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Lifetime of an emitting molecule near a partially reflecting surface*

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A classical treatment of energy transfer in metal insulator systems is presented. The approach involves the calculation of the radiation field of an emitting molecule near a partially reflecting surface. The modification of the image theory result produces a large correction when the molecule is near the surface. This in turn produces a correction to the calculated lifetime of the molecule as a function of distance from the surface that differs substantially from previous theoretical descriptions of this system and brings the theory into good agreement with experiment.

I. INTRODUCTION

The lifetime of an excited molecule has experimentally been found to vary dramatically as a function of distance from a metal mirror.[1,2] A number of authors[3,4,5,6] have examined this effect from the viewpoint of image theory. In recent work, Kuhn[7] also examined this effect, again using image theory, but modified to include, in an approximate way, energy transfer from the excited molecule to the metal mirror. In each case, and also in the present work, the basic calculation is concerned with the interaction between an excited molecule (assumed to be an oscillating dipole) and its own reflected radiation field. Image theory provides good agreement with experiment at large distances, but fails at short distances where energy transfer is important.

Image theory is only an approximation for a more complete electromagnetic theory of dipole radiation in the presence of a partially reflecting halfspace. This theory was developed much earlier in order to describe the radiation from an antenna in the presence of a partially conducting earth. The mathematical formulation of this problem is presented in the monograph of Banos,[8] the paper of Wise,[9] and was discussed originally by Sommerfeld, Weyl, and Van der Pol.[10] It was applied to an antenna of size small compared to the wavelength of the radiation so that the antenna could be taken as a point dipole. Although the expressions derived are somewhat inconvenient for describing the general electromagnetic field, we find that they are quite appropriate as a starting point to calculate the reflected field at the dipole position. In this paper we apply the treatment to an emitting molecule which is regarded as a radiating dipole in close proximity to a partially reflecting halfspace. We have recently[11] applied this theory to the Eu^{+3}/Ag system and in a very recent paper,[12] which appeared while the present paper was being prepared, Tews discusses this problem from basically the same point of view. The details are different from ours, but the results are basically the same. Nevertheless, we feel that our approach is sufficiently different and the problem of sufficient interest to warrant elaboration. It is to be noted that the theory is sufficiently general so that it applies to halfspaces other than metals: however, it is so restricted in this paper to metals because of the experimental systems available for comparison. Our final result contains a pure image term plus a correction term. The latter term is found to be extremely important at the short distances typical in energy transfer experiments involving metal–insulator systems.

When the present theory is incorporated into the description of damped oscillation of the emitting dipole, the result is a lifetime calculation which is valid at all reasonable distances between the dipole and the halfspace. A degree of simplicity has been lost but very good agreement with experiment is found.

II. THEORY

The equation of motion of the dipole (assumed to be a harmonically bound charge) is

$$\ddot{\mu} + \omega^2 \mu = (e^2/m) E_R - b\dot{\mu}\,, \tag{1}$$

where ω is the frequency of oscillation of the dipole in the absence of all damping, m is the effective mass of the dipole, E_R is the reflected electric field at the dipole, and b is the damping constant (inverse lifetime) in the absence of the mirror. The damping is composed of a radiative contribution b_r and a nonradiative contribution b_{nr}, so that the quantum yield of the emitting state in the absence of the mirror is given by $q = br/b$. The dipole moment μ is defined by the following:

$$\mu = \mu_0 e^{-i\Omega t} = \mu_0 e^{-i\Omega_R E t} e^{\Omega_m t} = \mu_0 e^{-i\omega' t} e^{-t/2\tau_d}\,, \tag{2}$$

where Ω is the complex oscillation frequency and τ_d is the lifetime in the presence of the mirror. Since E_R and μ oscillate at the same frequency Ω, we may write $E_R = E^0 \exp(-i\Omega t)$. Substituting Eq. (2) into Eq. (1) and performing the indicated operations, we obtain

$$\Omega^2 - \omega^2 - ib\Omega = -(e^2/\mu_0 m)E^0 , \tag{3}$$

and therefore

$$\Omega = -i\frac{b}{2} + \omega\left(1 - \frac{b^2}{4\omega^2} - \frac{e^2}{\mu_0 m\omega^2}E^0\right)^{1/2} , \tag{4}$$

where the branch of the square root has been chosen so that $\Omega = \omega$ in the absence of all damping.

