Electron-phonon interactions and ultrafast dynamics

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Selb
Summer School
of the CRC 1242

https://cs2t.de

Christian-Albrechts-Universität zu Kiel

Computational Solid-State Theory group

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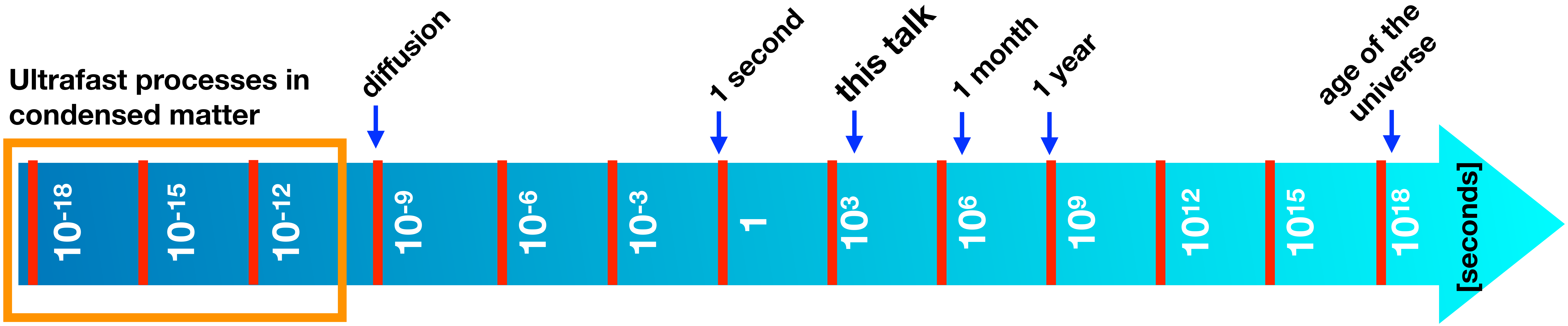
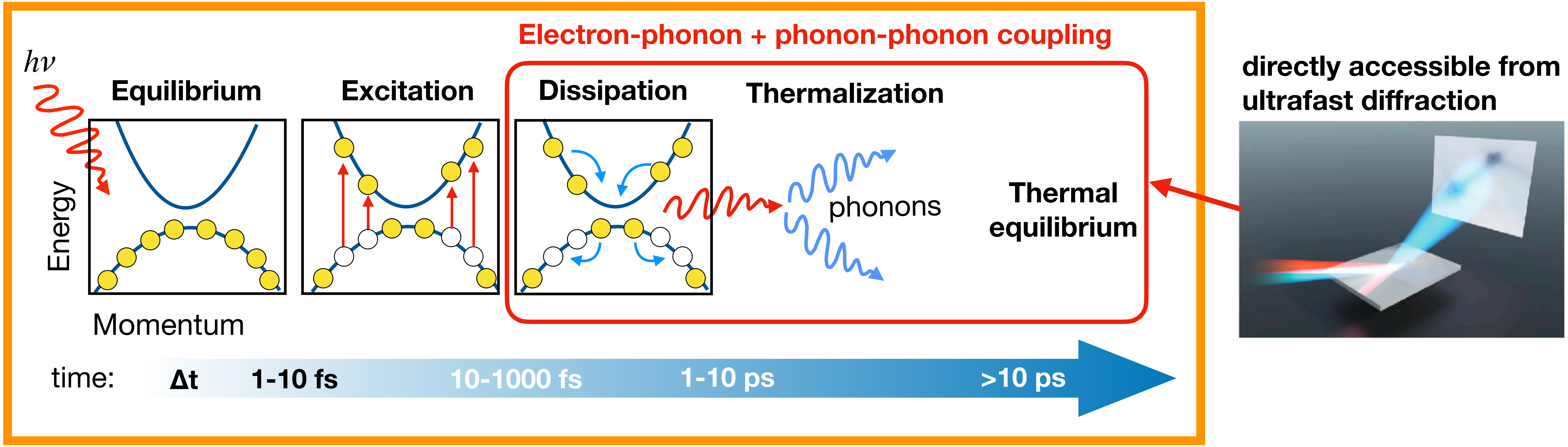
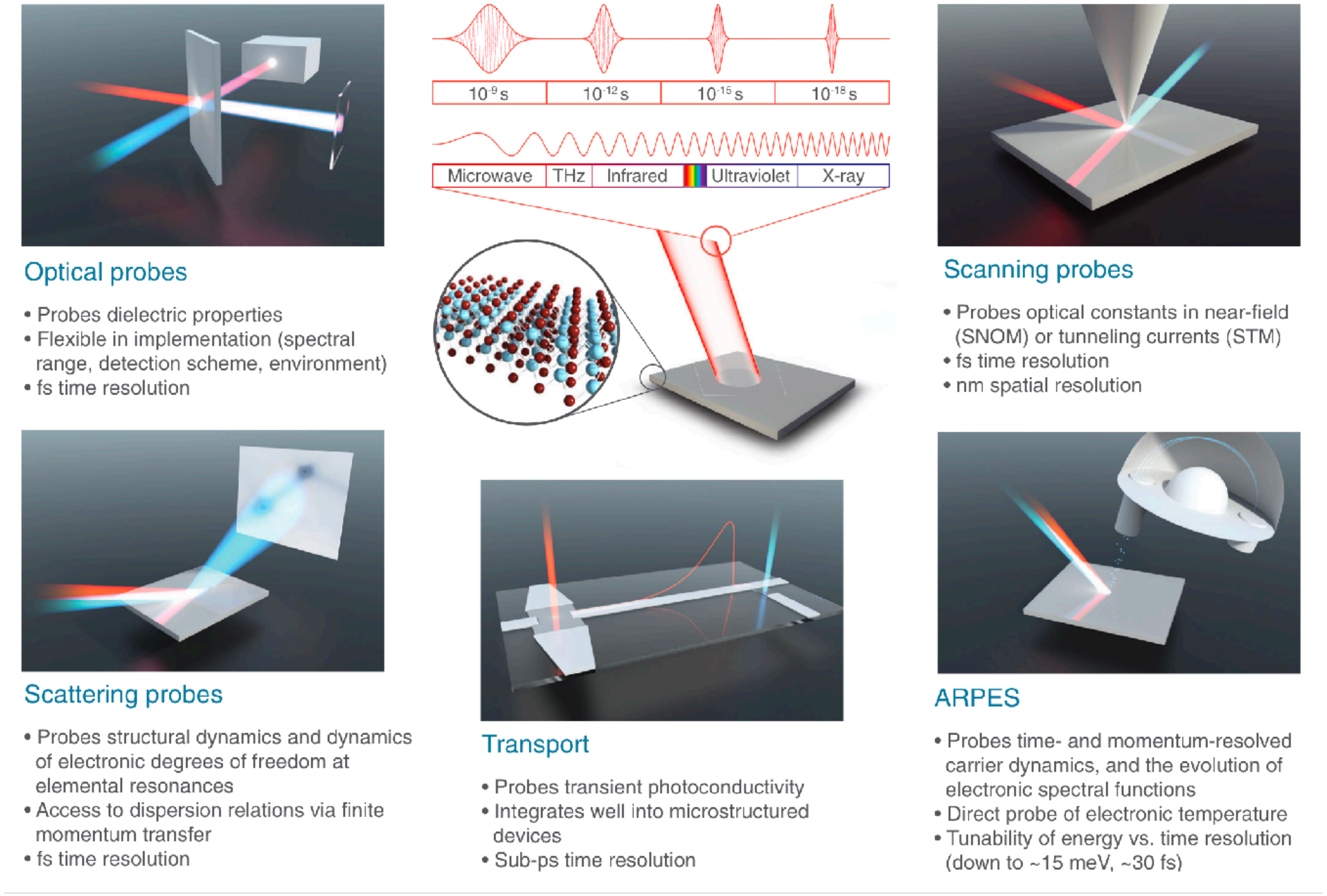
German Research Foundation

What's the time (scale)?





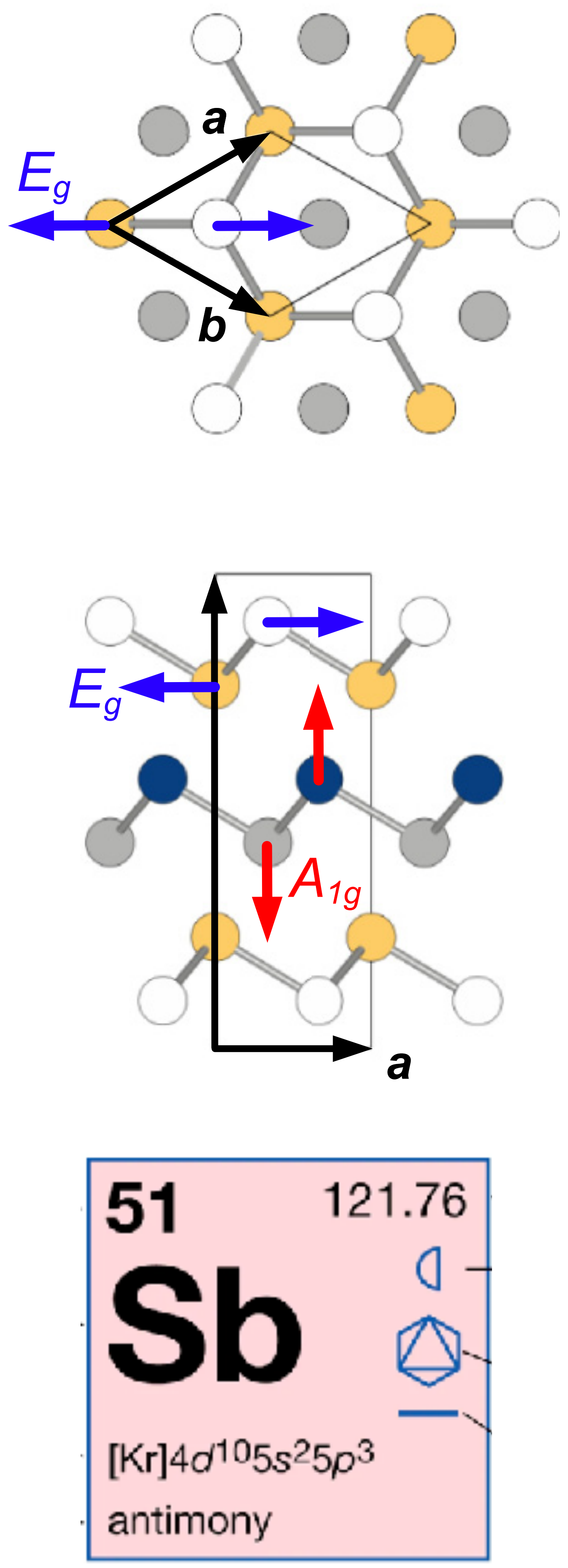
Ultrafast dynamics: a new frontier of condensed-matter research

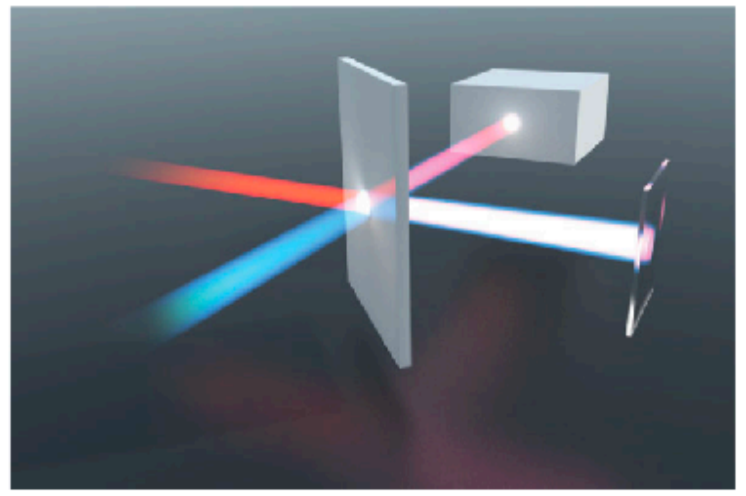


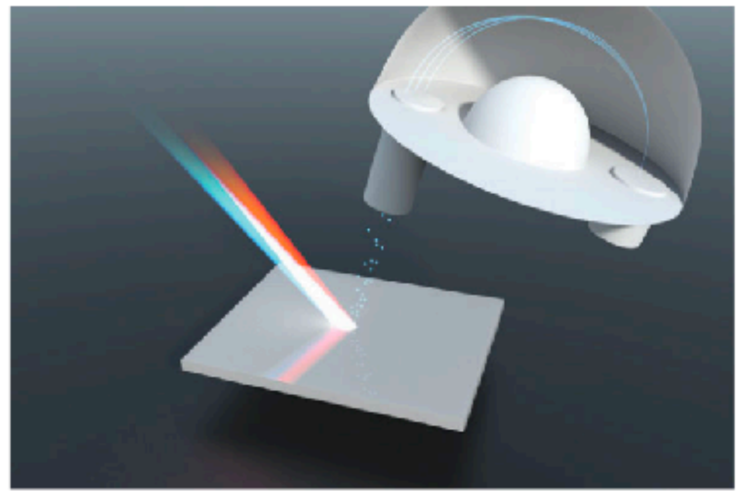
de la Torre, et al. Rev Mod. Phys. (2021)

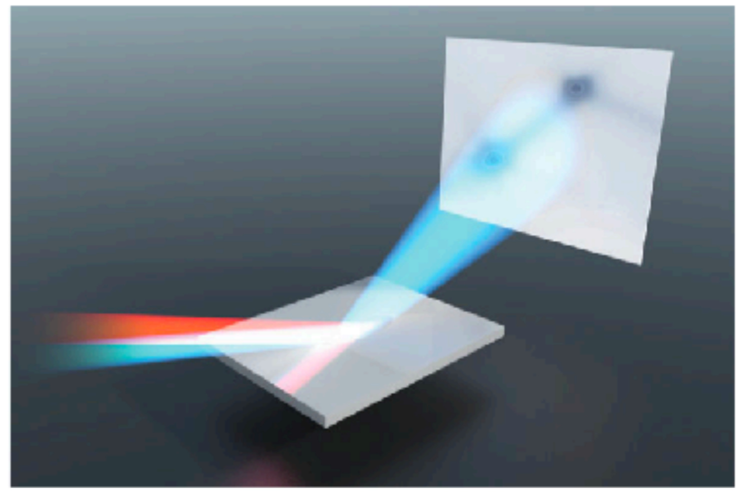
Coherent phonons in experiments: the example of antimony

Antimony (Sb)

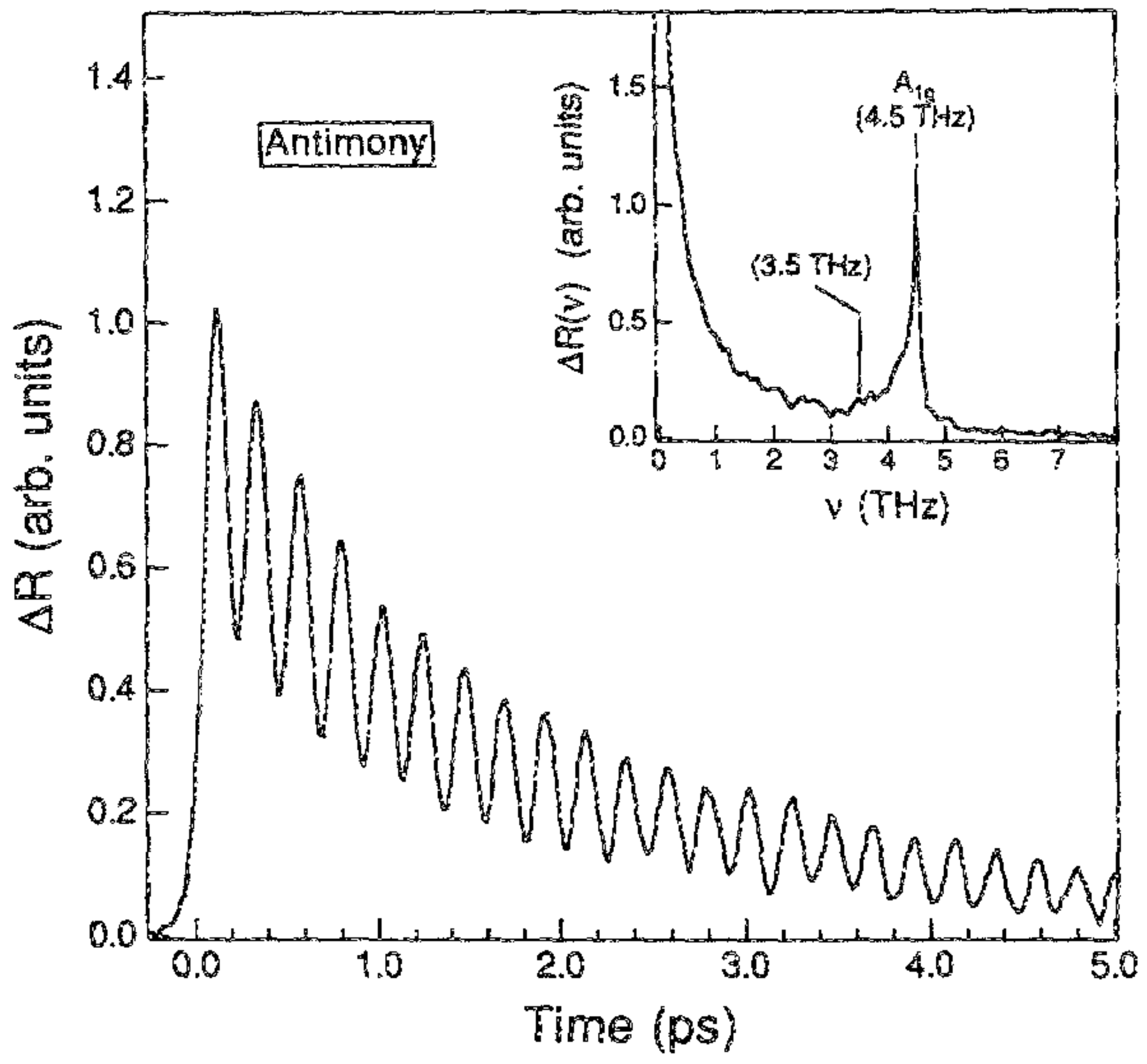






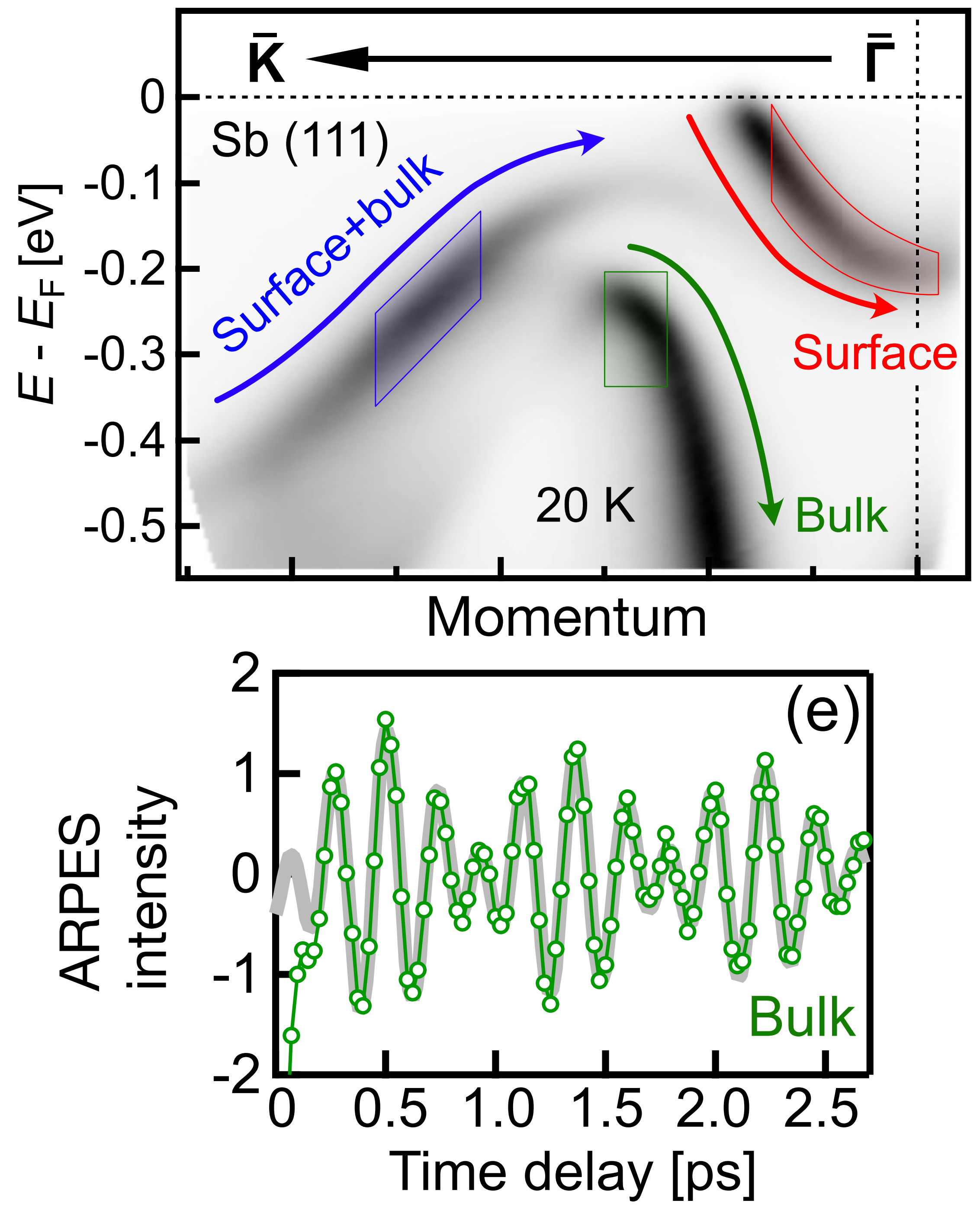


Transient Reflectivity



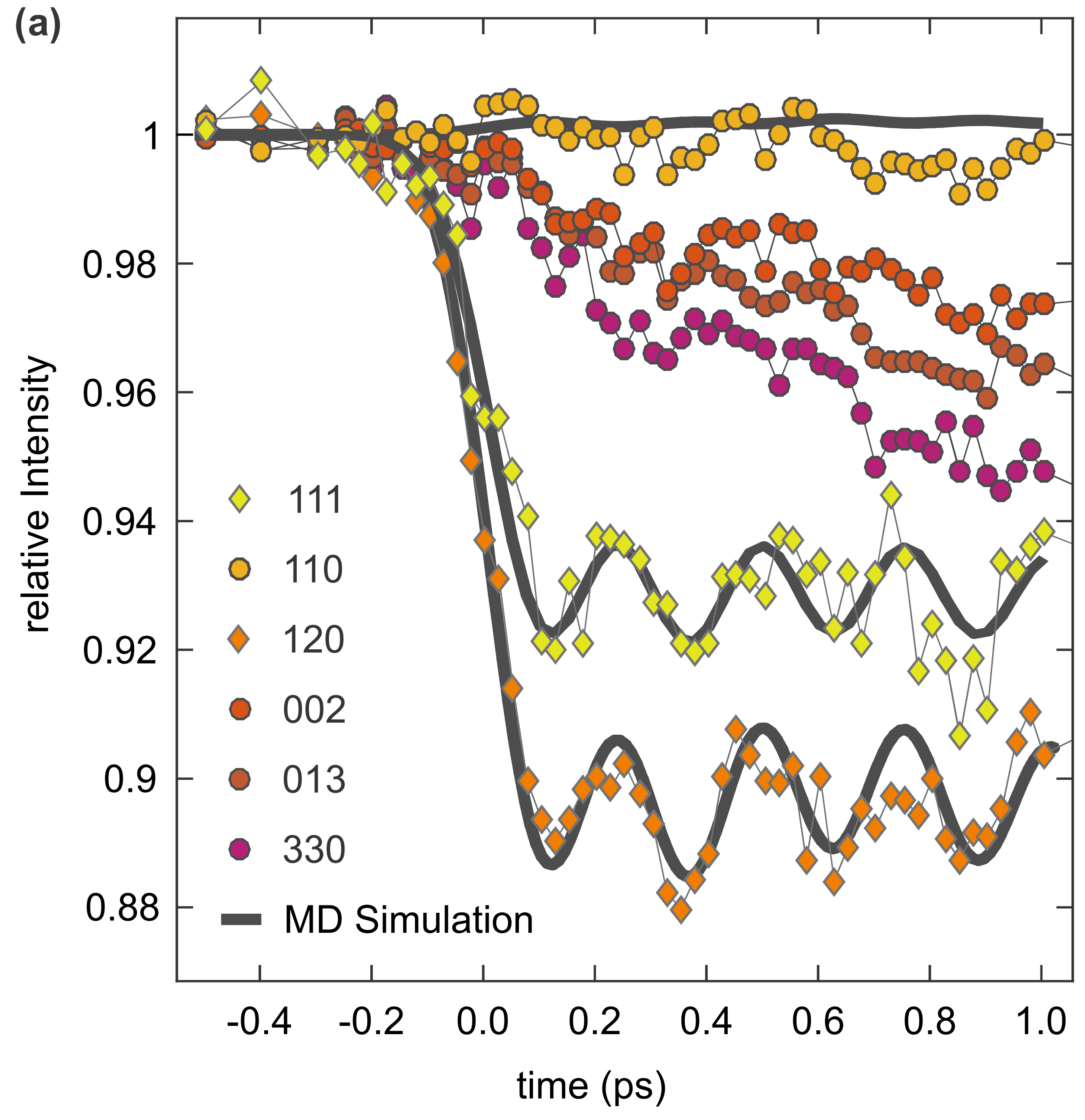
Cheng et al,
Appl. Phys. Lett. **57**, 1004 (1990)

Pump-probe ARPES



Sakamoto et al,
Phys. Rev. B **105**, L161107 (2022)

Ultrafast Diffraction

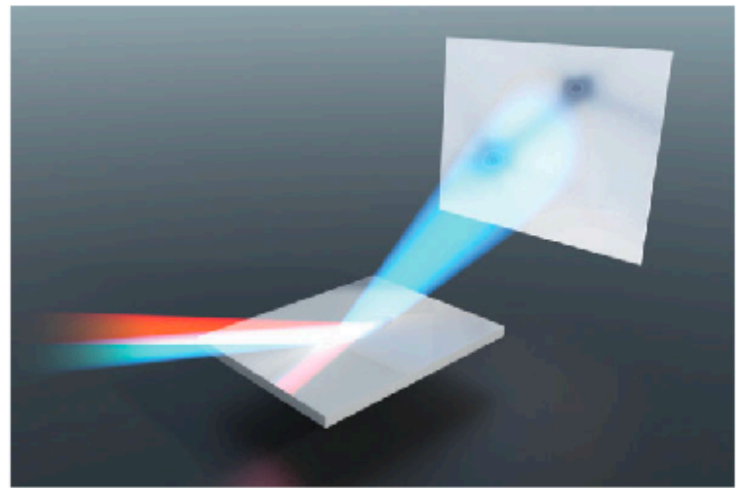


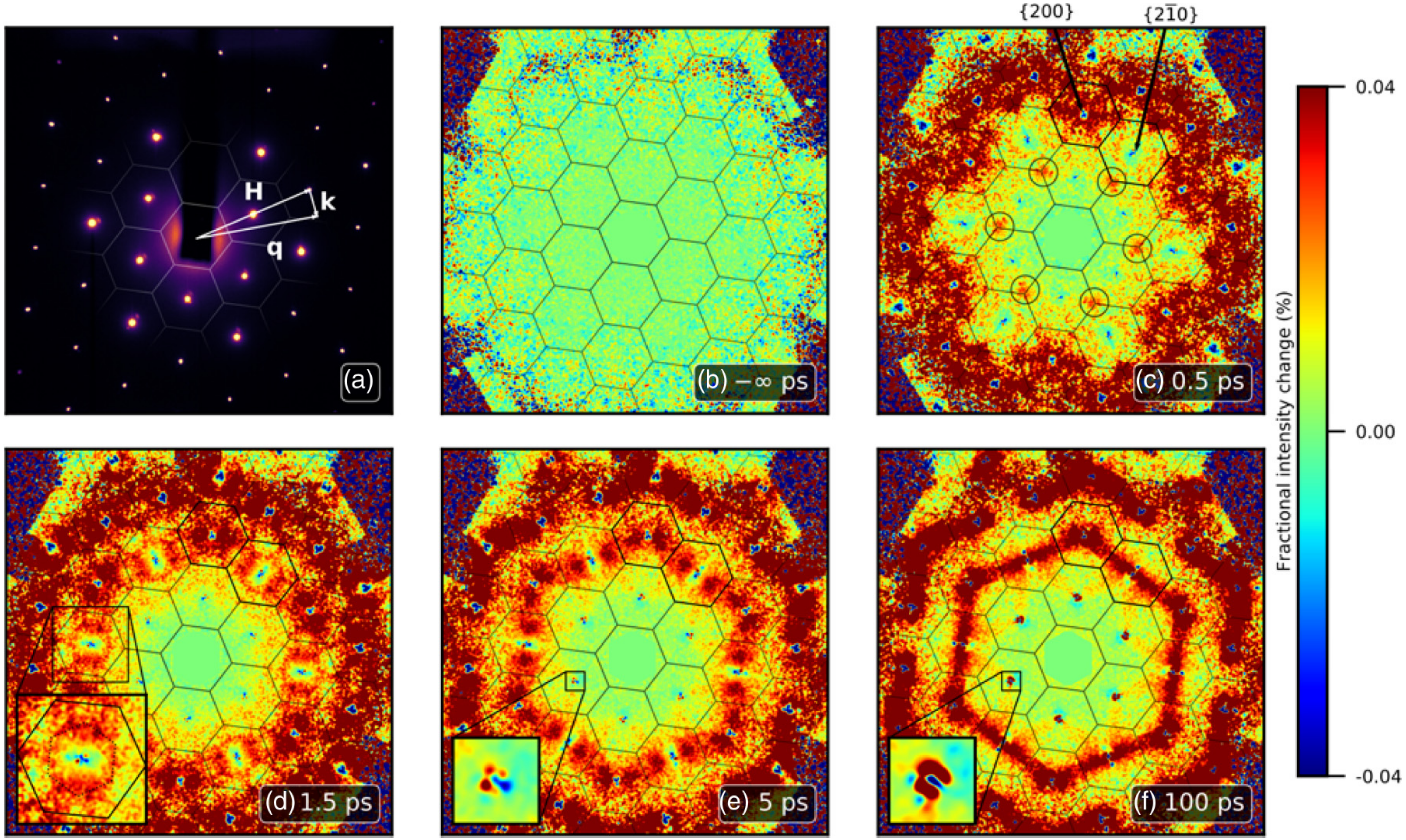
Waldecker, Ernstorfer, et al,
Phys. Rev. B **95**, 054302 (2017)

Incoherent phonons in diffraction experiments: the case of graphite

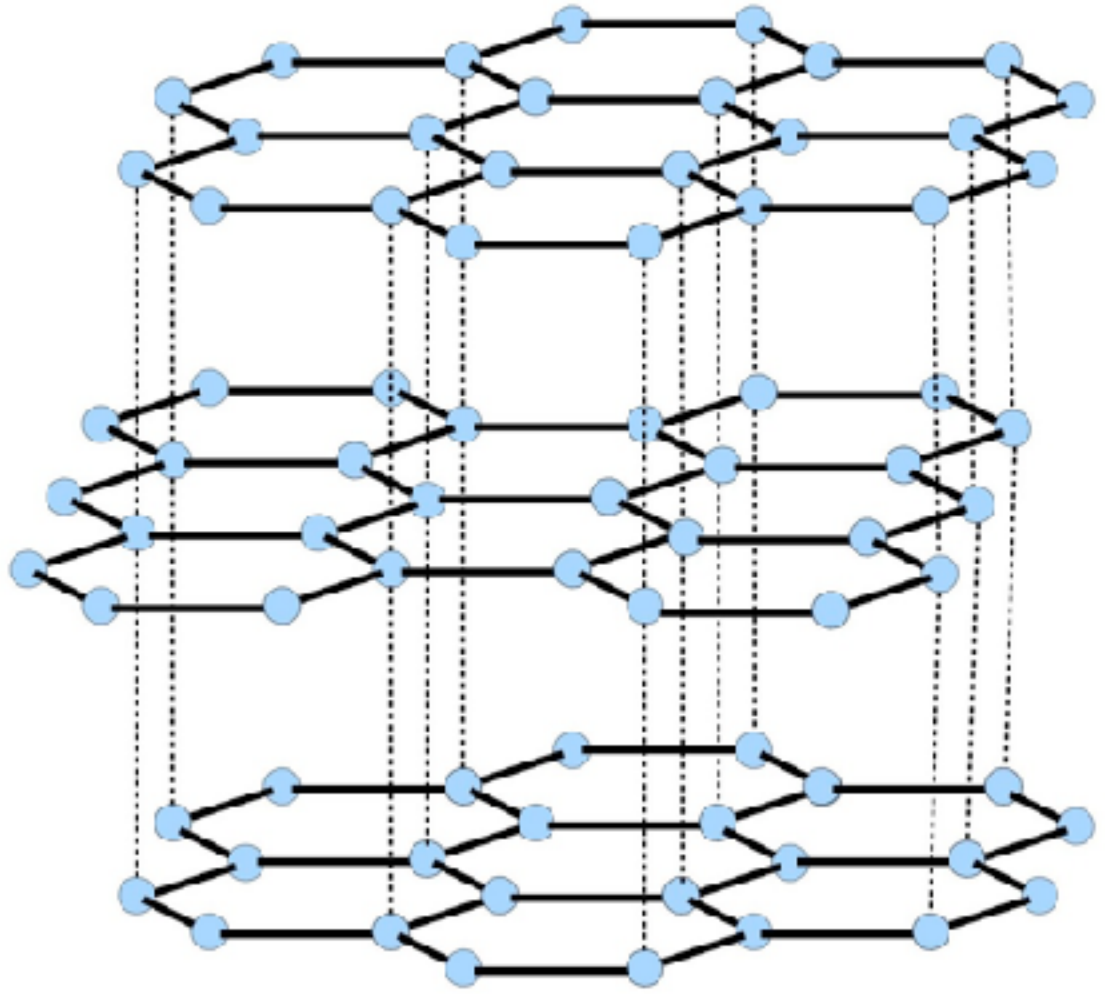
Ultrafast diffraction as a probe to non-equilibrium phonon population

$$n_{\mathbf{q}\nu}(t) \neq n_{\mathbf{q}\nu}^{\mathrm{BE}} = [e^{\hbar\omega_{\mathbf{q}\nu}/k_{\mathrm{B}}T} - 1]^{-1}$$





