

## Surface-enhanced Raman scattering in a two-oscillator electromagnetic model

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A two-oscillator model is considered to investigate the effect of a metal substrate of dielectric function  $\epsilon(\omega)$  on the Raman scattering from a molecule adsorbed on the metal surface. In the presence of the metal and an external electric field, the linear motion of the electronic and ionic oscillators in the molecule get coupled, in general. For obtaining Raman scattering at the Stokes frequency, a phenomenological nonlinear force term, which is bilinear in the oscillator amplitudes, is introduced in the equation of motion. The whole problem is considerably simplified when we use the fact that the ionic mass is much larger than the electronic mass and the ionic vibration frequency is much smaller than the electronic and optical frequencies. It is shown that because of different renormalization factors the frequency dependence of the enhancement factor  $F$ , taken to be the ratio of Raman intensity with and without the metal, is quite different from that calculated by using the familiar polarizability-derivative theory. Applying the well-known fluctuation-dissipation theorem, the new Raman line shape is also calculated to contrast it with the corresponding line shape in the absence of the metal.

### I. INTRODUCTION

The electromagnetic model involving the resonant excitation<sup>1</sup> of substrate surface-plasmon polaritons (SPP) and electron-hole pairs, together with the possible renormalization<sup>2</sup> of the molecular polarizability due to the presence of the substrate, is known to play an important role in the surface-enhanced Raman scattering (SERS) from molecules adsorbed at a metal surface. It is true that the first one or two monolayers next to the surface may have additional quantum-mechanical short-range enhancements due to specific metal-molecule bonding<sup>3</sup> and conduction-electron tunneling.<sup>4</sup> However, the electromagnetic model can describe quite accurately the classical long-range enhancement for the molecules away from the surface, and also a substantial part of the enhancement in many experimental situations involving molecules close to the surface. It is, therefore, useful to examine the dependence of the electromagnetic enhancement factor on the incident and Stokes frequencies  $\omega_I$  and  $\omega_S$ , respectively, in as much detail as possible.

Assuming a spatially nondispersive and uniform substrate dielectric function  $\epsilon(\omega)$ , a theory for the

electromagnetic enhancement factor for an arbitrary shape of the surface has been published recently by Agarwal, Jha, and Tsang.<sup>5</sup> The neglect of spatial dispersion may not be a severe restriction for the case of molecules away from the surface. However, in that paper<sup>5</sup> the Raman polarizability was calculated as the derivative of the linear electronic polarizability at the incident optical frequency  $\omega_I$  with respect to the ionic vibration amplitude  $\bar{Q}^*(\omega_0)$  from the equilibrium. This procedure is being used in most of the calculations of SERS, but it is quite well known that such a polarizability theory is correct only in the limit  $\omega_I \rightarrow \omega_S$ , i.e., in the limit in which the vibration frequency  $\omega_0 \rightarrow 0$ . Since in the electromagnetic model of SERS, one is particularly concerned with the resonances in the total enhancement factor with respect to  $\omega_I$  and  $\omega_S$ , it seems necessary to examine the situation beyond the usual polarizability-derivative approximation. For example, the renormalization of the Raman polarizability (dynamic image effect) need not depend only<sup>5</sup> on the incident frequency  $\omega_I$  [via the renormalization of the linear polarizability  $\alpha(\omega_I)$ ], but on both  $\omega_I$  and  $\omega_S$ . In order to investigate the nature of the frequency dependence of the Raman polarizability,

we consider here an exactly solvable simple two-oscillator model for SERS in which the electronic oscillator amplitude ( $\bar{x}$ ) is assumed to be coupled<sup>6</sup> to the ionic oscillator amplitude ( $\bar{Q}$ ) by a nonlinear force term which is bilinear in these amplitudes.

In Sec. II we introduce our two-oscillator model and discuss how, through the use of the fluctuation-dissipation theorem, one usually obtains the power spectrum of the Stokes radiation in terms of the frequency spectrum<sup>7</sup> of the fluctuation  $\langle |Q|^2 \rangle_\omega$  in the vibration amplitude. In the presence of the metal with an arbitrary shape of the surface and internal dielectric function  $\epsilon(\omega)$ , we then show the final results can be obtained by solving the coupled-oscillator equation in the presence of the local electric field  $\vec{E}^{(M)}(\omega_l)$  at the molecular site, together with relevant Maxwell's equations for the electromagnetic fields. Because of the coupling of the oscillators due to the general bilinear force term and because of the presence of the metal substrate, the general solution is quite complicated. However, in Sec. III we show that the results may be simplified considerably since the ionic mass  $M$  is much greater than the electronic mass  $m$ , and since  $\omega_0 \ll \omega_l, \omega_s$ . We then find that the renormalization factor indeed involves both  $\omega_l$  and  $\omega_s$ , and depending upon the value of the distance  $d$  of the molecule from the metal surface, the frequency dependence of the total enhancement factor may be quite different from that calculated using the polarizability-derivative theory.<sup>5</sup> As expected, the detailed shape of the Raman line is shown explicitly to be affected by the presence of the metal. To compare with earlier calculations, we briefly discuss our results in Sec. IV for the special case of a molecule adsorbed on a small metallic sphere.

