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Decay of molecules at corrugated thin metal films

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The problem of the decay rate for molecules at corrugated thin metal films is considered theoretically via a classical phenomenological approach by generalization of a previous theory for a single rough surface. In particular, numerical results are worked out in detail for grating films with various possible arrangements of the two grating surfaces, and for both cases with a supported and a free-standing film. Effects due to cross coupling into the long- and short-range surface plasmons are observed, and correlations to recent experiments performed by Gruhlke, Holland, and Hall are made. It is suggested that fluorescence experiments with pulsed-laser excitations should be carried out in order for the results in the present calculation to be observed.

I. INTRODUCTION

The problem of determining lifetimes for molecules in the proximity of metal surfaces has been investigated for the past twenty years due to its fundamental and practical importance.[1] Both cases of a flat[2] and a structured[3-5] surface have been thoroughly studied, though it seems to the present authors that for the latter type of surfaces, more experimental studies are needed to check the various results obtained from theoretical modeling.[2-5] Related to, but in itself a more interesting problem, is the case where the admolecules are placed close to a thin-film substrate. Roughly speaking, when the thickness is thin enough, a thin-film system is no more than two surfaces interfering with each other. For the case of a flat film, both the problems of molecular fluorescence lifetimes[2,6] and light-scattering by an external source[7] have been studied, with the latter having been extended to optically nonlinear films.[8] A system of perhaps even greater interest is a corrugated thin film, since the two surface plasmons supported by the two sides can now couple with each other leading to much richer proximity effects. This cross coupling effect has been studied recently by means of light-scattering experiments in which effects such as the couplings into long- and short-range surface plasmons[9-16] and the dramatic enhanced transparency[17,18] of a metallic film have been observed. The problem of molecular fluorescence in the vicinity of such a system has, however, received less attention. Only until very recently, being stimulated by a controversy among different groups as to whether cross coupling has really been observed from the asymmetry of the reflectance dips,[12] Gruhlke, Holland, and Hall have carried out successive experiments[19-21] to study the fluorescence of photoresist molecules in the vicinity of a Ag grating film, and it is claimed that cross coupling has been unambiguously observed in their experiments.

Motivated by the experiments in Refs. 19-21, we have set out here to perform a theoretical investigation of the decay rates (inverse lifetimes) for molecules near a metallic grating film by extending our previous theory for a grating surface.[5] We shall consider different structures of the system, including both the asymmetrically and symmetrically (free-standing) bound cases and films with only one surface roughened, and we shall make correlations with previous light-scattering[9-16] or fluorescence studies[19-21] wherever possible. In the following, we shall present in Sec. II a phenomonological theory, and numerical illustrations of various decay-rate spectra will follow in Sec. III. In Sec. IV we shall discuss the possible experimental implications from our calculations.

Before we present our formalism, we want to emphasize that whereas the theoretical treatment of the light-scattering problem usually incorporates all the dynamics of the problem,[10,11] the case for the calculation of the decay-rate problem in the vicinity of a rough surface has been simplified to work in the nonretarded (static) limit.[3,4] We have reevaluated the applicability of the nonretarded approach in terms of the substrate conductivity and the molecule-surface distances, and have emphasized the significance of applying a dynamic theory for such decay-rate calculations.[1] Very recently, we have further shown that the morphology-induced resonances in the decay-rate spectrum *can only occur in the dynamic treatment* but not in the static approach, due to the neglect of radiative energy transfer in the static theory.[22,23] Hence, we propose that to treat the cross-coupling effects (mediated by the grating period) in the decay-rate spectrum for the admolecules, it is necessary to impose a dynamic theory for the description, which we now proceed to develop in the following section.

