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A NEW PROBE FOR THE SURFACE ELECTRONIC STRUCTURE OF LIQUID METALS*

R.R. Chance

Materials Research Center, Allied Chemical Corporation, Morristown, NJ 07960, U.S.A.

A. Prock

Department of Chemistry, Boston University, Boston, MA 02215, U.S.A.

and

R. Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

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The fluorescent lifetime of an emitting molecule near a liquid mercury surface is proposed as a probe of the electronic structure of the mercury surface. It is shown that this property is very sensitive to the conductivity profile of the surface region.

THERE IS CURRENTLY an interest in the dielectric properties of the surface of liquid metals.[1–5] Bloch and Rice[1] have shown that the disagreement in the optical constants for liquid Hg obtained by ellipsometric and near normal-incidence reflection techniques[1,6–10] can be reconciled by assuming that the surface layer has a dielectric function which is quite different from the bulk. They interpret their results on the basis of an Epstein-like conductivity profile[11] for the surface region whose form is

$$\sigma(z) = \frac{W}{1+W}\left(\sigma_b + \frac{\sigma_s}{1+W}\right), \quad W \equiv \exp(2\pi z/\Delta), \tag{1}$$

where σ_b and σ_s are the bulk and surface conductivities, respectively. The quantity Δ determines the width of the profile measured in the z direction, i.e. normal to the Hg surface. The reflectivity of such a surface, particularly at normal incidence, is not markedly different from that of the sharp profile and is, therefore, not a sensitive probe of such profiles. It is therefore of interest to find new methods which are more sensitive to the details of the surface dielectric profile. In this note, we suggest such a method.

The reflectivity is a more sensitive function of the presence of the profile when the angle of incidence becomes complex. In the case of frustrated total refelction (FTR) a limited range of complex angles is accessible and some increased sensitivity to the dielectric profile of liquid Hg, relative to more conventional reflection techniques, is observed.[3–5,12] However, even with FTR it is difficult to distinguish between the Epstein profile and an ellipsometric-sharp profile (i.e. a sharp profile with the ellipsometrically determined optical constants).

In recent work we[13] and Tews[14] have found that the luminescent lifetime of an emitting molecule at a distance d_1 from a partially reflecting surface can be represented as an integral over all angles of incidence, real and complex. For example, the lifetime of a vertical dipole ($\perp$ to interface) is given as

$$\tau_d = \tau_\infty\left[1 - \tfrac{3}{2}q \operatorname{Im}\int_0^\infty R_{1,2}\, e^{-2l_1\hat{d}_1}\, u^3\, du/l_1\right]^{-1} \tag{2}$$

where τ_∞ and q are the lifetime and quantum yield in the absence of the mirror, $l_1 \equiv -i(1-u^2)^{1/2}$, $\hat{d}_1 \equiv \omega\sqrt{\epsilon_1}d_1/c$, $u = \sin\theta$, θ is the angle of incidence, and $R_{1,2}$ is the reflectivity (polarized parallel to plane of incidence). The form of equation (2) follows directly from the original formulation of Weyl.[15] As the distance d_1 becomes smaller, the range of complex angles that are important in the integration becomes larger. Therefore, from the remarks made above, we expect the lifetime to be a strong function of the dielectric profile of the surface in the small distance (energy transfer) region. In fact, it has recently been shown that the emitting molecule couples directly to the surface plasmon modes.[16,17]

We have recently extended the above mentioned calculations to the case of a multi-stratified medium.[18] From this work, in agreement with Wait,[19] we find for the lifetime of an emitting dipole oriented perpendicular to a medium made up of $k-1$ layers

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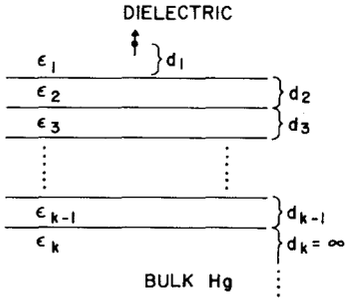

Fig. 1. Geometry of multi-layer problem. The dipole is perpendicular to and a distance d_1 from a multi layer system of $k - 1$ layers – the last layer being semi-infinite in extent.