## II. THE TWO-OSCILLATOR MODEL AND MATHEMATICAL FORMULATION FOR SERS

In the absence of any explicit coupling to the electronic motion, in the harmonic approximation we can describe the ionic motion by its normal modes. For a single mode, with an effective mass  $M$  and effective charge  $Z$ , the normal-model amplitude  $\bar{Q}$  satisfies the equation of motion

$$M(\ddot{\bar{Q}} + \omega_0^2 \bar{Q} + \gamma \dot{\bar{Q}}) = Z\vec{E}^{(M)}(t) \quad (1)$$

in the presence of a "local" field  $\vec{E}^{(M)}(t)$  at the molecular site. Here,  $\omega_0$  and  $\gamma$  are the experimentally observed "physical" resonance frequency and

damping of the mode under consideration in an isolated molecule, i.e., it includes the effect of the self-field on the corresponding "bare" quantities. In the absence of the metal, the local field  $\vec{E}^{(M)}(t)$  can be identified immediately with the incident field  $\vec{E}^{\text{inc}}$ , and the frequency spectra of fluctuations in Cartesian amplitudes  $Q_i$  are obtained from the generalized quantum-mechanical Nyquist formula<sup>7</sup>

$$\begin{aligned} \langle Q_i^* Q_j \rangle_\omega^0 &= \langle Q_i Q_j^* \rangle_\omega^0 \\ &= \frac{\hbar}{\pi} [n(\omega) + 1] \text{Im}[T_{ij}^{(0)}(\omega)] . \end{aligned} \quad (2)$$

Here,  $n(\omega)$  is the thermal factor

$$n(\omega) = \left[ \exp \left[ \frac{\hbar\omega}{k_B T} \right] - 1 \right]^{-1} \quad (3)$$

and the response function matrix (defined always as the displacement of coordinate  $i$  due to a unit external force of frequency  $\omega$  acting on the coordinate  $j$ ) is given by

$$T_{ij}^{(0)}(\omega) = \frac{Q_i(\omega)}{Z E_j^{\text{inc}}(\omega)} = \frac{\delta_{ij}}{M(\omega_0^2 - \omega^2 - i\omega\gamma)} . \quad (4)$$

The mean-square value of the fluctuating variable  $Q_i$  is given by

$$\langle Q_i^2(t) \rangle^0 = \int_{-\infty}^{\infty} d\omega \langle |Q_i|^2 \rangle_\omega^0 . \quad (5)$$

As already hinted at, in the presence of the metal substrate the local field  $\vec{E}^{(M)}$  is not the incident field  $\vec{E}^{\text{inc}}$ , and we will have to recalculate the modified fluctuation spectrum of  $\bar{Q}$  later in the paper.

The independent electronic motion in our model is described by an anisotropic harmonic oscillator of mass  $m$  and charge  $e$ . The Cartesian components of the electronic amplitude  $\bar{x}$  satisfy the equation of motion

$$m(\ddot{x}_i + \omega_e^2 d_{ij} x_j + \Gamma_{ij} \dot{x}_j) = e E_i^{(M)}(t) \quad (6)$$

in the presence of the local field  $\vec{E}^{(M)}$ . Here, and in what follows, unless explicitly stated otherwise, the summation over repeated indices is always implied. Again, electronic frequencies and damping are physical quantities observed in isolated molecule, and therefore,  $E_j^{(M)}$  is not the total field. Further, we assume  $\sum_i d_{ii} = 3$ .

The total induced dipole moment in the molecule involving both kinds of oscillators is given by

$$\vec{p} = e\bar{x} + Z\bar{Q} . \quad (7)$$

Since harmonic forces are already taken into account in writing Eqs. (1) and (6), the explicit non-

linear coupling between the two oscillators can be obtained from the lowest-order trilinear potential function<sup>6</sup>

$$V^{(3)}(\vec{x}, \vec{Q}) = A_{ijk} Q_i Q_j Q_k + B_{ijk} Q_i Q_j x_k + C_{ijk} x_i x_j Q_k + D_{ijk} x_i x_j x_k. \quad (8)$$

In terms of a six-dimensional generalized displacement vector defined by

$$\psi = \begin{bmatrix} x \\ Q \end{bmatrix}, \quad x = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}, \quad Q = \begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \end{bmatrix}, \quad (9a)$$

i.e.,

$$\begin{aligned} \psi_1 = x_1, \quad \psi_2 = x_2, \quad \psi_3 = x_3, \\ \psi_4 = Q_1, \quad \psi_5 = Q_2, \quad \psi_6 = Q_3, \end{aligned} \quad (9b)$$

the potential function can be rewritten in the form

$$V^{(3)}(\psi) = \frac{1}{3} \theta_{\lambda\mu\nu} \psi_\lambda \psi_\mu \psi_\nu. \quad (10)$$

As a convention we will use Greek indices running from one to six for the six-dimensional vector, and Latin indices for individual three-dimensional displacement vectors.

