Theoretical model for enhanced photochemistry on rough surfaces

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A simplified theory of enhanced ultraviolet, visible, and infrared photochemistry near rough dielectric and metallic surfaces is described and numerically investigated. Protrusions on a rough surface are modeled as isolated microscopic spheres. We formulate classical equations of motion for molecules interacting with electromagnetic fields and such material spheres. The model incorporates (a) dipole–dipole coupling between absorbing molecules and the large, induced dipoles created in microscopic spheres irradiated near Mie resonances, and (b) dissipative energy transfer from excited molecules to higher order $(l > 1)$ multipole resonances in the spheres. Calculations show that substantial enhancements in photochemical yields are possible for relatively slow chemical reactions as well as fast reactions. The similarities and differences between enhanced photochemistry and surface enhanced Raman scattering (SERS) are discussed in detail. Dielectric materials for enhanced infrared photochemistry at CO_2 laser wavelengths are proposed.

I. INTRODUCTION

Recent experimental and theoretical studies on surface enhanced Raman scattering (SERS)[1] have indicated that an important contributing mechanism is the intensified local electromagnetic field experienced by a molecule in the vicinity of surface protrusions on a rough metal substrate.[2] SERS due to field enhancement has also been observed for molecules adsorbed on microscopic metal islands[3] and near metallic particles imbedded in a solid matrix or in a colloidal solution.[4] In these situations a modified local electromagnetic field results from the image, the shape, and the plasmon resonance effects. The image effect, namely, the effect on the molecule due to the field induced by its own surface image, is a major cause for the short distance radiationless energy transfer from an excited molecule to a nearby surface.[5] However, the image contribution to the Raman enhancement is probably quite small.[6,7] The shape (also termed the lightening rod) effect is associated with the larger local field existing near sharp metallic edges and protrusions of a system lying in an external electromagnetic field. A molecule located near such a protrusion will feel this larger field and respond accordingly. It should be kept in mind that *on the average* the field intensity is not modified much by the presence of the metal boundaries.[8] "Lightening rod" enhancement will, however, be observed for processes which depend on high powers $(E^n, n \geq 2)$ of the field and also in cases where the molecules are preferentially adsorbed in higher field regions.[9]

Finally, plasmon resonance enhancement results from the interaction between an adsorbed molecule and the induced fields due to resonances excited in the substrate particles. These resonances may be localized in separate particles or surface protrusions[11(m),(o),(p)] or delocalized among many such centers.[1(a),(k)] While the use of the enhanced local field concept is valid for this case (the enhanced local field is caused by the plasmon resonance excitation in the substrate), one may also employ the more conventional (and equivalent) viewpoint of energy transfer between the excited plasmon resonance and the molecule.

Obviously, a theory which interprets SERS using an enhanced local electromagnetic field should predict that other phenomena associated with the interaction between molecules and an electromagnetic field should be affected by the proximity of such molecules to a suitable surface. Indeed, enhanced adsorption and luminescence have recently been reported.[10] In the present paper we investigate the feasibility of enhancing photochemical processes by the same mechanism.[11]

In order to understand the factors involved in enhancing electromagnetic processes on rough surfaces, it is useful to outline these experimental observations for SERS:

(a) The coinage metals (Ag, Au, and Cu) are the most efficient enhancing agents. This is related to their low plasma frequency, and we should expect similar behavior with alkali metals.

(b) Silver is by far the best enhancing substrate found to date. This results from its narrow, pronounced plasmon resonance.

(c) Surface roughness seems almost always to be necessary for SERS. Roughness implies both the excitability of surface plasmons and also field modification through the shape effect. The dependence of SERS on the incident frequency is strongly connected with the surface morphology which affects the plasmon resonance.

(d) While the enhancement is strongest at the closest approach to the surface, SERS has been observed also for molecules located as far as 100 Å from the surface in some cases.[12] SERS seems to be a *monotonically* decreasing function of the molecule surface distance.

(e) SERS is not normally molecule specific. The enhanced Raman cross section seems to be linearly dependent on the corresponding cross section of the free molecule. However, variation occurs due to the effect of surface selection rules, and to distortion and change in geometry of some adsorbed molecules.

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(f) The integrated intensity of SERS, like that of spontaneous Raman scattering from a free molecule, is linear in the incident radiation intensity.

All these factors may play an important role in any other surface enhanced electromagnetic process. However, some important differences should exist between SERS and enhanced photochemistry. These differences arise from the fact that SERS is, as far as the molecule is concerned, a nonresonant scattering process while photochemistry by its nature involves resonant adsorption and energy flow within the molecule. Furthermore, photochemistry often requires a finite accumulation of energy in the molecule before the desired process can take place. These ideas suggest the following qualitative consequences:

(a) The finite time needed for energy accumulation implies that unfavorable energy damping processes induced by the surface may compete with the desired photochemical reaction. In other words, even though an enhanced local electromagnetic field implies a larger integrated absorption by the molecule, this by no means guarantees that energy will be efficiently accumulated in the molecule. In particular, dissipation of the molecular energy via energy transfer to the substrate, being a very efficient process close to the surface, may compete successfully against the enhanced pumping process, thus preventing any substantial energy accumulation by the molecule.

(b) In addition to the competing energy damping, other processes may interfere with the desired photochemical reaction. These include surface induced thermal reactions, thermal and radiation induced desorption, and thermal surface degradation.

(c) The enhancement of resonant excitation of the molecule is expected to depend on the overlap between the molecular resonance and the excitable surface resonances. This implies that nonspecificity as far as the molecule is concerned will not hold. An efficient enhancement of a given resonance process will take place only on a suitably chosen substrate. It should also be noted that a broader (as opposed to narrower) plasmon resonance may sometimes by favorable as it overlaps better with the molecular resonance.

(d) Current electromagnetic theories of SERS treat a metal—vacuum (or other inert medium) interface disregarding the modification of dielectric properties of the medium outside the metal by the presence of the adsorbed molecules. While this is usually a good approximation in SERS, where the incident radiation is far from the molecular resonance, in photochemical situations this may not be true. This is particularly important in such situations where the molecules form a relatively thick adsorbed layer.

(e) Since the photochemical yield depends on the competition between the surface enhanced adsorption and surface induced damping processes, the molecule—surface distance dependence of surface enhanced photochemistry may be different from that of SERS.

We note that all these issues are relevant not only for surface enhancement photochemistry, but for all sur-face modified resonance optical phenomena. In particular, (c) and (d) above are important for surface enhanced resonance Raman scattering.

