Photoabsorption of molecules at corrugated thin metal films

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A phenomenological study has been carried out for the photoabsorption of molecules in the vicinity of a corrugated thin metal film. In particular, perturbative results for a grating silver film have been obtained to first order in the corrugation parameter, where the effect of the incident field coupled with the long-range surface plasmon is observed. Based on the different coupling nature between the radiations from the incident plane wave and from the molecular dipole to the substate film, it is proposed that, through control of the various parameters of the film, enhanced selective photoabsorption may be achieved.

I. INTRODUCTION

Since the discovery of surface-enhanced Raman scattering,[1] there has been in the past ten years a large number of investigations on the possibility for enhancing other photochemical processes at rough surfaces.[2] In particular, processes such as photolysis and photochemical degradation have been studied in great detail, both experimentally and through theoretical models which include both the cases of localized[3] and extended[4,5] surface structures. By now, it has become clear that for a first-order process, such as photoabsorption which includes photodissociation (direct dissociation) and resonance fluorescence, the ultimate outcome for the enhancement of the process generally depends on two competing factors: the enhanced surface electromagnetic field and the surface-induced decay rates for the admolecules. Detailed reviews of this subject are available in the recent literature[2,6]

Still another substrate of great interest is the case of a corrugated thin metal film. Although the problem of light scattering from such a film has been intensively studied within the past few years,[7-14] and to a less extent the problem of molecular decay,[15-17] the possibility of new photochemical processes in the vicinity of such a film has not been addressed.

In this work, we present a phenomenological study of the photoabsorption of molecules located near a corrugated thin metal film. Specifically, we shall consider the photoabsorption of a two-level system (modeled as a point dipole) above a metallic (taken as Ag throughout) grating film, with an incident laser field at an angle θ and a molecular dipole assumed to be oriented normal to the film (see Fig. 1). Our formulation will be based on a generalization of our previous model for a single grating surface[4] and an application of our recent work on the decay rates of molecules at such film systems.[17] As pointed out before, the full dynamics of the problems must be taken into account in order to treat the morphological induced effects.[17,18] We shall see that due to the different coupling natures of the radiations from the molecular dipole and the incident plane wave with the surface plasmons of the film, there is a possibility of achieving enhanced selective photoabsorption for the admolecules.

II. ABSORPTION CROSS SECTION

The configuration of our problem is shown in Fig. 1, where the molecule of dipole moment μ is located at $z = d$ above a thin metal (Ag) film bounded by two grating surfaces located at $z = 0$ and $z = -t$, respectively. Thus, the profile functions take the forms

$$\zeta_1 = \zeta_{0_1} e^{iQ_1 x}, \quad \zeta_2 = \zeta_{0_2} e^{iQ_2 x}, \tag{1}$$

where we shall assume small corrugations ($\zeta_{0_i} Q_i \ll 1$) so that perturbation theory can be applied. The optical properties of the three media are described by their dielectric functions ϵ_1, $\epsilon_2 = \epsilon'(\omega) + i\epsilon''(\omega)$ and ϵ_3. Let us consider p-polarized laser light of the form

$$\mathbf{E}_{in} = (E_{0x}\hat{e}_x + E_{0z}\hat{e}_z) e^{i(k_z^{(0)} z - \omega t)} e^{i\mathbf{k}_\parallel^{(0)}\cdot\mathbf{r}}$$

$$\equiv \mathbf{E}_0(\omega|z) e^{i\mathbf{k}_\parallel^{(0)}\cdot\mathbf{r}_\parallel}, \tag{2}$$

$$\mathbf{k}_\parallel^{(0)} = k_x^{(0)}\hat{e}_x, \quad \mathbf{r}_\parallel = (x,y) \tag{3}$$

which is incident on the system at an angle θ with respect to the normal direction. We want to calculate the absorption cross section of the molecule. For simplicity, we assume that μ is oriented perpendicular ($\mu = \mu\hat{e}_z$) to the film.

