AIP The Journal of Chemical Physics

Lifetime of an excited molecule near a metal mirror: Energy transfer in the Eu3+⁄silver system

R. R. Chance, A. Prock, and R. Silbey

Citation: J. Chem. Phys. 60, 2184 (1974); doi: 10.1063/1.1681335
View online: http://dx.doi.org/10.1063/1.1681335
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v60/i5
Published by the American Institute of Physics.

Lifetime of an excited molecule near a metal mirror: Energy transfer in the Eu^{3+}/silver system*

R. R. Chance

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755

A. Prock

Department of Chemistry, Boston University, Boston, Massachusetts 02215

R. Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 1 November 1973)

The effects of a metal mirror on the lifetime of an emitting molecule has been the subject of several recent investigations.[1-5] Experimental results show the lifetime to vary dramatically as a function of the distance from a metallic mirror. Though image theory adequately describes the large distance behavior, poor agreement is found at small distances due to near field effects.[1,4] We have extended the theory to include such effects; it is the purpose of this communication to briefly describe the theory and present some of the preliminary results.

Since the theory is that of an oscillating dipole near a reflecting half-space, we may use the enormous body of research which has been done on this problem due to its application to radio and radar wave propagation with the earth as a reflector.[6] Our final result for the reflected radiation field at a dipole oriented in a dielectric (region 1) parallel to, and a distance d from the dielectric-mirror surface (region 2) is

$$E_R = \frac{\mu n_1 \omega^3}{c^3}\left[\left(-\frac{1}{\gamma}+\frac{1}{\gamma^3}-\frac{i}{\gamma^2}\right)e^{i\gamma} + 2\int_0^\infty \frac{e^{-\gamma l}\sigma\, d\sigma}{l+m} - n_1^2\int_0^\infty \frac{e^{-\gamma l}\sigma^3\, d\sigma}{n_1^2 m + \tilde{n}_2^2 l}\right], \quad (1)$$

where $\gamma = 2n_1\omega d/c$, $m = (\sigma^2 - \tilde{n}_2^2/n_1^2)^{1/2}$, $l = (\sigma^2-1)^{1/2}$, μ is the dipole moment, n_1 is the real reflective index of region 1, $\tilde{n}_2$ is the complex refractive index of region 2, ($\tilde{n}_2 \equiv n_2 + ik_2$), and ω is the frequency of the dipole in the presence of the mirror.[7] The first term in Eq. (1) is the image field; the remainder are corrections to the image result which are extremely important at small distances and tend to zero for large distances. Assuming the emitting molecule to be a harmonically bound charge and proceeding in a fashion analogous to that of Kuhn,[1] we obtain $\tau_d/\tau_\infty = [1+(3q\beta/2)]^{-1}$, where $\beta = \mathrm{Im}(c^3E_R/\mu n_1\omega^3)$, τ_d is the lifetime of the emitting state in the presence of the mirror, τ_∞ is the lifetime in the absence of the mirror, and q is the quantum yield of the emitting state. A similar prescription may be followed for the case of the dipole oriented perpendicular to the mirror.

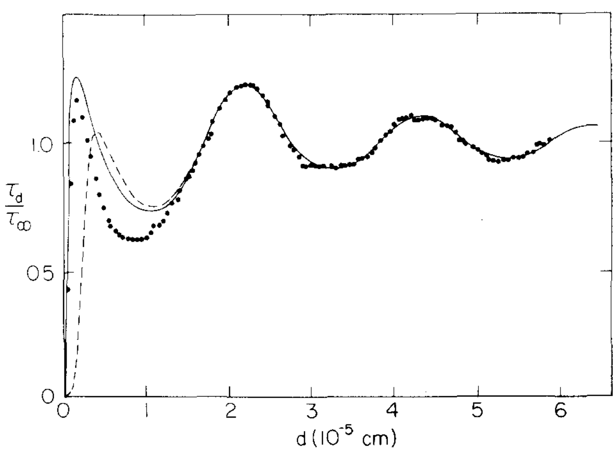

FIG. 1. Normalized lifetime of europium complex I as a function of distance from a silver mirror. The solid curve is our exact classical result; the dashed curve is Kuhn's asymptotic results. In both cases the dipole is assumed oriented parallel to the mirror with a quantum yield of 0.85. The experimental data are taken from Refs. 1 and 4; optical constants are taken from Refs. 5 and 8 ($n_1 = 1.50$, $n_2 = 0.06 \pm 0.02$, and $k_2 = 4.11 \pm 0.007$).

