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Coupling of an excited molecule to surface plasmons

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The decay of an excited molecule deposited at distances less than its dominant fluorescence wavelength λ_F from a metal surface is calculated including the interaction with surface charge-density oscillations. Both nonresonant and resonant cases, $\omega_0 \ll \omega_p$ and $\omega_0 \sim \omega_p$, are considered for ω_0, the electronic transition frequency in the visible part of the electromagnetic spectrum. The plasma frequency ω_p determines the dielectric response of a free-electron-gas metal, $\epsilon(\omega) = 1-\omega_p^2/\omega^2$, in the region $\omega < \omega_p$. We find considerable changes from the pure image-theory result given by us earlier, in particular for the molecular transition dipole moment oriented parallel to the metal surface. The coupling to the surface-plasmon excitation spectrum induces a rapidly increasing contribution to the linewidth of the decaying molecule with decreasing distance from the metal surface. As the image result for the case of a molecular transition dipole oriented parallel to the surface tends to zero with decreasing distance, the inclusion of the coupling to surface plasmons drastically affects the lifetime of this configuration. For both cases, i.e., transition dipole parallel and perpendicular to the metal surface, the contribution to the width due to coupling to surface excitations *diverges* with decreasing distance, leading to dramatic shortening of the lifetime of the decaying molecule due to conversion of the localized electronic energy into surface charge-density oscillations.

In this paper we consider the decay of an excited molecule, deposited at a fixed distance D from a metal surface for $\lambda_F \geq D \geq d$, where λ_F is the free-space fluorescence wavelength in the visible and d is of the order of atomic dimensions. In particular, we note at the outset that the presence of the metallic surface necessitates inclusion of the interaction of the electronic transition dipole with the coupled surface-plasmon–photon system,[1] which has been extensively investigated in recent years both by inelastic electron scattering[2] and by the method of frustrated total internal reflection.[3]

Drexhage, Kuhn, and Schaefer[4] have investigated radiative and nonradiative decay processes in a variety of molecular complexes by ingenious extensions of the Blodgett-Langmuir monolayer technique,[5] and we suggest that the particular effect we are calculating here should be observable by a suitable adaptation of their approach.

In an earlier paper[6] one of us has analyzed the experimentally observed distance-dependent modulation of the fluorescence decay time in terms of image theory and predicted a cooperative level shift analogous to the Lamb shift[6,7] by treating the metal surface as a perfect metal with infinite conductivity σ. This corresponds to perfect reflectivity $|R|=1$ and a phase shift $\delta=\pi$ of the electric field on reflection, assuming the field to vanish identically in the interior of the metal. The detailed electronic structure of real metals leads to an exponentially screened electric field in the interior of the metal. Kuhn[8] has generalized our model to the case $R\neq 1$, $\delta\neq\pi$ and Barton,[9] Philpott,[10] and Milonni and Knight[11] have considered the decay of an excited atom between two plane infinite mirrors, treated as perfect reflectors, by coupling the excited molecule to the quantized electromagnetic field expanded in the cavity modes of this geometry. The idea of using electronically excited molecules to probe surface plasmon structure occurred to both authors independently. Very recently the inclusion of the nonresonant coupling to surface waves has been shown to lead to improved agreement with the experimental data by Drexhage[4] by Tews[12] and Chance, Prock, and Silbey.[13]

The similarity of this problem, albeit scaled down by ten orders of magnitude, to the detailed treatment of A. Sommerfeld[14] of a radio antenna emitting over a conducting earth was noted by Refs. 6, 12, and 13. In the following, we use a semiclassical approach to treat the oscillating transition dipole of the excited molecule—a quantum-mechanical antenna which drives by its electromagnetic-field electronic charge-density oscillations on the metal-dielectric interface, and in turn is affected in its decay by the response of the surface. The coupling agent is the electromagnetic field of the electronic transition and we are particularly interested in the case of near degeneracy of electronic transition frequency and surface plasmon frequency. This near degeneracy will be shown to contribute a dominant new decay channel for the excited molecule by converting localized electronic energy into surface charge-density waves in the quasi two-dimensional metal-dielectric interface.