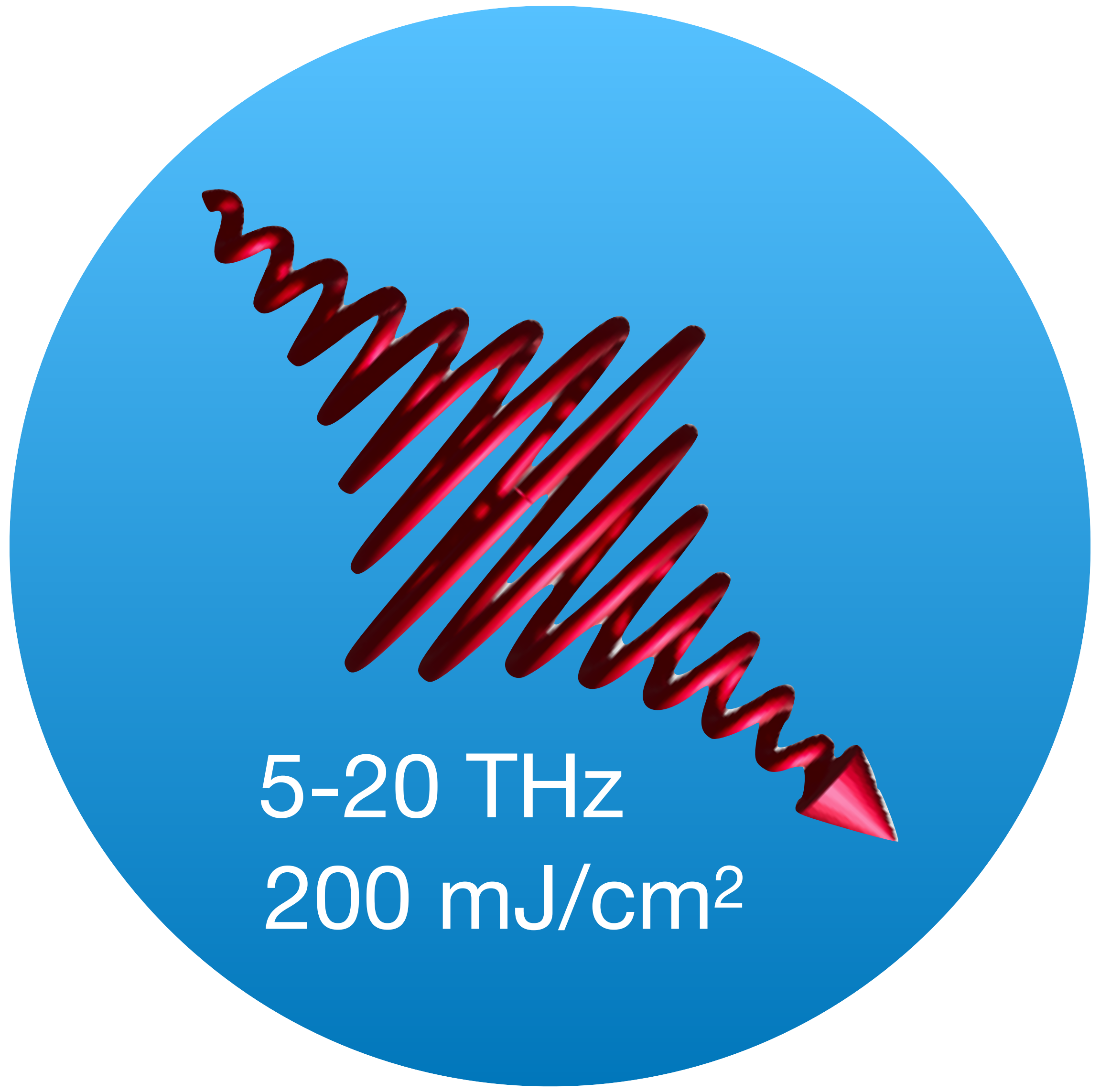
Graphite



Stern, Siwick, et al, Phys. Rev. B **97**, 165916 (2018)

Tailoring quasiparticle interactions on subpicosecond timescales

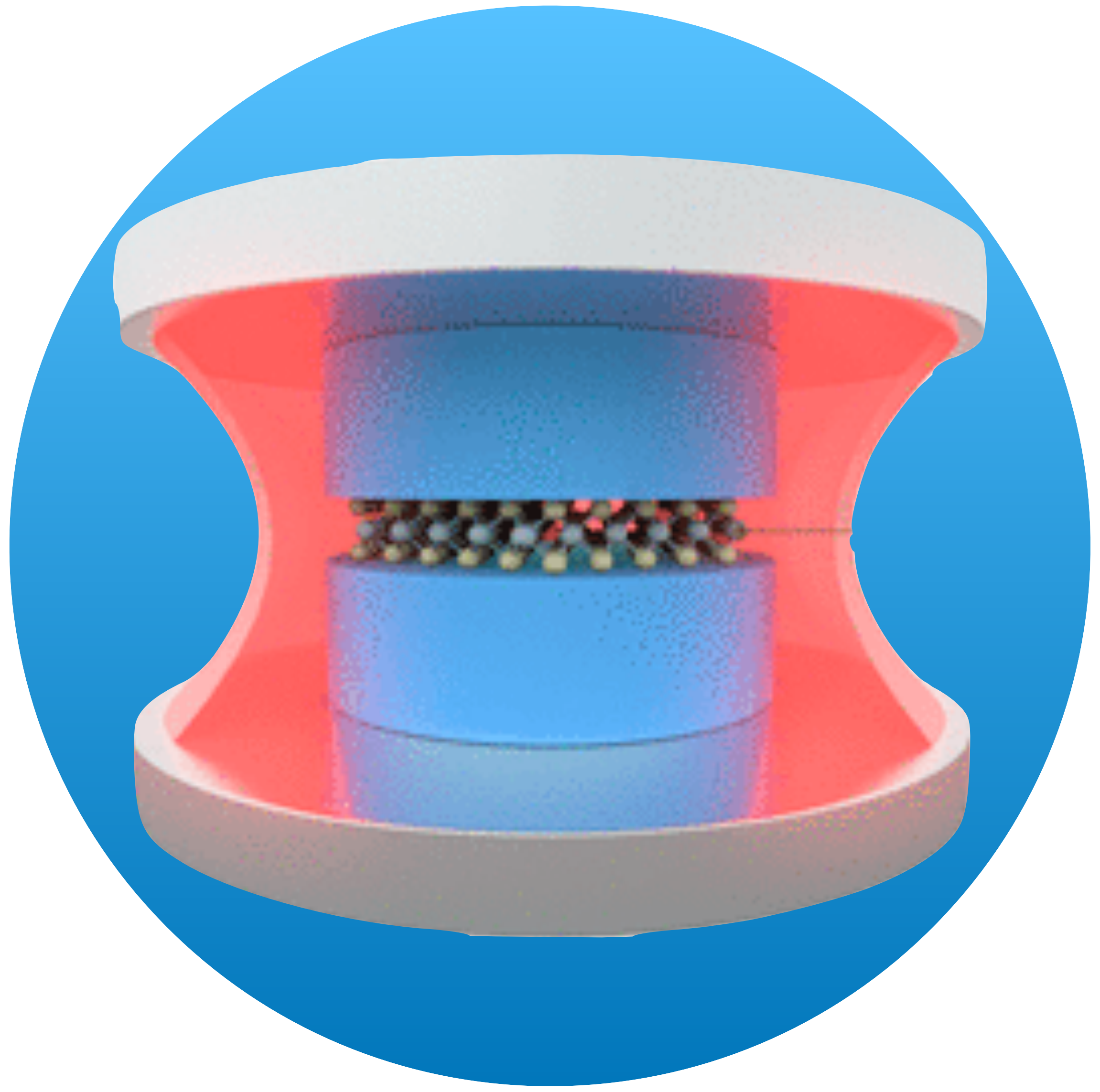
Intense THz pulses



Reversal of Ferroelectric polarization in $LiNbO_3$

Mankowsky, Cavalleri et al.,
Phys. Rev. Lett. **118**, 197601 (2017)

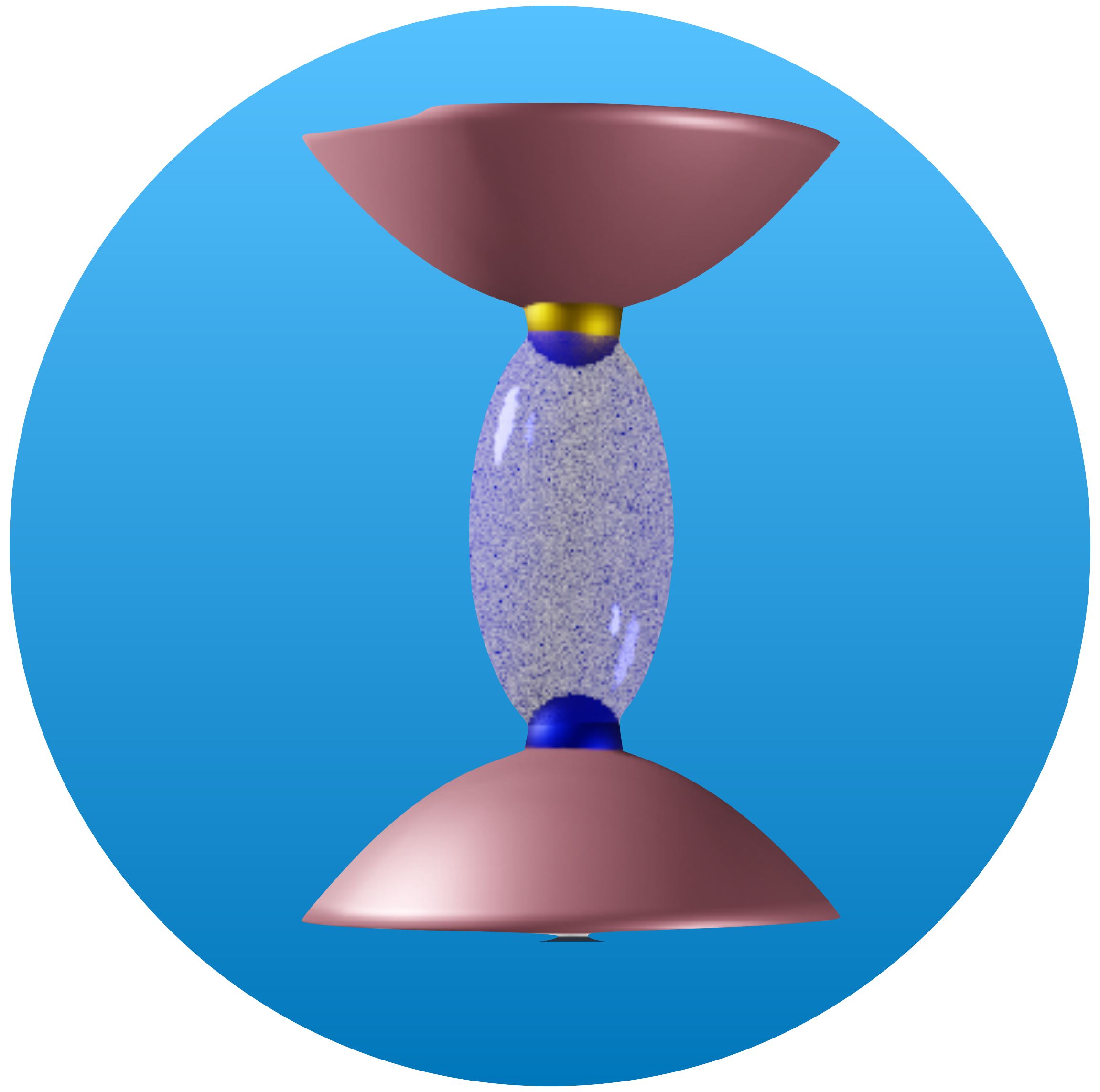
Cavity QED & Polaritons



Tunable phonon polaritons for hBN embedded in a optical micro-cavity

Barra-Burrillo, Hillenbrand et al.,
Nature Commun. **12**, 6206 (2021)

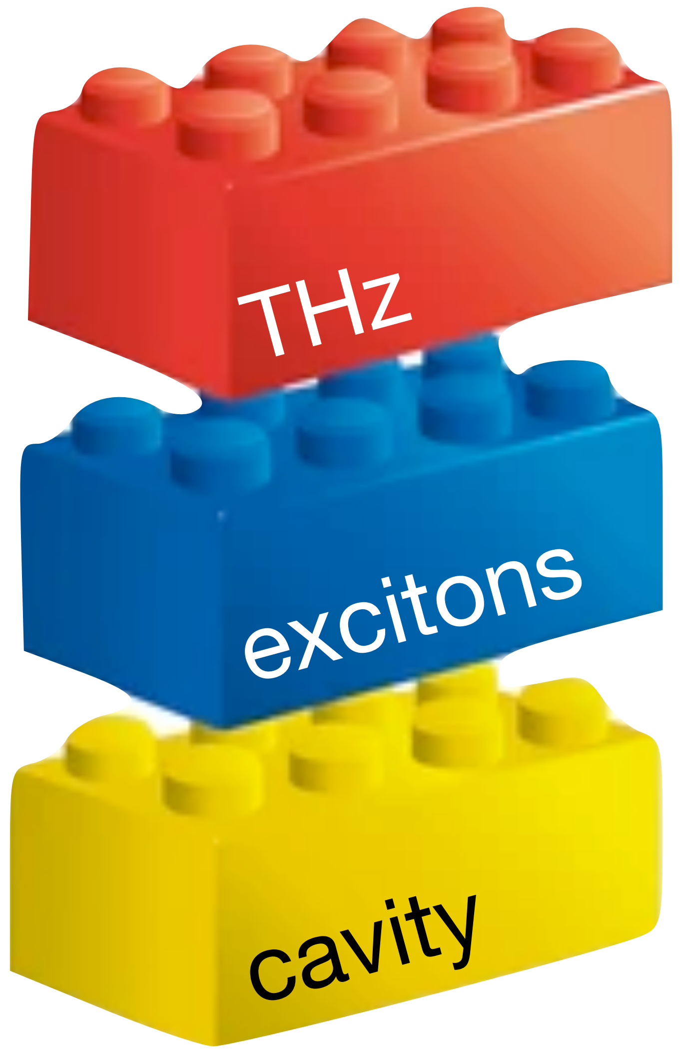
Optical excitations



Ultrafast lattice distortion during exciton formation in perovskites

Seiler, Ernstorfer et al.,
ACS Nano **17**, 1979 (2023)

coming soon:



Open challenges in ab-initio theory of light-driven structural control

1. Ab-initio description of excitation, dynamics, dissipation of the lattice
2. Novel paradigms for structural control require new theories
3. Many-body interactions and quasiparticle excitations in light-driven solids

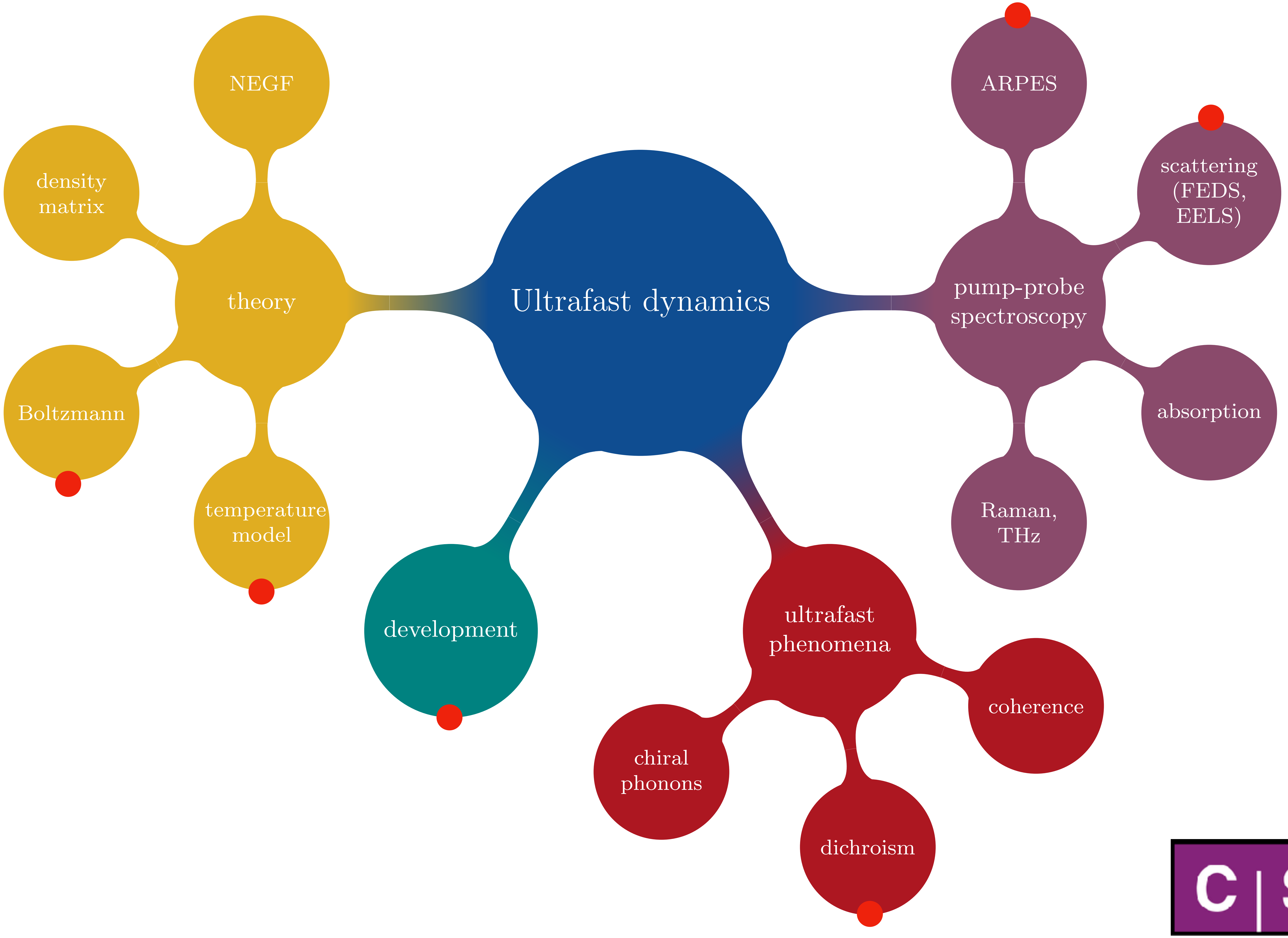
$$i\hbar\partial_t\Psi = \hat{H}\Psi$$

4. Develop open-access algorithms suitable for modern HPC infrastructure
5. Go FAIR: Findability, Accessibility, Interoperability, and Reuse of time-dependent data

... require efforts from an entire community!

- Scheffler, Draxl, et al, Nature **604**, 635 (2022)
- Schlavin et al., Appl. Phys. Rev. **9**, 011312 (2022)
- de la Torre, et al. Rev Mod. Phys. (2021)
- Disa et al., Nat. Phys. **17**,1087 (2021)
- Basov et al., Nat. Mater **16**, 1077 (2017)
- ... and many more

Challenges in ab-initio theory of ultrafast dynamics

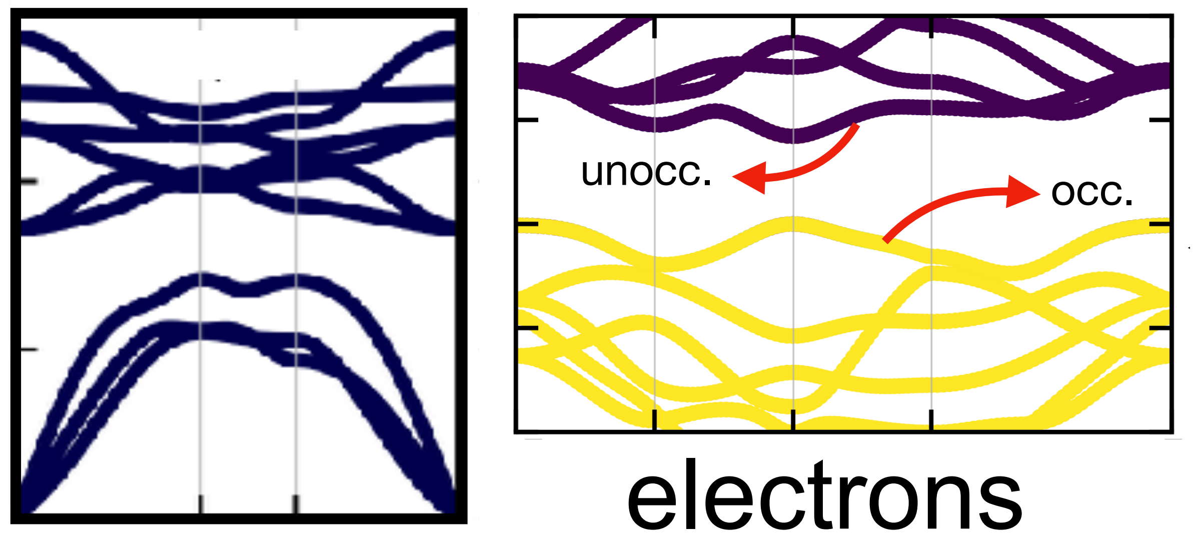


Computational Solid-State Theory group

Workflow for ultrafast dynamics simulations

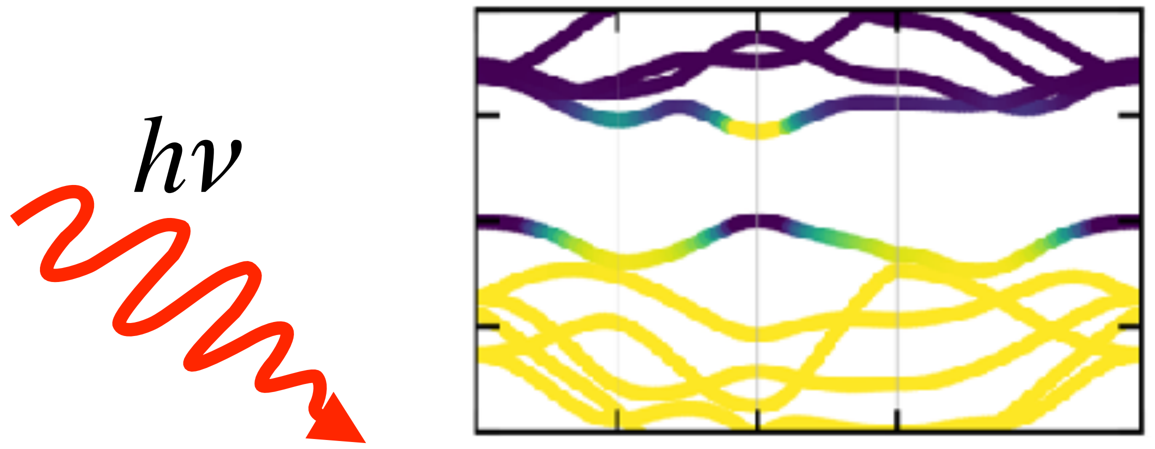
1. Band structure (DFT)
   Phonon dispersion (DFPT)
2. Model coupling to light pulse
   (or excited state Ansatz)
3. Time propagation
4. Transient many-body effects
   and emergent phenomena
5. Theoretical spectroscopy:
   tr-ARPES, Raman, scattering

1.



phonons electrons

2.



excitation

3.

two-temperature model

time-dependent Boltzmann equation

non-equilibrium Green's functions

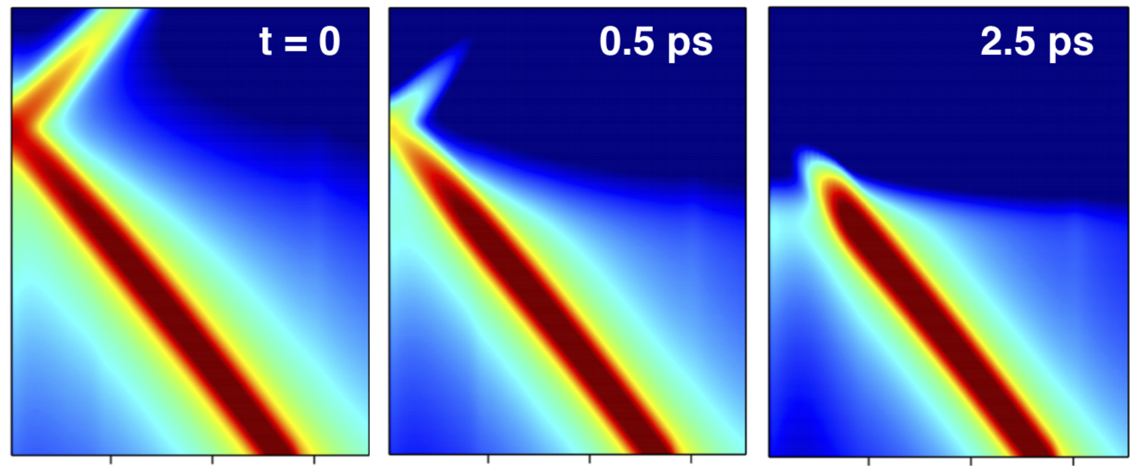
4.

Many-body perturbation theory and Green's functions

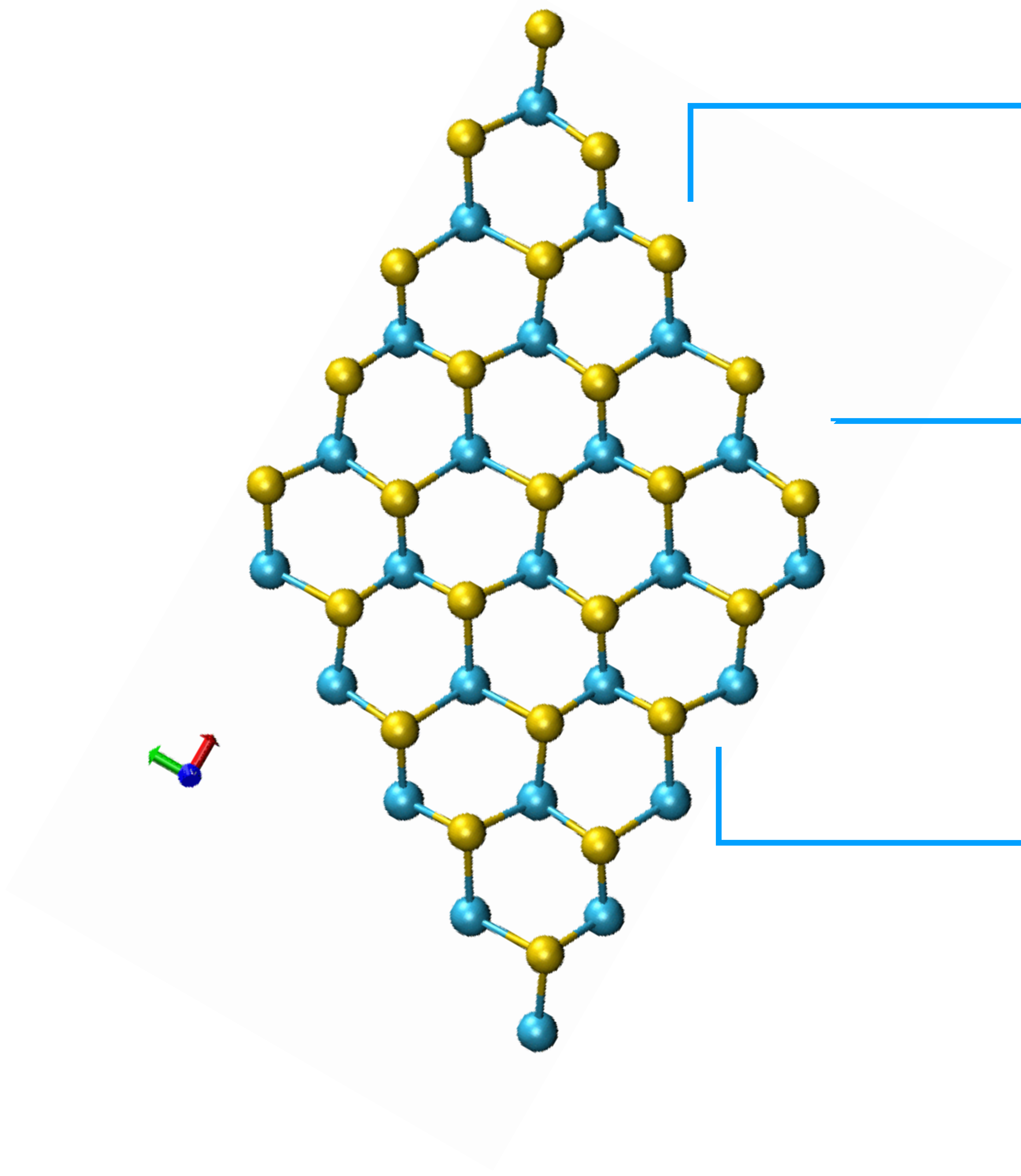
$$G(1,2) = -i\langle\Psi_0|\hat{T}\hat{\psi}(1)\hat{\psi}^\dagger(2)|\Psi_0\rangle$$

5.

tr-ARPES



Outline



The two-temperature model

The time-dependent Boltzmann equation

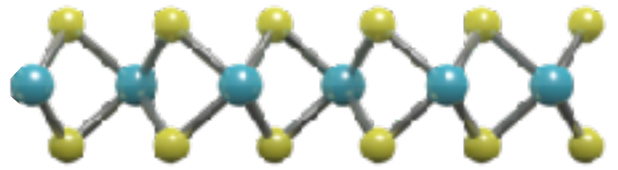
Ultrafast dynamics in 2D materials

Part 1

The two-temperature model (TTM)

Phonons at equilibrium: monolayer MoS_2

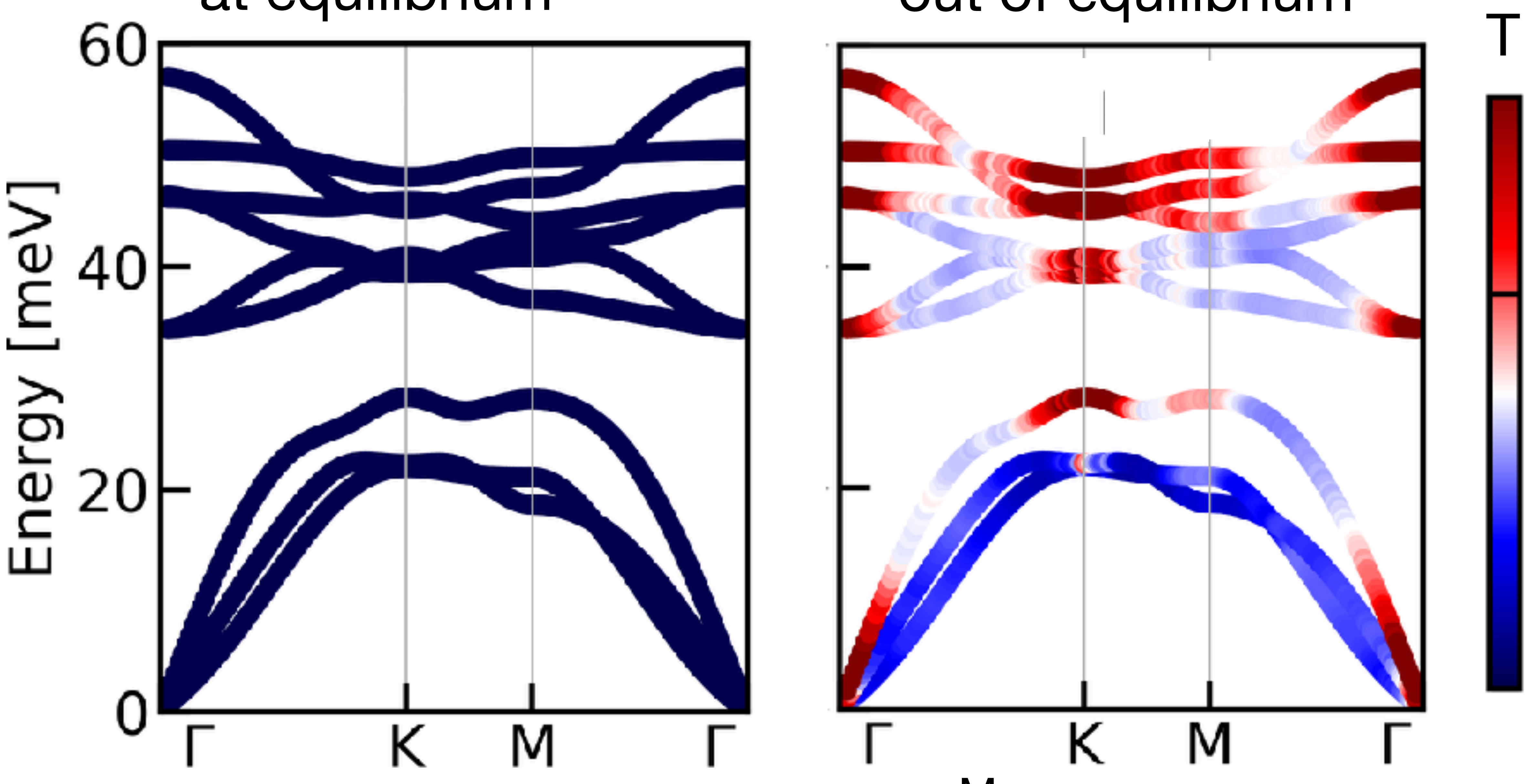
Monolayer MoS_2



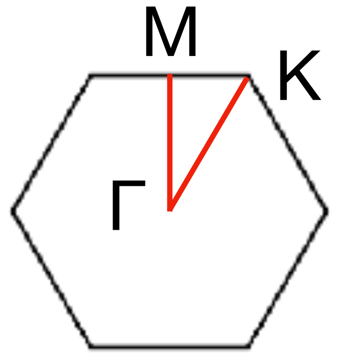
Bose-Einstein statistics: $n^0_{\mathbf{q}\nu}(T) = \left[e^{\hbar\omega_{\mathbf{q}\nu}/k_B T} - 1\right]^{-1}$

Vibrational temperature: $T_{\mathbf{q}\nu}(t) = \hbar\omega_{\mathbf{q}\nu}\{k_B \ln[1 + n_{\mathbf{q}\nu}(t)]\}^{-1}$

