A Developed Identities for the Enhancement Factor, the Spectral Variable and the Dissipation Parameter for Raman Bands From Semicontinuous Metal Films

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The behavior of enhanced Raman scattering for Raman active molecules on metallic surfaces have been investigated in view of a developed identities for the enhancement factors G^{Rs}, the spectral variable X, and the dissipation parameter of a monomer δ for Raman bands. A good agreement of our results with published data indicating that our suggested identities are fruitful.

Introduction

Surface enhanced Raman scattering (SERS) is one of the most intriguing optical effects [1,2]. However the most effective SERS systems are collections of interacting particles [2]. A fractal cluster is a system of interacting material particles called monomers. Fractals are particles in colloidal solutions, rough surfaces, disordered layers on surfaces [3]. The fractal excitation coherence length (L) within which the excitation of monomers are strongly correlated is limited by $R_o << L << R_c$, where R_o<, is a characteristic separation between nearest monomers, and R_c is the total radius of the cluster [3,4].

The aim of the present article is to develop identities to obtain the parameters G^{Rs}, X and δ for Raman bands of Raman active molecules on metallic surfaces.

Theory: We now deal to derive an identity for the enhancement factor G^{Rs} for a certain Raman signal of a semicontinuous metal film. Since the Raman active molecules are assumed to be uniformly distributed over the film. In this case G^{Rs} is equal to the ratio of the integrated band intensity of the considered signal I_R to that in the absence of metal grains $I_R°$ [1,5].

$$\therefore G^{Rs} = I_R / I_R{}^o$$

Since the major contribution to the enhancement is understood to originate from the large local fields that arise from optical excitation of surface plasmons [1,2]. The resulted local conductivity of the film takes either the metallic values $\sigma_{\mathbf{m}}$ on the metal grains or the dielectric values $\sigma_{\mathbf{d}}$ outside the metal grains inwhich $\sigma_{\mathbf{m}} >> \sigma_{\mathbf{d}}$. In this case [5]: $\sigma_{\mathbf{m}} = i\, \varepsilon_m\, \omega/4\pi$, $\sigma_d = i\, \varepsilon_d\, \omega/4\pi$, and ω: is the frequency of the incident wave.

A respective dependence of I_R, I_R° on $\sigma_{\mathbf{m}}$ and $\sigma_{\mathbf{d}}$ [5] has the consequence that

$$G^{RS}_{cal} \text{ depends on the optical quantity } \frac{\varepsilon^2_{m_1}}{\varepsilon_d \varepsilon_{m_2}} \qquad \varepsilon_m = \varepsilon_{m1} + i\, \varepsilon_{m2}$$

ε_m: The dielectric const, of the metal film.

Since G^{Rs} depends on the local fields which in turn depend on the external field (or the excitation frequency v_{ex}) [5, 6]. Inaddition the molecular transition frequency Δv_{mn} between two adjacent vibrational states (within the molecule in its electronic ground state) of respective quantum numbers m,n [7, 8, 9] is defined as:

$$\therefore \Delta v_{mn} = v_{ex} - v_{st}$$

v_{st}: The frequency of the Stokes mode (which is a Raman mode with a scattered frequency < v_{ex}) Furthermore the surface palsmon modes -in which the enhancement process must be affected - are very sensitive to any variations on the surface boundary metal/ dielectric whereby a limited infinitesimal density of these modes occurs around a unit frequency term I_v [10].
The above demonstrations have the consequence that G^{Rs} depends on the parameter P_v

$$P_v = \frac{\Delta v\, mn}{I_v}$$

Consequently G^{Rs} could be expressed as: $G^{RS} = \frac{\varepsilon^2_{m1} p_v}{\varepsilon_d\, \varepsilon_{m2}}$ (1)

Before dealing with an identity for the parameter X we must first of all define it, through the relation [2,3]

$$1/x_o = -(X + i\delta) \qquad (2)$$

x_o: Is the polarizability of a monomer on the investigated metal film. As shown below in Figs. (1,2) a continuous increase of G^{Rs} with increasing λ corresponding to continuous decrease of the dissipation factor δ as well as a decrease of the damping process of the surface plasma waves [15,16]. Hence the spectral variable X could be then postulated in a way taken into account the mechanism of the propagation of the surface plasma waves.

In this case, the surface waves propagated along the boundary metal/dielectric are localized waves transport no energy away from the boundary [15,17]. In addition the surface fields decay exponentially normal to the surface inside and outside the plasma [18,19]. Notice that the parameters X and δ are multiplied by R_o^3 to give dimensionless quantities [2] - From the above demonstrations $\boldsymbol{R_0^3}|X|$ could be represented as:

$$\boldsymbol{R_0^3}|X| = A\exp \frac{(h\omega - B)}{I} \text{ - I} = 1 \text{ eV} \qquad (3)$$

A: Is a damping parameter

$A = \sqrt{R_0^3\ \delta}$

B: Is an energetic parameter its behavior is shown in Fig. (4) as a function of λ. A maximum value of B(3.195 eV) is observed near the region of interband transitions for silver ($\lambda \sim 350$ nm). A continuous decrease of B with increasing λ whereas a negative values of B at $\lambda \geq 600$ nm may be due to abound energy states near the region of the surface plasmon resonance condition which is accepted [3,16,17].

