

## Comment on the Fluorescence of Trivalent Europium in D<sub>2</sub>O-H<sub>2</sub>O Mixtures

JOHN L. KROPP AND MAURICE W. WINDSOR

Chemical Sciences Department, TRW Systems, One Space Park  
Redondo Beach, California

(Received 28 February 1966)

IN a recent paper<sup>1</sup> Gallagher states that we found that the fluorescence intensity of the  ${}^5D_0 \rightarrow {}^7F_1$  emission of H<sub>2</sub>O/D<sub>2</sub>O solutions of europium salts increased linearly with the percentage of D<sub>2</sub>O, in disagreement with his observation of a clearly nonlinear relationship (Gallagher's Fig. 1). This is incorrect and arises from a confusion regarding the definition of  $I_D/I_H$  in Fig. 2 of our paper.<sup>2</sup>

In the footnotes of Tables I and II we define  $I_D/I_H$  as "the ratio of intensity in the specified solvent to that in H<sub>2</sub>O." For a D<sub>2</sub>O/H<sub>2</sub>O mixture, with  $I_D/I_H$  defined in this way,  $I_H$  is a constant and  $I_D$  varies with percentage of D<sub>2</sub>O (or H<sub>2</sub>O). In this case it would be better to write  $I_{D=a}/I_H$ , where  $a$  is the percentage of D<sub>2</sub>O in the mixture. In Fig. 2 we plot the parameters " $I_D/I_H$ " and " $\tau_D/\tau_H$ " for Eu(NO<sub>3</sub>)<sub>3</sub> as a function of the percentage of H<sub>2</sub>O in the mixture. In this case these parameters have the meaning we defined in Eq. (10) of our paper,

$$I_D/I_{H=b} = \tau_D/\tau_{H=b} = 1 + [bk_H/(k_F + k_D + k_X)] \quad (1)$$

With this definition  $I_D$  is the intensity in 100% D<sub>2</sub>O and is constant;  $I_{H=b}$  is the intensity in the mixture and varies with the percentage  $b$  of H<sub>2</sub>O in the mixture. To avoid confusion we should have used the terminology  $I_D/I_{H=b}$  in labeling the ordinate of Fig. 2.

Because  $I_D$  is a constant, plotting  $I_D/I_{H=b}$  is tantamount to plotting  $1/I_{H=b}$  vs percent H<sub>2</sub>O (or D<sub>2</sub>O). A linear relationship is indeed observed, but it is an *inverse* relationship with respect to the fluorescence intensity  $I_{H=b}$ . If we replot Gallagher's data in this manner it fits the linear relationship given by Eq. (1) quite well, as shown in Fig. 1. The slopes are different, since at 100% D<sub>2</sub>O he obtains  $I_D/I_H = 25$  compared to 18 in our case.<sup>3</sup> This is probably because Gallagher's method of preparing the salts in D<sub>2</sub>O gives less contamination by residual water of hydration than our method. With regard to the functional way in which the fluorescence intensity of Eu<sup>3+</sup> varies with percent D<sub>2</sub>O, in a D<sub>2</sub>O/H<sub>2</sub>O mixture, there is therefore no disagreement between Gallagher's measurements and ours.

We still differ from Gallagher with regard to observations of fluorescence lifetime. For EuCl<sub>3</sub> in D<sub>2</sub>O-H<sub>2</sub>O mixtures he reports a two-component decay which can be analyzed into two exponentials having lifetimes of 0.12 and 3.9 msec. We have re-examined the data from our paper,<sup>2</sup> together with more recent data on the lifetimes of rare-earth ions in D<sub>2</sub>O and H<sub>2</sub>O solutions containing acetate ions,<sup>4</sup> and cannot find any short-lived component with a lifetime longer than 20  $\mu$ sec,