The system considered, a single excited molecule deposited at a fixed distance D ($1\ \text{Å} \leq D \leq 10\,000\ \text{Å}$) from a metal surface, is composed of the 3 regions $z<0$, $0 \leq z \leq D$, $z>D$. We choose the z axis perpendicular to the metal surface at $z=0$ and take the metal to occupy the half-space $z \leq 0$. The regions I, II, and III are characterized by $\epsilon_{\rm I}=\epsilon_0$ (free space), $\epsilon_{\rm II}=\epsilon_{\rm I}>\epsilon_0$, $\epsilon_{\rm III}=1-\omega_p^2/\omega^2$ corresponding to the sections $z \geq D$, $0 \leq z \leq D$, and $z \leq 0$, respectively.

The existence of the metal surface and concomitant dielectric discontinuity removes conservation of the z component of the electromagnetic propagation vector $\vec{k}$ ($|k|=\omega_0/c$). In Fig. 1 we show the coupled photon-plasmon system, which results from the standard boundary condition of continuity of the tangential components of the field quantities $\vec{E}(\vec{r},t)$, $\vec{H}(\vec{r},t)$. The dielectric discontinuity at $z=0$ leads to the appearance of a new branch of the collective excitation spectrum of the metal, the surface plasmon branch, which corresponds to the quantized charge-density oscillations confined to the surface region. Due to the mixing of these surface charge-density oscillations with the solutions of the free Maxwell equation (transverse photons), the surface plasmons are lightlike, $\omega_s(k) \approx c|k|$ for small $|k| \ll \omega_p/c$, but asymptotically approach a constant value $\omega_k=\omega_p/(1+\epsilon_1)^{1/2}$ for $|k| \gg \omega_p/c$. It is worth pointing out that while the bulk plasmon excitations correspond to purely longitudinal fields ($\vec{E} \parallel \vec{k}$), the surface plasmons have components parallel and perpendicular to their two-dimensional propagation vector in the plane of the interface.

We consider the transition dipole moment $\vec{p}_1 = -e\langle\psi_e|\vec{x}|\psi_g\rangle$ of the excited molecule as the primary source of the electromagnetic field quantities $\vec{E}(\vec{r},t)$, $\vec{H}(\vec{r},t)$ and their material-dependent displacement and induction-field equivalents $\vec{D}(\vec{r},t)$, $\vec{B}(\vec{r},t)$. Neglecting magnetic effects by choosing $\mu_{\rm III}=\mu_{\rm II}=\mu_{\rm I}$, we have $\vec{D}_{\rm I}=\epsilon_0\vec{E}$, $\vec{D}_{\rm II}=\epsilon_1\vec{E}$, $\vec{D}_{\rm III}=\epsilon(\omega)\vec{E}$. We suppress the space-time dependence in the argument of E, D and use the free-electron-model dielectric function $\epsilon(\omega)=1-\omega_p^2/\omega^2$. We employ the Hertz vector $\vec{\Pi}(\vec{r},t)$, which is a solution of the wave equation with $\vec{p}_1$ as a source term, to derive $\vec{E}(\vec{r},t)$, $\vec{H}(\vec{r},t)$ in the standard manner by

$$\begin{aligned}\vec{E}(\vec{r},t)&=k_1^2\vec{\Pi}(\vec{r},t)+\vec{\nabla}[\nabla\cdot\vec{\Pi}(\vec{r},t)],\\ \vec{H}(\vec{r},t)&=(k_1^2/i\omega_0\mu_0)\vec{\nabla}\times\vec{\Pi}(\vec{r},t).\end{aligned} \tag{1}$$

We distinguish between two different configurations of the transition dipole moment with respect to the metal surface, namely, (I): $\vec{p}_1 \parallel \hat{z}$ and (II): $\vec{p}_1 \perp \hat{z}$ ($\hat{z}$ is a unit vector in the z direction).