In order to obtain experimental values of $\boldsymbol{R_0^3}|X|$, a two identities of both $\boldsymbol{R_0^3}|X|$, and $\boldsymbol{R_0^3}\ \delta$ have been derived from eq. 2 [2,3], whereas $\mathcal{X}_o$ is given by [2]:

$$\mathcal{X}_o = \boldsymbol{R_m^3}\ (\varepsilon_m - \varepsilon_d) / (\varepsilon_m + 2\varepsilon_d) \qquad (4)$$

R_m: Is the radius of the monomer.

Assuming $R_o \sim R_m$, one then obtains:

$$\boldsymbol{R_o^3}|X| \approx \left[\frac{\varepsilon_{m1} + 3.54}{\varepsilon_{m1} - 1.77}\right] \qquad (5)$$

$$\boldsymbol{R_0^3}\ \delta = \frac{5.31\ \varepsilon_{m2}}{(\varepsilon_{m1} - 1.77)2 + \varepsilon^2{}_{m2}} \qquad (6)$$

Consequently:

$$\langle \boldsymbol{R_0^3} |X| \rangle exp \approx \left| \frac{\left(\sqrt{R_0^3\,\delta}\right)_{exp}^{(\varepsilon_{m1}+3.54)}}{\sqrt{5.31\,\varepsilon_{m2}}} \right| \qquad (7)$$

A calculated values of G^{Rs}, δ and X could be obtained by considering the Raman band Δv_{mn} = 1400 cm^{-1} for adsorbed citrate on colloidal silver - for the boundary Ag/water ε_d=1.77 [13] whilst the values of ε_{m1}, ε_{m2} were obtained from [14] - Hence using eq. 1 one obtains different values of G^{Rs} for different excitation wavelengths.

Fig. (1) illustrates the relation between log G^{RS} and λ using our calculated values of G^{RS} and other values of published data [13,20] The calculated as well as the experimental values of $\boldsymbol{R_0^3}\ \delta$ could be obtained from the corresponding values of G^{RS} using the relation [2]: $\boldsymbol{R_0^3}\,\delta = 1/(G^{Rs})^{1/3}$. Fig. (2).

