EPFL

Electron-matter interactions: Vibrational EELS

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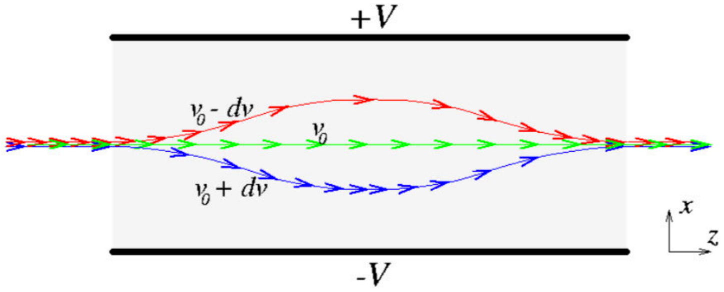
EPFL-IPHYS-LSME

Contents

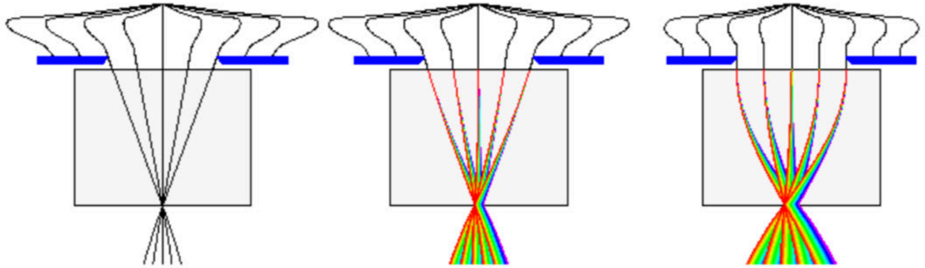
- Progress in TEM monochromation
- A new frontier: vibrational EELS and phonon modes
- Vibrational mode types and dipole or impact scattering
- Dipole scattering: aloof measurements of vibrational modes and dielectric theory
- Impact scattering: atomic resolution and thermal diffuse scattering
- Energy gain and temperature measurements

Electron probe monochromation

- First commercial monochromator: FEI Wien type filter – as used on Titan Themis at CIME, EPFL
- Basic Wien filter: perpendicular electric and magnetic deflection fields

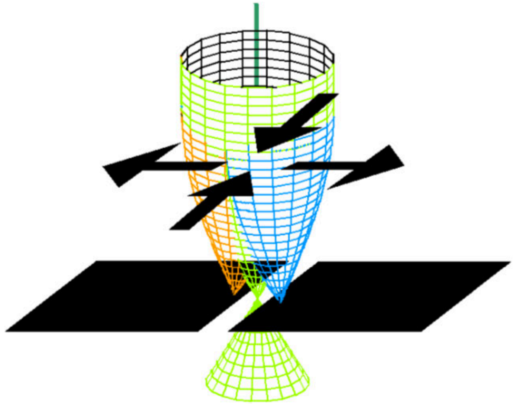


- Tuning excitation leads to energy dispersion



Excitation = 0 Excitation = π/4 = 0.78 Excitation = π/2 = 1.57

- Double focusing with electric quadrupole field leads to point focusing of electrons with different energies



Figures from *Monochromator manual Titan V1.2* by Peter Tiemeijer

Electron probe monochromation

- Wien filter acts on "soft" e⁻s – after FEG extraction, before acceleration by HT anode
- Higher HT (200–300 kV): ZLP FWHM of ~90–110 meV often achievable
- Lower HT (60 kV): 45–50 meV energy resolution has been tuned [1]
- Similar to 2010 state-of-the-art of 43 meV at 200 kV using unique Zeiss SESEM at Stuttgart MPI [2]
- Single Wien filter leads to e⁻ probe formation from "line object" ⟹ non-radially symmetric probe
- JEOL use double Wien filter to retrieve radial symmetry (30 meV FWHM at 30 kV achieved [3])

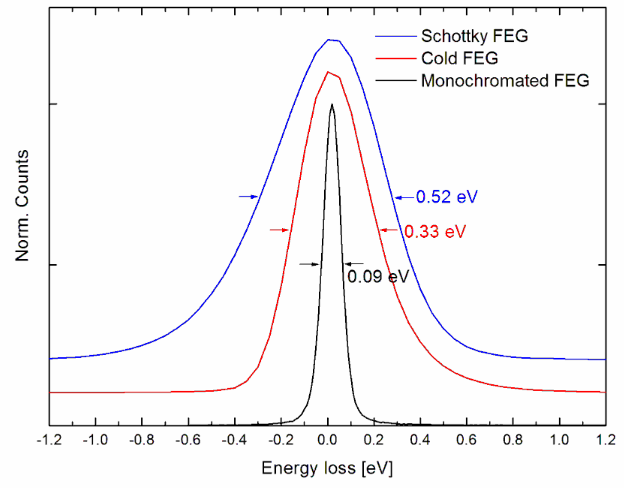
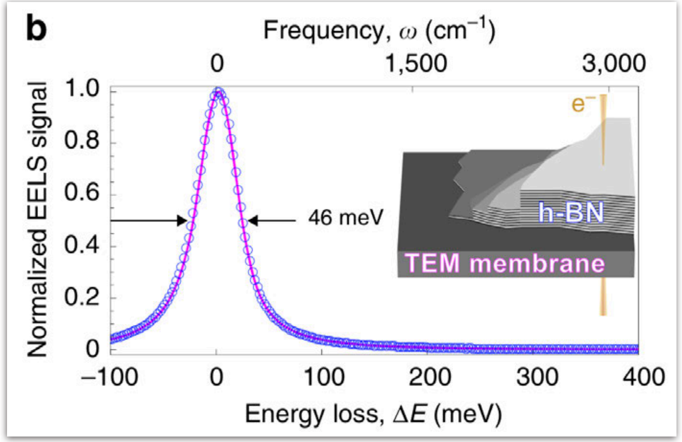
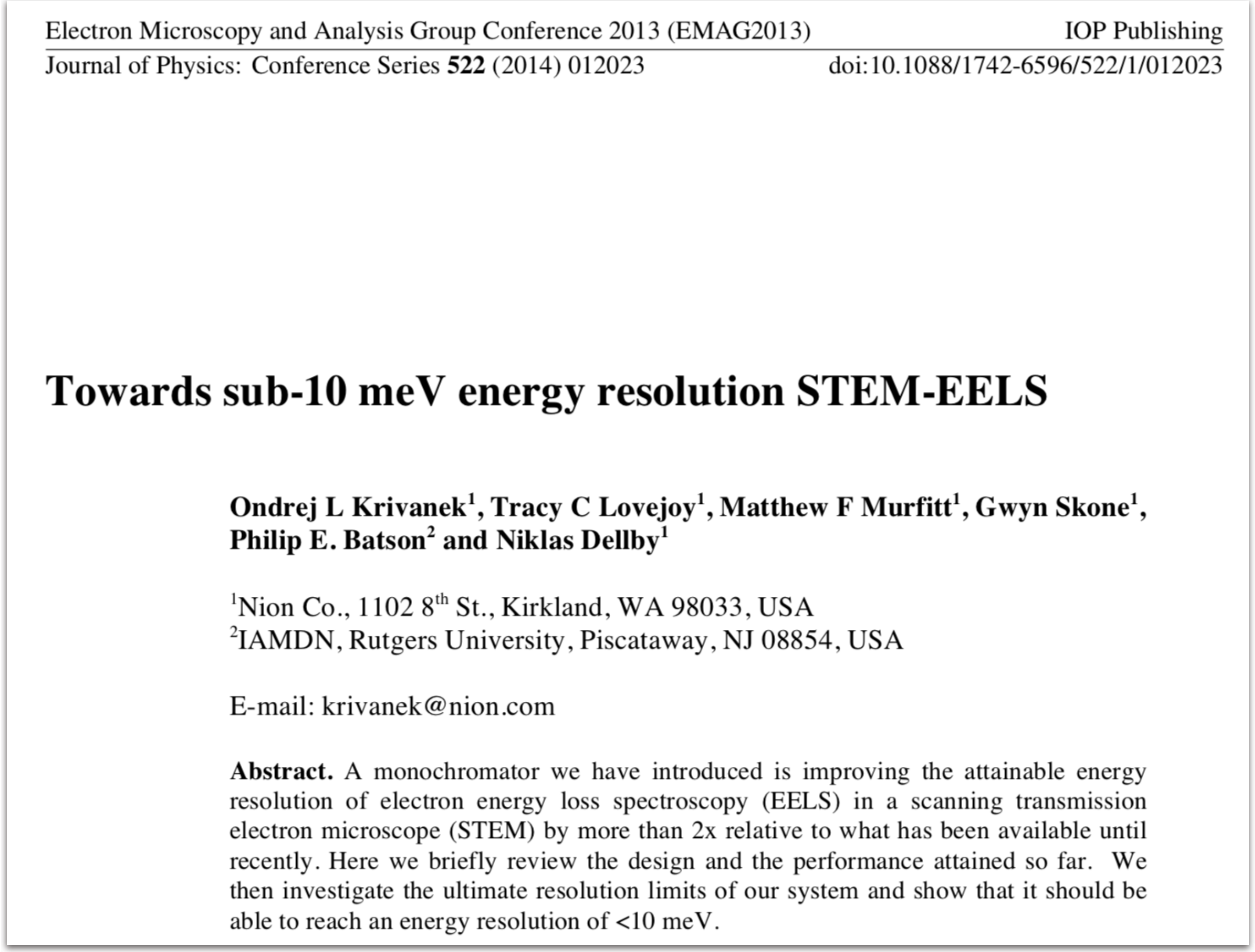


Figure courtesy of Rolf Erni, EMPA



[1] Govyadinov et al. *Nature Comm.* **8** (2017) 95; [2] Essers et al. *Ultramicroscopy* **110** (2010) 971–980; [3] Senga et al. *Nature* **573** (2019) 247–250

