

Lanthanide Ions as Sensitive Probes. Part III.¹ Triplet-energy Transfer from 2-Acetonaphthone and 2-Acetylfluorene to Europic Ions in Frozen Solution

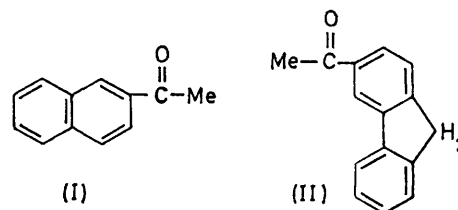
By Fredrick L. Minn,* George W. Mushrush, and Nicolae Filipescu, Departments of Chemistry, The George Washington University, Washington, D.C. 20006, and George Mason College, University of Virginia, Fairfax, Virginia 22030

Transfer of triplet energy from 2-acetonaphthone and 2-acetylfluorene to tervalent europium ions was investigated in rigid glass by measuring the quantum yields of donor phosphorescence and acceptor fluorescence and the decay of donor emission under selective excitation of the ketone at different Eu^{3+} concentrations. It is suggested that transfer originates in the n,π^* triplet, which is only slightly above the lowest π,π^* triplet of the sensitizer. A suggested photokinetic scheme, consistent with the presumed exchange mechanism, explains the observed behaviour and yields transfer rate constants of 2.3 and $10 \text{ l mol}^{-1} \text{ s}^{-1}$ for the two sensitizers. Spectroscopic observables predicted by statistical treatments were in very good agreement with experiment and were consistent with the assumed exchange mechanism. Alterations in the predicted time-dependence of phosphorescence intensity by donor self-quenching and by changes in the microscopic decay probability expression are considered.

TERVALENT lanthanide ions such as Eu^{3+} and Tb^{3+} are known to be efficient scavengers of triplet-state energy.¹⁻⁴ Since the excited rare-earth acceptors exhibit measurable fluorescence, they have been used for quantitative evaluation of the transfer process from aromatic ketone sensitizers and of competitive photochemical reactions.^{1,4} We now report our results on exchange transfer in a rigid matrix using tervalent europium as acceptor. The combination of the europic ion acceptor with either 2-acetonaphthone or 2-acetylfluorene sensitizers presents a number of unique features.

The 2-Acetonaphthone- Eu^{3+} Pair.—As found from fluid-solution experiments the lowest triplet of the donor is deactivated collisionally by Eu^{3+} ions at a somewhat less than diffusion-controlled rate.¹ A major advantage of 2-acetonaphthone (I) (AN) is that it emits long-lived $\pi^* \rightarrow \pi$ phosphorescence in a rigid matrix. Therefore, accurate decay-time measurements are possible. This contrasts with most other aromatic ketones, which

exhibit the usual millisecond $\pi^* \rightarrow n$ phosphorescence, and with other non-carbonyl compounds having lowest π,π^* triplets, which do not transfer energy to Eu^{3+} presumably because of comparatively low polarity.¹



In contrast to ordinary organic triplet acceptors, the europic ion is small, has no vibrational states, and is spherically symmetric. No apparent donor-acceptor complexation or association occurs even at high concentration. This was established not only by the usual absorbance-additivity and changes-in-donor-emission procedures but also by the absence of Eu^{3+} fluorescence

¹ Parts I and II, N. Filipescu and G. W. Mushrush, *J. Phys. Chem.*, 1968, **72**, 3516, 3522.

² A. Heller and E. Wasserman, *J. Chem. Phys.*, 1965, **42**, 949.

³ W. J. McCarthy and J. D. Winefordner, *Analyt. Chem.*, 1966, **38**, 848.

⁴ A. A. Lamola and J. Eisinger, 'Molecular Luminescence,' ed. E. C. Lim, W. A. Benjamin, New York, 1969, p. 801.

on selective acetonaphthone excitation in non-deaerated fluid solutions. Whenever a donor forms such a complex, the bright orange Eu^{3+} -emission is virtually unaffected by dissolved oxygen.⁵⁻⁷ Absence of triplet-state emission from organic acceptors in liquid solution almost always precludes use of this sensitive method for detecting complexation.

The acetonaphthone- Eu^{3+} pair has the additional advantage that the blue donor phosphorescence and the narrow-band acceptor luminescence do not overlap. Therefore, their intensities can be measured separately and accurately. Further, the donor can be selectively excited at a variety of frequencies where Eu^{3+} does not absorb.

The 2-Acetylfluorene- Eu^{3+} Pair.—Like acetonaphthone, 2-acetylfluorene (II) (AF) has a lowest π, π^* triplet state, does not complex the Eu^{3+} acceptor either at room temperature or at 77 K, can be selectively excited, and phosphoresces at wavelengths which do not overlap those of Eu^{3+} fluorescence. The study allows comparison of two similar organic donors of substantially different phosphorescent lifetimes in connection with the same monatomic acceptor.

EXPERIMENTAL

Europium(III) chloride (American Potash and Chemical Co., 99.99% grade) was used without further purification. 2-Acetonaphthone and 2-acetylfluorene (Eastman Organic) were recrystallized twice from ethanol. Standard solutions of EuCl_3 , acetonaphthone, and acetylfluorene in spectrograde methanol-absolute ethanol (1 : 4 v/v) were prepared. Samples of different concentrations were obtained from the standards by dilution. 1 ml samples of donor-acceptor mixtures were introduced into quartz low-temperature tubes, which fit inside the cold-finger Dewar vessel of the Amico-Bowman Spectrophotofluorimeter. The tubes were provided with a quartz-to-pyrex graded seal, a degassing side-reservoir, and a constriction. The sample in the degassing bulb was submitted to 30–40 cycles of freeze-and-thaw by repetitive immersion into liquid nitrogen under high vacuum and was flame-sealed. The bottom part of the tube was calibrated to allow accurate evaluation of the amount of solvent lost during degassing and the change in volume caused by glass formation in the Aminco Dewar vessel. The concentrations reported have been corrected for evaporation and contraction. High-quality frozen glasses were obtained. The emission spectra of the samples were obtained at 77 K upon excitation in a narrow band centred at 349 nm for acetonaphthone and 321 nm for acetylfluorene in a 90° geometry. These spectra were corrected by computer for the R136 photomultiplier response (S-20) and emission monochromator characteristics. The R136 response curve was supplied by the American Instrument Company and the monochromator correction factors were determined by monitoring spectra of numerous standards of known spectral distribution of emission.⁷⁻¹⁰ The quantum yields were obtained by comparison of the

areas under corrected emission curves with those of standards of known luminescence quantum yield⁷⁻¹⁰ (quinine sulphate and benzophenone for the organic materials and Rhodamine B for Eu^{3+}). Phosphorescence decay times were determined with the time-base XY-recorder Model 320T-1612 (Electro Instrument).

