

What Are the Applications of meV EELS ?

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The combination of high performance monochromators with energy loss spectrometers has opened up spectral windows in the visible and Infra-Red that were inaccessible in the transmission electron microscope for many years. It has been possible on occasion to achieve energy resolutions of 5 meV ($\sim 40 \text{ cm}^{-1}$) in the monochromated Nion UltraSTEM with probe currents of order 10 pA, and 10 meV is achievable on a routine basis. Although this is spectacular compared to EELS in the past, the energy resolution is still significantly inferior to 0.1 cm^{-1} ($\sim 0.01 \text{ meV}$) energy resolution of Raman or Infra-Red spectroscopy. However these bulk characterization techniques are unable to offer nanometer spatial resolution, except in specialized circumstances.

The new applications that are now possible can be broadly divided into three areas, nanophotonics, detection of point defects, and localized vibrational spectroscopy. The very small characteristic scattering angle for low energy dipole excitations means that the signal is delocalized over regions up to 10nm for signals in the optical part of the spectrum, and up to 100nm for signals in the IR region. Although this delocalization severely degrades spatial resolution it can be used to advantage in damage free vibrational spectroscopy and for probing effects of long-range electromagnetic fields that are relevant in nanophotonics. However there are significant differences, in EELS usually only the electrostatic field is significant whereas photons have related electric and magnetic fields perpendicular to each other.

Although lattice resolved images in phonon modes have been demonstrated, it is unlikely that defect modes arising from differences in bonding will be detected with the present resolution. Furthermore most of the interest in materials relates to thermal transport involving low energy phonons that are difficult to separate from the tail of the zero loss peak. It is still possible to extract information from the asymmetry of the zero loss peak. Fig 1 shows the mapping of the phonon dispersion of the acoustic phonon along [111] in Ge, showing the broadening of the dispersion from anharmonic interactions.

The situation is very different for organic compounds, including biological material [1]. An energy resolution of 5 meV is sufficient to make distinctions between different classes of organic compounds. It is even possible to determine the proportions of secondary structure in a protein using the technique pioneered by Byler and Susi [2] for IR spectroscopy. Fig 2 shows distinct spectra for vibrations related to the C=O on the protein backbone for bacteriorhodopsin which is largely β sheet and ompF porin that is predominately a helix.

Point defects have traditionally been a ‘blind spot’ in the TEM of materials. The ability to detect point defect states in band gaps of semiconductors and insulators is a significant advance. The first applications were color centers in alkali halides, though more recently detection of point defect states in semiconductors [3] and NV centers in diamond has been demonstrated. Although at present the spatial resolution is limited by delocalization, it might be possible to apply the techniques of ‘super resolution microscopy’ to localize a point defect with better than nm precision, should there be sufficient signal.

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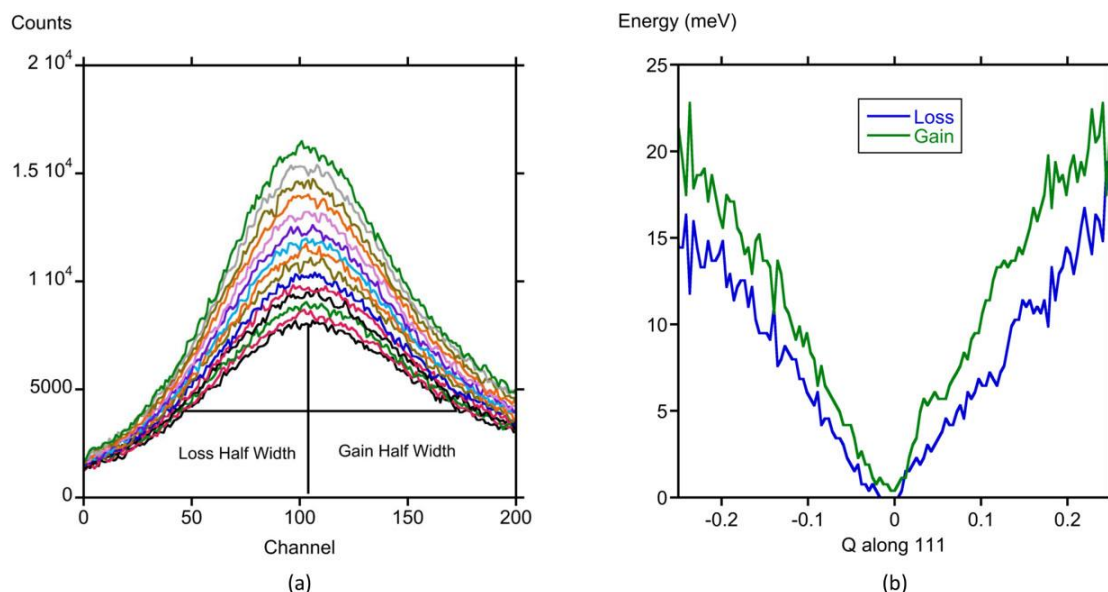


Figure 1. (a) Ω q EELS spectra from a Ge film acquired using a slot aperture with a dispersion of 0.38 meV per channel covering most of the 1st Brillouin Zone. (b) Extracted phonon dispersion for the LA mode, showing broadening due to anharmonic effects. The temperature could be extracted from the log of the ratio of intensities of the energy loss to energy gain [3,4]

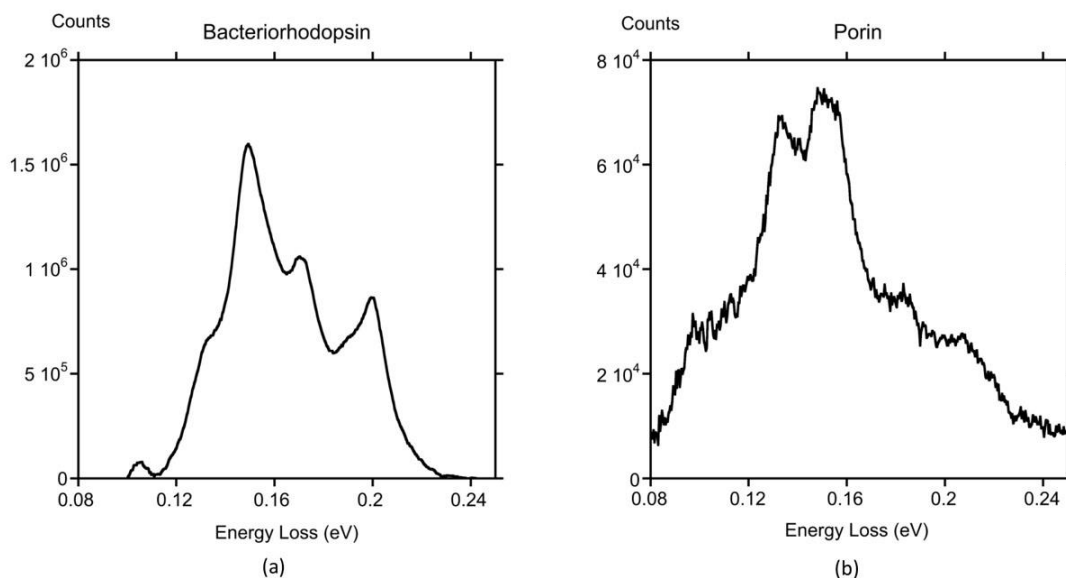


Figure 2. EELS spectrum from crystals of (a) Bacteriorhodopsin that is mainly α helix and (b) ompf Porin that is mainly β sheet showing clear differences in the amide peak region.

References

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