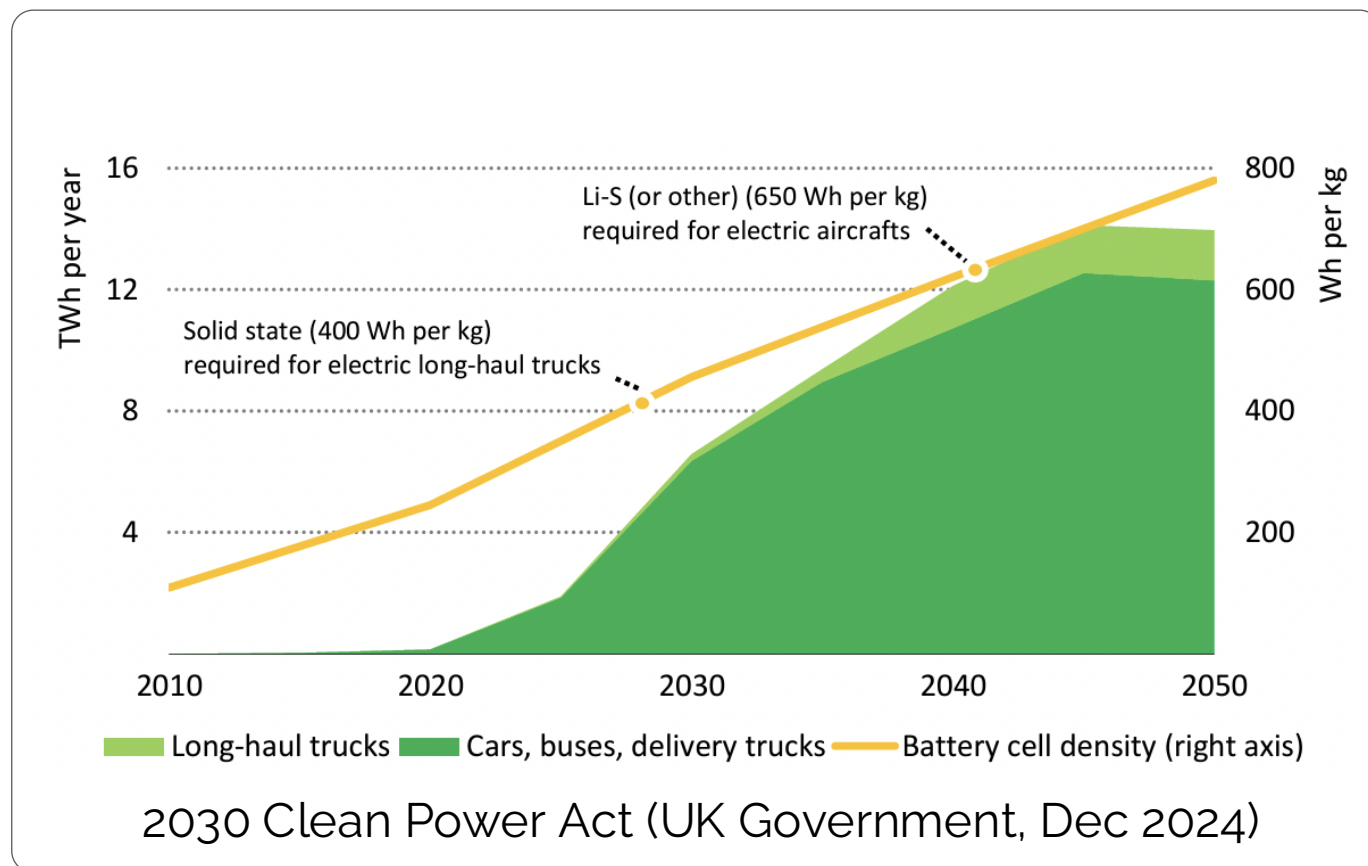
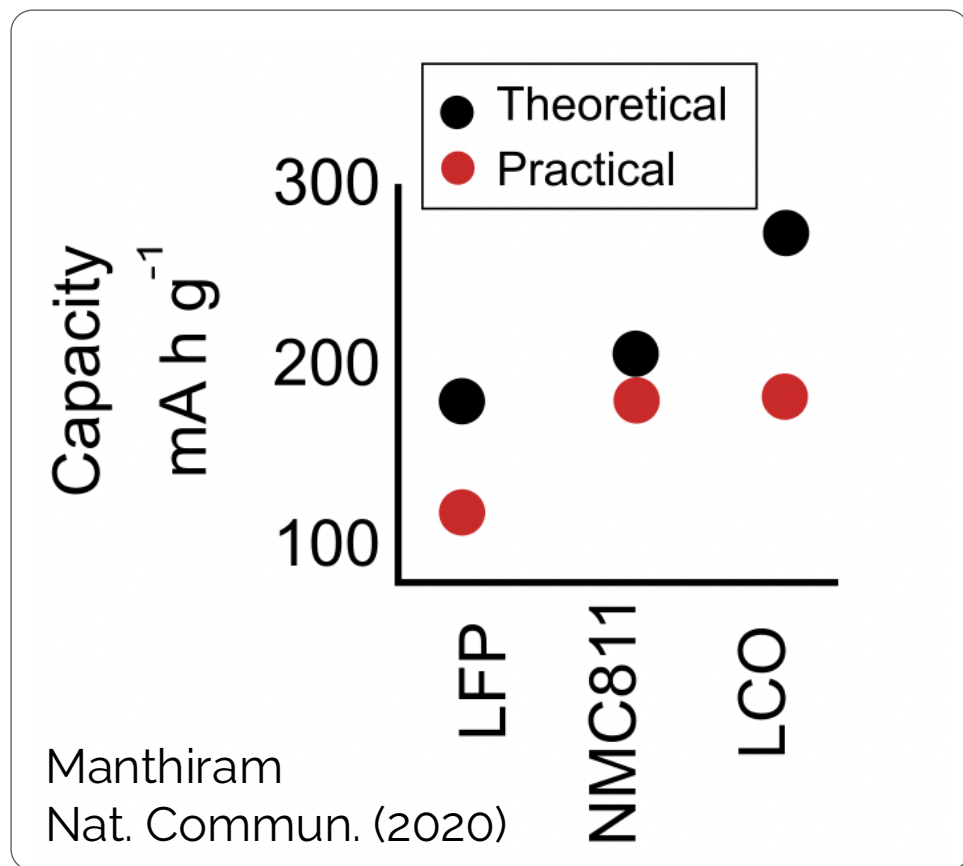


What can non-linear spectroscopy teach us about Li-ion batteries?

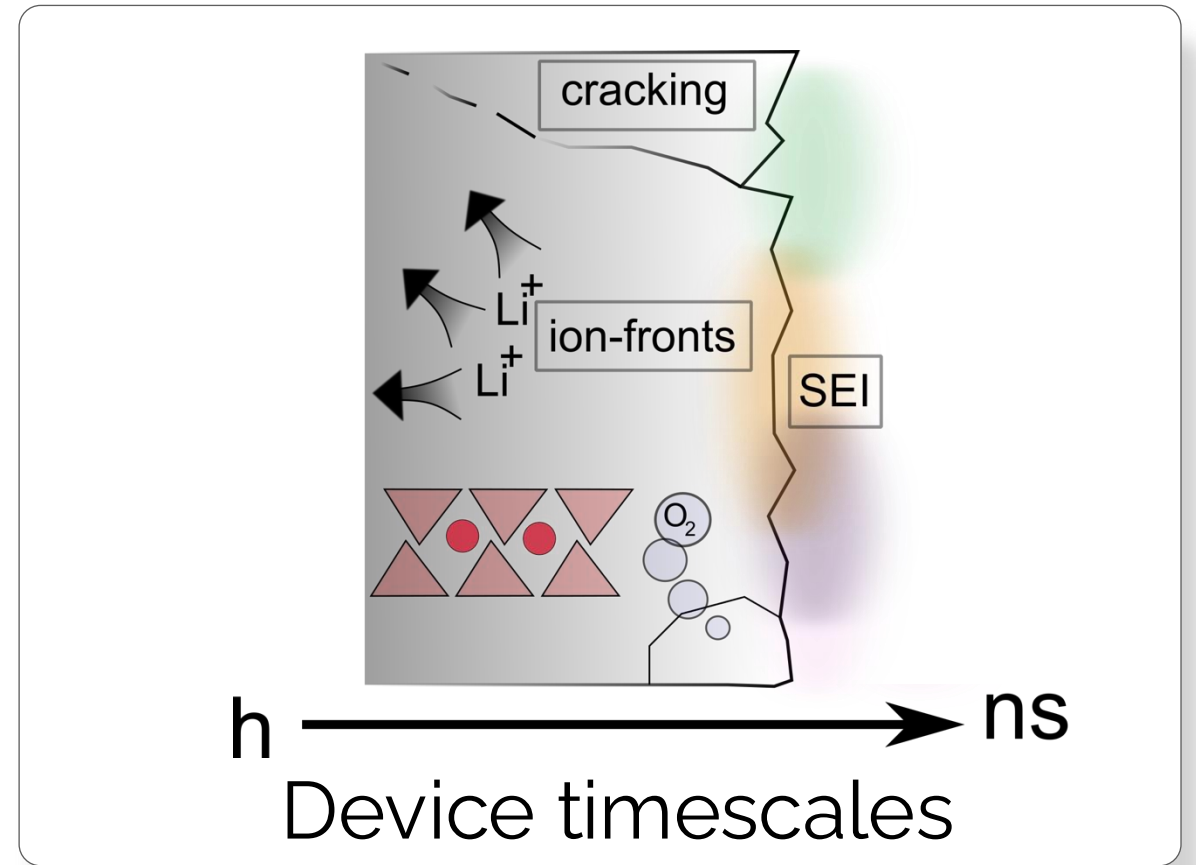
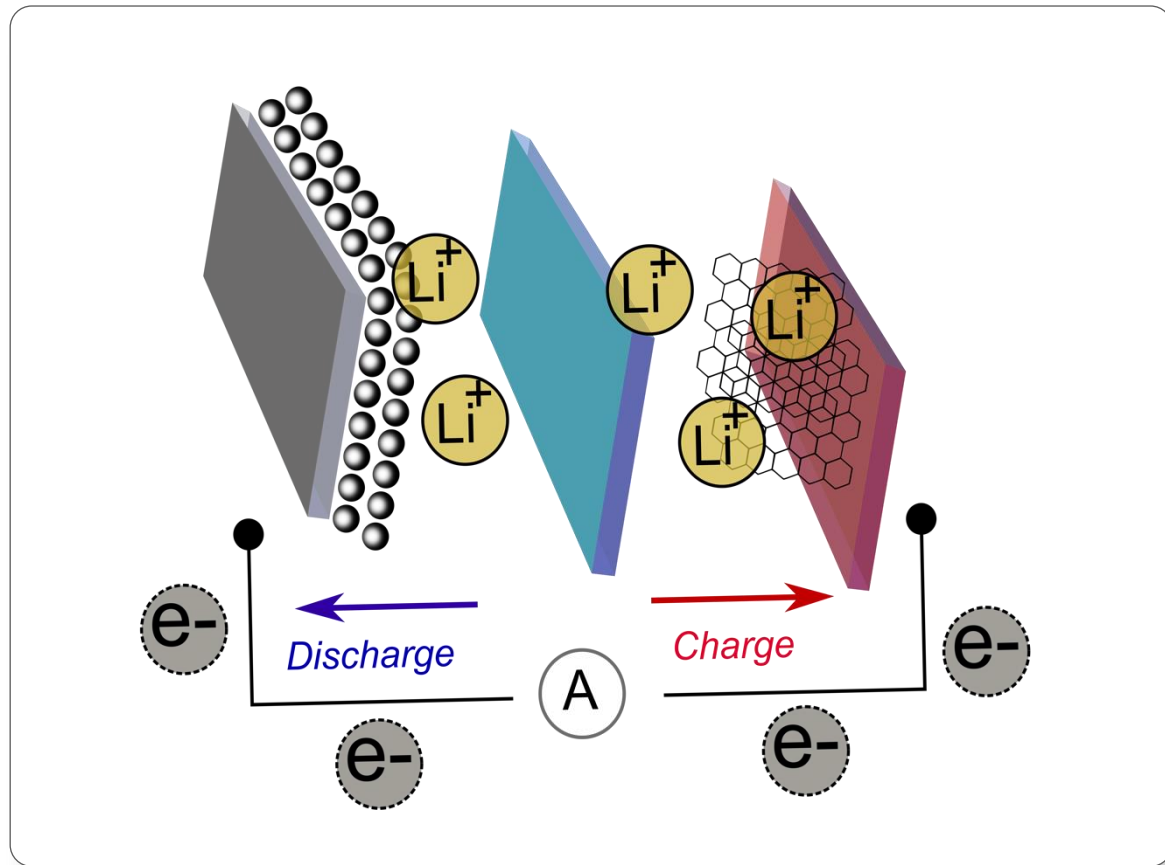
Raj Pandya
University of Warwick

