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Fluorescence and energy transfer near interfaces: The complete and quantitative description of the Eu^{+3}/mirror systems*

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The classical electromagnetic description of fluorescent emission and energy transfer in the Eu^{+3}/mirror systems is shown to be in quantitative agreement with the results of eight experimental systems studied by the fatty acid monolayer assembly technique. The emitter lifetime measured as a function of distance from the mirror(s) is found to be consistent with an isotropic spatial orientation for the emitter in all cases; furthermore, it is shown to be exclusively so in most of these cases. Both the quantum yield and the radiative lifetime of the luminescent state of the Eu^{+3} ion are determined by theoretical fits to the data. Whereas the quantum yield spans a range of 0.69–0.86, the radiative lifetime of the electric dipole transition at 612 nm is nearly constant, as required, with a value of 803 ± 29 μsec. Both the quantitative agreement between theory and experiment and the consistency among the eight experimental systems in predicting the radiative lifetime provide a clear demonstration of the utility of the fatty acid monlayer assembly technique as a method of measurement of emission properties of lunimescent systems and of dielectric properties of surfaces.

I. INTRODUCTION

The Langmuir–Blodgett technique[1,2] of monolayer spreading and deposition has been perfected by Kuhn and co-workers[3–10] as a method of assembling organized systems of molecules. This technique has been employed for studying various physical processes which require dimensional control on the molecular scale—short range energy transfer, for example. In the energy transfer studies, fatty acid monolayers are used as spacers to locate the emitter at a well defined distance from a thin absorbing layer. The distance dependence of the emitter lifetime yields information on the quantum yield and the multipole nature of the luminescent state.

The fatty acid spacer technique has also been used to study the effect of a thick metal mirror on the luminescent lifetime. In the original experiments[11,12] the lifetime of an europium complex (Eu^{+3} emission at 612 nm) was measured as a function of distance from silver, copper, and gold mirrors. Dramatic effects were observed at distances which were well beyond the energy transfer region. Since the original reporting of these experiments, the Eu^{+3}/silver data have appeared in at least twelve publications.[7,9,13–22]

The interaction of the dipole emitter and the mirror (or really the interaction of the dipole with its own reflected radiation field) has been discussed from several different points of view,[7,12,13,20] all of which are physically equivalent, though the results differ owing to the different approximations made in the description of the radiation field of the dipole. Drexhage's original approach[12,14] (the interference method) involved looking at the interference between a primary ray exiting directly from the dipole and a ray reflected from the mirror. Morawitz[13] described the phenomenon—both from a classical and a quantum mechanical point of view—as the coupling of an excited two-level system with itself through the radiation field of an electric dipole. Kuhn[7] discussed the effect as that of a driven harmonic oscillator where the oscillatory external force is the dipole's own reflected radiation field. The approximate form chosen by Kuhn for the reflected field included, for the first time, nonradiative energy transfer to the mirror—an effect which dominates the lifetime behavior at short distances. All of these approaches provided reasonable agreement with the Eu^{+3}/metal mirror experiments in the large distance range but poor agreement in the short distance range because of the approximate forms which were used to describe dipole radiation.

Actually, an enormous body of research had been done on the mathematical formulation of this problem by Sommerfeld,[23] Weyl,[24] and others[25–27] owing to its application to radio and radar wave propagation with the earth as a reflector. The analogy was pointed out by Mora-

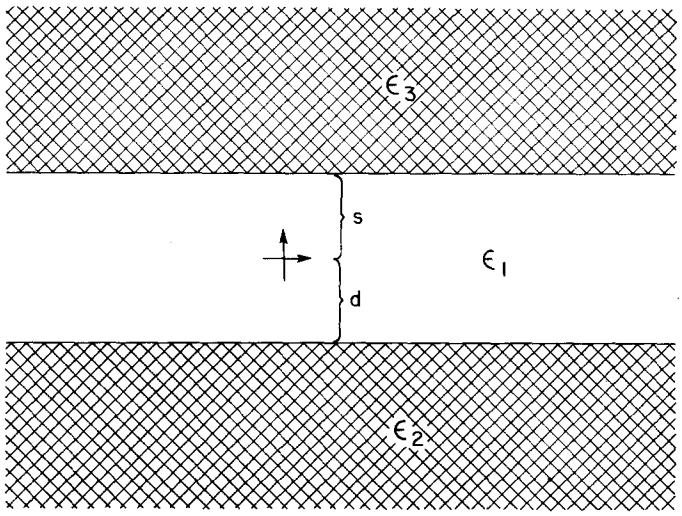


FIG. 1. Geometry of the two mirror problem. The quantities d and s are the distances between the dipole and the mirrors. The mirrors are parallel and infinite in extent.

