Molecular fluorescence in the vicinity of a gradient-index medium

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The problem of molecular fluorescence in the vicinity of a gradient-index medium is studied theoretically through classical modeling of a radiating dipole. A previously developed formulation involving the Green dyadic for an inhomogeneous medium is applied to the present problem. Normalized lifetimes for the admolecules are calculated and compared with those for a homogeneous medium. The results are illustrated by numerical examples assuming certain simple forms for the index profile. © 2000 Optical Society of America [S0740-3232(00)00305-7]

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1. INTRODUCTION

The problem of modeling radiating dipoles in the vicinity of a dielectric/metallic surface has continued to be of great interest since the first work by Sommerfeld published in 1909.[1] This interest is due in part to the theoretical simplicity of the problem as well as to the wide applicability of the model to realistic experimental situations. Examples range from the modeling of molecular fluorescence at interfaces[2] to emissions from semiconductor microcavities.[3]

Among the different approaches to the modeling of fluorescing molecules at interfaces, the phenomenological model formulated by Chance, Prock, and Silbey (CPS) and others,[2] using classical electrodynamics, stands out as a very efficient approach. In particular, the CPS theory can incorporate difficult aspects of the problem (e.g., surface morphological structure) with a minimum of effort. The general procedure according to this method is to obtain the Green dyadic for the radiating molecular dipole fitting the boundary conditions imposed by the layer interfaces.[2] This solution has been obtained previously for a variety of surface morphologies as well as for media with different dielectric properties. Examples include single and multilayer planar surfaces,[2] roughened surfaces with both extended [4] and localized[5] structures, and media of both isotropic and anisotropic dielectric properties.[2] In all previous studies a homogeneous dielectric medium has been assumed. The problem of fluorescing molecules in the presence of an inhomogeneous medium is yet to be studied.

One special class of inhomogeneous media (gradient-index medium) has an optical index that varies in only one of the spatial dimensions. Gradient-index optics has been an area of interest for quite some time, as both natural and manmade systems exist. These range from the lens of the human eye and the Earth's atmosphere to gradient-index fibers. The latter have found significant applications in many areas of modern technology, including imaging and communication.[6] For over 30 years a number of both experimental and theoretical studies have been devoted to the understanding of how electromagnetic waves propagate through such media.[7] In this regard, most theoretical formulations assume a plane wave incident on such a medium and perform calculations for the reflection and transmission coefficients. Both geometric optical[8] and wave optical[7] methods have been applied. Special approaches, such as the path-integral[9] and WKB[10] methods, have also been developed. To our knowledge, however, the theoretical modeling of molecular fluorescence in the presence of a gradient-index medium has never been studied. This requires calculation of the Green dyadic for such a medium; this dyadic was not established until recently.[11] It is our purpose in the present work to investigate this problem by using our recently formulated results for the Green dyadic. We hope that the results obtained from our modeling will stimulate measurement of fluorescence properties, such as lifetime and emission frequency shift, of molecules in the vicinity of such media. These measurements will be useful in probing the optical properties of such media with the fluorescence method. We limit our present theory to considering only the local dielectric response as in the CPS theory[12] and begin by giving a brief summary of previous results obtained for the Green dyadic method as applied to a gradient-index medium.

2. GREEN DYADIC FOR A GRADIENT-INDEX MEDIUM

To make our presentation self-contained, we start by reviewing the key equations from our previous formulation.[11] To begin, we recall our formulation of the