Sub-10 meV monochromation


Electron Microscopy and Analysis Group Conference 2013 (EMAG2013) IOP Publishing
Journal of Physics: Conference Series **522** (2014) 012023 doi:10.1088/1742-6596/522/1/012023

Towards sub-10 meV energy resolution STEM-EELS

Ondrej L Krivanek[1], Tracy C Lovejoy[1], Matthew F Murfitt[1], Gwyn Skone[1], Philip E. Batson[2] and Niklas Dellby[1]

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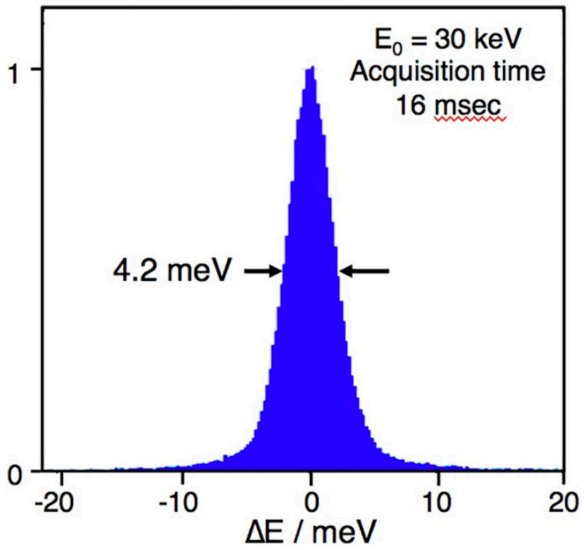
Abstract. A monochromator we have introduced is improving the attainable energy resolution of electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) by more than 2x relative to what has been available until recently. Here we briefly review the design and the performance attained so far. We then investigate the ultimate resolution limits of our system and show that it should be able to reach an energy resolution of <10 meV.



[4] Krivanek et al. *Ultramicroscopy* **203** (2019) 60–67

Sub-10 meV monochromation

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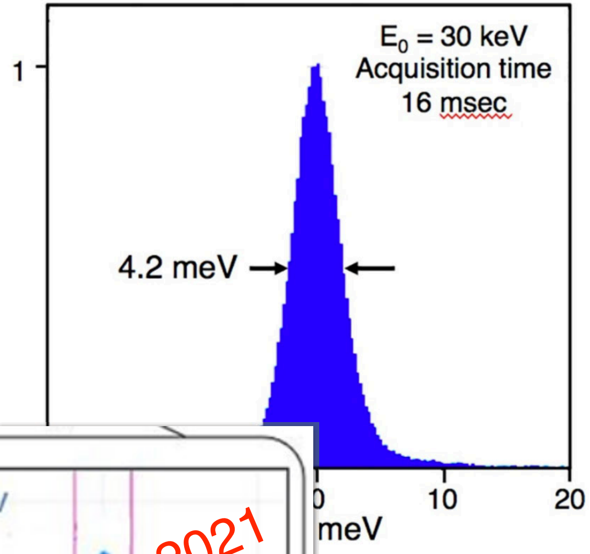
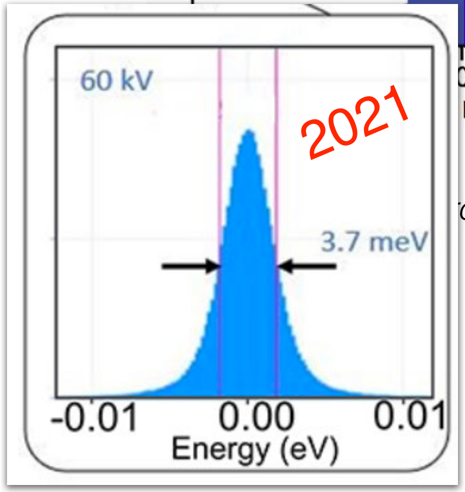


oscopy **203** (2019) 60–67



Nion Hermes monochromator

- Consists of back-to-back magnetic prisms in microscope column [5]
- Acts on accelerated "hard" e⁻s
- Uses quadrupole lenses to magnify smaller dispersion
- Employs multiple stabilisation schemes to make system "immune" to instabilities in: HT; monochromator and EELS filter prism power supplies
- 10–20 meV energy resolution now routinely achievable

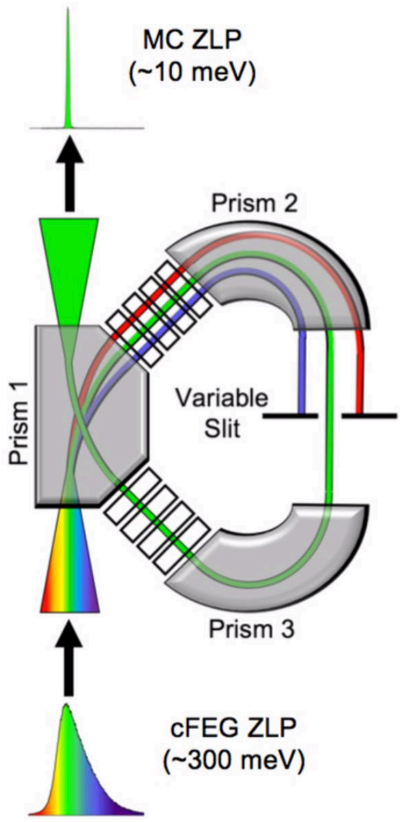


Figure from [6]:
Hachtel et al. *Sci. Rep.* **8** (2018) 5637

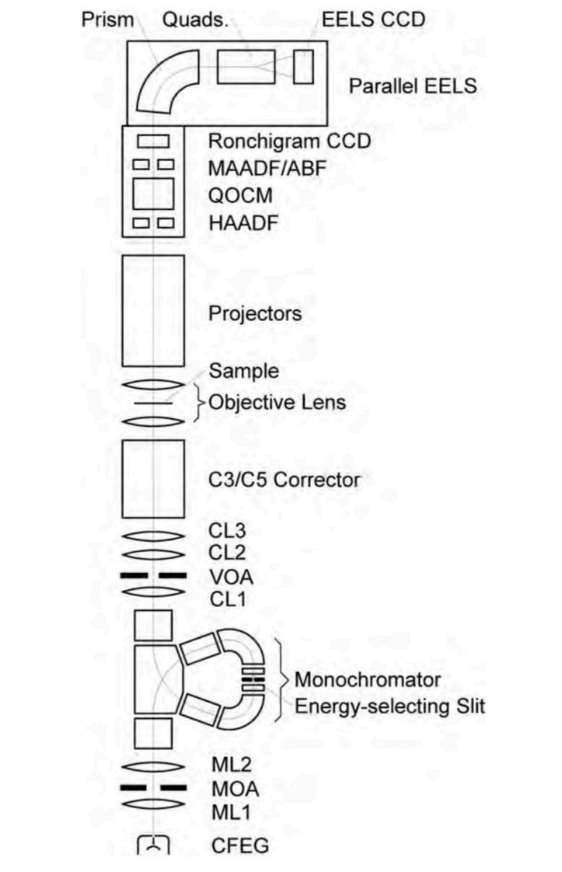


Fig. 3. Schematic cross-section of the monochromated column (Nion UltraSTEM™ 100MC).

Figure from [5]

[5] Krivanek et al. *Microsc.* **62(1)** (2013) 3–21

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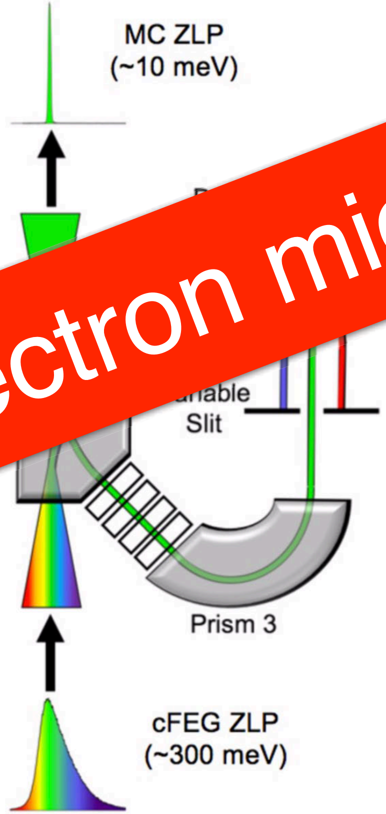
A new frontier in electron microscopy!!