witz[13] and later used by Tews[16,17] and Chance *et al.*[18,19] to obtain an exact classical description of the dipole/single mirror systems, i.e., the description of dipole radiation was exact within the classical framework. The agreement between experiment and theory improved dramatically when it was assumed that the dipole was oriented parallel to the mirror in the Eu^{+3}/metal systems. This conclusion was, however, inconsistent with other experiments in which the mirror was a nonabsorbing dielectric (air).[14,28] In that case only an isotropic distribution of dipole configurations was consistent with the experimental data. The existence of a second interface in the metal mirror systems (i.e., the system was actually metal/Eu^{+3}/air) was cited as a probable source of the discrepancies between theory and experiment.[13,19,29] Also, Drexhage has suggested the presence of this air layer as the explanation of the inconsistency between the different Eu^{+3} mirror systems in predicting the dipole orientation relative to the mirror.[29] To a large extent, it was this suggestion by Drexhage that prompted us to extend the theory to the case of an emitter between two parallel mirrors.

Philpott[30] and Milonni and Knight[31] have presented quantum mechanical treatments of the problem of an emitter between two parallel mirrors. More recently, Chance *et al.*[32] have presented the exact classical description of this same problem and have shown that the classical result is identical with the results of the quantum mechanical approach for the case of two perfectly reflecting mirrors. Drexhage[21] has used the interference method to treat the double mirror problem. Since only the far field component of the total radiation field is included in the interference method, this approach describes only the effects of the mirrors on the *radiative* component of the lifetime.[33]

In this paper, we have applied the exact classical description of the double mirror problem to eight experimental systems all involving the 612 nm emission of an europium ion complex in various mirror configurations. We are confident that the now complete theoretical description of these experimental systems contains all important aspects of the problem.

II. THEORY

The mathematical formulation of the dipole/single mirror systems has been described in some detail previously.[16–19,33] (See also Refs. 23, 34, and 35.) The treatment of two mirror problem differs only in complexity, and only the results will be given here.

The geometry of the problem is shown in Fig. 1. The emitter (assumed to be an oscillating electric dipole) is embedded in a nonabsorbing medium (Region 1) and is located at a distance d from Region 2 and a distance s from Region 3. No restrictions need be placed on the dielectric constants except that they be isotropic:

$$\epsilon_j = n_j^2 - K_j^2 + i2n_jK_j\,, \tag{1}$$

where n_j and K_j are the real and imaginary parts of the refractive index of Region j.

Two physically equivalent approaches may be taken to predict the effect of the mirrors on the lifetime of the emitting dipole.[33,36] In each case the Hertz vectors are constructed by matching the appropriate boundary conditions at the two interfaces. We may then follow Kuhn[7] and calculate the reflected radiation field at the dipole position. This is in turn inserted into the equation of motion of the dipole which is solved for the lifetime and frequency shift.[7,19] As the frequency shift is completely negligible in the systems of interest here,[19,37] we may alternately determine the lifetime by integrating the normal component of the complex Poynting vector over the planes of the two mirrors.[33,36] This method allows the determination of the radiative and nonradiative components of the total lifetime expression (and, therefore, also the effect of the mirror on the quantum yield).[33]

A third approach, which does not require the construction of the Hertz vectors, is based on Drexhage's interference method. If, in his integration over angles of incidence, complex angles of incidence are included, then the results of the previous two methods are obtained.[38] (See also Refs. 23 and 24.)

With any of the three methods outlined above, we find that the damping constants (inverse lifetimes) for dipoles oriented parallel and perpendicular to the mirrors are given by

$$b^{\perp,\parallel} = b^0(1 - qG^{\perp,\parallel})\,, \tag{2}$$

where b^0 is the damping constant in the absence of both mirrors and q is the quantum yield of the luminescent state—the latter being the primary parameter in the fit to the experiment data. The remaining quantity $G^{\perp,\parallel}$ depends only on the distances $\hat{d}\,(\equiv 2\pi n_1 d/\lambda)$ and $\hat{s}\,(\equiv 2\pi n_1 s/\lambda)$ and the optical constants of the three regions:

$$G^{\perp} = 1 - \tfrac{3}{2}\,\mathrm{Im}\int_0^{\infty} \frac{F(\hat{d}, -R_{12}^{\parallel})\,F(\hat{s}, -R_{13}^{\parallel})}{F(\hat{d}+\hat{s}, -R_{12}^{\parallel}R_{13}^{\parallel})}\,u^3\,du/l \tag{3}$$

