

## **Chapter-4**

# **Raman Scattering / Spectroscopy: A Brief Overview**

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This chapter highlights the historical development of Raman spectroscopy and detail of light scattering process involved with special emphasized on numerical explanation of Raman scattering process. Step by step development of Raman spectroscopy have been thoroughly discussed in the chapter. The mechanisms of surface enhanced Raman scattering (SERS) are also discussed here. Important parameters of SERS along with advantages of Raman spectroscopy and component of Raman system are discussed briefly.

### **1. INTRODUCTION**

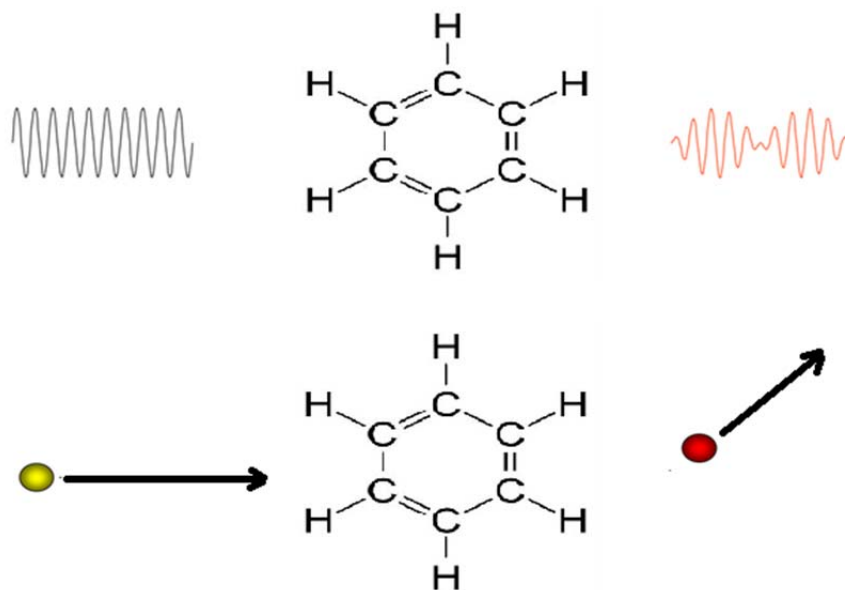
Raman spectroscopy, being a vibrational spectroscopic technique emerged as a convincing and reliable technique for label-free detection and identification of a specific molecule in unknown samples. This specific spectroscopy technique has been used in wide range of fields that includes explosives' detection, bacteria identification, living cell analysis, DNA and

RNA detection, protein-protein interaction and analysis etc.[1-7]. Raman spectroscopy has several advantages such as no or very little sample preparation steps are required, in-situ and in-vitro investigations for biological samples is possible, non-destructive and non-invasive investigations of samples etc. are possible with this technique. [8-10] Also, samples can be examined in a whole range of physical states such as solids, liquids or vapors, in hot or cold states, in bulk, as microscopic particles, or as surface layers. Raman spectroscopy is much like infrared (IR) spectroscopy, however, IR bands arise from a change in the dipole moment of a molecule whereas Raman bands arise from a change in the polarizability of the molecule due to interaction of light with the molecule.

The Raman scattering is a phenomenon of inelastic scattering of light from the molecules whose size is comparable to the wavelength of incident monochromatic light. Inelastic scattering is nothing but shifting of frequency in the scattered light from the incident light. The inelastic scattering of light was first postulated by Smekal in 1923 [11] and later in 1928 Raman and Krishnan [12] confirmed this phenomenon experimentally then onwards, this specific phenomenon has been referred to as Raman scattering and application of this phenomenon in different field of study has been referred as Raman spectroscopy. Originally in the experiment sunlight was focused by a telescope onto a sample and another lens was placed by the sample to collect the scattered radiation. To show the existence of scattered radiation with a shifting frequency from the incident frequency a system of optical filters were used.

## 2. THEORY OF RAMAN SCATTERING

Raman scattering can be think in two ways, the classical wave interpretation and the quantum particle interpretation. The light is considered as electromagnetic radiation in the classical wave interpretation. The light contains an oscillating electric field and it interacts with a molecule through its polarizability. The Polarizability of molecule is nothing but the ability to interact with an electric field which is determined by the electron cloud's. For example, soft molecules such as benzene tend to be strong Raman scatterers while harder molecules like water tend to be fairly weak Raman scatterers.