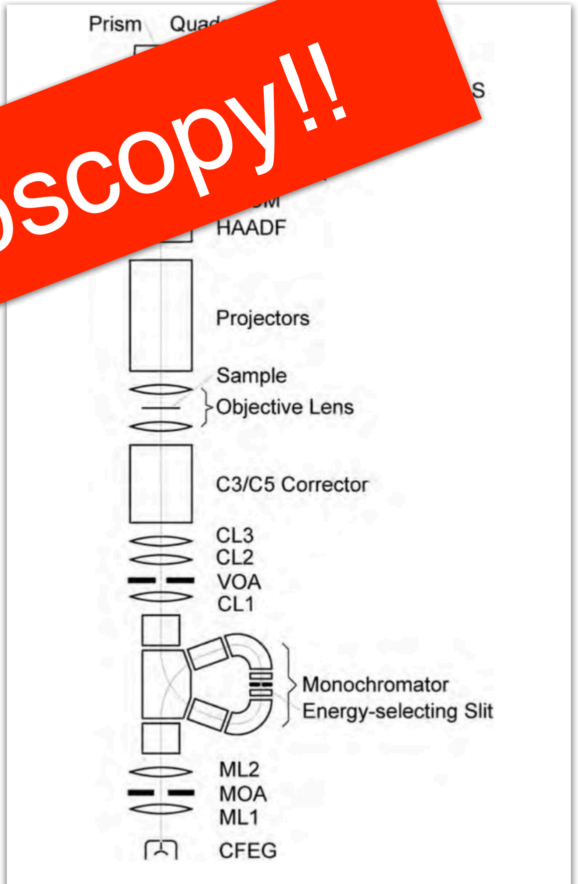


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Figure from [5]

Vibrational EELS

- First experimental results: demonstration of vibrational modes using STEM-EELS [7]
- Hachtel et al. extended this approach to site-specific isotopic label identification in ^{13}C-labeled L-alanine [8]
- Spectra comparable to FTIR – *but with better spatial resolution*

[7] Krivanek et al. *Nature* **514** (2014) 209–212;
[8] Hachtel et al. *Science* **363** (2019) 525–528

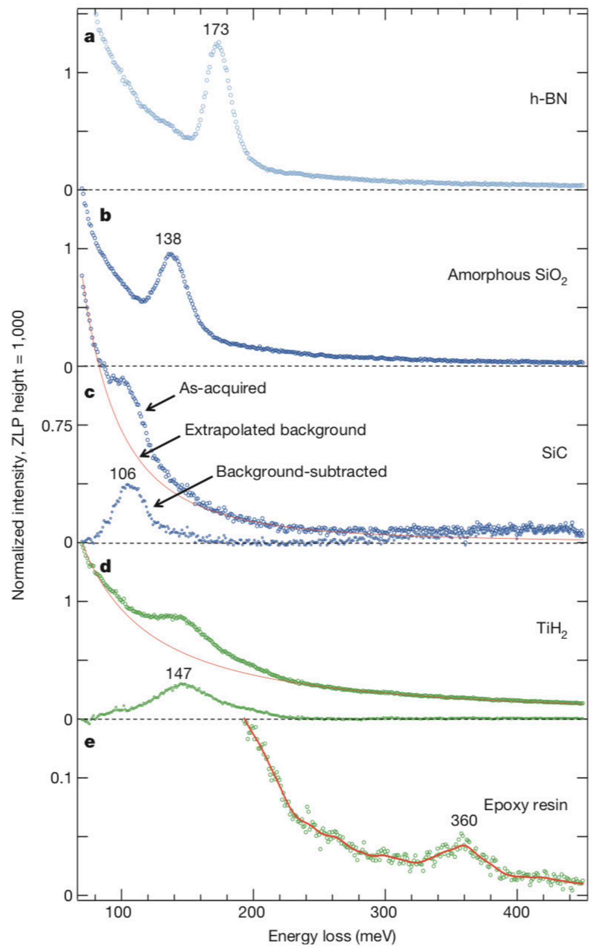


Figure 2 | **Vibrational spectra from various materials.** **a**, h-BN; **b**, amorphous SiO_2; **c**, SiC; **d**, TiH_2; and **e**, epoxy resin.

Figure from [7]

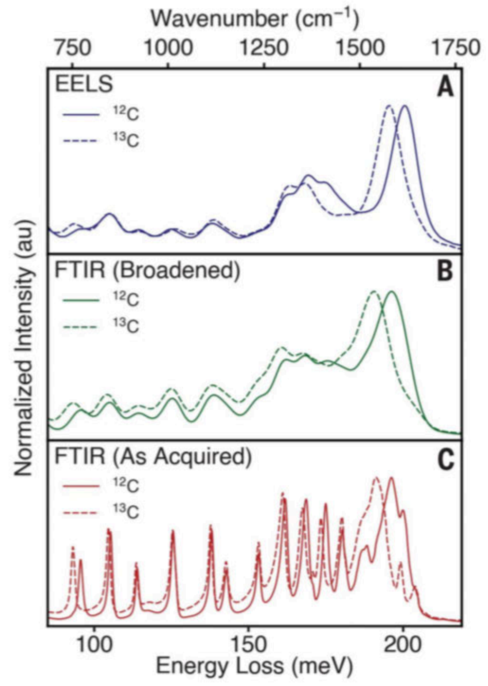
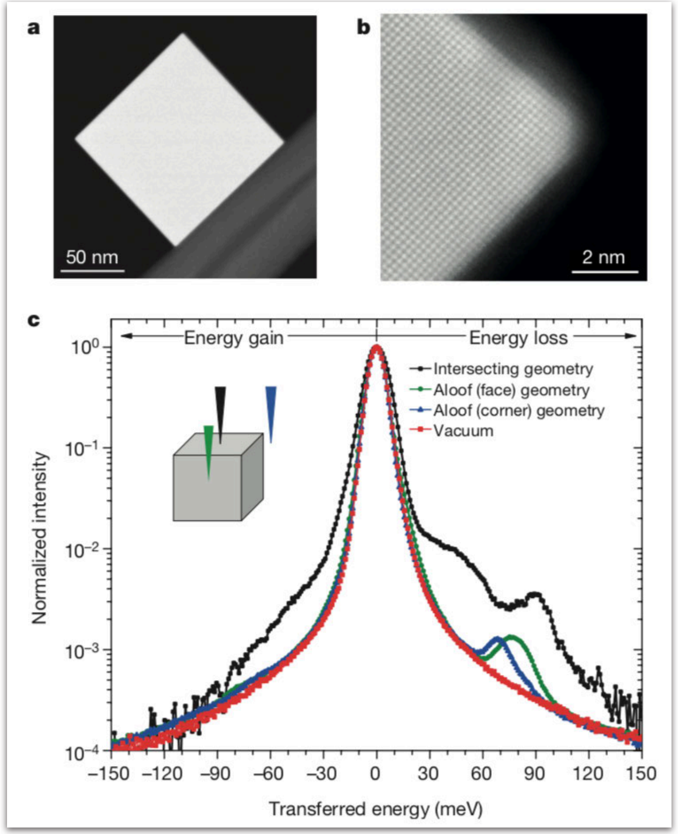


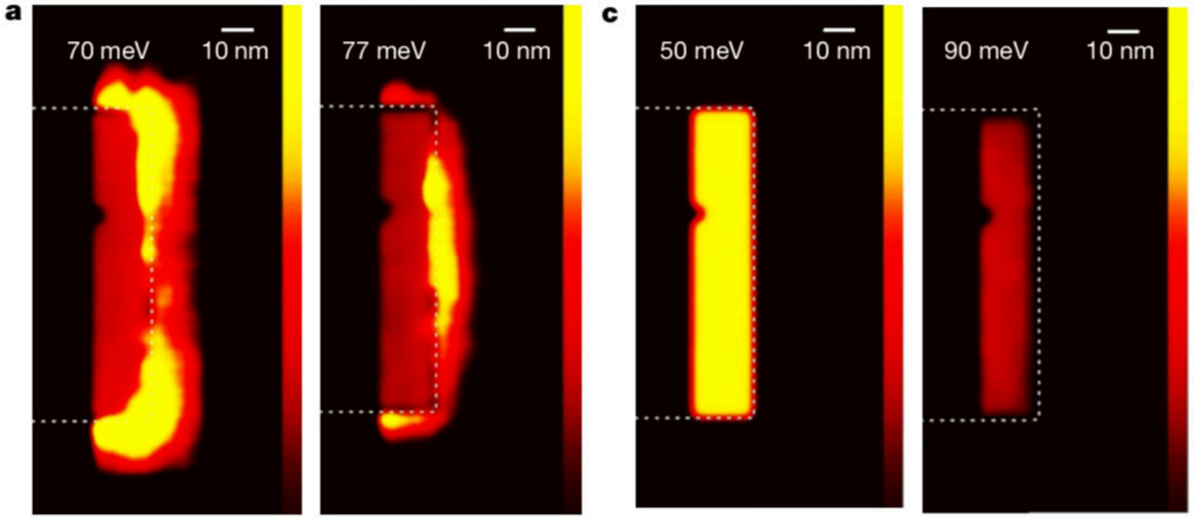
Fig. 1. Isotopic sensitivity in vibrational EELS. (**A**) Experimental vibrational spectra acquired with monochromated aloof EELS for ^{12}C L-Ala (solid line) and ^{13}C-labeled L-Ala (dashed line), exhibiting an observable isotopic shift of the dominant peak. (**B**) FTIR vibrational spectra from the same powders used for the EEL spectra in (A), broadened with a Gaussian filter to match the energy resolution in EELS (~6 meV) and showing a highly similar shift of the dominant peak. (**C**) FTIR spectra in the as-acquired energy resolution. Au, arbitrary units.

Figure from [8]

Imaging surface and bulk phonon modes

- Lagos et al. measured surface phonon polaritons modes and bulk phonon modes supported on the surface and in the volume of MgO nanocubes [9, 10]





[9] Lagos et al. *Nature* **543** (2017) 529–532; [10] Lagos et al. *Microscopy* **67(S1)** (2018) i3–i13

Acoustic vs optical phonons

- Taking case of material with two atom species [11]:
  - Acoustic modes:
    two atom types move in phase
  - Optical modes:
    two atom types vibrate out of phase
- If one atom has +ve charge and other equal –ve charge, optical mode gives oscillating dipole which can absorb/emit EM radiation
- Also specified: longitudinal (LA, LO), transverse (TA, TO) and out-of-plane (ZA, ZO) modes

