Surface-enhanced nonlinear-optical processes in molecules in a two-oscillator electromagnetic model

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A two-oscillator electromagnetic model is used to find the effect of a solid or a metal substrate of dielectric function $\epsilon(\omega)$ on several nonlinear optical processes in a molecule adsorbed on the surface. In particular, the case of the second-order optical mixing, the stimulated Raman scattering, the third-order polarizability for the four-wave mixing, and the case of two-photon absorption in the molecule have been considered explicitly in the approximation in which the ionic oscillator frequency is assumed to be small compared with both the electronic oscillator frequency and the optical frequencies involved. The two-oscillator model considered here, with a trilinear coupling potential function, is the same as the one recently used by us to investigate the spontaneous Raman process. From our analysis it is quite clear that the enhancement, if any, in each of the processes involves (1) the enhancement of each of the incident optical fields $\vec{E}^{\text{in}}$ to $\vec{E}^{(0)}$ at the molecular site, (2) the renormalization of the effective nonlinear polarizabilities at short molecular distances from the surface, and (3) the change of the outgoing radiation propagator (Green's function) from the free-space $\underline{G}_0$ to $\underline{G}$, due to the presence of the surface. For a metal surface of a given shape, each of these factors may contain possible surface-plasmon—polariton resonances at various frequencies involved.

I. INTRODUCTION

In a recent paper[1] (hereafter referred to as paper I) we have presented a two-oscillator model for calculating the electromagnetic part of the enhancement in the surface-enhanced Raman scattering (SERS) process. This model enables one to obtain rather easily the electromagnetic part of the enhancement of the Raman cross section of molecules in the presence of an arbitrary medium of dielectric function $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$ with any given surface profile. This simple model has the further advantage of relating the Raman enhancement factor to experimentally observed linear and Raman polarizabilities of the corresponding isolated molecule. In fact, such a model, described in paper I, is capable of describing not only the Raman process, but also a wide variety of nonlinear optical phenomena[2] in molecules in the presence of a metal or any other solid surface. In this paper we consider several such applications of the model.

In Sec. II we briefly review the essential features of the two-oscillator model and obtain general expressions for the second- and the third-order nonlinear molecular polarizabilities in the presence of a medium of dielectric function $\epsilon(\omega)$. Expressions for some special cases of these polarizabilities (susceptibilities) are derived in Secs. III and IV so that these could be used to discuss explicitly the second-order nonlinear-optical mixing process, the stimulated Raman process, the third-order polarizability for the four-wave mixing process, and the two-photon absorption process. In each case we have assumed that the ionic mass M is much greater than the electronic mass m, and the

ionic oscillator frequency ω_0 is much less than the electric oscillator frequency ω_e. The simplified expressions show exactly how the various enhancement factors involving the incident-field enhancement, the nonlinear polarizability renormalization, and the change in the outgoing radiation propagator appear in each of the nonlinear processes. We sum up our results in Sec. V and for completeness include a discussion of the linear absorption process in adsorbed molecules in the Appendix.

II. NONLINEAR POLARIZABILITIES $\chi^{(2)}$ AND $\chi^{(3)}$ FOR SURFACE-ENHANCED OPTICAL PHENOMENA IN THE TWO-OSCILLATOR MODEL

In the two-oscillator model discussed in detail in paper I, to the lowest order in coupling, the ionic motion described by the normal-mode amplitude $\vec{Q}$ and the electronic motion denoted by the amplitude $\vec{x}$, associated with a molecule located at $\vec{r}_0$, satisfy the equations of motion

$$M(\ddot{Q}_i+\omega_0^2 Q_i+\gamma\dot{Q}_i)=ZE_i^M(t)-\frac{\partial V^{(3)}}{\partial Q_i}, \qquad (2.1)$$

$$m(\ddot{x}_i+\omega_e^2 d_{ij}x_j+\Gamma_{ij}\dot{x}_j)=eE_i^M(t)-\frac{\partial V^{(3)}}{\partial x_i}, \qquad (2.2)$$

in the presence of an incident electromagnetic field $\vec{E}^{\text{inc}}(t)$ and the solid of dielectric function $\epsilon(\omega)$. Here $i,j=1,2,3$ denote Cartesian coordinates, ω_0 and γ are the experimentally observed "physical" resonance frequency and the damping constant for the ionic mode, $\omega_e^2 d_{ij}$ and Γ_{ij} are

the corresponding quantities in the nondiagonalized tensor forms for electronic motion ($\sum_i d_{ii} = 3$), and $\vec{\textbf{E}}^M(t)$ is the "local" electromagnetic field at the molecular site which must be related to $\vec{\textbf{E}}^{\text{inc}}$. The nonlinear coupling force terms in the above equation are obtained from the trilinear potential function

$$V^{(3)}(\vec{x}, \vec{Q}) = A_{ijk} Q_i Q_j Q_k + B_{ijk} Q_i Q_j x_k$$
$$+ C_{ijk} x_i x_j Q_k + D_{ijk} x_i x_j x_k$$
$$\equiv \tfrac{1}{3} \theta_{\lambda\mu\nu} \psi_\lambda \psi_\mu \psi_\nu \ , \tag{2.3}$$

where repeated indices mean summation (unless explicitly stated), and where as a convention we use greek indices taking values 1–6 in the six-dimensional amplitude space

$$\psi = \begin{bmatrix} x \\ Q \end{bmatrix}, \quad x = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}, \quad Q = \begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \end{bmatrix} \ . \tag{2.4}$$

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

$$\left[-\nabla^2 + \vec{\nabla} \vec{\nabla} \cdot - \epsilon(\vec{r}, \Omega) \frac{\Omega^2}{c^2} \right] \vec{\textbf{E}}^{(0)}(\vec{r}, \Omega) = 0 \ , \tag{2.5}$$

inside as well as outside the solid (metal), in the presence of the incident field $\vec{\textbf{E}}^{\text{inc}}(\Omega)$. Inside the solid the dielectric function $\epsilon(\vec{r}, \Omega) = \epsilon(\Omega)$, and outside it is equal to 1. This defines the Fresnel-type factors L_{ij} at the molecular site

$$E_i^{(0)}(\vec{r}_0, \Omega) = L_{ij}(\vec{r}_0, \Omega) E_j^{\text{in}}(\vec{r}_0, \Omega) \ , \tag{2.6}$$

relating the incident field to the external field present at the molecular site due to the presence of the metal (solid) surface. We must note that the local electromagnetic field $\vec{\textbf{E}}^{(M)}$ acting on the molecule, which occurs in Eqs. (2.1) and (2.2), is not the external field $\vec{\textbf{E}}^{(0)}$ since the former must also take into account the molecular dipole. In terms of the full Green's function $\underline{G}$ and the free-space Green's function $\underline{G}_0$, which satisfy the equations

$$\left[-\nabla^2 + \vec{\nabla} \vec{\nabla} \cdot - \epsilon(\vec{r}, \Omega) \frac{\Omega^2}{c^2} \right] \underline{G}(\vec{r}, \vec{r}_0, \Omega) = 4\pi\delta(\vec{r} - \vec{r}_0)\underline{I} \ , \tag{2.7a}$$

$$\left[-\nabla^2 + \vec{\nabla} \vec{\nabla} \cdot - \frac{\Omega^2}{c^2} \right] \underline{G}_0(\vec{r}, \vec{r}_0, \Omega) = 4\pi\delta(\vec{r} - \vec{r}_0)\underline{I} \ , \tag{2.7b}$$

