Comments on the classical theory of energy transfer

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Energy transfer from an emitting molecule to an absorbing half-space is considered from the viewpoint of electromagnetic theory. The lifetime of a dipole emitter in the presence of a mirror is determined through a calculation of the complex Poynting vector in the dielectric surrounding the dipole. This method has the advantage over previous approaches to this problem in that the radiative and nonradiative components of the lifetime expression may be rigorously separated. The influence on emitter lifetime of a mirror of finite thickness is also described. A simple expression is derived describing the energy transfer rate in these layered systems. It is shown that nonradiative energy transfer results from coupling of the near field of the dipole to the surface plasmon modes in the metallic absorber. The Förster energy transfer rate law is discussed in the context of the present theory.

I. INTRODUCTION

The lifetime of an emitting molecule located near a partially absorbing mirror has been analyzed recently in terms of a simple mechanical model.[1-5] The molecule is represented as an oscillating dipole whose reflected electric field produces a time dependent force which is incorporated into the equation of motion of the dipole. The equation is solved to find a damping (or lifetime) term which depends on the distance of the dipole from the mirror. At large distances (equal to or greater than the wavelength of the radiation), the damping shows an oscillatory behavior; while at short distances, the damping grows larger owing to nonradiative transfer of energy from the dipole to the partially absorbing mirror.

In this paper, we consider the general problem of the transfer of energy from an excited molecule to a metal or a dielectric. This problem has been treated previously by Kuhn[1] using an approximate image method. We derive these results from a more general viewpoint which is exact within the classical framework and further does not require the use of the mechanical model for the emitting molecule. We consider the energy flux from a dipole emitter in the presence of the mirror by calculating the Poynting vector in the dielectric surrounding the dipole.[6,7] The present method has the advantage in that it is now possible to separate the damping term into its radiative and nonradiative components. The latter represents primarily short-range energy transfer from the near field of the dipole.

For the case of a thick mirror, a simple expression is derived showing the dependence of the energy transfer rate on the optical constants of the system. This rate is maximized at the emitter frequency at which the imaginary part of the refractive index of the absorber (metal mirror) is equal to the refractive index of the

nonabsorbing dielectric in which the dipole is embedded, or equivalently, the real parts of the two dielectric constants are equal in magnitude and opposite in sign. This requirement appears in the theory of surface plasmons and, for the idealized case of real dielectric constants only, defines the frequencies of the nonradiative and radiative surface plasmon modes.[8,9] At the frequency of the nonradiative surface plasmon mode, the reflectivity for the photon field is maximized and trivial (radiational) energy transfer is minimum.

The theory is extended in this paper to treat partially absorbing mirrors of finite thickness. It is demonstrated that a (mirror) film which is relatively thin and thus somewhat transparent to the photon field can be sufficiently thick for the purposes of the energy transfer calculation so as to be indistinguishable from an infinitely thick film. In fact, these thin films can produce a greater energy transfer rate than a thicker film, and for a given dipole-film geometry, there is actually an optimum mirror film thickness which maximizes the transfer rate.

The paper is set out as follows: In Sec. II, results are derived for the energy flux through planes parallel to the mirror surface; the equivalence to the results from the mechanical model is shown. In Sec. III, the nonradiative effects are considered and discussed in some detail. The short-range energy transfer is shown to be equivalent to near field coupling of the dipole to surface plasmon modes in the mirror. In Sec. IV, the effects of finite metal film thickness are considered. In Sec. V, a derivation of the Förster energy transfer rate law is given from the present theory.

Throughout this work we will be primarily concerned with nonradiative energy transfer. In the discussion of the emitter/mirror systems, we will restrict the presentation to the vertical dipole (i.e., dipole oriented

perpendicular to the mirror), since the analysis is more straightforward and the mathematics less cumbersome than in the horizontal dipole case. This restriction has no effect on the conclusions reached herein and is consistent with the emphasis of this report, in that the only important differences between the horizontal and vertical cases involve radiative effects. The radiative aspects of the problem will be discussed in more detail in a later paper.

II. THE LIFETIME OF A DIPOLE EMITTER NEAR AN INTERFACE: ENERGY FLUX METHOD

The energy flux method to be described in this section requires there be a negligible shift in the emission frequency due to the presence of the mirror and the intrinsic damping of the dipole. Though the mechanical model discussed previously[4] does not require a negligible frequency shift as an initial assumption, the calculations using that model are straightforward only if this condition is met. Calculations using the mechanical model have shown that the shift is completely negligible for all cases of any physical significance[4] and may therefore be safely ignored with either approach. We will demonstrate here that either of the two methods may be used to determine the effects of the mirror on the lifetime of an emitting dipole. The energy flux method, however, allows the separation of these effects into their radiative and nonradiative components.

The case of a vertical dipole (i.e., dipole perpendicular to the mirror plane) will be considered. The geometry of the problem is shown in Fig. 1. The dipole is located at a distance d from the mirror and has a dipole moment given by

$$\mu = \exp(-i\omega t - bt/2) , \tag{2.1}$$

where $1/b$ is the lifetime of the dipole in the presence of the mirror. We have chosen the amplitude at $t = 0$ as unity for convenience. The dielectric containing the dipole has a real refractive index n_1 and a propagation constant $k_1 = 2\pi n_1/\lambda$. The metal has a complex refractive index $\tilde{n}_2 (\equiv n_2 + iK_2)$ and a propagation constant given by $k_2 = 2\pi \tilde{n}_2/\lambda$. The total energy flux through planes parallel to the mirror, above and below the dipole, will be calculated. Both planes are infinite in extent and thus account for all the energy flowing away from the dipole. The total energy flux out of the upper and lower planes will be labelled $F\!\uparrow$ and $F\!\downarrow$, respectively. Following Sommerfeld,[6] these are calculated using the complex Poynting vector, S^*, and integrating the normal component over the plane[7]:

$$F_{\uparrow,\downarrow} = \mathrm{Re} \int_{A_{\uparrow,\downarrow}} S^* \cdot \mathbf{n} \, dA , \tag{2.2}$$

where

$$S^* = (c/8\pi) E \times H^* . \tag{2.3}$$

The electric and magnetic fields are given by

$$E = (1/n_1^2)(k_1^2 \Pi + \mathrm{grad} \, \mathrm{div} \, \Pi) \tag{2.4}$$

and

$$H = -i(\omega/c) \mathrm{curl} \, \Pi , \tag{2.5}$$

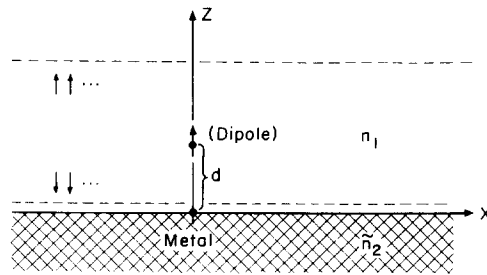where Π is the Hertz vector for this boundary value

