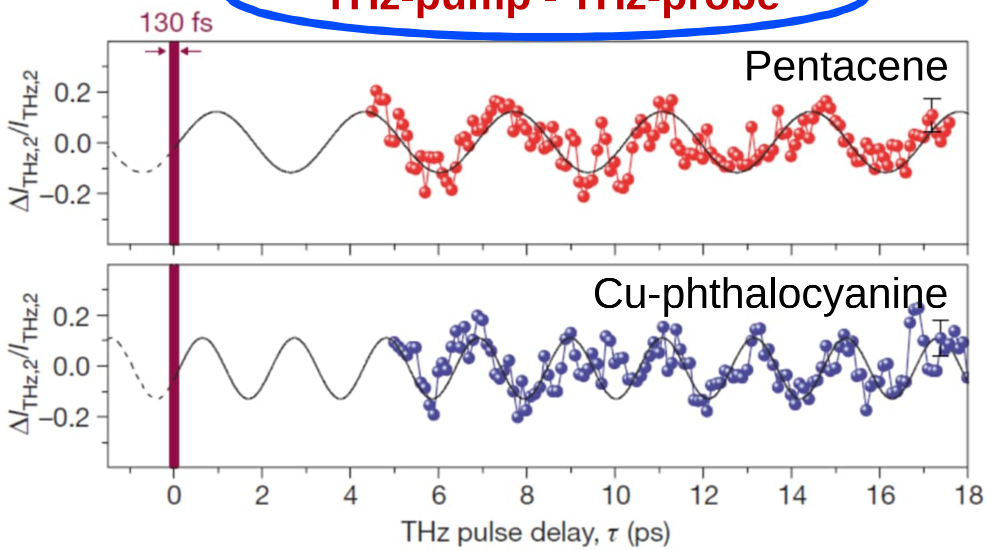


Pentacene(/NaCl/Au



THz-pump - THz-probe





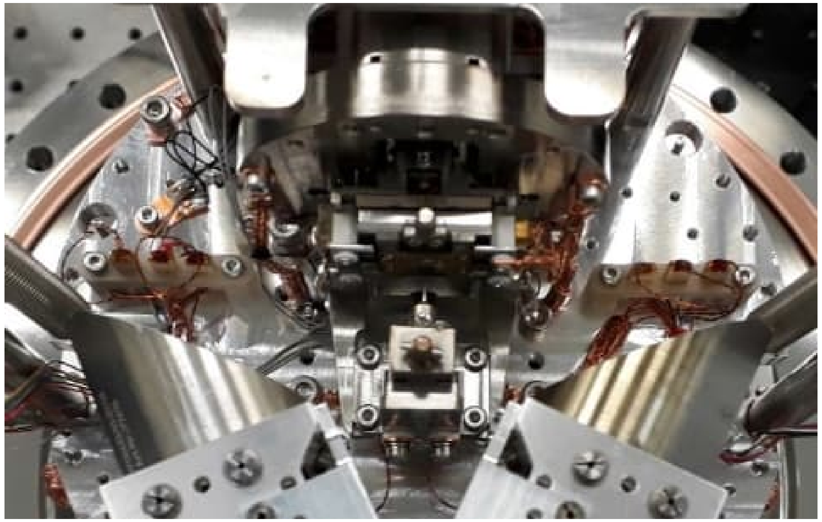
Optical excitation & probing in UHV LT-STM

Dr. Melanie Müller

Experimental setup (THz-STM):

- Exploit high stability and control of low-temperature STM (LT-STM)
- Precise **optical excitation** and **light detection** with motorized optics in UHV

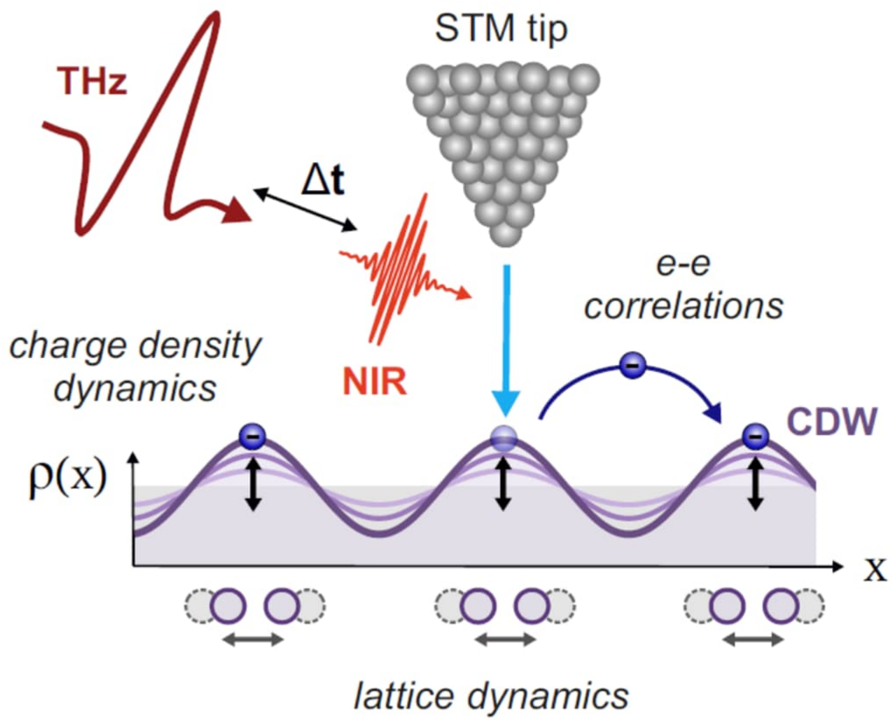
Parabolic mirrors integrated into LT-STM



- Unisoko STM platform with sample and optics at 5 K (or 80 K)
- Parabolic mirrors yield **high NA**
- Optical excitation with **visible fs pulses & THz STM probe**

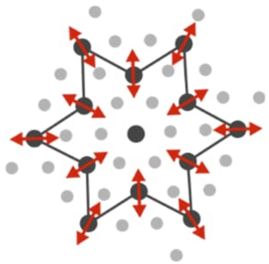
CDW dynamics probed by THz-STM

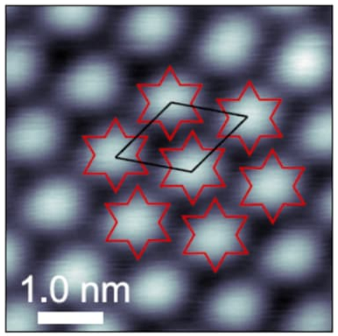
Goal: **Study ultrafast photoinduced CDW dynamics by THz light-wave STM**



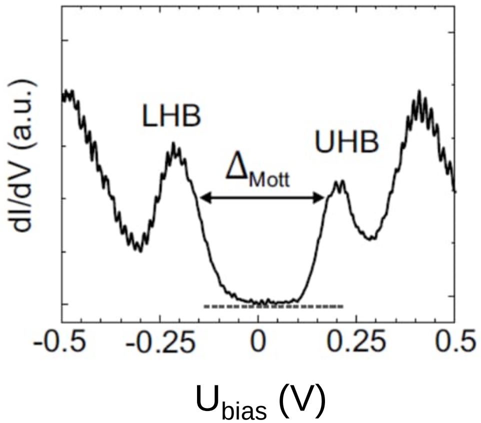
- Charge density wave (CDW) formation as a prototypical case of *e-ph* coupling
- Correlated electron-lattice dynamics
- Study **TaS_2 as model system** with rich phase diagram:
  - o Electronic structure strongly affected by stacking
  - o CDW formation accompanied Mott insulator physics

TaS_2
"Star-of-David"
amplitude mode
ν = 2.5 THz





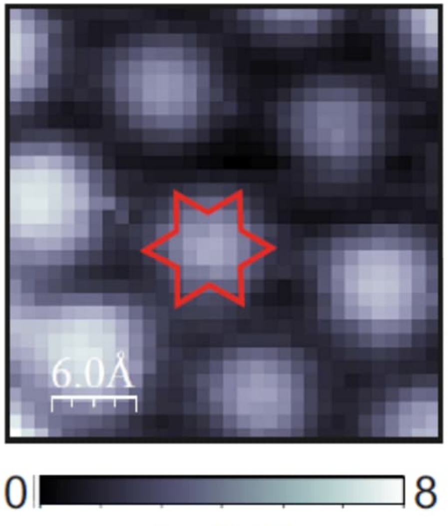
-500 mV, 10 pA



THz-STM of commensurate CDW on 1T-TaS_2

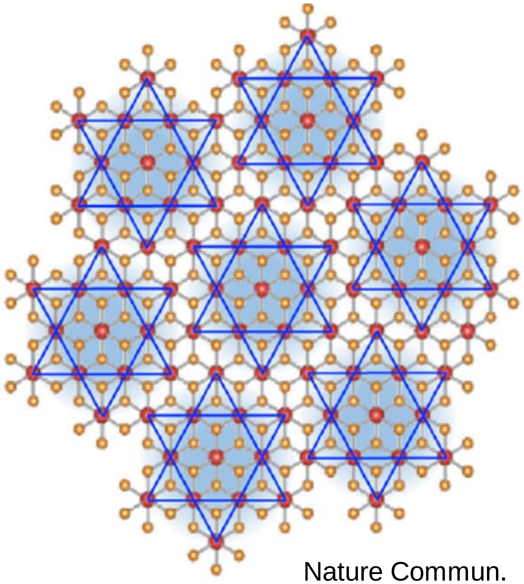
Imaging the CDW phase of TaS_2 with static STM and THz-STM

Static current



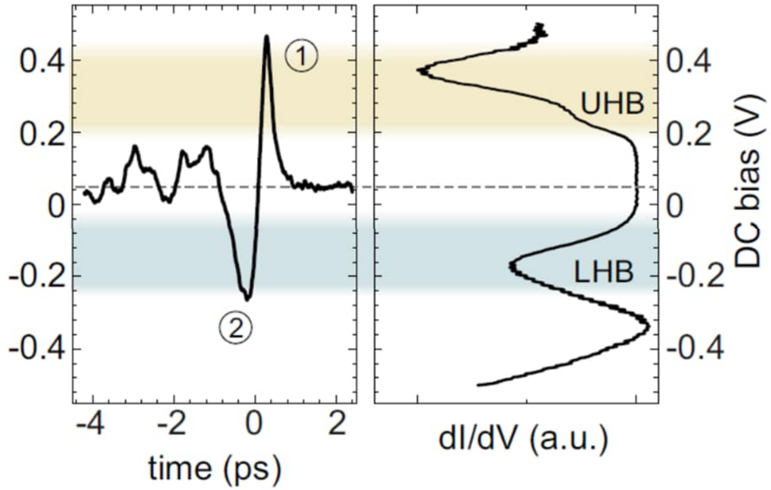
constant height mode, V_{DC} 50 mV

Star-of-David CDW of TaS_2



Nature Commun. **12**, 5873 (2021)

THz wave form and STS



THz-STM image:
Femtosecond snapshot of CDW in real space !

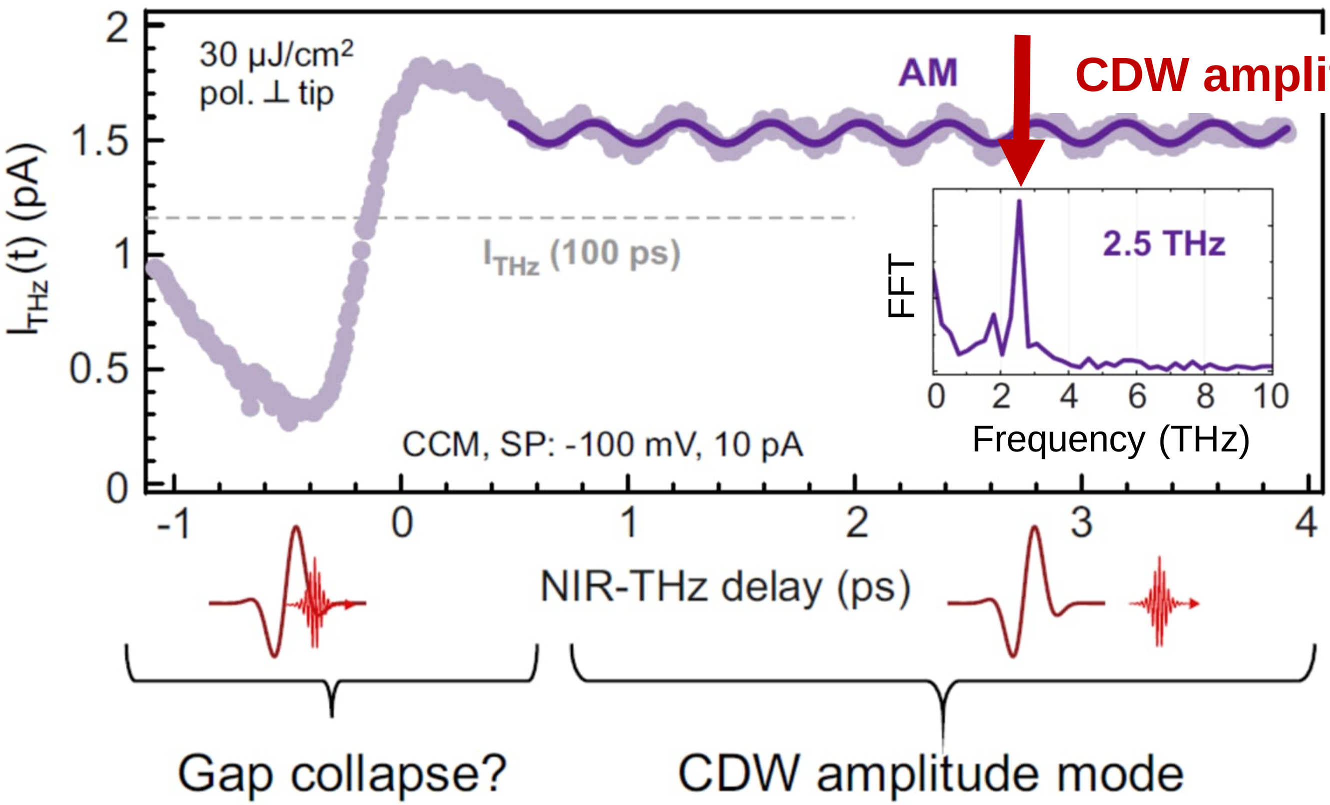
- Bipolar THz bias induced bi-directional tunneling into LHB and UHB
- THz bias calibrated via photoemission on Au(111) sample

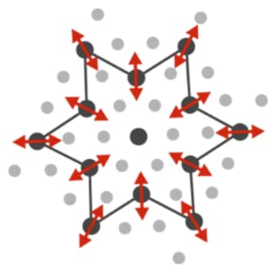
see M. Müller *et.al*, ACS Phot. **7**, 8 (2020)

Photoinduced dynamics probed by THz-STM

Photoexcitation of TaS_2 CDW phase with 30 fs, 1030 nm IR pulses:

CDW amplitude mode in TaS_2





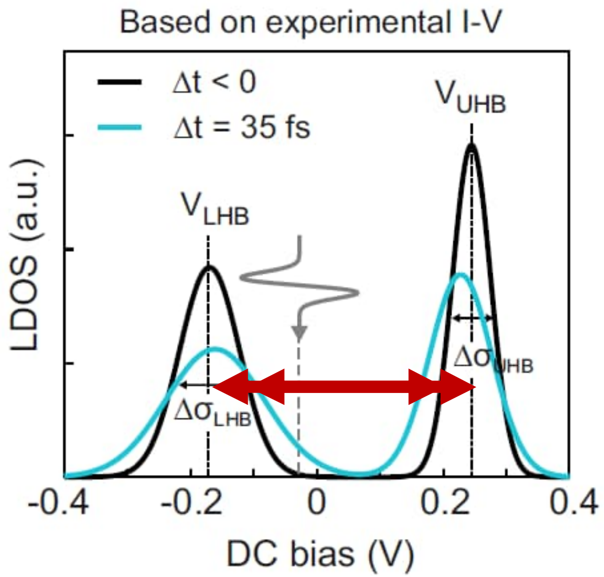
AM mode mainly observed in regions of enhanced rectified THz current *(defects/stacking?)*