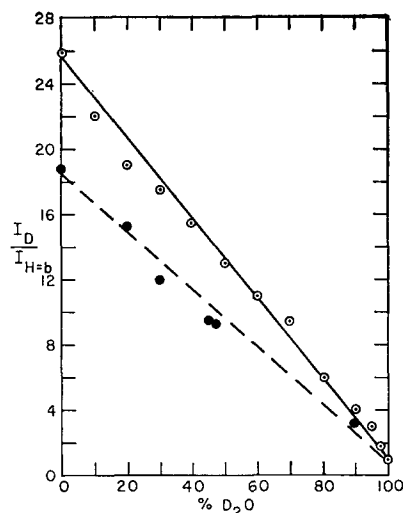


FIG. 1. Fit of Gallagher's data ( $\odot$ ) and data of Kropp and Windsor ( $\bullet$ ) to Eq. (1), showing the variation of  $I_D/I_{H=b}$  with increasing percent D<sub>2</sub>O.

which we attribute to the flash lamp. Gallagher suggests that this discrepancy is due to the difference in the observational techniques. The stroboscopic technique used by Gallagher is more sensitive than our single-flash technique and has a shorter resolving time of 2.5  $\mu$ sec. However, even with our 20- $\mu$ sec resolving time, we should have detected the 120- $\mu$ sec component reported by Gallagher. Further work is needed to resolve this discrepancy.

<sup>1</sup> P. K. Gallagher, J. Chem. Phys. **43**, 1742 (1965).

<sup>2</sup> J. L. Kropp and M. W. Windsor, J. Chem. Phys. **42**, 1599 (1965).

<sup>3</sup> Gallagher's data are for EuCl<sub>3</sub> and ours are for Eu(NO<sub>3</sub>)<sub>3</sub>; however, we find similar results for both compounds.

<sup>4</sup> J. L. Kropp and M. W. Windsor (unpublished results).

## Quantum Chemistry of Electrode Processes. II. Higher Activation Energies\*

P. P. SCHMIDT, JR., AND H. B. MARK, JR.

Department of Chemistry, The University of Michigan  
Ann Arbor, Michigan

(Received 14 March 1966)

IN Part I of this series the current of an electrode process was developed through examination of an assumed detailed model of the electrode interface.<sup>1</sup> In the nonadiabatic treatment presented, it was assumed that there is a steady-state population of an intermediate "metastable" state, and that the rate dependence of the current comes through a depopulation of the intermediate state leading to an emission transition to a final state. It was further assumed that the rate of depopulation could be given in terms of an analogy with Gouterman's radiationless transition mechanism.

In most cases the energy differences between the initial or the final state and the intermediate state for transitions in both directions, i.e., leading to a forward and reverse current, are of magnitudes much larger

than the phonon energies important in the depopulation step. In light of these facts, however, neither the original model, nor its treatment fail; rather the treatment must be modified to account for the prevailing physical conditions.

The modification is accomplished by realizing that the high-temperature approximation is valid only for phonons, and by noting the relative magnitudes of the electronic and phonon energies involved. It is seen that the dominant energies are the activation energies for either current:  $E_{12}$  and  $E_{43}$  in Part I. The energy of the phonon field *cannot* be identified with either of these two energies. If the energies of the phonon field are  $E''_{12}$  and  $E''_{43}$ , where  $E''$  represents the energy of a particular mode of the field, and  $E'' \ll E$ , and if they are substituted in the appropriate parts of expressions  $P_I$  and  $P_{IV}$  of (IV.10) in Part I, the re-evaluated current expressions become

$$j_f = c_{ox} A \mathcal{F} A_{34}^* (kT/E''_{43}) \exp[(E''_{43} - E_{12})/kT] \quad (1)$$

and

$$j_r = -c_{red} A \mathcal{F} A_{21}^* (kT/E''_{12}) \exp[+(E''_{12} - E_{43})/kT], \quad (2)$$

where

$$A_{nm}^* = (4\omega''_{nm}/3\hbar c_s^3) |\mathbf{u}_{mn}|^2. \quad (3)$$

Since  $E'' \ll E$ , it is readily seen that the phonon energies in the exponential can be ignored. Thus, the resulting current expressions are

$$j_f = c_{ox} A \mathcal{F} A_{34}^* (kT/E''_{43}) \exp(-E_{12}/kT) \quad (4)$$

and

$$j_r = -c_{red} A \mathcal{F} A_{21}^* (kT/E''_{12}) \exp(-E_{43}/kT). \quad (5)$$

All remaining expressions, such as the Nernst equation, are modified accordingly.

