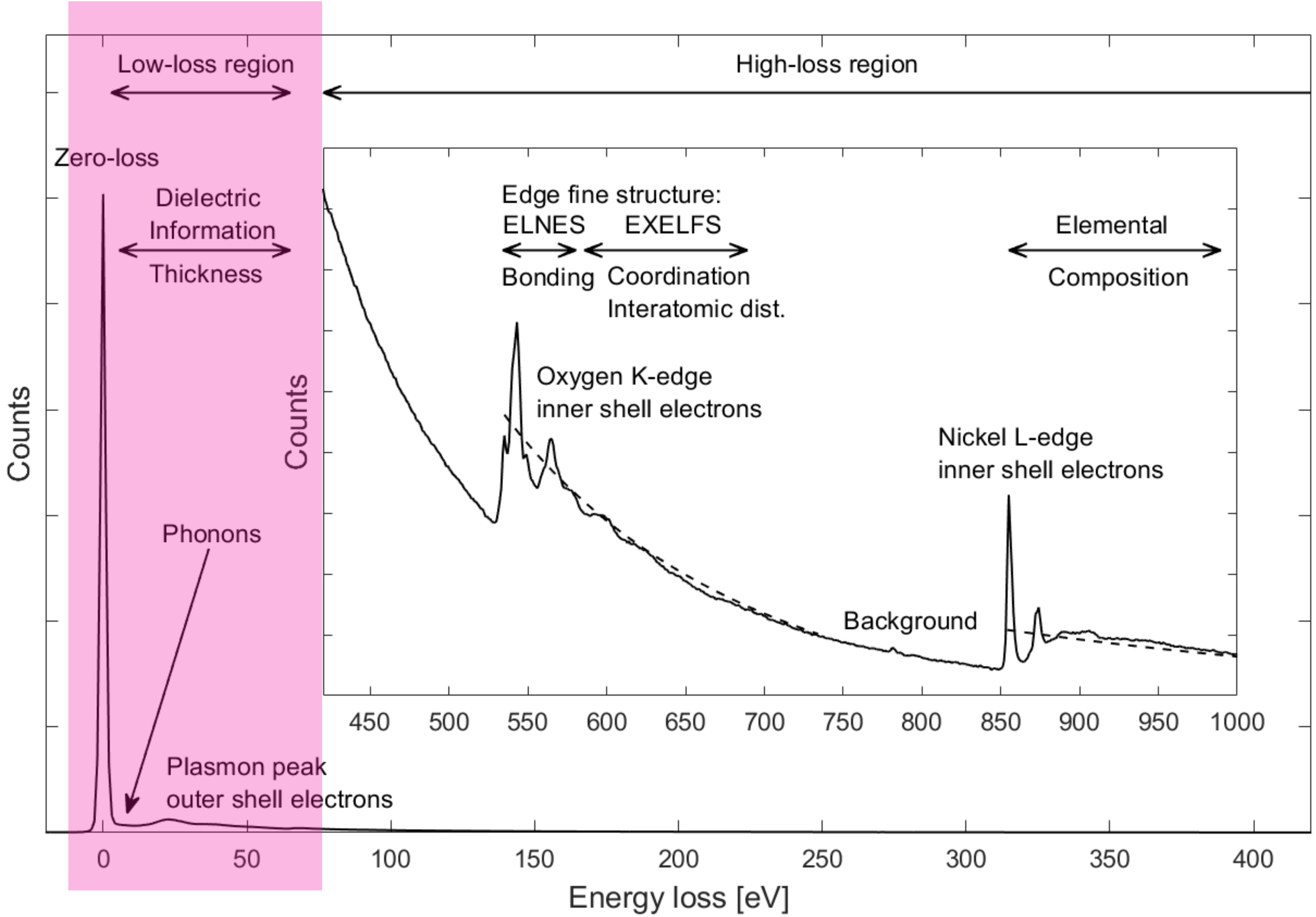
Quantitative Electron Microscopy 2025

Low-loss EELS and Cathodoluminescence

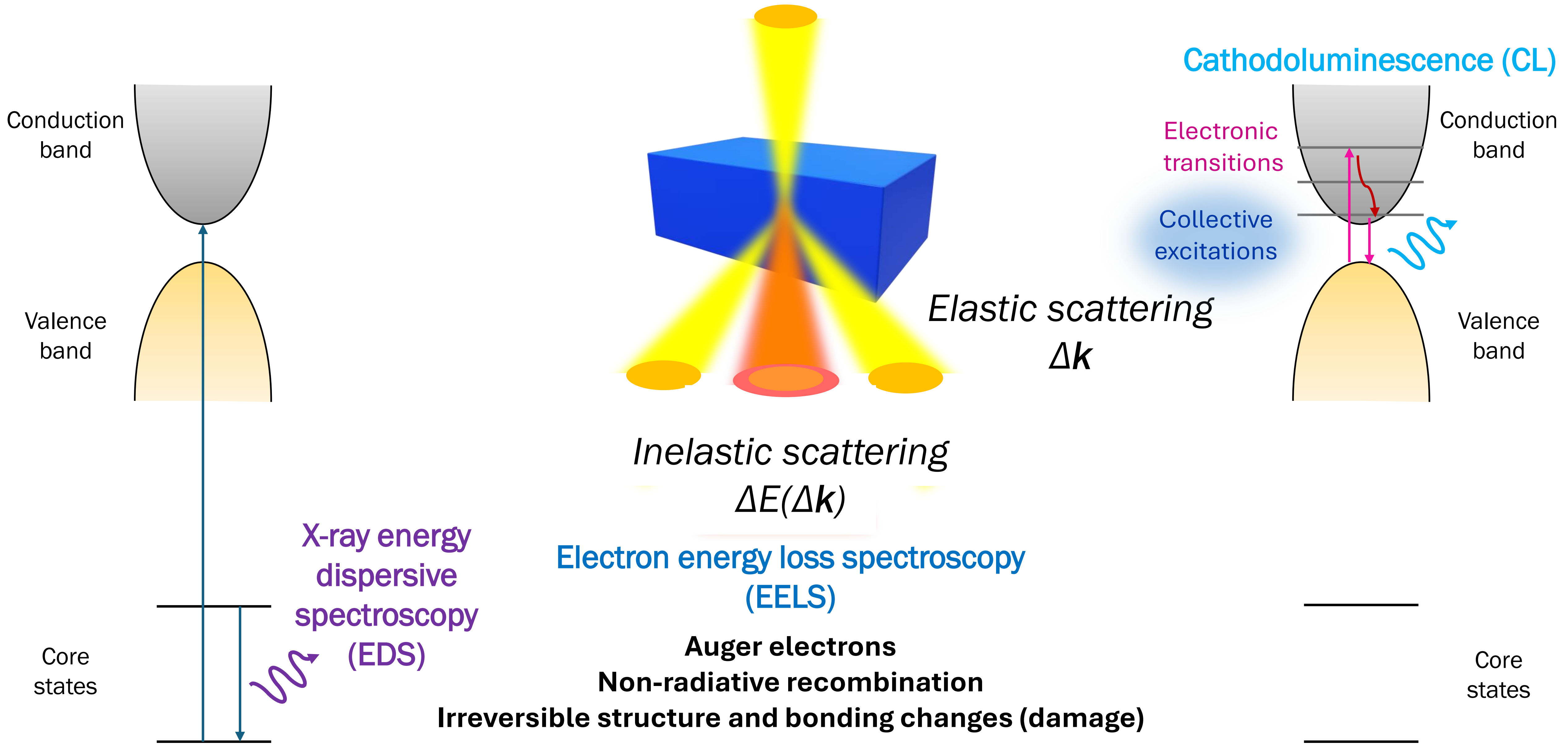
Sean Collins (s.m.collins@leeds.ac.uk)

Low-loss EELS

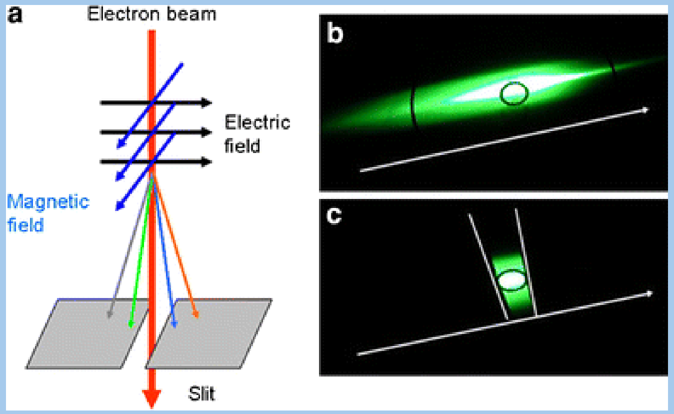


https://lampz.tugraz.at/~hadley/ss2/quasiparticles/eels/eels.php

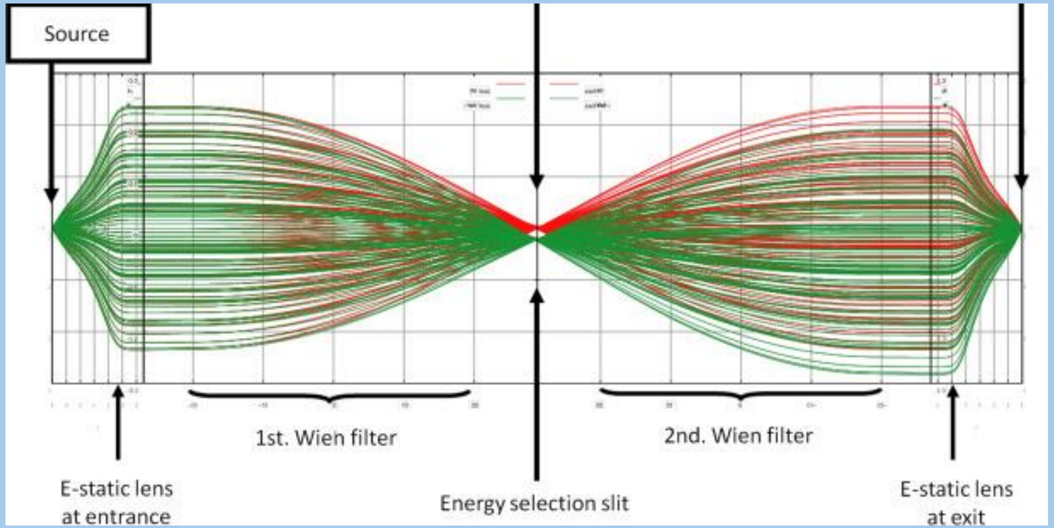
Overview of inelastic scattering processes in STEM: Excitation and relaxation pathways



Monochromators: Wien filter and magnetic sector approaches

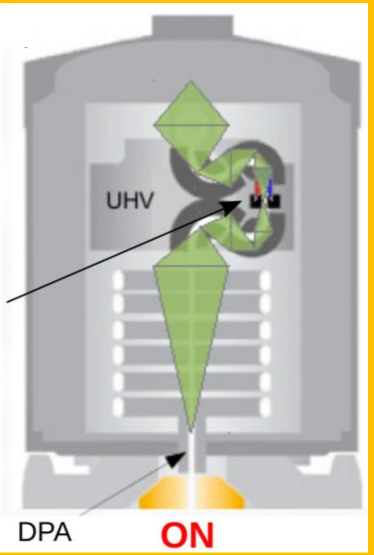


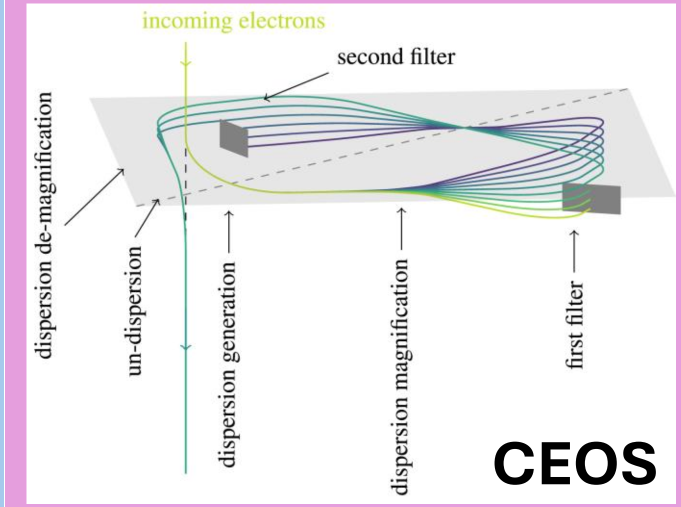
TFS



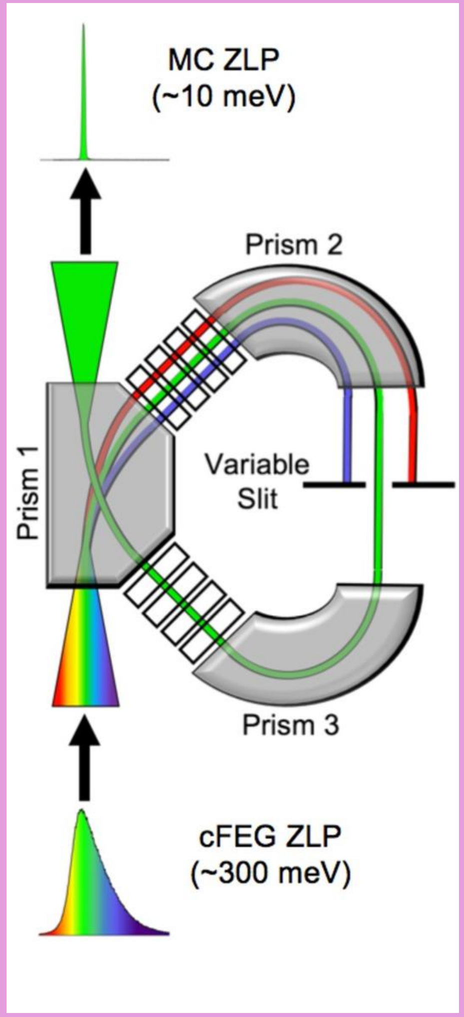
JEOL

CEOS





CEOS



Nion

https://link.springer.com/article/10.1007/s11244-008-9101-4
https://doi.org/10.1016/j.ultramic.2014.02.004

https://www.ceos-gmbh.de/en/produkte/monochromators
https://doi.org/10.1016/j.ultramic.2023.113805
https://www.nature.com/articles/s41598-018-23805-5

Reference points: Dielectric theory and Quantum descriptions

EELS of interband transitions, excitons & surface plasmons

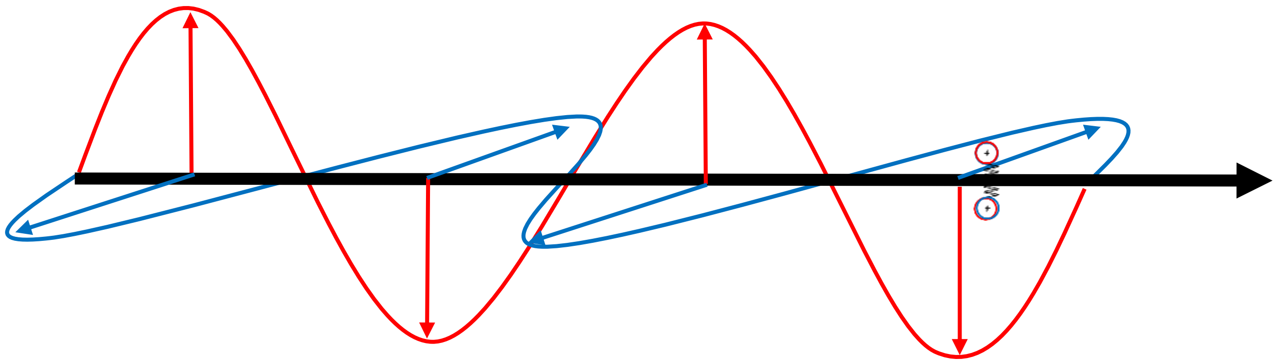
Demo: EELS of surface plasmon resonance modes

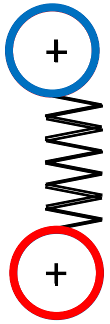
Light emission: Cathodoluminescence

Phonons

Light-driven transitions: Classical and Quantum pictures

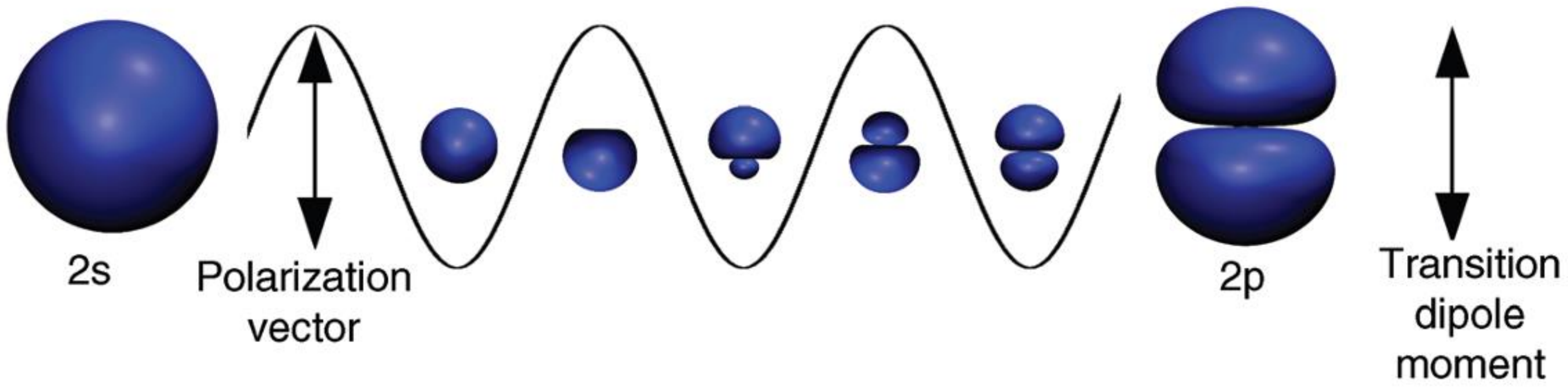
Classical picture: Oscillating electric and magnetic fields couple to charge oscillations (dipoles)





$$\Delta t \rightarrow \nu = \frac{c}{\lambda}$$

Quantum picture: Polarization in electric field couples to transition dipole

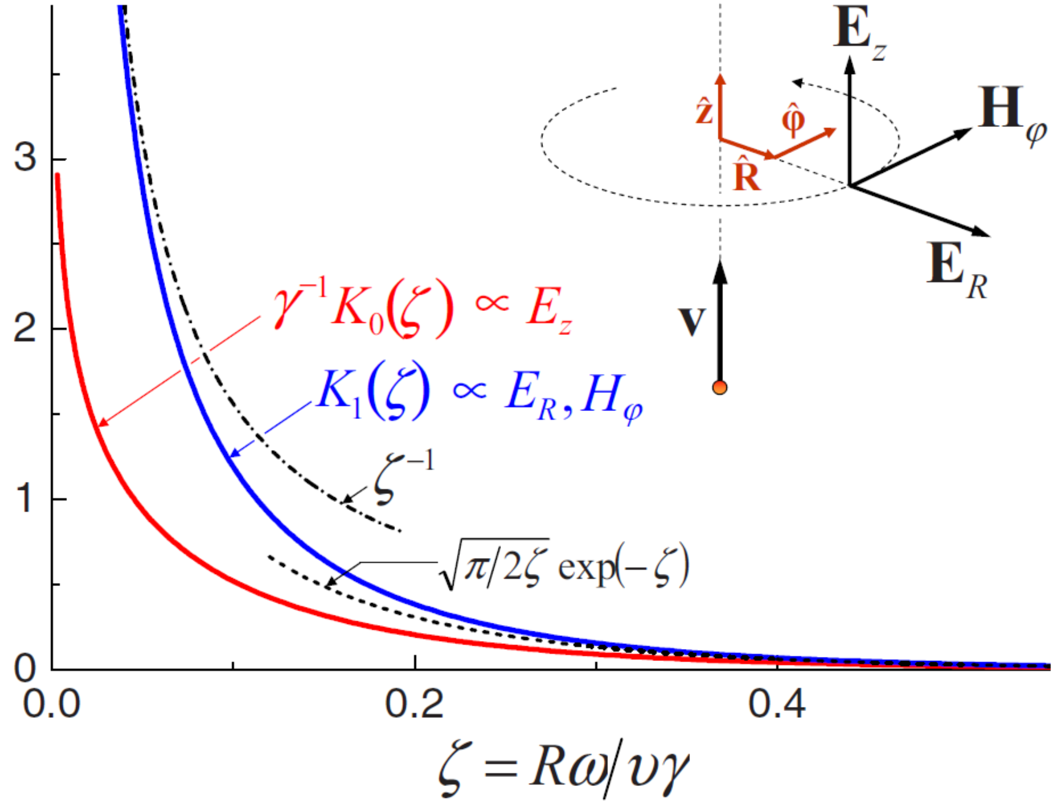


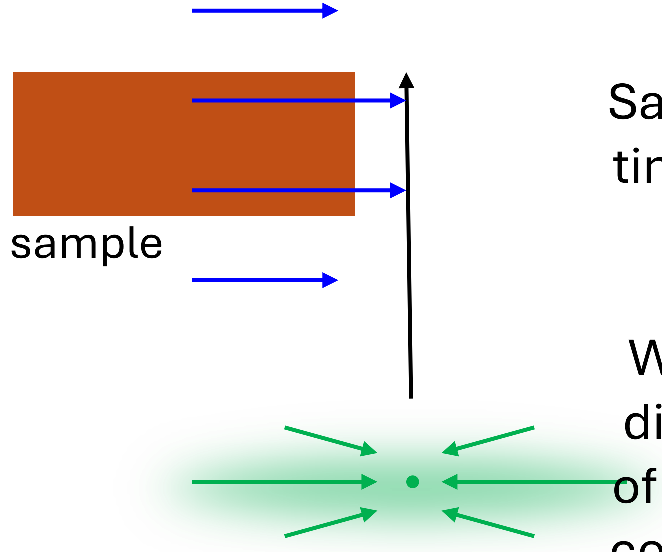
$$E = h\nu = \hbar\omega$$

P. J. Walla. *Modern Biophysical Chemistry: Detection and Analysis of Biomolecules*, Second Edition. Wiley-VCH, 2014.

Electron-driven transitions: Pulse-like excitation

Evanescent fields with transverse and longitudinal components





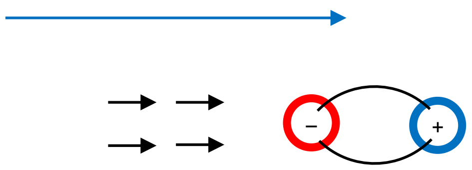
Sample sees time-varying **E**-field

With broad distribution of frequency components

J. García de Abajo *Rev. Mod. Phys.* **2010**, *82*, 209-275.

Dielectric response: Drude model for free electrons

Applied field (light, electron beam)



Material exhibits **polarization**
(drawn as dipoles emerging from electron density reorganisation in field)