RESULTS

Since the u.v. absorption spectra of acetonaphthone, acetylfluorene, and Eu^{3+} are well known, they will not be

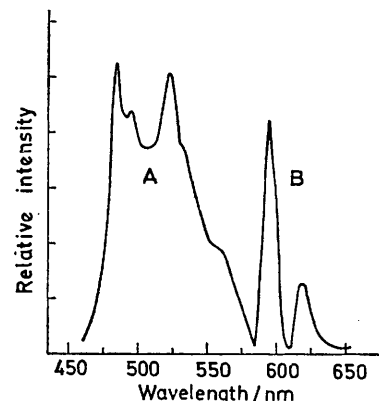


FIGURE 1 Emission spectra of 5.1×10^{-3} M-2-acetonaphthone and 0.30 M- EuCl_3 in degassed methanol-ethanol glass at 77 K upon excitation at 349 nm, uncorrected; A represents acetonaphthone phosphorescence and B represents Eu^{3+} fluorescence

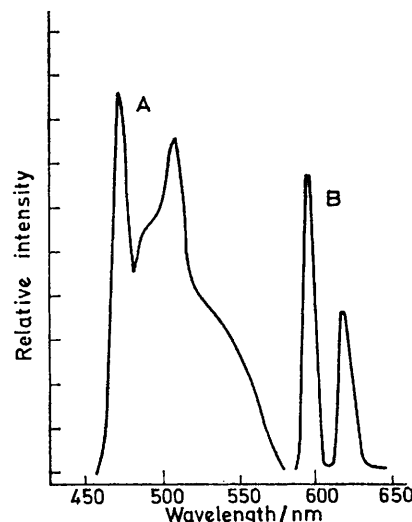


FIGURE 2 Emission spectrum of 5.1×10^{-4} M-2-acetylfluorene and 0.30 M- EuCl_3 in degassed methanol-ethanol glass at 77 K upon excitation at 321 nm, uncorrected; A represents acetylfluorene phosphorescence and B represents Eu^{3+} fluorescence

shown here. Typical emission spectra obtained under selective donor excitation for acetonaphthone- Eu^{3+} and acetylfluorene- Eu^{3+} mixtures are given in Figures 1 and 2, respectively. The $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions in

⁵ R. E. Whan and G. A. Crosby, *J. Mol. Spectroscopy*, 1962, **8**, 315.

⁶ N. Filipescu and N. McAvoy, *J. Inorg. Nuclear Chem.*, 1966, **28**, 253.

⁷ N. Filipescu, G. W. Mushrush, C. R. Hurt, and N. McAvoy, *Nature*, 1966, **211**, 960.

⁸ C. A. Parker and W. J. Barnes, *Analyst*, 1957, **82**, 606; C. A. Parker and W. T. Rees, *ibid.*, 1960, **85**, 587; C. A. Parker, *Analyt. Chem.*, 1960, **34**, 502.

⁹ C. E. White, M. Ho, and E. Q. Weiner, *Analyt. Chem.*, 1960, **32**, 438.

¹⁰ W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.

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Eu^{3+} are found in the orange-red region at 592 and 615 nm. On the other hand, the structured blue-green acetonaphthone phosphorescence displays peaks at 485, 494, 520, and 560sh nm and that of acetylfluorene at 472, 490sh, 510, and 540sh nm. The spectral separation of fluorescence and phosphorescence allows accurate individual intensity measurements. The decadic extinction coefficient of Eu^{3+} at the excitation wavelengths is of the order of $2 \text{ l mol}^{-1} \text{ cm}^{-1}$ whereas those of the organic sensitizers exceed $4 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Therefore, no correction for the direct excitation of Eu^{3+} ions is necessary. As the rare-earth-ion concentration was increased, the Eu^{3+} fluorescence became more intense with concomitant decrease in the long-lived donor phosphorescence. The original sensitizer concentration was the same in all mixed samples studied; however, because of slight variations in the amount of solvent evaporated during degassing, the final concentration varied within 3%. Besides additivity in donor and acceptor absorbance and absence of change in the shape of donor phosphorescence, evidence for lack of complex formation between Eu^{3+} and the two ketones was based on the absence of sensitized fluorescence from non-deaerated mixed solutions of EuCl_3 -AN or EuCl_3 -AF.⁵⁻⁷

The accuracy of quantum-yield measurements was limited mainly by sample geometry, spectral correction, and graphical integration. From reproducibility we estimate the quantum-yields values ϕ_p and ϕ_t listed in the Table to be correct within 15%. Concentrations listed for

Lifetimes of donor phosphorescence and luminescence quantum yields of donor and acceptor emission in different Eu^{3+} concentrations

Europic chloride concn. $[\text{F}]/\text{M}$	Ketone phosphorescence quantum yield ϕ_p	$^5\text{D} \rightarrow ^7\text{F}$ Eu^{3+} Fluorescence quantum yield ϕ_t	Phosphorescence e -decay time τ_p/s
$5 \times 10^{-3}\text{M}$ -2-Acetonaphthone			
0	0.380	—	6.80
0.053	0.255	9.2×10^{-4}	5.52
0.10	0.190	1.5×10^{-3}	4.19
0.15	0.169	2.0×10^{-3}	3.39
0.21	0.131	2.7×10^{-3}	3.30
0.31	0.110	3.4×10^{-3}	3.13
0.43	0.090	5.3×10^{-3}	2.36
0.52	0.072	6.9×10^{-3}	2.09
$5 \times 10^{-4}\text{M}$ -2-Acetylfluorene			
0	0.66	—	1.65
0.05	0.52	0.009	1.43
0.10	0.41	0.036	1.21
0.21	0.33	0.080	1.01
0.30	0.25	0.15	0.92
0.40	0.17	0.23	0.85
0.51	0.09	0.34	0.71

both donor and acceptor have been corrected for solvent evaporation and glass contraction.