The nonlinear force term for the equation of motion for the amplitude  $\psi_\lambda$  can be obtained from Eq. (10) as

$$f_\lambda^{\text{NL}} = -\frac{\partial V^{(3)}}{\partial \psi_\lambda} = -\theta_{\lambda\mu\nu} \psi_\mu \psi_\nu. \quad (11)$$

Although the above expression is more general, for the Raman scattering calculation only the term with the coefficient  $C_{ijk}$  in Eq. (8) is the most relevant one in the weak-coupling theory. In addition, for  $M \gg m$  and  $\omega_0 \ll \omega_e, \omega_l$ , only the corresponding force term in the electronic motion will be important. Thus in the simplified calculation to be described in the next section the coupling will be represented by the additional force on the electronic motion

$$F_i^{\text{NL}} = -2C_{ijk} x_j Q_k \quad (12)$$

on the right-hand side of Eq. (6), with no additional force for the ionic motion.

Before proceeding further, we must find an explicit relation between the local field  $\vec{E}^{(M)}$  acting at the molecular site and the incident field  $\vec{E}^{\text{inc}}(\omega_l)$  of frequency  $\omega_l$ , in the presence of both the metal and the molecule. For this we will introduce the field  $\vec{E}^{(0)}$ , defined as the external field anywhere in the *absence of the molecule* but in the presence of the met-

al, and the total field  $\vec{E}$  anywhere in the presence of both the metal and the molecule, which includes the self-field. For our purpose, the metal having an arbitrary surface shape is represented by the dielectric function

$$\epsilon(\vec{r}, \omega) = \begin{cases} \epsilon(\omega) & \text{inside the metal} \\ 0 & \text{outside the metal} \end{cases} \quad (13)$$

In the *absence* of the molecule the external field  $\vec{E}^{(0)}(\vec{r}_0, \omega_l)$  at the molecular site ( $\vec{r} = \vec{r}_0$ ) can be obtained by solving Maxwell's equations

$$\left[ -\nabla^2 + \vec{\nabla} \vec{\nabla} \cdot - \epsilon(\vec{r}, \omega_l) \frac{\omega_l^2}{c^2} \right] \vec{E}^{(0)}(\vec{r}, \omega_l) = 0 \quad (14)$$

inside as well as outside the metal, and by matching the tangential components of the electric and magnetic fields at the surface in the presence of the incident field  $\vec{E}^{\text{inc}}(\vec{r}, \omega_l)$ . Let us assume that this problem is solved, and that it leads to the Fresnel-type factors  $L_{ij}$  (which will depend on the explicit shape of the surface, etc.) defined by

$$E_i^{(0)}(\vec{r}_0, \omega_l) = L_{ij}(\vec{r}_0, \omega_l) E_j^{\text{inc}}(\vec{r}_0, \omega_l) \quad (15)$$

for the solution outside the metal.

In the presence of the molecule the local field  $\vec{E}^{(M)}$  is not the external local field  $\vec{E}^{(0)}$  acting at the molecular site. The relationship between these two can, however, be obtained<sup>5</sup> by first introducing the total field  $\vec{E}(\vec{r}, \omega_l)$  that satisfies Maxwell's equations

$$\begin{aligned} \left[ -\nabla^2 + \vec{\nabla} \vec{\nabla} \cdot - \epsilon(\vec{r}, \omega_l) \frac{\omega_l^2}{c^2} \right] \vec{E}(\vec{r}, \omega_l) \\ = \frac{4\pi\omega_l^2}{c^2} \vec{p}(\omega_l) \delta(\vec{r} - \vec{r}_0), \end{aligned} \quad (16)$$

where  $\vec{p}(\omega_l)$  is the induced dipole moment in the molecule. In terms of the well-known<sup>5</sup> free-space Green's function  $\underline{G}_0$  defined by

$$\begin{aligned} \left[ -\nabla^2 + \vec{\nabla} \vec{\nabla} \cdot - \frac{\omega_l^2}{c^2} \right] \underline{G}_0(\vec{r}, \vec{r}_0, \omega_l) \\ = 4\pi\delta(\vec{r} - \vec{r}_0) \underline{I}, \end{aligned} \quad (17)$$

and the full Green's function  $\underline{G}$  defined by

$$\begin{aligned} \left[ -\nabla^2 + \vec{\nabla} \vec{\nabla} \cdot - \epsilon(\vec{r}, \omega_l) \frac{\omega_l^2}{c^2} \right] \underline{G}(\vec{r}, \vec{r}_0, \omega_l) \\ = 4\pi\delta(\vec{r} - \vec{r}_0) \underline{I}, \end{aligned} \quad (18)$$

where  $\underline{I}$  is a unit dyadic, one has<sup>5</sup>

$$\vec{E}(\vec{r}, \omega_l) = \vec{E}^{(0)}(\vec{r}, \omega_l) + \frac{\omega_l^2}{c^2} \underline{G}(\vec{r}, \vec{r}_0, \omega_l) \cdot \vec{p}(\omega_l), \quad (19)$$

$$\vec{E}^{(M)}(\vec{r}, \omega_l) = \vec{E}^{(0)}(\vec{r}, \omega_l) + \frac{\omega_l^2}{c^2} \underline{G}^{(s)}(\vec{r}, \vec{r}_0, \omega_l) \cdot \vec{p}(\omega_l), \quad (20)$$

where the additional Green's function due to the metal surface is defined by

$$\underline{G}^{(s)} = \underline{G} - \underline{G}_0. \quad (21)$$

Note that the induced dipole moment  $\vec{p}(\omega_l)$  is related to  $e\vec{x}(\omega_l) + Z\vec{Q}(\omega_l)$  via Eq. (7), and that once the geometry of the metal surface is known, we can assume  $\vec{E}^{(0)}$  and  $\underline{G}$ , and hence  $\vec{E}^{(0)}$  and  $\underline{G}^{(s)}$ , to be known in principle. In other words, the unknown local field  $\vec{E}^{(M)}$  in Eqs. (1) and (6) can be eliminated in terms of  $\vec{x}$  and  $\vec{Q}$ , and in terms of known functions  $\vec{E}^{(0)}$  and  $\underline{G}^{(s)}$ .