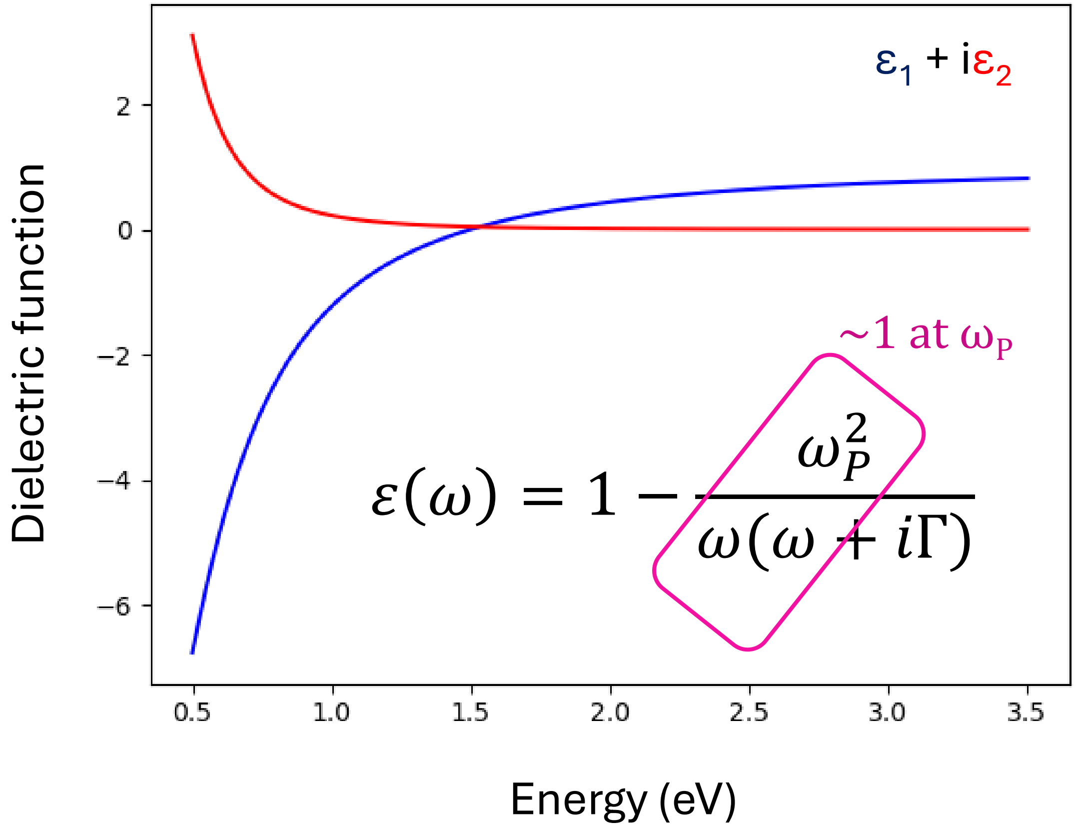
$$\mathbf{P} = (\varepsilon - \varepsilon_0)\mathbf{E}$$

$$\mathbf{P} = \varepsilon_0(\varepsilon_r - 1)\mathbf{E}$$

with $\varepsilon_r = \varepsilon/\varepsilon_0$

$$m_e\left[\frac{d^2}{dt^2}\mathbf{x} + \Gamma\frac{d}{dt}\mathbf{x}\right] = -q_e\mathbf{E}(t)$$

acceleration damping



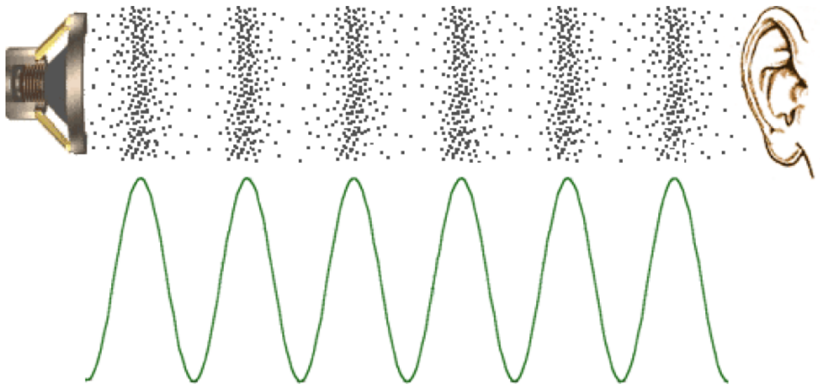
$$\varepsilon(\omega) = 1 - \frac{\omega_P^2}{\omega(\omega + i\Gamma)}$$

$$\omega_P = \sqrt{\frac{Nq_e^2}{m_e\varepsilon_0}}$$

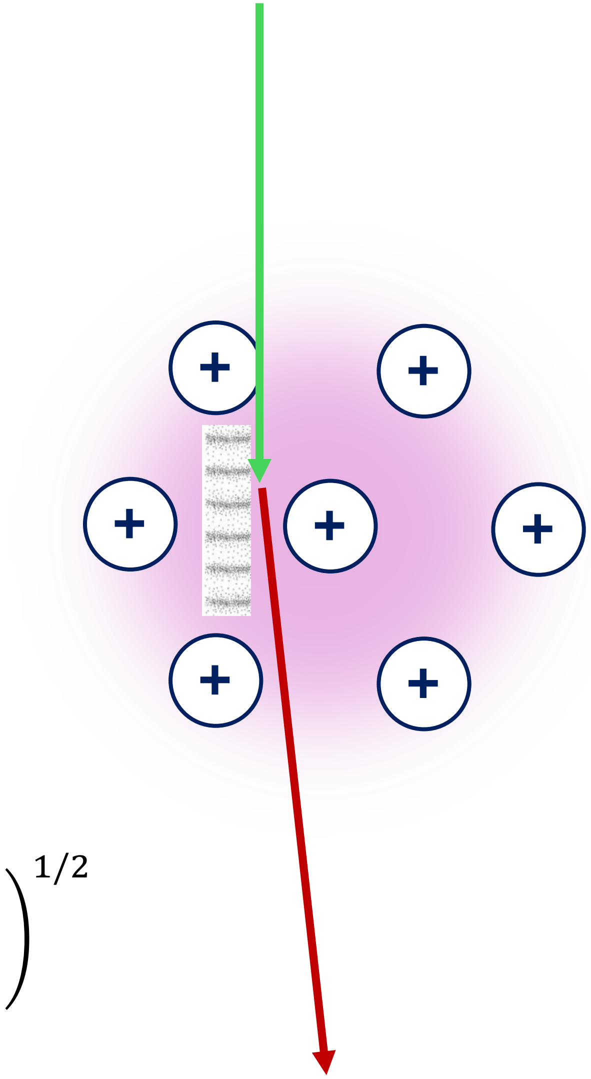
The plasma frequency: Longitudinal volume excitations

Collective excitations

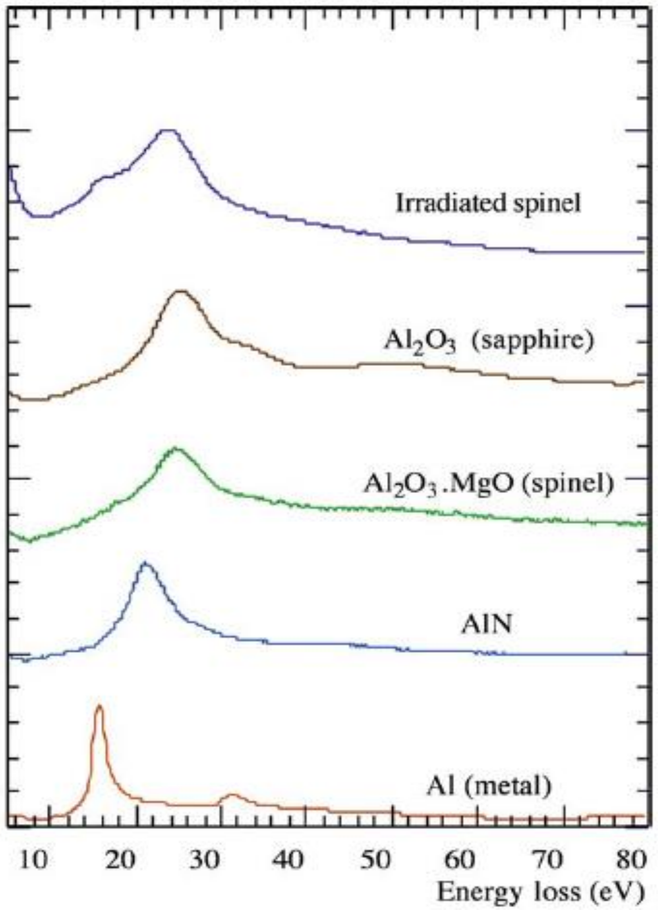
Bulk (volume) plasmons: longitudinal waves of valence electron density



http://musicweb.ucsd.edu/~trsmyth/sinusoids171/Sound_Wave.html



EELS



$$E_P^{met} = \hbar\sqrt{\frac{Nq_e^2}{m_e\varepsilon_0}}$$

Materials with bandgaps

$$E_P^{ins} = E_P^{met}\left(1 + \left(\frac{E_g}{E_P^{met}}\right)^2\right)^{1/2}$$

Bulk plasmon energies: a fingerprint of electron density

Asahina and Morita *J. Phys. C: Solid State Phys.* **1984**, *17*, 1839.

What does EELS measure?

When the bulk response dominates,
EELS tracks the loss function:

$$Loss = Im\left\{-\frac{1}{\varepsilon(\omega)}\right\}$$

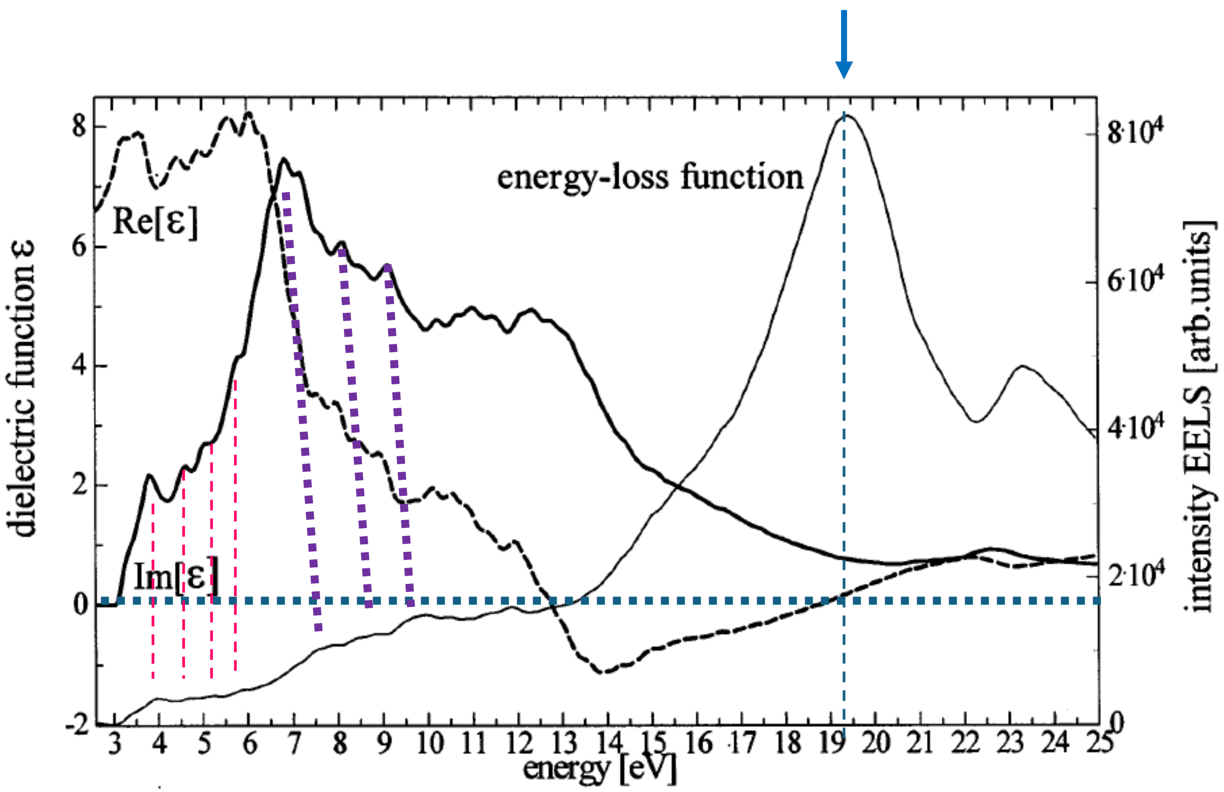
Assumes a single scattering distribution (SSD):
no ZLP tail, multiple scattering corrected

$$SSD = \frac{I_0 t}{\pi a_0 m_0 v^2} Im\left\{-\frac{1}{\varepsilon(\omega)}\right\} \ln\left[1+\left(\frac{\beta}{\theta_E}\right)^2\right]$$

t – thickness
β – collection angle
θ_E – characteristic angle (~$E/2E_0$)

a_0 – Bohr radius
m_0 – electron mass
v – electron velocity

Prominent bulk plasmon



$$Im\left\{-\frac{1}{\varepsilon}\right\} = Im\left\{-\frac{1}{\varepsilon_1 + i\varepsilon_2}\frac{\varepsilon_1 - i\varepsilon_2}{\varepsilon_1 - i\varepsilon_2}\right\} = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}$$

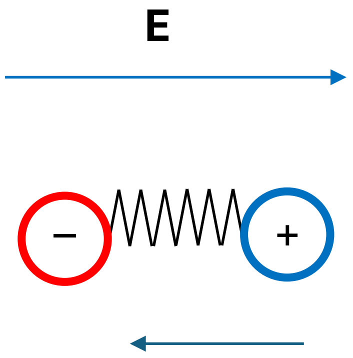
Denominator at minimum for $\varepsilon_1 = 0$

Where ε_1 ~ constant, ε_2 peaks match EELS peaks

Where ε_1 decreases (denominator decreases), EELS peaks slightly shifted relative to ε_2 peaks

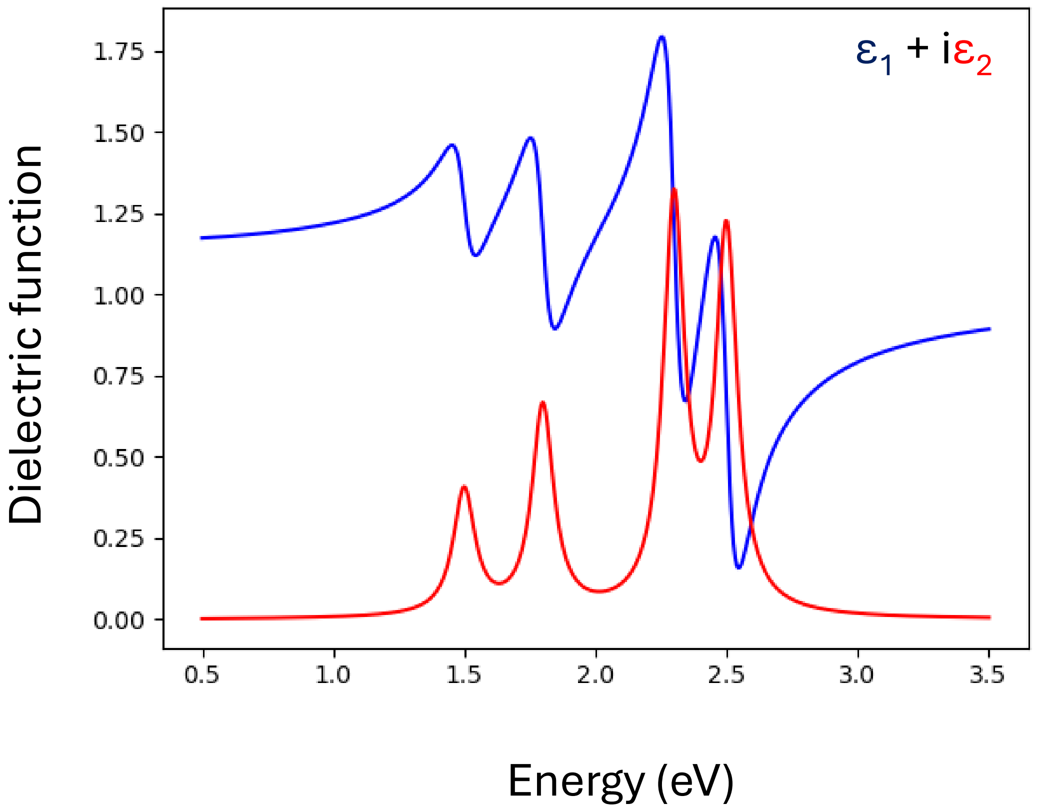
G. Brockt and H. Lakner. *Materials Science and Engineering* **1999,** *B59,* 155–158.

Lorenz Oscillator Model: Dielectric function with multiple transitions



Restoring force
(oscillator → resonance frequency)

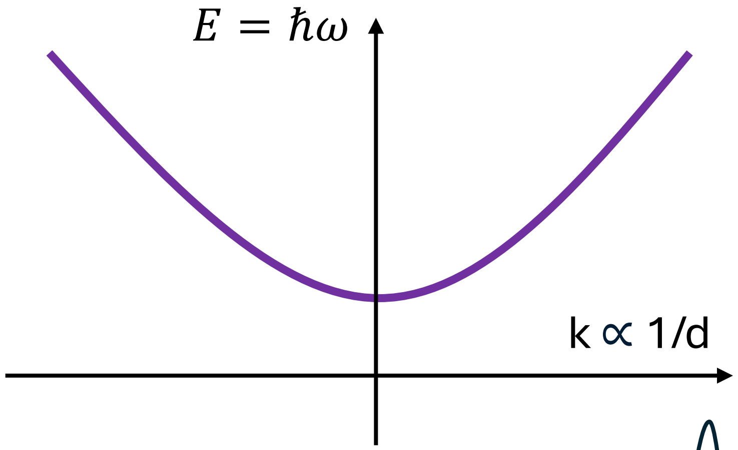
$$\tilde{\varepsilon}(\omega) = 1 + \omega_P^2 \sum_i \frac{f_i}{\omega_{0,i}^2 - \omega^2 - i\gamma\omega}$$



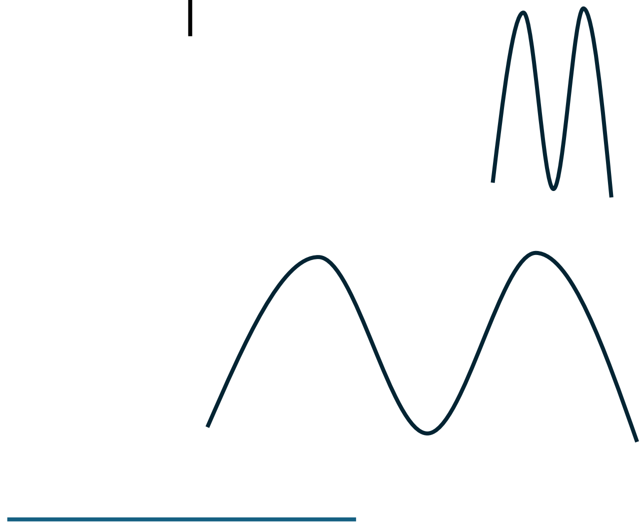
https://physics.byu.edu/faculty/colton/docs/phy442-resources/Lorentz-oscillator-model.pdf

Dispersion: Energy and momentum

Free electron gas (FEG)-like dispersion



Real-space:
Distance (d)



Tight binding picture

Reference points: Dielectric theory and Quantum descriptions

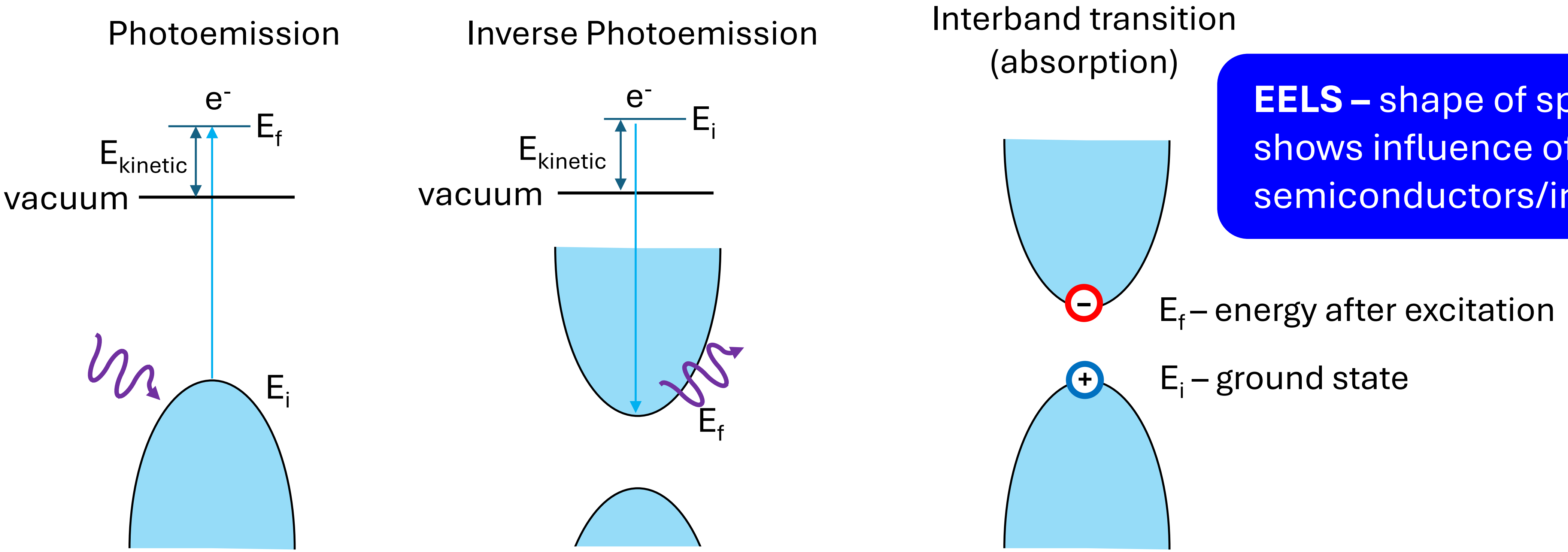
EELS of interband transitions, excitons & surface plasmons

Demo: EELS of surface plasmon resonance modes

Light emission: Cathodoluminescence

Phonons

Transitions – Independent particle picture



EELS – shape of spectra shows influence of JDOS for semiconductors/insulators

Ground state approximation – all transitions are between fixed states (not true)

One particle states for quasielectrons (quasiholes) approximation –
density of occupied (unoccupied) states with all remaining states' relaxations handled as renormalisation

Joint density of states (JDOS) – density of occupied and unoccupied states both taken into account
– necessary to describe absorption and other spectroscopies where initial and final states inside system
*possibly also need to consider electron-hole interaction (excitons)

Electronic transitions – the joint density of states

Both conduction and valence states

$$JDOS(E) \propto \int \delta(E_c(k) - E_v(k) - E)dk^3$$

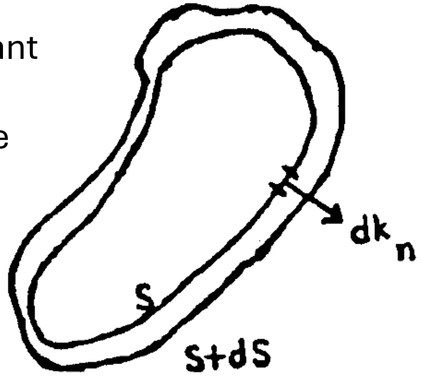
ε_2 as weighted JDOS

$$\varepsilon_2(E) \propto \int |\langle v|H'|c\rangle|^2 \delta(E_c(k) - E_v(k) - E)dk^3$$

Re-writing with
$dk^3 = dSdk_n$

$$JDOS(E) \propto \int \frac{dS}{|\nabla_k(E_c - E_v)|_{E_c - E_v = E}}$$

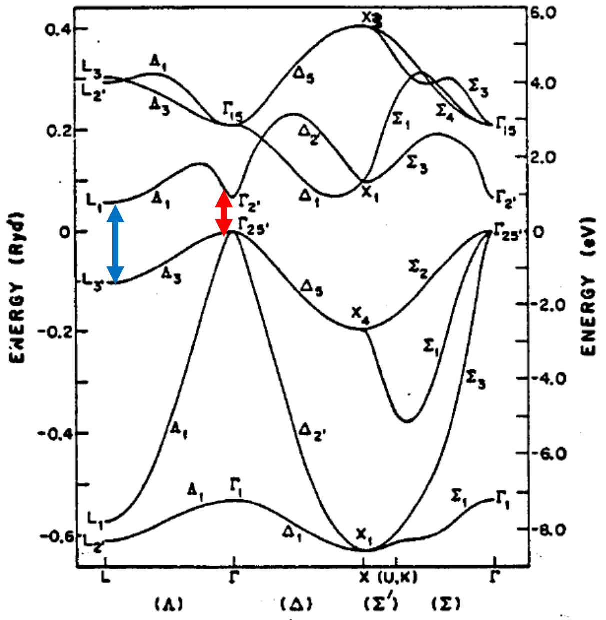
Constant energy surface

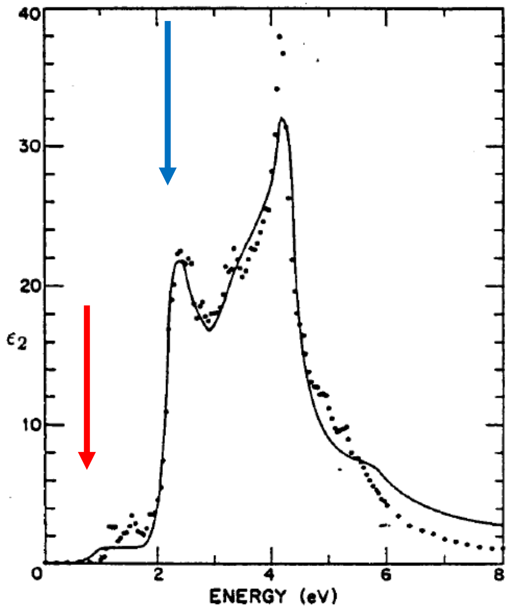


Lage where gradient in $E_c - E_v$ is flat

- Critical points
- Where bands follow each other

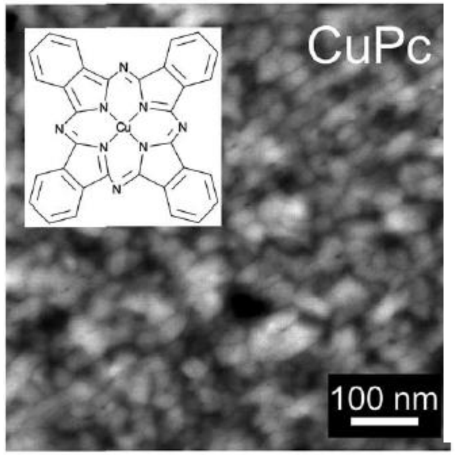
Germanium

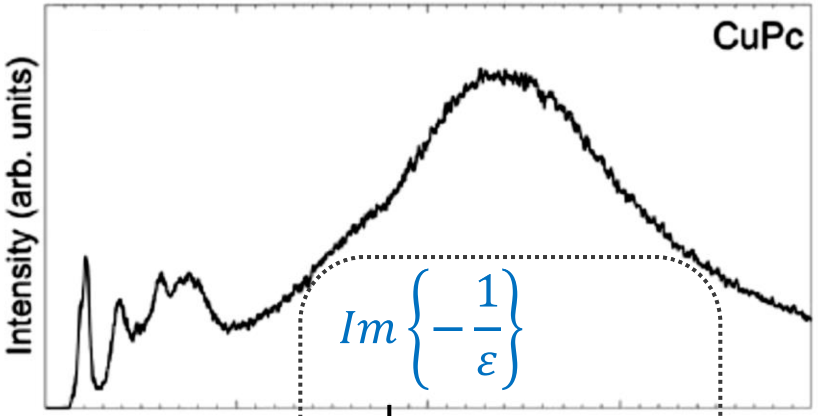


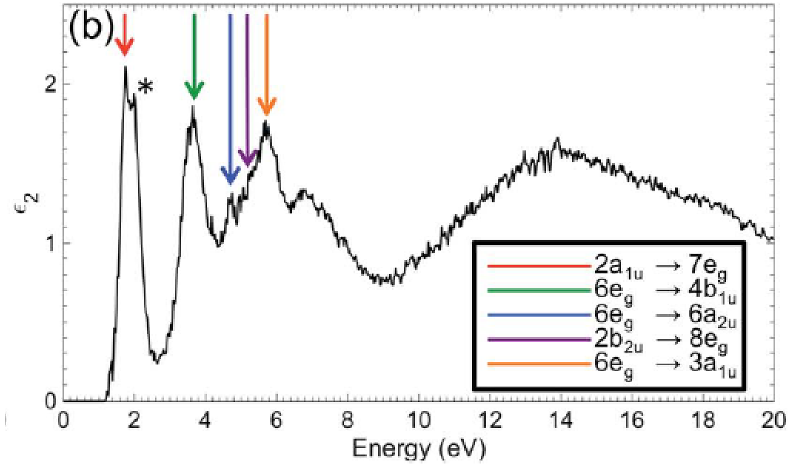


M.S. Dresselhaus, Solid State Physics Part II (MIT) http://web.mit.edu/course/6/6.732/www/6.732-pt2.pdf
Liang and Beal *J. Phys. C: Solid State Phys.* **1976**, *9*, 2823. | R. Nicholls et al. *J. Phys. Conf. Series* **2012**, *371*, 012062.