and

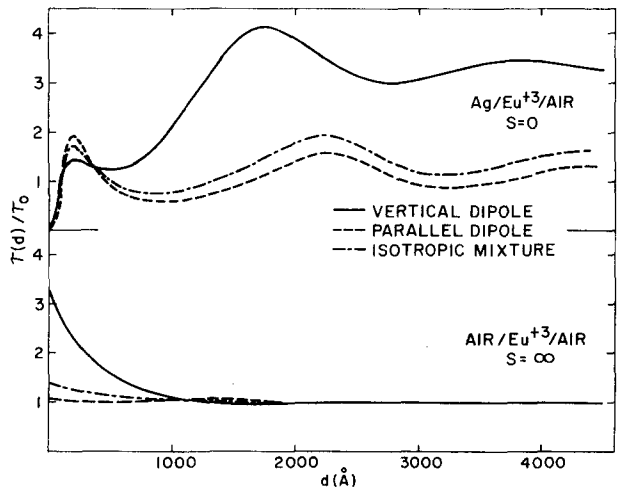


FIG. 2. Effect of dipole orientation on lifetime vs distance curves in single ($s=\infty$) and double ($s=0$) mirror systems with Eu^{+3} emission at 612 nm (quantum yield taken as unity). The lifetimes [$\tau(d)$] are in each case normalized to the value (τ_0) in the absence of both mirrors ($d, s \to \infty$). As $d \to \infty$, the lifetimes in the silver–air double mirror system approach the $d=0$ lifetimes in the air single mirror system for each of the three distributions of dipole orientations, respectively.

$$G^{\parallel} = 1 - \tfrac{3}{4}\,\mathrm{Im}\int_0^{\infty}\left[\frac{F(\hat{d}, R_{12}^{\perp})\,F(\hat{s}, R_{13}^{\perp})}{F(\hat{d}+\hat{s}, -R_{12}^{\perp}R_{13}^{\perp})} + (1-u^2)\,\frac{F(\hat{d}, R_{12}^{\parallel})\,F(\hat{s}, R_{13}^{\parallel})}{F(\hat{d}+\hat{s}, -R_{12}^{\parallel}R_{13}^{\parallel})}\right] u\,du/l\,, \tag{4}$$

where $F(x, y) \equiv 1 + y\exp(-2l_1 x)$. The reflectivities of the two interfaces are given as

$$R_{12}^{\perp} = (l_1 - l_2)/(l_1 + l_2), \tag{5}$$

$$R_{12}^{\parallel} = (\epsilon_1 l_2 - \epsilon_2 l_1)/(\epsilon_1 l_2 + \epsilon_2 l_1), \tag{6}$$

$$R_{13}^{\perp} = (l_1 - l_3)/(l_1 + l_3), \tag{7}$$

and

$$R_{13}^{\parallel} = (\epsilon_1 l_3 - \epsilon_3 l_1)/(\epsilon_1 l_3 + \epsilon_3 l_1), \tag{8}$$

where

$$l_j \equiv -i(\epsilon_j/\epsilon_1 - u^2)^{1/2}. \tag{9}$$

The experimental data for the Eu^{+3} systems have the form: lifetime [$\tau(d)$] as a function of distance (d) from one mirror (Region 2) with the distance (s) from the second mirror (Region 3) remaining constant. If we assume the optical constants are known quantities, we are left with the following unknowns: the quantum yield of the luminescent state, the orientation of the dipole relative to the mirrors, and the lifetime in the absence of the mirrors ($\tau_0 \equiv 1/b^0$), which is known at least approximately in each case. If the dipole is oriented at an angle θ relative to the mirror normal, then the lifetime is given as[17]

$$\tau(d, \theta) = \tau_0\,[\sin^2\theta b^{\parallel} + \cos^2\theta b^{\perp}]^{-1}, \tag{10}$$

or for an isotropic distribution of dipole configurations,

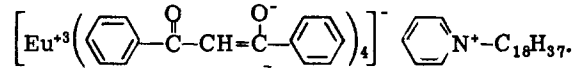
$$\tau(d) = \tau_0\,[\tfrac{2}{3}b^{\parallel} + \tfrac{1}{3}b^{\perp}]^{-1}. \tag{11}$$

As shown by Fig. 2, the lifetime behavior for the different dipole configurations is quite different. As pointed out in the next section, the experimental data are consistent only with the isotropic distribution.

