Luminescent Efficiency of Organic Solutions and Crystals

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IN a recent paper[1] a theory of luminescent efficiency has been proposed and applied to data on inorganic phosphors. Because the formulation is quite general, it can be used to interpret recent data[2-4] on luminescent organic solutions and crystals excited by gamma-rays. The excitation energy may be absorbed (I) directly by the luminescent molecules, or (II) by the solvent molecules which may (A) transfer the energy to the luminescent molecules or (B) lose the energy by radiationless processes. The luminescent molecules or "activators" lose the energy by (a) nonconcentration dependent radiationless processes, (b) radiationless processes resulting from interactions with nearby unexcited activators, and (c) emission.

The data of Kallman and Furst comprise mainly low activator concentrations; therefore (I) is insignificant. Also, (a) affects the absolute energy efficiency but not the concentration dependence of luminescence. Therefore, it is possible to apply the explicit expression for efficiency, η, as a function of gross activator concentration C:

$$\eta = C(1-C)^z/[C+(\sigma/\sigma')(1-C)], \qquad (1)$$

where z is the number of positions surrounding a given activator which if occupied by a second activator molecule quench luminescence, (b), and σ/σ' is the ratio of probabilities of processes (B) to (A) with unit concentrations of solvent and activator, respectively. Figure 1 shows the data of Kallman and Furst[2] and the calculated curve for anthracene in xylene. z is 270, indicating an interaction sufficient to quench luminescence between activators separated by three molecular diameters. That σ/σ' is only 0.0004 demonstrates that (A) is favored over (B), transfer of excitation energy occurring over as many as five solvent molecular diameters. The same values of z and σ/σ' are obtained from data[2] on carbazole in xylene. This is not surprising in view of the chemical similarity of anthracene and carbazole.

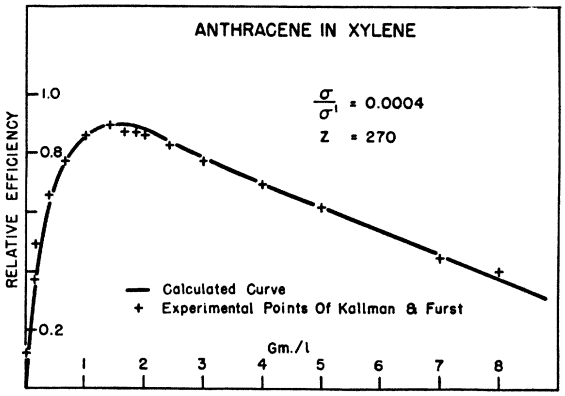

FIG. 1. Efficiency *vs.* activator concentration of anthracene in xylene.

The situation is different for naphthalene in xylene as shown by the data of Ageno, Chiozzotto, and Querzoli.[3] At high molecular concentrations of naphthalene, there is no evidence of a decrease in luminescent output; therefore, (b) is inoperative and z is zero. Also, at the high activator concentrations involved, (I) is important. The efficiency may be expressed as a linear combination of the efficiencies of the two excitation mechanisms (I) and (II):

$$\eta = f_I\eta_I + (1-f_I)\eta_{II}. \qquad (2)$$

The ratio, κ, of capture cross sections of activator and solvent for gamma-rays is approximately equal to the ratio of densities of napthalene and xylene. Equation 2 becomes:

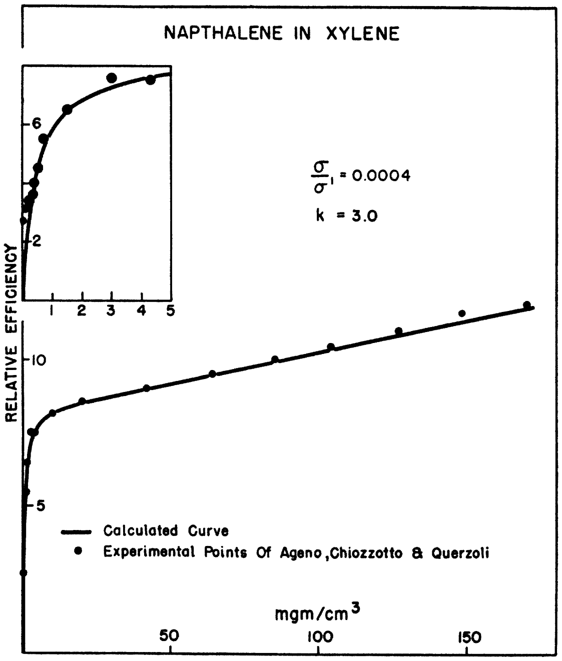

FIG. 2. Efficiency *vs.* activator concentration of naphthalene in xylene.

$$\eta = \left[\frac{\kappa C}{C(\kappa-1)+1}\right]\cdot k + \left[\frac{(1-C)}{C(\kappa-1)+1}\right]\left[\frac{C}{C+(\sigma/\sigma')(1-C)}\right]. \qquad (3)$$

Figure 2 demonstrates the agreement of Eq. (3) and the data[3] of Ageno, *et al.* The value of σ/σ' appears to be characteristic of xylene. The relative probabilities of (a) and (c) and of (I) and (II) determine k. That there is no interaction to quench luminescence is probably related to the chemical stability of naphthalene.