II. FORMALISM

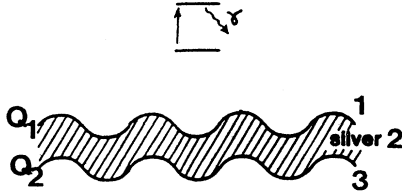The geometry of our problem is depicted in Fig. 1, where we consider a two-level system (modeled by a di-

FIG. 1. Configuration of the decay-rate problem at a corrugated thin film.

pole μ) located at a distance $z = d$ above a thin metal (taken as Ag) film bounded by two grating surfaces located at $z = 0$ and $z = -t$, respectively. Thus the profile functions take the simple forms

$$\zeta_1 = \zeta_{o_1} e^{iQ_1 x}, \quad \zeta_2 = \zeta_{o_2} e^{iQ_2 x} , \tag{1}$$

respectively, where we shall assume small corrugations ($\zeta_{o_i} Q_i \ll 1$) so that perturbation theory can be applied.[5] 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. According to the classical phenomenological (CP) ap-

proach, we must calculate the reflected field ($\mathbf{E}^r$) acting on the emitting dipole, which is then the cause of the induced decay, and we then obtain the normalized decay rate as[2]

$$\frac{\gamma}{\gamma_0} = 1 + \frac{3q\epsilon_1}{2k_1^3} \mathrm{Im} G(\omega) , \tag{2}$$

with

$$G(\omega) = \frac{E^r(\omega)}{\mu} , \tag{3}$$

and q being the quantum yield of the emitting state, $k_1 (= \sqrt{\epsilon_1} \omega/c)$ the emission wave number and γ_0 the decay rate for a free molecule. Since the details of similar calculations for a single grating surface have been given in a previous paper,[5] here we shall only sketch briefly the important steps in obtaining our final results, where as before, we shall consider the simple case with the dipole oriented perpendicular to the film.

By generalizing the original integral-equation theory for light scattering at a corrugated surface,[24] Mills and Maradudin have obtained for the corrugated film the μth component for the roughness contribution to $\mathbf{E}^r$ to first-order perturbation, given by[25]

$$E_\mu^r(\mathbf{r};\omega) = -\frac{k^2}{16\pi^3} \int d^2 k_\| e^{i\mathbf{k}_\| \cdot \mathbf{r}_\|} \int dz' d_{\mu\nu}(\mathbf{k}_\| \omega | zz') \{ [\epsilon_2 \Theta(z'+t) - \epsilon_1] \delta(z') \hat{\zeta}_1(\mathbf{k}_\| - \mathbf{k}_\|^{(0)})$$

$$+ [\epsilon_3 - \epsilon_2 \Theta(-z')] \delta(z'+t) [\hat{\zeta}_2(\mathbf{k}_\| - \mathbf{k}_\|^{(0)}) + t] \} E_\nu^{(0)}(\mathbf{k}_\|^{(0)} \omega | z') , \tag{4}$$

where $\|$ denotes any vector on the xy plane, $\hat{\zeta}_1$ and $\hat{\zeta}_2$ are Fourier transforms of Eq. (1), Θ is the Heaviside step function, and $d_{\mu\nu}$ is the Fourier transform of the two-dimensional "flat propagator" obtained in Ref. 25. $E_\nu^{(0)}$ in Eq. (4) denotes the total field for the dipole-substrate problem in the medium that contains z' for the case of a perfectly flat film, and expressions of which, in terms of the Green dyadic,[26] have already been worked out in the literature by Chance, Prock, and Silbey.[2] As pointed out before,[5] to evaluate the integral of $\delta(z')$ in Eq. (4) where $E_\nu^{(0)}$ may be discontinuous across the boundary of the films, one must adopt Agarwal's modifications[27] and not just take the mean value of the integrals at each side of the boundary.[24] It is straightforward to show that Agarwal's modifications to the theory of Maradudin and Mills[24] should be applicable to multilayered systems as well. Adopting further the normal incidence approximation ($\mathbf{k}_\|^{(0)} \approx 0$), which is good for shallow gratings,[5] we finally obtain the roughness contribution to the reflected field at the dipole site, given by ($k = \omega/c$)