In most of the experimental systems to be considered here, the remaining unknowns, τ_0 and q, can be determined essentially independently from the theoretical fits to the data. (They are completely independent at large distances where nonradiative energy transfer to the mirror does not affect the emitter lifetime.) As is obvious from the above discussion, τ_0 is simply a normalization factor. Though accessible experimentally, τ_0 has been determined accurately for only one of the eight systems considered here. The quantum yield of the luminescent state is then the primary parameter in the theoretical fits to the data and determines the magnitude of the oscillations about $\tau(\infty)$, the value that the lifetime approaches as d approaches ∞. [In single mirror systems, $\tau(\infty) = \tau_0$.]

III. COMPARISON TO EXPERIMENTAL DATA

The eight experimental systems are all of the form mirror/D fatty acid layers/emitter/S fatty acid layers/air, where D and S are the number of fatty acid layers deposited in the indicated positions. Since each layer is 26.4 Å thick, we have for the distances between the emitter and the two mirrors $d = D \times 26.4$ Å and $s = S \times 26.4$ Å. The emitter is in each case



The energy is absorbed in the four ligands and subsequently transferred nonradiatively to the Eu^{+3} which emits at 612 nm with a lifetime of about 1 msec. The mirror is either silver, gold, copper, or air. The optical constants of the metals are taken from Johnson and Christy.[39] The refractive index (n_1) of the fatty acid layers is taken to be 1.5 throughout.[8,12,40]

The lifetime of the Eu^{+3} is measured as a function of D with S fixed. In the systems considered here, $S=0$ $S=$ "∞" (single mirror), or $S=40$ ($s=1056$ Å). The rather

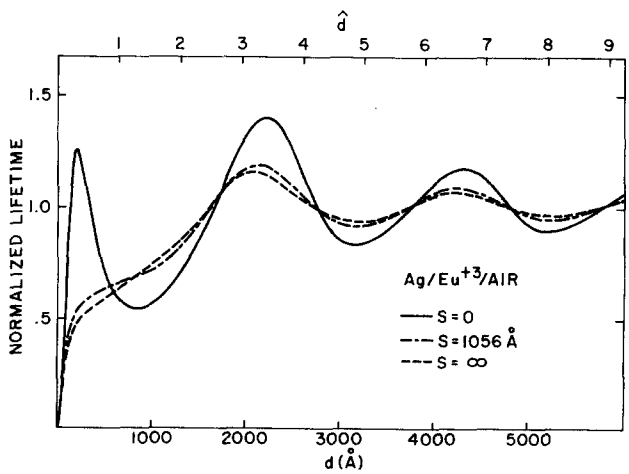


FIG. 3. Normalized lifetime vs distance for the Ag/Eu^{+3}/air system. Each curve has been normalized to approach unity as d approaches infinity. The quantity s is the distance between the emitter and the air/fatty acid interface.

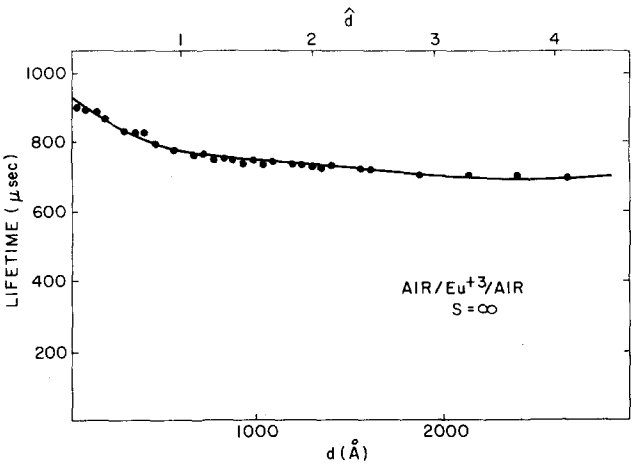


FIG. 4. Lifetime vs distance for System I. The experimental data are from Tews.[16,28] The solid curve represents the best fit to the data: $\tau_0 = 709$ μsec and $q = 0.857$.