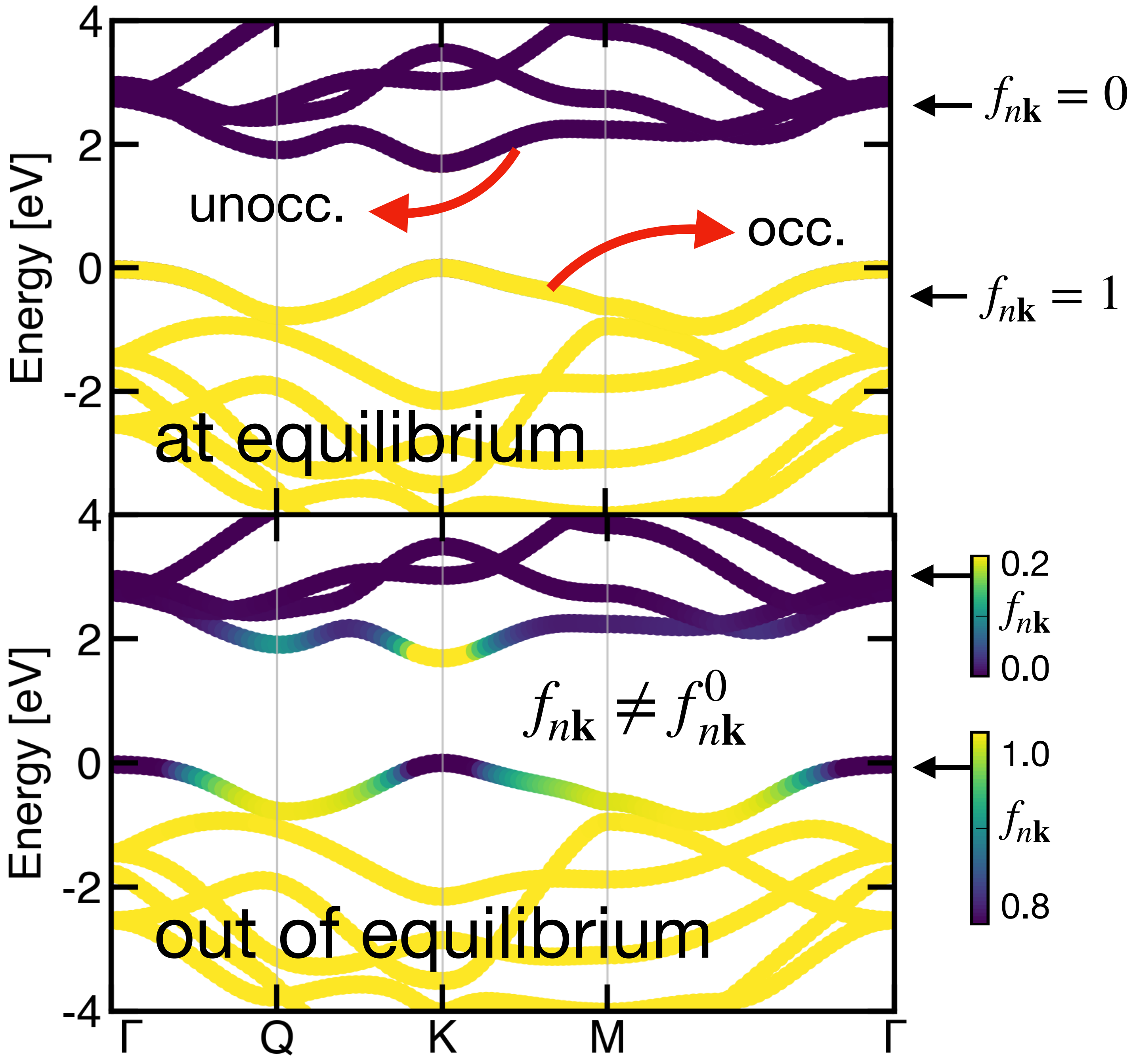
Phonons



from density functional perturbation theory

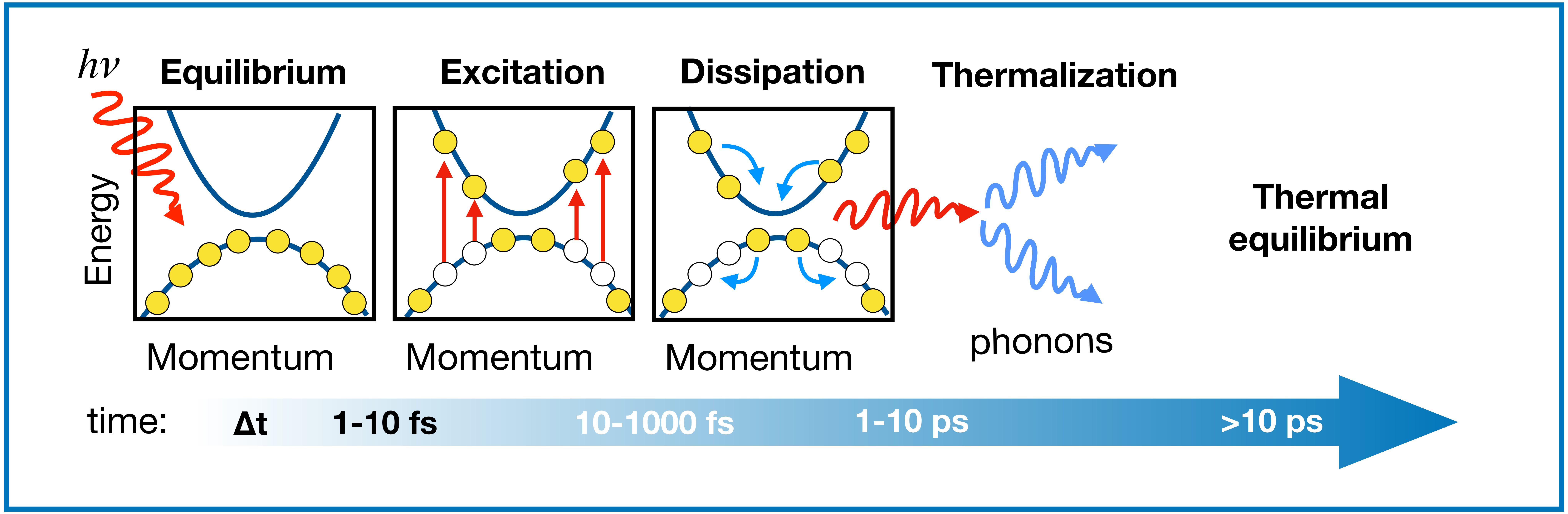


Electrons



Coupled dynamics of electrons and phonons

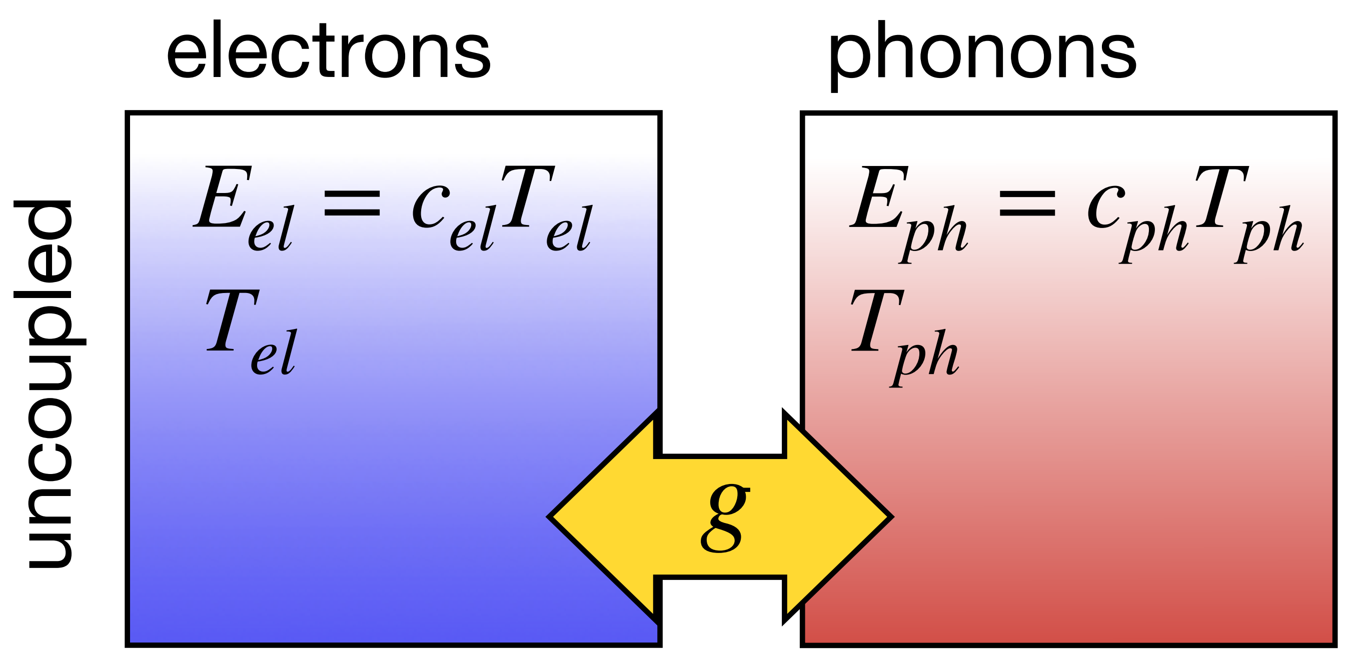
The coupled electron-phonon dynamics is triggered by a disturbance of equilibrium
(e.g., absorption of light at THz or UV frequencies)



Fundamental interactions restore a regime of thermal equilibrium:

- Electron-electron interactions (5-50 fs)
- Electron-phonon interactions (50-500 fs)
- Phonon-phonon interactions (0.5 - 200 ps)
- Radiative recombination (1ns)
- In magnetic materials: spin-phonon

Thermalization of electrons and lattice from the two-temperature model (TTM)



electrons and phonons as two thermal baths

① Dynamics as a thermalization of 2 thermal baths: $\frac{\Delta E_{el}}{\Delta t} = g_{el}(T_{ph} - T_{el})$ $\quad$ $\frac{\Delta E_{ph}}{\Delta t} = g_{ph}(T_{el} - T_{ph})$

② Energy conservation: $\Delta E_{el} = -\Delta E_{ph}$ → $g_{el} = g_{ph}$

③

$$c_{el}\frac{\Delta T_{el}}{\Delta t} = = g(T_{ph} - T_{el})$$

$$c_{ph}\frac{\Delta T_{ph}}{\Delta t} = = g(T_{el} - T_{ph})$$

infinitesimal time step → ④

Two-temperature model

$$c_{el}\frac{\partial T_{el}}{\partial t} = = g(T_{ph} - T_{el}) + S(t)$$

$$c_{ph}\frac{\partial T_{ph}}{\partial t} = = g(T_{el} - T_{ph})$$

TTM: coupled first-order differential equation for the temperature of the electrons and lattice

driving term (coupling to light)

All quantities available from first principles (parameter-free)

Electron heat capacity

$$C_{\mathrm{el}}(T) = \int_{\infty}^{\infty} d\varepsilon D_{\mathrm{el}}(\varepsilon)\varepsilon \frac{\partial f\left(\mu, \varepsilon, T_{\mathrm{el}}\right)}{\partial T_{\mathrm{el}}}$$

Phonon heat capacity

$$C_{\mathrm{ph}}(T) = \int_{0}^{\infty} d(\hbar\omega) D_{\mathrm{ph}}(\omega)\hbar\omega \frac{\partial n\left(\omega, T_{\mathrm{ph}}\right)}{\partial T_{\mathrm{ph}}}$$

Coupling constant

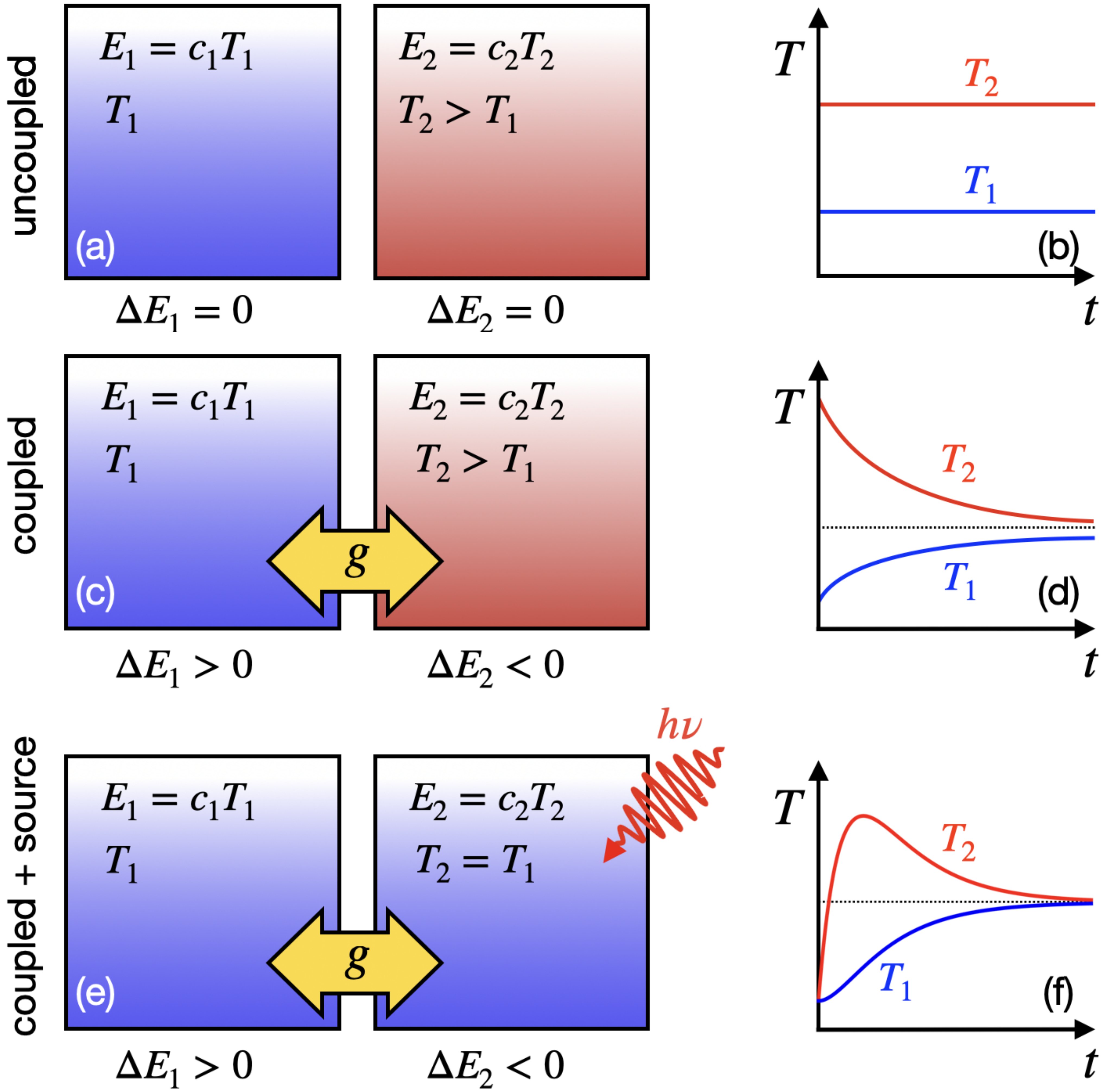
$$g = \frac{\pi k_B}{\hbar D_{\mathrm{el}}\left(\varepsilon_F\right)} \lambda \left\langle \omega^2 \right\rangle \int_{-\infty}^{\infty} d\varepsilon D_{\mathrm{el}}^2(\varepsilon)\left(-\frac{\partial f\left(\mu, \varepsilon, T_{\mathrm{el}}\right)}{\partial \varepsilon}\right)$$

Caruso, Novko, Adv. Phys. X **7**, 2095925 (2022)

Thermalization of electrons and lattice from the two-temperature model

Two-temperature model (TTM)

$$c_{el}\frac{\partial T_{el}}{\partial t} = = g(T_{ph} - T_{el}) + S(t) \qquad c_{ph}\frac{\partial T_{ph}}{\partial t} = = g(T_{el} - T_{ph})$$



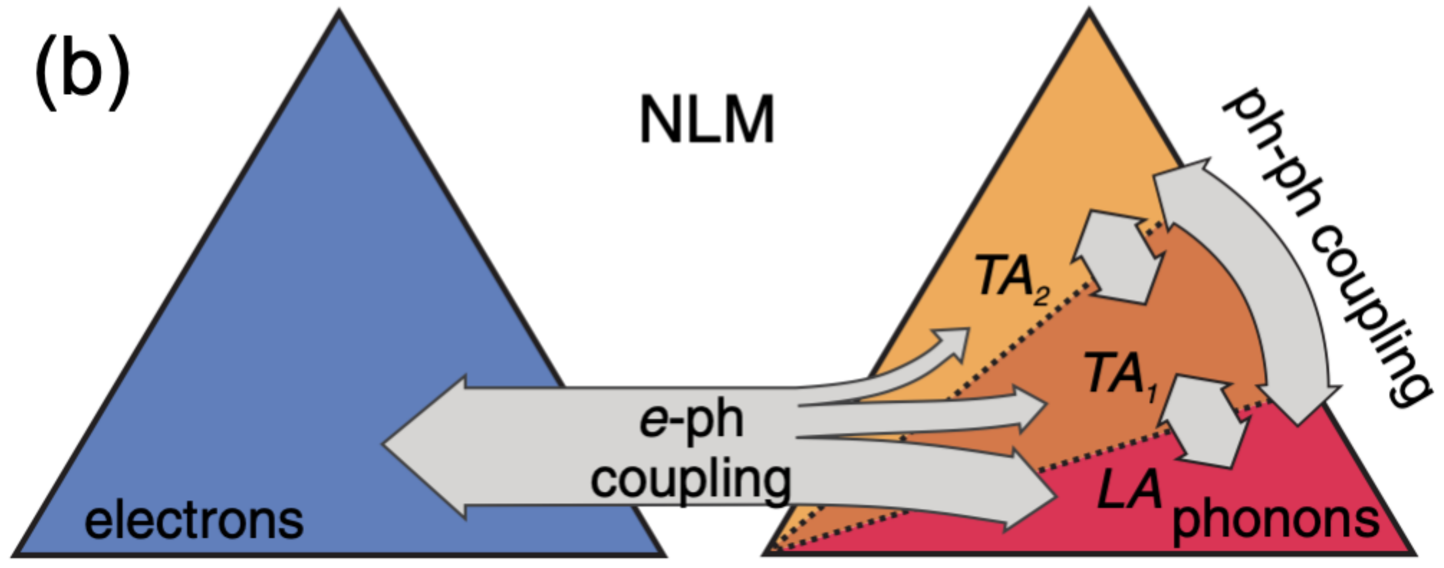
Caruso, Novko, Adv. Phys. X **7**, 2095925 (2022)

Limitations:

- Non-equilibrium states characterized by a single temperature
- The electron subsystem is at thermal equilibrium:
  $T_{el} \rightarrow f_{n\mathbf{k}}(T_{el}) = [e^{(\varepsilon_{n\mathbf{k}} - \mu)/k_B T_{el}} + 1]^{-1}$
- The phonon subsystem is at thermal equilibrium:
  $T_{ph} \rightarrow n_{\mathbf{q}\nu}(T_{ph}) = [e^{(\hbar\omega_{\mathbf{q}\nu})/k_B T_{ph}} - 1]^{-1}$
- Only applicable to metals

Generalizations:

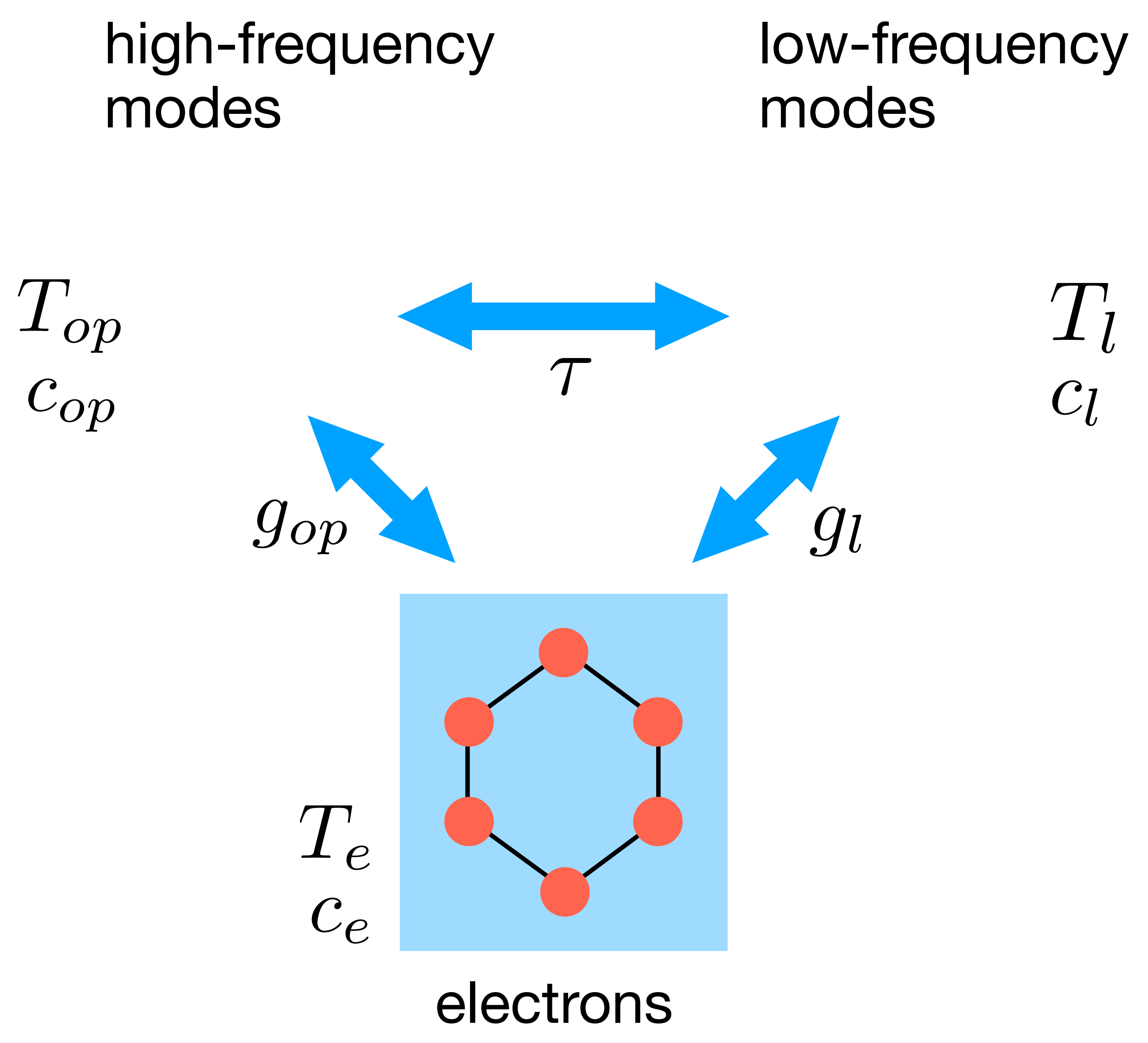
1. Non-thermal lattice model (NLM)

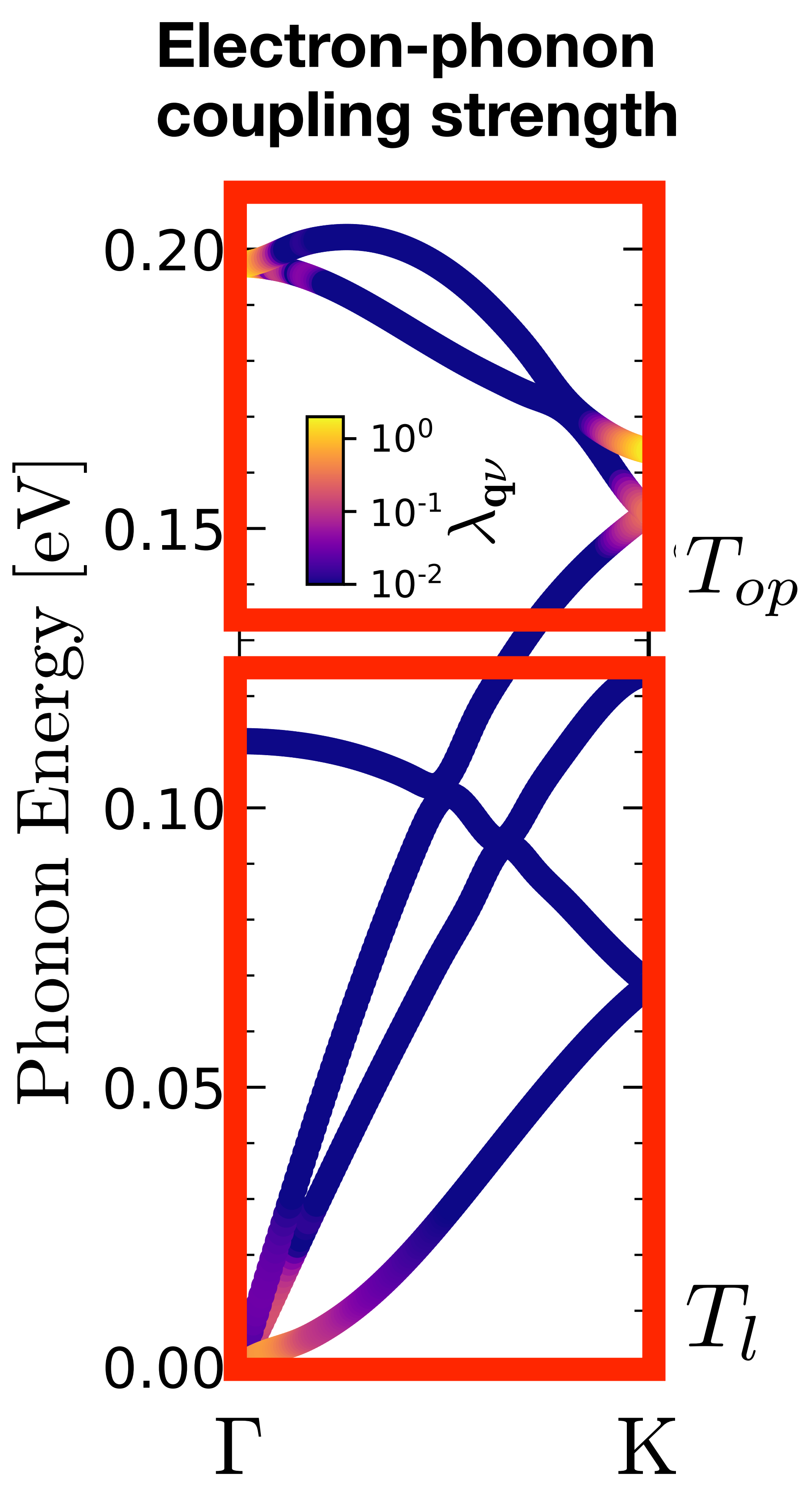


L. Waldecker, R. Bertoni, R. Ernstorfer, J. Vorberger, Phys. Rev. X **6**, 021003 (2016)

2. Distinct Fermi levels for electrons and holes (suitable for semiconductors)

Ultrafast dynamics in graphene via the three-temperature model





T_e T_{op} T_l temperatures (electrons, optical/acoustic phonons)

$$\frac{dT_e}{dt} = \frac{I(t)}{\beta c_e} - \frac{g_{op}}{c_e}(T_e - T_{op}) - \frac{g_l}{c_e}(T_e - T_l)$$

$$\frac{dT_{op}}{dt} = \frac{g_{op}}{c_{op}}(T_e - T_{op}) - \frac{T_{op} - T_l}{\tau},$$

$$\frac{dT_l}{dt} = \frac{g_l}{c_l}(T_e - T_l) + \frac{c_{op}}{c_l}\frac{T_{op} - T_l}{\tau}.$$

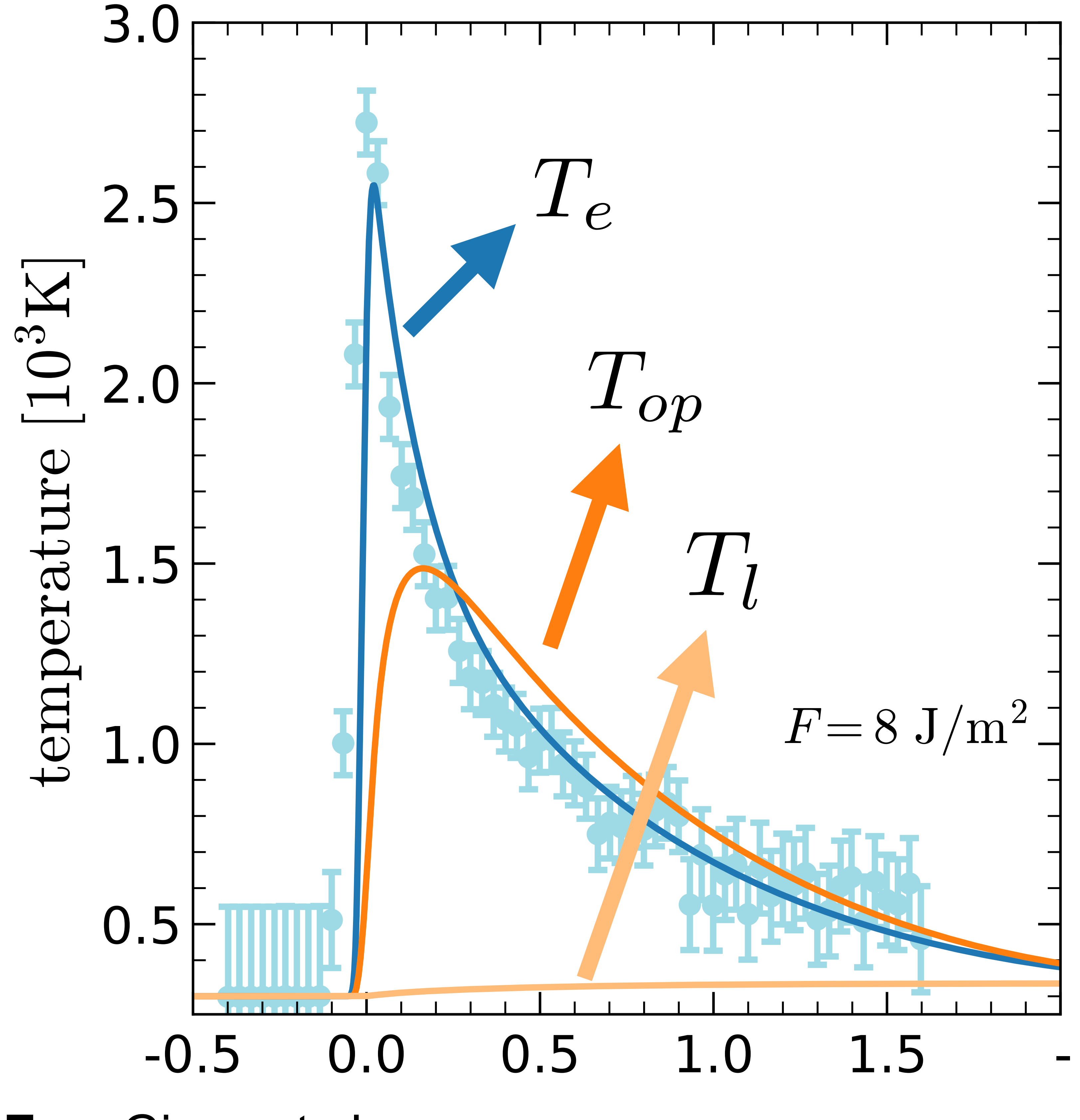
All parameters available from first principles

$I(t)$	pump (fluence/energy/duration)
g_{op} g_l	electron-phonon coupling to optical/acoustic phonons
c_e c_l c_{op}	heat capacity of electrons and phonons
τ	anharmonic coupling rate (from exp.)
β	pump energy density

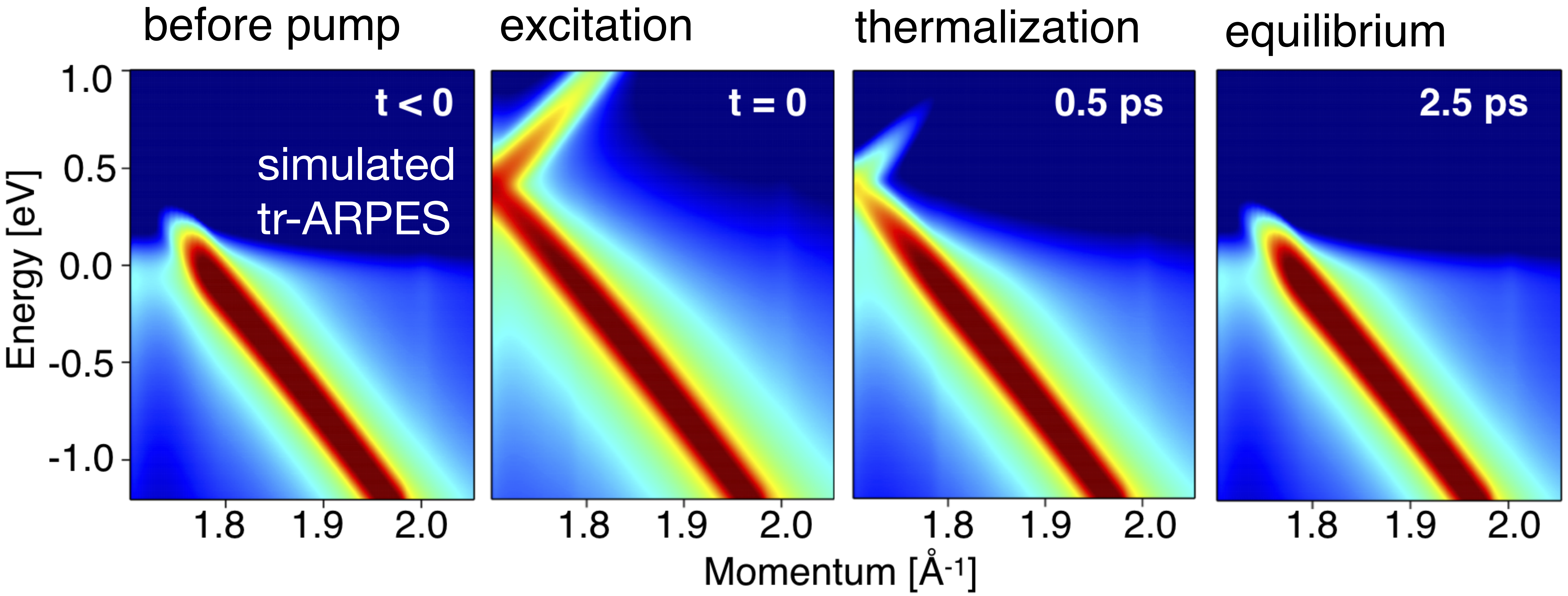
Parameter

Non-thermal lattice models and ultrafast dynamics in graphene

Calculated vs measured electronic temperature



Exp: Gierz, et al. Nature Materials, 12, 1119 (2013)



1. Electron phonon coupling self-energy

Bose / Fermi occupations

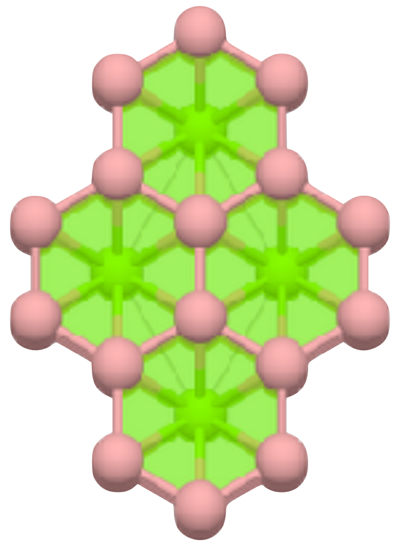
$$\Sigma^{\mathrm{e-ph}}_{n\mathbf{k}}(\omega) = \int \frac{d\mathbf{q}}{\Omega_{\mathrm{BZ}}} \sum_{m\nu} |g^{\mathrm{e-ph}}_{mn\nu}(\mathbf{k},\mathbf{q})|^2 \left[\frac{n_{\mathbf{q}\nu} + f_{m\mathbf{k}+\mathbf{q}}}{\omega - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \omega_{\mathbf{q}\nu} - i\eta} + \frac{n_{\mathbf{q}\nu} + 1 - f_{m\mathbf{k}+\mathbf{q}}}{\omega - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}\nu} - i\eta} \right]$$

2. Spectral function:

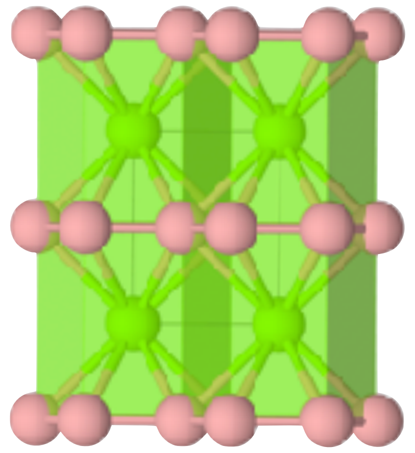
$$A_{n\mathbf{k}}(\omega, T) = \frac{1}{\pi} \frac{|\mathrm{Im}\,\Sigma^{\mathrm{e-ph}}_{n\mathbf{k}}(\omega)|}{[\omega - \varepsilon_{n\mathbf{k}} - \mathrm{Re}\,\Sigma^{\mathrm{e-ph}}_{n\mathbf{k}}(\omega)]^2 + [\mathrm{Im}\,\Sigma^{\mathrm{e-ph}}_{n\mathbf{k}}(\omega)]^2}$$

FC, D. Novko, C. Draxl, Phys. Rev. B 101 035128 (2020)