Figures 3 and 4 show the decrease of phosphorescence intensity with time following excitation cut-off for different acceptor concentrations. To exhibit the degree of exponentiality, we plotted the curves corresponding to different EuCl_3 concentrations on a logarithmic scale. Except for the initial few seconds the acetonaphthone graph

(Figure 3) indicates that the decay of the $T_1 \rightarrow S_0$ donor emission is exponential. In contrast, the straight lines in Figure 4 indicate virtually exponential behaviour for acetylfluorene even upon extrapolation to zero time. This

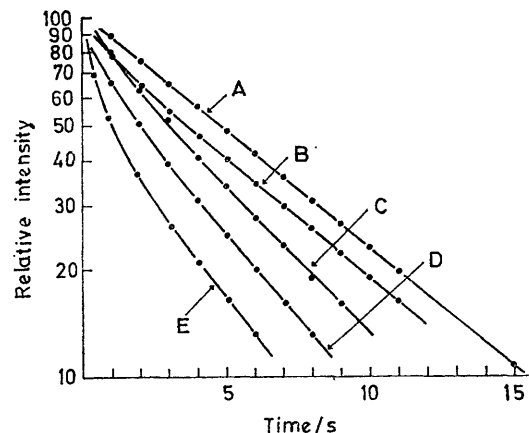


FIGURE 3 Semilogarithmic plots of decay curves for phosphorescence of $0.52 \times 10^{-3}\text{M}$ -2-acetonaphthone at EuCl_3 concentrations A, 0M; B, 0.053M; C, 0.10M; D, 0.21M; and E, 0.52M in degassed methanol-ethanol glass at 77 K. Other EuCl_3 concentrations of 0.15, 0.31, and 0.43M were omitted for clarity

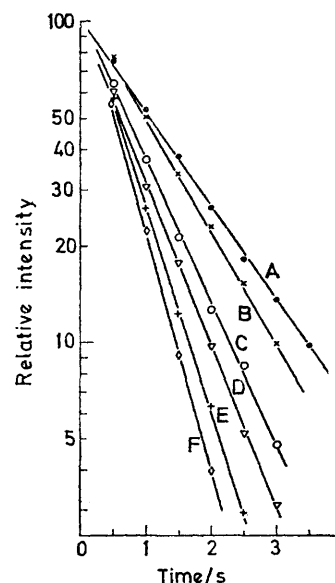


FIGURE 4 Semilogarithmic plots of decay curves for 2-acetylfluorene phosphorescence at different EuCl_3 concentrations in methanol-ethanol glass at 77 K; A, no EuCl_3 ; B, 0.10M- EuCl_3 ; C, 0.21M- EuCl_3 ; D, 0.30M- EuCl_3 ; E, 0.40M- EuCl_3 ; and F, 0.51M- EuCl_3 . The curve corresponding to the EuCl_3 concentration of 0.05M was omitted for clarity, since it was very close to curve A

behaviour contrasts with the highly non-exponential curves obtained by Terenin and Ermolaev^{11,12} for different pairs of organic donors and acceptors but agrees with the data of Eisenthal and Siegel.¹³⁻¹⁵

¹¹ A. Terenin and V. L. Ermolaev, *Trans. Faraday Soc.*, 1956, **52**, 1042.

¹² V. L. Ermolaev, *Soviet Phys. Uspekhi*, 1963, **80**, 333; English translation.

¹³ K. B. Eisenthal and R. Murashige, *J. Chem. Phys.*, 1963, **39**, 2108.

¹⁴ S. Siegel and H. S. Judeikis, *J. Chem. Phys.*, 1968, **48**, 1613.

¹⁵ S. Siegel and K. B. Eisenthal, *J. Chem. Phys.*, 1963, **38**, 2785.

The phosphorescence e -decay times τ_p are also listed in the Table for different acceptor concentrations, where we take the e -decay time to be the time necessary for the intensity of luminescence to reach $1/e$ of its original value and to be independent of the exponentiality of the decay curves. As usual, some variation in lifetime values was observed, depending on the method and extent of degassing. Therefore, we attempted to submit all samples to uniform degassing conditions.

DISCUSSION

n, π^* Transfer.—It was intriguing that of a variety of aliphatic and aromatic compounds tested as sensitizers for Eu^{3+} in both liquid and solid solutions the only efficient non-complexing donors were aromatic carbonyl compounds with lowest π, π^* triplet states, such as acetonaphthone, naphthaldehyde, acetylfluorene, and acetylphenanthrene.¹ The reason for this is not obvious. It is known that non-carbonyl compounds with π, π^* lowest triplet above the resonance levels of europium ion, such as naphthalene and terphenylene, do not sensitize acceptor fluorescence at all.¹ Further, aromatic carbonyl compounds with lowest n, π^* triplet of appropriate energy are poor sensitizers. Thus, it seems that an efficient non-chelating donor must have both a lowest π, π^* triplet and a nearby n, π^* T_2 state. In frozen mixed solution lowest n, π^* triplets of 'normal' ketones, such as benzophenone, are deactivated by phosphorescence and intramolecular thermal deactivation (rate constants *ca.* 10^3 s^{-1}) much more quickly than by intermolecular transfer to a nearby lanthanide ion (rate *ca.* 10^{-1} s^{-1} at 0.2M-acceptor concentration, see below). On the other hand, the major decay path of the $^3(n, \pi^*)$ level is to the long-lived nearby $^3(\pi, \pi^*)$ state. Since π, π^* triplets, such as those of naphthalene and fluorene, are unable to transfer energy to the europium ion,¹ it is natural to assume that the carbonyl substituent on acetonaphthone and acetylfluorene is instrumental in transfer. The role of the carbonyl group can be explained in one of two ways. Either it confers added polarity to the lowest π, π^* triplet necessary for 'penetration' of the solvation shell of the rare-earth ion, or its n, π^* triplet, situated slightly above the lowest $^3(\pi, \pi^*)$ state, is actually the level in which transfer originates. Since polar substituents other than carbonyl attached to aromatic nuclei do not make europium ion sensitizers of these compounds,¹⁶ the latter seems to us more probable.

It is known that for many ketones with a lowest π, π^* triplet level, lowering solvent polarity may bring about an inversion of the $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ states, as shown by a sharp decrease in the phosphorescence life-

time and a marked increase in the photoreduction quantum yield.¹⁷⁻²⁰ Because of their proximity, the $^3(\pi, \pi^*)$ and $^3(n, \pi^*)$ states are both populated by Boltzmann statistics ($RT = \text{ca. } 0.15 \text{ kcal mol}^{-1}$ at 77 K; for $E_{n, \pi^*} - E_{\pi, \pi^*}$ assumed to be about $0.2 \text{ kcal mol}^{-1}$, the relative populations are *ca.* 1:4, respectively). Since the lifetime of the $^3(\pi, \pi^*)$ state is on the order of several seconds, that of the $^3(n, \pi^*)$ is in effect also lengthened by virtue of their equilibrium. Consequently, transfer from the $^3(n, \pi^*)$ state to the lanthanide acceptor can be significant.