Batteries: fundamental performance challenge

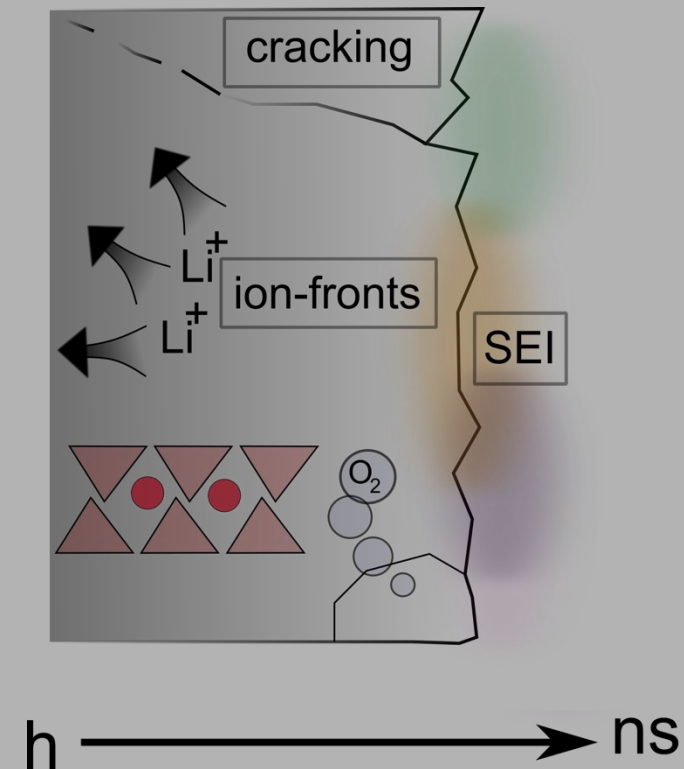


'Scale up alone will not be enough'

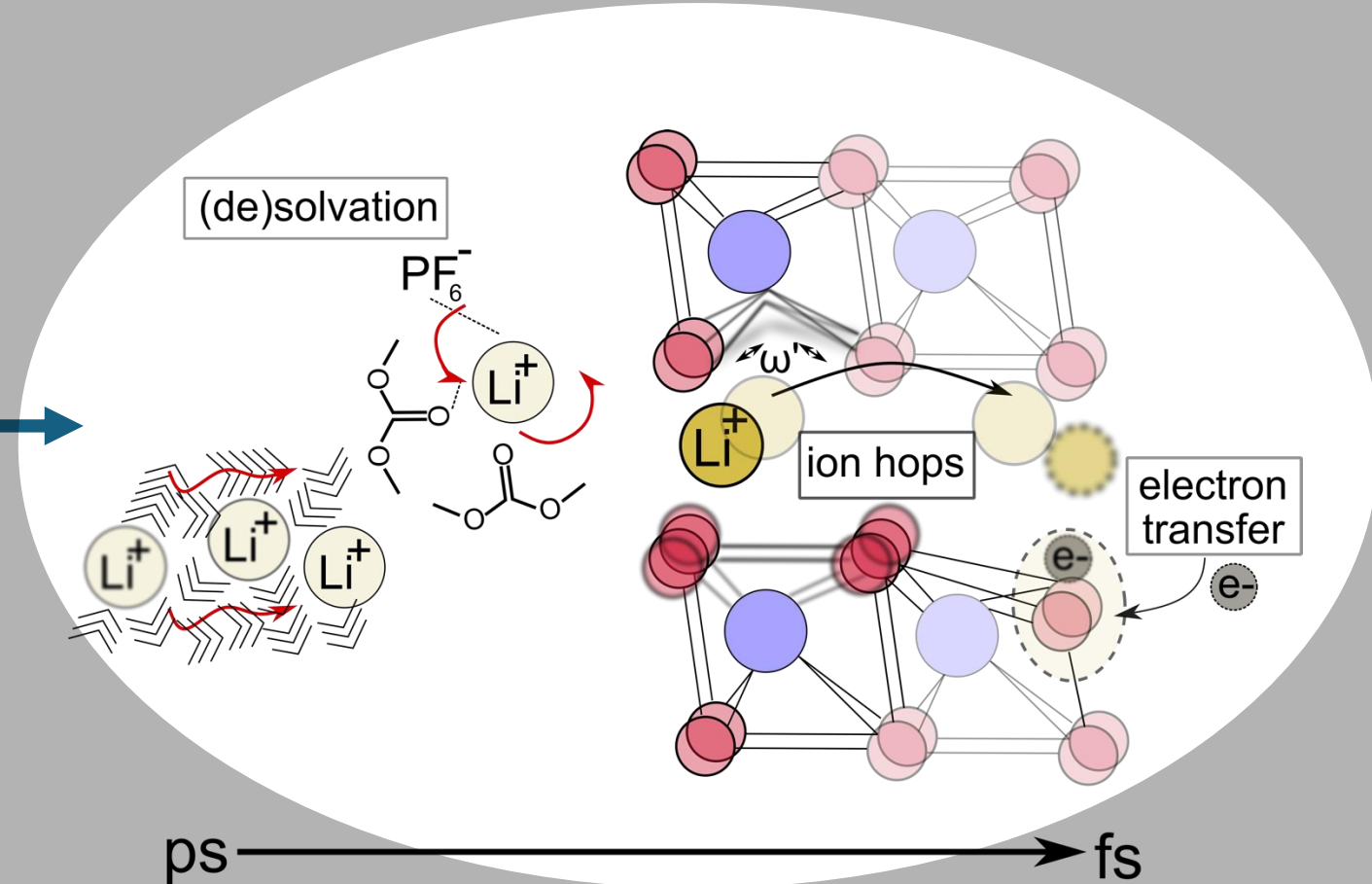
State-of-the-art in batteries



How does a battery (dis)charge?



State-of-the-art:
Device timescales

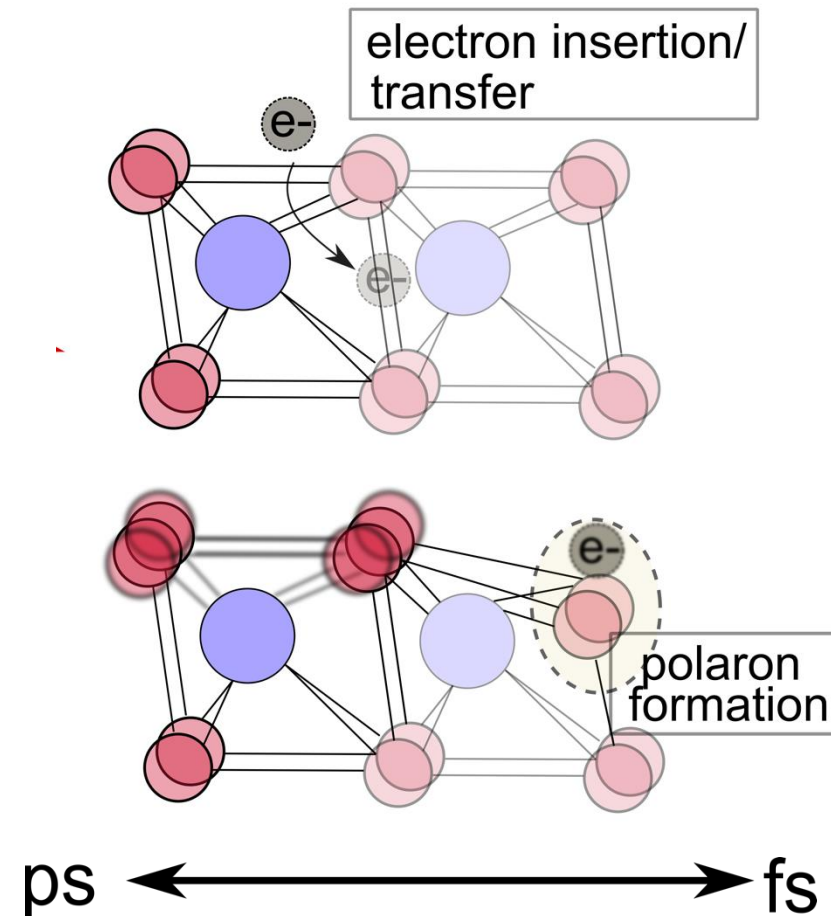


Missing gap: Chemical (ultrafast)
timescales

Why do these elementary steps matter?

**Femtosecond
electron transfer
governs:**

- ➔ capacity loss & voltage hysteresis through inactive redox intermediates
- ➔ electrode electronic conduction

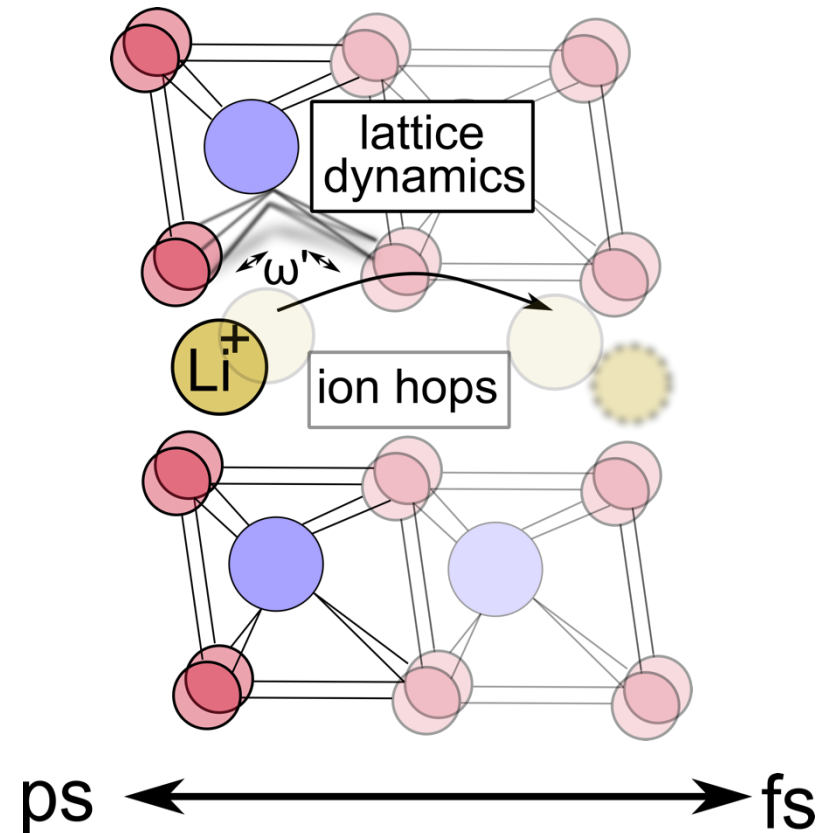


Why do these elementary steps matter?