$\vec{\textbf{E}}^M$ can be obtained from the knowledge of $\vec{\textbf{E}}^{(0)}$ by[1]

$$\vec{\textbf{E}}^M(\vec{r}, \Omega) = \vec{\textbf{E}}^{(0)}(\vec{r}, \Omega) + \frac{\Omega^2}{c^2} \underline{G}^{(s)}(\vec{r}, \vec{r}_0, \Omega) \cdot \vec{\textbf{p}}(\Omega) \ , \tag{2.8}$$

where

$$\underline{G}^{(s)}(\vec{r}, \vec{r}_0, \Omega) \equiv \underline{G}(\vec{r}, \vec{r}_0, \Omega) - \underline{G}_0(\vec{r}, \vec{r}_0, \Omega) \ , \tag{2.9}$$

and where the induced molecular dipole moment is

$$\vec{\textbf{p}}(\Omega) = e\vec{x}(\Omega) + Z\vec{Q}(\Omega) \ . \tag{2.10}$$

As explicitly worked out in paper I, it is now straightforward to show that the coupled electronic and ionic

equations of motion can be written in the form [$\phi(\Omega)$ denotes the Fourier transform of $\phi(t)$]

$$\underline{A}(\Omega)\psi(\Omega) = F^{(0)}(\Omega) + f^{\text{NL}}(\Omega) \ , \tag{2.11}$$

where various quantities are given by

$$f_\lambda^{\text{NL}}(t) = -\frac{\partial V^{(3)}}{\partial \psi_\lambda} = -\theta_{\lambda\mu\nu}\psi_\mu(t)\psi_\nu(t) \ , \tag{2.12}$$

$$F^{(0)}(\Omega) = \begin{bmatrix} eE^{(0)}(\Omega) \\ ZE^{(0)}(\Omega) \end{bmatrix} \ , \tag{2.13}$$

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

$$\underline{A}(\Omega) = \begin{bmatrix} \Lambda^{XX}(\Omega) & \Lambda^{XQ}(\Omega) \\ \Lambda^{QX}(\Omega) & \Lambda^{QQ}(\Omega) \end{bmatrix} \ , \tag{2.14}$$

$$\Lambda_{ij}^{XX}(\Omega) = m(-\Omega^2\delta_{ij} + \omega_e^2 d_{ij} - i\Omega\Gamma_{ij})$$
$$- \frac{e^2\Omega^2}{c^2} G_{ij}^{(s)}(\Omega) \ , \tag{2.15}$$

$$\Lambda_{ij}^{XQ}(\Omega) = \Lambda_{ij}^{QX}(\Omega) = -\frac{Ze\Omega^2}{c^2} G_{ij}^{(s)}(\Omega) \ , \tag{2.16}$$

$$\Lambda_{ij}^{QQ}(\Omega) = M(-\Omega^2 + \omega_0^2 - i\omega\gamma)\delta_{ij} - \frac{Z^2\Omega^2}{c^2} G_{ij}^{(s)}(\Omega) \ , \tag{2.17}$$

and where we have defined

$$G_{ij}^{(s)}(\Omega) \equiv G_{ij}^{(s)}(\vec{r}_0, \vec{r}_0, \Omega) \tag{2.18}$$

at the molecular site. Note that the Green's dyadic $\underline{G}^{(s)} = \underline{G} - \underline{G}_0$ depends explicitly on the shape of the solid (metallic) medium and vanishes in the absence of the medium.

From (2.12) it is clear that the nonlinear force term couples various frequency components, i.e.,

$$f_\lambda^{\text{NL}}(\Omega) = -\theta_{\lambda\mu\nu} \int \psi_\mu(\Omega - \Omega')\psi_\nu(\Omega')d\Omega' \ . \tag{2.19}$$

Thus, given the number of the impressed frequencies on the system, the nonlinear response can be calculated by using the standard perturbation methods. Let us write the incident field in the form

$$\vec{\textbf{E}}^{\text{in}}(\vec{r}, t) = \sum_l \vec{\textbf{E}}^{\text{in}}(\vec{r}, \omega_l)e^{-i\omega_l t} \ , \tag{2.20}$$

so that the external field at the molecular site is

$$\vec{\textbf{E}}^{(0)}(\vec{r}_0, t) = \sum_l \vec{\textbf{E}}^{(0)}(\vec{r}_0, \omega_l)e^{-i\omega_l t}$$
$$= \sum_l \underline{L}(\vec{r}_0, \omega_l) \cdot \vec{\textbf{E}}^{\text{in}}(\vec{r}_0, \omega_l)e^{-i\omega_l t} \tag{2.21}$$

since the medium has a linear dielectric function $\epsilon(\omega)$. In other words, (2.13) tells us that the external force term has the structure

$$F^{(0)}(t) = \sum_l F^{(0)}(\omega_l)e^{-i\omega_l t} \ , \tag{2.22}$$

From (2.11), the linear response can then be obtained in the form

$$\psi^{(1)}(t)=\sum_l e^{-i\omega_l t}\psi^{(1)}(\omega_l) , \tag{2.23}$$

$$\psi_\mu^{(1)}(\omega_l)=[\underline{\Delta}^{-1}(\omega_l)]_{\mu\nu}F_\nu^{(0)}(\omega_l) . \tag{2.24}$$

Assuming $\psi^{(3)}\ll\psi^{(2)}\ll\psi^{(1)}$, etc., we can then use the above result in (2.11) to obtain the second-order and third-order amplitudes as

$$\psi^{(2)}(t)=\sum_{l,m} e^{-i(\omega_l+\omega_m)t}\psi^{(2)}(\omega_l+\omega_m) , \tag{2.25}$$

$$\psi^{(3)}(t)=\sum_{l,m,n} e^{-i(\omega_l+\omega_m+\omega_n)t}\psi^{(3)}(\omega_l+\omega_m+\omega_n) , \tag{2.26}$$

where

$$\psi_\beta^{(2)}(\omega_l+\omega_m)=-[\underline{\Delta}^{-1}(\omega_l+\omega_m)]_{\beta\lambda}\theta_{\lambda\mu\nu}$$
$$\times\psi_\mu^{(1)}(\omega_l)\psi_\nu^{(1)}(\omega_m) , \tag{2.27}$$

$$\psi_\beta^{(3)}(\omega_l+\omega_m+\omega_n)=-2[\underline{\Delta}^{-1}(\omega_l+\omega_m+\omega_n)]_{\beta\lambda}$$
$$\times\theta_{\lambda\mu\nu}\psi_\mu^{(1)}(\omega_n)\psi_\nu^{(2)}(\omega_l+\omega_m) . \tag{2.28}$$

