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I. PRIGOGINE
STUART A. RICE

ADVANCES IN CHEMICAL PHYSICS

Advances in CHEMICAL PHYSICS

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INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more, and be broadly educated with respect to a large domain of science, has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, *Advances in Chemical Physics*, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

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MOLECULAR FLUORESCENCE AND ENERGY TRANSFER NEAR INTERFACES

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I. INTRODUCTION

The lifetime of an excited molecule fluorescing near an interface between two media can be altered substantially owing to reflection and absorption at the surface. The perfection of the fatty-acid monolayer assembly technique by Kuhn and co-workers [1-4] led to a series of beautiful experiments by Drexhage et al.,[5-9] in which the fluorescent lifetime of an excited molecule was measured near gold, silver, and copper surfaces. By the Langmuir–Blodgett dipping technique,[11,12] a number of layers of fatty acid were placed on a metal surface, and a layer of dye molecules was then put on top of this assembly. In this way the dye molecules were a known fixed distance from the metal. The dye molecules were then excited and their fluorescence was monitored. It was found that for large distances from the metal surface the fluorescence lifetime oscillated as a function of distance, while for small distances the lifetime went monotonically towards zero. The oscillations are explained qualitatively as being due to the metal surface acting as a mirror for the electric field of the emitter. The interference between the reflected wave and the initial wave gives rise to the observed oscillations in the lifetime.[5-8,12] The decrease in the lifetime when the distance becomes small is due to nonradiative transfer of energy from the excited molecule to the metal.[13,14] The nature of the states of the metal that accept this energy was unclear until the analogy between these experiments and the problem of radio-wave propagation near the surface of the earth became apparent.[13-15] The emitting molecule acts as an oscillating dipole (antenna) near a partially absorbing and partially reflecting surface (earth). Sommerfeld[16] provided the first theoretical treatment of the radio problem in 1909 and pointed out the possibility of a surface wave being present for the antenna close to the earth. In the same way it has been shown that the *surface-plasmon* modes of the metal dielectric interface are those that couple to the near field of the emitting molecule.[17-19] These modes have become of interest in recent years because of the experiments of Otto[20] and Burstein,[21] and the theoretical work of Ritchie[22] and others.[23]

In the present article the classical theory of an oscillating charge distribution near a dielectric interface is applied to the problem of molecules fluorescing near a surface. The experiments of Drexhage et al.[5-9] are explained quantitatively, and the connection between energy transfer and the surface modes is stressed. In addition, the possibility of resonant coupling to the surface plasmons is discussed for a variety of experimental situations.

In Section II the theory of a dipole antenna near a metal surface is given in detail and the terms in the decay-rate constant are separated into those due to energy transfer and those due to "radiative" effects. Detailed comparisons to the available experimental data are made. In Section III the dyadic Green's function method is used to derive damping rates for oscillating charge distributions near a single interface and near multiple interfaces. This method proves to be the most direct and elegant way to derive most of the formulas. In Section IV the coupling of the emitting molecule to the surface-plasmon modes of the metal/dielectric interface is discussed in detail for both isotropic and anisotropic media. Both nonresonant and resonant coupling are considered. Some experiments to test these predictions are suggested.

II. DIPOLE EMISSION NEAR INTERFACES

A. Theory for a Single Mirror

In this section we describe two methods for calculating the lifetime of an emitting dipole near a single interface (mirror). The first involves the use of Kuhn's model,[12] which requires the calculation of the reflected electric field at the dipole position. The second is the energy flux method.[18] Though the two approaches are physically equivalent, the energy-flux method has the advantage of allowing a rigorous separation of radiative and nonradiative lifetime components.

Following Kuhn[12] we first write the equation of motion of the dipole (assumed to be a harmonically bound charge)

$$\ddot{\mu}+\omega^2\mu=\frac{e^2}{m}E_R-b_0\dot{\mu} \tag{2.1}$$

where ω is the oscillation frequency in the absence of all damping, m is the effective mass of the dipole, E_R is the reflected field at the dipole position, and b_0 is the damping constant (inverse lifetime) in the absence of the mirror. The dipole moment μ and the reflected field E_R oscillate at the same (complex) frequency:

$$\mu=\mu_0\, e^{-i[\omega+\Delta\omega]t}\, e^{-bt/2} \tag{2.2}$$

and

$$E_R=E_0\, e^{-i(\omega+\Delta\omega)t}\, e^{-bt/2} \tag{2.3}$$

where $\Delta\omega$ and b are the frequency shift and the lifetime in the presence of the mirror. The problem is then one of a driven harmonic oscillator where the resonant external force is the reflected radiation field of the emitting dipole.

