

# Vibrational EELS in the electron microscope at atomic resolution

FS Hage<sup>1,2</sup>, G Radtke<sup>3</sup>, DM Kepaptsoglou<sup>2,4</sup>, M Lazzeri<sup>3</sup>, LJ Allen<sup>5</sup> and QM Ramasse<sup>2,6</sup>

<sup>1</sup>*Department of Physics/ Centre for Materials Science and Nanotechnology, University of Oslo, NO-0318 Oslo, Norway,*

<sup>2</sup>*SuperSTEM Laboratory, SciTech Daresbury Campus, Keckwick Lane, Warrington WA4AD, UK,*

<sup>3</sup>*Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, 75005 Paris, France,*

<sup>4</sup>*York JEOL Nanocentre and Department of Physics, University of York, Heslington, York YO10 5BR, United Kingdom*

<sup>5</sup>*School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia,*

<sup>6</sup>*School of Chemical and Process Engineering and School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, UK*

Corresponding author: [f.s.hage@fys.uio.no](mailto:f.s.hage@fys.uio.no)

Vibrational electron energy loss spectroscopy (EELS) in the (scanning) transmission electron microscope ((S)TEM) was first reported in 2014 [1] and has since been used by several groups to successfully probe the vibrational response of a wide range of materials at the nanoscale [2]. While  $\leq 1\text{\AA}$  electron probes are readily available in aberration-corrected instruments, it has proven to be somewhat of a challenge to go beyond the nanoscale and achieve atomic resolution in vibrational STEM-EELS. One of the complicating factors here is that beam electrons can undergo either “dipole” or “impact” scattering when interacting with vibrational modes in a sample. Dipole scattering occurs in polar materials, is delocalised ( $\sim 10\text{-}100\text{ nm}$ ) and dominates the vibrational loss spectrum for small scattering angles. Impact scattering, however, is localised at the atomic scale, occurs in polar and non-polar materials, and dominates for larger scattering angles.

In conventional STEM-EELS geometries, the bright field (BF) disc is centred on the EELS aperture, resulting in dipole scattering dominating the loss spectrum (for polar materials) and a large relative contribution of the elastic (zero loss) peak (for all materials). By using a dark field (DF) EELS collection geometry (i.e., the BF disc and EELS aperture do not overlap), the relative contributions of elastic and dipole scattering is significantly reduced, favouring instead impact scattering. Probing a thin sample of hexagonal boron nitride (hBN), we used DF-EELS to demonstrate that atomically resolved vibrational EELS is possible [3]. Our results also confirm that contrast in high-angle annular dark-field (HAADF) or Z-contrast imaging is based on phonon scattering. Furthermore, we used vibrational DF-EELS to probe the vibrational response of a single trivalent substitutional Si atom in a single layer of graphene [4]. The Si defect has a vibrational signature distinctly different from that of the surrounding carbon atoms, that is effectively localised to the defect atom itself. This is not simply due to vibrational modes being localised near the Si atom, but rather to defect-induced “pseudo-localised” modes: vibrational modes extended spatially over the whole system (as the “bulk” modes in graphene) which at the same time have an increased amplitude on the Si atom.

Returning now to vibrational BF-EELS, it turns out that, even for polar materials, impact scattering can be mapped at atomic resolution, albeit at the cost of a significant reduction in signal-to-noise as compared to DF-EELS [3, 5]. A further complication arises in that, at least for hBN, the atomically resolved contrast in a BF vibrational loss map can be reversed as a function of defocus [5]. This BF-EELS “contrast reversal” is due to channelling of the incident electron probe and does not occur in DF-EELS. In light of this, using a DF-EELS geometry clearly is advantageous when acquiring vibrational loss maps at atomic resolution in the

electron microscope [6].

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[2] O. L. Krivanek et al., *Ultramicroscopy* **203**, 60-67 (2019).

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[4] F. S. Hage et al., *Science* **367**, 1124-1127 (2020).

[5] F. S. Hage et al., *PRB* **102**, 214111 (2020).

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