Ultrafast ion transport is key for:

→ charging rates *via* maximizing ionic conduction

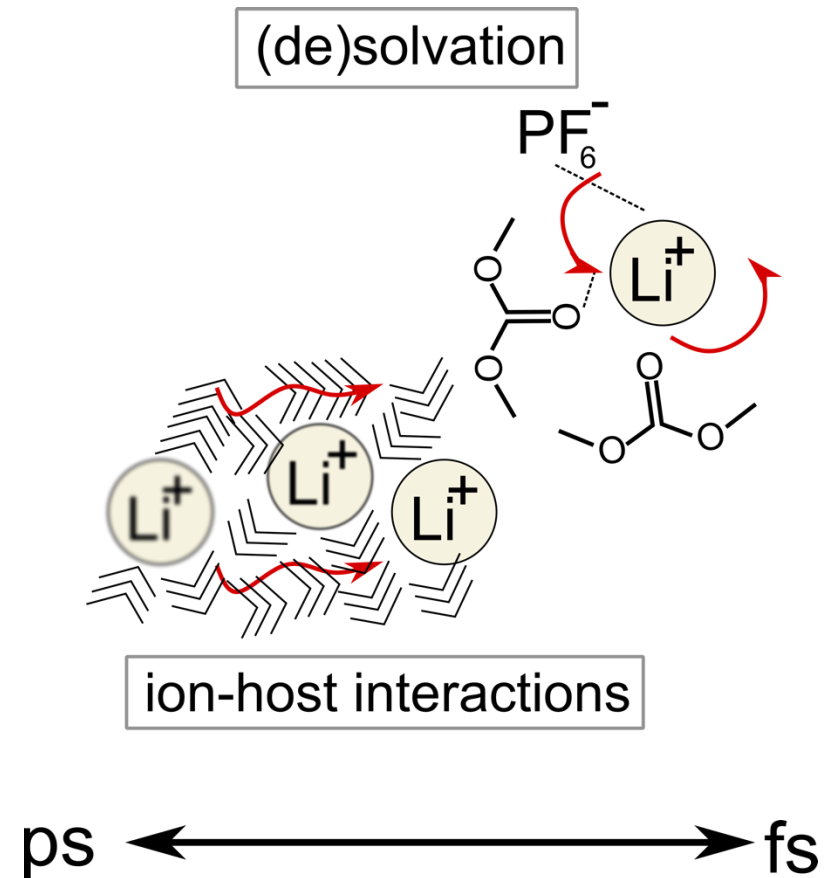
→ electrode/solid-electrolyte stability *via* mechanical strains



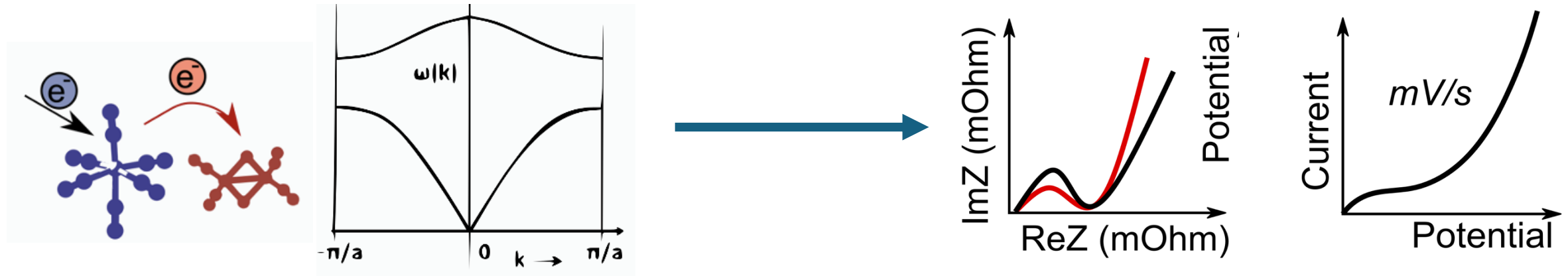
Why do these elementary steps matter?

Ultrafast (de)solvation controls:

- (dis)charging rate
- electrode/electrolyte and interface stability

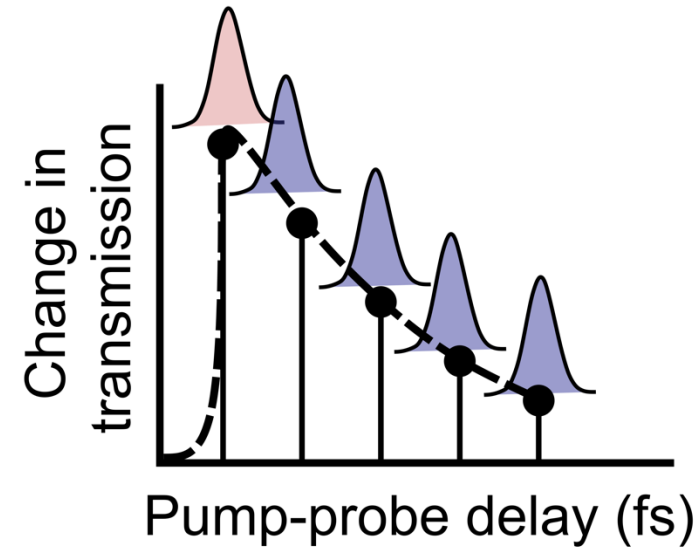
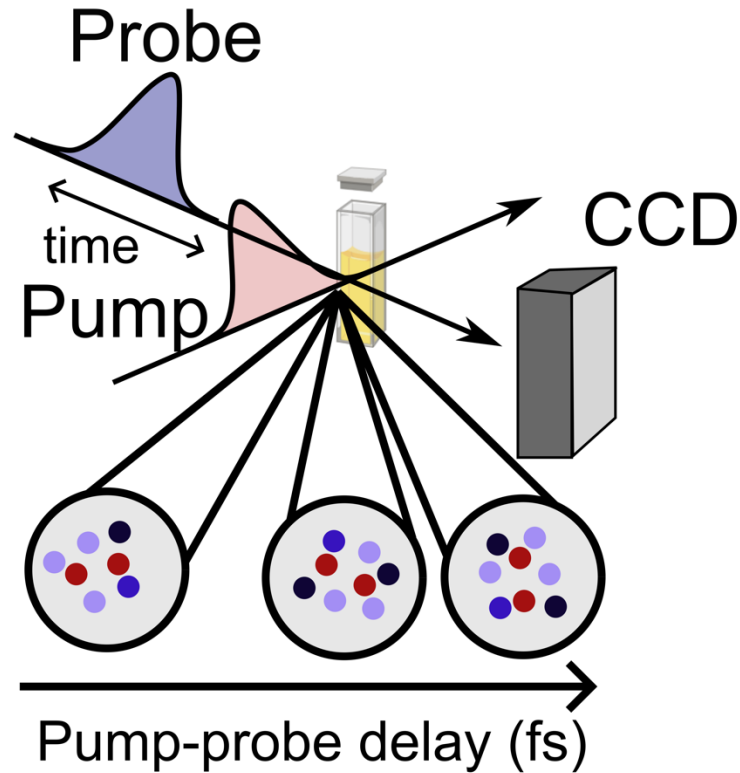


The importance of ultrafast timescales in batteries



We have a disconnect between microscopic observables (which we may calculate) and macroscopic parameters to control

How do we watch ultrafast processes?

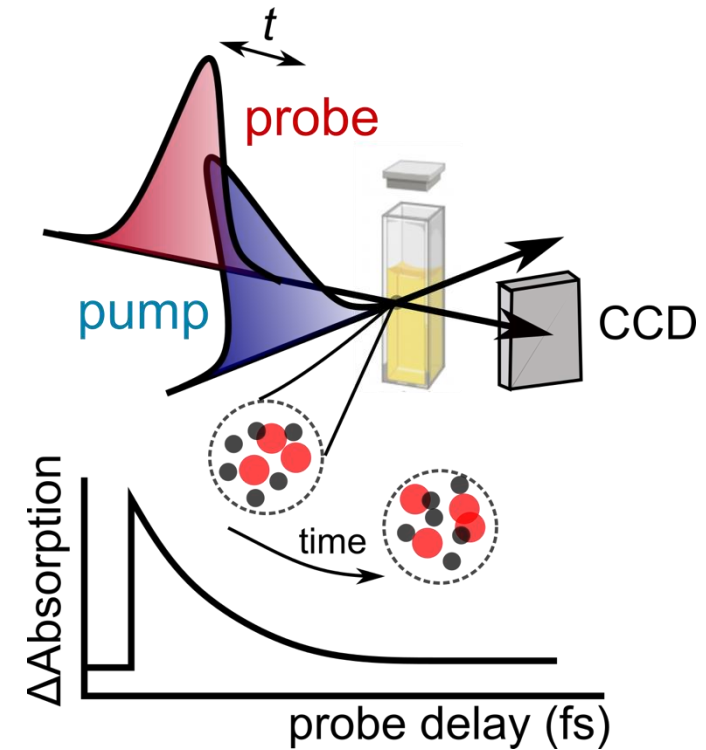
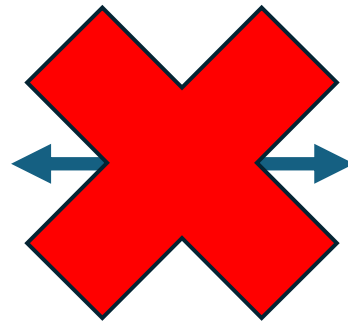
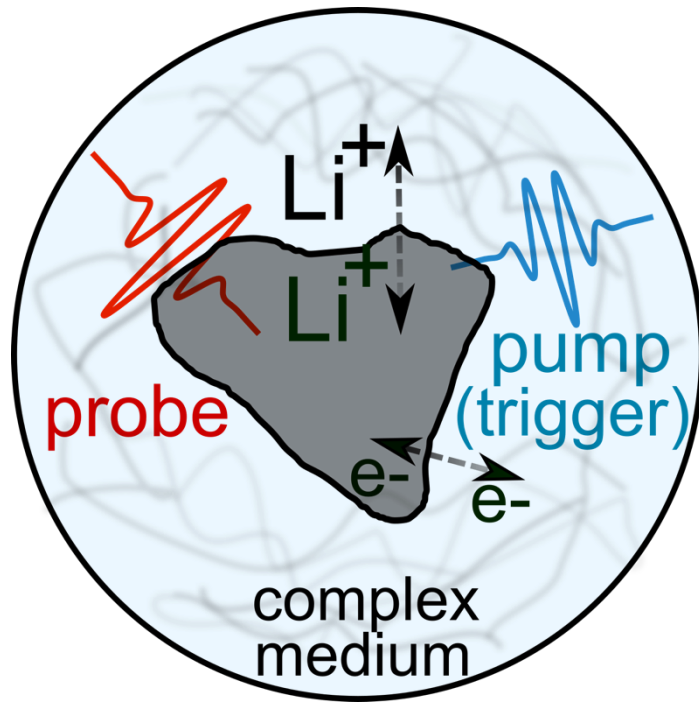


Time resolution set by pulse duration

Femtoseconds (Nobel Prize 1993), Attoseconds (Nobel Prize 2024)

Can we apply the pump-probe approach to batteries?

Battery?



Pump-probe spectroscopy:
light driven dynamics in solutions/films

How do we probe ultrafast processes in materials when they are not photoactivated?

What is non-linear spectroscopy and why do we need it?

$$H_{\text{int}}(t) = -\mu \cdot E(t)$$

Basic interaction dipole
for spectroscopy

$$P(t) = N \langle \mu(t) \rangle$$

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P}{\partial t^2}$$

We measure
polarisation density

$$P(t) = \epsilon_0 \left[\chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \dots \right]$$

Expanding in the
material response

What is non-linear spectroscopy and why do we need it?

$$P(t) = \int_{-\infty}^t dt' \chi^{(1)}(t - t') E(t')$$

The time correlations of the system are linked to their optical response

$$\chi^{(1)}(t) = \frac{i}{\hbar} \Theta(t) \langle [\mu(t), \mu(0)] \rangle$$

$$\mu(t) = \mu(Q(t))$$

$$C_Q(t) = \langle Q(t) Q(0) \rangle$$

Spectra are Fourier transforms of correlation functions

$$I(\omega) \propto \text{Im} \int_0^\infty dt e^{i\omega t} \langle \mu(t) \mu(0) \rangle$$

What is non-linear spectroscopy and why do we need it?

$$P^{(n)} \longleftrightarrow \langle \mu(t_n) \cdots \mu(t_1) \mu(0) \rangle$$

Higher-order polarization involves multi-time correlations

$$C_2(t) = \langle \mu(t) \mu(0) \rangle$$

“How similar is the system at time t to itself at time 0?”

$$C_4(t_3, t_2, t_1) = \langle \mu(t_3 + t_2 + t_1) \mu(t_2 + t_1) \mu(t_1) \mu(0) \rangle$$

