EELS and CL on the Nion ChromaTEM: Nano-optics with fast electrons

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Lab. de Physique des Solides (LPS), CNRS, U. Paris-Saclay, France

hBN from:
Kenji Watanabe, Takashi Taniguhui
NIMS Tsukuba, Japan

AlN/GaN nanowire from:
Eva Monroy
CEA, Grenoble, France

LPS ORSAY

HyperSpy

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Summary

Introduction: 20 minutes

Why nano-optics

Electron spectroscopy with fast electrons

Which equipment is needed?

Which samples are we looking at:

Light emission from excitons confined in quantum disks

Phonons in hBN flakes

Experiment: 30 minutes

Cathodoluminescence (CL) of GaN quantum disks in AlN nanowires

Electron energy loss spectroscopy of surface phonon polaritons in hBN flakes

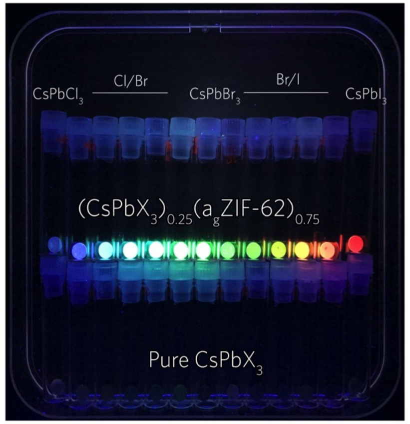
Data Analysis: 40 minutes

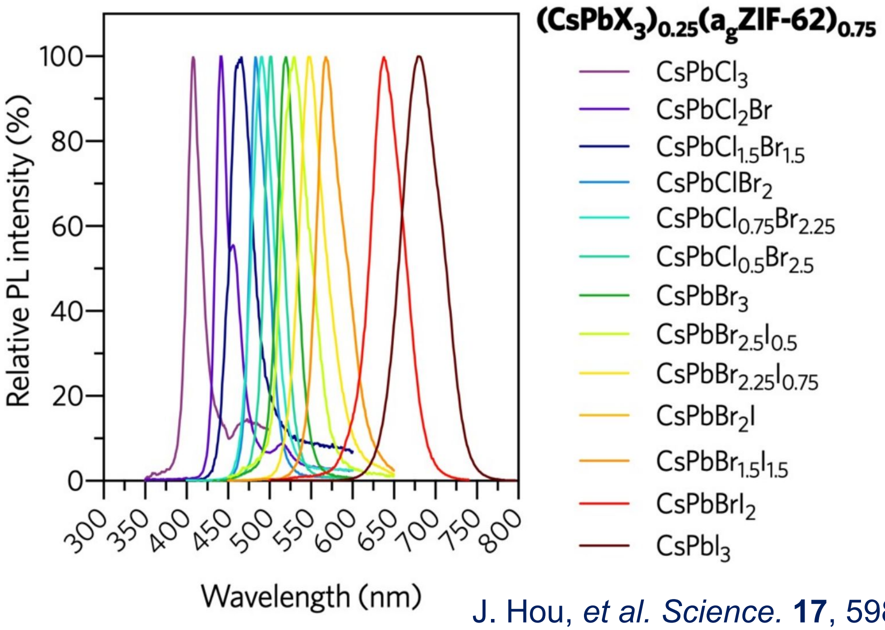
How to use python/hyperspy to analyze hyperspectral images

(we are around during the rest of the school, if you have questions, don't hesitate to contact us after the practical)

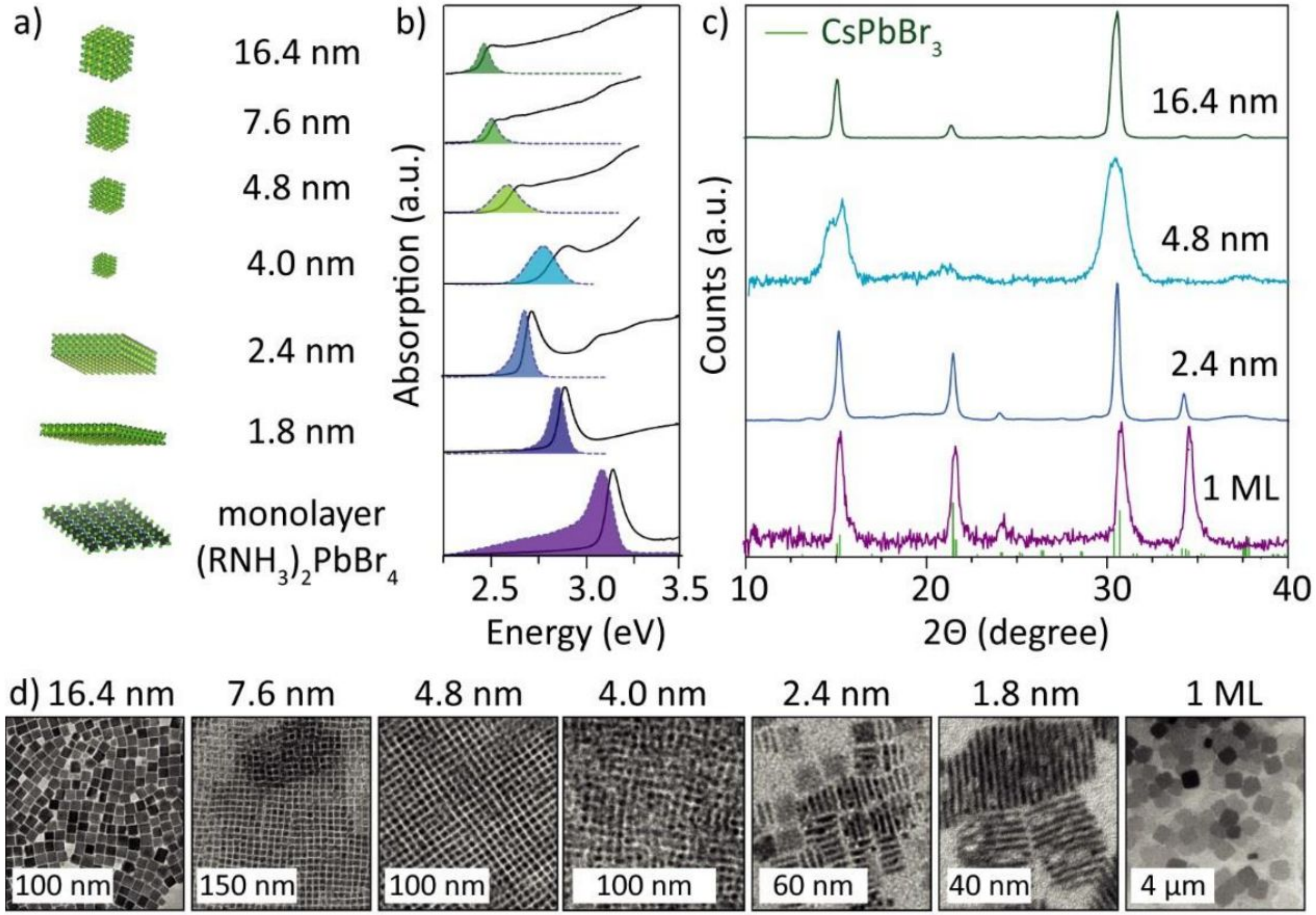
Why nano-optics?

Structure/chemistry and optics using complementary techniques: understanding through statistics





J. Hou, *et al. Science.* **17**, 598 (2021)



Single particles?

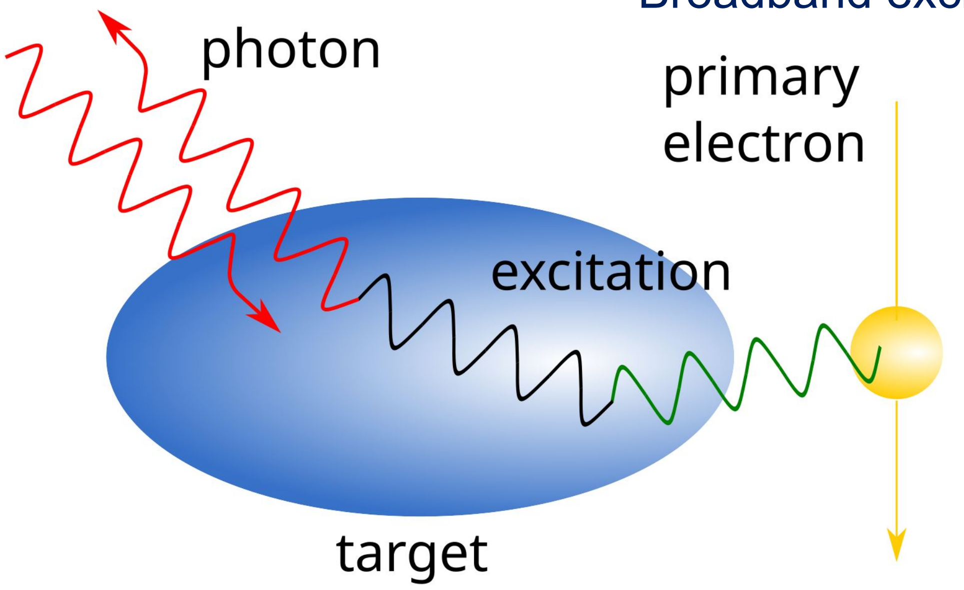
Q. A. Akkerman, *thesis: Lead Halide Perovskite Nanocrystals* , (2018)

Electron spectroscopies

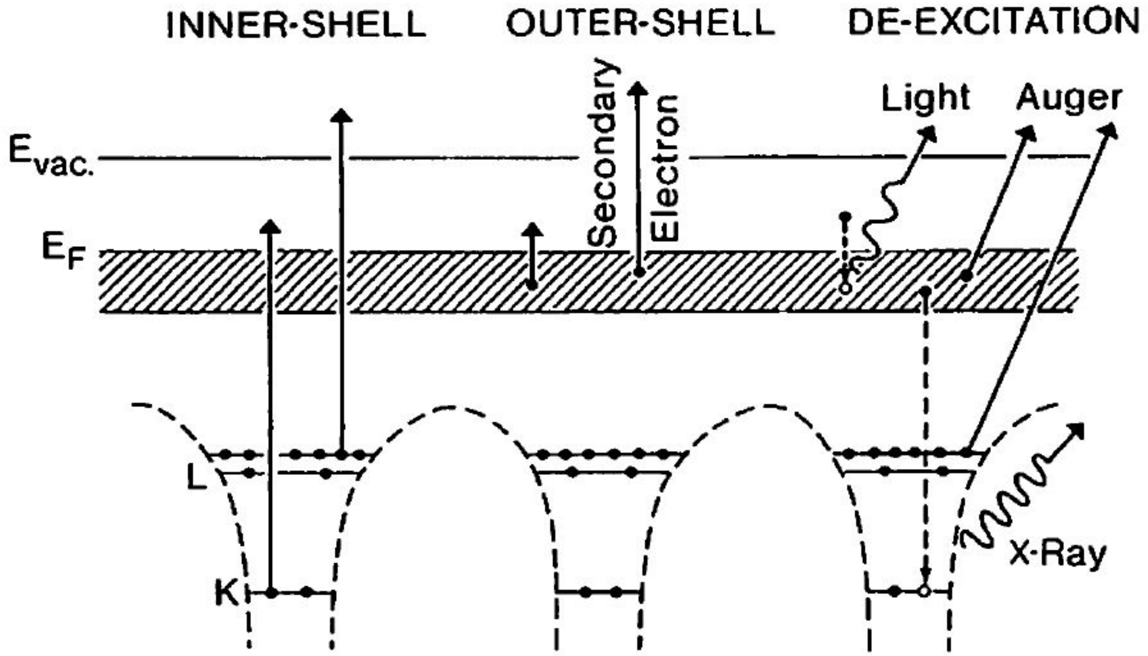
Either look at excitations creation or their decay

Decay: CL, EDS, EEGS,
Auger spectroscopy

Broadband excitation



Energy lost: EELS

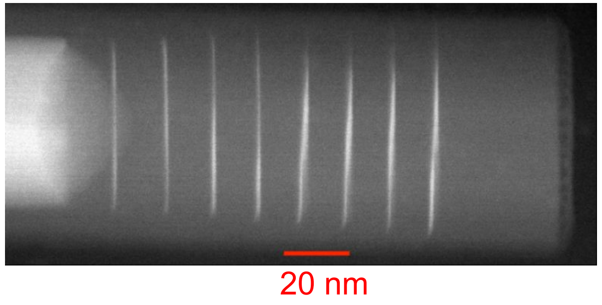


R. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, third edition (2011)

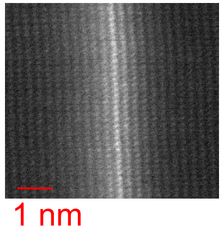
Typical kinetic energy:
100 keV (3.7 pm)

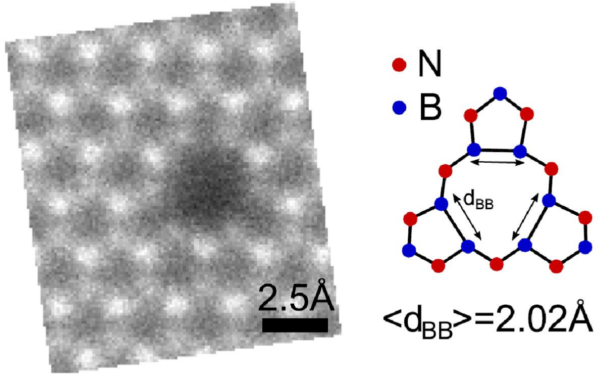
Experimental setup: STEMs

Elastic scattering (imaging)

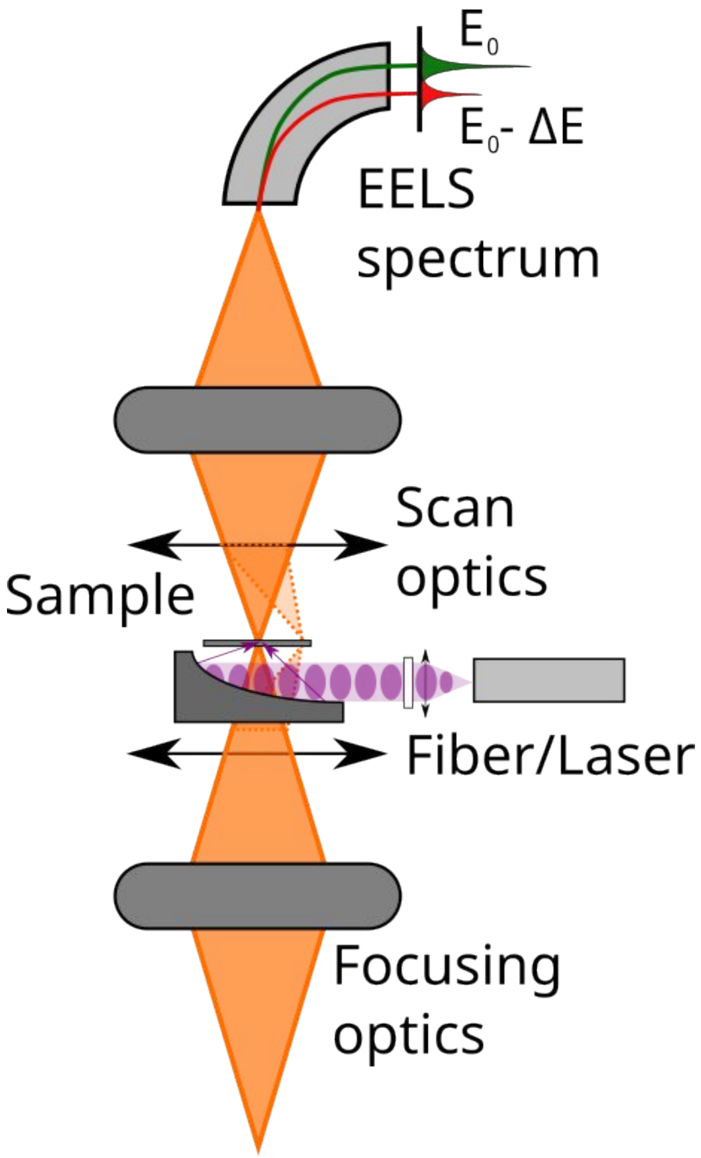


Crystal
structure
Atomic number
Morphology



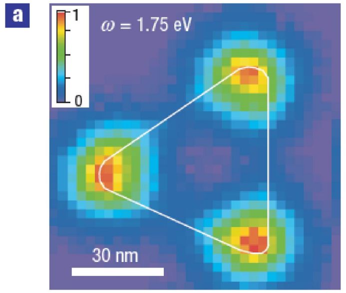


O. Cretu, et al *Phys. Rev. Lett.* (2015)



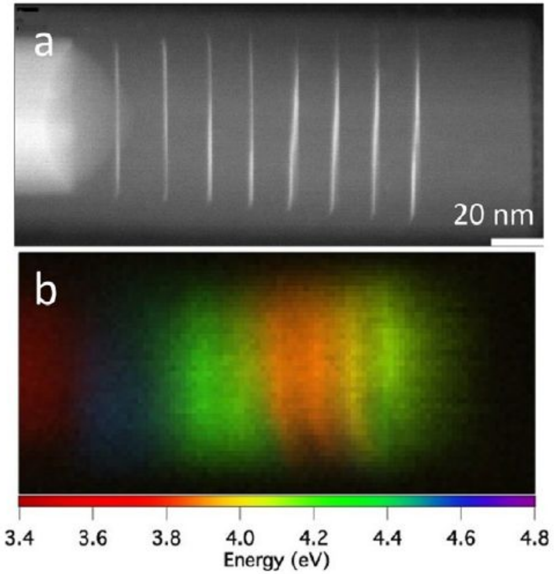
CL: L.F. Zagonel and M. Kociak *Ultramic.* **176** 112(2017)
EELS: J. Garcia de Abajo, *Rev. Mod. Phys.*, **82,** 209 (2010)

Inelastic scattering (spectroscopy)
EELS: absorption



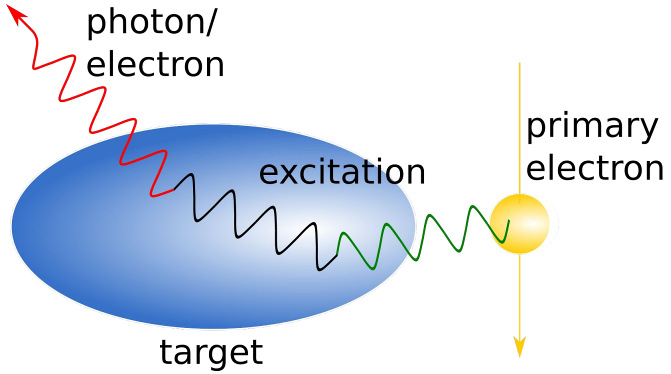
J. Nelayah, *et al. Nat. Phys.* **3** 348 (2007)

CL: excitation of a decay channel probability



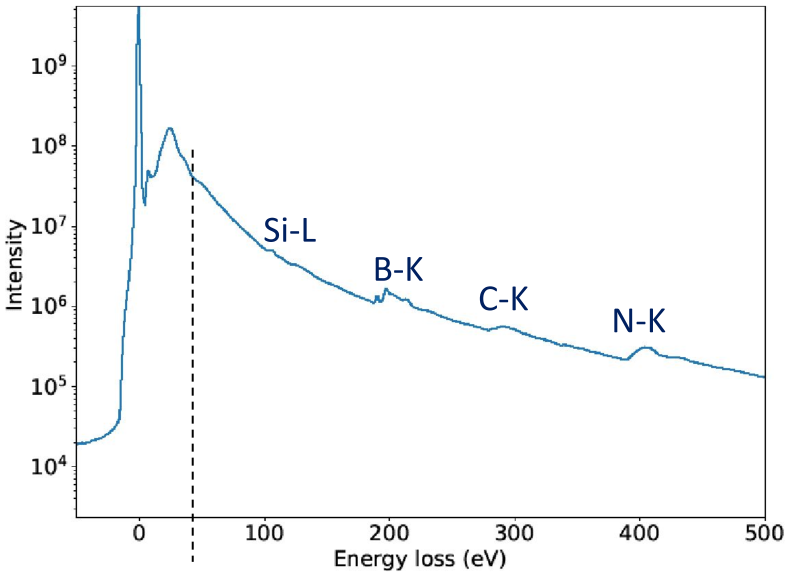
Also EEGS, EDS, Auger …

Electron spectroscopies: EELS



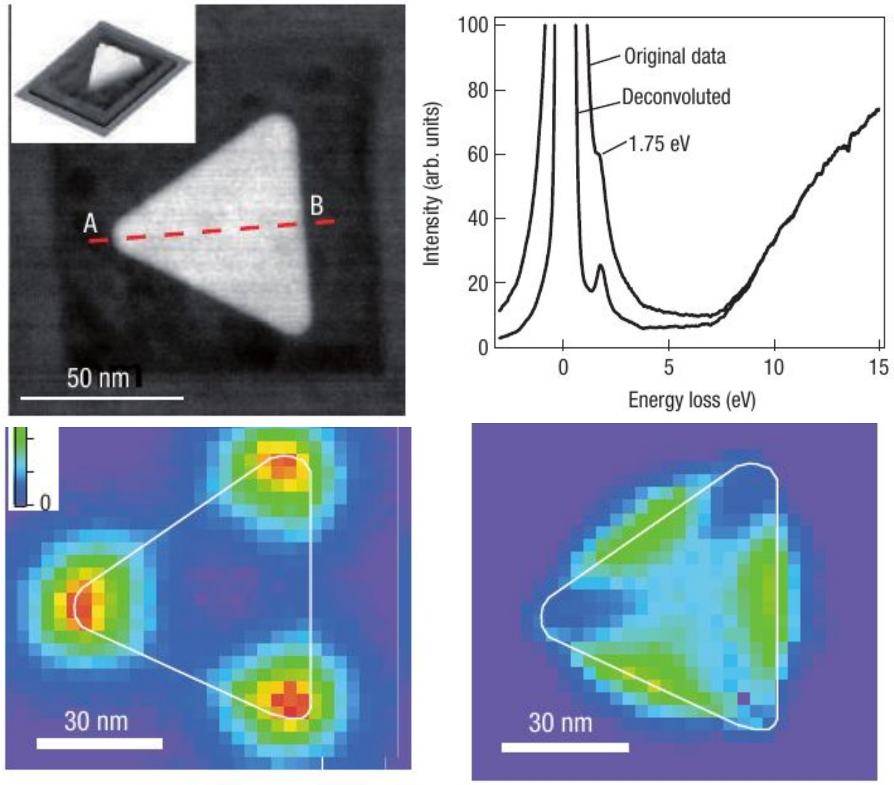
EELS of *h*-BN

By Steffi Woo



Low loss   Core loss

Plasmons in metallic structures



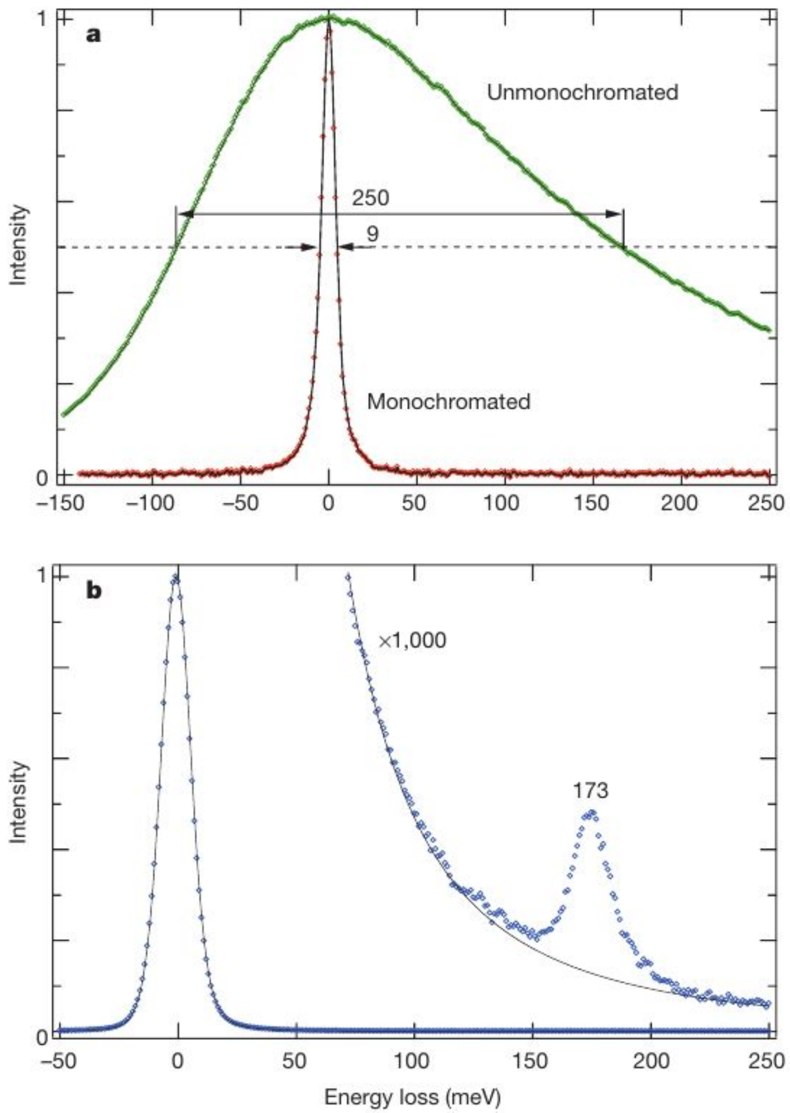
J. Nelayah, *et al.*, *Nat. Phys.*, **3**, 349 (2007)