Substituting into (2.1) and recognizing[18] that b^2 and the magnitude of $(e^2/\mu_0 m)E_0$ are very small compared to ω^2, we have

$$\Delta\omega = \frac{b^2}{8\omega} + \left[\frac{e^2}{2\mu_0 m\omega}\right] \mathrm{Re}\,(E_0) \tag{2.4}$$

and

$$b = b_0 + \left[\frac{e^2}{2\mu_0 m\omega}\right] \mathrm{Im}\,(E_0) \tag{2.5}$$

The frequency shift is found to be quite small[24] and so is unimportant for the purposes of the discussion in this section. We return to $\Delta\omega$ in Section IV. We now introduce the quantum yield of emitting state, $q \equiv b_r/b$ and the classical formula for the radiative decay constant[12,14]

$$b_r = \frac{2}{3}\frac{e^2 k_1^3}{m\omega n_1^2} \tag{2.6}$$

where n_1 is the refractive index of the medium containing the dipole and k_1 is the propagation constant ($k_1 = \omega n_1/c$). Equation 2.5 can now be rewritten in a more convenient form

$$\hat{b} \equiv \frac{b}{b_0} = 1 + \frac{3qn_1^2}{2\mu_0 k_1^3} \mathrm{Im}\,(E_0) \tag{2.7}$$

The problem is now reduced to that of calculating the reflected electric field at the dipole position.

The geometry of the problem of the single mirror is shown in Fig. 1. The two regions are half spaces with dielectric constants given as $\varepsilon_1 = n_1^2$ and $\varepsilon_2 = n_2^2 - \kappa_2^2 + i2n_2\kappa_2$, where n_2 and κ_2 are the real and imaginary parts of the refractive index of region 2. The electric field at any point in region 1 can be found as

$$\mathbf{E} = \frac{1}{\varepsilon_1}\left[k_1^2 \mathbf{\Pi}_1 + \nabla(\nabla \cdot \mathbf{\Pi}_1)\right] \tag{2.8}$$

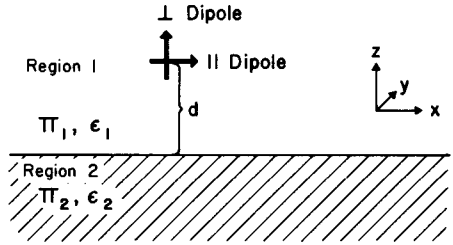

Fig. 1. Geometry for the single-mirror problem. Region 1 is a non-absorbing dielectric of refractive index $n_1(\varepsilon_1 = n_1^2)$. Region 2 is a half-space with no restrictions on the dielectric constant except that it be isotropic.

where $\mathbf{\Pi}_1$ is the Hertz vector of region 1, which we now construct.

We first consider the dipole oriented perpendicular to the interface. Following Sommerfeld[16] we write the Hertz vectors in the two media as follows (in cylindrical coordinates r, z, ϕ):

$$\mathbf{\Pi}_1 = \hat{e}_z \mu k_1 \int_0^\infty du\, J_0(ur) \frac{u}{l_1} (e^{\pm l_1(z-\hat{d})} + f_1\, e^{-l_1 z}) \tag{2.9}$$

$$\mathbf{\Pi}_2 = \hat{e}_z \mu k_1 \int_0^\infty f_2\, e^{l_2 z} J_0(ur) \frac{u}{l_1}\, du \tag{2.10}$$

where $\hat{d} \equiv k_1 d$, $l_j \equiv -i(\varepsilon_j/\varepsilon_1 - u^2)^{\frac{1}{2}}$ and $J_0(ur)$ is the zeroth-order Bessel function. The first term in (2.9) is the source term for the dipole; we take the minus sign in the region $z > \hat{d}$ and the plus sign in the region $z < \hat{d}$, which is the region of interest here for the reflected field calculation. The terms f_1 and f_2 are to be determined by fitting the boundary conditions at $z = 0$:

$$\varepsilon_1 \mathbf{\Pi}_1 = \varepsilon_2 \mathbf{\Pi}_2 \tag{2.11}$$

and

$$\frac{\partial \mathbf{\Pi}_1}{\partial z} = \frac{\partial \mathbf{\Pi}_2}{\partial z} \tag{2.12}$$

