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Cooperative Emission of an Excited Monolayer into Surface Plasmons

The cooperative emission of an excited molecular monolayer into surface plasmons of a metallic substrate is described. The effect arises from the very strong coupling of an electronically excited molecule to surface plasmons at distances that are short compared to the wavelength of the electronic transition. Strong resonant enhancement of this excited molecule-surface plasmon interaction occurs for near-degeneracy of the electronic transition frequency and the asymptotic surface plasmon frequency $\omega_p/2^{1/2}$. *It is shown theoretically how the two-dimensional analogue of superradiance can arise, leading to a highly directional and very intense surface plasmon pulse. This pulse or series of pulses has soliton-like characteristics and may be expected to propagate for considerably longer distances along the metal-vacuum interface than do individual surface plasmons.*

A. Introduction

The description of the cooperative emission of light from an assembly of excited atoms or molecules historically has had two distinct points of departure: the prediction of cooperative spontaneous emission by R. H. Dicke [1] in 1954 and the extension of microwave amplification concepts to the optical regime by Schawlow and Townes [2], which led to the laser. A broad range of gas-, liquid-, and solid-state lasers have since been developed with a large spectrum of performance parameters such as power, temporal operation, and wavelength tunability. The vast majority of these devices utilize the feedback aspect of a high Q cavity to force the stimulated emission of light from the incoherently excited active (lasing) region into the cavity modes with the largest gain.

In this paper, we discuss a new area of cooperative emission, which arises from a physical phenomenon characteristic of electronically excited molecules in the vicinity of metal surfaces. In its physical origin, this cooperative emission is related to Dicke superradiance and has evolved over the last ten years [3-7] from the realization and extension of these early concepts.

The fundamental difference between previously studied cooperative emission processes and the process discussed in this paper lies in the nature of the cooperatively generated field: not the radiation field in a single mode or super-position of many modes, but a quasi-particle field, the surface plasmon field, characteristic of metal-dielectric interfaces. Specifically, we consider surface plasmons, which arise as polariton modes, with exponentially decaying electric fields in both directions perpendicular to a metal-dielectric interface.

It has been shown by us [8] and others [9, 10] that the decay probability of electronically excited molecules, at distances D from a metal surface that are short compared to the wavelength of the corresponding transition λ_f, is strongly affected if the electronic transition frequency lies below the asymptotic surface plasmon (SP) frequency of the metal. The cause of this enhanced decay probability is the strong coupling of the electronic transition dipole of the excited molecule to the surface plasmon field. The patterns of the near-field transition dipole and the SP field both contain transverse as well as longitudinal components; this permits the efficient excitation of the SP field in the decay. In the vicinity of the surface, the SP field provides a new decay channel for an excited molecule, in addition to s- and p-polarized photons. For electronic transition frequencies near the asymptotic SP frequency $\omega_p/2^{1/2}$, this new nonradiant decay channel dominates the radiant channel by two or three orders of magnitude [8-10].

It is suggested here that the two-dimensional analogue of cooperative spontaneous emission (superfluorescence) can occur for a single monolayer of excited molecules over a metal surface. The initially inverted molecular system may be prepared by pumping a strongly allowed singlet-singlet transition of the molecules composing the monolayer(s).

Intersystem crossing, which can be enhanced by incorporating a heavy atom in the molecule to increase spin-orbit coupling, transfers the excitation energy into the long-lived triplet system. The emission into surface plasmons initially occurs spontaneously and eventually triggers the release of the energy stored in the triplet system in the preferred axial mode of the monolayer-metal surface system as a hyperbolic-secant-shaped, very intense surface plasmon pulse. Depending on initial conditions and the relevant dephasing and cooperative decay time scales, either a single soliton-like SP pulse or a series of pulses may be obtained.

The outline of this paper is as follows: Section B is a glossary of terms used in this paper; Section C is a brief introduction to the modification of radiative molecular decay due to the proximity of a metal surface. In Section D a model Hamiltonian is set up for the coupled molecule-photon-surface plasmon system, and a theoretical description is given of the time evolution of this system from a fully inverted initial state at time zero. In Section E a discussion is given of the physical parameters appropriate for surface plasmon superfluorescence. Section F contains a summary of the results and some general comments relating to other possible systems such as surface excitons, phonons, and magnons.

B. Glossary

ω_p	bulk plasmon frequency
D	distance from metal surface
λ_f	fluorescence wavelength of excited molecule
$\omega_p/2^{1/2}$	asymptotic surface plasmon frequency
κ	phase shift between direct and reflected wave
k_0	wave vector of phosphorescent photon
k	wave vector of photon
$\Sigma(\omega, D)$	self-energy of excited molecule at frequency ω and at distance D
ω_0	unrenormalized molecular transition frequency
γ_0	free-space decay rate of isolated molecule
$\omega_R^{\parallel}(D)$	renormalized molecular transition frequency for the transition dipole parallel to surface normal
$\gamma_R^{\parallel}(D)$	renormalized linewidth for transition dipole parallel to surface normal
$\omega_R^{\perp}(D)$	renormalized molecular transition frequency for transition dipole perpendicular to surface normal
$\gamma_R^{\perp}(D)$	renormalized linewidth for transition dipole perpendicular to surface normal
R	reflectivity of metal
ϵ_0	dielectric constant of medium adjacent to metal
$\epsilon(\omega)$	jellium dielectric function of metal
$(\gamma_s)^{-1}$	electron-electron scattering time
m	electron effective mass
n	conduction electron density of the metal
e	electronic charge
$\Omega_R^{\parallel}(D)$	renormalized molecular transition frequency including surface plasmons for transition dipole parallel to surface normal
$\Gamma_R^{\parallel}(D)$	renormalized linewidth including surface plasmons for transition dipole parallel to surface normal
$I^{\parallel}(\epsilon(\omega))$	surface plasmon contribution to linewidth
$J^{\parallel}(\epsilon(\omega))$	surface plasmon contribution to molecular transition frequency
$\xi^2(\omega)$	negative dielectric function of metal
$\mathcal{H}$	Hamiltonian for molecular monolayer-photon-surface plasmon system
$\mathcal{H}_0^{m}$	molecular Hamiltonian
$\mathcal{H}_0^{f}$	Photon and surface plasmon field Hamiltonian
$\mathcal{H}_1^{mf}$	interaction Hamiltonian for molecule-photon-surface plasmon
$\hbar$	Planck's constant × $(2\pi)^{-1}$
ω_k	photon frequency
ω_κ	surface plasmon frequency
$\sigma_3^{(j)}$	z component of pseudo-spin of the jth molecule
a_κ, a_κ^*	annihilation and creation operator of surface plasmons with wave vector κ
$b_{k\lambda}$, $b_{k\lambda}^*$	annihilation and creation operator for photons of wave vector k and polarization λ
$\vec{d}^{(j)}$	transition dipole of the jth molecule
$\vec{E}(\vec{r}_j, t)$	total electric field
$\psi_e^{(j)}$	excited state wavefunction of the jth molecule
$\psi_g^{(j)}$	ground state wavefunction of the jth molecule
$\vec{x}$	position operator of electron involved in the transition
$\vec{A}(\vec{r}_j, t)$	total vector potential at space-time point $\vec{r}_j$, t