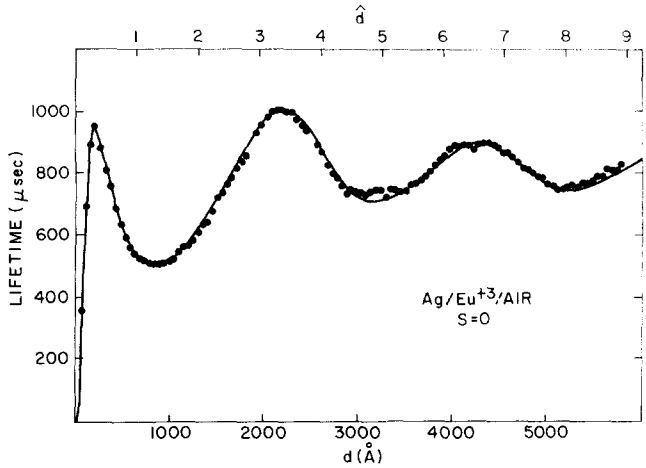


FIG. 6. Lifetime vs distance for System III. The experimental data are from Drexhage.[11,12] The solid curve represents the best fit to the data: $\tau_0 = 632$ μsec and $q = 0.760$.

dramatic effect of the air layer on the lifetime versus distance curves is illustrated in Fig. 3 for the silver mirror system.

Equation (11) is used to fit each set of experimental data. The quantities τ_0 (lifetime in absence of both mirrors) and q (quantum yield of the luminescent state) are varied to minimize the sum-of-squares deviation between theory and experiment. Theoretical and experimental results are compared for the following eight systems:

System I is air/d variable/Eu$^+$/$s = \infty$ as measured by Tews.[16,28] As is true of all eight systems, d is varied by introducing a specific number of fatty acid layers. The $s = \infty$ value results from assuming that the glass slide support has the same refractive index (1.5) as the fatty acid layers.

System II is also air/d variable/Eu^{+3}/$s = \infty$ as measured by Drexhage.[14] Though Systems I and II differ in some preparative details, they may be considered identical in the theoretical interpretation.

System III is silver/d variable/Eu^{+3}/air ($s = 0$) as measured by Drexhage.[12,14] The construction of this system proceeds as follows: (1) Silver is evaporated onto a glass slide to a thickness which is much greater than the absorption depth at 612 nm; (2) The desired number of fatty acid spacers are added by the monolayer assembly technique; and (3) A final layer is added containing the Eu^{+3} complex. Thus the dye layer is sandwiched between the fatty acid layers and an air half-space, i.e., $s = 0$.

System IV is silver/d variable/Eu^{+3}/$s = 1056$ Å/air as measured by Drexhage.[29] The construction is the same as System III except that, in a fourth step, 40 fatty acid cover layers are added. Since each layer is 26.4 Å thick, the Eu^{+3} complex is 1056 Å from the air half-space, i.e., $s = 1056$ Å. These data have not been published previously.

System V is gold/d variable/Eu^{+3}/air ($s = 0$) as measured by Drexhage.[12] The construction is the same as

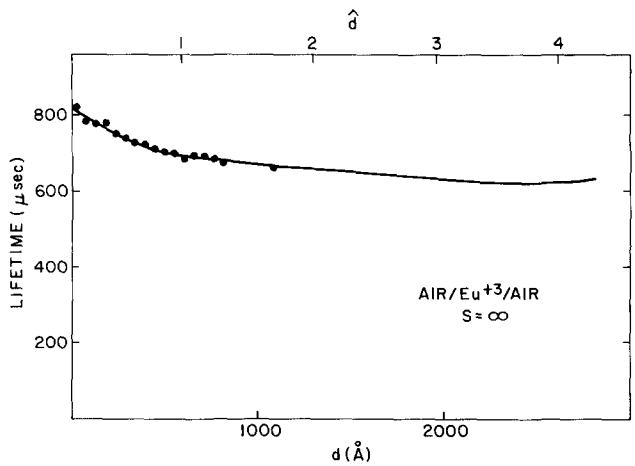


FIG. 5. Lifetime vs distance for System II. The experimental data are from Drexhage.[14] The solid curve represents the best fit to the data: $\tau_0 = 637$ μsec and $q = 0.777$.

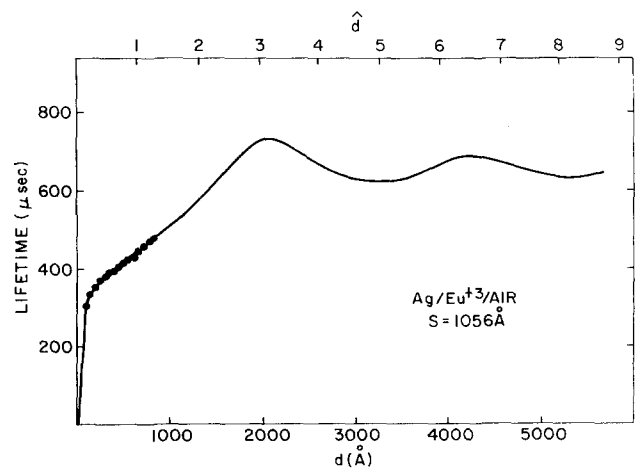


FIG. 7. Lifetime vs distance for System IV. The experimental data are from Drexhage.[29] The solid curve represents the best fit to the data: $q = 0.795$. The τ_0 value (625 μsec) is derived from Drexhage's estimate[29] and used without further adjustment.[41]