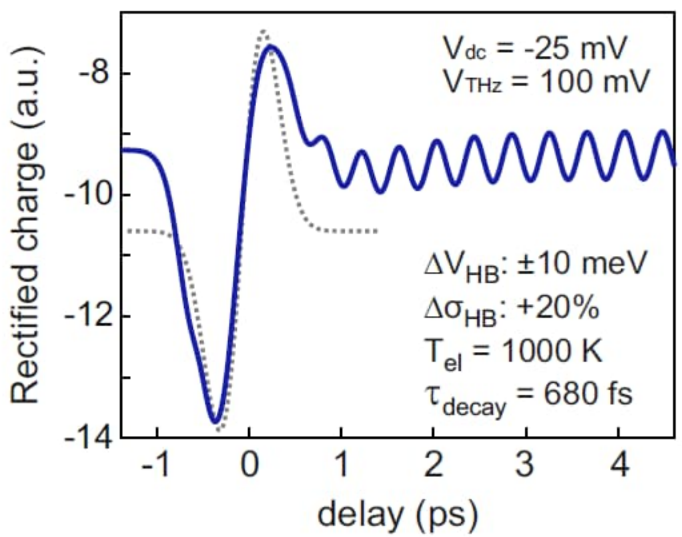
Time-resolved THz-STM: Real-time observation of coherent amplitude mode (AM) oscillation + Wave-like transient at t ~ 0: *Mott gap collapse ?*

Photoinduced dynamics: Modelling THz-STM

Qualitative model considering band shifts (LDOS) and population changes

$$I(t,\tau) \propto \int_{-\infty}^{\infty} \underbrace{\left[f_s(E_F - eV(t-\tau), T_{el,s}(t))\right.}_{\text{transient population}} - \left.f_t(E_F, T_{el,t}(t))\right] \underbrace{\rho_s(E_F - eV(t-\tau), t)}_{\text{LDOS modulation}} \rho_t(E_F) \underbrace{T(t)}_{\text{gap size modulation}} dE$$

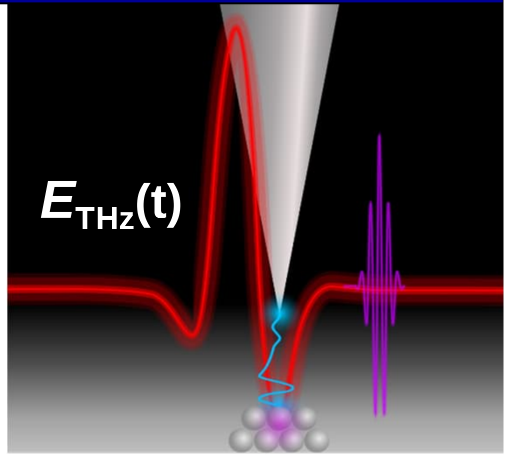


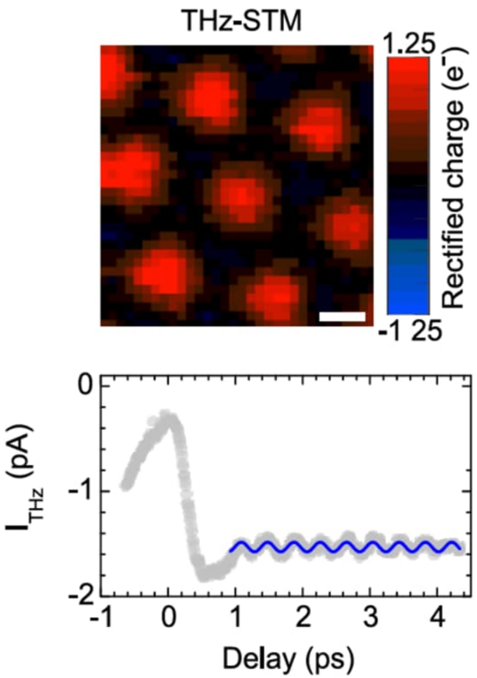


- ➢ Model qualitatively reproduces main observations.
- ➢ Bias dependent measurements show symmetric gap closing/opening with coupled to amplitude mode

Take home…

Ultrafast scanning probe microscopy can be realized by field-driven THz-STM or via photon-STM

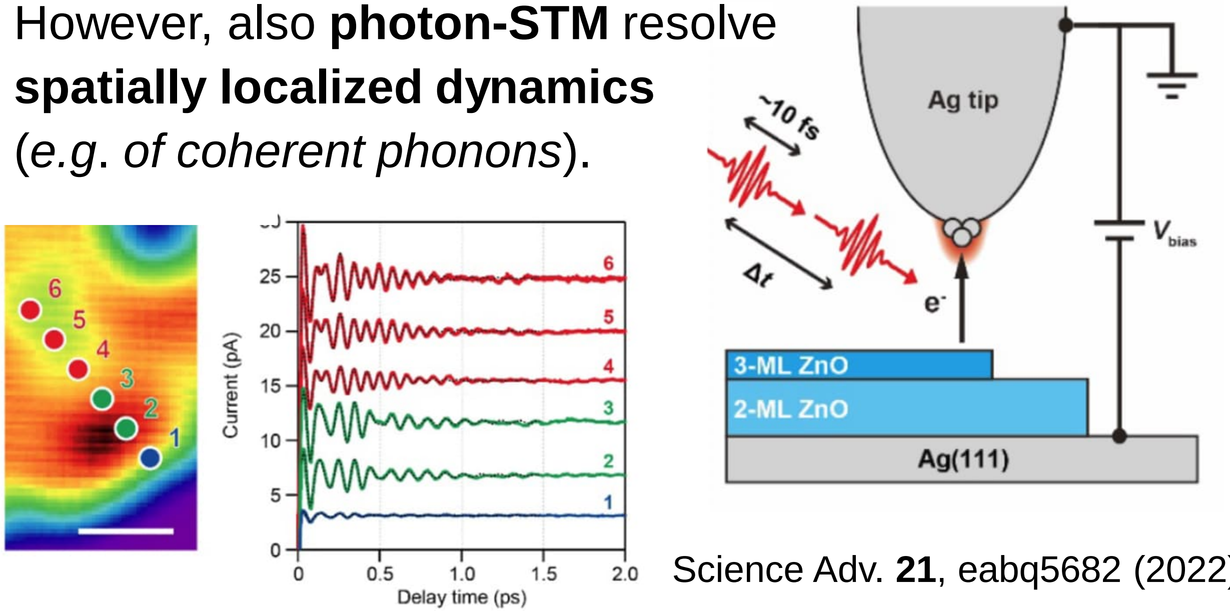




THz-STM implements a THz field as transient bias.

Promising tool to unravel **non-equilibrium dynamics at atomic scales**. (*e.g. CDW dynamics in TaS_2*)

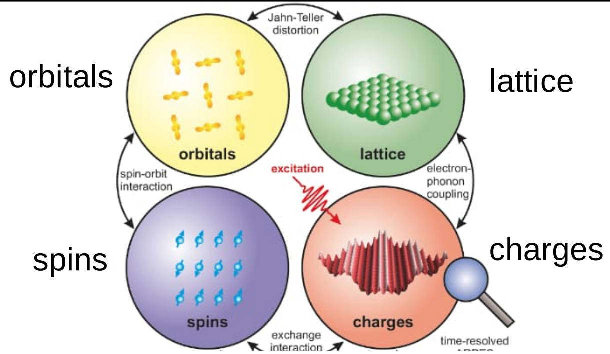
However, also **photon-STM** resolve **spatially localized dynamics** (*e.g. of coherent phonons*).



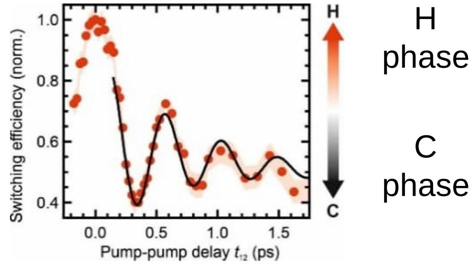
Science Adv. **21**, eabq5682 (2022)

Outline

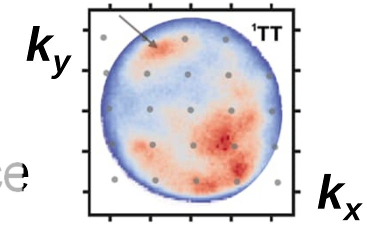
▶ **Motivation and general introduction:**
Material properties, fundamental excitations,
phase transitions & dynamics



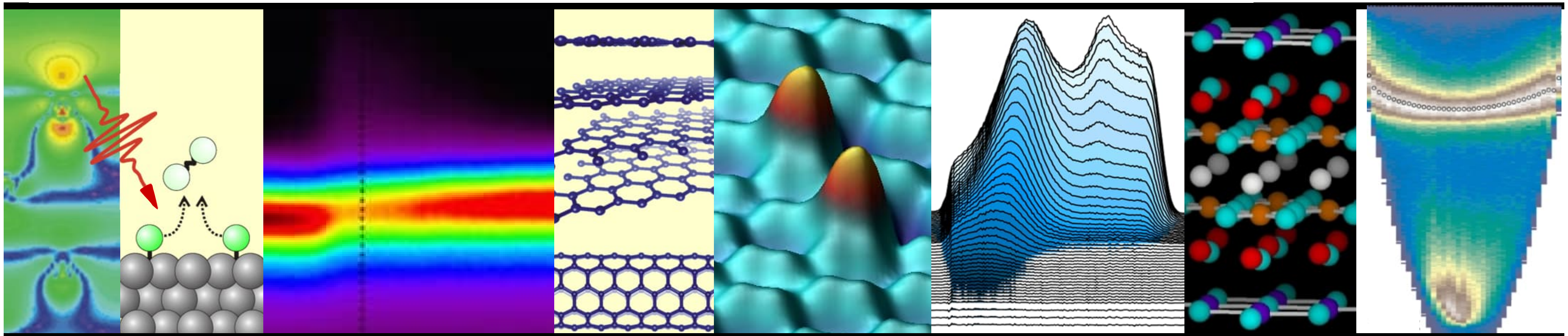
▶ **Charge density wave dynamics** in TaS_2 :
- Transition to metastable H phase probed by ARPES
- Local CDW dynamics probed by THz- STM



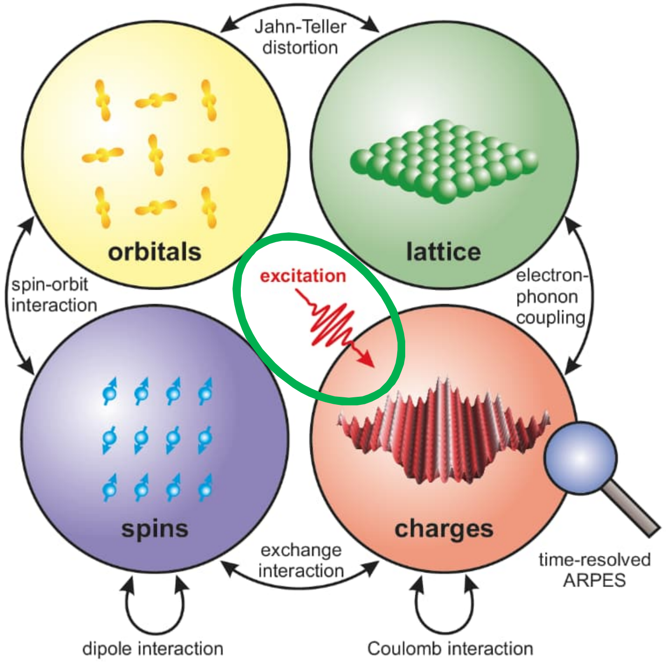
▶ **Exciton dynamics** in momentum space:
- Mechanism of singlet exciton fission in pentacene



▶ **Coupling between light and matter**:
- Phonon polaritons and strong coupling on SiC metasurface

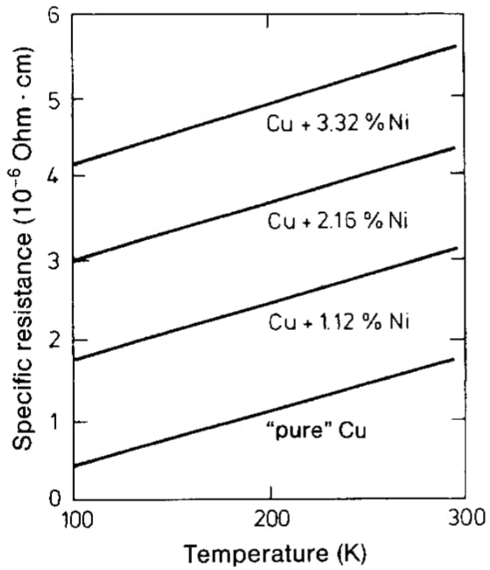


Elementary excitations of solids



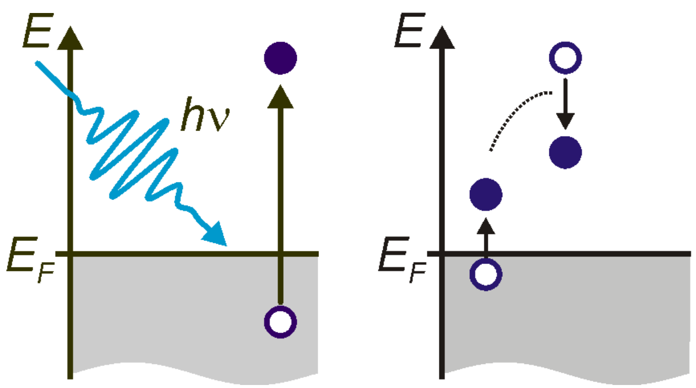
► Thermal excitations:

Example electrical resistivity of Cu:
e-ph coupling & defect scattering

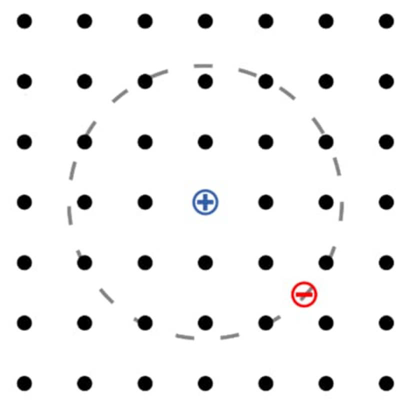


► Optical excitations in metals and semiconductors:

Metals



Semiconductors (Coulomb interaction)



Exciton formation:
- Frenkel exciton
- Wannier (localized)
- Charge transfer

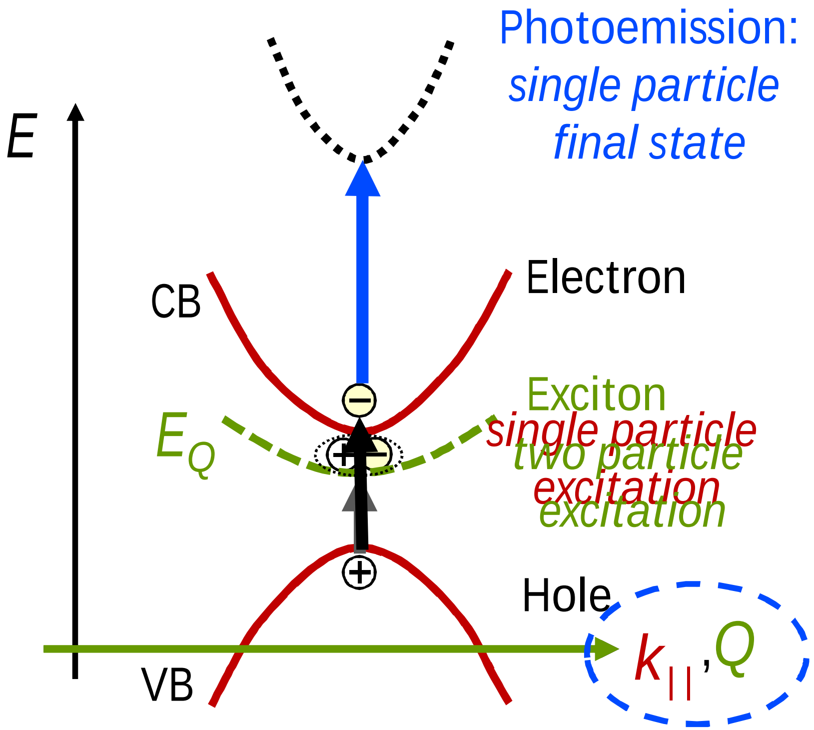
„two-body excitation“

Excitons probed in momentum space

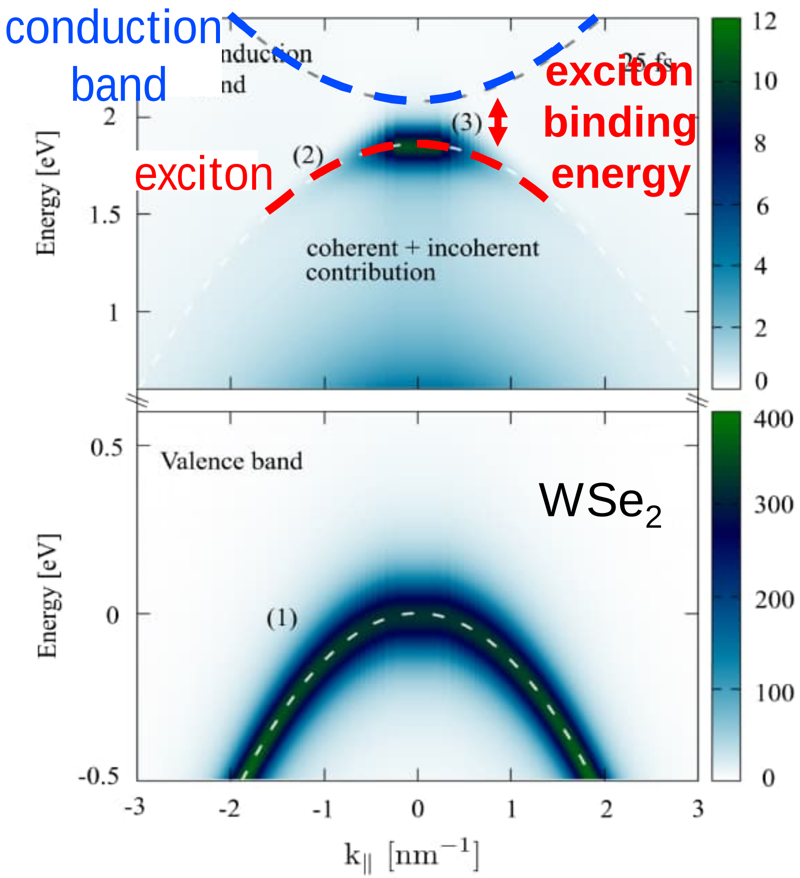
Excitons are typically probed optically (*i.e. no momentum resolution*)

…what is their signature in ARPES?