By symmetry, we expect $\vec{\Pi}(\vec{r},t)$ to be cylindrically symmetrical for case (I), i.e., $\vec{\Pi}^{\rm I}(\vec{r},t) = \Pi^{\rm I}[\rho=(x^2+y^2)^{1/2},z,t]\hat{z}$. We drop the time dependence, hereafter assuming a single Fourier component $\sim e^{-i\omega_0 t}$. Case II requires a more general Hertz vector[15] $\vec{\Pi}^{\rm II}(\vec{r})=(\Pi_x^{\rm II}(\vec{r}),0,\Pi_z^{\rm II}(\vec{r}))$, where we assumed $\vec{p}_1$ to define the x direction. The Hertz vector due to the primary source $\vec{p}_1$ is a solution of

$$(\nabla^2-\omega_0^2/c^2)\vec{\Pi}(\rho,z)=\vec{p}_1\delta(z-D)\delta(\rho)/\rho, \tag{2}$$

which can be written using the retarded Greens function solution of (2),

$$G(r,r')=e^{ik|r-r'|}/|r-r'|, \tag{2a}$$

$$\begin{aligned}\vec{\Pi}(\rho',z')&=\vec{p}_1\,e^{ikR}/R,\\ R&=[\rho'^2+(z'-D)^2]^{1/2},\end{aligned} \tag{3}$$

where ρ', z' are the cylindrical coordinates of the field observation point $\rho'=(x'^2+y'^2)^{1/2}, z'$.

The presence of the metallic surface and response of the metallic electrons in the half space $z \leq 0$ require consideration of the reflected field at the position of the molecular dipole. As the continuity of tangential components of D and H across the interface relate incident, reflected, and refracted (actually strongly attenuated in our case) field quantities by Fresnel's equations, we only require the form of the dielectric function $\epsilon(\omega)$ in region III, the metal, to solve for the additional contribution to the Hertz vector $\vec{\Pi}(\vec{r})$ ($z>0$) from the response of the surface charge. We use the simplest free electron, dispersionless form for $\epsilon(\omega)$ in $z \leq 0$, namely,

$$\begin{aligned}&\epsilon(\omega)=1-\omega_p^2/\omega^2,\\ &D(\rho,z)=\epsilon(\omega)E(\rho,z)\quad\text{for } z\leq 0.\end{aligned} \tag{4}$$

In the actual experiments the emitting molecule is trapped at the top monolayers of the dielectric $\epsilon_1>\epsilon_0$, the free space value. To simplify the theoretical treatment the optical properties of regions I and II are merged, i.e., they are assumed to be

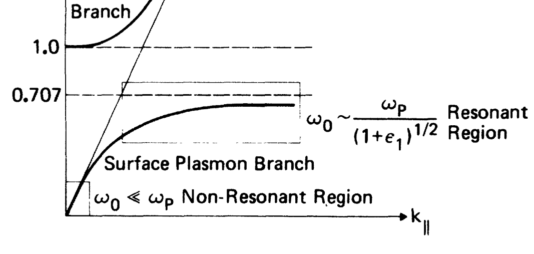

FIG. 1. Coupled two-dimensional photon–surface-plasmon dispersion curve $\omega_k^2=\frac{1}{2}\omega_p^2+k_{\parallel}^2c^2-(\frac{1}{4}\omega_p^4+k_{\parallel}^4c^4)^{1/2}$ (Ref. 2).

the same. In practice this is accomplished by performing the measurements in a liquid with a refractive index that matches that of region II.

We have neglected any interband contribution to $\epsilon(\omega)$ and neglected damping of the collective excitations, but it is straightforward to include both by using $\epsilon^{1B}(\omega) = 1 - \omega_p^2/\omega(\omega + i\gamma) + f/(\omega^2 - \omega_1^2)$ instead of (4). We are considering molecular transition frequencies $\omega_0 < \omega_p$, and $\epsilon(\omega)$ is therefore negative and the index of refraction $n(\omega) = \epsilon(\omega)^{1/2}$ *pure* imaginary. The electric field inside the metal decreases exponentially for $z < 0$, expressing the screening of the external field $E(r, t)$ by the response of the surface electrons. The mixed longitudinal and transverse character of the electromagnetic field components, which arises from its near field and induction components, which are normally ignored in radiation problems because of their $1/r^2$, $1/r^3$ dependence, are effective in coupling to surface charge-density waves (surface plasmons) if, as we suggest in this paper, the optical transition frequency is close to the surface plasmon frequency $\omega_s = \omega_p/(1 + \epsilon_1)^{1/2}$ (see Fig. 1). This can be attained by using a heavily doped semiconductor surface or an alkali metal, in which the plasma frequency $\omega_p^2 = 4\pi N e^2/m$ falls into the visible. With Sommerfeld[15] we use cylindrical eigenfunctions instead of the more standard plane-wave representation and obtain for the Hertz vector due to the primary dipole field and the surface response