The fact that ketones with lowest π, π^* triplets are efficient sensitizers in liquid solution as well could be understood in terms of the different quenching mechanism of n, π^* and π, π^* triplets. A carbonyl compound with lowest n, π^* triplet tends to react, reversibly^{21, 22} (*e.g.*, addition) or irreversibly^{23, 24} (*e.g.*, H-abstraction), with solvents in which the rare-earth salt is also soluble. Because this reactive pathway is not normally open to lowest, π, π^* triplets, such ketones tend to deactivate either by transfer to another solute or by self-quenching.²⁵ Nonetheless, even in the liquid state the nearby n, π^* second triplet can still be responsible for the actual transfer to solvated europic ion. This process is enhanced by the higher Boltzmann population of the T_2 state caused by temperatures higher than those required for frozen solution. The substantial concentration of acceptor used in these experiments will also favour transfer.

Photokinetics.—A steady-state treatment of the simplified mechanism of Scheme 1 leads to expressions (1)–(3),

$$\frac{1}{\phi_p} = \frac{1}{\phi_p^0} + \frac{(k_1 + k_2)k_5[{}^7F]}{k_1k_3} \quad (1)$$

$$\frac{1}{\tau_p} = k_3 + k_4 + k_5[{}^7F] \quad (2)$$

$$\frac{1}{\phi_i} = \frac{k_6 + k_7}{k_6} \frac{k_1 + k_2}{k_1} \left(1 + \frac{k_3 + k_4}{k_5[{}^7F]} \right) \quad (3)$$

where 7F and 5D represent the ground-state and the excited 5D_0 emitting level of Eu^{3+} , respectively; ϕ_p^0 , the phosphorescence quantum efficiency of donor in the absence of acceptor, is $k_1k_3/[(k_1 + k_2)(k_3 + k_4)]$; τ_p the donor e -decay time; the k 's the rate constants; and S_0 , S_1 , and T_1 the ground, excited singlet, and lowest triplet states, respectively, of the sensitizer. No differentiation was made in Scheme 1 between the phosphorescent $^3(\pi, \pi^*)$ T_1 level and the $^3(n, \pi^*)$ T_2 state

²¹ G. O. Schenk and R. Steinmetz, *Bull. Soc. chim. belges*, 1962, **71**, 781.

²² N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, 1968, **90**, 3264.

²³ For atom-abstraction reactions, see for example, D. C. Neckers in 'Mechanistic Organic Photochemistry,' Reinhold, New York, 1967, ch. 7, p. 163. For addition reactions of n, π^* carbonyl triplets, see N. C. Yang, *Pure Appl. Chem.*, 1964, **9**, 591.

²⁴ O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, 1969, **91**, 5390.

²⁵ R. E. Kellogg, *J. Chem. Phys.*, 1964, **41**, 3046.

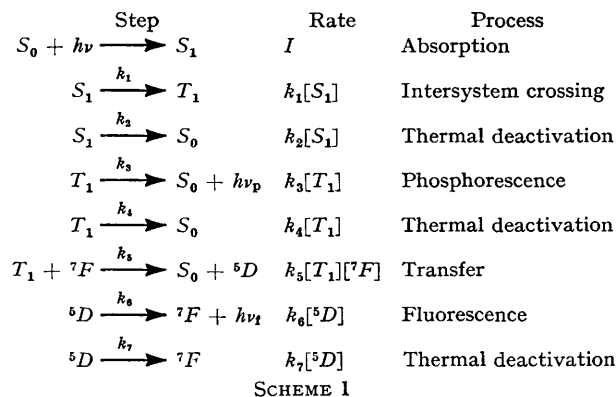
¹⁶ For example, halogeno-, amino-, and methoxy-naphthalenes do not sensitize europium fluorescence; unpublished results.

¹⁷ G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1962, **84**, 207.

¹⁸ G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, 1962, **66**, 1148.

¹⁹ K. Brederick, Th. Förster, and H. G. Oesterlin, 'Luminescence of Organic and Inorganic Materials,' Wiley, New York, 1962, p. 161.

²⁰ A. A. Lamola, *J. Chem. Phys.*, 1967, **47**, 4810.



presumably responsible for transfer, since under the assumption of a rapid equilibrium between T_1 and T_2 the rate expressions do not change in form. However in this interpretation, k_5 incorporates the equilibrium constant between the two triplets.

Plots of $1/\phi_p$ against $[{}^7F]$, $1/\tau_p$ against $[{}^7F]$, and $1/\phi_f$ against $1/[{}^7F]$ are good straight lines; this tends to substantiate the major features of the mechanism in Scheme 1. In fact, excellent straight lines can be drawn through the experimental points of both acetonaphthone and acetylfluorene with one exception: the high-concentration points in the plots of $1/\phi_p$ against $[{}^7F]$ lie above the linear extrapolation of low-concentration data. This seems to indicate a relatively efficient self-quenching process operative only when the concentration of ground-state donors is appreciable because of fast deactivation *via* transfer. In contrast, at low EuCl_3 concentration under steady illumination virtually the entire population is in the lowest triplet state.

There is good evidence supporting distant (40–50 Å) triplet-triplet annihilation^{25–27} and excimer formation for aromatic ketones having lowest π, π^* triplets.^{24,28} These processes could be included in the kinetics. For example, assuming that the energy of the excimer, formed by $T_1 + S_0 \longrightarrow$ excimer (k_{ex}), is below the 5D_0 level of the acceptor, the kinetic expression for $1/\phi_p$ becomes (4). Here, as previously defined, $\phi_p^0 =$

$$\frac{1}{\phi_p} = \frac{1}{\phi_p^0} + \frac{(k_1 + k_2)k_{ex}[S_0]}{k_1k_3} + \frac{(k_1 + k_2)k_5[{}^7F]}{k_1k_3} \quad (4)$$

$k_1k_3/(k_1 + k_2)(k_3 + k_4)$, where k_4 does not incorporate

* Because of the narrow-band fluorescence of Eu^{3+} , which has to be compared with broad-band emission of the standard, ϕ_f and ϕ_p^0 values are probably less accurate than phosphorescence data. Measurement of ϕ_f^0 by direct excitation of Eu^{3+} to 5D_3 at 394 nm in the absence of sensitizer gave values below 0.1; because of ϕ_f values of 0.34, we estimated ϕ_p^0 to be close to 0.35. The discrepancies are undoubtedly caused by errors in graphical integration and departure from monochromaticity in the exciting light in association with the sharp absorption and emission of the lanthanide ion. See, for example, H. J. Borchardt, *J. Chem. Phys.*, 1965, **42**, 3743.

