

Molecular Excitation Spectroscopy near Metallic Surfaces using Electron Energy Loss Spectroscopy

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Metallic particles and surfaces display complex optical properties. The interactions occurring at the surface of metallic particles and of 2D metal planes with molecular species have found extensive use in applications for sensitive molecular detection. Indeed, optical techniques such as surface enhanced Raman spectroscopy (SERS) or surface enhanced fluorescence (SEF) rely on the design of surfaces that, when in close vicinity to molecular systems, will ultimately produce improved molecular detection by changing the local electromagnetic environment of the molecules. These interactions are typically complex, as illustrated by the fact that in the case of SEF it can be challenging to predict whether a specific metallic structure will enhance or quench fluorescence. A new approach to perform molecular spectroscopy near metal surfaces is electron energy loss spectroscopy (EELS). This contribution will explore the ability of EELS to probe small volumes of molecules and to detect local changes in the excitation response of molecules near metallic surfaces with high spatial resolution.

Over the years, EELS has already proven an efficient means of detecting plasmons excited by an electron beam passing near or through a metallic surface. However, an electron beam also has the effect of exciting electronic transitions with high yields and inducing irreversible damage to the molecules as a result of the system relaxation. Using a new generation of electron monochromators, for which the energy spread of the electron beam can now be reduced to achieve nominal energy resolutions less than 10 meV [1], the vibrational signatures of organic systems can be detected using an aloof beam configuration aimed at avoiding ionization damage [2] and adsorbed inorganic species can be identified at the surface of nanoparticles [3]. Here we will present the prospects of using the strong effect of the electron beam to perform excitation spectroscopy prior to molecular damage.

In particular, monochromated EELS in a STEM was used to obtain information on the vibrational and electronic excited states of thiols and rhodamine dyes. We demonstrate that EELS can capture the molecular excited electronic states of immobilized molecules from nanometric areas, and that the technique is sensitive to the vibronic fine structure. We will include a discussion on electron doses required and support our findings with spatially resolved VIS spectra acquired from equivalent samples. We demonstrate the ability of EELS to probe electronic excitations of molecules at the vicinity of a metal surface where, typically, signals measured under UV-Vis excitation are dominated by scattering from the metal. Figure 1 shows an example where EELS register local variations of the excited electronic states of Rhodamine dyes and of the plasmon resonance of a gold planar surface with nanometric roughness [4].

References:

[1] O.L. Krivanek *et al.*, Nature **514** (2014), p. 209.

[2] P. Rez *et al*, Nature Comm. **7** (2016), p. 10945

[3] P.A. Crozier, Ultramicroscopy **180** (2017), p. 104

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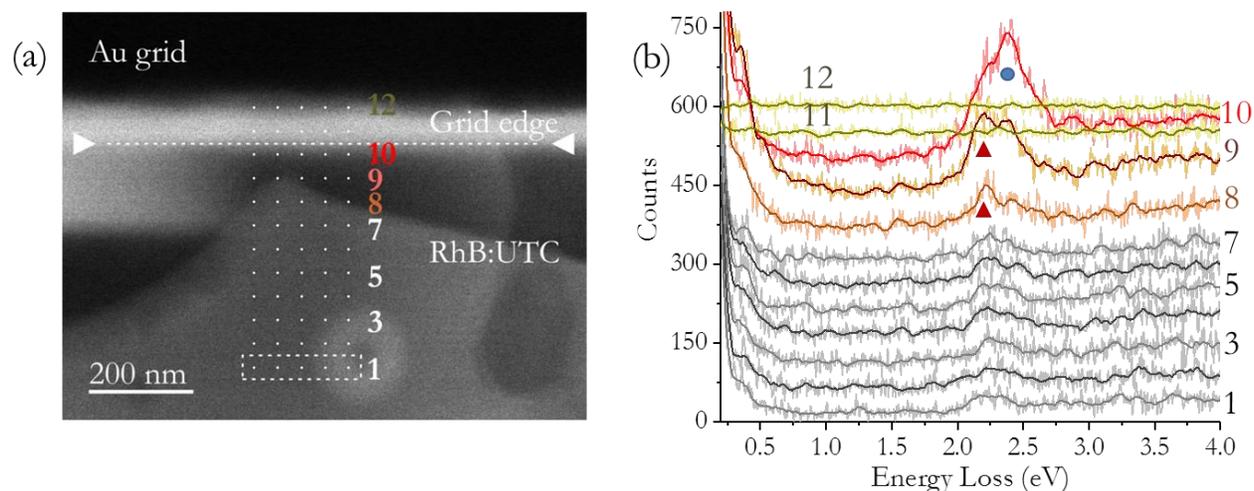


Figure 1. (a) HAADF image showing rhodamine B (RhB) molecules on ≤ 3 nm thick carbon film near the edge of a Au surface (observed local average roughness around 5 nm) indicated by a dashed line. The set of dots correspond to positions where EEL spectra were recorded with a 45 nm separation between position. (b) Excitation spectra of RhB molecules: EEL spectra recorded through the C membrane and averaged over 5 individual locations for each impact parameter. Dispersion was 0.002 eV/channel, the dwell time 0.6 seconds and the zero loss peak full width at half maximum was adjusted to 42 meV as a compromise between required energy resolution and beam current.