$$\vec{\Pi}^{\mathrm{I}}(\rho, z) = \vec{\mathrm{p}}_1\left(\frac{e^{ik_1R}}{R} + \frac{e^{ik_1R'}}{R'} - 2k_1^2\int_0^\infty \frac{J_0(\lambda\rho)[\exp-(\lambda^2 - k_1^2)^{1/2}(z + D)]\lambda(\lambda^2 - k_2^2)^{1/2}\,d\lambda}{(\lambda^2 - k_1^2)^{1/2}[k_2^2(\lambda^2 - k_1^2)^{1/2} + k_1^2(\lambda^2 - k_2^2)^{1/2}]}\right) \quad z \geq 0,$$
$$\vec{\Pi}^{\mathrm{I}}_{\mathrm{metal}}(\rho_1 z) = \vec{\mathrm{p}}_1 2k_1^2 \int_0^\infty \frac{J_0(\lambda\rho)[\exp(\lambda^2 - k_2^2)^{1/2}z][\exp-(\lambda^2 - k_1^2)^{1/2}D]\lambda\,d\lambda}{k_2^2(\lambda^2 - k_1^2)^{1/2} + k_1^2(\lambda^2 - k_2^2)^{1/2}}, \quad z < 0\,. \tag{5}$$

The pure image result[6] is contained in the first two terms of Eq. (5), as the integrals vanish as $k_2^2 = n_2^2 k_1^2 \to \infty$, $n_2^2 \to -\infty$ for infinite conductivity. The calculation for case II, $\vec{\mathrm{p}}_1 = |p_1|\hat{e}_x$, can be carried through in a similar manner, although the secondary Hertz vector now acquires both transverse ($\parallel e_x$) and longitudinal components ($\parallel e_z$). We find,[15] for $z < 0$, that

$$\Pi_x^{\mathrm{II}}(\rho, z) = \vec{\mathrm{p}}_1\left(\frac{\exp ik_1R}{R} - \frac{\exp ik_1R'}{R'} + 2\int_0^\infty \frac{\lambda\,d\lambda\,J_0(\lambda\rho)\exp-(\lambda^2 - k_1^2)^{1/2}(z + D)}{(\lambda^2 - k_1^2)^{1/2} + (\lambda^2 - k_2^2)^{1/2}}\right),$$
$$\Pi_z^{\mathrm{II}}(\rho, \phi, z) = -p_1 2\cos\phi\int_0^\infty \frac{\lambda^2 d\lambda\,[(\lambda^2 - k_1^2)^{1/2} - (\lambda^2 - k_2^2)^{1/2}][\exp-(\lambda^2 - k_1^{2\prime})^{1/2}(z + D)]J_1(\lambda\rho)}{k_2^2(\lambda^2 - k_1^2)^{1/2} + k_1^2(\lambda^2 - k_2^2)^{1/2}}, \quad \cos\phi = x/\rho. \tag{6}$$

The modification of the pure image result ($|R| = 1, \delta = \Pi$) to take account of nonperfect reflectivity $|R| < 1$ and angle-of-incidence dependent phase shift $\delta \neq \pi$ proposed in Ref. 8 on intuitive grounds can be rigorously derived from Eqs. (5), (6) by evaluating the integrals asymptotically using well-known saddle-point techniques.[16] The image term has the form

$$\pm\rho(k_1, \sin\theta)\, e^{ik_1R'}/R', \tag{7}$$

where ρ is the reflectivity amplitude for an angle of incidence θ,

$$\rho(k_1, \sin\theta) = \frac{(\xi^2 - \sin^2\theta)^{1/2} - \xi^2\cos\theta}{(\xi^2 - \sin^2\theta)^{1/2} + \xi^2\cos\theta}\,. \tag{8}$$

Since the molecule lies on the z axis, $\theta = 0$ and (8) reduces to

$$\rho(k_1, 0) = [1 - n(\omega)]/[1 + n(\omega)], \tag{8a}$$

where $\xi^2 = k_2^2/k_1^2 = n^2(\omega)$ is the square of the complex refractive index. We can rewrite (8a) in the form

$$\rho = |R|e^{i\delta}, \quad |R| < 1, \quad \delta \neq \pi, \tag{8b}$$

which is Kuhn's[8] *Ansatz* for the image term.