On solving, we find

$$f_1 = -R^{\parallel}\, e^{-l_1 \hat{d}} \tag{2.13}$$

$$f_2 = \frac{\varepsilon_1}{\varepsilon_2} (1 - R^{\parallel})\, e^{-l_1 \hat{d}} \tag{2.14}$$

where $R^{\parallel}$ is the reflection coefficient for an incident ray polarized parallel to the plane of incidence (p-polarized)[25]:

$$R^{\parallel} = \frac{\varepsilon_1 l_2 - \varepsilon_2 l_1}{\varepsilon_1 l_2 + \varepsilon_2 l_1} \tag{2.15}$$

Note that for the case of a perfect mirror ($R^{\parallel} = -1$), f_1 becomes $e^{-l_1 \hat{d}}$ and gives the image term in Sommerfeld's treatment.[16] Substituting into (2.8) and omitting the source term, we obtain the reflected field at the dipole position as

$$E_R^{\perp} = -\frac{k_1^3}{\varepsilon_1} \mu \int_0^\infty R^{\parallel}\, e^{-2l_1 \hat{d}} \frac{u^3}{l_1}\, du \tag{2.16}$$

Finally from (2.7), we have

$$\hat{b}_\perp = 1 - \frac{3}{2} q\, \mathrm{Im} \left(\int_0^\infty R^{\parallel}\, e^{-2l_1 \hat{d}} \frac{u^3}{l_1}\, du \right) \tag{2.17}$$

We next consider the dipole oriented parallel to the x-axis and the interface (Fig. 1). Again, following Sommerfeld we write the Hertz vectors as follows:

$$\Pi_1 = \hat{e}_x \mu k_1 \int_0^\infty (e^{\pm l_1(z-d)} + f_1 e^{-l_1 z}) \frac{u}{l_1} J_0(ur)\, du + \hat{e}_z \mu k_1 \frac{x}{r} \int_0^\infty g_1 e^{-l_1 z} J_1(ur)\, du \tag{2.18}$$

and

$$\Pi_2 = \hat{e}_x \mu k_1 \int_0^\infty f_2 e^{l_2 z} J_0(ur) \frac{u}{l_1}\, du + \hat{e}_z \mu k_1 \frac{x}{r} \int_0^\infty g_2 e^{l_2 z} J_1(ur)\, du \tag{2.19}$$

The boundary conditions at $z=0$ are

$$\frac{\partial \Pi_{1z}}{\partial z} - \frac{\partial \Pi_{2z}}{\partial z} = \frac{\partial \Pi_{2x}}{\partial x} - \frac{\partial \Pi_{1x}}{\partial x} \tag{2.20}$$

$$\varepsilon_1 \frac{\partial \Pi_{1x}}{\partial z} = \varepsilon_2 \frac{\partial \Pi_{2x}}{\partial z}, \tag{2.21}$$

$$\varepsilon_1 \Pi_{1x} = \varepsilon_2 \Pi_{2x}, \tag{2.22}$$

and

$$\varepsilon_1 \Pi_{1z} = \varepsilon_2 \Pi_{2z}. \tag{2.23}$$

On solving we find, again in agreement with Sommerfeld,[16]

$$f_1 = R^\perp e^{-l_1 \hat{d}} \tag{2.24}$$

$$f_2 = \frac{\varepsilon_1}{\varepsilon_2}(1 + R^\perp) e^{-l_1 \hat{d}} \tag{2.25}$$

and

$$g_1 = (R^\parallel - R^\perp) e^{-l_1 \hat{d}}; \qquad g_2 = \frac{\varepsilon_1}{\varepsilon_2} g_1 \tag{2.26}$$

where $R^\perp$ is the reflection coefficient for the incident ray polarized perpendicular to the plane of incidence (s-polarized)

$$R^\perp = \frac{l_1 - l_2}{l_1 + l_2} \tag{2.27}$$

Note again for a perfect reflector ($R^\perp = R^\parallel = -1$), we are left in (2.8) with source and image terms only, as expected.