**Fig. 1: Raman scattering classical wave and quantum particle interpretations**  
(<http://bwtek.com/raman-theory-of-raman-scattering/>)

On the other hand, in case of quantum particle interpretation the light is considered a photon that strikes the molecule and then scattered inelastically. The number of scattered photon depends on the molecular structure and environment such as atomic mass, bond order, molecular substituents, molecular geometry etc. Fig. 1 shows a visual comparison of the two methods.

To derive Raman mathematically, let us starts with the classical interpretation. To begin with let us consider a diatomic molecule as a mass on a spring (as shown in Fig. 2) where  $m$  represents the atomic mass,  $x$  represents the displacement, and  $K$  represents the bond strength.



**Fig. 2: Diatomic molecule as a mass on a spring.**

(<http://bwtek.com/raman-theory-of-raman-scattering/>)

Using Hooke's law the displacement of the molecule can be obtain as,

$$\frac{m_1 m_2}{m_1 + m_2} \left( \frac{d^2 x_1}{dt^2} + \frac{d^2 x_2}{dt^2} \right) = -K(x_1 + x_2) \dots \dots \dots (1)$$

Replacing the reduced mass ( $m_1 m_2 / [m_1 + m_2]$ ) and the total displacement ( $x_1 + x_2$ ) with  $\mu$  and  $q$  respectively, the equation can be obtain as,

$$\mu \left( \frac{d^2 q}{dt^2} \right) = -Kq \dots \dots \dots (2)$$

Solving this equation for  $q$  we have,

$$q = q_0 \cos(2\pi \nu_m t) \dots \dots \dots (3)$$

where  $q_0$  is the amplitude of the molecular vibration and  $\nu_m$  is the frequency of the molecular vibration and is defined as,

$$\nu_m = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \dots\dots\dots(4)$$

From equations 3 and 4, it is clearly seen that the molecular vibration is sinusoidal in nature and the frequency of the vibration is proportional to the bond strength and inversely proportional to the reduced mass. This ensures that every molecule will have their unique vibrational signatures, which are determined not only by the atoms in the molecule, but also the characteristics of the individual bonds [13].

When light i.e. electromagnetic (EM) radiation incident on material the electric field associated with the EM radiation induces an electric dipole moment  $M$  in the molecule, given by

$$M = \alpha E \dots\dots\dots(5)$$

where  $\alpha$  is the polarizability of the molecule.

The electric field  $E$  is given by

$$E = E_0 \cos \omega t = E_0 \cos(2\pi\nu t) \dots\dots\dots(6)$$

where  $E_0$  is the amplitude and  $\nu$  is the frequency of the of the incident electric field.

Therefore, from equations (5) & (6),

$$M = \alpha E_0 \cos(2\pi\nu t) \dots\dots\dots(7)$$

The dipole is oscillating in nature and oscillating dipole emits radiation at its own oscillating frequency  $\nu$ , giving the Rayleigh scattered beam. If, however, the polarizability varies slightly with molecular vibration, and is given by

$$\alpha = \alpha_0 + q \left( \frac{d\alpha}{dq} \right)_{q=0} + \dots \dots \dots (8)$$

where the q describes the molecular vibration as obtained in equation 2

From equations. 2 & 8, we have

$$\alpha = \alpha_0 + q_0 \left( \frac{d\alpha}{dq} \right)_{q=0} \cos(2\pi\nu_m t) \dots \dots \dots (9)$$

Substituting for alpha in (7), we have

$$M = \alpha_0 E_0 \cos(2\pi\nu t) + q_0 \cos(2\pi\nu_m t) E_0 \cos(2\pi\nu t) \left( \frac{d\alpha}{dq} \right)_{q=0} \dots \dots \dots (10)$$