FIG. 1. Geometry of the dipole–metal system for a vertical dipole; d is the distance from the dipole to the surface. The dashed lines represent the planes through which the flux is computed.

problem.[7] Using cylindrical coordinates (r, θ, z) and noting that in this case Π is along the z axis, we have

$$S = \frac{-i\omega}{8\pi n_1^2} \left[\frac{\partial}{\partial r} \left(\frac{\partial \Pi_z}{\partial z} \right) \right] \left(\frac{\partial \Pi_z^*}{\partial r} \right) . \tag{2.6}$$

We find that Π_z is given as[4,6,7]

$$\Pi_z = \mathbf{e}_z \mu \left[\frac{e^{ik_1 R_1}}{R_1} - \frac{e^{ik_1 R_2}}{R_2} + \int_0^\infty f_1 e^{-lz} J_0(\eta r) \, d\eta \right] , \tag{2.7}$$

where R_1 is the distance from the dipole to the point at which Π_z is being calculated (r, θ, z), R_2 is the distance from the image dipole to that point, and J_0 is the zeroth order Bessel function. The term f_1 is defined by the following:

$$f_1 = 2\eta k_2^2 e^{-ld}/(k_2^2 l + k_1^2 m) , \tag{2.8}$$

where

$$l \equiv -i(k_1^2 - \eta^2)^{1/2} \tag{2.9}$$

and

$$m \equiv -i(k_2^2 - \eta^2)^{1/2} . \tag{2.10}$$

The branch of the square root in the definition of l or m has been taken so that the real part is positive for all values of the integration variable η. It is more convenient to write

$$\Pi_z = \mathbf{e}_z \mu \int_0^\infty g_1 e^{-lz} J_0(\eta r) \, d\eta , \tag{2.11}$$

where

$$g_1 = (\eta/l)(e^{ld} - e^{-ld}) + f_1, \qquad z \geq d ,$$
$$g_1 = (\eta/l) e^{-ld}(e^{2lz} - 1) + f_1, \qquad 0 \leq z < d . \tag{2.12}$$

We then find upon integrating $S^* \cdot \mathbf{n}$ over the plane:

$$F_\uparrow = e^{-bt} \, \mathrm{Re}(i\omega/4n_1^2) \int_0^\infty \int_0^\infty d\eta d\eta' \, l(\eta') g_1(\eta') g_1^*(\eta)$$

$$\times \exp\{-[l^*(\eta') + l(\eta)]z\} \eta \delta(\eta - \eta') . \tag{2.13}$$

After some manipulation and noting that $F_\uparrow$ divided by the energy of the dipole (which we take as $|\mu|^2$ for convenience) is simply the rate constant $b_\uparrow$ associated with energy loss through the upper plane, we have

$$b_\uparrow = \frac{\omega k_1^3}{4n_1^2} \int_0^1 g_1 g_1^* (1 - \tau^2)^{1/2} \tau d\tau , \tag{2.14}$$

where $\tau = \eta/k_1$.

It is useful to normalize this result to that for a di-

pole in the absence of a mirror. In that case we may integrate Eq. (2.14) to yield for the radiative component of the intrinsic damping

$$b_r^0 \equiv 2b_t^0 = \omega k_1^3 / 3n_1^2 \ , \tag{2.15}$$

where b_t^0 is the rate constant in the absence of the mirror. We may also take into account at this point an unspecified nonradiative (thermal deactivation) contribution to the intrinsic damping and write for the total damping in the absence of the mirror

$$b^0 = \omega k_1^3 / 3n_1^2 + b_{nr}^0 = \omega k_1^3 / 3qn_1^2 \ . \tag{2.16}$$

We have used the usual definition for a quantum yield $q \equiv b_r^0/(b_r^0 + b_{nr}^0)$.

The normalized rate constant for energy loss through the upper plane is then

$$\hat{b}_t \equiv \frac{b_t}{b^0} = \frac{3q}{4} - \int_0^1 g_1 g_1^* (1 - \tau^2)^{1/2} \tau d\tau \ . \tag{2.17}$$

A similar prescription may be follwed for the rate constant b_t associated with the net energy flow through the lower plane in Fig. 1. Normalizing in the same manner, we find

$$\hat{b}_t = \frac{b_t}{b^0} = - \frac{3q}{4} \left[\int_0^1 f_1 f_1^* (1 - \tau^2)^{1/2} \tau d\tau + 2 \mathrm{Im} \int_0^\infty f_1^* e^{-l\hat{d}} \tau^2 d\tau \right] \ , \tag{2.18}$$

where (in the τ representation)

$$f_1 = 2\tau e^{-l\hat{d}} k_2^2 / (k_1^2 m + k_2^2 l) \ , \tag{2.19}$$

$$l \equiv - i(1 - \tau^2)^{1/2} \ , \tag{2.20}$$

$$m \equiv - i(k_2^2/k_1^2 - \tau^2)^{1/2} \ , \tag{2.21}$$

and

$$\hat{d} = k_1 d \ . \tag{2.22}$$

For comparison to our earlier results from the mechanical model[4] it is useful to rewrite Eqs. (2.17) and (2.18) as

$$\hat{b}_t = q - 3q \,\mathrm{Im} \int_0^1 (B + BB^* l) \tau^3 d\tau + 3q \,\mathrm{Im} \int_0^{1} \left(B - \frac{1}{2l} \right) e^{-2l\hat{d}} \tau^3 d\tau \tag{2.23}$$

and

$$\hat{b}_t = 3q \,\mathrm{Im} \int_0^1 (B + BB^* l) \tau^3 d\tau + 3q \,\mathrm{Im} \int_1^\infty Be^{-2l\hat{d}} \tau^3 d\tau, \tag{2.24}$$

where $B \equiv k_2^2/(k_1^2 m + k_2^2 l)$ [or, in terms of dielectric constants $B \equiv \epsilon_2/(\epsilon_1 m + \epsilon_2 l)$]. The total, normalized damping constant, including the intrinsic nonradiative component b_{nr}/b^0 (or $1 - q$), is then

$$\hat{b} \equiv b/b^0 = \hat{b}_t + \hat{b}_t + (1 - q) \ . \tag{2.25}$$

With slight changes in notation and some minor manipulation, we have from our earlier work with the mechanical model

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

$$+ 3q \,\mathrm{Im} \int_0^\infty Be^{-2l\hat{d}} \tau^3 d\tau \ . \tag{2.26}$$

Noting that the second term in Eq. (2.26) may be re-

written as $- 3/2 \,\mathrm{Im} \int_0^1 \exp(- 2l\hat{d}) \tau^3 d\tau / l$, it is straightforward to show the equivalence of Eqs. (2.25) and (2.26).

