

Vibrational spectroscopy in the electron microscope

Ondrej L. Krivanek^{1,2}, Niklas Dellby¹, Tracy C. Lovejoy¹, Toshi Aoki², Peter A. Crozier², Peter Rez², Maureen J. Lagos^{3,4}, and Philip E. Batson^{3,4}

1. Nion Co., 1102 Eighth St., Kirkland, WA 98033, USA
2. Department of Physics and Center for Solid State Science, Arizona State University, Tempe, AZ 85287, USA
3. Institute for Advanced Materials, Devices and Nanotechnology, Rutgers U., Piscataway, NJ 08854, USA
4. Departments of Physics and Materials Science, Rutgers U., Piscataway, NJ 08854, USA

E-mail: krivanek@nion.com

Working aberration correctors that first appeared in the 1990s have improved the resolution of electron microscopes by about 3x, before running into new limits such as chromatic effects and high order geometric aberrations. The improvement has greatly expanded the range of objects that electron microscopes can successfully resolve and analyse, and it has been called a “revolution in resolution”. More recently, monochromators with electron optics of similar quality to aberration correctors have improved the attainable energy resolution relative to unmonochromated electron microscopes by about 30x, and a further improvement of 3x appears feasible. Not surprisingly, the improved energy resolution is creating another “revolution”, by greatly expanding the analytical powers of monochromated microscopes.

The monochromator recently introduced by Nion as a part of its High Energy Resolution Monochromated EELS-STEM (HERMES) system employs electron optics corrected up to third order, two novel energy-stabilization schemes, plus ultra-stable electronics and further stability-enhancing measures [1]. It is giving ~10 meV resolution in electron energy loss spectra (EELS) recorded at 60 keV (Fig. 1), with a sub-nm electron probe. It is allowing new types of experiments to be performed in the electron microscope, such as exploring the vibrational properties of materials, detecting hydrogen by its vibrational signature, and potentially also detecting light elements such as hydrogen, lithium and carbon by the energy transfer that accompanies Rutherford scattering.

We are at the beginning of the exploration, and our preliminary results are very encouraging. We have been able to detect vibrational excitations (optical phonons) in a variety of materials (Fig. 2), at energy losses ranging from 70 to 400 meV [2]. We have also measured the spatial variation of the vibrational interaction and found good agreement with theory. There is a highly delocalized component, and optical phonons can be excited with an electron beam parked tens or even hundreds of nanometres in the vacuum outside a sample. This can be used for “alooof” spectroscopy, in which the energy transfer from the fast electron to the sample is restricted to typically less than 500 meV, and radiation damage is greatly reduced.

The phonon energy is proportional to the strength of the bonds being stretched or bent, and inversely proportional to the mass of the vibrating nucleus. This means that hydrogen gives higher energy vibrational peaks than other types of atoms, and is thus the easiest element to detect by its vibrational signature. Hydrogen-containing materials suffer major radiation damage when exposed to a beam of fast electrons, and the prospect of damage-free alooof spectroscopy of hydrogen is especially enticing.

There is also a more localized vibrational signal, which can be enhanced by selecting scattering angles of several mrad and higher. At scattering angles greater than about 50 mrad, the energy transfer that accompanies incoherent Rutherford scattering (normally used for forming high angle annular dark field (HAADF) images) provides another highly informative signal, with a large cross-section. The scattering occurs in less than an attosecond, and the nucleus behaves as free on this time scale. It can therefore be “weighed” by the magnitude of the energy transfer to it due to the scattering [3]. The instrumental requirements for this type of spectroscopy are especially demanding – excellent energy resolution must be combined with large EELS acceptance angles – but we are making progress in this direction too.

This short paper is dedicated to Professor Harald Rose, a true pioneer in advanced electron optics, on the occasion of his 80th birthday.

[1] O.L. Krivanek, T.C. Lovejoy, N. Dellby and R.W. Carpenter, “Monochromated STEM with a 30 meV-wide, atom-sized electron probe”, *Microscopy* **62** (2013) 3–21

[2] O.L. Krivanek et al., “Vibrational spectroscopy in the electron microscope”, *Nature* **514** (2014) 209-212

[3] T.C. Lovejoy et al., “Energy-Filtered High-Angle Dark Field Mapping of Ultra-Light Elements”, *Microsc. Microanal.* **20** (suppl. 3) (2014) 558–559

