LUMINESCENT LIFETIMES NEAR MULTIPLE INTERFACES: A QUANTITATIVE COMPARISON OF THEORY AND EXPERIMENT

R.R. CHANCE, A.H. MILLER *
Materials Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960, USA

A. PROCK
Department of Chemistry, Boston University, Boston, Massachusetts 02215, USA

and

R. SILBEY **
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

Received 3 February 1975

Results are presented for the classical theory of an emitting dipole located between two parallel mirrors. The calculated lifetime variations are in quantitative agreement with experiment for the silver/dielectric /Eu^{3+}/ air system.

Recently, there has been considerable interest in the emission lifetime of an excited molecule as a function of distance from a reflecting surface [1–16]. The experimental data of Drexhage [1–3] have been interpreted using various approximate theories for the dipole–mirror interaction. We have recently applied [9–12] the classical theory of wave propagation [17–20] near a single surface to this problem and found good agreement with experiment (as has Tews [5] using a similar approach). This agreement was not perfect, and it was suggested that the discrepancy was related to the presence in the experiments of a second interface – that between the emitting molecule on the dielectric and the air layer above. We have now completed the theoretical description of the experiment within the classical model by including this second interface. We find excellent agreement between experiment and theory (see fig. 1) from distances of ≈ 50 Å to 6000 Å. We feel confident that this more complete description contains all the important aspects of the problem. The best fit for the model obtains with an isotropic distribution (i.e., 2/3 parallel and 1/3 perpendicular) of dipoles on the surface. The difference between the results including the air–dielectric interface and those assuming a homogeneous dielectric medium surrounding the dipole is illustrated in fig. 2. The effect of introducing the second interface is to decrease the emission rate of a perpendicular dipole with little effect on that of a parallel dipole [2, 6]. For example, in the absence of the metal mirror, the ratio of lifetimes for the two orientations is approximately 3 in these systems.

The theoretical expression for the emission rate in the presence of two surfaces can be written in a form resembling that found for one surface by a suitable definition of the reflectivity. We find for the emission rate (divided by the rate in the absence of both surfaces),

* Present address: Department of Chemistry, Northwestern University, Evanston, Illinois 60201, USA.

** Research supported in part by the National Science Foundation.

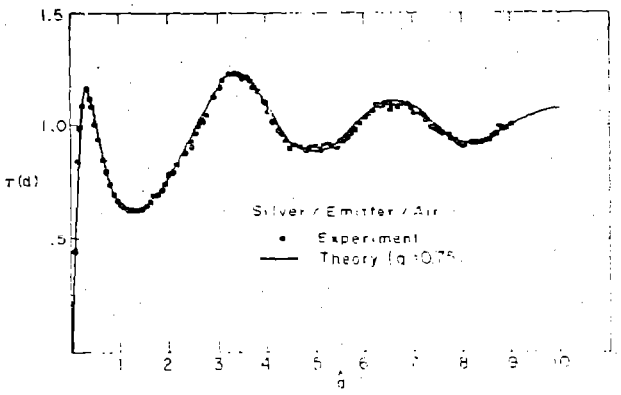

Fig. 1. Normalized lifetime versus distance ($\hat{d} \equiv 2\pi\epsilon_1^{1/2} d/\lambda$) for the silver mirror/fatty acid/Eu^{3+}/air system. The experimental data are those of Drexhage [1–3]; the theoretical curve represents our best fit to the data with an isotropic distribution of dipole orientations and the quantum yield (the only adjustable parameter) equal to 0.75. Both the data and the theoretical curve are normalized to approach one for large $\hat{d}$. The optical constants for silver are taken from Johnson and Christy [21] (λ = 6120 Å). To convert distance scale to Å multiply by 649.4 Å.

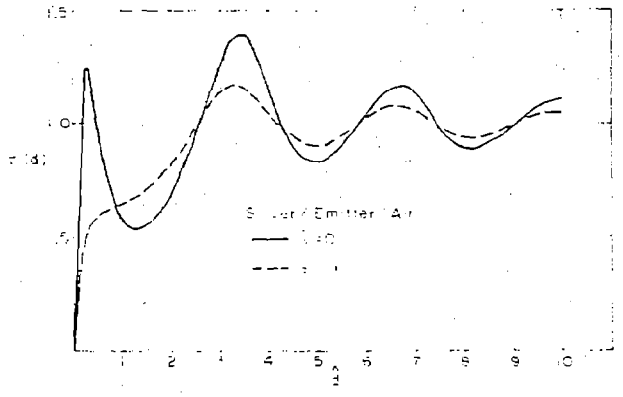

Fig. 2. Comparison of results for a single ($\hat{s} = \infty$) and double mirror systems ($\hat{s} = 0$) with an isotropic distribution of dipole orientations. The results are in each case normalized to approach unity at large $\hat{d}$. The solid curve is the same as that of fig. 1 except that here $q = 1$.