Green dyadic for the case of a continuously varying index medium obtained as the limit of the discrete multilayer model as slab thicknesses approach zero:

$$\mathbf{G}(\mathbf{R}, \mathbf{R}')\mathbf{J}(\mathbf{R}') = \frac{i}{4\pi}\int_{\lambda=0}^{+\infty} \mathrm{d}\lambda \sum_{n=0}^{+\infty} \frac{2-\delta(n, 0)}{\lambda h(\lambda, z')} \cdot \sum_{l=0}^{1} [\mathbf{M}_{l,n,\lambda}(h(\lambda, z)) \quad \mathbf{M}_{l,n,\lambda}(-h(\lambda, z)) \quad \mathbf{N}_{l,n,\lambda}(h(\lambda, z)) \quad \mathbf{N}_{l,n,\lambda}(-h(\lambda, z))]\begin{bmatrix}\mathbf{C}_{l,n,\lambda}(z)\\ \mathbf{F}_{l,n,\lambda}(z)\end{bmatrix}, \quad (1)$$

where

$$\mathbf{C}_{l,n,\lambda}(z) \equiv \begin{bmatrix} c_{l,n,\lambda}(z)\\ c'_{l,n,\lambda}(z)\end{bmatrix}, \qquad \mathbf{F}_{l,n,\lambda}(z) \equiv \begin{bmatrix} f_{l,n,\lambda}(z)\\ f'_{l,n,\lambda}(z)\end{bmatrix}$$

are the expansion coefficients and the definitions of the vector harmonics **M** and **N**, and other symbols are given in Refs. 11 and 13.

Now let us consider the case of a gradient-index film. Here we have $\epsilon \equiv \epsilon(z)$, where $\epsilon(z)$ is constant for $z \leqslant z_b$ and $z \geqslant z_t$ but varies continuously for $z_b \leqslant z \leqslant z_t$. Omitting the subscripts l, n, λ and indicating vector transposition by t, we previously obtained the following system of differential equations for **C** and **F**:

$$\frac{\mathrm{d}\mathbf{C}}{\mathrm{d}z} = \frac{dh}{\mathrm{d}z}\begin{bmatrix} -iz - \dfrac{1}{2h} & \dfrac{\exp(-2ihz)}{2h}\\ \dfrac{\exp(2ihz)}{2h} & iz - \dfrac{1}{2h}\end{bmatrix}\mathbf{C} + \delta(z - z_s)\begin{bmatrix}\mathbf{M}'(-h(z_s))^t\\ -\mathbf{M}'(+h(z_s))^t\end{bmatrix}\mathbf{J}$$

$$\equiv \mathbf{T}_c\mathbf{C} + \delta(z - z_s)\begin{bmatrix}\mathbf{M}'(-h(z_s))^t\\ -\mathbf{M}'(+h(z_s))^t\end{bmatrix}\mathbf{J}, \quad (2)$$

with boundary conditions

$$\mathbf{C}(z_b) = \begin{bmatrix}0\\ c'(z_b)\end{bmatrix}, \qquad \mathbf{C}(z_t) = \begin{bmatrix}c(z_t)\\ 0\end{bmatrix},$$

and

$$\frac{\mathrm{d}\mathbf{F}}{\mathrm{d}z} = \begin{bmatrix} -\left(iz + \dfrac{1}{2h}\right)\dfrac{\mathrm{d}h}{\mathrm{d}z} & \left(\dfrac{1}{2h}\dfrac{\mathrm{d}h}{\mathrm{d}z} - \dfrac{1}{k}\dfrac{\mathrm{d}k}{\mathrm{d}z}\right)\exp(-2ihz)\\ \left(\dfrac{1}{2h}\dfrac{\mathrm{d}h}{\mathrm{d}z} - \dfrac{1}{k}\dfrac{\mathrm{d}k}{\mathrm{d}z}\right)\exp(2ihz) & \left(iz - \dfrac{1}{2h}\right)\dfrac{\mathrm{d}h}{\mathrm{d}z}\end{bmatrix}\mathbf{F} + \delta(z - z_s)\begin{bmatrix}\mathbf{N}'(-h(z_s))^t\\ -\mathbf{N}'(+h(z_s))^t\end{bmatrix}\mathbf{J}$$

$$\equiv \mathbf{T}_f\mathbf{F} + \delta(z - z_s)\begin{bmatrix}\mathbf{N}'(-h(z_s))^t\\ -\mathbf{N}'(+h(z_s))^t\end{bmatrix}\mathbf{J}, \quad (3)$$

with boundary conditions

$$\mathbf{F}(z_b) = \begin{bmatrix}0\\ f'(z_b)\end{bmatrix}, \qquad \mathbf{F}(z_t) = \begin{bmatrix}f(z_t)\\ 0\end{bmatrix}.$$