It is further seen that the expressions for the current under the influence of an external polarization depend upon that polarization only through modification of the activation energies (electronic). Thus, the equations (VI.1), (VI.2), etc., follow from the basis, altered expression

$$J = A \mathcal{F} \left[ A_{34}^* c_{ox} \frac{kT}{E''_{43}} \exp(-E_{12} + \mathbf{u}_{12} \cdot \boldsymbol{\varepsilon}) / kT - A_{21}^* c_{red} \frac{kT}{E''_{12}} \exp(-E_{43} - \mathbf{u}_{43} \cdot \boldsymbol{\varepsilon}) / kT \right]. \quad (6)$$

Consequently, the activation energies given in I are not correct.

It should be noted further that for this system, as it has been considered, the identification made with the free energies of activation in I are impossible. Such identifications can only be made for the whole system, and not merely a part of it. This is a result of the conservation of energy, viz., the total system initial and final state energies are degenerate. Thus, for the specific model, which considers only a limited volume of the total electrode-plus-solution system, the identification made in I is meaningless, as is the expression for the factor  $\alpha$ .

Work on the consideration of more detailed descriptions of the interfacial system and the transitions leading to electrochemical currents is presently in progress. Further consideration is given there to the nature of the activation steps and the probabilities of transition.

\* This research was supported in part by a grant from the National Science Foundation, Grant No. GP-4620.

<sup>1</sup> P. P. Schmidt, Jr., and H. B. Mark, Jr., *J. Chem. Phys.* **43**, 3291 (1965).

## Errata

### Erratum: Charge Transfer between $N^+$ and O

[*J. Chem. Phys.* **44**, 414 (1966)]

WILLIAM J. KAUFMANN\*

*Astronomy Department, Indiana University, Bloomington, Indiana*

(Received 8 April 1966)

IT has been pointed out to me by D. Rapp (consultant) and R. Oman of the Research Department, Grumman Aircraft Engineering Corporation, Bethpage, New York, that the peaks observed in my theoretical cross sections are due to a mathematical artifact. These peaks arise from a resonance between the dominant abscissas in the Hermite-Gauss quadrature and a particular argument of the cosine term. The cross sections are, however, correct down to the energies where the peaks begin.

\* Formerly at: Research Department, Grumman Aircraft Engineering Corp. Bethpage, N.Y.

### Erratum: Local Equilibrium Approach to Transport Processes in Dense Media

[*J. Chem. Phys.* **43**, 4516 (1965)]

I. PRIGOGINE, G. NICOLIS, AND J. MISGUICH

*Faculté des Sciences, Université Libre de Bruxelles  
Brussels, Belgium*

(Received 8 April 1966)

IN the second line of the Appendix one should read "Expressions (3.2a) and (2.18)."

Also Formula (A2) of the Appendix reads

$$L_{th} = \frac{8\pi^3}{3kT} \int d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{l} \mathbf{J}_{12}^{V, \cdot} (-\mathbf{l}, \mathbf{v}_1, \mathbf{v}_2) \pi \delta(\mathbf{l} \mathbf{g}) \\ \times f_1^{eq}(\mathbf{v}_1) f_1^{eq}(\mathbf{v}_2) \left[ \frac{1}{2} m (v_1^2 v_1^2 + v_2^2 v_2^2) + \frac{1}{2} (v_1^2 + v_2^2) \right] \int d\mathbf{x}_1 d\mathbf{x}_2 \\ \times \delta(\mathbf{x} - \mathbf{x}_1) \delta(\mathbf{x} - \mathbf{x}_2) \\ \times \left( kT_1^2 \frac{\partial}{\partial T_1} + kT_2^2 \frac{\partial}{\partial T_2} \right) \ln n_2^{(0)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{l}) \Big] n_2^{(0)}(\mathbf{x}, \mathbf{l}).$$