† For example, for $\Delta E = 1 \text{ kcal mol}^{-1}$, k_5 becomes about $2 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ for the mechanism proceeding *via* the ${}^3(n, \pi^*)$ state. This value is still acceptable since it is close to those obtained with other organic sensitizers having lowest n, π^* triplets, such as benzophenone and benzaldehyde¹¹ and contrasts with the *ca.* 10^{-1} s^{-1} values reported for ${}^3(\pi, \pi^*)$ sensitizers, such as carbazole.¹¹

triplet deactivation by excimer formation; ϕ_p^0 actually represents the phosphorescence quantum yield of donor at low concentration in the absence of acceptor. The extra term $(k_1 + k_2)k_{ex}[S_0]/k_1k_3$ depends on the Eu^{3+} concentration. Since under steady-state illumination $[S_0]$ is small, this term is negligible at low acceptor concentration because of the relatively long lifetime of T_1 . In contrast, at high Eu^{3+} concentrations, the sensitizer triplet is deactivated by transfer at a higher rate and, therefore, even under steady illumination, $[S_0]$ is not negligible. At higher acceptor concentrations, this would be reflected in a faster increase of $1/\phi_p$ with $[{}^7F]$ than predicted by the low-concentration straight line. Such behaviour is suggested by the non-conforming points. Using an intersystem-crossing quantum yield,²⁹ $k_1/(k_1 + k_2)$, of 0.84 and a limiting fluorescence quantum yield* of Eu^{3+} , $\phi_f^0 = k_6/(k_6 + k_7)$, of 0.35, one can evaluate the rate constant for energy transfer k_5 from three different sets of data, namely, from slopes and intercepts of graphs of equations (1)–(3). We obtained $k_5 = 0.60$ and $1.5 \text{ l mol}^{-1} \text{ s}^{-1}$ for acetonaphthone and acetylfluorene respectively. These rate constants not only refer to transfer but include the equilibrium constant between the π, π^* and n, π^* triplets. At 77 K, assuming an energy difference † of 0.2 kcal mol^{-1} , we obtain a Boltzmann factor of *ca.* 0.26; therefore, the actual rate constants for transfer from ${}^3(n, \pi^*)$ are estimated to be 2.3 and 6.0 $\text{l mol}^{-1} \text{ s}^{-1}$. The plots also allow calculation of the rate constants of unimolecular deactivation processes, k_3 and k_4 . For acetonaphthone, we obtain $k_3 = 0.09 \text{ s}^{-1}$ and $k_4 = 0.06 \text{ s}^{-1}$. This gives a limiting value to the natural lifetime of acetonaphthone phosphorescence in the absence of all quenching processes (τ_0), of at least k_3^{-1} , *ca.* 11 s. Thus, it agrees with the estimated τ_0 values calculated from $S_0 \longrightarrow T_1$ absorption intensities for π, π^* triplets of aromatic compounds.³⁰ The experimental τ_0 value (6.80 s) is smaller than expected because of impurity quenching, mainly by traces of oxygen. On the other hand, under our experimental conditions, impurity quenching in solutions containing Eu^{3+} acceptor is slower than transfer to the rare-earth ion; therefore, τ_p values are reasonably accurate. This value for k_4 includes all first-order and pseudo-first-order radiationless deactivation processes. Bimolecular deactivation reactions such as triplet-triplet annihilation and excimer formation (or other self-quenching mechanisms) have been neglected. They are not expected to make significant contributions to the overall rate in frozen solutions except for the relatively few donor molecules trapped in close proximity to other other donors. Triplet-triplet annihilation requires two excited donors frozen near one another. But, if acetonaphthone does form excimers, the probability of

²⁶ R. G. Bennett, *J. Chem. Phys.*, 1964, **41**, 3048.

²⁷ T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, 1963, **39**, 1186.

²⁸ P. J. Wagner, *J. Amer. Chem. Soc.*, 1967, **89**, 5715.

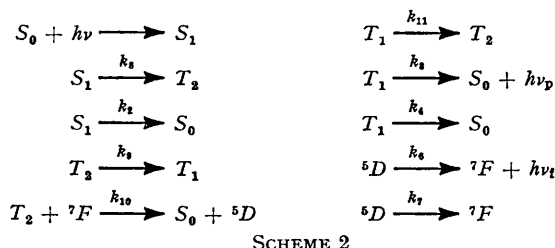
²⁹ A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 1956, **43**, 2129.

³⁰ S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 1966, **66**, 199.

excimer formation, requiring only single excitation, is higher.

For acetylfluorene, $k_3 + k_4 = 0.61 \text{ s}^{-1}$ with k_3 and k_4 comparable with one another. This is consistent with the competitive relationship between the radiative and radiationless deactivation of the lowest triplet of acetylfluorene, as determined from phosphorescence quantum-yield measurements ($\phi_p^0 = 0.66$) in alcoholic glass at 77 K.

A mechanism consistent with transfer from the second triplet is shown in Scheme 2. In this sequence the rate



constants corresponding to steps already in Scheme 1 are labelled with the same subscripts. In addition, the following assumptions were made. First, intersystem crossing from S_1 takes place exclusively to the T_2 state; this is substantiated not only by the energetic location^{31,32} of T_2 but especially by symmetry considerations.^{20,33,34} Secondly, the sensitizer fluorescence and the phosphorescence from the T_2 state are negligible; this is certainly supported by experiment. Finally, we assume that no transfer takes place from the π, π^* lowest triplet. We will discuss this scheme in connection with the acetylfluorene sensitizer.

Phosphorescence Decay.—The phenomenological rate expressions for the T_1 and T_2 levels from Scheme 2 are (5) and (6).

$$d[T_2]/dt = k_8[S_1] + k_{11}[T_1] - k_9[T_2] - k_{10}[{}^7F][T_2] \quad (5)$$

$$d[T_1]/dt = k_9[T_2] - (k_3 + k_4 + k_{11})[T_1] \quad (6)$$

Since after steady-state-illumination cut-off S_1 depopulates irreversibly in very short times compared to phosphorescence, we take $[S_1]$ to be zero. In addition, since T_2 is not depopulated suddenly, a steady-state approximation, $d[T_2]/dt = 0$, is certainly appropriate for this state. Eliminating $[T_2]$ between equations (5) and (6) and integrating equation (6), we obtain equation (7) or, since $k_3 + k_4 = 1/\tau_0$, where τ_0 is the donor

$$\frac{1}{\tau_p} = k_3 + k_4 + k_{11} - \frac{k_9 k_{11}}{k_9 + k_{10}[{}^7F]} \quad (7)$$

phosphorescent lifetime in the absence of EuCl_3 , equation (7a). A plot of $\tau_p \tau_0 / (\tau_0 - \tau_p)$ against $1/[{}^7F]$ for AF- Eu^{3+}

$$\frac{\tau_p \tau_0}{\tau_0 - \tau_p} = \frac{1}{k_{11}} + \frac{k_9}{k_{10} k_{11} [{}^7F]} \quad (7a)$$

³¹ W. Siebrand, 'The Triplet State,' ed. A. B. Zahlan, Cambridge Univ. Press, 1967, p. 31.