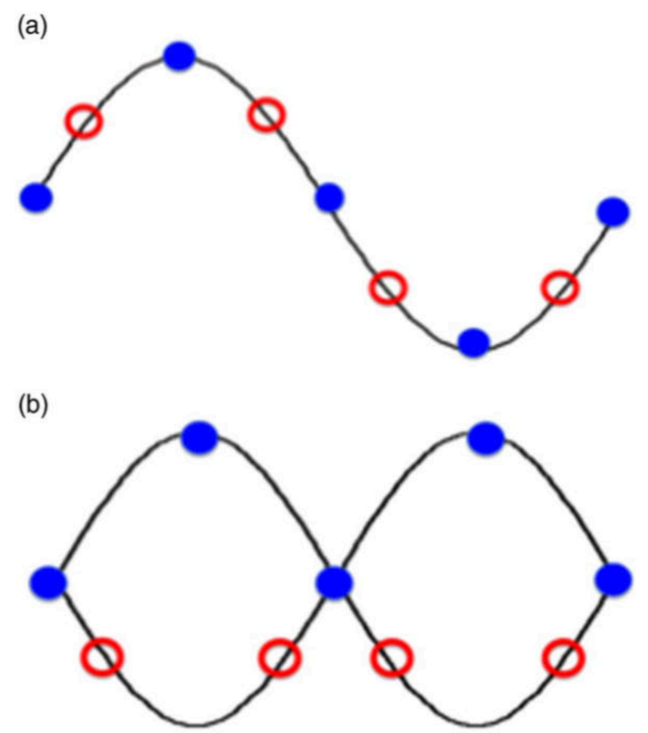
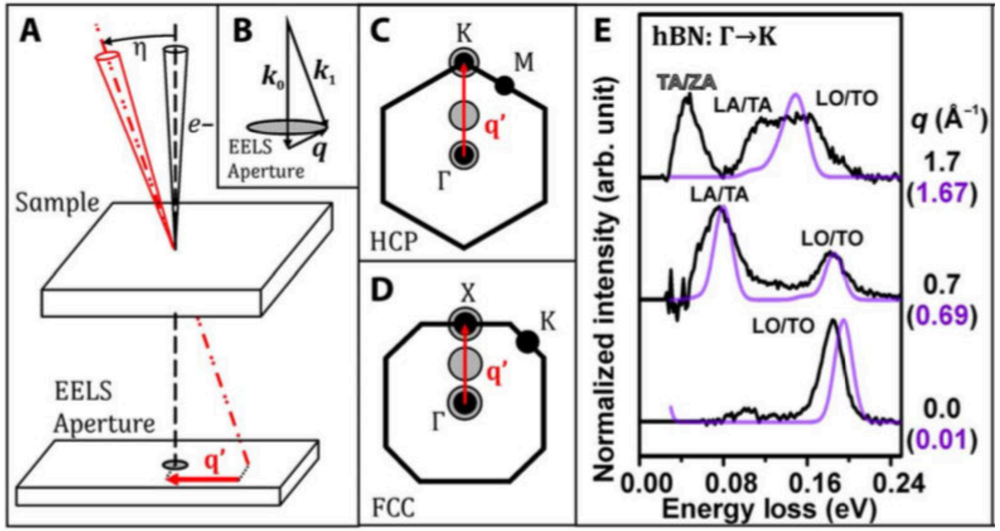


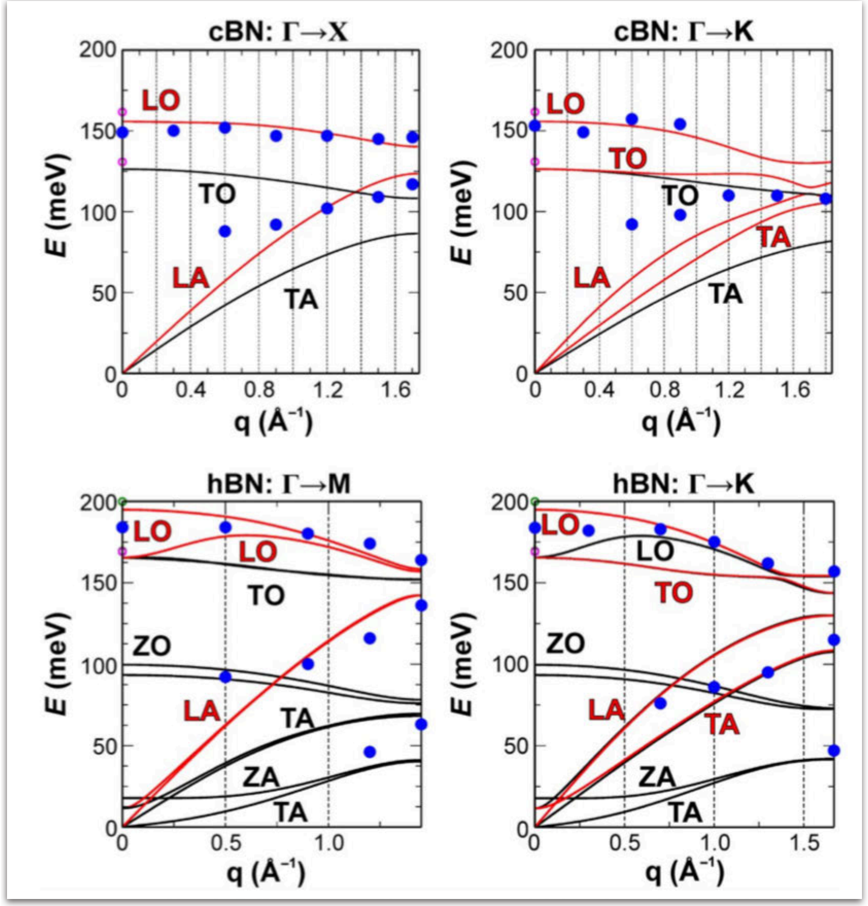
Figure 1. Vibrations of a linear chain with two types of atoms (shown as filled and open circles). The upper figure (**a**) shows an acoustic mode where all the atoms vibrate in phase, the lower figure (**b**) shows an optic mode where the two atom types vibrate in antiphase. If one atom is positively charged and the other negatively charged this clearly gives rise to an oscillating dipole.

[11] Rez *Microsc. Microanal* **20** (2014) 671–677

Momentum-resolved vibrational EELS

- By tilting the incident beam, Hage et al. measured phonon modes of cubic and hexagonal BN in ***q***-space [12]
  ⟹ mapping of optical and acoustic phonons across first Brillouin zone

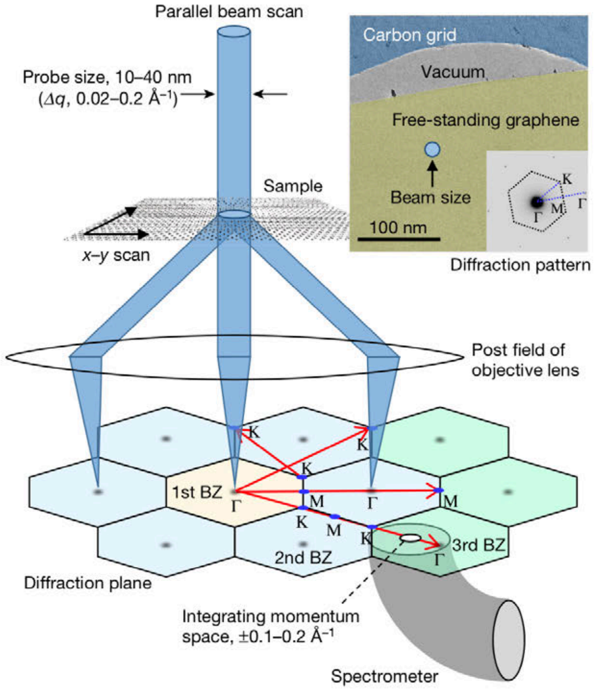


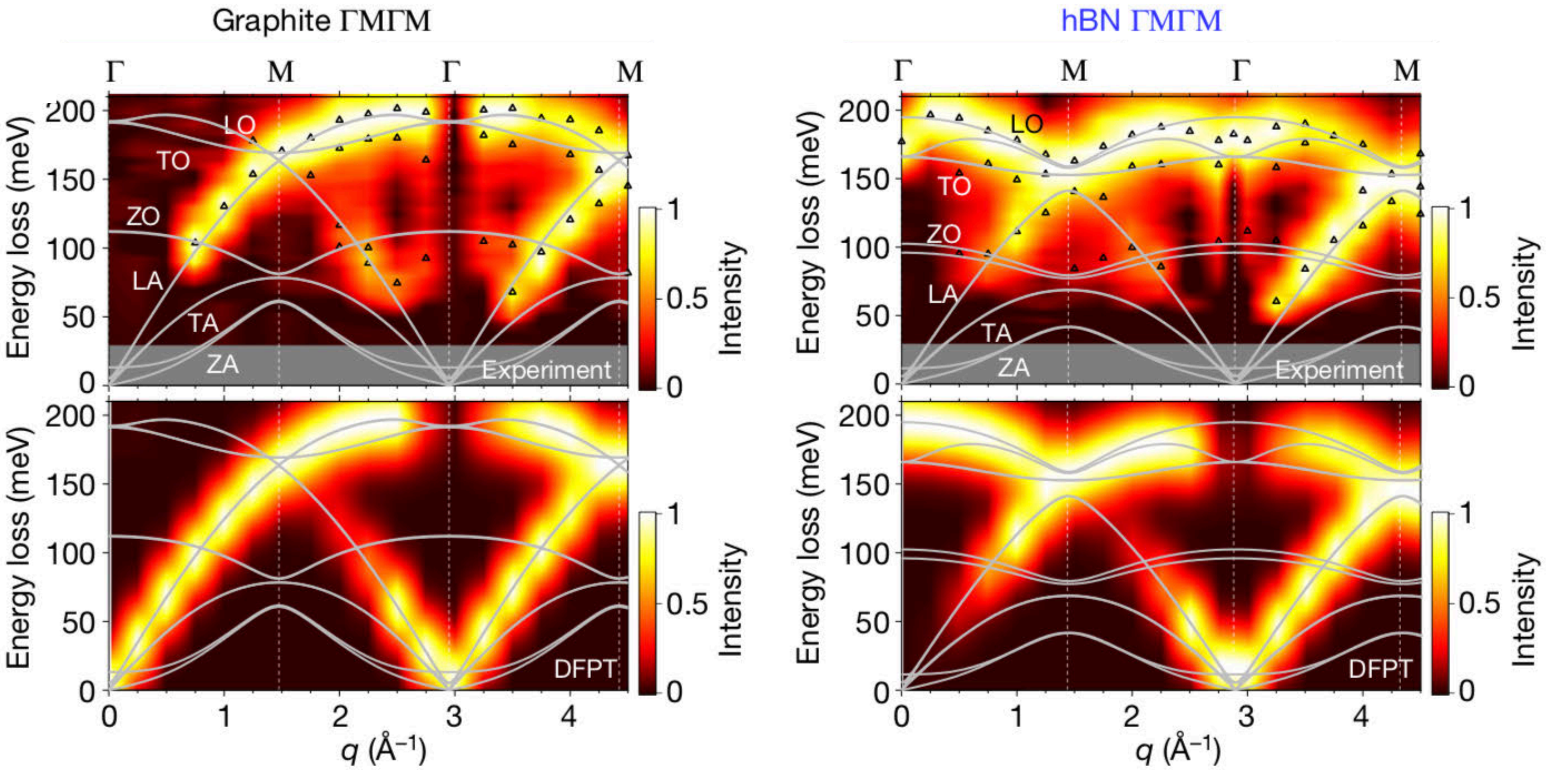


[12] Hage et al. *Sci. Adv.* **4** (2018) eaar7495

Momentum-resolved vibrational EELS

- Senga et al. extended approach across more Brillouin zones and to non-polar materials: graphite and even monolayer graphene [3]*