Substitution of (2.24) in (2.27) and (2.28) and writing $F^{(0)}$ in terms of $\underline{L}$ and $\vec{E}^{\text{in}}$ [using (2.13) and (2.21)] immediately allow us to obtain the induced nonlinear dipole moments in terms of $\vec{E}^{\text{in}}$ and the corresponding susceptibilities (polarizabilities), defined by

$$p_i^{(2)}(\omega_l+\omega_m)=e\vec{x}^{(2)}(\omega_l+\omega_m)+ZQ_i^{(2)}(\omega_l+\omega_m)\equiv\chi_{ijk}^{(2)}(\omega_l,\omega_m)E_j^{(0)}(\omega_l)E_k^{(0)}(\omega_m) , \tag{2.29}$$

$$p_i^{(3)}(\omega_l+\omega_m+\omega_n)=e\vec{x}^{(3)}(\omega_l+\omega_m+\omega_n)+ZQ_i^{(3)}(\omega_l+\omega_m+\omega_n)$$
$$\equiv\chi_{ijkl}^{(3)}(\omega_l,\omega_m,\omega_n)E_j^{(0)}(\omega_l)E_k^{(0)}(\omega_m)E_l^{(0)}(\omega_n) , \tag{2.30}$$

if we remember the relations

$$\psi_1=x_1, \quad \psi_2=x_2, \quad \psi_3=x_3, \quad \psi_4=Q_1, \quad \psi_5=Q_2, \quad \psi_6=Q_3 . \tag{2.31}$$

Note that the nonlinear polarizabilities are defined above in terms of the external fields $\vec{E}^{(0)}$ acting at the molecular site in the presence of the surface *instead* of the incident fields $\vec{E}^{\text{(in)}}$ for convenience in isolating the field enhancement factor via Eq. (2.6).

For the second-order polarizability, the explicit expression is then obtained in the form

$$\chi_{ijk}^{(2)}(\omega_l,\omega_m)=-\text{Sym}(j,\omega_l;k,\omega_m)(\{e[\underline{\Delta}^{-1}(\omega_l+\omega_m)]_{i\beta}+Z[\underline{\Delta}^{-1}(\omega_l+\omega_m)]_{i+3,\beta}\}$$
$$\times\theta_{\beta\mu\nu}\{e^2[\underline{\Delta}^{-1}(\omega_l)]_{\mu j}[\underline{\Delta}^{-1}(\omega_m)]_{\nu k}+eZ[\underline{\Delta}^{-1}(\omega_l)]_{\mu j}[\underline{\Delta}^{-1}(\omega_m)]_{\nu,k+3}$$
$$+Ze[\underline{\Delta}^{-1}(\omega_l)]_{\mu,j+3}[\underline{\Delta}^{-1}(\omega_m)]_{\nu k}+Z^2[\underline{\Delta}^{-1}(\omega_l)]_{\mu,j+3}[\underline{\Delta}^{-1}(\omega_m)]_{\nu,k+3}\}) \tag{2.32}$$

where Sym implies symmetrization with respect to the simultaneous interchange of $j\rightleftarrows k$ and $\omega_l\rightleftarrows\omega_m$, with the convention

$$\text{Sym}(AB)=\tfrac{1}{2}(AB+BA) , \tag{2.33}$$

etc. We should remind ourselves that roman indices take values 1, 2, or 3 whereas greek indices take values 1–6. The nonlinear polarization (2.29) will produce radiation at new frequencies $\omega_l+\omega_m$. Note the appearance of Fresnel-type factors $L_{pj}(\omega_l)L_{qk}(\omega_m)$ when one connects $\vec{E}^{(0)}$ to the incident fields $\vec{E}^{\text{in}}$ in (2.29), which may contain surface-plasmon—polariton (SPP) resonances at ω_l and ω_m, as in the case of SERS from molecules at a metal surface (discussed in paper I). Since the nonlinear dipole at $\omega_l+\omega_m$ radiates in the presence of the metal, with full

$\underline{G}=\underline{G}_0+\underline{G}^{(s)}$ there can be additional SPP resonance at $\omega_l+\omega_m$, via $\underline{G}^{(s)}$ in the outgoing wave. Apart from this, the resonant character of the susceptibility $\chi^{(2)}$ also arises from the $\underline{\Delta}^{-1}$ matrices. These lead to a resonance whenever one of the natural frequencies of the molecular vibrations, modified by the renormalization effects arising from the presence of the metal, coincides with either incident frequencies ω_l and ω_m or the final frequency $\omega_l+\omega_m$. The expression (2.32) for the second-order susceptibility can be used in a variety of mixing problems, including the second-harmonic generation,[3] sum or difference frequency generation, etc.

The expression for the third-order nonlinear molecular polarizability (susceptibility) $\chi_{ijkl}^{(3)}(\omega_l,\omega_m,\omega_n)$ in the presence of the metal can be obtained in a similar way. We find the result

$$\chi_{ijkl}^{(3)}(\omega_l,\omega_m,\omega_n)=\text{Sym}(j,\omega_l;k,\omega_m;l,\omega_n)(\{2e[\underline{\Delta}^{-1}(\omega_l+\omega_m+\omega_n)]_{i\lambda}+2Z[\underline{\Delta}^{-1}(\omega_l+\omega_m+\omega_n)]_{i+3,\lambda}\}$$

$$\times\theta_{\lambda\mu\nu}[\underline{\Delta}^{-1}(\omega_l+\omega_m)]_{\nu\alpha}\theta_{\alpha\beta\delta}\{e[\underline{\Delta}^{-1}(\omega_l)]_{\beta j}+Z[\underline{\Delta}^{-1}(\omega_l)]_{\beta,j+3}\}$$

$$\times\{e[\underline{\Delta}^{-1}(\omega_m)]_{\delta k}+Z[\underline{\Delta}^{-1}(\omega_m)]_{\delta,k+3}\}$$

$$\times\{e[\underline{\Delta}^{-1}(\omega_n)]_{\mu l}+Z[\underline{\Delta}^{-1}(\omega_m)]_{\delta,l+3}\}) , \tag{2.34}$$

where, as before, Sym is the symmetrization operator to make $\chi^{(3)}$ symmetric with respect to permutations $(j,\omega_l;k,\omega_m)$, etc., and $\underline{A}^{-1}$ is obtained from (2.14)–(2.17). Within our two-oscillator model, the above expression is the most general form for the third-order polarizability. It should be emphasized once again that the characteristics of the metal are contained in the Fresnel factors $\underline{L}$ which connect $\vec{E}^{(0)}$ with $\vec{E}^{in}$, and in $\underline{A}^{-1}$ (through the renormalization effect via $G^{(s)}$). The resonances at various frequencies $\{\omega_l\}$, $\{\omega_l+\omega_m\}$, and $\omega_l+\omega_m+\omega_n$ can occur due to possible resonances in $\underline{L}$ or in $\underline{A}^{-1}$, or due to the SPP resonance in outgoing propagator $\underline{G}$ at the frequency $\omega_l+\omega_m+\omega_n$. If the renormalization effects are not important, e.g., for molecular distances from the metallic surface much greater than 10–20 Å, $\underline{A}^{-1}$ may be replaced by $(\underline{A}^{free})^{-1}$ for an isolated molecule by taking the limit $\underline{G}^{(s)}\to\underline{0}$ in (2.15)–(2.17).