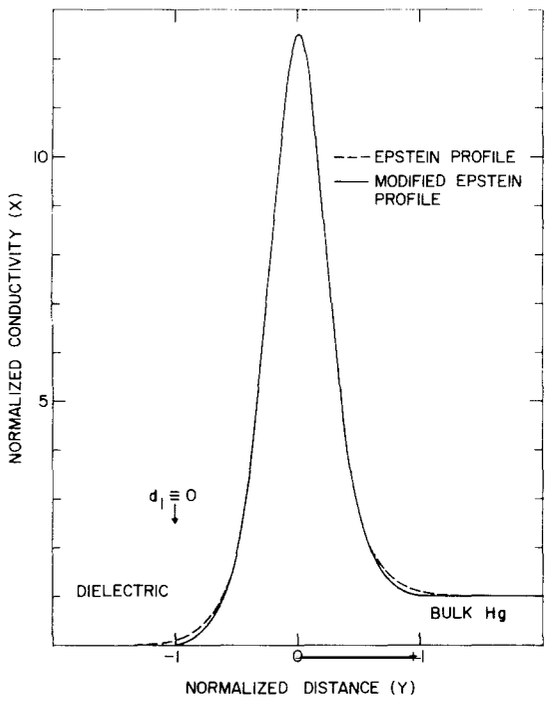

Fig. 2. Conductivity profile for liquid mercury surface. A linear extrapolation toward the points $Y = \pm 1$ has been used to obtain the modified profile which is used in all calculations.

$$\tau_d = \tau_\infty \left[1 - \tfrac{3}{2} q \, \mathrm{Im} \int_0^\infty \mathcal{R}_1 \, e^{-2 l_1 \hat{d}_1} \, u^3 \, du / l_1 \right]^{-1}, \quad (3)$$

where

$$\mathcal{R}_1 = \frac{R_{1,2} + \mathcal{R}_2}{1 + R_{1,2}\mathcal{R}_2}, \quad (4)$$

$$\mathcal{R}_j = \frac{R_{j,j+1} + \mathcal{R}_{j+1}}{1 + R_{j,j+1}\mathcal{R}_{j+1}} \, e^{-2 l_j \hat{d}_j}, \quad (5)$$

$$\mathcal{R}_{j,j+1} = \frac{\epsilon_j l_{j+1} - \epsilon_{j+1} l_j}{\epsilon_j l_{j+1} + \epsilon_{j+1} l_j}, \quad (6)$$

and

$$l_j \equiv -i(\epsilon_j/\epsilon_1 - u^2)^{1/2}. \quad (7)$$

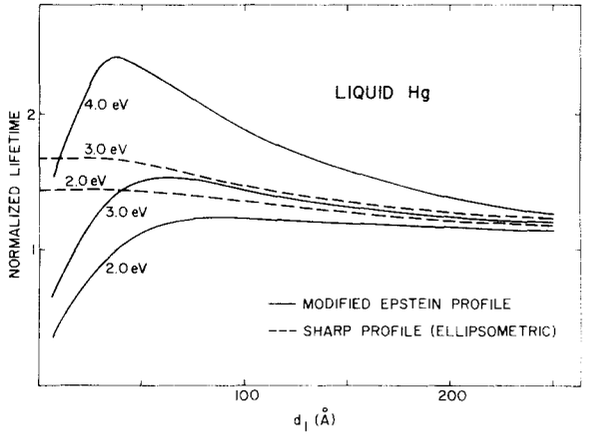

Fig. 3. Normalized lifetime vs distance for liquid mercury system with various emission frequencies. All lifetimes are normalized by the results for a sharp profile described by a Drude-like dielectric function with $\sigma_b = 9.4 \times 10^{15}$ and $\tau_b = 4.516 \times 10^{-16}$ sec. The optical constants for the elipsometric results are taken from reference 9.