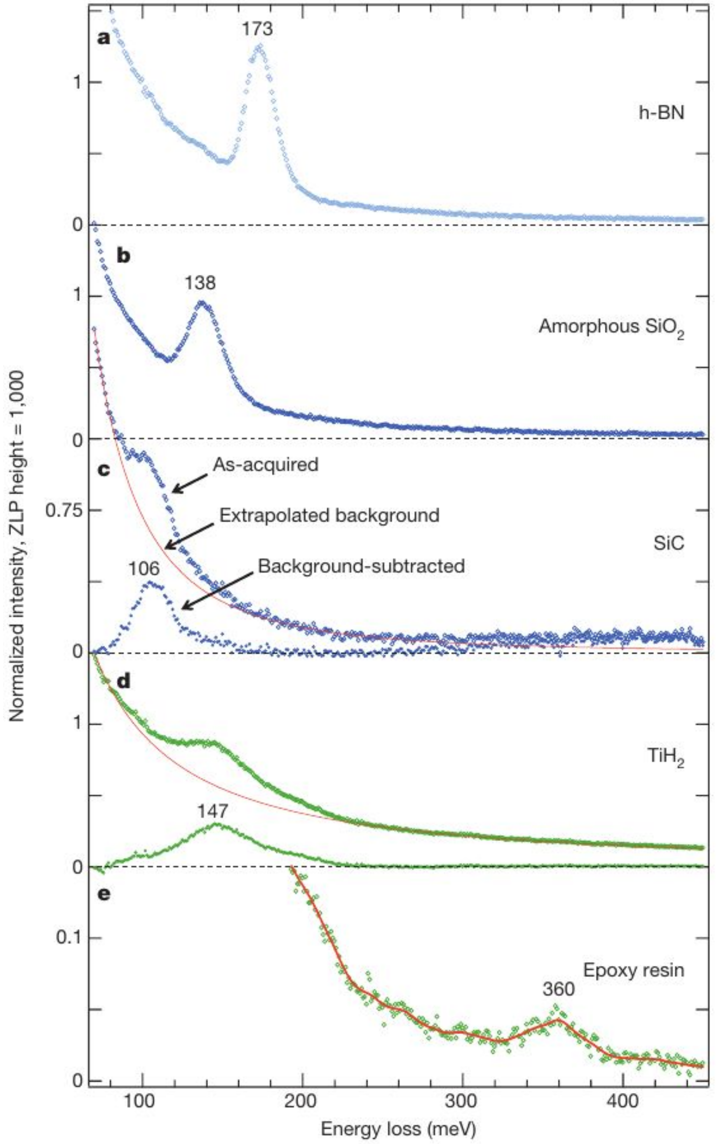
Bulk low loss EELS ~Im[-1/ε(ω)]

“Thin” low loss EELS ~Im[ε(ω)]

Vibrational EELS

Vibrational EELS at high spatial resolution
enabled by modern monochromators

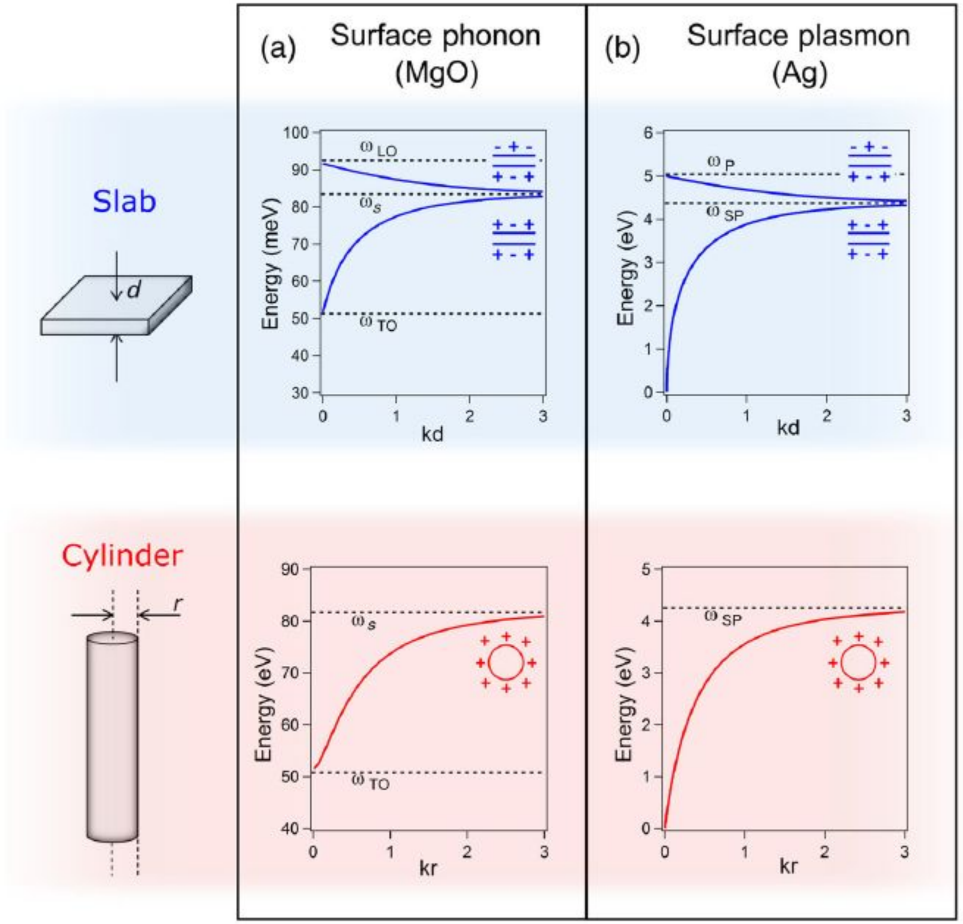




O. Krivanek, *et al.*,
Nature, **514**, 209 (2014)

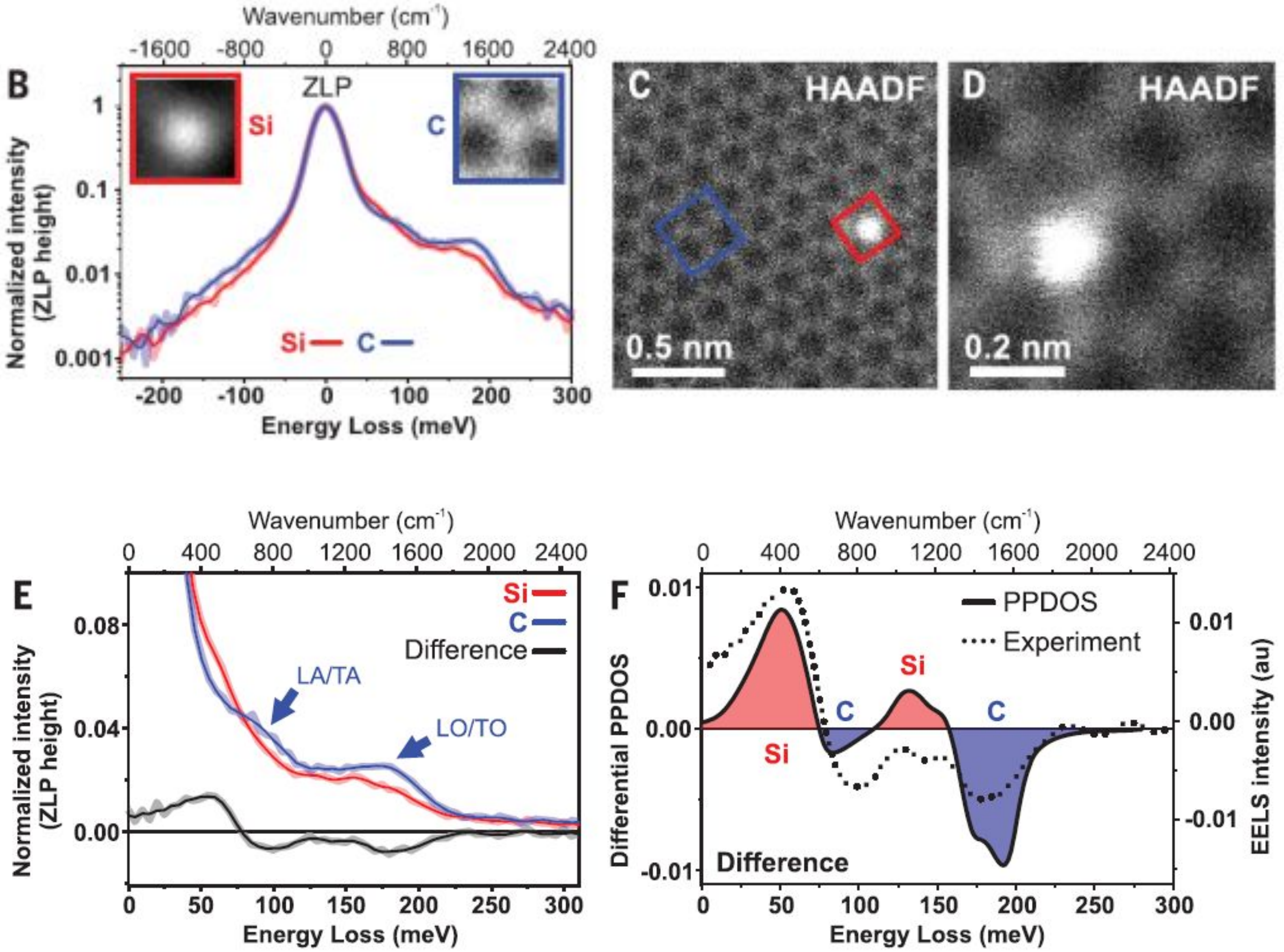
Vibrational EELS

Physics identical to plasmon polaritons/bulk plasmons



H. Lourenço-Martins and M. Kociak, *et al.*, *Phys. Rev. X*, **7**, 041059 (2017)

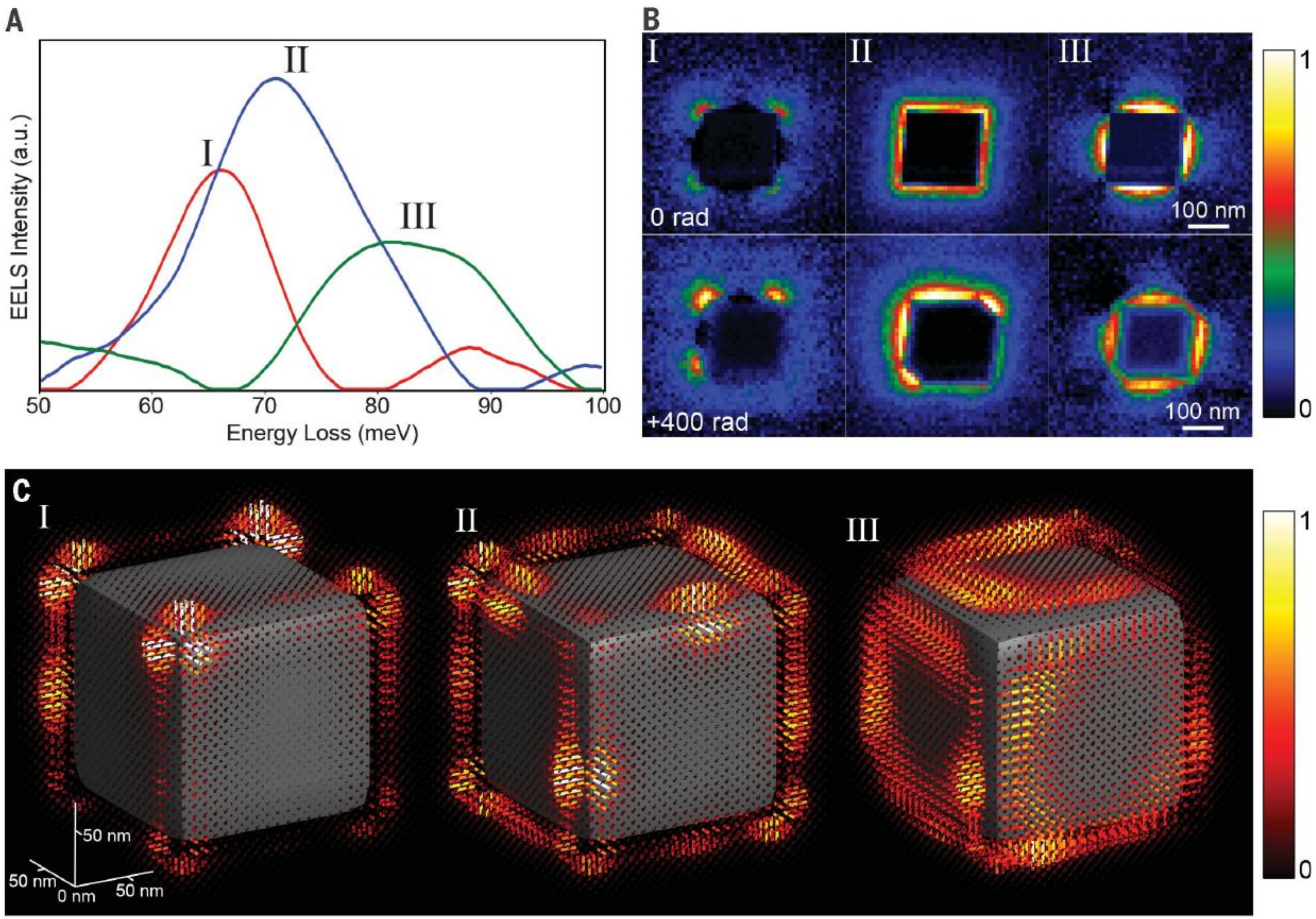
Phonon mapping at atomic resolution



F. Hage, *et al.*, *Science*, 367, 1124 (2020)

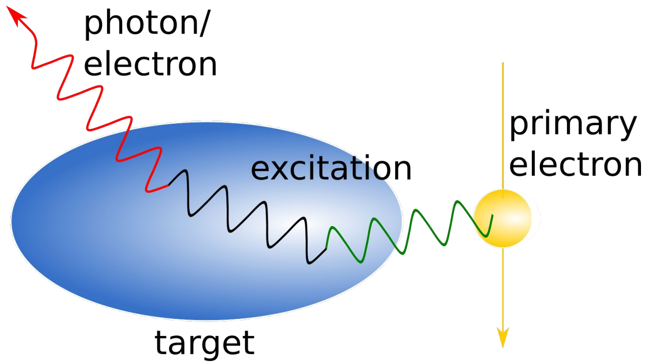
Vibrational EELS

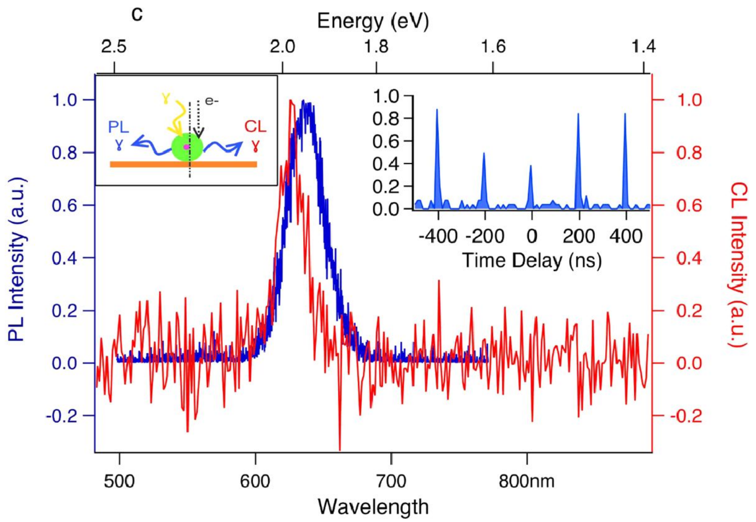
3D mapping of vibrational modes
in MgO cubes



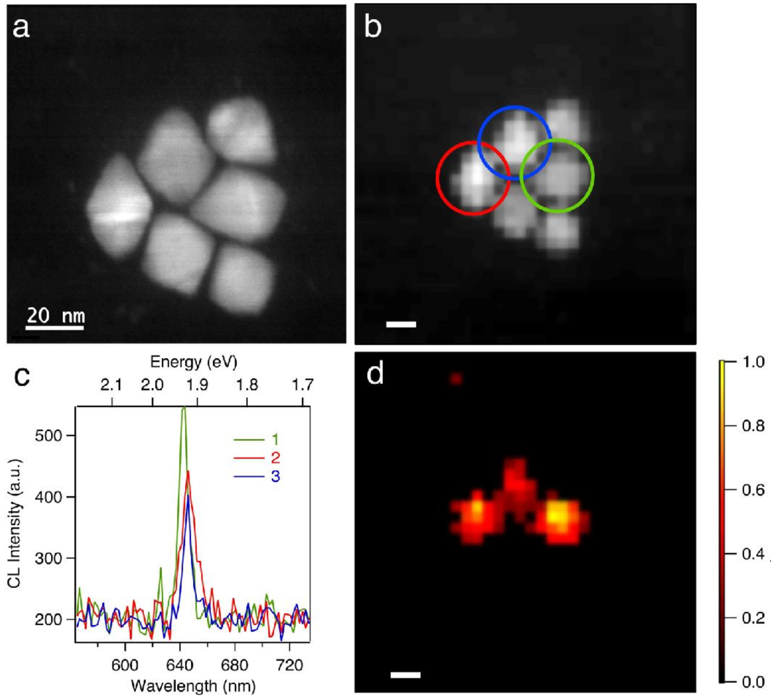
X. Li, *et al.*, *Science*, 371, 1264 (2021)

Electron spectroscopy: CL



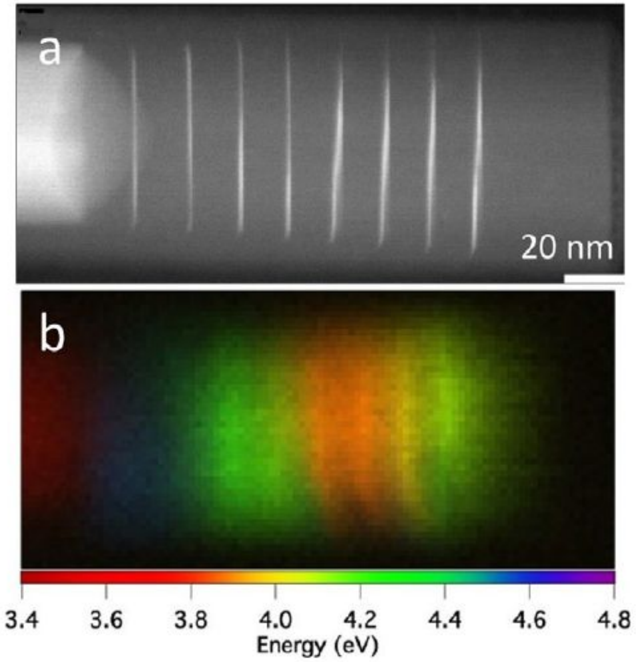


CL is linked to off-resonance photoluminescence



Z. Mahfoud, *et al.* J. Phys. Chem. Lett., **4** 4090 (2013)

CL: excitation x light extraction probabilities



S. Meuret, *et al. ACS Photon.* **3** 1157 (2016)
S. Finot, *et al. ACS Photon.* **9** 173 (2021)

The CHROMATEM Microscope

	A synchrotron in a STEM	Optical bench in a STEM
High resolution **EELS**	50 -100 meV	5 meV
High Resolution **imaging**	1.2 Å	Sub-nm
Low temperature (N_2) and soon Liquid He		
NanoCL & **Light** injection		1 meV
High resolution **monochromation**		Other specs, especially for reciprocal space measurements
High currents		20 pA @ 7 meV @ 5 Å

© Photo credit – Cyril FRESILLON / LPS / CNRS Photothèque

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INVESTISSEMENTS D'AVENIR

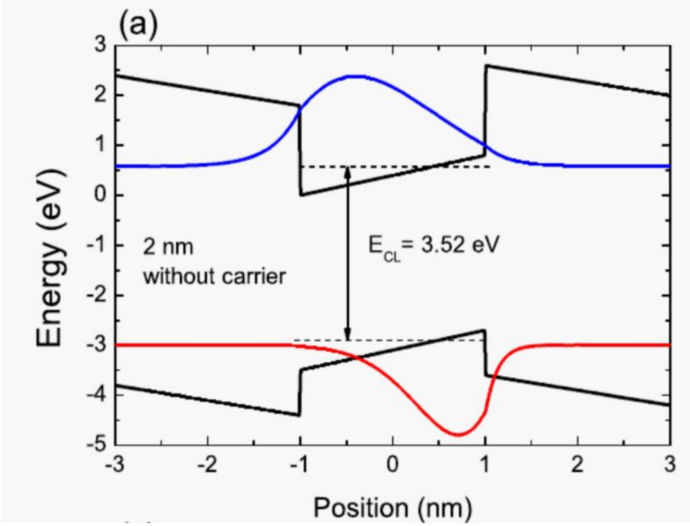
Equipement d'excellence

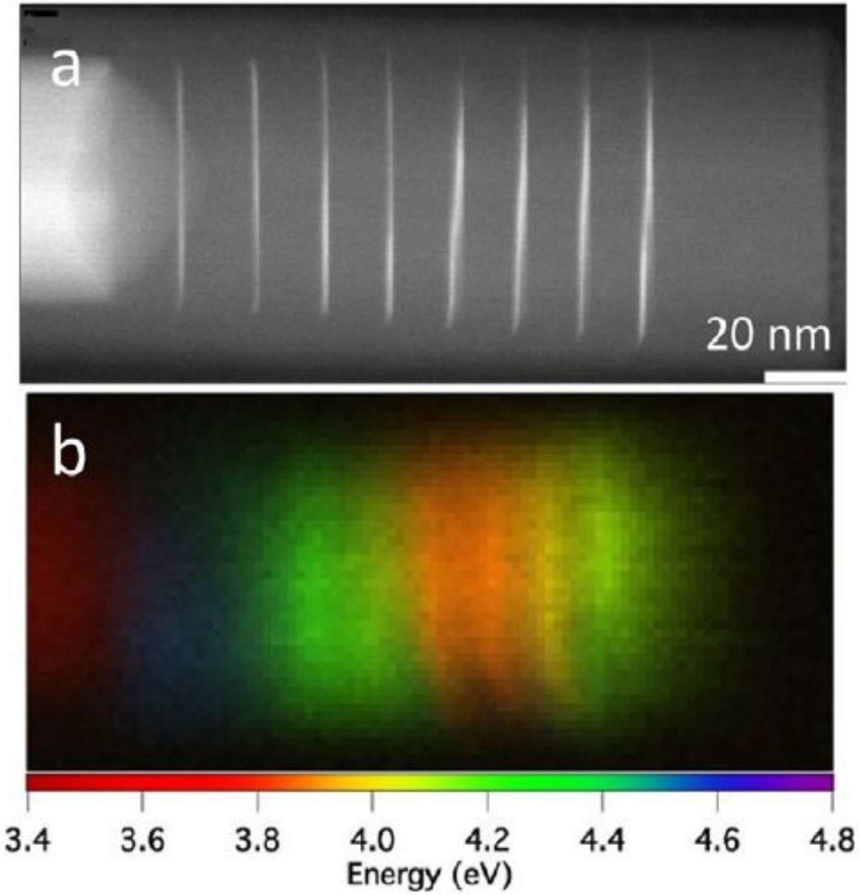
TEMPOS

Transmission Electron Microscopy at Palaiseau Orsay Saclay

CL GaN quantum disks in AlN nanowires

Light emission occurs due to electron and hole (missing electron) pair recombination, possibly with excitonic effects