Given Eqs. (5) and (6) we are now ready to analyze the conversion of the stored electronic energy of the excited molecule into radiative modes (photons) and excitation of the mixed two-dimensional photon-plasmon system of the metal surface, similar to the discussion given in our earlier treatment.[6] We imagine the molecule to be excited at $t = 0$, and the molecular transition dipole radiates for a time $t_{\mathrm{ret}} = 2D/c$, as if in free space ($D \to \infty$). The reflected field arises from the metal surface response to the initially emitted field. In contrast to the standing-wave boundary condition for the perfect reflector (pure image theory) the surface charge-density waves arrange themselves in such a way as to screen the external field inside the metal and set up a reflected field, which reaches the molecule starting at $t = t_{\mathrm{ret}}$ because of the causal nature of the retarded interaction. The molecule evolves now in the presence of the electric field of the surface-charge response and we have to calculate the time-evolution of the molecular dipole in this additional field. In our earlier treatment, we treated the interaction of the reflected (image) field on the initially excited dipole as a scattering problem with the possibility of reabsorption of the corresponding photon. We can also visualize the back reaction of the reflected field as an example of the radiation-reaction damping of classical electrodynamics. Simulating the electronic dipole by a damped harmonic oscillator with equation of motion

$$\ddot{p} + \gamma_0 \dot{p} + \omega_0^2 p = \frac{e^2}{m} E_{\text{ref}}(z = D)\,, \tag{9}$$

we find that the eigenfrequency of (9) is

$$\Omega = -\frac{i\gamma_0}{2} + \left(\omega_0^2 - \frac{e^2}{m} E_{\text{ref}} - \frac{\gamma_0^2}{4}\right)^{1/2}, \tag{9a}$$

where $\gamma_0 = \frac{2}{3} r_0 \omega_0^2$ ($r_0 = e^2/mc^2$ is the classical electron radius and γ_0 is the radiation damping width). As E_{ref} is complex, we find for the renormalized eigenfrequencies of the molecular dipole and width Ω^{ren}, γ^{ren}

$$\begin{aligned} \Omega^{\text{ren}} &= \omega_0 - \gamma_0 \operatorname{Re}[E_{\text{ref}}(\rho = 0, z = D)]\,, \\ \gamma^{\text{ren}} &= \gamma_0 \{1 + \operatorname{Im}[E_{\text{ref}}(\rho = 0, z = D)]\}\,. \end{aligned} \tag{9b}$$

We see by inspection of Eqs. (11) and (12) that the spherical wave terms $\pm e^{ikR'}/R'$ lead to the image-theory corrections to the renormalized molecular eigenfrequency and width. The integral terms, however, are additional contributions and have been considered for the nonresonant case $\omega_0 \ll \omega_p$ by Refs. 12 and 13. We emphasize the possibility of letting these terms become the dominant decay channel for short distances, as we are considering near degeneracy of electronic transition frequency and surface plasmon frequency. We have, for case I ($\vec{p}_1 \parallel \hat{z}$),

$$\frac{\gamma^{\parallel}(D)}{\gamma_0} = 1 + 3\left(\frac{\sin\kappa}{\kappa^3} - \frac{\cos\kappa}{\kappa^2}\right) - \frac{3}{1-\xi^2} I^{\parallel}(\xi^2); \tag{10a}$$

case II ($\vec{p}_1 \parallel \hat{x}$),

$$\frac{\gamma^{\perp}(D)}{\gamma_0} = 1 + \frac{3}{2}\left[\left(\frac{1}{\kappa^3} - \frac{1}{\kappa^2}\right)\sin\kappa - \frac{\cos\kappa}{\kappa^2}\right] - \frac{3}{2}\,\frac{1}{1-\xi^2} I^{\perp}(\xi^2), \tag{10b}$$

where $\xi^2 = k_2^2/k_1^2 = 1 - \omega_p^2/\omega_0^2$ and

$$I^{\parallel}(\xi^2) = I_P^{\parallel}(\xi^2) + I_N^{\parallel}(\xi^2), \tag{11a}$$

$$I^{\perp}(\xi^2) = I_P^{\perp}(\xi^2) + I_N^{\perp}(\xi^2), \tag{11b}$$

where $I_P^{\parallel}$, $I_N^{\parallel}$, $I_P^{\perp}$, $I_N^{\perp}$ are defined as