Transient phonon softening (Kohn anomaly) in MgB_2

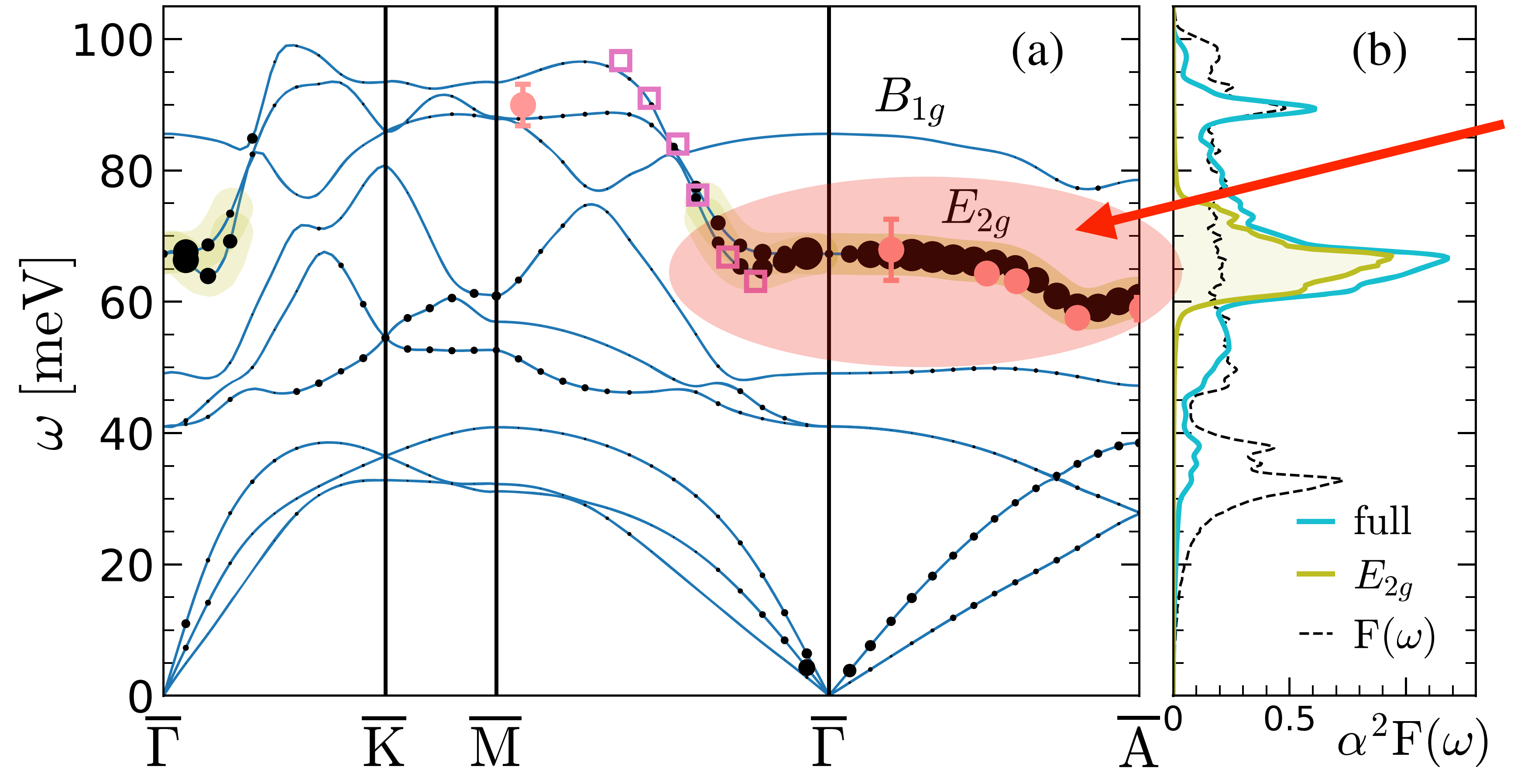


Facts about MgB_2
- Metal with hexagonal crystal structure
- BCS superconductor (T_c = 39 K)
- Highest known T_c for BCS superconductivity
- Strongly coupled E_{2g} modes



$$\Omega^2_{E_{2g}} = \omega^2_{E_{2g}} + 2\omega_{E_{2g}} \bar{\Pi}(\Omega_{E_{2g}}; \{T\}),$$

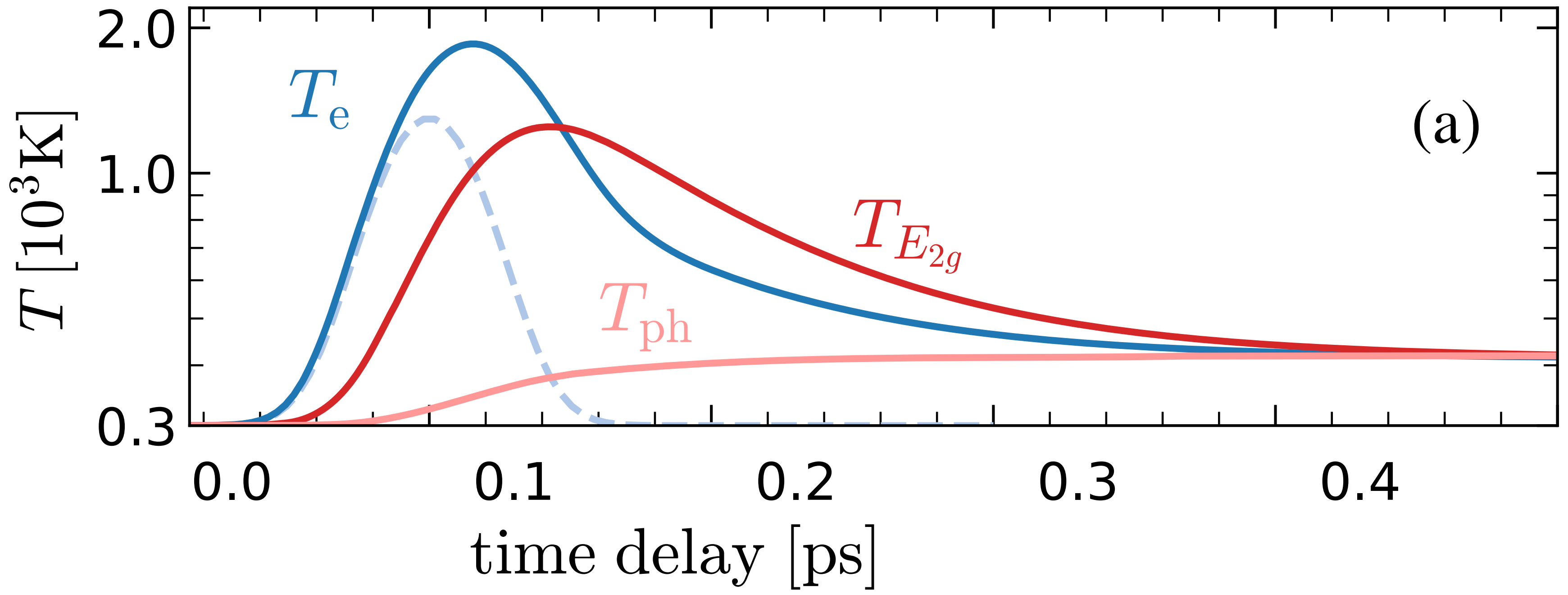
"dressed" phonon frequency — bare phonon frequency — phonon self-energy



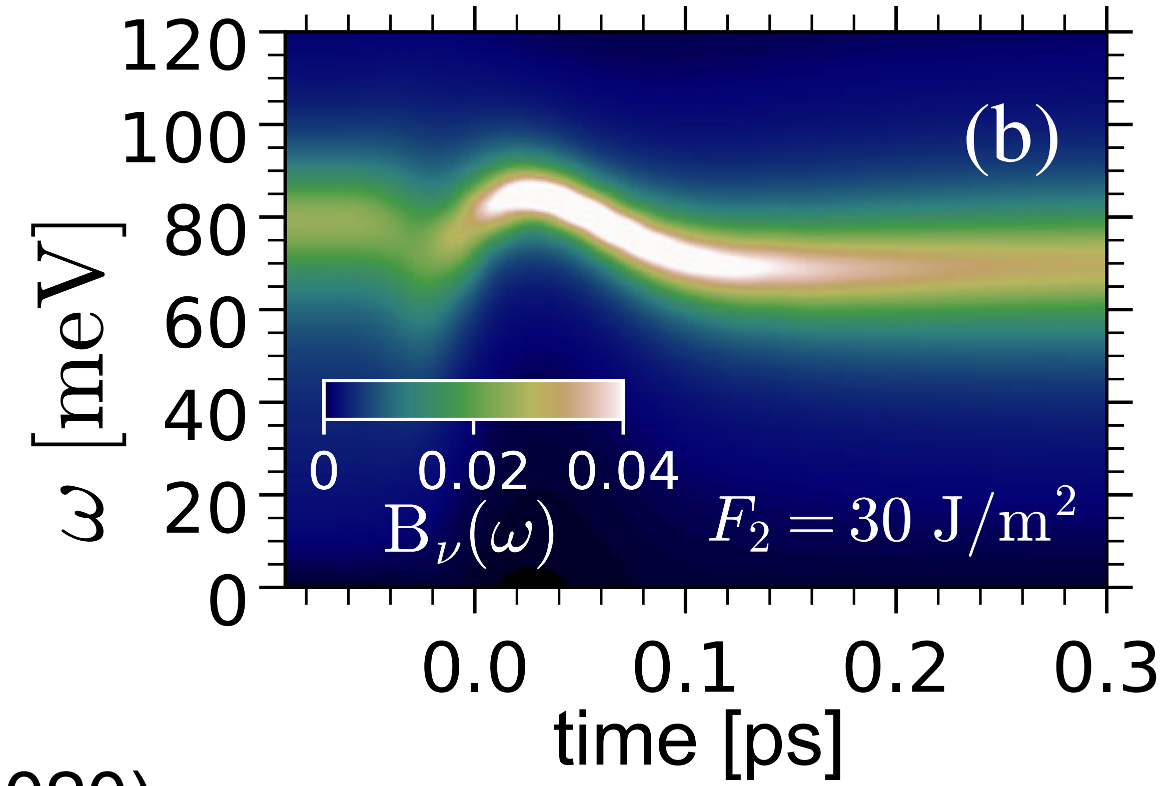
Kohn anomaly

Phonon spectral function

$$A_{\mathbf{q}\nu}(\omega) = \pi^{-1}\mathrm{Im}\left[\frac{2\omega_{\mathbf{q}\nu}}{\omega^2 - \omega^2_{\mathbf{q}\nu} - 2\omega_{\mathbf{q}\nu}\Pi^{\mathrm{NA}}_{\mathbf{q}\nu}(\omega)}\right]$$



Phonon spectral function @ Γ



Transient change of the E_{2g} phonon frequency due to the EPI: **"transient Kohn anomaly"**

D. Novko, FC, C. Draxl, E. Cappelluti, Phys. Rev. Lett. **124**, 077001 (2020)

Part 2

The time-dependent Boltzmann equation

Coupled electron-phonon dynamics beyond the non-thermal lattice models

Ab-initio description of ultrafast processes

Nonequilibrium Green's functions (& DMFT)
Time-dependent density-function theory
Time-dependent Boltzmann equation
Quantum Master equation
Molecular dynamics / Path integrals
Non-thermal lattice models

Check-list:

- ☑ Electron / phonon dynamics
- ☑ Electron-phonon coupling
- ☑ Full momentum resolution

Time-dependent Boltzmann equation (TDBE)

distribution function

collision integral

$$\frac{\partial f}{\partial t} = \Gamma_{\text{collisions}} + \text{other terms (fields, etc.)}$$

(In a gas:)

Equilibrium is re-established via collisions

Books:
Ziman, Electrons and phonons, Oxford Universisty Press (1960)
Hang, Jauho, Quantum Kinetics in Transport and Optics of Semiconductors, Springer (1996)
Bonitz, Quantum Kinetic Theory (1998)

Charge and thermal Transport:
Poncé, Li, Reichard, Giustino, Rep. Prog. Phys. 83, 036501 (2019)
Li, Carrete, Katcho, Mingo, Comp. Phys. Comm.185, 1747 (2014)
Mizokami, Togo, Tanaka Phys. Rev. B 97, 224306, (2018)
Chaput, Phys. Rev. Lett 110, 265506 (2013)
Togo, Chaput, Tanaka, Phys. Rev. B 91, 094306 (2015)

Ultrafast dynamics:
Sadasivam, Chan, Darancet, Phys. Rev. Lett. 119, 136602 (2017)
Bernardi, Eur. Phys. J. B 89, 239 (2016)
Jhalani, Zhou, Bernardi, Nano Letters 17, 5012 (2017)
FC, J. Phys. Chem. Lett. 12, 1274 (2021)

Time-dependent Boltzmann equation

Key assumption: Electronic and vibrational excitations are described via the corresponding distribution functions

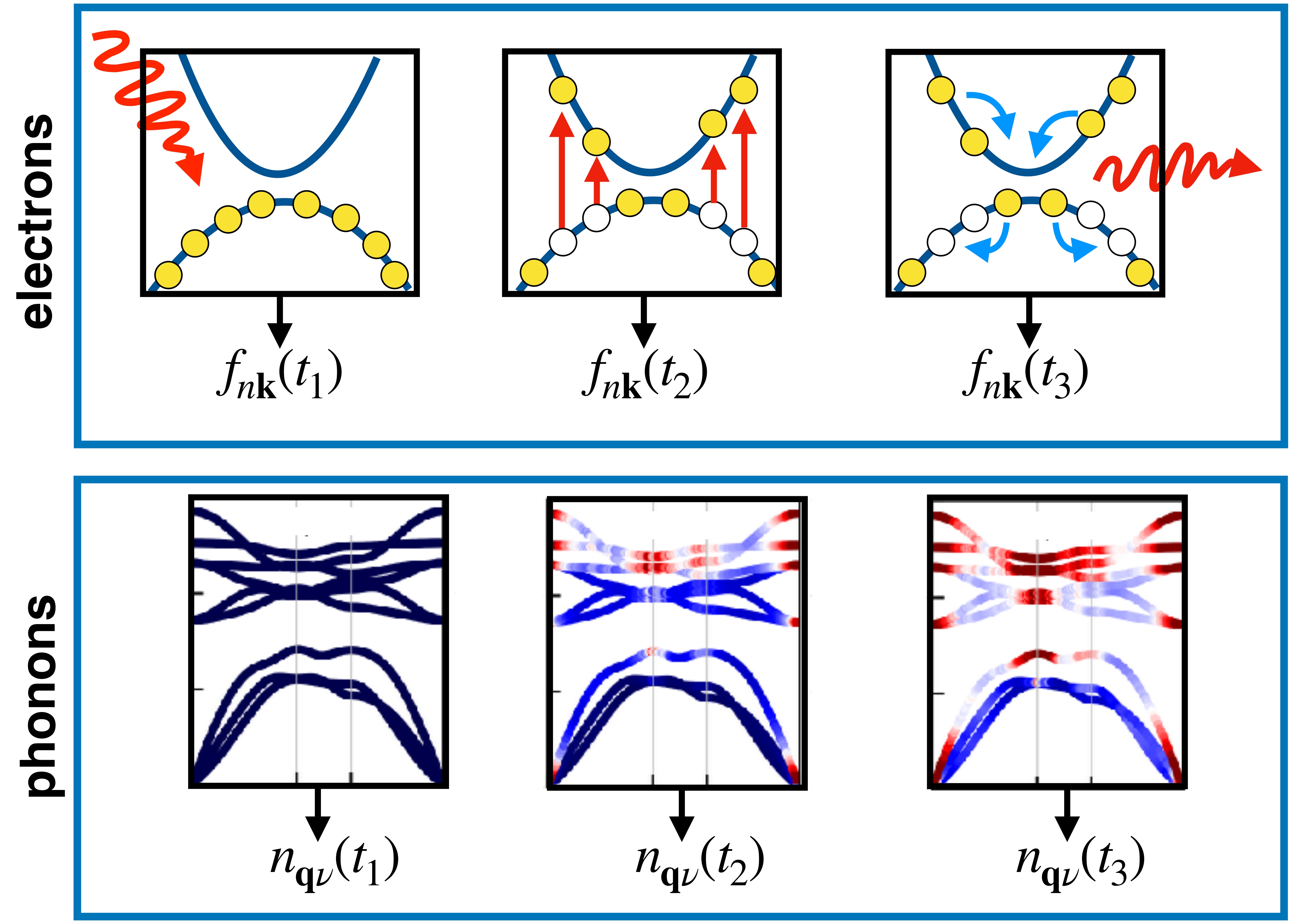
Thermal equilibrium

Bose-Einstein statistics: $n^{\rm eq}_{\mathbf{q}\nu} = [e^{\hbar\omega_{\mathbf{q}\nu}/k_{\rm B}T} - 1]^{-1}$

Fermi-Dirac statistics: $f^{\rm eq}_{n\mathbf{k}} = [e^{(\varepsilon_{n\mathbf{k}}-\mu)/k_{\rm B}T} + 1]^{-1}$

Out of equilibrium

$n_{\mathbf{q}\nu} \neq n^{\rm eq}_{\mathbf{q}\nu}$ **and/or** $f_{n\mathbf{k}} \neq f^{\rm eq}_{n\mathbf{k}}$



Rate of change of $n_{\mathbf{q}\nu}$ and $f_{n\mathbf{k}}$ from the TDBE

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I^{\rm e-ph}_{n\mathbf{k}}[f,n] + I^{\rm light}_{n\mathbf{k}}[f] + I^{\rm e-e}_{n\mathbf{k}}[f]$$

$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I^{\rm e-ph}_{\mathbf{q}\nu}[f,n] + I^{\rm ph-ph}_{\mathbf{q}\nu}[n]$$

- solved via Euler or Runge-Kutta algorithms.
- scattering rates are obtained ab initio

$I[f,n]$ collision integral

Review: F. Caruso, D. Novko, Adv. Phys. X **7**, 2095925 (2022)

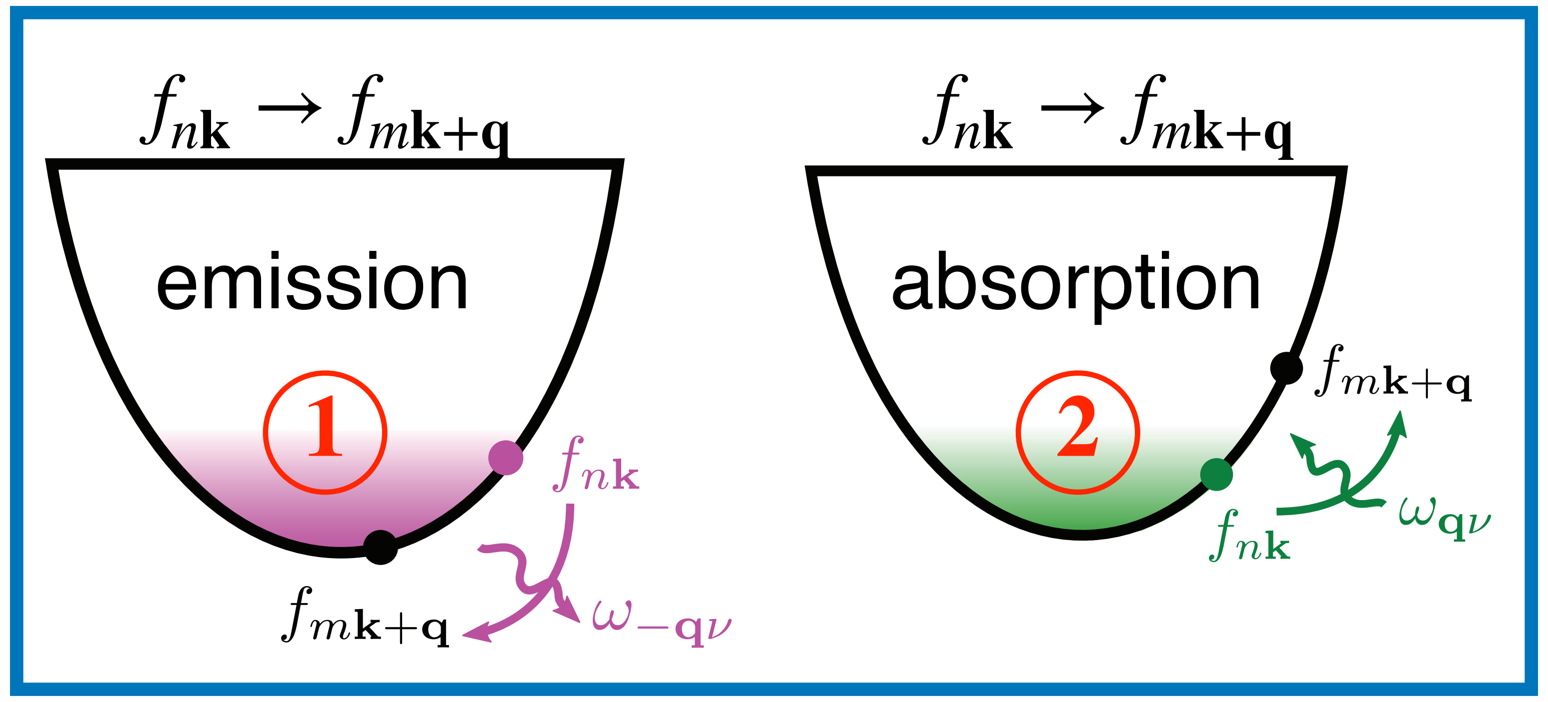
Collision integrals due to the electron-phonon interactions

Electron-phonon interaction $\hat{H}_{\text{eph}} = N_p^{-\frac{1}{2}} \sum_{mn\mathbf{k}} \sum_{\mathbf{q}\nu} g^{\nu}_{mn}(\mathbf{k},\mathbf{q}) \hat{c}^{\dagger}_{m\mathbf{k}+\mathbf{q}} \hat{c}_{n\mathbf{k}} [\hat{a}_{\mathbf{q}\nu} + \hat{a}^{\dagger}_{-\mathbf{q}\nu}]$

Electron-phonon coupling matrix elements

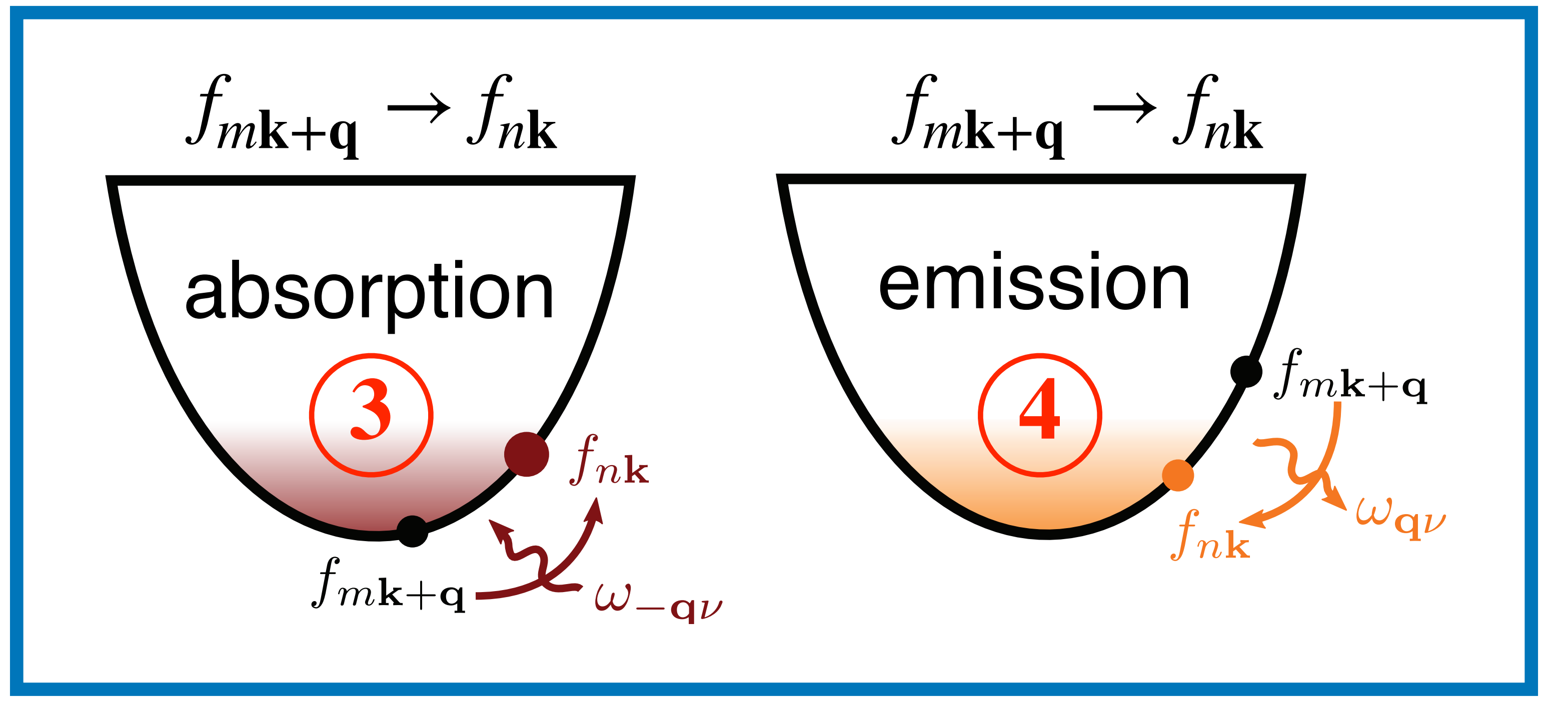
$$g^{\nu}_{nm}(\mathbf{k},\mathbf{q}) = \langle \psi_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\nu} V_{\text{KS}} | \psi_{n\mathbf{k}} \rangle$$

final electronic state — phonon perturbation — initial electronic state



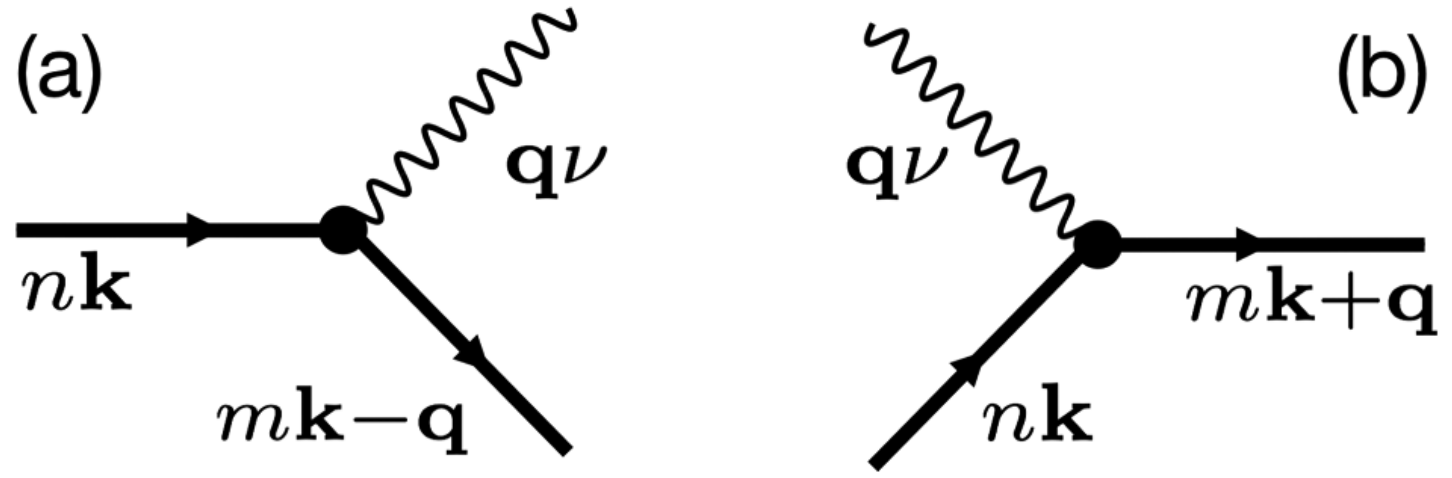
scattering out of $f_{n\mathbf{k}}$

rate of scattering out: $\Gamma^{\text{out}}_{n\mathbf{k}}$



scattering into $f_{n\mathbf{k}}$

rate of scattering out: $\Gamma^{\text{in}}_{n\mathbf{k}}$



phonon emission **absorption**

The total scattering rate due to the electron-phonon coupling: $\Gamma^{\text{eph}}_{n\mathbf{k}} = \Gamma^{\text{out}}_{n\mathbf{k}} + \Gamma^{\text{in}}_{n\mathbf{k}}$

At thermal equilibrium: $\Gamma^{\text{out}}_{n\mathbf{k}} = -\Gamma^{\text{in}}_{n\mathbf{k}} \rightarrow \Gamma^{\text{eph}}_{n\mathbf{k}} = 0$

Collision integrals from Fermi-golden rule $\Gamma_{i\to f} = \frac{2\pi}{\hbar} |\langle f | \hat{V} | i \rangle|^2 \delta(E^{\text{tot}}_f - E^{\text{tot}}_i)$

Collision integrals due to the electron-phonon interactions

Fermi-golden rule: $$\Gamma_{i\to f} = \frac{2\pi}{\hbar}|\langle f|\hat{H}_{eph}|i\rangle|^2\delta(E_f^{\text{tot}} - E_i^{\text{tot}})$$

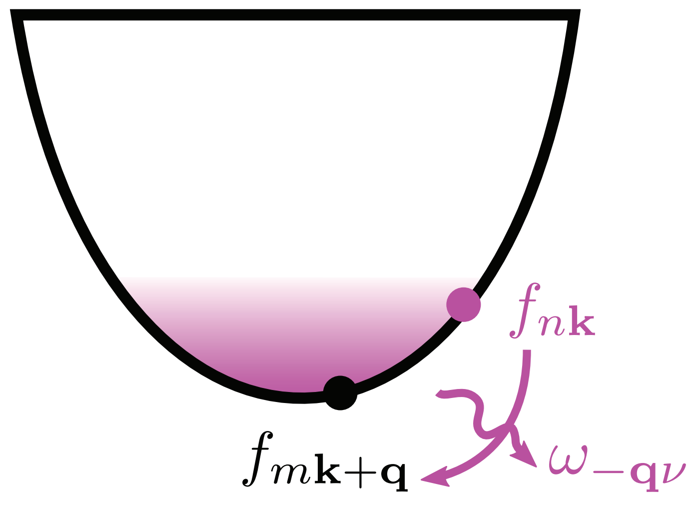
$$|i\rangle = |\Psi_i\rangle|\chi_i\rangle$$

① matrix elements: $$\langle f|\hat{H}_{\text{eph}}|i\rangle = N_p^{-\frac{1}{2}}\sum_{nm\nu}\sum_{\mathbf{kq}} g_{mn}^{\nu}(\mathbf{k},\mathbf{q})\langle\Psi_f|\hat{c}^{\dagger}_{m\mathbf{k}+\mathbf{q}}\hat{c}_{n\mathbf{k}}|\Psi_i\rangle\langle\chi_f|\hat{a}_{\mathbf{q}\nu} + \hat{a}^{\dagger}_{-\mathbf{q}\nu}|\chi_i\rangle$$

② energy difference: $$E_i^{\text{tot}} - E_f^{\text{tot}} = \varepsilon_{n\mathbf{k}} + \hbar\omega_{\mathbf{q}\nu} - \varepsilon_{m\mathbf{k}+\mathbf{q}}$$

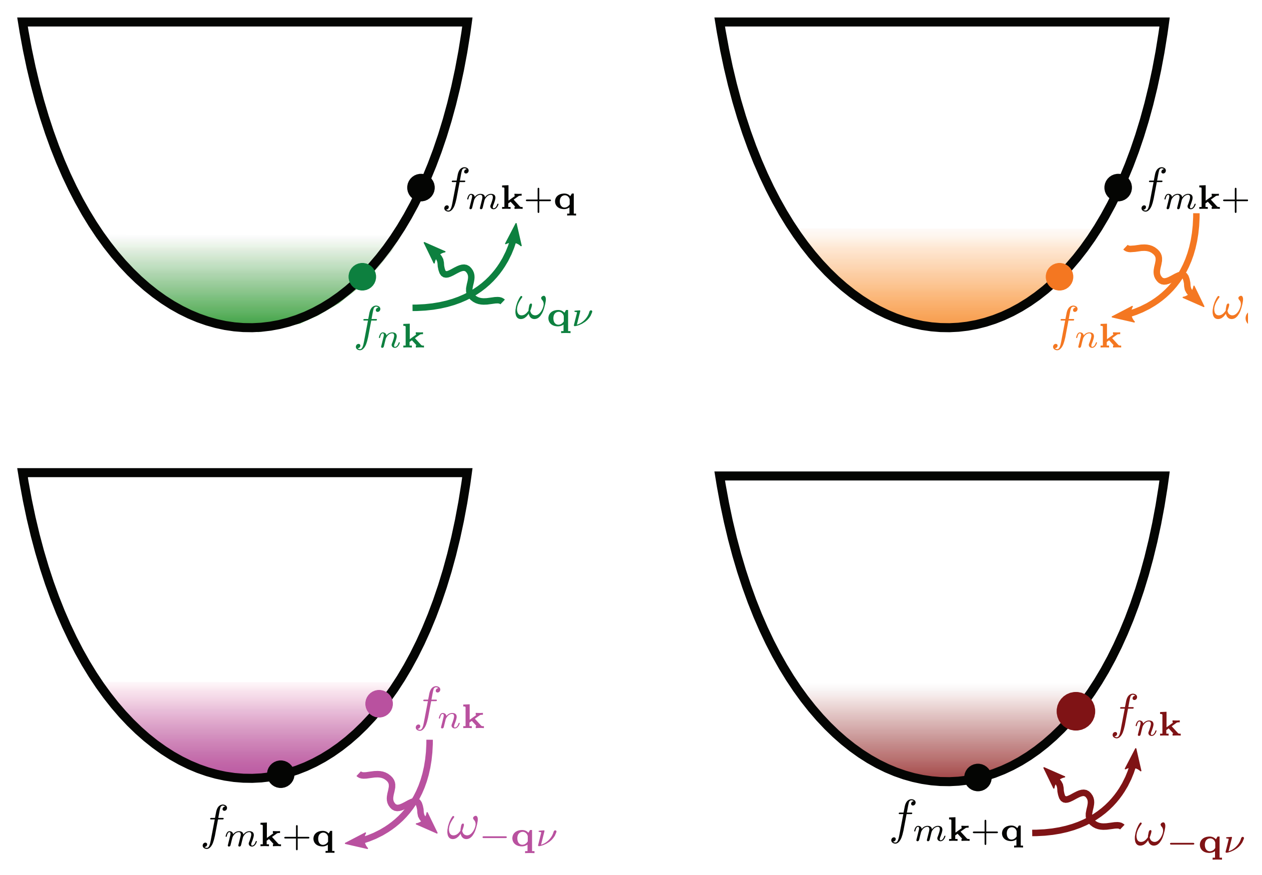
Scattering from $\psi_{n\mathbf{k}}$ to $\psi_{m\mathbf{k}+\mathbf{q}}$ via emission of a phonon $\omega_{\mathbf{q}\nu}$

transition rate from Fermi-Golden rule: $$\Gamma_{n\mathbf{k}\to m\mathbf{k}+\mathbf{q}} = \frac{2\pi}{\hbar}|g_{nm}^{\nu}(\mathbf{k},\mathbf{q})|^2 f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu})$$



Collision integral due to the EPI

$$\Gamma_{n\mathbf{k}}^{\text{e-ph}} = \frac{2\pi}{\hbar}\sum_{m\mathbf{q}\nu}|g_{nm}^{\nu}(\mathbf{k},\mathbf{q})|^2\Big[-f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu})$$
$$-f_{n\mathbf{k}}(1-f_{m\mathbf{k}+\mathbf{q}})\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu})$$
$$+(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\nu})$$
$$+(1-f_{n\mathbf{k}})f_{m\mathbf{k}+\mathbf{q}}\delta(\varepsilon_{n\mathbf{k}} - \varepsilon_{m\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\nu})\Big]$$



TDBE:

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = \Gamma_{n\mathbf{k}}^{\text{e-ph}}[f,n] + \Gamma_{n\mathbf{k}}^{\text{light}}[f] + \Gamma_{n\mathbf{k}}^{\text{e-e}}[f]$$

$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = \Gamma_{\mathbf{q}\nu}^{\text{e-ph}}[f,n] + \Gamma_{\mathbf{q}\nu}^{\text{ph-ph}}[n]$$

