CHAPTER - II

THEORETICAL INTERPRETATION OF SERS - I
[Electromagnetic Effect]

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2.1 General

Extensive research efforts have been devoted to the determination and understanding of the sources of surface-enhanced Raman scattering (SERS) effect. There is no single theoretical model capable of accounting for all the experimental observations related to SERS. The origin of the enormous Raman enhancement is believed to come from the result of several mechanisms. There are two major types of mechanism that contribute to the effect: (i) electromagnetic and (ii) chemical.

2.2 Electromagnetic Sources of SERS Effect

Electromagnetic interactions between the molecule and the substrate are believed to play a major role in the SERS process. During the interaction a large local electromagnetic field is created which enhances the Raman signals. A major contribution to electromagnetic enhancement is due to the surface plasmons. Surface plasmons are associated with the collective excitations of surface conduction electrons in metal [1]. Raman enhancements result from excitation of these surface plasmons by the incident radiation. Another enhancement is due to the excitation of surface plasmons by the Raman emission radiation of the molecule. Other types of electromagnetic enhancement mechanisms are due to (i) concentration of electromagnetic field lines near high-curvature points on the surface, that is, the
lightning-rod effect [2,3] (ii) polarization of the surface by dipole-induced fields in adsorbed molecules, that is, the image field effect [3,4,5] and (iii) Fresnel reflection effects.

2.3 Surface Plasmons

A plasma is an electrically neutral collection of electron and positive ions. A plasma can undergo oscillations due to an external source of excitation. A plasmon is nothing but a quantum of the plasma oscillations that occur in a plasma. At the surface between a plasma and material of dielectric constant \( \varepsilon_s \), a surface plasmon exists whose energy is given by

\[
E_s = \frac{\hbar \omega_p}{(1 + \varepsilon_0)^{\frac{1}{2}}}
\]

which is confined to within a screening length of the surface. Surface plasmons are the quanta of surface plasma oscillations, sometimes called surface electromagnetic waves, propagate parallel to the surface. For a free electron metal the surface plasma frequency \( \omega_s \) is given by

\[
\omega_s = \frac{\omega_p}{(1 + \varepsilon_0)^{\frac{1}{2}}}
\]

where \( \omega_p \) is the bulk plasma frequency [6]. When the metal is in contact with a vacuum,

\[
\omega_s = \frac{\omega_p}{2^{\frac{1}{2}}}
\]
The surface plasmon has the parallel momentum $K_\parallel$ which is given by the relation,

$$K_\parallel^2 = (\frac{\omega}{c})^2 \Re \frac{\epsilon_\omega}{\epsilon_\omega + \epsilon}$$  \hspace{1cm} (2.4)

where, $\epsilon$ is the complex dielectric function of the metal (or conductor) and $\epsilon_\omega$ is that of the ambient. Due to the requirement of the momentum conservation, surface plasmons cannot be excited optically, hence a surface plasmon does not radiate but is confined to the metal surface. Surface plasmon excitation becomes possible if the parallel momentum of the incident photon is modified to match that of the plasmon. This can be done by using a prism with carefully chosen refractive index or by constructing a grating on the surface to change the photon parallel momentum by diffraction. Making a surface randomly rough is also equivalent to ruling the grating on it. So, the surface plasmon can radiate under this condition.

Small particles have electromagnetic resonances similar to the surface plasmon. When the particle is small compared to the wavelength of the incident plane wave, a plasmon can be excited that has the symmetry of a time-varying dipole. Once excited, this dipolar plasmon can, of course, radiate. For a sphere this resonance occurs at the frequency $\omega_R$, for which the following condition is to be satisfied,

$$\Re [ \epsilon (\omega_R) ] = -2 \epsilon_\omega$$  \hspace{1cm} (2.5)
A sphere has also other resonances whose frequencies may be obtained from the relation,

$$\text{Re} \left[ \epsilon(\omega_N) \right] = -\left[ \frac{N^+1}{N} \right] \epsilon_0$$

(2.6)

where $N$ is an integer. Except for $N = 1$ resonance, which is dipolar, the others have symmetries corresponding to higher multipoles and therefore cannot radiate.