$\vec{A}^{s}(\vec{r}_j, t)$	vector potential due to s-polarized photons
$\vec{A}^{p}(\vec{r}_j, t)$	vector potential due to p-polarized photons
$\vec{A}^{SP}(\vec{r}_j, t)$	vector potential due to surface plasmons
c	speed of light
A	area of metal surface
$\hat{\kappa}$	unit vector in metal surface
$\hat{z}$	unit vector perpendicular to metal surface
$\vec{\kappa}$	two-dimensional wave vector in the reciprocal space to the metal surface
$\sigma_{\pm}^{(j)}$	step-up and step-down operators in Pauli pseudo-spin space for the *j*th molecule
U	time-evolution operator
δ_{κ}	frequency mismatch between molecule and surface plasmon of wave vector κ
$\vec{\rho}_j$	two-dimensional position vector of the *j*th molecule; inferior j' and ℓ denote other indices
p_{κ}	defined in text Section D
ν_0	defined in text Section D
$g_{\kappa}(t)$	function defined in Eq. (6)
$R_{\pm}(\vec{\alpha})$	collective transition operators for the monolayer at wave vector $\vec{\alpha}$
$\vec{\alpha}$	two-dimensional reciprocal lattice vector of monolayer
$L_{x,y}$	x, y dimensions of the monolayer
S, T	number of molecules in the x and y directions of the monolayer
a	lattice spacing of the monolayer
$f(\vec{\kappa} - \vec{\alpha}, t)$	reciprocal space and time shape function
$g(t)$	time correlation function of molecular transition
$G(\epsilon)$	single-molecule lineshape function
$\delta(\epsilon)$	Dirac delta function
$\delta_{\alpha\alpha'}$	Kronecker delta function
$A(\vec{\alpha})$, $A^{*}(\vec{\alpha})$	surface plasmon quasi-mode annihilation and creation operator
O	an operator defined in Eq. (14)
Λ_{F}	irreversible operator term in Liouville equation
$\kappa(\alpha)$	inverse surface plasmon escape time
v_{SP}	surface plasmon group velocity
ρ_{M}	areal density of monolayer
T_2^{*}	inhomogeneous dephasing time
γ_{inh}	$1/T_2^{*}$
γ	surface plasmon width
Tr	trace
$R_3(\vec{\alpha})$	collective population difference operator
ρ	total density matrix for monolayer-surface plasmon system
β	$(k_B T)^{-1}$; k_B is the Boltzmann constant, T the temperature
ρ_{SP}	surface plasmon density matrix
ρ_{m}	molecular monolayer density matrix
N	total number of molecules
E_i	internal energy of the system in units of $\hbar\omega_0$
$\psi(t)$	modified Bloch angle
τ_c	cooperation time
τ_d	total surface plasmon damping time
τ_0	phosphorescence lifetime

A tilde over symbols represents the canonical transformation to the interaction representation.

C. Molecular decay near a metal surface

Experimental work by Drexhage, Schaefer, Kuhn, and coworkers [11] on the decay of excited molecules deposited at fixed distances from various metal surfaces showed a strong distance dependence of the single-molecule decay rate. The dependence found was oscillatory and varied somewhat for the different metals used (Au, Al, Cu, Ag). At very short distances ($D < 50$ nm) the lifetime shortened dramatically, suggesting that the energy of the excited molecular complex was transferred to the metal.

The explanation of the oscillatory dependence of the decay rate on distance, suggestive of an interference effect, was given by Drexhage [11] by a classical calculation of the power radiated by a dipole oscillating at a fixed distance D from a reflector. The interference effect arises from the superposition of the directly emitted and reflected fields of the oscillator. Equivalent semiclassical and quantum-mechanical descriptions were given by us [12] for the case of a perfect metal. This approach maps the excited molecule-metal surface problem with its intractable many-body aspects into a much simpler two-body problem (the decay of a two-atom system, sharing one quantum of excitation). The analogy is made on the basis of image theory, which replaces the role of the surface with an image molecule placed at a distance D below the symmetry plane (metal surface).

Physically, the image molecule at a distance $2D$ from the source molecule represents the state of the decaying atom in its own radiation field, which has been reflected from the metal surface and has a relative phase shift of

$$\kappa = 2k_0 D; \qquad k_0 = 2\pi/\lambda_f.$$

From a quantum-mechanical viewpoint, however, the interference effect between directly emitted and reflected electromagnetic fields is similar to the analysis of a two-slit diffraction pattern arising from a single photon (the probability amplitudes for the two possibilities have to be added). The relative phase modulates the interference term when the absolute square of the total amplitude is taken, leading to constructive or destructive interference.