According to the phenomenological model,[3-5] the ab-

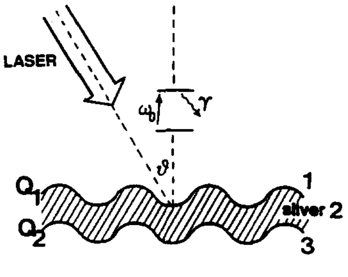

FIG. 1. Configuration of the photoabsorption problem at a corrugated thin film.

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sorption cross section for the free-molecule case (σ_0) can be obtained in Lorentzian form as

$$\sigma_0(\omega) = A\,|\mathbf{E}_{in}|^2 \sin^2\theta \frac{\gamma_M^0}{(\omega - \omega_M^0)^2 + (\gamma_M^0/2)^2}, \quad (4)$$

where A is a proportionality constant, and ω_M^0 and γ_M^0 denote the natural frequency and width, respectively, of the excited state of the free molecule.[4] In the presence of the substrate film, Eq. (4) then becomes

$$\sigma(\omega) = A\,|E_z(d,\omega)|^2 \frac{\gamma_M}{(\omega - \omega_M)^2 + (\gamma_M/2)^2}, \quad (5)$$

where $E_z(d,\omega)$ is now the total field driving the dipole, and ω_M and γ_M denote the dressed values for the frequency and width, respectively, due to the presence of the film substrate. Since these are usually dependent on the driving frequency ω, Eq. (5) is in general distorted from a Lorentzian shape.[3-5] Moreover, it is known that the induced frequency shift can most of the time be neglected compared to the induced decay rate,[19] and hence in the following we shall assume $\omega_M \approx \omega_M^0$ and take into account only the substrate-induced rate $\gamma(\omega)$. The remaining job then is to calculate $E_z(d,\omega)$ in Eq. (5). Following the perturbative approach of Maradudin and Mills,[20,21] we obtain to first order of roughness

$$E_z(d,\omega) = (1 + Re^{2ik_1 d})E_{in} \sin\theta + E_z^{(s)}(d,\omega)e^{ik_1 d}, \quad (6)$$

where R is the Fresnel reflectance for a flat film,[22] $k_1 = \sqrt{\epsilon_1}\omega/c$ is the wave number in the first medium, and $E_z^{(s)}$ is the contribution from the roughness to the scattered field, whose μth component is given by[20,21]

$$\begin{aligned} E_\mu^{(s)}(\mathbf{r};\omega) = & -\frac{k^2}{16\pi^3}\int d^2k_\| e^{i\mathbf{k}_\|\cdot\mathbf{r}_\|} \\ & \times \int dz' d_{\mu\nu}(\mathbf{k}_\|\omega|zz')\{[\epsilon_2\theta(z'+t) \\ & -\epsilon_1]\delta(z')\hat{\zeta}_1(\mathbf{k}_\| - \mathbf{k}_\|^{(0)}) \\ & + [\epsilon_3 - \epsilon_2\theta(-z')]\delta(z'+t) \\ & \times[\hat{\xi}_2(\mathbf{k}_\| - k_\|^{(0)}) + t]\}E_\nu^{(0)}(\mathbf{k}_\|^{(0)}\omega|z'), \end{aligned} \quad (7)$$

where $k = \omega/c$, $d_{\mu\nu}$ and $\hat{\zeta}_i$ are the Fourier transform of the "flat" propagators and profile functions, respectively, $E_\nu^{(0)}$ is the *total* field in the various media in the case of a flat film, and θ is the Heaviside step function. The integrals involving the δ functions must be carefully performed since $E_\nu^{(0)}$ is in general discontinuous across the various boundaries.

We have recently developed a method[23] of handling these integrals by applying the formalism of Agarwal,[24] from which we have obtained results which are a modified version of those in the original work of Maradudin and Mills[20] and are in agreement with those obtained from other approaches, including Mills'[25] subsequent modifications by applying the work of Juranek.[26] It is straightforward to show that such modifications for a single interface can be extended to the case of a multilayer structure. For the simplest case of a replicating grating film where we have

$$\zeta_1(\mathbf{r}_\|) = \xi_2(\mathbf{r}_\|) + t = \zeta_0 e^{i\mathbf{Q}\cdot\hat{e}_x}, \quad (8)$$