$$E_z^r(d;\omega) = -\frac{k^2}{4\pi} [(\epsilon_2 - \epsilon_1)\zeta_{o_1} I_1 + (\epsilon_3 - \epsilon_2)\zeta_{o_2} I_2] , \tag{5}$$

where I_1 and I_2 are integrals given by

$$I_1 = \frac{4\pi Q_1^2}{\alpha_1 k^2} \frac{\mu}{\epsilon_1^2} e^{i\alpha_1 d} \frac{(\epsilon_2/\epsilon_3 + \alpha_2/\alpha_3)e^{i\alpha_2 t} - (\epsilon_2/\epsilon_3 - \alpha_2/\alpha_3)e^{-i\alpha_2 t}}{(\alpha_2/\alpha_1 - \epsilon_2/\epsilon_1)(\alpha_2/\alpha_3 + \epsilon_2/\epsilon_1)e^{i\alpha_2 t} - (\alpha_2/\alpha_1 + \epsilon_2/\epsilon_1)(\alpha_2/\alpha_3 - \epsilon_2/\epsilon_3)e^{-i\alpha_2 t}} \int_0^\infty d\lambda \, \lambda^3 / h_1 e^{ih_1 d} f_1 , \tag{6}$$

$$I_2 = \frac{4\pi Q_2^2}{\beta_1 k^2} \frac{\mu}{\epsilon_1^2} (k_1/k_3)^{i\beta_1 d} \frac{2\beta_2/\beta_3}{(\beta_2/\beta_1 - \epsilon_2/\epsilon_1)(\beta_2/\beta_3 + \epsilon_2/\epsilon_3)e^{i\beta_2 t} - (\beta_2/\beta_1 + \epsilon_2/\epsilon_1)(\beta_2/\beta_3 - \epsilon_2/\epsilon_3)e^{-i\beta_2 t}} \int_0^\infty d\lambda \frac{\lambda^3}{h_1} e^{ih_2 d} f_2 , \tag{7}$$

where

$$\alpha_i^2 = \epsilon_i \frac{\omega^2}{c^2} - Q_1^2, \quad \beta_i^2 = \epsilon_i \frac{\omega^2}{c^2} - Q_2^2 , \tag{8}$$

and

$$h_i^2 = k_i^2 - \lambda^2$$

with

$$k_i = \sqrt{\epsilon_i} \frac{\omega}{c} . \tag{9}$$

Note that the signs of α_i and β_i must be carefully assigned so as to satisfy the boundary conditions for the

fields at infinity.[26] The functions f_1 and f_2 are defined as[2]

$$f_1 = \frac{2Sh_1\epsilon_2}{Sh_1\epsilon_2 + h_2\epsilon_1} ,$$ (10)

with

$$S = \frac{h_2\epsilon_3 - ih_3\epsilon_2\tan(h_2 t)}{h_3\epsilon_2 - ih_2\epsilon_3\tan(h_2 t)} ,$$ (11)

and

$$f_2 = \frac{k_2}{k_3}(f_3 e^{ih_2 t} + f_4 e^{-ih_2 t}) ,$$ (12)

with

$$f_3 = \frac{1}{2}\left[\frac{h_1 k_2}{h_2 k_1} + \frac{k_1}{k_2}\right] - \frac{f_1 - 1}{2}\left[\frac{h_1 k_2}{h_2 k_1} - \frac{k_1}{k_2}\right] ,$$ (13)

$$f_4 = \frac{1}{2}\left[\frac{k_1}{k_2} - \frac{h_1 k_2}{h_2 k_1}\right] + \frac{f_1 - 1}{2}\left[\frac{k_1}{k_2} + \frac{h_1 k_2}{h_2 k_1}\right] .$$ (14)