A method based on variation of constants has been developed in Ref. 11 to solve for **C** and **F**. Subtle points involving the jumps of $\epsilon(z)$ at the interfaces and the singularity at $h = 0$ must be handled with care. With the previous solution, numerical computation can be implemented to calculate **C** and **F** and hence the Green dyadic solution for a gradient-index medium. In the following section we apply the methodology of Ref. 11 to compute the lifetimes of admolecules in the vicinity of such an optically inhomogeneous film.

3. APPLICATION TO MOLECULAR FLUORESCENCE MODELING

Let us consider a fluorescing molecular dipole oriented perpendicular or parallel to the boundary $z = z_b$ of a gradient-index medium with complex refractive index $n(z)$. According to the classical phenomenological approach,[2] the normalized decay rate of the admolecule is obtained in terms of the imaginary part of the reflected field $\mathbf{E}_0$ at the dipole site as (in SI units):

$$\hat{b} = 1 + \frac{6\pi\epsilon_0 q n_s^{\,2}}{p_0 k_s^{\,3}}\Im(\mathbf{E}_0), \quad (4)$$

where q is the intrinsic quantum yield and $k_s = n_s\omega/c$, with n_s the purely real refractive index of the medium containing the dipole. Note that p_0 and ω are, respectively, the dipole moment and the emission frequency of the molecule, and the only quantity requiring calculation in this model is the imaginary part of the reflected field, $\Im(\mathbf{E}_0)$. This may be obtained from the Green dyadic of the problem as follows:

$$\mathbf{E}_0(\mathbf{R}) = i\omega\mu\int \mathbf{G}(\mathbf{R}, \mathbf{R}')\mathbf{J}(\mathbf{R}')\mathrm{d}V(\mathbf{R}'), \quad (5)$$

where μ is the (nonvarying) magnetic permeability of the medium. We first consider a dielectric medium with refractive index varying as shown in Fig. 1, where distance along the z axis is measured in units of inverse wave number $d \equiv c/n\omega$ with n being the real index of the source medium.

Let us first consider a vertically oriented dipole with moment $p_0\hat{\mathbf{z}}\exp(-i\omega t)$ at position $z_s < 0$ on the z axis. The current in this case will be given by

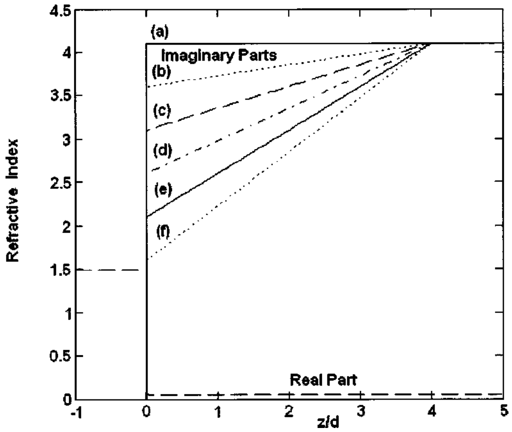

Fig. 1. Schematic illustration of the index profiles for the gradient-index medium considered in the modeling. The index for the medium that contains the molecule ($z < 0$) is fixed at 1.5, whereas the index for the film varies linearly with z for $0 \leqslant z \leqslant 4d$ in the form

$$n + ik = 0.06 + i\left[\frac{N}{2}\left(\frac{z}{4d} - 1\right) + 4.11\right],$$

$N = 0, 1, 2, 3, 4, 5$, for the cases (a)–(f). Thus case (a) corresponds to the homogeneous index value used in the computation of Fig. 2 of Ref. 2. The film thickness is fixed at $4d$. For $z > 4d$ the index is fixed at $0.06 + 4.11i$.

