Influence of Energy Transfer by the Exchange Mechanism on Donor Luminescence

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Influence of Energy Transfer by the Exchange Mechanism on Donor Luminescence*

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The decay of donor luminescence in a rigid solution when modified by electronic energy transfer by the exchange mechanism is treated theoretically. The rate constant for the elementary process of energy transfer is taken to be of the Dexter form, const $\exp(-2R/L)$, where R is the donor–acceptor distance and L is a positive constant. Calculations are made of the yield and decay time of the donor luminescence as functions of the acceptor concentration. The resulting relationship among the above quantities enables one to analyze experimental data in a quantitative manner, and thereby to obtain information about an intermolecular exchange interaction. As an example of such an analysis, Ermolaev's data on triplet–triplet transfer between some aromatic molecules are compared with our results, and very good agreement is found with a choice of the single parameter L.

I. INTRODUCTION

RESONANCE transfer of electronic excitation energy from one molecule (a "sensitizer," or "energy donor") to another (an "activator," or "energy acceptor") has been a subject of numerous investigations.[1-4] Theories have been developed which give formulas for the rate of energy transfer by electric-dipole–dipole interaction,[5,6] electric-dipole–quadrupole interaction,[6] and the exchange interaction.[6] While the former two of the interactions are electrostatic in origin, the last arises from requirement of the antisymmetry of the electronic wavefunction for the system consisting of a donor molecule and an acceptor molecule. These transfer mechanisms differ from one another in the dependence of the transfer rate on donor–acceptor distance, but common to all is the condition that an overlap between the donor emission spectrum and the acceptor absorption spectrum is essential for the transfer to occur. This is so even though we are concerned with virtual, not real, photon emission and reabsorption in the transfer process.

Experimental studies of resonance transfer in a condensed system have most frequently been made through luminescence measurements: donor molecules are excited in the presence of acceptor molecules, and the luminescence yield of donor and/or acceptor and the decay time of donor luminescence are measured as functions of the acceptor concentration. When one attempts to interpret an observed result, for instance, that of donor luminescence yield, it becomes necessary to have a theoretical relationship between the yield and the acceptor concentration. For dipole–dipole transfer, where the transfer rate is proportional to

the inverse sixth power of the donor–acceptor distance, Förster derived the following formula for the donor luminescence yield η:

$$\eta/\eta_0 = 1 - \sqrt{\pi}x\exp(x^2)[1 - \mathrm{erf}(x)],$$

$$x = \tfrac{1}{2}\sqrt{\pi}c/c_0, \qquad (1)$$

where η_0 is the luminescence yield in the absence of acceptors, c the acceptor concentration, c_0 a parameter called the "critical transfer concentration" which is related to the transfer rate, and $\mathrm{erf}(x)$ the error function.[1,7,8] The efficiency of energy transfer is simply $1 - \eta/\eta_0$. Equation (1) has been found to explain a number of observations on *sensitized fluorescence* in condensed systems.

The phenomenon of *sensitized phosphorescence*, or energy transfer between triplet states, was discovered by Terenin and Ermolaev,[9,10] who interpreted it as arising from the exchange mechanism.

We can briefly summarize their findings in a long series of investigations[9-20] by indicating those features

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[1] Th. Förster, Discussions Faraday Soc. **27**, 7 (1959).

[2] Th. Förster, Radiation Res. Suppl. **2**, 326 (1960).

[3] A. N. Terenin, Usp. Fiz. Nauk **43**, 47 (1951) [English transl.: AEC-tr-3031 (1958)].

[4] A. N. Terenin and V. L. Ermolaev, Usp. Fiz. Nauk **58**, 37 (1956) [English transl.: AEC-tr-3031 (1958)].

[5] Th. Förster, Ann. Physik **2**, 55 (1948).

[6] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[7] Th. Förster, Z. Naturforsch. **4a**, 321 (1949).

[8] M. D. Galanin, Zh. Eksperim. i Teor. Fiz. **28**, 485 (1955) [English transl.: Soviet Phys.—JETP **1**, 317 (1955)].

[9] V. L. Ermolaev and A. N. Terenin, *Pamiati S. I. Vavilova* (Moscow, 1952) p. 137 [English transl.: In Memory of S. I. Vavilova, NRC TT-540].

[10] A. N. Terenin and V. L. Ermolaev, Dokl. Akad. Nauk SSSR **85**, 547 (1962) [English transl.: NRC TT-529].

