Smart Design of Zero-Mode Waveguide Nanodevices for Effective Detection of Single-Molecule Fluorescence

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The spontaneous decay rate of an excited molecule placed near a circular nanoaperture in a metal film of finite thickness and finite conductivity lying on a dielectric substrate (zero-mode waveguide, ZMW) is investigated. A significant influence of the molecule position and the presence of the substrate on the spontaneous emission rate of the molecule is shown. The asymptotes, which can be used to describe this process, are found. Total, radiative, and nonradiative channels of spontaneous decay rates of the excited molecule are extracted and analyzed. It is shown that a special choice of the substrate and the material of metal film leads to the appearance of "leaky" surface plasmon waves and substantial enhancement of the radiative decay rate. The results can be useful in the design of alternative ZMW optical nanodevices for effective detection of single-molecule fluorescence.

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I. INTRODUCTION

Nanoapertures of different shapes in a metal film are widely used in optical and plasmonic nanodevices [1–5]. Such nanoapertures do not support propagating modes and are often called zero-mode waveguides (ZMW, Fig. 1).

ZMW are basic elements of a scanning near-field optical microscope (SNOM) [6–10], devices for DNA sequencing [11,12] and single-molecule spectroscopy [13–27]. A nanoaperture has been also used in the experiment on a single photon transport by a moving atom [28,29]. Chan *et al*. have investigated a new type of plasmon-atomic two-dimensional metamaterial based on a perforated plasmonic metasurface in an atomic gas [30]. Methods for precise positioning of a molecule inside a nanoaperture [31] create alternative opportunities to control the radiation of a single quantum emitter.

Despite a considerable number of experiments on the fluorescence of a single molecule near a single nanoaperture (see e.g., [6–10,13–25,32,33]), as far as the author knows, there are no detailed theoretical studies of such problems, and the interpretation of the experimental results and design of effective ZMW are not easy tasks. In the ZMW experiments on a single-molecule fluorescence, a nanoaperture plays a dual role: it modifies (1) the excitation field and (2) the spontaneous emission rate of the molecule [23,34]. Usually, the authors pay the most attention to enhancement of the excitation field by a nanoaperture. However, the modification of the spontaneous emission rate of the molecule is also of great importance in the single-molecule fluorescence. The problem of spontaneous emission rate modification by a nanoaperture (Purcell effect [35]) is more complicated in comparison with the calculation of the excitation rate and is independent of it. Analytical and numerical approaches to the problem of the spontaneous emission rate of a single molecule located near an aperture in a perfectly conducting and infinitely thin screen are presented in Refs. [36,37]. However, in a real experiment, an approximation of a real metal film with a perfectly conducting and infinitely thin screen is not good enough, and one should take into account the finite conductivity of the metal and finite thickness of the metal film and also of the dielectric substrate. Taking these factors into account leads to the surface plasmon excitation at the interface of the metal film and the dielectric and to Joule's losses inside the metal.

There are many works in this direction. In particular, single-molecule fluorescence near rectangular nanoapertures has been studied in [13,20]. A single-molecule fluorescence in even more complicated geometries of "antenna-in-box" or bowtie apertures has been investigated in Refs. [21] and [25], respectively. Several other geometries have been considered in Ref. [17]. Unfortunately, the influence of radiative decay rate on a single-molecule fluorescence has not been studied in detail in these and related works.

In the present work, we will present a detailed study of the influence of a circular aperture in the metal film of finite thickness and conductivity on the radiative and nonradiative channels of spontaneous emission rate of a molecule located near it (see Fig. 2). To provide a substantial enhancement of the spontaneous emission rate and as a consequence of the fluorescence rate, we will consider a wide range of materials. which are constituent parts of