we obtain from Eq. (7)

$$\begin{aligned} E_z^{(s)}(d,\omega) = & -\frac{k^2}{4\pi}\zeta_0\{(\epsilon_2 - \epsilon_1)[d_{zx}(\mathbf{k}_\|\omega|d,0_-) \\ & \times E_x^{(0)}(\omega|0_+) + d_{zz}(\mathbf{k}_\|\omega|d,0_-) \\ & \times E_z^{(0)}(\omega|0_+)]E_x^{(0)}(\omega|0_+) \\ & + (\epsilon_3 - \epsilon_2)[d_{zx}(\mathbf{k}_\|\omega|d,-t_+) \\ & \times E_x^{(0)}(\omega|-t_-) + d_{zz}(\mathbf{k}_\|\omega|d,-t_+) \\ & \times E_z^{(0)}(\omega|-t_-)]\}, \end{aligned} \quad (9)$$

$$\begin{aligned} \mathbf{k}_\| &= \mathbf{Q} + \mathbf{k}_\|^{(0)}, \\ k_\| &= Q + k_1 \sin\theta. \end{aligned} \quad (10)$$

The expressions for the propagators $d_{\mu\nu}$ can be found in Ref. 21, and the results for various $E^{(0)}$'s for a flat film are also available in the literature.[22,27] Using these available results, we can finally compute $E_z(d,\omega)$ in Eq. (6) in terms of E_{in} (see the Appendix), and together with the relation between γ_M and γ_M^0 which we have obtained in a previous work,[17] we can finally calculate the absorption cross section $\sigma(\omega)$ in Eq. (5) in the presence of the substrate film in comparison to a given free-molecule absorption profile $\sigma_0(\omega)$.

III. POSSIBILITY OF ENHANCED SELECTIVE PHOTOABSORPTION

Instead of showing some straightforward model calculation based on Eqs. (4) and (5), here we shall pay attention to a very interesting feature of the problem which may lead to the realization of a mechanism for enhanced selective photoabsorption for adsorbed molecules. In a recent study of the decay rate spectrum for admolecules near such a grating film,[17] we pointed out that the coupling of the molecular fluorescence radiation to the two thin film surface plasmons is governed by a very different dispersion relation as compared to those in the case of plane wave light scattering experiments.[15,16] The difference arises from the dipole nature of the molecular emission which consists of a superposition of all the plane wave harmonics. Hence the resonance peaks due to the cross-coupling of the plasmons on the two film surfaces into the long-(and short-)range surface plasmons in the decay-rate spectrum are in general at *different positions* as compared to those in the light scattering spectrum.[17] Since these peak positions (in both spectrums) are very sensitive to the geometrical (roughness, thickness,...) and dielectric properties of the film, for a given absorption level one can then try to adjust these parameters so that the cross-coupling peak of the scattered field lies close to the natural frequency ω_M^0 of the system, and that of the induced decay rate stays away from ω_M^0. Under optimal conditions enhanced selective photoabsorption of this particular level (ω_M^0) may be achieved, since the other levels close to ω_M^0 would now be strongly damped due to the fact that they can experience large induced decay rates. We shall illustrate this below through a numerical model calculation.