$$b^{\perp} = 1 - \tfrac{3}{2} q \,\mathrm{Im} \int_0^{\infty} \mathrm{d}\tau (\tau^3/l)\, \mathcal{R}_-^{\perp} , \tag{1a}$$

$$b^{\parallel} = 1 + \tfrac{3}{4} q \,\mathrm{Im} \int_0^{\infty} \mathrm{d}\tau (\tau/l)[\mathcal{R}_+^{\perp} + (1-\tau^2)\,\mathcal{R}_+^{\parallel}] , \tag{1b}$$

where q is the quantum yield of the luminescent state. The remaining quantities are given by the following:

$$\mathcal{R}_{\pm}^{\perp,\parallel} = [R_{12}^{\perp,\parallel} \mathrm{e}^{-2l_1\hat{d}} (1 \pm R_{13}^{\perp,\parallel} \mathrm{e}^{-2l_1\hat{s}}) + R_{13}^{\perp,\parallel} \mathrm{e}^{-2l_1\hat{s}} (1 \pm R_{12}^{\perp,\parallel} \mathrm{e}^{-2l_1\hat{d}})] \times [1 - R_{12}^{\perp,\parallel} R_{13}^{\perp,\parallel} \mathrm{e}^{-2l_1(\hat{d}+\hat{s})}]^{-1} , \tag{2}$$

$$R_{ab}^{\perp} = (\epsilon_b l_a - \epsilon_a l_b)/(\epsilon_b l_a + \epsilon_a l_b) , \tag{3}$$

$$R_{ab}^{\parallel} = (l_a - l_b)/(l_a + l_b) , \tag{4}$$

and

$$l_a = -\mathrm{i}[(\epsilon_a/\epsilon_1) - \tau^2]^{1/2} . \tag{5}$$

In the above, $\hat{d}$ is the distance from the dipole to region 2 in units of wavelength ($\hat{d} \equiv 2\pi\epsilon_1^{1/2} d/\lambda$) and $\hat{s}$ is the distance from the dipole to region 3 in the same units. In the present case (fig. 1) we have a silver mirror in region 2, air in region 3, dielectric in region 1, and $\hat{s} = 0$. In the absence of the second interface, we have $\hat{s} = \infty$ and recover our earlier results. The present form of the expression for the emission rate is written so as to resemble closely that which would obtain when only the wave zone contribution is considered [2, 3]. In that case the upper limit of the integral would be unity instead of infinity (and the calculated decay rate would correspond to the radiative component of the total decay rate [12]).

The present theory can be readily extended to describe many interfaces and a variety of experimental conditions. The experimental data of Drexhage [1–3] for other metal mirrors, dielectric interfaces (see also ref. [6]), and dielectric matching (i.e., removal of the air interface) can now be quantitatively understood. We will present these results in a future publication.

We would like to thank Dr. K.H. Drexhage and Dr. K.H. Tews for helpful discussions. We would also like to thank the Chemistry Department of Northwestern University for support and use of their computer facilities.

References

[1] K.H. Drexhage, Habilitations-Schrift, Marburg (1966).
[2] K.H. Drexhage, J. Luminescence 1, 2 (1970) 693.
[3] K.H. Drexhage, in: Progress in optics, Vol. 12, ed. E. Wolf (North-Holland, Amsterdam, 1974) p. 165.
[4] H. Morawitz, Phys. Rev. 187 (1969) 1792.
[5] K.H. Tews, Thesis, Marburg/Lahn (1972); Ann. Physik (Leipzig) 29 (1973) 97; J. Luminescence 9 (1974) 223; Ann. Physik (Leipzig), to be published,
[6] K.H. Tews, C. Inacker and H. Kuhn, Nature 228 (1970) 276.
[7] H. Kuhn, J. Chem. Phys. 53 (1970) 101.
[8] H. Bucher, K.H. Drexhage, M. Fleck, H. Kuhn, D. Mobius, F.P. Shafer, J. Sondermann, W. Sperling, P. Tillmann and J. Wiegard, Mol. Cryst. 2 (1967) 199.
[9] R.R. Chance, A. Prock and R. Silbey, J. Chem. Phys. 60 (1974) 2184.
[10] R.R. Chance, A. Prock and R. Silbey, J. Chem. Phys. 60 (1974) 2744.
[11] R.R. Chance, A. Prock and R. Silbey, J. Chem. Phys. 62 (1975) 771.
[12] R.R. Chance, A. Prock and R. Silbey, J. Chem. Phys. 62 (1975) 2245.
[13] P.W. Milonni and P.L. Knight, Opt. Commun. 9 (1973) 119.
[14] M. Philpott, Chem. Phys. Letters 19 (1973) 435.
[15] H. Morawitz and M. Philpott, Coupling of an Excited Molecule to Surface Plasmons, Phys. Rev., to be published.
[16] G. Barton, Proc. Roy. Soc. A320 (1970) 251.
[17] A. Sommerfeld, Ann. Physik (Leipzig) 28 (1909) 665; 81 (1926) 1135.
[18] H. Weyl, Ann. Physik (Leipzig) 60 (1919) 481.
[19] A. Baños, Dipole radiation in the presence of a conducting half space (Pergamon, New York, 1966).
[20] J.R. Wait, Electromagnetic waves in stratified media (MacMillan, New York, 1962).
[21] P. Johnson and R. Christy, Phys. Rev. B6 (1972) 4370.