$$I_P^{\parallel}(\xi^2) = -\pi \frac{|\xi|^6}{(|\xi|^2 - 1)^{5/2}} \exp\left(-\frac{\kappa}{(|\xi|^2 - 1)^{1/2}}\right), \tag{12a}$$

$$\begin{aligned} I_N^{\parallel}(\xi^2) = \int_0^1 \frac{dx\,(1-x^2)}{x^2(\xi^2+1)-1} &[(1 - x^2 - \xi^2)\cos\kappa x \\ &- \xi^2 x (1 - x^2 - \xi^2)^{1/2} \sin\kappa x], \end{aligned} \tag{12b}$$

$$I_P^{\perp}(\xi^2) = -\pi \frac{|\xi|^4}{(|\xi|^2 - 1)^{5/2}} \exp\left(-\frac{\kappa}{(|\xi|^2 - 1)^{1/2}}\right), \tag{12c}$$

$$\begin{aligned} I_N^{\perp}(\xi^2) = \int_0^1 &\frac{dx}{x^2(\xi^2+1)-1} \\ &\times \{x^2[2(1-x^2) - \xi^2(1+x^2)]\cos\kappa x \\ &+ (x^2 + 2x^2\xi^2 - 1)(1 - x^2 - \xi^2)^{1/2} \sin\kappa x\}, \end{aligned} \tag{12d}$$

where $\kappa = 2k_1 D$ is the phase delay at the dipole location due to the metallic surface. The contributions from the surface plasmon pole at $x_s = 1/(|\xi|^2 - 1)^{1/2}$, Eqs. (12a) and (12c) for the parallel and perpendicular geometry, dominate the numerical integrals (12b) and (12d) for small distances $D < 500$ Å. We point out that the importance of these terms will be diminished if we consider a more general dielectric function for the free-electron metal including damping as it moves the location of the surface pole off the real axis.[17] The integrals $I_N^{\parallel}(\xi^2)$, $I_N^{\perp}(\xi^2)$ are evaluated by standard 16 point Gaussian integration for 1 Å$< D <$10 000 Å and are plotted in Figs. 2 and 3 for the two geometries considered and the values of the dimensionless frequency variable $x = \omega_0/\omega_p = 0.7$ [the surface plasmon (Fig. 1) occurs at $\omega_s = \omega_p/(1+\epsilon_1)^{1/2} = 0.707\omega_p$ for $\epsilon_1 = 1.0$] and $x = 0.1$.[16] The contribution of the near-resonant surface term drastically changes the widths $\gamma^{\parallel}(D)$, $\gamma^{\perp}(D)$ and hence the fluorescence lifetime

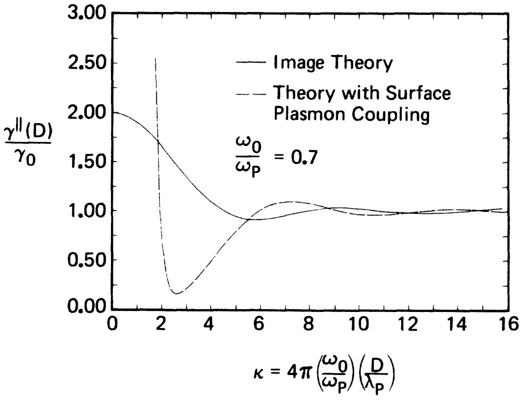

FIG. 2. Renormalized width $\gamma^{\parallel}(D)/\gamma_0$ [Eq. (10a)] plotted as a function of $\kappa = 4\pi(\omega_0/\omega_p)D/\lambda_p$ and the pure image result (Ref. 6) near the surface plasmon resonance $\omega_0/\omega_p = 0.7$.