The above discussion merely serves to show that the mechanical model correctly reproduces the solution to Maxwell's equations. Though the two approaches give identical expressions for the lifetime of the dipole in the presence of a mirror, the energy flux method is advantageous since, as will be seen shortly, the radiative and nonradiative (energy transfer) components in Eq. (2.25) may be rigorously separated.

Obviously, we already have enough information to calculate an *observed* quantum yield: $q_{\mathrm{obs}} \approx \hat{b}_t / \hat{b}$. This, however, is not the quantum yield as it is usually defined, namely $q =$ number of photons emitted per luminescent state created by the incident light or, in other words, the radiative decay rate constant divided by the total decay rate constant. (The ratio of this and the number of photons emitted/ the number absorbed is merely the inverse of the probability of creation of the luminescent state.[1,5,10]) Here we must, of course, distinguish between the "real" photons associated with the radiation field of the dipole and the "virtual" photons associated with the near field of the dipole. A certain fraction of the photons emitted by the dipole will be absorbed in the mirror, i.e., "trivially" transferred to the mirror. Equation (2.23) must take this into account, and in fact, the second term in that equation is due solely to the absorption of real photons in the mirror. This particular assignment for the second term may be seen qualitatively from the following observations: (1) it is independent of $\hat{d}$; (2) it equals zero for a perfect reflector and $q/2$ for a nonreflecting mirror (no boundary); and (3) it reappears in the equation for b_t with the opposite sign so that a cancellation of terms results in Eq. (2.25), as it should.

These arguments then allow us to separate our expression for $\hat{b}$, the total damping rate constant, into its radiative ($\hat{b}_r$) and nonradiative ($\hat{b}_{nr}$) components:

$$\hat{b}_r = q + 3q \,\mathrm{Im} \int_0^1 \left(B - \frac{1}{2l} \right) e^{-2l\hat{d}} \tau^3 d\tau \tag{2.27}$$

and

$$\hat{b}_{nr} = (1 - q) + 3q \,\mathrm{Im} \int_1^\infty Be^{-2l\hat{d}} \tau^3 d\tau \ . \tag{2.28}$$

Note that we have included in Eq. (2.28) the intrinsic nonradiative component, which is of course not related to the presence of the mirror. The quantum yield is then simply $\hat{b}_r/\hat{b}$ and differs from the observed quantum yield by a factor [given by the second term in Eq. (2.23)] that is independent of the distance between the dipole and the mirror. We note that our separation of b into b_r and b_{nr} differs from that adopted by Kuhn[1] in the treatment of this factor.

We can quantify the preceding argument by a direct calculation, using the Fresnel formulas, of the absorption of photons from the radiation field of a dipole placed in front of a mirror. The calculation is straightforward and verifies the above conclusions. Alternately, we may calculate the photon flux through the

upper plane by again using Fresnel formulas and considering only the radiation field of the emitter. This is basically the approach adopted by Kuhn[1] and by Drexhage[10] and will be but briefly summarized here. It involves looking at the interference between a primary ray exiting directly from the dipole and a reflected ray from the metal. We simply calculate the amplitude which results, convert to intensity, and integrate over all angles. After normalization by the result for a dipole in the absence of the mirror, we obtain

$$\hat{b}'_t = \frac{3q}{4} \int_0^{\pi/2} \left| 1 + \frac{R_\shortparallel}{A_\shortparallel} e^{i2\hat{d}\cos\theta} \right|^2 \sin^3\theta d\theta, \qquad (2.29)$$

where θ is the angle between the primary ray and a normal to the mirror plane, i.e., for the vertical dipole case, the direction of the dipole. $R_\shortparallel/A_\shortparallel$ is the ratio of amplitudes for the reflected and incident ray. After changing variables (let $\cos\theta = il$) and noting that $R_\shortparallel/A_\shortparallel = (k_2^2 l - k_1^2 m)/(k_2^2 l + k_1^2 m)$, it is straightforward to show that $\hat{b}'_t = \hat{b}_t$. Therefore, all the terms in Eqs. (2.23) and (2.24) except one may be derived from the far field of the dipole. The one exception must, therefore, have its origins in the near field of the dipole and we conclude that it represents the normalized rate constant for nonradiative energy transfer to the mirror:

$$\hat{b}_{ET} = 3q \, \mathrm{Im} \int_1^\infty B e^{-2i\hat{d}} \tau^3 d\tau . \qquad (2.30)$$

This equation shows the correct behavior in the various limiting cases and also, as will be discussed in the next section, varies as d^{-3} at small values of d, as would be expected from simple considerations of the dimensionality of the problem. We note, however, that a calculation of the total transfer of energy to the mirror via the electromagnetic field of the dipole would proceed from Eq. (2.24) and would therefore include the energy transferred by the far field of the dipole in addition to $\hat{b}_{ET}$.

A completely analogous derivation can be made for the horizontal dipole case (i.e., dipole parallel to the mirror). The mechanical model and present method, of course, give identical results. As in the vertical case, the radiative and nonradiative components are, respectively, the $0 \to 1$ and $1 \to \infty$ portions of the integral expression for the total decay rate as given in Ref. 3. In both the horizontal and vertical dipole cases, the $0 \to 1$ portions of the integrals give precisely the formulas of Drexhage[10] which were obtained through the interference method.

III. NONRADIATIVE EFFECTS

A. Energy transfer rate constant in the limiting case of small distance

Nonradiative energy transfer has been discussed by a number of authors[11,12] as an effective decay channel for an emitting molecule located near a metallic surface. For example, Vaubel et al.[11] find that the experimentally determined energy transfer rate constant in the anthracene–aluminum system may be expressed as

$$\dot{b}_{ET} = \beta d^{-3} , \qquad (3.1)$$

where d is the distance in centimeters between the emitter and the mirror. As we have recently pointed out,[4] the same large increase in decay rate at small distances is seen in the Eu^{+3}/metal systems examined by Drexhage.[13] Since the energy transfer rate was not the emphasis of that work, there is not sufficient data availabele to derive a limiting form for the dependence on d in the small distance range.

Simple considerations of the dimensionality of dipole-dipole transfer (Förster transfer)[14] predict the cubic dependence. However, this approach is not adequate to predict the value of β, even qualitatively, for the layered systems because of the presence of the interface between emitter and receiver. In this section, we present the derivation of a simple expression for β which is widely applicable to experiments involving emission near metallic electrodes or other absorbing media.

