

Vibrational STEM-EELS at the atomic scale

Quentin Ramasse^{1,2}, Fredrik S. Hage¹, Demie Kepaptsoglou^{1,3}, Guillaume Radtke⁴ and Michele Lazzeri⁴

¹ SuperSTEM Laboratory, SciTech Daresbury Campus, Daresbury, United Kingdom

² School of Chemical and Process Engineering and School of Physics, University of Leeds, Leeds, United Kingdom

³ Department of Physics, University of York, York, United Kingdom

⁴ Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC) Sorbonne Universités – UPMC Univ Paris 06, UMR CNRS 7590, Muséum National d'Histoire Naturelle, IRD UMR 206, 4 Place Jussieu, F-75005 Paris, France

The functional properties of materials are increasingly controlled and tuned through defects whose engineering takes place quite literally at the atomic level. In particular, it is believed that even at the single atom level the structure and chemistry of these defects can affect the nature, frequency and dispersion of phonons in materials, thus potentially affecting essential physical phenomena such as superconductivity, thermal transport or even structural phase transitions. However, conventional vibrational (optical) spectroscopy techniques typically only provide insights on bulk systems, where information is averaged over much larger length scales.

Recent methodological developments have shown how electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) can be used to study the dispersion of phonons at the nm-scale, by carefully adjusting optical parameters to balance spatial and momentum resolution [1,2]. A related technical approach was also recently used to achieve atomic resolution in phonon spectroscopy. By displacing the EELS collection aperture away from the optic axis of the instrument to angles similar to those used for Z-contrast image detectors, the contribution of electrons that have undergone dipole scattering as well as elastic scattering is minimised and this optical geometry favours instead the highly localised impact transitions in the recorded vibrational spectrum [3].

This has now been extended to observe how a single substitutional Si impurity in graphene induces a characteristic, localized modification of the vibrational response. Extensive ab initio calculations reveal the measured spectroscopic signature arises from defect-induced pseudo-localized phonon modes, whose energies can be directly matched to experiments. This truly realizes the promise of vibrational spectroscopy in the electron microscope by demonstrating single atom sensitivity and spatial resolution, with wide-reaching implications across the fields of physics, chemistry and materials science [4].

References

[1] F.S. Hage, R.J. Nicholls, J.R. Yates *et al.*, *Science Advances* **4** (2018), eaar7495.

[2] RJ Nicholls, FS Hage, DG McCulloch *et al.*, *Phys. Rev. B* **99** (2019), 094105.

[3] F.S. Hage, D.M. Kepaptsoglou, Q.M. Ramasse *et al.*, *Phys. Rev. Lett.* **122** (2019), 016103.

[4] F.S. Hage, G. Radtke, D.M. Kepaptsoglou *et al.*, Submitted (2019).

[5] SuperSTEM is the UK National Research Facility for Advanced Electron Microscopy, supported by the Engineering and Physical Sciences Research Council.