The main result [12] for the effect of a metal surface on the energy levels of a molecule can be described in terms of a complex self-energy $\Sigma(\omega, D)$, which renormalizes the energy ω_0 and free-space decay rate γ_0 of the isolated molecule:

$$\omega_R^{\parallel}(D) = \omega_0 - \frac{3}{2}\gamma_0\left(\frac{\cos\kappa}{\kappa^3} + \frac{\sin\kappa}{\kappa^2}\right),$$

$$\gamma_R^{\parallel}(D) = \gamma_0\left[1 + 3\left(\frac{\sin\kappa}{\kappa^3} - \frac{\cos\kappa}{\kappa^2}\right)\right], \tag{1a}$$

for the case of the transition dipole of the excited molecule parallel to the normal to the metal surface. For the second geometry, the molecular transition dipole perpendicular to the surface normal, one finds [12]:

$$\omega_R^{\perp}(D) = \omega_0 - \frac{3}{4}\gamma_0\left[\left(\frac{1}{\kappa^3} - \frac{1}{\kappa}\right)\cos\kappa + \frac{1}{\kappa^2}\sin\kappa\right],$$

$$\gamma_R^{\perp}(D) = \gamma_0\left\{1 + \frac{3}{2}\left[\left(\frac{1}{\kappa^3} - \frac{1}{\kappa}\right)\sin\kappa - \frac{1}{\kappa^2}\cos\kappa\right]\right\}. \tag{1b}$$

It should be noted that this result is exact, apart from the neglect of molecular recoil in the emission of the photon, which will couple a continuum of field modes (instead of a single one) to the electronic transition. This type of effect is, however, very small and has only recently been observed in nonlinear high resolution gas-phase spectroscopy [13].

The assumption of a perfectly reflecting surface made in Ref. [12] was relaxed in Ref. [14] to include a reflectivity $R < 1$ and a phase shift on reflection unequal to π. These early treatments have the common element of treating the metal surface as playing a static role in the decay of the electronically excited molecule.

A significant advance occurred with the inclusion of the dynamic response of the metal surface. The similarity of the quantum-mechanical problem to the one of an antenna radiating over a conducting earth [15] was already noted in Ref. [12]. Application of the full sophisticated apparatus of radiation theory by Tews [9] and by Chance, Prock, and Silbey [10] implicitly includes a significant additional aspect of the decay: the generation of electromagnetic modes (which propagate in the metal-dielectric interface) with electric fields decaying exponentially in *both* directions perpendicular to the metal surface. These modes, which are polaritons, exist in the entire frequency range from 0 to $\omega_p(1 + \epsilon_0)^{-1/2}$ [15], where ϵ_0 is the dielectric constant of the dielectric adjoining the metal. These modes directly account for the different effects found for different metals in the small distance regime because ω_p, the bulk plasma frequency of the metal, describes the collective response of the metallic electrons and therefore depends on their number density and effective mass.

The first explicit discussion of the consequences of the surface plasmon spectrum on the decay of an excited molecule was given in Ref. [8]. It was shown there, in an adaptation of classical electromagnetic theory [16], that use of a jellium description of the metallic electrons produced resonance effects in the region $\omega_0 \approx \omega_p(1 + \epsilon_0)^{-1/2}$. These resonance effects arise from singularities in the polarization response of the metal surface corresponding to excitation of real surface plasmons in the molecular decay. The same effects were also discussed by Chance, Prock, and Silbey [10] and by others [9].

This section is intended as a review of the single molecule-metal surface interaction; therefore, we will only exhibit the modification of the image theory (static) results due to excitation of surface plasmons in the decay (dynamic effects). The dielectric function for the metal will be chosen in the simplest jellium form:

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_s\omega},$$

$$\omega_p = 4\pi ne^2/m,$$

where γ_s^{-1} is the electron scattering time, m is the electron effective mass, n is the electron density of the metal, and e is the electron charge.

The image theory results given in Eqs. (1a) and (1b) are modified by additional terms due to the coupling to surface plasmons, and to the appearance of the optical response of the metal (which is no longer treated as a perfect conductor) in the reflectivity and phase shift on reflection.

The renormalized energy eigenvalues including the imaginary part of the self-energy are given by

$$\Omega_R^{\parallel}(D) = \omega_R^{\parallel}(D) + \frac{3}{1 + \epsilon(\omega)}\, J^{\parallel}(\epsilon(\omega)),$$

$$\Gamma_R^{\parallel}(D) = \gamma_R^{\parallel}(D) - \frac{3}{1 + \epsilon(\omega)}\, I^{\parallel}(\epsilon(\omega)), \tag{2a}$$

for the transition dipole parallel to the normal of the metal surface. The contribution $I^{\parallel}$ is defined by the expressions

$$I^{\parallel}(\epsilon(\omega)) = I_P^{\parallel}(\xi^2) + I_N^{\parallel}(\xi^2),$$

$$\xi^2 = -\epsilon(\omega),$$

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

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

The appearance of a singularity at $\epsilon(\omega) = -1$ is transparent in these expressions, as is the recovery of the image result ($|\epsilon(\omega)| \rightarrow \infty$ corresponds to a perfect conductor). The contribution $J^{\parallel}$ and the modification of the second arrangement (transition dipole perpendicular to the metal-surface normal) are analogous and we refer the reader to earlier papers [8, 17].

The results of these calculations for the width of electronically excited molecules with transition frequencies close to the asymptotic surface plasmon frequency $\omega_p/2^{1/2}$ are shown in Figs. 1(a) and (b).