Now we are in a position to solve the two-oscillator problem in the presence of the metal. Eliminating  $\vec{E}^{(M)}$  from the equations of motions (1) and (6) in favor of  $\vec{E}^{(0)}$  or  $\vec{E}^{\text{inc}}$  via Eqs. (20) and (7), and by adding the bilinear force term (11), it is straightforward to rewrite these equations of motion. In the six-dimensional space of the generalized displacement vector  $\psi$ , the Fourier transform of the combined equations of motion, written in the matrix notation, has the form

$$\Lambda(\Omega)\psi(\Omega) = F^{(0)}(\Omega) + f^{\text{NL}}(\Omega). \quad (22)$$

Here,  $F^{(0)}(\Omega)$  is the six-dimensional force vector

$$F^{(0)}(\Omega) = \begin{bmatrix} eE^{(0)}(\Omega) \\ ZE^{(0)}(\Omega) \end{bmatrix}, \quad (23)$$

$$E^{(0)}(\Omega) = \begin{bmatrix} E_1^{(0)}(\vec{r}_0, \Omega) \\ E_2^{(0)}(\vec{r}_0, \Omega) \\ E_3^{(0)}(\vec{r}_0, \Omega) \end{bmatrix},$$

and  $f^{\text{NL}}(\Omega)$  is the Fourier transform of the nonlinear force term (11). Here, the  $6 \times 6$  matrix  $\Lambda$  can be written in terms of four  $3 \times 3$  matrices as

$$\Lambda(\Omega) = \begin{bmatrix} \Lambda^{XX}(\Omega) & \Lambda^{XQ}(\Omega) \\ \Lambda^{QX}(\Omega) & \Lambda^{QQ}(\Omega) \end{bmatrix}, \quad (24)$$

$$\Lambda_{ij}^{XX}(\Omega) = m(-\Omega^2\delta_{ij} + \omega_e^2 d_{ij} - i\Omega\Gamma_{ij}) - \frac{e^2\Omega^2}{c^2} G_{ij}^{(s)}(\Omega), \quad (25)$$

$$\Lambda_{ij}^{XQ}(\Omega) = \Lambda_{ij}^{QX}(\Omega) = -\frac{Ze\Omega^2}{c^2} G_{ij}^{(s)}(\Omega), \quad (26)$$

$$\Lambda_{ij}^{QQ}(\Omega) = M(-\Omega^2 + \omega_0^2 - i\Omega\gamma)\delta_{ij} - \frac{Z^2\Omega^2}{c^2} G_{ij}^{(s)}(\Omega), \quad (27)$$

where we have used the convention

$$\underline{G}^{(s)}(\vec{r}_0, \vec{r}_0, \Omega) \equiv \underline{G}^{(s)}(\Omega) \quad (28)$$

at the molecular site.

It must be noted that due to the presence of the metal two types of oscillators become coupled, even in the absence of the nonlinear force term. Also, the resonance conditions are changed due to the presence of the term proportional to  $\underline{G}^{(s)}$  in Eqs. (25) and (27). In the absence of the metal,  $\underline{G}^{(s)}$  of course vanishes identically, by definition.

First, let us consider the linear problem in the absence of the nonlinear force term in (22). For an incident field  $\vec{E}^{\text{inc}}(\omega_l)$  varying with the frequency  $\omega_l$ , Eq. (22) then immediately leads to the solution for induced (linear) displacements

$$\psi(\omega_l) = \begin{bmatrix} x(\omega_l) \\ Q(\omega_l) \end{bmatrix} = \Lambda^{-1}(\omega_l) F^{(0)}(\omega_l). \quad (29)$$

The frequency spectrum of the fluctuation in generalized displacements is obtained by calculating the response function  $T_{\mu\nu}(\omega)$  as the displacement  $\psi_\mu(\omega)$  due to a unit external force of frequency  $\omega$  at the molecular site acting on the index  $\nu$ , and then using the Nyquist formula. We find

$$\langle \psi_\mu^* \psi_\nu \rangle_\omega = \langle \psi_\mu \psi_\nu^* \rangle_\omega = \frac{\hbar}{\pi} [n(\omega) + 1] \text{Im}[\Lambda^{-1}(\omega)]_{\mu\nu}. \quad (30)$$