The quantity $\mathcal{R}_1$ is the parallel component of the reflectivity of the multilayer system at a particular value of θ ($u \equiv \sin\theta$). The geometry of the system is shown in Fig. 1. The close analogy between equations (2) and (3) is obvious. Indeed, the expression for a parallel dipole can be inferred from this analogy and the earlier single mirror equations.[13,14] For simplicity we will restrict ourselves to the perpendicular case, (though there is a simple factor-of-two relationship between the lifetimes for the two orientations in the energy transfer region).[16]

For illustrative purposes, we have applied equation (3) to a model of the liquid Hg problem using a slightly modified version of the Epstein profile. We assume a Drude dispersion relation and take the parameters for the profile [equation (1)] from reference 5: $\Delta = 6.28$ Å, $\sigma_s = 48\sigma_b$, $\tau_s \approx \tau_b = 4.516 \times 10^{-16}$ sec, and $\sigma_b \simeq 9.4 \times 10^{15}$ esu. The normalized conductivity is then

$$x \equiv \frac{\sigma(z)}{\sigma_b} = \frac{W(49 + W)}{(1 + W)^2} \quad (8)$$

and is shown in Fig. 2 as a function of Y ($\equiv z/\Delta$). Also shown in Fig. 2 is the slightly modified version of the Epstein profile which we will use in the present series of calculations. We have then for the distance dependent dielectric constant

$$\epsilon(\omega, z) = \epsilon_1(1 - x) - x \frac{4\pi\tau\sigma_b}{1 + \omega^2\tau^2} + ix \frac{4\pi\sigma_b}{\omega(1 + \omega^2\tau^2)}. \quad (9)$$

The lifetime of the fluorescence of a molecule emitting at a distance d_1 from such a surface was computed using

equation (3). Up to 400 strata are necessary in some cases for adequate numerical convergence.

The results are shown in Fig. 3 for $\epsilon_1 = 1.50$. All lifetimes are normalized by the results for a sharp Drude profile. As d_1 gets smaller, the lifetime for the surface with the Epstein profile differs significantly from that for the sharp profile surface. This is in agreement with our earlier remarks about the inclusion of complex angles of incidence. Results are also shown in Fig. 3 for the ellipsometric profile and are seen to be easily distinguishable from the Epstein profile results especially in the small distance region ($d_1 < 60$ Å).

From the above, we see that the lifetime of an emitting molecule near the surface of liquid mercury will be strongly affected by the surface dielectric profile and thus will be a sensitive probe of such a profile.

REFERENCES

1. BLOCH A.N. & RICE S.A., *Phys. Rev.* **185**, 933 (1969).
2. CROZIER E.D. & MURPHY E., *Can. J. Phys.* **50**, 1914 (1972).
3. GUIDOTTI D., RICE S.A. & LEMBERG H.L., *Solid State Commun.* **15**, 113 (1974).
4. LEMBERG H.L., RICE S.A. & GUIDOTTI D., *Phys. Rev.* **B10**, 4079 (1974).
5. RICE S.A., GUIDOTTI D., LEMBERG H.L., MURPHY W.C. & BLOCH A.N., in *Advances in Chemical Physics* (Edited by PRIGOGINI I.). Wiley-Interscience (1974).
6. SCHULZ L.G., *J. Opt. Soc. Amer.* **47**, 64 (1957).
7. HODGSON J.N., *Phil. Mag.* **4**, 189 (1959).
8. WILSON E.G. & RICE S.A., *Phys. Rev.* **145**, 55 (1966).
9. FABER T.E. & SMITH N.V., *J. Opt. Soc. Amer.* **58**, 102 (1968).
10. BOIANI J. & RICE S.A., *Phys. Rev.* **185**, 931 (1969).
11. EPSTEIN P.S., *Proc. Natl. Acad. Sci.* **16**, 627 (1930).
12. LEMBERG H.L., Ph.D. thesis, University of Chicago (1973).
13. CHANCE R.R., PROCK A. & SILBEY R., *J. Chem. Phys.* **60**, 2184, 2744 (1974); CHANCE R.R., MILLER A., PROCK A. & SILBEY R., *J. Chem. Phys.* **63**, 1589 (1975).
14. TEWS K.H., *Ann. Phys. (Leipz.)* **29**, 97 (1973); Thesis, Marburg/Lahn (1972).
15. WEYL H., *Ann. Phys. (Leipz.)* **60**, 481 (1919).
16. CHANCE R.R., PROCK A. & SILBEY R., *J. Chem. Phys.* **62**, 2245 (1975).
17. MORAWITZ H. & PHILPOTT M.R., *Phys. Rev.* **B10**, 4863 (1974).
18. CHANCE R.R., PROCK A. & SILBEY R. (to be published).
19. WAIT J.R., *Electromagnetic Waves in Stratified Media.* MacMillan, New York (1962).