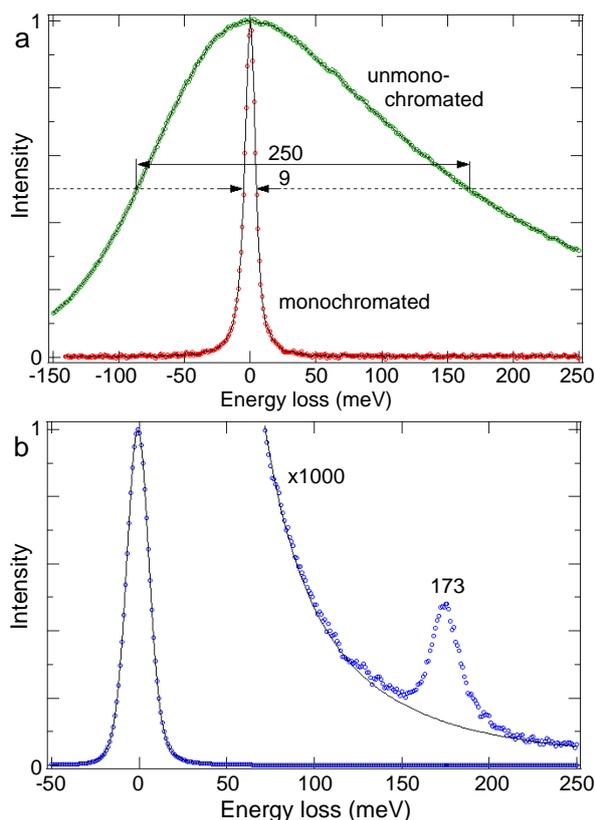


Fig. 1. a) 9 meV wide monochromated EELS zero loss peak (ZLP) recorded by the Nion HERMES system at 60 keV primary energy, compared to an unmonochromated ZLP produced by the instrument's cold field emission gun (CFEG). b) vibrational spectrum of hexagonal boron nitride (BN). Reproduced from Nature [2], by permission.

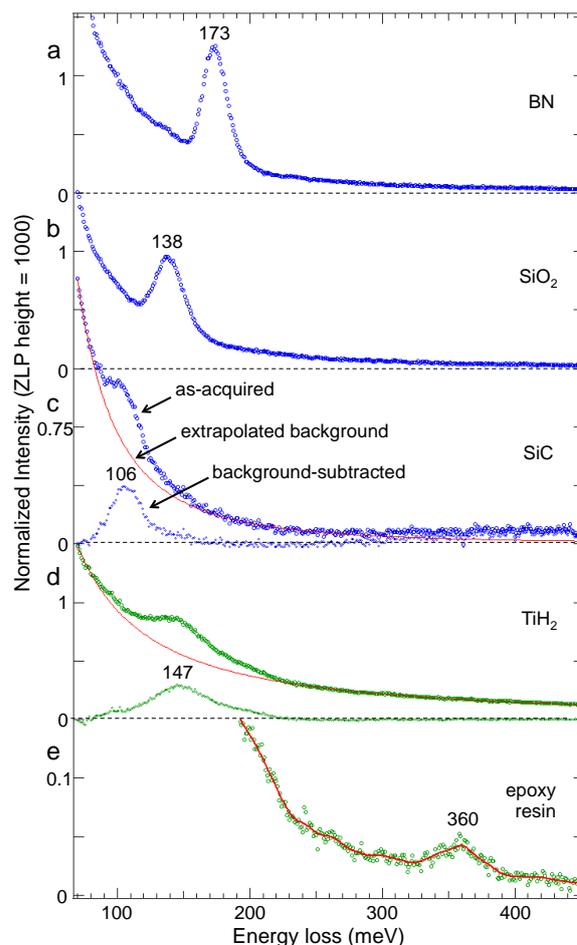


Fig. 2. Vibrational spectra of various materials. Nion HERMES, 60 keV. Reproduced from Nature [2].

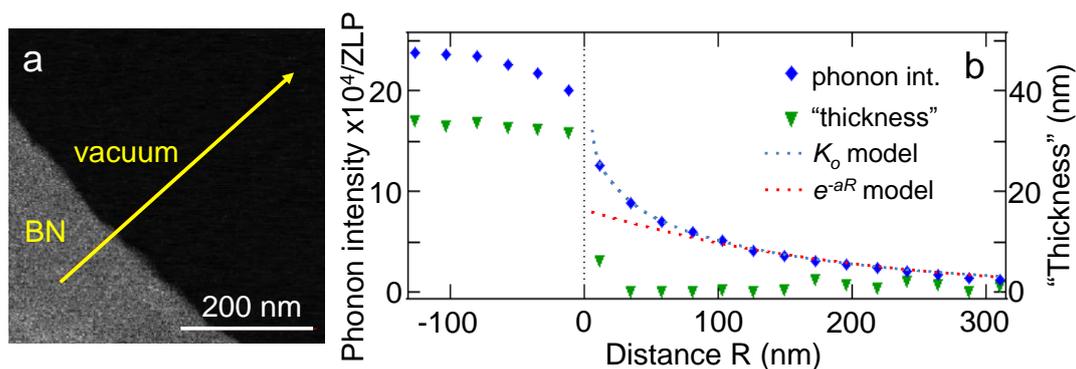


Fig. 3. Vibrational signal in BN extending outside a BN particle. a) Annular dark field (ADF) image of a BN particle and adjacent vacuum; yellow arrow shows the location of the line-profile. b) Line profile of the variation of the 173 meV BN LO (longitudinal optical) phonon compared to the thickness variation, determined by comparing the measured total inelastic intensity to the EELS mean free path. Two models for the fall-off of the phonon signal in the vacuum are shown: modified Bessel function of the second kind (K_0), and simple exponential function. At >100 nm outside the particle, both models fit well; closer to the particle, only the Bessel function, which has a sharp maximum at the particle surface, provides a good fit. Reproduced from Nature [2].