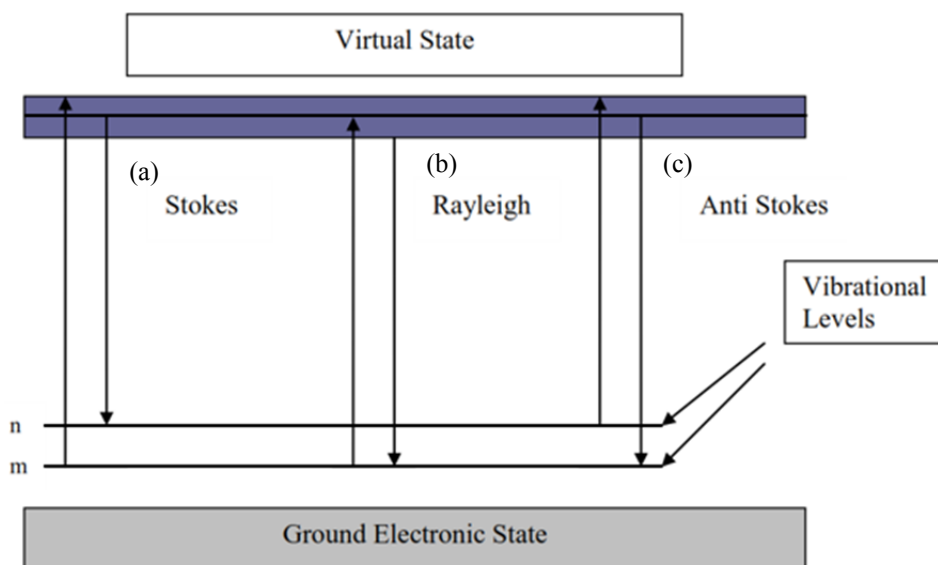
Using the trigonometric identity,  $\cos A + \cos B = \frac{1}{2}(\cos(A + B) + \cos(A - B))$  this equation can be obtained as-

$$M = \alpha_0 E_0 \cos(2\pi\nu t) + \frac{1}{2} q_0 E_0 \left( \frac{d\alpha}{dq} \right)_{q=0} [\cos\{2\pi(\nu + \nu_m)t\} + \cos\{2\pi(\nu - \nu_m)t\}] \dots \dots \dots (11)$$

Thus, we find that the oscillating dipole has three distinct frequency components- The exciting frequency  $\nu$ , with amplitude  $\alpha_0 E_0$ ,  $\nu + \nu_m$  and  $\nu - \nu_m$  with very small amplitude of  $\frac{1}{2} q_0 E_0 \left( \frac{d\alpha}{dq} \right)_{q=0}$ . From equation 11, it has been observed that due to the interaction of the molecule and the incident light, there are two resultant effects. The first effect is called Rayleigh scattering, which is the dominate effect and results in no change in the frequency of the incident light. The second one is the Raman scattering effect. When expanded to,  $\frac{1}{2} q_0 E_0 \left( \frac{d\alpha}{dq} \right)_{q=0} [\cos\{2\pi(\nu + \nu_m)t\} + \cos\{2\pi(\nu - \nu_m)t\}]$  the shift of the incident light frequency by plus or minus the frequency of the molecular vibration. The increase in frequency is

known as an Anti-Stokes shift and the decrease in frequency is known as a Stokes shift. Thus, Raman spectrum can directly give the vibrational frequency of a molecular bond.

If the molecular vibration does not change the polarizability of the molecule then  $\left(\frac{d\alpha}{dq}\right)_{q=0} = 0$ . In this case, the dipole oscillates only at the frequency of the incident (exciting) radiation. The same is true for the molecular rotation. It can be concluded that to have Raman Spectrum of the molecule the molecular vibration or rotation must cause a change in the molecular polarizability.



**Fig. 3: Energy level diagram for Raman scattering; (a) Stokes Raman scattering, (b) Rayleigh scattering and (c) anti-Stokes Raman scattering.**

The classical interpretation of Raman effect satisfactorily describes the Rayleigh scattering, stokes and anti-stokes shift with their frequency and amplitudes. It can be seen that the amplitudes of stokes and anti-stokes shifted Raman scattering are equal, practically the intensity of anti-stokes shifted Raman scattering is much weaker than stokes shifted Raman scattering. The reason behind this anomaly cannot be explain by the classical interpretation, therefore, the quantum particle interpretation come into picture.