Numerical implementation

① **Real time propagation (Heun or Runge Kutta algorithm)** $\frac{\partial f}{\partial t} = \Gamma_{\text{collisions}}$ Euler: $f(t + \Delta t) = f(t) + \Gamma_{\text{collisions}} \Delta t$

② **Electron and phonon energies ($\varepsilon_{n\mathbf{k}}$ and $\hbar\omega_{\mathbf{q}\nu}$) from DFT and DFPT.**

- Spin-orbit coupling effects included
- Norm-conserving Vanderbiit (ONCV) pseudopotential
- Band structure are fixed, $\varepsilon_{n\mathbf{k}}$ and $\omega_{\mathbf{q}\nu}$ are time-independent (weakly perturbed system)

QUANTUMESPRESSO

③ **Ultra-dense k- and q-point meshes (maximally-localized Wannier functions)**

- in 2D materials $120 \times 120 \times 1$ up to $200 \times 200 \times 1$

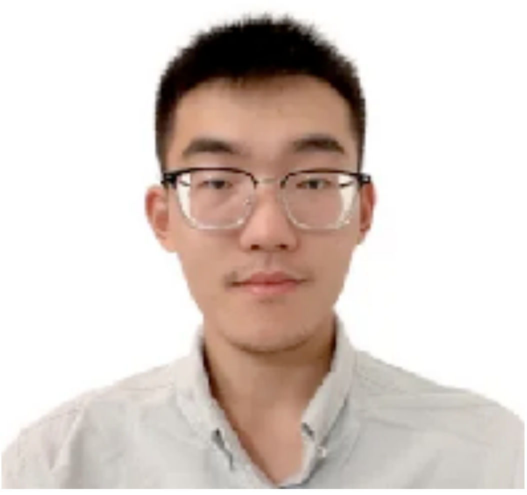
WANNIER90

④ **Electron-phonon and phonon-phonon coupling matrix elements from first principles**

EPW

BTE

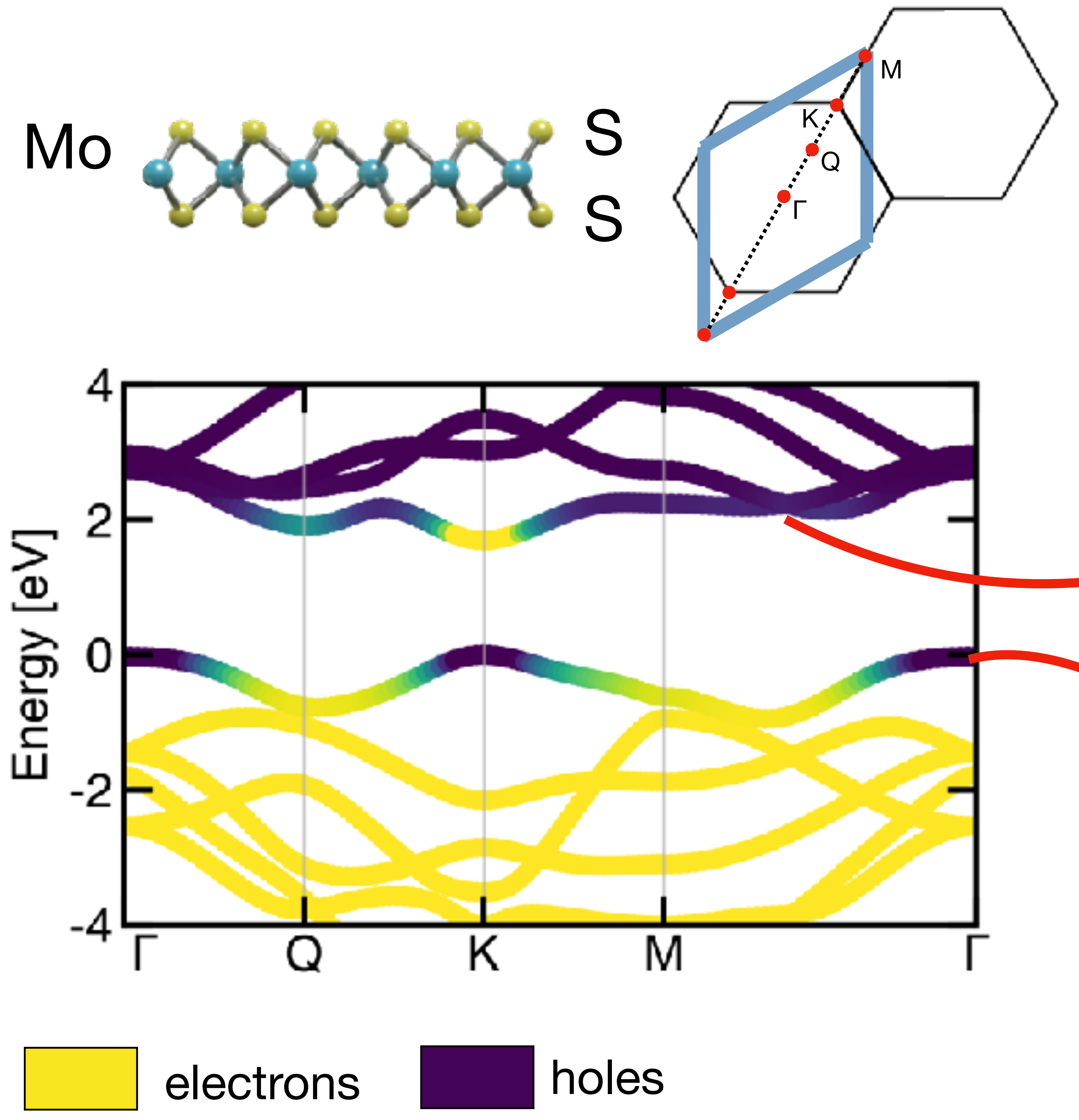
⑤ **Implemented in EPW by Yiming Pan (check out his poster!)**

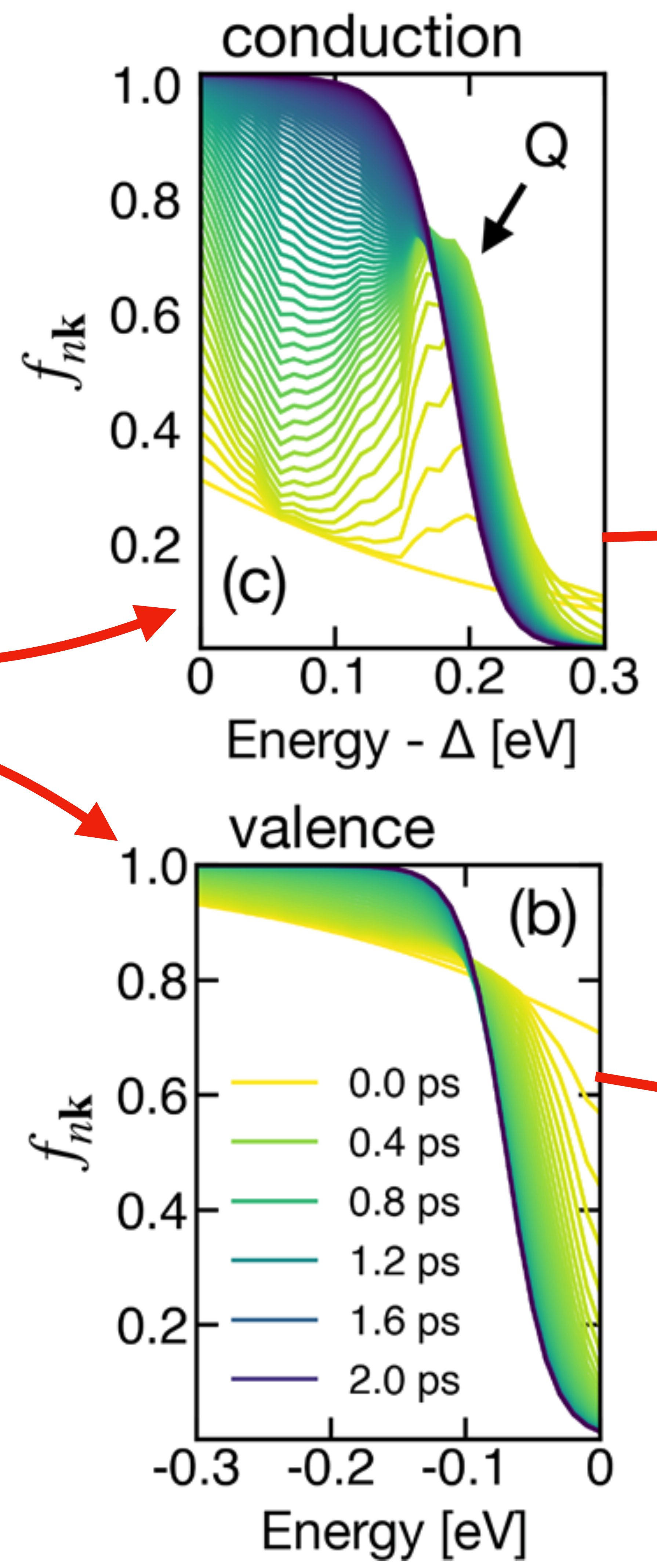


Part 3

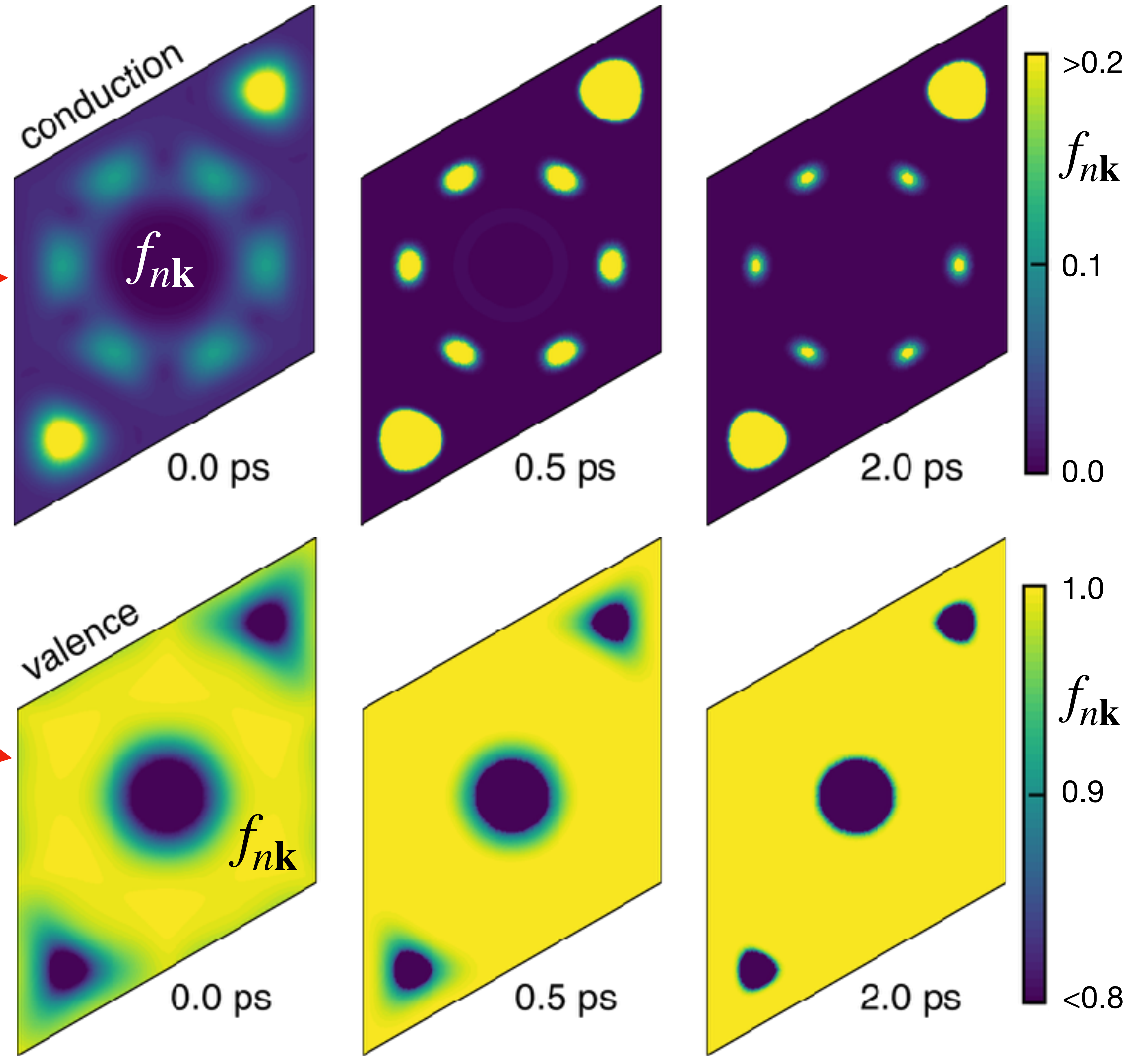
Ultrafast phonon dynamics 2D and van-der-Waals materials

Nonequilibrium <u>ELECTRON</u> dynamics in monolayer MoS_2





Electron and hole dynamics with momentum resolution



Estimated timescales for electron relaxation: $< 2\,\mathrm{ps}$

Experiments from (*) (fs-electron diffraction): $1.7 \pm 0.3\,\mathrm{ps}$

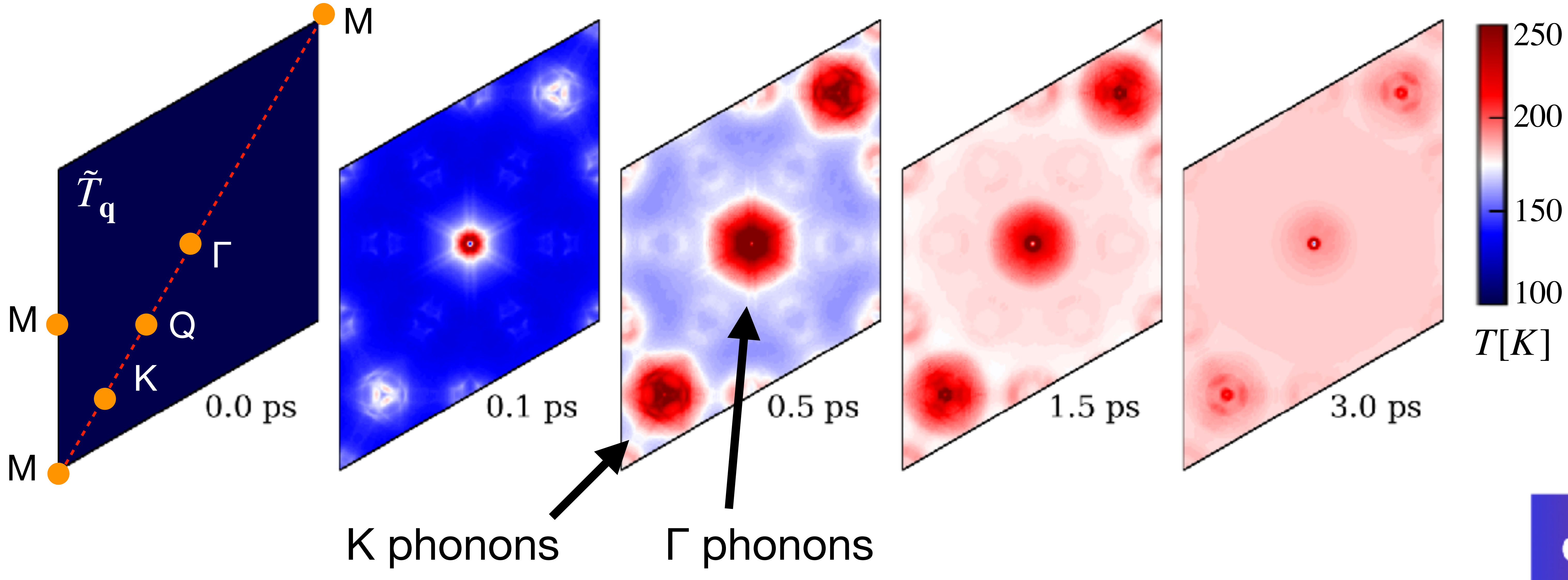
$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I^{\mathrm{e-ph}}_{n\mathbf{k}}[f, n]$$

(*) Mannebach et al., Nano Lett. 15, 6889 (2015)

F. Caruso, J. Phys. Chem. Lett. **12**, 1274 (2021)

Nonequilibrium PHONON dynamics in monolayer MoS_2

Phonon TEMPERATURE in the Brillouin zone

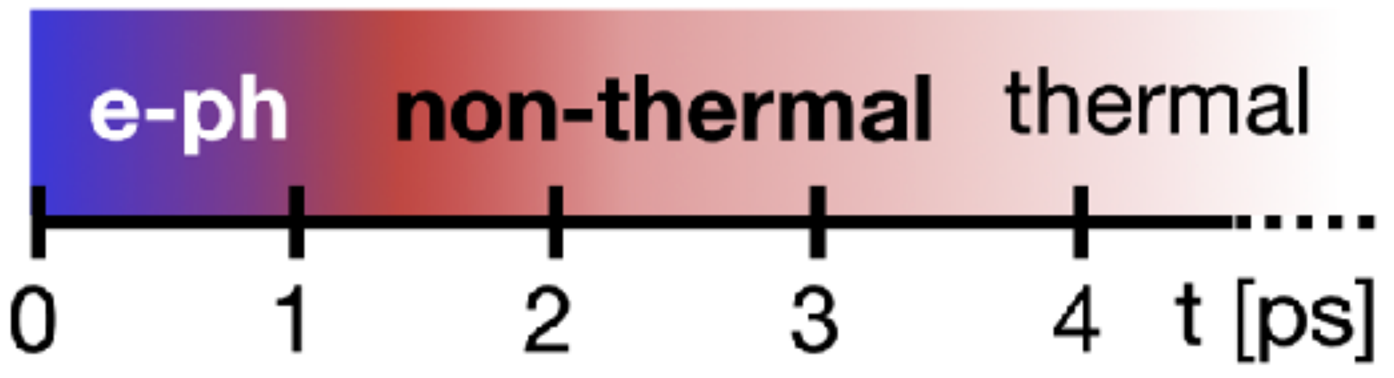


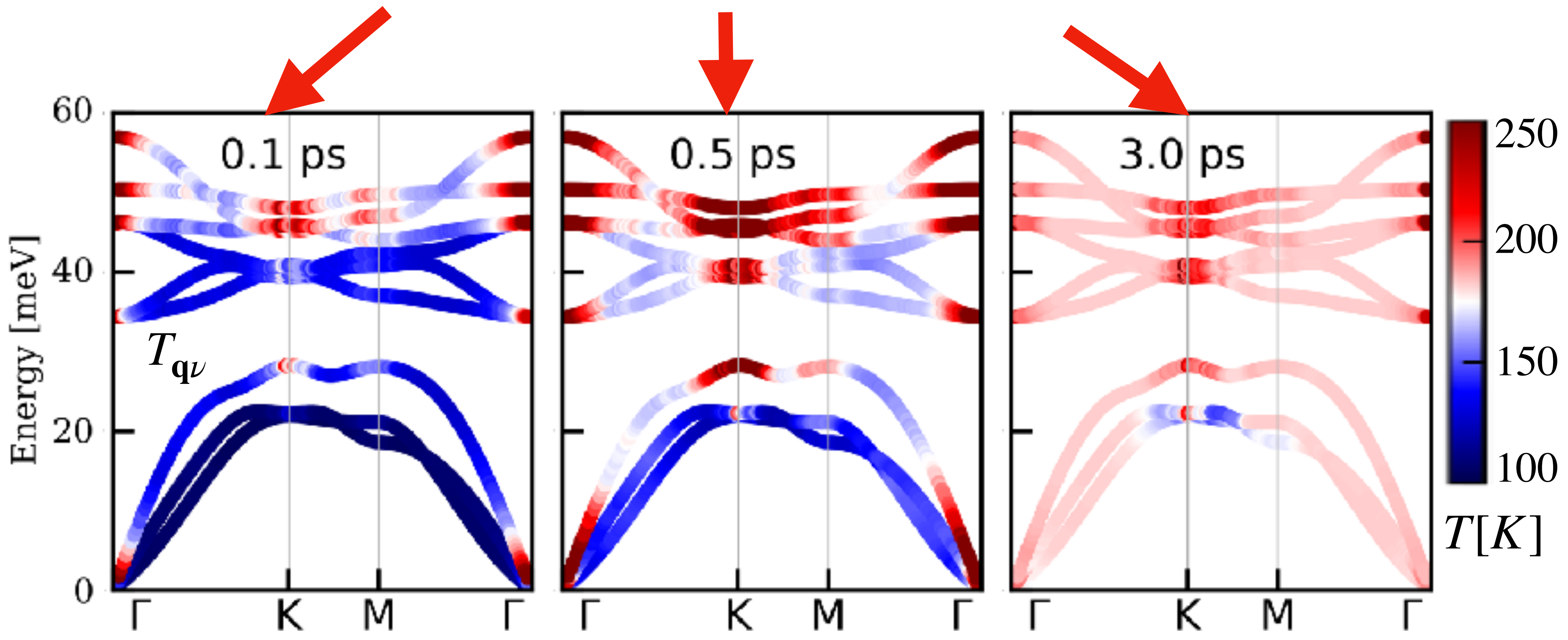
Phonon temperature

$$T_{\mathbf{q}\nu} = \hbar\omega_{\mathbf{q}\nu}[k_B \ln(1 + n_{\mathbf{q}\nu})]^{-1}$$

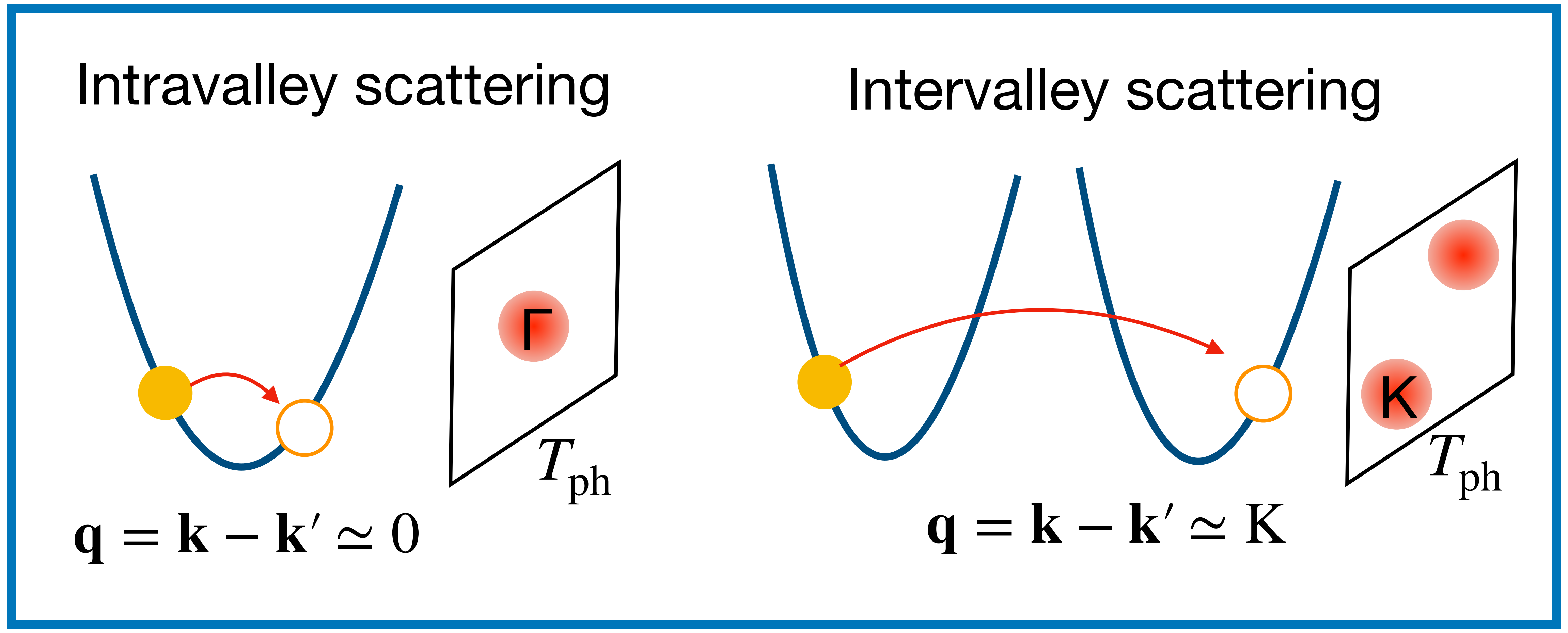
(averaged for all phonon polarizations)

$$T_{\mathbf{q}\nu} \neq \text{const} \longrightarrow n_{\mathbf{q}\nu} \neq n^{\text{eq}}_{\mathbf{q}\nu}$$





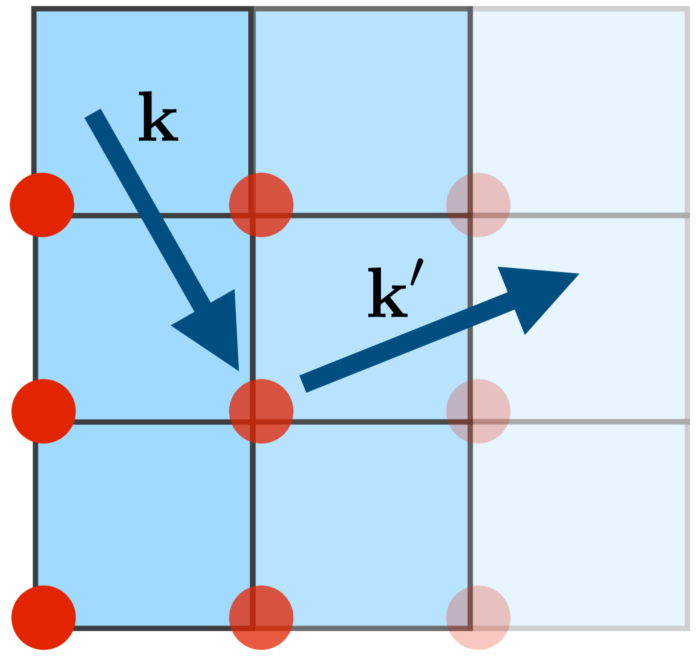
Momentum selectivity in the phonon emission:



F. Caruso, J. Phys. Chem. Lett. **12**, 1274 (2021)

A crash course in the theory diffraction

Static lattice (1 atom per cell)



Bragg's law:

$$A(\mathbf{q}) = \sum_{p}^{N_p} f_0 \exp\left[i\mathbf{q}\cdot\mathbf{R}_p\right]$$

amplitude

Scattering cross section

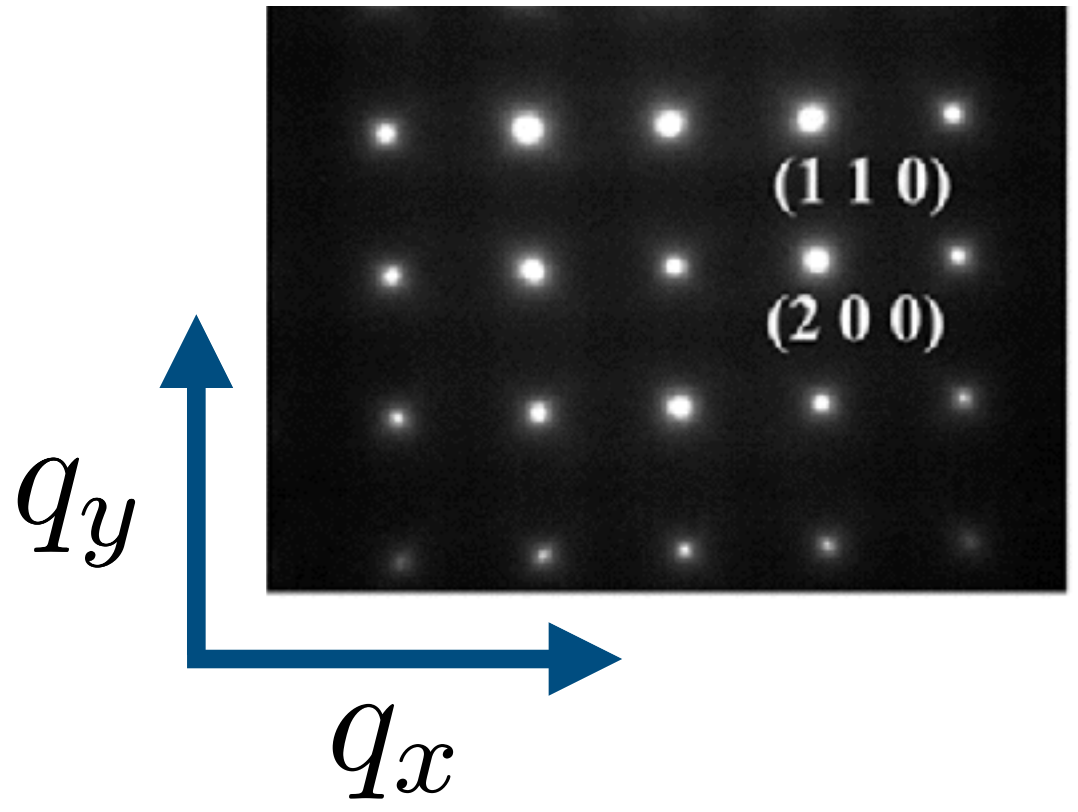
Lattice vector

Scattering intensity for a perfect lattice:

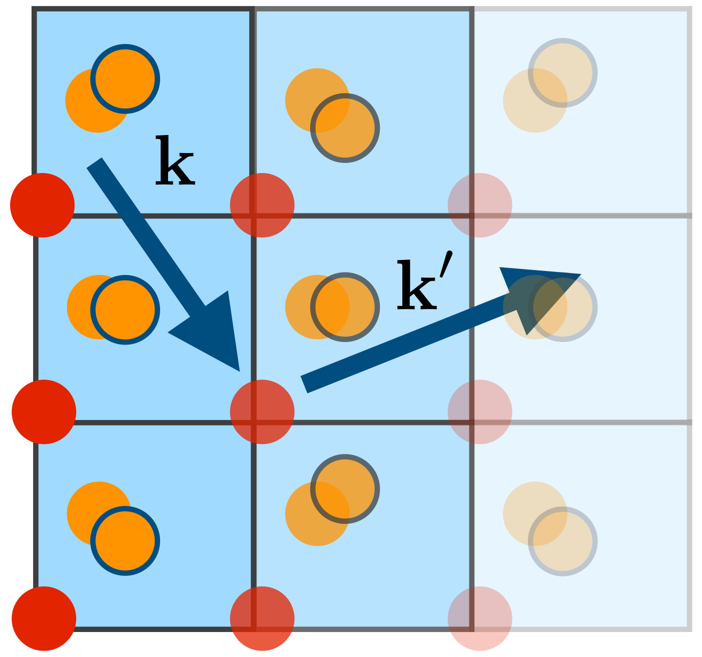
$$I(\mathbf{q}) = |A(\mathbf{q})|^2 \simeq \delta_{\mathbf{q},\mathbf{G}}$$

Reciprocal lattice vector

example: Cubic lattice



Vibrating lattice (>1 atom per cell)



$$I(\mathbf{Q},\tau) = I_0(\mathbf{Q},\tau) + I_1(\mathbf{Q},\tau) + \cdots$$

Zero-phonon

One-phonon

Zero-phonon term:

$$\langle I_0(\mathbf{S})\rangle_T \quad = \quad N_p^2 |f_0|^2 \exp(-2W_T)\delta_{\mathbf{S},\mathbf{G}}$$

One-phonon term:

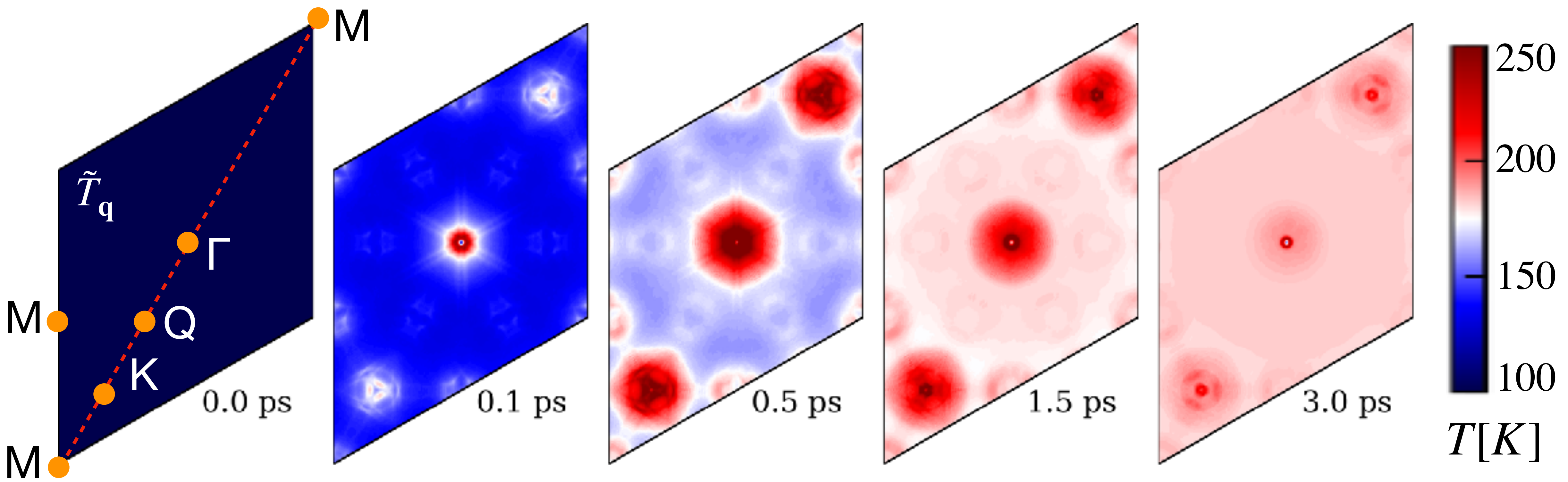
$$\langle I_1(\mathbf{S},E)\rangle_T = |f_0|^2\exp(-2W_T)\frac{\hbar^2 N_p}{2M_\kappa}\sum_{\mathbf{q}\nu}\left[\sum_{\alpha\alpha'} S_\alpha S_{\alpha'} e^{\nu}_{\kappa\alpha}(\mathbf{q}) e^{\nu *}_{\kappa\alpha'}(\mathbf{q})\right]\frac{1}{\hbar\omega_{\mathbf{q}\nu}} \times \left[\delta(\mathbf{S}+\mathbf{q})n_{\mathbf{q}\nu,T}\delta(E+\hbar\omega_{\mathbf{q}\nu}) + \delta(\mathbf{S}-\mathbf{q})(n_{\mathbf{q}\nu,T}+1)\delta(E-\hbar\omega_{\mathbf{q}\nu})\right]. \quad (16)$$

phonon occupation (available from the TDBE)

G.L. Squires, Introduction to the Theory of Thermal Neutron Scattering (Cambridge University Press)

