

Surface Enhanced Raman Spectroscopy (SERS)

Theory of surface enhanced Raman scattering

Surface Enhanced Raman Spectroscopy (SERS) is a form of Raman spectroscopy which involves the study of samples adsorbed to or interacting in some manner with metal surfaces, typically nanoscale featured gold or silver surfaces, or gold or silver colloids. Under the correct conditions, SERS may give rise to spectral enhancements of 10^5 or even 10^6 compared to normal Raman scattering, working at PPB or femtomol concentration is often straightforward and single molecule detection is widely reported.

Although now a widely accepted and utilized technique, the first SERS experiment was serendipitously performed as recently as 1974. The initial discovery by Fleischmann reported very intense spectra for pyridine on a roughened silver electrode. The intensity of the spectra was initially attributed to an increase in molecular packing on the surface, which (due to successive oxidation and reduction cycles) had an increased surface area. Further research showed that this increased packing density alone could not account for the intensity increase and in 1977 two independently developed theories were published.

“Surface roughness” is essential for SERS. In this context “roughness” means that a surface must have regions with a certain curvature. For example, colloidal silver with an average particle diameter of 40 nm is considered rough, although each colloidal particle is essentially smooth (atomically rough). Other types of SERS active, rough surfaces include metal substrates, which have undergone

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repeated oxidation and reduction cycles, lithographic assemblies and vapor deposited surfaces. All of these surfaces can be treated as spheres, either in isolation or as an assembly on a flat substrate.

The details of the several proposed mechanisms of enhancement remain a matter of debate. It is considered that the “Electromagnetic Model” (EM) operates in the majority of cases, although the “Charge Transfer Model” (CT) is often also involved. As Raman scattering is governed by the relationship $\mu = E\alpha$, then SERS must involve an increase in either or both of the terms E (amplitude of the electric field), and α (molecular polarizability). The EM theory essentially addresses the enhancement of E , and the CT model is concerned with the enhancement of α . One common feature between these two theories is that both require surface roughness for spectral enhancement to occur.

The electromagnetic model

The EM model deals with E , the amplitude of the electric field of light (a molecule independent factor) and proposes that enhancement is due to the structure of the surface, and interaction of adsorbed molecules with surface plasmons.

Surface plasmons are oscillating electromagnetic fields which exist at interfaces and decay exponentially on each side of the interface. Their amplitude can be resonantly enhanced by radiation of a suitable wavelength. For a plasmon to be excited its momentum and frequency must be maintained. On smooth surfaces, plasmon excitation energy is lost as heat, whereas rough surfaces allow a portion of the plasma energy to be radiated. If the scale of surface roughness is small in comparison to the wavelength of the incident radiation (λ), then a dipolar plasmon will radiate. If this radiation is resonant with the Raman and Rayleigh scatter of a molecule on the surface (this scatter also caused by λ), then the scatter will become substantially amplified.

The charge transfer (chemical) model

Measured enhancement factors are often in good agreement with values calculated using the EM model, but in some cases it is apparent that there is also a second mechanism contributing to the enhancement. While the existence of a CT enhancement is itself not in doubt, the level to which it contributes to SERS signals is still a matter of debate.

The CT model is based around the principle that an adsorbed molecule can, under specific conditions, interact with a metal surface in such a way that there is a large increase in molecular polarizability, α .

In the charge transfer model, an incident photon excites an electron from the metal surface into an adsorbed molecule, creating a negatively charged excited molecule. The molecular geometry of this excited molecule differs from that of the neutral species. This charge transfer induces a nuclear relaxation within the excited molecule, which results in, the return of the electron to the metal surface, the creation of an excited neutral molecule and the emission of a wavelength shifted (Raman) photon.

It is possible to prove the existence of CT enhancement. For example the observation of SERS on silver coated rhodium and platinum surfaces, which themselves do not exhibit EM enhancement. But as CT enhancements must be calculated by quantum mechanical techniques, the level to which CT enhancement contributes to total SERS intensity is typically difficult to ascertain.

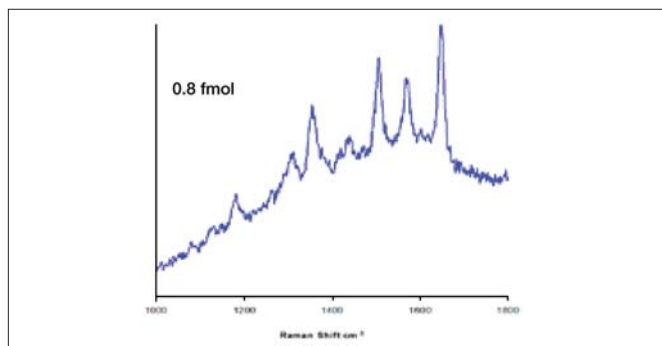


Figure 1. Spectrum of 0.8 fmol concentration solution of Rhodamine labeled oligonucleotide.