In Eq. (2.30) we have an expression for $\hat{b}_{ET}$ valid at all distances. For small $\hat{d}$ ($\equiv k_1 d$) this term dominates the total damping constant in Eq. (2.25). We have, in fact, shown numerically that the total damping varies as d^{-3} in this region, and will now derive β, the coefficient of d^{-3}. We proceed by evaluating the integral in (2.30) in the limit of small d. Since the leading term is proportional to d^{-3}, we multiply by d^3 and then let d approach zero. This leads to

$$\lim_{d \to 0} \hat{b}_{ET} = \frac{3q}{4\hat{d}^3} \, \mathrm{Im} \left(\frac{-k_1^2}{k_1^2 + k_2^2} \right) \qquad (3.2)$$

for a vertical dipole and

$$\lim_{d \to 0} \hat{b}_{ET} = \frac{3q}{8\hat{d}^3} \, \mathrm{Im} \left(\frac{-k_1^2}{k_1^2 + k_2^2} \right) \qquad (3.3)$$

for a horizontal dipole. Thus, in general, we may write

$$\beta = \frac{3q}{32} \frac{\lambda^3 \Theta}{\pi^3 n_1} \left[\frac{n_2 K_2}{(n_1^2 + n_2^2 - K_2^2)^2 + 4n_2^2 K_2^2} \right], \qquad (3.4)$$

where $k_1 = 2\pi n_1/\lambda$, $k_2 = 2\pi \tilde{n}_2/\lambda$, and $\tilde{n}_2 \equiv n_2 + iK_2$. The quantity Θ is a parameter varying with orientation and equals 1 for a horizontal dipole, 2 for a vertical dipole, and 4/3 for randomly oriented dipoles. Equation (3.4) requires that the system be describable in terms of the optical constants of the two media. If the emission is not confined to a narrow band, Eq. (3.4) may be rewritten as an integral over the emission spectrum in a fashion analogous to the well-known Förster expression (see Sec. V). Note that Eq. (3.4) allows a ± 33% estimate of β without any knowledge of the dipole orientation. This expression differs from one derivable from the approximations of Kuhn[1] and shows a sharper and larger peak in β vs K_2 than would that approximate expression. The two expressions agree in the limit of weak absorbers (K_2 small).

Though the effects of energy transfer in layered systems have been noted in many instances, only a few quantitative evaluations of β have been made. These are shown in Table I along with the theoretical estimates from Eq. (3.4). (We have taken $q = 1$ as a good approximation for each of these systems.) The agreement is good in the Eu^{+3}/metal systems where the comparison

TABLE I. Comparison of theory and experiment for energy transfer rate parameter β.

System	n_1	n_2[a]	K_2[a]	β(Theory)[b]	β (Exptl)[b]
Eu^{+3}/Au	1.5	0.22	3.22	4.9	5.0[c]
Eu^{+3}/Cu	1.5	0.33	3.14	7.9	7.2[c]
Eu^{+3}/Ag	1.5	0.06	4.11	0.53	≥ 0.19[c,d]
Anth/Au	2.1	1.46	1.96	7.5	≥ 2.6[e]
Anth/Al	1.5	0.43	4.64	0.77	5.2[f]

[a]Optical constants taken from Johnson and Christy[15] and Hass and Waylonis.[16]

[b]Units on β are 10^{-18} cm^3; the dipole is assumed to be parallel to the mirror, i.e., $\Theta = 1$.

[c]K. H. Drexhage, private communication (see also Ref. 10).

[d]Insufficient data in small distance range so that only a lower limit estimate could be made.

[e]Indirect measurement[12] allowing only a lower limit estimate of β.

[f]Direct fluorescence measurement; however, the system was actually anthracene/fatty acid spacer/aluminum.[11]

is straightforward, but not as good in the anthracene/metal systems. In the latter case, other effects may be important, such as exciton diffusion and a complex n_1 over much of the emission range.

B. Dielectric constant matching and surface plasmons

The equation for the energy transfer rate constant for small distances exhibits an intersting resonance behavior. If, in Eq. (3.2) or (3.3), $k_1^2 + k_2^2$ is zero or near zero, the rate constant becomes very large. In terms of the dielectric constants of the two layers, ϵ_1 and ϵ_2,
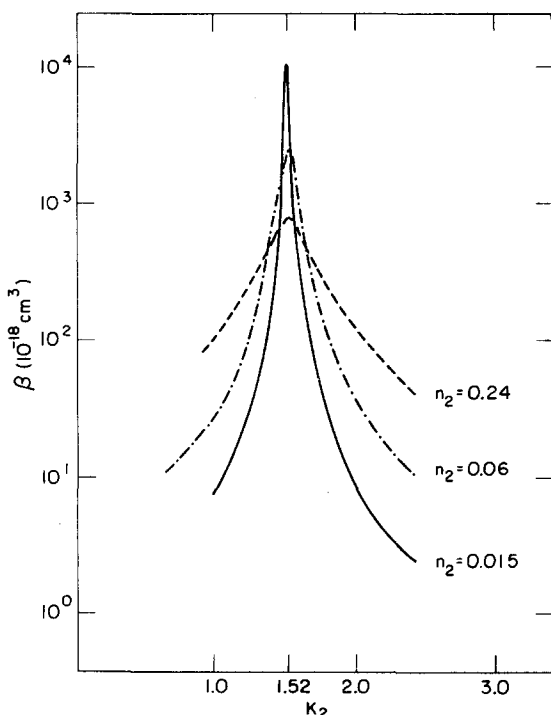

FIG. 2. The short range energy transfer rate parameter β as a function of K_2, the imaginary part of the refractive index of the metal. The dipole is assumed to be that of the Eu^{+3} complex emitting at 612 nm in a fatty acid layer of refractive index $n_1 = 1.52$.
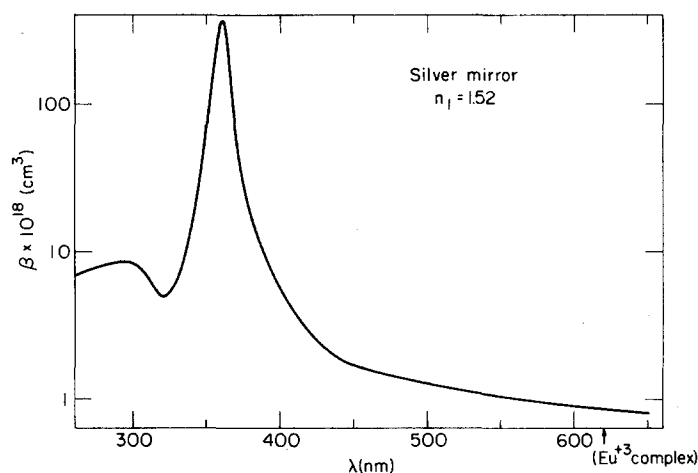

FIG. 3. The energy transfer rate parameter β vs wavelength for dipole emitters of varying wavelength. The metal is silver; the dielectric containing the dipole has a refractive index 1.52 (fatty acid layers).

this translates into a matching condition,

$$\epsilon_1 + \epsilon_2 = 0 , \tag{3.5}$$

where

$$\epsilon_1 = n_1^2 = (k_1 c/\omega)^2 \tag{3.6}$$

and

$$\epsilon_2 = \tilde{n}_2^2 = (k_2 c/\omega)^2 . \tag{3.7}$$

To illustrate the dramatic increase in the energy transfer rate near the matching condition [Eq. (3.5)], we have computed β for the Eu^{+3} complex (with dipole perpendicular to the mirror) on the fatty acid layer near metal mirrors of varying K_2. The results are shown in Fig. 2 for various values for n_2. These results indicate the sensitivity of β to the optical constants of the metal near the matching condition.

