



UNDERSTANDING OF ENHANCEMENT MECHANISM IN THE PHENOMENA OF SURFACE ENHANCED RAMAN SCATTERING (SERS)

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Abstract

Objective of the article is to support the understanding and identification of the mechanism involved in the SERS phenomenon. It is usually believed that two types of enhancement mechanisms involved for the huge enhancement of SERS spectra over Raman spectra. One is a long-range electromagnetic (EM) effect and the other is a short-range chemical (CHEM) effect, are simultaneously operative. The EM mechanism is established on the amplified electromagnetic field produced by optical excitation of surface plasmon resonance of nano-scale surface roughness. On the other hand, the photo induced transfer of the electrons (transfer of charge) from the Fermi level of the metal to the unoccupied molecular orbital of the molecule or molecule to metal is depended completely on the energy of the photon and the electric potential of the interface.

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1. Introduction

Most photons are elastically scattered when light is scattered from a molecule. In elastic scattering the scattered photons have the same energy as the incident photons. However, a very small fraction of light (roughly 1 in 10^7 photons) is scattered at optical frequencies different from the frequencies of the incident photon (usually lower than the frequency of the incident photons). The effect involving to this inelastic scattering is called the Raman Effect. The change in vibrational,

rotational or electronic energy of a molecule are the very responsible parameter to occur Raman scattering. C. V. Raman and Krishnan observed this phenomenon when monochromatic light passes through a liquid [1].

It can be realized that, the energy of a vibration of the scattering molecule is equal to the difference in energy between the incident photon and the Raman scattered photon. A plot of intensity of scattered light versus energy difference is a Raman spectrum.

Figure 1 shows quantum mechanical energy level diagram of Rayleigh and Raman scattering.

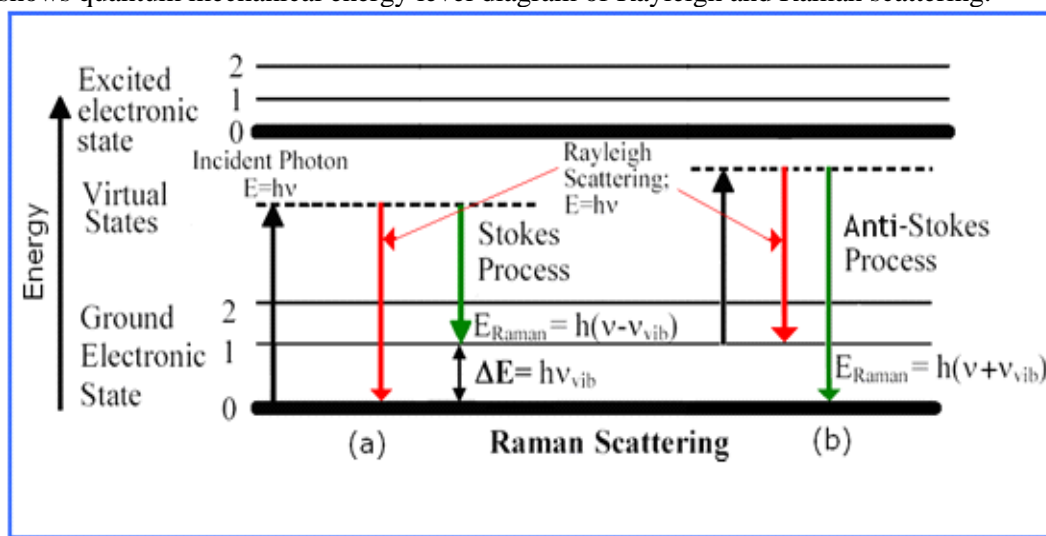


Figure 1 Quantum mechanical Energy level diagrams of Rayleigh and Raman scattering. The vibrational states show the difference in emission photons associated with Rayleigh scattering and Raman scattering. (a) Stokes Raman scattering (b) Anti-Stokes Raman scattering