The dramatic dominance of the new decay channel is apparent from these figures and shows that for distances less than $\lambda_f/10$ (λ_f is the fluorescence wavelength), which corresponds to tens of nanometers in the optical region, molecules will predominantly decay by emission of surface plasmons, for either polarization of the transition dipole. It is this very strong resonance effect between a localized electronic excitation and the delocalized surface-charge density oscillations that forms the basis of the new type of cooperative emission discussed in this paper.

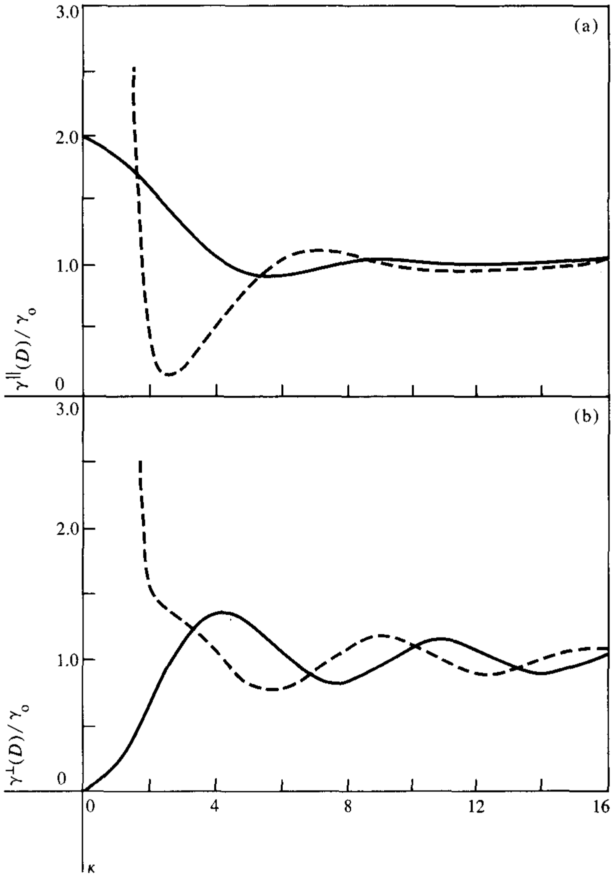

Figure 1 Modification of the image theory width due to SP coupling for (a) parallel transition dipole and surface normal; (b) perpendicular transition dipole and surface normal; image theory (——) and theory with SP coupling (- - -); $\omega_0/\omega_p = 0.7$; $\kappa = 4\pi(\omega_0/\omega_p)(D/\lambda_p)$.

D. Molecular monolayer-surface plasmon superfluorescence

This section addresses the possibility of using the strong coupling between electronically excited molecules and electronic surface plasmons propagating in the metal-dielectric interface to generate coherent, intense pulses by the analogue of superfluorescence in the two-dimensional surface geometry [17].

The theoretical description of the decay of a highly excited system of atoms, leading to the emission of very intense pulses without the feedback of a cavity, has seen considerable advances [3-5] since the early work by R. H. Dicke [1]. These are based on utilizing the reduced master equation for the coupled atom-field system.

The system to be studied is a monomolecular array deposited at a distance $D << \lambda_f$ from a metal surface. The molecules are described as two-level systems coupled to the total electric field, expanded in terms of creation and destruction operators for s- (TE mode) and p- (TM mode) polarized transverse photons and surface plasmons. The well-known representation of the two-level system in terms of pseudo-spin Pauli matrices is used. The Hamiltonian for the entire photon-surface plasmon monolayer system can be written as

$$\mathscr{H} = \mathscr{H}_0^{\mathrm{m}} + \mathscr{H}_0^{\mathrm{f}} + \mathscr{H}_{\mathrm{I}}^{\mathrm{mf}},$$

$$\mathscr{H}_0^{\mathrm{m}} = \hbar\omega_0 \sum_{j=1}^{N} \sigma_3^{(j)},$$

$$\mathscr{H}_0^{\mathrm{f}} = \sum_{k,\lambda} \hbar\omega_k b_{k\lambda}^* b_{k\lambda} + \sum_{\kappa} \hbar\omega_\kappa a_\kappa^* a_\kappa,$$

$$\mathscr{H}_{\mathrm{I}}^{\mathrm{mf}} = -\hbar \sum_{j=1}^{N} \vec{d}^{(j)} \cdot \vec{E}(\vec{r}_j, t). \tag{3}$$

Coulomb gauge has been used for the electric field $\vec{E}(\vec{r}_j, t)$, and electric dipole coupling to the total electric field has been assumed for the molecular transition dipole $\vec{d}^{(j)}$:

$$\vec{d}^{(j)} = -e\langle\psi_{\mathrm{e}}^{(j)}|\vec{x}|\psi_{\mathrm{g}}^{(j)}\rangle,$$

$$\vec{E}(\vec{r}_j, t) = -\left(\frac{1}{c}\right)\frac{\partial\vec{A}(\vec{r}_j, t)}{\partial t},$$

$$\vec{A}(\vec{r}_j, t) = \vec{A}^{\mathrm{s}}(\vec{r}_j, t) + \vec{A}^{\mathrm{p}}(\vec{r}_j, t) + \vec{A}^{\mathrm{SP}}(\vec{r}_j, t), \tag{4}$$

where c is the speed of light. The coupling to the radiative field modes is neglected in the calculation because it is negligible in the near-resonant energy region, $\omega_0 \approx \omega_p/2^{1/2}$ (see Section C). The contribution to the vector potential from the surface plasmon part of the field can be expressed [18] as:

$$\vec{A}^{\mathrm{SP}}(\vec{r}_j, t) = \sum_{\kappa} \left(\frac{4\pi\hbar c}{Ap_{\kappa}}\right)^{1/2} \left(i\hat{\kappa} + \frac{\kappa}{\nu_0}\hat{z}\right)[a_{\kappa} \exp(-i\omega_{\kappa}t) + a^*_{-\kappa} \exp(i\omega_{\kappa}t)] \exp(-\nu_0 z + i\vec{\kappa} \cdot \vec{\rho}), \quad (5)$$