On substituting into (2.8) and omitting the source term, we obtain

$$E_R^\parallel = \frac{k_1^3 \mu}{2\varepsilon_1} \int_0^\infty [(1-u^2)R^\parallel + R^\perp] e^{-2l_1 \hat{d}} \frac{u\, du}{l_1} \tag{2.28}$$

and

$$\hat{b}_{\parallel} = 1 + \frac{3q}{4} \operatorname{Im} \int_0^{\infty} [(1-u^2)R^{\parallel} + R^{\perp}] \, e^{-2l_1 \hat{d}} \frac{u \, du}{l_1} \tag{2.29}$$

(Equations 2.17 and 2.29 with some minor, but tedious, manipulation are in agreement with our previous work and with that of Tews.[15])

Though we now have the theoretical description of the effect of a single mirror on the lifetime, the mirror has significant effects both on the radiative and nonradiative components of the lifetime—the latter being a result of nonradiative energy transfer. The method that we now describe gives a rigorous separation of these two effects. The geometry is the same as in Fig. 1, except now we imagine a plane above the dipole ($z > d$) and a plane below the dipole ($0 < z < d$). The total energy flux through these planes is now calculated. Since the planes are infinite in extent, this calculation accounts for all the energy flowing away from the dipole by way of the radiation field. The flux through each plane, $F\uparrow$ or $F\downarrow$, is calculated by integrating the normal component of the complex Poynting vector, $\mathbf{S}^*$, over the plane[25]:

$$F_{\uparrow,\downarrow} = \operatorname{Re} \int_{A\uparrow,\downarrow} \mathbf{S}^* \cdot \mathbf{n} \, dA \tag{2.30}$$

where

$$\mathbf{S}^* = \left(\frac{c}{8\pi}\right) \mathbf{E} \times \mathbf{H}^*$$

$$\mathbf{H} = -\mathrm{i}\left(\frac{\omega}{c}\right) \operatorname{curl} \boldsymbol{\Pi}$$

and $\mathbf{E}$ is given by (2.8). The Hertz vector $\boldsymbol{\Pi}$ is given by (2.9) for the perpendicular dipole and by (2.18) for the parallel dipole. We begin with a detailed discussion of the perpendicular dipole. In that case we have

$$\mathbf{S}^* \cdot \mathbf{n} = -\frac{i\omega}{8\pi\varepsilon_1} \left[\frac{\partial}{\partial r}\left(\frac{\partial \Pi_{1z}}{\partial z}\right)\right]\left(\frac{\partial \Pi_{1z}^*}{\partial r}\right) \tag{2.31}$$

Substituting from (2.9) for Π_{1z} and integrating over the plane, we have for $F_{\uparrow}$ (take minus sign in exponent of source term in Π_1):

$$F_{\downarrow} = k_1^3 |\mu| \operatorname{Re} \int_{A\uparrow} dr \, r \, d\phi \int_0^{\infty} \frac{i\omega}{8\pi\varepsilon_1} [e^{-l_1(z-\hat{d})} - R^{\parallel\prime} \, e^{-l_1(z+\hat{d})}]$$

$$\times u'^2 J_1(u'r) \, du' [e^{-l_1^*(z-\hat{d})} - R^{\parallel *} \, e^{-l_1^*(z+\hat{d})}] \frac{u^2}{l_1^*} J_1(ur) \, du \tag{2.32}$$

On changing the order and integrating over ϕ, we have

$$F_\uparrow = k_1^3|\mu|^2 \,\mathrm{Re}\int_0^\infty\int \frac{i\omega}{4\varepsilon_1}\left[e^{-l_1(z-\hat{d})} - R^{\parallel\prime}\, e^{-l_1^*(z+\hat{d})}\right]$$

$$\times\left[e^{-l_1^*(z-\hat{d})} - R^{\parallel *}\, e^{-l_1^*(z+\hat{d})}\right]$$

$$\times u'^2\,\frac{u^2}{l_1^*}\,du'\,du\int_0^\infty dr\, r\, J_1(u'r)J(ur) \tag{2.33}$$