EELS of interband transitions: Kramers Kronig Analysis (KKA)





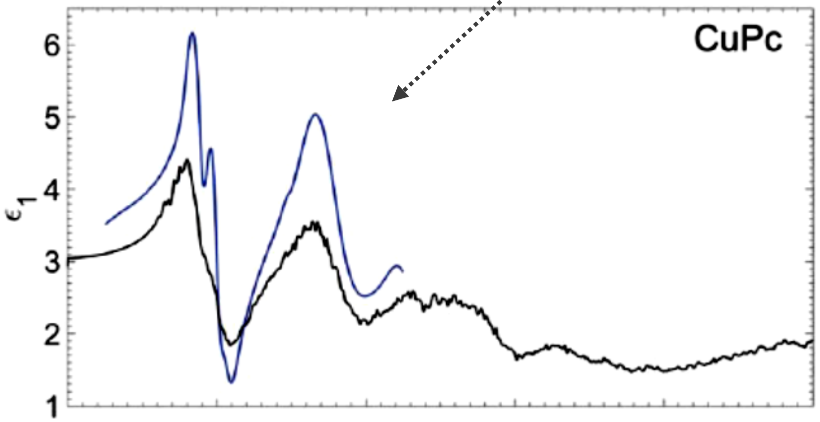


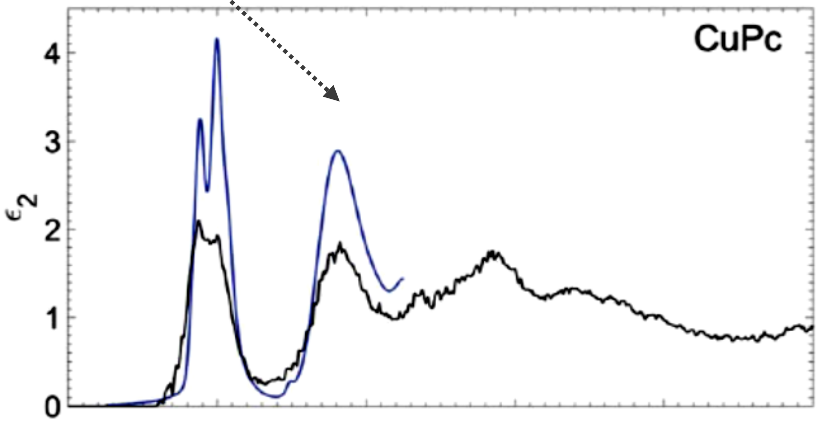
$$Im\left\{-\frac{1}{\varepsilon}\right\}$$

$$Re\left\{-\frac{1}{\varepsilon}\right\}$$

KKA Step 1: *Use sum rules that complex functions must satisfy to construct real part*

KKA Step 2: *Recover* $\varepsilon_1 + i\varepsilon_2$ *from complex* $1/\varepsilon$





Solid blue: From spectroscopic ellipsometry

J. Alexander et al. *J. Mater. Chem. A* **2016**, *4*, 13636-13645.

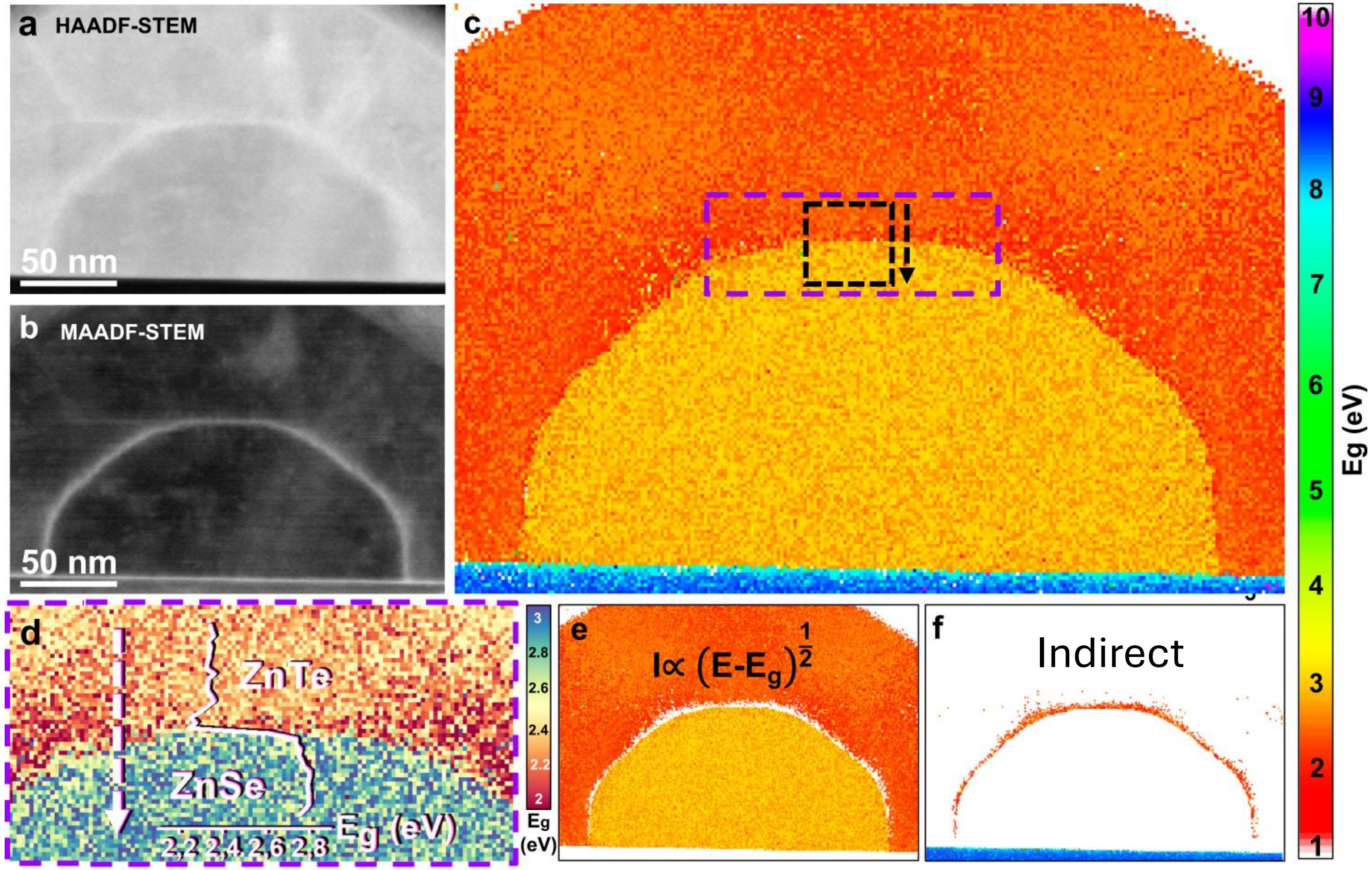
EELS for bandgap mapping

Direct gaps

$I \propto (E - E_g)^{1/2}$

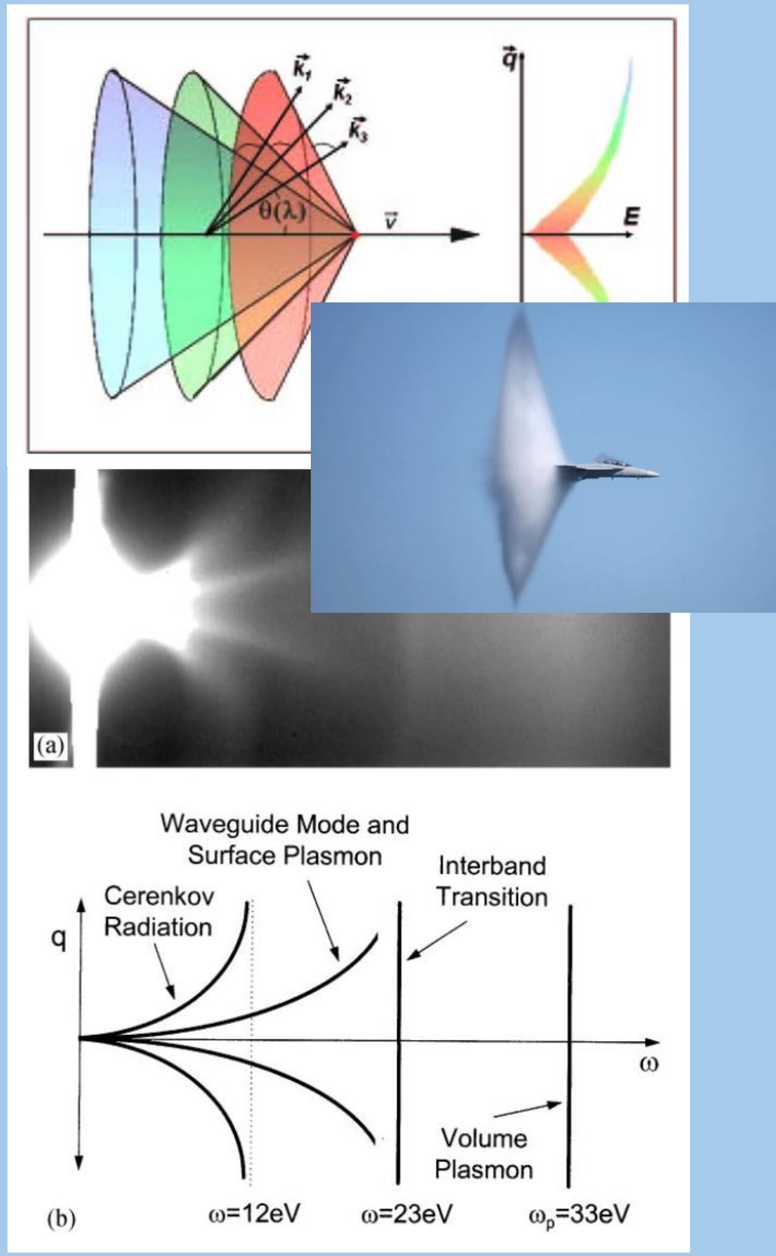
Indirect gaps

$I \propto (E - E_g)^{3/2}$



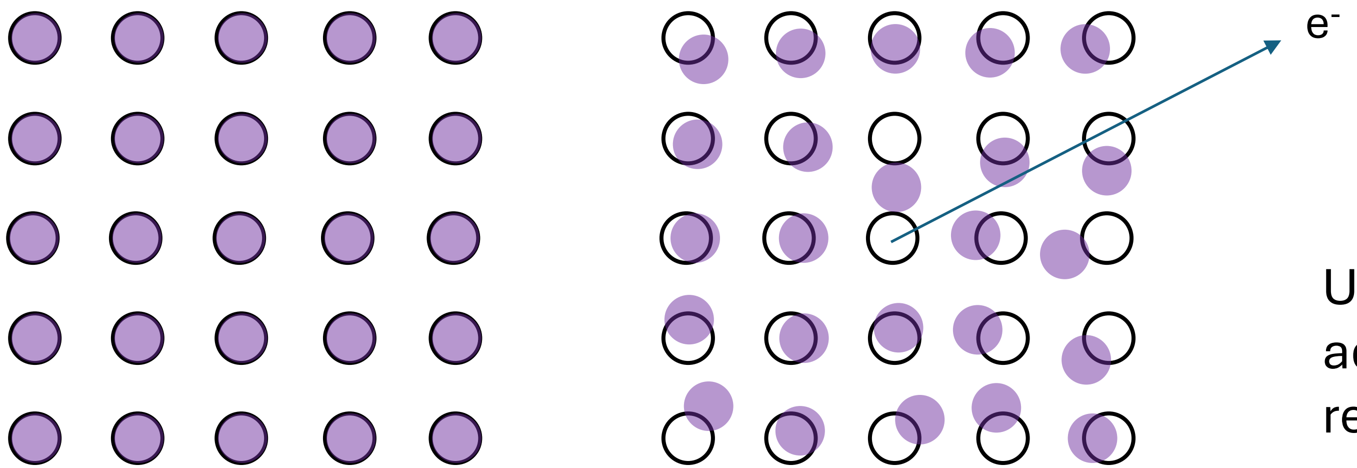
Rafferty and Brown *Phys. Rev. B* **1998**, *58*, 10326-10337.
S. Martí-Sánchez et al. *Nat. Commun.* **2022**, *13*, 4089.

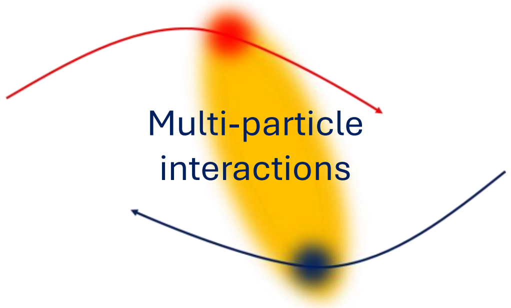
Beware: Cerenkov losses



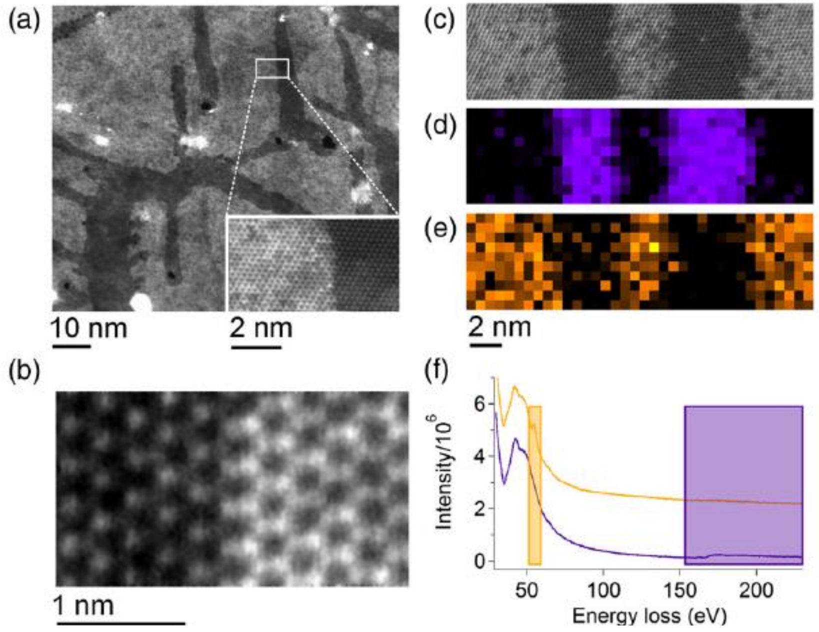
M. Stöger-Pollach et al. *Micron* **2006**, *37*, 396-402.
P.A. Midgley *Ultramicroscopy* **1999**, *76*, 91-96.

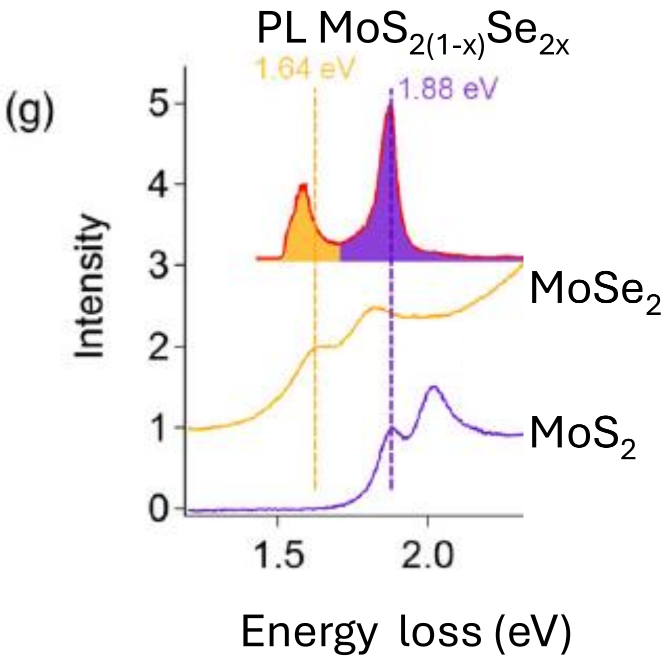
EELS of excitons

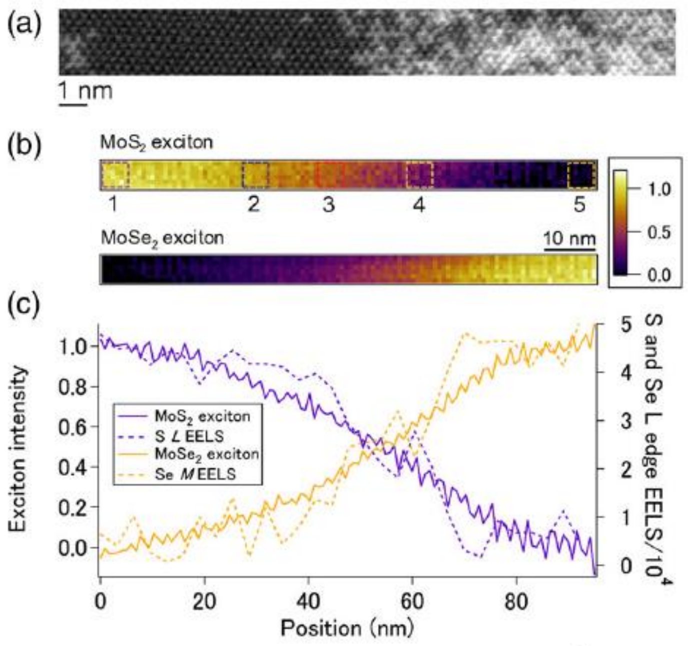




Upon removal of a charge from VB (or addition of charge in CB) there will be reaction, polarization, and screening

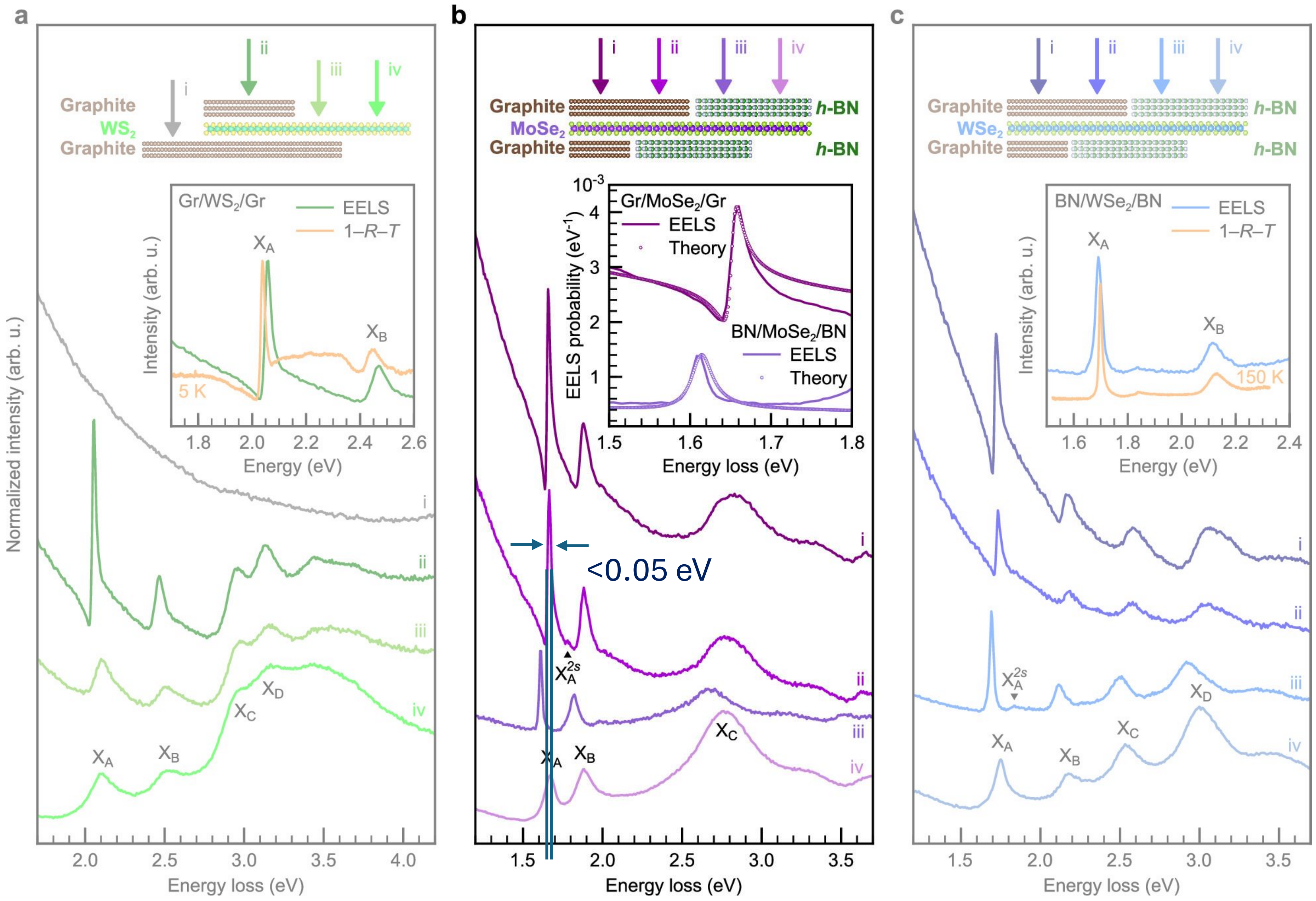


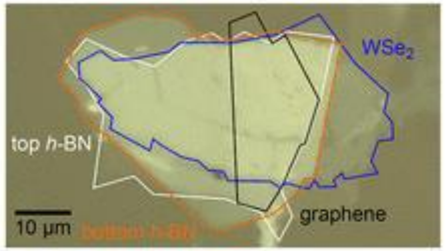




L.H.G. Tizei et al. *Phys. Rev. Lett.* **2015**, *114*, 107601.