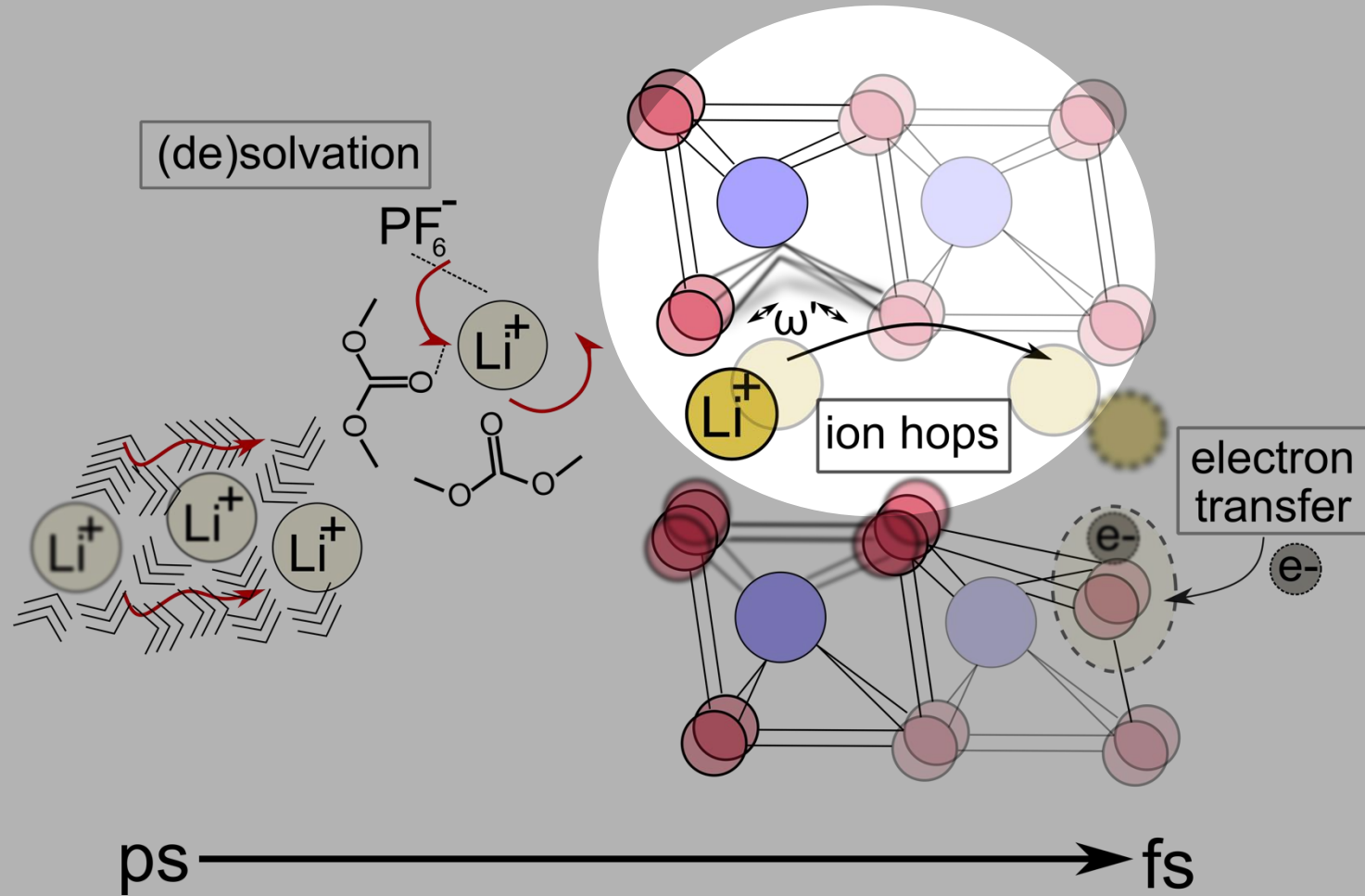
“If the system had frequency ω_1 earlier, how correlated is it with its frequency later?”

Two-point statistics fully
characterize a process
**only if it is Gaussian and
stationary**

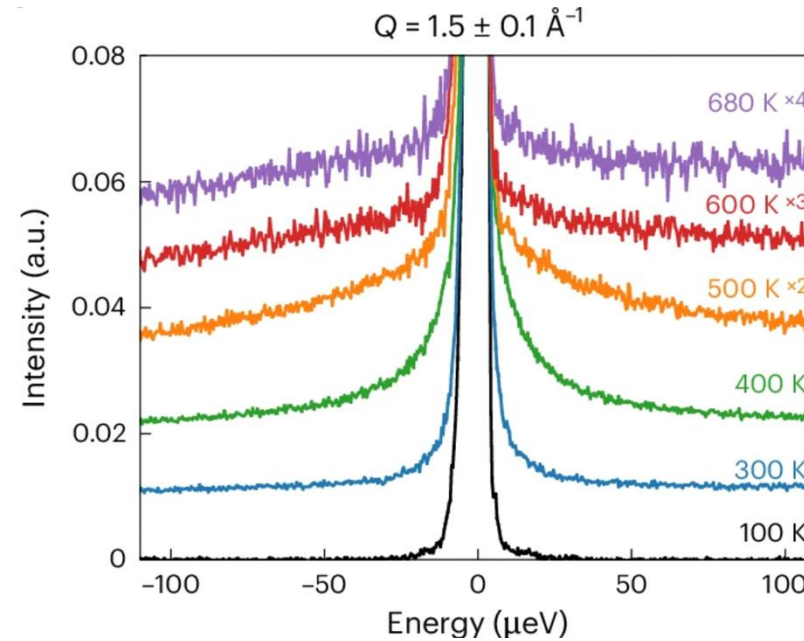
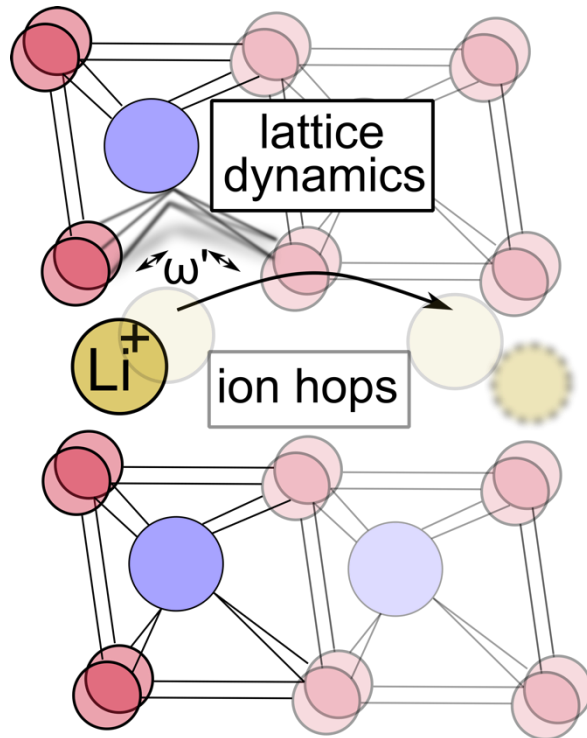
Four-point function
measures **fluctuation
correlations across time
intervals.**

= Non-linear
spectroscopy

Ultrafast dynamics in batteries



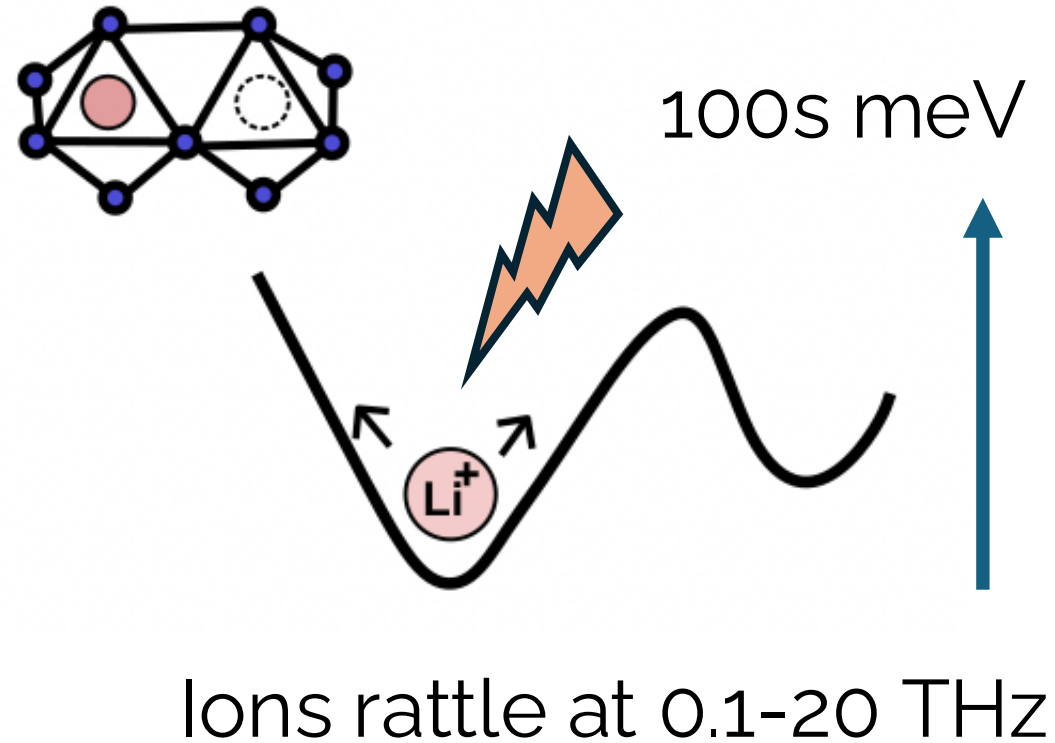
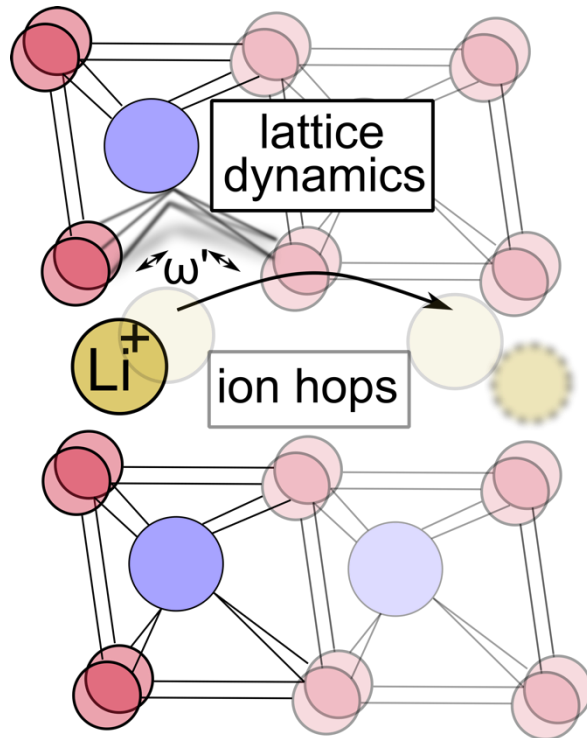
Linear spectroscopies are still powerful



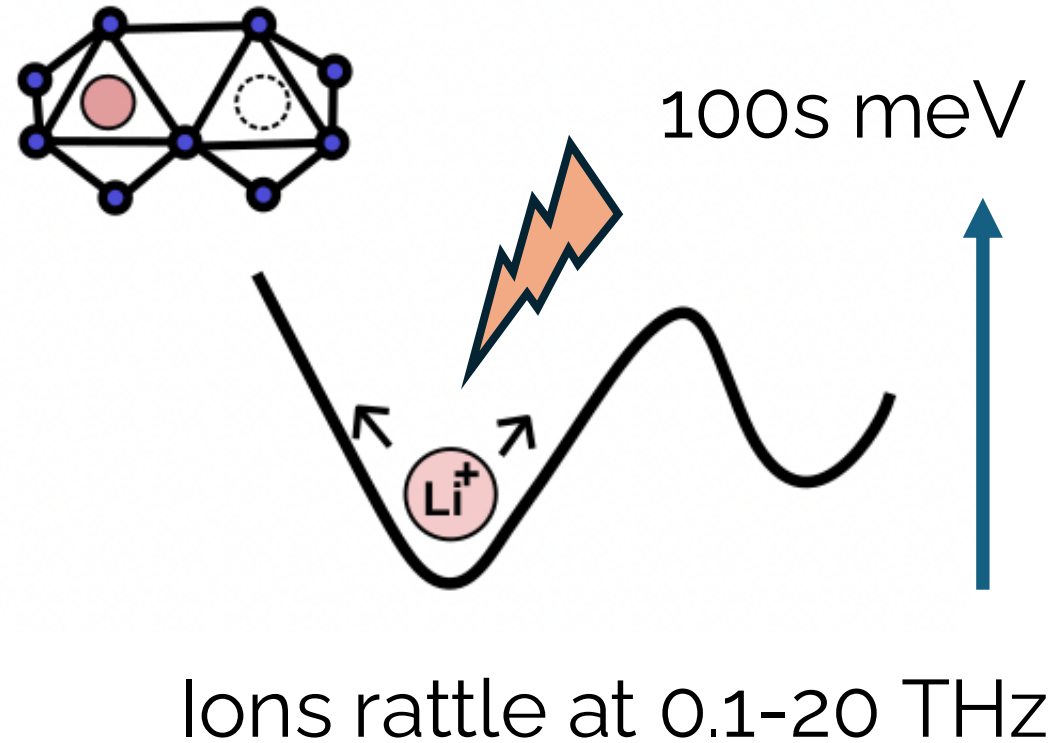
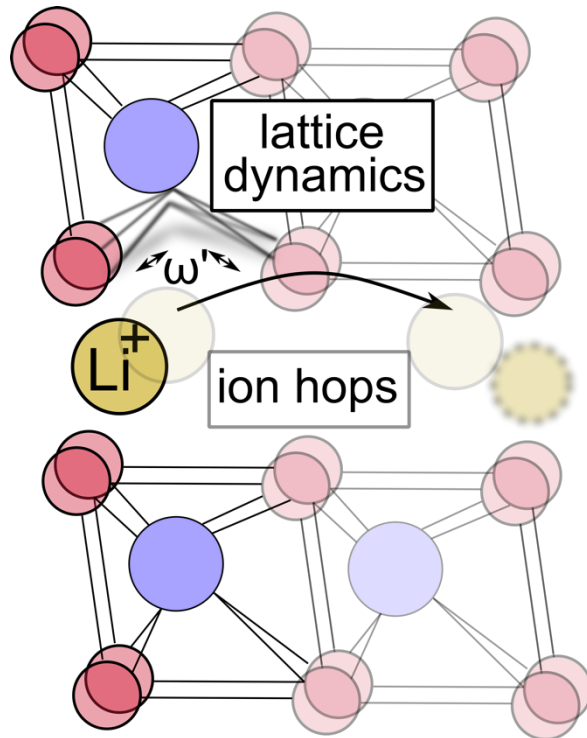
$$D = \frac{1}{3} \int_{-\infty}^{\infty} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle dt,$$

How do we probe ultrafast processes in materials when they are not photoactivated?