with the following definitions for p_{κ}, ν_0, and ω_{κ}:

$$p_{\kappa} = \frac{\epsilon^4(\omega_{\kappa}) - 1}{[-\epsilon(\omega_0) - 1]^{1/2}} \left[\frac{1}{\epsilon^2(\omega_{\kappa})}\right],$$

$$\nu_0 = [\kappa^2 - (\omega_{\kappa}^2/c^2)]^{1/2},$$

$$\omega_{\kappa}^2 = \frac{1}{2}\omega_p^2 + c^2\kappa^2 - \left(\frac{1}{4}\omega_p^4 + c^4\kappa^4\right)^{1/2},$$

and $\vec{\kappa}$ is a two-dimensional wave vector in the reciprocal space of the metal surface A.

We have now cast the excited molecular monolayer-metal surface plasmon system in a form externally identical with the standard quantum-optical superfluorescence case [5]. We have, of course, made several approximations in our treatment of the metal surface, which has been taken to be perfectly flat. We have neglected the coupling of the SP system to electron-hole pairs and to lattice vibrations that leads to damping of these quasi-particles. We introduce shortly a phenomenological damping term to include these effects. The inclusion of surface roughness would lead to additional damping of the SP due to conversion into photons by the wave vector transfer perpendicular to the surface.

Most interesting to us is the case of an initially highly excited molecular monolayer and its time-evolution towards cooperative spontaneous decay into SP. The use of the Pauli (pseudo-spin) and Bose-Einstein commutation relations for the molecular and field operators $\sigma_{\pm}^{(j)}$, $\sigma_3^{(j)}$ and a_{κ}, a_{κ}^* respectively, allows the canonical transformation of the Hamiltonian to the interaction representation

$$\tilde{\mathscr{H}} = \mathrm{U}^{-1}\mathscr{H}\mathrm{U} = \hbar \sum_{\kappa} \{\delta_{\kappa}\tilde{a}^*_{\kappa}\tilde{a}_{\kappa} + g_{\kappa}[\tilde{a}^*_{\kappa}\sigma_-^{(j)} \times \exp(-i\vec{\kappa} \cdot \vec{\rho}_j) - \mathrm{h.c.}]\},$$

$$\delta_{\kappa} = \omega_{\kappa} - \omega_0,$$

$$\mathrm{U} = \exp(i\mathscr{H}_0 t),$$

$$\mathscr{H}_0 = \hbar\left[\sum_{j=1}^{N} \omega_0\sigma_3^{(j)} + \sum_{\kappa} \omega_{\kappa}a^*_{\kappa}a_{\kappa}\right],$$

$$g_{\kappa}(t) = \left(\frac{4\pi\omega_{\kappa}^2}{\hbar c p_{\kappa} A}\right)^{1/2} \left[\hat{\kappa} \cdot \hat{d}^{(j)} + i(\hat{z} \cdot \hat{d}^{(j)})\frac{\kappa}{\nu_0}\right] \times \exp(-\nu_0 D - i\delta_{\kappa}t), \quad (6)$$

where h.c. stands for Hermitian conjugate. The rotating-wave approximation has been invoked to omit the anti-resonant terms $a^*_{\kappa}\sigma_+^{(j)}$, $a_{\kappa}\sigma_-^{(j)}$. The next step is to use a reciprocal space representation for the local molecular operators $\sigma_{\pm}^{(j)}$:

$$R_{\pm}(\vec{\alpha}) = \sum_{j'=1}^{N} \exp[\pm i\vec{\alpha} \cdot \vec{\rho}_{j'}]\sigma_{\pm}^{(j')}, \quad (7)$$

in terms of the two-dimensional reciprocal lattice vector $\vec{\alpha} = (\alpha_x^s, \alpha_y^t)$ with

$$\alpha_x^s = \frac{2\pi s}{L_x}, \qquad \alpha_y^t = \frac{2\pi t}{L_y}, \qquad -\frac{1}{2}S \le s \le \frac{1}{2}S,$$

$$-\frac{1}{2}T \le t \le \frac{1}{2}T, \qquad N = ST.$$

The L_x and L_y are the x and y dimensions of the monolayer, *i.e.*, $L_x = Sa$, $L_y = Ta$.

The commutation relations of the local operators $\sigma_{\pm}^{(j)}$, $\sigma_3^{(j)}$ can be used to derive commutation relations for the collective operators $R_{\pm}(\vec{\alpha})$:

$$[R_+(\vec{\alpha}), R_-(\vec{\alpha}')] = \sum_{j',\ell} \exp[i(\vec{\alpha} \cdot \vec{\rho}_{j'} - \vec{\alpha}' \cdot \vec{\rho}_{\ell})] \times [\sigma_+^{(j')}, \sigma_-^{(\ell)}] = 2R_3(\vec{\alpha} - \vec{\alpha}'). \quad (8)$$

We now express the Hamiltonian $\tilde{\mathscr{H}}$ in the interaction representation in terms of the collective operators $R_{\pm}(\vec{\alpha})$:

$$\tilde{\mathscr{H}} = \hbar \sum_{\kappa} \delta_{\kappa}a^*_{\kappa}a_{\kappa} + \hbar \sum_{\kappa,\alpha} g_{\kappa}[a^*_{\kappa}R_-(\vec{\alpha})f(\vec{\kappa} - \vec{\alpha}, t) - \mathrm{h.c.}], \quad (9)$$

with the definition

$$f(\vec{\kappa} - \vec{\alpha}, t) = \frac{1}{N}\sum_{j'=1}^{N} \exp[i(\vec{\kappa} - \vec{\alpha}) \cdot \vec{\rho}_{j'} + i\delta_{j'}t]. \quad (9a)$$