From the above discussion it is clear that the feasibility of surface enhanced photochemistry depends not only on our ability to insure that an enhanced pumping rate will subsequently result in a larger photochemical yield, but also on the availability of dielectric substrates with plasmon resonances ranging throughout the photochemically interesting spectral regime (i. e., from the UV to the infrared). In Sec. II we briefly discuss such possible dielectrics. Actual model cases are investigated in Secs. III and IV. Generally, two extreme situations may be envisioned. In the first, the chemical process following the adsorption step is very fast (e. g., direct photodissociation). In this relatively simple case enhanced photochemistry is essentially synonymous with enhanced absorption. In the second extreme case the chemical reaction requires the accumulation of a certain threshold energy equivalent to a few absorbed photons (e. g., infrared multiphoton dissociation). The ability of the molecule to actually store energy near the surface becomes crucial for this case.

In the present study we limit ourselves to situations where the dielectric environment of the substrate is assumed not to be affected by the photochemically active molecules. This situation occurs when the molecules are present in low density (e. g., gas phase), or for weakly absorbing molecules present in somewhat higher concentrations.

The effect of the dielectric surface is modeled by considering a single microscopic particle of a given size and dielectric material as a substrate for the chemically interesting molecule. Such a particle represents a surface protrusion, or an island in a surface island film. The molecule is classically modeled as a point dipole with an internal coordinate capable of storing energy. Similar models have been used in electromagnetic theories of SERS. A summary of our model assumptions, their limitations, and an outline of the future directions of this research is provided in Sec. IV.

II. DIELECTRIC SUBSTRATES

Investigations of SERS have demonstrated the crucial role play by the substrate in this phenomenon. Both experimental and theoretical results have pointed out the close relationship between SERS and Mie resonances or "conduction electron resonances" (a term used by several authors to describe delocalized Mie resonances in electromagnetically interacting metal particles)[13] in the substrate particles. The energy and shape (intensity and width) of these resonances are very sensitive to the type of substrate used and to the morphology of its surface. In what follows, we assume that the bulk dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ of the substrate may be used to investigate the electromagnetic properties of its surface and of small substrate particles.

Consider a small (relative to the radiation wavelength) dielectric sphere which very roughly models a surface protrusion or an isolated island in an island film de-

posited on some inert surface. A Mie resonance in the light adsorption and scattering by this sphere occurs at frequency ω_S such the $\epsilon_1(\omega_S) = -2$. Excitation of the sphere is actually characterized by a series of multipole resonances with $l \geq 1$, and the Mie resonance at ω_S is the dipolar $l = 1$ member of this series. Only the dipole member of the series can be excited in the limit that the sphere is small with respect to the radiation wavelength. The width of this resonance is given approximately by

$$\gamma = [2\epsilon_2(\omega)/\epsilon_1'(\omega)]_{\omega = \omega_S} , \qquad (\text{II.1})$$

where $\epsilon_1'(\omega) = d\epsilon_1(\omega)/d\omega$. For a molecule adsorbed on this sphere, SERS as well as other electromagnetic phenomena (e.g., enhanced absorption and luminescence) dependent upon intensified local fields are expected to be most pronounced for $\omega = \omega_S$, where ω is the incident or the emitted frequency. The magnitude of the induced oscillating dipole in the sphere is maximized at the Mie resonance, and thus the magnitude of the induced local electromagnetic fields is also maximized at ω_S.

Having in mind the possible enhancement of resonance molecular processes, we should be able to provide dielectric substrates such that $\omega_S \simeq \omega_M$, where ω_M is the given molecular resonance frequency. For free electron metals $\epsilon(\omega) = \epsilon_\infty[1 - \omega_p^2/(\omega^2 + i\omega/\tau_e)]$, where $\omega_p^2 = 4\pi Ne^2/m^*\epsilon_\infty$ (N, e, and m^* are the electron density, charge, and effective mass, respectively). ω_p is the plasma frequency, τ_e is the electron relaxation time, and ϵ_∞ is the dielectric constant associated with tightly bound core electrons. If $\tau^{-1} \ll \omega$, we get $\omega_S = \omega_p/\sqrt{(1 + 2/\epsilon_\infty)}$. Keeping in mind that ϵ_∞ is on the order of 1–10 and that $\omega_p \sim 5$–20 eV, we see that rough metal surfaces may be useful in the UV and the far UV ranges, though exceptions in real metals do result from the existence of low energy interband transitions leading to a modified $\epsilon(\omega)$ (e.g., in silver, copper, and gold).

In the IR regime nonmetallic dielectrics suggest themselves as potentially more useful substrates. The following two classes of materials may prove particularly useful.

A. Ionic crystals

The dielectric function of ionic crystals is given by

$$\epsilon(\omega) = \epsilon_\infty \frac{\omega_L^2 - \omega^2 - i\omega\tau_n^{-1}}{\omega_T^2 - \omega^2 - i\omega\tau_n^{-1}} , \qquad (\text{II.2})$$

where ω_L and ω_T are the long wavelength longitudinal and transverse optical phonon frequencies, respectively, and where τ_n is the relaxation time associated with the lattice nuclear motion. ω_L and ω_T are related by the Lyddane–Sachs–Teller expression

$$\omega_L/\omega_T = (\epsilon_0/\epsilon_\infty)^{1/2} , \qquad (\text{II.3})$$

where ϵ_0 is the static ($\omega = 0$) dielectric constant. For $\tau_n^{-1} \ll \omega$ we get

$$\omega_S = \omega_T[(\epsilon_0 + 2)/(\epsilon_\infty + 2)]^{1/2} . \qquad (\text{II.4})$$

Since $\epsilon_0 > \epsilon_\infty$, we see that

$$\omega_T < \omega_S < \omega_L . \qquad (\text{II.5})$$

As an example, consider MgO^{14} with $\epsilon = 10$, $\epsilon_\infty = 2.95$,

and $\omega_T = 578$ cm^{-1}. Equation (4) yields $\omega_S = 900$ cm^{-1}. For SiC,[15] $\epsilon_0 = 10$, $\epsilon_\infty = 6.7$, and $\omega_T = 794$ cm^{-1}, implying $\omega_S = 932$ cm^{-1}. Note that these values are close to CO_2 laser frequencies and thus these materials may be suitable for enhancing processes induced by this laser. We also note that these resonances are quite sharp. For the SiC data we get, from Eq. (1), $\gamma = 9.5$ cm^{-1}.