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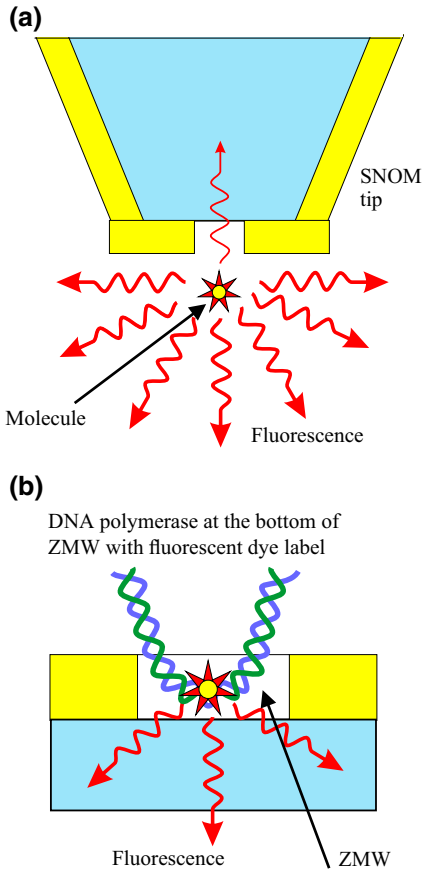

FIG. 1. (a) Schematic view of a SNOM tip. (b) Schematic view of ZMW device for DNA sequencing [11,12].

ZMW. This will allow us to make use of the effect of the large enhancement of the spontaneous decay rate by means of leaky plasmonic waves [38] to develop a principle of operation of alternative types of ZMW devices of different kinds.

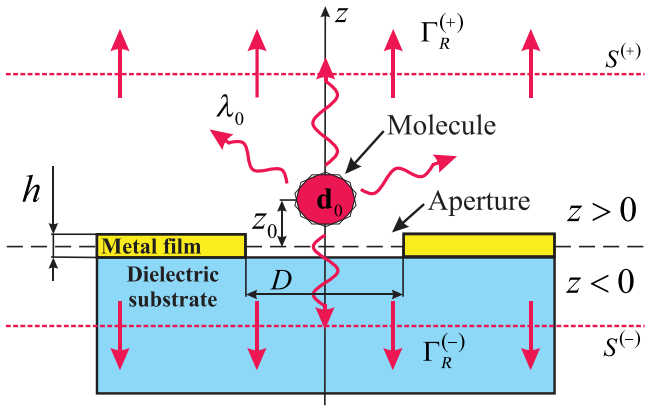

FIG. 2. Schematic view of our model of a ZMW device or a SNOM tip.

It is well known that all organic fluorescent dyes and fluorescent proteins are dipoles whose orientations are closely related to the structure of their labeled target proteins (see e.g. [39]). That is why we will use a classical oscillating dipole as a model of a dye molecule. Within this model of the molecule, its decay rate can be found within well-known approaches ([40–44] and Sec. II). In the case of a real metal, there are no analytical solutions, and we have mainly treated this problem numerically. However, where it is possible, we have found asymptotic expressions. The geometry of the problem under consideration is shown in Fig. 2.

The rest of the article is organized as follows. Section II describes the general approach to the study of spontaneous emission near a nanoaperture. In Sec. III, the spontaneous decay rate of the molecule near an aperture in the metal film on a dielectric substrate is investigated. In this section, it is shown that for some parameters, a large enhancement of the spontaneous emission rate of the molecule is possible. The SNOM tip design based on this effect is suggested to detect molecules more effectively in comparison with existing SNOMs.

II. GENERAL CONSIDERATION OF A MOLECULE RADIATION IN NANOENVIRONMENT

In the case of a weak electromagnetic interaction of the molecule with a nanoaperture in the real metal film, the total spontaneous decay rate of the molecule ($\Gamma_T = \gamma_T/\gamma_0$) consists of radiative ($\Gamma_R = \gamma_R/\gamma_0$) and nonradiative ($\Gamma_{\rm NR} = \gamma_{\rm NR}/\gamma_0$) rates of spontaneous emission, where $\gamma_0 = (4k_0^3/3\hbar)|\mathbf{d}_0|^2$ is the rate of spontaneous emission of the molecule in vacuum [see Fig. 2].