Multi-particle effects: Excitons in transition metal dichalcogenides





Sample cooling (LN_2)

Electron beam monochromator (10 meV resolution)

Direct electron detector for EELS (Medipix3)

S. Y. Woo et al. *Nano Lett.* **2024**, *24*, 3678-3685.

EELS of surface plasmons

Collective excitations

$$\Delta E = \int_{-\infty}^{\infty} dt q_e (\mathbf{v} \cdot \mathbf{E}_{\mathbf{ind}}[\mathbf{r}(t), t]) = \int_{0}^{\infty} d\omega \hbar\omega \Gamma^{EELS}(\omega)$$

$z = vt$

$dz = v\,dt$

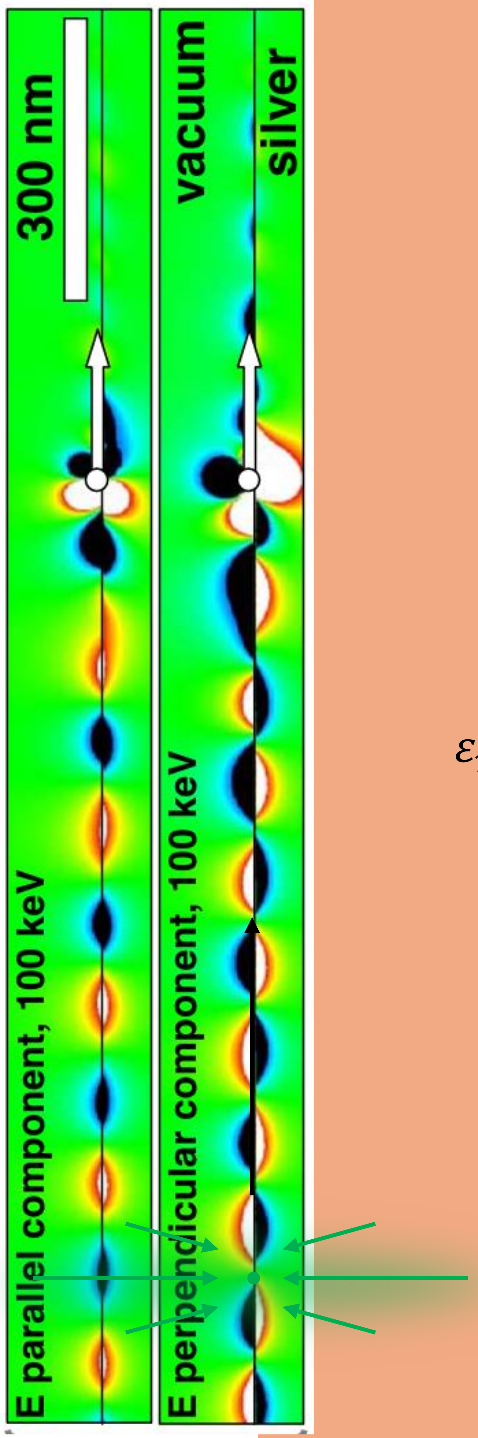
$$\Gamma^{EELS} = \frac{q_e}{v\pi\hbar\omega} \int_{-\infty}^{\infty} dz \; \mathrm{Re}\{e^{-i\omega\frac{z}{v}} \mathbf{v} \cdot \mathbf{E}_{\mathbf{ind}}[\mathbf{r}(t), \omega]\}$$

$$\varepsilon_{metal} + \varepsilon_{vacuum} = 0$$

$$1 - \frac{\omega_P}{\omega^2} + 1 = 0$$

$$\omega_{surface} = \frac{\omega_P}{\sqrt{2}}$$

ε_{vacuum}



ε_{metal}

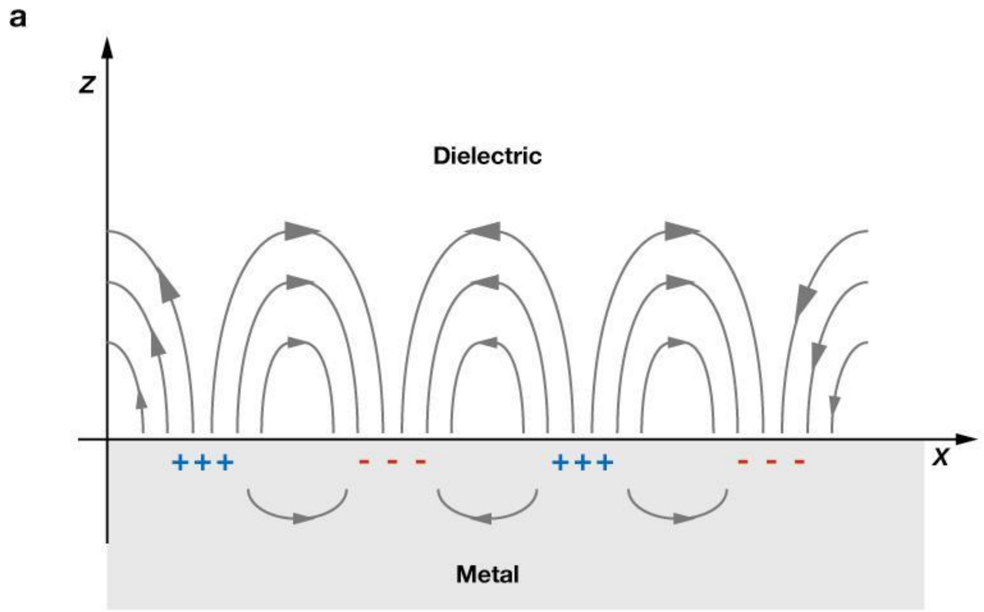
J. García de Abajo *Rev. Mod. Phys.* **2010**, *82*, 209-275.

Surface plasmons in nanoparticles

Dielectric and metal nano- and microparticles show size and shape-dependent scattering

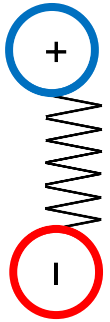
Surface plasmon polaritons

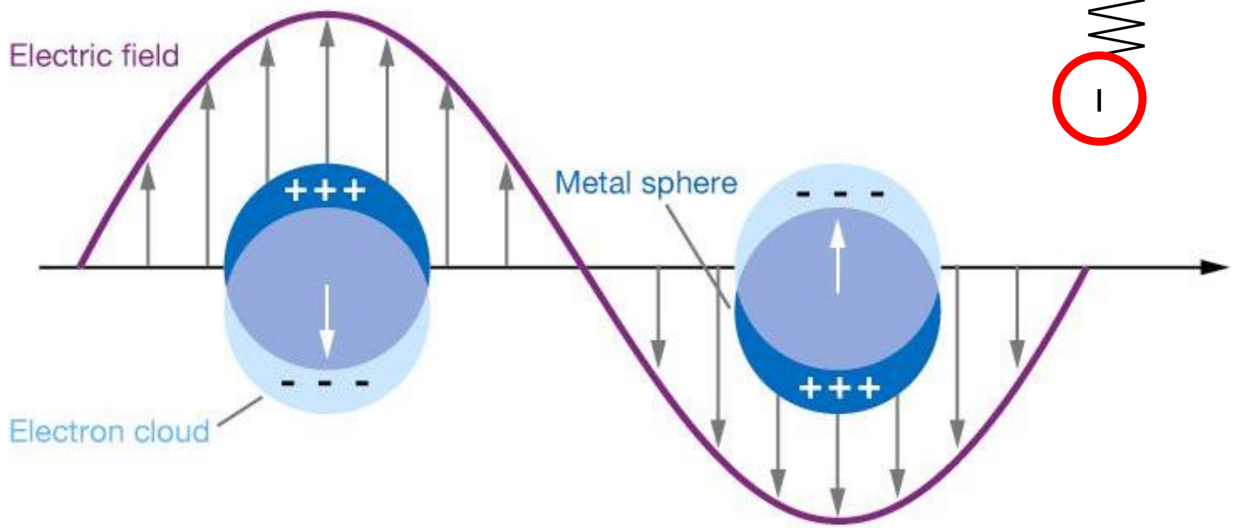
Propagating oscillations on a surface



Localised surface plasmon

Standing wave resonance



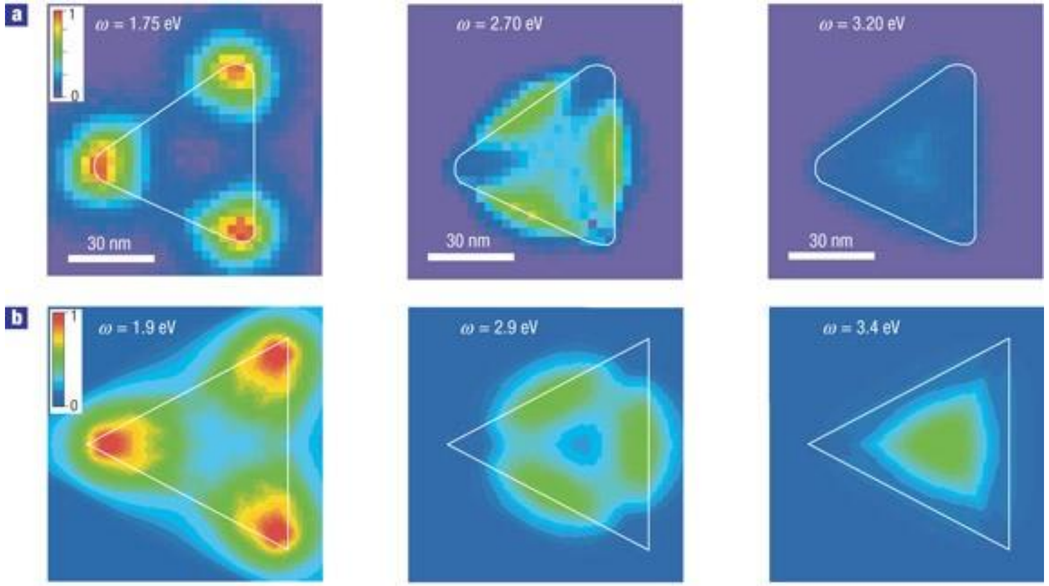


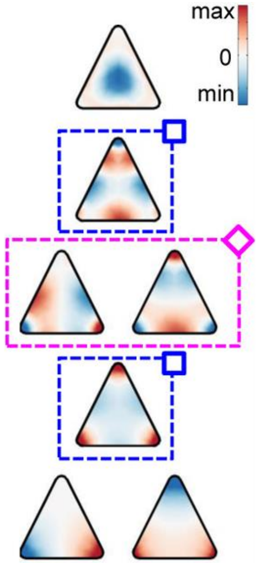
Polarisation ⟶ restoring force at particle surface

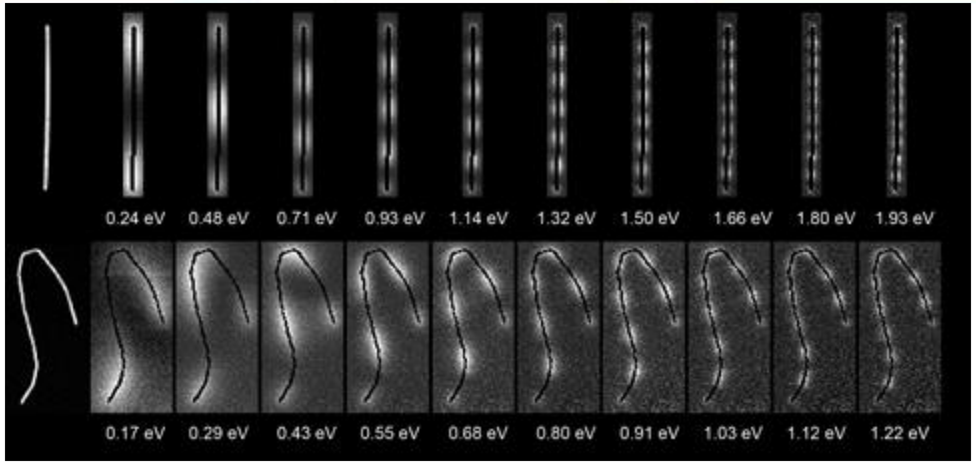
K. A. Willets and R. P. Van Duyne *Annual Review of Physical Chemistry* **2007**, *58*, 267-297.

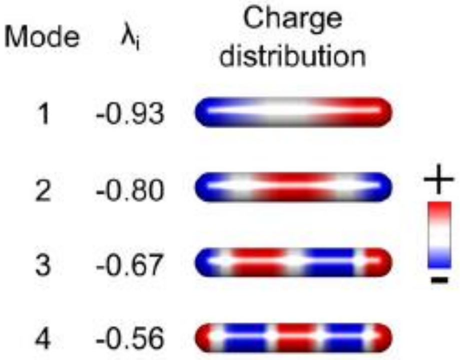
EELS of surface plasmons

Collective excitations





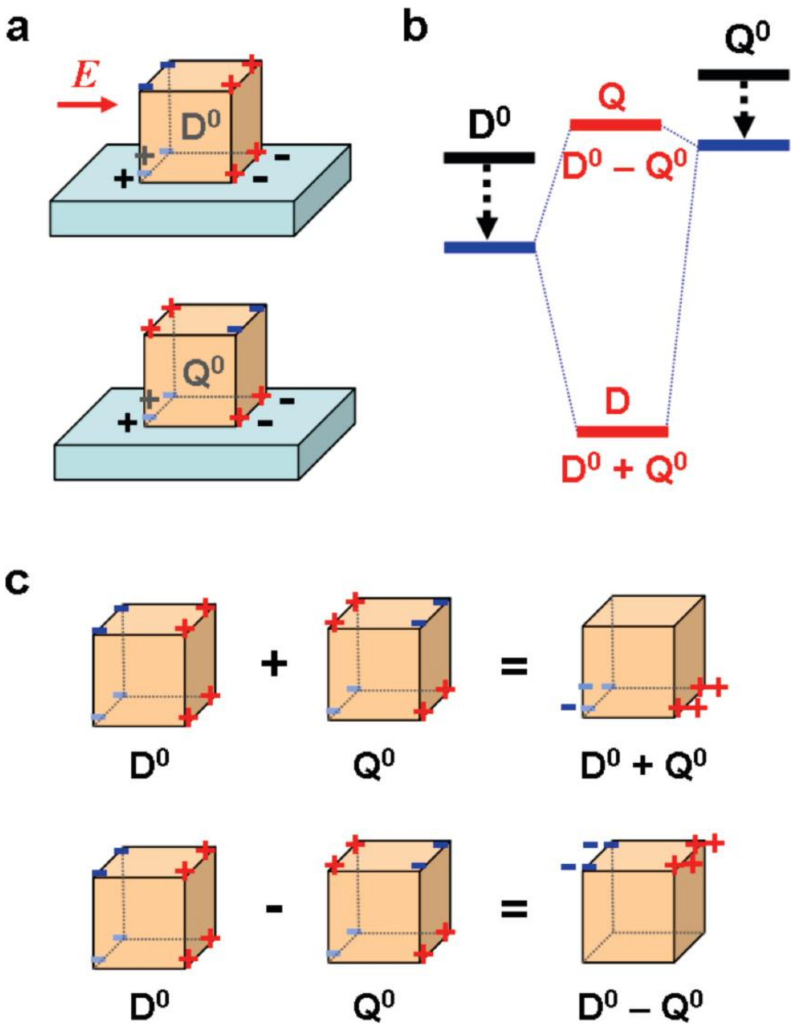


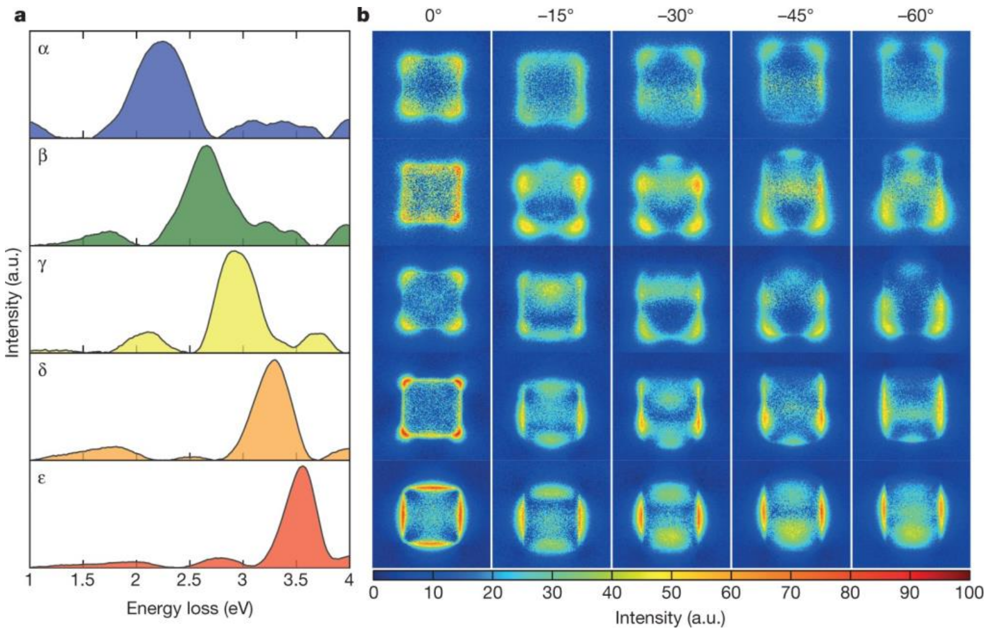


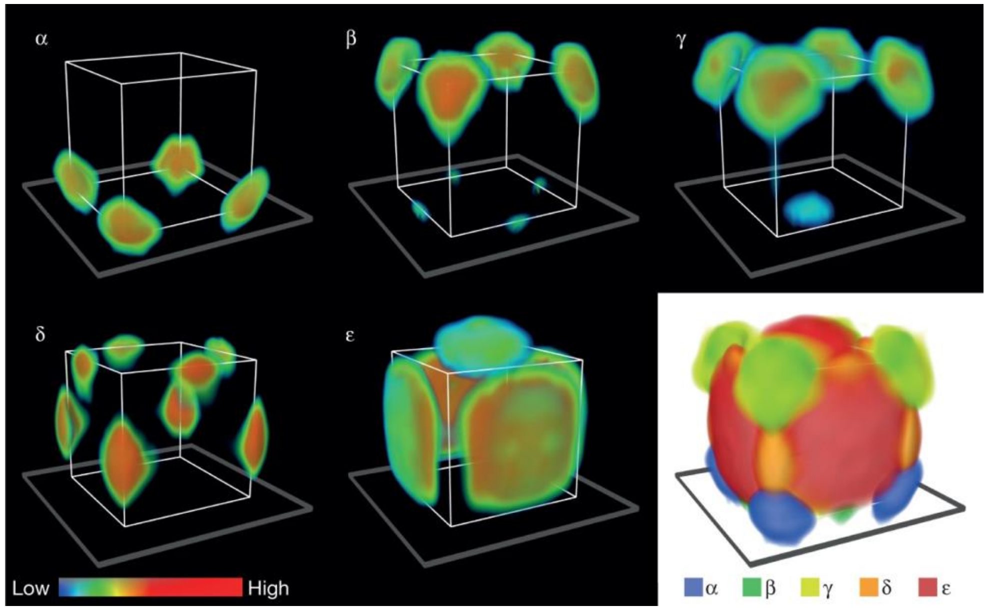
J. Nelayah et al. *Nat. Phys.* **2007**, *3,* 348-353.
F. P. Schmidt et al. *Nano Lett.* **2014**, *14*, 4810-4815.
D. Rossouw and G. Botton *Phys. Rev. Lett.* **2013**, *110*, 066801.
H. Lourenço-Martin and M. Kociak *Phys. Rev. X* **2017**, *7*, 041059.

EELS of surface plasmons

Collective excitations



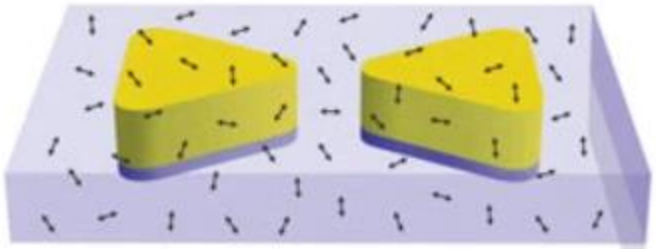


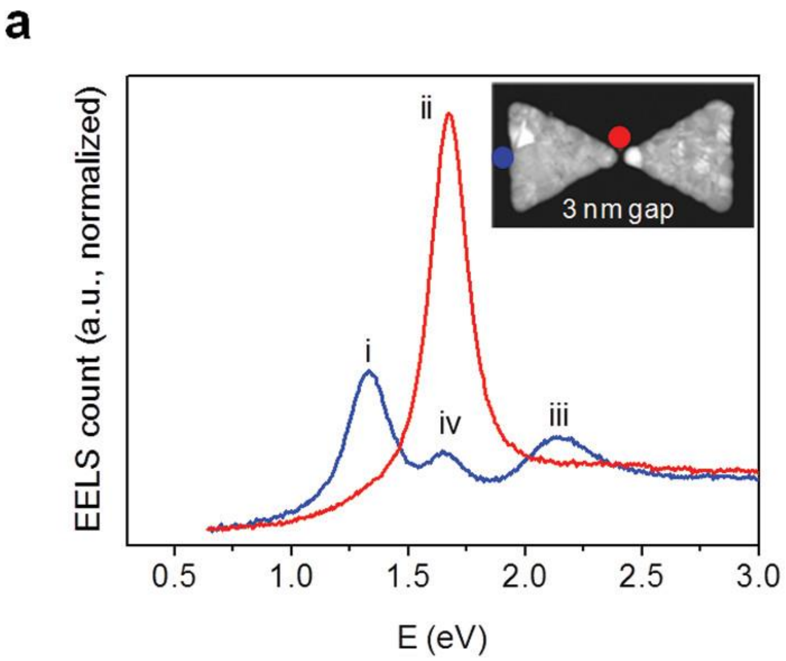


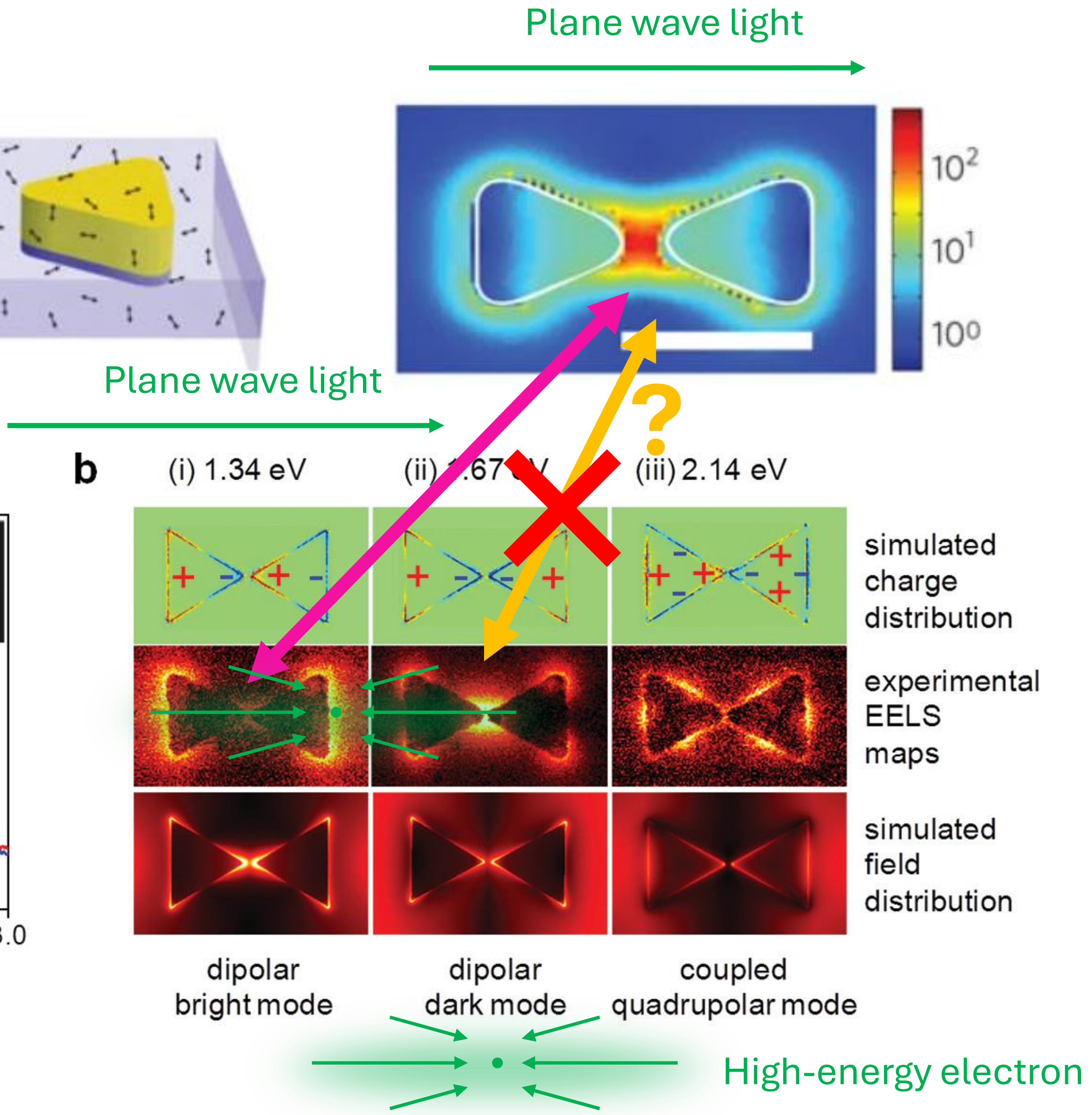
O. Nicoletti et al. *Nature* **2013**, 502, 80-84.
S. Zhang et al. *Nano Lett.* **2011**, *11*, 1657-1663.