B. Doped semiconductors

In ionic semiconductors both optical phonons and free charge carriers contribute to the dielectric function, a simple model for which is

$$\epsilon(\omega) = \epsilon_\infty \left(1 - \frac{\omega_p^2}{\omega^2 + i\omega\tau_e^{-1}} + \frac{\omega_L^2 - \omega^2 - i\omega\tau_n^{-1}}{\omega_T^2 - \omega^2 - i\omega\tau_n^{-1}}\right) . \qquad (\text{II.6})$$

Due to the low carrier concentrations, the characteristic plasma frequencies are much lower than those of metals and ω_S may again take values in the IR range. Furthermore, the ability to adjust ω_p via doping makes these materials potentially versatile. As an example, consider n-type InSb[16] ($\epsilon_0 = 17.9$, $\epsilon_\infty = 15.7$, $\omega_T = 179$ cm^{-1}, $\tau_n^{-1} = 2.7$ cm^{-1}, $\tau_e^{-1} = 30$ cm^{-1}, and $m^* \simeq 0.03 m_e$). If we fix the carrier concentration so that $\omega_p = 1028$ cm^{-1} ($N \simeq 5.5 \times 10^{18}$ cm^{-3}), we obtain $\omega_S = 967$ cm^{-1} and $\gamma = 33.6$ cm^{-1}. This resonance also lies within the CO_2 laser range.

Obviously, these numbers principally serve for illustration. The resonance behavior of real substrate particles will be substantially modified due to nonspherical shapes, the effect of the underlying surface, the interactions between the dielectric particles, the dielectric solvent around the particle, and so on. A better understanding of these optical effects may eventually provide us with tools to control the dielectric properties of a substrate for our photochemical purposes. For the case of a semiconductor substrate it is important to mention the complication arising from the strong temperature dependence of the dielectric function, which may lead to a change in this function in the course of the photochemical process due to heating effects.

III. DIRECT PHOTODISSOCIATION

As discussed in the Introduction, enhanced photochemistry is a direct implication of enhanced absorption in cases where the photochemical reaction in the excited molecular state is fast relative to all the damping processes which affect the excited molecule. Direct photodissociation, which takes place on a time scale on the order of 10^{-14} sec following the absorption, belongs to this case. Other examples include direct photoionization, and internal isomerizations taking place within essentially one vibrational period. Here the yield of the reactive process is unity to a good approximation, i.e., the reaction cross section is equal to the absorption cross section.

We invoke a highly simplified model where the molecule is represented by a classical point dipole with static polarization α_M lying at a distance d from the surface of a dielectric sphere of radius a. The sphere is characterized by a dielectric function

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) . \tag{III.1}$$

We limit ourselves to the case where a and d are much smaller than the radiation wavelength. The molecule is taken to lie on the z axis (with the sphere center at the origin) and the induced molecular dipole is assumed to lie in the zx plane and to form an angle θ_M with this axis. The incident radiation field is assumed to be plane polarized with its electric field component pointing in the (θ, ψ) direction.

Our starting point is the equations of motion for the molecule and the sphere polarizations given by (in the Drude approximation for the sphere and the harmonic model for the molecule)[17]

$$\ddot{\mu} + \tilde{\omega}_M^2 \mu + \Gamma \dot{\mu} = \omega_M^2 \alpha_M \left[\left(\frac{2}{R^3} \mu_{sz} + E_z \right) \cos\theta_M \right.$$
$$\left. + \left(-\frac{1}{R^3} \mu_{sx} + E_x \right) \sin\theta_M \right] , \tag{III.2a}$$

$$\ddot{\mu}_{sz} + (\omega_S^2 + \gamma^2/4)\mu_{sz} + \omega\dot{\mu}_{sz} = \omega_x^2 \alpha_s \left(\frac{2}{R^3}\mu\cos\theta_M + E_z \right) , \tag{III.2b}$$

$$\ddot{\mu}_{sx} + (\omega_S^2 + \gamma^2/4)\mu_{sx} + \omega\dot{\mu}_{sx} = \omega_S^2 \alpha_s \left(\frac{1}{R^3}\mu\sin\theta_M + E_x \right) . \tag{III.2c}$$

μ is the induced molecular dipole, $\tilde{\omega}_M = \omega_M + D$, where ω_M is the molecular resonance frequency and D is a surface induced shift, α_M is the static molecular polarizability, E_z and E_x are the z and x components of the incident radiation field, respectively, $R = d + a$, μ_{sz} and μ_{sx} are the z and x components of the dipole moment induced on the sphere, respectively, and α_s is the apparent static sphere polarizability.[17] α_M and α_s may be expressed

$$\alpha_M = \tfrac{3}{2}(C/\omega_M)^3 (\Gamma_r^{(f)}/\omega_M) \tag{III.3}$$

and

$$\alpha_s = \frac{6a^3}{\omega_s[\partial\epsilon_1(\omega_S)/\partial\omega_S]} , \tag{III.4}$$

where $\Gamma_r^{(f)}$ is the radiative decay rate of the free molecule and c is the speed of light. Finally, Γ appearing in Eq. (III.2a) is the molecular decay rate resulting from all processes which are not associated with the interaction between the molecule and the dipolar sphere resonance:

$$\Gamma = \Gamma^{(f)} + \Gamma'_{nr,s} \tag{III.5}$$

In Eq. (III.5), $\Gamma^{(f)}$ is the (radiative and nonradiative) intrinsic decay rate of the isolated free molecule, and $\Gamma'_{nr,s}$ is the nonradiative decay rate of the molecule resulting from energy transfer from the molecule to the nonradiative, higher multipole $(l > 1)$ sphere resonances. For $d \ll a$ $(d \leq 0.2a$, approximately), $\Gamma'_{nr,s}$ approximately equals $\Gamma_{nr,s}$ (the rate for nonradiative energy transfer from the molecule to all the sphere modes) and, in fact, is given to a good approximation by $\Gamma_{nr,pl}$ (the corresponding rate for a molecule on a plane surface). This result is demonstrated in Fig. 1, where typical calculated values of $\Gamma_{nr,pl}$, $\Gamma_{nr,s}$, and $\Gamma'_{nr,s}$ for a model sys-
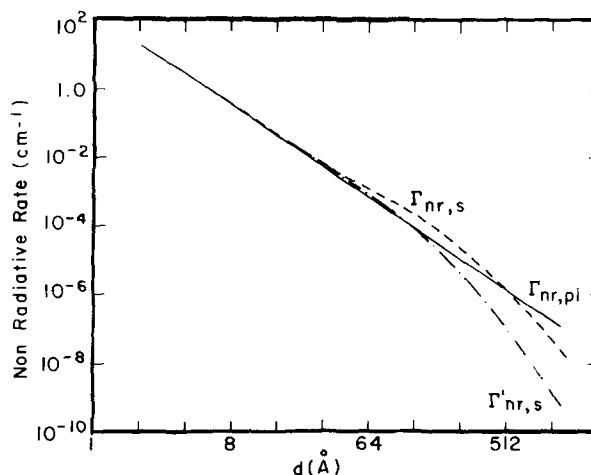

FIG. 1. Log–log plot of the distance dependence of various nonradiative decay rates of a molecule near a dielectric surface. $\Gamma_{nr,pl}$ is the decay rate near a planar surface; $\Gamma_{nr,s}$ is the rate near a 200 Å sphere. $\Gamma'_{nr,s}$ is similar to $\Gamma_{nr,s}$ but the contribution of the $l = 1$ sphere plasmons is not included. Parameters used are for a model SF_6 molecule near doped InSb with $\omega_p = 1027$ cm^{-1} (Table I). All rates are for a molecule perpendicular to the surface.

tem are presented. The method of Ref. 17 has been used for this calculation. Similarly, the shift D results from the interaction of the molecule with the $l > 1$ sphere resonances but may be approximated for $d \ll a$ by the frequency shift calculated for a plane. In what follows we shall assume that $D \ll \omega_M$ and take $\tilde{\omega}_M \simeq \omega_M$. (This is usually true at distances for which the present classical theory is valid.)