[11] V. L. Ermolaev, Dokl. Akad. Nauk SSSR **102**, 925 (1955).

[12] A. N. Terenin and V. L. Ermolaev, Trans. Faraday Soc. **52**, 1042 (1956).

[13] V. L. Ermolaev, Izv. Akad. Nauk SSSR Ser. Fiz. **20**, 514 (1956) [English transl.: Bull. Acad. Sci. USSR Phys. Ser. **20**, 471 (1956)].

[14] V. L. Ermolaev and A. Terenin, J. Chim. Phys. **55**, 698 (1958).

[15] V. L. Ermolaev, Opt. i Spektroskopiya **6**, 642 (1959) [English transl.: Opt. Spectry. (USSR) **6**, 417 (1959)].

[16] V. L. Ermolaev, Dokl. Akad. Nauk SSSR **139**, 348 (1961) [English transl.: Soviet Phys.—Doklady **6**, 600 (1962)].

[17] V. L. Ermolaev, Opt. i Spektroskopiya **13**, 90 (1962) [English transl.: Opt. Spectry. (USSR) **13**, 49 (1962)].

[18] A. N. Terenin and V. L. Ermolaev, Izv. Akad. Nauk SSSR Ser. Fiz. **26**, 21 (1962) [English transl.: Bull. Acad. Sci. USSR Phys. Ser. **26**, 21 (1962)].

[19] V. L. Ermolaev and E. B. Sveshnikova, Izv. Akad. Nauk SSSR Ser. Fiz. **26**, 29 (1962) [English transl.: Bull. Acad. Sci. USSR Phys. Ser. **26**, 29 (1962)].

[20] V. L. Ermolaev, Usp. Fiz. Nauk **80**, 3 (1963) [English transl.: Soviet Phys.—Usp. **80**, 333 (1963)].

which are distinct from dipole–dipole transfer. (1) The donor luminescence yield does not obey Eq. (1), but varies roughly as $\exp(-ac)$, where c is the acceptor concentration and a is a positive constant. (2) The decay time of the donor luminescence decreases much more slowly with increase in the acceptor concentration than it does for dipole–dipole transfer. To be more precise, if the acceptor with concentration c causes a decrease $\delta\tau$ in the decay time τ and decrease $\delta\eta$ in the luminescence yield η, the quantity

$$\lim_{c\to 0}\frac{\delta\tau/\tau}{\delta\eta/\eta}$$

is much smaller (about 0.1) than the corresponding value (theoretically 0.5[8]) for dipole–dipole transfer. (3) The efficiency of transfer is independent of the oscillator strength of the acceptor. Items (1) and (2) indicate that the transfer rate depends strongly on the donor–acceptor distance R and is of much shorter range than R^{-6} (see Appendix I). Item (3) rules out an electromagnetic mechanism of transfer. All these facts are exactly in accord with Dexter's theoretical predictions[6] on transfer by the exchange mechanism.[21]

Independent studies of energy transfer between triplet states under different experimental conditions[22,23] and by means of the ESR method[24–28] support the view of Terenin and Ermolaev.

The present work consists in calculation of the yield and the decay time of donor luminescence as functions of the acceptor concentration, for energy transfer by the exchange mechanism. It is hoped that the result will provide a sound, quantitative basis for analyzing experimental data for this kind of energy transfer, just as Förster's formula (1) has long been doing for dipole–dipole transfer. Our results indicate, in particular, that careful measurement of the decay time is of vital importance to attainment of a full knowledge of energy transfer by the exchange mechanism.

Section II starts with a discussion of a general relationship between the transfer rate and the luminescence decay, and then treats the specific case of energy transfer by the exchange mechanism. Section III presents some numerical results, and Sec. IV describes a procedure for analyzing experimental data on the basis of the present calculation. Appendix I gives a unified treatment of some simple cases including transfer by dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interaction. An extensive tabulation of numerical results will be presented elsewhere.[29]

II. FORMULATION

Generalities

Consider a system in which two different kinds of molecule, energy donors, and energy acceptors, are randomly distributed in an inert medium. Both the donor and the acceptor molecules are assumed to have only one excited electronic state in the pertinent energy region. Throughout the following discussion, three basic assumptions are made: (a) Brownian translational motion of all the molecules is slow enough so that each individual energy-transfer process may be considered to occur at a definite donor–acceptor distance. (b) The rate constant for energy transfer is taken as independent of the molecular orientation. This assumption is permissible when the rate constant averaged over the molecular orientation may be used, for example, when molecular rotation is fast enough compared with the energy-transfer process. (c) Energy transfer occurs only from a donor to an acceptor (i.e., donor–donor transfer is negligible).