EELS versus light excitation

Single molecule fluorescence design







A. Kinkhabwala et al. *Nat. Photon.* **2009**, *3*, 654-657.
H. Duan et al. *Nano Lett.* **2012**, *12*, 1683-1689

Demo: EELS of surface plasmons resonances

Reference points: Dielectric theory and Quantum descriptions

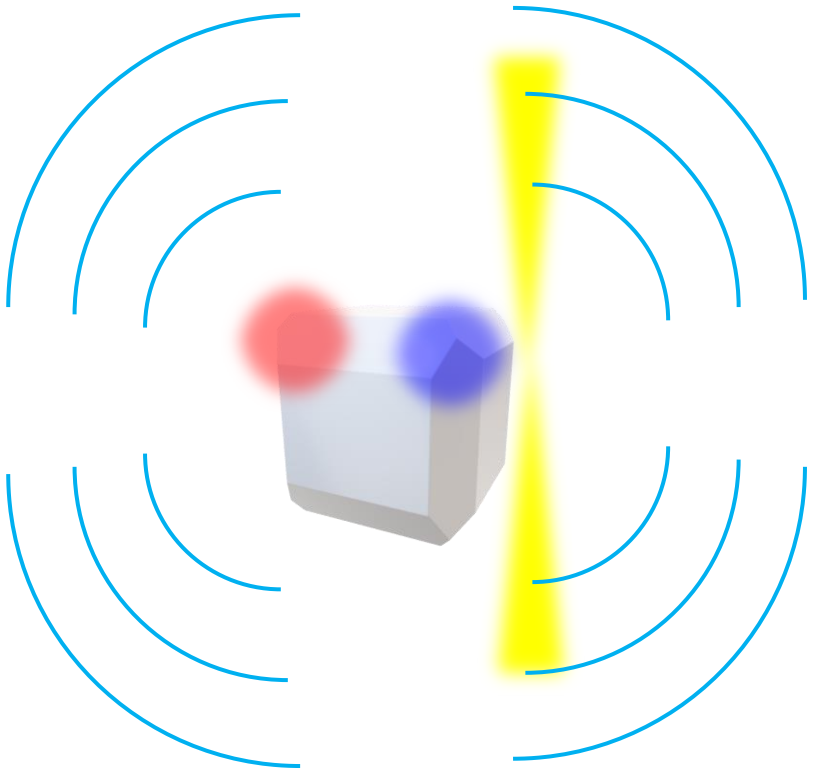
EELS of interband transitions, excitons & surface plasmons

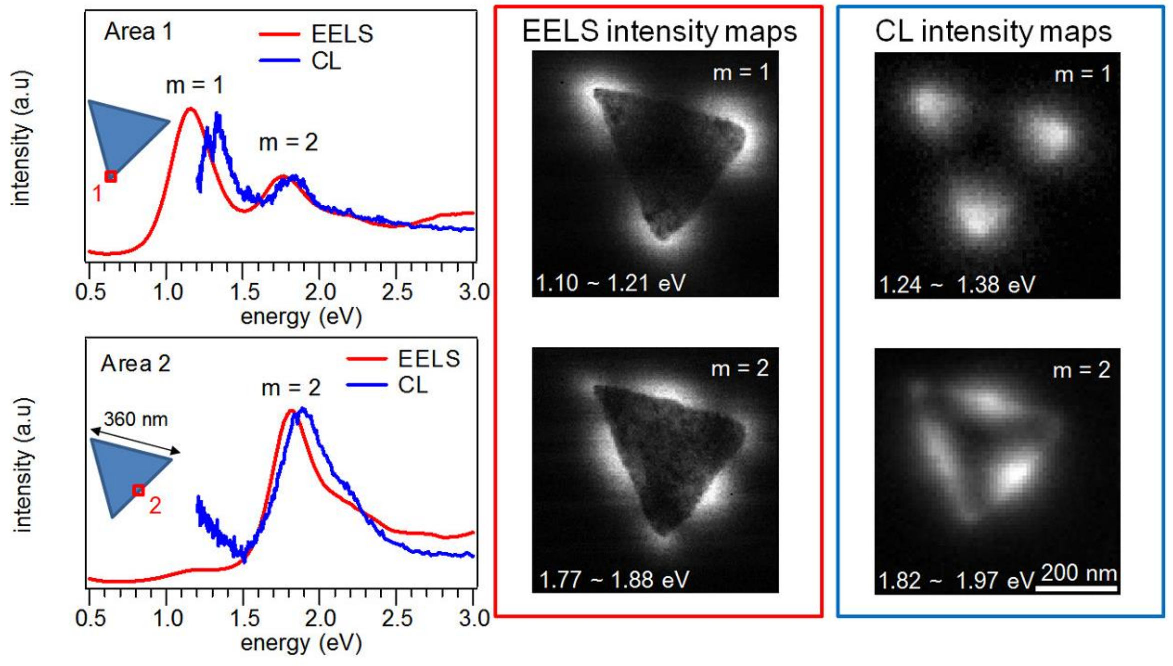
Demo: EELS of surface plasmon resonance modes

Light emission: Cathodoluminescence

Phonons

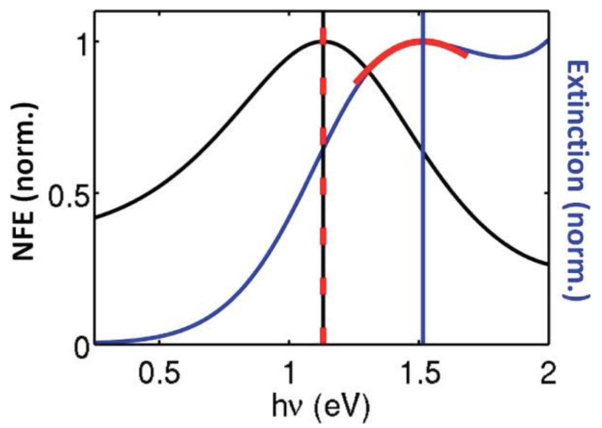
Cathodoluminescence of plasmonic particles





$$\Gamma^{CL} \propto \left| \int_{-\infty}^{\infty} dz \, \mathrm{Re}\{e^{-i\omega z/v} \, \mathbf{E_z} \, [\mathbf{r}, \omega]\} \right|^2$$

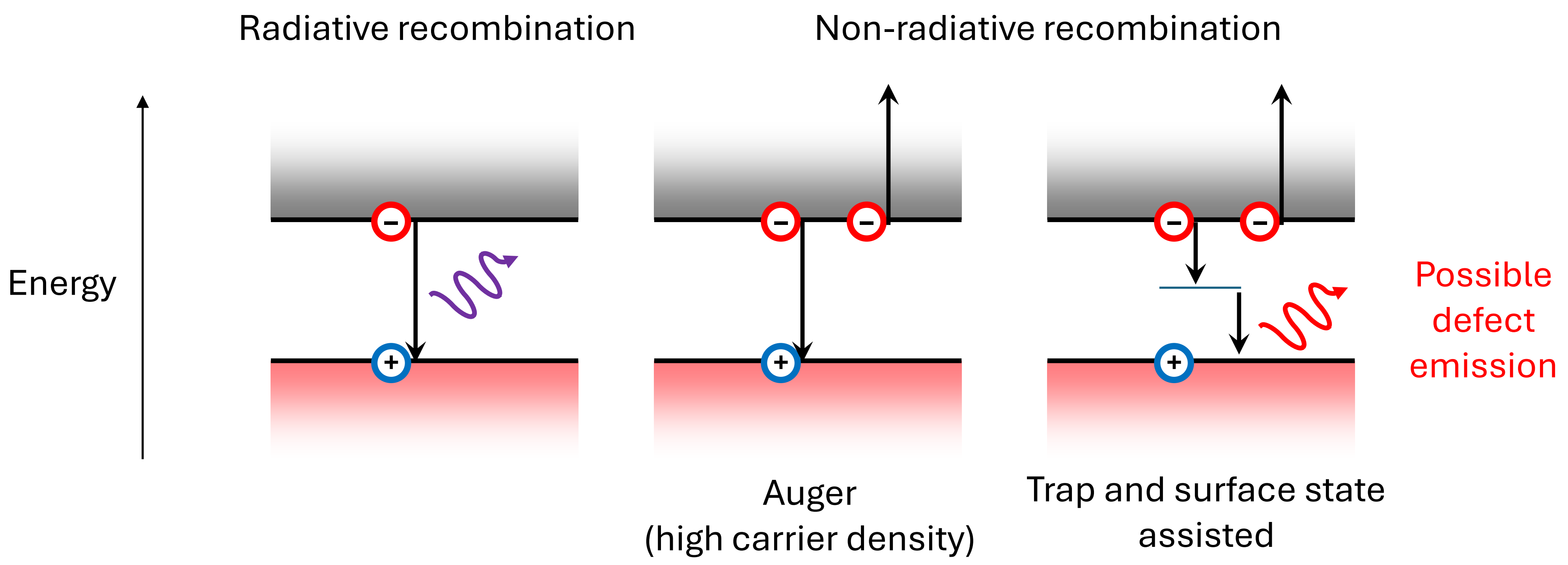
Near field



Far field

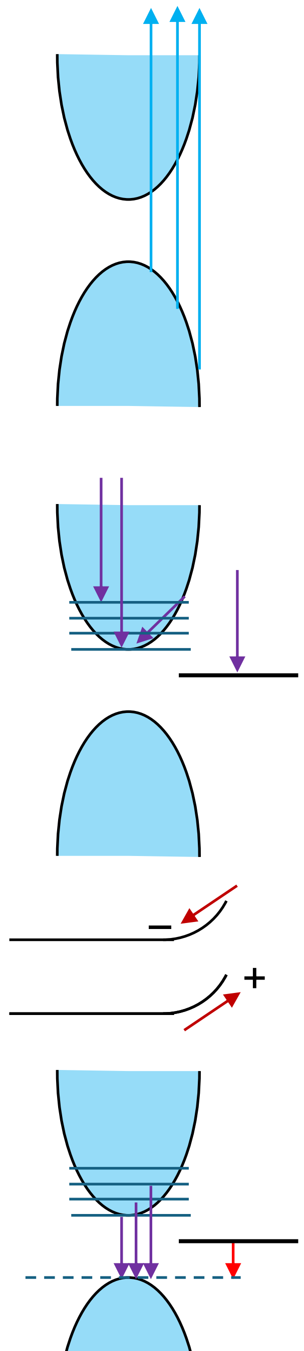
E. Akerboom et al. *ACS Nano* **2024**, *18*, 13560-13567.
N. Kawasaki et al. *ACS Photon*. **2016**, *3,* 1654-1661.
Zuloaga and Nordlander *Nano Lett*. **2011**, *11*, 1280-1283.

After excitation – what next?



Excited state lifetime – depends on relative rates of competing recombination pathways
e.g. High trap density will shorten observed lifetime (as will efficient emission)

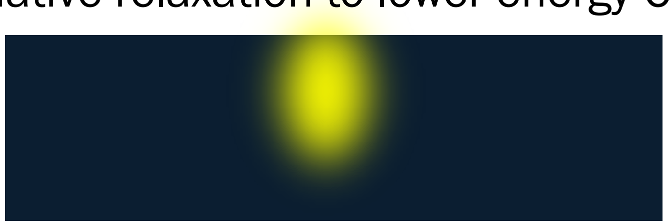
CL: Overview



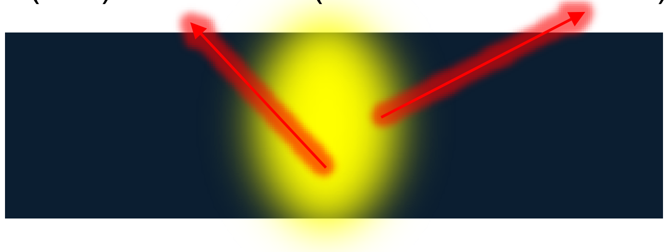
1 Excitation of electrons from ground state |0>
to high energy bound states |n>

Backscattered & secondary electrons may cause further excitations

2 Non-radiative relaxation to lower energy CB, bound states



3 Diffusion (3D) and drift (in external fields)

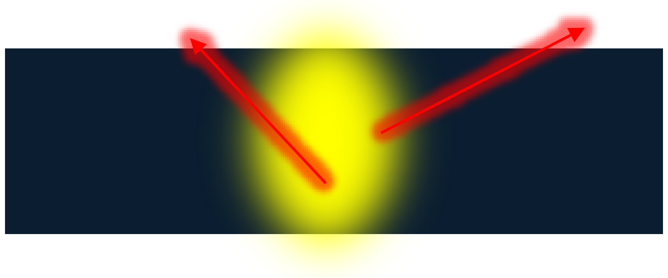


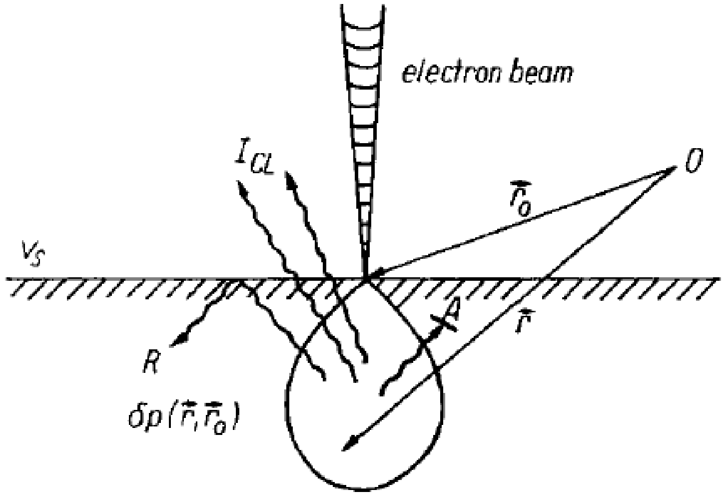
4 Radiative recombination (light emission)
Competing with non-radiative recombination and charge separation

Different excited state vibrational energies

- ➢ Possible emissions split by phonon energies

CL: Outcoupling and generation volumes





$$I_{CL}(\boldsymbol{r_0}) = C \int_V AR\eta(\boldsymbol{r})\delta p(\boldsymbol{r},\boldsymbol{r_0}) d^3r$$

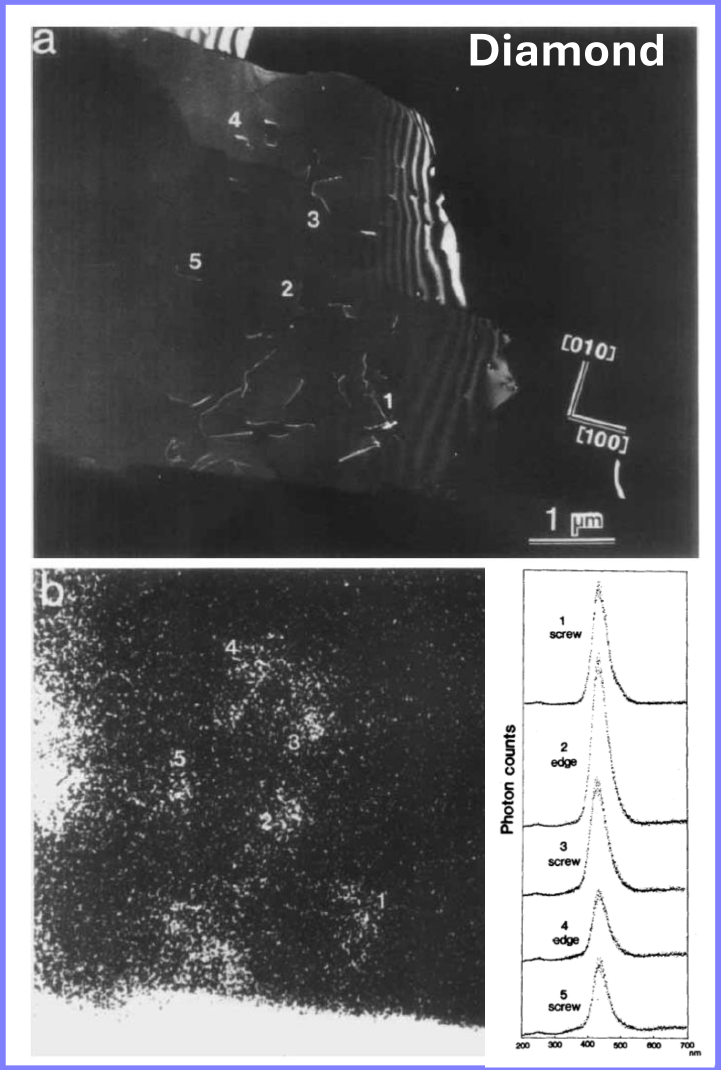
V($\mathbf{r}$, $\mathbf{r_0}$) – generation volume

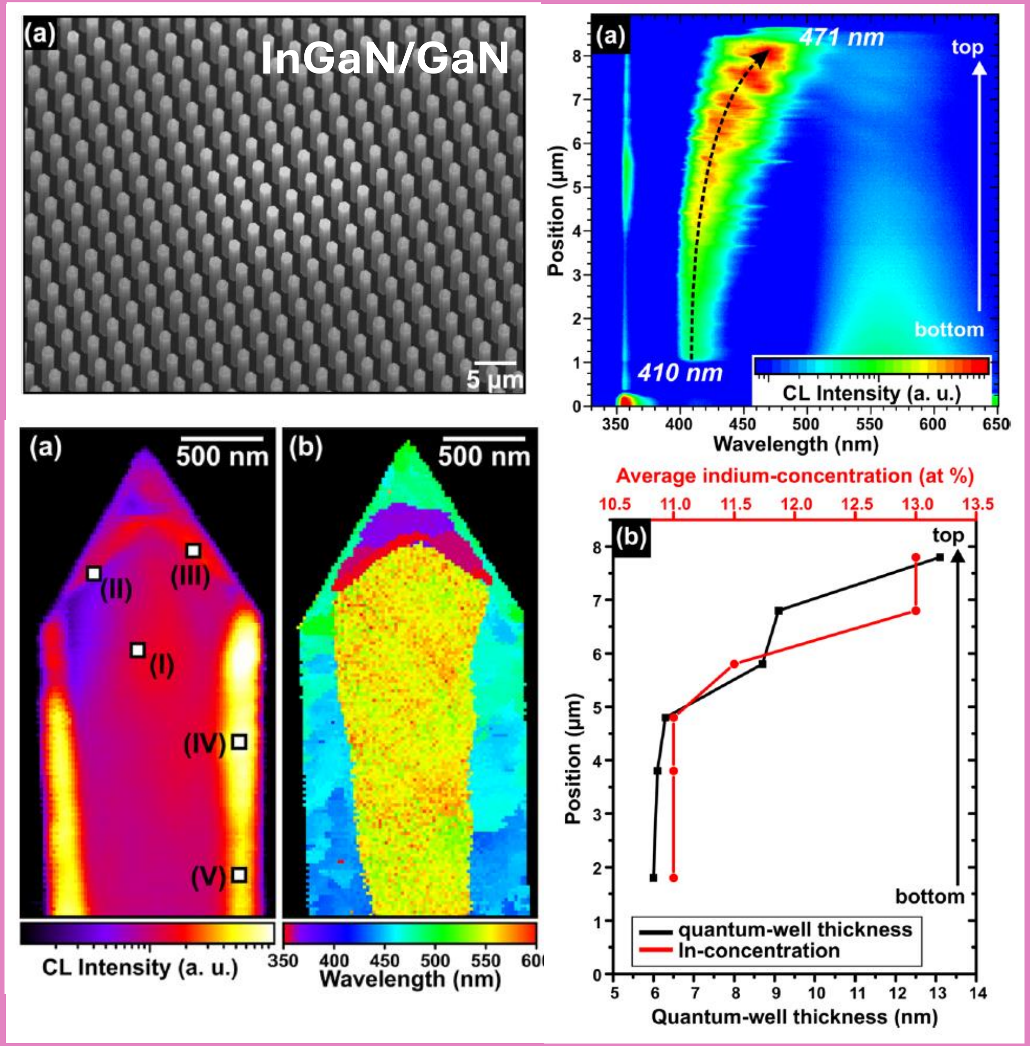
A – re-absorption
R – reflection
} *Outcoupling of light*

$\eta(\boldsymbol{r})$ – internal quantum efficiency (IQE)
$\delta p(\boldsymbol{r},\boldsymbol{r_0})$ – excess carriers

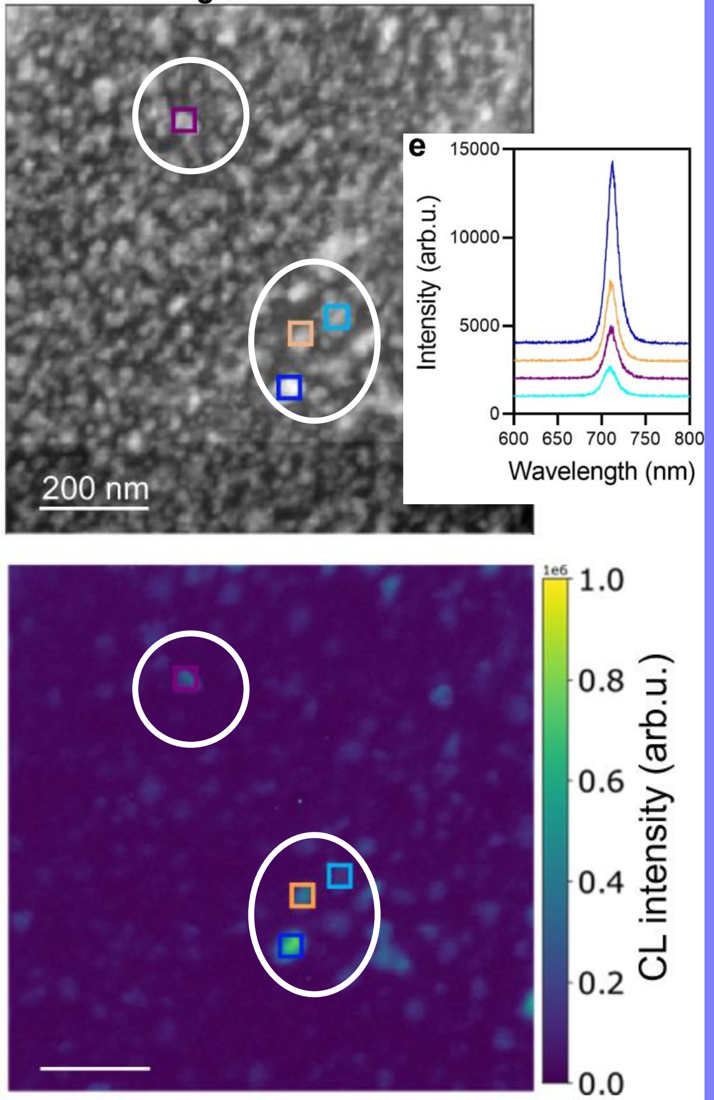
K. Löhnert and E. Kubalek *Phys. Stat. Sol. A* **1984**, *83*, 307.