The energies corresponding to the excited molecule (W_M) and to the dipolar sphere resonance are given by

$$W_M = \frac{1}{2\lambda_M}[(\dot{\mu}/\omega_M)^2 + \mu^2] , \tag{III.6}$$

$$W_s = W_{sx} + W_{sz} ,$$

$$W_{sn} = \frac{1}{2\alpha_s}[(\dot{\mu}_{sn}/\omega_s)^2 + \mu_{sn}^2] , \quad n = x, z . \tag{III.7}$$

In the Appendix we derive an expression for the absorption cross section of the molecule as determined from Eq. (III.2). The result is

$$\sigma_{ab}(\omega) = \frac{4\pi}{3}\frac{\omega}{C}\text{Im}[D_1(\omega)D_3(-\omega) + D_2(\omega)D_4(-\omega)] , \tag{III.8}$$

where $D_i(\omega)$ $(i = 1, \ldots, 4)$ are defined in Eqs. (A10)–(A15). The result (III.8) is obtained for the case where the molecule–sphere system is oriented at random directions relative to the incident field $E = E_0\cos(\omega t)$.

Figures 2–7 display results of calculations on various model systems based on Eq. (III.8). In Figs. 2–4 we show $\sigma_{ab}(\omega)$ obtained for a model I_2 molecule located at different distances from silver, copper, and gold spheres. The molecular parameters correspond to the I_2 molecule above its photodissociation threshold, where the actual molecular line shape was replaced by a Lorentzian with a width approximately corresponding to the dissociation rate of the excited molecule. For com-
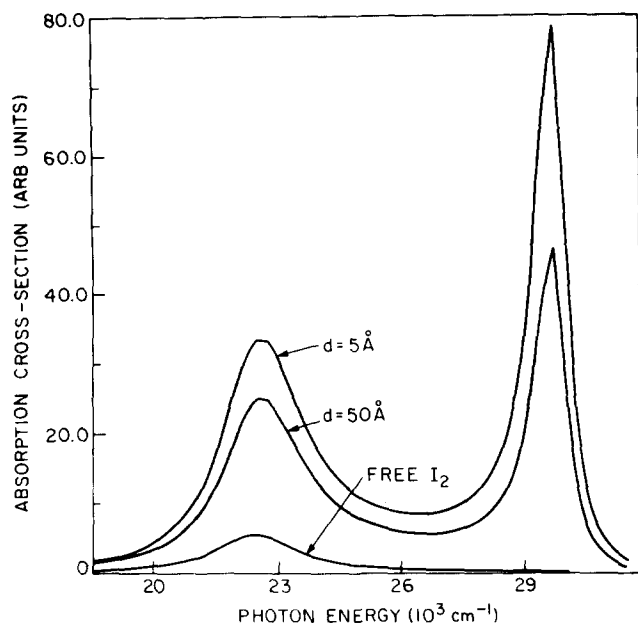
FIG. 2. Visible absorption cross section of a model I_2 molecule near a silver sphere ($a = 500$ Å). The molecule is perpendicular to the surface.

FIG. 4. Absorption cross section of a model I_2 molecule near a gold sphere ($a = 500$ Å). The molecule is perpendicular to the surface.

pleteness we also show a similar plot for the absorption cross section of a model SF_6 molecule (a harmonic molecule with parameters corresponding to the $v = 0 \rightarrow 1\,965\,cm^{-1}$ transition of SF_6) located at different distances from a InSb sphere, even though enhancement in this case of a long-lived excited state does not directly imply that photochemistry is also enhanced.

The dependence of the integrated absorption cross section on the molecule–sphere spearation d is shown in Fig. 6 for the model iodine molecule near the silver, copper, and gold spheres and in Fig. 7 for the model SF_6 molecule near spheres made of InSb and of SiC. The
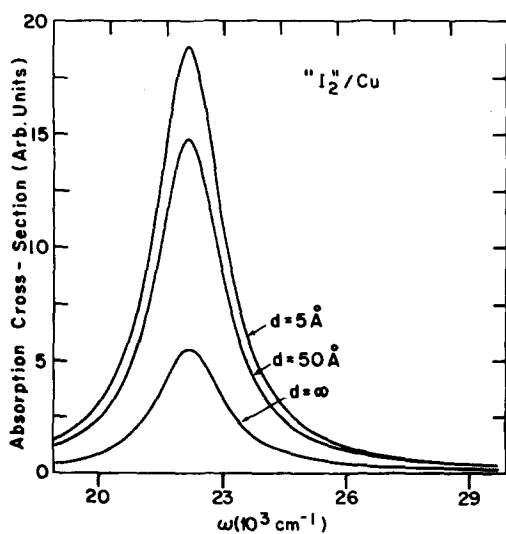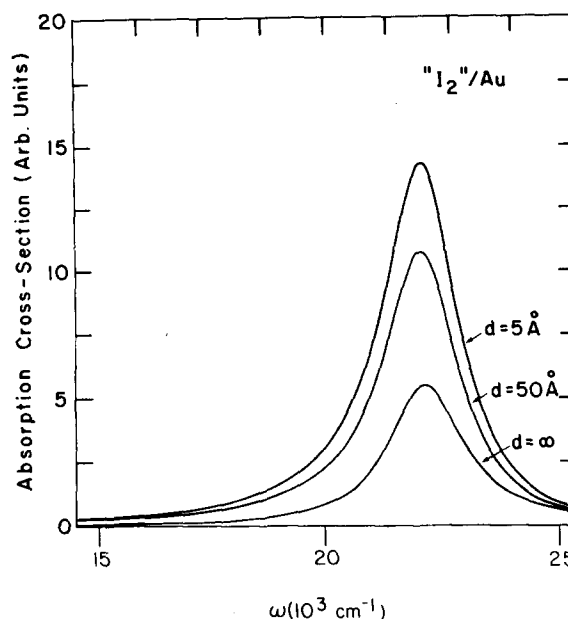
parameters used in these calculations are given in Table I. It should be kept in mind that the present theory which approximates the sphere response to an incident homogeneous field as a Lorentzian function peaked at the dipolar Mie resonance (the "Drude approximation")[17] is valid only for $\gamma \ll \omega_S$. There the results for copper and gold should be viewed only as order of magnitude estimates.