Since, for all reasonable distances, both b^2 and the magnitude of $(e^2/\mu_0 m)E^0$ are very small compared with ω^2, a simple expansion of the square root is appropriate, yielding the following results:

$$\Delta\omega \cong \omega - \omega' = b^2/8\omega + (e^2/2\mu_0 m\omega)\,\mathrm{Re}(E^0) , \tag{5}$$

and

$$\tau_d^{-1} = b + (e^2/\mu_0 m\omega)\,\mathrm{Im}(E^0) . \tag{6}$$

The frequency shift ($\Delta\omega$), given by Eq. (5), is found to be negligible for all cases of physical significance, so that we may take $\omega' = \omega$ as a good approximation.

Introducing the classical expression for b_r[7],

$$b_r = 2e^2\omega^2 n_1/3c^3 m , \tag{7}$$

we may write Eq. (6) in terms of the quantum yield. The result, which is now in a form convenient for numerical computation, is

$$\frac{\tau_d}{\tau_\infty} = \left[1 + \frac{3qc^3}{2\mu_0\omega^3 n_1}\,\mathrm{Im}E^0\right]^{-1} , \tag{8}$$

where $\tau_\infty (\cong 1/b)$ is the lifetime when the mirror is absent and n_1 is the refractive index of the medium containing the dipole.

The reflected electric field of the dipole can be found by analogy with the problem of the reflection of radio waves from the surface of the earth. We merely modify the result here for application to the energy transfer problem.

The geometry is the following: The dipole is embedded in a nonabsorbing dielectric (region 1) and is located at a distance d from the mirror (region 2). A perpendicular to the mirror defines the z direction. The origin of the coordinate system is taken to be on the interface between region 1 and region 2. We will first consider the parallel case, i.e., the dipole is oriented in the x direction parallel to the mirror. The Hertz vector Π at a point R (coordinates x, y, z) is given for this geometry as[9]:

$$\Pi^{\parallel} = \hat{e}_x\mu\left(\frac{e^{ik_1R_1}}{R_1} - \frac{e^{ik_1R_2}}{R_2} + \int_0^\infty \frac{2}{l+m}J_0(\rho\eta)e^{-\sigma l}\eta d\eta\right) + \hat{e}_z\mu\left(\frac{-2x}{\rho}\int_0^\infty \frac{(k_2^2 - k_1^2)J_1(\rho\eta)e^{-\sigma l}\eta^2 d\eta}{(l+m)(k_2^2 l + k_1^2 m)}\right), \tag{9}$$

where R_1 is the distance from the dipole to the point R, R_2 is the distance from the image dipole to the point R, and J_n is the nth order Bessel function. The remaining quantities are defined by

$$k_1 = \Omega n_1/c , \tag{10}$$

$$k_2 = \Omega\tilde{n}_2/c , \tag{11}$$

$$\tilde{n}_2 = n_2(1 + i\kappa_2) , \tag{12}$$

$$l = (\eta^2 - k_1^2)^{1/2} , \tag{13}$$

$$m = (\eta^2 - k_2^2)^{1/2} , \tag{14}$$

$$\rho = (R_2^2 - \sigma^2), \tag{15}$$

and

$$\sigma = z + d , \tag{16}$$

where n_1 is the real refractive index of region 1 and $\tilde{n}_2$ is the complex refractive index of region 2. The branch of the square root in l and m is determined so that the image field cancels when $k_1 = k_2$ (no boundary).

The Hertz vector $\Pi^{\perp}$ for the case in which the dipole is oriented perpendicular to the plane of the mirror is[9]:

$$\Pi^{\perp} = \hat{e}_z\mu\left[\frac{e^{ik_1R_1}}{R_1} + \frac{e^{ik_1R_2}}{R_2} + \int_0^\infty \frac{2k_2^2}{k_2^2 l + k_1^2 m}J_0(\rho\eta)e^{-\sigma l}\eta d\eta - \frac{2e^{ik_1R_2}}{R_2}\right] . \tag{17}$$

For both $\Pi^{\parallel}$ and $\Pi^{\perp}$, the first term represents the direct field of the dipole, the second represents the field of the image dipole, and the remaining two terms are corrections to the image result. The electric field at any point in the dielectric (region 1) can be found as

$$\mathbf{E} = \frac{1}{n_1^2}\left[k_1^2\Pi + \nabla(\nabla\cdot\tilde{\Pi})\right] . \tag{18}$$