Hence, from Eqs. (2) and (3), we finally obtain to first order in roughness the reduced total decay rate for the admolecule, given by (assuming $q \simeq 1$)

$$\frac{\gamma}{\gamma_0} = \gamma^F + \gamma^R ,$$ (15)

with

$$\gamma^F = 1 + \frac{3\epsilon_1}{2k_1^3}\mathrm{Im}G^F ,$$ (16)

$$\gamma^R = \frac{3\epsilon_1}{2k_1^3}\mathrm{Im}G^R ,$$ (17)

where

$$G^F(\omega) = \frac{i}{\epsilon_1}\int_0^\infty d\lambda\, \frac{\lambda^3}{h_1}(f_1 - 1)e^{2ih_1 d} ,$$ (18)

$$G^R(\omega) = \frac{E_z^r(d;\omega)}{\mu} ,$$ (19)

and $E_z^r(d;\omega)$ as given in Eq. (5). The correctness of this result can be checked by taking various limits such as by letting one of the ζ_{o_i}'s go to zero and by making any of the two neighboring ϵ's to be identical, and the limiting results can then be checked with those obtained previously for a single grating surface.[5]

III. NUMERICAL RESULTS

Here we apply our general results in Sec. II to several film systems of interest, each of which has been studied previously in the literature for light-scattering properties.

A. Film with only one grating surface

This system has recently been studied by Friar and co-workers[15] for the reflectance from an impinging plane wave. To investigate our decay-rate problem, we simple set $\zeta_{o_1} = 0$ in Eq. (1) and are hence left with only the term

$\zeta_{o_2}I_2$ in Eq. (5). Furthermore, we take $\epsilon_1 = 1.0$ and $\epsilon_3 = 3.6$, and $\epsilon_2 = \epsilon' + i\epsilon''$ for silver can be found from various source books.[28] Other parameters are as given in the figure captions.

Figure 2 shows the total decay (γ, solid line) as well as the separate contributions from the flat (γ^F, dotted line) and rough (γ^R, dashed line) components of the film. Here various resonance peaks can be clearly observed corresponding to the single-surface nonradiative transfer (~ 3.6 eV),[5] the flat-film interference resonance,[2] and the morphology-induced resonance[22] due to the grating surface, respectively.

Figure 3 shows, for the same system, the total rate γ for different thicknesses of the film. It is obvious that as $t \to \infty$, the single flat surface result (dotted line) is recovered, where both the flat-film interference and grating-induced resonance disappear. Similar effects on the light-scattering resonances due to the variation of film thickness in this system have been observed in Ref. 15. Likewise, similar results are obtained if we set $\zeta_{o_2} = 0$ but $\zeta_{o_1} \neq 0$ in our expressions in Sec. II,[14] except that, of course, in the limit $t \to \infty$, the grating induced peak (~ 2 eV) still shows up, in agreement with our previous investigations.[22]

B. Supported grating film

Figure 4 shows results for γ, γ^F, and γ^R, where we have assumed $\zeta_{o_1} = \zeta_{o_2} = 5$ Å. This asymmetrically bound system ($\epsilon_1 = 1$, $\epsilon_3 = 3.6$) is known for its "inefficiency" of cross coupling between the two surface
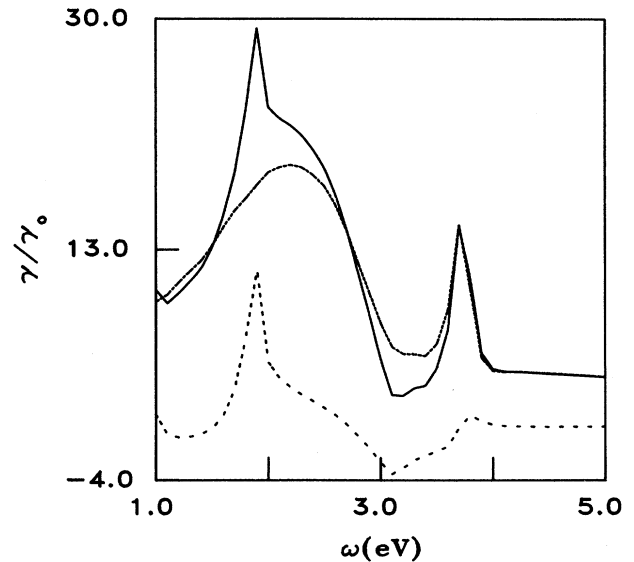