Applications of CL in STEM



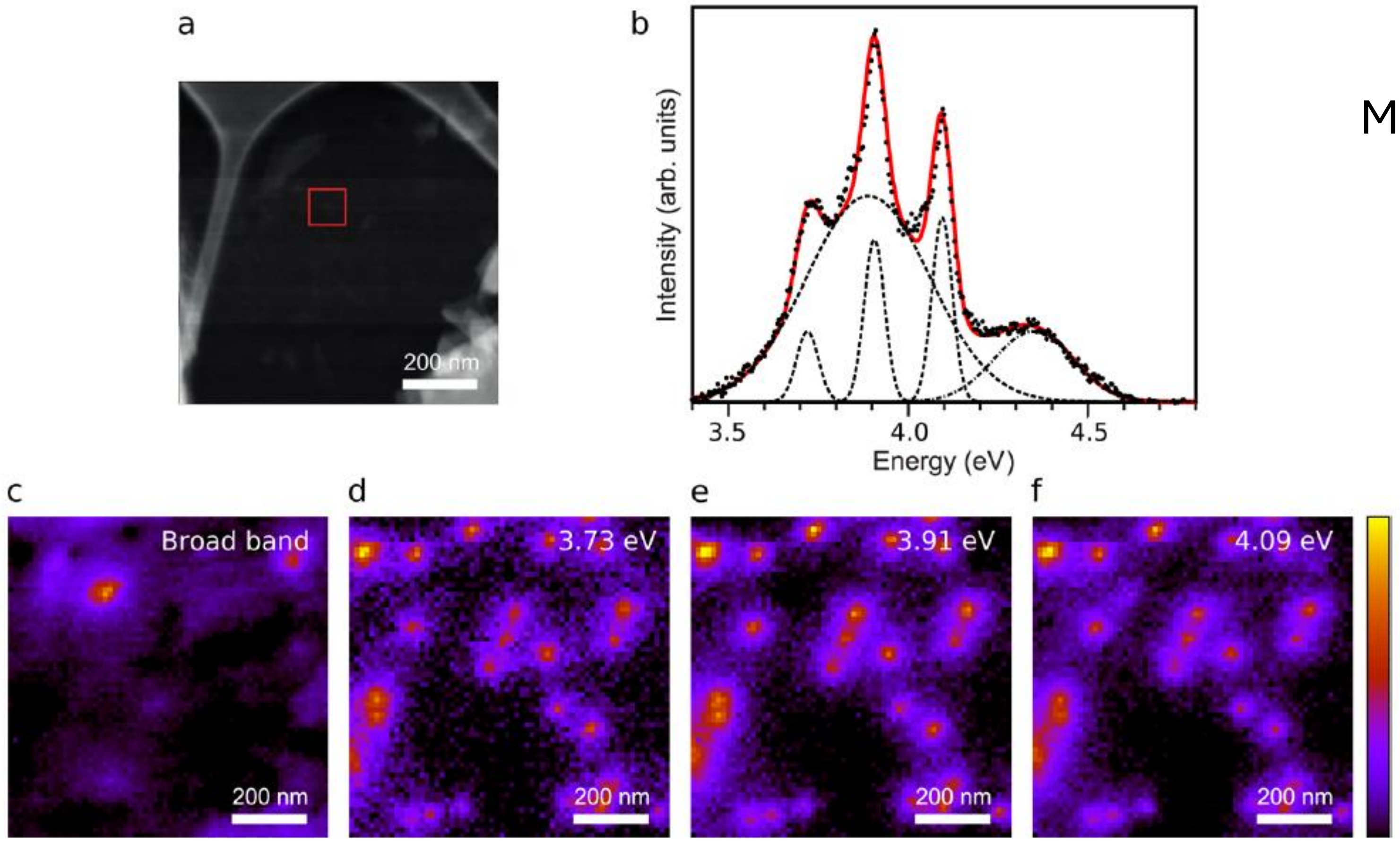


$CsPbI_3$ perovskites



N. Yamamoto, J.C.H. Spence, and D. Fathy. *Philos. Mag. B* **1984**, *49,* 609-629.
M. Müller et al. *Nano Lett.* **2016**, *16*, 5340-5346.
X. Li et al. *Nat. Commun.* **2023**, *14,* 7612.

Defect emission: example in hexagonal BN (h-BN)



Match for three sharp emission lines indicates common origin (phonon replica, ~180 meV)

Mid-gap emissions – excitonic emissions quenched at same locations

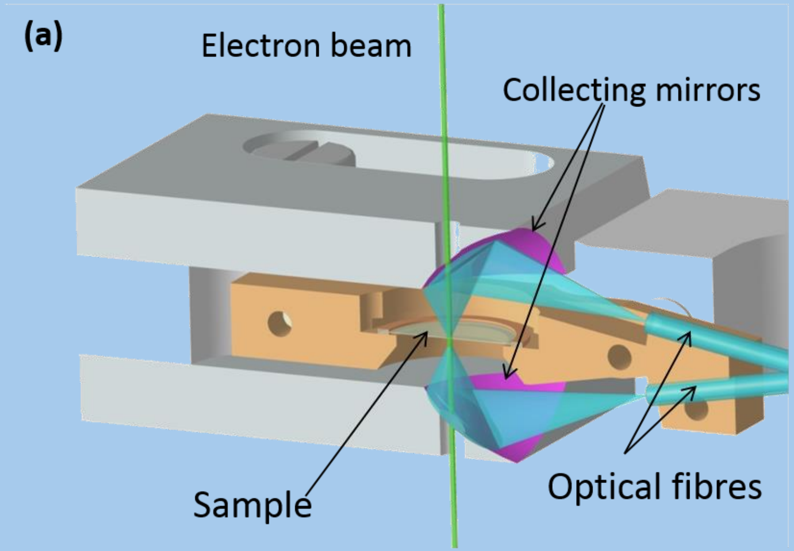
Likely at C-substitution defects in h-BN

R. Bourrellier et a. *Nano Lett*. **2016**, *16*, 4317-4321.

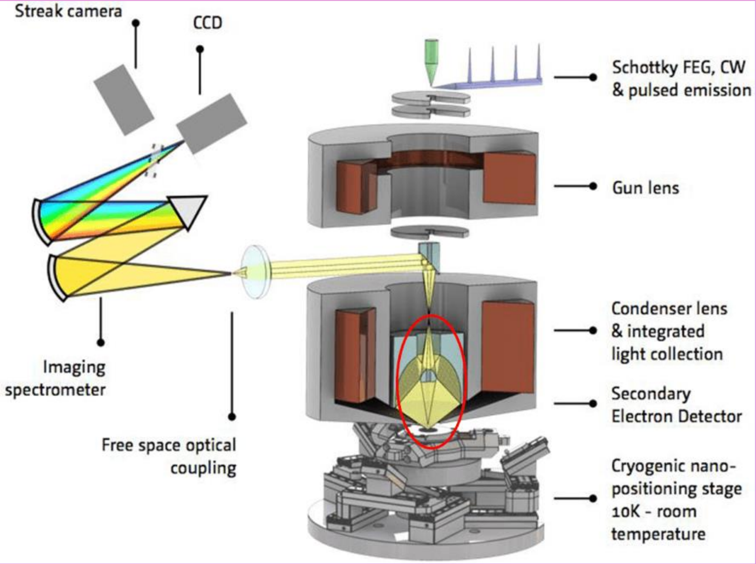
CL light extraction: Mirrors + optical fibres or free space coupling

Attolight (STEM)

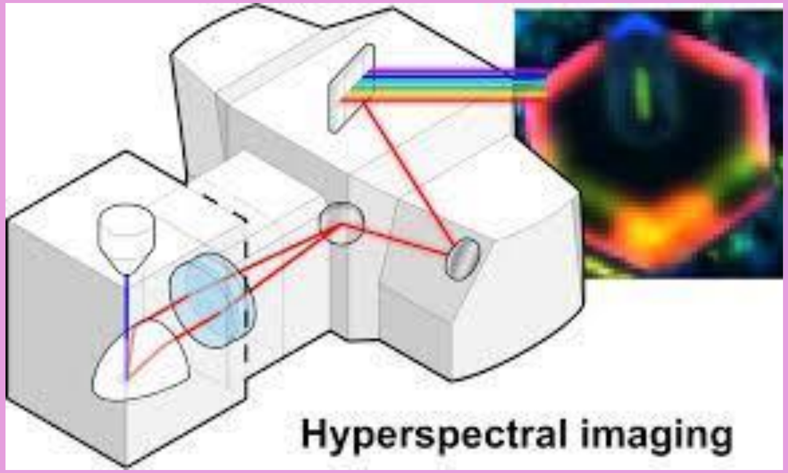
Gatan (STEM)



Attolight (SEM)



Delmic (SEM)



Reference points: Dielectric theory and Quantum descriptions

EELS of interband transitions, excitons & surface plasmons

Demo: EELS of surface plasmon resonance modes

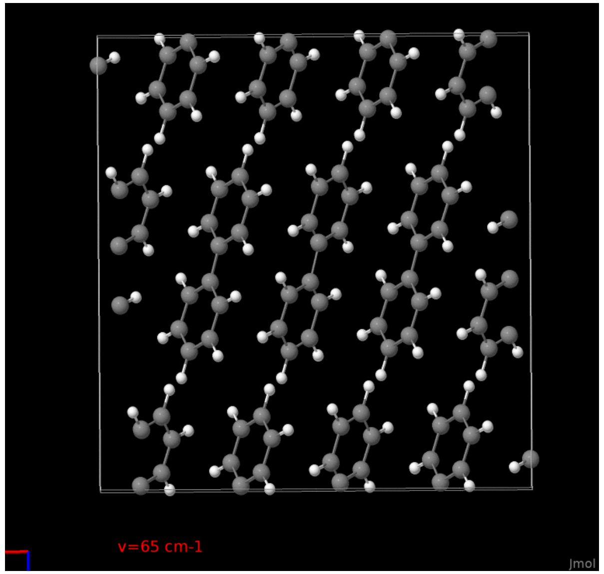
Light emission: Cathodoluminescence

Phonons

Phonons: Lattice vibrations

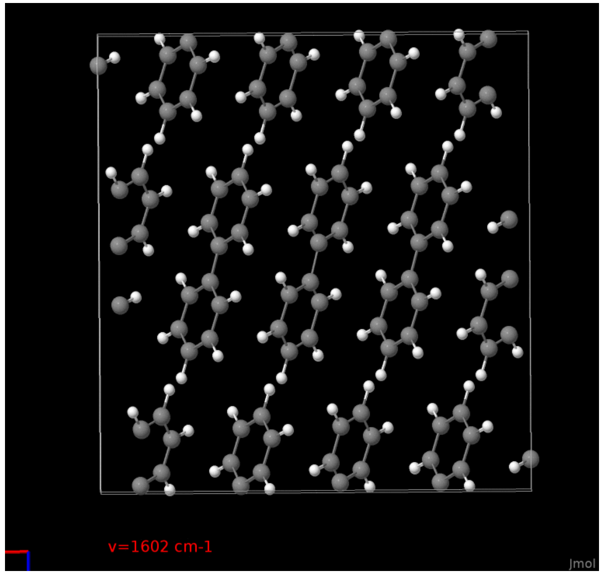
Γ

65 cm^{-1}



Γ

1602 cm^{-1}



2D Antimony

Out-of-plane acoustic

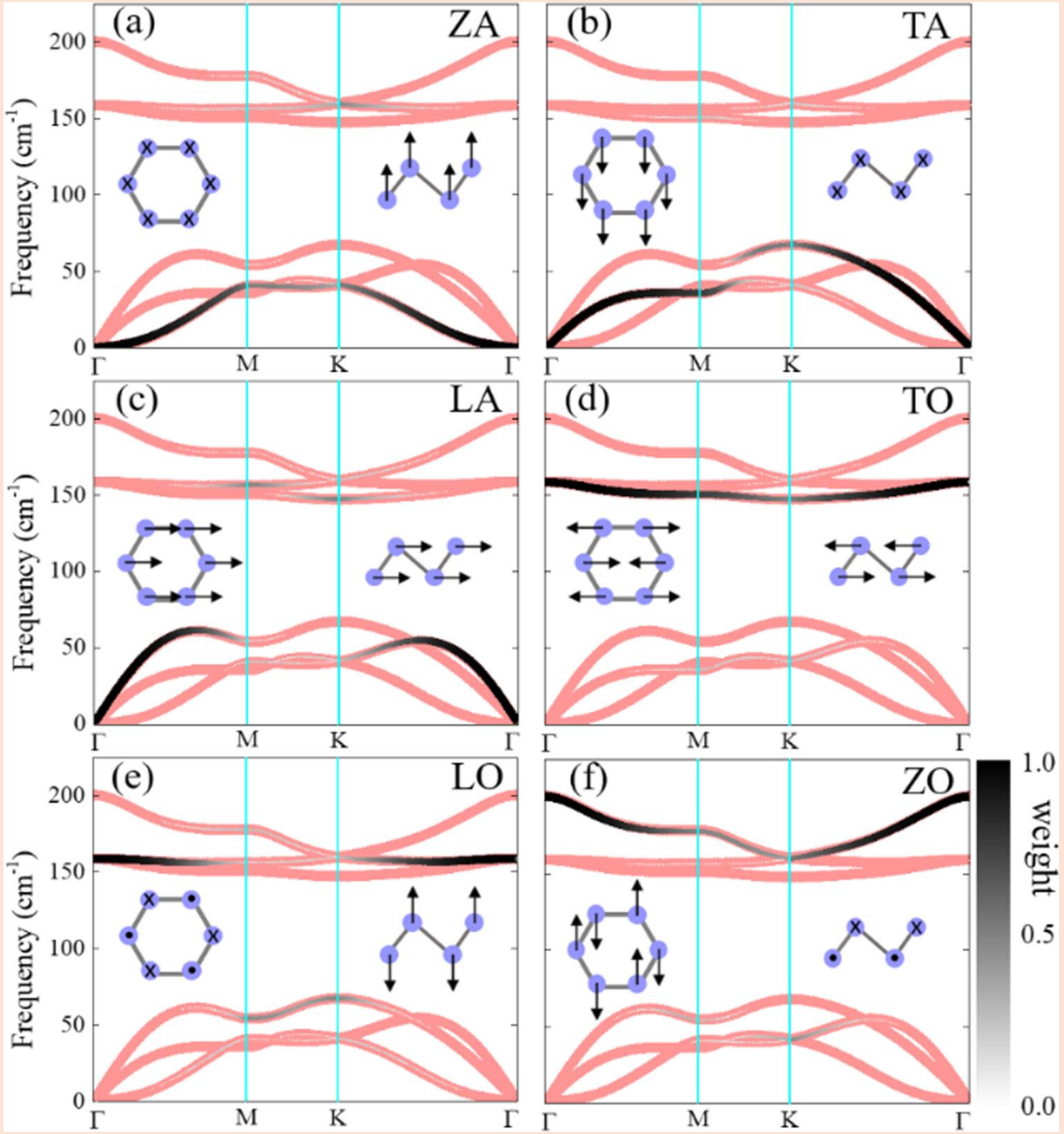
Transverse acoustic

Longitudinal acoustic

Transverse optical

Longitudinal optical

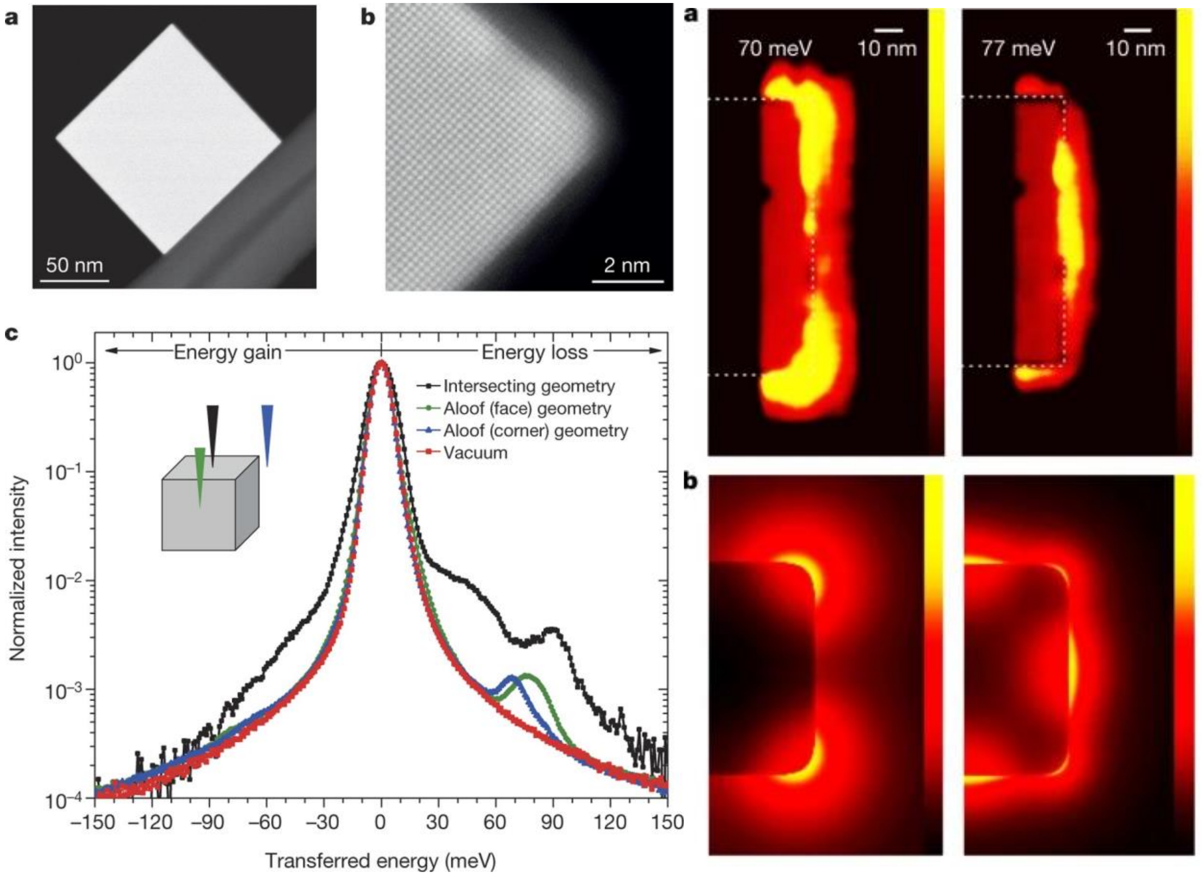
Out-of-plane optical



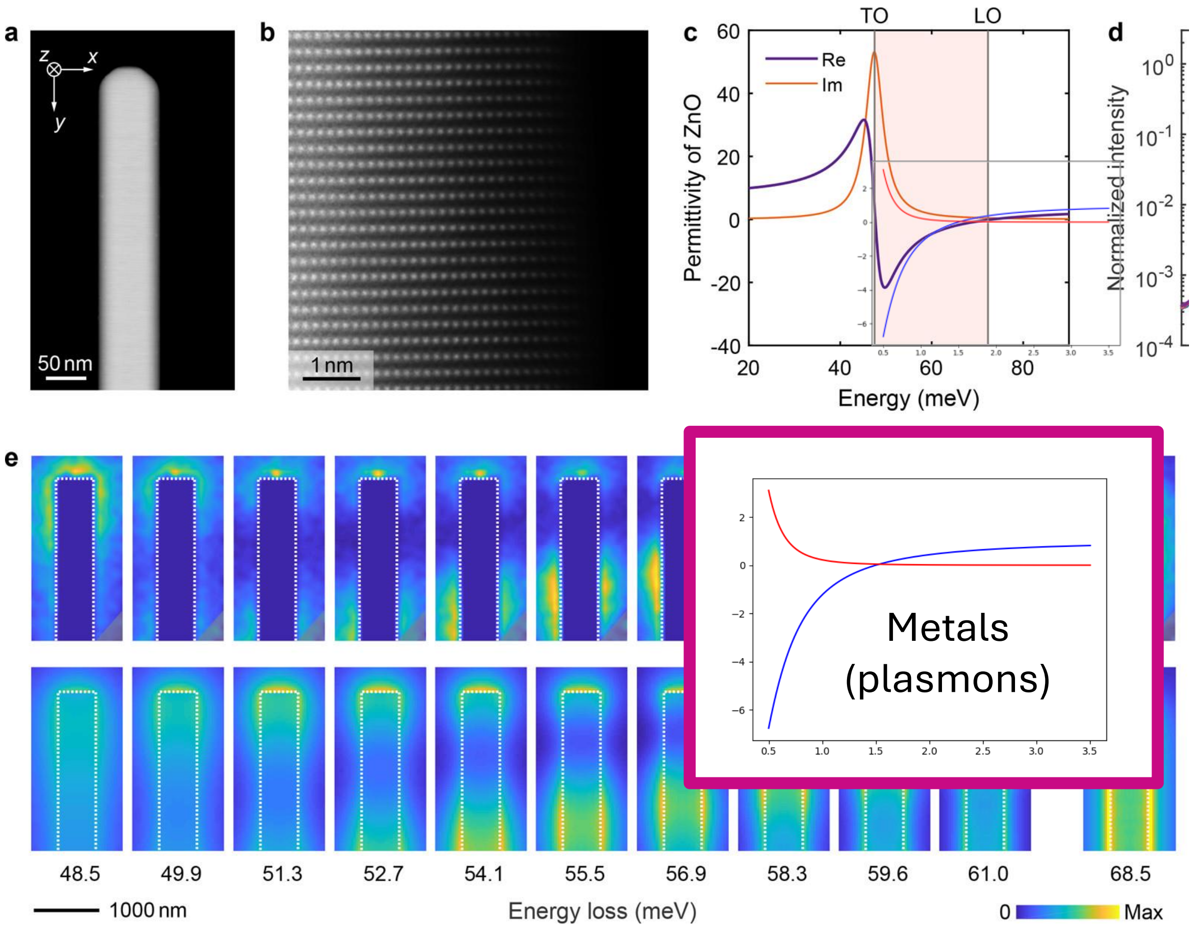
L. Cheng et al. *J. Phys. Mater.* **2019**, *2*, 045005.