Figures 3–5 show the typical enhancement in the absorption cross section (and photochemistry) obtained for cases characterized by good overlap between the molecular and the dielectric resonance. Figure 2 shows a more interesting case obtained for intermediate separations ($|\omega_M - \omega_S| \gtrsim \Gamma + \gamma$) between the two resonances. We recall that what is plotted is essentially the rate of
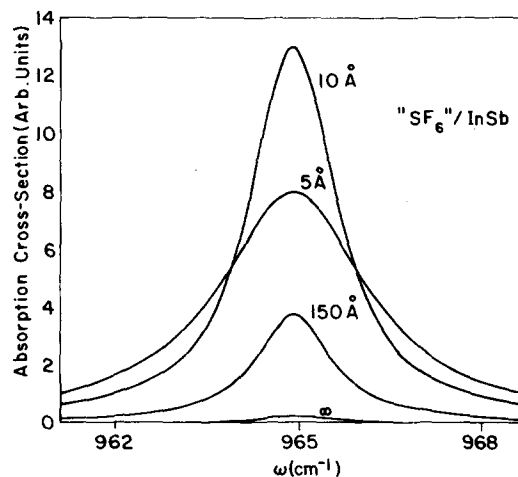

FIG. 3. Absorption cross section of a model I_2 molecule near a copper sphere ($a = 300$ Å). The molecule is perpendicular to the surface.

FIG. 5. Absorption cross section of a model SF_6 molecule near a InSb sphere ($a = 500$ Å). The molecule is perpendicular to the surface.
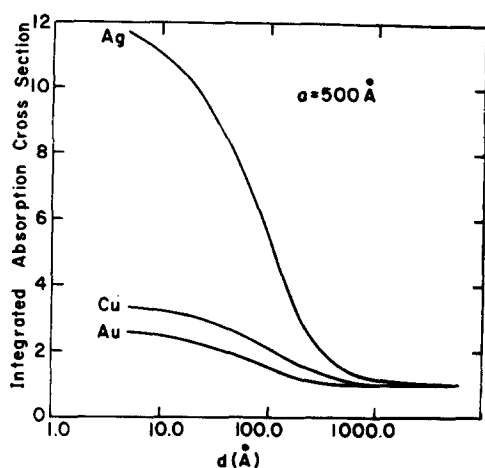
FIG. 6. Integrated absorption cross sections for the model I_2 molecule perpendicular to Ag, Cu and Au spheres ($a = 500$ Å) as a function of the molecule–surface separation. The cross sections are normalized to I as $d \to \infty$.

FIG. 7. Integrated absorption cross sections for the model SF_6 molecule perpendicular to SiC and InSb spheres ($a = 500$ Å) as a function of the molecule–surface separation.

energy pumping into the molecule. We may interpret the peak near the free molecular resonance as direct absorption by the molecule enhanced because of the increased local electromagnetic field near the sphere. The other peak located near the dipolar Mie resonance of the silver sphere may be heuristically interpreted as energy absorption by the sphere followed by energy transfer from the sphere to the molecule. We see that in this case the more efficient photodissociation may be achieved by irradiating the system near the silver sphere resonance. This doubly peaked curve has no analog in the theory of SERS near a silver sphere, and demonstrates a novel effect which appears in the theory of enhanced photochemistry.

Figure 7 shows another remarkable feature. The effect of the sphere on the molecular absorption can add either destructively or constructively to the absorption of the free molecule. Destructive interference in the SF_6/SiC system leads to a reduction in the absorption cross section relative to that of the free molecule for intermediate molecule–sphere surface separations in Fig. 7.

A simple approximate estimate for these effects can be obtained by neglecting the μ dependent terms on the rhs of Eqs. (III.2b) and (III.2c). The terms containing
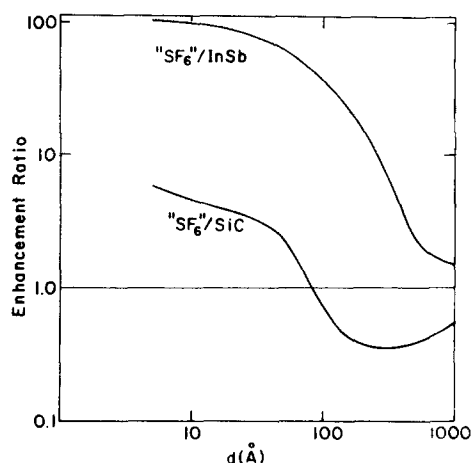
μ_{sx} and μ_{sz} in Eq. (III.2a) then become simple correction terms for the local field and since σ_{ab} is proportional to $|E_{loc}|^2$, we can easily calculate the enhancement ratio. Limiting ourselves to the case $\theta_M = 0$ (molecule normal to the sphere surface), we obtain (putting $\tilde{\omega}_s^2 = \omega_s^2 + \gamma^2/4$)

$$\frac{\sigma_{ab}}{\sigma_{ab}^{(f)}} = \left[1 + \frac{2\omega_S^2(\tilde{\omega}_S^2 - \omega^2)}{(\tilde{\omega}_S^2 - \omega^2)^2 + (\omega\gamma)^2} \frac{\alpha_S}{R^3} \right]^2$$
$$+ \left[\frac{2\omega_S^2 \omega\gamma}{(\tilde{\omega}_S^2 - \omega^2)^2 + (\omega\gamma)^2} \frac{\alpha_S}{R^3} \right]^2 , \quad \text{(III.9)}$$

where $\sigma_{ab}^{(f)}$ is the absorption cross section of the free molecule. For large R, Eq. (III.9) takes the asymptotic form (provided $\tilde{\omega}_S \neq \omega$)

$$\frac{\sigma_{ab}}{\sigma_{ab}^{(f)}} \sim 1 + \frac{4\omega_S^2(\tilde{\omega}_S^2 - \omega^2)}{(\tilde{\omega}_S^2 - \omega^2)^2 + (\omega\gamma)^2} \frac{\alpha_S}{R^3} . \quad \text{(III.10)}$$

We see that a destructive interference occurs for $\tilde{\omega}_S < \omega$.

Finally, we call attention to the relatively mild dependence of these effects on the molecule–surface separation d, as is evident from the figures as well as from Eq. (9). This is in accord with both experimental and theoretical observations on SERS.

IV. DYNAMICAL CALCULATIONS

When the chemical process which follows the molecular excitation is not fast relative to the surface induced

TABLE I. Parameters for the dielectrics and the model molecules used in the calculations.