$$\mathbf{J} = -i\omega p_0 \hat{\mathbf{z}} \exp(-i\omega t)\delta(\mathbf{R}' - z_s\hat{\mathbf{z}}). \tag{6}$$

For field computations at the source we need the following fundamental solution matrices as generalized to handle discontinuity at $z = z_b = 0$, noting that

$$\mathbf{\Phi}_c \equiv \mathbf{\Phi}_c(+\infty, -\infty) \equiv \mathbf{\Pi}_c(z_b+, z_b-)\mathbf{\Phi}_c(z_t, z_b),$$

$$\mathbf{\Phi}_f \equiv \mathbf{\Phi}_f(+\infty, -\infty) \equiv \mathbf{\Pi}_f(z_b+, z_b-)\mathbf{\Phi}_f(z_t, z_b).$$

Details for these matrices $\mathbf{\Pi}$ and $\mathbf{\Phi}$ can be found in Ref. 11. Only the summand in Eq. (1) involving $\mathbf{N}_{0,0,\lambda}(-h_s)$ is nonzero at $z_s\hat{\mathbf{z}}$; hence its coefficient, $f'_{0,0,\lambda}(-\infty)$, is the only one needed. For the case where the scattered rather than total field is desired at the source, we have

$$\begin{bmatrix} f_{0,0,\lambda}(+\infty) \\ f'_{0,0,\lambda}(-\infty) \end{bmatrix} = \begin{bmatrix} (\mathbf{\Phi}_f)_{11} & 0 \\ (\mathbf{\Phi}_f)_{21} & -1 \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{N}_{0,0,\lambda}(-h_s)^t\mathbf{J} \\ 0 \end{bmatrix}, \tag{7}$$

where $()_{ij}$ refers to the ijth element of the matrix. Dropping the 0, 0, λ subscripting for simplicity and solving, we have

$$\begin{aligned} f'(-\infty) &= \frac{(\mathbf{\Phi}_f)_{21}}{(\mathbf{\Phi}_f)_{11}} \mathbf{N}(-h_s)^t\mathbf{J} \\ &= \frac{(\mathbf{\Phi}_f)_{21}}{(\mathbf{\Phi}_f)_{11}} [-i\omega p_0 \exp(-i\omega t)][\mathbf{N}(-h_s)^t\hat{\mathbf{z}}] \\ &\quad \times \delta(\mathbf{R}' - z_s\hat{\mathbf{z}}). \end{aligned}$$

From Eqs. (1) and (5) we have

$$\begin{aligned} \hat{\mathbf{z}}^t\mathbf{E}(z_s\hat{\mathbf{z}}) &= \frac{i\omega^2\mu}{4\pi}[p_0 \exp(-i\omega t)] \\ &\quad \times \int_{\lambda=0}^{+\infty} \frac{(\mathbf{\Phi}_f)_{21}}{(\mathbf{\Phi}_f)_{11}} \frac{[\mathbf{N}(-h_s)^t\hat{\mathbf{z}}]^2}{\lambda h_s(\lambda)} \mathrm{d}\lambda. \end{aligned} \tag{8}$$

Noting that

$$\mathbf{N}(-h_s)^t\hat{\mathbf{z}} = \frac{\lambda^2 \exp(-ih_sz_s)}{k_s},$$

we may substitute Eq. (8) into Eq. (4) to obtain

$$\hat{b}_\perp = 1 + \left(\frac{3q}{2k_s^3}\right)\Re\left[\int_{\lambda=0}^{+\infty} \frac{(\mathbf{\Phi}_f)_{21}}{(\mathbf{\Phi}_f)_{11}} \frac{\lambda^3 \exp(-2ih_sz_s)}{h_s(\lambda)} \mathrm{d}\lambda\right],$$

where $\Re(\,)$ denotes the real part.