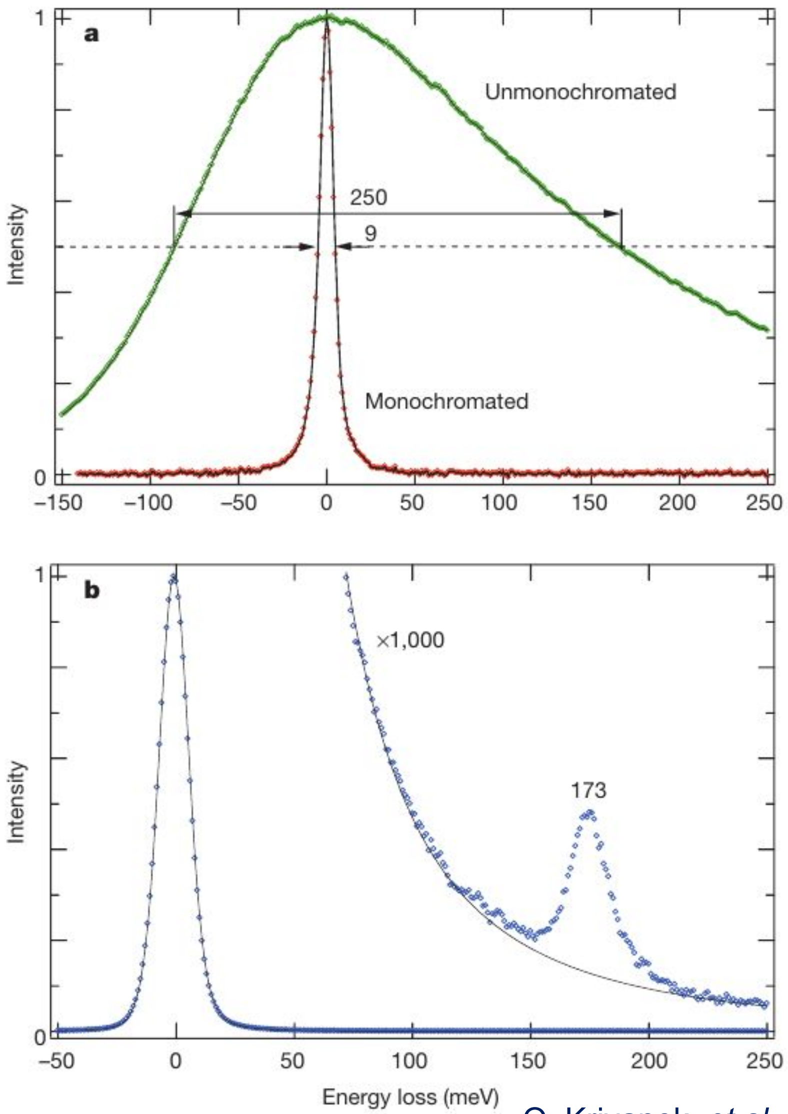


S. Meuret, *et al. ACS Photon.* **3** 1157 (2016)

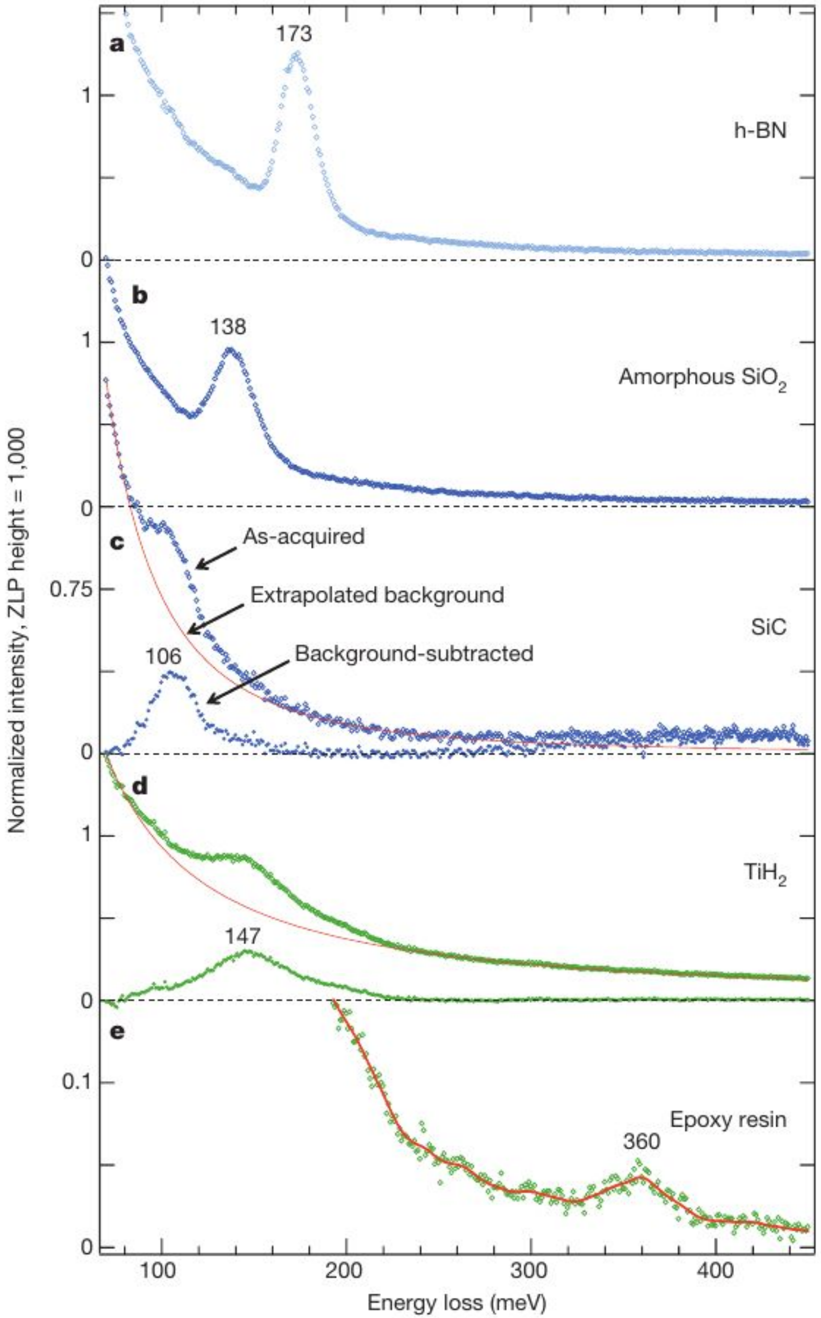
1) **Electron and holes** are represented by **wavefunctions** of a given size (nanometric here)
2) In a bulk material, the difference in energy between electrons and holes is the forbidden energy band gap (consequence of crystal structure + Schrödinger equation)
3) When they are in a **confined** space, their **energy is increased** (consequence of Schrödinger equation)
4) So the **emission energy** depends on the quantum well size

N. Ashcroft and N. D. Mermin, Solid State Physics
M. Cardona, Fundamentals of Semiconductors

EELS of phonons

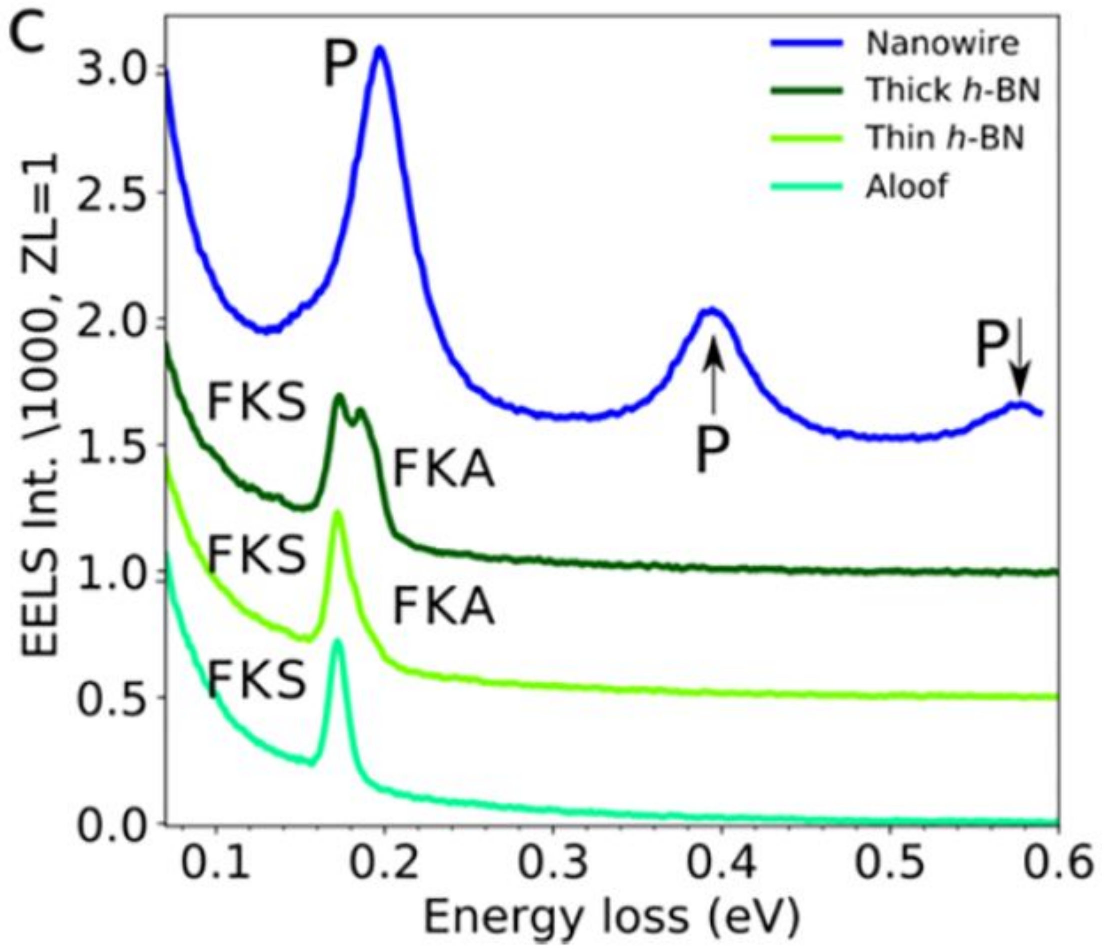


O. Krivanek, *et al.*, *Nature*, **514**, 209 (2014)



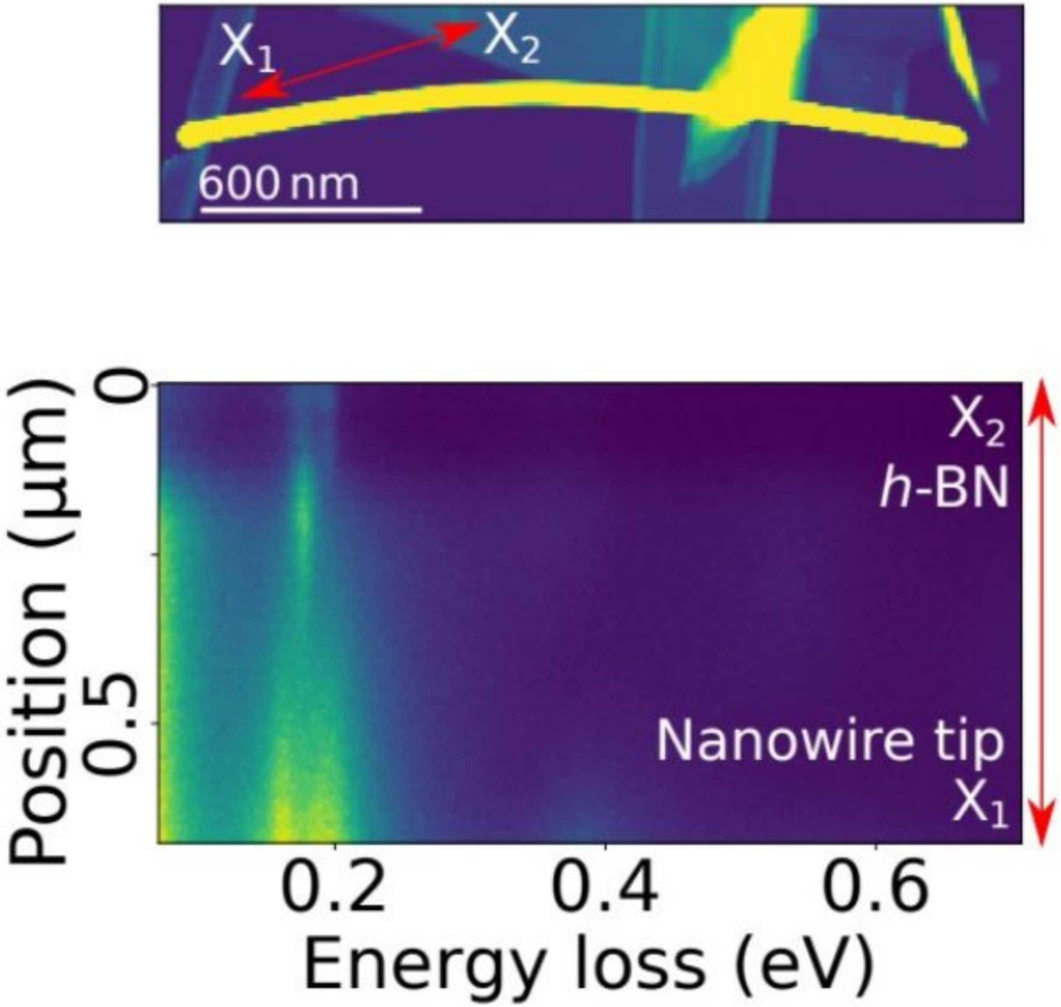
EELS of phonons in hBN

Fuchs Kliewer modes in hBN



L. H. G. Tizei, *et al., Nano Lett.*, **20**, 2973 (2020)

Mapping of vibrational modes



Experiments

Data analysis

Acknowledgements

STEM group - LPS

université PARIS-SACLAY

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LPS ORSAY

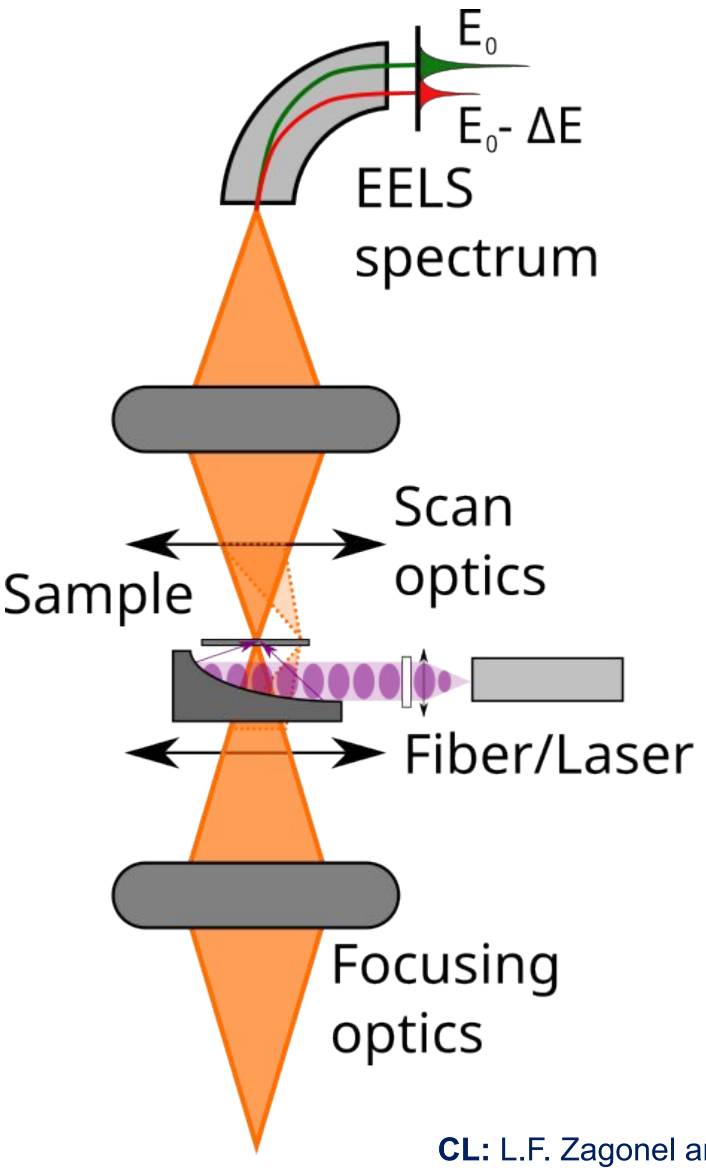
Thank you for your attention!

HyperSpy

Extra slides

Experimental setup

© Photo credit – Cyril FRESILLON / LPS / CNRS Photothèque



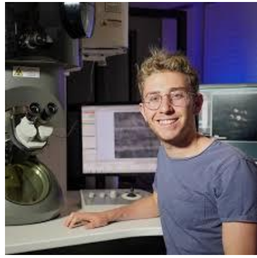
Fast blanking (5 ns) and TPX3 (1.5 ns) for time-resolved spectroscopy

Different spectroscopies: EELS, CL, EEGS…

Focused laser injection (~µm spot size)

CL: L.F. Zagonel and M. Kociak *Ultramic.* **176** 112(2017)
EELS: J. Garcia de Abajo, *Rev. Mod. Phys.*, **82,** 209

Laser-EELS synchronized experiments

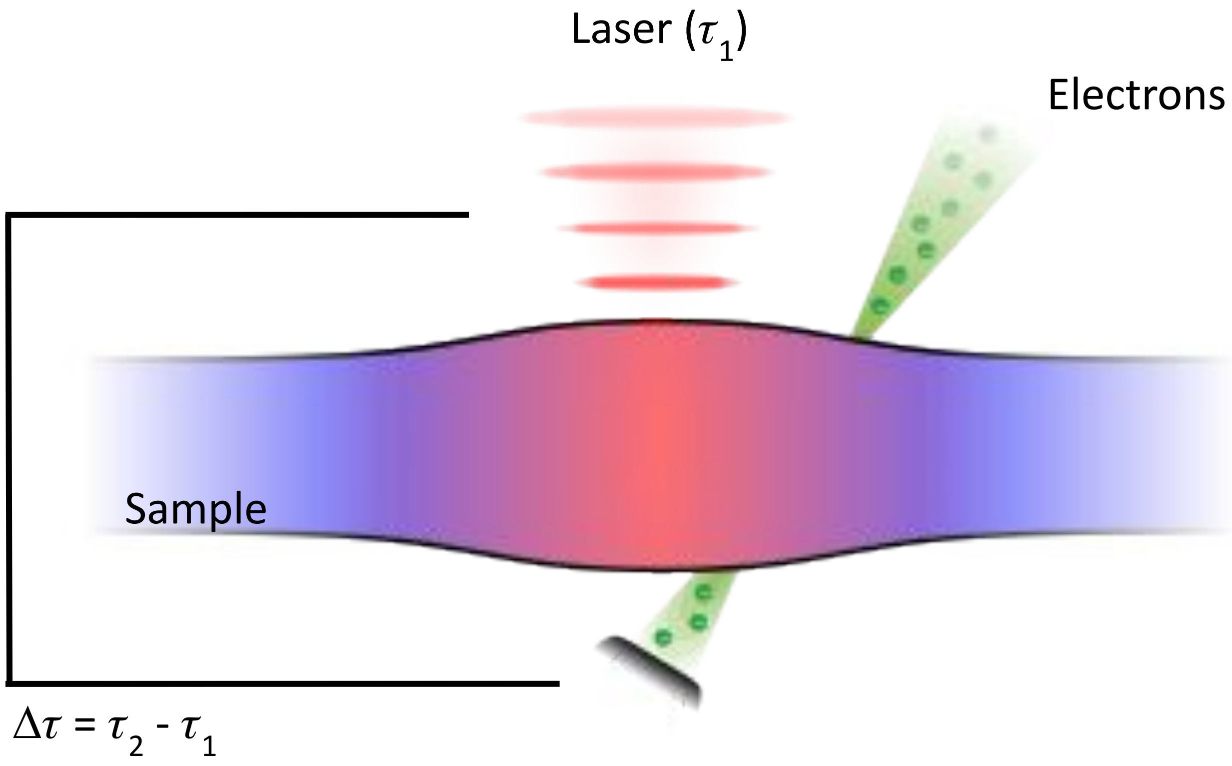


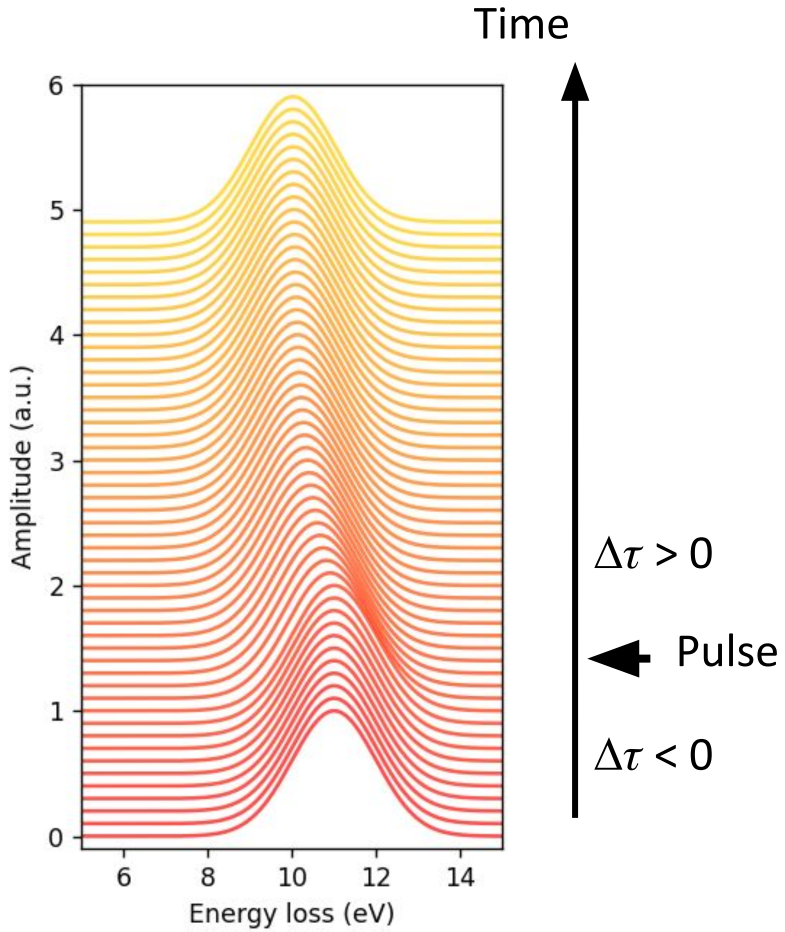
→ The sample is heated with a **focused ns-pulsed laser**

→ A nm-scaled area is probed with a **continuous electron beam**

→ A synchronized even-based detector gives the **time delay between laser pulse and electron scattering**

We follow a spectroscopy signature (EELS)

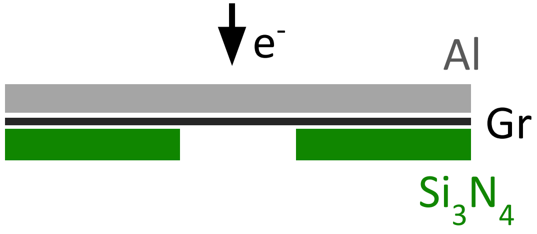




F. Castioni *et al.*, Nano Lett. **25**, 1601 (2025)

Plasmon shift in Al films

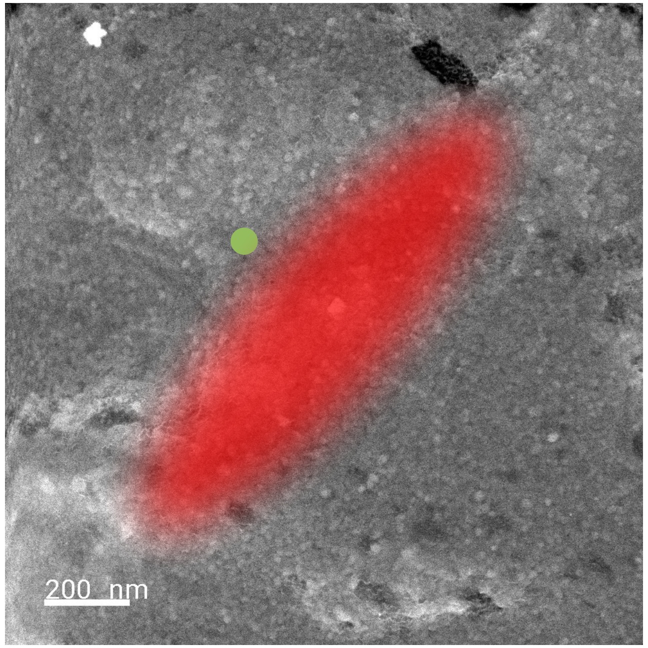
Metal heating → thermal expansion → lower free electron density → plasmon shift

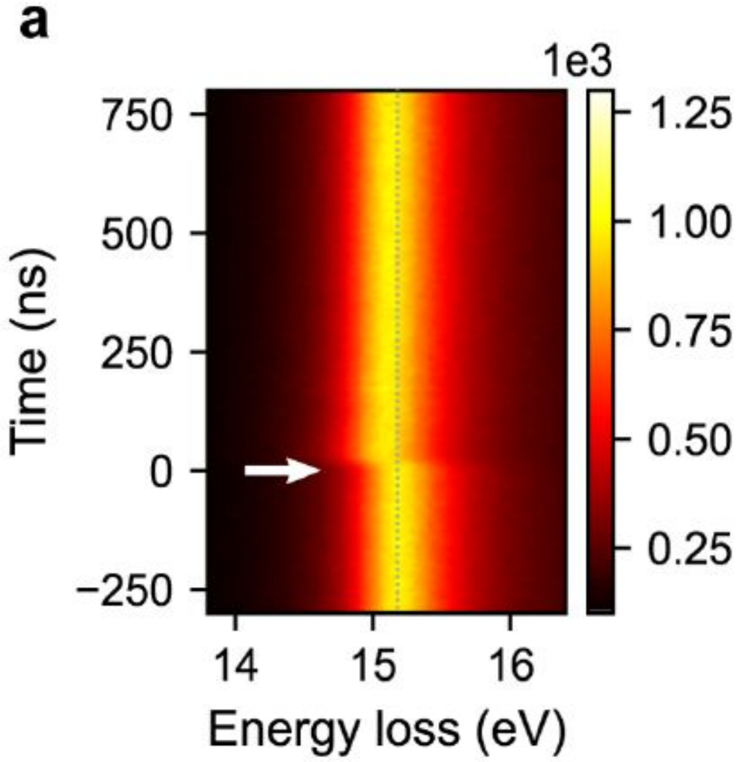


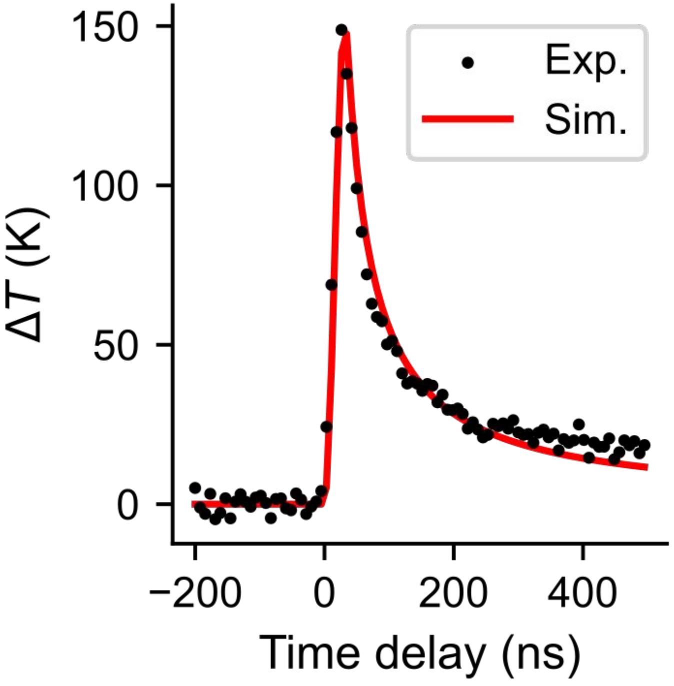
$$E_p(T) = \hbar\omega_p(T) = \hbar\sqrt{\frac{4\pi \boldsymbol{n}(\boldsymbol{T})e^2}{m}}$$

$$n(T) \approx n(T_0)\left(1 - 3\int_{T_0}^{T} \boldsymbol{\alpha}(\boldsymbol{T})\,dT\right)$$