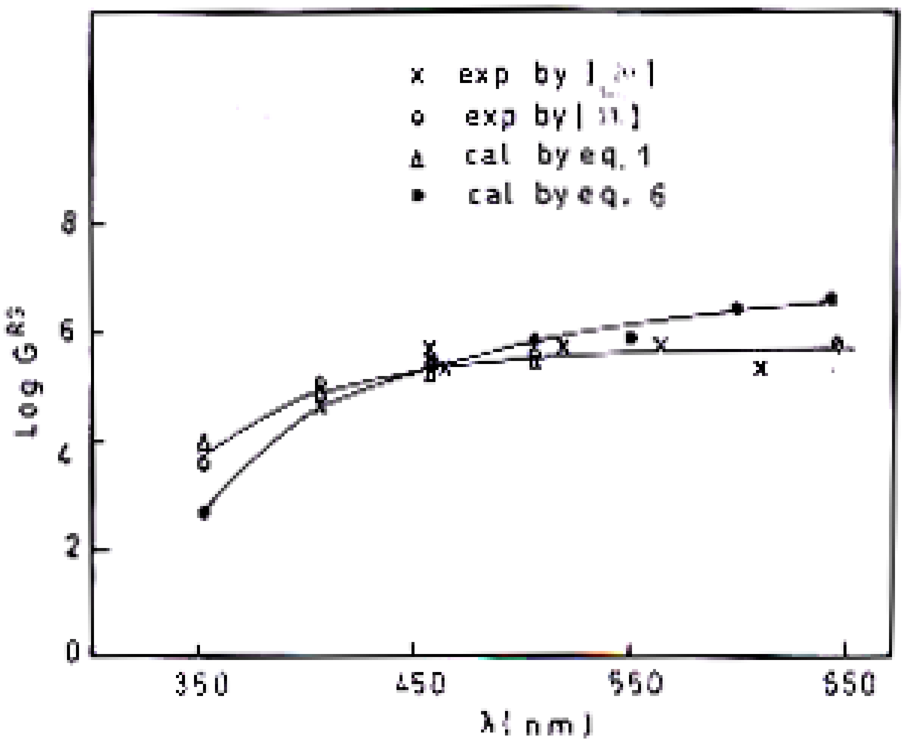

Fig.(1) : The variation of log G^{Rs} against the investigated wavelength λ

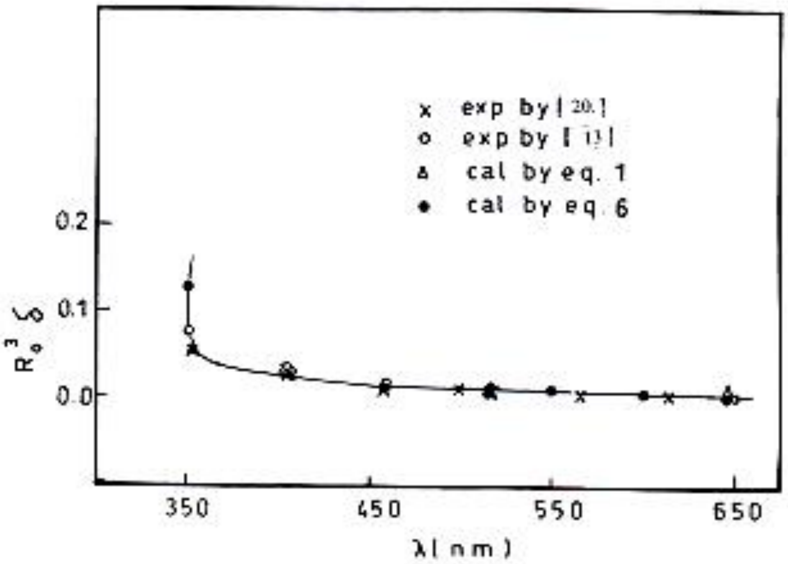

Fig.(2) : The variation of $R^3_0\,\delta$ against λ

shows the variation of $R_0^3\delta$ against λ Fig. (3) reveals the spectral variable R_0^3|x| against λ using the calculated values obtained from eqs (3,5), the experimental values by [13,20] with the help of eq. [7]. It is observed from Figs. (1-3) that the behavior for our calculated values of G^{Rs}, $R_0^3\delta$ and R_0^3|x| are in accordance with published data [2,13,20], indicating that our suggested identities 1, 3 are useful and physically meaningful. It is observed from Fig. (3) that, the condition R_0^3|x|~1 corresponds to λ ~ 6250 A^o which nearly equals the resonance wavelength of the surface plasmons λ_s(6300 A^0) for the boundary Ag/ water in accordance with the observations of [3].

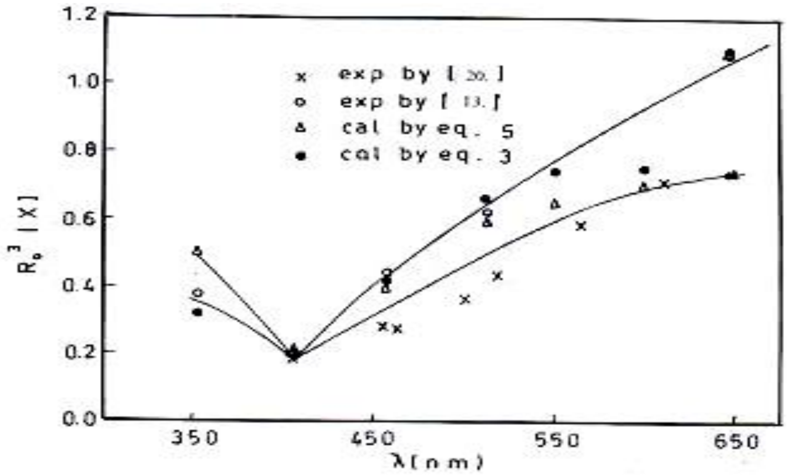

Fig.(3) : The variation of $R^3_0\,|\chi|$ against λ

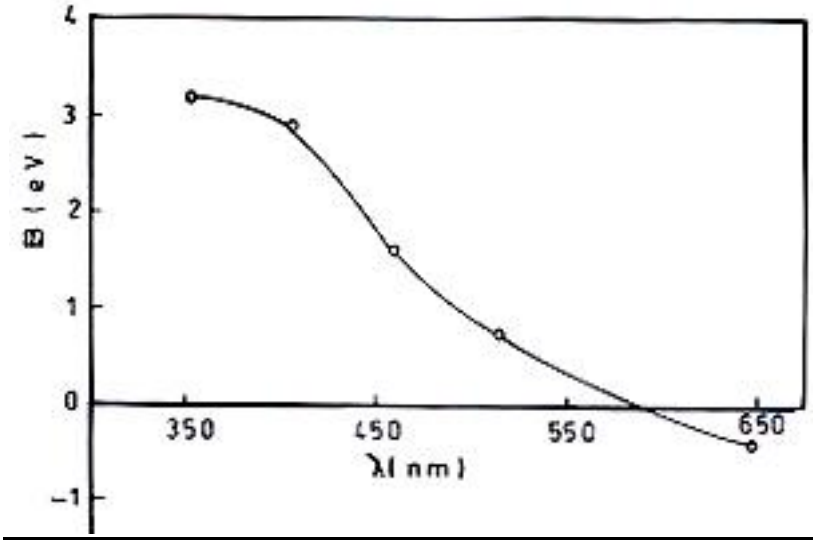

Fig.(4) : The variation of the energetic parameter B against λ

Conclusion:

A developed identities for the three parameters G^{Rs}, X and δ have been obtained. At long wavelengths an increase of G^{Rs} is accompanied with a propagation of surface plasma waves as well as with a decrease of δ. The condition $R_0^3|x|\sim 1$ corresponds to surface plasmon resonance condition.

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