Dielectric	ω_S (cm^{-1})	ϵ_1 (ω_S) (cm)	ϵ_2 (ω_S)	γ (cm^{-1})	α_s/a^3
Ag	28 230	7.45×10^{-4}	0.284	763	0.29
Cu	27 300	2.43×10^{-4}	5.35	44 000	0.90
Au	20 690	5.43×10^{-4}	4.32	16 000	0.53
SiC	932	0.061	0.29	9.5	0.11
InSb[a]	967	0.034	0.55	32.4	0.18

Molecule	ω_M (cm^{-1})	$\Gamma_r^{(f)}$ (cm^{-1})	$\Gamma_{nr}^{(f)}$ (cm^{-1})	α_M (cm^3)
Model I_2	22 220	1.9×10^{-6}	2125	4.71×10^{-26}
Model SF_6	965	1.33×10^{-10}	0	9.27×10^{-25}

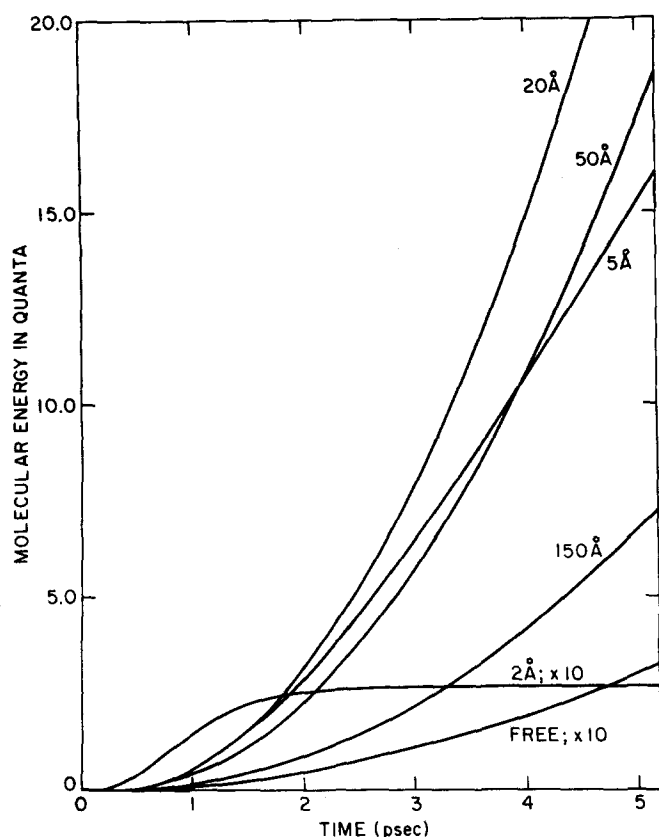[a]Doped to have $\omega_p = 1027$ cm^{-1}.

FIG. 8. The time evolution of the molecular energy for the model SF_6 molecule near a InSb sphere. The incident field intensity is 10^8 W/cm^2 and the incident frequency is 965 cm^{-1} (10.4 μm). The molecular dipole is normal to the surface.

damping processes, enhanced molecular absorption does not necessarily imply enhanced photochemical yield. Examples of slower processes include reactions proceeding from thermally relaxed excited electronic states, and reactions proceeding from vibrationally excited ground state molecules. We have to investigate whether the molecule can absorb enough energy and store it for a sufficiently long time for the chemical process to occur. To study this aspect of the problem we have performed a direct numerical integration of Eq. (III.2). Figure 8 shows the internal energy of our model SF_6 molecule as a function of time near a doped InSb sphere.[18] It is seen that a rapid excitation and efficient energy storage can be achieved *if* the molecule is not too close to the surface. Thus, at small separations energy transfer to the dielectric sphere is fast and the molecular energy saturates at a low excitation level. This occurs because the surface induced damping rate decreases as d^{-3} (for $d \ll a$) with increasing molecule surface separation, while the resonance induced local field enhancement depends on d through a $(d+a)^{-3}$ factor (for a sphere) and decreases more slowly with increasing d. *Therefore, a larger separation becomes advantageous for energy accumulation in long lived molecular states.* Obviously, an optimum distance d exists. With the parameters used in Fig. 8, it is seen to be on the order of $\sim 0.05a$.

More insight into the effect of surface damping can be

obtained by considering the saturation energy of the excited oscillator in a given indident field. An important question here is whether sufficient energy can be accumulated to allow ground state isomerization or bond breaking to occur. At saturation the dissipation and pumping rates of the molecule are equal. Limiting ourselves to the normal configuration and using Eqs. (A4) and (A5), we obtain

$$\dot{\mu} = \frac{\alpha_M \omega_M^2}{\Gamma} \left(\frac{2}{R_3} \mu_{sz} + E_z \right) . \qquad (IV.1)$$

This corresponds to the energy

$$W_M^{(sat)} = \frac{1}{\alpha_M} \left(\frac{\dot{\mu}}{\omega_M} \right)^2 = \frac{\alpha_M \omega_M^2}{\Gamma^2} \left[1 + 4 \frac{\omega_s}{\gamma^2} \left(\frac{\alpha_s}{R^3} \right)^2 \right] |E_z|^2 , \qquad (IV.2)$$

where we have used Eq. (III.2b) (without the μ dependent term) and assumed that $\omega_s \simeq \omega$. Equation (IV.2) can be written in the form

$$W_M^{(sat)} = W_M^{(sat, f)} \left(\frac{\Gamma^{(f)}}{\Gamma} \right)^2 \left[1 + \frac{4 \omega_s^2}{\gamma^2} \left(\frac{\alpha_s}{R^3} \right)^2 \right] \qquad (IV.3)$$

and

$$W_M^{(sat, f)} = \frac{\alpha_M \omega_M^2 |E_z|^2}{(\Gamma^{(f)})^2} \qquad (IV.4)$$

is the saturation energy for the free oscillator. With typical parameters $\omega_M = 960$ cm^{-1} and $\Gamma^{(f)} = \Gamma_r^{(f)} \sim 10^2$ sec^{-1}, and for a field corresponding to a flux $\sim 10^8$ W/cm^2, we obtain $\omega_M^{(sat, f)}/\hbar \omega_M \sim 2 \times 10^{20}$ quanta. (This obviously is an unphysical result not applicable to real SF_6 molecules.) Near the dielectric sphere, we approximate the surface as a plane, and $\Gamma/\Gamma^{(f)} \sim 10^{-12}/d^3$, where d is the distance in cm. Using also the estimates $\alpha_s/R^3 \sim 0.15$ (for $d \ll a$) and $(W_x/\gamma)^2 \sim 1000$, we get $W_M^{(sat)}/\hbar \omega_M \sim 0.02[d(\text{Å})]^3$, where $d(\text{Å})$ is the distance expressed in Å. Thus, we need $d > 12$ Å to get above typical dissociation energies (32 quanta for SF_6) at saturation. It should be kept in mind that this calculation does not provide any information concerning the time it takes to reach saturation.