In Secs. III and IV we will try to simplify our general expressions for $\chi^{(2)}$ and $\chi^{(3)}$ for applications to particular nonlinear processes when we assume that the ionic mass M is much greater than the electronic mass m, and the corresponding ionic frequency ω_0 is small compared to the electronic and optical frequencies. It has to be noted, however, that until now our expressions are general enough to be used, for example, to obtain more general expressions for the nonlinear electronic polarizabilities at optical frequencies by considering both the oscillators in the model to be electronic (with $M=m,Z=e$).

III.. SECOND-ORDER ELECTRONIC POLARIZABILITY AND THE THIRD-ORDER POLARIZABILITY FOR STIMULATED RAMAN SCATTERING, WITH LARGE IONIC MASS

When the ionic mass M is assumed to be large compared to the electronic mass m, with $\omega_0\ll\omega_e$, the general expressions for various physical processes of interest simplify considerably. In paper I we have already considered the case of spontaneous Raman scattering. In this section we will consider the case of the second-order electronic polarizability and the stimulated Raman process. The Raman susceptibility for four-wave mixing and the two-photon absorption process, under the same approximation, will be considered in Sec. IV.

A. Second-order electronic polarizability

For ionic frequencies small compared to the electronic and optical frequencies, to calculate the second-order optical polarizability it is enough to consider the response of the electronic oscillators. In our model one can thus retain only the last term in the coupling potential function (2.3), so that for this process,

$$\theta_{\lambda\mu\nu}=0, \quad \text{any of } \lambda,\mu,\nu>3 \ , \tag{3.1a}$$

$$\theta_{ijk}=3D_{ijk}, \quad i,j,k=1,2,3 \ . \tag{3.1b}$$

In terms of the linear electronic polarizability of the isolated molecule,

$$\underline{\alpha}(\Omega)=\frac{e^2}{m}(-\Omega^2\underline{I}+\omega_e^2\underline{d}-i\Omega\underline{\Gamma})^{-1} \ , \tag{3.2}$$

and its inverse (in matrix form),

$$\underline{\alpha}^{-1}(\Omega)=\frac{m}{e^2}(-\Omega^2\underline{I}+\omega_e^2\underline{d}-i\Omega\underline{\Gamma}) \ , \tag{3.3}$$

where $\underline{I}$ is the unit matrix; $\underline{A}^{-1}$ matrices needed in (2.32) for calculating $\chi^{(2)}$ are now given by

$$[\underline{A}^{-1}(\Omega)]_{ij}=\left[\left[e^2\underline{\alpha}^{-1}(\Omega)-\frac{e^2\Omega^2}{c^2}\underline{G}^{(S)}(\Omega)\right]^{-1}\right]_{ij} \ . \tag{3.4}$$

In terms of the renormalized (due to the presence of the surface) linear polarizability tensor,

$$\underline{\alpha}^{eff}(\Omega)=\underline{N}^{-1}(\Omega)\cdot\underline{\alpha}(\Omega) \ , \tag{3.5}$$

where the renormalization denominator is defined by

$$\underline{N}(\Omega)\equiv\left[\underline{I}-\frac{\Omega^2}{c^2}\underline{\alpha}(\Omega)\cdot\underline{G}^{(S)}(\Omega)\right] \ , \tag{3.6}$$

$\underline{A}^{-1}$ can be rewritten as

$$[\underline{A}^{-1}(\Omega)]_{ij}=\frac{1}{e^2}[\underline{\alpha}^{eff}(\Omega)]_{ij}$$

$$=\frac{1}{e^2}[\underline{N}^{-1}(\Omega)\cdot\underline{\alpha}(\Omega)]_{ij} \ . \tag{3.7}$$

Setting $Z=0$ (i.e., ignoring the ionic contributions) in the general expression (2.32) for $\chi^{(2)}$, the second-order electronic polarizability is thus found to be

$$\chi_{ijk}^{(2)e}(\omega_l,\omega_m)=-\text{Sym}(j,\omega_l;k,\omega_m)\frac{3}{e^3}D_{stu}$$

$$\times\alpha_{is}^{eff}(\omega_l+\omega_m)\alpha_{tj}^{eff}(\omega_l)\alpha_{uk}^{eff}(\omega_m) \ . \tag{3.8}$$

The radiation signal at $\omega_l+\omega_m$ in the outgoing direction $\hat{n}$ due to the second-order dipole moment

$$p_i^{(2)}(\omega_l+\omega_m)=\chi_{ijk}^{(2)}(\omega_l,\omega_m)E_j^{(0)}(\omega_l)E_k^{(0)}(\omega_m) \tag{3.9}$$

is now proportional to

$$|\vec{E}(\omega_l+\omega_m)|^2=\frac{(\omega_l+\omega_m)^4}{c^4}$$

$$\times|\underline{G}(r\to\infty,\hat{n};\vec{r}_0;\omega_l+\omega_m)\cdot\vec{p}^{(2)}(\omega_l+\omega_m)|^2 \ , \tag{3.10}$$

where $\underline{G}$ is the full Green's function of (2.7a) in the presence of the surface.

The net enhancement factor in the signal at $\omega_l+\omega_m$ can be obtained from (3.8)–(3.10) by dividing (3.10) by the corresponding expression with $G^{(s)}=0$, $\vec{E}^{(0)}\to\vec{E}^{in}$, and $\underline{\alpha}^{eff}\to\underline{\alpha}$. This expression again simplifies considerably in the coordinate system in which $\underline{\alpha}$ and $\underline{G}^{(s)}$ may happen to be diagonal. In such a case, in our model the second-order polarizability for an isolated molecule (free) is given by[4]

$$\chi_{ijk}^{(2)free}(\omega_l,\omega_m)=-\frac{3}{e^3}D_{ijk}\alpha_{ii}(\omega_l+\omega_m)$$

$$\times\alpha_{jj}(\omega_l)\alpha_{kk}(\omega_m) \ , \tag{3.11}$$

where there are no summations present, and the second-order susceptibility in the presence of the surface is related to it by

$$\chi_{ijk}^{(2)e}(\omega_l,\omega_m)=\frac{\chi_{ijk}^{(2)\text{free}}(\omega_l,\omega_m)}{N_{ii}(\omega_l+\omega_m)N_{jj}(\omega_l)N_{kk}(\omega_m)} \ ,$$

(3.12a)

where there are no summations present and where the renormalization denominator is

$$N_{pp}(\Omega)\equiv 1-\frac{\Omega^2}{c^2}\alpha_{pp}(\Omega)G_{pp}^{(s)}(\Omega) \ .$$

(3.12b)

The total enhancement factor obtained from (3.10) thus contains the factors due to the renormalization of $\chi^{(2)e}$ from $\chi^{(2)\text{free}}$ via (3.12), change of $\vec{E}^{\text{in}}(\omega_l)$ and $\vec{E}^{\text{in}}(\omega_m)$ to fields $\vec{E}^{(0)}(\omega_l)$ and $\vec{E}^{(0)}(\omega_m)$, respectively, via Eq. (2.6), and the change of the outgoing propagator from $\underline{G}_0$ to $\underline{G}=\underline{G}_0+\underline{G}^{(s)}$, each of which may contain SPP resonances discussed in paper I.