HAADF Image

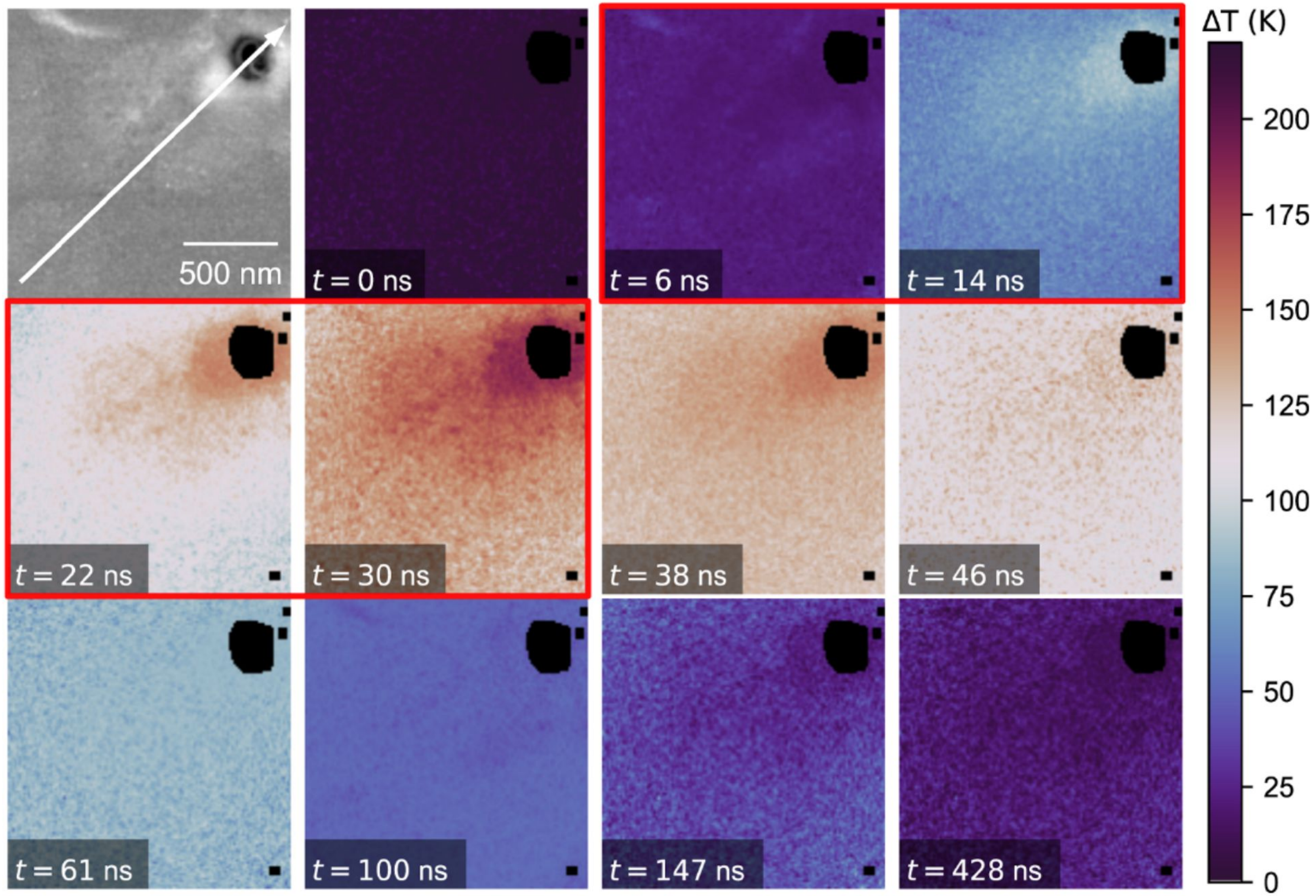


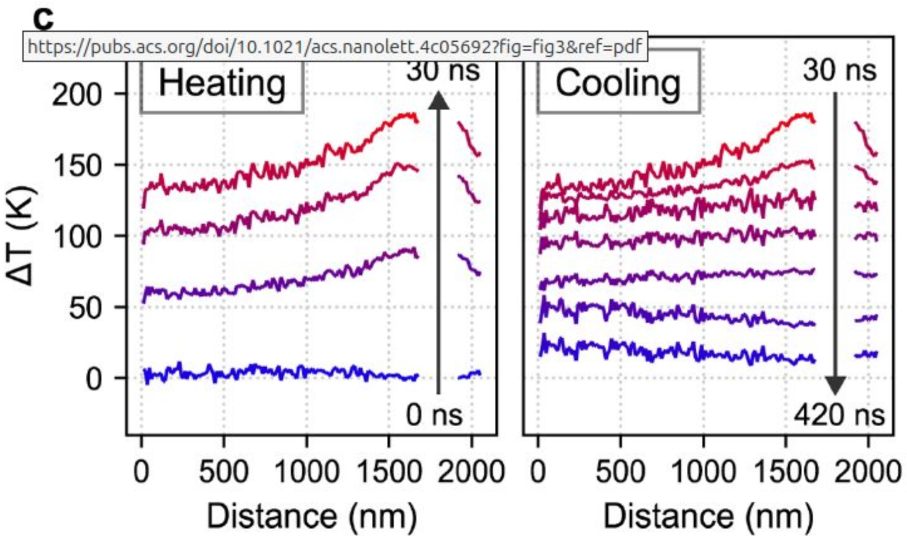




F. Castioni *et al.*, Nano Lett. **25**, 1601 (2025)

Space and time resolved heating





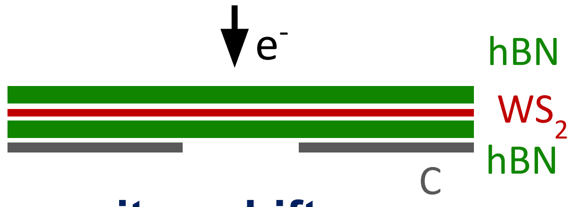
Localized heating during laser pulse

Temperature becomes homogenous in FOV following the pulse

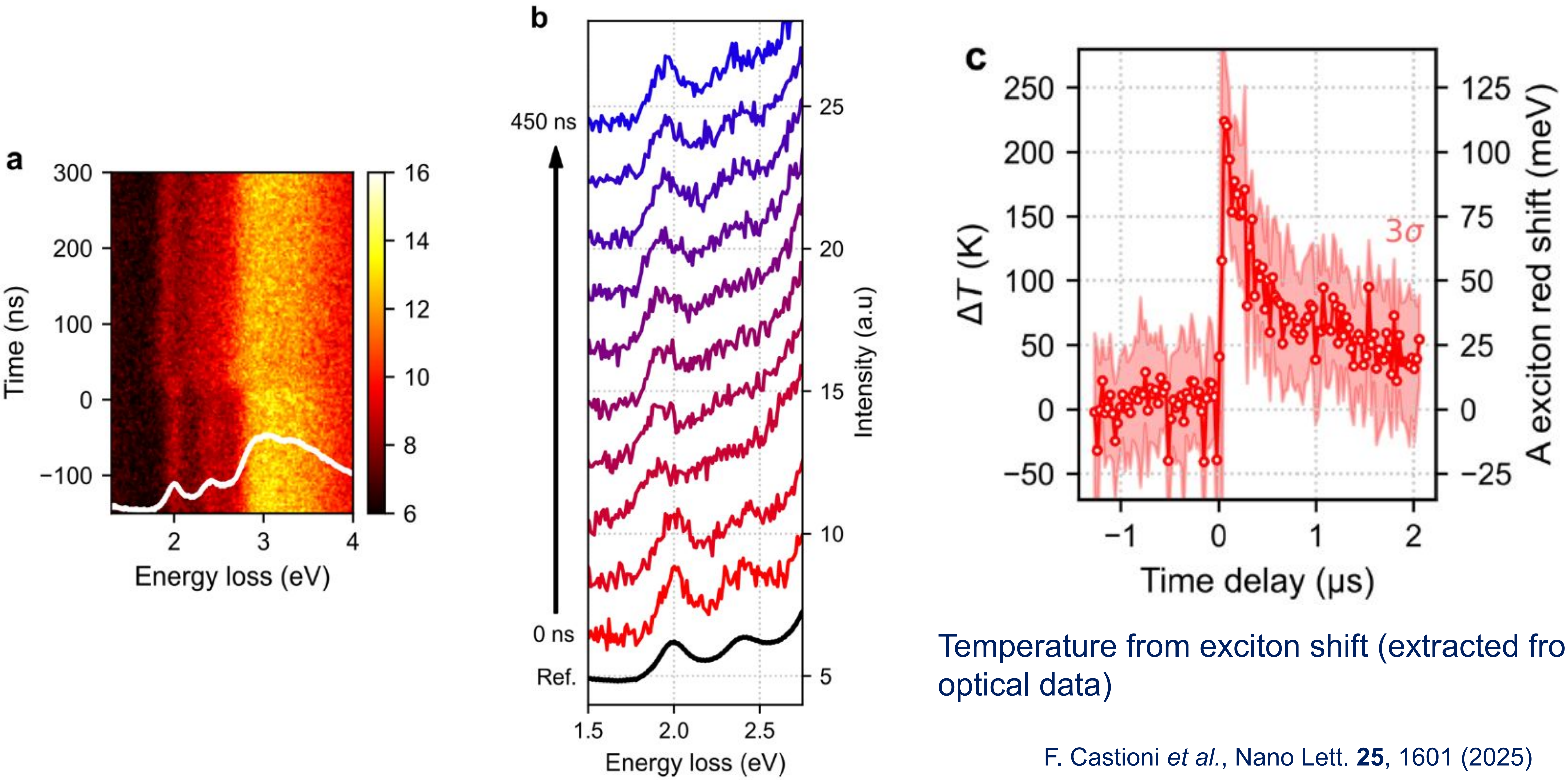
Long thermalization (> 10 μs)

F. Castioni *et al.*, Nano Lett. **25**, 1601 (2025)

WS_2 exciton shift



Semiconductor heating → thermal expansion → band-gap modification → exciton shift



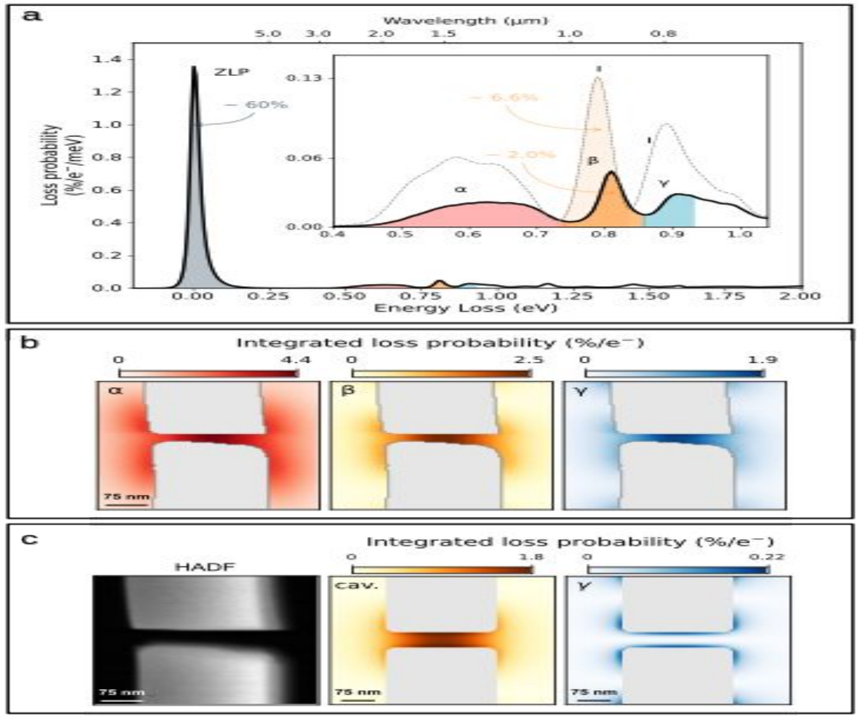
Temperature from exciton shift (extracted from optical data)

F. Castioni *et al.*, Nano Lett. **25**, 1601 (2025)

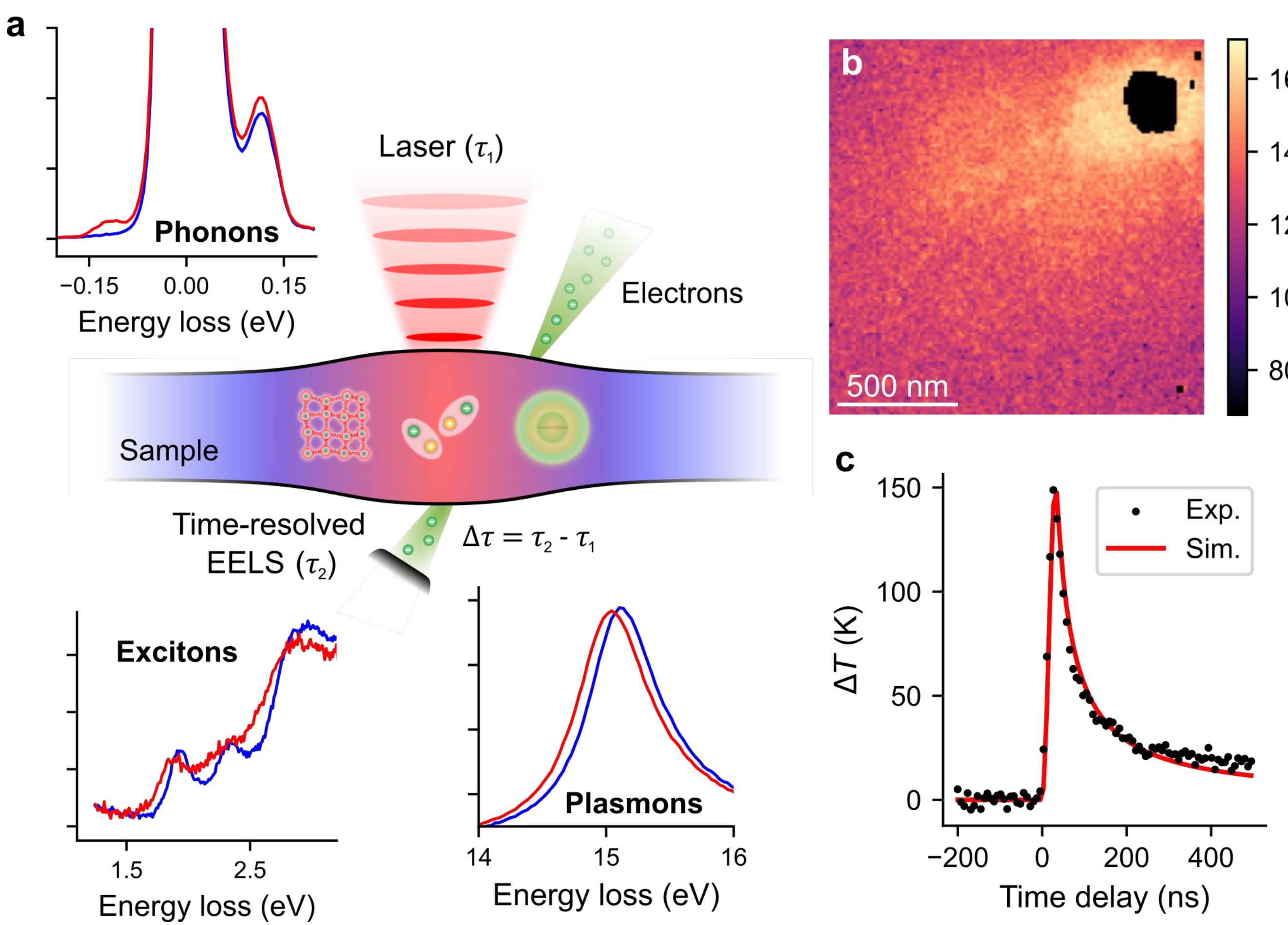
Conclusion

A new method for nanosecond-resolved nanothermometry

High quality factor Si photonic cavity for high electron coupling probability (1 % for the cavity mode)



M. Bézard, *et al.* *ACS Nano* . **18,** 10417 (2023)



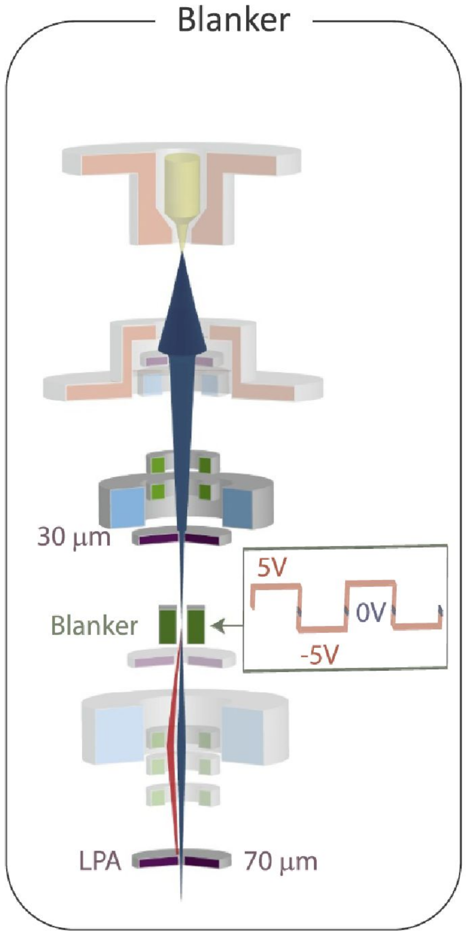
F. Castioni *et al.*, Nano Lett. **25**, 1601 (2025)

Thank you!

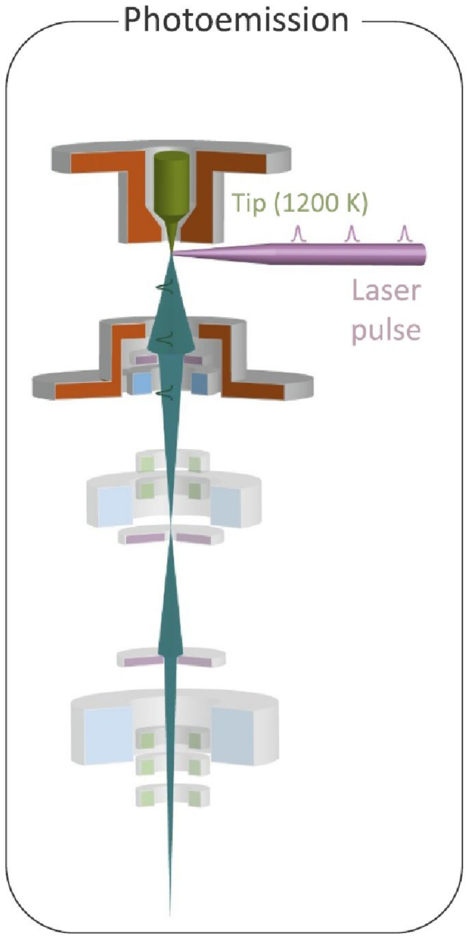
Time-resolved electron spectroscopy

Blanker technologies
(down to ~1s ps nowadays)

S. A. Reisbick, *et al. Ultramicroscopy* **235** 113497 (2022)
A. Lassise, *et al.* Rev. Sci. Inst. **83** 043705 (2012)



Laser-driver sources
(fs-as scales)



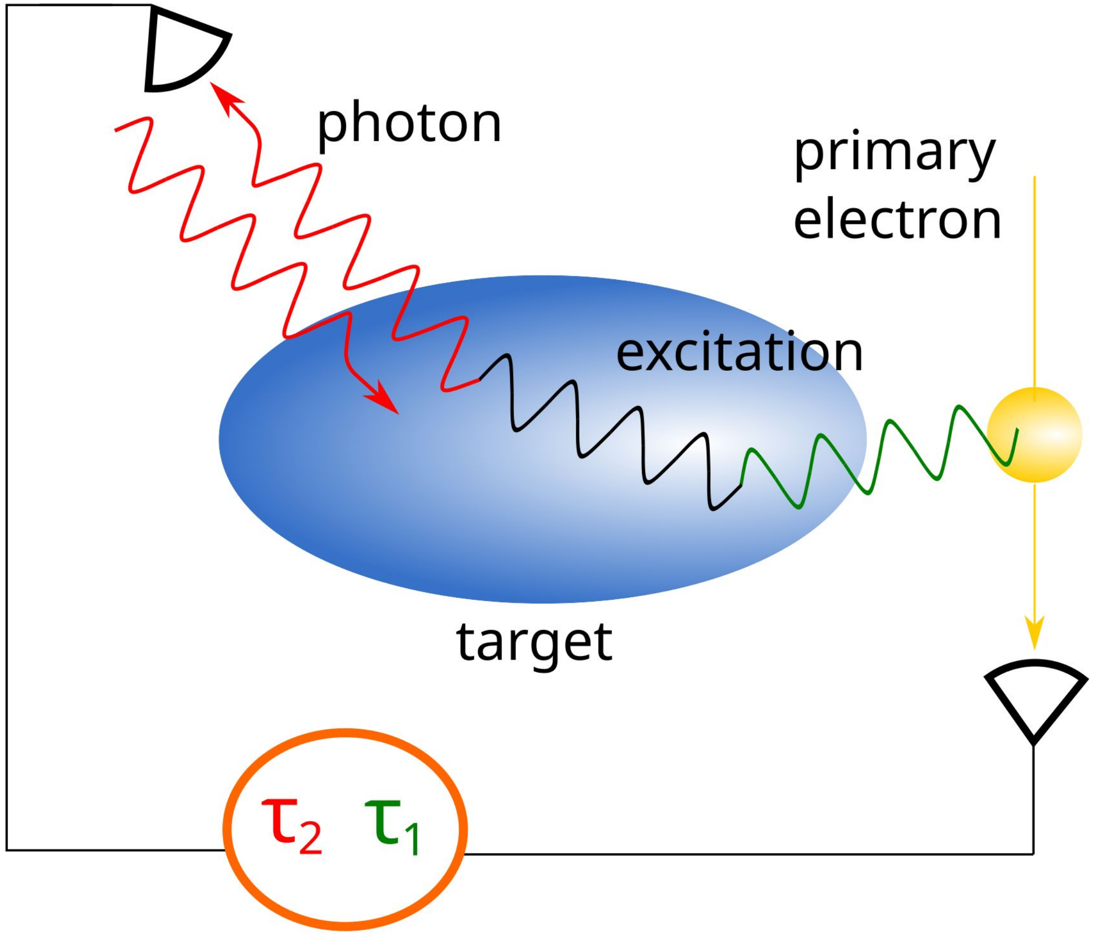
O. Bostanjoglo *et al.* Ultramicroscopy, 2000
B. Barwick *et al. Nature*, 2009.
A. Feist *et al. Nature*, 2015.
B. Arbouet *et al.* Adv. Im. Elec. Phys. (2018)
(a review)

That is not how we do it

S. Meuret, *et al. Ultramicroscopy* **197** 28 (2019)

Time-resolved experiments with a continuous electron source?