- Photoemission is often viewed in a single particle picture:



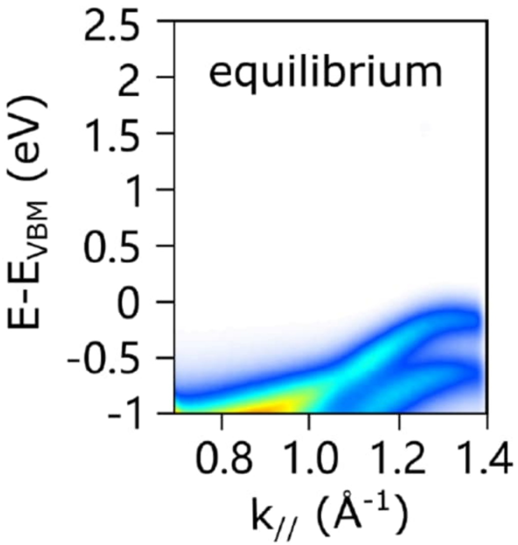
Simulation of trARPES signal
(*E. Malic & coworkers*)

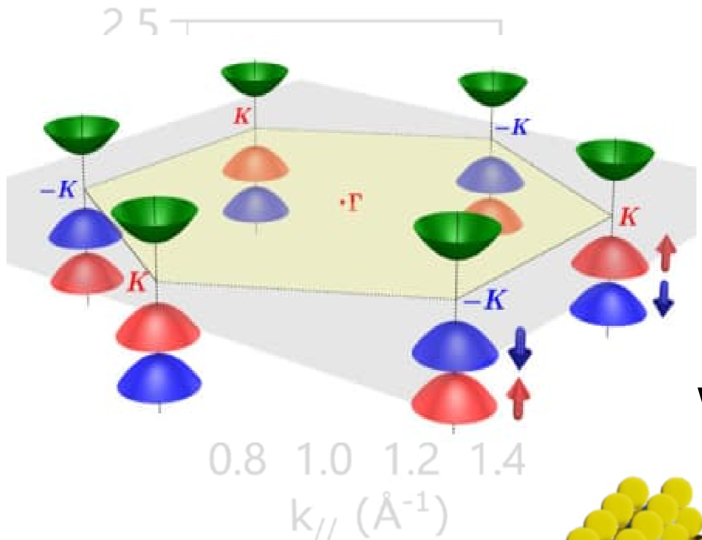


Phys. Rev. B **100**, 205401 (2019)

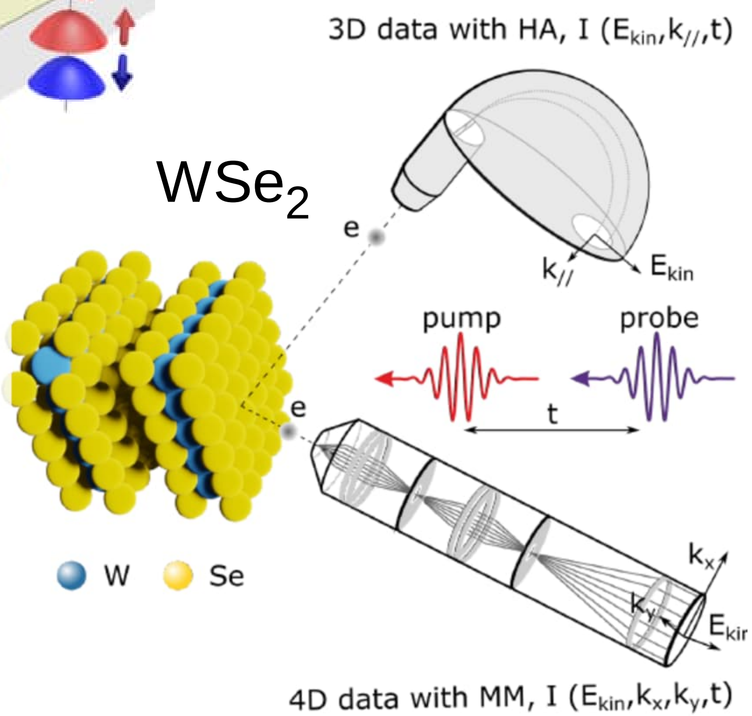
Momentum resolved trARPES form WSe_2

Excitation of A exciton probed with HA and MM analyzers





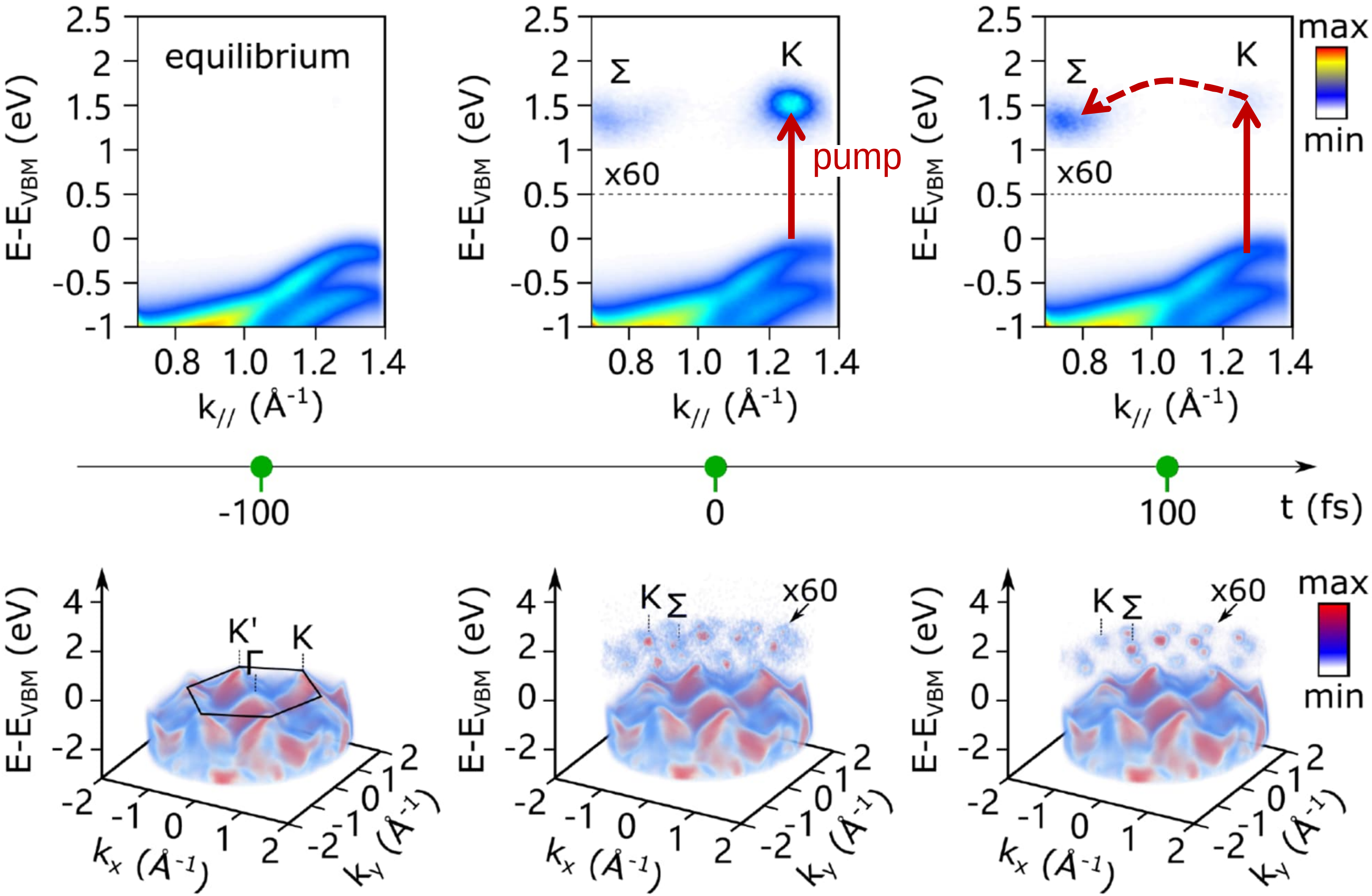
Hemispherical analyzer



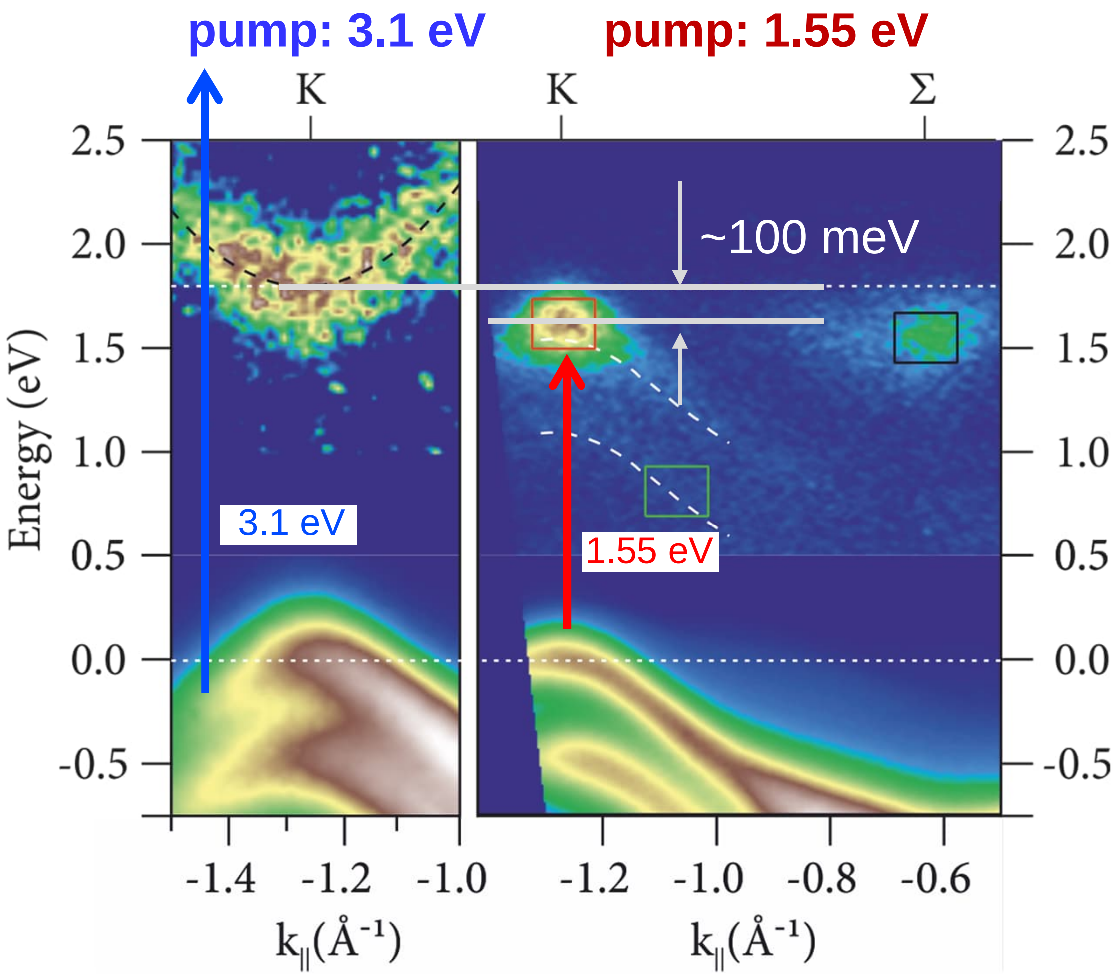
Momentum microscope

Momentum resolved trARPES form WSe_2

Excitation of A exciton probed with HA and MM analyzers



Signature of excitons in trARPES ?



Direct **measurement** of the **exciton binding energy:** **100 meV**

Calculated A exciton binding energy (for BL WSe_2): **91 meV**

Christiansen *et al.*, PRB **100**, 205401 (2019).

Dong *et al.*, Natural Sci. **1**, e10010 (2021)

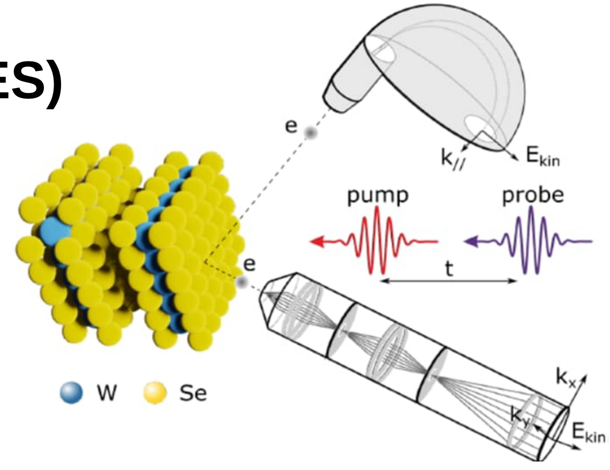
K valley excited state character depends on pump photon energy:

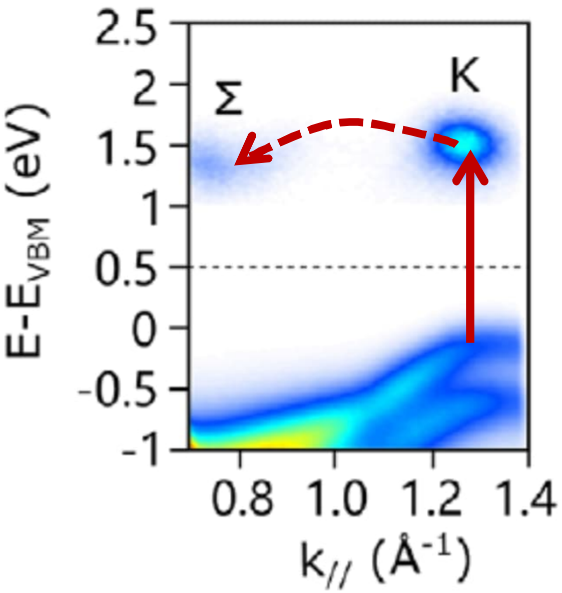
3.1 eV excitation → single-particle excited state

1.55 eV excitation → excitonic excited state *(A exciton)*

Take home…

Time- and angle-resolved photoemission (trARPES) using momentum microscopy



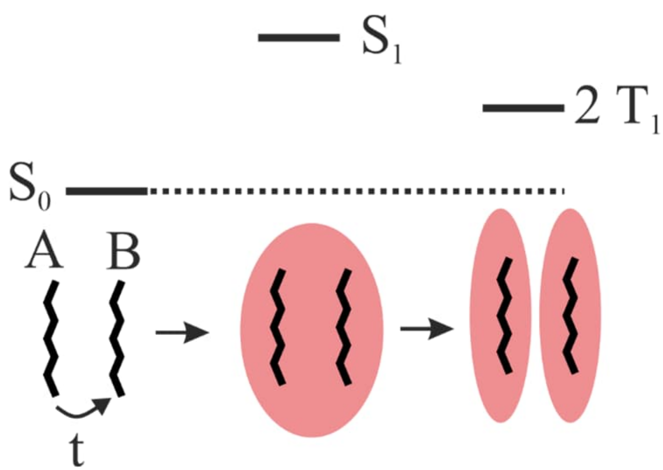


trARPES applicable to many-body states 'beyond' a single-particle picture (*e.g. excitons*)

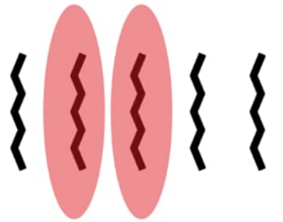
Natural Science **1**, e10010 (2021)

Singlet exciton fission in molecular crystals

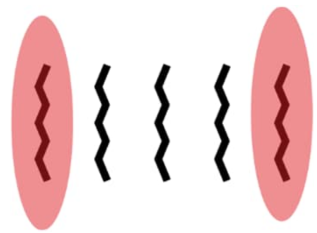
Singlet exciton fission (SF): conversion of a singlet excitation to two triplets
→ carrier multiplication (*e.g.* in solar cells)
Conditions for singlet fission: proximity of molecules and low-lying triplet states



Bitriplet exciton ^1TT (spin allowed formation)



Spatially separated, spin correlated $^1T\cdots T$



excitation of S_1	electron & spin correlated	spin correlated	uncorrelated

$$S_0 + h\nu \rightarrow S_1 \rightarrow {}^1TT \rightarrow {}^1T\cdots T \rightarrow T_1 + T_1$$

Here focus on the “primary step” in pentacene

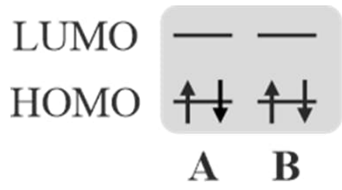
Singlet fission in pentacene crystals

What is the mechanism of the primary step in pentacene?