In Fig. 3 the calculated values of β are presented for emitter/silver systems with $n_1 = 1.52$ (fatty and layers), $\theta = 2$ (vertical dipole), $q = 1$, and λ variable. As the wavelength of the emission is swept through a small range, a resonance is seen in β. Consequently a sharp dip in the lifetime and quantum yield would result. This striking effect should be observable with an adsorbed molecule which emits at about 360 nm. This resonance wavelength in the emitter/silver system increases slightly as n_1 is increased ($\lambda \approx 400$ nm for n_1 $n_1 = 2.0$). For the hypothetical case of a Drude electron gas metal, we have $\epsilon_2(\omega) = 1 - \omega_p^2/\omega^2$, where ω_p is the bulk plasmon frequency. Thus, for this case, the resonance occurs at $\omega = \omega_p/(1 + \epsilon_1)^{1/2}$.

This resonance or matching condition was first noted by Sommerfeld in the radio wave case and is related to his famous surface wave.[6] We note that the denominator $k_2^2 l + k_1^2 m$ in the expression for the electric field[4] has a zero which gives rise to a term which becomes large for small d and near the dielectric matching condition. This latter condition is well known from the theory of surface plasmons[8] where it is the equation for the dispersion relation of the surface plasmon modes.

The interpretation is now straightforward: the short range dipole field is coupling to the surface modes causing them to oscillate and thus absorb energy.[17,18] The normal condition that surface plasmons are not coupled to the *radiation* field (because the phase velocity of these modes is less than light for all k and ω) is not violated here because the *short range* dipole field is not a radiation field and contains all Fourier components (i.e., k vectors).

Another manifestation of this coupling of surface waves to the short range field is the distance dependence of the energy flux through planes in the metal. For the radiation case this is governed by the skin depth and hence has an exponential dependence on distance. However, for the short range field, a different dependence occurs. If a plane is drawn parallel to and a distance d_2 below the surface of the metal, and the flux through it computed as in Sec. II, we find for small d and d_2 that

$$\hat{b}(d_2) = \frac{3q\Theta}{8k_1^3(d+d_2)^3} \, \mathrm{Im}\left(\frac{-k_1^2}{k_1^2+k_2^2}\right). \tag{3.8}$$

This is in agreement with Eq. (3.2), and contrasts markedly with the radiation case. We note once again the strong dependence on the matching condition.

IV. FILMS OF FINITE THICKNESS

Many experiments in photoconductivity and fluorescence quenching which have been done on single crystals of aromatic molecules[11,12] have used semitransparent films of evaporated metals. It becomes important to investigate the effect of the finite film thickness on the various energy transfer rates and on the emitter lifetime. Bucher *et al.*[19] have discussed a theory for this effect based on the short range dipolar field only. This present section gives the theory including the entire dipole field and so is an exact classical theory. We discuss limiting cases at the end of this section.

Figure 4 illustrates the geometry of the problem. The dipole is again embedded in a nonabsorbing medium of refractive index n_1, the absorber is characterized by a
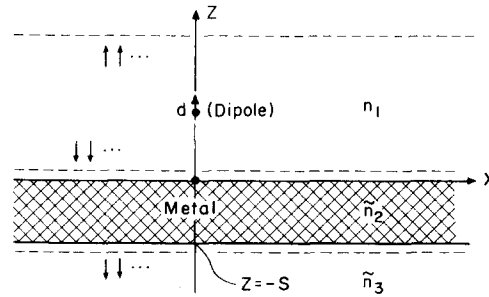

FIG. 4. Geometry of the dipole—thin metal mirror system; d is the dipole—mirror distance and s is the metal thickness.

refractive index $\tilde{n}_2$(complex), and below the film is a region of refractive index $\tilde{n}_3$. The Hertz vectors in the three regions are given by (vertical dipole case):

$$\Pi_1 = \mathbf{e}_z \mu \int_0^\infty \left\{ \frac{\tau}{l} e^{l(\hat{z}-\hat{d})} - \frac{\tau}{l} e^{-l(\hat{z}+\hat{d})} + f_1 e^{-l\hat{z}} \right\} J_0(\tau\hat{r})\,d\tau , \tag{4.1}$$

$$\Pi_2 = \mathbf{e}_z \mu \int_0^\infty \left\{ f_2 e^{m\hat{z}} + f_3 e^{-m\hat{z}} \right\} J_0(\tau\hat{r})\,d\tau , \tag{4.2}$$

and

$$\Pi_3 = \mathbf{e}_z \mu \int_0^\infty f_4 e^{n\hat{z}} J_0(\tau\hat{r})\,d\tau , \tag{4.3}$$

where

$$l = -i(1-\tau^2)^{1/2} , \tag{4.4}$$

$$m = -i[(\epsilon_2/\epsilon_1)-\tau^2]^{1/2} , \tag{4.5}$$

and

$$n = -i[(\epsilon_3/\epsilon_1)-\tau^2]^{1/2} . \tag{4.6}$$

(For notational convenience here and in the equations to follow, we have replaced the square of the refractive indices with the dielectric constants.) On fitting the appropriate boundary conditions at each of the two boundaries and using the relationship which connects the Hertz vector with the electric field,[6,7] we find for the reflected field at the dipole

$$E_R = \frac{\mathbf{e}_z \mu k_1^3}{\epsilon_1}\left\{ 2\left(\frac{i}{(2\hat{d})^2} - \frac{1}{(2\hat{d})^3}\right)e^{i2\hat{d}} + 2\epsilon_2 \int_0^\infty \frac{e^{-2l\hat{d}}\tau^3 d\tau}{\epsilon_1 m + \epsilon_2 l}\left[\frac{1 - e^{-2m\hat{s}}(\epsilon_2 n - \epsilon_3 m)(\epsilon_2 n + \epsilon_3 m)^{-1}}{1 + e^{-2m\hat{s}}(\epsilon_2 n - \epsilon_3 m)(\epsilon_2 n + \epsilon_3 m)^{-1}(\epsilon_1 m - \epsilon_2 l)(\epsilon_1 m + \epsilon_2 l)^{-1}} \right] \right\} . \tag{4.7}$$

Here $\hat{d} = k_1 d$ and $\hat{s} = k_1 s$, where s is the thickness of the film. From the mechanical model[4] we then have

$$\hat{b} = 1 + \frac{3q}{2}\frac{\epsilon_1}{k_1^3}\,\mathrm{Im}(E_R/\mu) . \tag{4.8}$$

Figure 5 shows the calculated results through this formalism for the normalized lifetime $(1/\hat{b})$ vs dipole—emitter distance for various thicknesses of film. Optical constants are for the Eu$^+$/Ag system,[15] $\tilde{n}_2 = 0.06 + i4.11$; the emission wavelength is 6120 Å. Media above and below the metal are taken to be the same, i.e., $n_1 = n_3 = 1.52$.