Using Eq. (18), we find the following expressions for the reflected field at the original dipole (that part of $\mathbf{E}$ which comes from all of Π except the direct term):

$$E_R^{\parallel} = \frac{\mu\hat{e}_x}{n_1^2}\left[\left(-\frac{k_1^2}{\sigma} + \frac{1}{\sigma^3} - \frac{ik_1}{\sigma^2}\right)e^{ik_1\sigma} + k_1^2\left(2\int_0^\infty \frac{e^{-\sigma l}\eta d\eta}{l+m} - \int_0^\infty \frac{e^{-\sigma l}\eta^3 d\eta}{k_1^2 m + k_2^2 l}\right)\right] , \tag{19}$$

and

$$E_R^{\perp} = \frac{\mu\hat{e}_z}{n_1^2}\left[\left(\frac{2}{\sigma^3} - \frac{2ik_1}{\sigma^2}\right)e^{ik_1\sigma} - 2k_1^2\int_0^\infty \frac{me^{-\sigma l}\eta^3 d\eta}{(k_2^2 l + k_1^2 m)l}\right] , \tag{20}$$

where σ is now simply the distance between the dipole and its image, i.e., $\sigma = 2d$. $E_R^{\parallel}$ and $E_R^{\perp}$ refer to the cases of the dipole oriented parallel to the mirror and perpendicular to the mirror respectively. The terms containing $e^{ik_1\sigma}$ are in each case the image terms; the remaining terms are corrections to the image result which are extremely important at small distances and tend to zero at large distances.

Our results seem very different from Kuhn's approximate expressions for the reflected field which he takes to be the field of the image dipole modified by a phase factor δ at reflection and by a reflectivity R^2. He obtains, for example, in the parallel case

$$E_R = \hat{e}_x\frac{\mu R e^{-i\delta}}{n_1^2}\left(\frac{k_1^2}{\sigma} - \frac{1}{\sigma^3} + \frac{ik_1}{\sigma^2}\right)e^{ik_1\sigma} . \tag{21}$$

However, in the limit of perfect reflection ($k_2 \to \infty$), we have $R^2 = 1$ and $\delta = \pi$; similarly, m approaches infinity and the two expressions agree. For the case $k_2^2 \gg k_1^2$, an asymptotic expansion of the exact expression gives a

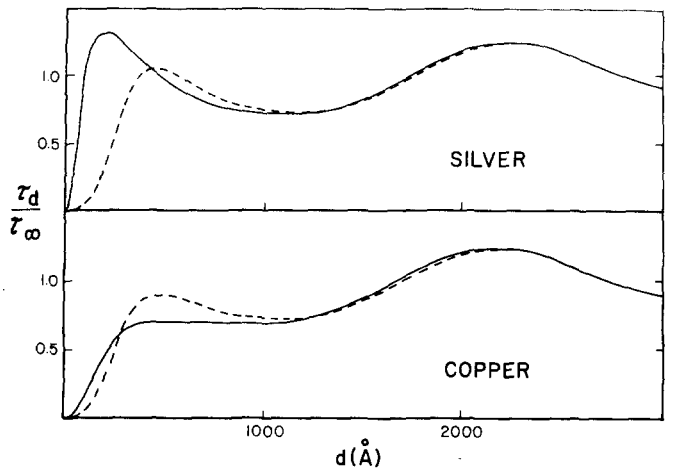

FIG. 1. Comparison of our theory (—) with Kuhn's theory (— —) for the normalized lifetime of an excited molecule oriented parallel to an a distance d from a metal mirror. The molecule is oriented in a nonabsorbing medium with $n_1 = 1.50$ and $\lambda = 612$ nm.

correction term which is proportional to d^{-3}; thus, we expect deviations of Kuhn's result from the exact result at small d. Both Eq. (20) and Eq. (21) are proportional to σ^{-3} for small σ; however the factor multiplying σ^{-3} is different in the two cases. For $n(=k_2/k_1)$ large, we find the difference to be $2\mu\hat{e}_x \exp(ik_1\sigma)/(n\sigma^3 n_1^2)$. It is this difference which gives rise to the dramatic differences in lifetime for small σ calculated from Eq. (20) and Eq. (21). This is indeed borne out by the calculations reported in the following sections.