In the case of the parallel dipole with moment $p_0\hat{\mathbf{x}}\exp(-i\omega t)$, the current will be given by

$$\mathbf{J} = -i\omega p_0 \hat{\mathbf{x}} \exp(-i\omega t)\delta(\mathbf{R}' - z_s\hat{\mathbf{z}}). \tag{9}$$

Only the two summands in Eq. (1) involving $\mathbf{N}_{0,1,\lambda}$ and $\mathbf{M}_{1,1,\lambda}$ are nonzero in the x direction at $z_s\hat{\mathbf{z}}$. We have from Eq. (1),

$$\begin{aligned} &\hat{\mathbf{x}}^t\mathbf{G}(z_s\hat{\mathbf{z}}, z_s\hat{\mathbf{z}})\mathbf{J}(z_s\hat{\mathbf{z}}) \\ &\quad = \frac{i\hat{\mathbf{x}}^t}{4\pi}\int_{\lambda=0}^{+\infty} \frac{2}{\lambda h_s(\lambda)} \\ &\qquad \times [c'_{1,1,\lambda}\mathbf{M}_{1,1,\lambda}(-h_s) + f'_{0,1,\lambda}\mathbf{N}_{0,1,\lambda}(-h_s)]\mathrm{d}\lambda. \end{aligned} \tag{10}$$

In addition to Eq. (7), with subscripts 0, 1, λ, we have

$$\begin{bmatrix} c_{1,1,\lambda}(+\infty) \\ c'_{1,1,\lambda}(-\infty) \end{bmatrix} = \begin{bmatrix} (\mathbf{\Phi}_c)_{11} & 0 \\ (\mathbf{\Phi}_c)_{21} & -1 \end{bmatrix}^{-1} \begin{bmatrix} \mathbf{M}_{1,1,\lambda}(-h_s)^t \cdot \mathbf{J} \\ 0 \end{bmatrix},$$

resulting in the following (with subscripts dropped again for simplicity):

$$\begin{aligned} c'(-\infty) &= \frac{(\mathbf{\Phi}_c)_{21}}{(\mathbf{\Phi}_c)_{11}} \mathbf{M}(-h_s)^t\mathbf{J} \\ &= \frac{(\mathbf{\Phi}_c)_{21}}{(\mathbf{\Phi}_c)_{11}} [-i\omega p_0 \exp(-i\omega t)] \\ &\quad \times [\mathbf{M}(-h_s)^t\hat{\mathbf{x}}]\delta(\mathbf{R}' - z_z\hat{\mathbf{z}}). \end{aligned}$$

We have at the source,

$$\hat{\mathbf{x}}^t\mathbf{M}(-h_s) = \frac{\lambda \exp(-ih_sz_s)}{2},$$

$$\hat{\mathbf{x}}^t\mathbf{N}(-h_s) = \frac{-ih_s\lambda \exp(-ih_sz_s)}{2k_s}.$$

From Eqs. (1), (5), and (10) we have

$$\begin{aligned} \hat{\mathbf{x}}^t\mathbf{E}(z_s\hat{\mathbf{z}}) &= \frac{i\omega^2 p_0\mu}{8\pi}\exp(-i\omega t)\int_{\lambda=0}^{+\infty} \frac{\lambda \exp(-2ih_sz_s)}{h_s(\lambda)} \\ &\quad \times \left[\frac{(\mathbf{\Phi}_c)_{21}}{(\mathbf{\Phi}_c)_{11}} - \left(\frac{h_s}{k_s}\right)^2 \frac{(\mathbf{\Phi}_f)_{21}}{(\mathbf{\Phi}_f)_{11}}\right]\mathrm{d}\lambda. \end{aligned} \tag{11}$$

Substitution of Eq. (11) into Eq. (4) yields

$$\begin{aligned} \hat{b}_\parallel = 1 + \frac{3q}{4k_s}\Re\bigg\{ &\int_{\lambda=0}^{+\infty} \frac{\lambda \exp(-2ih_sz_s)}{h_s(\lambda)} \\ &\times \left[\frac{(\mathbf{\Phi}_c)_{21}}{(\mathbf{\Phi}_c)_{11}} - \left(\frac{h_s}{k_s}\right)^2 \frac{(\mathbf{\Phi}_f)_{21}}{(\mathbf{\Phi}_f)_{11}}\right]\mathrm{d}\lambda\bigg\}. \end{aligned}$$