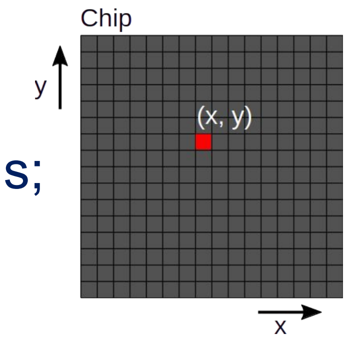
Measure the excitation time

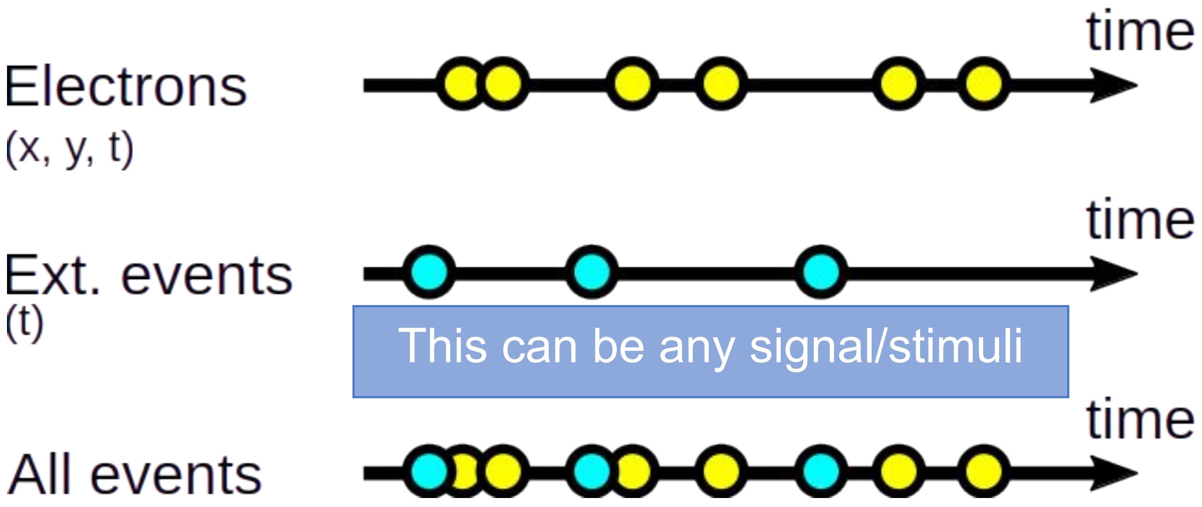


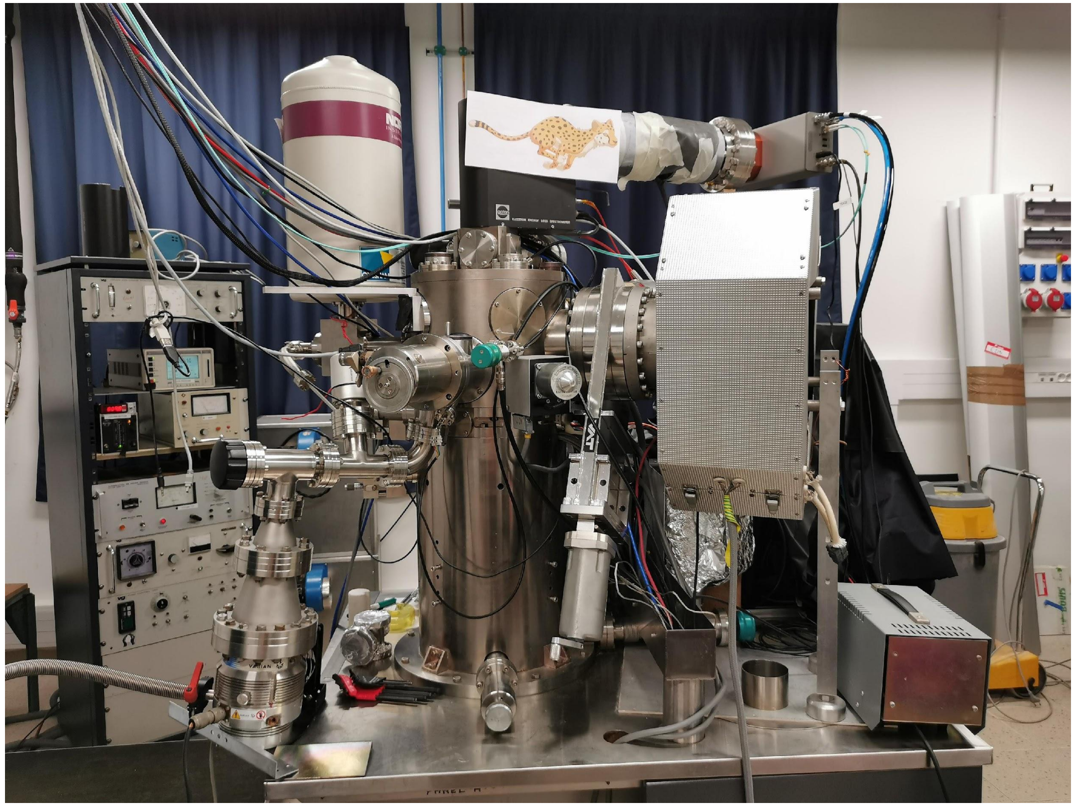
Similar ideas:
S. Meuret, *et al. ACS Photon.* **3** 1157 (2016) S. Finot, *et al. ACS Photon.* **9** 173 (2021) S. Yanagimoto, *et al.*, *Comm. Phys.* 6, 260 (2023) *S.* Fiedler, *et al., Nanophotonics,* 12, 2231 (2023)

Event-based detection for EELS

- ✔ Event-based:
  - Outputs electron (x, y, t)
  - Maximal temporal resolution ~1.5625 ns;
- ✔ CheeTah:
  - 1024 x 256 pixels;
  - Count rate as high as 120 million hits/s (~20 pA)*;
  - Read-out speed does not apply;
  - Two time-to-digital converter inputs (TDCs);



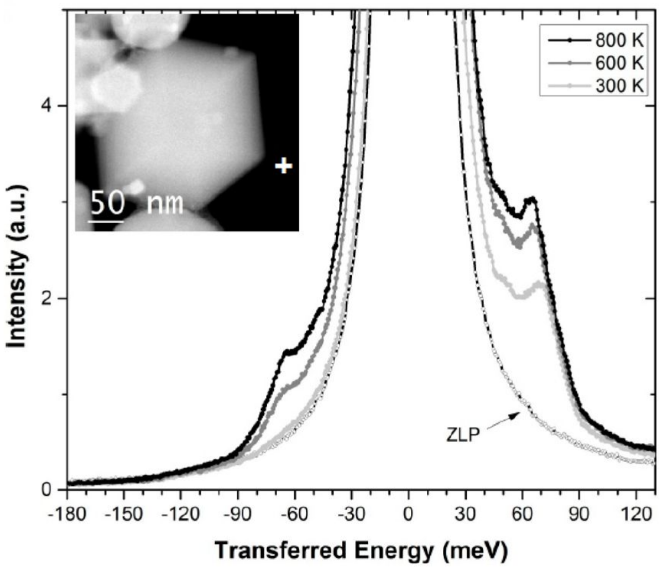


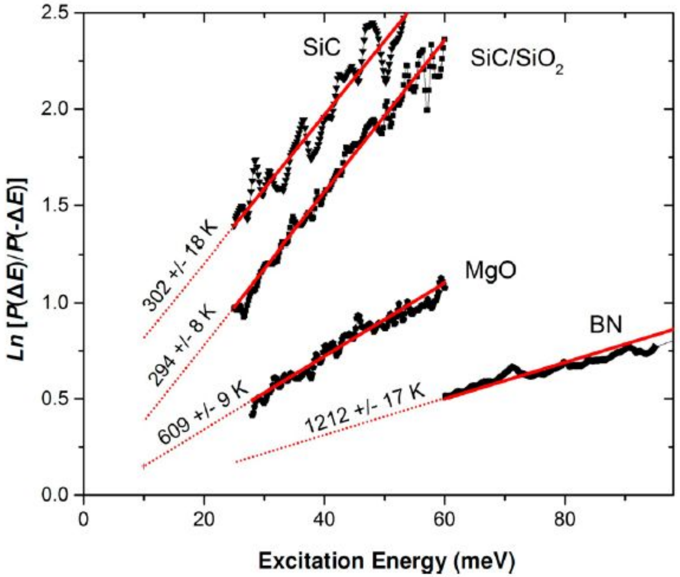


Y. Auad, *et al. Ultramicroscopy.* ***239*****,** 113539 (2021)
See also: D. Jannis. Vol. 233. Ultramicroscopy. 2022.

AMSTERDAM SCIENTIFIC INSTRUMENTS

Principle of detailed balance

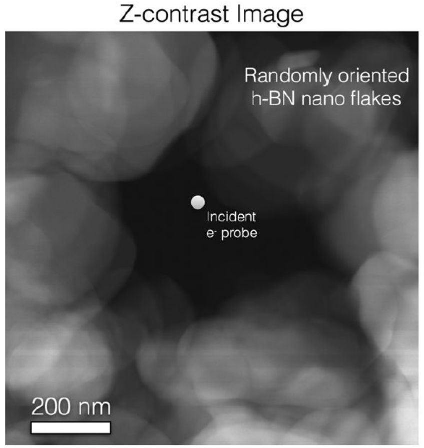


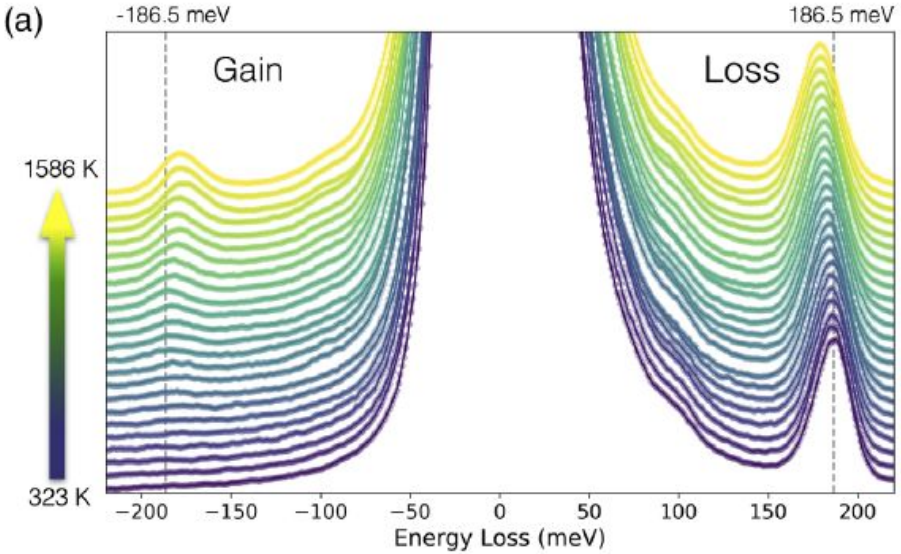


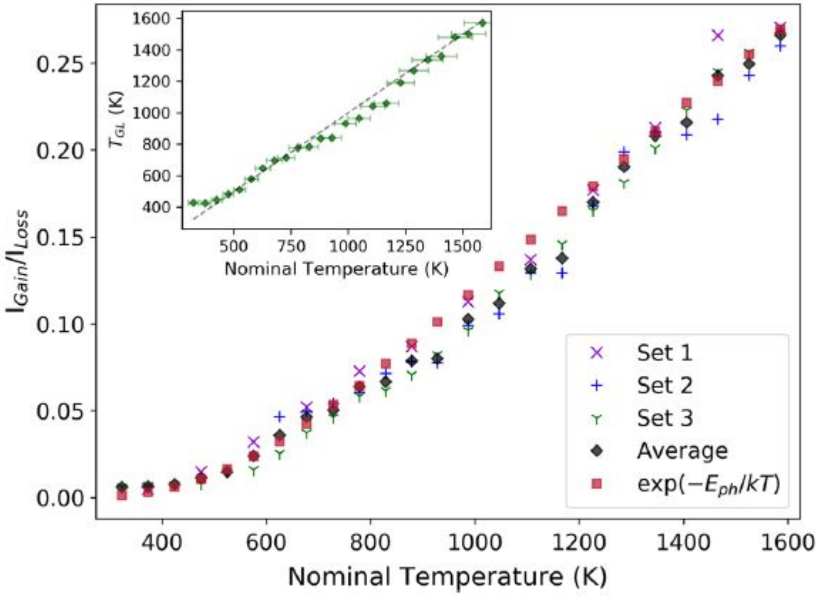
Spontaneous loss and gain ratio

$$\frac{P(\Delta E)}{P(-\Delta E)} = e^{\Delta E/K_bT}$$

M. J. Lagos, P. E. Batson, *Nano Lett.* **18**, 4556–4563 (2018)

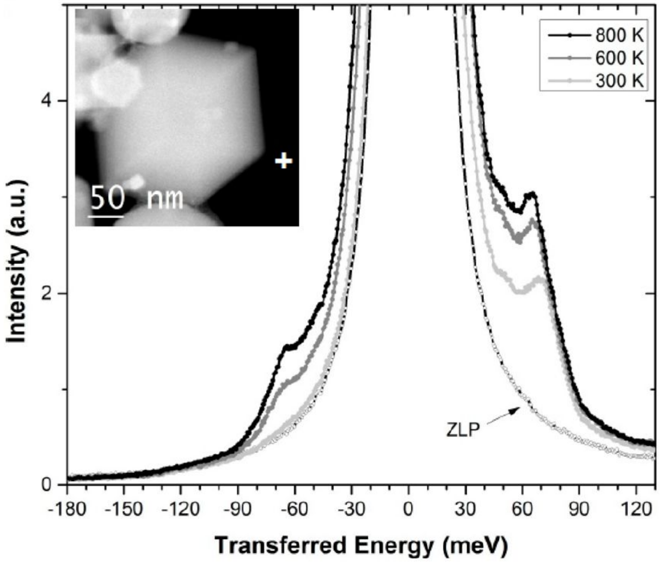


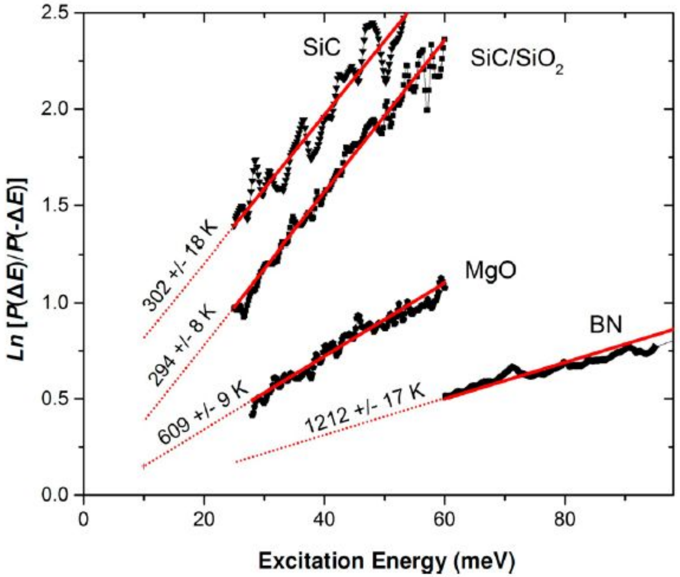




J. C. Idrobo *et al.*, *Phys. Rev. Lett.* **120**, 095901 (2018)

Principle of detailed balance



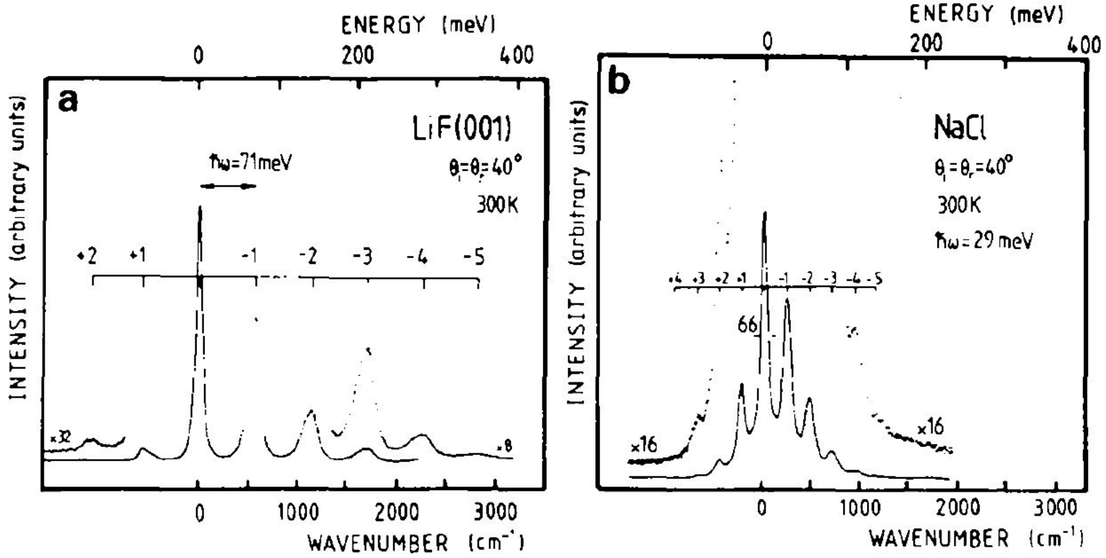


Spontaneous loss and gain ratio

$$\frac{P(\Delta E)}{P(-\Delta E)} = e^{\Delta E/K_b T}$$

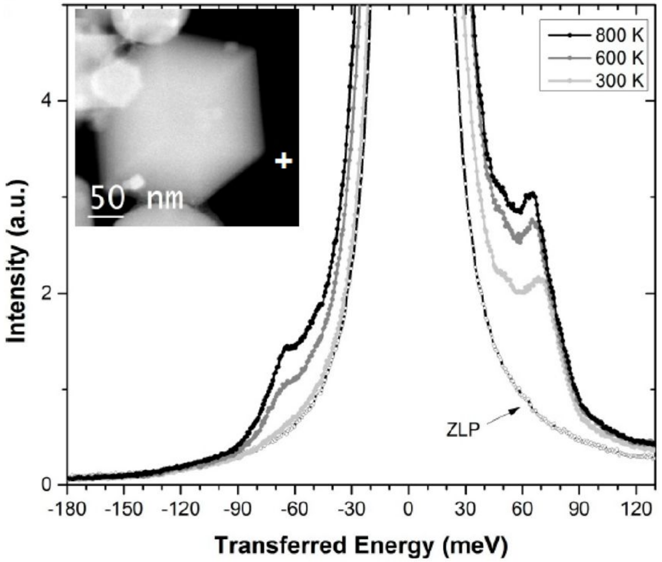
M. J. Lagos, P. E. Batson, *Nano Lett.* **18**, 4556–4563 (2018)

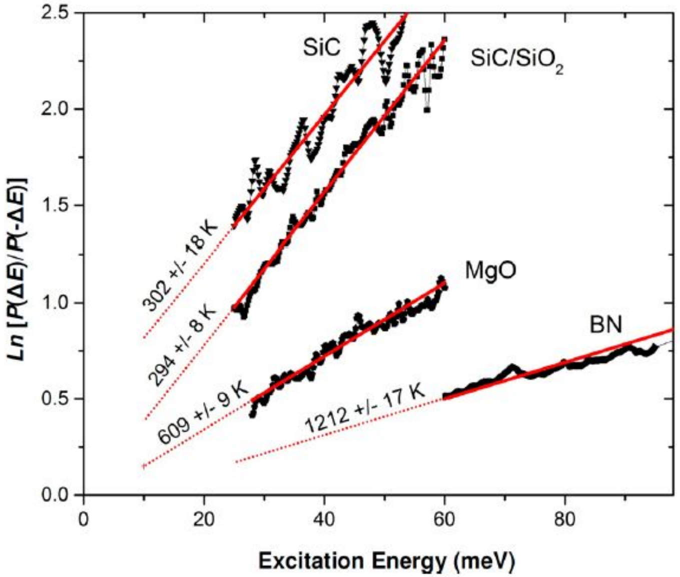
These are spontaneous thermal gain events