In the linear problem the displacement induced by the incident field, and hence the induced dipole moment  $\vec{p}$ , vary with the frequency  $\omega_l$  of the incident field. To obtain a dipole moment at a frequency other than  $\omega_l$ , which would give rise to Raman scattering, we must include the nonlinear force term  $f^{\text{NL}}$ , defined by Eq. (11), in the equation of motion (22). Since there is no external field at the Stokes frequency,  $\omega_s = \omega_l - \omega$  and  $F^{(0)}(\omega_s) = 0$  in (22). In the weak-coupling theory the Fourier transform of (22) at  $\omega_s$  can then be written as

$$\Lambda_{\lambda\delta}(\omega_s)\psi_\delta(\omega_s) = -2\theta_{\lambda\mu\nu}\psi_\mu(\omega_l)\psi_\nu^*(\omega), \quad (31)$$

$$\omega_s = \omega_l - \omega,$$

where  $\psi_\mu(\omega_l)$  is the linear displacement obtained in Eq. (29) and where  $\psi_\nu(\omega)$  is the fluctuating field whose correlations are given by Eq. (30). The above equation can be solved in the form

$$\psi_\delta(\omega_S) = -2[\Lambda^{-1}(\omega_S)]_{\delta\lambda} \theta_{\lambda\mu\nu} \psi_\mu(\omega_l) \psi_\nu^*(\omega) \quad (32)$$

to obtain the Cartesian components ( $i=1,2,3$ ) of the Raman dipole moment

$$p_i(\omega_S) = -2\{e[\Lambda^{-1}(\omega_S)]_{i\lambda} + Z[\Lambda^{-1}(\omega_S)]_{i+3,\lambda}\} \theta_{\lambda\mu\nu} \psi_\mu(\omega_l) \psi_\nu^*(\omega) \quad (33)$$

$$\equiv S_{i\mu\nu}(\omega_S) [\Lambda^{-1}(\omega_l)]_{\mu\delta} F_\delta^{(0)}(\omega_l) \psi_\nu^*(\omega). \quad (34)$$

In the presence of the metal the above Raman dipole moment (when inserted in Maxwell's equations) gives the Stokes radiation field in the form

$$\vec{E}(\omega_S) = \frac{\omega_S^2}{c^2} \underline{G}(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_S) \cdot \vec{p}(\omega_S). \quad (35)$$

This determines the frequency spectrum of the scattered radiation in the form

$$|\vec{E}(\omega_S)|^2 = \frac{\omega_S^4}{c^4} G_{ij}(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_S) G_{ik}^*(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_S) S_{j\mu\nu}(\omega_S) S_{k\mu'\nu'}^*(\omega_S) [\Lambda^{-1}(\omega_l)]_{\mu\delta} [\Lambda^{-1}(\omega_l)]_{\mu'\delta'}^* \times F_\delta^{(0)}(\omega_l) F_{\delta'}^{(0)}(\omega_l) \langle \psi_\nu^* \psi_{\nu'} \rangle_\omega. \quad (36)$$

Here  $S_{i\mu\nu}$  is defined via Eqs. (33), (34), and (23),  $F^{(0)}(\omega_l)$  is related to the incident field via Eqs. (23) and (15), and the quantum fluctuation correlation function  $\langle \psi_\nu^* \psi_{\nu'} \rangle_\omega$  is obtained from Eq. (30). The enhancement factor for SERS at a given frequency  $\omega_S$  is obtained from Eq. (36) by comparing it to the corresponding expression in the absence of the metal, i.e., with  $\vec{G}^{(s)} \rightarrow 0$  and  $\vec{E}^{(0)} \rightarrow \vec{E}^{\text{inc}}$ . We will discuss a simplified version of the above general result in the next section.

### III. ENHANCEMENT FACTOR FOR HEAVY IONIC MASS

Until now, we have not assumed anything about the nature of the mass ratio  $M/m$  or about the frequency ratio  $\omega_0/\omega_e$ . We will consider this important point in this section.

In the absence of the metal,  $\vec{E}^{(M)} \rightarrow \vec{E}^{\text{inc}}$ , and the linear equations of motions (1) and (6) are uncoupled. In such a case, the induced electronic and ionic dipole moments induced by  $\vec{E}^{\text{inc}}(\Omega)$  have the form

$$e\vec{x}(\Omega) = \frac{e^2}{m} [(-\Omega^2 \underline{I} + \omega_e^2 \underline{d} - i\Omega \underline{\Gamma})^{-1}] \cdot \vec{E}^{\text{inc}}(\Omega), \quad (37)$$

$$Z\vec{Q}(\Omega) = \frac{Z^2}{M} (-\Omega^2 + \omega_0^2 - i\Omega\gamma)^{-1} \vec{E}^{\text{inc}}(\Omega), \quad (38)$$

in the matrix notation. These two expressions define the electronic and ionic physical polarizabilities, respectively, of an isolated molecule. In the matrix notation, it has the form

$$\underline{\alpha}(\Omega) = \frac{e^2}{m} (-\Omega^2 \underline{I} + \omega_e^2 \underline{d} - i\Omega \underline{\Gamma})^{-1}, \quad (39)$$

$$\underline{\alpha}_{\text{ion}}(\Omega) = \frac{Z^2}{M} (-\Omega^2 + \omega_0^2 - i\Omega\gamma)^{-1} \underline{I}, \quad (40)$$

in our model. In fact, in terms of the inverse matrices

$$\underline{\alpha}^{-1}(\Omega) = \frac{m}{e^2} (-\Omega^2 \underline{I} + \omega_e^2 \underline{d} - i\Omega \underline{\Gamma}), \quad (41)$$

$$\underline{\alpha}_{\text{ion}}^{-1}(\Omega) = \frac{M}{Z^2} (-\Omega^2 + \omega_0^2 - i\Omega\gamma) \underline{I}, \quad (42)$$