For simplicity, we have assumed that the molecular monolayer consists of a square array of molecules with lattice constant a. The electronic transition frequency ω_0 is taken to be homogeneously broadened. To simplify the subsequent treatment, the further assumption is made that the spatial and temporal dependence of $f(\vec{\kappa} - \vec{\alpha}, t)$ is separable, *i.e.*,

$$f(\vec{\kappa} - \vec{\alpha}, t) = F(\vec{\kappa} - \vec{\alpha})g(t),$$

$$g(t) = \int_{-\infty}^{+\infty} d\epsilon G(\epsilon) \exp(i\epsilon t),$$

$$F(\vec{\kappa} - \vec{\alpha}) = \frac{1}{N}\sum_{j'=1}^{N} \exp[i(\vec{\kappa} - \vec{\alpha}) \cdot \vec{x}_{j'}] = \sum_{j'=x,y} \frac{\sin\left[\frac{1}{2}(\kappa_{j'} - \alpha_{j'})L_{j'}\right]}{N_{j'}\sin\left[\frac{1}{2}N_{j'}^{-1}(\kappa_{j'} - \alpha_{j'})L_{j'}\right]}, \quad (10)$$

where $G(\epsilon)$ is the single-molecule lineshape function. For the case of only homogeneous broadening, $G(\epsilon) = \delta(\epsilon)$, and $g(t) = 1$.

The interaction between the collective molecular operators $R_\pm(\vec{\alpha})$ and the SP modes a_κ, a^*_κ is modulated by the diffraction function $F(\vec{\kappa} - \vec{\alpha})$. It is this modulation of the interaction term g_κ that brings about the highly mode-selective decay in superfluorescence [5]. By analogy to these treatments, we introduce an SP quasi-mode operator $A(\vec{\alpha})$:

$$A(\vec{\alpha}) = \left(\frac{L_x L_y}{A}\right)^{1/2} \sum_{\kappa} a_\kappa F(\vec{\kappa} - \vec{\alpha}). \qquad (11)$$

The quasi-mode operators $A(\vec{\alpha})$, $A^*(\vec{\alpha})$ obey Bose-Einstein commutation relations, which arise from the statistics of the SP operators a_κ, a^*_κ and the ortho-normality of the diffraction functions $F(\vec{\kappa})$:

$$\frac{L_x L_y}{4\pi^2} \int d^2\kappa F(\vec{\kappa} - \vec{\alpha}) F(\vec{\kappa} - \vec{\alpha}') = \delta_{\alpha\alpha'} \, . \qquad (12)$$

The two-dimensional diffraction function $F(\vec{\alpha})$ is sharply peaked about $\vec{\alpha} = 0$ and has a width in reciprocal space of order $1/S$. By construction, it has the periodicity of the reciprocal lattice of the molecular monolayer, but we will neglect coupling to points outside the first Brillouin zone.

Because of the narrow width of the diffraction function, we can neglect the κ dependence of the coupling constant g_κ and replace it with an average coupling constant evaluated at $\vec{\kappa} = \vec{\alpha}$, reducing the interaction Hamiltonian $\mathcal{H}_{\mathrm{I}}^{\mathrm{m\text{-}SP}}$:

$$\mathcal{H}_{\mathrm{I}}^{\mathrm{m\text{-}SP}} = \left(\frac{\hbar}{L_x L_y}\right)^{1/2} \sum_{\vec{\alpha}} g_{\vec{\alpha}}(t) [A^*(\vec{\alpha}) R_-(\vec{\alpha}) - \mathrm{h.c.}]. \qquad (13)$$

The definition of the surface plasmon quasi-mode operators in Eq. (11), in terms of a weighted sum over a finite range of κ values for individual surface plasmon modes, is equivalent to the expansion of the complete set of radiation field operators in a large quantization volume in terms of modes defined in the active [5] region of a superradiant medium. Due to the escape of the field into the surrounding space, the quasi-modes are damped and the Hamiltonian is no longer *unitary*.

The calculation of the time-evolution of the coupled molecular monolayer-surface plasmon system proceeds by using the Liouville equation, which includes a dissipative term describing the irreversible aspects of the motion. The master equation for any operator O is defined

$$dO/dt = (1/i\hbar)[\mathcal{H}_0 + \mathcal{H}_{\mathrm{I}}, O] + \Lambda_{\mathrm{F}} O,$$

$$\Lambda_{\mathrm{F}} O = \sum_{\alpha} \{\kappa(\vec{\alpha}) + \gamma\} \{[A(\vec{\alpha}), OA^*(\vec{\alpha})] + \mathrm{h.c.}\}. \qquad (14)$$

Here, square brackets stand for the commutator and the $\Lambda_{\mathrm{F}} O$ term introduces irreversibility into the time-evolution due to the various damping processes.

There are two explicitly exhibited terms in the dissipative part of Eq. (14). The first, given by

$$\kappa(\vec{\alpha}) = \frac{v_{\mathrm{SP}}}{2L_x} \qquad \text{where } v_{\mathrm{SP}} = \left.\frac{\partial \omega_\kappa}{\partial \kappa}\right|_{\vec{\kappa} = |\vec{\alpha}|},$$

is related to the transit time of the resonant surface plasmon mode across the excited monolayer. It is similar to the damping of the electromagnetic quasi-mode in superfluorescence, which occurs on a time scale of $L/c = 1/\kappa$ and has to fulfill the set of inequalities [5]:

$$\frac{1}{\kappa} << (g_{\alpha_0} \rho_{\mathrm{M}}^{1/2})^{-1} << \gamma^{-1}_{\mathrm{inh}},$$

where $\gamma_{\mathrm{inh}} = 1/T^*_2$ and is the inhomogeneous dephasing time.

