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DualEELS at High Energy Losses: Exploring Lower Accelerating Voltages and Absolute Cross Sections

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EELS has typically been performed at relatively low energy losses. The majority of studies are at losses of less than 1 kV and there are quite a few between 1 and 2 kV. High quality studies above 2 kV are rarer, and above 3 kV there are fewer than ten published studies known to the authors. Apart from the obvious point that there is relatively little signal out there, and therefore counting times will be long, there are also electron optical issues that make transferring the signal into the spectrometer more difficult with increasing loss. Specifically, the electron optics of STEM columns are often not explicitly tuned to transfer high energy losses into the spectrometer with the same efficiency as the zero loss electrons. Recently, we reported the detailed characterisation and optimisation of the post-specimen lenses in a modern aberration-corrected STEM for spectroscopy, nominally out to 3 kV at 200 kV beam energy [1]. We then reported some possible applications of this high loss EELS [2]. In this paper, we report further advances in extending high loss EELS to 80 kV beam energy, and in using high loss Dual EELS at 200 kV to measure absolute cross sections for some Pt-group metals.

Following our earlier work at 200 kV, we have optimized our 2 cm camera length at 80 kV to improve the transfer of loss electrons into the spectrometer. Figure 1a shows a spectrum recorded with the original 2cm camera length. As seen previously at 200 kV [1], extra background intensity perturbs the background shape, here from about 1500 eV, making EELS analysis of Si or other semiconductors problematic. Figure 1b shows that the problem is fixed with the new 2cmC camera length. Figure 1c) shows why. For the 2cm camera length, the EELS stripe folds inwards rather rapidly, and extra intensity from the edges is folded into the EELS entrance aperture. A crossover occurs around 3500 eV. For the optimized 2 cmC camera length, this effect is much delayed with the crossover happening between 5000 and 5500 eV, potentially allowing good quality EELS out to close to 3000 eV.

Previously, we reported characterization of the $L_{2,3}$ EELS edges of some 2nd row transition elements, including changes with oxidation and calculation of absolute differential cross sections of two 2nd row transition elements: Zr and Mo [2, 3]. We now extend this to three further 2nd row transition elements, all of which are platinum group metals with applications in catalysis: Ru, Rh and Pd. The cross sections were calculated as in our previous publications [3, 4] using DualEELS to provide a low loss spectrum to go with the core-loss spectrum. This allows deconvolution of plural scattering, normalization by the zero loss intensity, and determination of thickness to allow normalization by the areal density of atoms. To allow for optimal sharpness of both the zero loss peak and the core loss edges, two datasets were recorded for each area, one using an F_x value for the spectrometer suitable for the low loss, and the other used one optimized for the core loss, as described previously [3]. The F_x change for the core loss was +0.4 in the GIF Quantum for all datasets shown here. Figure 2 shows background-subtracted cross sections for the three elements. Both Ru and Rh show significant white lines at the L_3 and L_2 edges, as is typical for transition elements due to the significant density of empty *d*-states just above the Fermi level. Rh, however, shows a significant decline in the white line intensity relative to the continuum background as compared to Ru – this is entirely expected as there will be fewer empty *d*-states per atom in Rh – there are nominally 2 empty *d*-states per atom in Rh as opposed to 3 per atom in Ru. Pd, on the other hand, shows no strong white lines, which accords well with simple chemistry models of the isolated atom electronic structure of [Kr] $4d^{10}$ leaving no empty *d*-states whatsoever. This trend of decreasing and finally disappearing white lines is rather similar to that previously observed in $L_{2,3}$ edges for 1st row transition elements from Sc-Zn [5,6].