Capturing ion motion in batteries



Capturing ion motion in batteries

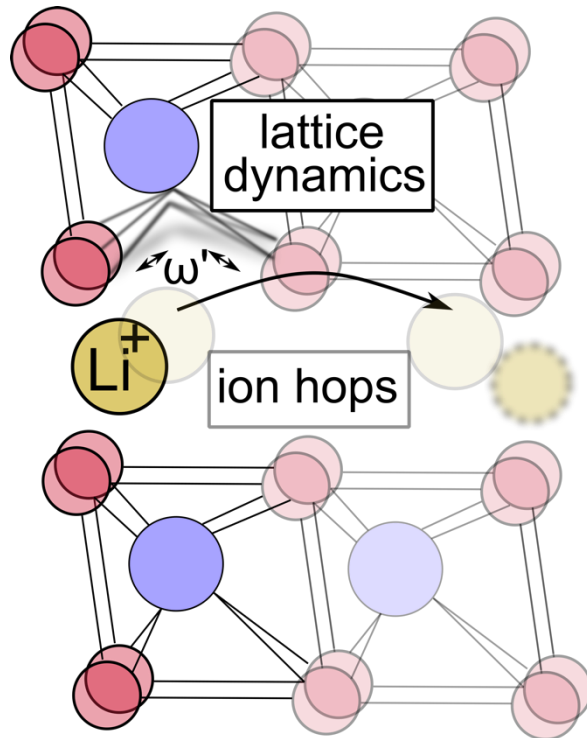


Exciting ions with THz light: 0.1-3 THz limit

The driving field is slow compared to the intrinsic vibrational or relaxation rates of ionic motion

How can THz light induce ion motion.

Case 1

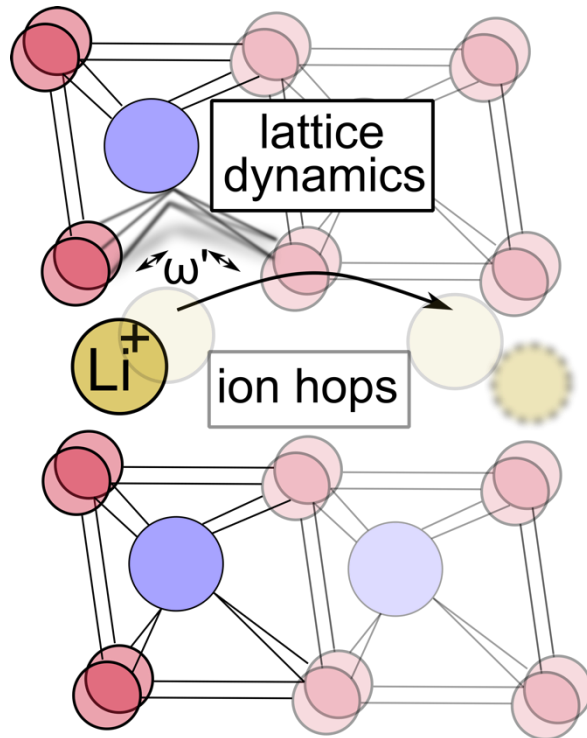


$$m\ddot{x} + m\gamma\dot{x} + m\omega_0^2x = qE(t)$$

Ion (or an effective
normal-mode
coordinate)
with charge q and
displacement $x(t)$ along
the field $E(t)$:

How can THz light induce ion motion.

Case 1

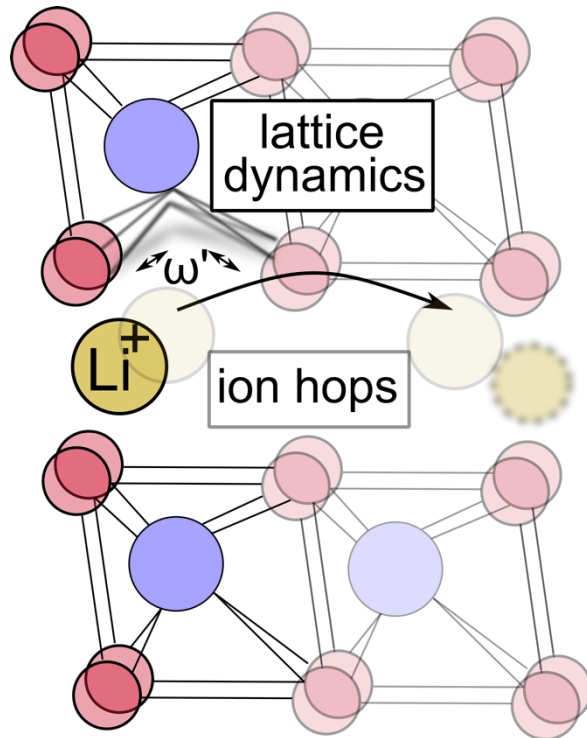


$$\chi(\omega) = \frac{Nq^2}{\epsilon_0 m} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

If ω_0 is in the THz range (soft phonon, rattling mode, intersite vibration), the response is resonantly large

How can THz light induce ion motion.

Case 2

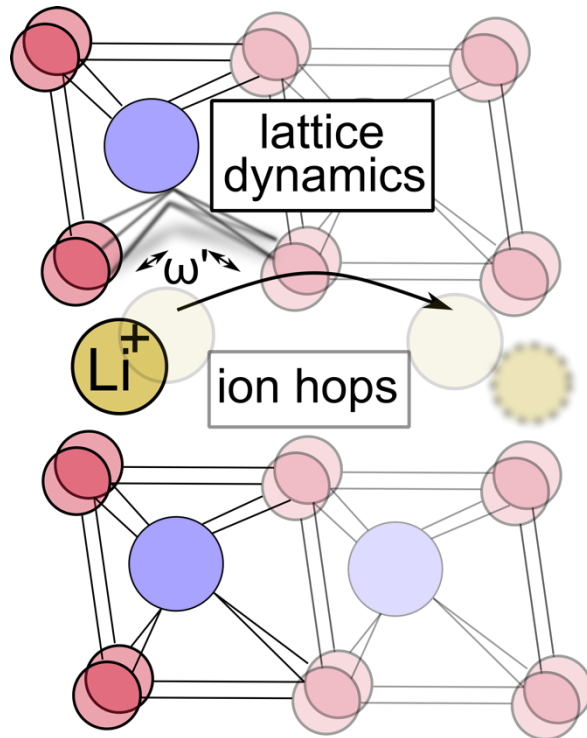


$$M\ddot{Q} + M\Gamma\dot{Q} + M\Omega^2Q = Z^*E(t)$$

For an IR-active phonon/ionic normal mode Q with effective charge Z^* and reduced mass M

How can THz light induce ion motion.

Case 2

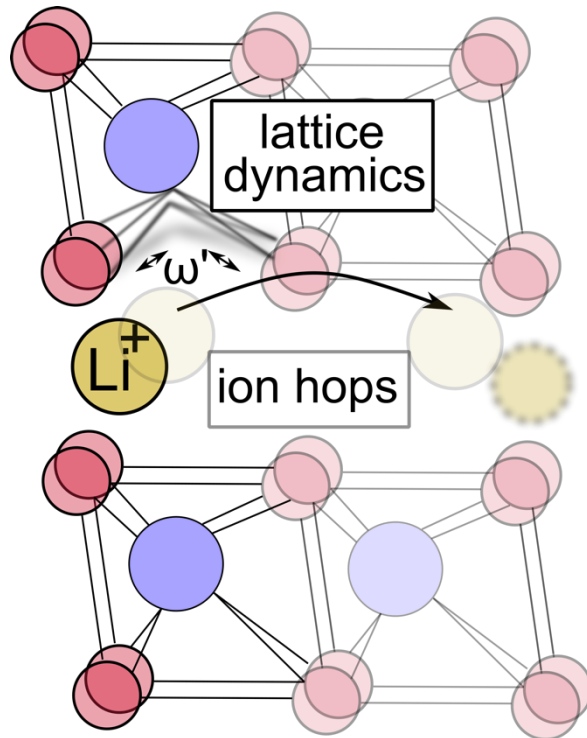


$$\chi(\omega) = \frac{N(Z^*)^2}{\epsilon_0 M} \frac{1}{\Omega^2 - \omega^2 - i\Gamma\omega}$$

THz couples to
polar phonons

How can THz light induce ion motion.

Case 3

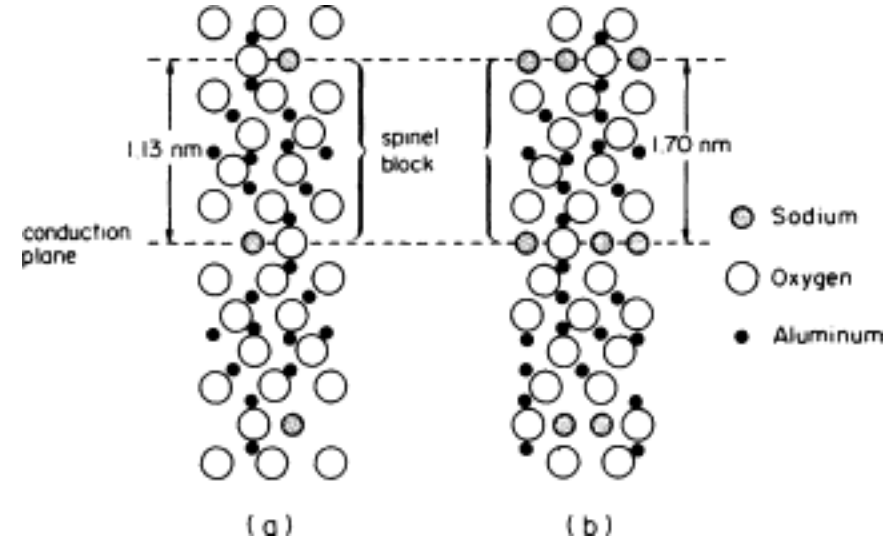
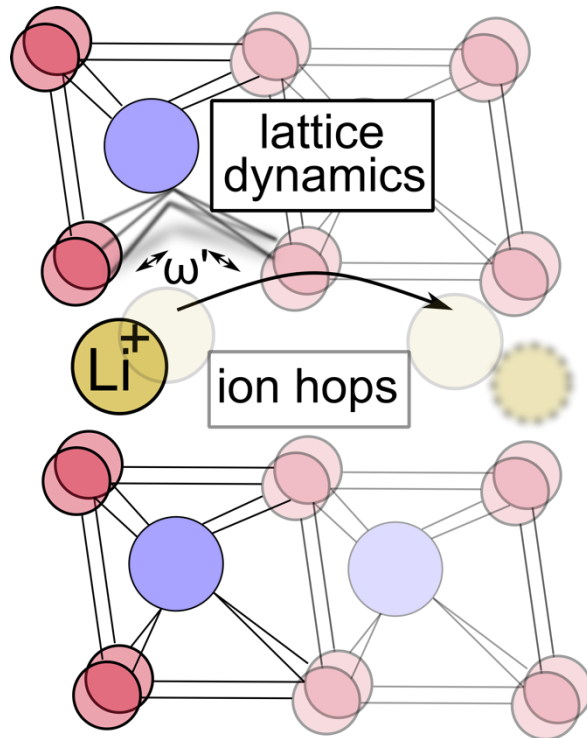


$$m\dot{v} + \frac{m}{\tau}v = qE(t)$$

$$\epsilon(\omega) = \epsilon_{\text{lat}}(\omega) + \frac{i\sigma(\omega)}{\epsilon_0\omega}$$