The first arrow shows the energy contained in the incident photon, which strikes the molecule. The molecule is excited to a virtual excitation state and not a fully excited state. This occurs in both Rayleigh and Raman scattering. In Rayleigh scattering, a photon is released with the same amount of energy as in the incident photon. If the incident photon of frequency ν strikes the molecule then the total energy of the photon is $E_{total} = h\nu = h\frac{c}{\lambda}$ where h is Planck's constant, c is the speed of light, and λ is the wavelength in centimeters. This is also called elastic scattering. Raman scattering is indicated in Figure 1 by the second emission arrow. The decrease in energy is smaller than in Rayleigh scattering. In Raman (inelastic) scattering, the exciting photon leaves the molecule with less energy than the incident photon. The energy, due to the inelastic scattering, is lost for the vibrations of the molecular bonds after the transfer of energy to the molecule: $\Delta E = h\nu_{vib}$ where ΔE is the difference in energy and ν_{vib} is the vibrational frequency of the molecular bond that is vibrating. The Raman scattered photon has less

energy and is at a longer wavelength as the total energy of the incident photon must be conserved. Monitoring these inelastically scattered photons will give the information about the vibrations occurring in the molecule, which is nothing but a Raman spectrum [2, 3] where

$$E_{Raman} = h(\nu - \nu_{vib}) \quad (1)$$

In other words, the Raman Effect arises when a photon is incident on a molecule and interacts with the electric dipole of the molecule. Although the spectrum contains vibrational frequencies, it is a form of electronic spectroscopy. Classically the interaction can be observed as a perturbation of the electric field generated by the molecules. In quantum mechanical system, the phenomena of scattering is observed due to excitation of virtual state which has lower energy than a real electronic transitional energy. This energy also nearly equal to the de-excitation energy and a change in vibrational energy. The scattering event occurs within a very short period of time and it is 10^{-14} seconds or less. The virtual state and ground state

transition involved in scattering phenomena is shown in Figure 1a

The thermal population of vibrational excited states is low, but not zero at room temperature. Consequently, the first state is the ground state and the scattered photon will have lower energy than the energy of the exciting photon. In Raman spectroscopy this Stokes shifted scatter is usually observed. Figure 1a depicts Raman Stokes scattering.

There are very small fraction of the molecules exist in the vibrationally excited states. In Raman scattering the vibrationally excited molecules leaves the molecules in the ground state. The scattered photon appears at higher energy, as shown in Figure 1b. The intensity of anti-Stokes Raman spectrum is always less than the Stokes spectrum, but at room temperature, it is sufficiently strong to be used in various applications for vibrational frequencies less than about 1500 cm^{-1} . Since the Stokes and anti-Stokes lines provide the same frequency information we generally use Stokes lines for their high intensity. At a particular vibrational frequency the temperature of the molecular system can be measured with the ratio of anti-Stokes to Stokes intensity.

Raman spectroscopy is complementary to another vibrational spectroscopy method, infrared spectroscopy. Infrared spectroscopy also gives bond vibration information but it is based on the absorption of infrared light by the molecule. The peaks in each of the forms of spectroscopy describe similar vibrational bands in a spectrum and occur in comparable locations within the spectrum [2].

2. Understanding the mechanisms involved in the SERS phenomenon.

More than 20 years after the first observation of enhanced Raman spectra of pyridine, the method has now reached an advanced stage of development yet the exact mechanism of SERS is still under controversy. As Raman scattering arises from the induced dipole moment produced by the interaction of electromagnetic field of light with the molecular polarizability, mathematically connected as, where α and β are vectors and is a tensor of rank 2. So the origin of tremendous enhancement in Raman scattering is obviously due to any type of perturbation in either one or both of E and β . Based on this important idea, it is mostly recognized that two enhancement mechanisms, a long-range electromagnetic (EM) effect and the other a short-range chemical (CHEM) effect, are operative simultaneously.

(a) Classical Electromagnetic Mechanism

When discussing the EM mechanism, we have to mention the localized surface plasmon resonance (LSPR) which is responsible for it. Surface plasmon is defined as the collective oscillation due to excitation of the electron gas of a metal confined to the near surface. Localized surface plasmon resonance is the excitation of surface plasmons by incident light at nanometer-sized metallic structures. Once the wavelength of the incident light is close to the LSPR of metallic surface, the molecules adsorbed or close to the surface yield a large electromagnetic field which is responsible for the enhancement in the Raman signal. Electromagnetic mechanism is a result of an enhanced electromagnetic field produced at the metal surface [4].