V. DISCUSSION AND CONCLUSION

In this paper we have invoked a very simple model for the study of spectroscopic and photochemical phenomena associated with an irradiated molecule located near a rough dielectric surface or near a dielectric particle in a composite dielectric system. Our model includes a polarizable point dipole lying near a dielectric sphere with all distances much smaller than the radiation wavelength. The sphere represents the dielectric particle or a protrusion on a rough dielectric surface, and we have assumed that its electromagnetic properties are determined by the bulk dielectric function $\epsilon(\omega)$. Furthermore, we have invoked the Drude approximation whereupon the sphere resonances are assumed to obey Drude type equations of motion with parameters determined by $\epsilon(\omega)$. In the calculations reported in the present work, we have used a harmonic molecule and assumed that the molecular dipole is linear in the intramolecular coordinates; however, these assumptions may be easily relaxed. Finally, we note that our approach is completely classical.

The equations of motion (III. 2) in the Drude approximation describe a molecular dipole μ coupled to two sphere dipoles μ_{sx} and μ_{sz} (associated with x and z components of the dipolar sphere plasmons, respectively). The lack of coupling with the y component results from our choice of coordinates where μ lies in the xz plane. It is important to notice that Eqs. (III. 2) are classical Drude equations describing energy transfer in a Förster–Dexter type model. There are, however, several important differences from the normal Förster–Dexter model as applied to two interacting molecules:

(a) The dipolar response of the sphere corresponds to three degenerate dipolar resonances ($l = 1$; $m = 0, \pm 1$) so that in general we are concerned with the interaction between the molecule and these three resonances (as stated above, we can represent the sphere with two degrees of freedom only because of our particular choice of coordinate system).

(b) The sphere, on the molecular scale, is almost a macroscopic object and its polarizability is orders of magnitude larger than that of the molecule (for a 200 Å radius silver sphere $\alpha_s \simeq 10^7 \alpha_{r_2}$). Thus, there is a huge asymmetry in the model which does not appear in molecular Förster–Dexter systems. In fact, this asymmetry leads to a change of description on our part as observers: What constitutes an energy transfer process in one case appears to be an enhancement phenomenon in the other.

(c) The particle is characterized by higher multipole $l > 1$ modes, which are not coupled to the incident field because the field is homogeneous on the sphere scale. These modes, however, provide a sink for the molecular energy and their effect emerges in the parameter Γ of Eq. (III. 2a). The presence of both radiative and nonradiative modes in the dielectric particle leads to a competition between two processes: the transfer of energy from the radiative particle modes to the molecule on one hand, and the damping of molecular energy due to transfer into the nonradiative particle modes on the other.

The occurrence of this competition, which has no effect on nonresonant processes like SERS, leads to important consequences for resonance absorption and photochemistry. The different distance d dependence of the energy transfer and of the damping processes leads to the existence of optimal molecule–surface separation for the enhancement of photochemical reactions. This optimal distance depends on the energy threshold for the reaction, on the lifetime of the activated molecule, and on the shape and intensity of the exciting pulse. Even when photochemistry occurs on a slow time scale, we have seen that under reasonable excitation conditions enhanced photochemistry is possible provided that the adsorbed molecule is not too close to the surface. This may be achieved by using appropriately coated surfaces and particles.

Even though we have used a sphere as a model for the dielectric particles, our general equations (III. 2) will be valid in many other situations: Only the values of α_s and of Γ will change depending on the particle shape and α_s may be replaced by a tensor for less symmetric particles.[19] We do not expect our general conclusions to change, although the detailed estimates concerning the size of the enhancement and the value of the optimal distance will, of course, be affected. When the concentration of dielectric particles becomes large so that interactions between them can no longer be neglected or when the underlying bulk substrate strongly modifies the dielectric response of the surface protrusions, we still expect the final outcome of a photochemical experiment to be determined by surface induced pumping and damping processes in much the same way as with the examples studied here. A detailed theoretical evaluation of the desired cross section for such complicated optical cases still constitutes a theoretical challenge both here and in SERS. A worthwhile generalization of the present work in a more modest direction is a study of the phenomena discussed here for cases where the size of the dielectric particle becomes comparable to the radiation wavelength.

In addition to the factors discussed here, the feasibility of surface enhanced photochemistry will depend on our ability to control surface heating. In strong incident fields and particularly in the case of nonmetallic substrates of low heat conductivity, radiation induced heating following absorption by the dielectric may become a serious problem as it can lead to thermal desorption, thermal reaction, and to surface degradation. The fact that optical excitation is highly efficient and proceeds at high speed on the surface implies that the photochemical process may be achieved during a few picoseconds under a moderately strong field (see Fig. 8), so it may compete successfully with thermal processes if short light pulses are employed. Surface degradation may still become the main technological problem of surface enhanced photochemistry.

An experimental demonstration of surface enhanced photochemistry may be difficult in the presence of bulk photochemically active matter since the enhancement ratios are far smaller than in SERS (10–10^2 instead of $\sim 10^4$). This problem may be circumvented by focusing the laser beam on the surface so as to favor molecules located close to it, or alternatively by working without a bulk (where desorption may constitute a problem). It is also possible to cross a laser and a molecular beam on a rough surface, e. g., in a typical laser assisted field induced ionization configuration but without applying the dc field. It is interesting to note that there are some reports in the literature of unusual photochemical activity on rough surfaces,[20] though it is too early to judge whether these experiments are related to the phenomena discussed here.

ACKNOWLEDGMENT

APPENDIX: ABSORPTION CROSS SECTION OF A MOLECULE LOCATED NEAR A DIELECTRIC SPHERE

Starting from Eq. (III. 6) for the molecular energy,

$$W_M = \frac{1}{2\alpha_M}\left[\left(\frac{\dot{\mu}}{\omega_M}\right)^2 + \mu^2\right]. \tag{A1}$$