Equation (11) of reference 1 predicts that the temperature dependence of luminescent efficiency should be greater at lower activator concentration because of a higher activation energy for (b). Also, this activation energy should change less rapidly with concentration at lower concentrations. Both predictions are in agreement with the data of Liebson and Farrar[4] on the temperature dependence of luminescence of mixtures of naphthalene and anthracene.

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[2] H. Kallman and M. Furst, Phys. Rev. 79, 857 (1950).
[3] Ageno, Chiozzotto, and Querzoli, Phys. Rev. 79, 720 (1950).
[4] S. H. Liebson and R. J. Farrar, Phys. Rev. 79, 733 (1950).

The Isotopic Weight of Helium

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A TABLE of isotopic weights obtained by the combination of nuclear reaction Q values and mass spectrograph doublets has been published by Tollestrup, Fowler, and Lauritsen.[1] It is the purpose of this letter to show (1) that a more satisfactory isotopic weight scale can be based on a different approach, in which the value for He^4 is obtained from the mass spectrographic $(2D^2-He^4)$ doublet,[2-4] and (2) that apparent gross errors which exist in the Q values can reasonably be attributed to the values associated with the $Li^7(p,\alpha)He^4$ and $Li^6(d,\alpha)He^4$ reactions.

Table I of reference 1 should be utilized to obtain the Q values needed in the discussion which follows. The reactions of column 1 of Table I should be numered in sequence. The "as measured" Q values in column 2 are the input values in Mev from which the mass equivalents in milli-mass units are secured by multiplying by the usual conversion factor 1.074.

The mass difference ($2D^2-He^4$) can be obtained from disintegration data alone by the combination in "cycles" of Q values from reactions from which all atoms other than D and He have been eliminated by subtraction of identities.[5] One such cycle utilizing n, H^1, D^2, He^3, He^4, Li^6, and Li^7 yields

$$\begin{aligned}(2D^2-He^4)&=0.025522\pm0.000045\text{MU}\\&=(Q_1+Q_4+Q_{10}+Q_{13}-Q_9)\times1.074.\qquad\text{(a)}\end{aligned}$$

A second cycle involving H^1, D^2, He^4, Li^7, Be^8, and Be^9 yields

$$\begin{aligned}(2D^2-He^4)&=0.025536\pm0.000039\text{MU}\\&=(Q_{13}+Q_{21}-Q_{15}-Q_{18})\times1.074.\qquad\text{(b)}\end{aligned}$$

A third cycle which includes H^1, D^2, He^4, Li^6, Be^8, and Be^9 yields

$$\begin{aligned}(2D^2-He^4)&=0.025431\pm0.000042\text{MU}\\&=(Q_{11}+Q_{19}-Q_{15}-Q_{18})\times1.074.\qquad\text{(c)}\end{aligned}$$

These three cycles are sufficient for the argument. If (a), (b), and (c) are combined, the result would be represented approximately by 0.02550 ± 0.000023.

In the case of the four measurements of the ($2D^2-He^4$) doublet by four different instruments, the values (in MU) are 0.02551 ± 0.00008;[6] 0.02561 ± 0.00004;[2] 0.025604 ± 0.000009;[3] 0.025612 ± 0.000008.[4] The recent measurements of Nier and Ewald may be weighted equally to give

$$0.025608\pm0.000006=(2D^2-He^4).\qquad\text{(d)}$$

The differences between this value and those given by Eqs. (a), (b), and (c) are 12 to 30 times the probable errors of the Ewald-Nier measurement and 2 to 4 times the probable errors of the combined Q values of Eqs. (a), (b), and (c). Q_{11} and Q_{13} naturally come under suspicion as they represent the only Q values obtained from range-energy measurements, while all other Q values are from electrostatic or magnetic deflection studies.[1] Also, Q_{11} should equal $Q_{10}+Q_{13}$; and the fact that the probable errors do not overlap, $Q_{11}-Q_{10}-Q_{13}>\epsilon_{11}+\epsilon_{10+13}$, has indicated that Q_{13} or Q_{11} or both may be away from their true values by more than the assigned probable errors. Equations (a), (b), and (c), considered with the Ewald-Nier value for ($2D^2-He^4$), Eq. (d), furnish a strong indication that Q_{13} and Q_{11} are *both* too small, where hitherto only one or the other of these values or their difference has been under suspicion. An error of the magnitude indicated above in the mass spectrograph result of Ewald would correspond to an error in the doublet separation of $\frac{1}{2}$ the width of a line or an error in the dispersion of $\sim\frac{1}{4}$ percent. An examination of Ewald's remarkable spectra shows how remote is the possibility of any error of that magnitude. Equivalent possibilities in Nier's excellent work are equally unlikely.