The radiative decay rate (Γ_R) consists of radiative rates into the upper ($\Gamma_R^{(+)} = \gamma_R^{(+)}/\gamma_0$) and lower ($\Gamma_R^{(-)} = \gamma_R^{(-)}/\gamma_0$) half spaces [see Fig. 2]. The radiative decay rate corresponds to the photon emission to infinity in the upper or lower half spaces, respectively. The nonradiative decay rate of the molecule corresponds to the emission of a photon, which is absorbed in the metal film. Total energy balance can be expressed by the following formula

$$\Gamma_T = \Gamma_R + \Gamma_{\rm NR} = (\Gamma_R^{(+)} + \Gamma_R^{(-)}) + \Gamma_{\rm NR}. \qquad (1)$$

The total spontaneous decay rate of the molecule (Γ_T) in vacuum near the aperture can be calculated with the help of the solution of the classical problem of the diffraction of an electromagnetic field of the oscillating dipole (with a frequency ω_0 and a dipole momentum $\mathbf{d}_0$) on the aperture in a real metal film [40–44]. If the oscillating dipole is defined by the

current density [41])

$$\mathbf{j} = -i\omega_0 \mathbf{d}_0 \delta(\mathbf{r} - \mathbf{r}_0) \exp(-i\omega_0 t), \tag{2}$$

where $\delta(\mathbf{r} - \mathbf{r}_0)$ is the Dirac delta function, $\mathbf{r}_0$ is the coordinate of the dipole position, then the total rate of the spontaneous emission of the molecule can be represented by the expression

$$\Gamma_T = \frac{\gamma_T}{\gamma_0} = \frac{3}{2}\mathrm{Im}\left\{\frac{\mathbf{d}_0 \cdot \mathbf{E}(\mathbf{r}_0, \mathbf{r}_0, \omega_0)}{k_0^3 |\mathbf{d}_0|^2}\right\} = 1 + \frac{3}{2}\mathrm{Im}\left\{\frac{\mathbf{d}_0 \cdot \mathbf{E}^{(1)}(\mathbf{r}_0, \mathbf{r}_0, \omega_0)}{k_0^3 |\mathbf{d}_0|^2}\right\}, \tag{3}$$

where $\mathbf{E}(\mathbf{r}, \mathbf{r}_0, \omega_0)$ is the electric field, which is found from a full system of the Maxwell's equations with the oscillating dipole current (2) located near the aperture in a real metal film; $\mathbf{E}^{(1)}(\mathbf{r}_0, \mathbf{r}_0, \omega_0)$ is the scattered part of the electric field; $k_0 = \omega_0/c_0 = 2\pi/\lambda_0$, where c_0 and λ_0 are the speed of light and the wavelength in vacuum, respectively; Im describes the imaginary part.

Equation (3) describes the total spontaneous decay rate of the molecule, that is, it takes into account the processes of absorption of the emitted photon by the metal film and the processes of real radiation where the photon goes to the detector.

The radiative part of the spontaneous emission rate (Γ_R) can be expressed in terms of the energy flow to infinity [41]

$$\Gamma_R = \Gamma_R^{(+)} + \Gamma_R^{(-)} = \frac{3}{8\pi k_0^4 |\mathbf{d}_0|^2} \times \int_{S^{(+)} \cup S^{(-)}} dS \mathrm{Re}\{[\mathbf{E}(\mathbf{r}, \mathbf{r}_0, \omega_0) \times \mathbf{H}^*(\mathbf{r}, \mathbf{r}_0, \omega_0)]_z\}, \tag{4}$$

where $S^{(+)}$ and $S^{(-)}$ are plane surfaces parallel to the interface [see Fig. 2], $\mathbf{E}(\mathbf{r}, \mathbf{r}_0, \omega_0)$ and $\mathbf{H}(\mathbf{r}, \mathbf{r}_0, \omega_0)$ are the electric and magnetic fields at the observation point $\mathbf{r}$ where the asterisk denotes the complex conjugation, the subscript z describes the z component of the vector, and Re describes the real part.

The nonradiative decay channel (Γ_{NR}) corresponds to the absorption of photons in a metal film, which results in metal heating. It is calculated by the volume integration

$$\Gamma_{\mathrm{NR}} = \frac{3\varepsilon''_{\mathrm{film}}(\omega_0)}{8\pi} \frac{\int_V |\mathbf{E}(\mathbf{r}, \mathbf{r}_0, \omega_0)|^2 dV}{k_0^3 |\mathbf{d}_0|^2}, \tag{5}$$

where $\varepsilon''_{\mathrm{film}}(\omega_0)$ is the imaginary part of the permittivity of the film, $\varepsilon_{\mathrm{film}}(\omega_0) = \varepsilon'_{\mathrm{film}}(\omega_0) + i\varepsilon''_{\mathrm{film}}(\omega_0)$, and V is the metal film volume.