J. J. Pireaux *et al.*, Surface Science **162**, 32 (1985)

Principle of detailed balance





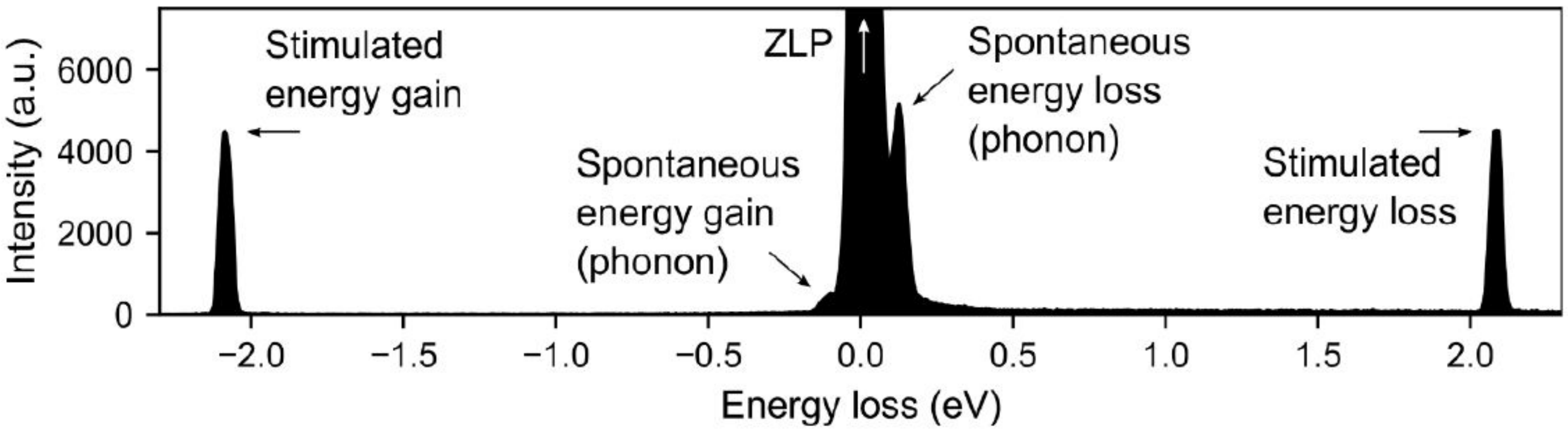
Spontaneous loss and gain ratio

$$\frac{P(\Delta E)}{P(-\Delta E)} = e^{\Delta E/K_b T}$$

M. J. Lagos, P. E. Batson, *Nano Lett.* **18**, 4556–4563 (2018)

These are spontaneous thermal gain events

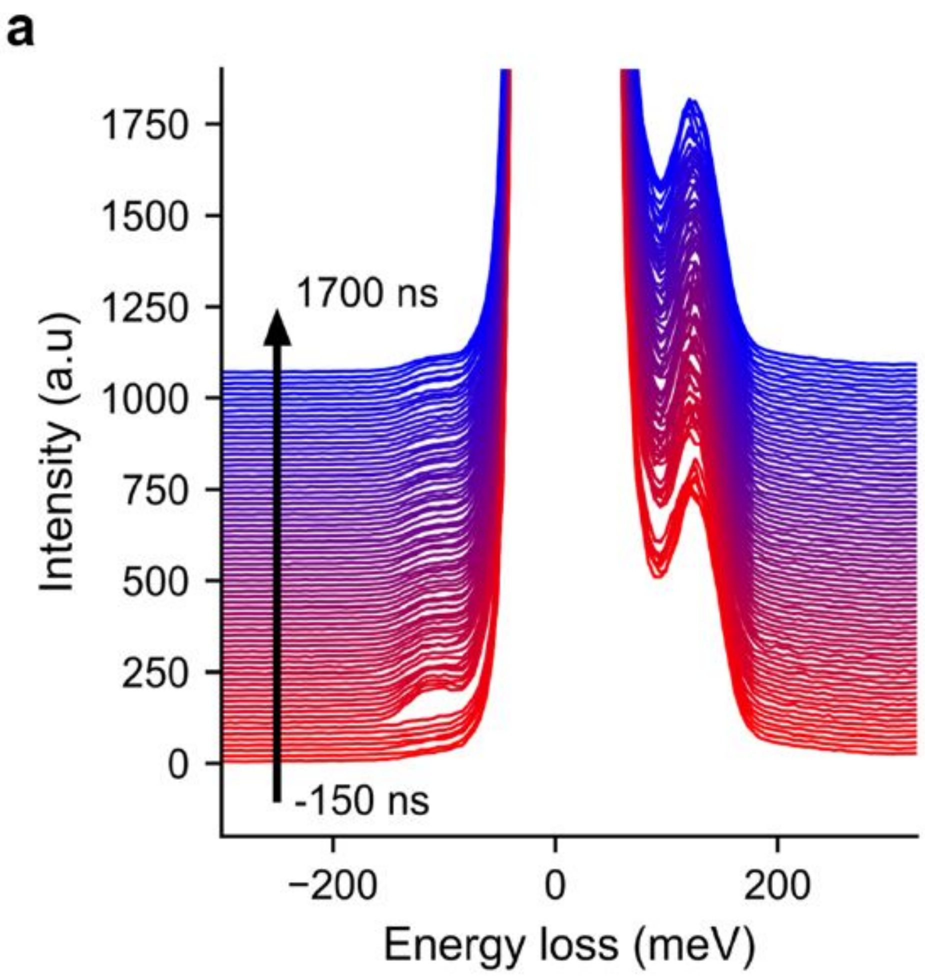
b

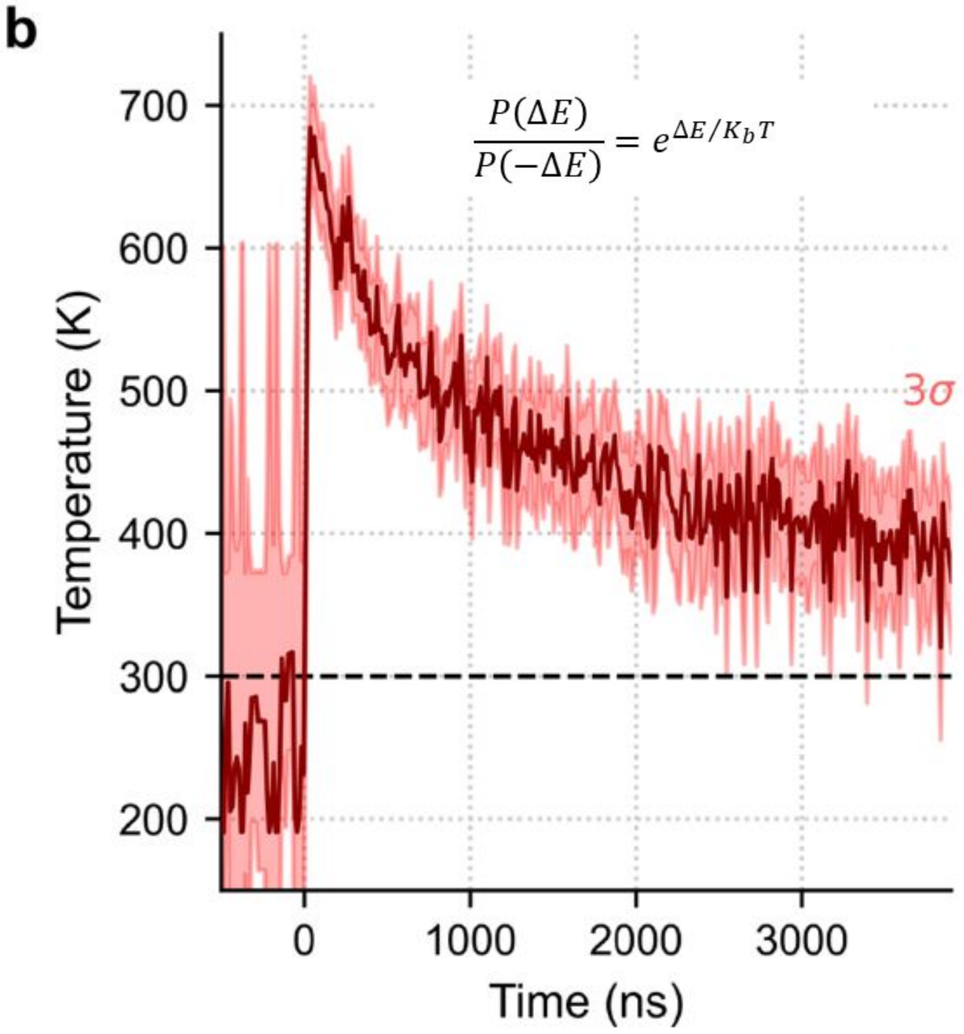


F. Castioni *et al.*, Nano Lett. **25**, 1601 (2025)

Quantitative temperature from phonons

SiN_x film

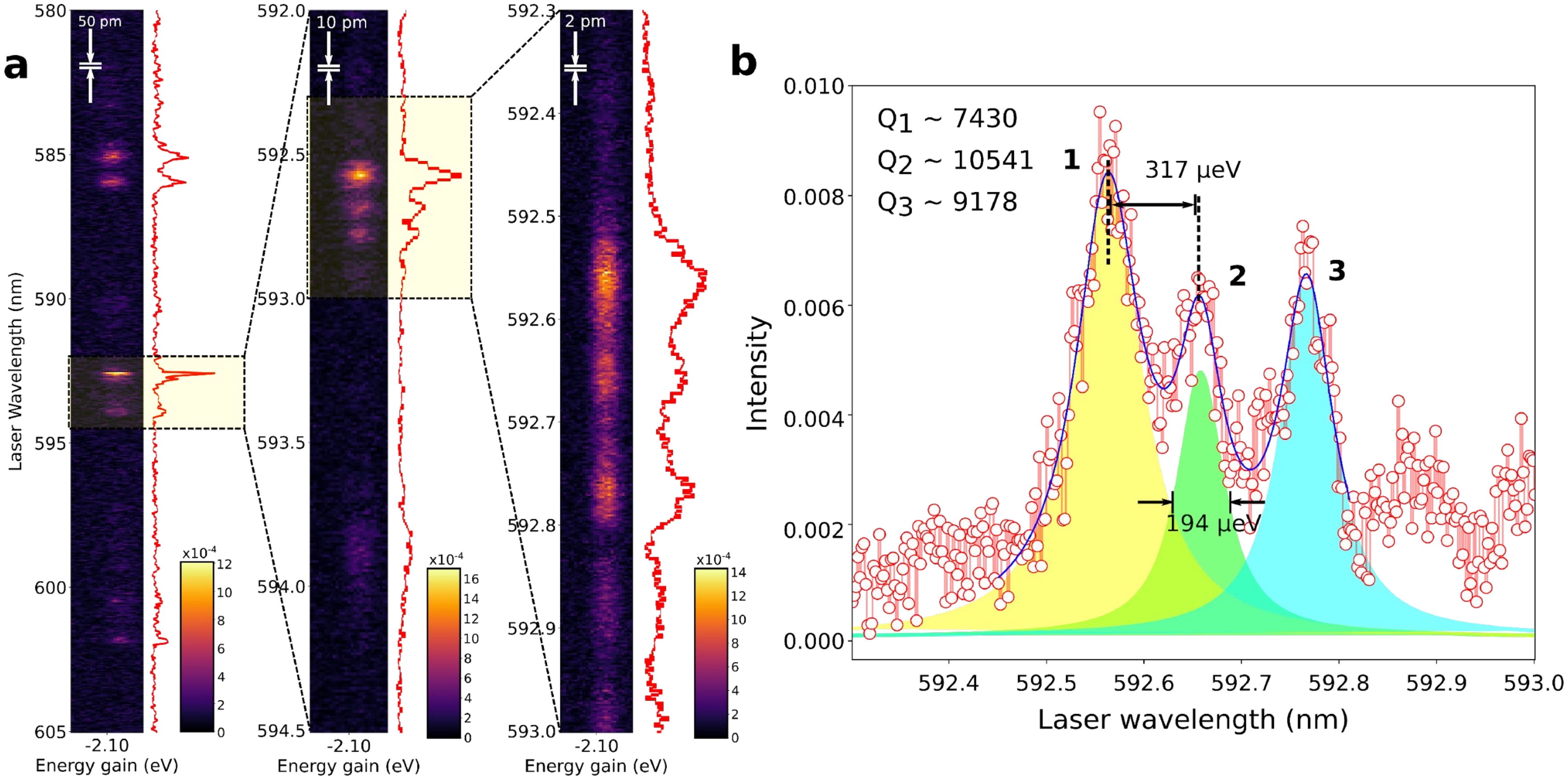




F. Castioni *et al.*, Nano Lett. **25**, 1601 (2025)

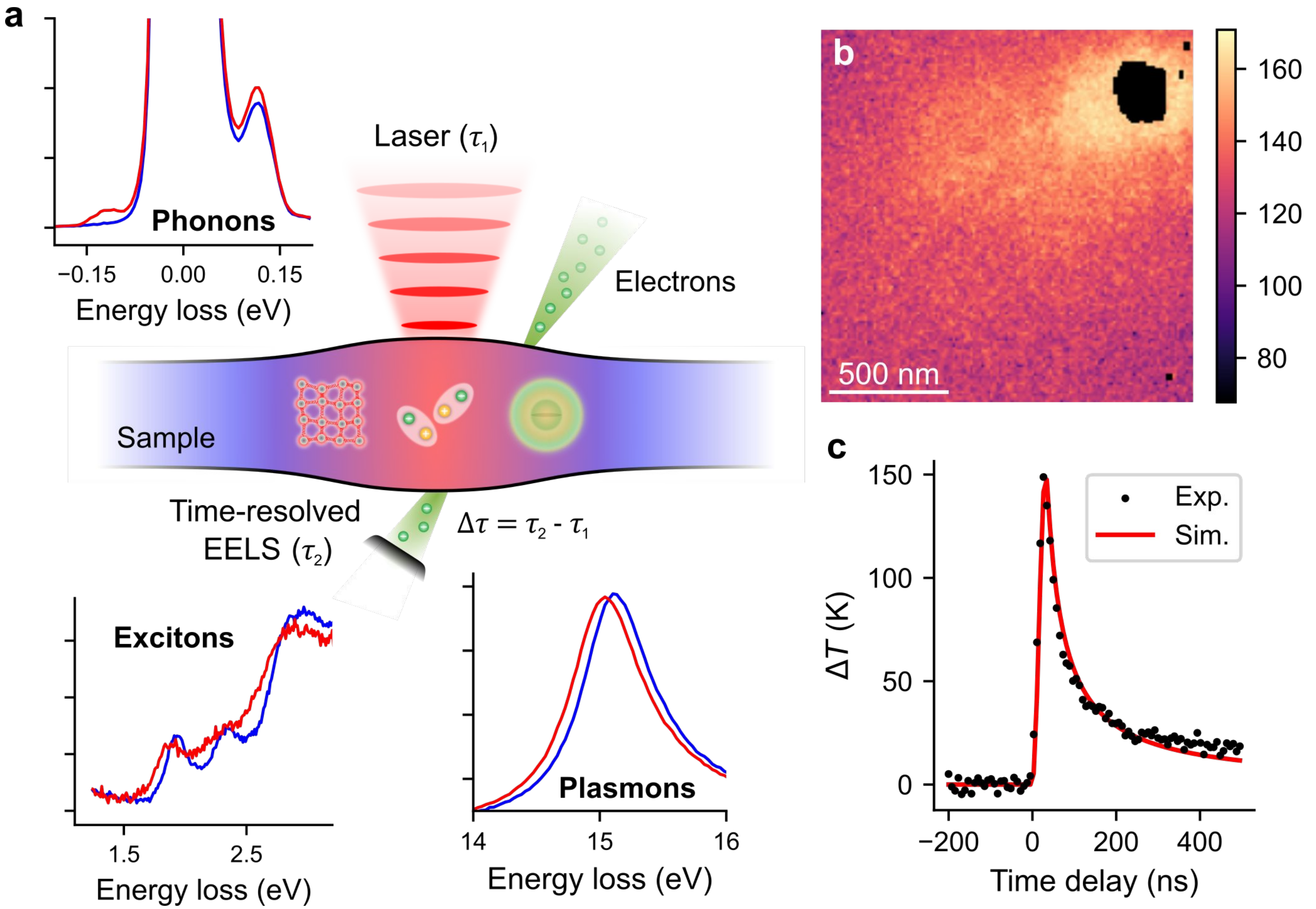
Electron energy gain spectroscopy

High quality factor optical modes in
dielectric spheres



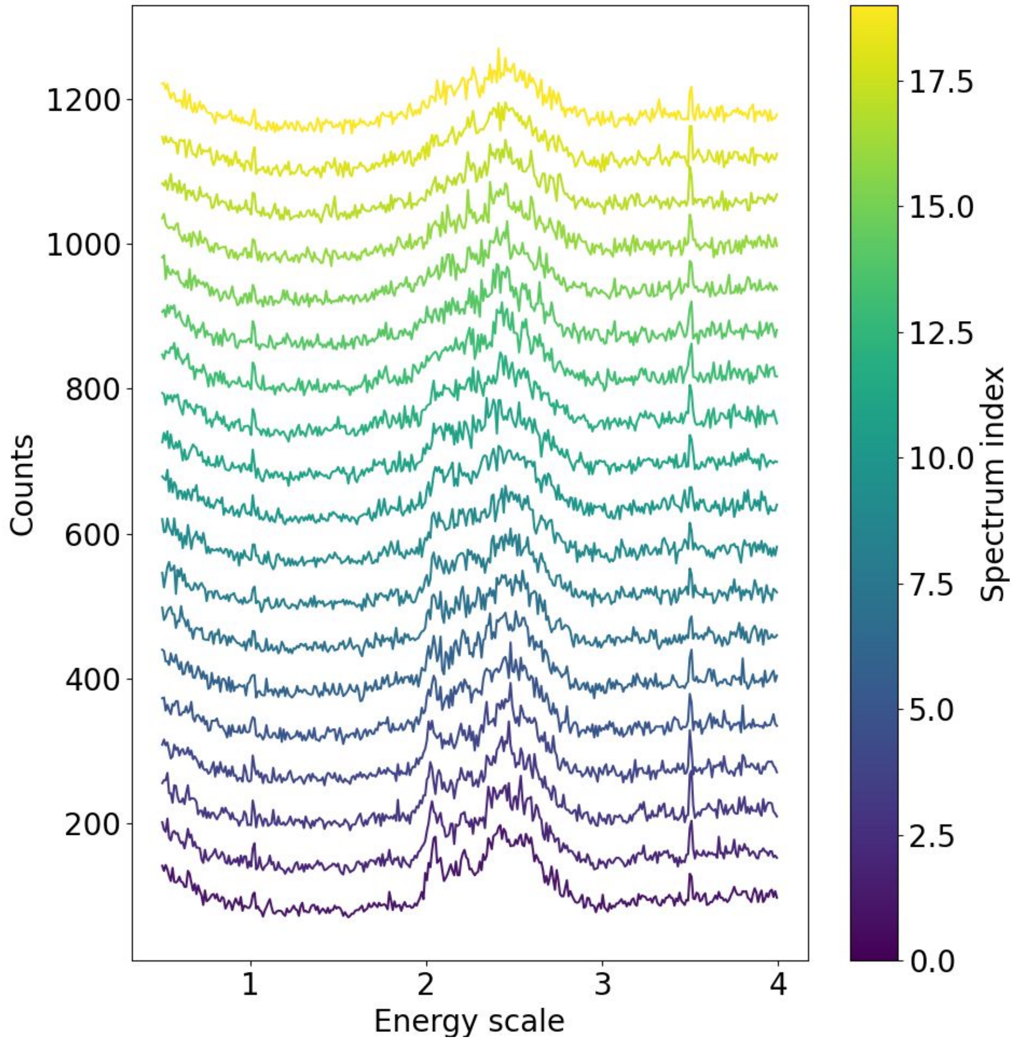
Y. Auad, *et al, Nat. Comm.* **14** 4442 (2023)

Laser-EELS synchronized experiments



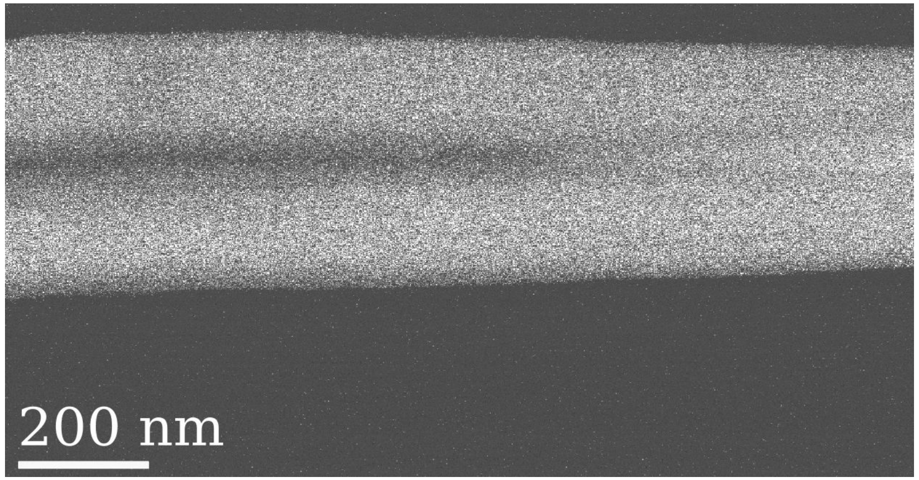
F. Castioni *et al.*, Nano Lett. **25**, 1601 (2025)

Optical signature of molecular crystals (PDI: perelyne diimide)



- About 1.5e6 electrons per spectrum
- 0.44 μm^2 scanned area with 2 nm wide pixels, using a 2 nm probe (defocused)
- 3 fA current (measured on TPX)
- Total dose: 1.58 e/$Å^2$
- Dose per spectrum: 0.03 e/$Å^2$

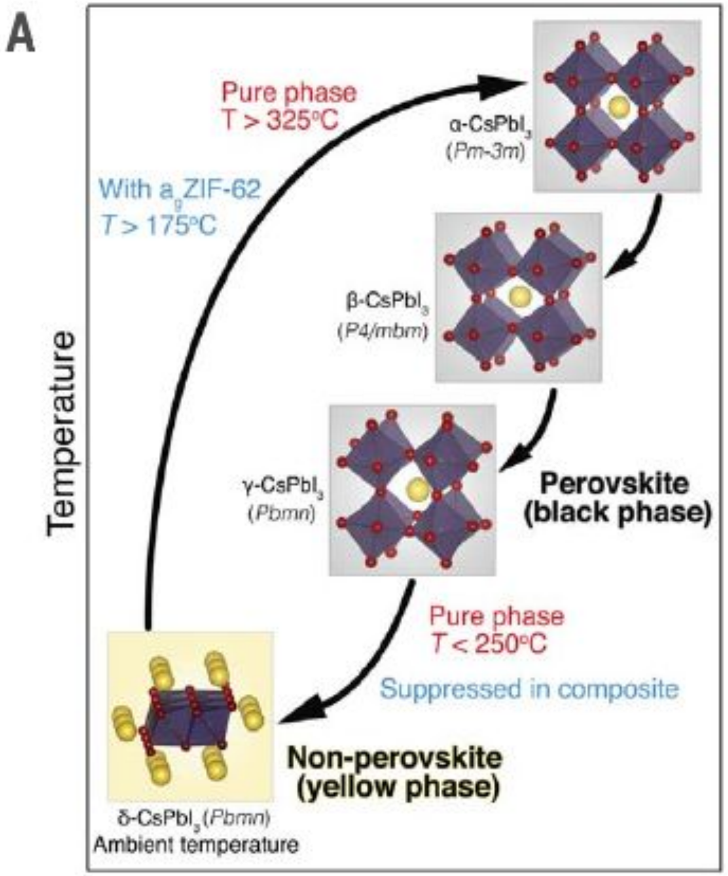
PDI ribbon (HAADF)

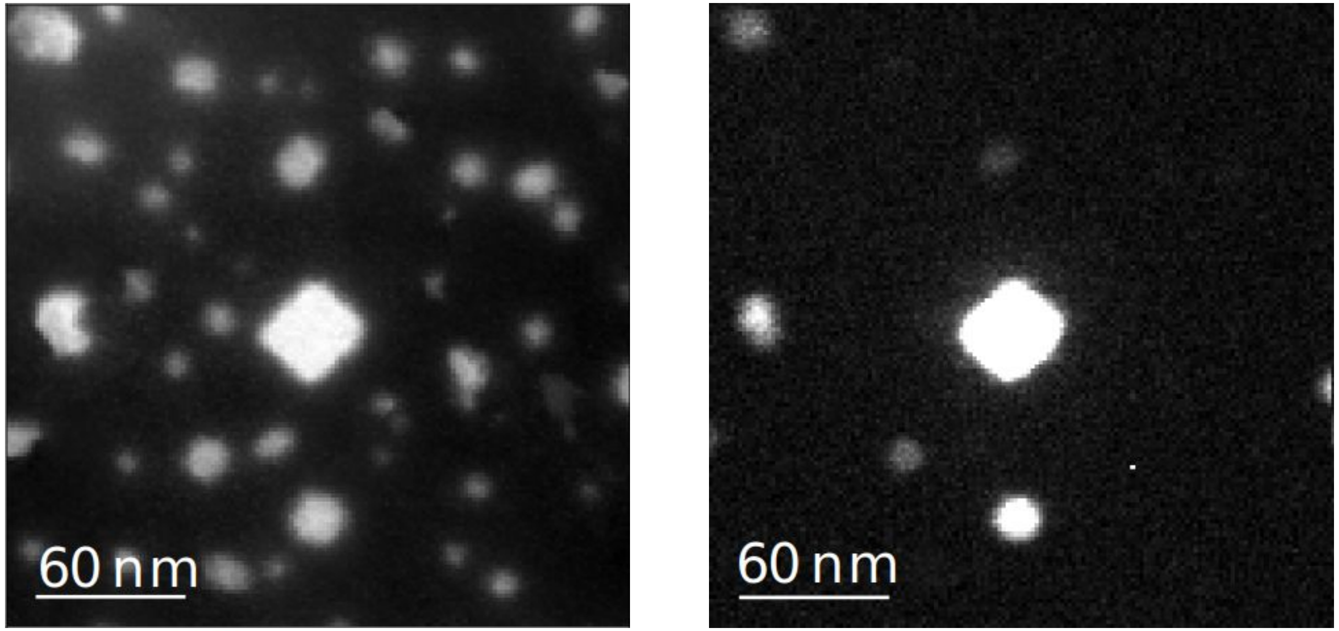


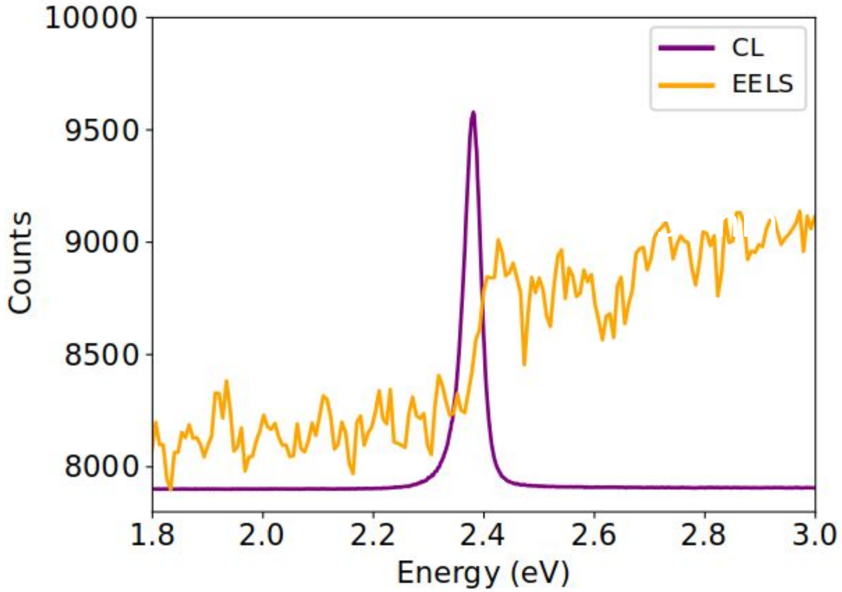
Collaboration with Sean Collins (Leeds)

Stokes shift in lead halide perovskites

MOF composite





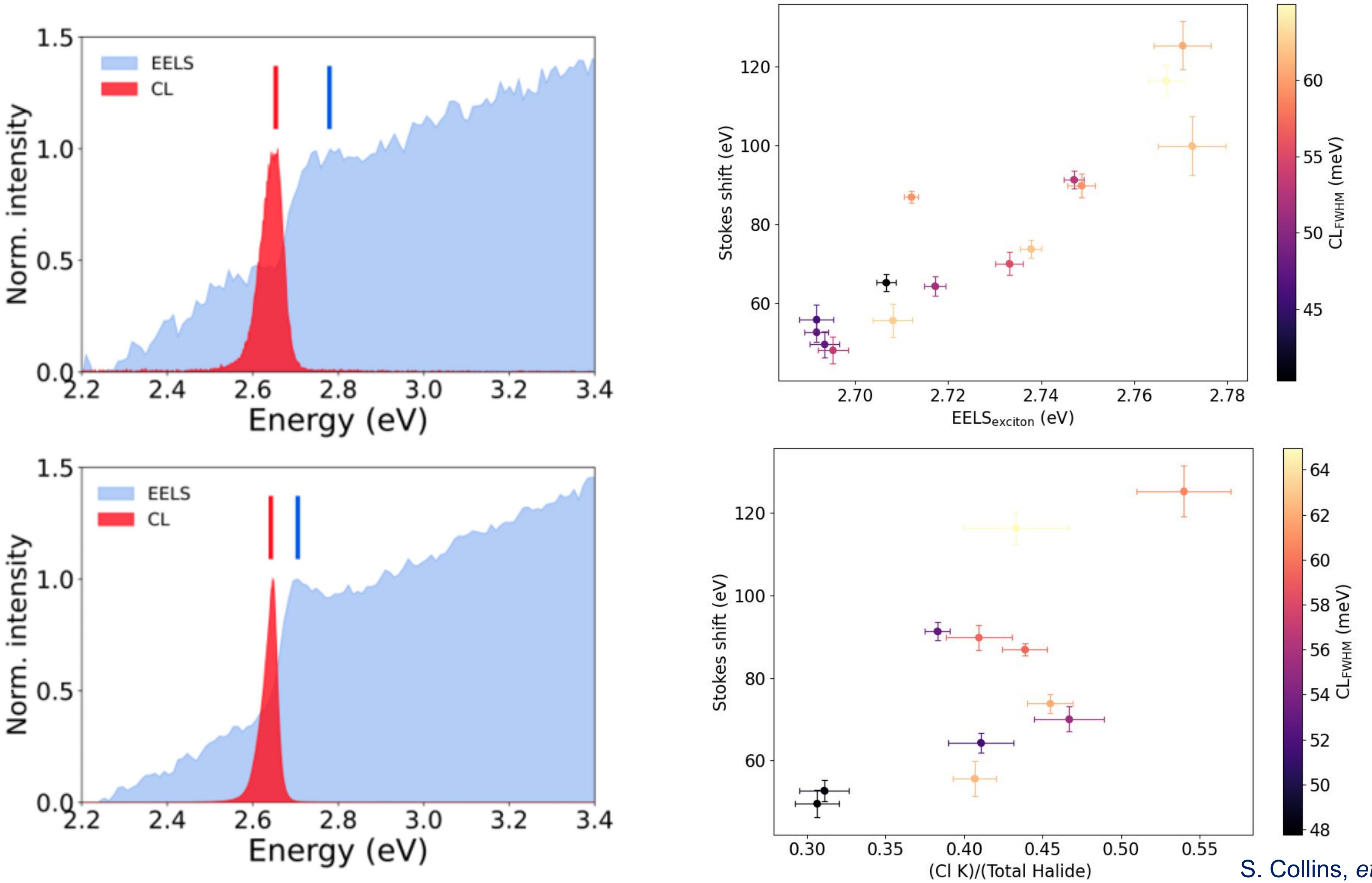


Jingwei House (Queensland University) and Sean Collins (Leeds University)