which may be more readily available, the general matrix  $\Lambda(\Omega)$  of Eq. (24) can be rewritten in the more convenient form

$$\Lambda(\Omega) = \begin{pmatrix} e^2 \underline{\alpha}^{-1}(\Omega) - \frac{e^2 \Omega^2}{c^2} \underline{G}^{(s)}(\Omega) & -Ze \frac{\Omega^2}{c^2} \underline{G}^{(s)}(\Omega) \\ -Ze \frac{\Omega^2}{c^2} \underline{G}^{(s)}(\Omega) & Z^2 \underline{\alpha}_{\text{ion}}^{-1}(\Omega) - \frac{Z^2 \Omega^2}{c^2} \underline{G}^{(s)}(\Omega) \end{pmatrix}. \quad (43)$$

Here, each term, of course, represents a  $3 \times 3$  matrix.

Now, let us consider the physical fact that  $M \gg m$ , and that the ionic resonance frequency  $\omega_0 \ll \omega_e, \omega_l, \omega_s$ , the optical frequencies. Since  $Z$  and  $e$  are of the same order, it is clear from Eqs. (37) and (38) that the induced ionic displacement can be neglected in comparison to the induced electronic displacement if  $\Omega \gg \omega_0$ . In other words, the optical fields directly couple only to the electrons. For  $\Omega \sim \omega_e, \omega_s$ , only  $x_i(\Omega)$  can be kept in the equations of motion;  $Q(\Omega)$  is important only at low frequencies  $\Omega \sim \omega_0$ .

Because of the great simplification discussed above, we can neglect terms proportional to  $\vec{Q}(\omega_l)$  and  $\vec{Q}(\omega_s)$  everywhere. The solution for the linear displacements given by Eq. (29) then simplifies immediately to

$$\vec{x}(\omega_l) = \frac{1}{e} \left[ \underline{\alpha}^{-1}(\omega_l) - \frac{\omega_l^2}{c^2} \underline{G}^{(s)}(\omega_l) \right]^{-1} \cdot \vec{E}^{(0)}(\omega_l), \quad (44)$$

$$\vec{Q}(\omega_l) \simeq 0 \quad (45)$$

in the tensor notation. Again, as explained in Sec. II, if we keep only the nonlinear force term (12) in the electronic equation of motion, at Stokes frequency we find

$$\vec{x}(\omega_s) = -\frac{2}{e^2} \left[ \underline{\alpha}^{-1}(\omega_s) - \frac{\omega_s^2}{c^2} \underline{G}^{(s)}(\omega_s) \right]^{-1} \cdot \underline{C} : \vec{x}(\omega_l) \vec{Q}^*(\omega), \quad (46)$$

$$\vec{Q}(\omega_s) \simeq 0, \quad (47)$$

in place of the more general expression (32). This leads to the Raman dipole moment

$$\vec{p}(\omega_s) = -\frac{2}{e^2} \underline{N}^{-1}(\omega_s) \cdot \underline{\alpha}(\omega_s) \cdot \underline{C} : \underline{N}^{-1}(\omega_l) \cdot \underline{\alpha}(\omega_l) \cdot \vec{E}^{(0)}(\omega_l) \vec{Q}^*(\omega), \quad (48)$$

where  $\underline{N}$  is the renormalization tensor (matrix)

$$\underline{N}(\Omega) \equiv \left[ \underline{I} - \frac{\Omega^2}{c^2} \underline{\alpha}(\Omega) \cdot \underline{G}^{(s)}(\Omega) \right]. \quad (49)$$

Note that the expression (48) contains the renormalization denominators both at  $\omega_l$  and  $\omega_s$ . The above expression for the Raman dipole moment can be compared with the Raman polarizability for an isolated molecule (in the same model)

$$\vec{p}^{(0)}(\omega_s) = -\frac{2}{e^2} \underline{\alpha}(\omega_s) \cdot \underline{C} : \underline{\alpha}(\omega_l) \cdot \vec{E}^{\text{inc}}(\omega_l) \vec{Q}^{(0)*}(\omega). \quad (50)$$

In our simple model, for  $\omega \ll \omega_l, \omega_s$ , the frequency spectra of the correlations  $\langle Q_i^* Q_j \rangle_\omega$  are the only ones to be considered. In the absence of the cross terms in (43) this may be obtained directly from the equation of motion

$$\left[ M(-\omega^2 + \omega_0^2 - i\omega\gamma) \underline{I} - \frac{Z^2 \omega^2}{c^2} \underline{G}^{(s)}(\omega) \right] \cdot \vec{Q}(\omega) = Z \vec{E}^{(0)}(\omega). \quad (51)$$

This leads to

$$\langle Q_i^* Q_j \rangle_\omega = \frac{\hbar}{\pi} [n(\omega) + 1] \times \text{Im} \left[ \left[ M(-\omega^2 + \omega_0^2 - i\omega\gamma) \underline{I} - \frac{Z^2 \omega^2}{c^2} \underline{G}^{(s)}(\omega) \right]^{-1} \right]_{ij} \quad (52)$$

Note that the correlations will remain diagonal if  $\underline{G}^{(s)}(\omega)$  is diagonal. Also, if  $(Z^2 \omega^2 / c^2) \underline{G}^{(s)}(\omega)$  is small in comparison, the nondiagonal part may be negligible. However, it must be emphasized here that because of the presence of the metal, the Raman line shape determined primarily by Eq. (52) is changed from the case of the isolated molecule. The real part of  $\underline{G}^{(s)}(\omega)$  is responsible for a possible frequency change, whereas the imaginary part determines the change in shape and width.