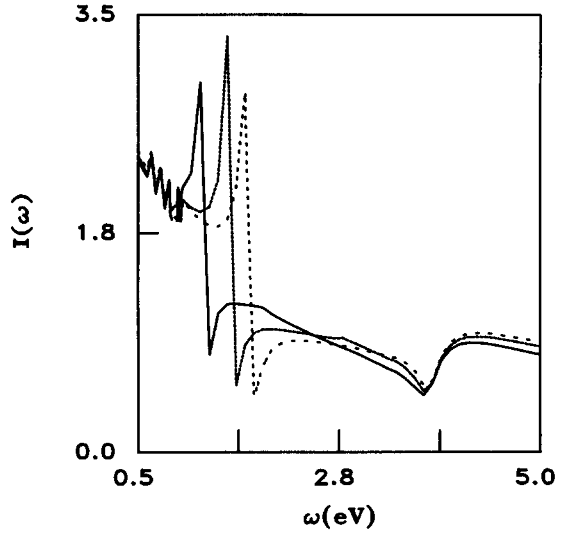

FIG. 2. Intensity of the electric field at $z = d = 150$ Å from a supported grating film ($\epsilon_1 = 1.0$, $\epsilon_3 = 3.6$) as a function of frequency at fixed film thickness $t = 100$ Å and grating amplitude $\zeta_0 = 40$ Å. The angle of incidence θ is set at 1 rad, and the grating wave number is varied as: $Q = 1.0 \times 10^{-3}$ Å^{-1} (solid line); $Q = 1.5 \times 10^{-3}$ Å^{-1} (dotted line); and $Q = 2.0 \times 10^{-3}$ Å^{-1} (dashed line). The y axis on each graph is in arbitrary units.

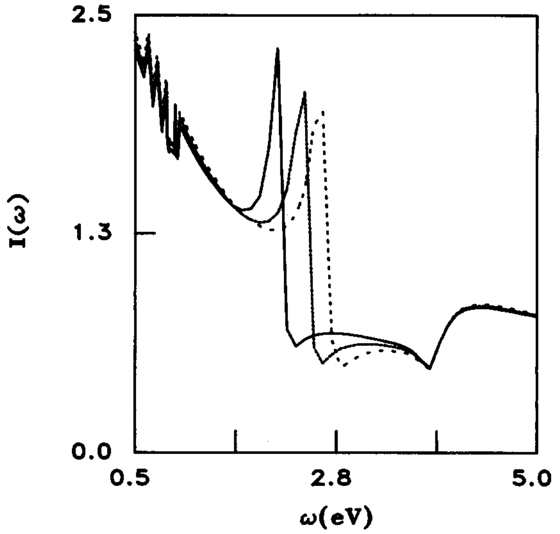

FIG. 4. Same as in Fig. 2, except that the results are for a free-standing film, $\epsilon_1 = \epsilon_3 = 1.0$.

IV. NUMERICAL ILLUSTRATIONS

To illustrate the sensitivity of the cross-coupling peaks to the film parameters, let us first study the intensity of the total field at the molecule site ($z = d$). Defining $I(\omega) = |E_z(d,\omega)|^2$ with E_z given in Eq. (6), Fig. 2 shows the spectrum of $I(\omega)$ at $d = 150$ Å for different grating periods Q for a supported (asymmetrically bound) film. It shows, aside from the well-known "dip" at $\omega \sim 3.6$ eV for Ag due to the excitation of the nonradiative surface plasmon mode, that the long-range evanescent surface plasmon (LRSP) mode due to the cross coupling is manifested clearly in the spectrum, where its peak moves as Q is varied. At such a distance, the short-range cross-coupling mode almost vanishes completely. Figure 3 shows similar variation of this LRSP peak with the thickness (t) of the film for a fixed value of Q, where the peak is seen to disappear as t tends to infinity. Figure 4 shows similar effects as in Fig. 2, except that we now have a free-standing (symmetrically bound) film, which is known to be a very efficient system for cross-coupling between the two film surface plasmons.[16,17] Figure 5 shows similar effects as in Fig. 3 for the free-standing film in Fig. 4. To illustrate the possible selective enhanced mechanism as discussed in Sec. III, we consider a hypothetical molecular system with Lorentzian absorption lines $\sigma_0(\omega)$ as illustrated in Fig. 6. Let us consider the photoabsorption spectrum of this system when being located at $d = 150$ Å from a supported grating film as that in Figs. 2 and 3, and with $Q = 1.5 \times 10^{-3}$ Å^{-1}. Using the results for the decay rate worked out previously,[17] the decay rate spectrum for the same grating film system is plotted in Fig. 7, from which the peak due to cross coupling into LRSP located at $\omega \sim 1.1$ eV is clearly seen to be located at a different position than that for

