

Aloof-beam Vibrational Electron Energy-loss Spectroscopy of Adsorbate/Metal Particle Systems

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The ability to perform high resolution mapping of adsorbate molecules or layers and correlate this with atomic structure would provide a transformative new tool for investigating the surface chemistry taking place on nanoparticles. Such a tool can be used to detect dissociative and non-dissociative sites on adsorbent surfaces and study different bonding arrangements between the adsorbate and the adsorbent. Recent work using high resolution electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) has shown how surfaces and interfaces modify the spatial extent of vibrational excitations [1]. For a comprehensive understanding of the detection of such vibrational signals, experiments need to be performed on simple model systems. The spectra need to be compared with results from conventional vibrational spectroscopies like Fourier-transform infrared (FTIR) spectroscopy to understand how electron excitation differs from photon excitation. Radiation damage may be substantial when an electron probe is placed directly on the adsorbate layer of interest. We adopt the aloof beam EELS technique that makes use of the long-range Coulomb interaction between electrons and adsorbate molecules to minimize damage when the probe is placed just outside the adsorbate layer [2]. We explore two classes of adsorbate/substrate systems because of their overall scientific importance and their suitability 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 μm average diameter, 99.99% pure) were purchased from Sigma-Aldrich. Surface pre-treatment involved heating the Pt powder to 400°C in flowing H₂ for 3 hours. CO was chemisorbed on Pt by flowing the gas (20 cc/min) through a bed of adsorbent powder 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 beam 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 similar to the FTIR spectrum [3] in shape, which shows a peak at ~160 meV corresponding to the CH₂ wag and the C–N stretch, another peak at ~177.5 meV corresponding to the CH₂ scissor and a third peak at 210 meV corresponding to the C=O and C–N stretch vibrational modes. 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. The sample was stable in air as the CO

signal was detectable with DRIFTS two weeks after initial CO exposure making it ideal for EELS. 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 [4, 5].

References:

- [1] K. Venkatraman *et al*, *Microscopy* (2018), p. 1-10, doi: 10.1093/jmicro/dfy003.
 [2] P.A. Crozier, *Ultramicroscopy*, **180** (2017), p. 104.
 [3] Y. Borodko *et al.*, *J. Phys. Chem. B*, **110** (2006), p. 23052.
 [4] F.J.G. de Abajo, *Rev. Mod. Phys.* **82** (2010), p. 209.
 [5] The support from National Science Foundation CHE-1508667 and the use of (S)TEM at Eyring Materials Center at Arizona State University is gratefully acknowledged.

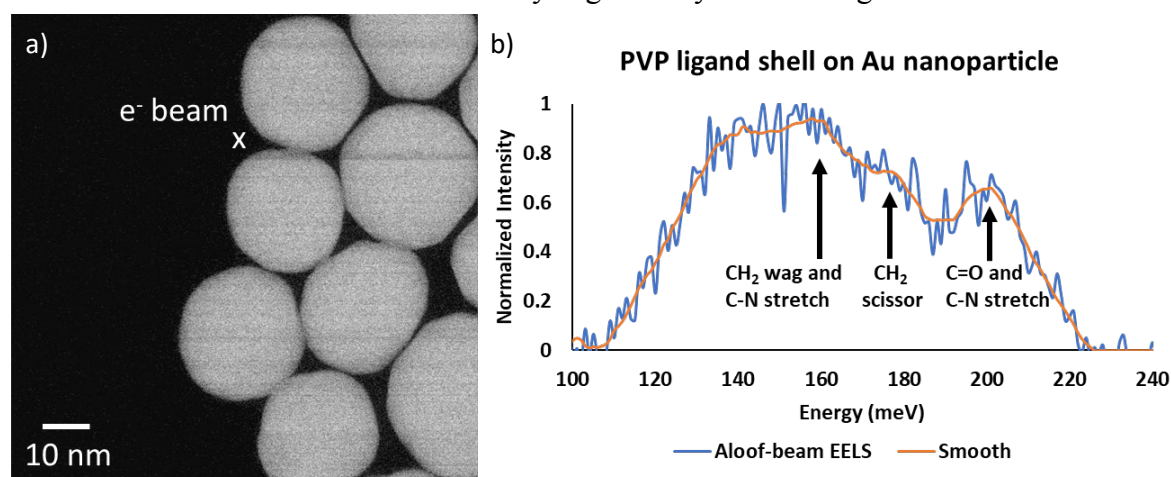


Figure 1. a) ADF image of the PVP/Au system showing the position of the electron beam relative to the Au surface. b) Typical aloof-beam vibrational energy-loss spectrum from the PVP/Au system.

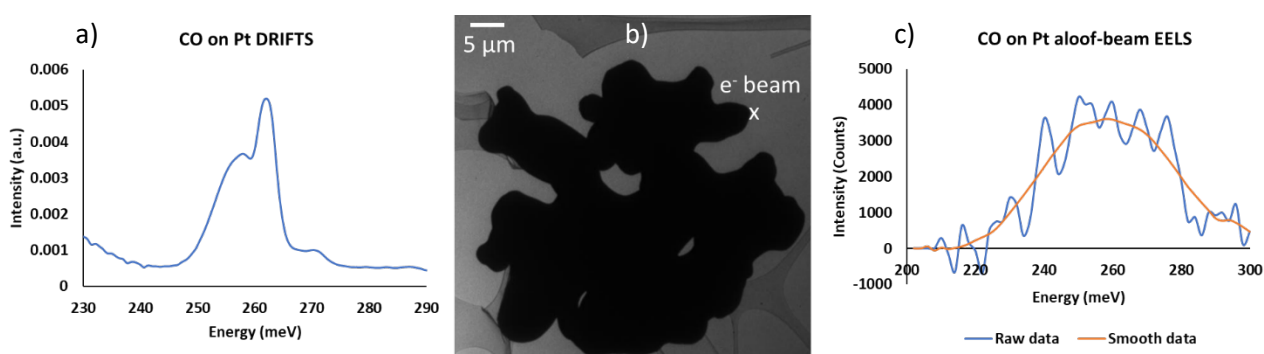


Figure 2. a) DRIFTS spectrum from the CO/Pt system showing the CO vibrational signal at ~ 261 meV. b) Ronchigram of the Pt particle showing the relative position of the electron beam. c) Aloof-beam vibrational energy-loss spectrum showing the CO signal at ~ 260 meV.