To have better visualization of the Raman effect and determine additional information, we can use the quantum particle interpretation. As discussed earlier in the quantum interpretation, the Raman effect is described as inelastic scattering of a photon from a molecule. From Fig. 3, we can see that this results from the incident photon exciting the molecule into a virtual energy state. There are three different potential outcomes when it occurs. First, the molecule can bounce back to the ground state by emitting a photon of equal energy to that of the incident photon, which is referred as Rayleigh scattering. Secondly, the molecule can relax to a state and real phonon emit a photon with less energy than the incident photon; this is called Stokes shifted Raman scattering. The third potential outcome is that the molecule is already in an excited phonon state, is excited to a higher virtual state, and then back to the ground state by emitting a photon with more energy than the incident photon; this is called Anti-Stokes Raman scattering. As the population of molecules in the ground state more at room temperature, therefore probability that a photon will be Anti-Stokes scattered much low, hence, anti-stokes shifted Raman scattering intensity is



low as compared to Stokes shifted Raman scattering intensity. As a result, most Raman measurements are performed considering only the Stokes shifted light.

Further it has been observed that the power of the scattered light,  $P_s$ , is equal to the product of the intensity of the incident photons,  $I_o$ , and a value known as the Raman cross-section,  $\sigma_R$ . The Raman cross section is given by

$$\sigma_R \propto \frac{1}{\lambda^4} \dots\dots\dots (12)$$

where  $\lambda$  equals the wavelength of the incident photon. Therefore,

$$P_s \propto \frac{I_o}{\lambda^4} \dots\dots\dots (13)$$

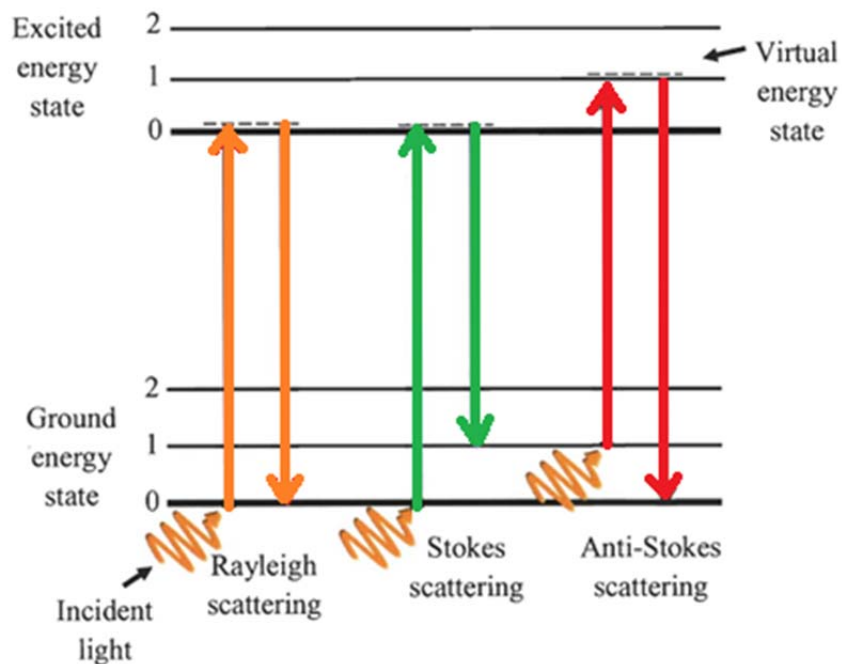
From equation 13 it is seen that the power of the scattered light is directly proportional to the intensity of the incident light and inversely proportional to fourth power wavelength. Therefore, it is always desirable to use a short excitation wavelength and a high power excitation source based on these relationships. However, this is not always the case.

### 3. RAMAN SPECTRUM AND RAMAN SHIFT

The energy difference between incident and scattered photons is called Raman shift and it is positive for Stokes scattering and negative for Anti-Stokes scattering. Numerically the Raman shift is expressed in wave number ( $\bar{\nu}$ ) unit is in  $\text{cm}^{-1}$ , which is given as  $\bar{\nu} = \frac{1}{\lambda} - \frac{1}{\lambda_s}$ , where  $\lambda$  is the incident wavelength and  $\lambda_s$  is scattered wavelength. In most cases, a Raman shift is shown as a function of Raman intensity.