The second term responsible for the irreversible decay of the system is the phenomenological term γ, which accounts for the intrinsic width of the SP, and which arises from the coupling of these collective degrees of freedom of the metallic electron gas to electron-hole pairs and phonons. The leakage term in Eq. (14) is responsible for the highly directional SP pulse, in correspondence with the dominant role of the Dicke end-fire mode in superradiance [1, 5]. The additional damping term dissipates part of the emitted electronic energy into other elementary excitations of the total system, such as electron-hole pairs, phonons, and heat.

A more complete theory than the one presented here would explicitly include these additional degrees of freedom and would eliminate the coupling to them by performing averages of the total density matrix over the corresponding variables. Such a theory has not yet been developed, but it is clear that our phenomenological inclusion of the quasi-particle nature of the SP field in terms of a finite width for decay would emerge at an early stage of such a calculation. In addition, a more complete theory would provide a way of calculating γ from the theory in terms of the coupling constants and final states of the electron-hole and phonon systems.

In the absence of such a theory we consider γ to be a phenomenological parameter, which can be estimated from experimental data on SP damping [18]. We note, however, that such an experimental value for SP damping is a *single* quasi-particle property and does not necessarily imply that the highly nonlinear propagating SP pulse obeys the same decay laws. From the stability of solitons, once formed, it seems reasonable to expect that SP soli-

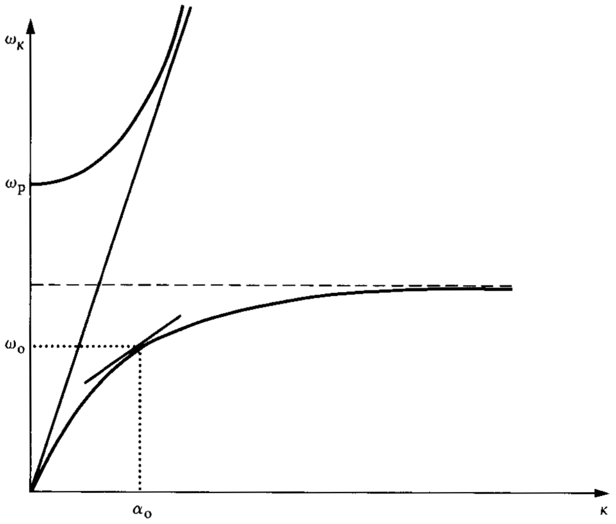

Figure 2 Surface plasmon dispersion relations; the definition of surface plasmon group velocity is $\omega_\kappa \approx \omega_0 + (\kappa - \alpha_0) \times (\partial\omega_\kappa/\partial\kappa|_{\kappa=\alpha_0})$; bulk plasmon frequency is given by ω_p and molecular transition frequency by ω_0. Asymptotic surface plasmon frequency (- - -) is given by $\omega_p/2^{1/2}$. The linear diagonal line between the two curves is given by $\omega = 2^{1/2}c\kappa$.

ton damping is less than the single SP damping, leading to larger propagation distances of the SP pulse or pulses.

The physical origin of soliton behavior in the monolayer-metal surface system is the nonlinear coupling between the excited monolayer and the surface plasmons, which arises from the cooperative polarization of the decaying atoms. In the simple pendulum description of superradiant decay, the equatorial projection of the Bloch vector $\langle R_3(t)\rangle$ [see Eq. (19), derived later] is the driving term $\propto \sin\psi$ [Eq. (20)] in the time-evolution of the system.

The competition between the SP leakage term, $\kappa(\vec{\alpha}) = v_{\text{SP}}/2L_x$, and the intrinsic SP damping term γ requires $\gamma \leq \kappa(\vec{\alpha})$ for the formation of a highly directional SP pulse.

By inspection of Fig. 2, which displays the surface plasmon dispersion relations, it is clear that this condition can be met in the cross-over region, where the group velocity of the SP is still comparable to c ($v_{\text{SP}} \approx c/5$) and the SP damping is small [18]. The master equation (14) can be used to calculate the time-evolution of $\langle R_3(\vec{\alpha})\rangle$, the excitation density-ensemble average of the molecular monolayer. We find

$$\frac{d\langle R_3(\vec{\alpha})\rangle}{dt} = \left(\frac{1}{i\hbar}\right)\text{Tr}_{\text{SP}}\{[\mathscr{H}_0 + \mathscr{H}_{\text{I}}^{\text{m-SP}}, R_3(\vec{\alpha})] + \sum_{\alpha'}[\kappa(\vec{\alpha}\,') + \gamma] \times [A(\vec{\alpha}\,'), R_3(\vec{\alpha})A^*(\vec{\alpha}\,') + \text{h.c.}]\rho\}. \tag{15}$$

The density matrix for the monolayer-SP system is defined in the standard manner:

$$\rho = \frac{\exp(-\beta\mathscr{H})}{\text{Tr}\exp(-\beta\mathscr{H})} = \rho_{\text{SP}} \otimes \rho_{\text{m}}.$$

The SP degrees of freedom have been traced over in Eq. (15).

We now select the single resonant mode $\vec{\alpha}_0$ that is resonant with the SP field ($\omega_0 = \omega_{\kappa=\alpha_0}$), has the largest gain, and couples to the quasi-mode operators A_{α_0}, $A^*_{\alpha_0}$ of the SP field.