?

$S_1 \rightarrow {}^1TT$

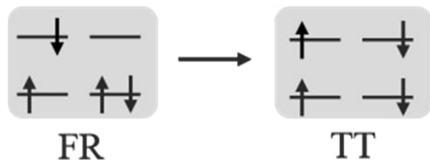
We will consider two molecules only:



a) Direct two-electron coupling of Frenkel exciton (FR) and ^{1}TT states → coherent superposition state

$$V_{\text{eff}} \propto \langle FR|V|\,{}^1TT\rangle$$

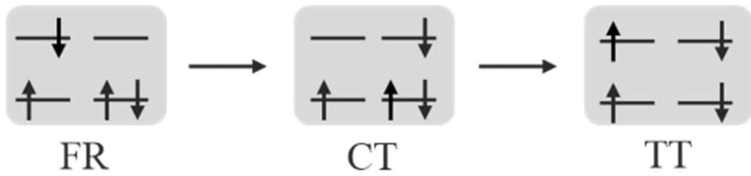
Chan et al., Science 334, 1541 (2011).



b) Charge-transfer-state (CT) mediated coupling

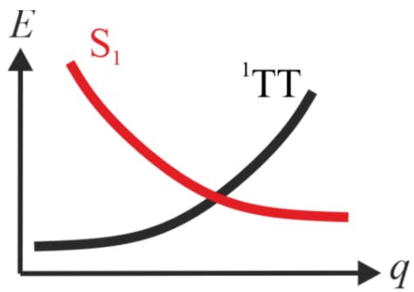
$$V_{\text{eff}} \propto \langle FR|V|CT\rangle\langle CT|V|\,{}^1TT\rangle$$

Berkelbach et al., JCP 138, 114103 (2013).



c) Conical intersection

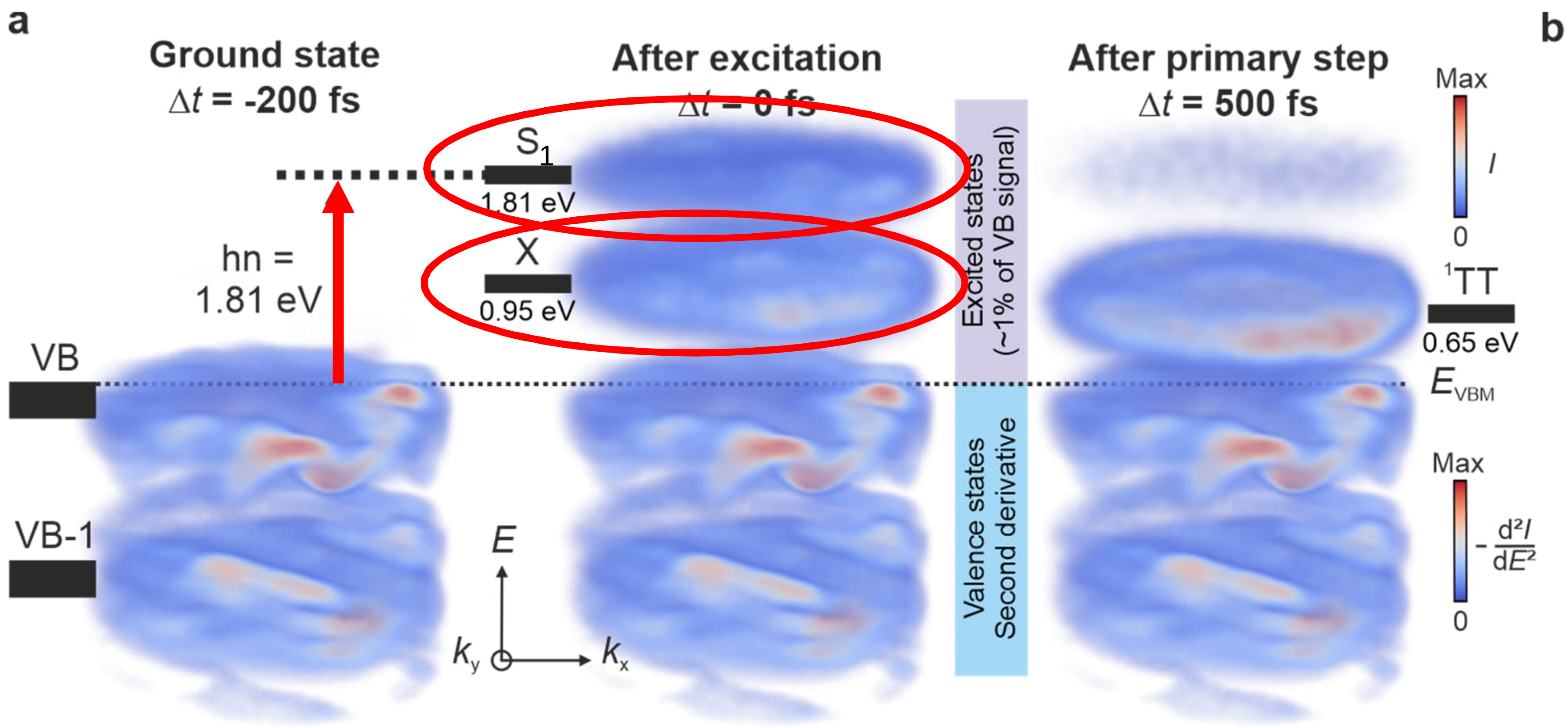
Muser et al., Nature Phys. 11, 352 (2015).
Duan et al., Science Adv. 6, eabb0052 (2020).



⇨ New insights using momentum resolution

Momentum-resolved observation of singlet fission

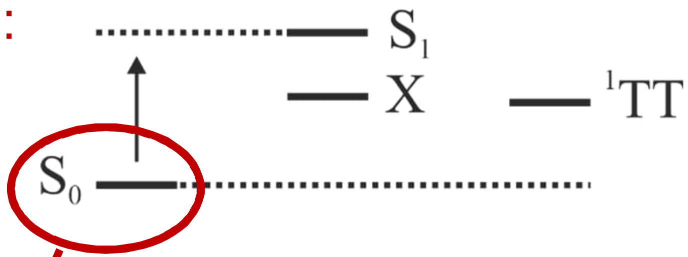
trARPES data of singlet fission in pentacene:

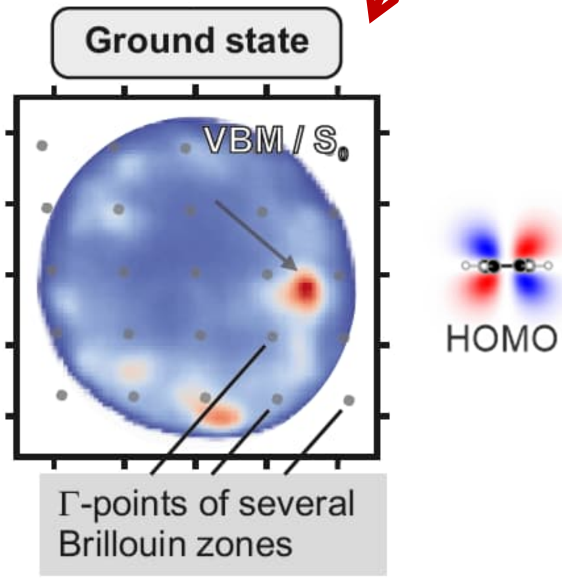


Neef *et al.*, Nature **616**, 275 (2023)

Momentum-maps of electronic states in pentacene

Snapshots of photoelectron momentum maps:



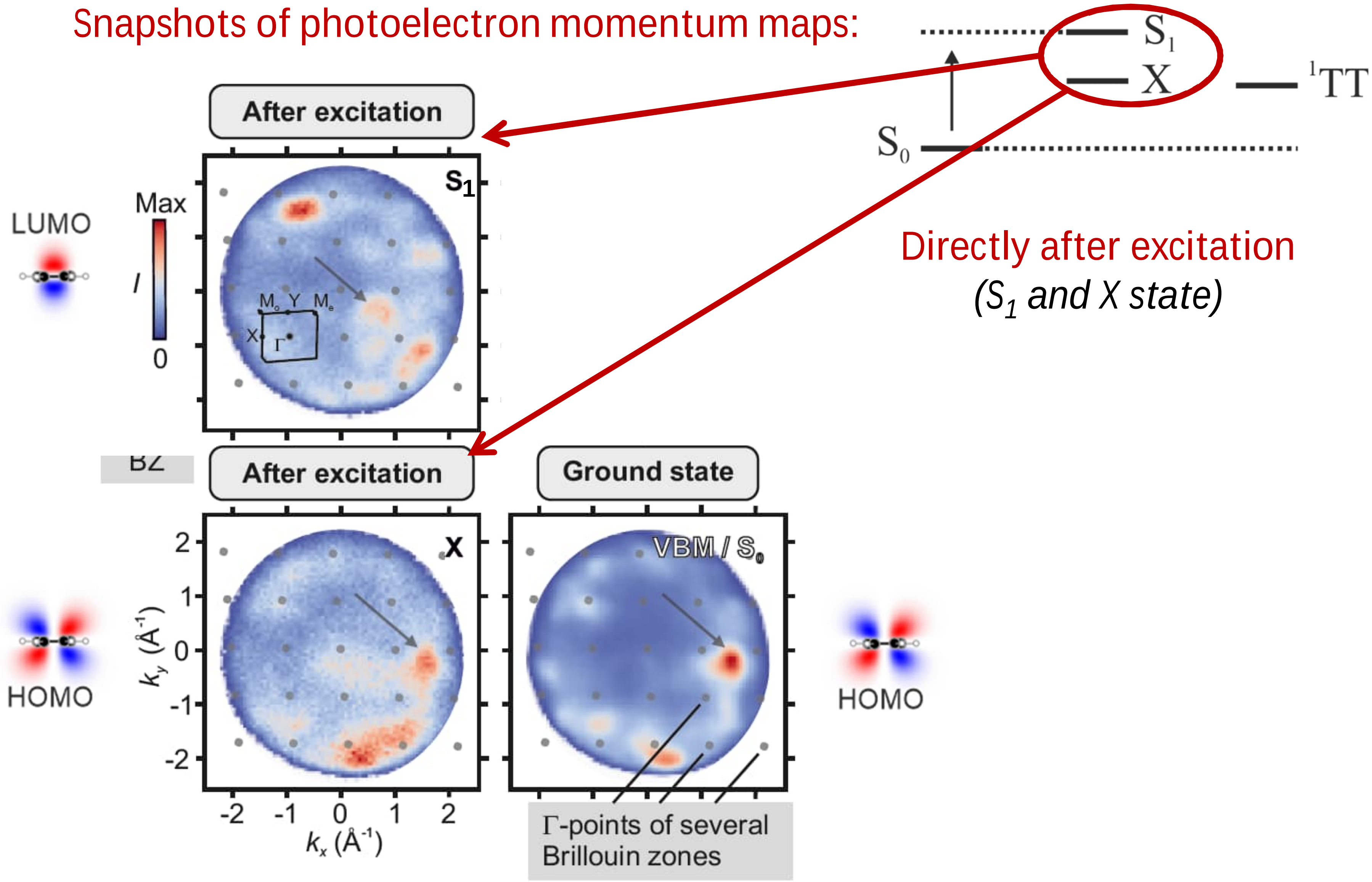


Before excitation
(S_0 state)

A. Neef *et al.*, Nature **616**, 275 (2023)

Momentum-maps of electronic states in pentacene

Snapshots of photoelectron momentum maps:



A. Neef *et al.*, Nature **616**, 275 (2023)

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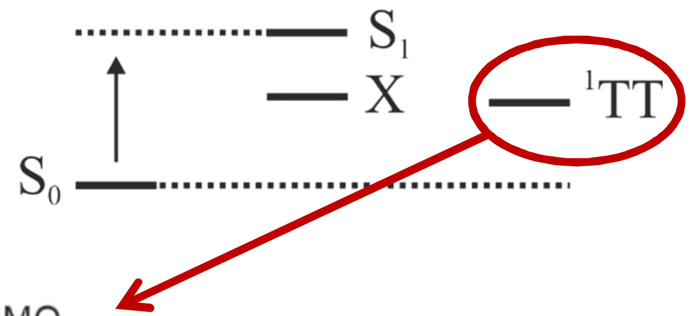
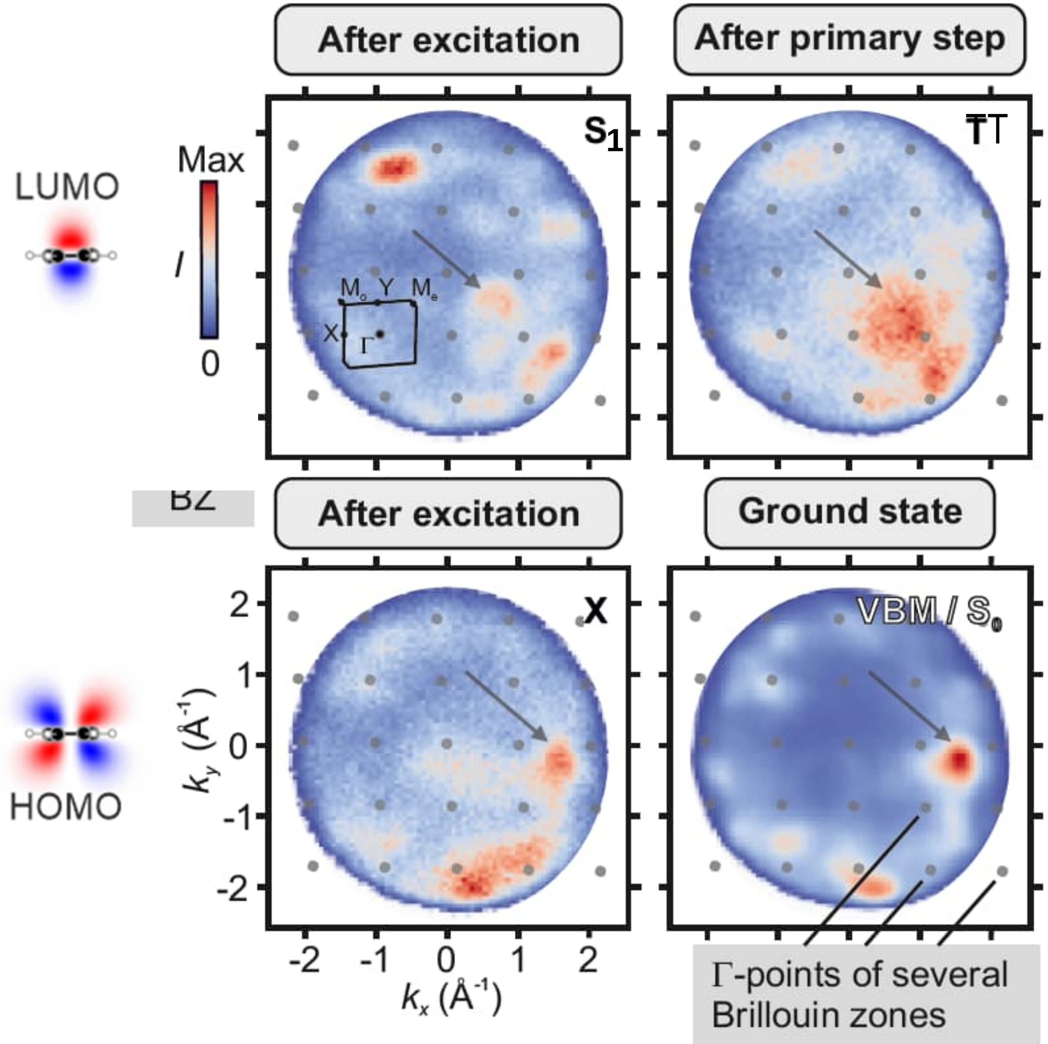