The first point to note is that for $\hat{s} \geq 1.0$ the lifetime versus $\hat{d}$ curves are indistinguishable. Actually for

$\hat{s} \geq 0.5$ (corresponding to a thickness of about 320 Å for this case) there is no significant difference in lifetime vs $\hat{d}$. This is reasonable, since the calculated transmission for a photon field for such a film is around 10%. Secondly, it is shown that for $\hat{s} = 0.1$ (or $s = 64$ Å, corresponding to photon field transmission of 58%) the reduction in lifetime of the emitter is actually greater than in the "thick" film case up to a distance, $\hat{d}$, of about 1.5, or a physical distance of about 960 Å. Using the energy flux method described in Sec. II, it can be shown unequivocally that, as was the case for an infinitely thick metal, the dominating effect as the small d range is nonradiative energy transfer to the absorbing film. Calculations for the example given in Fig. 5 show
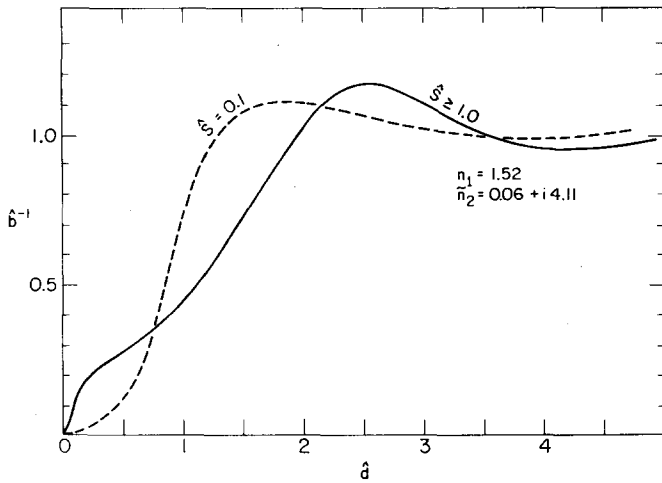
FIG. 5. The effect of the thickness of the metal mirror on the lifetime of the dipole. The two curves represent the normalized lifetime $(1/\hat{b})$ vs distance, $\hat{d} \equiv k_1 d$. The dashed curve is for $\hat{s} = 0.1$; the full curve for $\hat{s} \geq 1.0$, where $\hat{s} \equiv k_1 s$.

that it is the large increase in b_{ET} which accounts precisely for the large decrease in the normalized lifetime as the film thickness $\hat{s}$ decreases from ∞ to 0.1.

Using the procedure outlines in Sec. III, β, the coefficient of the d^{-3} (energy transfer) term, may be evaluated (vertical dipole case):

$$\beta \equiv \hat{b}_{ET} d^3 = \frac{3q}{k_1^3} \mathrm{Im} \left[\epsilon_2 \int_0^\infty e^{-2\tau} \tau^2 d\tau \right.$$
$$\left. \times \frac{(\epsilon_1 + \epsilon_2) + (\epsilon_1 - \epsilon_2) \exp(-2\tau s/d)}{(\epsilon_1 + \epsilon_2)^2 - (\epsilon_1 - \epsilon_2)^2 \exp(-2\tau s/d)} \right] , \quad (4.9)$$

where we have taken $n_1 = n_3$ for convenience. Note that Eq. (4.9) correctly reduces to Eq. (3.2) for $s = \infty$ and gives $\beta = 0$ for $s = 0$.

Results are shown in Fig. 6 for a range of values of $\bar{n}_2$. The real part is selected as 0.06 and the imaginary part covers a span from the value 4.11 (silver film) to the "matching" value of 1.52. The family of curves shows an interesting development. The monotonically decreasing curve (with decreasing s/d) which describes the matching condition is seen to develop a peak as K_2 moves away from the matching condition. This peak in the case of the silver film $(K_2 = 4.11)$ is seen to be quite high, rising more than 2 orders of magnitude over the value for a thick film. Further, since the energy transfer region is of the order of 100 Å, it is clear that the corresponding film is a very thin one for maximum rate of energy transfer.

In the limit that $\hat{d}$ is small, and s/d is much less than 1, a formula for $\hat{b}_{ET}$ can be derived which resembles that of Kuhn[1] and Bücher et al.[19] In this case, the result is

$$\hat{b}_{ET} = d_0^4/d^4 , \quad (4.10)$$

where

$$d_0 = \alpha \frac{\lambda}{n_1} (Aq)^{1/4} \left[\frac{n_2}{2n_1} \left(1 + \frac{\epsilon_1^2}{|\epsilon_2|^2} \right) \right]^{1/4} , \quad (4.11)$$

$$A = 4\pi K_2 s/\lambda , \quad (4.12)$$

and α is a geometric factor which is equal to $(1/4\pi)(9)^{1/4}$ for a vertical dipole. This expression is quite similar to that of Kuhn[1] and reduces to it for the case $n_1 = n_2 \gg K_2$. However, for $n_2 \ll n_1$, for example, d_0 computed from (4.11) will be very different from that computed with the formula of Kuhn. In addition, the transition from the d^{-4} (small s/d) behavior to the d^{-3} behavior (large s) is not monotonic, as shown in Fig. 6.

Another limiting case of interest is that for $n_1 = n_2 \gg K_2$ and for general s/d. We find this case

$$\hat{b}_{ET} = \frac{3k_2 q}{8k_1^3 d^3 n_1} [1 - (d/d+s)^3] . \quad (4.13)$$

Thus there is a smooth transition from d^{-3} to d^{-4} in this case.

Bücher et al.[19] have examined the effect of increasing the absorptivity of evaporated gold films on the energy transfer rate. The absorptivities of the films used in their experiments correspond to gold thicknesses in the range of 1–50 Å. However, an *evaporated* gold film of thickness less than 200 Å is not formed in a homogeneous layer, but in small islands. These islands may be distributed randomly and may be relatively thin, so that a substantial part of the surface is covered by thin gold layers. It is not clear how the present theory should be modified to take the inhomogeneity into account. However, the results of the experiments of Bücher et al.[19] are in qualitative agreement with Eq. (4.10). This may indicate that the effect of the inhomo-
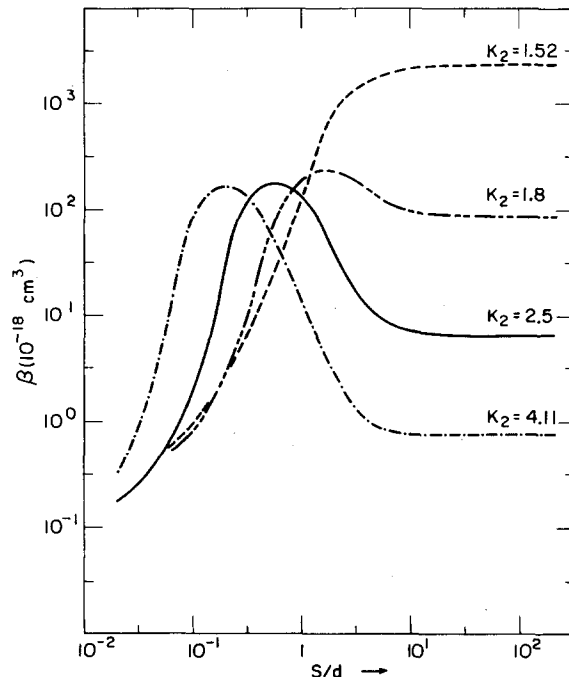