Since in the radiation zone the Stokes field is given by

$$\vec{E}(\omega_S) = \frac{\omega_S^2}{c^2} \underline{G}(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_S) \cdot \vec{p}(\omega_S), \quad (53)$$

the enhancement factor for the Raman scattering in the presence of the metal is given by

$$F(\omega_S) = \frac{|\underline{G}(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_S) \cdot \vec{p}(\omega_S)|^2}{|\underline{G}_0(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_S) \cdot \vec{p}^{(0)}(\omega_S)|^2}, \quad (54)$$

$$p_i(\omega_S) = R_{ijk}(\omega_S, \omega_I) E_j^{(0)}(\omega_I) Q_k^*(\omega), \quad (58)$$

$$R_{ijk}(\omega_S, \omega_I) = \frac{R_{ijk}^{(0)}(\omega_S, \omega_I)}{[1 - (\omega_S^2 / c^2) \alpha_{ii}(\omega_S) G_{ii}^{(s)}(\omega_S)] [1 - (\omega_I^2 / c^2) \alpha_{jj}(\omega_I) G_{jj}^{(s)}(\omega_I)]} \quad (59)$$

with no summations. Because of this simplification, the enhancement factor can now be obtained completely in terms of the experimentally available parameters for the isolated molecule. Note that Eq. (59) represents the renormalization of the Raman polarizability from  $\underline{R}^{(0)}$  to  $\underline{R}$ , due to the presence of the metal. The renormalization factor is symmetrical between  $\omega_I$  and  $\omega_S$ .

The net enhancement factor (54) now has the reduced form

$$F(\omega_S) = \frac{|\underline{G}(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_S) \cdot \underline{R}(\omega_S, \omega_I) : \vec{E}^{(0)}(\omega_I) Q^*(\omega)|^2}{|\underline{G}_0(\vec{r} \rightarrow \infty, \vec{r}_0, \omega_S) \cdot \underline{R}^{(0)}(\omega_S, \omega_I) : \vec{E}^{\text{inc}}(\omega_I) Q^{(0)*}(\omega)|^2}. \quad (60)$$

Because of the metal, the incident field is changed from  $\vec{E}^{\text{inc}}(\omega_I)$  to  $\vec{E}^{(0)}(\omega_I)$  at the molecular site, the Raman polarizability is renormalized from  $\underline{R}^{(0)}$  to  $\underline{R}$  [see Eq. (59)], the scattering propagator for the outgoing field is changed from  $\underline{G}_0$  to  $\underline{G} = \underline{G}_0 + \underline{G}^{(s)}$  and the frequency spectrum of the fluctuation in  $Q$

where  $p$  and  $p_0$  are obtained in our model in Eqs. (48) and (50). The above expression involves the fluctuation correlations given by (52), with and without  $\underline{G}^{(s)}(\omega)$ , in the numerator and denominator, respectively.

Instead of considering the expression (54) for arbitrary  $\underline{\alpha}$  and  $\underline{G}^{(s)}$ , it is very interesting to study the special case in which we may have a coordinate system in which  $\underline{\alpha}$  and  $\underline{G}^{(s)}$  are diagonal tensors. In such a case, it is possible to eliminate the unknown coupling tensor  $\underline{C}$  in favor of the experimentally observed Raman polarizability tensor  $R^{(0)}$  of an isolated molecule, defined by

$$p_i^{(0)}(\omega_S) = R_{ijk}^{(0)}(\omega_S, \omega_I) \times E_j^{\text{inc}}(\omega_I) Q_k^{(0)*}(\omega). \quad (55)$$

In the polarizability derivative approach, one has the connection

$$R_{ijk}^{(0)} \rightarrow \frac{\partial \alpha_{ij}(\omega_I)}{\partial Q_k^{(0)*}(\omega)}. \quad (56)$$

In our model, for  $\underline{\alpha}$  diagonal, we have

$$R_{ijk}^{(0)}(\omega_S, \omega_I) = -\frac{2}{e^2} C_{ijk} \alpha_{ii}(\omega_S) \alpha_{jj}(\omega_I), \quad (57)$$

with no summations, in terms of which the Raman dipole moment (48) can be written as

is modified. Depending on the nature of the substrate and the frequencies involved, each of the first three of these changes may contain surface-plasmon-polariton resonances, discussed in Ref. 5.

