Nanoplasmonics and surface enhanced spectroscopy

Adsorbate-induced background and missing first layer effect in surface enhanced Raman scattering (SERS)

P. G. Gucciardi, C. D'Andrea, M. Cottat, A. Toma, B. Fazio, E. Di Fabrizio, Nathalie Lidgi.M. Lamy de La Chapelle, and A. Otto[1] *

[1]Institut für experimentelle Physik der kondensierten Materie, Heinrich-Heine-Universität Düsseldorf, 40225 Düsseldorf, Germany

The SERS spectra of adsorbates on plasmonic nanostructures are composed of a discrete Raman spectrum and an adsorbate induced background (1). Apart from classical local electromagnetic field enhancement a homogeneous extra first layer effect is not existing (2). This is surprising in view of all the experimental evidence for transient electron transfer between metals and adsorbates, e.g. covalent bonding of an adsorbate by spontaneous electron transfer (allowed by Heisenberg's uncertainty principle in the so-called Newns-Anderson model), ultrafast electron transfer between adsorbate and metal after X ray excitation of core electrons of the adsorbate, electronic damping of vibrations, adsorbate induced surface resistance, harpooning of molecules approaching a surface, desorption of molecules, photochemistry of adsorbates, quenching of fluorescence at surfaces , electron transfer reactions at metal electrodes, scanning tunneling microscopy, and friction.

Points (1) and (2) become explicable by the requirement of coherence in Raman scattering. Coherence is only kept during an ultra short electron transfer from metal to the adsorbate and back within the surface plasmon dephasing time of about 6 fs. This time is too short to excite a vibration of the adsorbate, only the excitation of electron hole pairs is still possible. This limit is known as impulse scattering.
Adsorbed molecules are Raman excited only by via intra-molecular transitions, like the molecules in the second and further layers. Both the long range Raman intensity and the inelastic background are enhanced in the same way by the enhanced local electromagnetic fields.

The adsorbate induced background is also observed in the infrared spectral region in reflection spectroscopy at grazing incidence. [1]

[1] Hein, M.; Dumas, P.; Otto, A.; Williams, G. P., Friction of conduction electrons with adsorbates - Simultaneous changes of DC resistance and broadband IR reflectance of thin Cu(111) films exposed to CO. *Surface Science* **1999,** *419* 308