For the case of a small sphere, as disussed by several authors (see paper I and other references therein), the renormalization factors have been shown to be insignificant for molecular distances $d>20$ Å from the surface of the sphere. In such a case, the enhancement of (3.10) comes mainly from enhancement factors in $\underline{G}$ and $\vec{E}^{(0)}$. Each of these factors has the structure

$$\frac{E_j^{(0)}(\omega)}{E_z^{\text{in}}(\omega)}=\delta_{j3}-(3-\delta_{j3})\left[\frac{a}{a+d}\right]^3 g(\omega,a) \ ,$$

(3.13a)

where a is the radius of the sphere and

$$g(\omega,a)=\frac{\epsilon(\omega)-1}{\epsilon(\omega)+2+\frac{12}{5}(\omega^2/c^2)a^2}\simeq\frac{\epsilon(\omega)-1}{i\epsilon_2(\omega)}$$

(3.13b)

at the SPP resonance, in the case in which the incident wave is assumed to be polarized in the direction

$\vec{r}_0=(a+d)\hat{z}$, the position vector of the molecule. The center of the sphere is assumed to be at the origin. In the visible frequency region, for Ag the SPP enhancement factor is of the order of 50. The net enhancement for the harmonic generation will depend on how many of the frequencies ω_l, ω_m, and $\omega_l+\omega_m$ are resonant with the SPP of the metallic substrate. One may have a situation where both ω_l and ω_m are resonant but $\omega_l+\omega_m$ is nonresonant, leading to net enhancement factor of the order of 50^4 for the case of silver substrate. It may also happen that both ω_l and ω_m are nonresonant, but $\omega_l+\omega_m$ is resonant, leading to an enhancement factor $\sim 10^3$. It is already known that such enhancement factors are expected to be smaller for the case of a grating by at least 1 or 2 orders of magnitude.

B. Stimulated Raman scattering

To consider Raman scattering from ionic vibrations in the molecule, as was already done in Sec. III of Ref. 1, one keeps only the third term in the coupling potential function (2.3), so that

$$V^{(3)}=C_{ijk}x_i x_j Q_k \ .$$

(3.14)

Also the Raman polarization at $\omega_s=\omega_l-\omega$ is obtained in such a way that the ionic amplitudes at optical frequencies ω_l and ω_s and the electronic amplitudes at the vibration frequency ω are neglected. At the incident frequency ω_l, one obtains

$$\vec{x}^{(1)}(\omega_l)=\frac{1}{e}\underline{N}^{-1}(\omega_l)\cdot\underline{\alpha}(\omega_l)\cdot\vec{E}^{(0)}(\omega_l) \ ,$$

$$\vec{Q}^{(1)}(\omega_l)\simeq 0 \ ,$$

(3.15)

where the renormalization matrix $\underline{N}(\Omega)$ is already defined in (3.6). The reduced form of the relation (2.27) then leads to the Raman dipole moment

$$\vec{P}_{\text{Raman}}(\omega_l-\omega=\omega_s)\simeq e\vec{x}^{(2)}(\omega_l-\omega)=-\frac{2}{e^2}\underline{N}^{-1}(\omega_s)\cdot\underline{\alpha}(\omega_s)\cdot\underline{C}:\underline{N}^{-1}(\omega_l)\cdot\alpha(\omega_l)\cdot\vec{E}^{(0)}(\omega_l)\vec{Q}^*(\omega)$$

$$\equiv\underline{R}(\omega_s,\omega_l):\vec{E}^{(0)}(\omega_l)\vec{Q}^*(\omega) \ ,$$

(3.16)

where $\underline{R}(\omega_s,\omega_l)$ is the third-rank Raman tensor.

In the case of spontaneous Raman scattering considered in paper I, $\vec{Q}(\omega)$ was the random variable having its correlation functions determined from the analysis of thermal fluctuations at ω (with the use of fluctuation-dissipation theorem). For the stimulated case, $\vec{Q}(\omega)$ is the ionic amplitude which is produced due to the nonlinear force term in the ionic motion, proportional to $-C_{ijk}x_j^{(1)}(\omega_l)x_k^{*(1)}(\omega_s)$, i.e., due to the interaction between the fields $\vec{E}^{(0)}(\omega_l)$ and $\vec{E}^{(0)*}(\omega_s)$. For this we must solve the reduced form of the ionic equation of motion (in the absence of the homogeneous electric field at ω), to the second order in the fields

$$\Lambda_{ij}^{QQ}(\omega)Q_j(\omega)=-C_{kli}x_k^{(1)}(\omega_l)x_l^{(1)*}(\omega_s) \ ,$$

(3.17)

where Λ_{ij}^{QQ} is given by (2.17). This, with the use of (3.15) for both $x^{(1)}(\omega_l)$ and $x^{(1)}(\omega_s)$, immediately leads to

$$Q_i^*(\omega)=-\frac{2}{e^2}\Lambda_{ij}^{QQ}(-\omega)C_{klj}$$

$$\times[\underline{N}^{-1}(\omega_l)\cdot\underline{\alpha}(\omega_l)\cdot\vec{E}^{(0)}(\omega_l)]_k^*$$

$$\times[\underline{N}^{-1}(\omega_s)\cdot\underline{\alpha}(\omega_s)\cdot\vec{E}^{(0)}(\omega_s)]_l \ .$$

(3.18)

Substitution of (3.18) into (3.16) then gives the Raman dipole moment for the stimulated process and the corresponding third-order nonlinear polarizability in the form

$$p_i^{\text{SR}}(\omega_s)=\chi_{ijkl}^{(3)\text{SR}}(\omega_l,-\omega_l,\omega_s)E_j^{(0)}(\omega_l)E_k^{(0)*}(\omega_l)E_l^{(0)}(\omega_s) \ .$$

(3.19)

The full expression for $\chi^{(3)\text{SR}}$ can be simplified considering the case in which $\underline{\alpha}$ and $\underline{G}^{(s)}$ are diagonal. In such a case one finds

$$\chi_{ijkl}^{(3)SR}=\sum_{m}R_{ijm}(\omega_s,\omega_l)R_{klm}(\omega_s,-\omega_l)\left[\left[M(-\omega^2+\omega_0^2+i\omega\gamma)-\frac{Z^2\omega^2}{c^2}G_{mm}^{(s)}(-\omega)\right]^{-1}\right],$$

(3.20)

where the Raman tensor $\underline{R}$ is related to the corresponding tensor for the free molecule,

$$R_{ijk}(\omega_s,\omega_l)=\frac{R_{ijk}^{free}(\omega_s,\omega_l)}{[1-(\omega_s^2/c^2)\alpha_{ii}(\omega_s)G_{ii}^{(s)}(\omega_s)][1-(\omega_l^2/c^2)\alpha_{jj}(\omega_l)G_{jj}^{(s)}(\omega_l)]},$$

(3.21)

where there are no summations present. Thus, in this case, the Raman polarizability $\chi^{(3)SR}$ has been expressed completely in terms of the known Raman tensors $\underline{R}^{free}$, renormalization denominators $N_{ii}(\omega_s)$ and $N_{jj}(\omega_l)$, and the line-shape functions

$$[M(-\omega^2+\omega_0^2-i\omega\gamma)-(Z^2\omega^2/c^2)G_{mm}^{(s)}(-\omega)].$$

The result in the absence of the metal is relatively simple: $\underline{R}\rightarrow\underline{R}^{free}$, $\vec{E}^{(0)}\rightarrow\vec{E}^{in}$, and $\underline{G}^{(s)}\rightarrow0$.