Suppose that a donor is excited at time $t=0$. When no acceptors are present, the probability $\rho(t)$ of finding the donor in the excited state at time t declines exponentially, namely, $\rho(t)=\exp(-t/\tau_0)$, where τ_0 is the reciprocal of the rate constant for spontaneous deactivation (by light emission and internal quenching) of the donor. When acceptors are present, the probability decreases more rapidly because of the additional competing process of energy transfer. Let $n(R_k)$ be the rate constant for energy transfer from a donor D to an acceptor A_k at a distance R_k. Then we have

$$\rho(t) = \exp\left(\frac{-t}{\tau_0}\right)\prod_{k=1}^{N}\exp[-tn(R_k)], \qquad (2)$$

where N is the total number of acceptors in a finite volume around the donor. The mode of decay described by $\rho(t)$ depends on the environment of the particular donor considered. Macroscopically significant is the statistical average $\phi(t)$ of $\rho(t)$ over an infinitely large number of donors. If $w(R)$ is the probability distribution of the donor–acceptor distance R in the volume V, we can write

$$\phi(t) = \exp\left(\frac{-t}{\tau_0}\right)\lim_{N\to\infty, V\to\infty}\left\{\int_V \exp[-tn(R)]w(R)dV\right\}^N.$$

$$(3)$$

[21] Since the phosphorescence from a large organic molecule is of electric-dipole character, which arises from singlet–triplet mixing due to spin–orbit coupling [S. Weissman and D. Lipkin, J. Am. Chem. Soc. **64**, 1916 (1942)], it would seem that a triplet–triplet transfer could, in principle, result also from the dipole–dipole interaction. Actually, however, the mixing seems to be too small to make this mechanism significant, at least for the most cases studied by Terenin and Ermolaev.

[22] H. L. J. Bäckström and K. Sandros, Acta Chem. Scand. **14**, 48 (1960).

[23] G. Porter and F. Wilkinson, Proc. Roy. Soc. (London) **A264**, 1 (1961).

[24] J. B. Farmer, C. L. Gardner, and C. A. McDowell, J. Chem. Phys. **34**, 1058 (1961).

[25] B. Smaller and J. R. Remko, Organic Crystal Symposium, National Research Council of Canada, Ottawa, Canada (October 1962).

[26] K. B. Eisenthal and R. Murashige, J. Chem. Phys. **39**, 2108 (1963).

[27] S. Siegel and K. B. Eisenthal, J. Chem. Phys. **38**, 2785 (1963).

[28] S. Siegel and H. Judeikis, J. Chem. Phys. **41**, 648 (1964).

[29] M. Inokuti and F. Hirayama, "Tables for Analyzing Luminescence Data in Energy Transfer Studies," ANL–6996 (to be published).

Here the volume V over which integration is carried out should be chosen large enough to contain a macroscopic number of acceptors, and thus the limit $N \to \infty$, $V \to \infty$ should be taken so that N/V, the acceptor concentration, is finite. Assuming a random spatial distribution of acceptors around a donor, we put $w(R)dV = 4\pi R^2 dR/V$ and take the volume V as a sphere with radius R_V ($V = 4\pi R_V^3/3$) to obtain

$$\phi(t) = \exp\left(\frac{-t}{\tau_0}\right) \lim_{N \to \infty, V \to \infty} \left\{ \frac{4\pi}{V} \int_0^{R_V} \exp[-tn(R)] R^2 dR \right\}^N.$$

(4)

The function $\phi(t)$ is proportional to the intensity of the donor luminescence and therefore shall be called hereafter the decay function of donor luminescence. It is not, in general, an exponential function for the following reason: As the decay proceeds, excited donors having unexcited acceptors in their close neighborhood tend to become exhausted, since the rate constant $n(R)$ usually decreases with increasing distance R. Equation (4) enables one to calculate the decay function as soon as a dependence of the rate constant on the distance is specified. Our formalism so far is a straightforward generalization of Förster's treatment[7] of dipole–dipole transfer. A further generalized version including the dependence of the rate constant on the molecular orientation can be developed, as was done by Maksimov and Rozman.[30]