To clarify the problem of molecule radiation located near the aperture of the SNOM tip, we investigate a metal film with a nanoaperture lying on an infinite dielectric substrate (see Sec. III). The z axis coincides with the axis of symmetry of the aperture. The coordinate $z = 0$ nm is in the middle of the metal film of thickness h. In the numerical simulations, we use the optical properties of the gold metal film from [45]. In what follows, a "vertical" dipole means that the dipole moment $\mathbf{d}_0$ has the same direction as the z axis. A "horizontal" dipole means that the dipole moment $\mathbf{d}_0$ is perpendicular to the z axis.

In our numerical simulations, we use the finite element method (COMSOL Multiphysics) for solving Maxwell's equations with a point oscillating electric dipole defined by current density (2). We use two-dimensional modeling with axisymmetric formulation of the problem. For the case of a vertical dipole moment, the solution does not have angular dependence. For the case of a horizontal dipole moment, the solution has angular dependence proportional to $\cos(\varphi)$ or $\sin(\varphi)$.

To understand the effect of the nanoaperture on the spontaneous emission of the molecule and checking our calculations, we compare our results with three cases that have analytical solutions.

The first case is spontaneous emission of the molecule located near the solid metal film of finite thickness and finite conductivity. In this case, the expressions for the total rate of spontaneous emission are obtained first by using the classical approach [46])

$$\Gamma_T = 1 + \frac{3}{2k_0^3}\mathrm{Re}\int_0^\infty r^p(q) \frac{q^3 \exp\left(2i\tilde{z}_0\sqrt{k_0^2 - q^2}\right)}{\sqrt{k_0^2 - q^2}} dq \quad \text{(for the vertical dipole moment)} \tag{6}$$

and

$$\Gamma_{\mathrm{T}} = 1 - \frac{3}{4k_0^3}\mathrm{Re}\left\{\int_0^\infty [(k_0^2 - q^2)r^p(q) - k_0^2 r^s(q)] \times \frac{q \exp\left(2i\tilde{z}_0\sqrt{k_0^2 - q^2}\right)}{\sqrt{k_0^2 - q^2}} dq\right\} \quad \text{(for the horizontal dipole moment)}, \tag{7}$$

where $\tilde{z}_0 = z_0 - h/2$, r^p and r^s are reflection coefficients for p and s polarized waves for a three-layer system [42]

$$r^{(p,s)}(q) = \frac{r_{12}^{(p,s)}(q) + r_{23}^{(p,s)}(q)\exp\left(2ih\sqrt{\varepsilon_{\rm film}k_0^2 - q^2}\right)}{1 + r_{12}^{(p,s)}(q)r_{23}^{(p,s)}(q)\exp\left(2ih\sqrt{\varepsilon_{\rm film}k_0^2 - q^2}\right)}, \tag{8}$$

where $r_{i,j}^{(p,s)}$ are the reflection and transmission Fresnel coefficients for the single interface (i,j)

$$r_{ij}^{p}(q) = \frac{\varepsilon_j\sqrt{\varepsilon_i k_0^2 - q^2} - \varepsilon_i\sqrt{\varepsilon_j k_0^2 - q^2}}{\varepsilon_j\sqrt{\varepsilon_i k_0^2 - q^2} + \varepsilon_i\sqrt{\varepsilon_j k_0^2 - q^2}},$$

$$r_{ij}^{s}(q) = \frac{\sqrt{\varepsilon_i k_0^2 - q^2} - \sqrt{\varepsilon_j k_0^2 - q^2}}{\sqrt{\varepsilon_i k_0^2 - q^2} + \sqrt{\varepsilon_j k_0^2 - q^2}}, \tag{9}$$

where $\varepsilon_1 = 1$ (the vacuum), $\varepsilon_2 = \varepsilon_{\rm film}(\omega_0)$ (the metal film), and $\varepsilon_3 = \varepsilon_{\rm sub}$ (the dielectric substrate).