The Raman gain for the stimulated process can now be obtained by using the optical theorem. The gain is defined as the rate at which the energy of the field $\vec{E}(\omega_s)$ increases divided by the incident flux at ω_s. The optical theorem[5,6] then leads to the expression

$$q=-\frac{4\pi c}{\omega_s}\frac{\text{Im}[\vec{E}^{(in)*}(\omega_s)\cdot\vec{a}(\hat{n}_s)]}{|\vec{E}^{in}(\omega_s)|^2}$$

(3.22)

for the gain. Here $\hat{n}_s$ is the direction of propagation of the incident field at ω_s and $\vec{a}$ gives the scattering amplitude. The scattering amplitude is related to the field at ω_s as

$$\vec{E}(\omega_s)=\frac{\omega_s^2}{c^2}\underline{G}(r\rightarrow\infty,\hat{n}_s;\vec{r}_0,\omega_s)\cdot\vec{p}^{\ SR}(\omega_s)$$

$$\equiv\frac{\omega_s^2}{c^2}\underline{\mathscr{G}}(\hat{n}_s,\vec{r}_0,\omega_s)\cdot\vec{p}^{\ SR}(\omega_s)\frac{e^{i\omega_s r}}{r}$$

$$\equiv\frac{e^{i\omega_s r}}{r}\vec{a}(\hat{n}_s),$$

(3.23)

where

$$\underline{G}(\vec{r}\rightarrow\infty,\hat{n}_s;\vec{r}_0,\omega_s)\equiv\frac{e^{i\omega_s r}}{r}\underline{\mathscr{G}}(\hat{n}_s,\vec{r}_0,\omega_s).$$

(3.24)

On combining (3.24) and (3.19), we find that the net enhancement factor for the stimulated Raman scattering is similar in magnitude to that for the spontaneous Raman scattering, already considered by several authors.[7,8]

IV. RAMAN SUSCEPTIBILITY FOR FOUR-WAVE MIXING AND $\chi^{(3)}$ FOR TWO-PHOTON ABSORPTION

In this section we will first discuss the case of the third-order Raman susceptibility for the four-wave mixing case when the ionic mass M is much greater than the electronic mass m and the ionic frequency ω_0 is much less than the electronic frequency ω_e. Later on, we will also obtain the purely electronic third-order nonlinear-optical susceptibility to describe the two-photon absorption case.

A. Raman susceptibility for four-wave mixing

We now calculate the simplified form of the third-order susceptibility $\chi^{(3)}(\omega_l,\omega_l,-\omega_s)$ to describe the four-wave mixing case in which $\omega_l-\omega_s=\omega$ is close to the ionic frequency equal to ω_0, and which is responsible for producing a signal at $2\omega_l-\omega_s$. The derivation follows similar steps as given in Sec. III for the stimulated Raman process. As in (3.16), the induced dipole moment at $2\omega_l-\omega_s$ is given by

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

$$\equiv\underline{R}(2\omega_l-\omega_s,\omega_l):\vec{E}^{(0)}(\omega_l)\vec{Q}(\omega).$$

(4.1)

Again $\vec{Q}(\omega)$ is given by (3.18), i.e.,

$$Q_i(\omega)=-\frac{2}{e^2}\left[\left[M(-\omega^2+\omega_0^2-i\omega\gamma)\underline{I}-\frac{Z^2\omega^2}{c^2}\underline{G}^{(s)}(\omega)\right]_{ij}^{-1}\right]C_{klj}[\underline{N}^{-1}(\omega_l)\cdot\underline{\alpha}(\omega_l)\cdot\vec{E}^{(0)}(\omega_l)]_k[\underline{N}^{-1}(\omega_s)\cdot\underline{\alpha}(\omega_s)\cdot\vec{E}^{(0)}(\omega_s)]_l^*.$$

(4.2)

The four-wave mixing process can then be rewritten as

$$p_i(2\omega_l-\omega_s)=\chi_{ijkl}^{(3)4W}(\omega_l,\omega_l,-\omega_s)E_j^{(0)}(\omega_l)E_k^{(0)}(\omega_l)E^{(0)*}(\omega_s),$$

(4.3)

which defines the corresponding susceptibility.

The dipole moment (4.3) would radiate a signal at $2\omega_l-\omega_s$. It may be noted that in the usual treatment of a four-wave mixing signal in nonlinear optics one deals with the so-called phase-matched signal. In the present case, because of the presence of the metal surface, it may not be possible to obtain phase matching.

In case $\underline{\alpha}$ and $\underline{G}^{(s)}$ are diagonal, the expression for $\chi^{(3)4W}$ obtained from (4.1)–(4.3) can be simplified considerably. One finds

$$\chi^{(3)4W}(\omega_l,\omega_l-\omega_s)=\sum_m R_{ijm}(2\omega_l-\omega_s,\omega_l)R_{klm}(-\omega_s,\omega_l)\left[M(-\omega^2+\omega_0^2-i\omega\gamma)-\frac{Z^2\omega2}{c^2}G_{mm}^{(s)}(\omega)\right]^{-1},\qquad(4.4)$$

where the Raman tensor $\underline{R}$ is related to the corresponding tensor $\underline{R}^{\text{free}}$ for an isolated molecule by (3.21). The emitted radiation at $2\omega_l-\omega_s$ is proportional to the square of the full Green's function $\underline{G}$ at $2\omega_l-\omega_s$ and the dipole moment (4.3). The enhancement in this case can be much larger than SERS, since now there are three field factors at ω_l, ω_l, and $-\omega_s$ apart from the outgoing propagator at $2\omega_l-\omega_s$. Each of these can have SPP resonance provided that ω_l, $\omega_l-\omega=\omega_s$, and $\omega_l+\omega$ are close to the SPP frequency of the substrate.

B. Two-photon absorption

To obtain the two-photon absorption coefficients we must calculate the third-order nonlinear susceptibility $\chi^{(3)}(-\omega_1,\omega_1,\omega_2)$ or $\chi^{(3)}(-\omega_2,\omega_2,\omega_1)$, where ω_1 and ω_2 are the incident-wave frequencies (which may be same as a special case). If all these frequencies are optical, it is enough to calculate only the electronic part of the nonlinear response by setting $Z=0$ in our expression (2.34). However, for obtaining $\chi^{(3)e}$, it may be necessary to con-

sider more than one electronic oscillator varying with different frequencies, and to also take into account the additional potential function $V^{(4)}$, quadrilinear in these amplitudes. However, for simplicity we will take only one oscillator in our model, hoping that our final result when converted in terms of the physical electronic linear polarizability $\underline{\alpha}$ is approximately correct even in the more general case.