FIG. 2. Results for the various reduced decay rates for a film with one grating surface where we have chosen $d = 200$ Å, $t = 100$ Å, $\epsilon_1 = 1.0$, $\epsilon_3 = 3.6$, $\zeta_{o_1} = 0$, $\zeta_{o_2} = 50$ Å, and $Q_2 = 10^{-3}$ Å^{-1}. The solid line represents the total rate, and the dotted and dashed lines represent the contributions from the flat and rough components of the film, respectively.
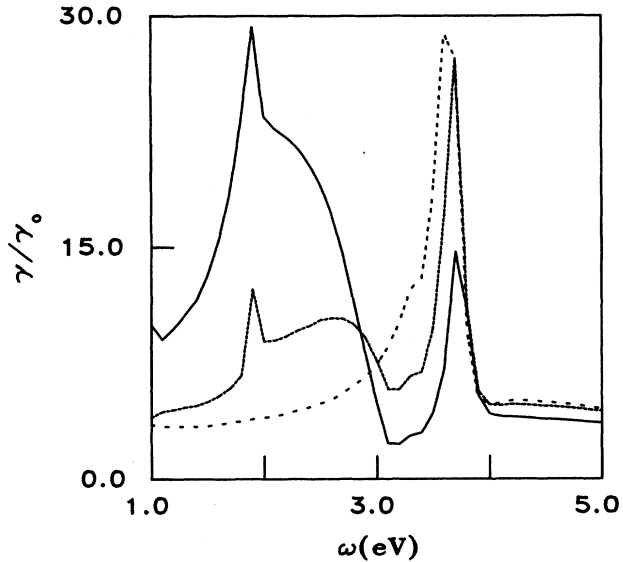
FIG. 3. Same as in Fig. 2, but only the total rates for various film thicknesses are shown: solid line, $t = 100$ Å; dotted line, $t = 200$ Å; dashed line, $t \to \infty$.

FIG. 5. Same as in Fig. 4, but only the total rates for various film thicknesses are shown: a, $t = 100$ Å; b, $t = 150$ Å; c, $t = 200$ Å; d, $t \to \infty$.

plasmons supported by each grating surface.[21] In fact, the resonance peaks that appear in Figs. 4 and 5 are not much different (except in strength) when compared with the results in case A. This fact can be easily understood in the case of plane-wave incidence, where the dispersion relations for the two surface plasmons are simpler, from which serious restrictions are found to be imposed on the coupling condition when the film is bounded by two different dielectric media.
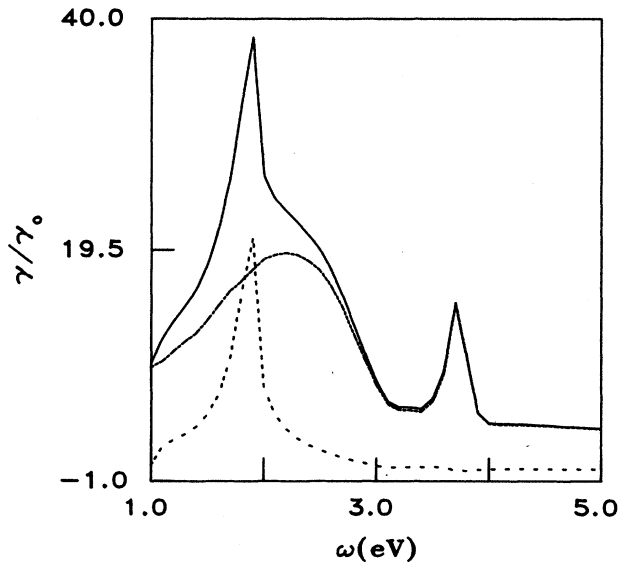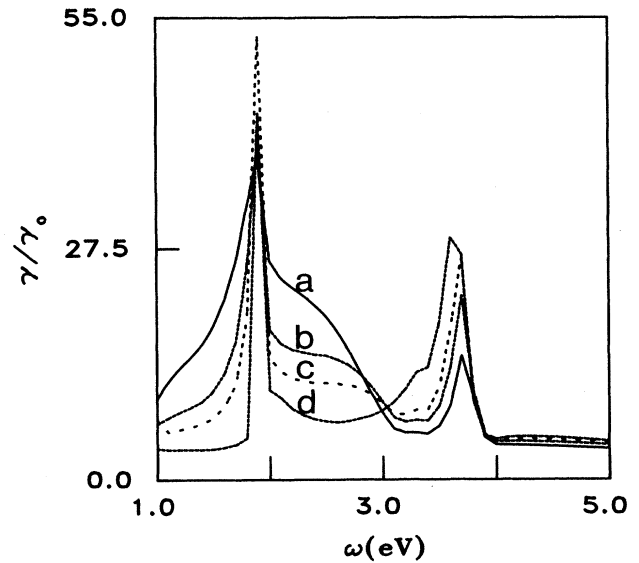
C. Free-standing grating film