The second case is the spontaneous emission of the molecule located near a perfectly conducting infinitely thin screen without an aperture [37,43,44]. For this geometry, the problem has a simple solution for the total rate of spontaneous emission

$$\Gamma_T = 1 - 3\left(\frac{\cos(2k_0\tilde{z}_0)}{(2k_0\tilde{z}_0)^2} - \frac{\sin(2k_0\tilde{z}_0)}{(2k_0\tilde{z}_0)^3}\right)$$

(for the vertical dipole moment) (10)

and

$$\Gamma_T = 1 - \frac{3}{2}\left(\frac{\sin(2k_0\tilde{z}_0)}{(2k_0\tilde{z}_0)} + \frac{\cos(2k_0\tilde{z}_0)}{(2k_0\tilde{z}_0)^2} - \frac{\sin(2k_0\tilde{z}_0)}{(2k_0\tilde{z}_0)^3}\right)$$

(for the horizontal dipole moment). (11)

The third case is the spontaneous emission of the molecule with a vertical dipole moment located near a perfectly conducting infinitely thin screen with an aperture. This problem has an analytical solution for the total rate of spontaneous emission within the quasistatic approximation for an arbitrary position and orientation of the dipole moment. For the case of a dipole with z orientation, the expression for the total decay rate has the following form [36,37]

$$\Gamma_T = \frac{1}{2}\left(1 + \frac{2}{\pi}\left[\frac{a\tilde{z}_0}{(\tilde{z}_0^2 + a^2)} + \arctan\left(\frac{\tilde{z}_0}{a}\right)\right]\right)^2 + \frac{1}{2}\left(1 - \frac{2}{\pi}\left[\frac{a\tilde{z}_0}{(\tilde{z}_0^2 + a^2)} + \arctan\left(\frac{\tilde{z}_0}{a}\right)\right]\right)^2, \tag{12}$$

where $a = D/2$ is the radius of the aperture.

As we will show, all these asymptotes (6)–(12) can be useful for estimation of the total decay rate near the SNOM tip or ZMW.

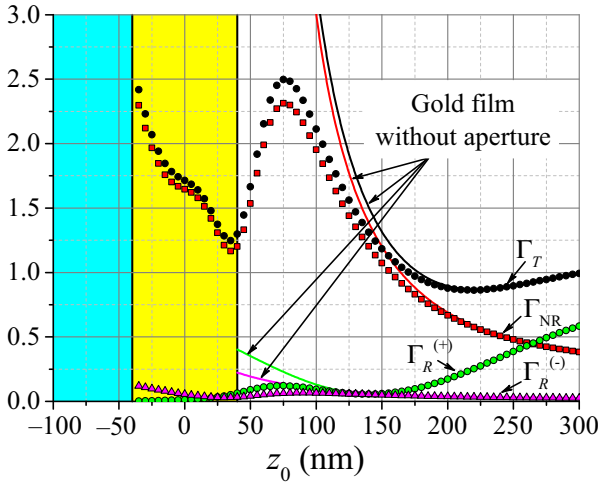

FIG. 3. Total (Γ_T) (black color), radiative into the upper ($\Gamma_R^{(+)}$) (green color), and into the lower ($\Gamma_R^{(-)}$) (magenta color) half-spaces, nonradiative ($\Gamma_{\rm NR}$) (red color) rates of spontaneous emission of the molecule located on the axis of symmetry of the aperture in the gold film as a function of the position of the molecule z_0. The points are the case of the metal film with an aperture. The solid lines are the case of the metal film without an aperture [see Eq. (6)]. The yellow stripe stands for the molecule position in the area inside the aperture in the gold film. The cyan stripe is the area of the dielectric substrate ($\varepsilon_{\rm sub} = 2.25$). The radiation wavelength $\lambda_0 = 500$ nm, $\mathbf{d}_0 \parallel z$, $D = 100$ nm, $\varepsilon_{\rm film} = -2.13 + i2.42$ [45].