[3] Senga et al. *Nature* **573** (2019) 247–250

**Using a JEOL, not a Nion!!*

Dipole vs impact scattering

- Electron-phonon interactions commonly assigned to regimes of: *dipole scattering* or *impact scattering* [13]

- Dipole scattering:
  - associated with long-range Coulomb field, vibrational modes excited by polarising the medium
  - spectral features like IR spectroscopy
  - spatially delocalised

- Impact scattering:
  - vibrational modes that appear in neutron scattering, but not IR spectroscopy
  - e.g. acoustic modes, optical modes in non-ionic materials, symmetric stretching and deformation modes in ionic materials
  - spatially localised

[13] Venkatraman et al. *Nature Phys.* **15** (2019) 1237–1241

Dipole scattering

- Dipole theory predicts a Lorentzian angular distribution of intensity:

$$\frac{\mathrm{d}I}{\mathrm{d}\Omega} \propto \frac{1}{\theta^2 + \theta_{\mathrm{E}}^2} \qquad \text{where} \qquad \theta_{\mathrm{E}} \approx \frac{\Delta E}{2E_0}$$

$\Longrightarrow$ scattering angles very small

- Suppose θ_{50} is median angle of inelastic scattering where: $\theta_{50} \approx \left(\theta_{\mathrm{E}}\theta_{\mathrm{c}}\right)^{1/2}$
- Half of scattered e⁻ acquire transverse momentum within range [14]: $\Delta p_x = \pm\left(h/\lambda\right)\theta_{50}$
- From Heisenberg uncertainty relation: $L_{50} \approx \Delta x \approx \lambda/2\theta_{50}$
- Observed $L_{50} \approx$ 100 nm for E_0 = 60 keV and ΔE = 150 meV

$\Longrightarrow$ dipole scattering interaction highly delocalised; can be measured in *aloof* mode

[14] Egerton *Ultramicroscopy* **159** (2015) 95–100

Aloof measurements

- Scattering wave vector along beam direction:

$$q_z = k_0 \frac{\Delta E}{mv^2} = \frac{\omega}{v}$$

- For impact parameter d, classical dielectric response theory gives scattering cross-section [15]:

$$\sigma(d) \propto K_0\left(\frac{2\omega}{\gamma v} d\right)$$

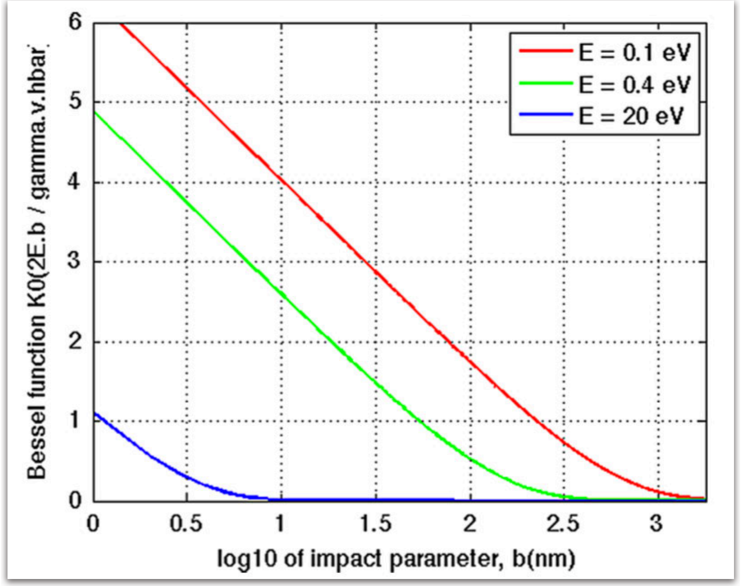


Figure from [14]

- Crystals: strongest intensity from LO modes with ionic displacement in specimen plane [11]

- Molecular vibrations (no dispersion/wavevector dependence): still measure displacements in specimen plane – but can be simple bond stretching or torsional vibrations with displacements ⊥ to bond

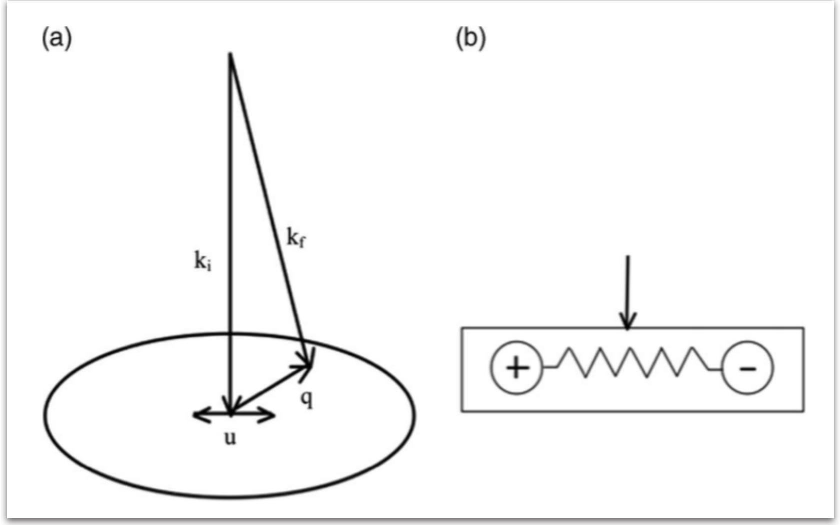
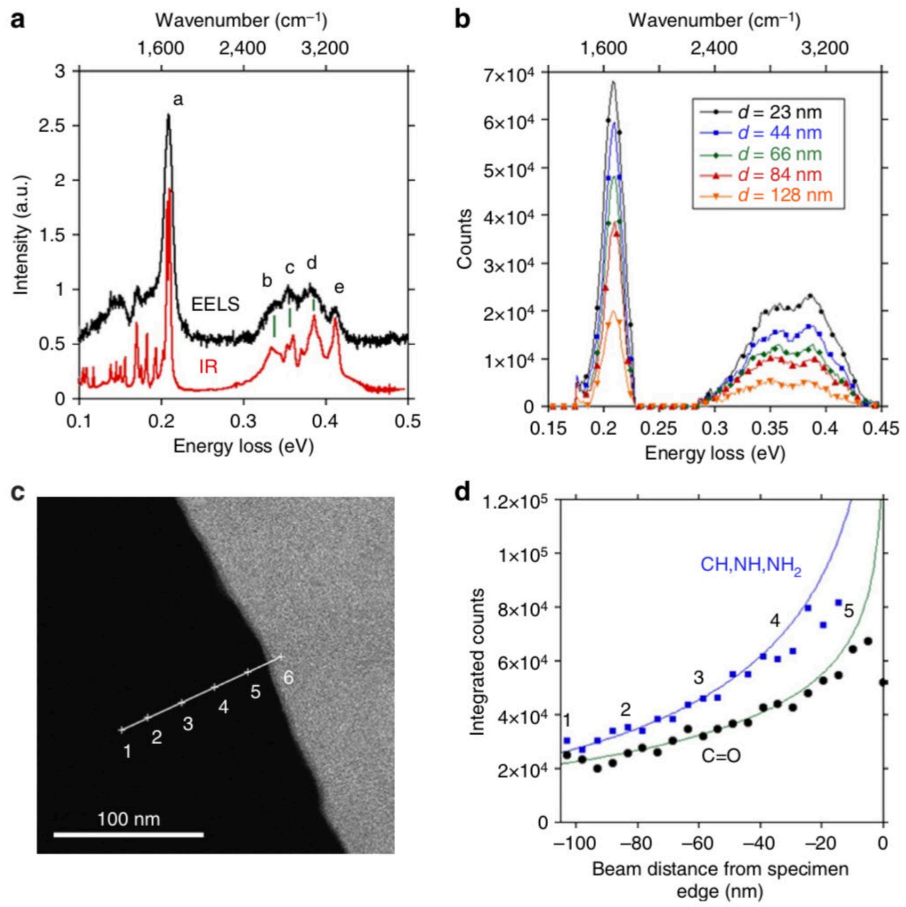


Figure from [11]

[15] Rez et al. *Nature Comm.* **7** (2016) 10945

EPFL Beam sensitive studies

- Using aloof mode with large impact parameter (e.g. $d \approx 30$ nm) allows vibrational modes to be studied with significantly reduced damage (radiolysis) in e⁻-beam sensitive samples
- Demonstrated by Rez et al. on *biogenic guanine* crystals [15]
- Note:
  - lighter elements
    $\Longrightarrow$ larger vibrational displacements
    $\Longrightarrow$ larger σ
    – can be comparable to that for C K-edge
  - stretching modes of H bonded to other atoms have highest frequencies; $\Delta E \approx 300$–400 meV