Recipe for ab-initio simulation of UEDS intensities

Step 1: Obtain the non-equilibrium phonon population from the TDBE



Step 2: Evaluate the structure factor for the instantaneous phonon population

$$I(\mathbf{Q},\tau) = I_0(\mathbf{Q},\tau) + I_1(\mathbf{Q},\tau) + \cdots$$

Zero-phonon   One-phonon

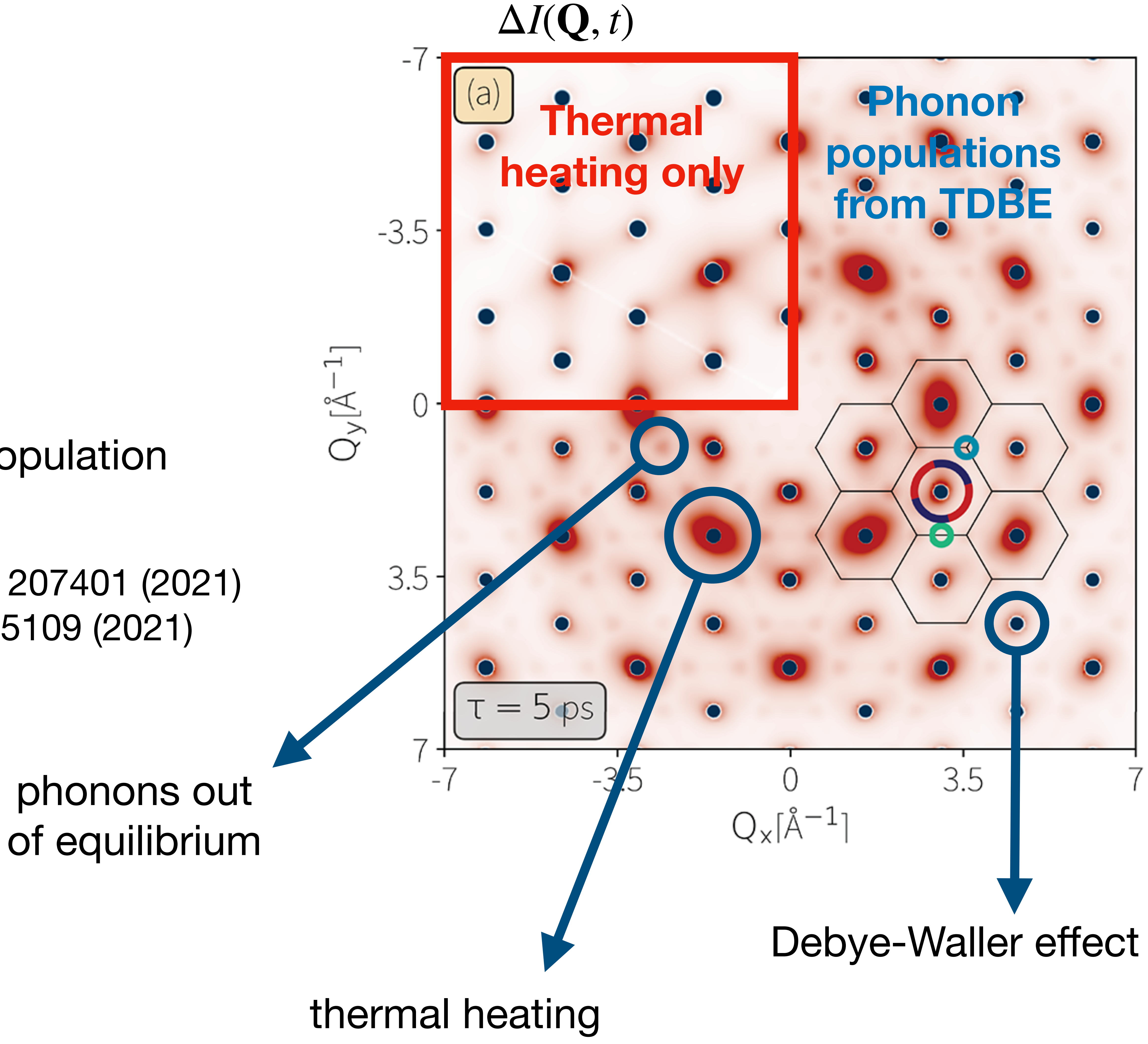
M. Zacharias, et al.,
Phys. Rev. Lett. **127**, 207401 (2021)
Phys. Rev. B **104**, 205109 (2021)

Step 3: Subtract the initial structure factor

Intensity difference: $$\Delta I(\mathbf{Q},t) = I(\mathbf{Q},t) - I(\mathbf{Q},t=0)$$

T. Britt, F. Caruso et al,, Nano Lett. **22**, 4718 (2022)

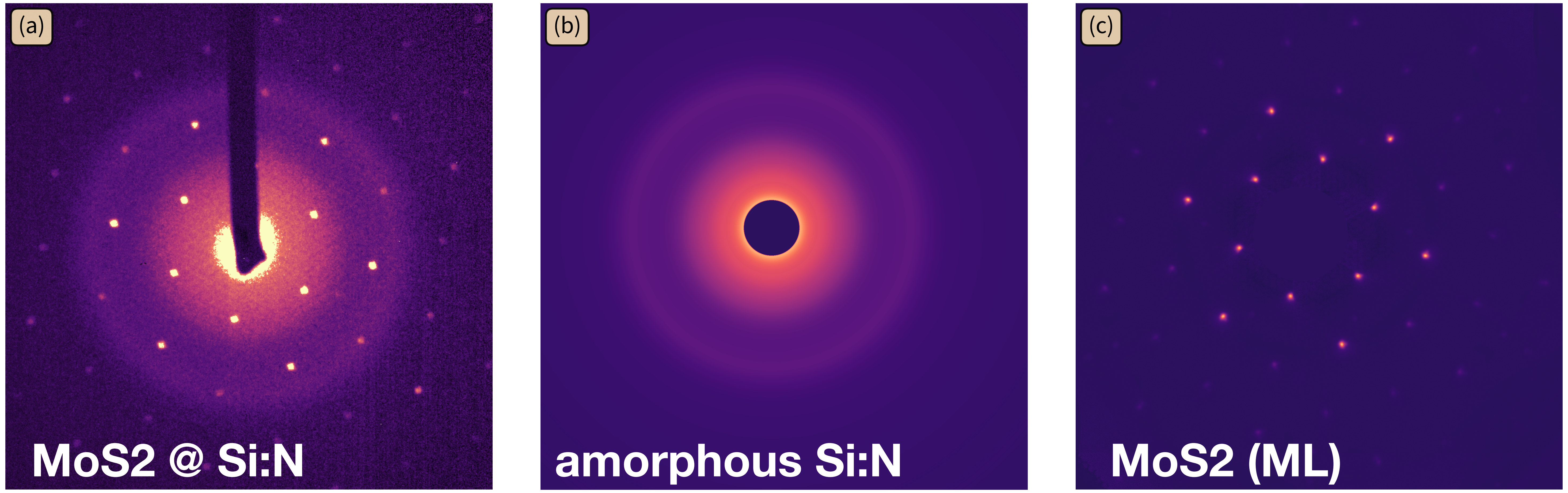
Simulated UEDS for monolayer MoS_2



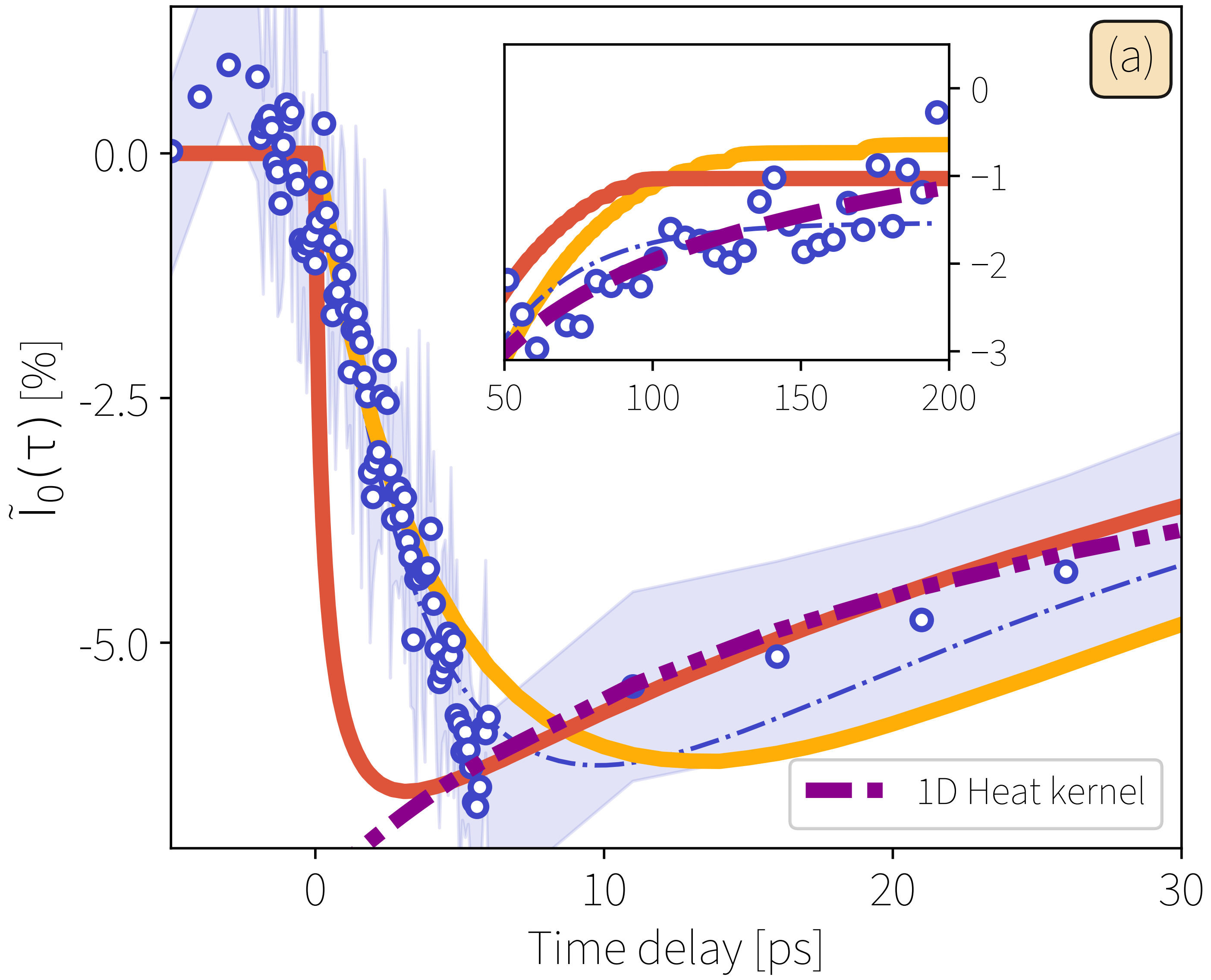
Direct view of phonon dynamics in MoS_2 monolayer

Experiments

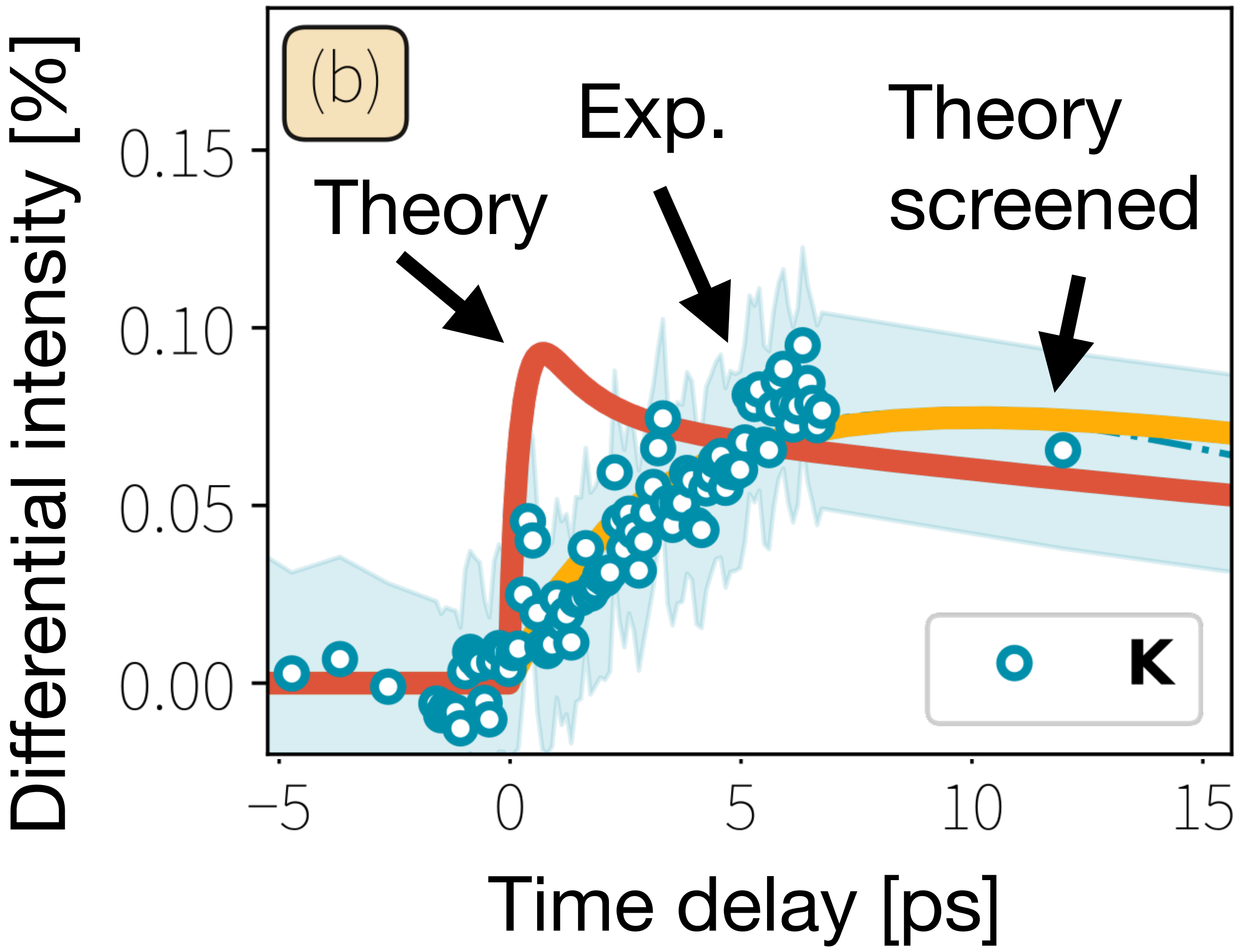
Tristan Britt Bradley Siwick
(McGill University)



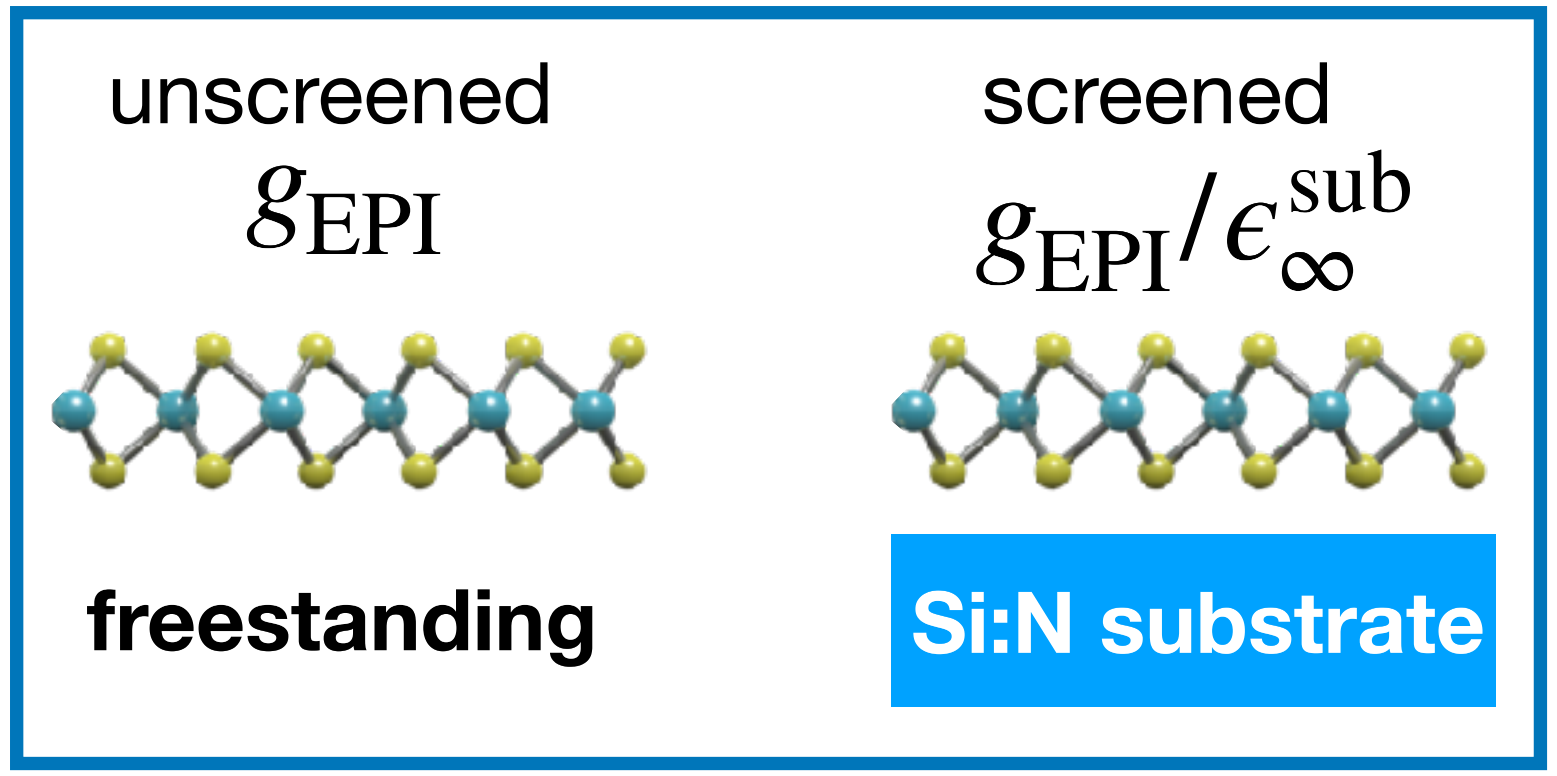
Bragg peak dynamics (Debye Waller effect)



Diffuse scattering at K

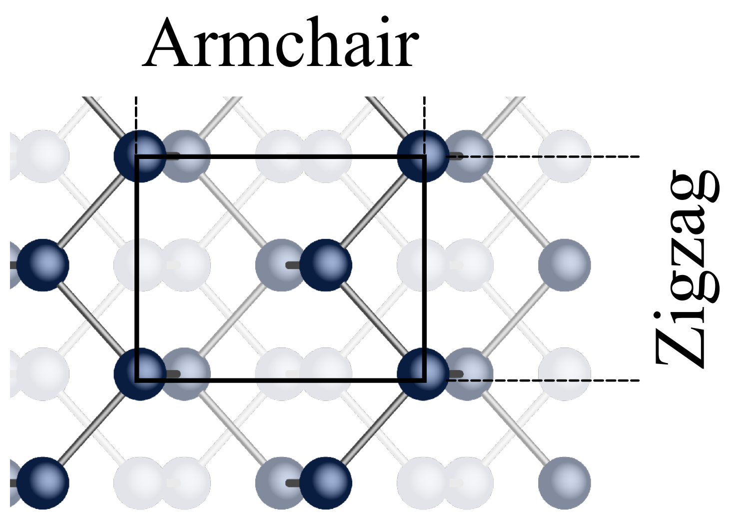


Measured energy transfer to the lattice: ~7 times slower than theory.

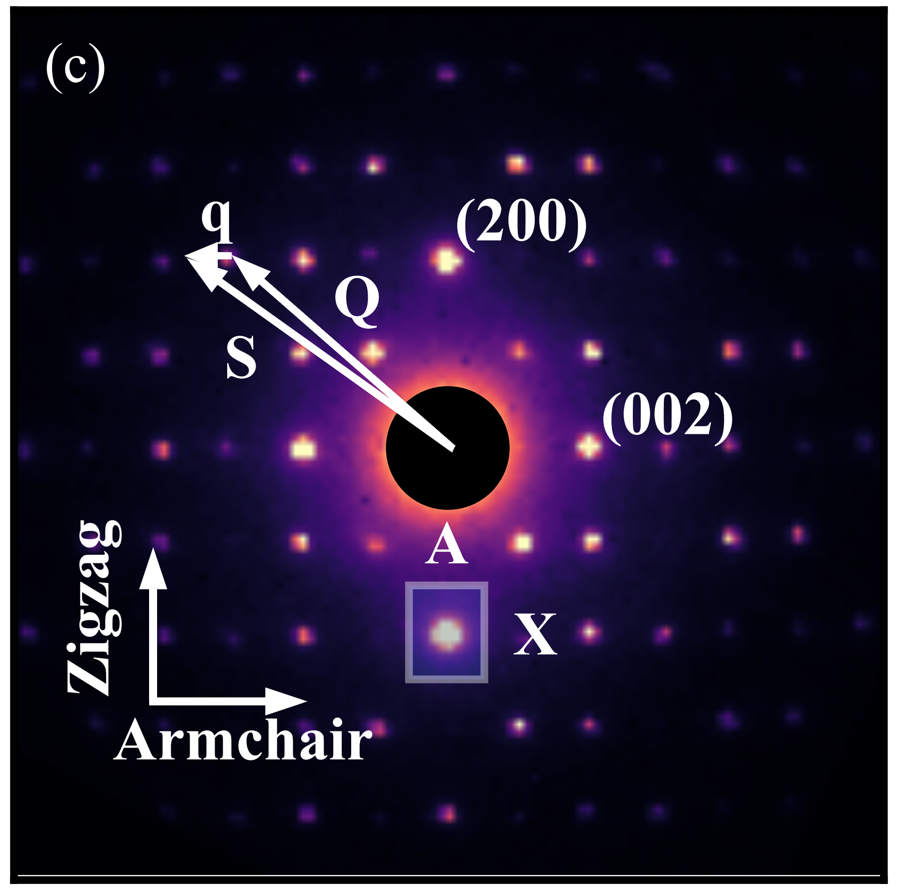


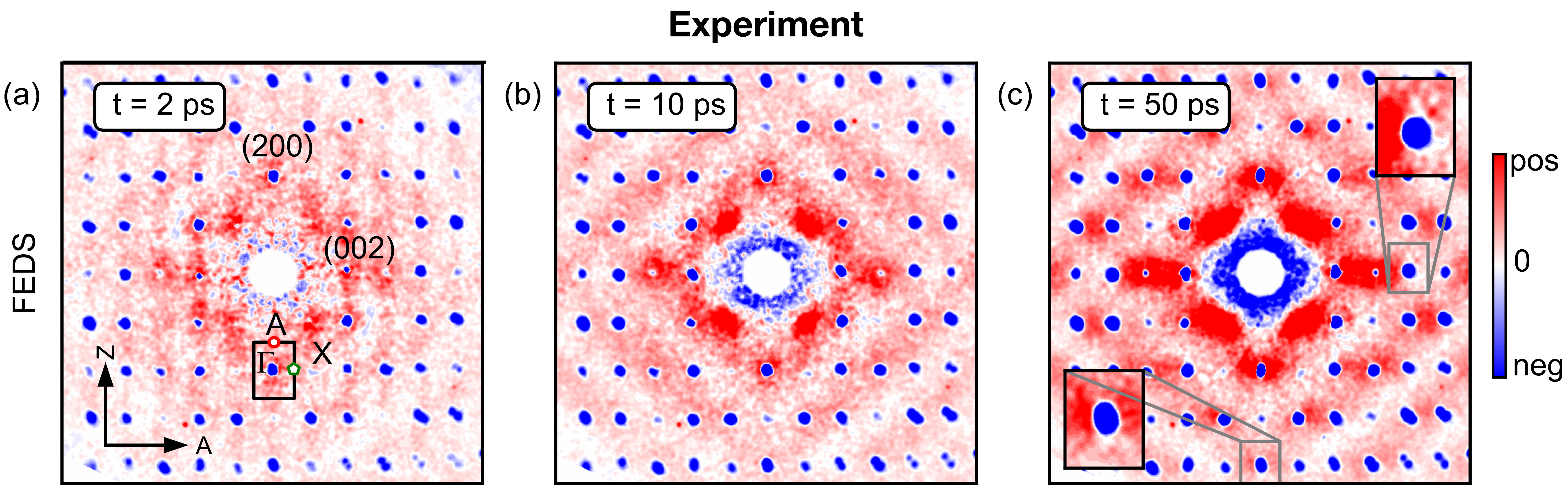
T. Britt, (...) F. Caruso, XYZ, B. Siwick, Nano Lett. **22**, 4718 (2022)

Ultrafast electron diffuse scattering: black Phosphorus



Black phosphorus





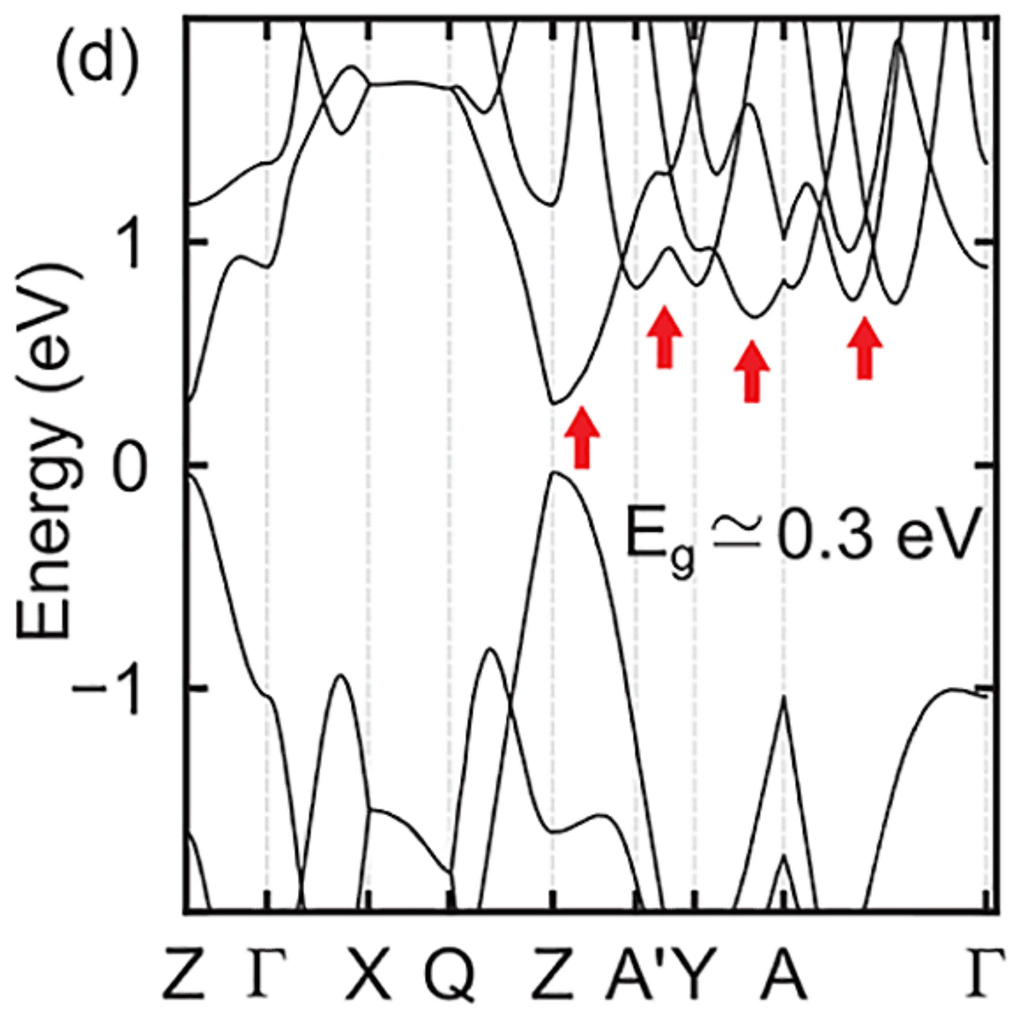
Experiments: FHI Berlin

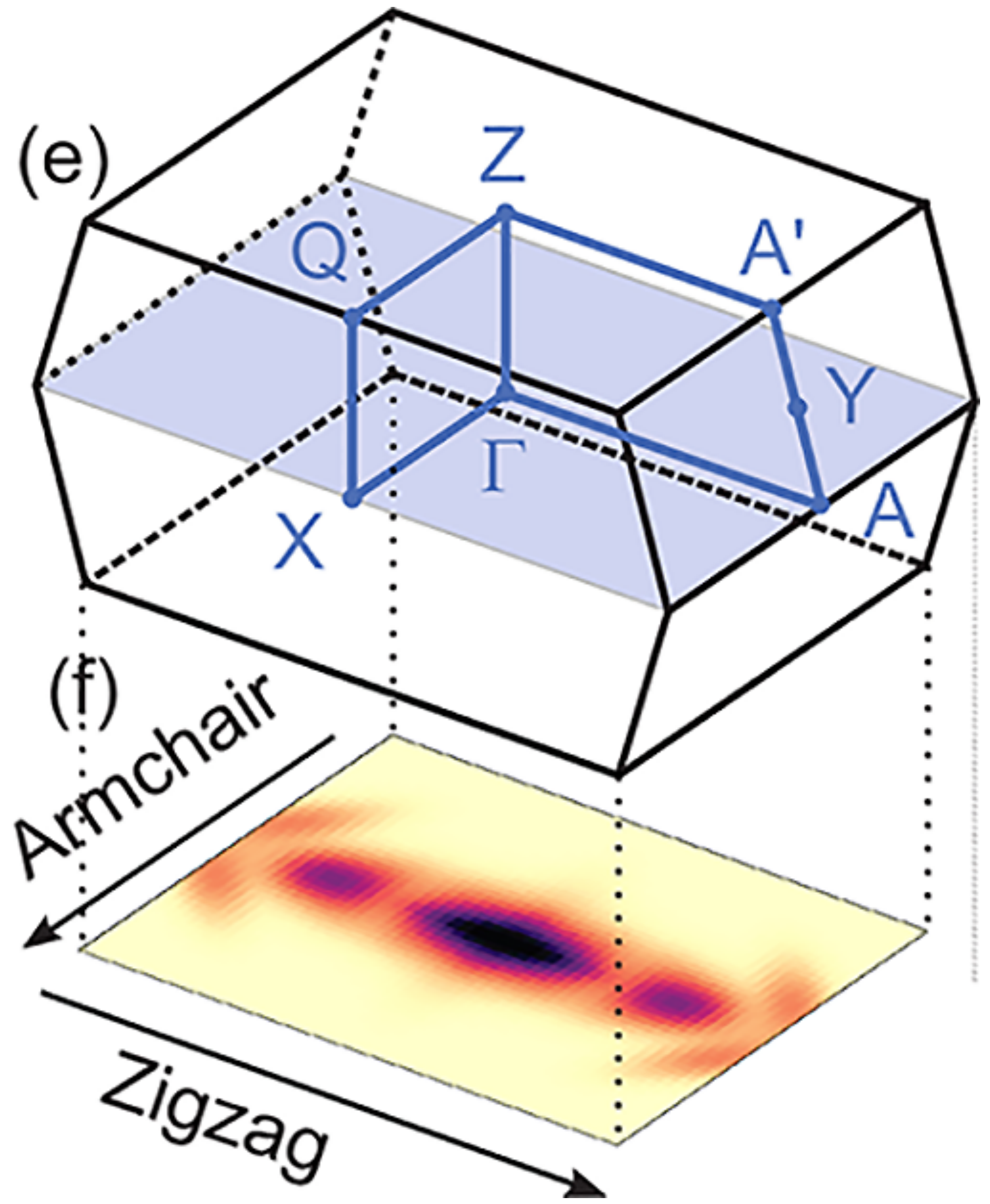
Helene Seiler

Ralph Ernstorfer

H. Seiler et al., Nano Lett. **21**, 6171 (2021)

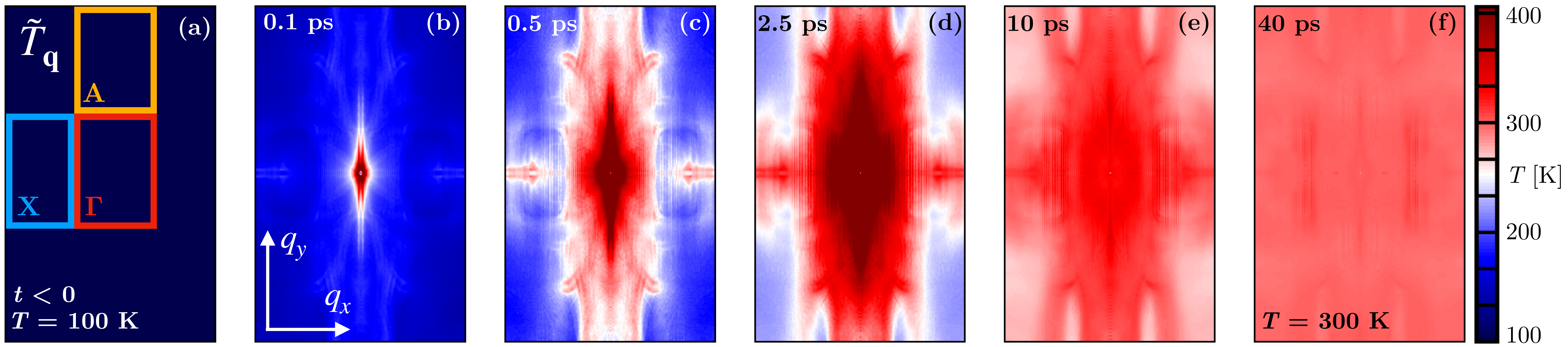
Non-equilibrium lattice dynamics in bP from first-principles