To demonstrate our formulation for molecular fluorescence in the presence of a gradient-index film, we have considered a film with a simple linear index profile as shown in Fig. 1 and have calculated lifetimes for such an

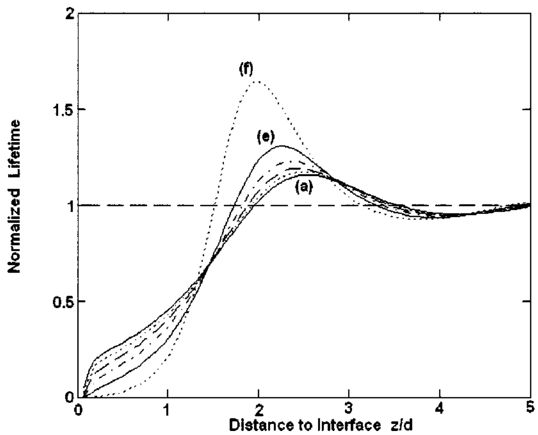

Fig. 2. Computed normalized lifetimes for an admolecule as a function of distance to the gradient-index film as described in Fig. 1. The molecular orientation is perpendicular to the film surface. Results with gradual variation corresponding to cases (a)–(f) in Fig. 1 are shown, with the labels (a), (b), and (f) indicated explicitly.

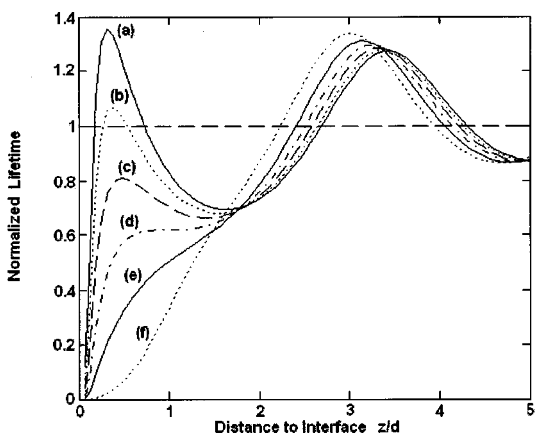

Fig. 3. Same as in Fig. 2, except for a parallel-oriented molecule.

admolecule. As indicated in Fig. 1, a film of $4d$ thickness having refractive index with a constant real part $n(z)$ and a constant or linearly increasing imaginary part $k(z)$ is assumed. Such films can be fabricated by various codeposition techniques as detailed in Ref. 7. Curves (a)–(f) exhibit increasing slopes into the film. For each case we have computed normalized lifetimes ($\hat{b}^{-1}$) versus distance from the dipole to the interface. Our computed results are shown in Fig. 2 for the perpendicular-dipole case and Fig. 3 for the parallel-dipole case. These results are similar to those presented in Fig. 2 of Ref. 2, for which the emitting dipole is located in glass with silver (possessing a constant complex refractive index) on the other side of the interface. While the results for a gradient-index film preserve the characteristics of a homogeneous film,[2] the effects of optical film inhomogeneity are observed in the fluorescence lifetimes of the admolecules. In particular, for short distances the molecular lifetimes decrease as the imaginary part of the index becomes smaller at the interface and hence more steeply sloped into the medium. This indicates that more significant nonradiative transfer between the excited molecule and the surface is taking place.

4. CONCLUSION

We have applied our results[11] for the Green dyadic to field computations involving a gradient-index medium in order to model the effect of the medium on the lifetimes of fluorescing molecules. Since the methodology for experimental preparation of this kind of gradient-index film has been well established, even with desirable index profile control[7] we expect that the present theoretical results can be checked against experiment in the near future. This combination of experimental and computational methodology may facilitate new ways of optically studying these films, as well as controlling the fluorescence properties of admolecules situated nearby.

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