³² M. Bixon and J. Jortner, *J. Chem. Phys.*, 1968, **48**, 715.

is shown in Figure 5. The slope of the straight line is 0.53 mol/l . Since the two nearby triplets are thermally equilibrated through rapid phonon interaction with solvent, the T_1 and T_2 populations satisfy the Boltzmann equation. Thus, the k_{11} activation energy is just the endothermicity of the $T_1 \rightarrow T_2$ transition and the rate constants k_{11} and k_9 have identical frequency factors determined by the transition probability. Consequently, k_9/k_{11} is given by $\exp [(E_{T_1} - E_{T_2})/RT]$. Arbitrarily assuming³⁵ that $E_{T_1} - E_{T_2} = ca. 0.2 \text{ kcal mol}^{-1}$, we have that $k_9/k_{11} = ca. 4$. Using this value, we obtain the rate constant for energy transfer k_{10} to be $7.9 \text{ l mol}^{-1} \text{ s}^{-1}$.

Because of the advantages of the AF- EuCl_3 pair there are two alternative ways of estimating the transfer rate

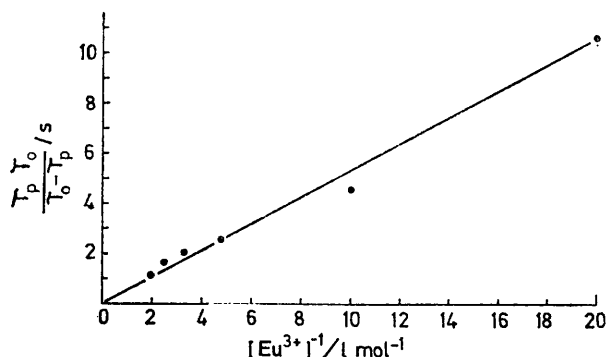


FIGURE 5 2-Acetylfluorene

constant k_{10} , namely, from the quantum efficiency data for donor phosphorescence or acceptor fluorescence, both obtained under continuous excitation.

Luminescence Quantum Yields.—A steady-state treatment of Scheme 2 gives expressions (8) and (9), for the

$$\frac{1}{\phi_p} = \frac{1}{\phi_p^0} + \frac{(k_3 + k_4 + k_{11})k_{10}}{\phi_p^0(k_3 + k_4)k_9} [{}^7F] \quad (8)$$

$$\frac{1}{\phi_t} = \frac{1}{\phi_t^0 \phi_{isc}} + \frac{k_9(k_3 + k_4)}{\phi_t^0 \phi_{isc}(k_3 + k_4 + k_{11})k_{10} [{}^7F]} \quad (9)$$

quantum yields of acetylfluorene phosphorescence ϕ_p and Eu^{3+} fluorescence ϕ_t , where $\phi_p^0 = k_3 k_8 / (k_2 + k_8)(k_3 + k_4)$, $\phi_t^0 = k_6 / (k_6 + k_7)$, and $\phi_{isc} = k_8 / (k_2 + k_8)$. Now, $k_3 + k_4 = 1/\tau_0 = 0.61 \text{ s}^{-1}$, $k_{11} \gg k_3 + k_4$, $\phi_p^0 = 0.66$, and $\phi_{isc} \approx 0.8$. In addition, we assume that $\phi_t^0 \approx 0.35$ and, as above, that $k_9/k_{11} \approx 4$ (cf. footnote, p. 67). The slope of the line in Figure 5 gives $k_{10} \approx 13 \text{ l mol}^{-1} \text{ s}^{-1}$; this value is within a factor of 2 of that derived from lifetime data. A less reliable value is obtained from the graph of $1/\phi_t$ against $1/[{}^7F]$ graph, namely, $3.2 \text{ l mol}^{-1} \text{ s}^{-1}$. Probably $k_{10} \approx 10 \text{ l mol}^{-1} \text{ s}^{-1}$ is representative of the transfer rate. This is about four times larger than that determined for the AN- Eu^{3+}

³³ N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1967, p. 72.

³⁴ R. Shimada and L. Goodman, *J. Chem. Phys.*, 1965, **43**, 2027.

³⁵ N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenberger, *J. Amer. Chem. Soc.*, 1967, **89**, 5468.

pair under similar experimental conditions. Since the intersystem-crossing quantum efficiency is already nearly unity in acetophenone and since the nature of the T_1 and T_2 states in both acetylfluorene and acetophenone should be very much alike, differences in these factors are probably not responsible for the increase. In view of our mechanism, a natural explanation is provided by slight differences in the $^3(n,\pi^*) - ^3(\pi,\pi^*)$ energy gaps in the two ketones. It should be mentioned that the lowest triplets of the two sensitizers have slightly different energies relative to the Eu^{3+} levels. The problem of energy-level matching will be considered in more detail elsewhere. It is clear that the rate constant is very sensitive to small changes in ΔE , since at 77 K the value of RT is only 0.15 kcal mol $^{-1}$. The linearity of the plots and the magnitude of the transfer rate constant are consistent with a mechanism based on transfer from the n,π^* triplet of the sensitizer.

Statistical Analysis.—The above results were interpreted in terms of the statistical models developed by Inokuti and Hirayama³⁶ and Minn and Filipescu.³⁷ In Inokuti and Hirayama's model the emission intensity at time t , $P(t)$, is $P(t) = \exp[-t/\tau_0 - (c/c_0\gamma^3)g(e\tau t/\tau_0)]$, where the 'critical concentration' c_0 and γ are parametric-fit quantities, c the acceptor concentration, and g a function defined by $g(z) = -z \int_0^1 \exp(-zy) (\ln y)^3 dy$.