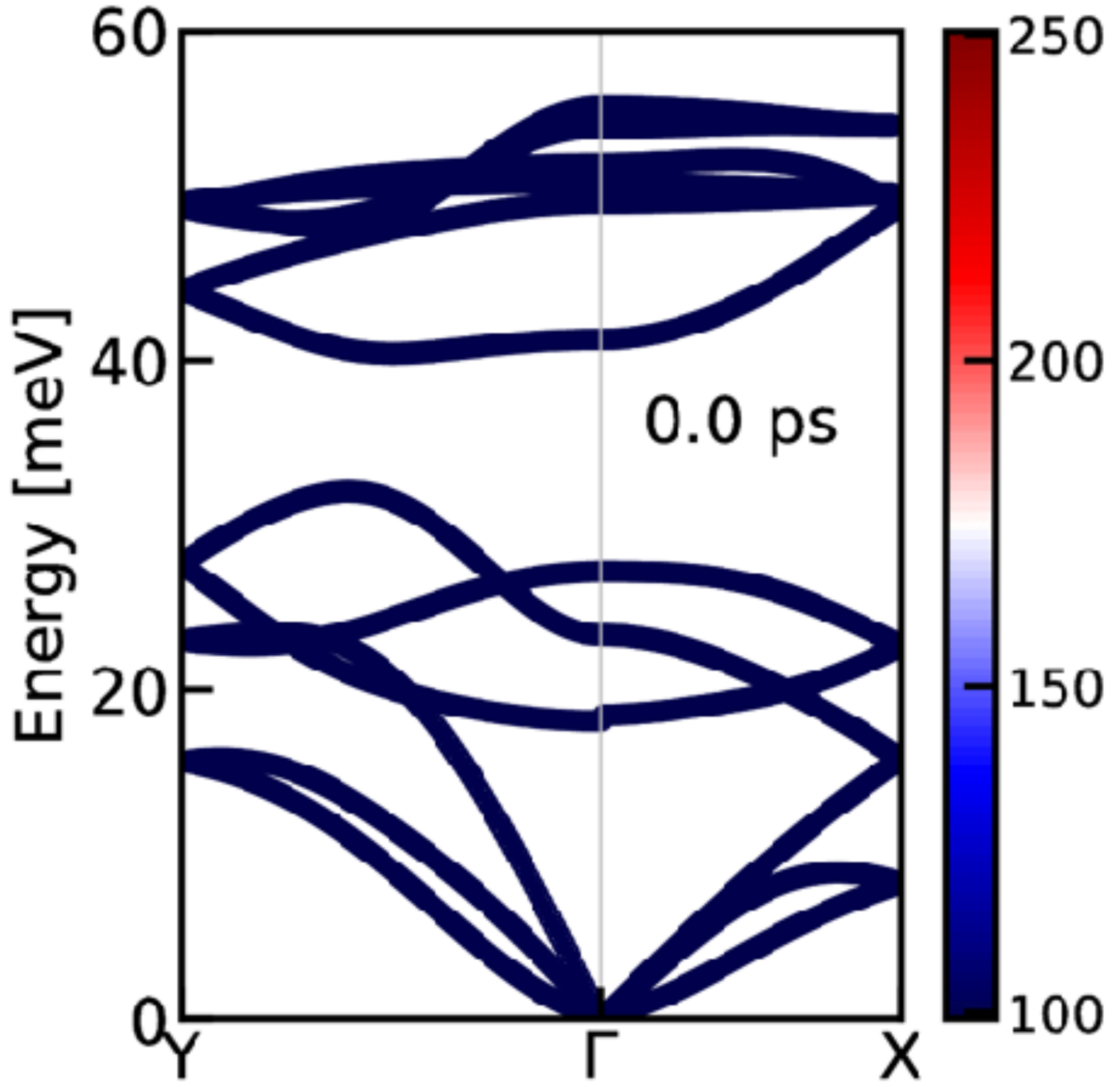


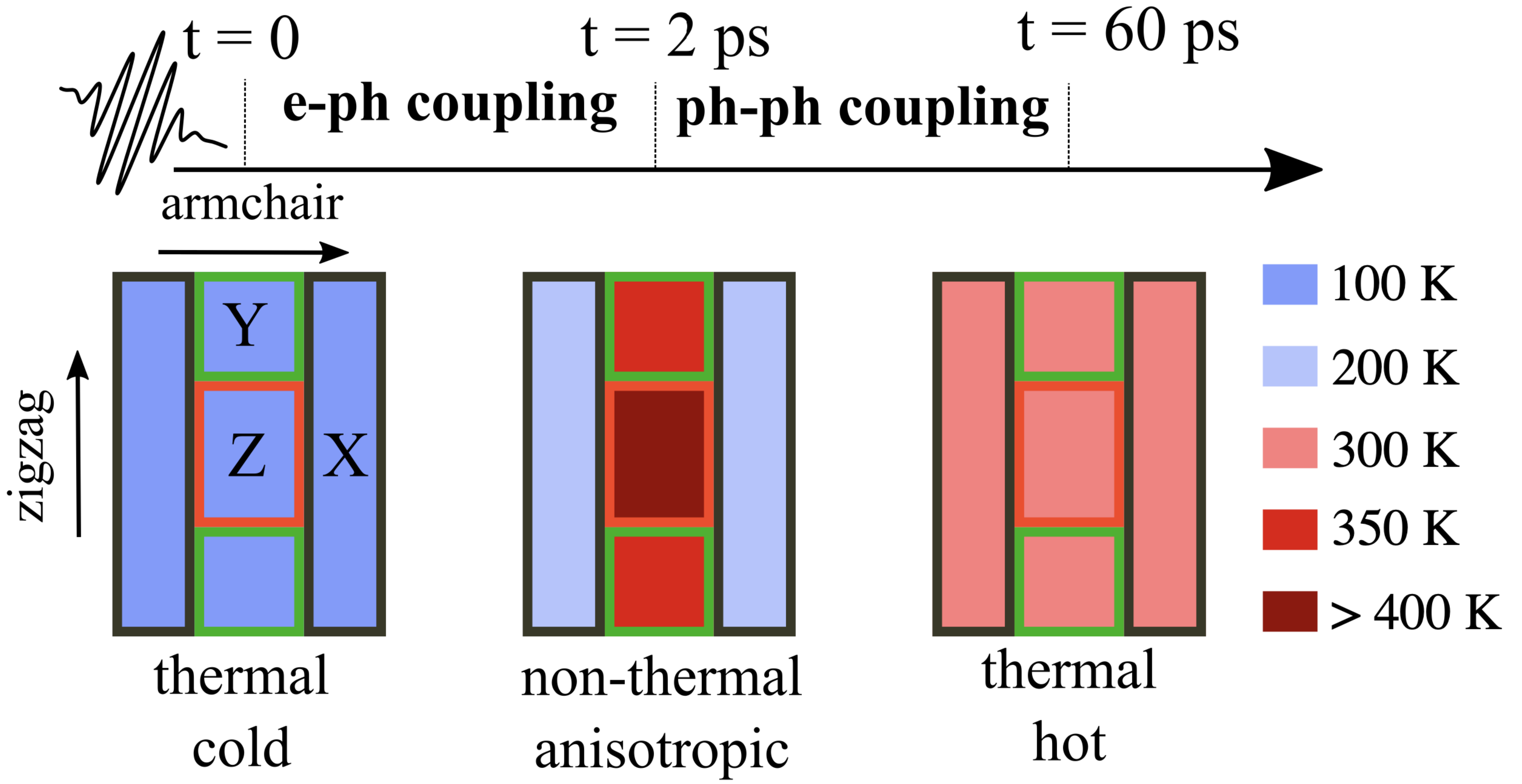


$$\frac{\partial n_{\mathbf{q}\nu}}{\partial t} = I_{\mathbf{q}\nu}^{\mathrm{e-ph}}[f,n] + I_{\mathbf{q}\nu}^{\mathrm{ph-ph}}[n]$$

Effective vibrational temperature

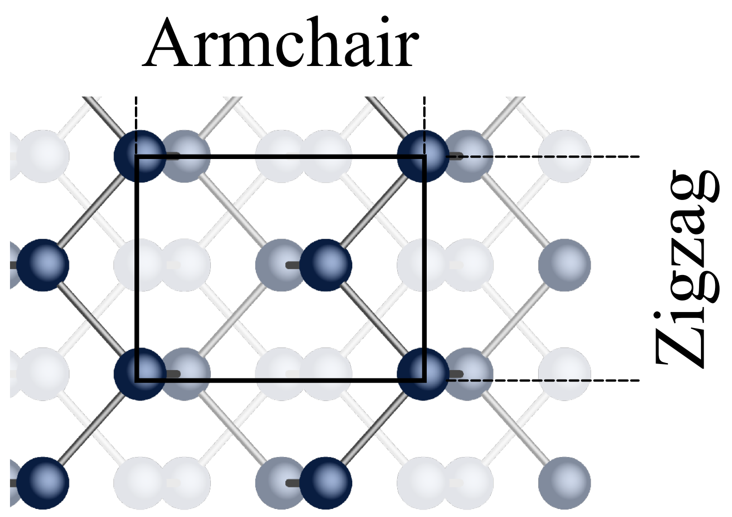




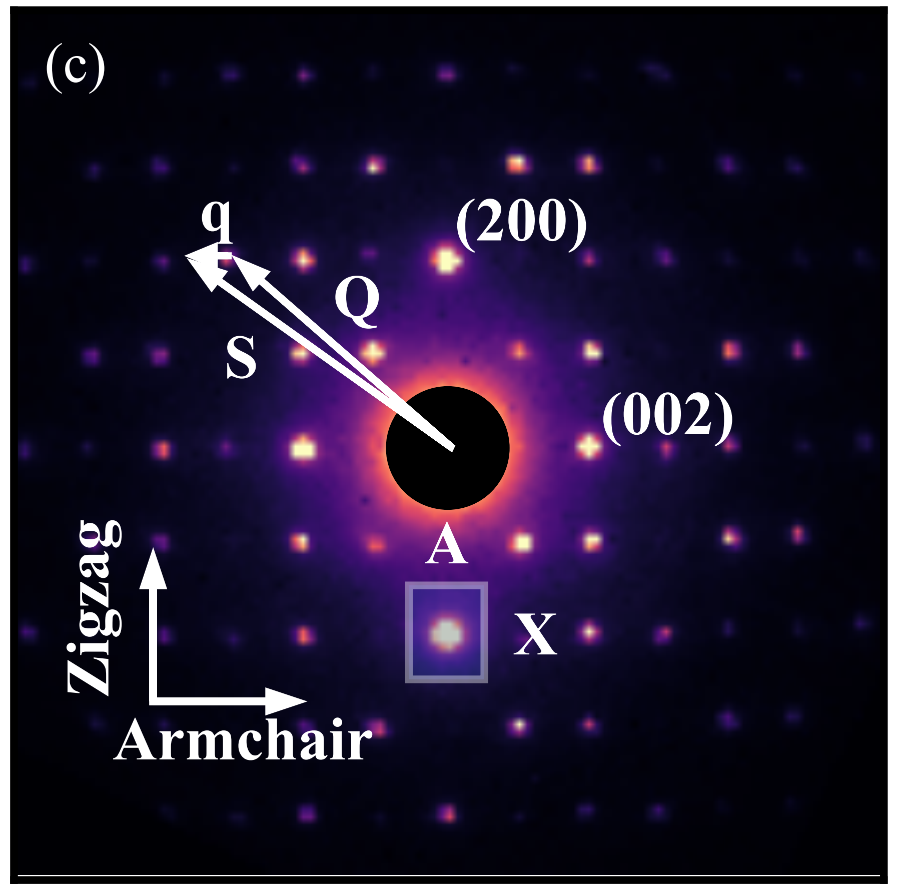


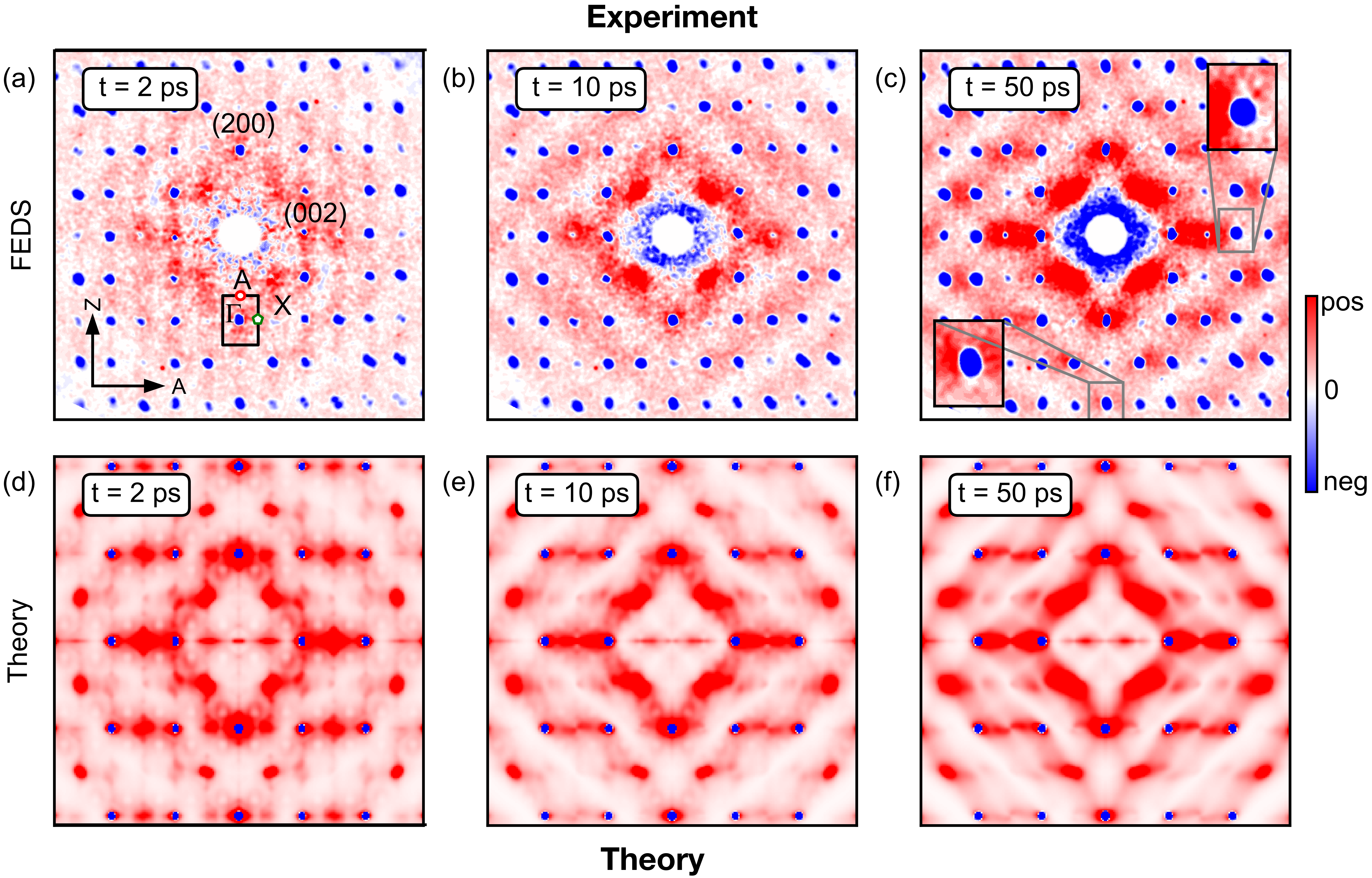
H. Seiler et al., Nano Lett. **21**, 6171 (2021)

Ultrafast electron diffuse scattering: black Phosphorus



Black phosphorus





Experiments: FHI Berlin

Helene Seiler

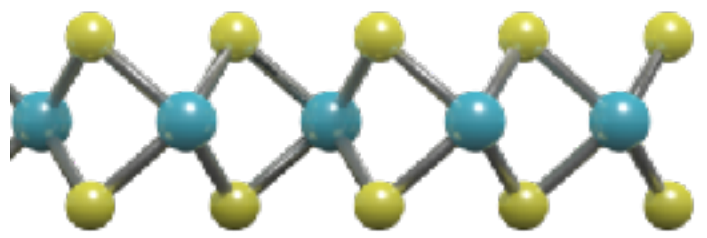
Ralph Ernstorfer

H. Seiler et al., Nano Lett. **21**, 6171 (2021)

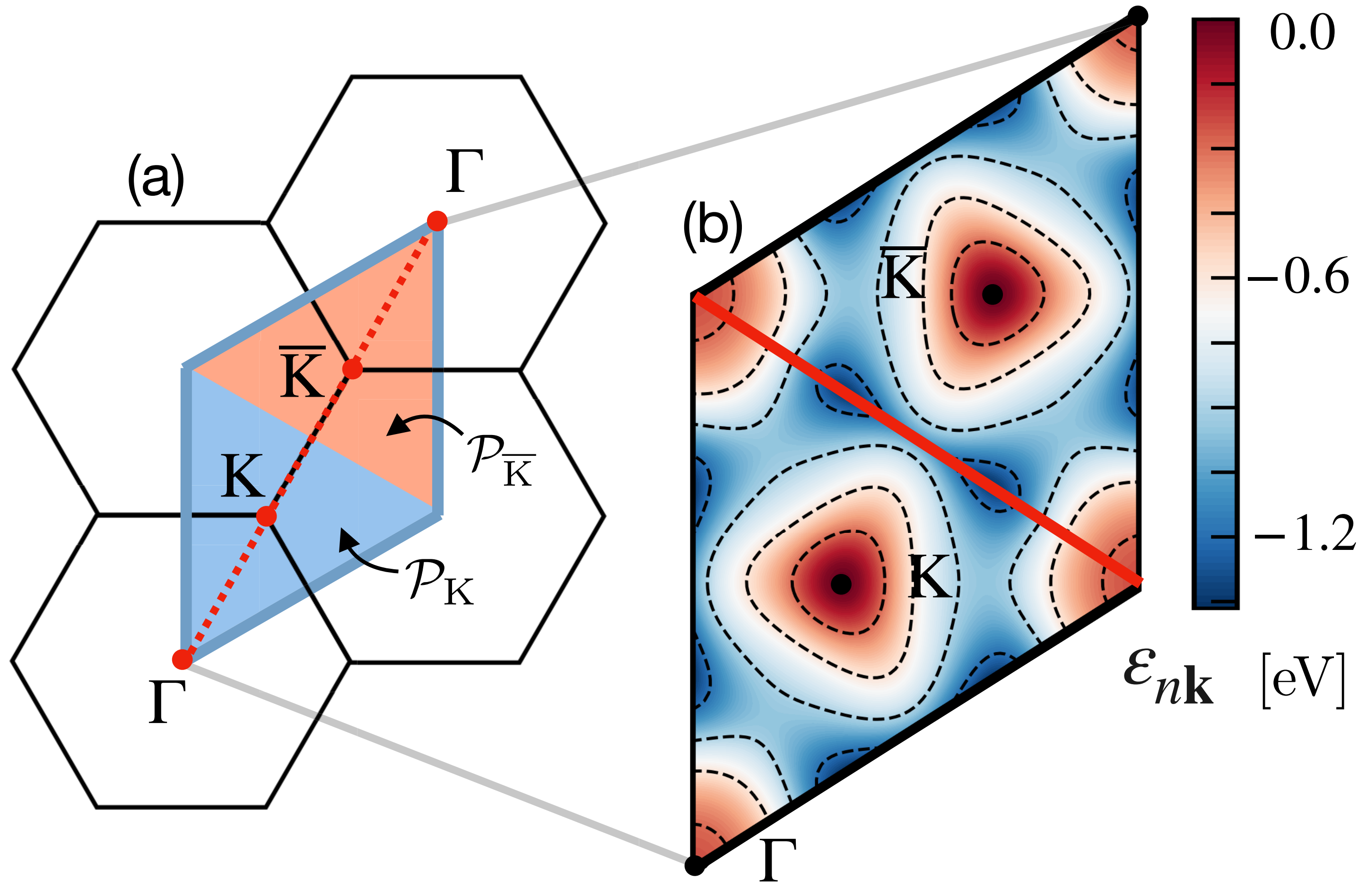
Part 4

Vibrational dichroism of chiral valley phonons

Valley selective circular dichroism in TMDs and chiral valley excitons



monolayer MoS_2



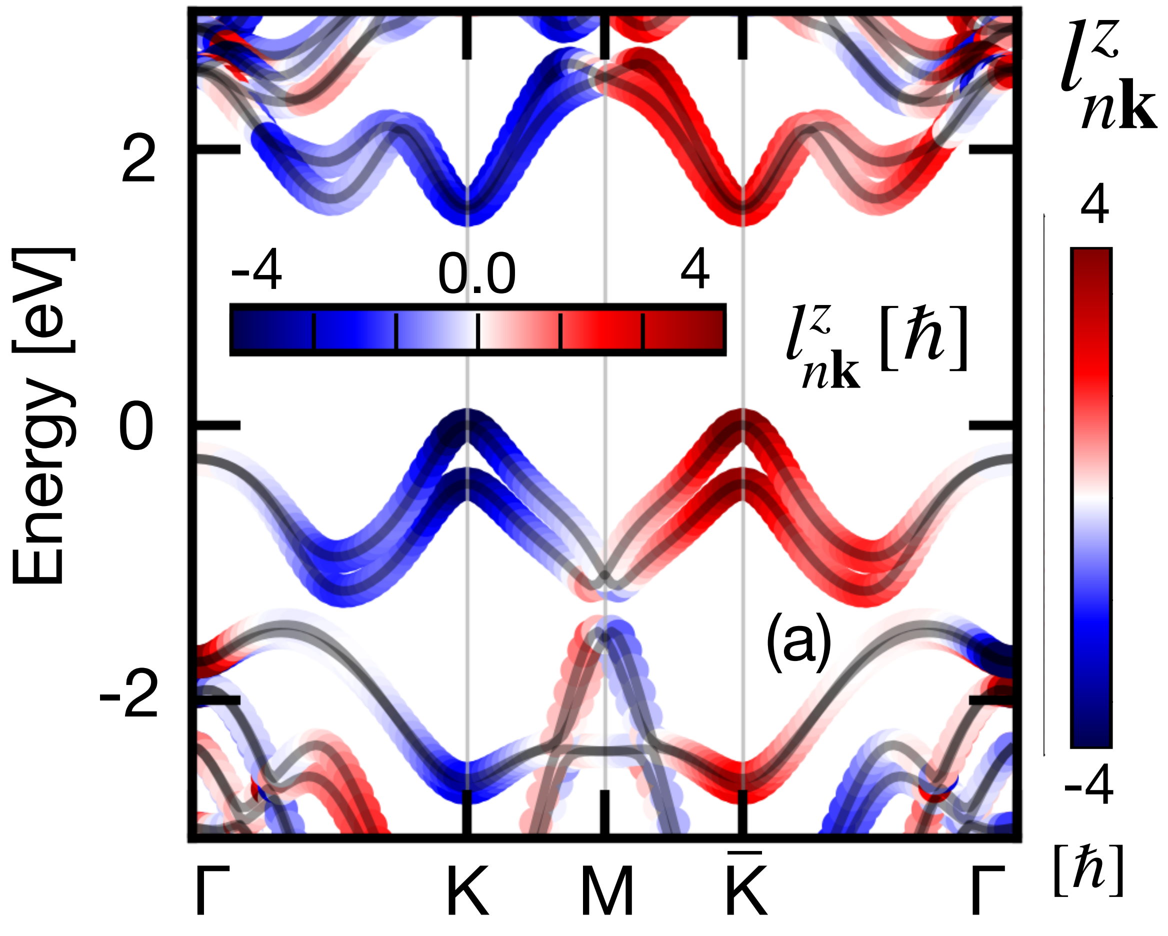
top valence band

Orbital angular momentum (OAM): $\mathbf{l} = \mathbf{r} \times \mathbf{p}$

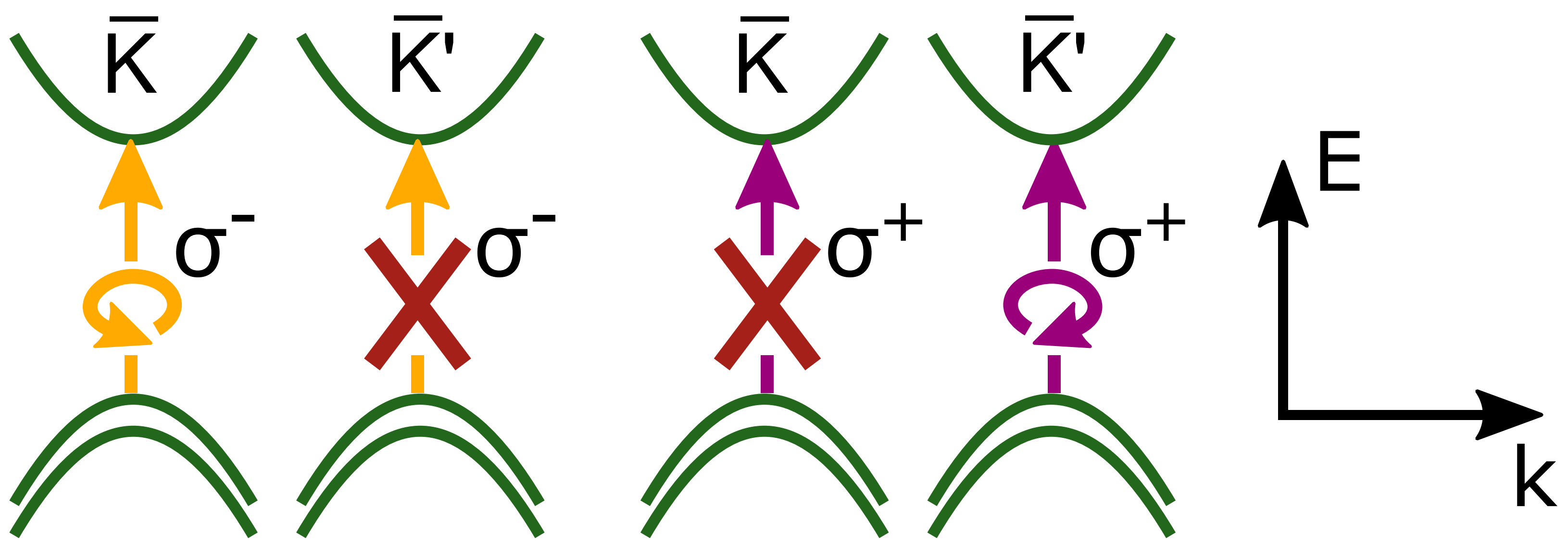
$$l^z_{n\mathbf{k}} = \frac{2\hbar}{m_e} \sum_{m \neq n} \frac{\mathrm{Im}\left[M^x_{nm} M^y_{mn}\right]}{\varepsilon_{m\mathbf{k}} - \varepsilon_{n\mathbf{k}}}$$

Modern theory of OAM:

Thonhauser et al., Phys. Rev. Lett. (2005)



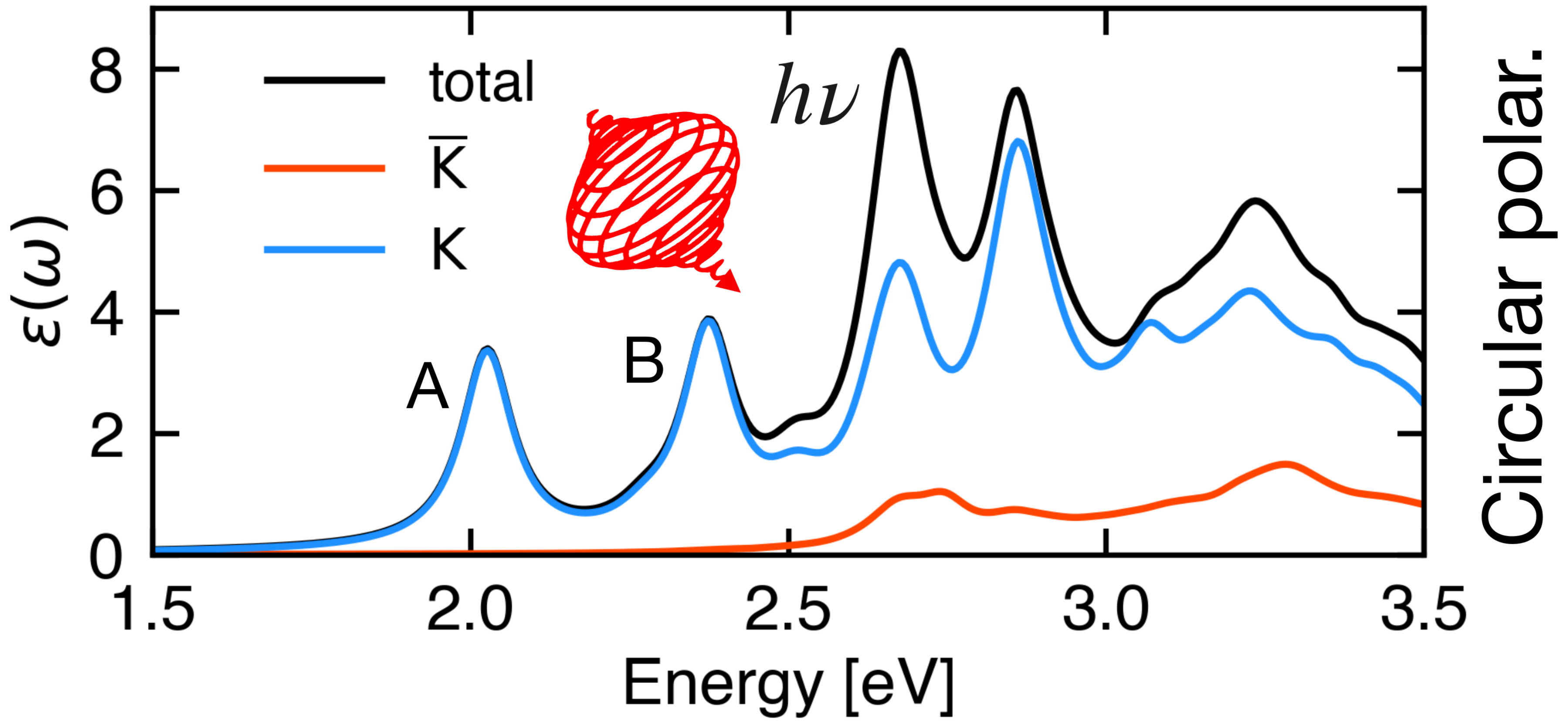
Valley-selective circular dichroism

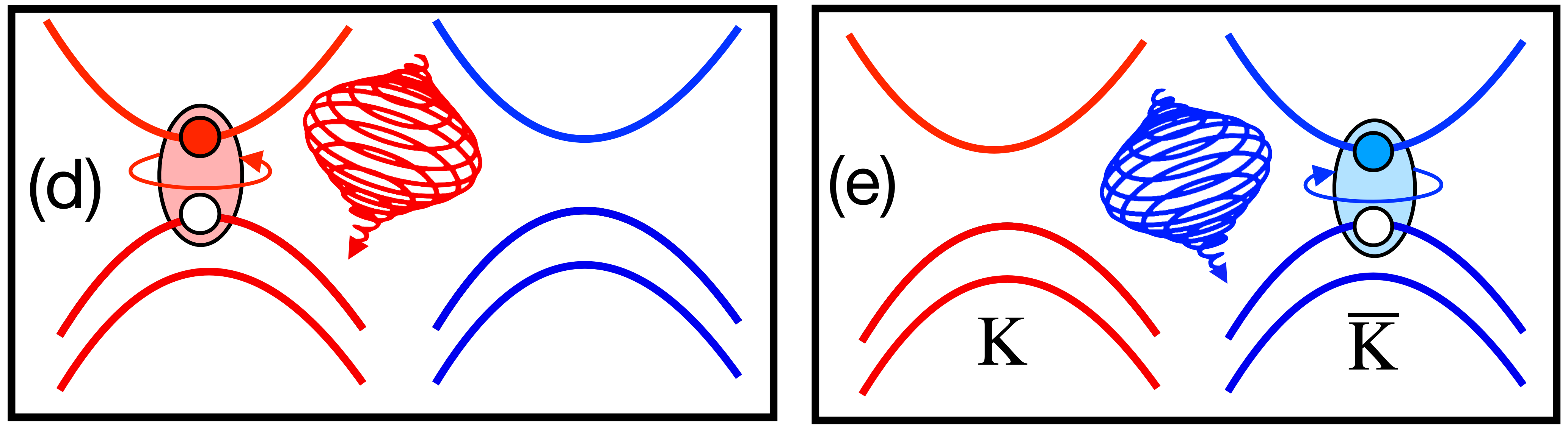


Yao, Xiao, Niu, Phys. Rev. B **77**, 235406 (2008)

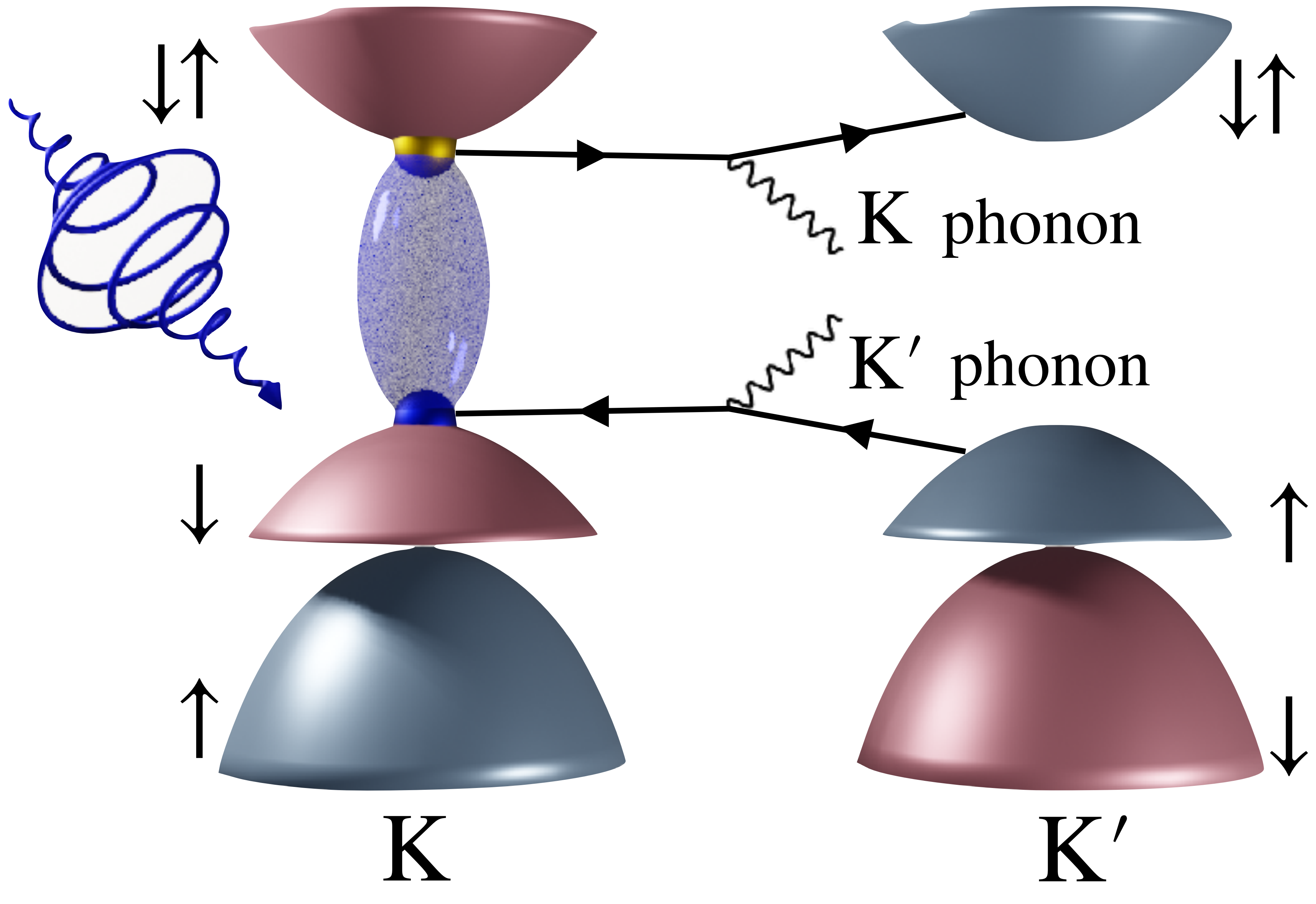
Valley selective circular dichroism in TMDs and chiral valley excitons

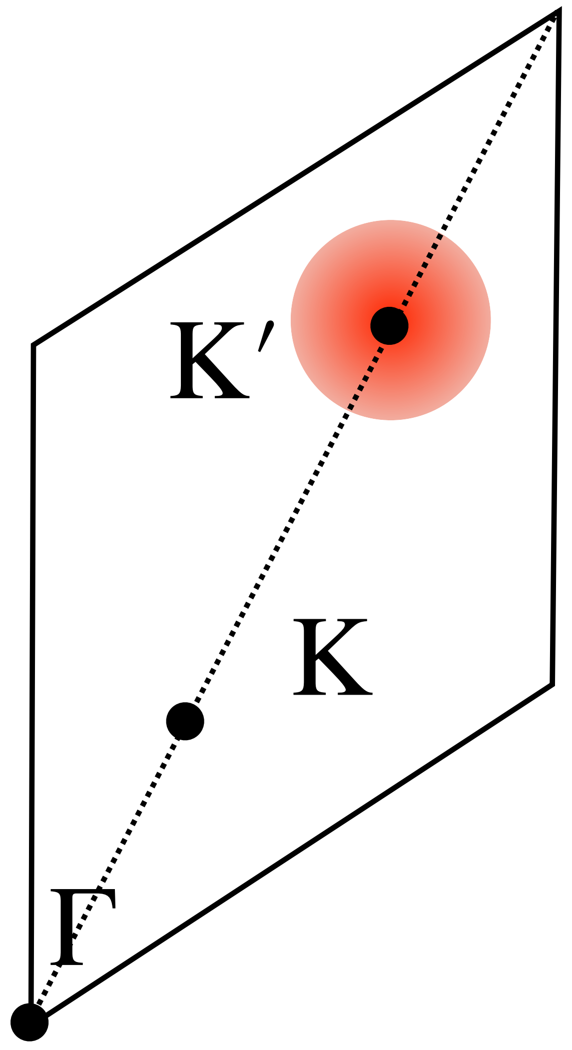
Ab-initio theory of chiral valley excitons:





F. Caruso et al., J. Phys. Chem Lett. **13**, 5894 (2022)





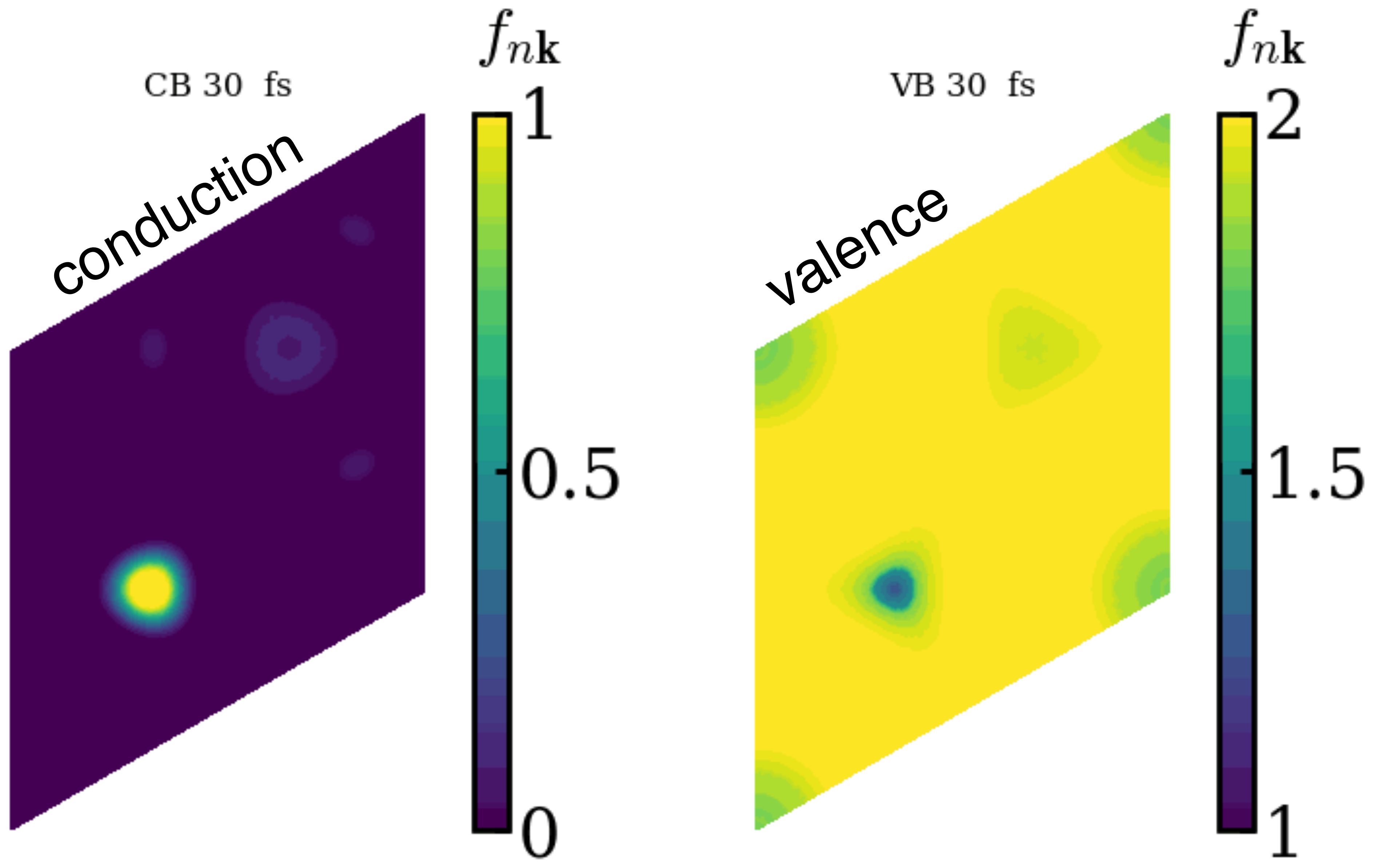
Q1: How is the lattice dynamics influenced by valley selective circular dichroism

Q2: Can we extend valleytronics paradigm to vibrational excitations of the lattice?