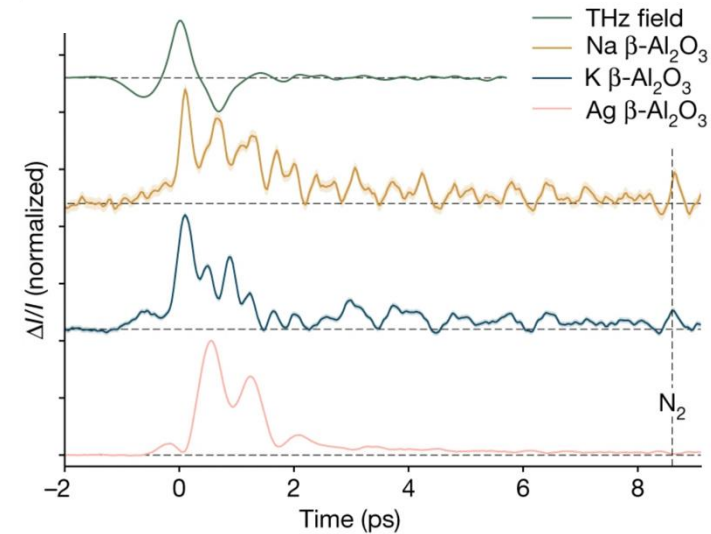
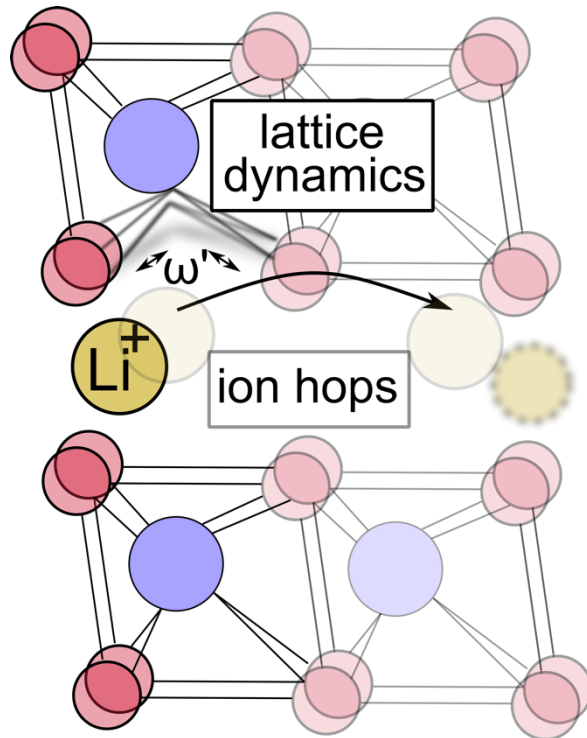
THz excites ionic motion as an AC conduction response

Example 1: Sodium Beta Alumina – applying case 1



Distinct phonon modes in 0.1-3 THz range = polarization dominated by ionic motion

Example 1: Sodium Beta Alumina – applying case 1

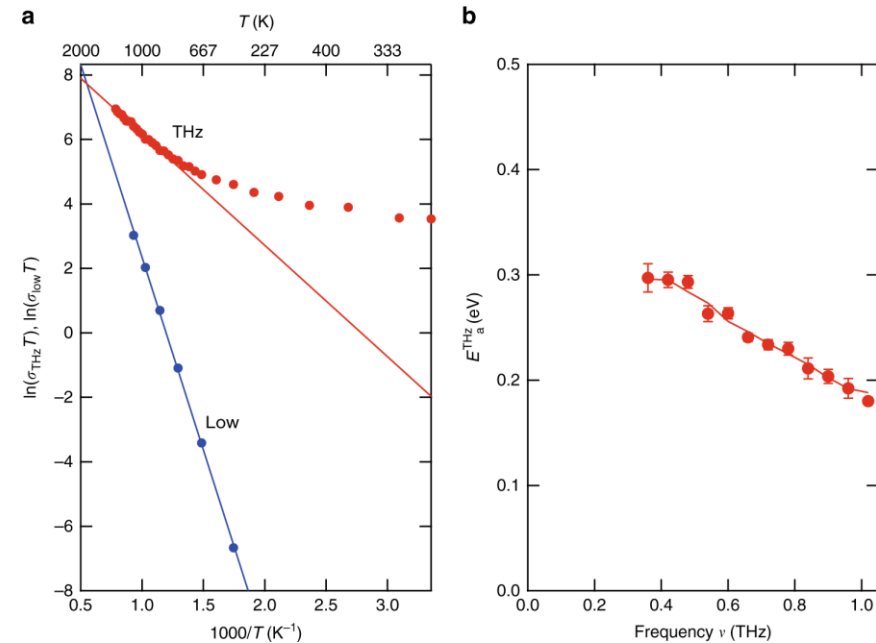
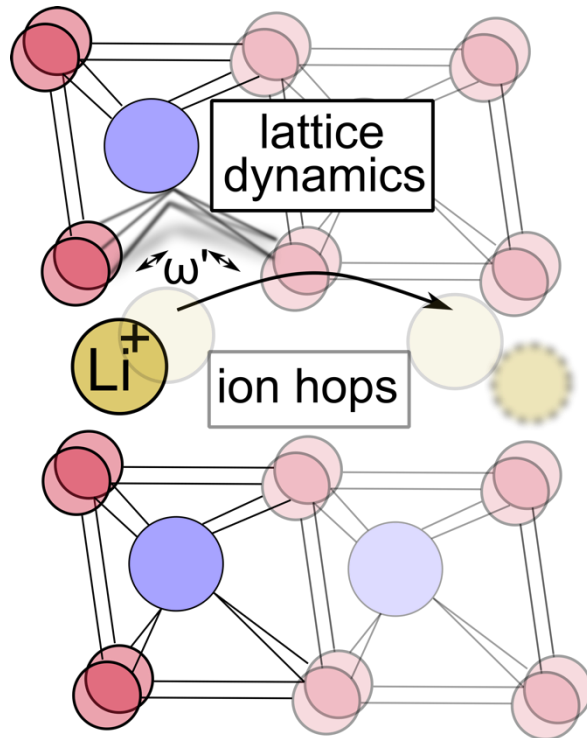


THz-Kerr spectroscopies reveal:

- Time scales of ion hops
- Anisotropy in ion dynamics and memory of ion hops
- Kerr directly probes polarisation

Key refs: Nature 625, 691–696 (2024)
Phys. Rev. Lett. 124, 147401 (2020)

Example 2: Zirconia – applying case 2

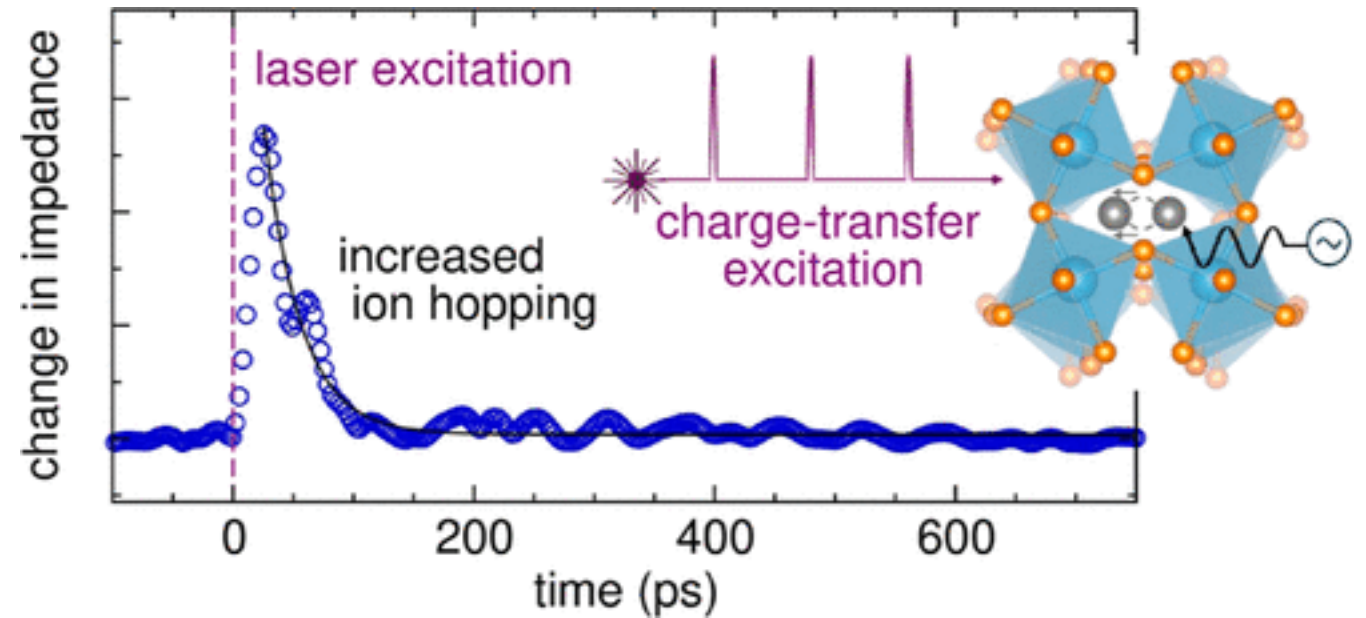
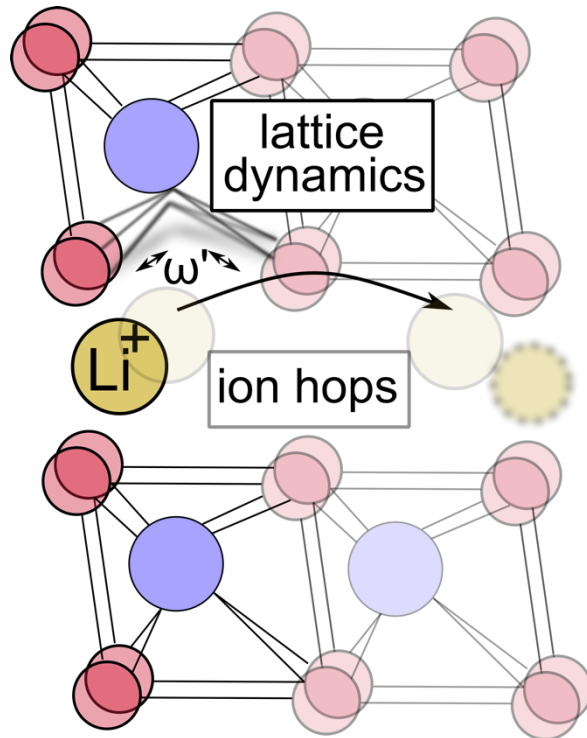


Field-resolved THz spectroscopies also reveal:

- ➔ Microscopic ionic conductivities
- ➔ Deviation from Arrhenius

Key ref: Nat. Commun.
10, 2662 (2019)

Example 3: LLTO – applying case 3*

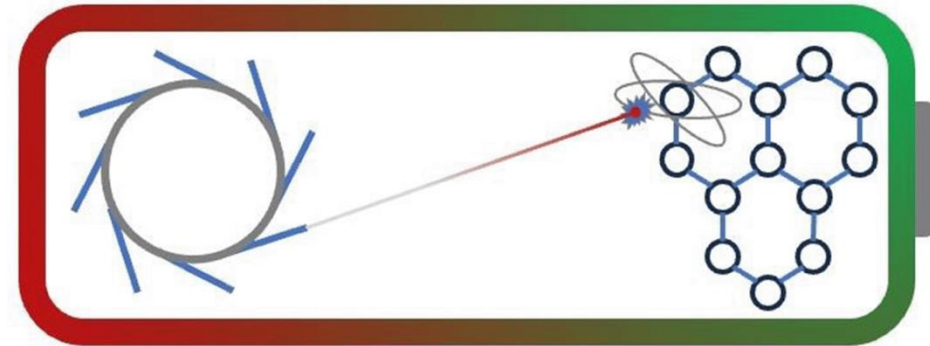
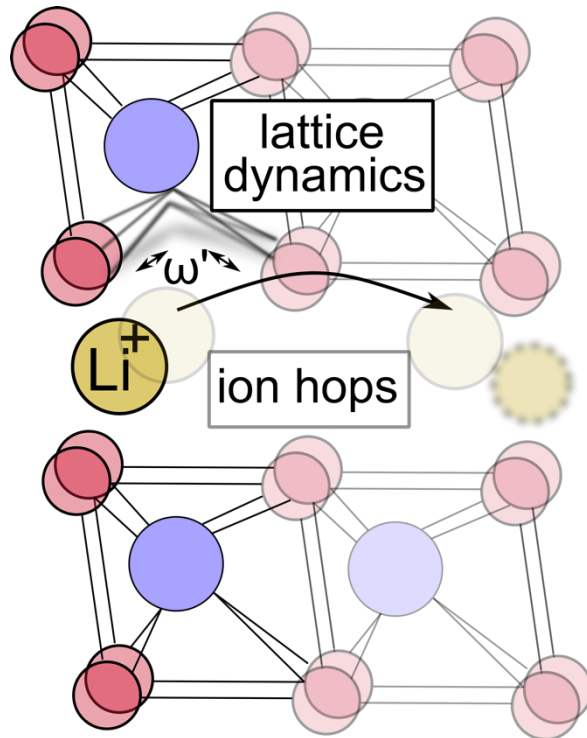