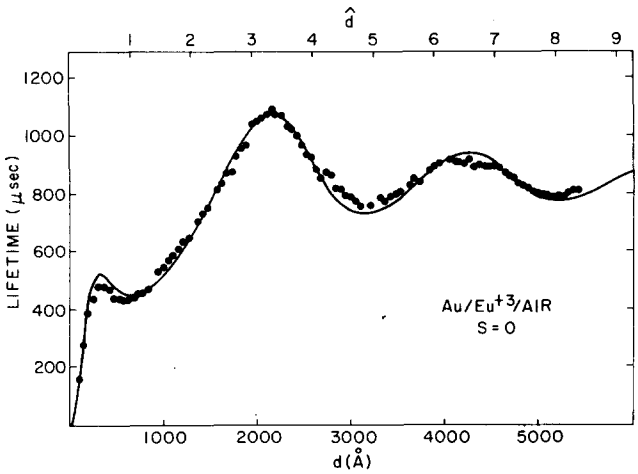


FIG. 8. Lifetime vs distance for System V. The experimental data are from Drexhage.[11,12] The solid curve represents the best fit to the data: $\tau_0 = 639$ μsec and $q = 0.818$.

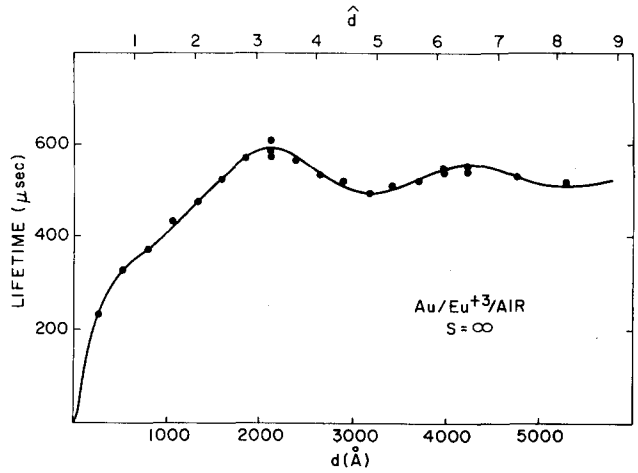


FIG. 10. Lifetime vs distance for System VII. The experimental data are from Drexhage.[21] The solid curve represents the best fit to the data: $\tau_0 = 536$ μsec and $q = 0.688$.

System III.

System VI is gold/d variable/Eu^{+3}/$s = 1056$ Å/air as measured by Drexhage.[29] The construction is the same as System IV. These data have not been published previously.

System VII is gold/d variable/Eu^{+3}/$s = \infty$ as measured by Drexhage.[21] The construction is the same as System IV (or VI), except that the entire assembly is immersed in a dielectric matching liquid, i.e., $s = \infty$.

System VIII is copper/d variable/Eu^{+3}/air ($s = 0$) as measured by Drexhage.[12] The construction is the same as System III.

The results for System I are shown in Fig. 4 along with the experimental data from Tews.[16,28] The best fit obtains for $\tau_0 = 709$ μ sec and $q = 0.857$. This is the only system for which anything more than an estimate of τ_0 has been determined in the course of the experiment. Tews reports the experimental value as $\tau_0 = 720$ μ sec. The 1.5% deviation between his value and our best-fit value is well within experimental precision of the measurements (about 3%–4%).[16,28,29] Referring back to Fig. 2, it is quite clear that only the isotropic distribution of dipole configurations can explain the experimental data.