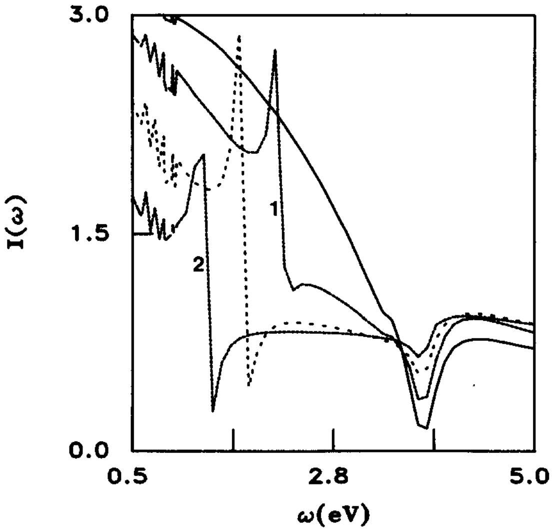

FIG. 3. Same as Fig. 2, except that Q is fixed at 2.0×10^{-3} Å^{-1} and t is varied: dotted line 2 ($t = 50$ Å); dashed line ($t = 100$ Å); dotted line 1 ($t = 200$ Å); solid line ($t \to \infty$).

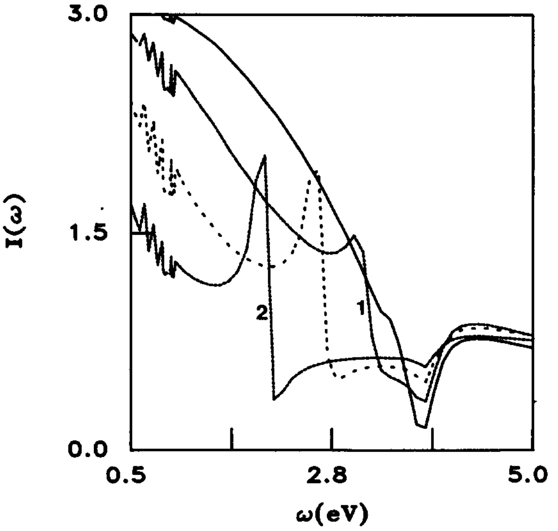

FIG. 5. Same as Fig. 3, except that the results are for a free-standing film, $\epsilon_1 = \epsilon_3 = 1.0$.

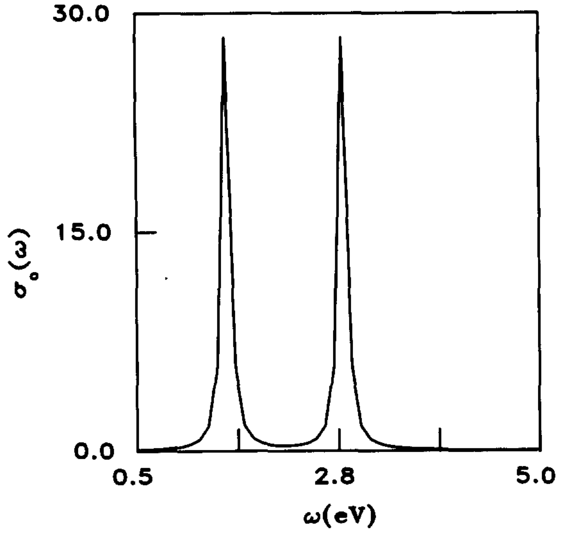

FIG. 6. Hypothetical molecular system with two Lorentzian absorption lines.

light scattering in Fig. 2 where the spectrum peaks at $\omega \sim 1.6$ eV. Figure 8 shows the distorted absorption line shape $\sigma(\omega)$ for the molecular system in Fig. 6 located in the vicinity of the above grating film. It can be seen that one of the absorption lines is suppressed while only the one with $\omega_M^0 \sim 1.5$ eV is excited. Moreover, there is not much enhancement for this line since the corrugation amplitude $\zeta_0 \simeq 40$ Å used in this calculation is too small. We have tried to increase this to go beyond 100 Å where we do have enhancement, but then the result is not very meaningful due to the limitation of the present perturbative approach. Nevertheless, the present results do give very strong indications that such selective enhanced photoabsorption may indeed be possible for deeper grating films, in which case a nonperturbative treatment must be adopted. We plan to reformulate this problem using a nonperturbative approach to calculate the fields and decay rates in the future.