FIG. 6. The effect of thickness of metal mirror on the energy transfer rate parameter, β; s is the mirror thickness, d is the dipole–mirror separation, and K_2 is the imaginary part of the refractive index of the metal. In all cases $n_1 = n_3 = 1.52$ and $n_2 = 0.06$.

geneity is relatively small for these experimental conditions.

V. FÖRSTER TRANSFER THEORY FROM CLASSICAL ELECTRODYNAMICS

As Kuhn[1] has pointed out, the classical theory of an oscillating dipole in an absorbing dielectric can also be used to derive the expression for the rate of energy transfer from an excited molecule to a host molecule of the dielectric. In this section, we reiterate this using a different approach which shows the complete equivalence of the classical and quantum methods. The excited molecule is represented by the oscillating dipole (or a set of dipoles each oscillating at a different frequency) and the molecule in the absorbing dielectric will be represented by a unit cell volume of the classical continuous dielectric.

The rate of energy (heat), Q, absorbed at a point $\mathbf{R}$ per second per unit volume by a classical dielectric, when an electric field oscillating at frequency ω is impressed on it at point $\mathbf{R}$, is given as[20]

$$\frac{dQ}{dt} = \frac{\omega}{4\pi} \mathbf{E}(\mathbf{R}) \cdot \boldsymbol{\epsilon}''(\omega) \cdot \mathbf{E}^*(\mathbf{R}) , \tag{5.1}$$

where $\boldsymbol{\epsilon}''(\omega)$ is the imaginary (absorptive) part of the dielectric constant of the dielectric. The electric field, for $|\mathbf{R}|$ small compared to $k(= 2\pi n/\lambda)$, can be written as

$$\mathbf{E}(\mathbf{R}) = \frac{1}{n^2 R^3} \boldsymbol{\mu} \cdot (1 - 3\hat{R}\hat{R}) e^{ik|R|} , \tag{5.2}$$

where n is the refractive index of the dielectric medium. Thus, Eq. (5.1) reduces to

$$\frac{dQ}{dt} = \frac{\omega}{4\pi} \frac{1}{n^4 R^6} \boldsymbol{\mu} \cdot (1 - 3\hat{R}\hat{R}) \cdot \boldsymbol{\epsilon}''(\omega) \cdot (1 - 3\hat{R}\hat{R}) \cdot \boldsymbol{\mu} , \tag{5.3}$$

where $\boldsymbol{\mu}$ is the transition dipole moment (represented by the oscillating dipole) for the excited guest molecule for frequency ω.

We may proceed from here in two ways: (a) Equation (5.3) can be interpreted immediately as the overlap of the host absorption [proportional to $\boldsymbol{\epsilon}''(\omega)$] and the guest emission (proportional to $\mu\mu$ for the oscillating dipole); the expression can then be summed over all emission frequencies of the guest with the appropriate weighting factors. This reproduces the final Förster rate expression; or (b) we can proceed in the same spirit as Förster.[14] We will proceed in the latter manner and return to (a) at the end.

We note that the absorptive part of the dielectric constant can be written approximately as[21]

$$\boldsymbol{\epsilon}''(\omega) = \frac{4\pi}{\hbar V} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \langle \mu_M \mu_M(t) \rangle_M , \tag{5.4}$$

where V is the volume of the dielectric; μ_M is the dipole moment operator of the dielectric medium, and $\mu_M(t)$ is $\exp(iH_M t)\mu_M \exp(-iH_M t)$, where H_M is the Hamiltonian of the medium and the average is over the states of the medium with appropriate weights. We take to the lowest order

$$\mu_M = \sum_i \mu_i^{(M)} \tag{5.5}$$

and

$$H_M = \sum_i h_i^{(M)} , \tag{5.6}$$

where $\mu_i^{(M)}$ is the dipole moment operator for molecule i in the medium and $h_i^{(M)}$ is the Hamiltonian for the ith molecule in the medium. We have then

$$\boldsymbol{\epsilon}''(\omega) = \frac{4\pi N}{\hbar V} \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \langle \mu_i^M \mu_i^M(t) \rangle , \tag{5.7}$$

where we have assumed that all the host molecules are identical and we need only consider the single molecule excitations at the frequencies of interest. If we now assume the statistical weight for the state α of the medium molecule with energy $\hbar\omega_\alpha$ is $\rho(\omega_\alpha)$ and expand the average, we find

$$\boldsymbol{\epsilon}''(\omega) = \frac{4\pi N}{\hbar V} \int_{-\infty}^{+\infty} dt e^{-i\omega t} \sum_{\alpha,\beta} \rho(\omega_\alpha) \mu_{\alpha\beta} \mu_{\beta\alpha} e^{i(\omega_\beta - \omega_\alpha)t} \tag{5.8}$$

or

$$\boldsymbol{\epsilon}''(\omega) = \frac{8\pi^2 N}{\hbar V} \sum_{\alpha,\beta} \mu_{\alpha\beta} \mu_{\beta\alpha} \delta(\omega - \omega_\beta + \omega_\alpha) , \tag{5.9}$$

where

$$\mu_{\alpha\beta} = \langle \alpha | \mu_i^M | \beta \rangle . \tag{5.10}$$

Substituting this into Eq. (5.3), we find

$$\frac{dQ}{dt} = \frac{N}{V} \frac{\omega}{n^4 R^6} \frac{2\pi}{\hbar} \sum_{\alpha,\beta} \rho(\omega_\alpha) [\mu_{\alpha\beta} \cdot (1 - 3\hat{R}\hat{R}) \cdot \mu_{\beta\alpha}]^2 \delta(\omega - \omega_\beta + \omega_\alpha). \tag{5.11}$$

This represents the amount of energy transferred to the medium per unit volume per unit time. If we multiply by V/N (the unit cell volume) and divide by $E = \hbar\omega$, we find the *rate* of energy transfer,

$$\gamma_{ET} = \frac{2\pi}{n^4\hbar^2} \frac{1}{R^6} \sum_{\alpha,\beta} \rho(\omega_\alpha)[\mu \cdot (1 - 3\hat{R}\hat{R}) \cdot \mu_{\alpha\beta}]^2 \delta(\omega - \omega_\beta + \omega_\alpha) . \tag{5.12}$$

This is exactly the *Golden Rule Expression* for energy transfer between guest and host molecules separated by R, via the dipole–dipole interaction, which is the starting point for Förster's theory. Notice that $E_\beta - E_\alpha$ is the energy difference in the medium and is equal to $\hbar\omega$, the energy emitted by the excited molecule.