The collective molecular operators $R_\pm$, R_3 define a constant of the motion:

$$\langle R_+(\vec{\alpha}_0)R_-(\vec{\alpha}_0) + R_3^2(\vec{\alpha}_0) - R_3(\vec{\alpha}_0)\rangle = \frac{N}{2}\left(\frac{N}{2} + 1\right). \tag{16}$$

The equation of motion for the monolayer excitation density $\langle R_3(\vec{\alpha}_0)\rangle$ relates the total internal energy in units of $\hbar\omega_0$ of the system,

$$E_{\text{i}} = \langle A^*_{\alpha_0}A_{\alpha_0}\rangle + \langle R_3(\vec{\alpha}_0)\rangle,$$

to the loss term,

$$2\{\kappa(\alpha_0) + \gamma\}\langle A^*_{\alpha_0}A_{\alpha_0}\rangle.$$

Specifically,

$$\frac{d}{dt}[\langle A^*_{\alpha_0}A_{\alpha_0}\rangle + \langle R_3(\alpha_0)\rangle] = -2\{\kappa(\alpha_0) + \gamma\}\langle A^*_{\alpha_0}A_{\alpha_0}\rangle. \tag{17}$$

This equation is obtained from Eq. (15) by using the commutation relations for the collective operators,

$$[R_3(\vec{\alpha}), R_\pm(\vec{\alpha}\,')] = \pm 2R_\pm\delta_{\alpha\alpha'}. \tag{18}$$

The collective operators $R_\pm$, R_3 and the SP quasi-mode operators A_{α_0}, $A^*_{\alpha_0}$ commute.

To gain insight into the implications of the equation of motion for the excitation density, we introduce a modified Bloch angle as the dynamic variable for the decay by defining

$$\langle R_3(t)\rangle = [1 + (N + 1)\cos\psi(t)]/2. \tag{19}$$

Use of the self-consistent field approximation allows the decoupling of ensemble averages of higher-order products of operators into products of ensemble averages such as $\langle R_3\rangle$ and $\langle A^*_{\alpha_0}A_{\alpha_0}\rangle$ to lead to a Sine-Gordon equation [19] with damping for the Bloch angle $\psi(t)$:

$$\ddot{\psi} + [\kappa(\alpha_0) + \gamma]\dot{\psi} - (g^2_{\alpha_0}/L_xL_y)(N + 1)\sin\psi = 0. \tag{20}$$

It is well known from a large number of recent papers [20] that the solutions of this equation describe a variety of nonlinear systems with highly unusual properties (solitons).

E. Experimental conditions for the occurrence of SP superfluorescence

The dynamic equation for the time-evolution of the Bloch angle $\psi(t)$ derived in Section D is of direct relevance to the prediction of cooperative decay for a highly excited molecular monolayer into SP.

The appearance of the inertial term $\ddot{\psi}$ in the pendulum equation (20) is due to the inclusion of higher-order correlation functions of the field-matter system [5] and corresponds in physical terms to reabsorption in the active medium.

The overdamped pendulum solution for $\psi(t)$, found by completely neglecting the inertial term $(\approx\ddot{\psi})$, leads to a single hyperbolic-secant solution already obtained in Ref. [1]. The occurrence of either a single "superfluorescent" SP pulse or a damped SP pulse train is determined by the relative size of τ_c and τ_d. The cooperation time,

$$\tau_c = (g_{\alpha_0}\rho^{1/2})^{-1}, \tag{21a}$$

arises from the collective spontaneous decay of the molecules, and

$$\tau_d = [\kappa(\alpha_0) + \gamma]^{-1} \tag{21b}$$

is the damping time accounting both for the escape of the excitation pulse from the excited region and for the intrinsic damping of SP. A single soliton-like SP pulse occurs if $\tau_c >> \tau_d$, while several pulses of decreasing amplitude are expected for $\tau_c \gtrsim \tau_d$.

We consider the following set of parameters:

$$v_{SP} \approx c/5, \qquad \gamma \approx 10^{12}\ \mathrm{s}^{-1}, \qquad L_x = 3 \times 10^{-3}\ \mathrm{cm},$$

and find $\tau_d \approx 0.5 \times 10^{-12}$ s. For a molecular monolayer of areal density $\rho_M \approx 10^{12}$ molecules per cm^2 and a typical phosphorescence lifetime $\tau_0 \approx 10^{-3}$ s, a value for the cooperation time that meets the condition for single-pulse superfluorescence ($\tau_c >> \tau_d$) is $\tau_c \approx 2 \times 10^{-11}$ s.

Our calculation has neglected inhomogeneous broadening for simplicity (inhomogeneous dephasing time $T_2^* \to \infty$), implying systems with dephasing times longer than 10^{-10} s. We expect that such conditions can be met in a low-temperature experiment.

The metal surface most suitable for experimental demonstration of SP superfluorescence is silver, with an asymptotic SP at $\hbar\omega_{SP} = 3.6$ eV and relatively small damping. This frequency may be further reduced by an overlayer of high dielectric constant ϵ_0 because of the factor $\omega_{SP} = \omega_p(1 + \epsilon_0)^{-1/2}$.

Planar organic molecules such as benzene, naphthalene, and anthracene have their lowest triplet transition in the same energy range and can be chemically modified by heavy-atom substitution to enhance spin-orbit coupling. Thus, intersystem crossing to the triplet state gives the initial state of the system after pumping into a singlet state with a laser.

The detection of single or multiple hyperbolic-secant SP pulses propagating in the metal-dielectric interface may be possible by use of the inverse attenuated total reflection technique used by Burstein *et al.* [21].

F. Summary and conclusions

We have demonstrated that cooperative spontaneous emission may occur in a new domain: the metal-dielectric interface. Significant modification occurs in the properties of excited molecules in such an environment, particularly for near-degeneracy of the molecular transition frequency ω_0 and the asymptotic SP frequency $\omega_p/2^{1/2}$. The generation of a soliton-like pulse of surface excitations propagating in the metal-dielectric interface is of potentially great importance for surface-wave generation and low-loss propagation.

The effect described for the specific case of electronically excited molecules and the SP of a metal is more general than the model. For example, vibrationally excited molecules over crystal surfaces or radicals over a magnetic surface with a suitable spin-wave spectrum are expected to show similar potential for cooperative emission of the appropriate strongly coupled polaritons. It is our hope that the discussion given in this paper will stimulate experimental work to define such systems.

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