The last integral equals $\delta(u'-u)/u'$ and the integration over u' can be done to yield

$$F_\uparrow = k_1^3|\mu|^2\,\mathrm{Re}\int_0^\infty\left(\frac{i\omega}{4\varepsilon_1}\right)\frac{u^3}{l_1^*}\left|e^{-l_1(z-\hat{d})} - R^{\parallel}\, e^{-l_1(z+\hat{d})}\right|^2 du \tag{2.34}$$

After noting that the $1\to\infty$ portion of the integral is imaginary and carrying out some minor manipulation, we divide by the total energy of the dipole $(\frac{1}{2}\omega^2 m|\mu|^2/e^2)$ to obtain $b_\uparrow$

$$b_\uparrow = \left(\frac{2e^2k_1^3}{3m\omega n_1^2}\right)\left[1 - \frac{3}{4}\,\mathrm{Im}\int_0^1 (1-|R^{\parallel}|^2)\,\frac{u^3\,du}{l_1} - \frac{3}{2}\,\mathrm{Im}\int_0^1 R^{\parallel}\, e^{-2l_1\hat{d}}\,\frac{u^3\,du}{l_1}\right] \tag{2.35}$$

Note that the first term in parentheses is just b_r from (2.6) and that for $R^{\parallel}=0$, $b=b_r/2$ as it should. Normalizing to the decay rate in the absence of mirror, $b_0=b_r/q$, we have the final form:

$$\hat{b}_\uparrow = q - \frac{3}{4}\,q\,\mathrm{Im}\int_0^1 (1-|R^{\parallel}|^2)\,\frac{u^3\,du}{l_1} - \frac{3}{2}\,q\,\mathrm{Im}\int_0^1 R^{\parallel}\,\frac{e^{-2l_1\hat{d}}}{l_1}\,u^3\,du \tag{2.36}$$

A similar prescription may be followed to obtain $\hat{b}_\downarrow$ (the only modifications necessary are to change signs from minus to plus in the exponent of the source term for $\mathbf{\Pi}_1$ and to change the sign of $\mathbf{S}^*$)

$$\hat{b}_\downarrow = \frac{3}{4}\,q\,\mathrm{Im}\int_0^1 (1-|R^{\parallel}|^2)\,\frac{u^3\,du}{l_1} - \frac{3}{2}\,q\,\mathrm{Im}\int_1^\infty R^{\parallel}\, e^{-2l_1\hat{d}}\,\frac{u^3\,du}{l_1} \tag{2.37}$$

These results can be compared with our results from the earlier calculation for $\hat{b}_\perp$ of (2.17) according to the relation[18]

$$\hat{b} = b_\uparrow + b_\downarrow + (1-q) \tag{2.38}$$

where we have included the intrinsic nonradiative damping constant, $b_{nr}/b_0 \equiv 1-q$. Equation 2.38 correctly reproduces (2.17) and the same is true for the parallel dipole. We only give the results for the parallel case:

$$\hat{b}_{\uparrow}=q-\frac{3}{8}q\,\mathrm{Im}\int_0^1 du\,\frac{u}{l_1}\left[(1-|R^{\perp}|)^2+(1-u^2)(1-|R^{\parallel}|^2)\right]$$
$$+\frac{3}{4}q\,\mathrm{Im}\int_0^1 du\,\frac{u}{l_1}\,e^{-2l_1\hat{d}}\left[R^{\perp}+(1-u^2)R^{\parallel}\right] \tag{2.39}$$

and

$$\hat{b}_{\downarrow}=\frac{3}{8}q\,\mathrm{Im}\int_0^1 du\,\frac{u}{l_1}\left[(1-|R^{\perp}|^2)+(1-u^2)(1-|R^{\parallel}|^2)\right]$$
$$+\frac{3}{4}q\,\mathrm{Im}\int_1^{\infty} du\,\frac{u}{l_1}\left[R^{\perp}+(1-u^2)R^{\parallel}\right]e^{-2l_1\hat{d}} \tag{2.40}$$

We now have enough information to calculate an apparent quantum yield, $q_a\equiv\hat{b}_{\uparrow}/\hat{b}$, which is the value that could be determined experimentally by measuring the emission intensity integrated over the half space of region 1 in Fig. 1. We show in Fig. 2 the variation of q_a with distance from a silver mirror (optical constants taken for an emission wavelength of 612 nm).[26] At large distances q_a approaches a value less than 1.0 because of "trivial" transfer to the silver mirror.[18] The dip in q_a at $\hat{d}\sim 1.7$ is caused by a dramatic decrease in $\hat{b}_{\uparrow}$ in this region (see Refs. 2 and 27). We return to this point later in this section. There are no experimental data for q_a available at this time.