The results for System II are shown in Fig. 5. The best-fit values of τ_0 and q are 637 μ sec and 0.777, respectively. The results for Systems I and II would seem to be in disagreement, since, except for preparative details, they are identical. However, the quantum yield may well depend on the details of the preparation of the dye and fatty acid monolayers. (In fact, q could vary within a given experimental run; this fluctuation probably makes a significant contribution to the precision of the measurements.) The radiative lifetime ($\tau_r \equiv \tau_0/q$) of the

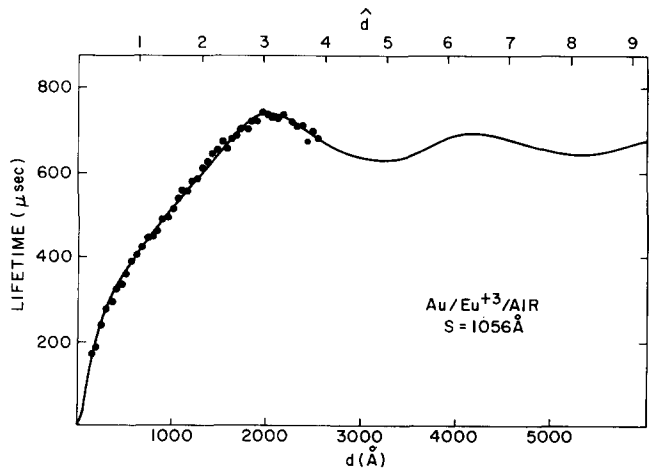


FIG. 9. Lifetime vs distance for System VI. The experimental data are from Drexhage.[29] The solid curve represents the best fit to the data: $q = 0.767$. The τ_0 value (625 μsec) is derived from Drexhage's estimate[29] and used without further adjustment.[41]

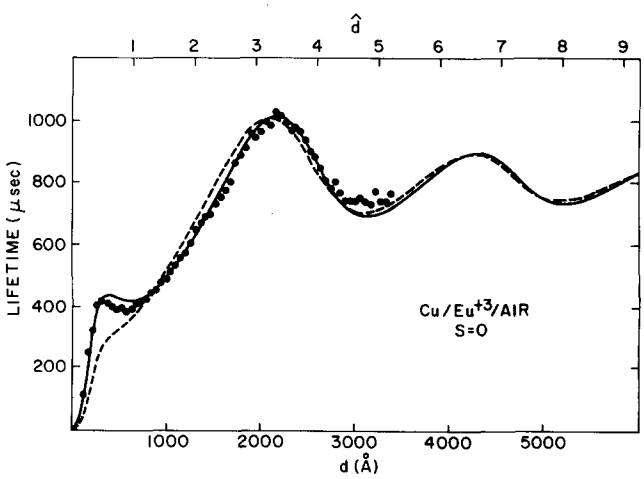


FIG. 11. Lifetime vs distance for System VIII. The experimental data are from Drexhage.[11,12] The solid curve represents the best fit to the data: $\tau_0 = 620$ μsec and $q = 0.801$. The dashed curve results when an alternate set of optical constants is chosen for copper. (See Table I.) The large reduction in the lifetime in the short distance range, as predicted by the dashed curve, results from an increased probability of nonradiative transfer to the copper.[33]

TABLE I. Optical constants of silver, copper, and gold at 612 nm.

Metal	n_2 [a]	K_2 [a]
Silver	0.06 (0.10)	4.11 (4.00)
Gold	0.215 (0.047)	3.22 (3.60)
Copper	0.327 (0.35)	3.14 (2.60)

[a]Taken from Johnson and Christy[39] (with small interpolation). The values shown in parenthesis were used previously by Tews[17] in fitting the lifetime data.

612 nm transition in Eu^{+3} would be expected to be the same regardless of the system. We find $\tau_r = 827$ μsec from Tew's data and $\tau_r = 820$ μsec from Drexhage's data. (Within the classical description, the radiative lifetime is expected to be inversely proportional to the refractive index of the surrounding medium.[7,19] All τ_r values reported herein refer to a medium of refractive index 1.50.)

The agreement between theory and experiment for System III is shown in Fig. 6 and is well within experimental error at all distances. The experimental data for System IV (Fig. 7) have been supplied to us by Drexhage and have not been published previously. The two data sets clearly illustrate the dramatic effect the air layer has on the lifetime variations (see Fig. 3). Because of the small number of data points in System IV, all of which were restricted to the short distance range, a fairly wide range of q and τ_0 combinations give an adequate representation of the data. Therefore, Drexhage's estimate[29] of τ_0 was corrected for the presence of the air layer and used without further adjustment.[41] (The same is true for System VI discussed below.)

The results illustrated in Fig. 6, taken alone, strongly suggest an isotropic distribution of dipole orientations, since, if the distribution deviates significantly from isotropic, the goodness of the fit is destroyed. Also, the previously discussed results with air mirrors (Figs. 4 and 5) predict a radiative lifetime ($\tau_r \equiv \tau_0/q$) of about 825 μsec. If the data of Fig. 6 are fit with the theoretical results for a parallel dipole $\tau_r = 1006$ μsec is obtained. The isotropic case yields $\tau_r = 832$ μsec, in good agreement with the air mirror results. The same argument holds true for the other metal mirrors. Further, in comparing Figs. 6 and 7, the almost complete disappearance of the first peak in the lifetime at $d \approx 200$ Å can only be explained with the isotropic distribution.