The numerical computations were performed using Eqs. (8), (19), and (20). Both direct complex integration and real integration following an initial extraction of $\mathrm{Im}(E^0)$ yielded the same results. Gauss's formula was used to evaluate all integrals.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show a comparison of our theory with Kuhn's theory for the parallel and perpendicular cases,

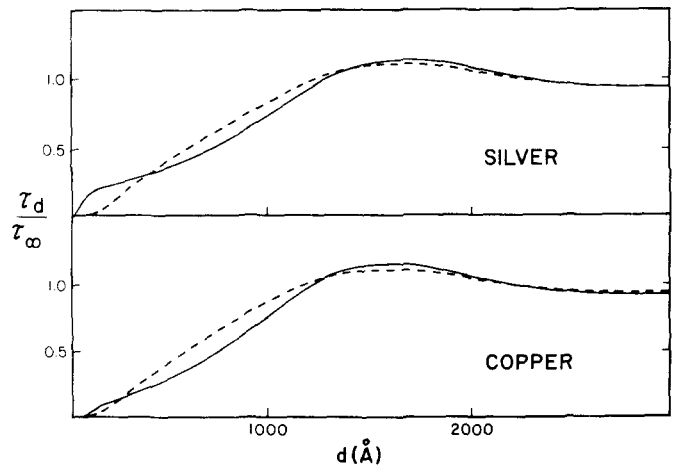

FIG. 2. Comparison of our theory (—) with Kuhn's theory (— —) for the normalized lifetime of an excited molecule oriented perpendicular to and a distance d from a metal mirror.

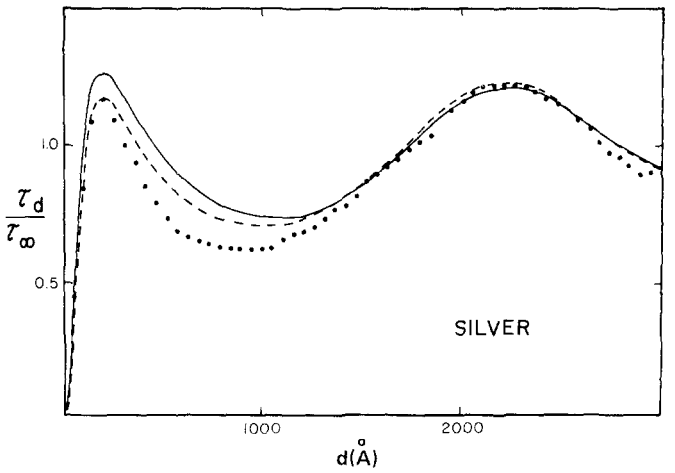

FIG. 3. Normalized lifetime versus distance for the Eu^{+3}/silver system. The solid curve corresponds to a quantum yield, q, of 0.85 and a parallel dipole component fraction ($F_{\parallel}$) of unity. The dashed curve corresponds to $q = 1.0$ and $F_{\parallel} = 0.89$. The optical constants ($n_1 = 1.50$, $n_2 = 0.06$, and $n_2 k_2 = 4.11$) are taken from Refs. 13 and 14.

respectively. The normalized lifetime results are shown for two sets of values for the optical constants of the mirror[13]: $n_2 = 0.06$, $n_2\kappa_2 = 4.11$ (silver) and $n_2 = 0.327$, $n_2\kappa_2 = 3.14$ (copper). In the range of distances close to the mirror, up to a few hundred angstroms, our results are much more sensitive to changes in the optical constants than are results which are based on the image theory. Note that the substantial differences between the two theories which occur for small distances gradually disappear at large distances, as expected.

Figures 3–5 show how the present theory compares with the experimentally measured[1,2] lifetime for europium complex I (emission at $\lambda = 612$ nm) as a function of distance from silver, gold, and copper mirrors. Cadmium arachidate layers ($n_1 = 1.50$ and $n_1\kappa_1 = 0$)[14] were used as spacers to establish the emitter–mirror distance. In the comparison of his modified image theory

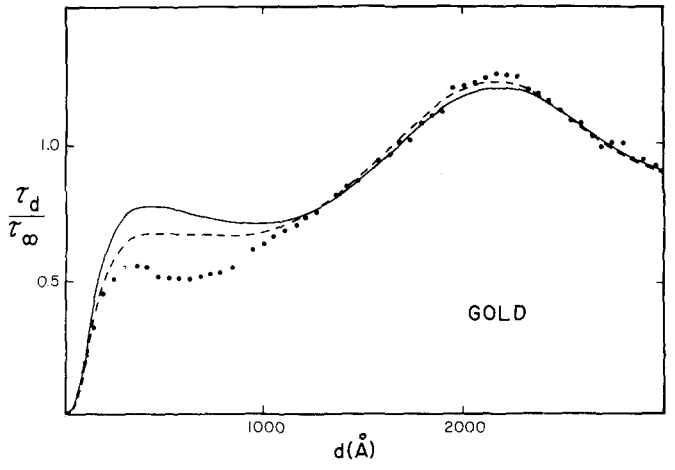

FIG. 4. Normalized lifetime versus distance for the Eu^{+3}/gold system. (—), $q = 0.85$, $F_{\parallel} = 1.0$; (— —), $q = 1.0$, $F_{\parallel} = 0.89$. The optical constants of gold ($n_2 = 0.215$ and $n_2 k_2 = 3.22$) are taken from Ref. 13.