#### 4. RESONANCE RAMAN SCATTERING

The resonance Raman scattering is a process in which the intensity of Raman scattered signal is enhanced by several order. Generally in this type of Raman scattering the energy level of incident photon is close to the level of electronic transitions of the molecule, the virtual state will resonant with one of the electronic levels. This phenomenon, which is shown in Fig. 4. [14,15]



**Fig. 4. Resonance Raman scattering phenomenon [16]**

#### 5. SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS)

SERS is a phenomenon in which the Raman signal intensity of molecule is greatly enhanced when the molecule is absorbed or very closed proximity to

the roughened metal surface. SERS can be used for a wide range of physical and biological applications; therefore, it has become an area of great interest with the number of publications in the field rising year after year.

### **5.1 Brief History**

In the year 1974, Fleischmann and co-workers [17] first observed the SERS effect. In their experiment they have observed that pyridine adsorbed onto an electrochemically roughened silver surface give rise to intense Raman signals. Fleischmann et al., interpreted in their original paper that the amplified Raman signal of pyridine is due to increased surface area caused by the roughening of silver electrodes. Still there were many unanswered questions regarding this hypothesis. Approximately three years later in 1977 two independent groups, Jeanmarie and R Van Duyne [18] and Albrecht and A Creighton [19] confirmed the result –a Raman enhancement of about a million –compared with the signal from the pyridine molecules in the absence of metal and documented that the observed Raman enhancement could not be accounted for by increased surface area, instead other mechanisms exist. Several enhancement mechanisms were proposed by different researcher since advent of SERS, however only two mechanisms, Electromagnetic (EM) mechanism and Chemical Enhancement (CE) mechanism are now broadly accepted. The Electromagnetic (EM) mechanism contributes dominantly (can contribute ten or more orders of magnitude) in the enhancement mechanism which is based on the collective oscillation of free electron density generating localized surface plasmons (LSPs)[20]. The CE mechanism describes the chemical interaction between

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probe molecules and the noble metal and is contribute only up to 2-3 orders of magnitude [21].

## 6. MECHANISMS OF SERS

As mentioned earlier, two enhancement mechanisms have explain the reason why metallic nanoparticles or roughened metallic surfaces give rise to an increased Raman signal intensity. The two mechanisms are describes below.

### 6.1 The Electromagnetic Mechanism of SERS

It is important to recall the phenomenological approach to Raman scattering to understand the EM enhancement mechanism. When monochromatic radiation of frequency  $\nu$  with an electric field  $E$  interacts with a molecule, it induces a dipole oscillating at a frequency  $\nu_m$ . The dipole moment is given by

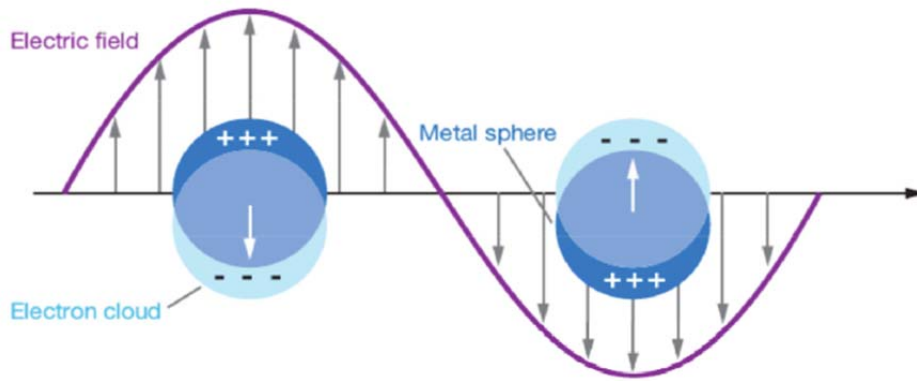
$$M = \alpha E \dots \dots \dots (14)$$

The oscillating dipole radiates power proportional to  $M$  at frequency  $\nu_m$  and the frequency detected as Raman signal in far-field. The same concept can be used to describe SERS. However, the roughened metal surface alters the effects as[22]-

- (a) There is a local field enhancement because of electromagnetic enhancement at the metallic surface.
- (b) The properties of radiation of the dipole is affected by the metallic environment resulting a possible radiation enhancement.