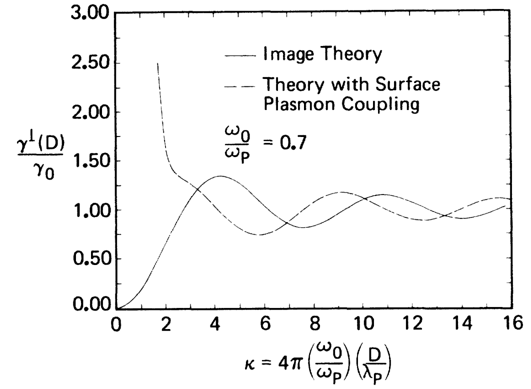

FIG. 3. Renormalized width $\gamma^{\perp}(D)/\gamma_0$ [Eq. (10b)] plotted as a function of $\kappa = 4\pi(\omega_0/\omega_p)D/\lambda_p$ and the pure image result (Ref. 6) near the surface plasmon resonance $\omega_0/\omega_p = 0.7$.

$$\tau^{\parallel}(D), \tau^{\perp}(D) \sim \pi/\gamma^{\parallel}(D), \quad \pi/\gamma^{\perp}(D).$$

In fact, both cases, parallel and perpendicular dipole orientation, lead to divergent expressions for the linewidth, in contrast to the image results,[6] which indicate a limit of $2\gamma_0$ for case I ($\vec{p}_{\rm I} \parallel \hat{z}$) and 0 for case II ($\vec{p}_{\rm I} \parallel \hat{x}$). In Figs. 2 and 3 we plot the renormalized widths $\gamma^{\parallel}(D)/\gamma_0$, $\gamma^{\perp}(D)/\gamma_0$ as a function of the phase delay $\kappa = 2k_1 D = 4\pi(\omega_0/\omega_p)(D/\lambda_p)$ in the dimensionless variables ω_0/ω_p, D/λ_p (λ_p is the plasmon wavelength). It is evident that the inclusion of the coupling of the transition dipole moment to the mixed photon–surface-plasmon excitation spectrum strongly modifies the image-theory results plotted for comparison. In particular, the subradiant energy-trapping state of image theory corresponding to the transition dipole oriented parallel to the metal surface couples very efficiently to the two-dimensional surface plasmon mode, which becomes the dominant decay channel.

Experimental verification of the effect calculated in this paper should be attempted by orienting the transition dipole of an excited molecule parallel to an alkali metal or doped semiconductor surface at distances less than 500 Å and choosing a molecular transition frequency ω_0 close to the surface plasmon frequency $\omega_p/\sqrt{2}$. We find, for example, that for $x = \omega_0/\omega_p = 0.16$ the pure image width for case II is only $8\times10^{-3}\gamma_0$, while the combined surface contributions (11b) are $9.5\times10^{-2}\gamma_0$, i.e., a factor of 10 larger at a distance of 500 Å. Near the surface plasmon resonance, however, at $x = \omega_0/\omega_p = 0.7$, the image width is $0.148\gamma_0$, while the surface resonance induced width is $95.5\gamma_0$. The corresponding results for case I, in which the contribution of the primary dipole field and the image dipole are in phase (super-radiant combination, in the parlance of Dicke superradiance theory,[18] of a pair of radiators acting as a single quantum-mechanical radiator) are pure image width $1.996\gamma_0$, the surface excitation induced width (11a) is $0.87\gamma_0$ leading to a total width of $2.87\gamma_0$ at $D = 500$ Å, $x = \omega_0/\omega_p = 0.16$; while near the surface plasmon frequency $x = \omega_0/\omega_p = 0.7$ the corresponding numbers are $1.925\gamma_0$ for the pure image width and $198.9\gamma_0$ for the contribution of the surface plasmon coupling. We note that the coupling to surface charge-density oscillations becomes the dominant decay channel near the metal surface, leading to drastic lifetime shortening of the excited molecule by several orders of magnitude.

Very similar considerations can be made for magnetic dipole transitions, with the main difference arising from the interchange of the symmetric and antisymmetric combination of magnetic image dipoles for parallel and perpendicular orientation with respect to the symmetry plane of the metal surface.

We have thus found an effective way of transferring electronic localized excitation energy into surface charge-density waves spreading out along the metal-dielectric interface. As similar resonant molecular electronic and vibrational dipole coupling to other surface excitations (surface polaritons) occurs in dielectric and magnetic materials, this type of excitation transfer may provide an alternative method for studying the structure of the surface excitation spectrum in such systems.

In a different vein, coupling of electromagnetic field energy in the form of uv light quanta is made possible by absorption into highly excited electronic states of a molecule close to a surface, which then decouples the external field by intersystem crossing and could transfer its energy by the process discussed in this letter to surface excitations. We are intending to explore these possibilities in subsequent publications.

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