

Detection and Characterization of OH Vibrational Modes using High Energy Resolution EELS

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The recent detection of vibrational excitations in monochromated electron energy-loss spectroscopy recorded from scanning transmission electron microscopes has opened up new opportunities for nanoscale materials characterization [1]. The enhanced energy resolution has the greatest impact on the low-loss EELS and it is now possible to probe vibrational and electronic excitations at the nanometer level. For example, localized bandgap mapping and detection of interband states is now possible providing a new tool to correlate optical properties with atomic structure [2,3]. Vibrational spectroscopy allows hydrogen containing species to be identified and correlated with materials structure. Detection of water and OH species on nanoparticle surfaces is important for developing a fundamental understanding of solar water splitting catalysts. The delocalized nature of the low-loss spectrum also makes it possible to use the aloof beam spectral acquisition mode (i.e. with the electron probe positioned outside the sample) dramatically reducing electron beam damage. To investigate the feasibility of OH detection, a series of hydroxide and hydrates have been investigated.

Samples of $\text{Ca}(\text{OH})_2$, H_3BO_3 and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were prepared for TEM by crushing the powders and dispersing over holey carbon films. Spectra were recorded from these samples using a Nion UltraSTEM fitted with a monochromator, an aberration corrector and a Gatan Enfium spectrometer. The microscope was operated at 60 kV and the typical energy resolution was between 15 – 30 meV (the larger resolution was sometimes employed to increase the signal to noise in the spectrum) with a typical dwell time of 30 – 60 s. Spectra were acquired in both transmission mode and in aloof beam mode. In some cases, linescans were recorded in which a series of spectra were recorded as the beam was moved from the vacuum into the bulk.

The OH stretch mode at 452 ± 2 meV was easily detected from $\text{Ca}(\text{OH})_2$ using aloof beam EELS as shown in Figure 1a. The peak full width half maximum (FWHM) was around 24 meV and the linescan (Figure 1b and c) shows that the OH signal is maximized when the probe is positioned just outside the sample and falls to less than 10% of its maximum when the probe is 35 nm away from the surface. The vibrational signal also falls off rapidly as the probe moves into the sample due mostly to electrons being elastically scattered outside the spectrometer entrance aperture and possibly radiation damage. The OH stretch was also observed in H_3BO_3 (Figure 1d) at an energy of about 453 ± 2 meV with a FWHM of 20 meV. (A smaller peak at around 350 meV may be due to hydrocarbon contamination). The aloof beam mode is also useful for minimizing radiation damage for valence-loss spectroscopy. Figure 2a shows the low-loss spectrum from the $\text{Ca}(\text{OH})_2$ recorded in aloof mode (beam 6 nm outside sample) and in transmission mode (beam 10 nm inside sample). Both spectra show a bandgap of approximately 6.5 eV but the aloof mode spectrum shows prominent peaks at 7.3 and 8.4 eV which do not show up in the transmission spectrum. The leading tail on the edge of the conduction band in the transmission spectrum is consistent with a large number of defects introduced as a result of beam damage.

Figure 2b shows the OH vibrational fingerprint for $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The peak center at around 430 meV is almost 25 meV below the corresponding stretch for the hydroxides. It is also asymmetric and much broader with a FWHM of around 80 meV suggesting a variation in the molecular environment around the OH species. The sample was in the microscope high vacuum system of 10^{-9} Torr for several days and there may have been selective loss of water from the surface region probed which is primarily probed by a loof beam EELS. During the presentation other factors influencing the detection of OH species especially on oxide surfaces will be discussed. The ultimate goal is to detect hydroxide species locally on the surface of water splitting catalysts.

References

- [1] O.L. Krivanek et al. *Nature* **514**, 209-212 (2014).
- [2] W.J. Bowman et al, these proceedings
- [3] Q. Liu et al, these proceedings
- [4] The support from US Department of Energy (DE-SC0004954) and the use of ETEM at John M. Cowley Center for HR Microscopy at Arizona State University is gratefully acknowledged.

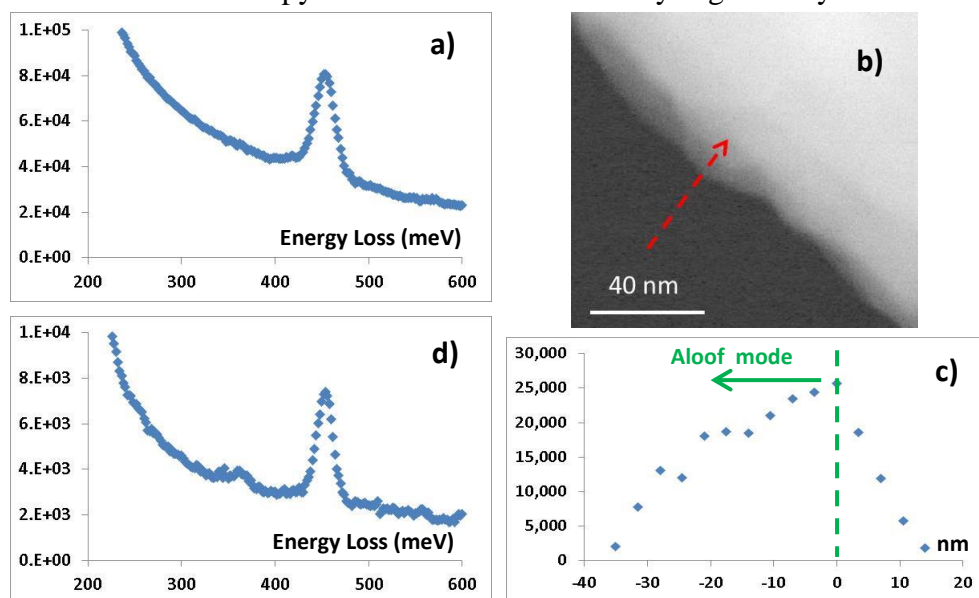


Figure 1: a) ALOOF mode spectrum showing OH vibrational peak at 454 meV from $\text{Ca}(\text{OH})_2$. b) Z-contrast image and c) OH peak intensity as a function of position from $\text{Ca}(\text{OH})_2$. c) OH peak recorded in a loof beam mode from H_3BO_3 .

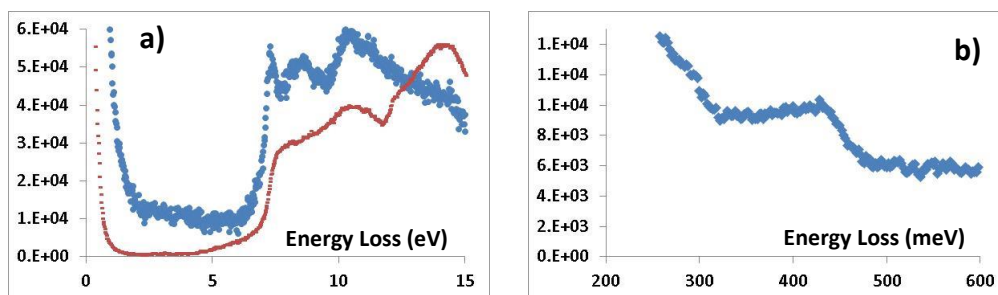


Figure 2: a) Low-loss spectrum from $\text{Ca}(\text{OH})_2$ recorded 6 nm outside the sample (blue) and in transmission mode (red). b) OH vibrational peak from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.