Fundamentals and Applications of Surface-Enhanced Raman Spectroscopy (SERS)

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When a molecule is adsorbed on some metallic nanostructured surfaces such as silver, copper or gold, it can undergo an enormous enhancement of the Raman signal giving rise to the so called *Surface-Enhanced Raman Scattering* (SERS). The high sensitivity of this effect allows an accurate structural study of adsorbates at very low concentrations. The SERS effect has historically been associated with the substrate roughness on two characteristic length scales. Surface roughness on the 10 to 100 nm length scale supports localized plasmon resonances which are considered as the dominant enhancement mechanism of SERS (Electromagnetic Enhancement Mechanism: SERS-EM). It is usually accepted that these electromagnetic resonances can increase the scattered intensity by an average factor of ca. 10^4 to 10^7.

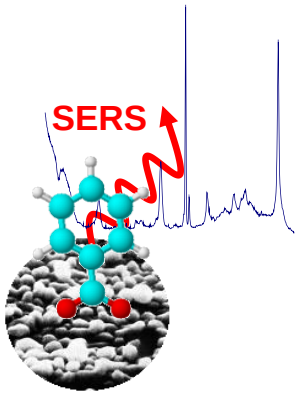

Figure 1. SERS effect.

A secondary mechanism often thought to require atomic scale roughness is referred to as Charge Transfer (CT) Enhancement Mechanism (SERS-CT). This mechanism involves the photoinduced transfer of an electron from the metal to the adsorbate or vice versa and involves new electronic excited CT states which result from adsorbate–substrate chemical interactions. It is also estimated that such SERS-CT mechanism can enhance the scattering cross-section by a factor of ca. 10 to 10^2. These two mechanisms can operate simultaneously, depending on the particular systems and experimental conditions, making difficult to recognize each one and to estimate their relative magnitude in a particular spectrum. [1]

From the point of view of the metal nanostructures, electromagnetic interaction of light with nanoscale metals can generate collective oscillations of conduction electrons generally known as localized surface plasmon resonances (LSPRs) which constitute the basis of new fundamental research and applications, i.e. catalysis, plasmonic solar cells or nanodevices for bio-applications. Additionally, Raman scatterers molecules located at the interparticle junctions may experience SERS enhancement that exceeds that of the isolated nanoparticles by several orders of magnitude enabling the detection of single molecules. [2]

References:

[1] M.R. Lopez-Ramirez, D. Aranda Ruiz, F.J. Avila Ferrer, J.F. Arenas, J.C. Otero, J. Soto, *J. Phys. Chem. C* 120 (2016) 19322−19328.

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