Peak	Energy (meV)	Frequency (cm^{-1})	Assignment
a	209	1,666	C=O stretch
b	334	2,663	C-H stretch
c	357	2,846	N-H stretch
d	386	3,078	Symmetric NH_2
e	411	3,277	Antisymmetric NH_2

[15] Rez et al. *Nature Comm.* **7** (2016) 10945

Dielectric theory

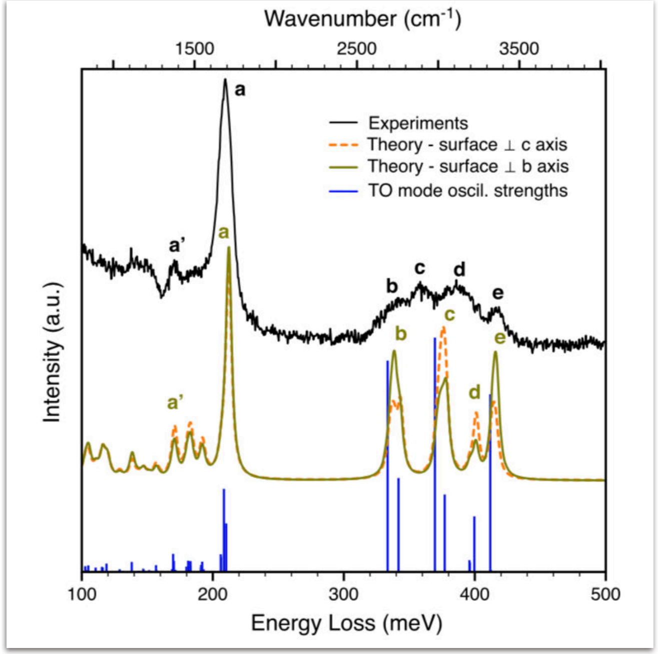
- Starting from classical Lorentz force approach work done:

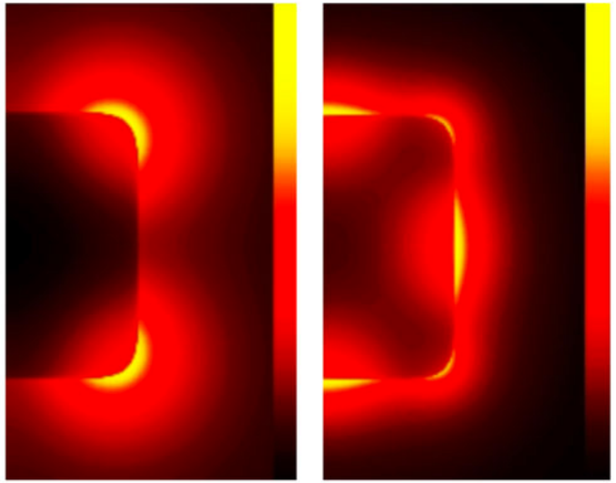
$$W = -e\int_{-\infty}^{\infty} \vec{\boldsymbol{v}} \cdot \vec{\boldsymbol{E}}^{ind}\left(\vec{\boldsymbol{r}}_e\right) dt$$

  Radtke et al. simulated guanine EELS response using quantum mechanical DFT calculations of dielectric response of specimen [16]

- Local dielectric response-based BEM also successfully simulates the surface and corner supported surface phonon polaritons observed in aloof geometry on MgO nanocubes [9]

- However, other approaches must be used for the bulk phonons [17]

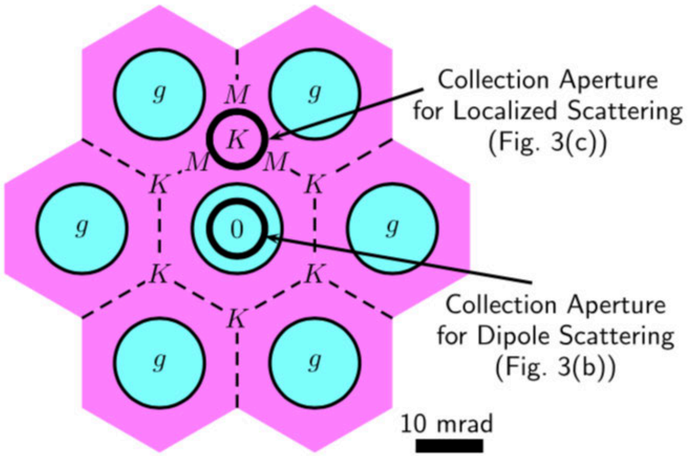


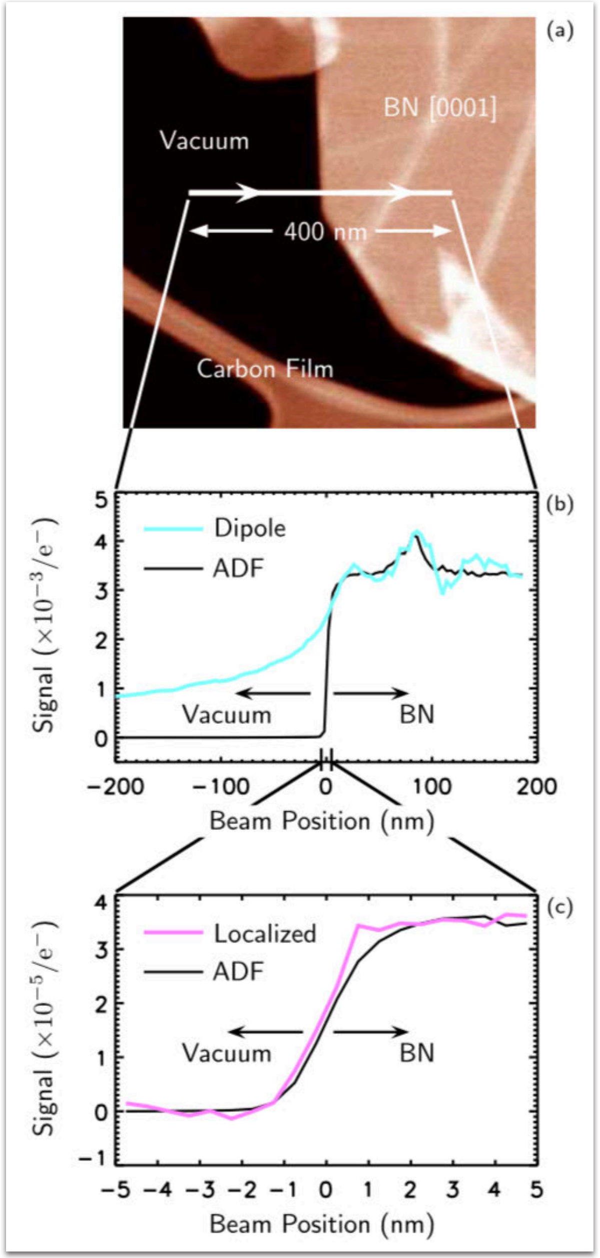


[16] Radtke et al. *PRL* **119** (2017) 0247402; [17] Hohenester et al. *PRB* **97** (2018) 165418

Impact scattering

- Impact scattering should give access to much more localised signal
- Can isolate by selecting large wave vectors which involve rapidly modulating atomic (cation-anion) displacements which lack long range $\vec{E}$ fields
- That is: localised scattering $\Longleftrightarrow$ large Δp / large θ
- First demonstrated on *h*-BN by Dwyer et al. [18]:

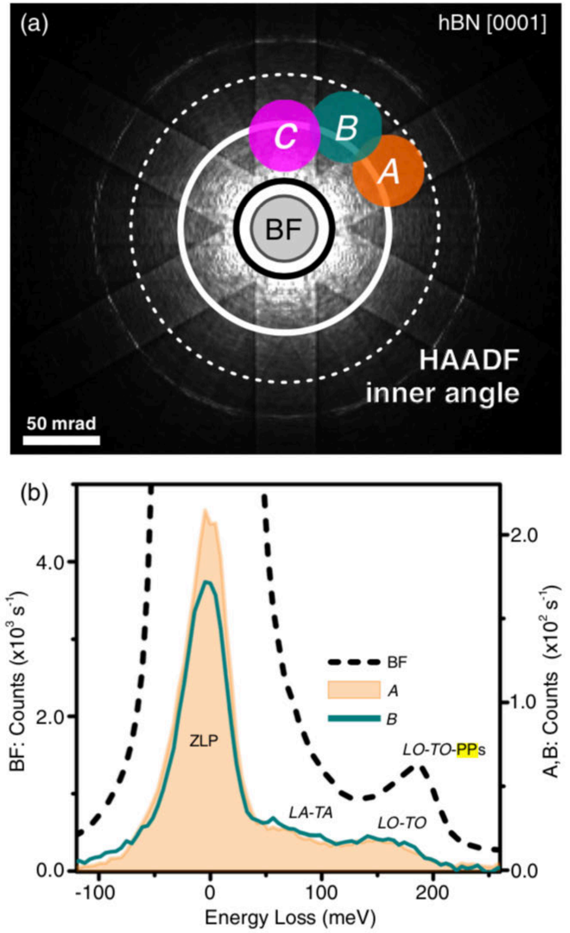


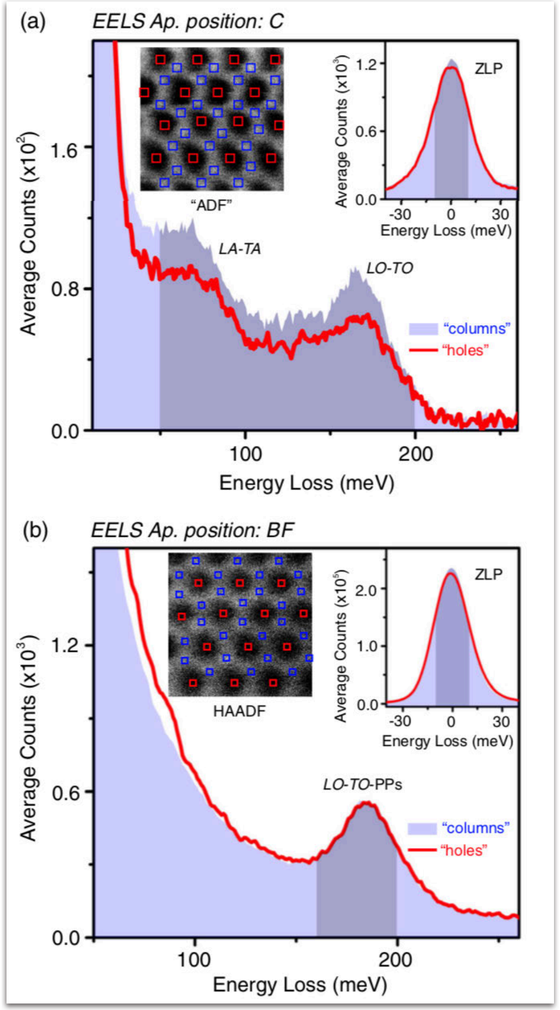


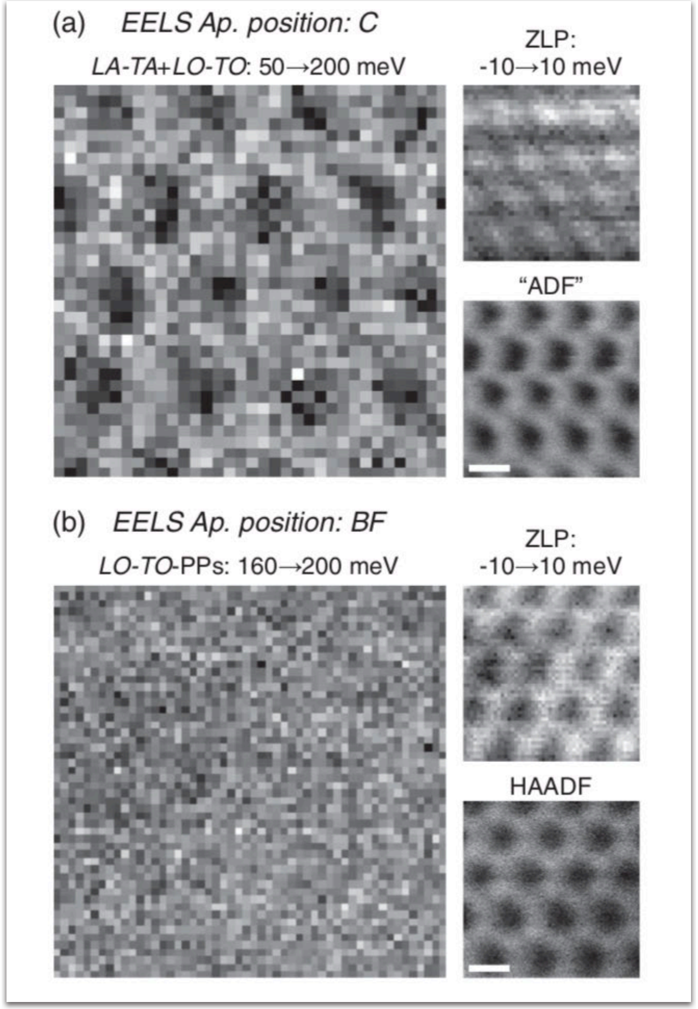
[18] Dwyer et al. *PRL* **117** (2016) 256101

Atomic resolution phonon scattering

- Hage et al. pushed this approach to atomic resolution on *h*-BN [19]







[19] Hage et al. *PRL* **122** (2019) 016103

Week 3 recap!

QM model of phonon excitation

- Les Allen et al. introduced quantum mechanically correct model of phonon scattering: Forbes et al. PRB **82** (2010) 104103
- Introduces the QM exchange of phonon excitation into the Schrödinger equation
- Schrödinger equation modified to:

$$\left[-\frac{\hbar^2}{2m}\nabla^2_{\vec{r}} + H_c(\vec{\tau}) + H'(\vec{r},\vec{\tau})\right]\Psi(\vec{r},\vec{\tau}) = E(\vec{r},\vec{\tau}) \qquad (3.27)$$

H_c is the Hamiltonian for all the crystal particles

H' describes the interaction of the incident e⁻ with the crystal particles

E is total energy of system

$\vec{r}$ is coordinate of incident e⁻

$\vec{\tau} = \{\vec{r}_1,\ldots,\vec{r}_N\}$ is set of all position vectors referring to particles in the crystal

Week 3 recap!

QM model of phonon excitation

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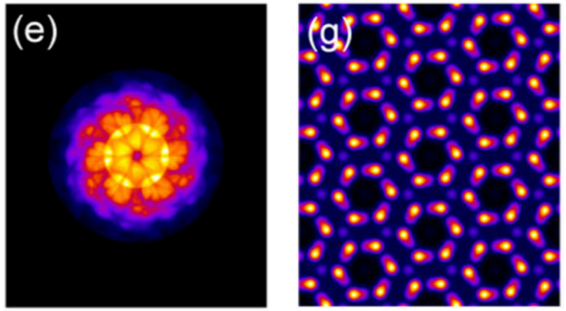
$\vec{r}$ is coordinate of incident e−

$\vec{\tau} = \{\vec{r}_1,\ldots,\vec{r}_N\}$ is set of all position vectors refer

QM model of phonon excitation

- Term-by-term analysis shows that the frozen phonon and QM models are actually equivalent for the end result.
- However, the fully elastic approach of the frozen phonon is physically incorrect. This has now been proven using ultra-low-loss electron energy-loss spectroscopy! TDS corresponds to a phonon excitation with ΔE.
- The QM model that correctly represents the inelastic nature of phonon scattering is available for use in the μSTEM simulation software, which can simulate diffraction patterns, HRTEM and STEM images, EDXS, EELS…

PACBED HAADF STEM

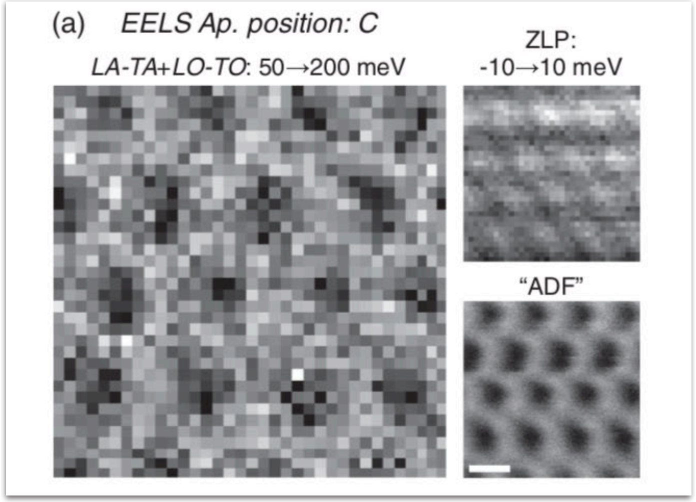


Les J. Allen et al. Ultramicroscopy **151** (2015) 11–22

Proof that HAADF TDS is inelastic!

- Quoting the authors:

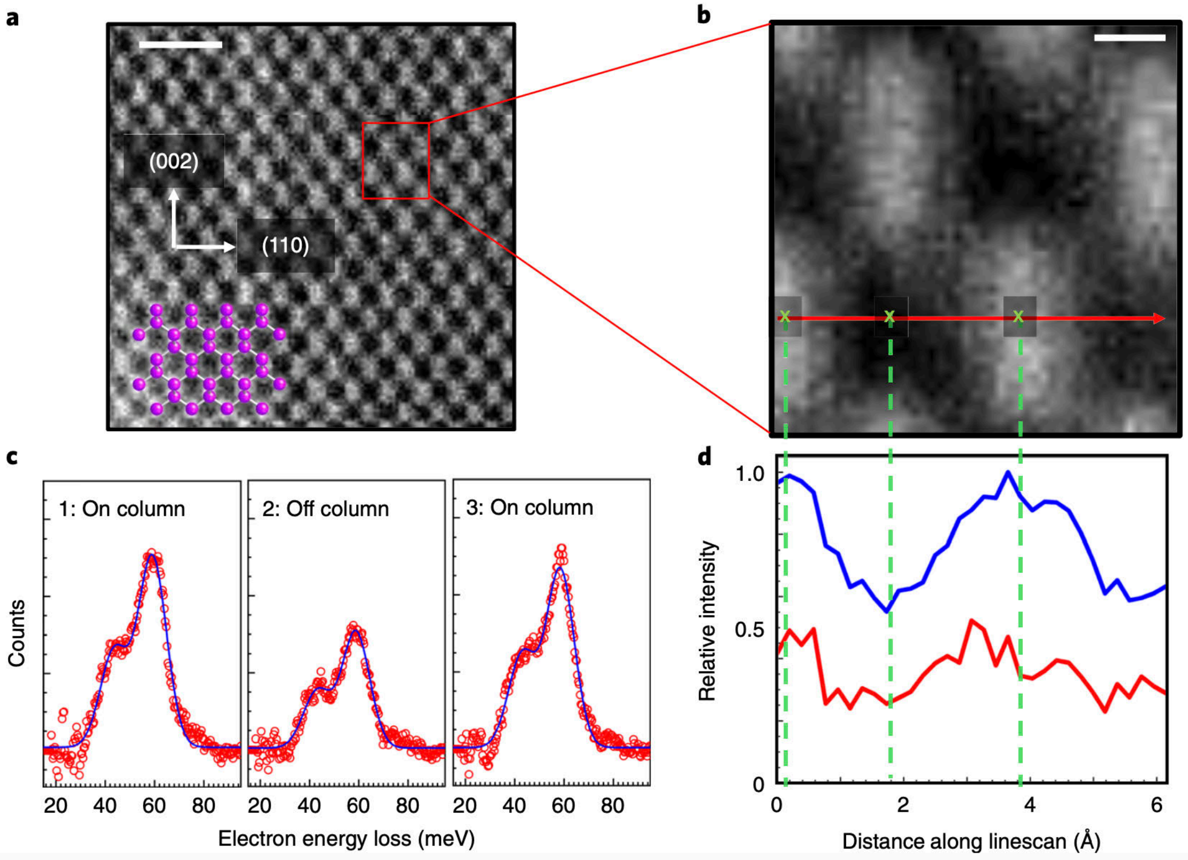
  "*these results support the quantum excitation of phonons model and confirm that the standard technique of Z-contrast imaging is based on the inelastic scattering associated with phonon excitations, not consistent with the frozen phonon model which assumes elastic scattering from different configurations of the atoms in the specimen*"