It is essential to illuminate the SERS phenomena as a five step process. In the first step, light is incident on a surface at a certain angle and can excite a surface plasmon. Second, the large electric field of the plasmon will polarize molecules bound to the surface, creating large effective dipole moments within them. Third, if a molecule now changes its vibrational state then, the molecular polarisation will be altered. Forth, this change in polarisation subsequently affects the emitted plasmon, leading to a new plasmon surface field. Finally the surface plasmon can couple into an outgoing Raman scattered photon [4-6]. The EM does not depend on the nature of specific molecule-metal interactions on the surface, nor on their adsorption properties and are characterized by distances considerably exceeding the atomic size. Therefore, where the EM is operative, the SERS spectra are not different from the Raman spectra of free molecules [4]

Figure 2 shows a sketch of electric field localization in colloids and sharp point samples. The field intensity depends on the inter-particle distance and particle shape. Figure 3 shows pictorially the SERS process steps

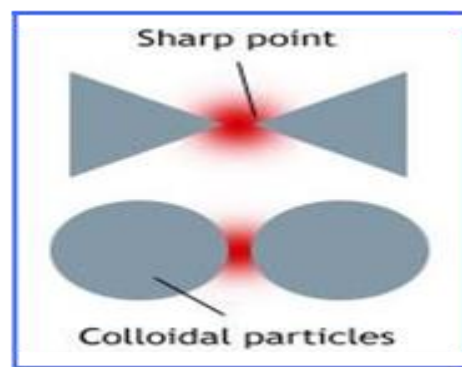


Figure 2 A sketch of electric field localization in colloids and sharp point samples

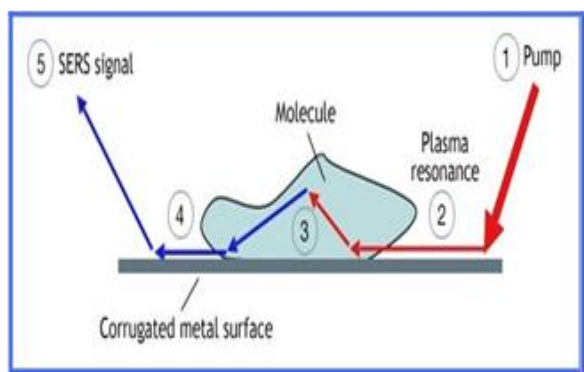


Figure 3 SERS process steps: (1) laser light incident on the metal substrate (2) plasmons excitation (3) light scattered by the molecule (4) Raman scattered light transferred back to plasmons and (5) scattered in air

In this mechanism the enhancement factor E at each molecule is (approximately) given by

$$E = |E(\omega)|^2 |E(\omega')|^2 \quad (2)$$

where $E(\omega)$ is the local electric-field enhancement factor at the incident frequency ω and $E(\omega')$ is the corresponding factor at the Stokes-shifted frequency ω' . More elaborate mathematical expressions for the electromagnetic enhancement factor, which do not include a product of fields at various frequencies, have been given by Kerker [7]. However, numerical values of the enhancements based on this more accurate expression are only slightly different, so (2) is almost exclusively used. In conventional SERS, E be an average over the surface area of the particles where molecules can adsorb to produce the experiential enhancement factor $\langle E \rangle$, while in single-molecule SERS (SMSERS) it is the maximum enhancement E_{\max} that is of great interest. Note that E_{\max} can be orders of magnitude larger than E , so the distinction between these two enhancement estimates is important. Another point is that $E(\omega)$ and $E(\omega')$ are often approximated by assuming that $E(\omega)$ and $E(\omega')$ are the same, and hence $E = |E(\omega)|^4$. The plasmon width is often large compared to the Stokes shift which is benefited by the approximation of the above mentioned expression. However, in studies of SERS on isolated homogeneous particles, this assumption leads to an overestimate of the enhancement factor by factors of 3 or more.

Most of the early enhancement factor estimates were based on analytical theory (either Mie theory for spheres or quasistatic approximations for spheroids). A number of theoretical estimates of SERS enhancement factors have been made in the last few years for non-resonant molecules on

nanoparticle surfaces using computational electrodynamics methods such as the discrete dipole approximation (DDA) [8], semi-analytic approach to T-matrix, known as extended boundary condition method (EBCM) [9-14] and the finite difference time-domain (FDTD) [15-16] method to solve Maxwell's equations to determine the local fields $E(\omega)$. In these approaches the structures of the particle were characterized using finite elements so it is not tough enough to describe a particle of any shape, and sizes up to a few hundred nm are within regular computational skills. These theories can also be utilized to describe many particles, but finally they are limited by the total number of elements required to meet the accuracy of calculation. However, it is possible to couple many particles together using coupled multipole expansions.