2.4 Electromagnetic Enhancement on Flat Surfaces: Image Field Model

Electromagnetic interaction between a molecule and a flat surface plays a vital role in the enhancement of the Raman signals. King and his collaborators [7] calculated this enhancement by the help of a model which is known as "image-field model". According to this model, the dipole moment induced in the molecule by the incident field and its image field is given by,

$$\mu = \alpha ( E + E_{\text{im}} )$$

(2.7)

where $E$ and $E_{\text{im}}$ are the incident and image fields, and $\alpha$ is the ZZ component of the molecular polarizability, $E_{\text{im}}$ is given by

$$E_{\text{im}} = \frac{\epsilon - \epsilon_0}{\epsilon + \epsilon_0} \cdot \frac{\mu}{4\pi r^3}$$

(2.8)

where $r$ is the distance between the point dipole and the surface.
Substituting and rearranging we can get,

\[
\mu = \frac{\alpha}{1-(\alpha/4\pi^3)(\epsilon - \epsilon_0)/\epsilon(\epsilon + \epsilon_0)} \cdot \mathbf{E} \tag{2.9}
\]

This expression resembles to a conventional expression for a dipole moment \( \mu \) induced by a field \( \mathbf{E} \) except that in place of the polarizability \( \alpha \) one has an effective polarizability,

\[
\alpha_{eff} = \frac{\alpha}{1-(\alpha/4\pi^3)(\epsilon - \epsilon_0)/\epsilon(\epsilon + \epsilon_0)} \tag{2.10}
\]

This expression has a pole at the frequency at which

\[
\text{Re} \left[ \frac{\alpha(\epsilon - \epsilon_0)}{4\pi^3(\epsilon + \epsilon_0)} \right] = 1 \tag{2.11}
\]

In fact this is related to surface-plasmon excitation in the metal surface at the frequency for which the condition \( \text{Re} \left( \epsilon \right) = -\epsilon_0 \) obtains [8]; otherwise, the quantity \( \alpha(\epsilon - \epsilon_0)/4\pi^3(\epsilon + \epsilon_0) \) would not approach 1 except for unrealistically small values of \( \epsilon \). Using reasonable parameters, King et al [7] showed that on silver, Raman enhancements in excess of \( 10^6 \) are possible at or below \( \epsilon = 1.65 \) \( \AA \), the enhancement dropping to around \( 10^2 \) for \( \epsilon = 2 \) \( \AA \).

Feibelman [9] finds practically no image-field enhancement in a model that uses linear response theory to treat the response of the metal electrons to the time-varying induced dipole due to the adsorbed molecule. Lee and Birman [10,11] have considered the image-field problem as part of their general
coupled-state quantum formalism for treating SERS. So, according to them the image-field enhancement is not an important contributor to SERS.

A decidedly real surface-enhancement process, electromagnetic in origin, which occurs at flat metal surfaces is due to the fact that the molecule near the metal surface is illuminated by both a direct and a reflected field, coherently superimposed to give an intensity upto four times the incident intensity. Likewise, the Raman scattered field is composed of a direct and reflected field yielding upto four-fold an increase in its intensity for a total maximum enhancement of 16. Efrima and Metiu [12,13,14] has called this effect as 'minor' enhancement.

2.5 Electromagnetic Enhancement for Spherical Metal Particles

Let us consider a metallic spherical particle. A molecule, treated as a classical electric dipole, is placed at a position \( r' \), outside the particle. Upon irradiation with a plane wave of frequency \( \omega_0 \), the molecular dipole will radiate at the Raman frequency \( \omega \) with a dipole moment

\[
\vec{p} \left( \vec{r}', \omega \right) = \alpha' \vec{E}_p \left( \vec{r}', \omega_0 \right)
\]

(2.12)

where \( \alpha' \) is the Raman polarizability of the molecule and \( \vec{E}_p \left( \vec{r}', \omega_0 \right) \) is the field at the exciting frequency \( \omega_0 \) at the location of the molecule [15].
Fig. 2.1: Schematic view of electric fields near a sphere of radius 'a' and refractive index 'm'. At the incident frequency $\omega_0$ there are the incident, Lorentz-Mie, and primary fields, $E_i(\omega_0)$, $E_{LM}(\omega_0)$ and $E_p(r', \omega_0)$. At the shifted frequency $\omega$ there are the dipole, scattered, and Raman fields, $E_{DIP}(\omega)$, $E_{SC}(\omega)$ and $E_R(r, \omega)$, where $r'$ and $r$ are the positions of the dipole and observer respectively.
The exciting field in turn is comprised of the incident field \( \vec{E}_1 (\vec{r}', \omega) \) plus the elastically scattered field \( \vec{E}_{LM} (\vec{r}', \omega) \) called the Lorentz-Mie field. Hence,

\[
\vec{E}_p (\vec{r}', \omega) = \vec{E}_i (\vec{r}', \omega) + \vec{E}_{LM} (\vec{r}', \omega) \quad (2.13)
\]

The electric field associated with the Raman radiation at an observation point \( \vec{r} \) is given by

\[
\vec{E}_R (\vec{r}, \omega) = \vec{E}_{\text{dip}} (\vec{r}, \omega) + \vec{E}_{\text{sc}} (\vec{r}, \omega) \quad (2.14)
\]

where \( \vec{E}_{\text{dip}} \) is the field of the oscillatory dipole \( \vec{F} (\vec{r}', \omega) \) in the absence of the particle and \( \vec{E}_{\text{sc}} (\vec{r}, \omega) \) is a secondary or scattered field that must be computed by solving the appropriate boundary value problem at the Raman frequency