It is customary and convenient for practical purposes to introduce a "decay time" which characterizes the behavior of the decay function. Since the above $\phi(t)$ is not in general an exponential function, there is no unique way of defining a decay time. We can consider at least the following two kinds of decay times. One is the "mean duration"[8] τ_m of donor luminescence, defined by[31]

$$\tau_m = \int_0^\infty t\phi(t) dt \Big/ \int_0^\infty \phi(t) dt.$$

(5)

The other is the "$1/e$-decay time" τ_e, or the time interval after which the donor luminescence has decreased by a factor of e from its value at $t=0$. Thus τ_e is defined

as the root of the equation

$$\phi(\tau_e) = e^{-1}.$$

(6)

If the decay function happens to be purely exponential, then τ_m and τ_e coincide. Otherwise, they are in general different.

So far we have dealt with luminescence decay after flash excitation. Under certain experimental circumstances, it is convenient to observe the luminescence decay after turning off a continuous exciting light, by which the system has been brought to a steady state with respect to the concentration of excited molecules. If the system has been excited with a constant intensity for a time interval much longer than τ_0, and the exciting light is then turned off at time $t=0$, the intensity of luminescence at a later time t is proportional to[37]

$$\int_t^\infty \phi(t') dt',$$

where $\phi(t)$ is the decay function for flash excitation. For convenience we may consider

$$\phi_s(t) = \int_t^\infty \phi(t') dt' \Big/ \int_0^\infty \phi(t') dt',$$

(7)

which is normalized in such a way that $\phi_s(0) = 1$. If the decay function $\phi(t)$ for flash excitation is purely exponential, then $\phi_s(t) = \phi(t)$. Otherwise, $\phi_s(t)$ generally differs from $\phi(t)$.

We can define the "mean duration" τ_{ms} of the donor luminescence after turning off a steady-state excitation by

$$\tau_{ms} = \int_0^\infty t\phi_s(t) dt \Big/ \int_0^\infty \phi_s(t) dt,$$

(8)

in analogy with τ_m for flash excitation. It is easily seen that τ_{ms} can be evaluated directly from $\phi(t)$ by

$$\tau_{ms} = \frac{1}{2} \int_0^\infty t^2 \phi(t) dt \Big/ \int_0^\infty t\phi(t) dt.$$

(9)

[30] M. Z. Maksimov and I. M. Rozman, Opt. i Spektroskopiya **12**, 606 (1962) [English transl.: Opt. Spectry. **12**, 337 (1962)].

[31] A phase fluorometer using sinusoidally modulated exciting light measures τ_m as long as it is operated at a low modulation frequency ω such that $\omega\tau_m \ll 1$. (See, e.g., Refs. 32–36).

[32] E. Gaviola, Z. Physik **35**, 748 (1926); Ann. Physik **81**, 44 (1926).

[33] L. A. Tumerman, J. Phys. USSR **4**, 151 (1941).

[34] S. F. Kilin, G. P. Prosin, and I. M. Rozman, Pribory i Tekhn. Eksperim. No. 2, 57 (1959) [English transl.: Instr. Exptl. Tech. USSR **1959**, 234].

[35] A. Yu. Borisov and L. A. Tumerman, Izv. Akad. Nauk SSSR Ser. Fiz. **23**, 97 (1959) [English transl.: Bull. Acad. Sci. USSR Phys. Ser. **23**, 94 (1959)].

[36] J. B. Birks and D. J. Dyson, J. Sci. Instr. **38**, 282 (1961).

[37] The intensity $I(t)$ of luminescence, in appropriate units, resulting from exciting light whose intensity $J(t)$ varies with time t in an arbitrary way can be expressed by a Duhamel integral

$$I(t) = \int_0^\infty J(t-t') \phi(t') dt',$$

(a)

where $\phi(t)$ is the decay function for flash excitation. This is generally valid under the condition that the number of excited molecules is small enough compared with the total number of molecules in the system and that the system does not undergo a permanent change such as a photochemical reaction. For a particular case of steady-state excitation turned off at $t=0$, we put $J(t)=1$ for $t<0$ and $J(t)=0$ for $t>0$ in the above equation (a) to obtain

$$I(t) = \int_t^\infty \phi(t') dt'.$$

Reference 38 gives an explicit verification of the above result for a particular case of dipole–dipole transfer.

[38] K. B. Eisenthal and S. Siegel, J. Chem. Phys. **41**, 652 (1964).