[19] Hage et al. *PRL* **122** (2019) 016103

On-axis atomic resolution vib. EELS

- Si viewed on [110] zone axis (showing Si dumbbells)
- Atomic resolution signal observed even for an on-axis detector configuration
- *Difference*: although both optic and acoustic modes, no charge transfer that gives rise to the oscillating dipole: *apolar* material
- Rez and Singh implicate the role of Umklapp scattering from the second Brillouin Zone back to the first Brillouin Zone for lattice resolution with the on axis detector



From: [13] Venkatraman et al. *Nature Phys.* **15** (2019) 1237–1241

[27] Rez and Singh. *Ultramicrosc.* **220** (2021) 113162

Vibrational EELS treatments

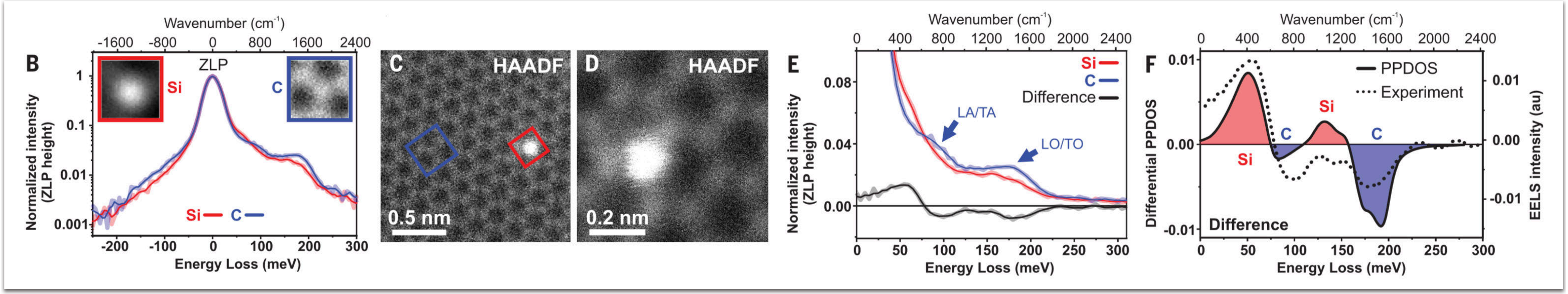
- Allen's group has extended the quantum excitation of phonons model to isolate the inelastic phonon excitation and de-excitation in order to simulate EELS in the phonon sector [20], and applied a correlated model for atomic motion of the vibrational modes [21].

- However, as pointed out by Dwyer in presenting an alternative quantum mechanical treatment, they omitted dipole scattering. In Dwyer's approach the dipole scattering from long-wavelength optical vibrations is included [22].

[20] Lugg et al. *PRB* **91** (2015) 144108
[21] Forbes and Allen *PRB* **94** (2016) 014110
[22] Dwyer *PRB* **96** (2017) 224102

Vibrational EELS treatments

- Saavedra and García de Abajo used an electron-phonon Hamiltonian to study vibrational EELS of nanographenes. They identified that the loss probability is closely related to the local density of vibrational states [23].
- Hage et al. also implicated the projected phonon density of states (PPDOS) in their analysis of single-atom vibrational spectroscopy using off-axis EELS [24]:



[23] Saavedra and García de Abajo *PRB* **92** (2015) 115449
[24] Hage et al. Science **367** (2020) 1124–1127

Energy gain peak

- Idrobo et al. measured loss and *gain* peaks for an optical phonon mode in *h*-BN using aloof mode [25]
- Intensity ratio is proportional to occupation probability of the state, i.e.:

$$\frac{I_{\text{gain}}}{I_{loss}} = \frac{P_{\text{gain}}}{P_{\text{loss}}} = \exp\left(-\frac{\Delta E_{\text{Ph}}}{k_{\text{B}}T}\right)$$

- Can use as nanoscale temperature probe!

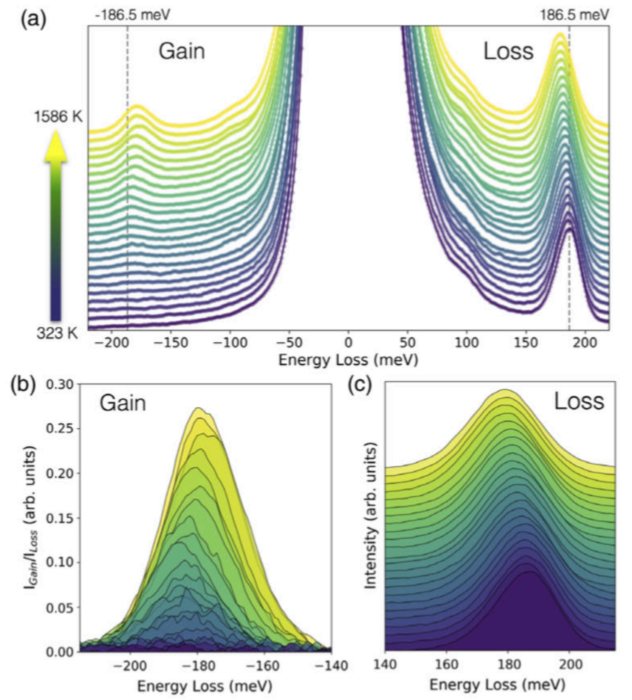


FIG. 2. Electron energy-loss and energy-gain spectra of *h*-BN as a function of temperature. (a) Spectra acquired as a function of temperature from 323 to 1586 K, with average increment steps of 55 K. (b) Electron energy-gain spectra shown in (a) after the background has been subtracted. The intensity of each gain peak (I_{Gain}) has been normalized with the intensity of the loss peak (I_{Loss}) obtained at the same nominal temperature. (c) Electron energy-loss peaks shown in (a). The loss peak corresponds to a *h*-BN high-energy optical-phonon mode.

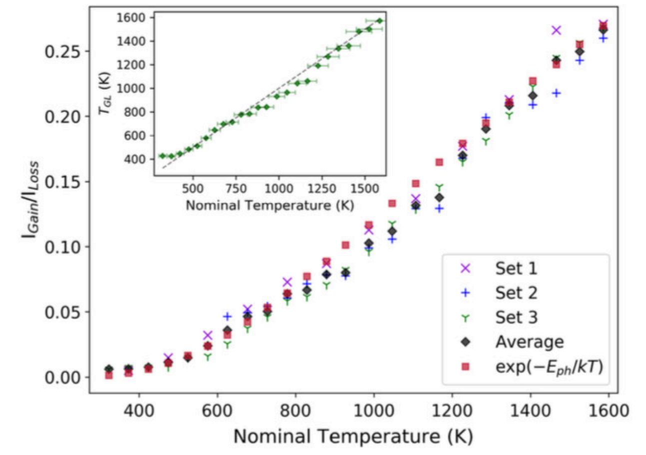


FIG. 3. Gain and loss phonon peak intensity ratios. Gain and loss phonon peak intensity ($I_{\text{Gain}}/I_{\text{Loss}}$) ratios of three different sets of measurements performed at different times (and the respective average) compared with the Boltzmann factor $\exp(-E_{ph}/kT)$.

[25] Idrobo et al. *PRL* **120** (2018) 095901

What's new is old…

- Boersch, Geiger and Stickel, 1966:
  Interaction of 25 keV e⁻s with lattice vibrations in LiF [26]

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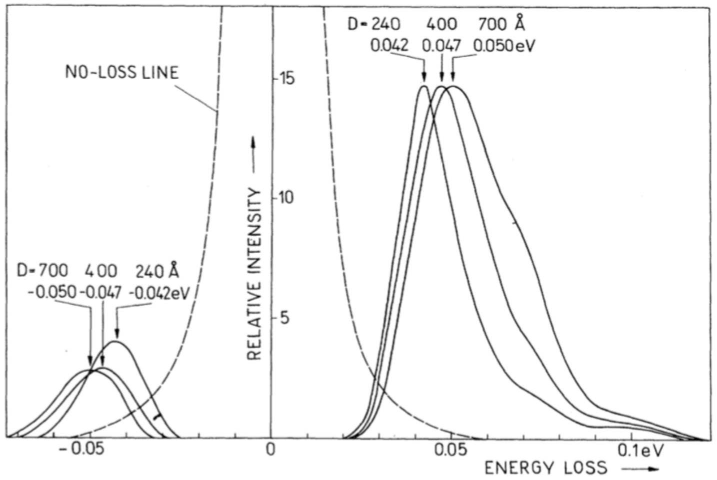

FIG. 2. Energy gains and energy losses of 25-keV electrons in LiF for different foil thicknesses D on carbon substratum. $\theta \geq 10^{-4}$. $T = 300°K$.

However, this was with a µm size e⁻ beam, rather than an imaging, diffraction and analytical tool with a (sub-)Å size e⁻ probe and near synchrotron like capabilities!

[26] Boersch et al. *PRL* **17** (1966) 379