Momentum maps exhibit different orbital character

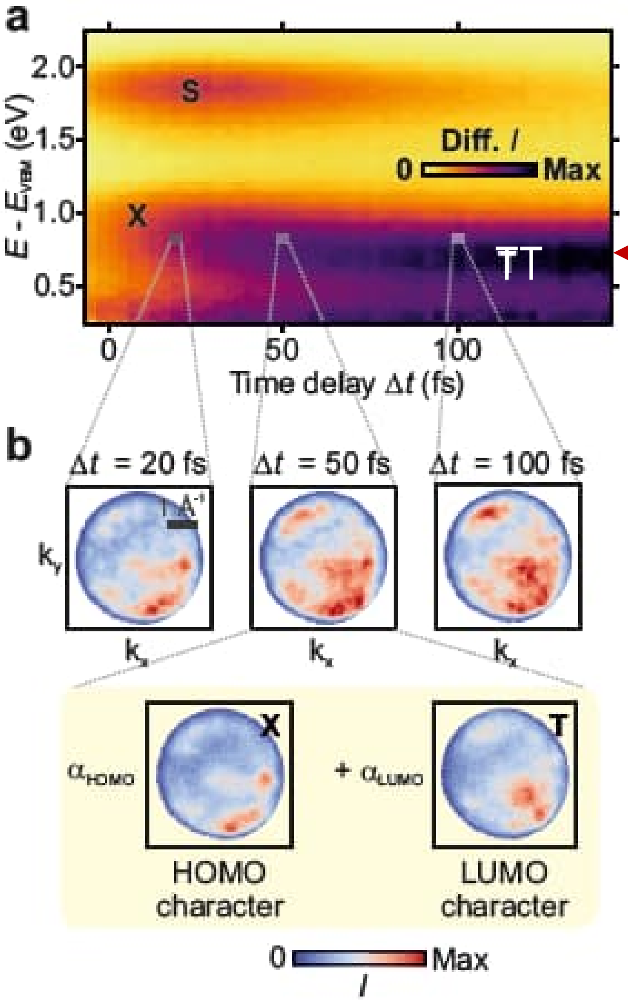
S_1 and ^{1}TT with:
LUMO character

X and VBM/S_0 state:
HOMO character

A. Neef *et al.*, Nature **616**, 275 (2023)

Decomposition of overlapping states

Observation and orbital-based decomposition in S, X and TT:

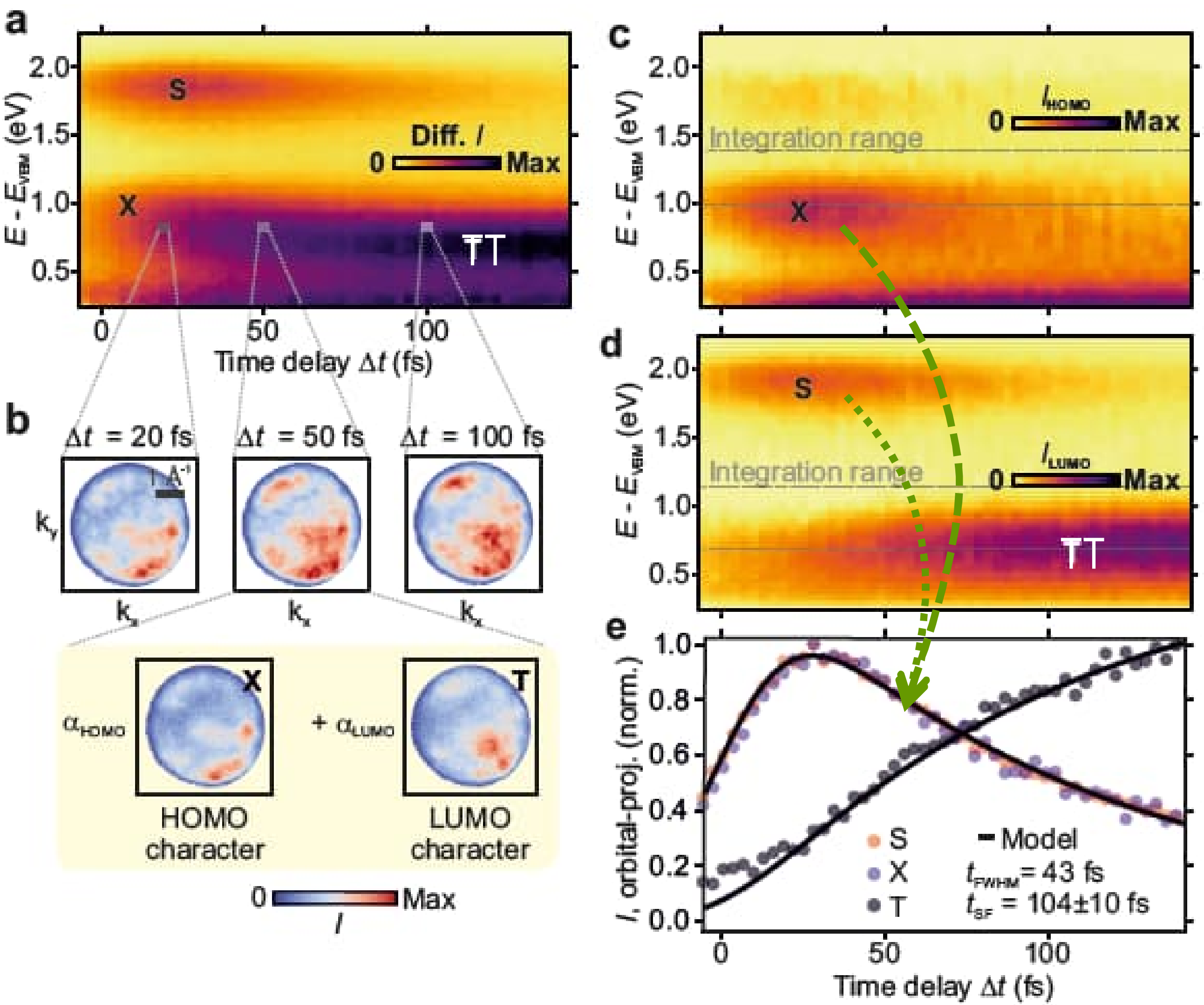


Overlapping signals X and TT

A. Neef *et al.*, Nature **616**, 275 (2023)

Decomposition of overlapping states

Observation and orbital-based decomposition in S, X and TT:

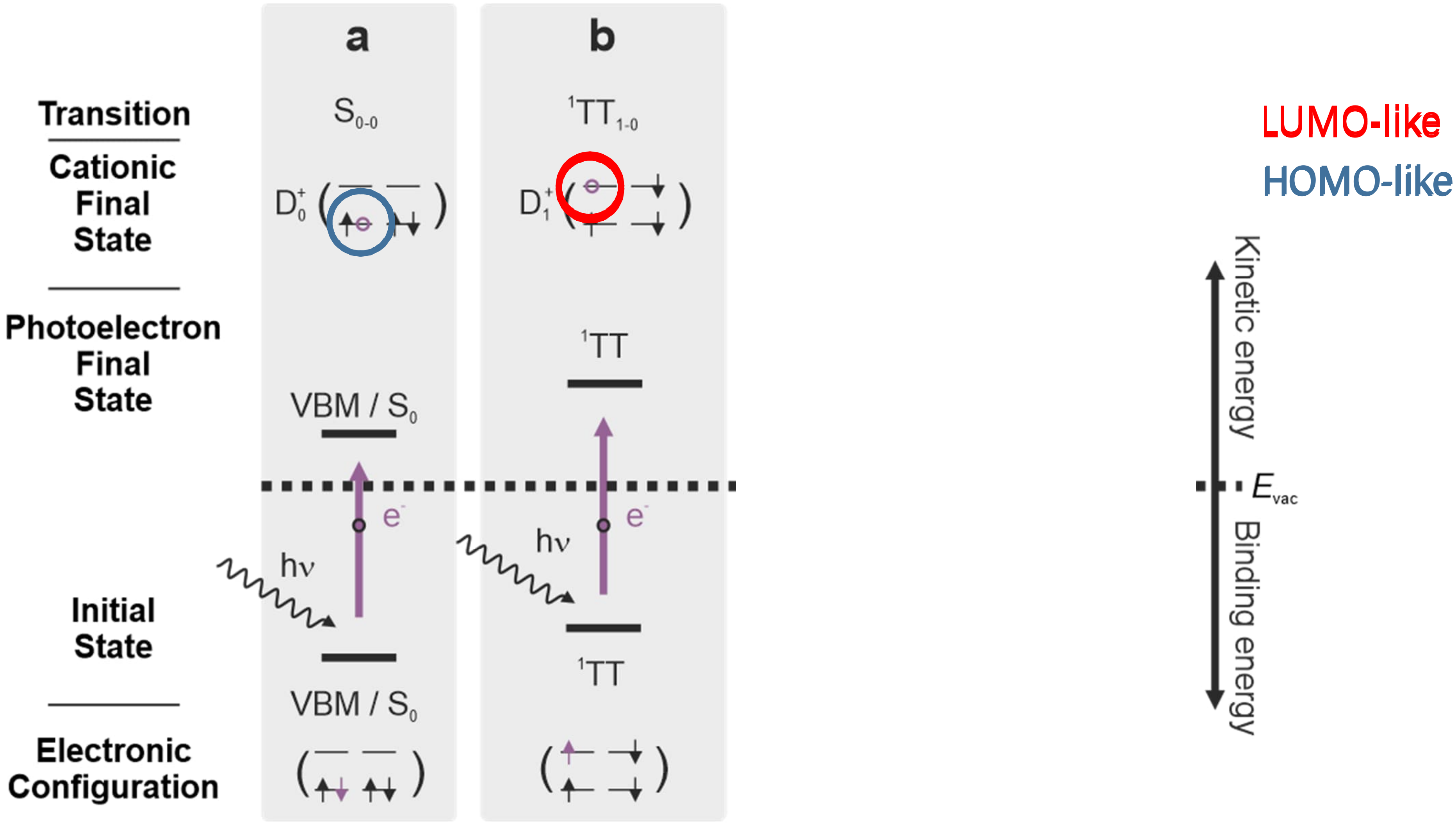


- X signal can only arise from CT state
- signature of charge-transfer character of the singlet exciton
- singlet exciton has both Frenkel + CT character !!

Singlet fission shows monoexponential dynamics with $\tau_{SF} = 104 \pm 10$ fs

A. Neef *et al.*, Nature **616**, 275 (2023)

Signatures of different excitonic states



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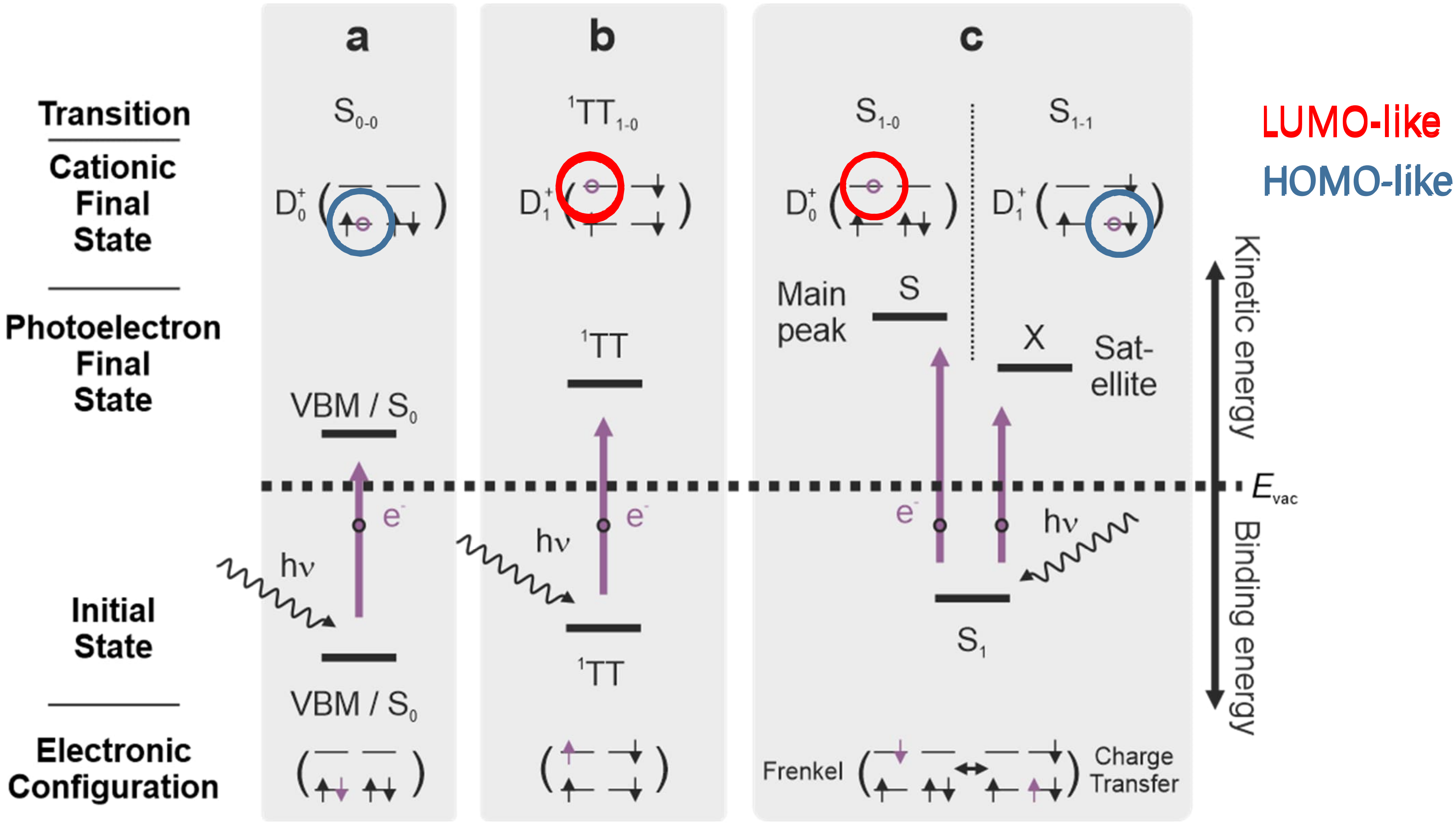


Hybridization

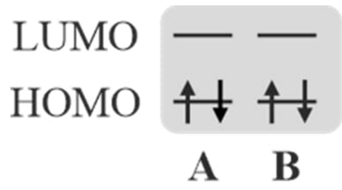
Singlet fission in pentacene crystals

What is the mechanism of the primary step in pentacene?

?

