Aloof beam vibrational electron energy-loss spectroscopy of adsorbate/metal particle systems.

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The detection of vibrational signals from adsorbate molecules or layers using high resolution electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) would provide a transformative new tool for investigating the surface chemistry taking place on nanoparticles. To develop this technique, experiments need to be performed on simple model systems. The spectra need to be compared with results from Fourier-transform infrared (FTIR) spectroscopy. We adopt the aloof beam EELS technique that uses the long-range Coulomb interaction between electrons and adsorbate molecules to minimize radiation damage when the probe is placed just outside the adsorbate layer. We explore two classes of adsorbate/substrate systems for developing the aloof beam vibrational EELS technique, viz. polyvinylpyrrolidone (PVP) ligand shell on Au nanoparticles and CO on Pt particles.

Commercially synthesized Au nanoparticles (40 nm diameter) with a 5-7 nm thick PVP ligand shell were purchased from nanoComposix. Commercial Pt particles (10 m average diameter, 99.99% pure) were purchased from Sigma-Aldrich. CO was chemisorbed by flowing (20 cc/min) it through a bed of Pt particles at room temperature for 30 min in a RIG 150 micro-reactor. A NION UltraSTEM 100 aberration-corrected electron microscope equipped with a monochromator (15-20 meV energy resolution) was used to perform aloof-beam EELS. The microscope was operated at 60 kV, with probe convergence and collection semi-angles of 28 and 12 mrad respectively. The data was processed for background subtraction using the Gatan Microscopy Suite.

Figure 1a is an ADF image showing the probe position relative to the nanoparticles. Figure 1b shows the background subtracted aloof-beam spectrum recorded from the PVP/Au system. The energy-loss spectrum looks like the FTIR spectrum [1] in shape, convolved with the EELS energy-resolution. We will perform diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) on our PVP/Au system and compare it with our EELS measurements.

DRIFTS performed on the CO/Pt system confirmed a CO signal peak at ~261 meV corresponding to on-top bonding of the CO molecule to Pt, as is observed in Figure 2a. Figure 2b is a ronchigram of a Pt particle showing the relative position of the electron beam. Figure 2c shows a preliminary background-subtracted aloof-beam energy-loss spectrum from the CO/Pt system. Comparison with DRIFTS measurements suggests that the signal in the energy-loss spectrum at ~260 meV comes from CO. Broadening of the signal might arise from small changes in the relative orientation of the CO molecule to the Pt. We will discuss experiments for more well-defined geometries and detailed simulations based on relativistic and non-relativistic dielectric theory [2].

References:

1. Y. Borodko et al., J. Phys. Chem. B, **110** (2006), p. 23052.

2. F.J.G. de Abajo, Rev. Mod. Phys., **82** (2010), p. 209.

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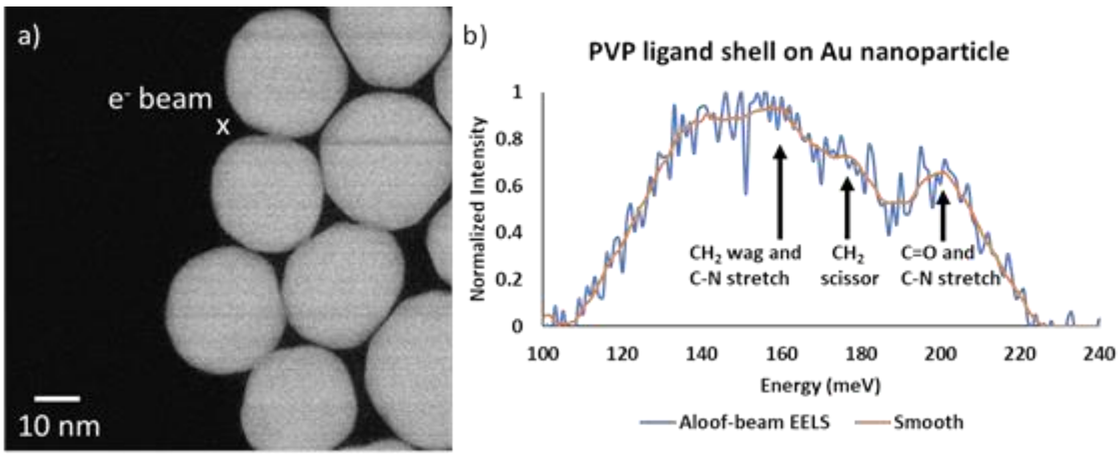

Fig. 1: a) ADF image of the PVP/Au system. b) Energy-loss spectrum from the PVP/Au system.

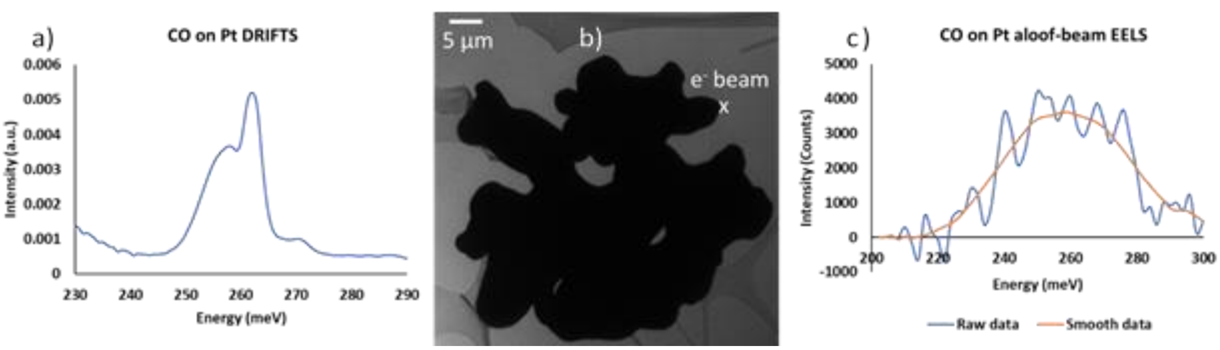

Fig. 2: a) DRIFTS spectrum from the CO/Pt. b) Ronchigram of the Pt particle. c) Aloof-beam vibrational energy-loss spectrum from CO on Pt.