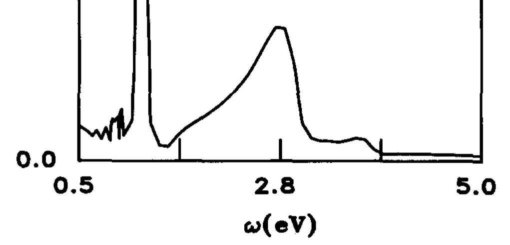

FIG. 7. Decay rate spectrum for the system as in Figs. 2 and 3 with $Q = 1.5 \times 10^{-3}$ Å^{-1} and $t = 100$ Å.

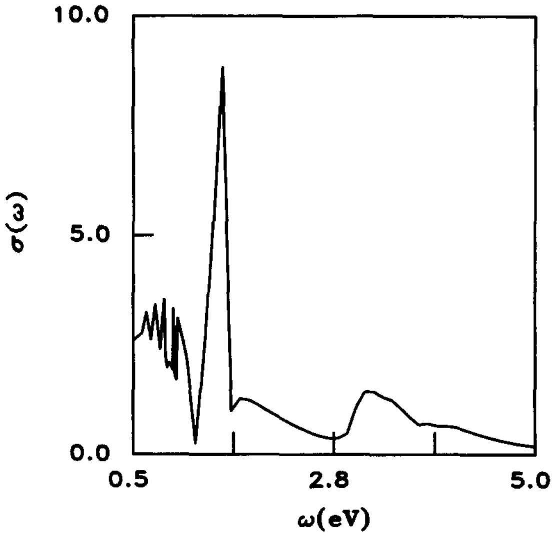

FIG. 8. Distorted photoabsorption line shape for the molecular system in Fig. 6 in the presence of the grating film as described in Fig. 7.

V. CONCLUSION

In this paper, we have studied phenomenologically the photoabsorption of a molecule in the vicinity of a grating film. Our main result here is the speculation of the possibility of enhanced selective photoabsorption. It is well known that due to its monochromaticity and tunability, the laser has found great applications in various selective photochemical processes. Nevertheless, to have the selective absorption enhanced, one requires a highly intense laser source, which may then lead to multiphoton processes and hence weakens the selectivity in the photoprocess. In this present mechanism which we are proposing, however, we have made use of the fact that the induced decay rate and the enhanced LRSP field have very different resonance structures, and hence the excitation of other levels may be suppressed by the enhanced decay rates at their natural frequencies. Hence, we conclude that it is worth pursuing the problem further using a nonperturbative approach to allow large grating amplitudes for the film and to recalculate $\sigma(\omega)$ for such a system, so that a realistic enhanced selective photoabsorption may be exhibited.

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APPENDIX

Here we give a brief account on how the final expression for $E_z^{(s)}(d,\omega)$ may be obtained from Refs. 21 and 22. From Ref. 22 it is straightforward to show that

$$E_x^{(0)}(\omega|0_+) = (1-R)E_{in}\cos\theta; \qquad E_x^{(0)}(\omega|-t_-) = TE_{in}\cos\beta;$$
$$E_z^{(0)}(\omega|0_+) = (1+R)E_{in}\sin\theta, \qquad E_z^{(0)}(\omega|-t_-) = TE_{in}\sin\beta, \tag{A1}$$

where

$$R=\frac{(1-\Delta_1)(1+\Delta_2)\,e^{-ik_2t\cos\alpha}-(1+\Delta_1)(1-\Delta_2)\,e^{ik_2t\cos\alpha}}{(1+\Delta_1)(1+\Delta_2)\,e^{-ik_2t\cos\alpha}-(1-\Delta_1)(1-\Delta_2)\,e^{ik_2t\cos\alpha}}, \tag{A2}$$

and

$$T=\frac{4\Delta_2\,e^{-ik_3t\cos\beta}}{(1+\Delta_1)(1+\Delta_2)\,e^{-ik_2t\cos\alpha}-(1-\Delta_1)(1-\Delta_2)\,e^{ik_2t\cos\alpha}}, \tag{A3}$$