In Minn and Filipescu's model $P(t)$ is given by $P(t) = c \exp(-t/\tau_0) \int_0^1 [\exp(-Ate^{-2r/L})] [\exp(-4\pi cr^3/3)] 4\pi r^2 dr$, where the frequency A and the 'effective Bohr radius' L are essentially adjustable parameters with vaguely defined physical significance. The parameters in these two formulae for $P(t)$ are related by $A = e\tau/\tau_0$ and $c_0 = 3/(4\pi L^3)$ and come ultimately from Dexter's expression³⁸ for the transfer rate constant $k_{10}(r) = A \exp(-2r/L)$.

The shape of the decay curve $P(t)$ is determined by the probability $p(t)$ [equation (10)] of finding the $p(t) =$

$$\exp[-(k_3 + k_4 + k_{11})t] \exp\left(\frac{k_9 k_{11} t}{k_9 + k_{10}[^7F]}\right) \quad (10)$$

emitting T_1 state still populated at time t after excitation cut-off.^{36,37} For T_2 transfer from a single donor molecule, $p(t)$ is given by $p(t) = \exp(-t/\tau_p)$, where $1/\tau_p$ is given by equation (7). One of the rate constants, k_{10} , is dependent on the donor-acceptor separation distance r . For the ensemble, the phosphorescence intensity $P(t)$ is given by the distance-averaged probability, $P(t) = \int p(t) dV$ or, equation (11), where $w(r) P(t) = \exp[-(k_3 + k_4 + k_{11})t]$

$$\int \exp\left(\frac{k_9 k_{11} t}{k_9 + k_{10}[^7F]}\right) w(r) 4\pi r^2 dr \quad (11)$$

is the density of acceptors³⁶ or of nearest-neighbours³⁷ at r . The integration is difficult to carry out, even numerically, because of the parametric dependence of

k_{10} on r and because of only incomplete knowledge of k_9 and k_{11} . However, one can see that if $k_{10}[^7F]$ is either small compared with k_9 or relatively r -independent, the decay curves will be exponential.

The experimentally measurable quantities, the phosphorescence-yield ratio ϕ_p/ϕ_p^0 and the decay-time ratio τ_p/τ_0 , are obtained from the equations $\phi_p/\phi_p^0 = \int_0^\infty P(t) dt / \tau_0$ and $\int_{\tau_p}^\infty P(t) dt / \int_0^\infty P(t) dt = e^{-1}$.

Values of ϕ_p/ϕ_p^0 and τ_p/τ_0 at different Eu^{3+} concentrations are compared with theoretically predicted curves in Figures 6–9. Although Minn and Filipescu's

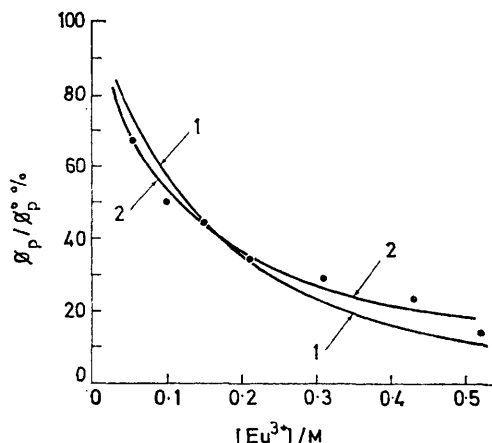


FIGURE 6 Comparison of ϕ_p/ϕ_p^0 against EuCl_3 concentration with the theoretically predicted curves for acetophenone; ●, Experimental; 1, Inokuti and Hirayama's model with $\gamma = 5.44$ and $L = 4.47 \text{ \AA}$; 2, Minn and Filipescu's model with $A = 8.5 \text{ Hz}$ and $L = 6.65 \text{ \AA}$

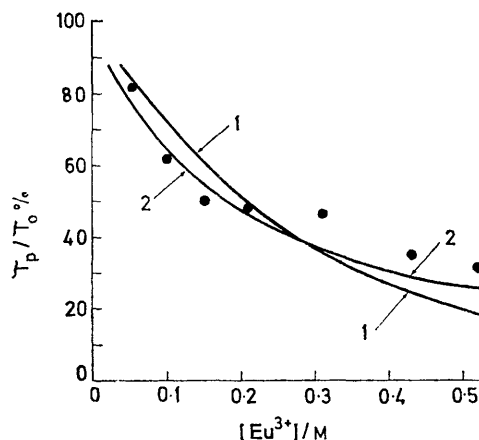


FIGURE 7 Comparison of curve of τ_p/τ_0 against EuCl_3 concentration with the theoretically predicted curves for acetophenone; ●, Experimental; 1, Inokuti and Hirayama's model with $\gamma = 5.44$ and $L = 4.47 \text{ \AA}$; 2, Minn and Filipescu's model with $A = 8.5 \text{ Hz}$ and $L = 6.65 \text{ \AA}$

model gives slightly better fits, both models give very good agreement. The experimental decay curves for

³⁶ M. Inokuti and F. Hirayama, *J. Chem. Phys.*, 1965, **43**, 1978.

³⁷ F. L. Minn and N. Filipescu, *J. Chem. Soc. (A)*, 1970, 1016.

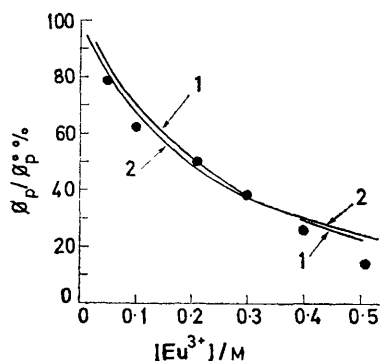


FIGURE 8 Comparison of experimental and theoretical ϕ_p/ϕ_p^0 at different EuCl_3 concentrations for acetylfluorene; \bullet , Experimental; 1, Inokuti and Hirayama's model with $\gamma = 5.75$ and $L = 3.60 \text{ \AA}$; 2, Minn and Filipescu's model with $A = 175 \text{ Hz}$ and $L = 4.00 \text{ \AA}$

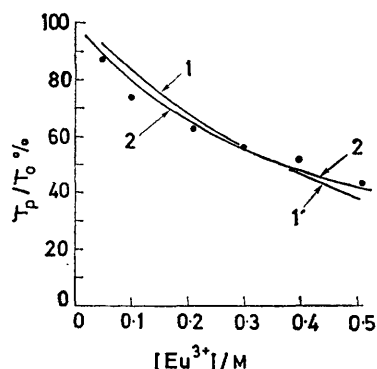


FIGURE 9 Comparison of experimental and theoretical curves of τ_p/τ_0 against EuCl_3 concentration for acetylfluorene; \bullet , Experimental; 1, Inokuti and Hirayama's model with $\gamma = 5.75$ and $L = 3.60 \text{ \AA}$; 2, Minn and Filipescu's model with $A = 175 \text{ Hz}$ and $L = 4.00 \text{ \AA}$