III. SPONTANEOUS EMISSION OF A MOLECULE LOCATED NEAR THE SINGLE APERTURE IN THE METAL FILM PLACED ON A DIELECTRIC SUBSTRATE

Let us consider the rate of spontaneous emission of the molecule located near a single aperture in a metal film placed on the semi-infinite dielectric substrate ($\varepsilon_{\rm sub} = 2.25$). This situation is very close to the case of a real SNOM tip [see Fig. 1(a)] or ZMW device [see Fig. 1(b)]. In this section, the thickness of the metal layer is chosen to be 80 nm and dipole orientation is along the axis symmetry (z axis). We have chosen such thickness and orientation for comparison with the study of radiative decay rates enhancement due to "leaky" surface plasmon waves in a multilayer structure without an aperture [38]).

Figures 3 and 4 show the dependence of the total, radiative, and nonradiative parts of the decay rate as a function of the molecule position on the axis of the aperture for different permittivities of the metal film.

From Fig. 3 (for the vertical orientation of the dipole moment), it can be seen that in the presence of finite conductivity, the nonradiative contribution becomes very significant or even predominant. The radiation contribution begins to prevail over the nonradiative one only at large distances when the coordinate z_0 is greater than $3D$.

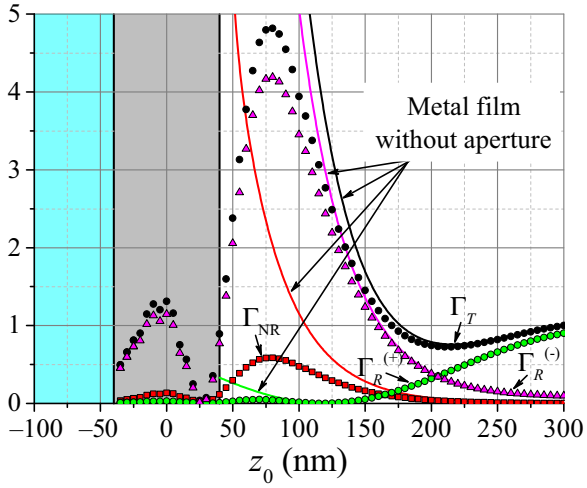

FIG. 4. Total (Γ_T) (black color), radiative into the upper ($\Gamma_R^{(+)}$) (green color), and into the lower ($\Gamma_R^{(-)}$) (magenta color) half-spaces, nonradiative (Γ_{NR}) (red color) rates of spontaneous emission of the molecule located on the axis of symmetry of the aperture in a hypotheticl metal material film as a function of the position of the molecule z_0. The points are the case of the metal film with an aperture. The solid lines are the case of the metal film without an aperture [see Eq. (6)]. The gray stripe corresponds to the molecule position in the area inside the aperture in the metal film. The cyan stripe is the area of the dielectric substrate ($\varepsilon_{sub} = 2.25$). The radiation wavelength $\lambda_0 = 500$ nm, $\mathbf{d}_0 \,||\, z$, $D = 100$ nm, $\varepsilon_{film} = -1.72 + i0.001$.

It can be seen that when z_0 is greater than $2D$, the molecule ceases to feel the presence of the aperture, and for the calculation of total, radiative, nonradiative rates the approach "molecule located near the metal plane" [see Eq. (6)] starts to work well. Note that for a large enough distance between the dipole and the metal surface, the total rate of spontaneous emission of the molecule tends to the asymptote "molecule near a perfectly conducting infinitely thin screen without an aperture" [see Eq. (10)]. Also, from a comparison of the total rates for the perfect electric conducted film and gold film cases with the aperture, one can see that they have the maximum before the metal film.

However, for other parameters of a dielectric substrate and a metal film, the excitation of a "leaky" surface plasmon wave becomes possible [38,47]). Such "leaky waves" make it possible to obtain a substantial increase in the spontaneous radiative decay rate into the lower half space (that is, inside the SNOM tip or ZMW). To excite the "leaky" surface plasmon wave for a dielectric substrate with $\varepsilon_{sub} = 2.25$, one needs to take a specially selected metal film (for example, $\varepsilon_{film} = -1.72 + i0.001$). The results of the calculations for this case are shown in Fig. 4.