Its rate of change is

$$\dot{W}_M = \frac{\dot{\mu}}{\alpha_M \omega_M^2}(\ddot{\mu} + \omega_M^2 \mu) \tag{A2}$$

and, using Eq. (III. 2a) (with $\tilde{\omega}_M = \omega_M$), we get

$$\dot{W}_M = (\dot{W}_M)_{\text{dis}} + (\dot{W}_M)_{\text{pump}} , \tag{A3}$$

where

$$(\dot{W}_M)_{\text{dis}} = -\Gamma(\dot{\mu})^2/(\alpha_M \omega_M^2) \tag{A4}$$

describes the loss of molecular energy due to the dissipation process and where

$$(\dot{W}_M)_{\text{pump}} = \dot{\mu}\left[\left(\frac{2}{R^3}\mu_{sz} + E_z\right)\cos\theta_M + \left(\frac{1}{R^3}\mu_{sx} + E_x\right)\sin\theta_M\right] \tag{A5}$$

corresponds to the gain in molecular energy due to its interaction with external forces. The absorption line shape is associated with the pumping term. Defining

$$F = \left(\frac{2}{R^3}\mu_{sz} + E_z\right)\cos\theta_M + \left(\frac{1}{R^3}\mu_{sx} + E_x\right)\sin\theta_M , \tag{A6}$$

and introducing the Fourier transform $\hat{f}(u)$ of the function $f(t)$, i.e.,

$$f(t) = \int_{-\infty}^{\infty} e^{-iut}\hat{f}(u)\,du , \tag{A7}$$

we may write Eq. (A5) in the form

$$(\dot{W}_M)_{\text{pump}} = -i\int_{-\infty}^{\infty} dv\,\exp(-ivt)\int_{-\infty}^{\infty} du\,u\hat{\mu}(u)\hat{F}(v-u) . \tag{A8}$$

The Fourier transform $\hat{\mu}$ and $\hat{F}$ can be found from Eqs. (III. 2). These equations yield

$$\hat{\mu}(u) = D_1(u)\hat{E}_z(u) + D_2(u)\hat{E}_x(u) ,$$
$$\hat{F}(u) = D_3\hat{E}_z(u) + D_4(u)\hat{E}_x(u) , \tag{A9}$$

where

$$D_1(u) = \alpha_M\frac{\omega_M^2[2\omega_s^2\alpha_s/R^3 + B(u)]\cos\theta_M}{A(u)B(u) - \omega_M^2\omega_s^2(\alpha_M\alpha_s/R^6)(3\cos^2\theta_M + 1)} , \tag{A10}$$

$$D_2(u) = \alpha_M\frac{\omega_M^2[-\omega_s^2\alpha_s/R^3 + B(u)]\sin\theta_M}{A(u)B(u) - \omega_M^2\alpha_s^2(\alpha_M\alpha_s/R^6)(3\cos^2\theta_M + 1)} , \tag{A11}$$

$$D_3(u) = \cos\theta_M + \frac{\omega_s^2\alpha_s}{B(u)R^3}\left[\frac{D_1(u)}{R^3}(3\cos^2\theta_M + 1) + 2\cos\theta_M\right] , \tag{A12}$$

$$D_4(u) = \sin\theta_M + \frac{W_s^2\alpha_s}{B(u)R^3}\left[\frac{D_2(u)}{R^3}(3\cos^2\theta_M + 1) + \sin\theta_M\right] , \tag{A13}$$

in which

$$A(u) = \omega_M^2 - u^2 - iu\Gamma \tag{A14}$$

and

$$B(u) = (\omega_s^2 + \gamma^2/4) - u^2 - iu\gamma . \tag{A15}$$

For an incident field of the form

$$E_n(t) = E_{0n}\cos(\omega t + \eta) \quad (n = x, z) , \tag{A16}$$

we have

$$\hat{E}_n(u) = \frac{1}{2}E_{0n}[e^{i\eta}\delta(u + \omega) + e^{-i\eta}\delta(u - \omega)] . \tag{A17}$$

Inserting Eqs. (A9) and (A17) into Eq. (A8) and using

$$\hat{E}_n(u)\hat{E}_m(v-u) = \frac{1}{4}E_{0n}E_{0m}[\delta(u+\omega) + \delta(u-\omega)]\delta(v) , \tag{A18}$$

we obtain after some algebra

$$(\dot{W}_M)_{\text{pump}} = \frac{1}{2}\omega\{E_{0z}^2\,\text{Im}[D_1(\omega)D_3(-\omega)] + E_{0x}^2\,\text{Im}[D_2(\omega)D_4(-\omega)]$$
$$+ E_{0x}E_{0z}\,\text{Im}[D_1(\omega)D_4(-\omega) + D_2(\omega)D_3(-\omega)]\} . \tag{A19}$$

Finally, the absorption cross section is obtained as

$$\sigma_{ab} = \frac{1}{S}(\dot{W}_M)_{\text{pump}} , \tag{A20}$$

where S is the absolute magnitude of the Poynting vector

$$S = \frac{c}{8\pi}|E_0|^2 , \tag{A21}$$

where c is the speed of light. Using $E_{0z} = E_0\cos\theta$ and $E_{0x} = E_0\sin\theta\cos\psi$ and averaging over all orientations of the molecule–sphere system relative to the incident field, we get

$$\sigma_{ab} = \frac{4\pi}{3}\frac{\omega}{c}\,\text{Im}[D_1(\omega)D_3(-\omega) + D_2(\omega)D_4(-\omega)] . \tag{A22}$$

As a test, consider the isolated molecule $(R \to \infty)$ case. Then Eqs. (A10)–(A13) yield $D_1D_3 + D_2D_4 = \alpha_M\omega_M^2/A$ and using $\text{Im}(1/A) \sim (\Gamma/4\omega)/[(\omega_M - \omega)^2 + (\Gamma/2)^2]$, we obtain the free molecule absorption cross section

$$\sigma_{ab}^{(f)} = \frac{\Gamma_r^{(f)}}{4}\left(\frac{2\pi c}{\omega_M}\right)^2\frac{\Gamma/2\pi}{(\omega_M - \omega)^2 + (\Gamma/2)^2} . \tag{A23}$$

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¹⁸The harmonic molecule model described in Sec. III and in Table I has been used. This is of course an oversimplified picture of multiphoton excitation. A more general anharmonic model with a realistic dependence of μ on the intramolecular coordinate can be used, utilizing the formalism of Ref. 17.

¹⁹For example, for a molecule lying along the long axis of a spheroid [characterized by long and short axes $2a$ and $2b$, respectively, with $f = (a^2 - b^2)^{1/2}$ and $\xi_0 = a/f$] such that μ is perpendicular to the spheroid surface, the molecule is coupled to the dipolar plasmon directed along the long axis. For this plasmon we get $\alpha_S = [1/\omega_S \epsilon_1(\omega_S)] [(2/3)\xi_0/(\xi_0^2 - 1) Q_1^2(\xi_0)] f^3$, where $Q_1(\xi) = (\xi/2)\ln[(\xi+1)/(\xi-1)] - 1$ and where ω_S satisfies $\epsilon_1(\omega_S) Q_1(\xi_0) = \xi_0 (dQ_1/d\xi)_{x\xi_0}$ [A. Nitzan (unpublished result)]. The corresponding Γ may be calculated using the procedure of Ref. 18.

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