Both Kuhn's model and the energy flux method give the effect of the mirror on the lifetime of the dipole. However, with the energy flux method we have separated and can now identify the individual terms. In (2.36), (2.37), (2.39), and (2.40), the first integral expression is, in each case, directly related to the transfer of energy to the mirror by way of the far field of the dipole ("trivial" transfer). This is obvious from the behavior of these terms in a number of limiting cases. For example, it is important to note that these terms are independent of distance, so that for large $\hat{d}$ they are dominant in the equations for $\hat{b}_{\downarrow}$. Therefore, the transfer must be by way of the far field of the dipole. We have verified this assignment by a direct calculation of the absorption of photons from the far field of a dipole placed in front of the mirror.[18]

With the assignment of these distance-independent terms clear, we can now write expressions for the radiative, b_r, and nonradiative, b_{nr}, decay-rate constants in the presence of the mirror:

$$\hat{b}_r(\perp)=q-\frac{3}{2}q\,\mathrm{Im}\int_0^1 R^{\parallel}\,e^{-2l_1\hat{d}}\,\frac{u^3\,du}{l_1} \tag{2.41}$$

and

$$\hat{b}_{nr}(\perp)=(1-q)-\frac{3}{2}q\,\mathrm{Im}\int_1^{\infty} R^{\parallel}\,e^{-2l_1\hat{d}}\,\frac{u^3\,du}{l_1} \tag{2.42}$$

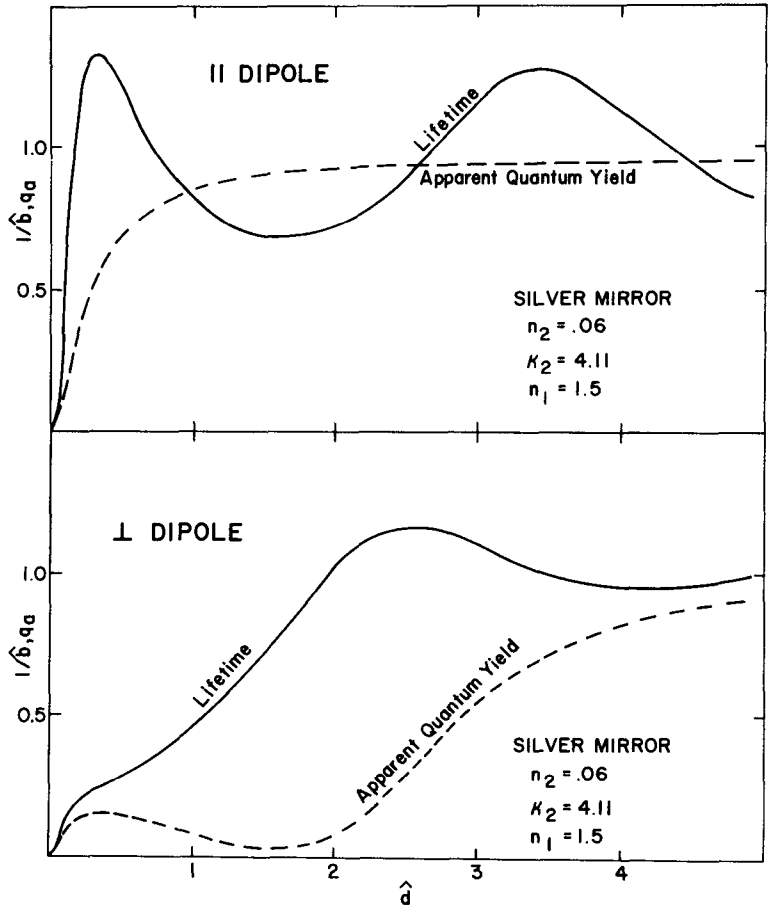

Fig. 2. Apparent quantum yield q_a and normalized lifetime $1/\hat{b}$ versus distance $\hat{d}$ ($d = 2\pi n_1 d/\lambda$) from a silver mirror ($n_2 = 0.06 + i4.11$) from (2.36 through 2.40). Results are shown for electric dipoles oriented perpendicular to the interface and parallel to the interface. The quantum yield of the emitting state, q, is taken to be unity here and in the figures to follow unless noted otherwise.