This is the most efficient system for cross coupling studies, since the two surface plasmons are coupled for all energies in the case of plane-wave incidence.[21] The fabrication of such a film has been described by Inagaki and co-workers.[13] For simplicity, we have assumed $\epsilon_1 = \epsilon_3 = 1$ and $\zeta_{o_1} = \zeta_{o_2} = 5$ Å. It is clearly seen from Fig. 6 that the two surface plasmons on each grating surface are coupled

FIG. 4. Results for a supported ($\epsilon_1 = 1.0$; $\epsilon_3 = 3.6$) grating film, where we have taken $d = 200$ Å, $t = 100$ Å, $\zeta_{o_1} = \zeta_{o_2} = 5$ Å, $Q_1 = Q_2 = 10^{-3}$ Å^{-1}, and the graphical notations are as given in Fig. 2.
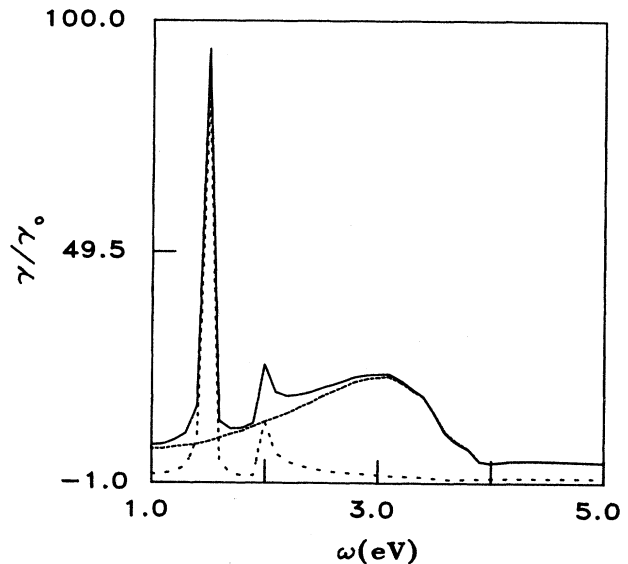

FIG. 6. Results for a free-standing film ($\epsilon_1 = \epsilon_3 = 1.0$), where all other parameters and notations are as in Fig. 4.

to the long- ($\omega \sim 1.5$ eV) and short-range ($\omega \sim 2.0$ eV) surface plasmons. Similar features have been observed in a light-scattering experiment[13] in which the photoacoustic technique has been applied to monitor the excitation of such cross-coupled plasmons. However, the splitting of higher-order peaks observed there does not show up in our calculation due to the different dispersion relations which we have here for the coupling of the dipole radiations to the film, instead of the plane-wave couplings as in the light-scattering case, where one has multiple branches of dispersion relations.[13] Figure 7 shows results for the same system with different film thicknesses, where again the cross-coupling effect disappears for a thick film, just as in the experiments of Inagaki and co-workers.[13]