The numerical results are shown in Fig. 1 along with the experimental results[2] for the Eu^{3+}/silver system. Also shown in Fig. 1 are the results from Kuhn's theory[1] for the same set of optical constants.[5,8] Our theory agrees well at all distances with the experimental data; in particular, the rising edge and the location of the first peak in the data are reproduced almost exactly.

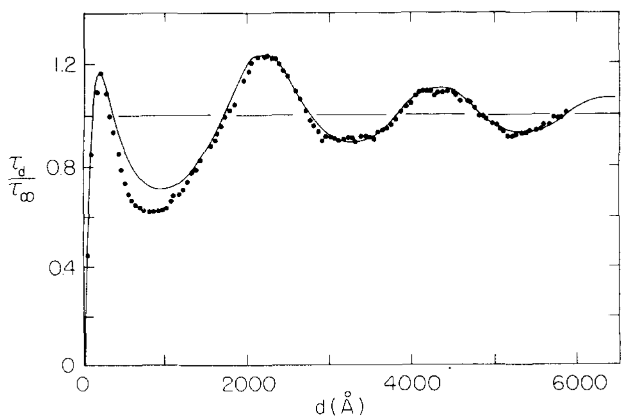

FIG. 2. Normalized lifetime of europium complex I as a function of distance from a silver mirror, and as a function of parallel component fraction ($F_\parallel = 0.89$) and perpendicular component fraction (0.11). The quantum yield is taken as unity.

Both theories are adequate for large distances.

Drexhage[4] has analyzed the same data in terms of a parallel component fraction ($F_{\parallel}$) and a perpendicular component fraction ($F_{\perp}$). Assuming a random arrangement of dipoles ($F_{\parallel} = 0.67$; $F_{\perp} = 0.33$), he obtained a reasonable fit for the large distance behavior but again, since the metal was assumed to be a perfect reflector, poor agreement at small distances. We have proceeded in an analogous fashion and find for a reasonable fit to the experimental data, that $F < 0.15$. The optimum valvalue is about $F = 0.11$ assuming a quantum yield of unity (see Fig. 2). We have applied the same theory to copper and gold mirrors[3] with good results.[9]

*This research was supported in part by NSF and by the Research Corporation.

[1](a) H. Morawitz, Phys. Rev. 187, 1792 (1969); (b) H. Kuhn, J. Chem. Phys. 53, 101 (1970).
[2]K. H. Drexhage, H. Kuhn, and F. P. Schäfer, Ber. Bunsenges. Phys. Chem. 72, 329 (1968); K. H. Drexhage, M. Fleck, H. Kuhn, F. P. Schäfer, and W. Sperling, *ibid.* 70, 1179 (1966).
[3]K. H. Drexhage (private communication).
[4]K. H. Drexhage, J. Lumin. 1, 693 (1970).
[5]H. Kuhn and D. Möbius, Angew. Chem. 10, 620 (1971).
[6]A. Banos, *Dipole Radiation in the Presence of a Conducting Half Space* (Pergamon, New York, 1966).
[7]Since the frequency shift is found to be negligible for any case that would have physical significance, we have explicitly assumed the frequency shift to be zero.
[8]P. Johnson and R. Christy, Phys. Rev. B 6, 4370 (1972).
[9]The referee has kindly pointed out an article by K. Tews [Ann. Physik 29, 97 (1973)] which has just appeared. Tews also takes into account the nonideal reflectively of the mirror and finds similar results to ours.