The magnitudes and assigned probable errors of the Q values other than Q_{11} and Q_{13} make it appear that the difficulties lie with Q_{11} and Q_{13} in the disagreement between the mass spectrograph and the disintegration mass scales. The source of the possible errors in Q_{11} and Q_{13} might be in the range energy curve.

However, as is well known, the measurement of Q_{13} for the reaction $Li^7(p,\alpha)He^4$ is essentially a measurement of the small range difference between the alpha particles from the Li^7 reaction and the alpha-particles of ThC′. The energy of the latter has been measured with very high precision by Briggs,[7] and Rosenblum and Dupouy.[8] Also, indirect checks of several kinds exist for the ThC′ measurements. The only reasonable change in Q_{11} from the ThC′ experiments is associated with the change in $2e/M$ for alpha-particles to conform to the weight of helium given below. There is no significant change in Q_{13} from this consideration. A detailed survey emphasizes that the $Li^7(p\alpha)He^4$ and $Li^6(d\alpha)He^4$ reaction Q values should be brought to the same high order of accuracy as is obtained by deflection methods for the other Q values listed in Table I of reference 1.

A mass scale for H^1, D^2, He^4, C^{12}, and O^{16} obtained chiefly from doublet measurements is appended. The input data also includes the important results of Bell and Elliott[9,10] for Q_1 for $H^1(n\gamma)D^2$, and Taschek, *et al.*,[11] and others[12] for $n-H^1$ combined to give $2H^1-D^2=1.555\pm0.006\times10^{-3}$ MU. This is averaged with Roberts and Nier's[13] measurement $1.549\pm0.006\times10^{-3}$ MU.

The baic mass-spectrographic doublets are as follows:

$$\begin{aligned}(H^1)_2-D^2&=\ 15.52\pm0.04\times10^{-4}\text{ MU}^{9,11,13}\\(D^2)_3-\tfrac{1}{2}C^{12}&=422.28\pm0.19\times10^{-4}\text{ MU}^{10}\\C^{12}+(H^1)_4-0&=364.5\ \ \pm0.22\times10^{-4}\text{ MU}^{13}.\end{aligned}$$

The corresponding mass scale is as follows:

$$\begin{array}{ccc}n=1.0089785; & H^1=1.0081386; & D^2=2.0147252;\\ \qquad\qquad 38 & \qquad\qquad 32 & \qquad\qquad 57\end{array}$$

$$\begin{array}{cc}He^4=4.003842; & C^{12}=12.003895.\\ \qquad\qquad 13 & \qquad\qquad 19\end{array}$$

A complete table of isotopic weights derived from both reaction Q-values and mass spectrograph doublets is in preparation for the Nuclear Science Series of the National Research Council.

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The Perfect Diamagnetism of Free Electrons with Application to Superconductivity

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CALCULATIONS have been made on the Fermi-Dirac statistics of free charged particles in a uniform magnetic field in a *finite* box, and of free particles in a magnetic field which decays exponentially from the applied field at the surface of the box. Particular attention is paid to using $\psi=0$ rather than ψ periodic as the boundary condition on the walls of the box.

Considering the first problem above, it follows from the rigorous application of this boundary condition to a finite cylinder of dimensions R, L_z, with H along the axis, that the total number of particles and the energy $U-MH$ at absolute zero are, for an orbit radius smaller than the dimensions of specimen: $\alpha=kc\hbar/eH$,

$$\begin{aligned}N&=(Vk^3/6\pi^2)[1+(3\pi/8R)\alpha+(2/5R^2)\alpha^2]\\U-MH&=(\hbar^2Vk^5/20m\pi^2)[1+(5\pi/12R)\alpha+(10/21R^2)\alpha^2].\end{aligned}$$

Here, $k=(2m\zeta)^{\frac{1}{2}}/\hbar$, where ζ is the energy of the highest occupied state.

The last two terms in brackets correspond to orbits whose centers are just outside (<orbit radius) the specimen[1] (with periodic boundary conditions, these would be counted in the adjoining "big cell"), and orbits which encircle the origin.[2] These extra terms vanish in the limit $V\rightarrow\infty$, N/V finite, so that they depend on the size and the shape of the specimen. For macroscopic specimens they still make a large contribution to the magnetic moment, shown in Fig. 1.

If one assumes that Fig. 1 gives M as a function of $H_{\text{effective}}$ and uses the relation $H_{\text{eff}}=H_{\text{appl}}+4\pi M(H_{\text{eff}})$ to obtain $H_{\text{appl}}=f(H_{\text{eff}})$, and then $M=f(H_{\text{appl}})$, one obtains Fig. 2, curve (1), which indicates almost perfect diamagnetism up to a critical field and then a triple-valued transition (similar to the condensation of a Van der