As in (3.1) and (3.7), we now have

$$\theta_{\lambda\mu\nu}=0,\quad\text{any of }\lambda,\mu,\nu>3\qquad(4.5a)$$

$$\theta_{ijk}=3D_{ijk},\quad i,j,k=1,2,3\qquad(4.5b)$$

and

$$[\underline{\Delta}^{-1}(\Omega)]_{ij}=\frac{1}{e^2}[\underline{\alpha}^{\text{eff}}(\Omega)]_{ij}=\frac{1}{e^2}[\underline{N}^{-1}(\Omega)\cdot\underline{\alpha}(\Omega)]_{ij}.\qquad(4.6)$$

From (2.36), with $Z=0$, the required third-order electronic polarizability reduces to

$$\chi_{ijkl}^{(3)e}(-\omega_1,\omega_1,\omega_2)=\text{Sym}(j-\omega_1,k\omega_1,l\omega_2)\frac{18}{e^6}D_{stu}D_{s't'u'}$$

$$\times[\alpha_{is}^{\text{eff}}(-\omega_1+\omega_1+\omega_2)\alpha_{us'}^{\text{eff}}(\omega_1+\omega_2)\alpha_{tj}^{\text{eff}}(-\omega_1)\alpha_{u'k}^{\text{eff}}(\omega_1)\alpha_{t'l}^{\text{eff}}(\omega_2)],\qquad(4.7)$$

with the corresponding dipole moment

$$p_i^{2\text{ph}}(\omega_2)=\chi_{ijkl}^{(3)e}(-\omega_1,\omega_1,\omega_2)E_j^{(0)*}(\omega_1)E_k^{(0)}(\omega_1)E_l^{(0)}(\omega_2).\qquad(4.8)$$

Again, in the simplified case in which the free polarizability $\alpha(\Omega)$ and $\underline{G}^{(s)}(\Omega)$ are diagonal and $\underline{N}(0)$ is a scalar, $\chi^{(3)e}$ may be written approximately in terms of $\chi^{(3)\text{free}}$. For two-photon absorption at $\omega_1+\omega_2$, one finds

$$\chi_{ijkl}^{(3)e}(-\omega_1,\omega_1,\omega_2)\cong\frac{\chi_{ijkl}^{(3)\text{free}}(-\omega_1,\omega_1,\omega_2)}{[N_{ii}(\omega_2)N_{jj}(-\omega_1)N_{kk}(\omega_1)N_{ll}(\omega_2)]N(\omega_1+\omega_2)},\qquad(4.9)$$

where

$$N_{pp}(\Omega)=\left[1-\frac{\Omega^2}{c^2}\alpha_{pp}(\Omega)G_{pp}^{(s)}(\Omega)\right],\qquad(4.10)$$

$$N(\omega_1+\omega_2)\simeq\sum_p N_{pp}(\omega_1+\omega_2)/3.\qquad(4.11)$$

The two-photon cross section, as in the case of linear absorption[9,10] discussed in the Appendix, can be obtained[6] in the form

$$\sigma_{2\text{ph}}(\omega_2)=\frac{4\pi\omega_2}{c\,|\vec{E}^{\text{in}}(\omega_2)|^2}$$

$$\times\text{Im}[\vec{E}^{\text{in}}(\omega_2)\cdot\underline{\mathscr{G}}(\hat{n}_2,\vec{r}_0,\omega_2)\cdot\vec{p}^{2\text{ph}}].\qquad(4.12)$$

When this is compared with the corresponding case of an isolated molecule, one immediately obtains the surface-enhancement factor for the two-photon absorption case.[2]

Again one finds possible SPP resonances in the fields $\vec{E}^{(0)}$ at frequencies ω_1 or ω_2, the enhancement arising from the renormalization of $\chi^{(3)\text{free}}$ via (4.9), and the SPP resonance in the outgoing propagator $\mathscr{G}$. Except for the nature of the frequencies involved, the enhancement is similar to the case of the Raman process.

For the case of a small sphere (radius a is less than the wavelength of light), the enhancement discussed above will be of the order of $|g(\omega_1)|^2|g(\omega_2)|^2$. At an exact SPP resonance at either ω_1 or ω_2, this leads to a factor $\sim10^3-10^4$ for the case of molecules on a silver substrate. The somewhat smaller enhancement factor estimated by Glass et al.[11] in a recent experiment may be arising basically due to a broad distribution of shapes on metal ellipsoids, and hence of the SPP resonances in their experiment.

CONCLUSIONS

In the preceding sections we have considered several nonlinear-optical processes in molecules adsorbed on a

metal (or any other solid) surface of dielectric function $\epsilon(\omega)$, within the framework of a simple two-oscillator model with the trilinear potential coupling. Similar to the case of the spontaneous Raman scattering considered in paper I, we found that in each of the nonlinear processes one has three distinct types of changes.

(i) In each case, the fields acting at the molecular site $\vec{r}_0$ become modified from the incident $\vec{E}^{in}(\Omega)$ to $\vec{E}^{(0)}(\Omega) = \underline{L}(\vec{r}_0,\Omega)\cdot\vec{E}^{in}(\vec{r}_0,\Omega)$, due to the presence of the solid surface. If one is dealing with a rough metallic surface or metal spheres, etc., the Fresnel-type factors $\underline{L}$, and hence $\vec{E}^{(0)}(\Omega)$, contain SPP resonances. This is the so-called local-field enhancement. This involves more than one field and frequency in nonlinear processes.

(ii) The outgoing Green's function (propagator) for the radiation of frequency Ω' being detected is modified from the free Green's function $\underline{G}_0(r \to \infty, \hat{n}'; \vec{r}_0; \Omega')$ to the full Green's function

$$\underline{G}(r \to \infty, \hat{n}'; \vec{r}_0; \Omega') \equiv \underline{G}_0 + \underline{G}^{(s)}(r \to \infty, \hat{n}'; \vec{r}_0; \Omega') ,$$

in the presence of the surface. The additional Green's function $\underline{G}^{(s)}(\vec{r}, \vec{r}_0, \Omega')$ contains SPP resonances.[1]

(iii) The intrinsic nonlinear polarizability for each of the processes becomes renormalized, which may be important to take into account at molecular distances up to approximately 20 Å from the surface. The renormalization is similar to the renormalization of the linear polarizability $\underline{\alpha}$,

$$\alpha_{ii}^{eff}(\Omega) = \frac{\alpha_{ii}(\Omega)}{1 - (\Omega^2/c^2)\alpha_{ii}(\Omega)G_{ii}^{(s)}(\vec{r}_0,\vec{r}_0,\Omega)}$$

$$= [\underline{N}^{-1}(\Omega)]_{ii}\alpha_{ii}(\Omega) , \qquad (5.1)$$

except that several denominators $N_{pp}(\Omega)$ occur for nonlinear susceptibilities, depending on the order and the nature of the nonlinearity.