If we now assume that the energy levels of the medium are a quasicontinuum, we can replace the sum by an integral. We also change the notation somewhat to agree with Förster:

$$\mu_{\alpha\beta} \equiv \mu(\omega_\alpha, \omega_\alpha + \omega) = \mu_{elec}^{(M)} S(\omega_\alpha, \omega_\alpha + \omega) . \tag{5.13}$$

In the above, $\mu_{elec}^{(M)}$ represents the electronic part of the transition dipole moment for the medium molecule, and S represents the Franck–Condon factor for the respective transition. In replacing the sum by an integral, we much replace $\rho(\omega_\alpha)$ by a function which gives the density of states at ω_α as well as the statistical weight of the state α, which we call $g^{(M)}(\omega_\alpha)$:

$$\gamma_{ET} = \frac{2\pi}{\hbar^2} \frac{1}{n^4 R^6} \int d\omega_\alpha g^{(M)}(\omega_\alpha) S^2(\omega_\alpha, \omega_\alpha + \omega)$$
$$\times [\mu \cdot (1 - 3\hat{R}\hat{R}) \cdot \mu_{elec}^{(M)}]^2 . \tag{5.14}$$

The excited molecule emits at more than one frequency.

To take this into account, we sum over all possible emission frequencies of the excited molecule. By writing

$$\mu = \mu_{elec}^{(d)} S(\omega_\gamma, \omega_\gamma - \omega) , \qquad (5.15)$$

where $\mu_{elec}^{(d)}$ is the electronic transition dipole moment

and $S(\omega_\gamma, \omega_\gamma - \omega)$ is the Franck–Condon factor for the transition from ω_γ to $\omega_\gamma - \omega$ in the guest molecule, we can write the total rate for energy transfer:

$$\gamma_{tot} = \int d\omega \int d\omega_\gamma g^{(d)}(\omega_\gamma) \gamma_{ET} , \qquad (5.16)$$

or

$$\gamma_{tot} = \frac{2\pi}{n^4 \hbar^2 R^6} \int d\omega \left\{ \int d\omega_\gamma g^{(d)}(\omega_\gamma) S^2(\omega_\gamma, \omega_\gamma - \omega) \right\} \left\{ \int d\omega_\alpha g^{(H)}(\omega_\alpha) S^2(\omega_\alpha, \omega_\alpha + \omega) \right\} \left| \mu_{elec}^{(d)} \cdot (1 - 3\hat{R}\hat{R}) \cdot \mu_{elec}^{(H)} \right|^2 . \qquad (5.17)$$

This agrees with Förster (except for our last factor, which is the exact geometric factor analogous to Förster's K). To proceed, all that is done is to make the connection of the first term in brackets with the emission spectrum of the guest and the second term with the absorption spectrum of the host (a factor of ω^{-4} comes out because of the difference in Einstein A and B coefficients). Since this is well known, we will leave it out.

The conclusion of this study is that the Förster transfer rate formula which has been found to be extremely useful in many contexts can be derived from a *completely* classical (electrodynamical) point of view. The final Förster form, with emission and absorption spectra, could have been derived directly from Eq. (5.1) with no recourse to quantum mechanics, as stated above, by merely noting that $\epsilon''(\omega)$ is proportional to the *absorption* of the host and integrating over the *emission* frequencies of the guest with appropriate weights. We see, then, as Kuhn[1] has emphasized, that the Förster transfer rate is a classical phenomenon. This is not surprising in view of the vast literature on the calculation of van der Waals forces from a classical viewpoint.[22] We note however that the classical equation, Eq. (5.1), does not depend on a model for the dielectric constant of the medium, and so can be more general than the second order perturbation result.

ACKNOWLEDGMENTS

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[1]H. Kuhn, J. Chem. Phys. 53, 101 (1970).
[2]H. Morawitz, Phys. Rev. 187, 1792 (1969).
[3]R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. 60, 2184 (1974).
[4]R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. 60, 2744 (1974).
[5]K. H. Tews, Ann. Phys. (Leipz.) 29, 97 (1973); Thesis, Marburg/Lahn, 1972.
[6]A. Sommerfeld, *Partial Differential Equations of Physics* (Academic, New York, 1949).
[7]J. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941).
[8]R. H. Ritchie, Phys. Rev. 106, 874 (1957); R. A. Ferrell, Phys. Rev. 111, 1214 (1958); E. A. Stern and R. A. Ferrell, Phys. Rev. 120, 130 (1960).
[9]S. A. Rice, D. Guidotti, H. L. Lemberg, W. C. Murphy, and A. N. Bloch, "Some Comments on the Electronic Properties of Liquid Metal Surfaces" (to be published).
[10]K. Drexhage, J. Lumin, 1-2, 693 (1970). Habilitationschrift, Marburg/Lahn, 1966.
[11]G. Vaubel, H. Baessler, and D. Möbius, Chem. Phys. Lett. 10, 334 (1971) and references therein.
[12]R. Chance and A. Prock, Phys. Status Solidi B 57, 597 (1973).
[13]K. H. Drexhage (private communication).
[14]T. Forster, Ann. Phys. 2, 55 (1948); also in *Modern Quantum Theory*, edited by O. Sinanoğlu (Academic, New York, 1965), Vol. III.
[15]P. Johnson and R. Christy, Phys. Rev. B 6, 4370 (1973).
[16]G. Hass and J. Waylonis, J. Opt. Soc. Am. 51, 719 (1961).
[17]H. Morawitz and M. Philpott[18] have also noted this interpretation by following Sommerfeld's arguments through in the modern language of plasma oscillations.
[18]H. Morawitz and M. Philpott, "Coupling of an Excited Molecule to Surface Plasmons" (preprint 1974).
[19]H. Bücher, K. Drexhage, M. Fleck, H. Kuhn, D. Möbius, F. Schäfer, J. Sondermann, W. Sperling, P. Tillmann, and J. Wiegand, Mol. Cryst. 2, 199 (1967).
[20]L. Landau and I. Lifshitz, *Electrodynamics of Continuous Media* (Addison Wesley, Reading, 1960).
[21]See, for example, R. G. Gordon, Adv. Mag. Reson. 3, 1 (1968).
[22]See, for example, A. McLachlan, R. D. Gregory, and M. A. Ball, Mol. Phys. 7, 119 (1964).