(b) Charge-transfer mechanism of SERS

The observations, which cannot be explained by the Electromagnetic mechanism alone, strongly suggest the existence of an additional mechanism in the SERS signal enhancement. Gersten et al [17] were the first group of scientists who suggested in 1979 this additional mechanism, generally termed as the charge-transfer (CT) mechanism or "chemical" mechanism. Mainly two types of CT interactions have been proposed: (i) Ground state charge transfer, (ii) Excited state charge transfer.

(i) Ground state charge transfer

According to Aussenegg and Lippitsch [18] the ground state charge transfer (CT) may also give rise to enhancement of Raman signals. Charges may be transferred between the molecule and the metal surface depending upon the distance between them.

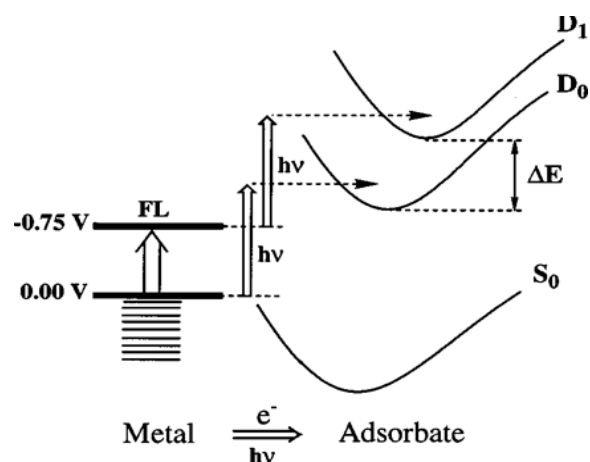


Figure 4 Approximate scheme of the relative position of the Fermi level of the metal controlled by the electrode potential.

The molecular vibration modulates this CT and corresponding change in the polarizability depends considerably on the vibrational co-ordinate resulting in huge enhancement of the associated molecular vibrational mode in the SERS spectra.

Other researchers suggest similar mechanism also [19-21]. A slightly different type of ground state CT mechanism has also been reported by Otto [22].

Their concept is that the in-phase coupled vibrations of groups of surface molecules push and pull electron density to and from the surface, which modulates the surface reflectivity.

However, the ground state CT model leads to the formation of surface-molecule complex. According to this model, the enhancements are expected only for the vibrations that are symmetric with respect to the symmetry elements of this complex.

(ii) Excited state charge transfer

Another type of CT model proposed that an electron from a state below the Fermi level in the metal is excited to an unoccupied state of the adsorbed molecule [23, 24]. If the energy of the incident photon matches with the CT transition energy then there will be possibilities of creation of resonance. Avouris and Demuth [25], Schmeisser *et al* [26] established the existence of such charge transfer excitation by electron-energy-loss-spectroscopy (EELS).

They observed a broad band starting at 1.4 eV and peaked at 2.3 eV for pyridine adsorbed on silver. For a metal (D) to molecule (A) charge transfer, the CT contribution to the polarizability derivative of the system with respect to a normal co-ordinate Q_A of the molecule as estimated by Avouris and Demuth [25] is given by

$$\left(\frac{\delta\alpha_{total}}{\delta Q_A}\right)_{CT} = \left(\frac{\delta q_A}{\delta R}\right) \left(\frac{\delta\alpha_A}{\delta q_A}\right) \left\{ \frac{\delta\alpha_A}{\delta q_A} - \frac{\delta\alpha_D}{\delta q_D} \right\} \quad (3)$$

Where α is the Raman polarizability of a metal-molecule complex, q represents charge and R the donor-acceptor separation.