Given the nature of the surface shape and the medium, the enhancement factor in each of the processes can be obtained immediately by first finding once and for all the Fresnel-type factors $L_{ij}(\vec{r}_0,\Omega)$ and Green's functions $\underline{G}^{(s)}(r \to \infty, \hat{n}; \vec{r}_0, \Omega)$ and $\underline{G}^{(s)}(\vec{r}_0, \vec{r}_0, \Omega)$. For specific geometries, these are known from the papers in Refs. 1 and 7. A detailed numerical investigation of the renormalization effects arising in spherical geometries has been carried out recently in Ref. 8. It may be added that at present there are no direct experiments available for comparison of our theoretical results in the case of most of the nonlinear optical processes taking place in molecules adsorbed on a solid surface, which we have discussed in this paper. A detailed numerical calculation for these processes depends on the particle sizes and shapes of the substrate and on the distribution of molecular distances from the substrate, which will characterize future experiments on these nonlinear processes.

Before concluding this paper a line regarding the use of the words "polarizability" and "susceptibility" in this paper is on order. Although we have sometimes used the word susceptibility (a concept useful for a bulk medium) and used the symbols $\chi^{(2)}$, $\chi^{(3)}$, etc., all our expressions and calculations are for the *polarizabilities* of a given mol-

ecule at the molecular site $\vec{r}_0$. Since these depend on $\vec{r}_0$ in our case, the corresponding expressions for the usual bulk susceptibilities can be obtained by first multiplying these polarizabilities by the local differential densities of these molecules and then integrating over the spatial positions of the molecules. The dimensions of the bulk susceptibilities differ from the dimensions of the corresponding polarizabilities (obtained in this paper) by a factor of number density (L^{-3}).

APPENDIX: COMMENTS ON THE (LINEAR) ABSORPTION BY ADSORBED MOLECULES ON METAL SURFACES

In Secs. III and IV we have analyzed the problem of nonlinear absorption or gain. We could also analyze the much simpler problem of the linear absorption by adsorbed molecules.[9,10] We comment briefly on this in this appendix. The linear optical absorption can be expressed in terms of the linear electronic polarizability. We will ignore the ionic contribution. The absorption (extinction) cross section at the incident frequency ω_l can be defined in analogy to (3.22) as

$$\sigma_{abs} = + \frac{4\pi\omega_l}{c \mid \vec{E}^{in}(\omega_l) \mid^2}$$

$$\times \text{Im}[\vec{E}^{in}(-\omega_l)\cdot\mathscr{G}(\hat{n}_l; \vec{r}_0; \omega_l)\cdot\vec{p}(\omega_l)] . \qquad (A1)$$

Hence the ratio of the extinction cross section in the presence of the metal to that in the absence of the metal becomes

$$F_{abs}(\omega_l) = \frac{\text{Im}[\vec{E}^{in*}(\omega_l)\cdot\mathscr{G}(\hat{n}_l; \vec{r}_0; \omega_l)\cdot\underline{\alpha}^{eff}\cdot\underline{L}\vec{E}^{in}(\omega_l)]}{\text{Im}[\vec{E}^{in*}(\omega_l)\cdot\underline{\alpha}\cdot\vec{E}^{in}(\omega_l)]}$$

$$\qquad (A2)$$

where $\underline{\alpha}$ is the free-electronic polarizability and $\underline{\alpha}^{eff}$ is the polarizability in the presence of the metal

$$\underline{\alpha}^{eff}(\omega) = \left[\underline{I} - \frac{\omega^2}{c^2}\underline{\alpha}(\omega)\cdot\underline{G}^{(s)}(\omega)\right]^{-1}\cdot\underline{\alpha} . \qquad (A3)$$

For the case of a small metallic sphere (radius $a \ll c/\omega$) and the field polarized along X axis and the molecule located along Z axis, (A2) becomes[1]

$$F_{abs}(\omega_l) = \frac{\text{Im}\{[1 - (\epsilon_l - 1/\epsilon_l + 2)(a/r_0)^3]^2 N_{XX}(\omega_l)\alpha_{XX}\}}{\text{Im}(\alpha_{XX})} ,$$

$$\qquad (A4)$$

where all the quantities are to be taken at the frequency ω_l. Note that in the region of the excitation of SPP, $\epsilon_l + 2 \sim 0, F_{abs}(\omega_l)$ is negative, whereas for far away frequencies, e.g., near the frequency ω_e (resonance of α_{XX}), $\epsilon_l + 2$ is largely real and hence $F_{abs}(\omega_l)$ is positive. It should be remembered that the contribution (A1) is solely due to the presence of the molecule. There is also a contribution (usual one occurring in Mie theory) due to the presence of the sphere, which is always positive. Since

molecular polarizabilities are generally fairly small, it is clear that for $\omega_l \sim \omega_{SP}$ (where SP represents surface plasmon) (SPP frequency), the net absorption will be reduced whereas for $\omega_l \sim \omega_e$, the net absorption will be more. This result is in agreement with the work of Wang and Kerker[9] who treated the dye molecules as another coating of a dielectric layer (spherical) on top of a silver sphere.

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[1]G. S. Agarwal and S. S. Jha, Phys. Rev. B 26, 4013 (1982). Hereafter, this paper is referred to as paper I.

[2]C. G. B. Garrett, IEEE J. Quantum Electron. QE-4, 70 (1968).

[3]A. Wokaun, J. G. Bergman, J. P. Heritage, A. M. Glass, P. F. Liao, and D. H. Olson, Phys. Rev. B 24, 849 (1981).

[4]This is in the spirit of Miller's rule. See, e.g., Ref. 2.

[5]See, for example, M. Born and E. Wolf, Principles of Optics (Pergamon, Oxford, 1970), p. 658.

[6]D. Boggett and R. Loudon, Phys. Rev. Lett. 28, 1051 (1972).

[7]M. Moskovits, J. Chem. Phys. 69, 4159 (1978); S. S. Jha, J. R. Kirtley, and J. C. Tsang, Phys. Rev. B 22, 3973 (1980); S. L. McCall, P. M. Platzman, and P. A. Wolff, Phys. Lett. 77A, 381 (1980); D. S. Wang, M. Kerker, and H. Chew, Appl. Opt. 19, 2315 (1980); J. L. Gersten and A. Nitzan, J. Chem. Phys.

[73], 3023 (1980); C. Y. Chen and E. Burstein, Phys. Rev. Lett. 45, 1287 (1980); G. S. Agarwal, S. S. Jha, and J. C. Tsang, Phys. Rev. B 25, 2089 (1982); B. J. Messinger, K. Ulrich von Raben, R. K. Chang, and P. W. Barber, ibid. 24, 649 (1981); P. K. Arvind and H. Metiu, Chem. Phys. Lett. 74, 301 (1980).

[8]G. S. Agarwal and S. V. Oneil, Phys. Rev. B 28, 487 (1983).

[9]D. Wang and M. Kerker, Phys. Rev. B 25, 2433 (1982).

[10]A. J. Sievers, Phys. Rev. B 22, 1600 (1980); A. M. Glass, P. F. Liao, J. G. Bergman, and D. H. Olsen, Opt. Lett. 5, 368 (1980); S. Garoff, D. A. Weitz, T. J. Gramila, and C. D. Hanson, ibid. 6, 245 (1981); C. K. Chen, A. R. B. deCastro, and Y. R. Shen, Phys. Rev. Lett. 46, 145 (1981).

[11]A. M. Glass, A. Wokaun, J. P. Heritage, J. G. Bergman, P. F. Liao, and D. H. Olson, Phys. Rev. B 24, 4906 (1981).