$S_1 \rightarrow {}^1TT$

We will consider two molecules only:



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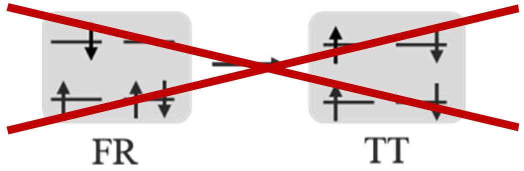

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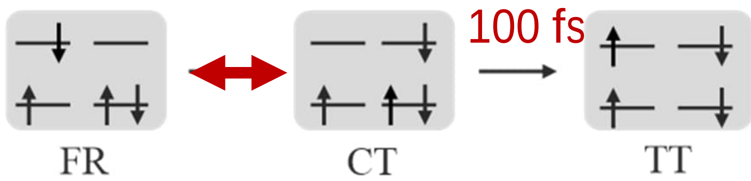

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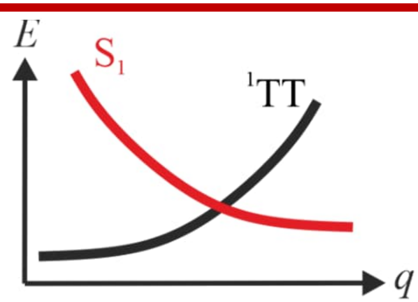
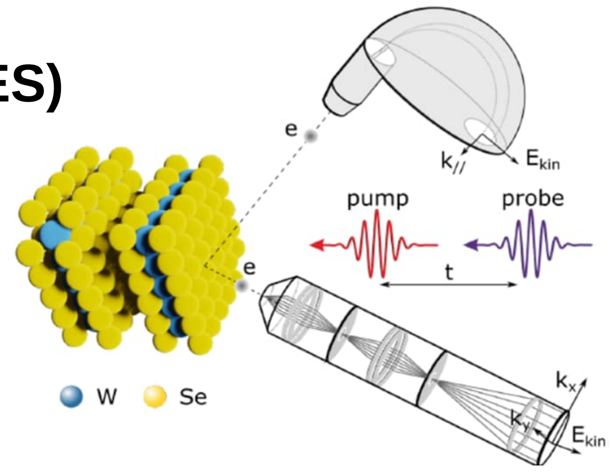
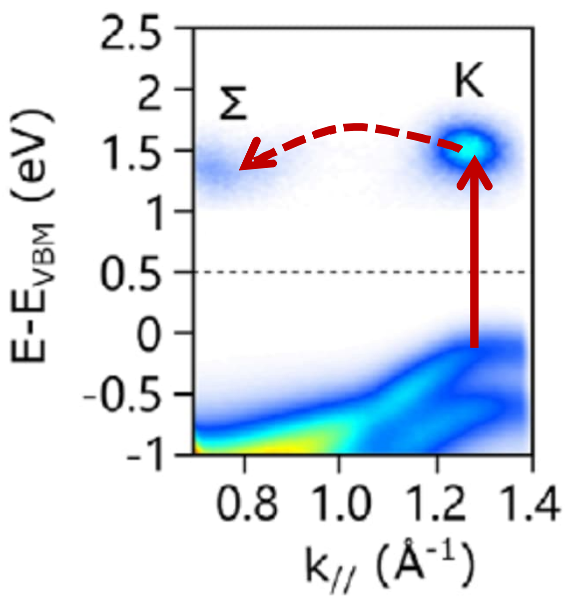


Take home…

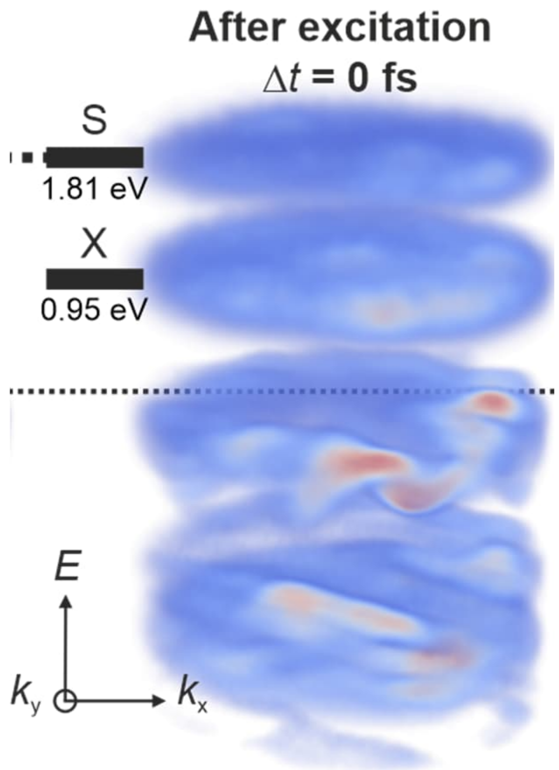
Time- and angle-resolved photoemission (trARPES) using momentum microscopy





trARPES applicable to many-body states 'beyond' a single-particle picture (*e.g. excitons*)

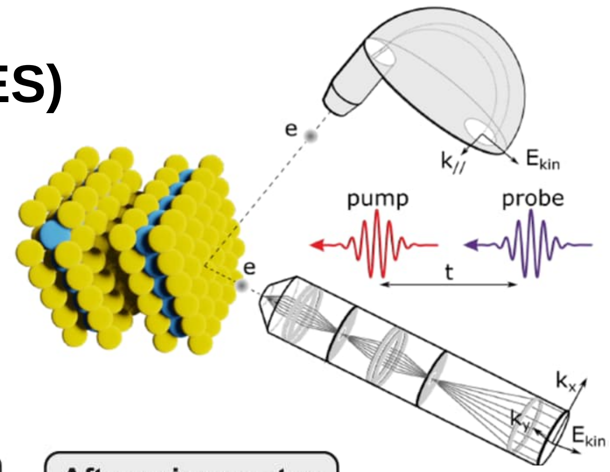
Natural Science **1**, e10010 (2021)



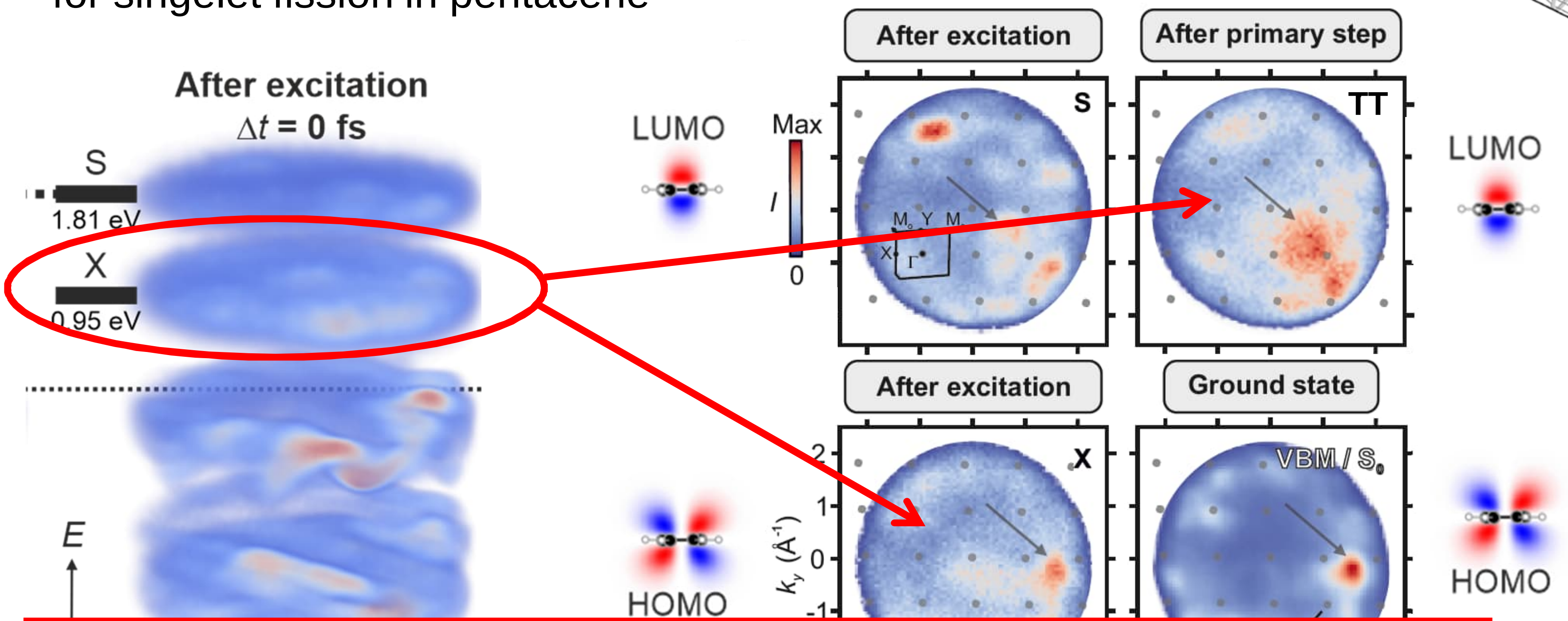
Orbital-resolved perspective of exciton fission exemplified for a molecular crystal (*pentacene*)

Nature **616**, 275 (2023)

Time- and angle-resolved photoemission (trARPES) using momentum microscopy



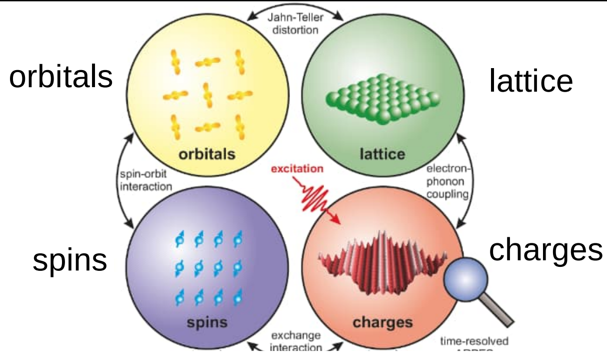
Orbital-resolved decomposition:
Orbital-resolved of exciton dynamics examplified for singelet fission in pentacene



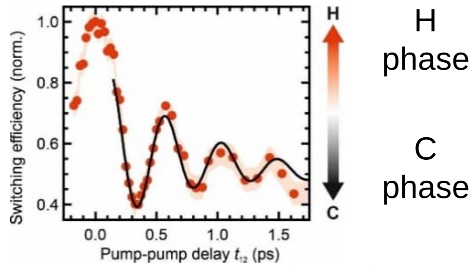
In general: Photoelectron momentum distributions may allow to disentangle overlapping states (or congested spectra)

Outline

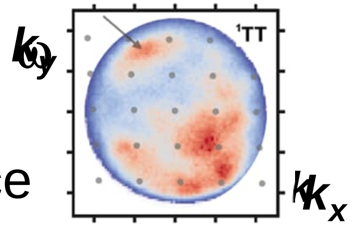
- **Motivation and general introduction:**
  Material properties, fundamental excitations, phase transitions & dynamics



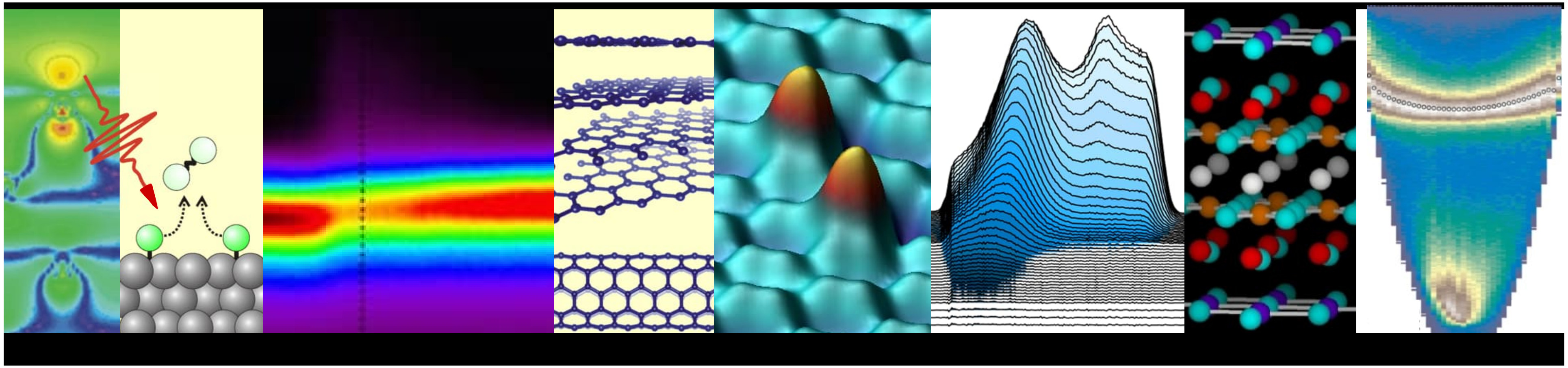
- **Charge density wave dynamics** in TaS_2:
  - Transition to metastable H phase probed by ARPES
  - Local CDW dynamics probed by THz- STM



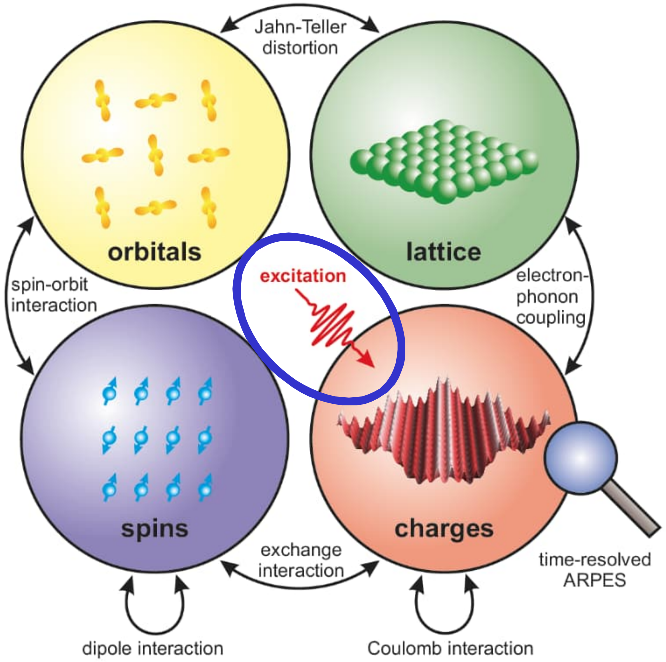
- **Exciton dynamics** in molecular crystals:
  - Singlet fission in pentacene in momentum space



- **Coupling between light and matter**:
  - Phonon polaritons and strong coupling on SiC metasurface

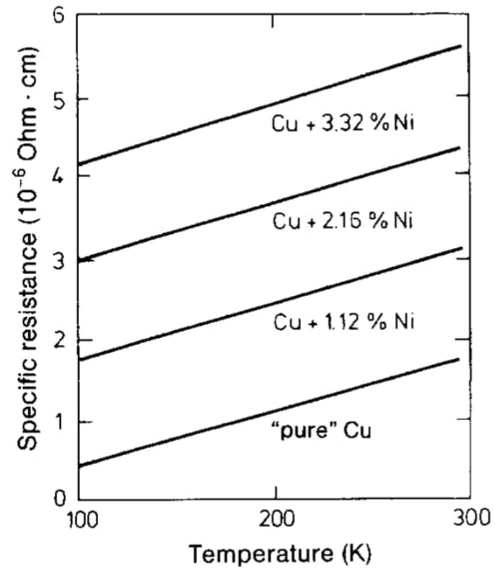


Elementary excitations of solids



- ▶ Thermal excitations:

  Example electrical resistivity of Cu:
  e-ph coupling & defect scattering

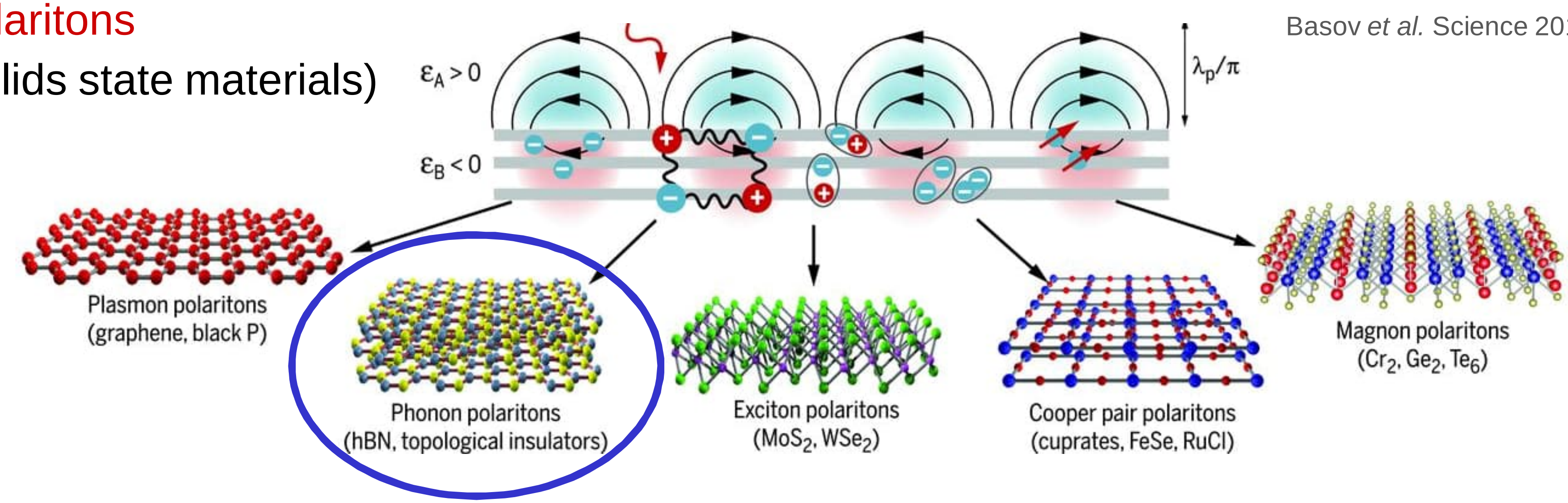


- ▶ Optical excitations:

  coupling of light and matter

Polaritons
(solids state materials)