Optical pulse can maybe be used to drive ions:

- ➔ Involves complex charge transfer mechanism
- ➔ Route to light driven charging and further ultrafast probing

Key ref: J. Am. Chem. Soc.
2025, 147, 30, 26456–26467
Mater. Horiz., 2026, Advance Article

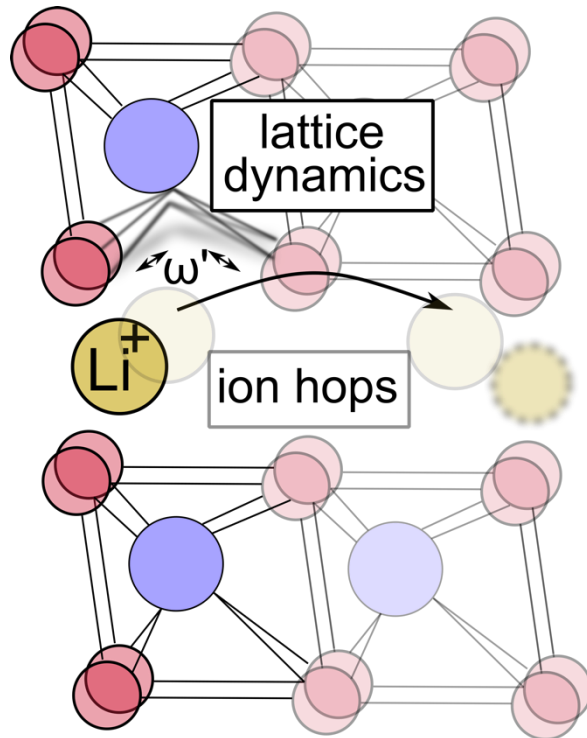
Trying to bring things together



UltraBat

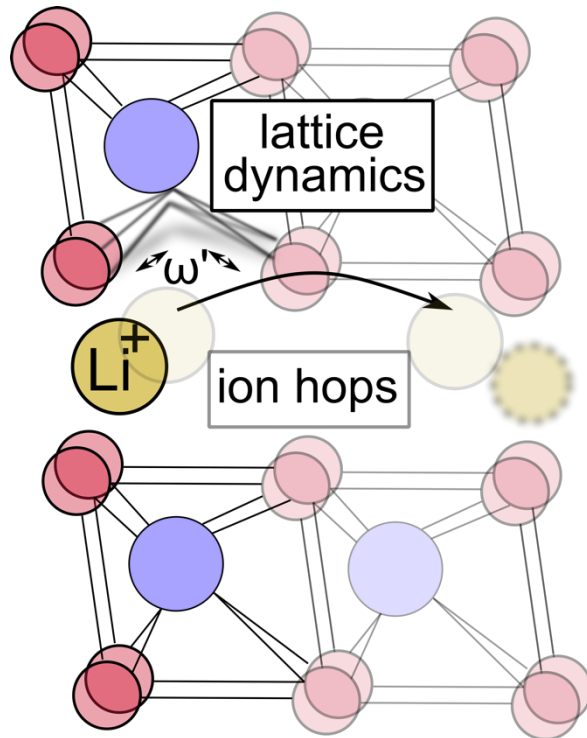
Can we come up with
other, more general
approaches?

Open questions



Does ion motion couple to the lattice motion?

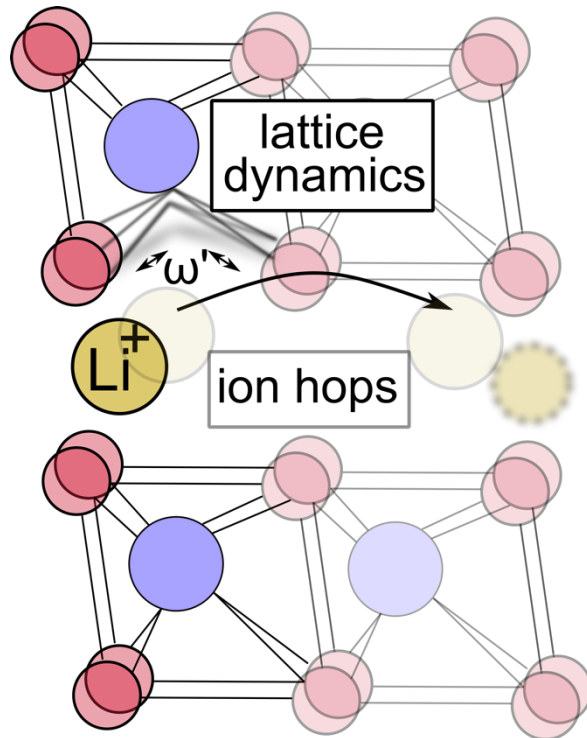
Open questions



Does ion motion couple to the lattice motion?

Can we read out structures of transition states?

Open questions

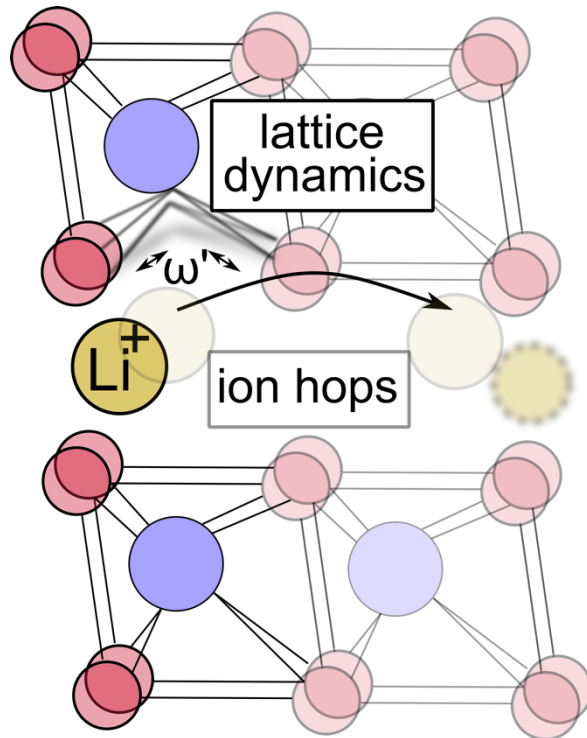


Does ion motion couple to the lattice motion?

Can we read out structures of transition states?

Can we macroscopically change ion conduction?

Open questions



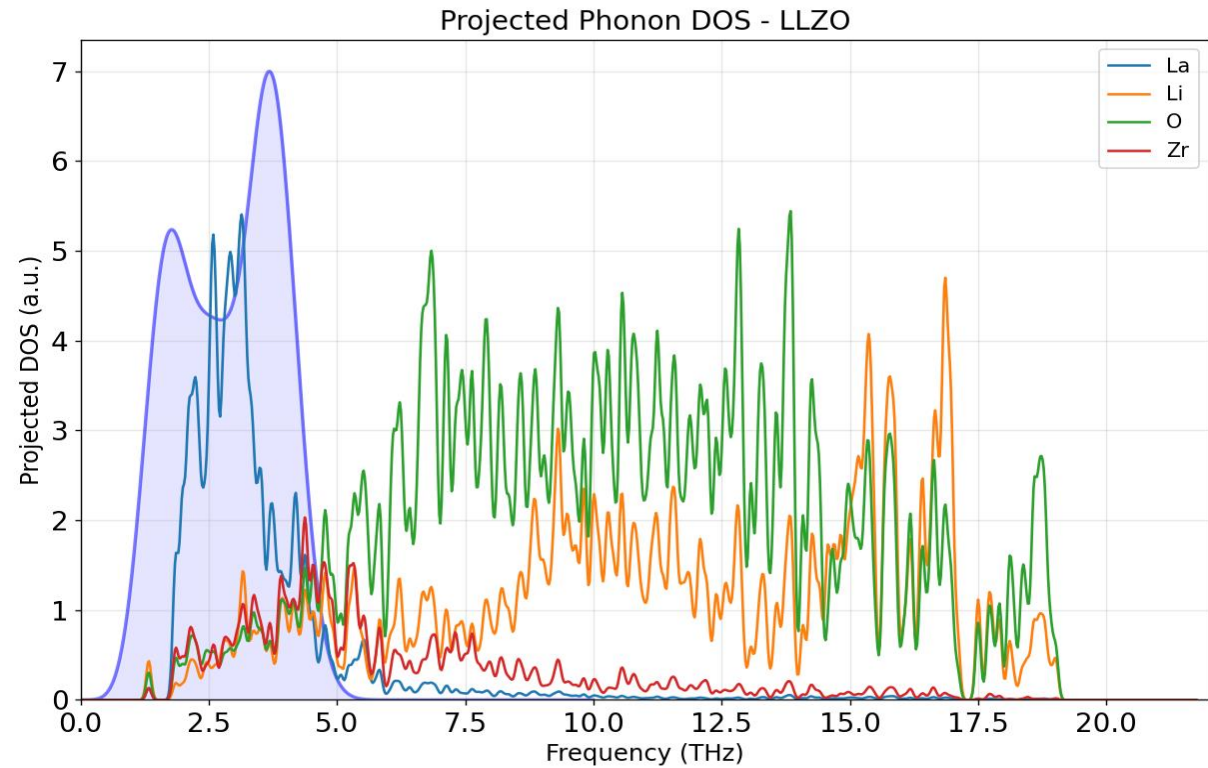
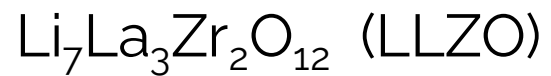
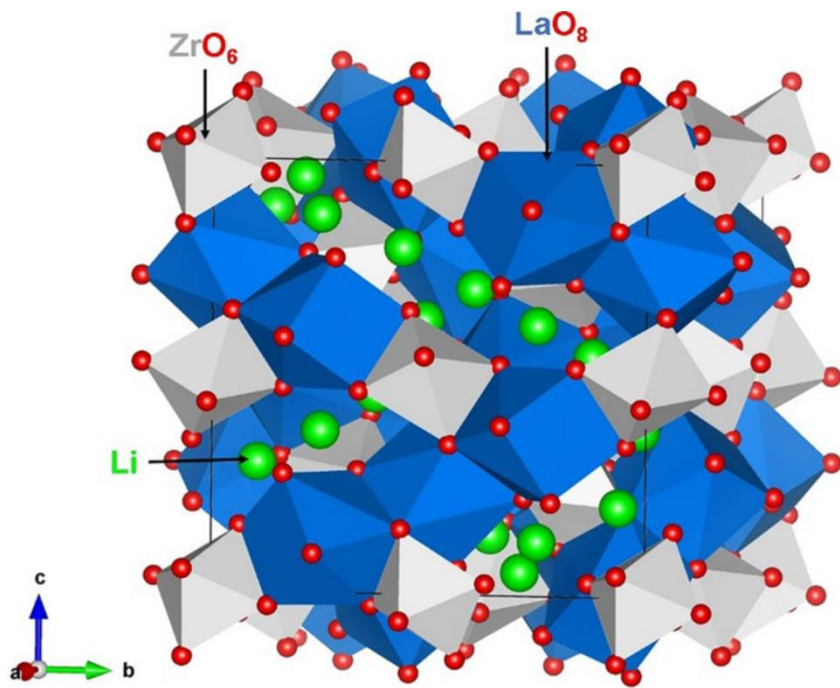
Does ion motion couple to the lattice motion?

Can we read out structures of transition states?

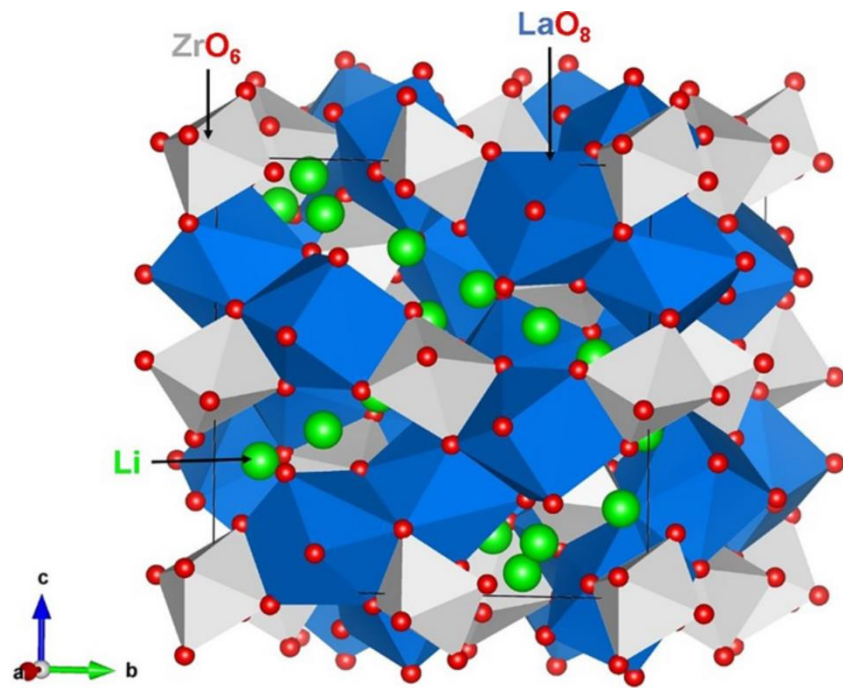
Can we macroscopically drive ion motion?