J. Hou, *et al. Science.* **17**, 598 (2021)

Stokes shift in lead halide perovskites

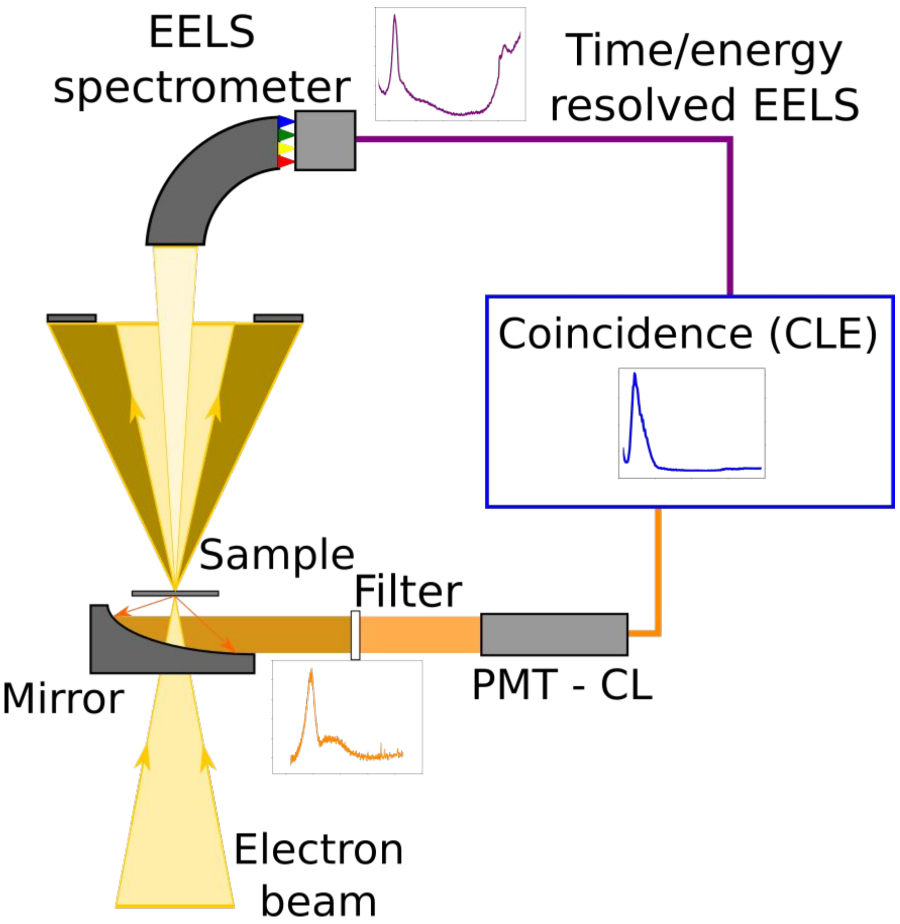
Absorption, emission (LPS) and chemistry (Leeds)



S. Collins, *et al. in preparation* (2025)

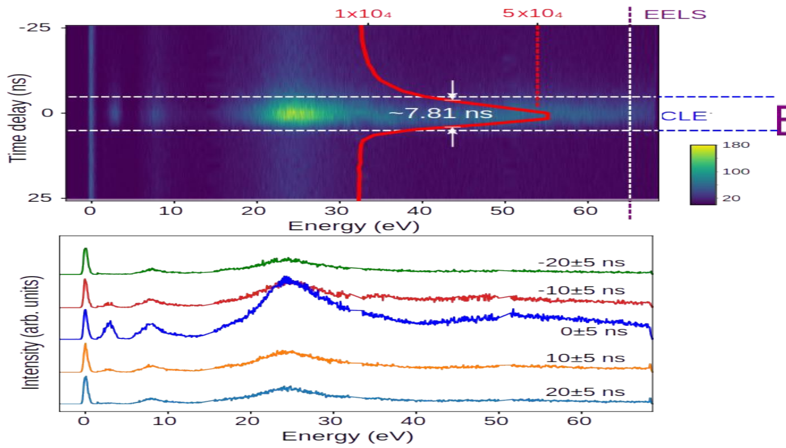
Cathodoluminescence excitation spectroscopy

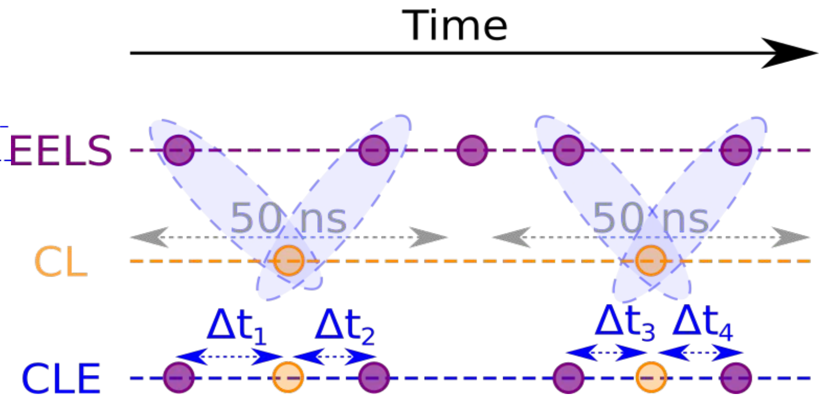
Establish the link between energy lost *per electron* to photon emission



2 ns time resolution and coincidences with external triggers (Timepix3)

Y. Auad, *et al. Ultramicroscopy.* ***239*****,** 113539 (2021)

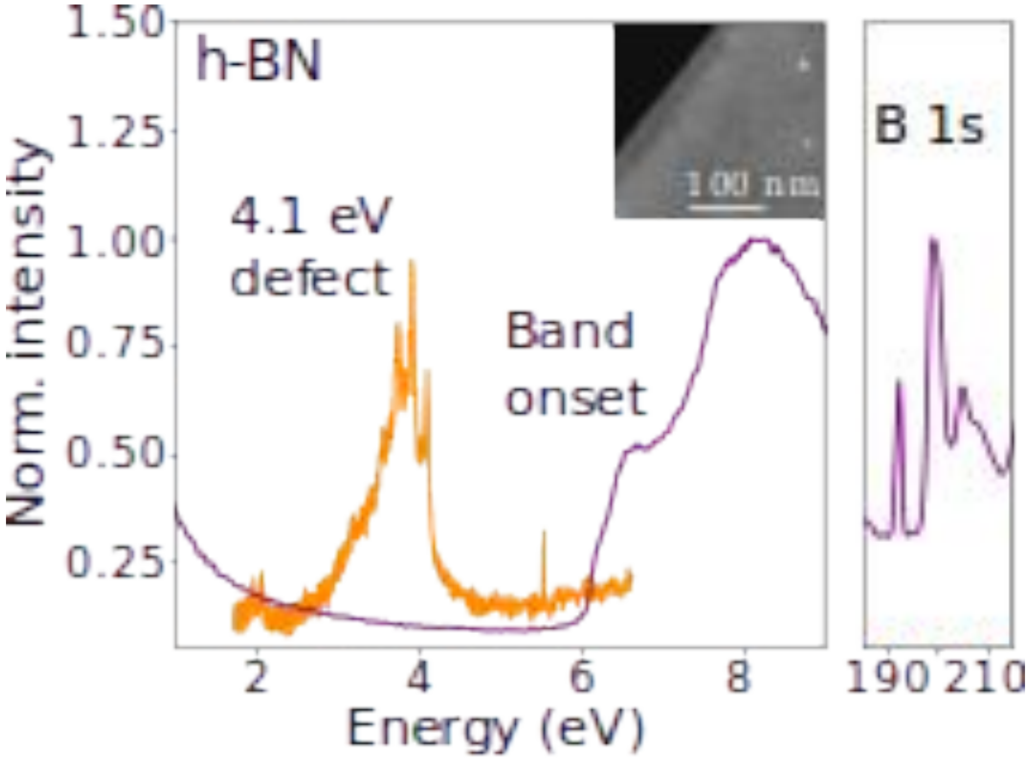


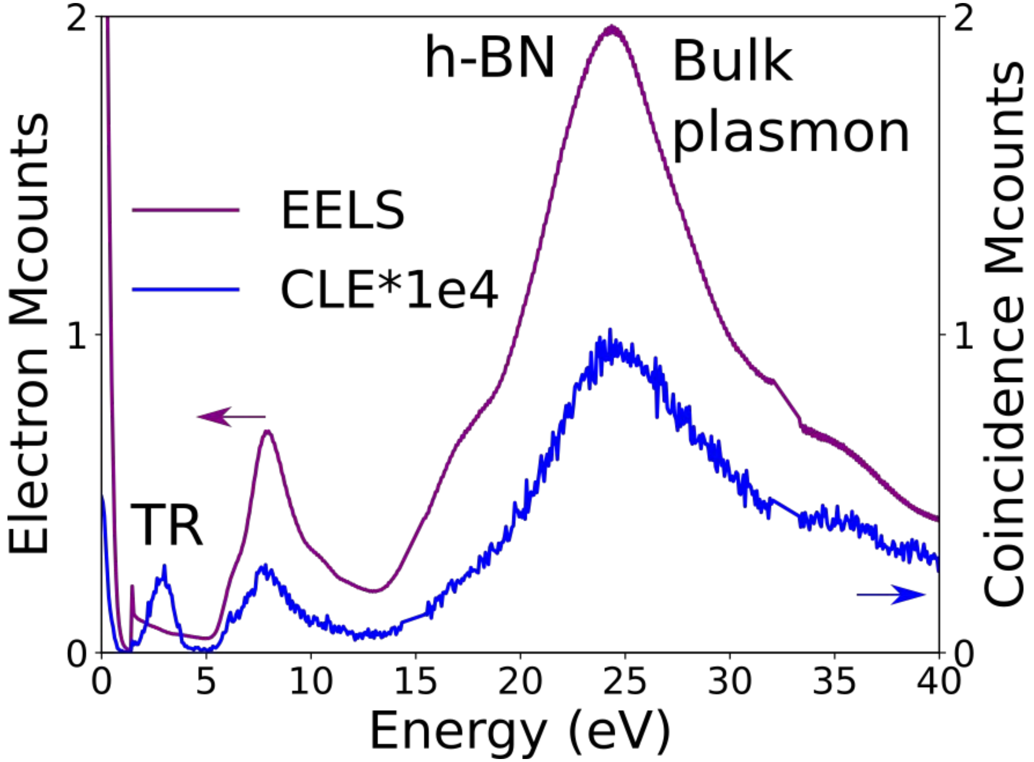


N. Varkentina, Y. Auad, *et al Sci. Adv.* abq4947 (2022)
See also: A. Feist, *et al., Science,* **377,** 777 (2022)

Experiments: N. Varkentina and Y. Auad

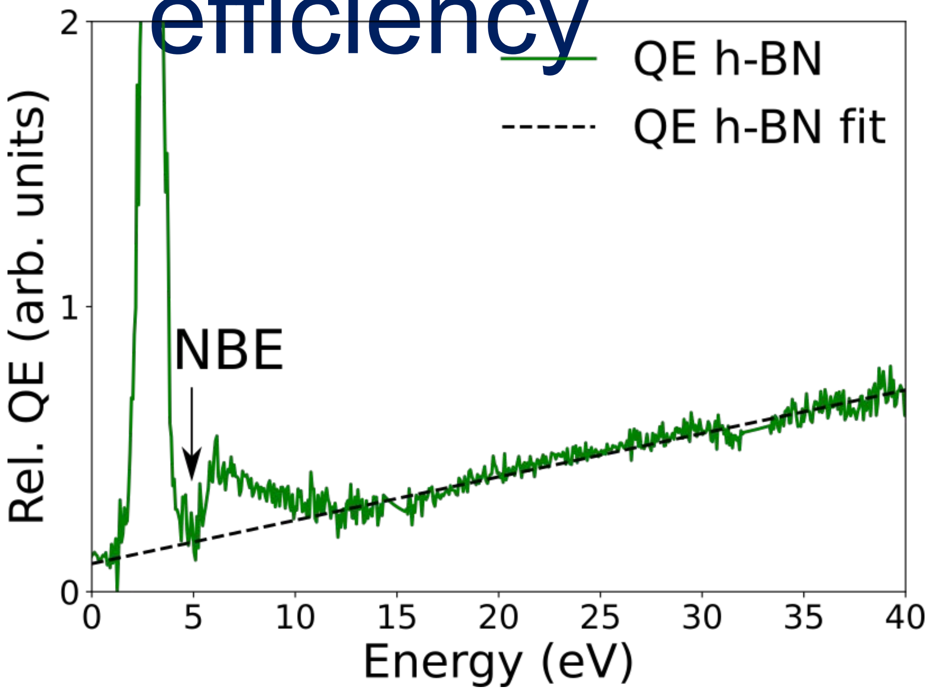
Coincidence spectra (CLE)



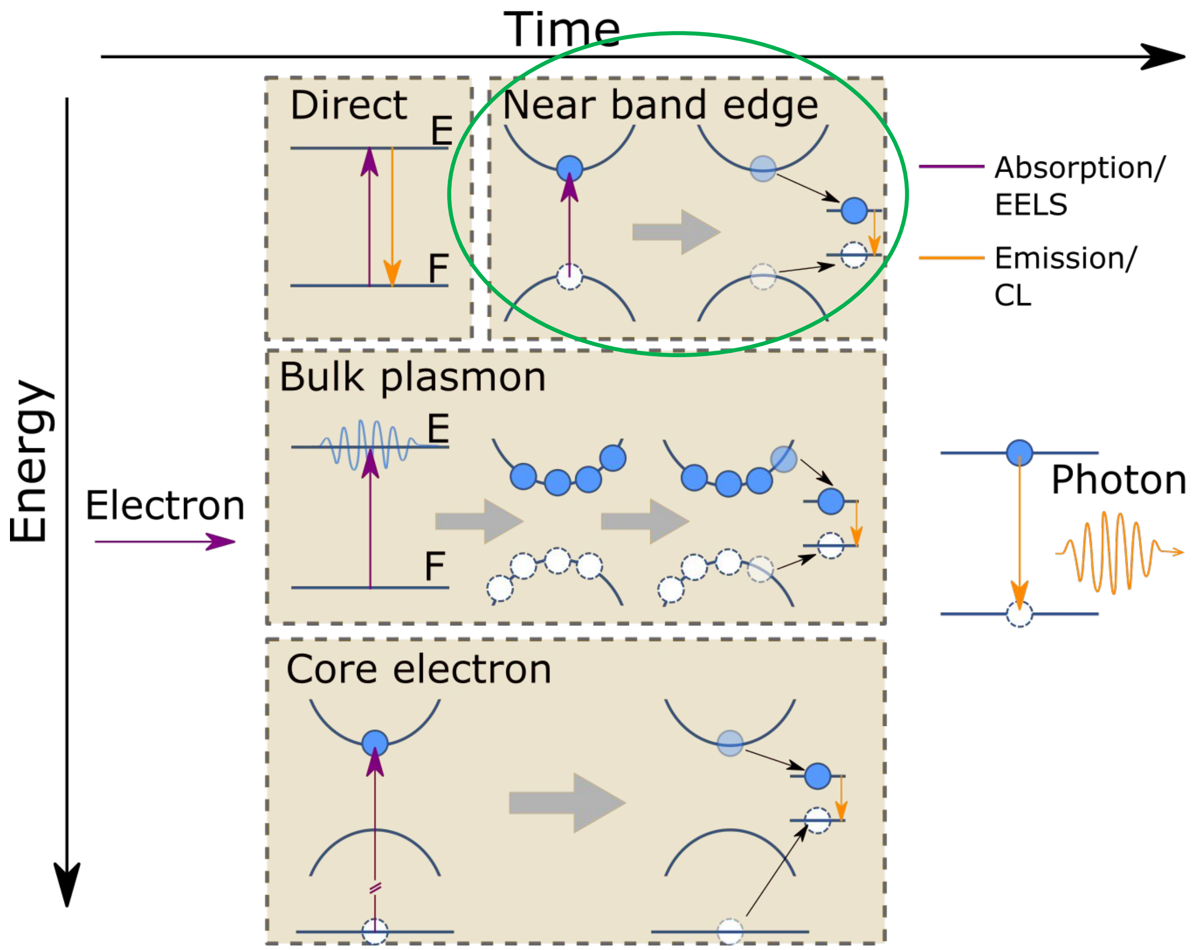


N. Varkentina, Y. Auad, *et al Sci. Adv.* abq4947 (2022)

Relative quantum efficiency

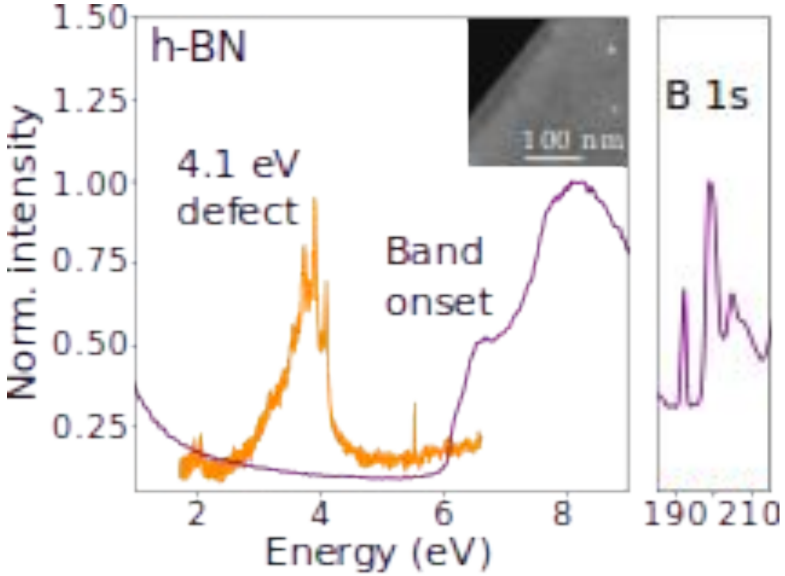


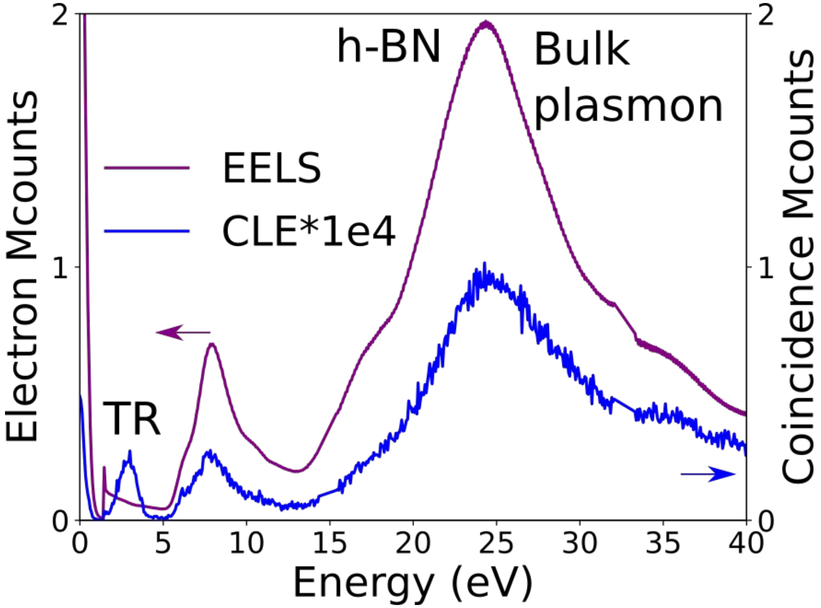
Whole range "in **one** measurement"
Easy access to VUV and soft X-ray
(IR harder because of photon part)



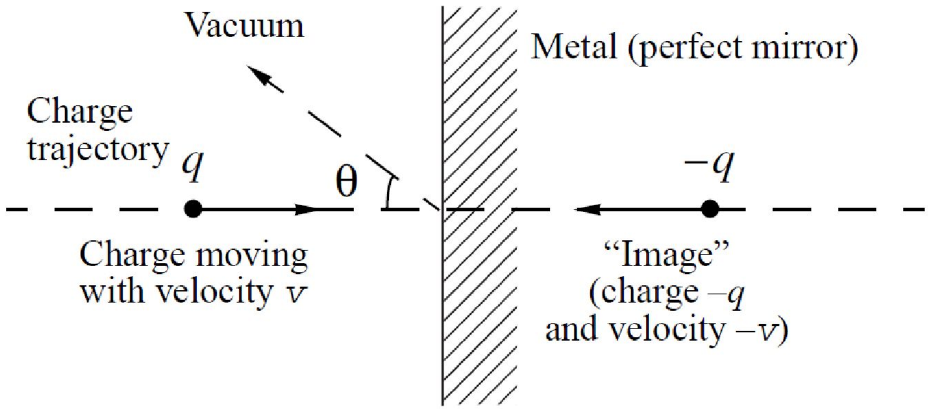
N. Varkentina, Y. Auad, *et al Sci. Adv.* abq4947 (2022)

Can we detect in gap excitations?





No… but



Transition radiation: **fast** scattering in the **forward and backwards** directions

$$W_1(\omega, \theta) = \frac{q^2 v^2 \sin^2\theta}{\pi^2 c^3 [1 - (v^2/c^2)\cos^2\theta]^2},$$

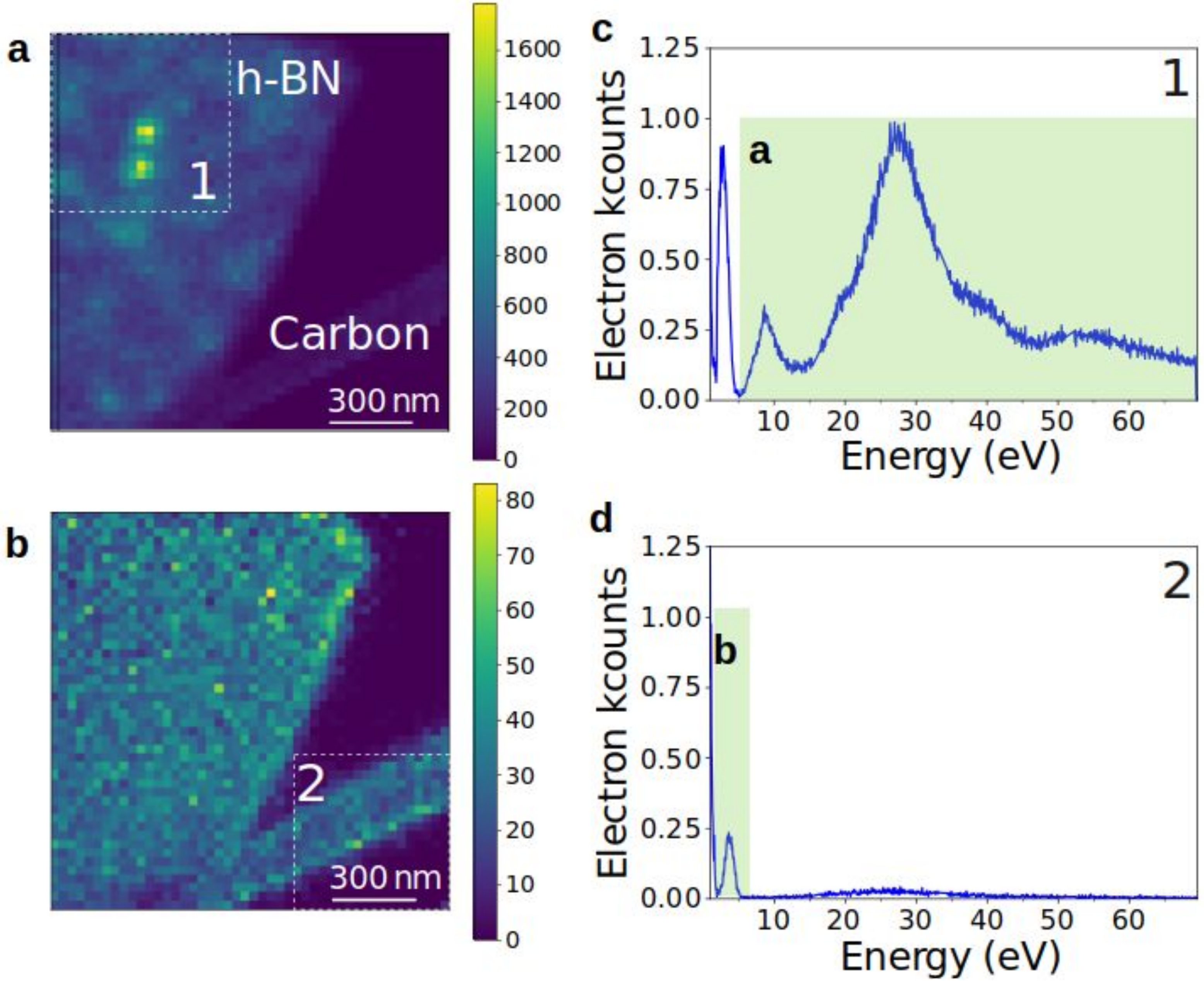
A. Freilinger

Filtering in **angle** or **time**

V. L. Ginzbourg and I. M. Frank, Zh. Eksp. Teo. Fiz. 16,15 (1946)
V. L. Ginzbourg, *Acoustics.* 51,11 (2005)

With high spatial resolution

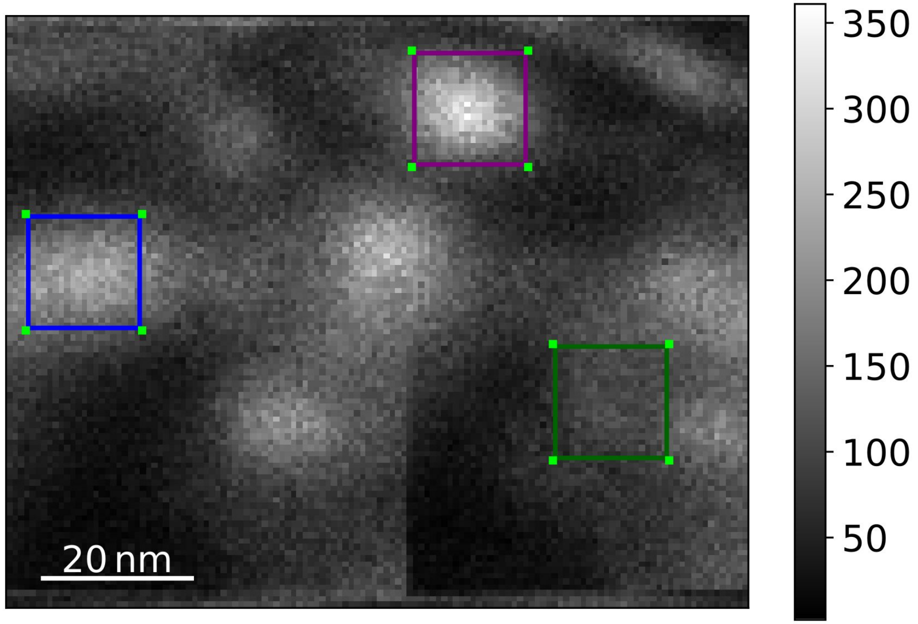
"Two defects" separated by 125 nm



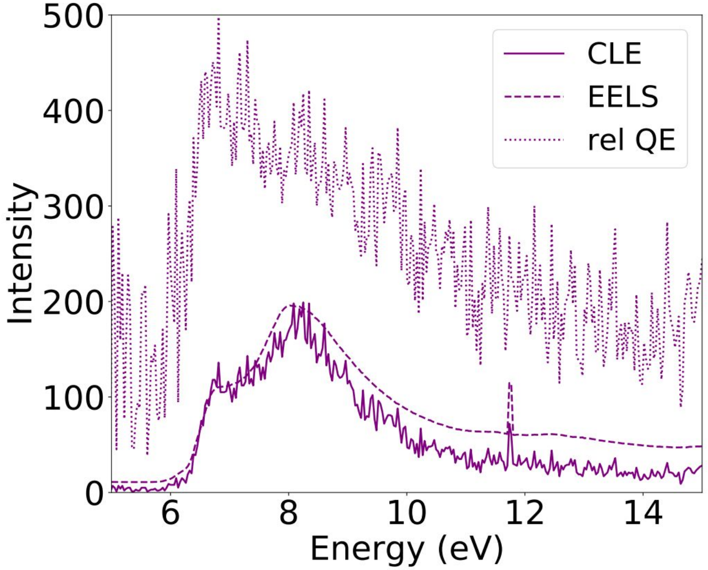
4.1 eV defect: R. Bourrellier, *et al.*, Nano Lett. (2016)
N. Varkentina, Y. Auad, *et al Sci. Adv.* abq4947 (2022)