The suffixes A and D denote the acceptor (regularly the adsorbate) and the donor (generally the metal)

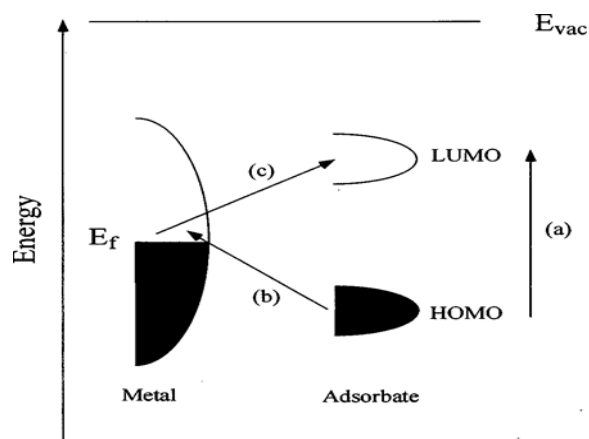


Figure 5: Typical energy level diagram for a molecule adsorbed on a metal surface. The occupied and unoccupied molecular orbitals are broadened into resonances by their interaction with the metal states. Orbital occupancy is determined by the Fermi energy. Possible charge transfer excitations are shown

The charge transfer (CT) mechanism of SERS can be explained by the resonant Raman mechanism in which charge transfer excitations from the metal to the adsorbed molecule or vice versa occur at the energy of the incident laser frequency [27, 28]. Campion and Kambhampati [27] proposed a hypothesis to understand the CT mechanism of SERS. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the probe molecule are symmetrically disposed in energy with respect to the Fermi level of the metal (Figure 5).

In this case, charge transfer excitations (either from the molecule to metal or vice versa) can take place at around half the energy of the intrinsic intramolecular excitations of the molecule. In their reports they enlightened their justification by a resonance Raman mechanism in which either (a) the electronic states of the molecule are shifted and widened by their interaction with the rough surface or (b) new electronic states which arise from chemisorption serve as resonant intermediate states in Raman scattering.

Both Franck-Condon (FC) factor and Herzberg-Teller (HT) couplings are operative in CT mechanism [29]. Overlap of different vibrational substrates of the ground and excited electronic states are considered in the FC mechanism and mixing of different vibrational states by vibrationally induced changes in the electronic wave functions results in the HT coupling. The calculated enhancement factors are very small compared to the experimentally observed values, which indicates that the CT mechanism usually operates in conjunction with the electromagnetic effects.

Persson considered Newns-Anderson resonances of an adsorbate on a silver surface and calculated the ratio of Raman scattering intensity of the adsorbed molecule with respect to the free molecule. [24] The discrete energy level of the lowest unoccupied orbital of the adsorbate is shifted and broadened into a resonance by short time excursions of electrons from the metal into this orbital $|a\rangle$ is equivalent to a partial filling of this broadened level by electrons. The charge transfer interaction involves the excitation of an electron from a metal state below the Fermi energy to about the maximum of ρ_a where ρ_a denotes the electron density of the adsorbate.

The phonon-electron interaction is simply given by,

$$H_{\text{photon-electron}} = -edE_z\hat{n}_Q \quad (4)$$

Where d is the distance between the centre of charge of the orbital $|a\rangle$ and the metal image plane, E_z is the incident field normal to the surface and \hat{n}_Q is an operator which describes the number of electrons in the orbital $|a\rangle$

The molecule-vibration interaction is given by,

$$H_{\text{electron-vibr}} = \epsilon'_a(0)Q\hat{n}_Q \quad (5)$$

Where ϵ'_a is obtained from the expansion of energy ϵ'_a of the orbital $|a\rangle$ of the free molecule with respect to the normal co-ordinate of the vibration. The chemical contribution to the enhancement factor is obtained by Persson as

$$\epsilon_a(Q) = \tilde{\epsilon}_a + \epsilon'_a(0)Q + \dots(6)$$

$\alpha'(0)$ is the derivative of the electronic polarizability of the free molecule with respect to Q and this term governs the ordinary non-resonant Raman scattering ω_L , is the incident laser frequency w , is the Stokes frequency and contains the resonant Raman scattering caused by the charge transfer interactions.

3. Conclusion

Surface Enhanced Raman Scattering or Spectroscopy (SERS) is a very highly effective techniques or tools to identify the presence of molecules down to the single molecular detection level. It can also provide very useful information regarding metal-molecule interaction.

The adsorptive site/sites and the orientation of the adsorbed molecule can be determined qualitatively by comparing the relative intensities and positions of the bands in the SERS with those in the Raman

spectrum of the pure or solvated analyte. The involvement of mechanism in the phenomena of SERS explore the exact cause and its effect on metal-molecule complexes.

The classical electromagnetic mechanism along with short range chemical charge transfer mechanism has been discussed here. The detail mathematical expression and pictorial representation of ground and excited state charge transfer mechanism has been explained here.

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