How do we get more dynamical information, can we go beyond THz?

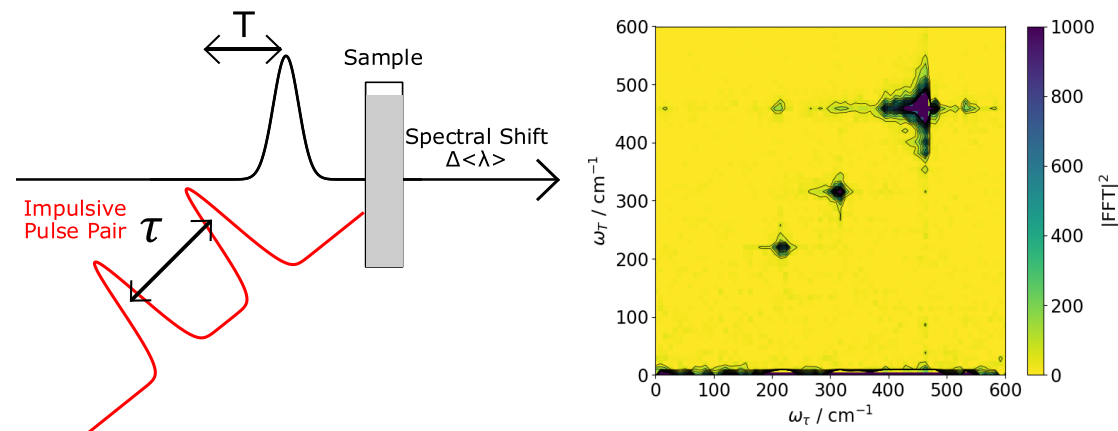
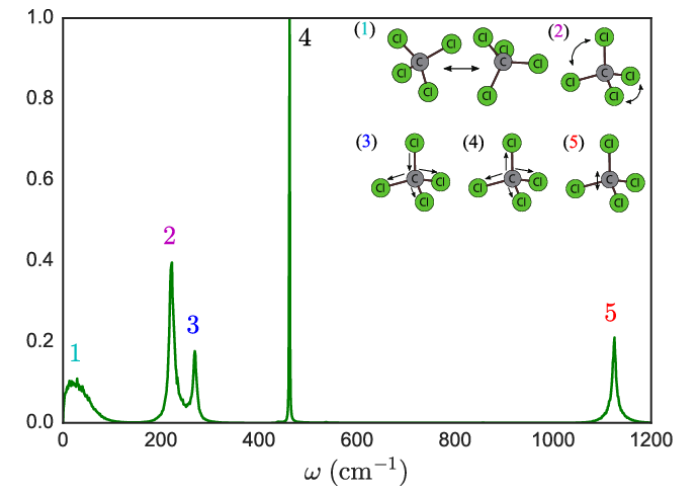
LLZO



LLZO – can we explore coupling between the lattice and ion motion



$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)

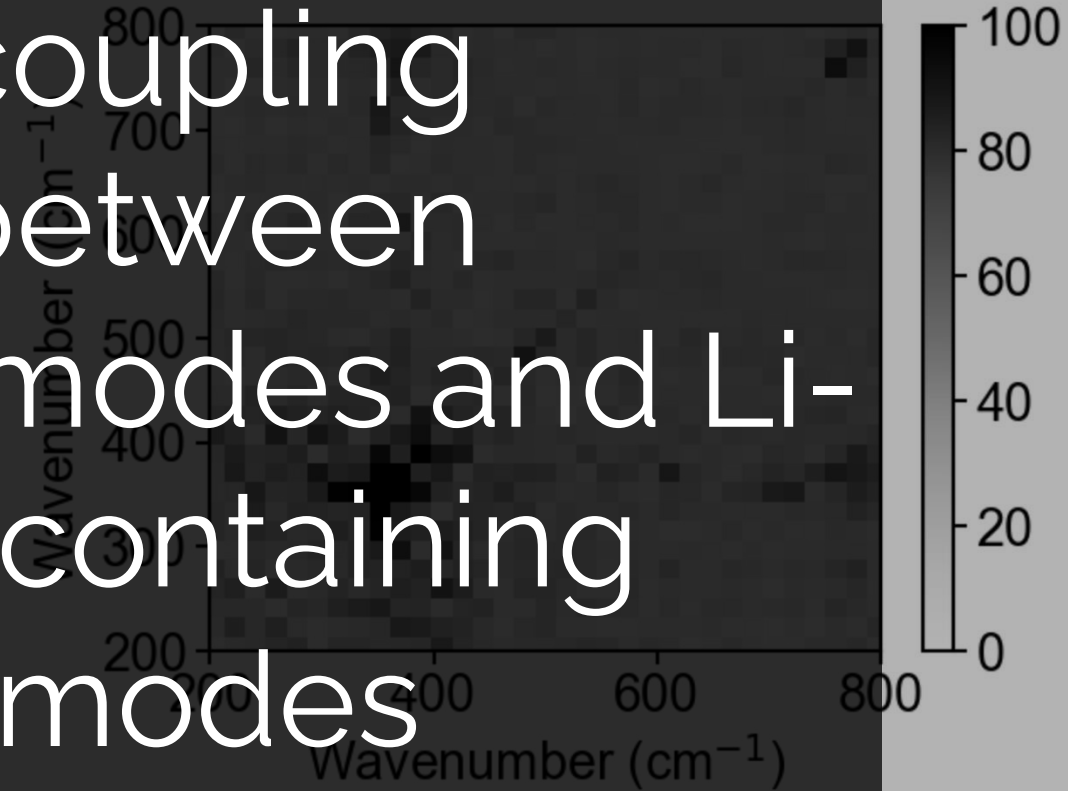
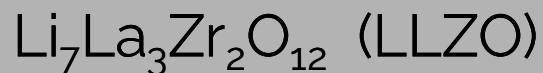
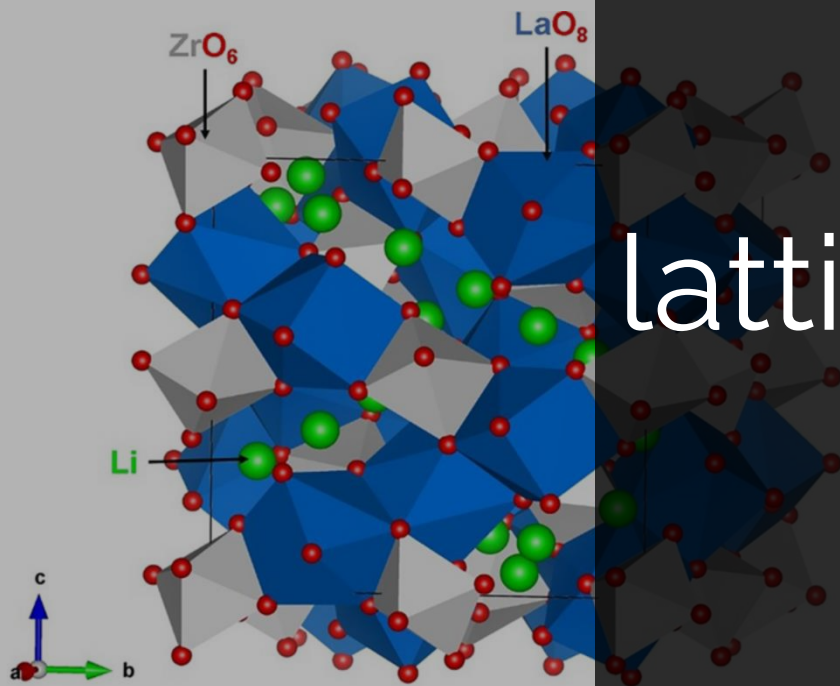


LLZO – can we explore coupling between the lattice and ion motion

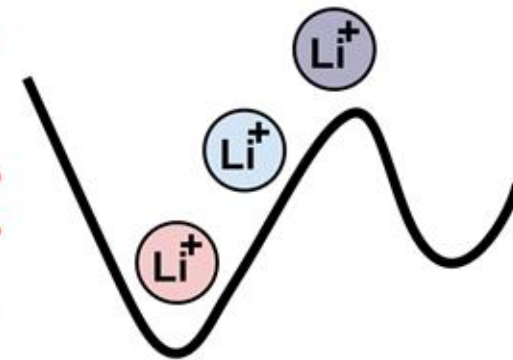
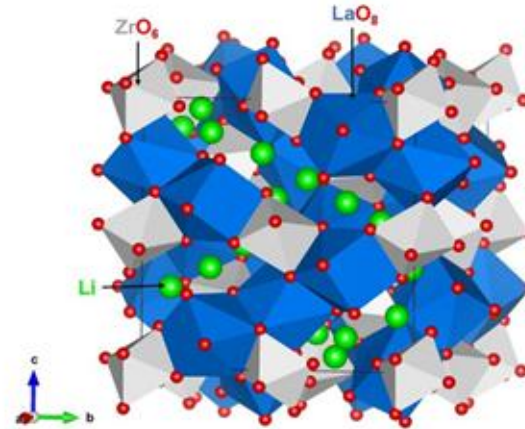
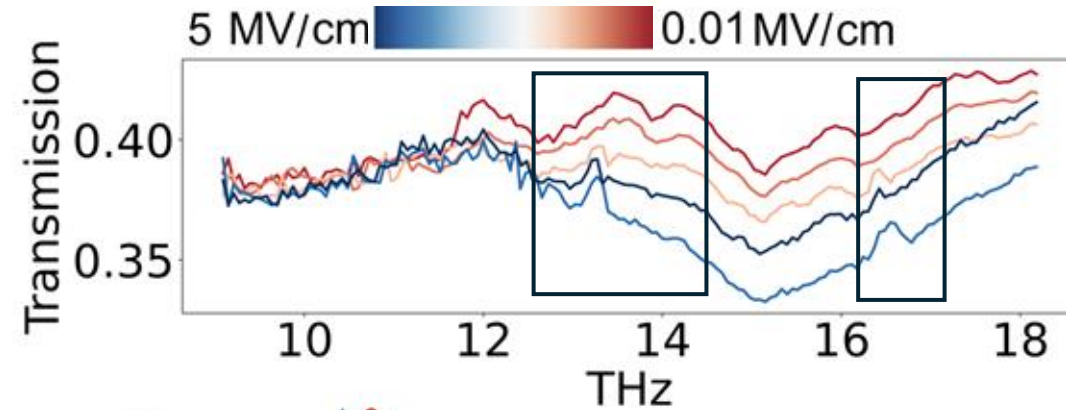
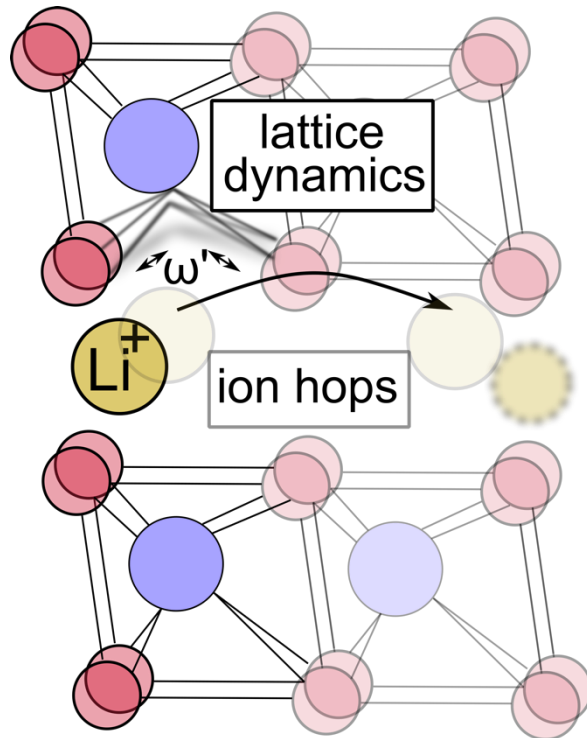
We do have

coupling
between

lattice modes and Li-
ion containing
modes



THz hole burning



THz pump diffraction probe