It can be seen that in this case, the radiative rate in the lower half space starts to make a prevailing contribution to the total spontaneous decay rate. In particular, at $z_0 \approx 80$ nm (the distance from the surface of the metal film is 40 nm) $\Gamma_R^{(-)} \approx 4.19$. In the case of the gold film, at the same distance $\Gamma_R^{(-)} \approx 0.07$ (see Fig. 3). Thus, one can see an enhancement by a factor of 60 in the case of a proper selection of materials.

This large enhancement is due to 2 factors:

(1) Plasmonic leaky-wave excitation [38]
(2) Transformation of near fields in vacuum into propagating waves in dielectrics ("forbidden light") [48,49].

This effect is observed only for small losses. Such low losses are difficult to implement in an experiment. Nevertheless, to check this result, one can use the gallium-doped zinc oxide as an example (it has $\varepsilon_{film} \approx -1.05 + i0.6$ [50]) and a permittivity of the substrate of $\varepsilon_{sub} \approx 10$ (which is the case of semiconductors in the infrared range of the wavelength). For these materials even in the case without an aperture, one can obtain a radiative decay enhancement in the lower half space equal to eight [38], which substantially exceeds the radiative rate achievable in other configurations considered in this paper. Even better results can be achieved with dysprosium-doped cadmium oxide at a wavelength of around 1950 nm ($\varepsilon''_{film} \approx 0.2$ [51]) or with crystalline silicon carbide in the midinfrared ($\varepsilon''_{film} \approx 0.15$ [52]). For these materials in the case without an aperture, one can expect the radiative decay rate to be enhanced 30-fold with the same substrate ($\varepsilon_{sub} \approx 10$) [38]. Moreover, the concept of loss compensation is currently widely discussed [53] and can be used to achieve the conditions of realization of the found effect.

The presence of the substrate can radically change the relation between the radiative and nonradiative channels of the spontaneous emission. As is clearly seen, this effect is manifested in the excitation of "leaky" surface plasmon wave in this system.

IV. CONCLUSION

We have investigated the spontaneous emission of a single molecule located near a zero-mode waveguide in the

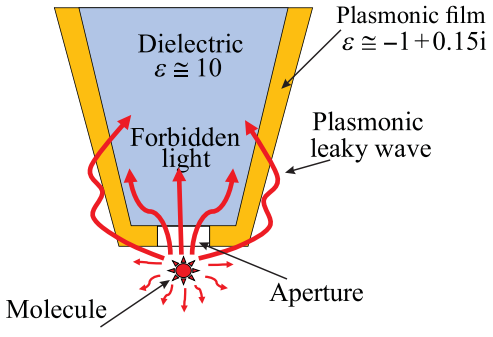

FIG. 5. Design of a smart SNOM tip for effective single-molecule detection by excitation of leaky plasmonic waves and forbidden light.

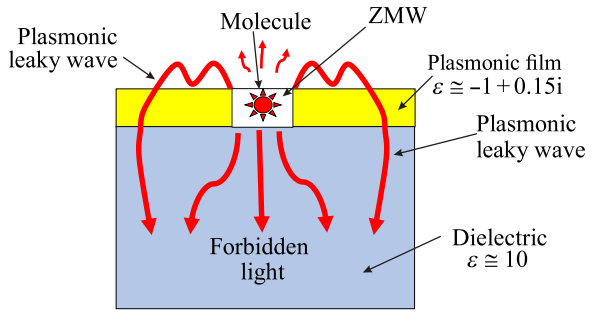

FIG. 6. Design of a smart ZMW device for an effective single-molecule detection by excitation of leaky plasmonic waves and forbidden light.

finite thickness plasmonic film on a dielectric substrate for a wide range of their permittivities.

We demonstrate that a special choice of permittivities of the metal film and the dielectric substrate results in the excitation of a "leaky" surface plasmon wave and a "forbidden light," which substantially change the relation between the radiative and nonradiative decay channels. As a result, the "leaky" wave significantly increases the radiative rate into the dielectric substrate. The effect found can be used for designing a smart ZMW device with high efficiency of a single-molecule detection (see Figs. 5 and 6).

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