https://lampz.tugraz.at/~hadley/ss1/phonons/natalia/modes.php

Ionic crystals: Phonon polariton and surface phonon polaritons

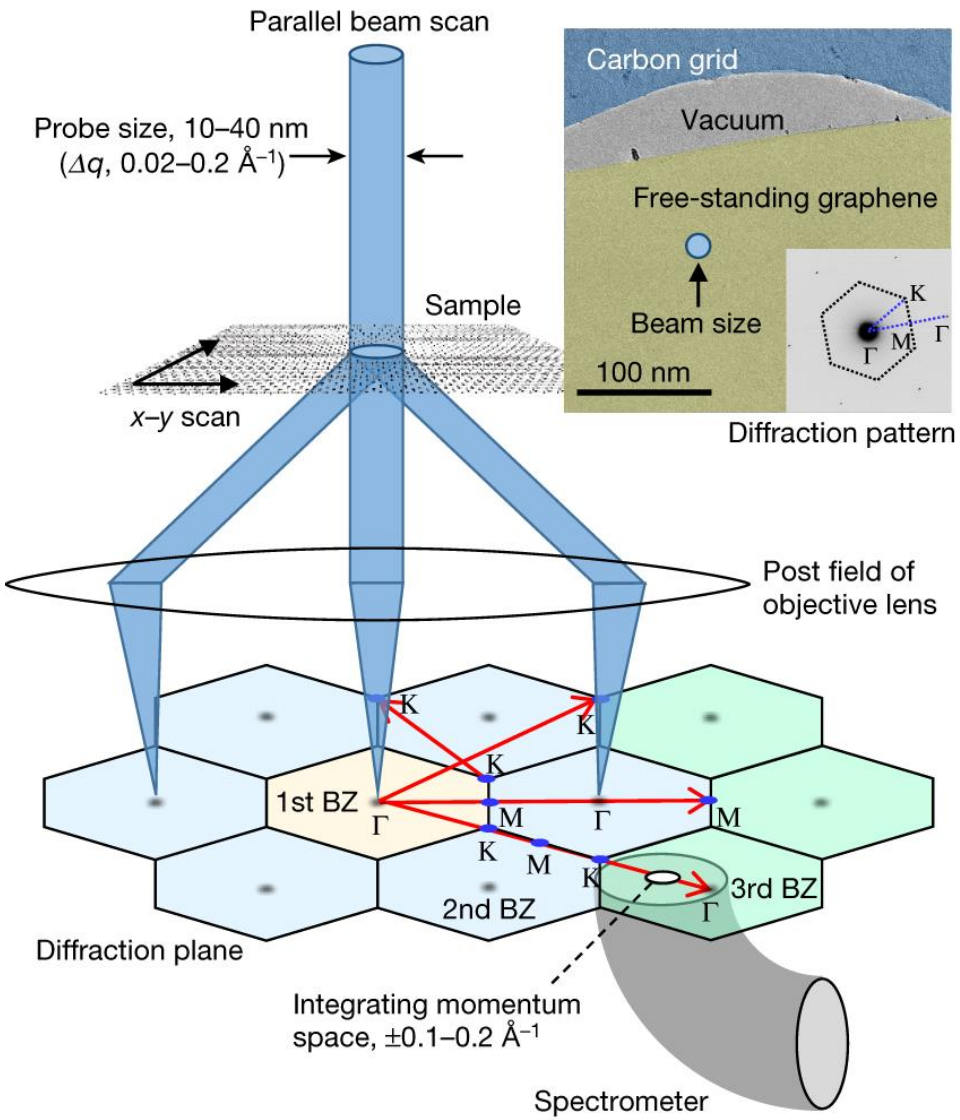


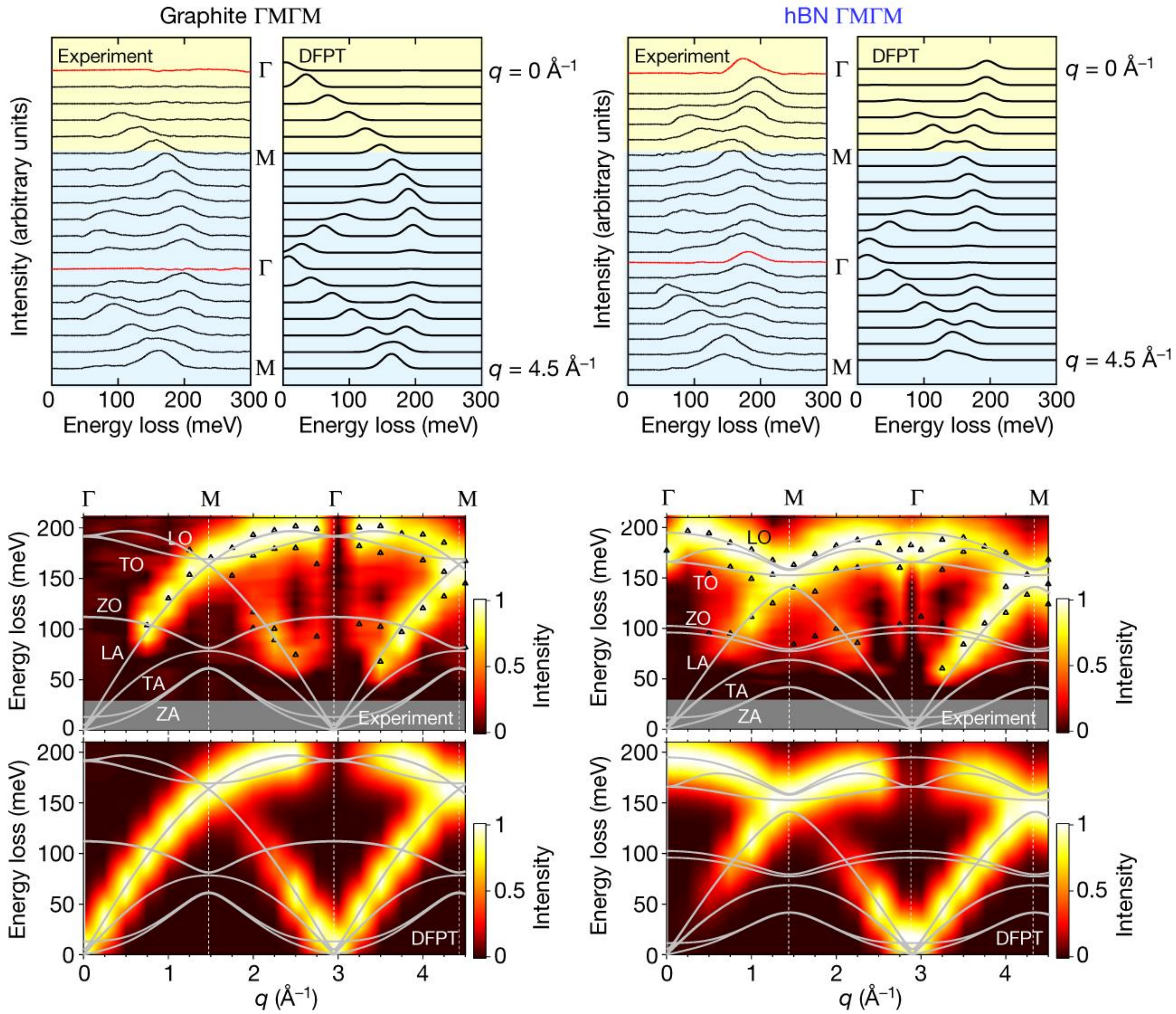
M. Lagos et al. *Nature* **2017**, *543*, 529-532.



R. Qi et al. *Nano Lett.* **2019**, *19*, 5070-5076.

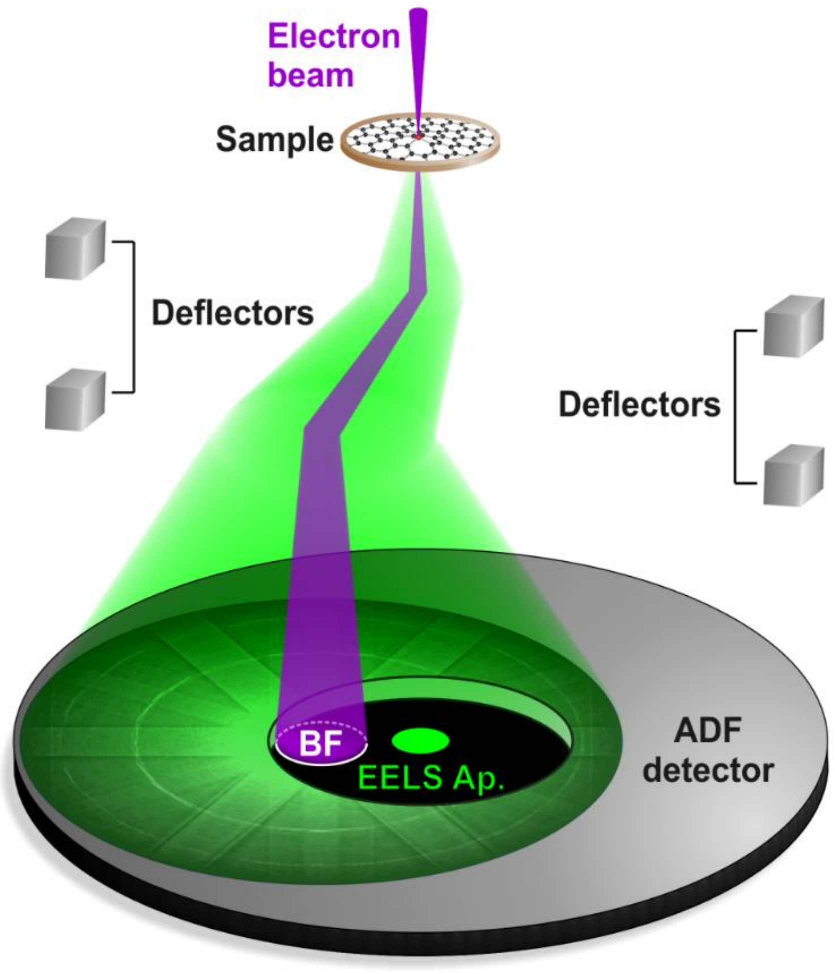
Phonons: Measuring dispersion

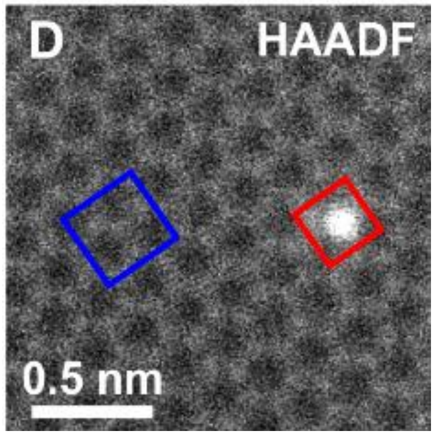


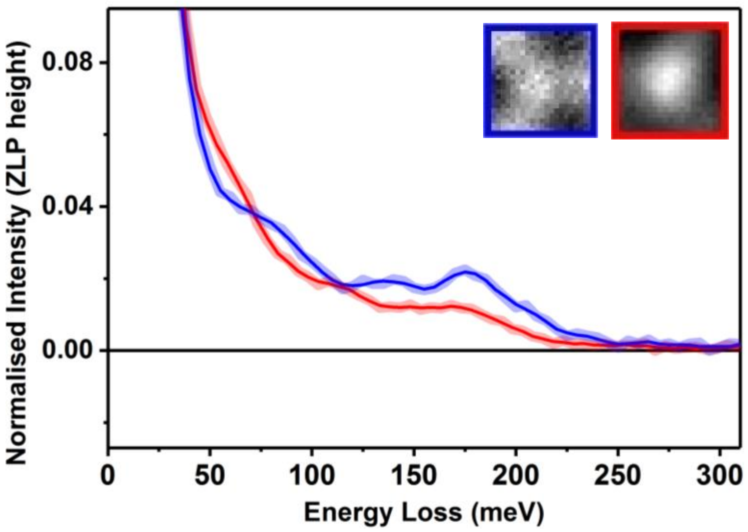


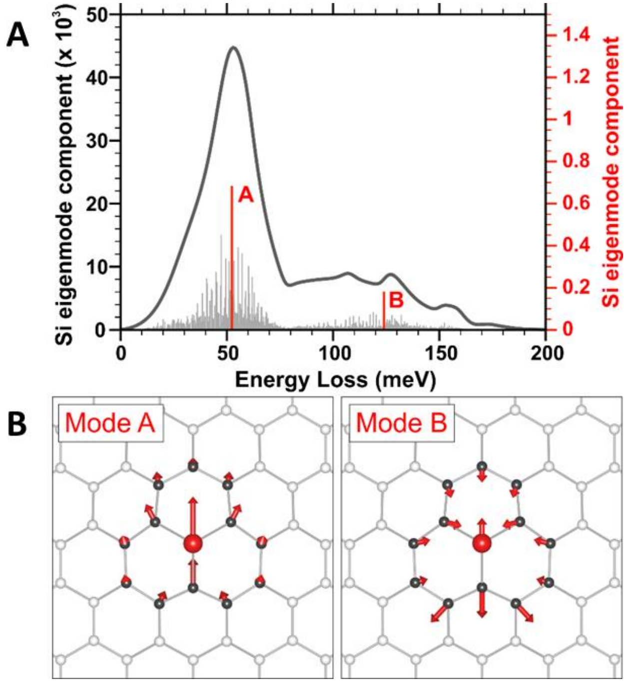
R. Senga et al. *Nature* **2019**, *573*,247-250.

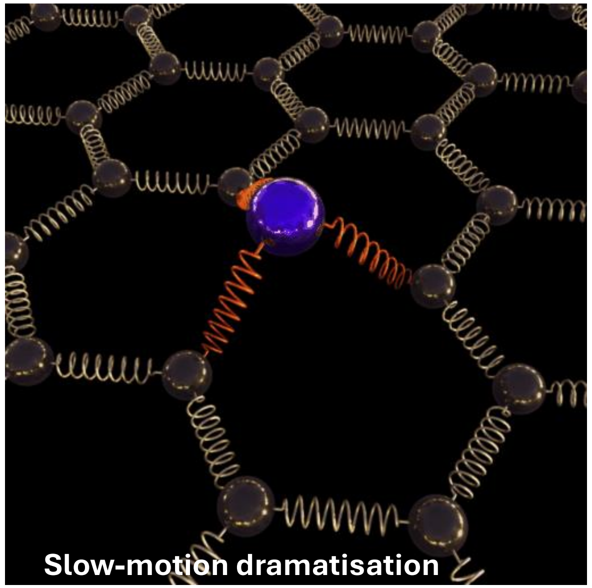
Phonons: Off-axis for localisation





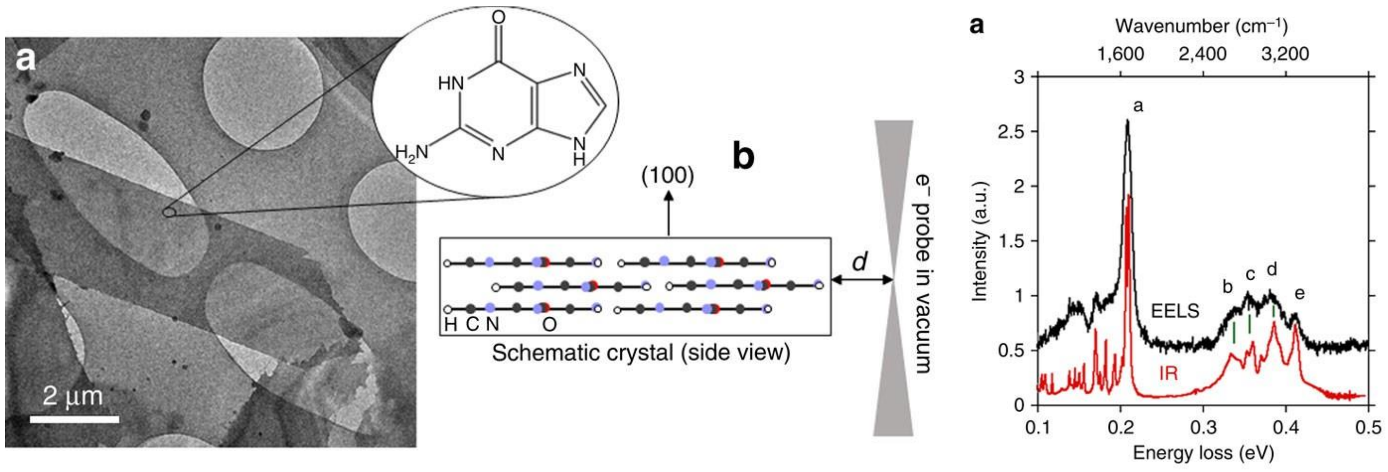


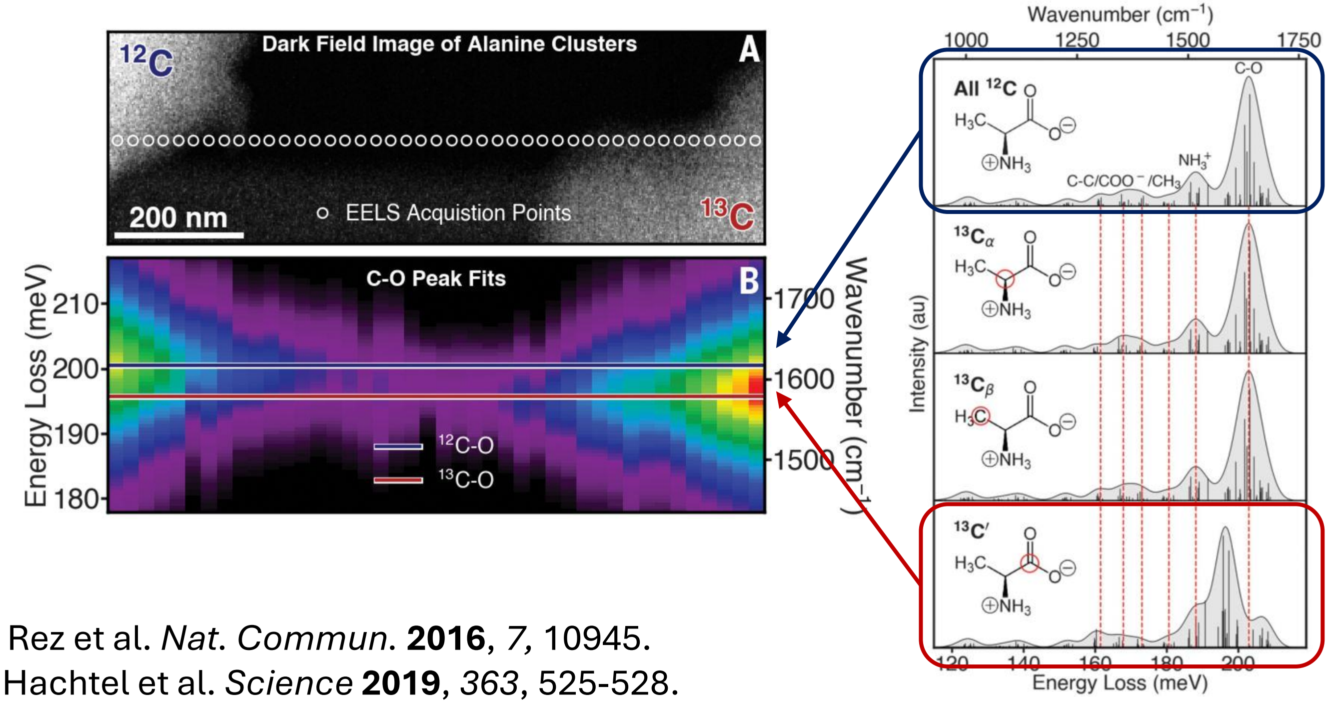


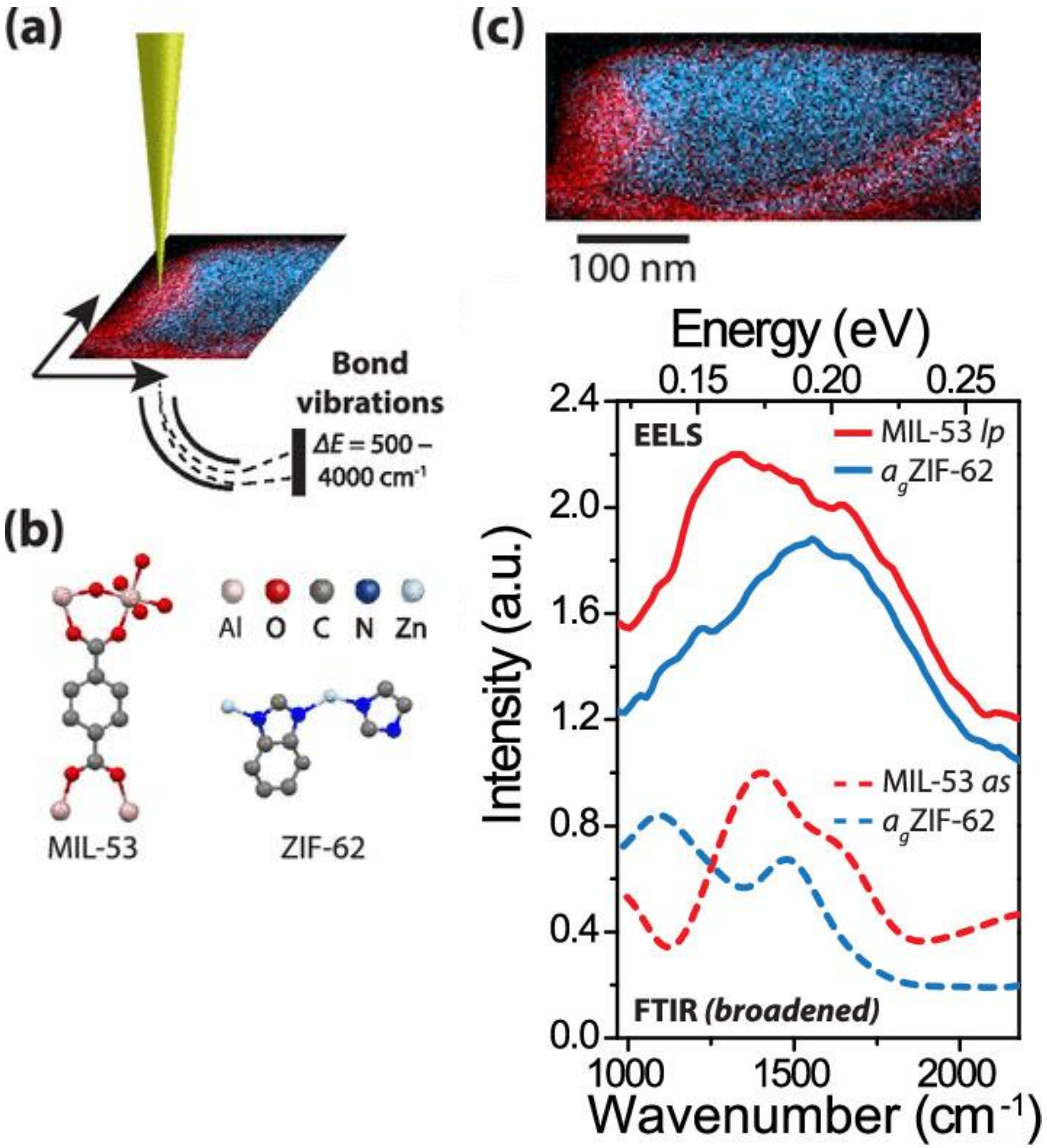


F.S. Hage et al. *Science* **2020,** *367,* 1124-1127.