Again let us consider that the radius of the particle is 'a' and \( \epsilon_i \) and \( \epsilon_s \) are the complex dielectric function of the particle i.e. metal and of the surrounding medium. In the small-particle limit, the electric field at \( \omega_s \) and \( r' \) may be considered equivalent to the field of an electric dipole at the center of the sphere with dipole moment

\[
\vec{P}_o = a^3 g_o \vec{E}_1 (\vec{r}', \omega) \quad (2.15)
\]

where,

\[
g_o = \frac{\epsilon_i (\omega_o) - 1}{\epsilon_i (\omega_o) + 2} = \frac{\epsilon - 1}{\epsilon + 2} \quad (2.16)
\]
in which $\epsilon$ is the ratio of the complex dielectric function of the material comprising the particle to that of the ambient.

\[ \mathbf{E}_p \] will force the molecule at $r'$ to oscillate at the shifted frequency $\omega$ with dipole moment

\[ \mathbf{P}_1(\omega) = \alpha \mathbf{E}_p(r', \omega) \]  \hspace{1cm} (2.17)

where $\alpha$ is the Raman tensor of the free molecule and $\mathbf{E}_p(r', \omega)$ is the incident field plus the Lorentz-mie field, which is now due to the dipole $\mathbf{P}_o$.

Again, the scattered field $\mathbf{E}_{SC}(r, \omega)$ is the field of an electric dipole which is located at the center of the particle with a dipole moment,

\[ \mathbf{P}_2(\omega) = a^3 g \mathbf{E}_d(0, \omega) \]

where,

\[ g = \frac{\epsilon_1(\omega)-1}{\epsilon_1(\omega)+2} = \frac{\epsilon(\omega)-1}{\epsilon(\omega)+2} \]  \hspace{1cm} (2.18)

in which $\mathbf{E}_d$ is the field of $\mathbf{P}_2(\omega)$ at the origin $r' = 0$ in the absence of the sphere. The total Raman emission is given by the coherent addition of the field of $\mathbf{P}_1(\omega)$ and $\mathbf{P}_2(\omega)$.

In the most favourable configuration when the molecule is on the surface of the sphere ($r' = a$) and the polarization of the incident and scattered wave is perpendicular to the scattering
plane, the Raman enhancement factor $G$ for the adsorbed molecule is given by Kerker et al [16] as

$$G = 5\left| (1 + 2g_o)(1 + 2g) \right|^2 \quad (2.19).$$

When a sphere is entirely covered with adsorbed molecules, one must extend this analysis by averaging the Raman scattered light emanating from every molecule. Kerker et al [16] and Wang et al [17] have performed this averaging with the assumption that each admolecule to be an oscillating dipole normal to the surface. This yields the result,

$$G = \left| (1 + 2g)(1 + 2g_o) \right|^2 \quad (2.20)$$

independent of the choice of polarization direction of the incident or scattered light.

Now, let us focus to the eqn. (2.19) which is the expression for the enhancement when a single molecule is adsorbed on the sphere. Here, the quantity $g$ (or $g_o$) becomes large when $\text{Re} (\epsilon)$ approaches $-2$. This is precisely the condition for the excitation of localized surface plasmons in the sphere. When that condition obtains, eqn. (2.19) is dominated by the $g.g_o$ term and $G$ becomes

$$G = 80\left| g.g_o \right|^2 \quad (2.21).$$
Hence according to this model, large SERS signals are expected when both the frequency of the incident and Raman scattered beams approaches the surface-plasmon resonance conditions. In this case the quantity $G$ becomes proportional to 

$$[ \frac{\epsilon' - 1}{\epsilon''} ]^4 \text{ i.e.}$$

$$G \propto \frac{\epsilon' - 1}{\epsilon''} \quad (2.22)$$

where $\epsilon'$ and $\epsilon''$ are respectively, Re ( $\epsilon$ ) and Im ( $\epsilon$ ). Hence the metals which provide the greatest enhancement, according to this model, are those that have small $\epsilon''$ values and large $\epsilon'$ values at the frequency at which Re ( $\epsilon$ ) = -2. This condition immediately brands the alkali metals (gr. Ia) and the coinage metal (gr. Ib) as good enhancers, producing $G$ values in excess of $10^5$.

Lastly, the size of the particle is an important factor for observing the enhancement. In the electromagnetic theory of SERS observed from molecules adsorbed on spherical metal particles, a strong enhancement will be observed when the particle size remains smaller than the exciting wavelength. It should be mentioned that for larger spherical particles, the enhancement factor decreases due to (i) radiation damping and (ii) dynamic depolarization i.e. the partially destructive interference between radiation emitted at different points of the particle.
References

8. M. Moskovits; Rev. of Mod. Phys. 57 783 (1985).