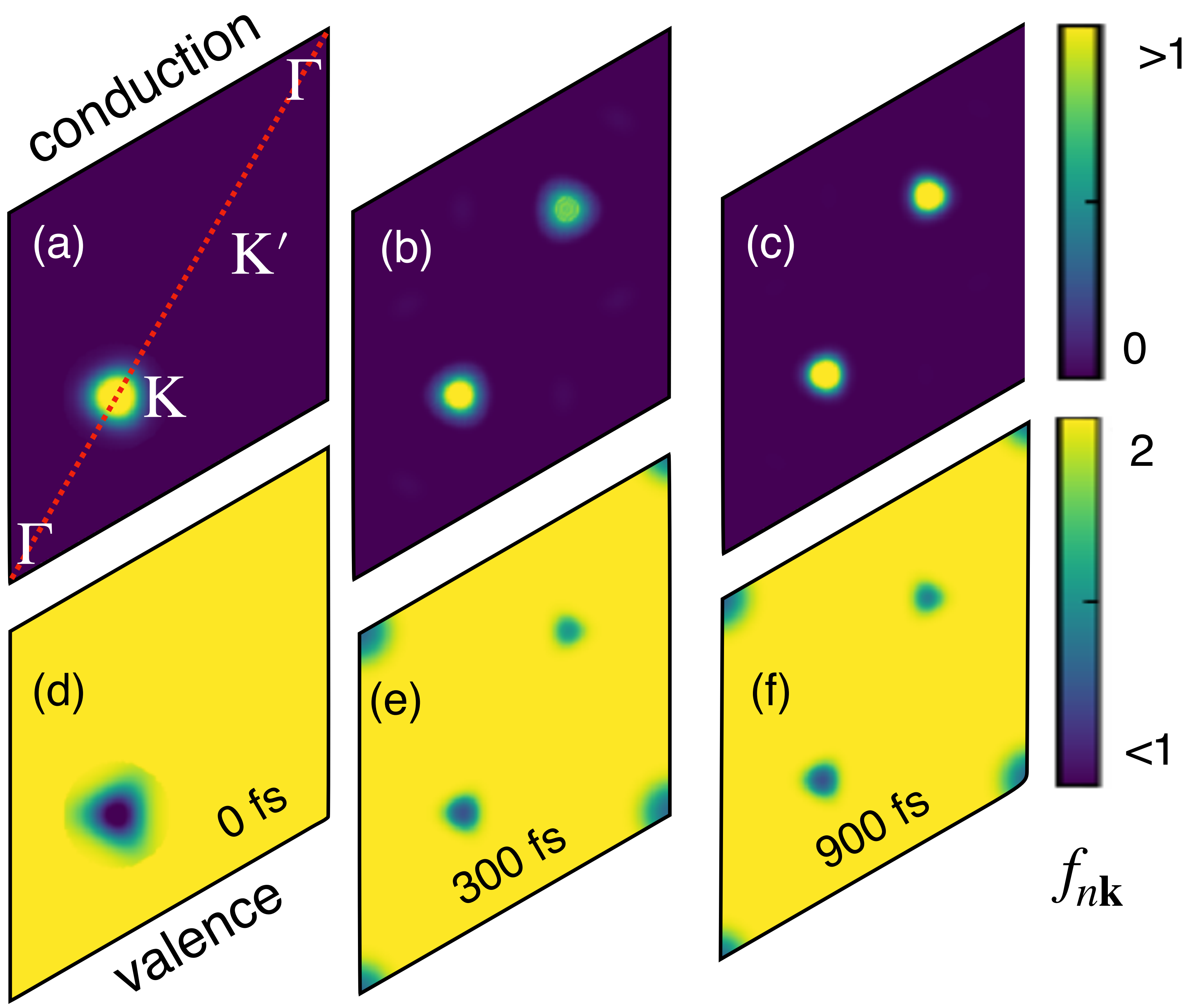
Electron dynamics: ultrafast valley depolarization

Ultrafast electron dynamics from the TDBE

$$\frac{\partial f_{n\mathbf{k}}}{\partial t} = I^{\text{e-ph}}_{n\mathbf{k}}[f, n]$$



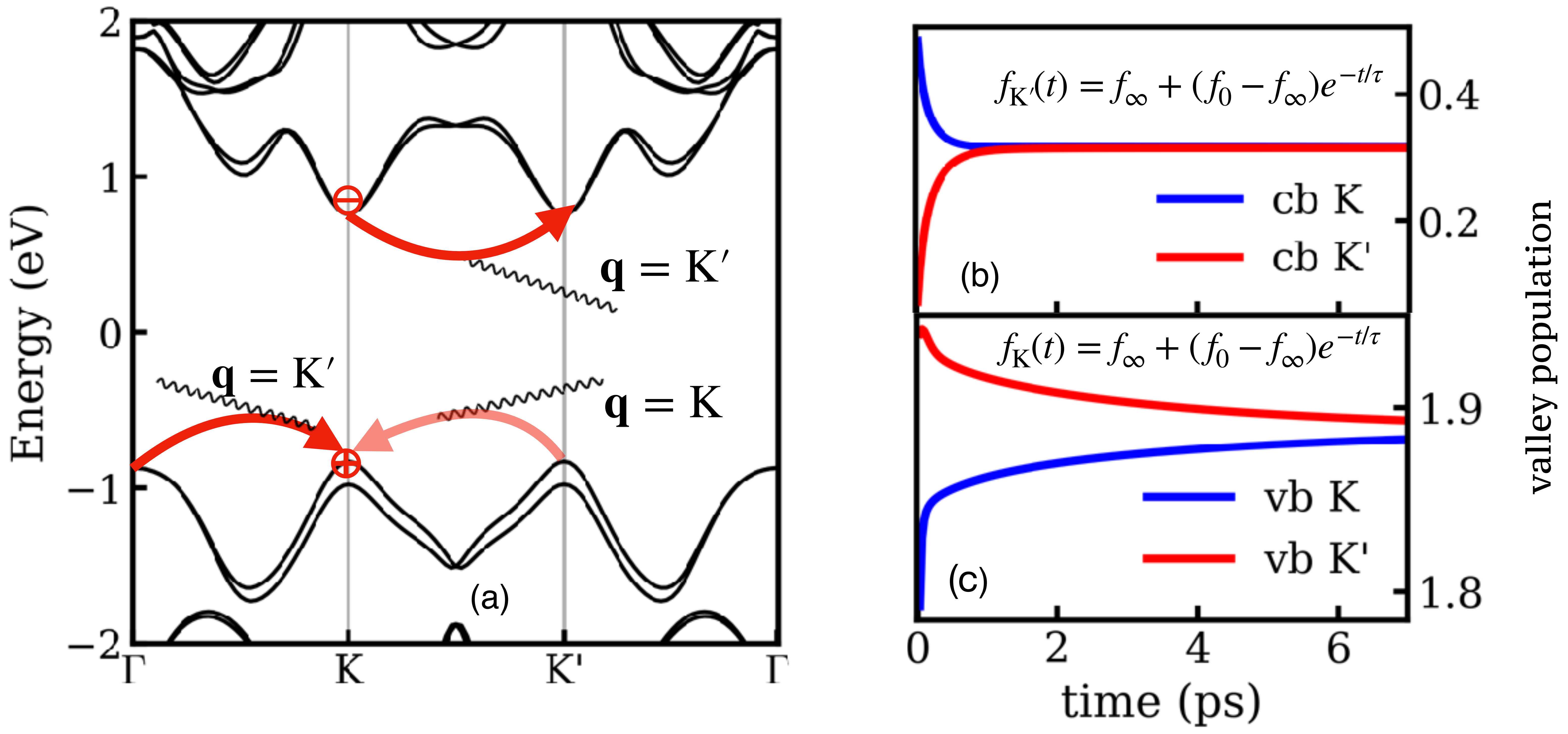
Starting point:
valley-polarized electron excitation



- Ultrafast valley depolarization dynamics
- Different timescales for valence and conduction band

Electron dynamics: ultrafast valley depolarization

- Valley depolarization of photoexcited carriers
  - conduction bands: fast K-K' intervalley scattering, the decaying time is 150 fs
  - valence bands: Γ-K and K to K', the decaying time is 2 ps
  - Results consistent with other calculations and experiments:



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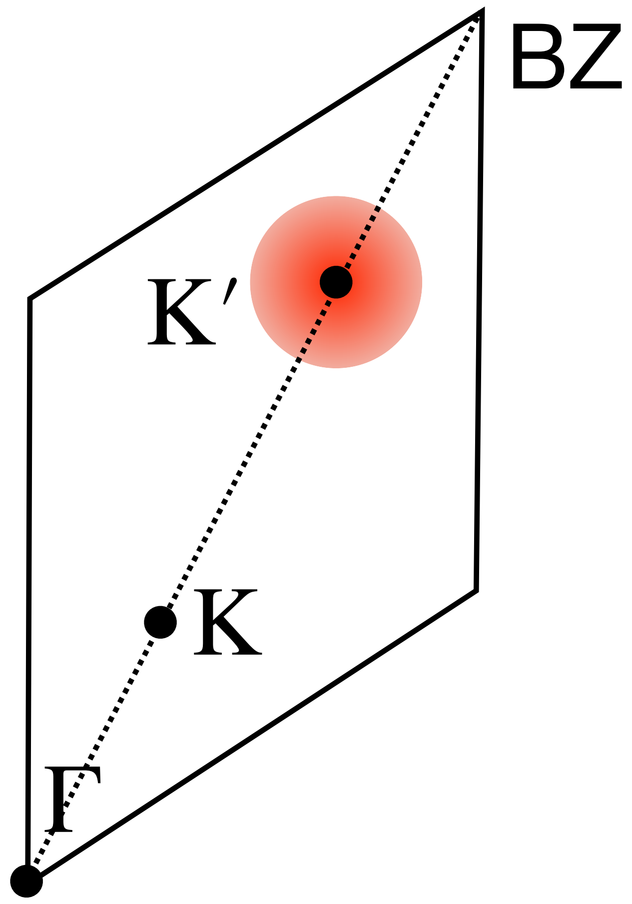
Phonon dynamics: excitation of chiral valley phonons

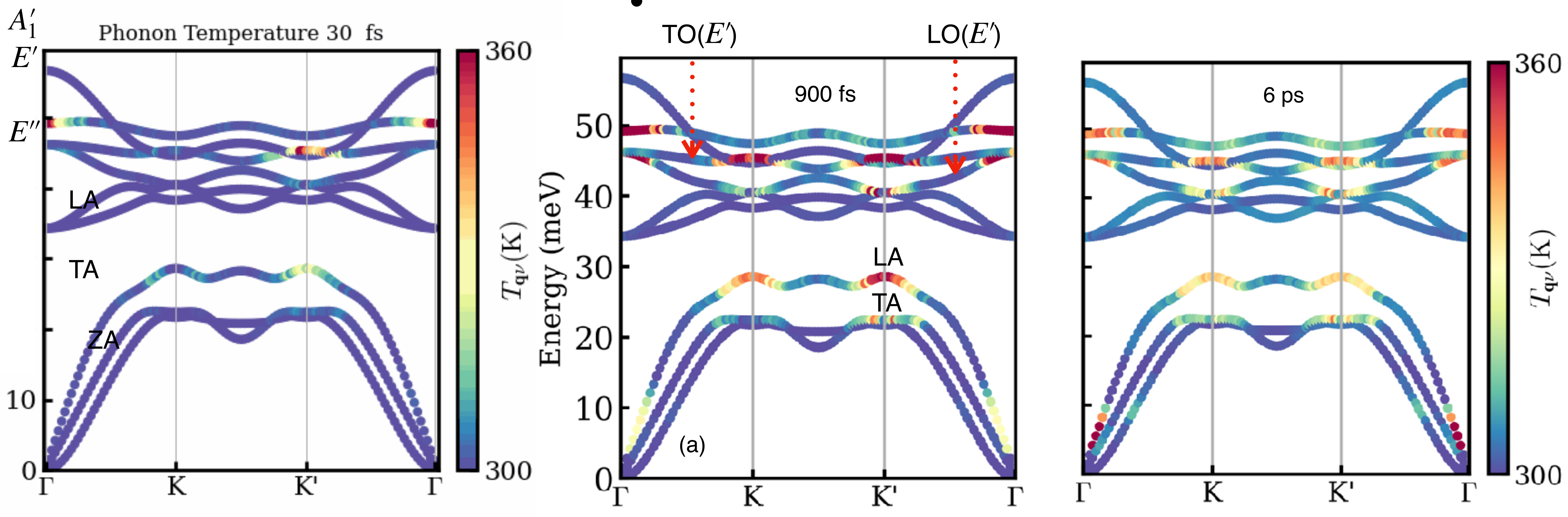
Phonon TEMPERATURE in the Brillouin zone

$$T_{\mathbf{q}\nu} = \hbar\omega_{\mathbf{q}\nu}[k_{\mathrm{B}} \ln(1 + n_{\mathbf{q}\nu})]^{-1}$$

(averaged for all phonon polarizations)



population imbalance between phonons at the K and -K high-symmetry points



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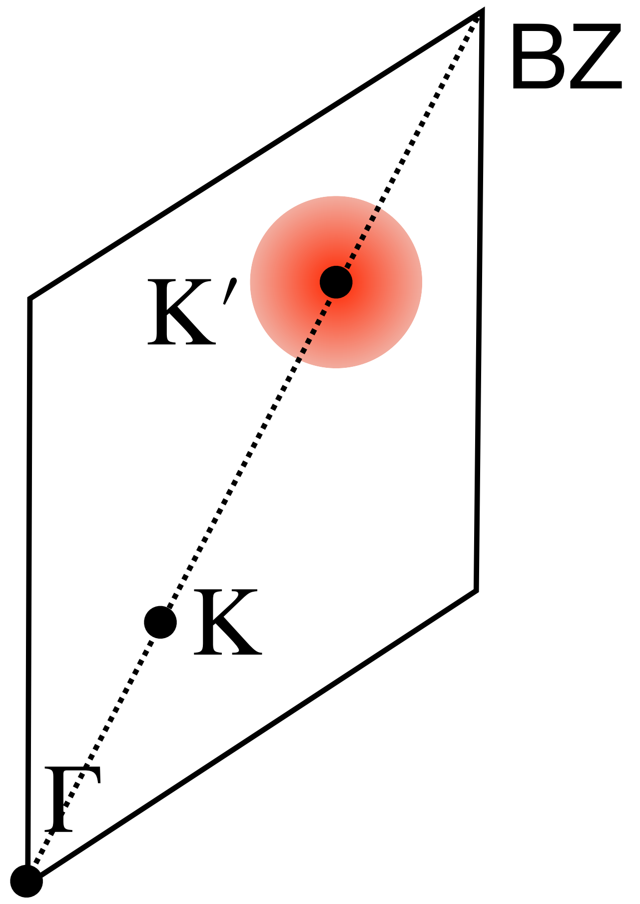

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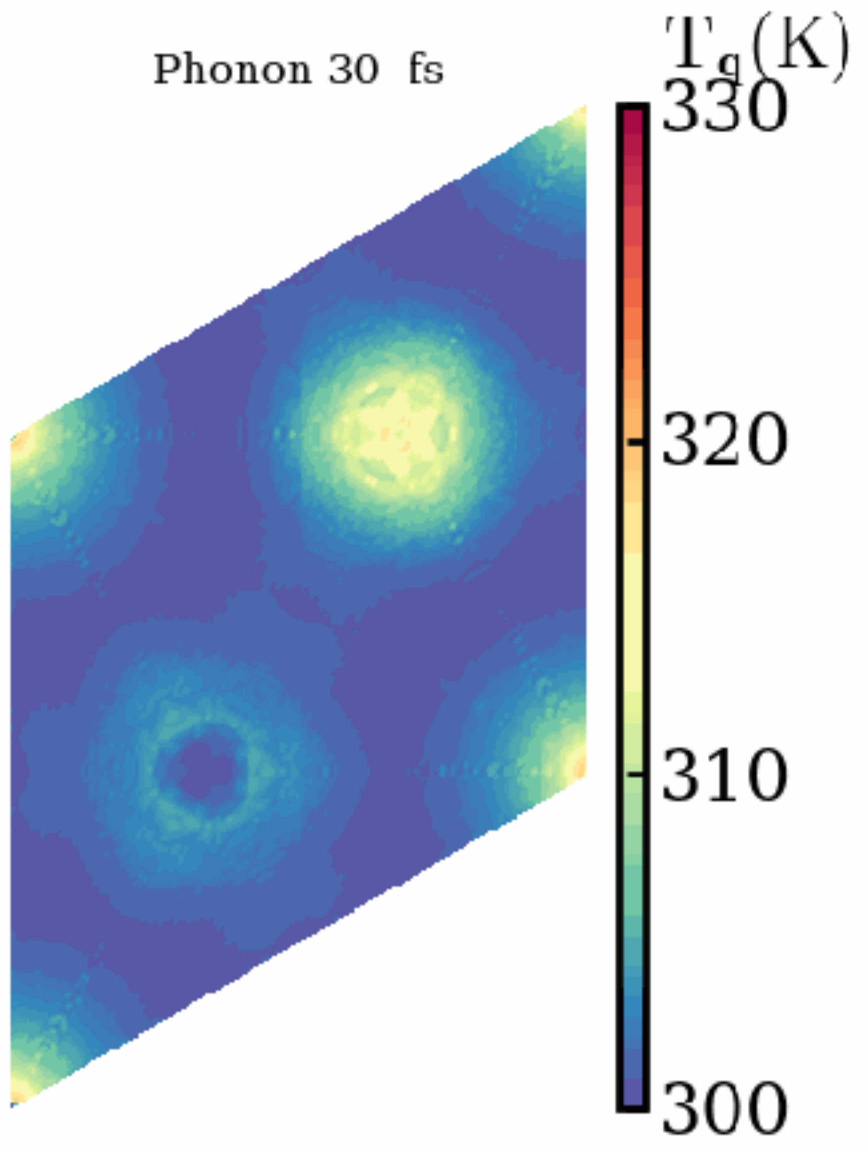
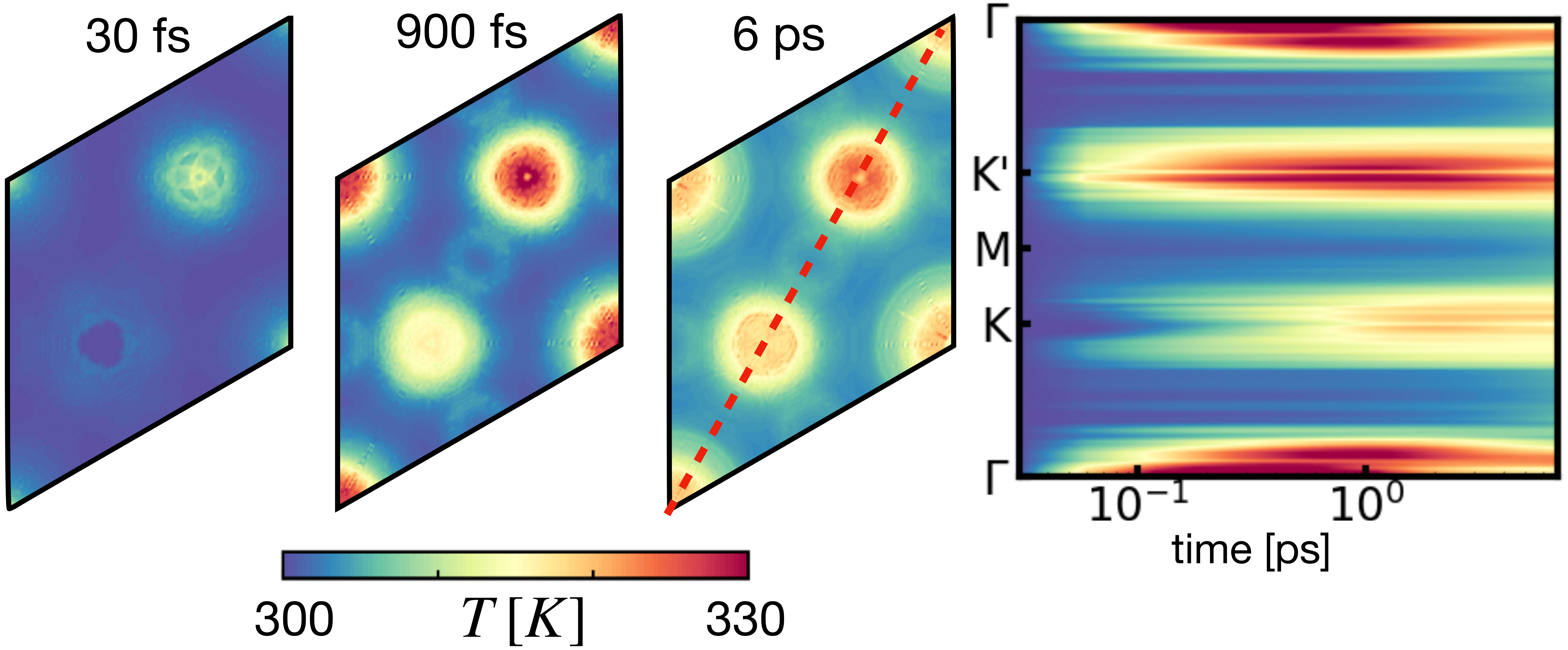
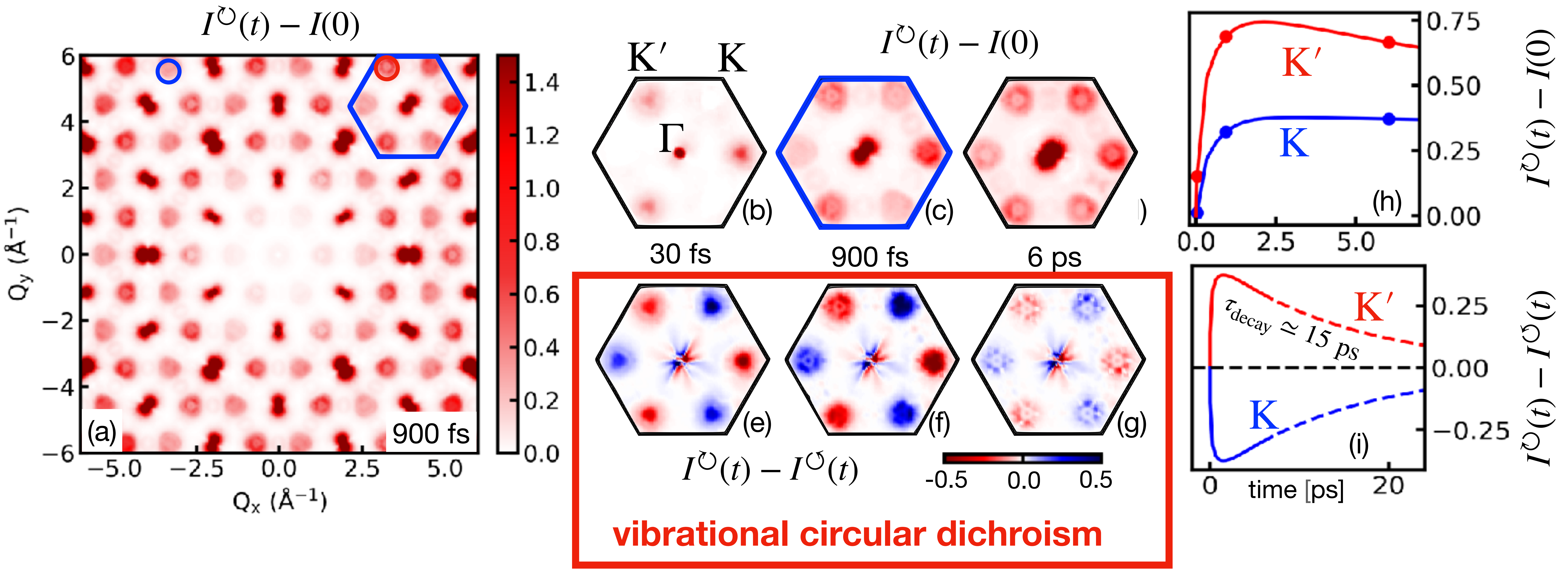




Fingerprints of vibrational dichroism in ultrafast diffraction experiments

Ultrafast electron diffuse scattering signal (simulations)



$I^{\circlearrowright}(t) - I(0)$ **: transient diffraction intensity (change relative to equilibrium)**

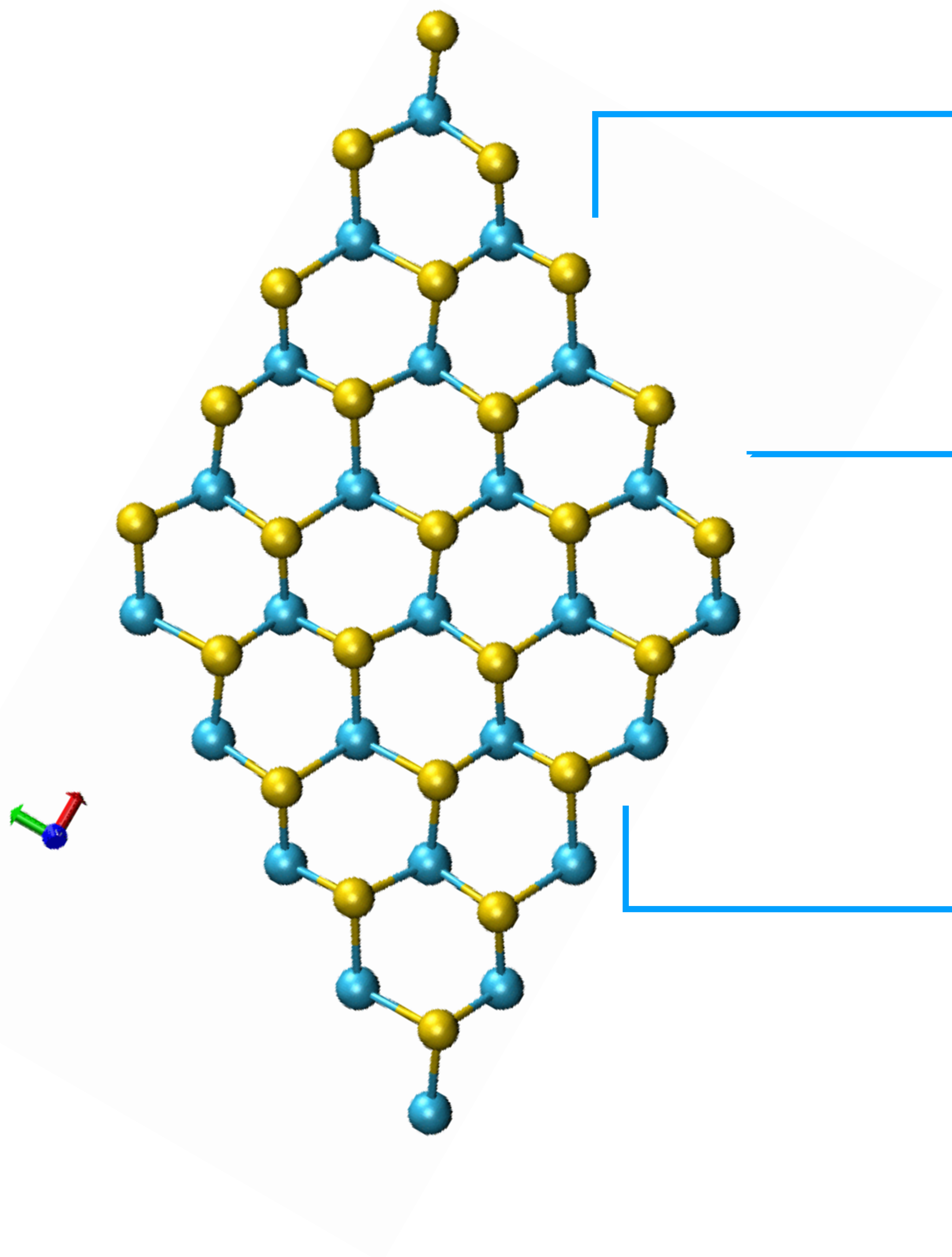
$I^{\circlearrowright}(t) - I^{\circlearrowleft}(t)$ **: dichroic diffraction intensity (changes by switching polarization)**

Take-home message:

Vibrational dichroism persisting for tens of picoseconds.

Phonon valleytronics?

Outline

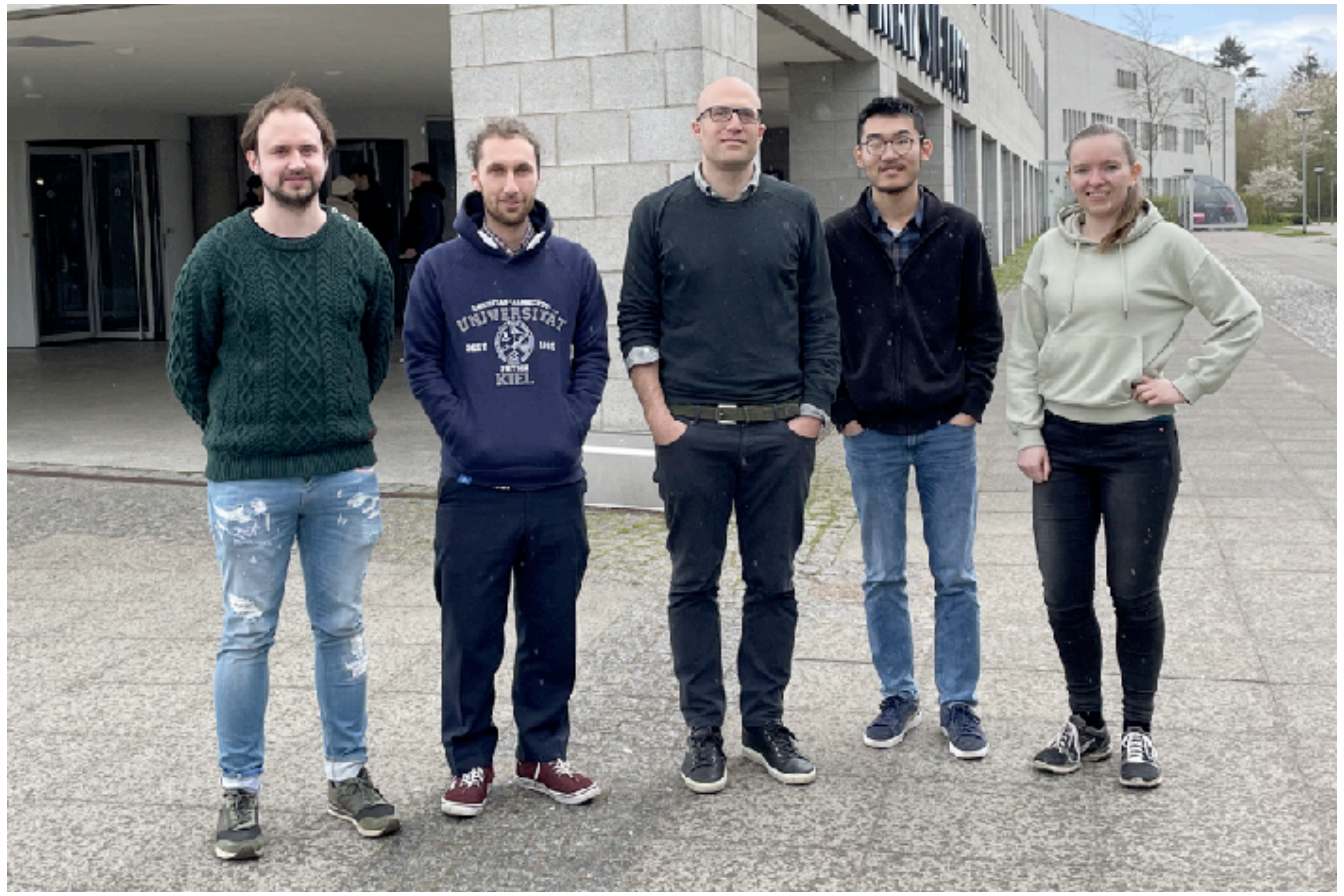


The two-temperature model

The time-dependent Boltzmann equation

Ultrafast dynamics in 2D materials

Acknowledgements



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- Michael Bauer (Uni Kiel)

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