Molecular vibrations: Isotopic effects and functional group chemistry

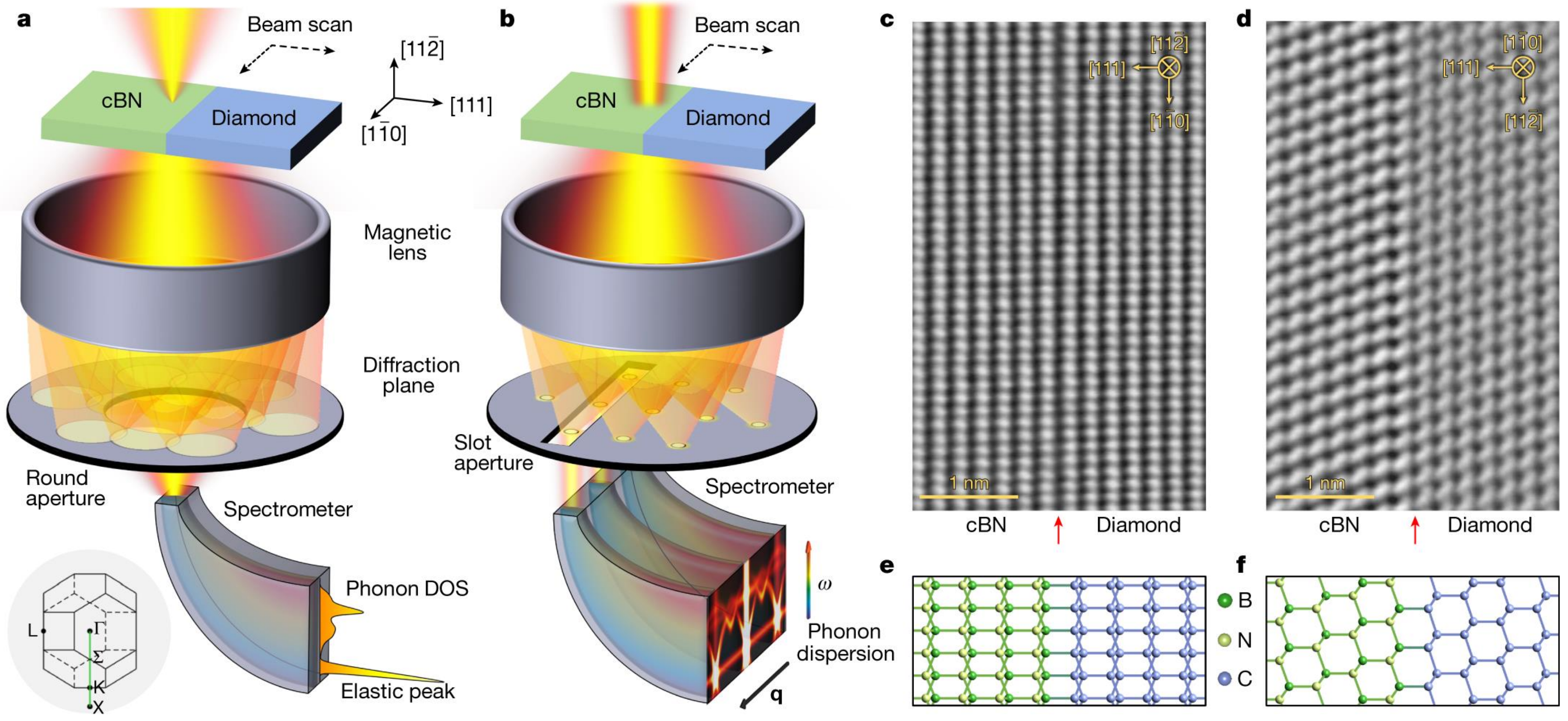






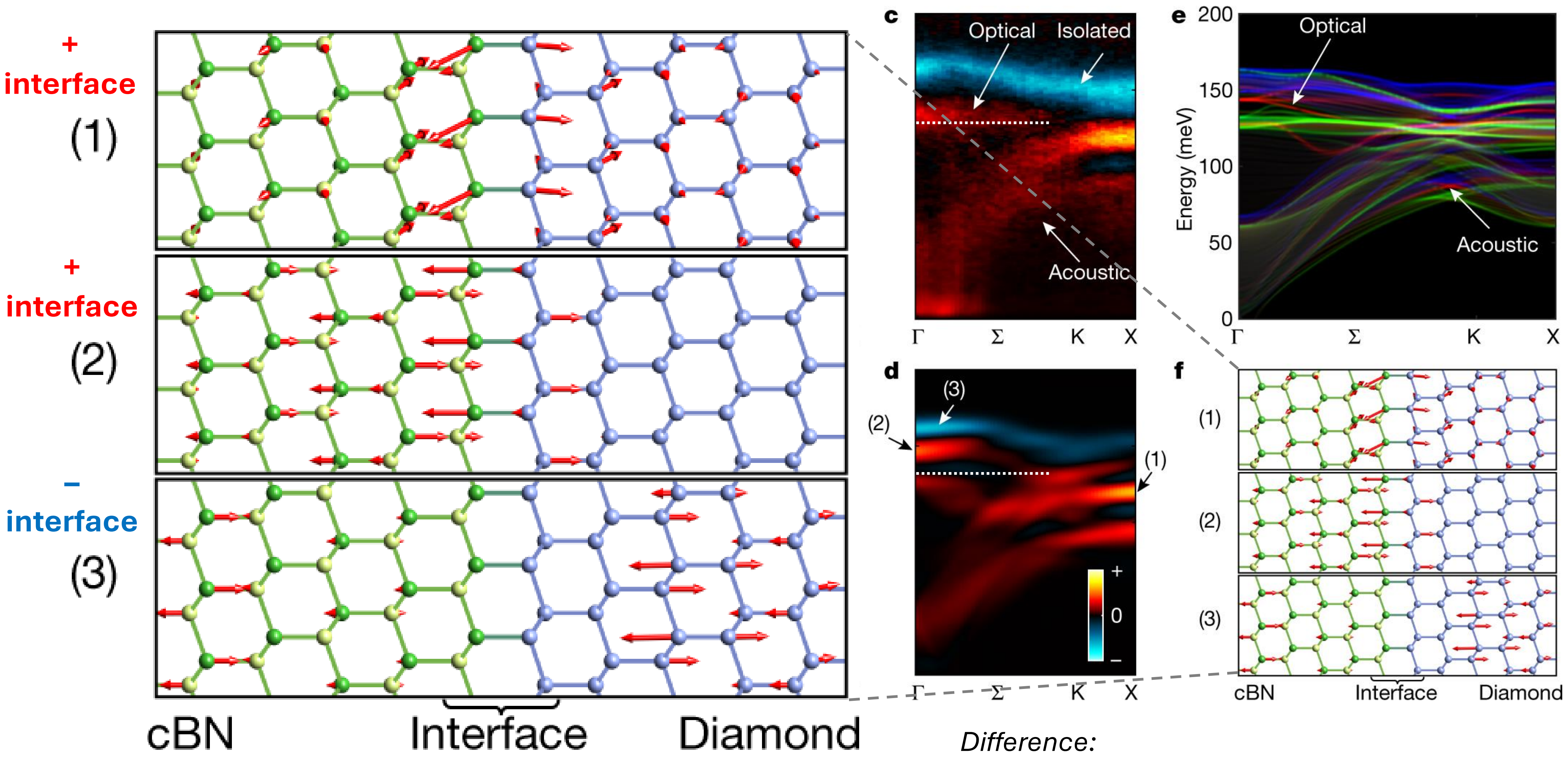
P. Rez et al. *Nat. Commun.* **2016**, *7,* 10945.
J. Hachtel et al. *Science* **2019**, *363*, 525-528.
S. M. Collins et al. *Nano Lett.* **2020**, *20*, 1272-1279.

4D-EELS: Spatially resolved phonon dispersion



R. Qi et al. *Nature* **2021**, *599,* 399-403.

4D-EELS: Spatially resolved phonon dispersion



Difference: Interface – average of two bulk

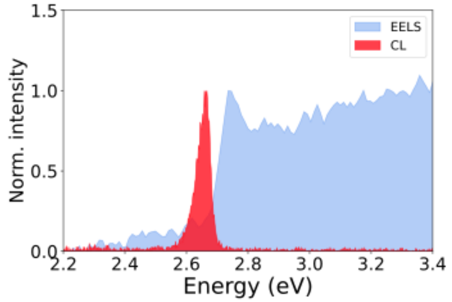
R. Qi et al. *Nature* **2021**, *599*, 399-403.

Summary

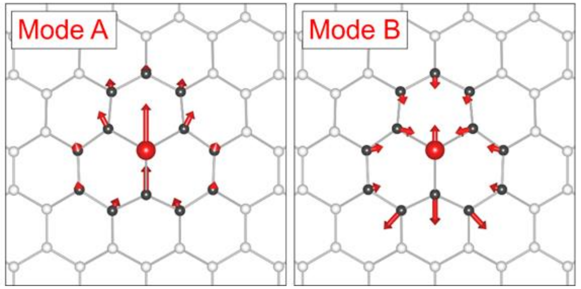
- Low loss EELS and CL detect a variety of excitations of valence electrons
  - Bulk plasmons provide a fingerprint of each phase’s electronic structure
  - Surface plasmons in metals appear in slabs and nanoparticles
  - Materials with bandgaps: Interband transitions and excitons
- CL captures light emission arising from electron interaction
  - Far field radiation from plasmonic resonators
  - Electron-hole recombination (after relaxation and diffusion)
- At IR energies EELS explores phonons and vibrations
  - Surface phonon polaritons (ionic crystal: phonon analogue to surface plasmons)
  - Dispersion
  - Interfaces, domains, and single atom localisation
  - Isotope sensitivity

Metals

Semiconductors



Vibrations

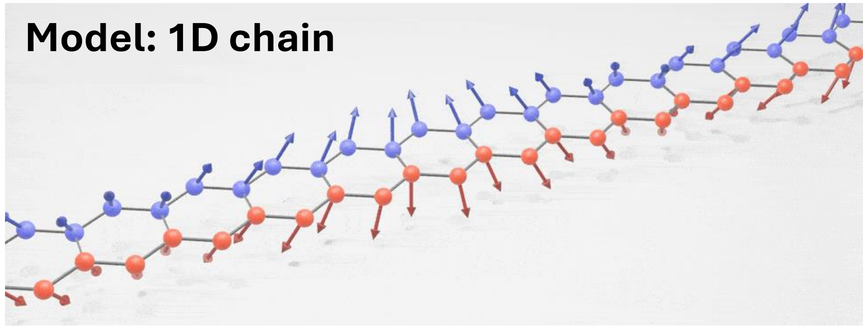


Key references and wider reading

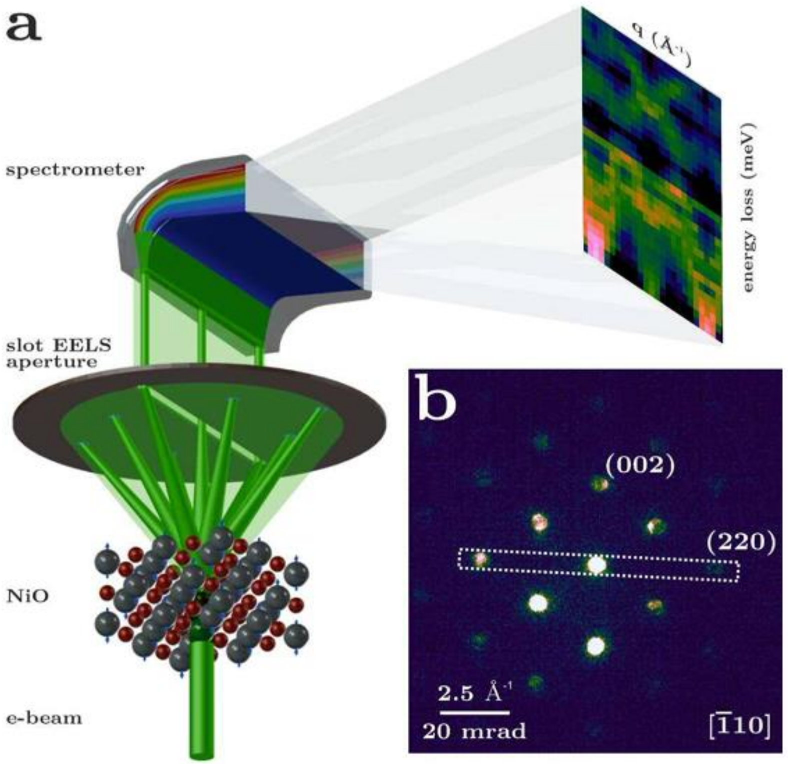
1. F. J. García de Abajo *Rev. Mod. Phys.* **2010**, *82*, 209-275.
   https://doi.org/10.1103/RevModPhys.82.209
2. F. J. García de Abajo and V. Di Giulio *ACS Photon*. **2021**, *8,* 945-974.
   https://doi.org/10.1021/acsphotonics.0c01950
3. A. Polman, M. Kociak, and F. J. García de Abajo *Nat. Mater.* **2019**, *18*, 1158-1171.
   https://doi.org/10.1038/s41563-019-0409-1
4. M. Kociak and O. Stéphan *Chem. Soc. Rev.* **2014**, *43*, 3865-3883.
   https://doi.org/10.1039/C3CS60478K
5. H. Lourenço-Martins and M. Kociak *Phys. Rev. X* **2017**, *7*, 041059.
   https://doi.org/10.1103/PhysRevX.7.041059
6. J. A. Hachtel et al. *Microscopy Today* **2021,** *29*, 36-41.
   https://doi.org/10.1017/S1551929520001789
7. R. Nicholls et al. *Phys. Rev. B* **2019**, *99*, 094105.
   ttps://doi.org/10.1103/PhysRevB.99.094105
8. R. Egerton *Electron Energy-Loss Spectroscopy,* 3rd Ed. Springer 2011.
   https://link.springer.com/book/10.1007/978-1-4419-9583-4

Additional examples

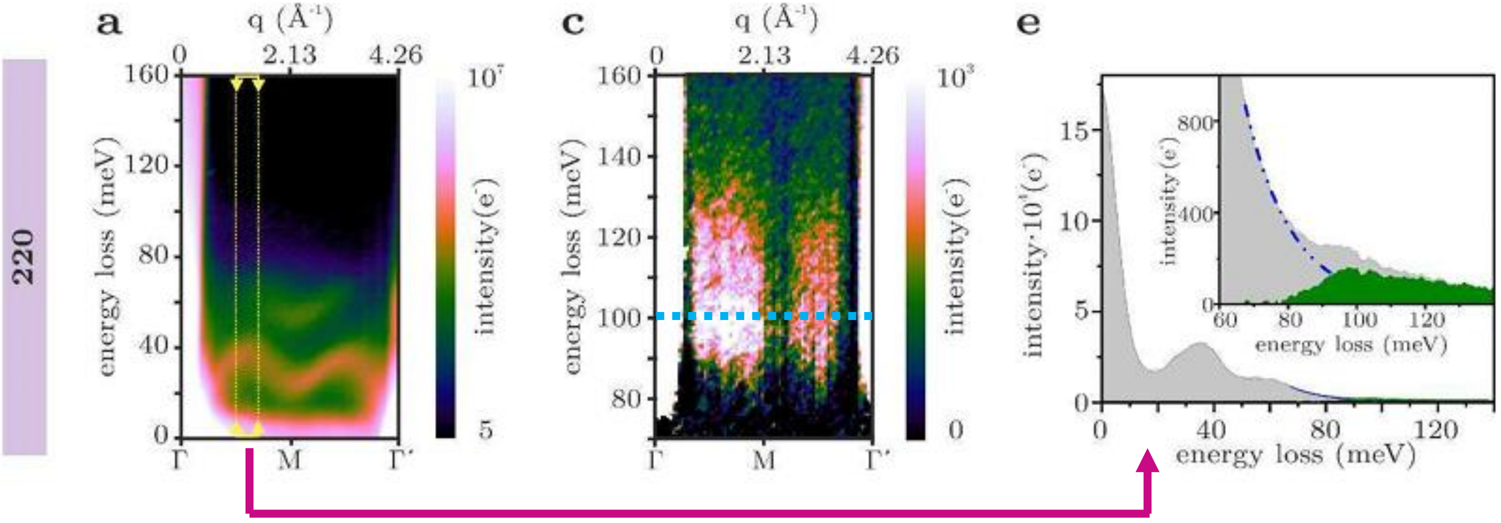
Magnons: Spin waves



https://www.nist.gov/image/magnon-animation\



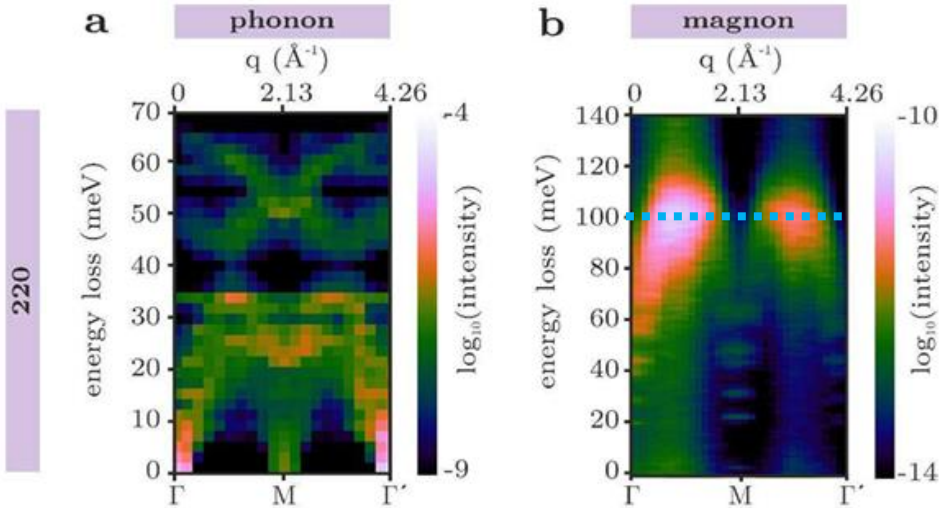
Experiment



Profile through ω-q

$E = \hbar\omega$

Calculations

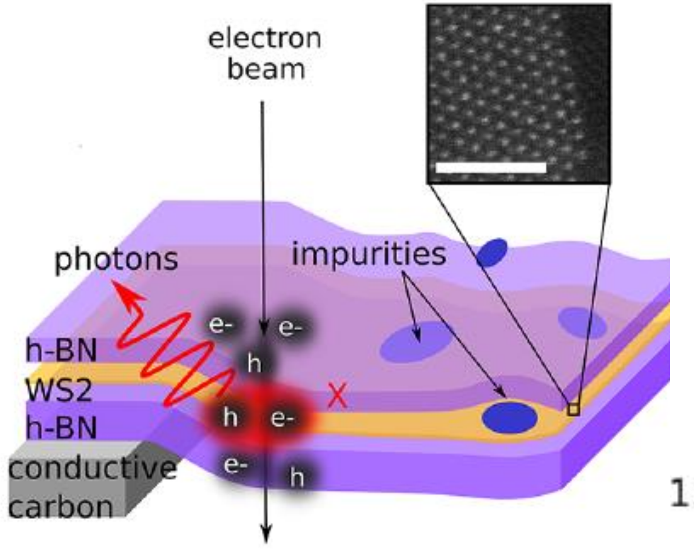


Note differences in vertical axis scales for visualisation

D. Kepaptsoglou et al. https://arxiv.org/abs/2410.02908.

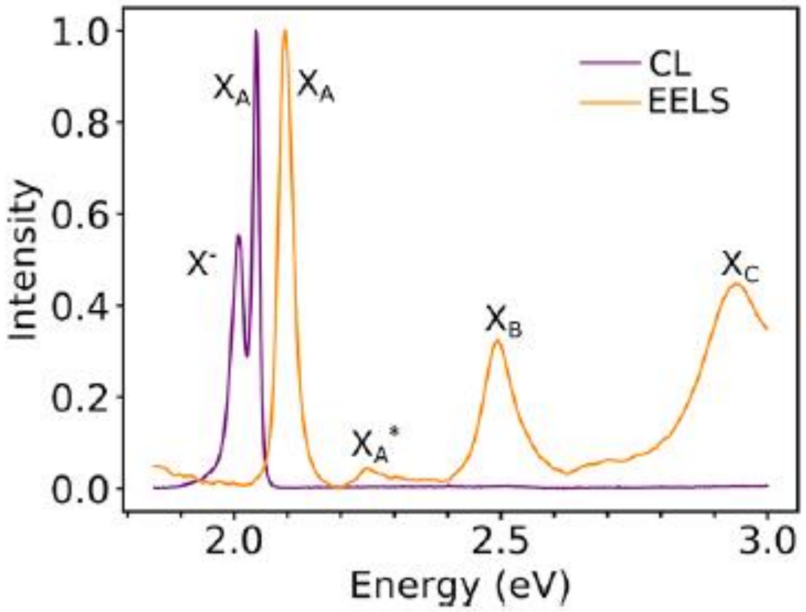
EELS+CL of sandwiched TMD layers

Sample: exfoliated WS_2 encapsulated in h-BN (5/10 nm top/bottom) on carbon filled with 2 μm holes



h-BN encapsulation:

- Increases interaction volume (more signal, esp in CL)
- High purity/quality gives sharp lines

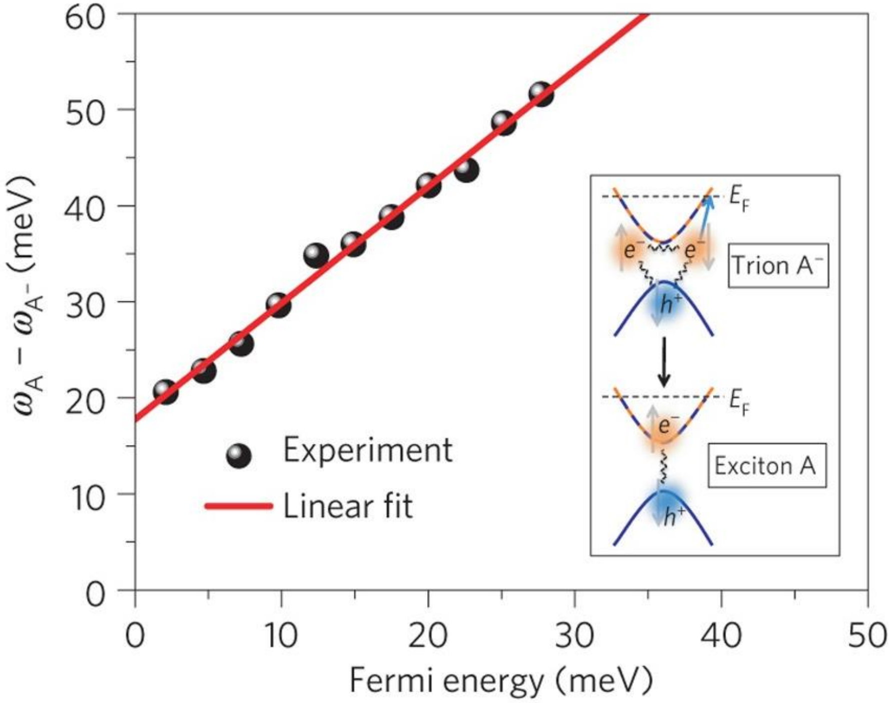


Peak position and decrease in X⁻ peak at room temperature used to assign features

N. Bonnet et al. *Nano Lett*. **2021**, *21*, 10178-10185.

Attolight Mönch CL system

What is a trion?

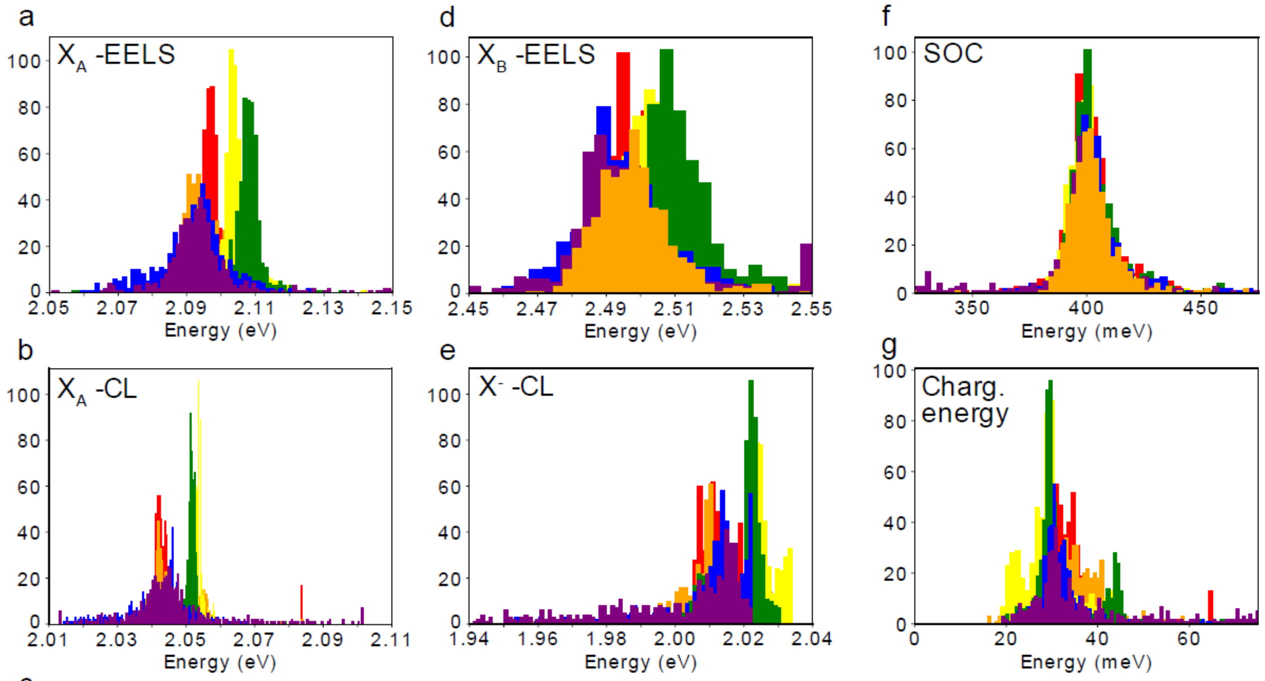


Fermi energy controlled through applied bias (gating). Trions form in the presence of excess electrons (doping or gating)

K.F. Mak *Nat*. *Mater*. **2013**, *12,* 207-211.

EELS+CL of sandwiched TMD layers

Gaussian fitting of peaks with both EELS and CL data enables several further optical parameters to be extracted

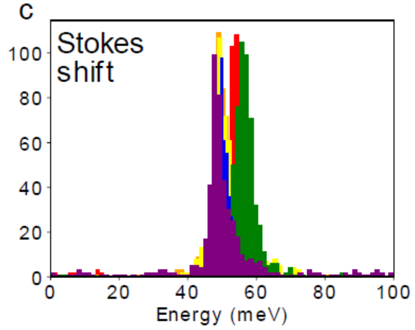


$X_A - X_B$

Energy difference arising from spin-orbit coupling (energy splitting)

$X_A - X^-$

Energy shift due to additional charge in trion



Stokes shift – difference in absorption and emission energies ($E_{abs} - E_{PL}$)
Key optical parameter as reflects relaxation and dissipation of excited state

$X_{A,\ EELS} - X_{A,\ CL}$

Small energy shifts consistent with PL observations – broadly differences in chemical environment, strain (lattice distortions)

N. Bonnet et al. *Nano Lett.* **2021**, *21*, 10178-10185.