The relative yield η/η_0 of donor luminescence, defined as the ratio of the luminescence yield in the presence of acceptor to that in its absence, is expressed by[39]

$$\eta/\eta_0 = \tau_0^{-1} \int_0^\infty \phi(t)\, dt. \qquad (10)$$

The efficiency of energy transfer is given by $1 - \eta/\eta_0$.

Energy Transfer by the Exchange Mechanism

Dexter[6] has derived the following expression for the rate constant for energy transfer by the exchange mechanism:

$$n(R) = \frac{2\pi}{\hbar} Z^2 \int f_D(E)\, F_A(E)\, dE \qquad (11)$$

with

$$Z^2 = K^2 \exp(-2R/L), \qquad (12)$$

where K is a constant with the dimension of energy, L a constant called the "effective average Bohr radius," $f_D(E)$ the donor emission spectrum, and $F_A(E)$ the acceptor absorption spectrum.[40] The spectra should be normalized on the photon energy scale so that

$$\int f_D(E)\, dE = \int F_A(E)\, dE = 1. \qquad (13)$$

Integration in Eqs. (11) and (13) extends over the relevant spectral band, which is assumed to be well separated from other bands. In Eq. (12), Z is an asymptotic form of an exchange integral for the donor–acceptor pair, and the exponential dependence, which is valid for large values of R, arises from the fact that electronic wavefunction of a molecule generally declines exponentially. (See Sec. V of Ref. 6 for details.) For

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[39] Integration of Eq. (a) of Footnote 37 with respect to t gives

$$\int_{-\infty}^\infty I(t)\, dt = \int_0^\infty \phi(t)\, dt \int_{-\infty}^\infty J(t)\, dt.$$

This means the total luminescence energy emitted in a sufficiently long time interval is proportional to the total energy of the exciting light in the same interval, and the proportionality constant

$$\int_0^\infty \phi(t)\, dt$$

corresponds, apart from a trival factor, to the luminescence yield, which is obviously independent of the mode of excitation. This has been explicitly verified for a particular case of dipole-dipole transfer in Ref. 38.

[40] The function $F_A(E)$ is difficult, if not entirely impossible, to determine directly from experiment, because the absorption associated with the forbidden transition is obviously weak. However, the emission band, which is more easily observed, serves as a basis for inferring an approximation to the function. Furthermore, the function $F_A(E)$ appearing in the expression (11) for the transfer rate may be equated with the shape of the absorption spectrum only under certain conditions, because the mechanism of transfer (exchange interaction) is different from that of light absorption (dipole interaction resulting from singlet–triplet mixing). (See Footnote 21.)

small distances, the exchange integral depends on details of the molecular wavefunction and behaves in too complicated a way to permit a general statement. It may also depend on molecular orientation. However, in evaluating $\phi(t)$ by (4), it is important to know only the behavior of the rate constant for large distances. Contributions from small distances, where the rate constant $n(R)$ is in general high, are not significant, because, in Eq. (4), $n(R)$ appears in the exponent, and besides there is a volume element factor R^2.

It is convenient for our analysis to rewrite the above rate constant in the form

$$n(R) = (1/\tau_0)\, \exp\{\gamma[1 - (R/R_0)]\}, \qquad (14)$$

where R_0 and γ are constants related to Dexter's quantities by

$$\gamma = 2R_0/L, \qquad (15)$$

$$\frac{e^\gamma}{\tau_0} = \frac{2\pi}{\hbar} K^2 \int f_D(E)\, F_A(E)\, dE. \qquad (16)$$

We may, following Förster's terminology, call R_0 "a critical transfer distance" in the sense that, for an *isolated* donor–acceptor pair separated by R_0, the energy transfer occurs with the same rate as the spontaneous deactivation in the donor.

In order to calculate the decay function $\phi(t)$, we insert (14) into (4) and obtain, after changing integration variables,

$$\phi(t) = \exp\left(\frac{-t}{\tau_0}\right) \lim_{N\to\infty, R_V\to\infty} \left[3\gamma^{-3}\left(\frac{R_0}{R_V}\right)^3 \right.$$
$$\left. \times \int_{y_V}^1 \exp(-zy)\,(\ln y)^2 y^{-1}\, dy \right]^N, \qquad (17)$$

where

$$z = e^\gamma t/\tau_0, \qquad (18)$$

$$y_V = \exp[-\gamma(R_V/R_0)]. \qquad (19)$$

The integral in (17) can be evaluated for small y_V values in the following manner:

$$\int_{y_V}^1 \exp(-zy)\,(\ln y)^2 y^{-1}\, dy = -\tfrac13 \exp(-zy_V)\,(\ln y_V)^3$$
$$+ \tfrac13 z \left[\int_0^1 \exp(-zy)\,(\ln y)^3\, dy - \int_0^{y_V} \exp(-zy)\,(\ln y)^3\, dy \right]$$
$$= -\tfrac13 (\ln y_V)^3 - \tfrac13 g(z) + O[y_V(\ln y_V)^3]. \qquad (20)$$