$$\Delta_1=\frac{k_1\cos\alpha}{k_2\cos\theta},\quad \Delta_2=\frac{k_3\cos\alpha}{k_2\cos\beta},\quad k_i=\sqrt{\epsilon_i}\,\frac{\omega}{c}, \tag{A4}$$

and θ, α, and β are the angles made by the light rays with respect to the normal direction in media 1, 2, and 3, respectively. By using the Green dyadics worked out in Ref. 21, we obtain

$$\begin{aligned}E_z^{(s)}(d,\omega) = {} & -\frac{k^2}{4\pi}\zeta_0\{(\epsilon_2-\epsilon_1)[C_1C_2E_x^{(0)}(\omega|0_+)+C_4E_z^{(0)}(\omega|0_+)] \\ & +(\epsilon_3-\epsilon_2)[C_1C_3E_x^{(0)}(\omega|-t_-)+C_5E_z^{(0)}(\omega|-t_-)]\}\,e^{i\alpha_1 d},\end{aligned} \tag{A5}$$

where the coefficients C_i are given by:

$$C_1=\frac{k_1\sin\theta}{Q+k_1\sin\theta}, \tag{A6}$$

$$C_2=\frac{2\alpha_2\epsilon_2\rho\,\{1+[(\alpha_3\epsilon_2-\alpha_2\epsilon_3)/(\alpha_3\epsilon_2+\alpha_2\epsilon_3)]\,e^{-2i\alpha_2t}\}}{2\alpha_2\epsilon_1-(\alpha_2\epsilon_1+\alpha_1\epsilon_2)\{1-[(\alpha_3\epsilon_2-\alpha_2\epsilon_3)/(\alpha_3\epsilon_2+\alpha_2\epsilon_3)]\,e^{-2i\alpha_2t}\}}, \tag{A7}$$

$$C_3=\frac{2\alpha_2\epsilon_2\rho\,e^{-i\alpha_2t}\{1+[(\alpha_3\epsilon_2-\alpha_2\epsilon_3)/(\alpha_3\epsilon_2+\alpha_2\epsilon_3)]\}}{2\alpha_2\epsilon_1-(\alpha_2\epsilon_1+\alpha_1\epsilon_2)\{1-[(\alpha_3\epsilon_2-\alpha_2\epsilon_3)/(\alpha_3\epsilon_2+\alpha_2\epsilon_3)]\,e^{-2i\alpha_2t}\}}, \tag{A8}$$

$$\begin{aligned}C_4={} & \frac{4\pi}{i\alpha_1}\left(\frac{c^2}{\epsilon_2\omega^2}\alpha_2^2-1\right)\left(\frac{\epsilon_2}{\epsilon_1}\right) \\ & \times\frac{[(\epsilon_2/\epsilon_3)+(\alpha_2/\alpha_3)]\,e^{i\alpha_2t}-[(\epsilon_2/\epsilon_3)-(\alpha_2/\alpha_3)]\,e^{-i\alpha_2t}}{[(\alpha_2/\alpha_1)-(\epsilon_2/\epsilon_1)][(\alpha_2/\alpha_3)+(\epsilon_2/\epsilon_3)]\,e^{i\alpha_2t}-[(\alpha_2/\alpha_1)+(\epsilon_2/\epsilon_1)][(\alpha_2/\alpha_3)-(\epsilon_2/\epsilon_3)]\,e^{-i\alpha_2t}},\end{aligned} \tag{A9}$$

$$\begin{aligned}C_5={} & \frac{4\pi}{i\alpha_1}\left(\frac{c^2}{\epsilon_2\omega^2}\alpha_2^2-1\right)\left(\frac{\epsilon_2}{\epsilon_1}\right) \\ & \times\frac{2(\alpha_2/\alpha_3)}{[(\alpha_2/\alpha_1)-(\epsilon_2/\epsilon_1)][(\alpha_2/\alpha_3)+(\epsilon_2/\epsilon_3)]\,e^{i\alpha_2t}-[(\alpha_2/\alpha_1)+(\epsilon_2/\epsilon_1)][(\alpha_2/\alpha_3)+(\epsilon_2/\epsilon_3)]\,e^{-i\alpha_2t}},\end{aligned} \tag{A10}$$

where

$$\rho=\frac{2\pi ic^2}{\epsilon_2\omega^2}\,(Q+k_1\sin\theta), \tag{A11}$$

and $\alpha_i^2=\epsilon_i(\omega^2/c^2)-(Q+k_1\sin\theta)^2$, with the sign of α_i being carefully taken to meet various boundary conditions at infinity.