### 6.1.1 Local field Enhancement

The electromagnetic field at the vicinity of the metallic surfaces get strongly modified upon incident of electromagnetic radiation on a suitable metal surface (that possess a negative real and small positive imaginary dielectric constant). This specific modification in the electromagnetic field is due to the coherent oscillation of free electrons that generate surface plasmons. Surface plasmons can be of two types, surface plasmon polariton (or propagating plasmon) that propagates along the metal-dielectric interface [23,24] or localized surface plasmon which localized on the surface of a nanoparticle (Fig. 5) with a frequency known as the localized surface plasmon resonance (LSPR) [25,26].



**Fig. 5: Schematic diagram of localized surface plasmon generation. [22]**

The local electric field  $E_L$  is different from incident field  $E$ , in terms of both magnitude and orientation. Generally, the magnitude of  $|E_L|$  can be much larger than  $|E|$ . The local field induces a dipole of dipole moment given by

$$M_R = \alpha E_L(\nu_m) \dots \dots \dots (15)$$

Therefore, the dipole is enhanced by a factor of  $|E_L(v_m)|/|E|$  as compared to the dipole induced due to incident field. If such dipole radiates in free-space (i.e., in absence of metallic environment), the radiated energy which is proportional to  $|M_R|^2$ , would enhance by a factor

$$EF_L = \frac{|E_L(v_m)|^2}{|E|^2} \dots\dots\dots(16)$$

The local electric field enhancement factor  $EF_L$  is characterizes the enhancement of the electric field intensity, here we ignore any changes in the electric field polarization.

**6.1.2 Radiation Enhancement**

The dipole induced due to local field radiates in presence of metallic objects in case of SERS. Therefore, dipole radiation alters significantly. Depending on the relative dielectric function  $\epsilon(r)$  of the object, its geometry, and the dipole position, orientation and its emission frequency,  $v_{rad}$  the total power radiated by the dipole,  $P_{rad}$  can be either increase or decrease (relative to that in free space,  $P_0$ ). Due to coupling to the LSPR of metallic objects [27] there is an enhancement in the radiated power. Therefore, the radiation enhancement factor is given by

$$EF_{rad} = \frac{P_{rad}}{P_0} \dots\dots\dots(17)$$

**6.1.3  $|E|^4$  Approximation**

Combining local electric field enhancement and radiation enhancement, EM enhancements of single-molecule SERS (SMSERS) can be expressed as [27]

$$\text{Enhancement factor (EF)} \approx EF_L(v_m) \times EF_{rad}(v_{rad}) \dots\dots\dots(18)$$

By solving the electromagnetic problem under specific external excitation conditions with an incident field  $E$ ,  $EF_L(\nu_m)$  can be calculated. However, to estimate  $EF_{rad}(\nu_{rad})$  one has to solve the electromagnetic problem of dipolar emission, instead of external excitation, which is a very complicated task. To avoid these complications, it is often assumed that local electric field enhancements and radiation enhancements are approximately equal. Hence, SERS enhancements can be expressed as

$$EF \approx EF_L(\nu_m) \times EF_{rad}(\nu_{rad}) \approx \frac{|E_L(\nu_m)|^2}{|E|^2} \frac{|E_L(\nu_R)|^2}{|E|^2} \dots \dots \dots (19)$$

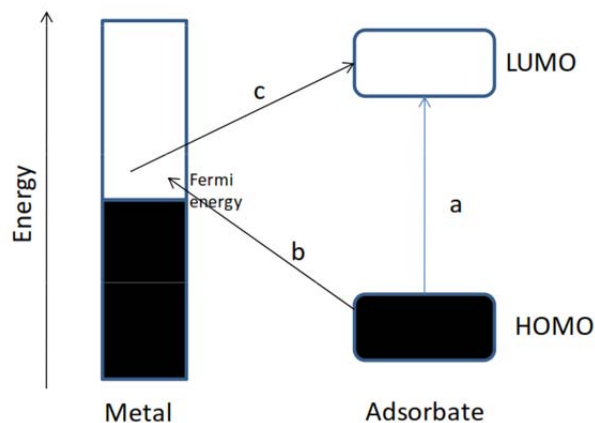
An additional approximation can be made, i.e.  $\nu_m = \nu_R$ , which, results into famous expression of the SERS enhancement