In order to get a better idea about our final expression, let us apply our formula to the simple case

of a molecule adsorbed on a small metallic sphere of radius  $a \ll c/\omega_l$ . If the origin of the coordinate system is taken to be the center of the sphere, we can define the molecular position by

$$\vec{r}_0 = r_0 \hat{z} = (a+d)\hat{z}, \quad d > 0. \quad (61)$$

For this position the local external field at the molecular site is related to the incident field by

$$\begin{aligned} \vec{E}^{(0)}(\vec{r}_0, \omega_l) \simeq & \vec{E}_{\text{inc}}(\vec{r}_0, \omega_l) + \frac{a^3}{r_0^3} g(\omega_l, a) \\ & \times [3\hat{z}(\hat{z} \cdot \vec{E}_{\text{inc}}) - \vec{E}_{\text{inc}}] \end{aligned} \quad (62)$$

$$g(\Omega, a) = \frac{\epsilon(\Omega) - 1}{\epsilon(\Omega) + 2 + \frac{12}{5}(\Omega^2/c^2)a^2}. \quad (63)$$

The above expression is valid only for small spheres

$$F^{\text{zz}}(\omega_S) = \frac{|1 + 2(a/r_0)^3 g(\omega_S, a)|^2 |1 + 2(a/r_0)^3 g(\omega_l, a)|^2}{|N^2(\omega_S, a, r_0) N^2(\omega_l, a, r_0)|} f(\omega) \quad (65)$$

where the renormalization denominator

$$N(\Omega, a, r_0) = 1 - \frac{\alpha_{\text{zz}}}{r_0^3} \sum_l \frac{l(l+1)^2(\epsilon-1)}{l+1+l\epsilon(\Omega)} \frac{a^{2l+1}}{r_0^{2l+1}} \quad (66)$$

and the ratio of the vibrational line-shape functions is given by

$$\begin{aligned} f(\omega) &= \frac{\sum_k |R_{\text{zzk}}^{(0)}|^2 \langle Q_k^* Q_k \rangle_\omega}{\sum_k |R_{\text{zzk}}^{(0)}|^2 \langle Q_k^* Q_k \rangle_\omega^0} \\ &= \frac{\sum_k |R_{\text{zzk}}^{(0)}|^2 \text{Im}[M(-\omega^2 + \omega_0^2 - i\omega\gamma) - (Z^2\omega^2/c^2)G_{kk}^{(s)}(\omega)]^{-1}}{\sum_k |R_{\text{zzk}}^{(0)}|^2 \text{Im}[M(-\omega^2 + \omega_0^2 - i\omega\gamma)]^{-1}}. \end{aligned} \quad (67)$$

We will discuss and compare our results with the earlier calculations in the next section.

#### IV. DISCUSSION

If we compare our explicit results for the case of the small sphere with the earlier calculation in Ref. 5, it is clear that these two differ in the renormalization factors for the Raman polarizability, apart from the line-shape modification function  $f(\omega)$ . Whereas both the results contain the  $l=1$  SPP resonance factors at  $\omega_l$  and  $\omega_S$ , which occur due to the

( $a \ll \lambda$ ). For  $|\epsilon|^{1/2}a \sim \lambda$ , one must take care of higher-order terms, including the effect of radiation damping, properly. Even for very small spheres, the imaginary part  $\epsilon_2(\Omega)$  is, of course, different than that for the bulk metal. This must be kept in mind while obtaining numerical values. In the non-retardation limit, at the molecular site

$$\begin{aligned} \frac{\Omega^2}{c^2} \underline{G}^{(s)}(\Omega) \simeq & \sum_{l=0}^{\infty} \frac{l[\epsilon(\Omega) - 1]}{l+1+l\epsilon(\Omega)} \frac{a^{2l+1}}{r_0^{2l+4}} \\ & \times \left[ (l+1)^2 \hat{z}\hat{z} + \frac{l(l+1)}{2} \hat{x}\hat{x} \right. \\ & \left. + \frac{l(l+1)}{2} \hat{y}\hat{y} \right]. \end{aligned} \quad (64)$$

For diagonal  $\underline{\alpha}$  and the incident and scattered radiation polarized along  $\hat{r}_0 = \hat{z}$ , it can be shown that the enhancement factor  $F(\omega_S)$  given by (60) reduces to

enhancement of the external field and the scattering propagator, respectively, the renormalization factor is symmetrical as a function of the frequencies  $\omega_S$  and  $\omega_l$  in the present case. The two renormalization factors are the same only in the limit  $\omega_l \rightarrow \omega_S$ . In case there is a resonance involved in the renormalization factor, with  $d < 20 \text{ \AA}$  or so,<sup>5</sup> this difference is important to determine the frequency dependence accurately. Similarly, the *modification in the line shape also becomes important at short distances*. Compared to many other available calculations<sup>1,2,8</sup> for the case of a small sphere, our expression seems to be the most complete. However, note that for



spheres with  $a |\sqrt{\epsilon}| \sim \lambda$ , we must include radiation damping for obtaining  $\bar{E}^{(0)}(\omega_I)$ .

Although we have presented the calculation of the electromagnetic enhancement factor in the two-oscillator model, we believe that most of our conclusions should be correct qualitatively, even in the more general case. In fact, in the coordinate system in which  $\underline{\alpha}$  and  $\underline{G}^{(s)}(\vec{r}_0, \vec{r}_0, \omega)$  are diagonal, we believe that the formulas (58)–(60) for the enhancement factor should also be exact in the more general case. This is because in such a case the final formula can be rewritten in terms of the physical polarizabilities of the isolated molecule, without involving any unknown parameters of our model.

Because of the ease with which the two-oscillator model can be handled in the presence of the metal, it is possible to study other linear as well as non-linear processes occurring in the molecule using this model. Some of these molecular processes will be discussed in a planned future publication to investigate the effect of a metal or an insulator with an arbitrary shape of the surface.

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