[1] M. Fleischmann, P. J. Handra, and A. J. McQuillan, Chem. Phys. Lett. **26**, 163 (1974).

[2] For reviews, see G. M. Goncher, C. A. Parsons, and C. B. Harris, J. Phys. Chem. **88**, 4200 (1984); D. A. Jelski, P. T. Leung, and T. F. George, Int. Rev. Phys. Chem. **7**, 179 (1988).

[3] J. I. Gersten and A. Nitzan, Surf. Sci. **158**, 165 (1985), and references therein.

[4] P. T. Leung and T. F. George, J. Chem. Phys. **85**, 4729 (1986).

[5] P. T. Leung and T. F. George, Chem. Phys. Lett. **134**, 375 (1987).

[6] See also, P. T. Leung and T. F. George, Spectroscopy **4**, 35 (1989).

[7] I. Pockrand, Opt. Commun. **13**, 311 (1975); I. Pockrand and H. Raether, Appl. Opt. **16**, 1784 (1977).

[8] D. Sarid, Phys. Rev. Lett. **47**, 1927 (1981).

[9] G. S. Agarwal, Phys. Rev. B **31**, 3534 (1985); S. D. Gupta, G. V. Varada, and G. S. Agarwal, Phys. Rev. B **36**, 6331 (1987).

[10] M. G. Weber and D. L. Mills, Phys. Rev. B **32**, 5057 (1985).

[11] T. Inagaki, M. Motosuga, E. T. Arakawa, and J. P. Goudonnet, Phys. Rev. B **31**, 2548 (1985); **32**, 6238 (1985).

[12] I. A. Avrutskii, A. S. Svarhin, and V. A. Sychugov, Opt. Spectrosc. (USSR) **63**, 198 (1987).

[13] M. G. Cavalcante, G. A. Farias, and A. A. Maradudin, J. Opt. Soc. Am. B **4**, 1372 (1987).

[14] Z. Chen and H. J. Simon, J. Opt. Soc. Am. B **5**, 1396 (1988).

[15] R. W. Gruhlke, W. R. Holland, and D. G. Hall, Phys. Rev. Lett. **56**, 2838 (1986); Opt. Lett. **12**, 364 (1987).

[16] R. W. Gruhlke and D. G. Hall, Appl. Phys. Lett. **53**, 1041 (1988).

[17] P. T. Leung, Y. S. Kim, and T. F. George, Phys. Rev. B (in press); A preliminary account of this and the present work may be found in Proc. Soc. Photo-Opt. Instrum. Eng. (in press).

[18] P. T. Leung, Y. S. Kim, and T. F. George, Phys. Rev. B **38**, 10032 (1988);

Y. S. Kim, P. T. Leung, and T. F. George, Chem. Phys. Lett. **152**, 453 (1988).

[19]See, for example, R. R. Chance, A. Prock, and R. Silbey, Adv. Chem. Phys. **37**, 1 (1978).

[20]A. A. Maradudin and D. L. Mills, Phys. Rev. B **11**, 1392 (1975).

[21]D. L. Mills and A. A. Maradudin, Phys. Rev. B **12**, 2943 (1975).

[22]See, for example, L. N. Hadley and D. M. Dennison, J. Opt. Soc. Am. **37**, 451 (1947).

[23]P. T. Leung and T. F. George, Phys. Rev. **36**, 4664 (1987).

[24]G. S. Agarwal, Phys. Rev. B **14**, 846 (1976).

[25]D. L. Mills, Phys. Rev. B **12**, 4036 (1975).

[26]E. Juranek, Z. Phys. **233**, 324 (1970).

[27]See also, M. Born and E. Wolf, *Principles of Optics*, 6th ed. (Pergamon, New York, 1980).