The results for Systems V,[12] VI,[29] and VII[21] are shown in Figs. 8, 9, and 10, respectively. The large effect of the air layer is again shown clearly in comparing Systems V and VII. (In the case of the System VI, Drexhage's estimate of τ_0 was used.)[41] The data of System VI were supplied to us by Drexhage and have not been published previously.

The results for System VIII[12] are shown in Fig. 11. As is true of the gold/$s = 0$ results, the agreement in the short distance range is not as striking as is the case for the silver data and, in certain regions of the copper and gold/$s = 0$ data, is probably outside of the expected experimental error. In this short distance region, nonradiative energy transfer occurs from the emitter to the absorbing mirror. This process is extremely sensitive to the optical constants of the metal.[33] Errors in the optical constants (or contamination of the surface region of the metal) would most strongly affect the curve shape in the short distance region. The effect of varying the optical constants is shown clearly by the dashed curve in Fig. 11 which represents the best fit, for data points at distances greater than 650 Å only, when the alternate set of optical constants shown in Table I is used for copper. No further attempt has been made for finding the best optical constants for copper (or gold) to improve the fit. If the alternate set of optical constants is used for the gold data, the fit in the short distance region improves slightly.

IV. SUMMARY AND CONCLUSIONS

The results are summarized in Table II. Though the quantum yield varies from 0.69–0.86, the radiative life-

TABLE II. Summary of results.

System[a]	Mirror	d(Å)	s(Å)	q[b]	τ_0(μsec)[b,c]	τ_r(μsec)[e]	S.D. (%)[f]
I	Air	26–2666	∞	0.857	709[d]	827	1.4
II	Air	26–1082	∞	0.777	637	820	1.1
III	Silver	53–5861	0	0.760	632	832	2.2
IV	Silver	105–845	1056	0.795	625	786	3.5
V	Gold	158–5438	0	0.818	639	781	2.9
VI	Gold	158–2534	1056	0.767	625	815	2.4
VII	Gold	264–5280	∞	0.688	536	779	2.1
VIII	Copper	158–3379	0	0.801	620	774	3.7

[a]All data are from Drexhage[12,21,29] with the exception of the System I data, which are taken from Tews[16,28].
[b]The quantities q and τ_0 (with exceptions noted for Systems IV and VI[c]) are obtained as best fits of Eq. (11) to the experimental data.
[c]Drexhage's estimate of τ_0 was corrected for the presence of the air layer and used without further adjustment in Systems IV and VI. (See text).[41]
[d]Tews obtained 720 μsec experimentally.[28]
[e]Radiative lifetime ($\tau_r \equiv \tau_0/q$) of the Eu^{+3} emitter at 612 nm in a dielectric medium of refractive index n_1 (1.50).
[f]Relative standard deviation.

time is relatively constant for an average value of 803 ±29 μsec. As can be seen from Table II and the corresponding figures 4–11, the experimental data from all eight systems can be quantitatively explained using classical electromagnetic theory. Of the three parameters mentioned above (orientation of the emitter, quantum yield of luminescent state, and radiative lifetime in the medium), two have been fixed in order to obtain agreement in all cases: the orientation must be assumed random and the radiative lifetime is 803 ± 29 μsec. The other parameter, quantum yield, varies from 0.69 to 0.86—a fluctuation which we assume to result from the many steps involved in the preparative procedure. This agreement shows that this method is capable of quantitatively determining the properties of luminescent states, is useful in probing the dielectric properties of interfaces, and can be important in the future in studying surface properties. Furthermore, these conclusions are not restricted to electric dipole radiation nor to the particular mirror configurations discussed herein. We have recently extended the theory to include magnetic dipole and electric quadrupole radiation and to multicomponent stratified media.[38]

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[37]For the case of an europium complex emitting at 612 nm and located 26.4 Å (one fatty acid spacer) from a silver mirror, the predicted frequency shift is only about 10^6 Hertz.[38]
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[41]In general, it is felt that the parameterization of the τ_0 value is a useful approach only when it amounts to essentially an extrapolation of the data points at large distances, i.e., the parameters of q and τ_0 would be essentially independent of each other. When only short distance data are available, small uncertainties in the optical constants of the metal mirrors can affect the results considerably.