Analogous expressions can be written, by inspection, for the parallel dipole. Our results for $\hat{b}_r(\perp)$ and $\hat{b}_r(\parallel)$ are the same as those given previously by Drexhage[6-9] who used a method based on the far field of the dipole (the interference method). This approach involves looking at the interference between the primary ray exiting directly from the dipole and the reflected ray from the mirror. The amplitude that results is converted to intensity and integrated over all angles θ. After normalizing to the result in the absence of

the mirror and changing variables so that $u=\sin\theta$, we obtain (2.36) in the perpendicular case, and by neglecting d independent terms we get (2.41) as before. The same is true for the parallel case, as well as for more complicated mirror configurations and for multipole emission, which are discussed later. It is now clear that the interference method gives the effect of the mirror on the *radiative* decay-rate constant of the emitter. Furthermore, the interference method is a useful and sometimes convenient technique (see appendix, Section III.D) for obtaining the total decay-rate expression $\hat{b}_{\perp,\parallel}$, since we only need in that case to extend the integration to complex angles of incidence ($\cos\theta=0$ to $i\infty$ or $u=1$ to ∞).

Finally, the integral expression in (2.42) for $\hat{b}_{nr}(\perp)$ gives the nonradiative rate constant for energy transfer to the mirror. At small $\hat{d}$, $\hat{b}_{nr}$ is proportional to $\hat{d}^{-3}$ as expected from the dimensionality of the problem. We discuss the small distance behavior in more detail later in this section and in Section IV.

We now discuss briefly how our results compare to earlier approximate theories.[27] We showed earlier that Drexhage's formulas are identical to ours in the radiation zone limit ($\hat{d}$ large). Other approaches have used image methods, assuming perfect reflection ($R^{\perp}=R^{\parallel}=-1$). Taking this limit for (2.17) and (2.29), we find

$$\hat{b}_{\perp}=1-3q\ \mathrm{Im}\left[\left(\frac{1}{(2\hat{d})^3}-\frac{i}{(2\hat{d})^2}\right)e^{i2\hat{d}}\right] \tag{2.43}$$

and

$$\hat{b}_{\parallel}=1+\frac{3}{2}q\ \mathrm{Im}\left\{\left[\frac{1}{(2\hat{d})^3}-\frac{i}{(2\hat{d})^2}+\frac{1}{(2\hat{d})}\right]e^{i2\hat{d}}\right\} \tag{2.44}$$

in agreement with other work—including quantum mechanical treatments of the perfect mirror problem.[17,28,29]

None of these approximate theories mentioned above takes energy transfer into account. Kuhn[12] modified the image theory in a manner that, for the first time, reproduces some of the aspects of energy transfer—principally that $\hat{b}$ varies as $\hat{d}^{-3}$ at small $\hat{d}$. He inserted an amplitude and phase factor into the perfect-mirror equations to obtain, for example, in the parallel case

$$\hat{b}_{\parallel}=1+\frac{3}{2}q|R|\ \mathrm{Im}\left\{\left[\frac{-1}{(2\hat{d})^3}+\frac{i}{(2\hat{d})^2}+\frac{1}{(2\hat{d})}\right]e^{i(2\hat{d}-\delta)}\right\} \tag{2.45}$$

where $Re^{-i\delta}$ is the reflection coefficient of the mirror at normal incidence, that is, $R^{\parallel}$ or $R^{\perp}$ at $\theta=0$ ($u=0$). For a perfect mirror $|R|=1$ and $\delta=\pi$, so that (2.44) and (2.45) agree in this limit. Equation 2.45 can be shown to be an asymptotic limit of (2.29) for large $\hat{d}$. The same is true for the perpendicular dipole case.

In Fig. 3 we compare results from the exact classical theory,[14,15] Kuhn's