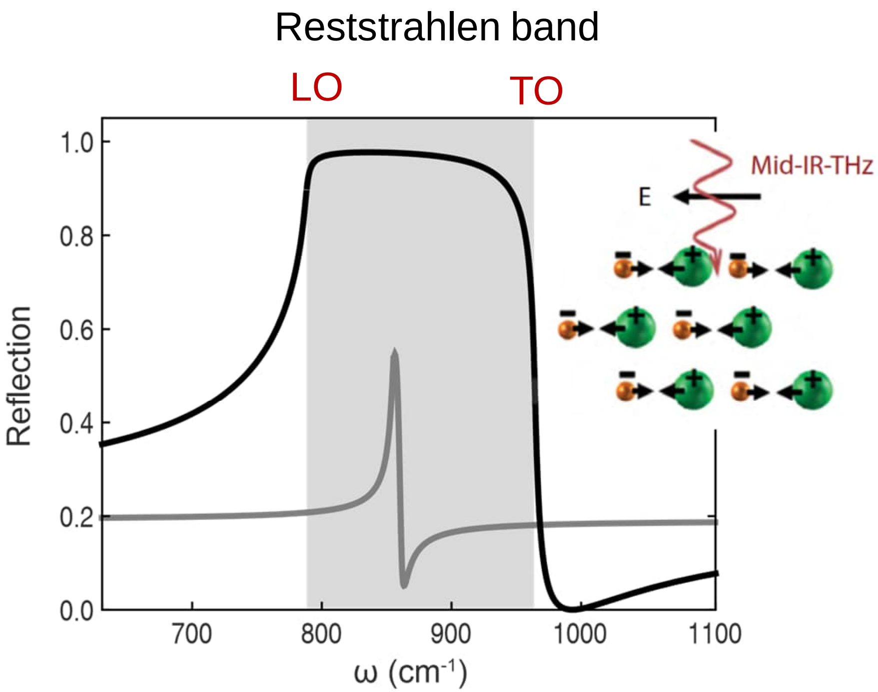
Basov *et al.* Science 2016

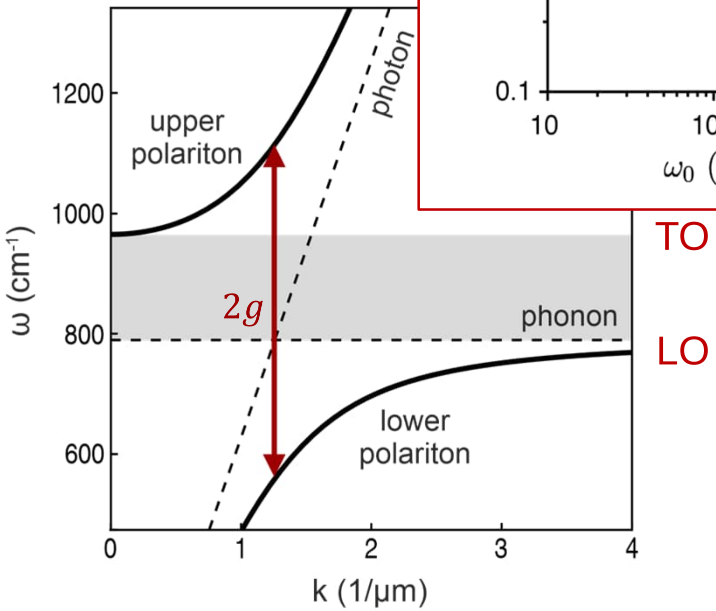


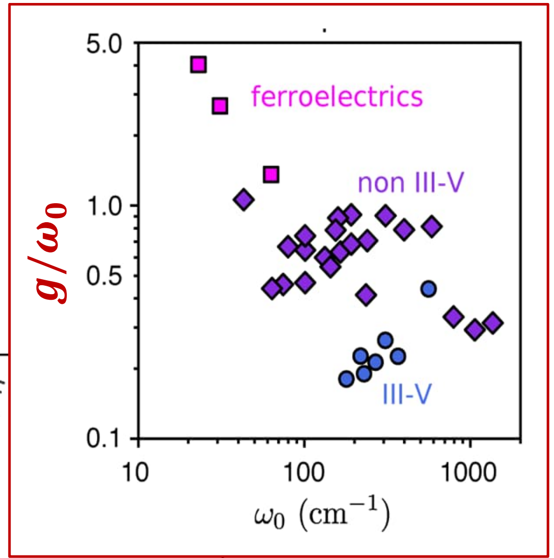
Phonon polaritons

Bulk Phonon Polaritons

- **Strong coupling of light and optical phonons in polar semiconductors**







Recent review:

Galiffi et al. Nat. Rev. Mater. 2024

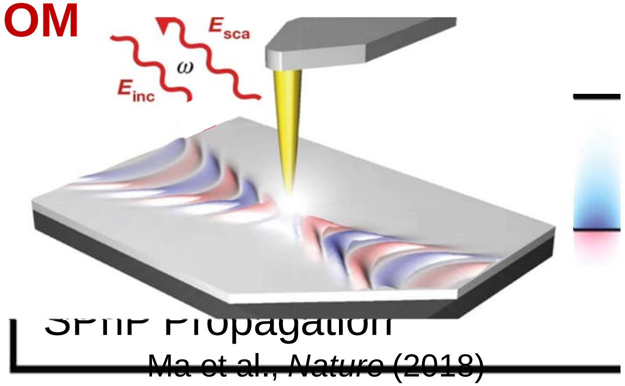
- Light-matter coupling comparable to excitation frequency

(Surface- / Localized-) Phonon Polaritons

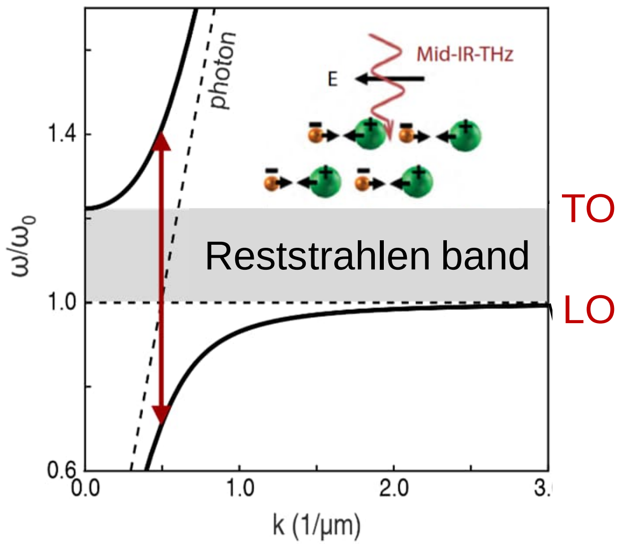
Phonon Polaritons (PhP):

- Bulk PhP exhibit band gap (Reststrahlen band) giving rise to surface modes
- Propagating Surface Phonon Polaritons (SPhP) located in Reststrahlen band
- Localized Phonon Polaritons (LPhP)

Imaging: SNOM

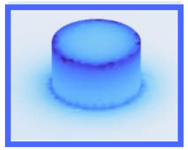


Bulk



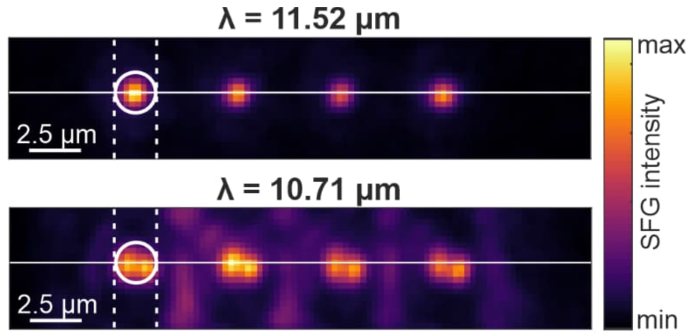
Imaging: SFG microscopy

monopole



SiC pillars

dipole



Recent review:

Galiffi et al. Nat. Rev. Mater. 2024

Subdiffractional spatial resolution

Niemann et al. *APL* 120, 131102 (2022)

Wide-field SFG microscopy

Setup: Far-IR FEL source synchronized with VIS laser

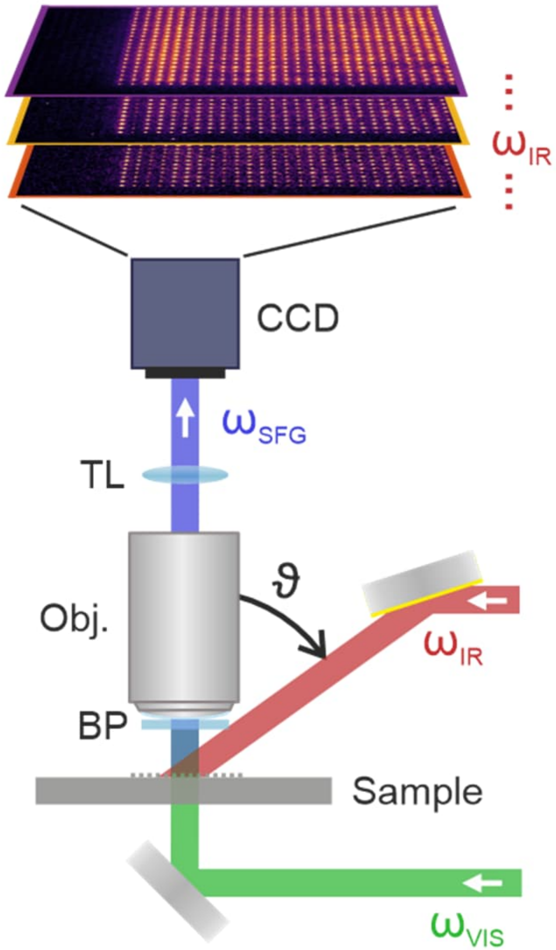
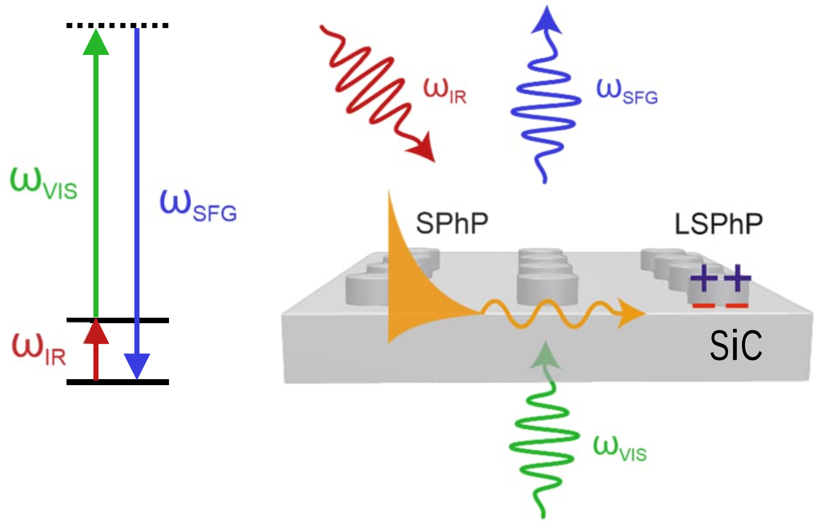


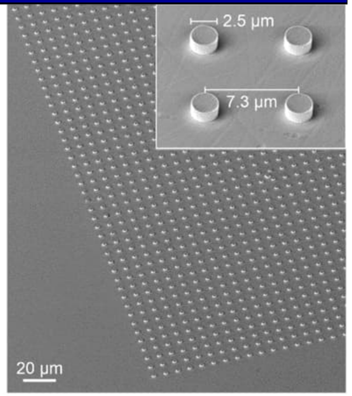
Image **surface phonon polaritons** (SPhP) excited on meta-surfaces exhibiting also localized SPhP

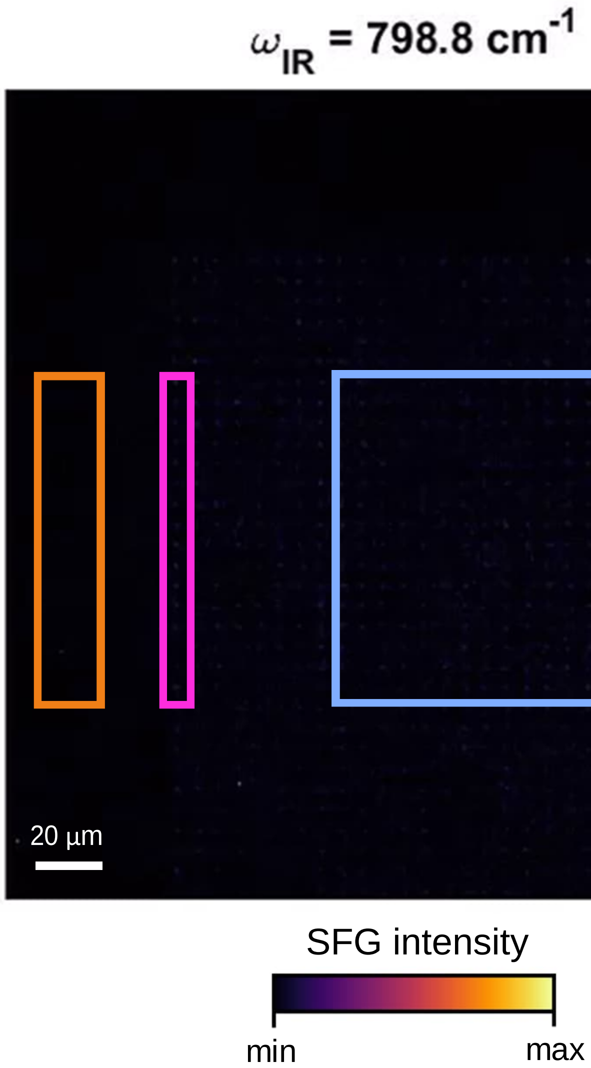


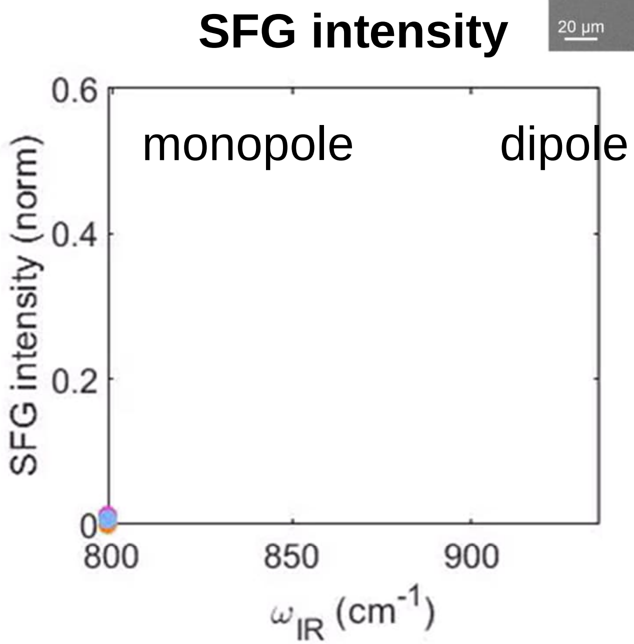
- SFG nonlinear mixing upconverts polaritonic near fields to visible frequencies
- Free electron laser (FEL) source provides access to Far-IR (ω_{IR} = 3000 – 200 cm^{-1})