D. Remarks on the Rochester experiments

In three recent investigations,[19−21] a group at the University of Rochester has performed beautiful experiments in which cross coupling of the two surface plasmons from the sides of a thin grating Ag film is unambiguously observed, through the scattered (transmitted) light from the molecular fluorescence of a photoresist in the vicinity of the film. Both asymmetrically- and symmetrically-bound films have been studied. We have performed a calculation of the decay rates [Eqs. (5)–(19)] for one of their systems using their parameters for the optical constants and the silver grating of different periods, and our results are shown in Fig. 8. Although we observe a similar qualitative feature to that in Fig. 1 of Ref. 19, the positions of the peaks are quite different in the two cases. We suspect that the type of experiments we are referring to would be quite different from the Rochester experiments, since in the latter the dispersion relations are still guided by those derived from an incident plane wave, and the fluorescent molecules are simply undergoing Rayleigh scattering by
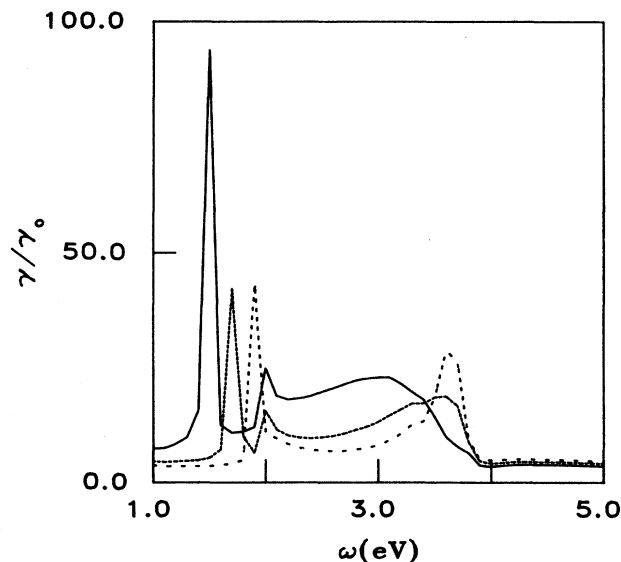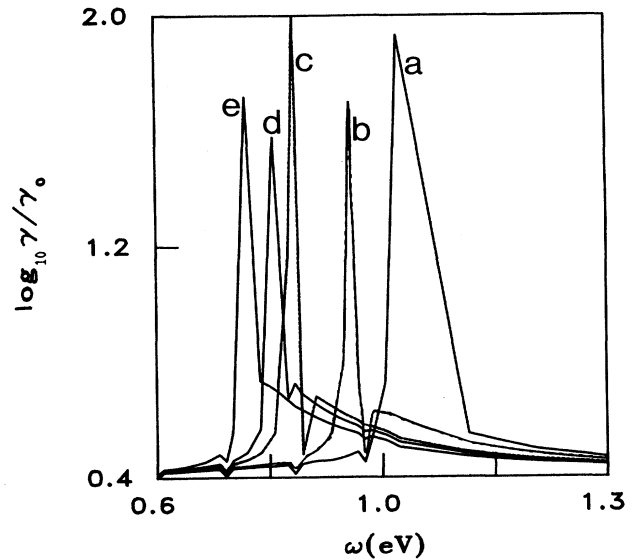

FIG. 8. Calculation of the (total) decay-rate spectrum using the parameters given in Ref. 19 with $t = 500$ Å. The various graphs correspond to different grating periods ($\Lambda = 2\pi/Q$): a, $\Lambda = 760$ nm; b, $\Lambda = 814$ nm; c, $\Lambda = 900$ nm; d, $\Lambda = 926$ nm; e, $\Lambda = 976$ nm. Note that the logarithmic scale is used for the reduced decay rates.