$$EF \approx \frac{|E_L(\nu_m)|^4}{|E|^4} \dots \dots \dots (20)$$

## 6.2 The Chemical Enhancement

Different researcher has given many explanation of chemical enhancement but mostThe mostly accepted explanation of CE is a charge-transfer (CT) mechanism [27,28] Due to adsorption of analyte on the metal surface, metal adsorbate complex is formed. There is a form covalent bond between adsorbate and metal surface (chemisorption). This bonding produces new electronic states and serves as resonant intermediate states. In other words, with the Fermi level of the metal the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the adsorbate are symmetrically disposed. And, Charge transfer (CT)s from Fermi level to LUMO and retro-donation of electron from HOMO to Fermi level of the metal. Under certain conditions, the laser energy can also be

directly in resonance with the electronic excitation of the metal-adsorbate complex. The process descriptions are summarized in Fig. 6 [22].



**Fig. 6: Schematic of charge transfer mechanism**

## 7. IMPORTANT PARAMETERS FOR SERS

Some important parameters for such as substrate and analyte are briefly discussed below.

### 7.1 Substrate

The substrate that supports high Plasmon resonance and enhances a weak Raman signal is called SERS substrate. SERS substrates provide a high amplification of Raman signal. Depending upon generation process SERS substrates can be classified into three types-

- Metallic particles in solution such as a colloidal solution
- A planar metallic structure which is array of nanoparticle that are supported by a planar structure such as glass and silicon
- Metallic electrodes.



Electrodes have played an important role in the SERS process and even its discovery, but because of their low enhancement factor, they are not being used as much as before.

### **7.2 SERS analyte (probe)**

In selecting appropriate probes for SERS the intensity of Raman scattering plays a vital role. Arrangement of the molecule on the substrate and toward to the incident light affect the intensity of Raman spectrum significantly. Raman signal intensity is also depends on the power of laser source. If electromagnetic field of molecules are close to exciting laser energy then the molecule can be considered as a good candidate to be used as a SERS analyte. The probe should be able to absorb on the SERS substrate. Generally, the molecule can be attached to the metallic surface without any treatment, however some of them might need a chemical process and treatment.

## **8. ADVANTAGES OF RAMAN SPECTROSCOPY**

There are several reasons behind the popularity of Raman spectroscopy in the different field of applications-

**Specificity:** As Raman detects fundamental vibrations of molecules, Raman bands have a good signal-to-noise ratio and no overlapping.

**Aqueous systems analysis:** The Raman spectrum of water is very weak; therefore, it is easier to get Raman spectra of aqueous solution.

**Organic and inorganic analysis:** Unique Raman signature may be produced for different types of chemical bonds.

**Wide Concentration Range:** The Raman signal intensity is directly proportional to the concentration of analytes. Raman analysis measures a species concentration from a fraction of 1% to 100% without sample dilution.

**No sample preparation:** Raman requires no special preparation of the sample.

**Non-destructive and non-invasive analysis:** As Raman analysis involves only illuminating a sample, often through a window, with a laser and collecting the scattered photons this makes Raman spectroscopy *non-destructive*. The Raman analysis is not spread harmfully over the analyzing area.

**In situ and in vitro analysis:** It is possible to get Raman signal of biological sample by doing analysis inside the analyte or on the area where the analyte present.

**Quantitative Raman:** Raman band can be used to provide a measure of the concentration of a molecule as the Raman intensity is proportional to the number of molecules contributing in the Raman band.

**Short measurement times:** Raman spectrum can be acquired in a fraction of seconds, which enables real time monitoring of chemical reaction.

## **2.0. Basic Components of a Raman System**

Raman system contains the following main components

1. A laser excitation source
2. Excitation delivery optics
3. A sample

4. Collection optics
5. A wavelength separation device
6. A detector and associated electronics
7. A recording device.

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