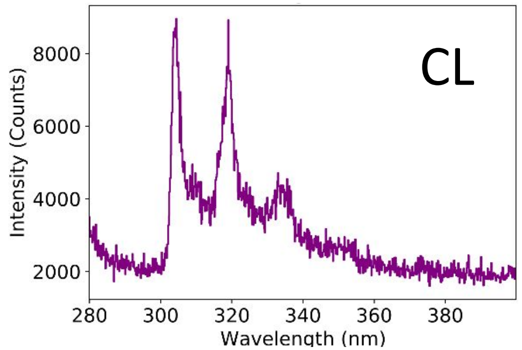
Defects absorption mapping

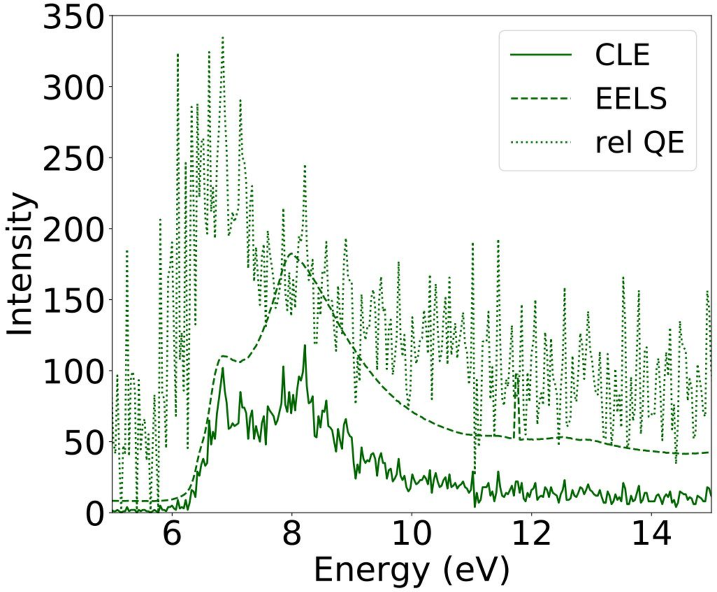
Nion monochromated microscope
+ Timepix3 (ASI) + light
injector/collector (Attolight)

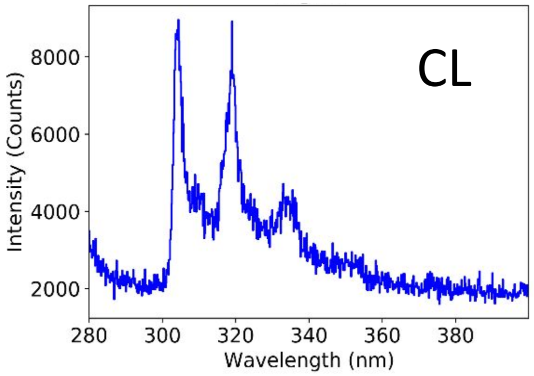


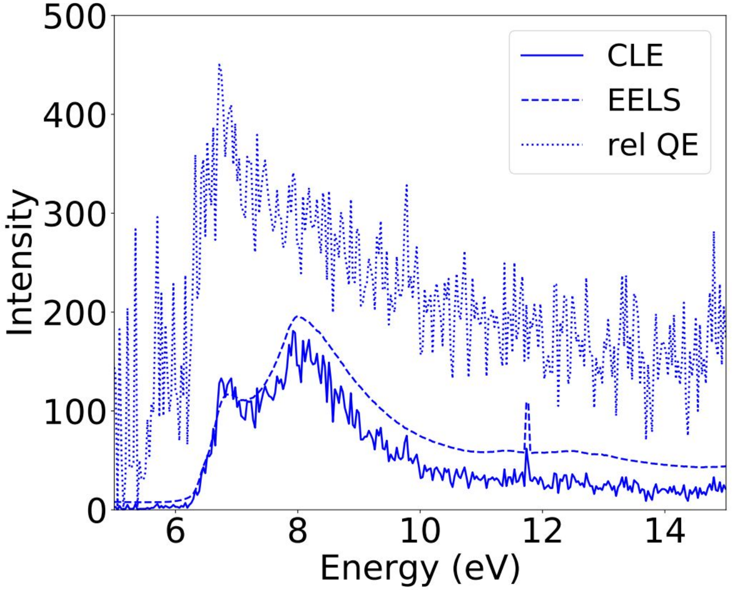
L. H. G. Tizei, *et al.*, *unpublished* (2023)

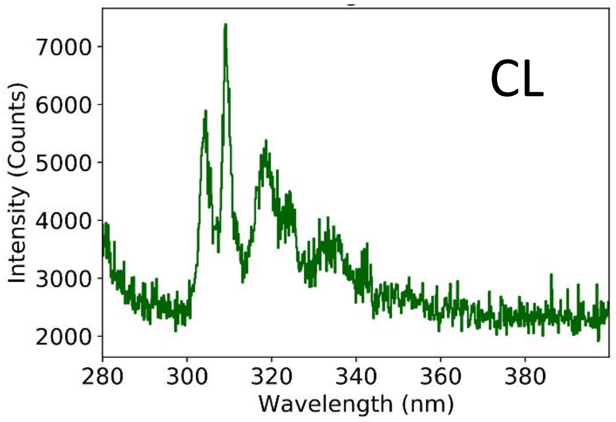












So what do EEGS measure?

Electron coupling strength

$$\beta(\mathbf{R},\omega) = \frac{e}{\hbar\omega}\int_{-\infty}^{\infty} dz E_z(\mathbf{r},\omega) e^{-i\omega z/v}$$

Induced field → Spontaneous EELS

Scattered field → Stimulated EEGS/EELS

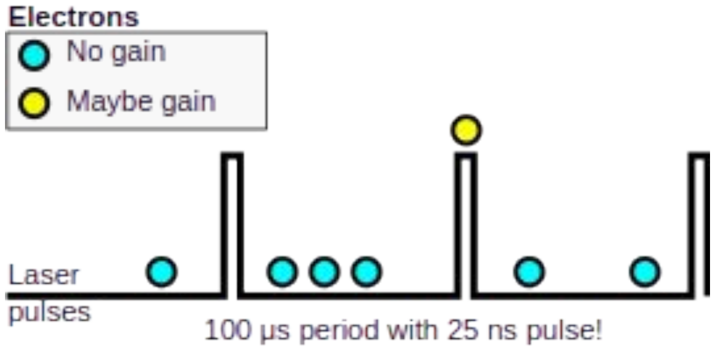
The scattered field will have maxima where there are resonances

So by sweeping a laser beam which is sharp in energy << meV EEGS is feasible

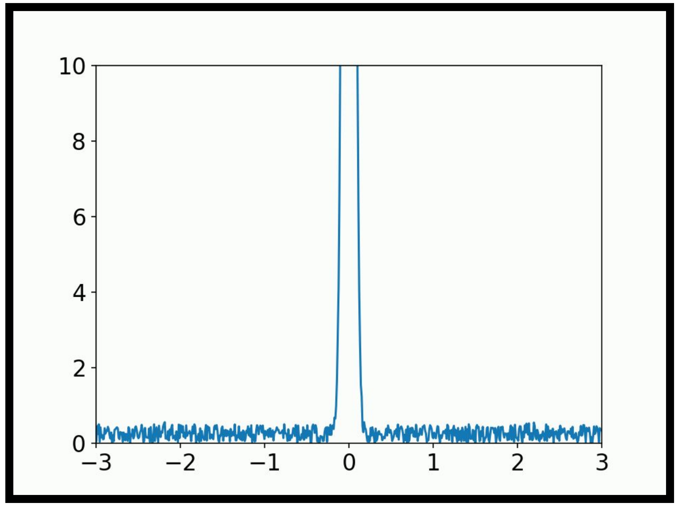
J. F. Garcia de Abajo and M. Kociak, *New Journal of Physics*, 2008
Y. Auad, *et al, Nat. Comm.* **14** 4442 (2023)

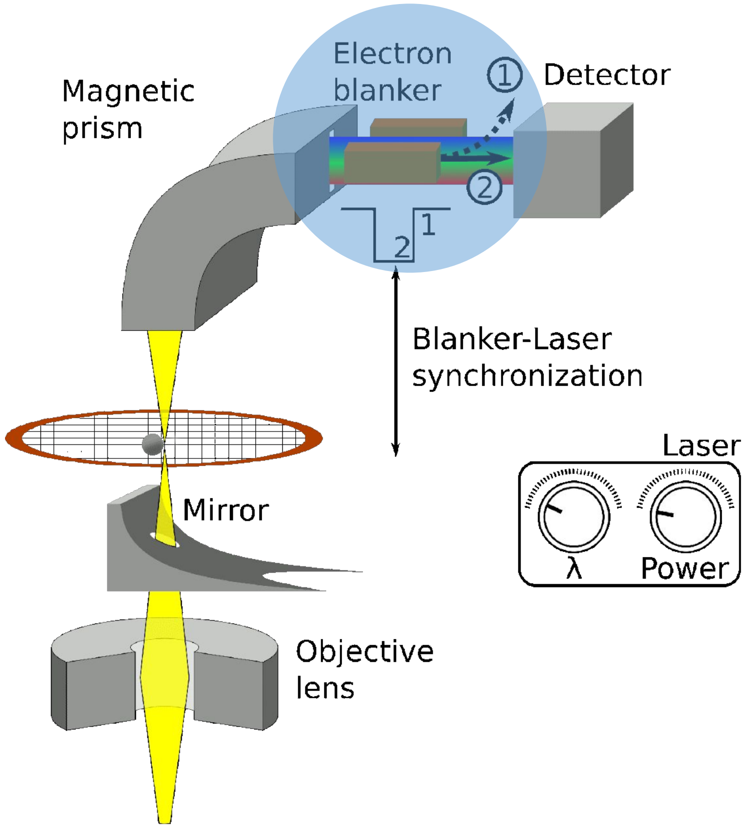
Electron energy gain spectroscopy

1. (Change wavelength + EELS) x n;
2. Use the blanker to improve SNR;



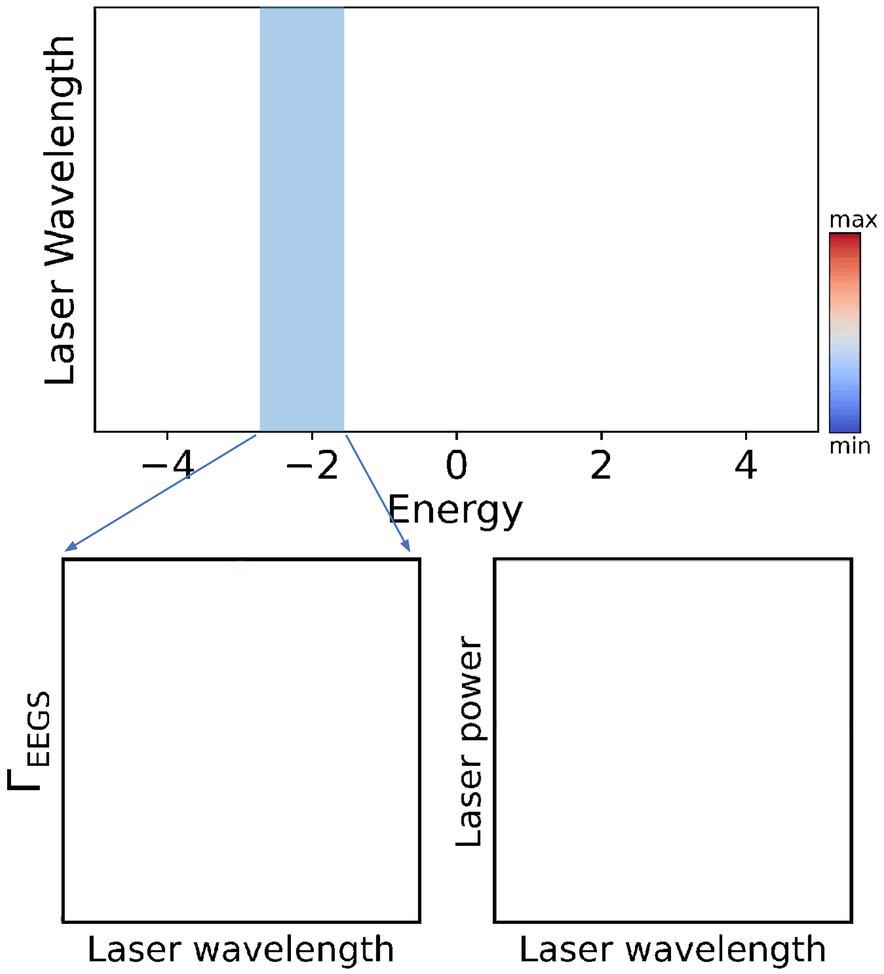
EELS Camera





✔The laser:
- Tunable wavelength;
- Nanosecond-pulsed;
- μeV spectral resolution;

Wavelength-series of EELS spectra



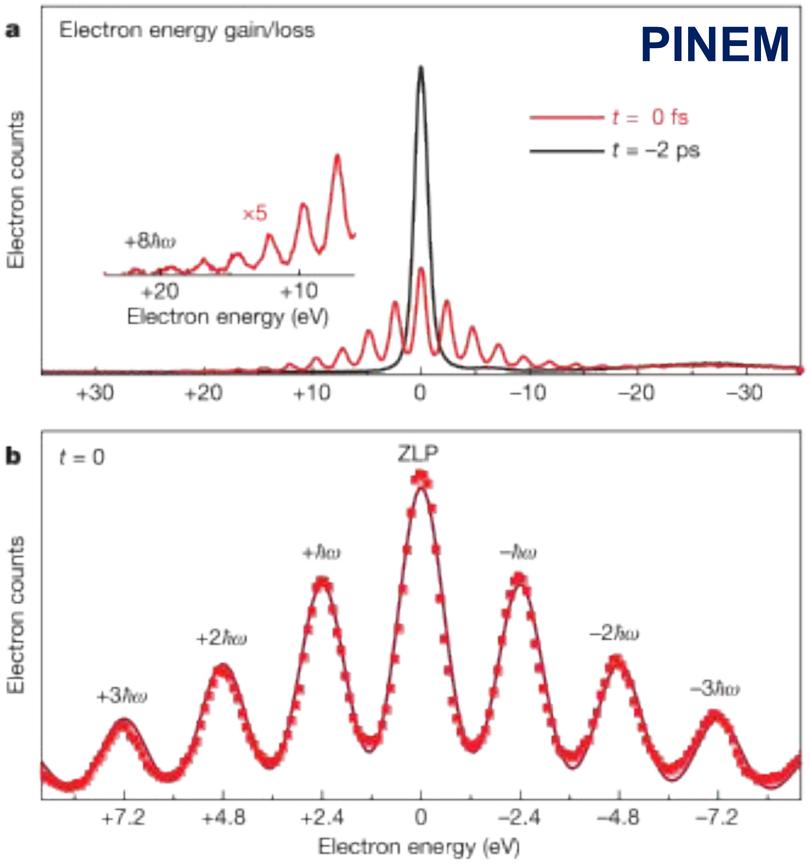
Y. Auad, *et al*, *Nat. Comm.*, **14**, 4442 (2023)

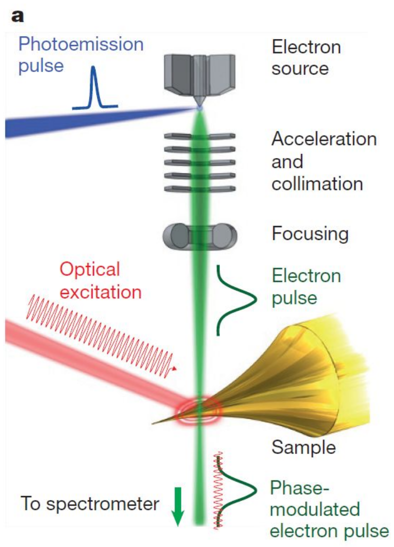
Previous work

Femtosecond laser (UEM)

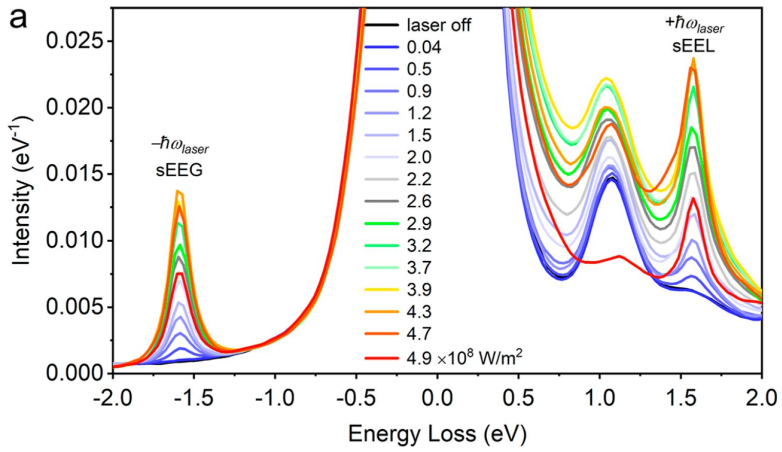
“Bad for spectroscopy!”

PINEM

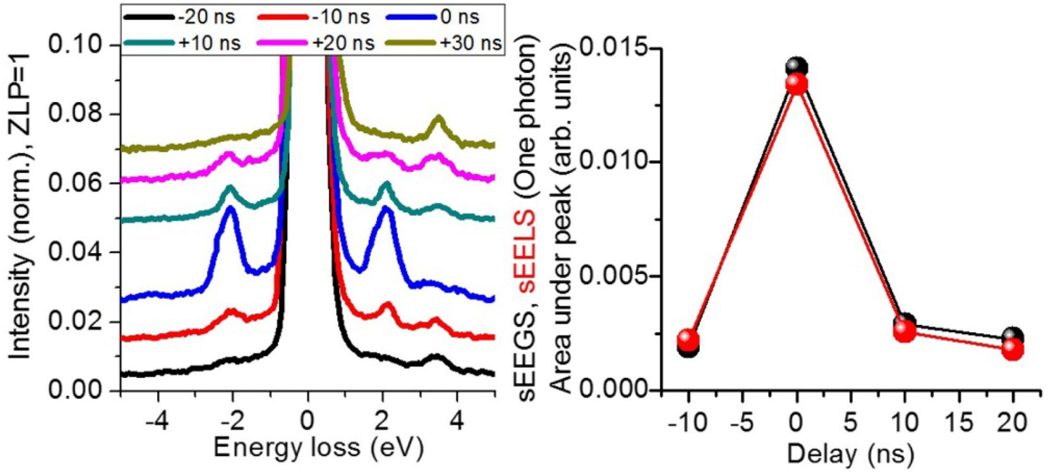




Continuous-wave

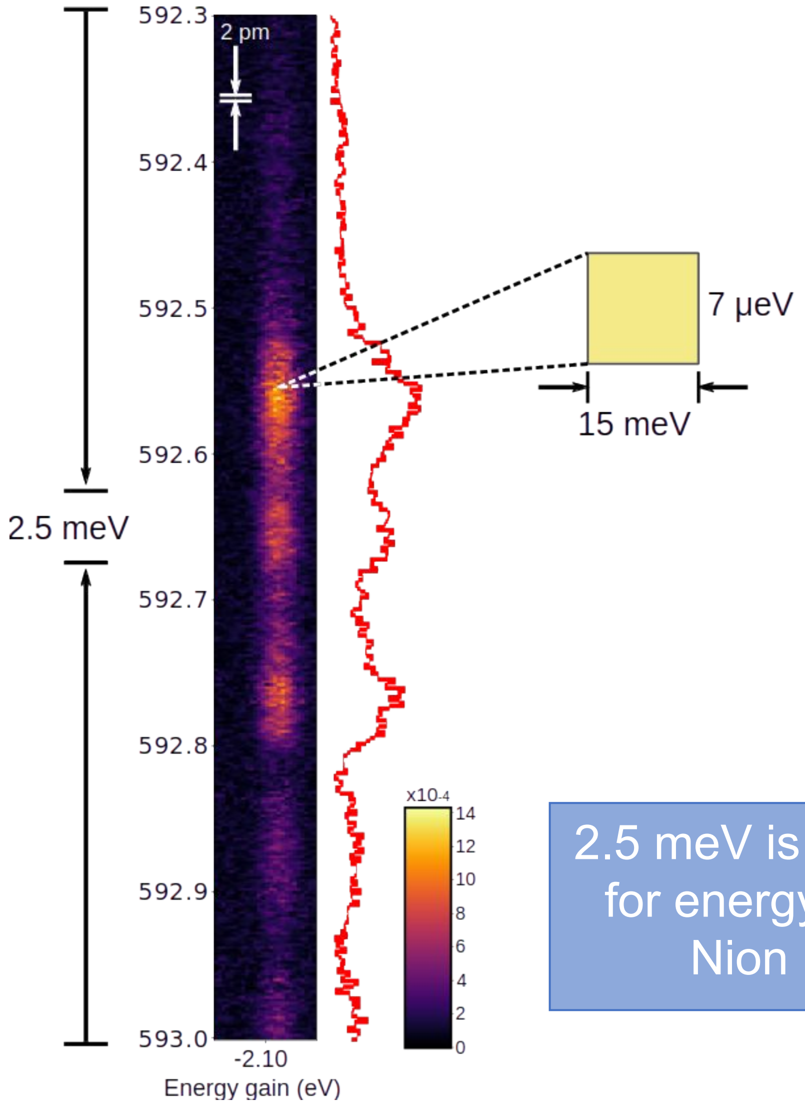


Nanosecond laser



B. Barwick et al. *Nature*, 2009.
A. Feist et al. Nature, 2015.
P. Das et al. Ultramicroscopy. 2019.
C. Liu et al. ACS Photonics. 2019.

µeV electron spectroscopy



✓ Sampling of 7 µeV from the laser is three orders of magnitude better than the ultimately spectral resolution of the microscope (5 meV);

✓ This system is capable of measuring $Q_0 > 10^5$;

2.5 meV is about the record for energy resolution in a Nion microscope

Y. Auad, *et al, Nat. Comm.* **14** 4442 (2023)
See also: J.-W. Henke, *et al.*, *Nature* (2021)