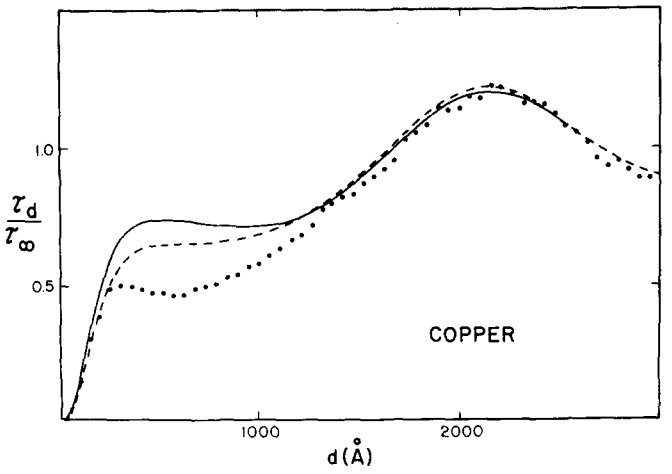

FIG. 5. Normalized lifetime versus distance for the Eu^{+3}/copper system. (—), $q=0.85$, $F_{\parallel}=1.0$; (— —), $q=1.0$, $F_{\parallel}=0.89$. The optical constants ($n_2=0.327$ and $n_2k_2=3.14$) are taken from Ref. 13.

to these experimental results, Kuhn[7] assumed that the emitting dipole was oriented parallel to the mirror. Morawitz[4] and Drexhage,[15] analyzed the same data in terms of a parallel dipole component fraction ($F_{\parallel}$) and a perpendicular component fraction ($F_{\perp}$). Assuming a random arrangement of dipoles ($F_{\parallel}=2/3$; $F_{\perp}=1/3$), they obtained reasonable agreement with the large distance behavior but again, since the metal was assumed to be a perfect reflector, poor agreement at small distances.

The solid curves in Figs. 3–5 are our results assuming the dipole to be oriented parallel to the mirror. The only adjustable parameter in these calculations is the quantum yield[16]; setting $q=0.85$ gives a good fit to all these sets of data. As indicated earlier,[11] the quantum yield sets the amplitude scale for the lifetime oscillations and is therefore, determined essentially by the large distance behavior of the experimental lifetime measurements.[17]

If we assume a quantum yield of unity and allow the parallel component fraction to vary, the fit is imporved somewhat as shown by the dashed curves in Figs. 3–5; $F_{\parallel}=0.89$ is found to give a good fit to all three sets of data.[18] Again, this parameter is determined essentially from the large distance behavior.[17]

In both approaches outlined above, the agreement between the present theory and the experimental observation is quite adequate at all distances. In particular, the rising edge and the location of the first maximum in the lifetime data are reproduced almost exactly. The latter point is especially evident in the case of silver, where a well defined maximum in the data is discernible. Other theoretical approaches have failed to explain the large differences in the experimental results for silver, gold, and copper mirrors at small distances. Our theory is seen to describe this behavior very well.

There does, however, seem to be a small but significant deviation between theory and experiment in the 200–1000 Å range consistent through all three sets of data. This may result from the fact that the experiments were done in air without the use of any index matching immersion liquid. Thus, the experiments introduce another interface—Cd arachidate/air—which may significantly perturb the results at small distances.[19]

IV. CONCLUSIONS

We have shown that a classical approach, including near field effects, is adequate to describe the observed lifetime vs emitter–mirror distance in these metal insulator systems. The deviations from the image theory result are very important at small distances, but decrease as d^{-3} when the emitter is moved away from the mirror. This result is in agreement with the experimental systems discussed here, and also with the observations made by other workers in more complicated systems,[20,21,22] as well as the recent work of Tews.[12]

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[17]The experiment data for the silver and gold mirrors are available to about $d = 6000$ Å and are included in these determinations. As shown earlier,[11] the agreement in the 3000–6000 Å range is quite good.

[18]The theoretical lifetime for these two component systems is determined from the best single exponential representation of a similated emission versus time profile.

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