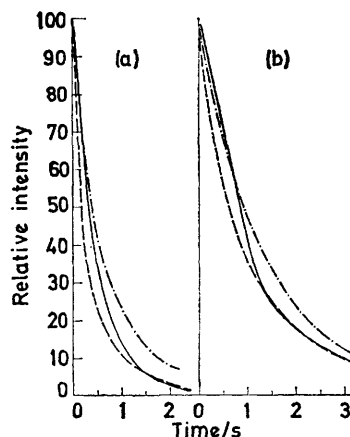


FIGURE 10 Experimental and theoretical phosphorescence decay curves following steady-state excitation cut-off; (a) 0.51M- EuCl_3 ; (b) 0.10M- EuCl_3 ; (—) Experimental; (---) Minn and Filipescu's model; (-·-·-) Inokuti and Hirayama's model. Excitation of acetylfluorene at 321 nm.

the highest and lowest acceptor concentrations are compared in Figure 10 for acetylfluorene with those

predicted by the both treatments. Again, the two probability expressions give satisfactory agreement without reproducing the curves in detail. A fit with experimental decay curves is a very sensitive check not only on the physical model but also on the assumed mechanism of transfer. To our knowledge this is the first time such agreement has been reported for decay curves in an exchange mechanism. The above results tend to confirm that transfer occurs by exchange. However, it should be pointed out that for acetophenone the decay curves predicted by both models fail to agree with those observed; the statistical treatments give a faster decay.

The fact that the phosphorescence decay curves become exponential very rapidly, in times short compared with τ_0 , deserves comment. Both Inokuti and Hirayama's and Minn and Filipescu's models, as well as the sphere-of-quenching model,³⁸ predict exponential decay of donor emission at long times. However, the shapes of these curves would differ. In one extreme, corresponding to the active-volume with instantaneous transfer within the sphere of quenching, the phosphorescence intensity $P(t)$ should be of the form $P(t) = 1$ for $t = 0$ and $P(t) = \exp(-t/\tau_0 - c/c')$ for $t > 0$ where c' is a constant with dimensions of concentration. The semilogarithmic plot of such curves for different acceptor concentrations c gives roughly parallel lines which do not pass through the point $P(0) = 1$. At the other extreme, in which the transfer is independent of donor-acceptor separation distance,³⁹ the luminescence intensity is given by $P(t) = \exp[-(1 + c/c'')t/\tau_0]$, where c'' is another constant, and the corresponding semilogarithmic plot consists of a number of straight lines of different slopes radiating from $P(0) = 1$. Figure 3 suggests that the AN- Eu^{3+} system is between these two extremes but closer to the Perrin model since the slopes of the long-time portion of the lines are roughly the same. The non-linearity in the first few seconds could be interpreted as originating in a transfer probability less than unity within the sphere of quenching. The radius of the active volume derived from quantum-yield data is approximately 12 \AA , essentially that reported for other organic-chromophore pairs. On the other hand, the radial disposition of the straight lines in Figure 4 suggests that the AF- EuCl_3 system behaves in a manner close to that predicted by the Stern-Volmer model.⁴⁰ A transfer-rate law independent of donor-acceptor separation distance r seems incompatible with the presumed exchange mechanism; however, even some r -dependence can be accommodated to give straight lines. It is obvious that for very small values of A or very large values of L , $k_{10}(r)$ is not severely dependent on r . The best fits between experimental and theoretical spectroscopic quantities were obtained with $A = \text{ca. } 10 \text{ Hz}$ and $L = \text{ca. } 5 \text{ \AA}$ for acetophenone and $A = \text{ca. } 200 \text{ Hz}$ and $L = \text{ca. } 4 \text{ \AA}$ for acetylfluorene. These values resemble those estimated for inorganic ionic

³⁸ D. L. Dexter, *J. Chem. Phys.*, 1953, **21**, 836.

³⁹ F. Perrin, *Compt. rend.*, 1924, **178**, 1978.

⁴⁰ O. Stern and M. Volmer, *Phys. Z.*, 1919, **20**, 183.

crystals⁴¹ ($A \sim 10$ Hz, $L \sim 4.5$ Å) but contrast markedly with those reported for organic mixtures^{11,12} ($A > 10^6$ Hz, $L < 2.0$ Å). It is difficult to single out the causes for the substantial differences found on replacing an organic acceptor with a lanthanide ion. The reason may lie in the nature of the rare-earth-ion acceptor (energy levels, paramagnetisms, high atomic number, etc.) or in its spherical symmetry and small size.

Although the physical meaning of A is elusive, the L value is presumably related to the spacial extension of both the excited-state donor and the ground-state acceptor wave functions. The fact that the effective Bohr radius is found to be smaller for excited acetylfluorene than for acetonaphthone with the same europic ion acceptors suggests that excitation delocalization is more extensive in acetonaphthone. In the valence-bond picture, this can be easily visualized on comparing alternant naphthalene with 2-substituted fluorene, since one cannot write resonance structures with charge separation or unpaired spins involving both the carbonyl substituent and the unsubstituted benzene ring in fluorene. Consequently, the size of the energy-donating section of the excited acetonaphthone may well exceed that of acetylfluorene.

Although the AN-EuCl₃ system gives agreement with Perrin's model³⁸ and yields a sphere-of-quenching radius of about 12 Å, the AF-EuCl₃ pair does not behave

accordingly. The fact that the decay curves in Figure 4 seem to fit a Stern-Volmer model, which takes k_{10} virtually independent of r , is probably because most donor molecules have an acceptor of ion within 8–15 Å in the EuCl₃ concentration range used.

Such a situation in the sphere-of-quenching model would lead to instantaneous total transfer. However, if the transfer probability has a finite value in the active volume, the rate constant may be nearly separation independent. Using the Stern-Volmer expression $\tau_p/\tau_0 = (1 + [^7F]/C)^{-1}$, where C is the acceptor concentration at which the phosphorescence decay is twice as fast as in the absence of quencher, one obtains the constant $C = 0.35$ M. Indirectly, this value corresponds to an average nearest-neighbour distance of *ca.* 11 Å, essentially the same as the radius of the active volume for the AN-EuCl₃ system.

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[0/525 Received, April 1st, 1970]

⁴¹ N. Riehl, International Conference on Luminescence, Newark, Delaware, 1969; *J. Luminescence*, 1970, **1**, **2**, 1.