Spectro-microscopy of polaronic meta-surface

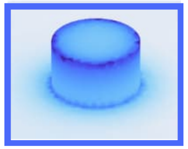
SFG imaging of polaronic modes as function of IR wavelength







monopole

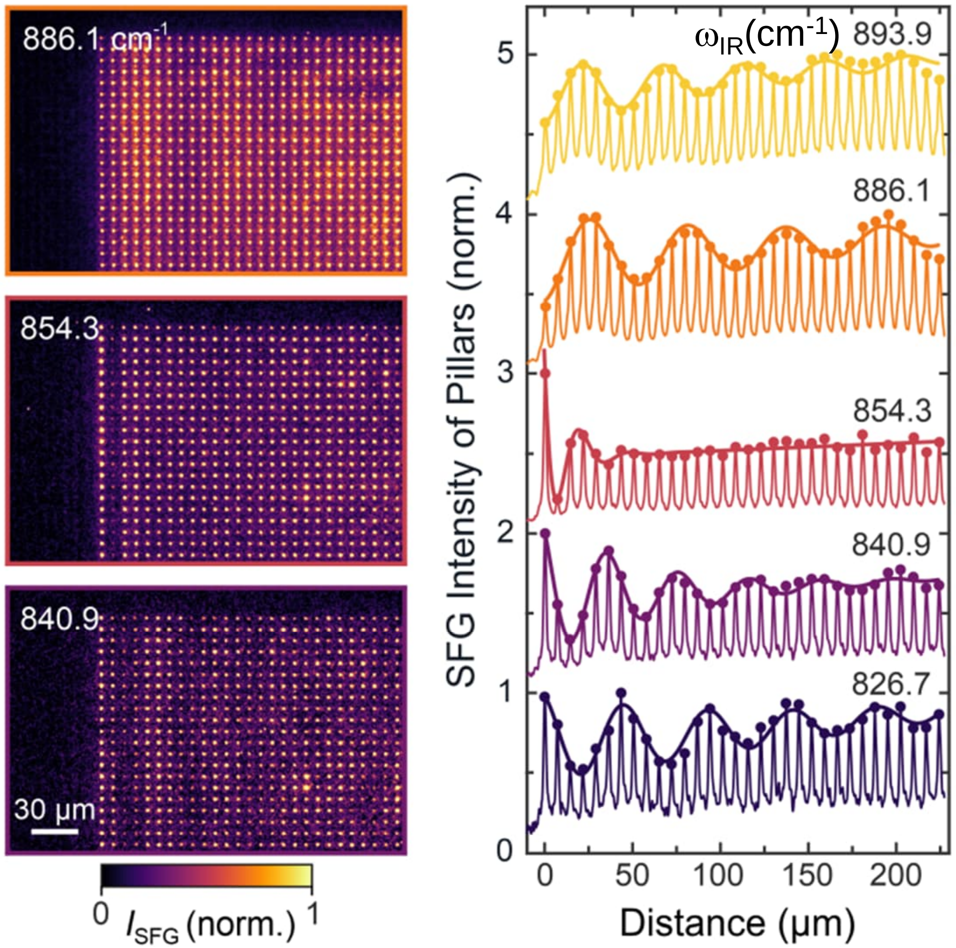


SiC pillars

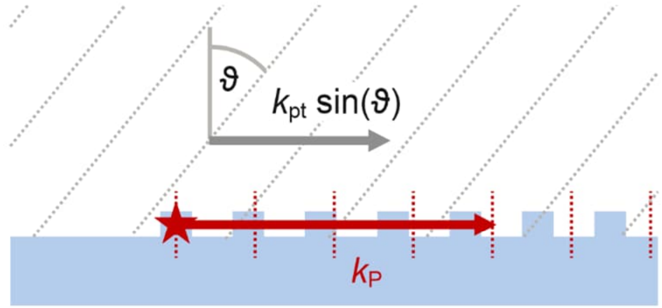
dipole

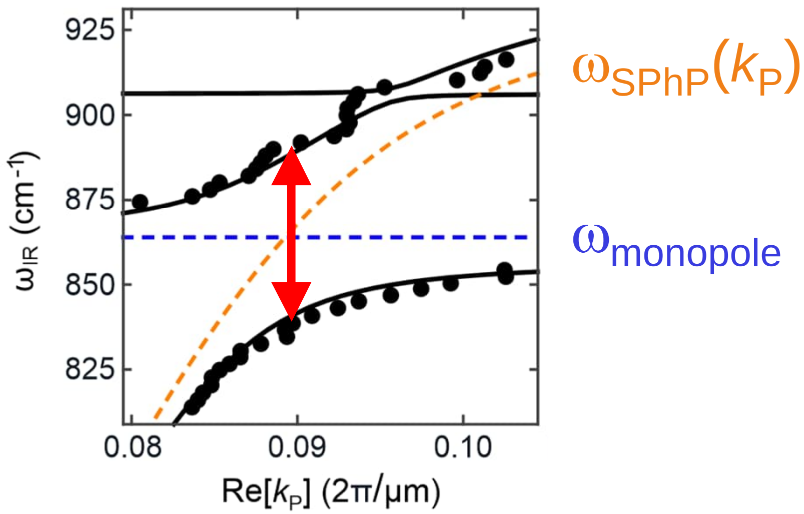
Real space imaging of strong coupling

Interferometry of localized and edge launched propagating polaritons



$$I(x) = |Ae^{ik_{\rm P}x + i\xi} + Be^{ik_{\rm pt}\sin\vartheta x}|^2$$



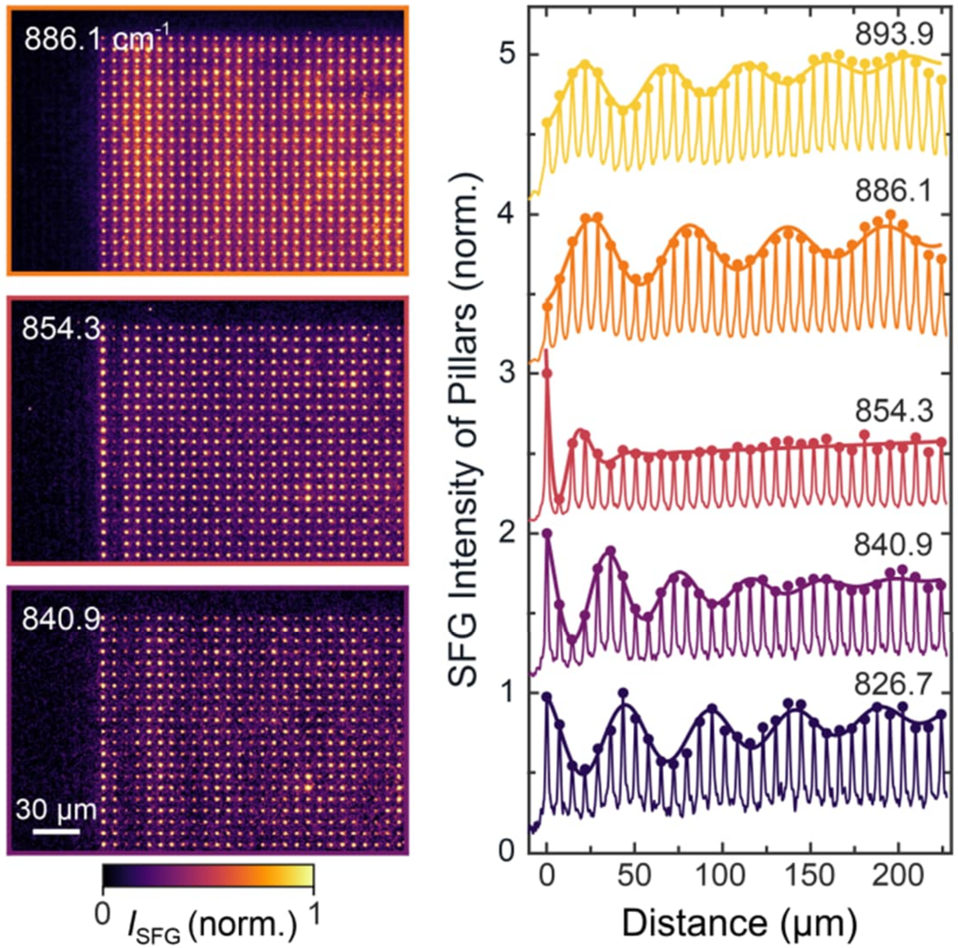


- Strong coupling determines polariton propagation length **up to 150 μm**

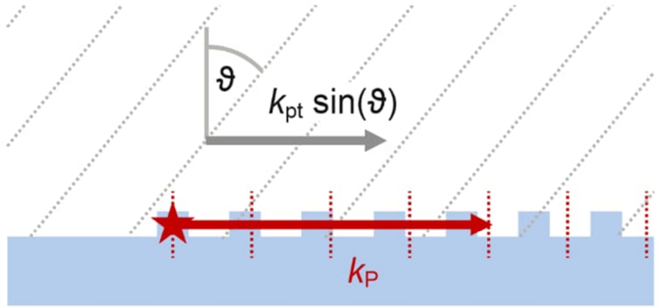
See: Lu et al. *Nano Lett.* 21, 1831 (2021), Gubbin et al. *PRL* 116, 246402 (2016)

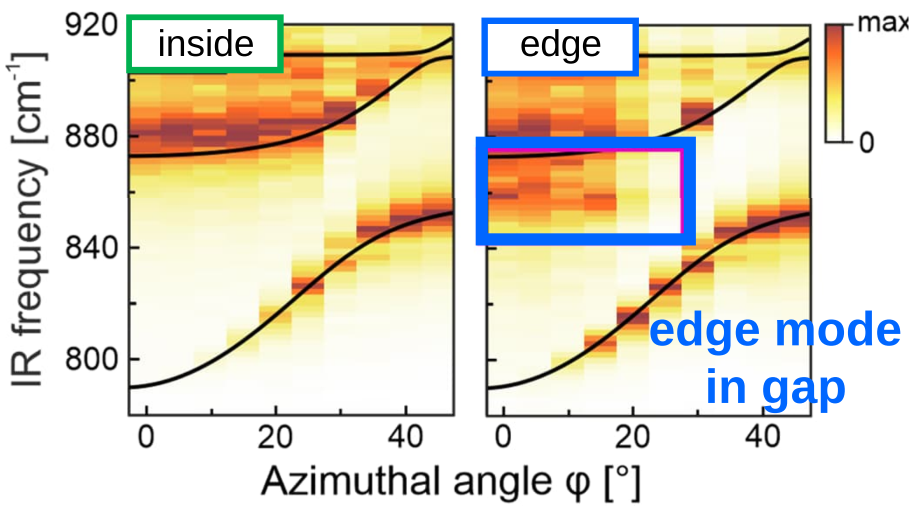
Real space imaging of strong coupling

Interferometry of localized and edge launched propagating polaritons



$$I(x) = |Ae^{ik_P x + i\xi} + Be^{ik_{pt}\sin\vartheta x}|^2$$

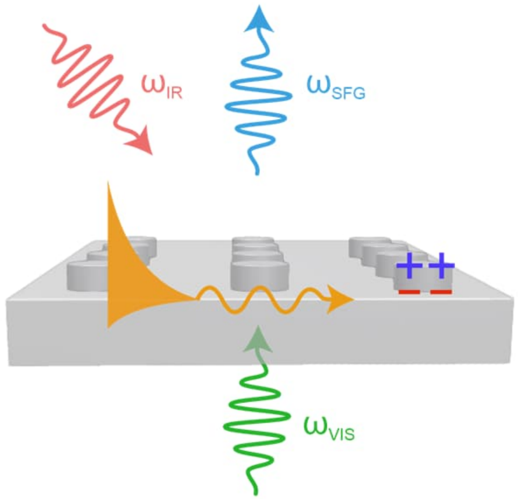


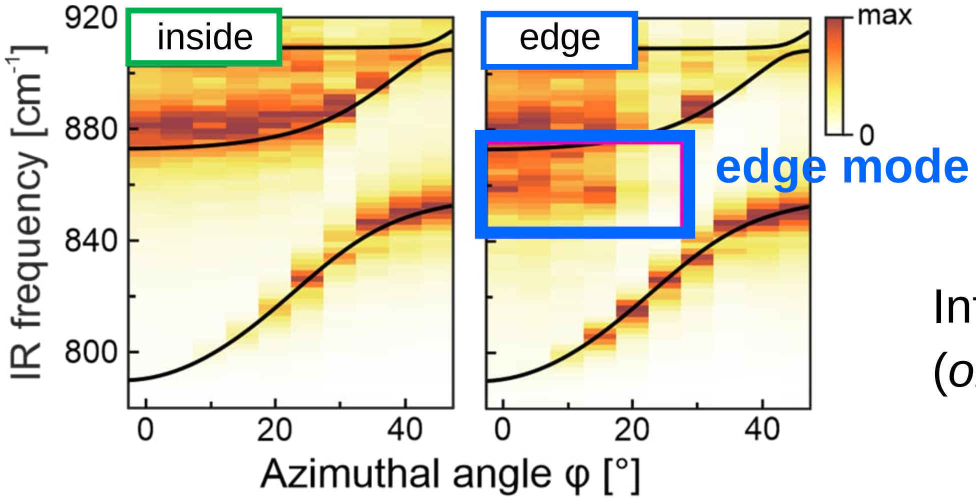


- Localizatian at edge when strong coupling prevents propagation

Take home...

Wide-field SFG microscopy shows global dynamics and symmetry properties beyond IR diffraction limit

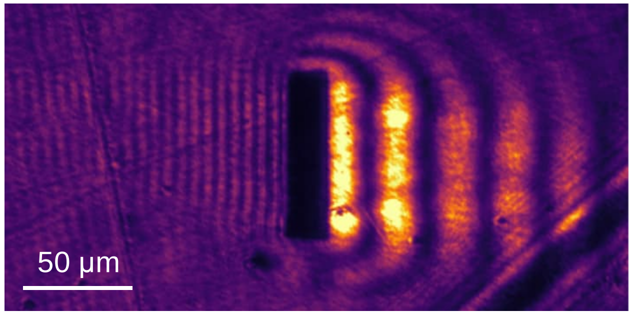


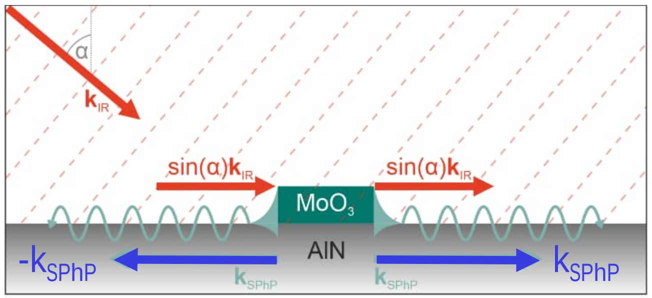


Interferometry of edge lauchned SPhP (*on SiC metasurface*)

Advanced Materials (2024 accepted)

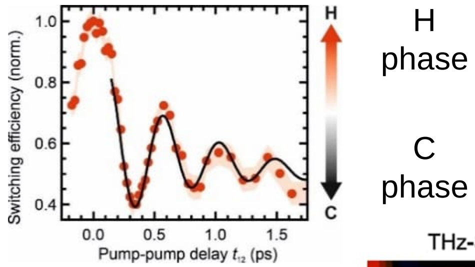
Real space imaging of propating SPhP modes



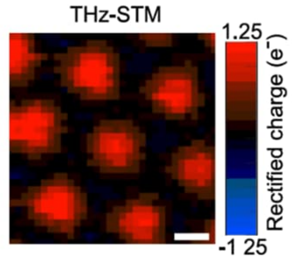


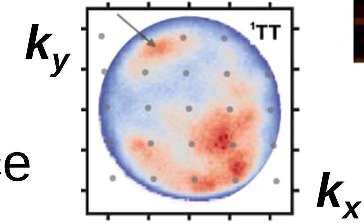
Summary

- **Overview:** Material properties, excitations, phase transitions & dynamics

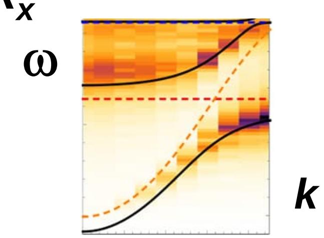


- **Charge density wave dynamics** in TaS_2:
  - Transition to metastable H phase probed by ARPES
  - Local CDW dynamics probed by THz- STM

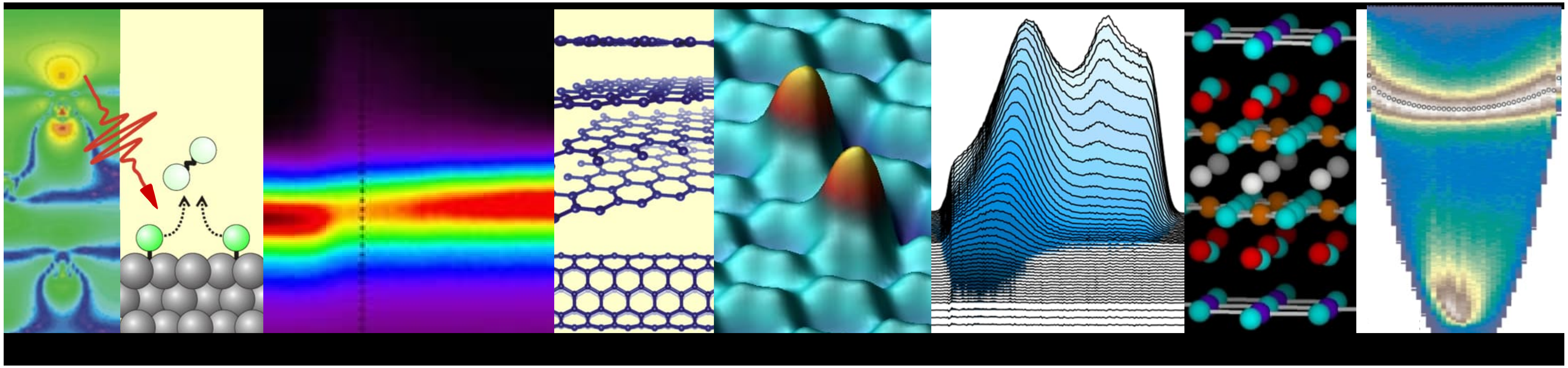




- **Exciton dynamics** in molecular crystals:
  - Singlet fission in pentacene in momentum space



- **Coupling between light and matter**:
  - Phonon polaritons and strong coupling on SiC metasurface



Acknowledgements

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HHG-based trARPES

L. Parra Lopez, A. Vaitsi, V. Sleziona, A. Hammud & M. Müller
Fritz-Haber-Institut der MPG, Berlin

ultrafast STM

R. Niemann, N. Müller, S. Wasserroth & A. Paarmann
Fritz-Haber-Institut der MPG, Berlin
G. Lu & J. Caldwell, *Vanderbuildt University, Nashville*

Phonon polaritons

S. Hammer, J. Pfaum *(University of Würzburg)*
F. Bonafe, H. Apelt, Angel Rubio *(MPI Hamburg)*

Theory