which the incident light from the optical fiber is transmitted through the grating film. Here, as discussed above, we are instead referring to the coupling between the surface plasmons and the dipole fields of the decaying molecules in which a superposition of all the harmonics are involved, and hence we expect the resonances to be governed by different dispersion relations. As a matter of
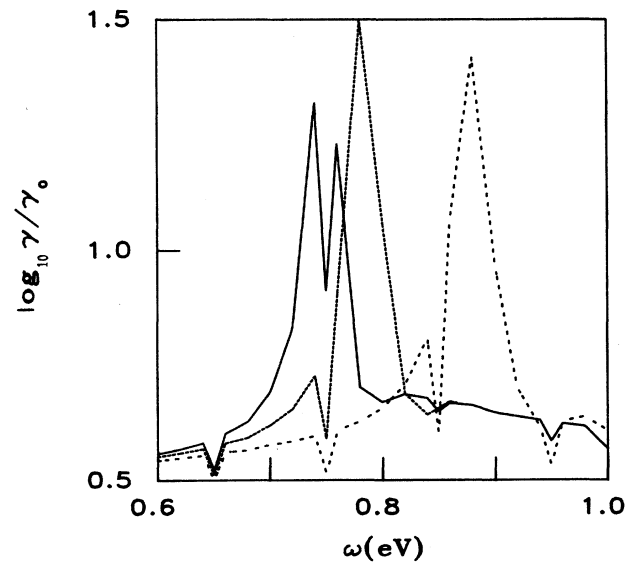

FIG. 7. Same as in Fig. 6, but only the total rates for various film thicknesses are shown: solid line, $t = 100$ Å; dotted line, $t = 200$ Å; dashed line, $t \rightarrow \infty$.

FIG. 9. Cross coupling into the long- and short-range surface plasmons for the configuration as in Fig. 8 for thinner film thicknesses ($t = 150$ Å). Only the cases b (dashed line), d (dotted line), and e (solid line) of Fig. 8 are shown.

fact, one of the Rochester experiments[21] indeed shows that for the symmetrically-bound case, multiple resonances due to higher-order dispersions do appear in their transmittance spectrum, much as in the case of plane-wave scattering as studied by Inagaki et al.[13] In fact, the peaks shown here for the decay-rate spectrum in Fig. 8 are not much different from those due to single-surface (thick-film) couplings (cf. Figs. 3 and 5). Cross coupling into the split modes of the long- and short-range surface plasmons can only be seen here if the film thickness is further decreased, as shown in Fig. 9.

We would like to propose that for the observation of the peaks calculated in this present work, fluorescence experiments have to be performed in which the molecules are excited by a short-pulse laser and the emission intensity is monitored by various time-resolved techniques.[29] In this fashion, the decay-rate values can then be deduced by assuming appropriate forms for the decay curves that fit the intensity data. In such experiments, the pulse width of the laser must be considerably shorter than the lifetimes ($\sim 1/\gamma$) of the admolecules, and the molecule decaying from its excited state (after being "pumped up" by the laser pulse) can then be modeled as a radiating dipole.[2] The reflected field from the substrate film acted on the dipole (which leads to the induced decay of the molecule) can then be correctly described by the present formalism, and hence the peak positions from the present work can be checked by exciting various fluorescent molecules of different natural frequencies.

IV. CONCLUSION

We have performed calculations of the decay-rate spectrum for fluorescent molecules near a corrugated metal film for both supported and unsupported systems, and appropriate types of experiments have been suggested. While many qualitative features observed here are similar to the case of light-scattering analyses of such film systems,[9-16] we emphasize that a distinct feature of the present problem is the dipole nature of the radiation coupled to the surface plasmons of the film. Because of the difference between this coupling and the plane-wave coupling to the grating modes, we expect that interesting phenomena will arise if one studies the photoabsorption of these admolecules in which an external laser field (plane wave) is introduced to drive the admolecules with *both* the external and molecular (dipolar) fields coupled to the surface plasmon modes at the same time. We have obtained some preliminary results for such a problem, and details will be presented in a separate paper.[30]

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