References:

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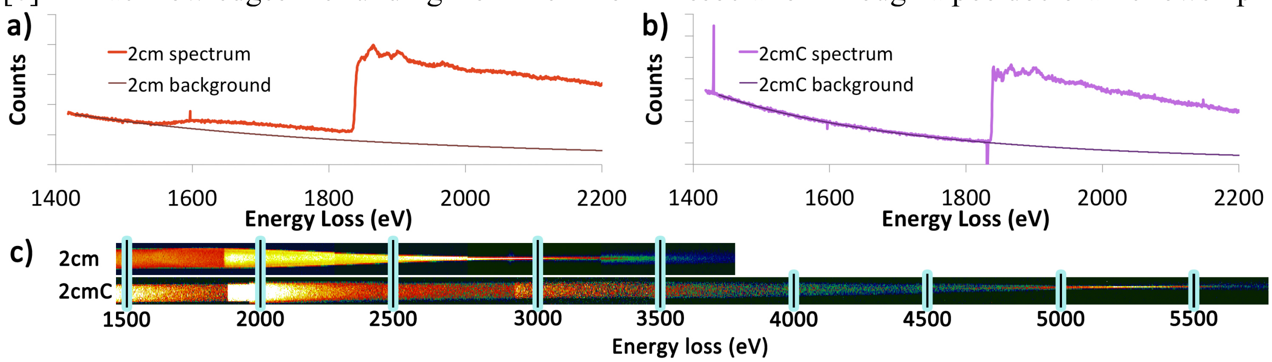

Figure 1. 80 kV EELS characterization: a) a silicon K-edge recorded using the standard 2cm camera length; b) the same spectrum recorded using the optimized 2cmC camera length; c) EELS stripe images from Si showing that at 2cm camera length, a crossover is reached around 3500 eV, whereas this happens at about 5000-5500 eV for the optimized 2cmC camera length.

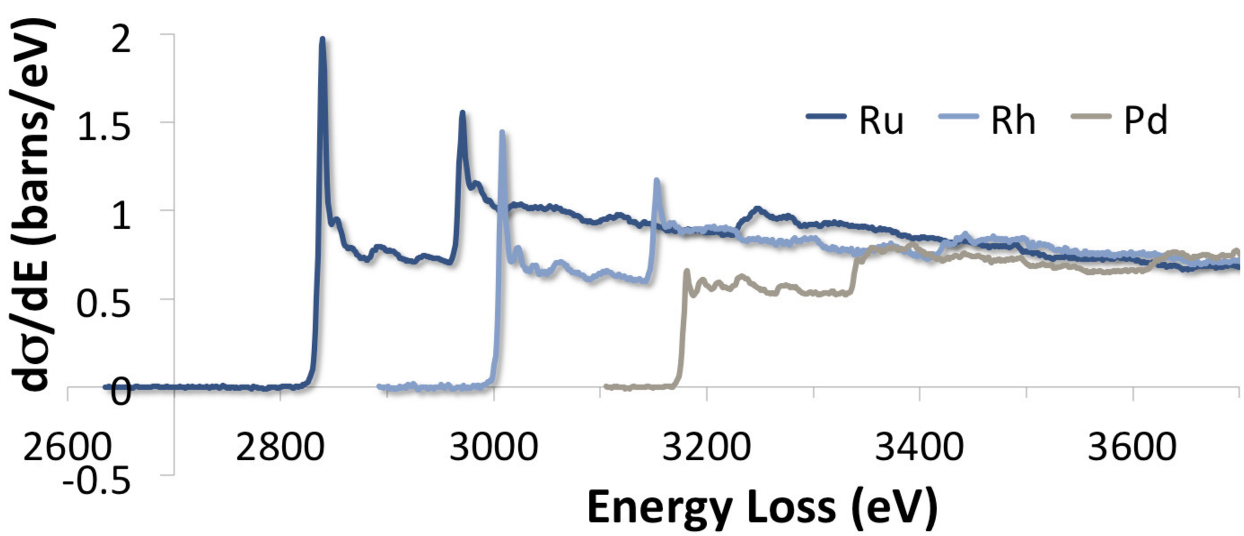

Figure 2. Absolute differential cross sections for three platinum group metals: Ru, Rh and Pd.