Here we have defined a function $g(z)$ by

$$g(z) = -z \int_0^1 \exp(-zy)\,(\ln y)^3\, dy. \qquad (21)$$

Thus, by use of (17) through (21), we can write $\phi(t)$ in the form

$$\phi(t) = \exp(-t/\tau_0) \lim_{N\to\infty, R_V\to\infty} [1-\gamma^{-3}(R_0/R_V)^3 g(z)]^N.$$

$$(22)$$

The result, after taking the limit, is conveniently expressed as

$$\phi(t) = \exp[-t/\tau_0 - \gamma^{-3}c/c_0 g(e^\gamma t/\tau_0)], \qquad (23)$$

where c is the acceptor concentration

$$c = 3N/(4\pi R_V^3), \qquad (24)$$

and c_0 is a parameter, which is called the critical transfer concentration, defined by

$$c_0 = 3/(4\pi R_0^3). \qquad (25)$$

Note that the above c and c_0 are in units of centimeters^{-3}. If concentration in units of moles per liter is used, then we have

$$R_0 = 7.346 c_0^{-1/3} \text{ (angstrom)}. \qquad (26)$$

We now give properties of the function $g(z)$ relevant to numerical evaluation. First, it is easy to see that $g(z)$ is positive and monotonically increasing for any $z > 0$. Second, expansion of the exponential in the integrand in (21) followed by term-by-term integration gives a Taylor series

$$g(z) = 6z \sum_{m=0}^{\infty} \frac{(-z)^m}{m!(m+1)^4}, \qquad (27)$$

which is absolutely convergent for any z. Finally, for sufficiently large values of $z > 0$, $g(z)$ can be expressed by

$$g(z) = (\ln z)^3 + h_1(\ln z)^2 + h_2(\ln z) + h_3 + O[e^{-z}(\ln z)^3 z^{-2}],$$

$$(28)$$

where the coefficients h_1, h_2, and h_3 are related to derivatives of the gamma function of argument unity:

$$h_1 = -3\Gamma'(1) = 1.73164699,$$

$$h_2 = 3\Gamma''(1) = 5.93433597,$$

$$h_3 = -\Gamma'''(1) = 5.44487446. \qquad (29)$$

The derivation of (28) is given in Appendix II.

Thus numerical evaluation of $g(z)$ is simple. For small values of z, the Taylor series (27) converges rapidly, while, for large values of z, the leading terms in (28) give $g(z)$ with excellent accuracy. An absolute accuracy of 10^{-8} is achieved by use of (27) for $z \le 10$, and (28) for $z > 10$.

Substitution of (23) into (5), (6), (9), and (10) gives τ_m/τ_0, τ_e/τ_0, τ_{ms}/τ_0, and η/η_0 as functions of c/c_0. This stage of the calculation must be done numerically.
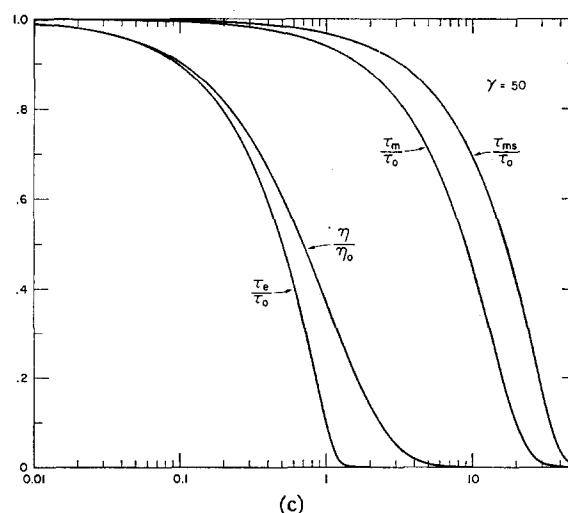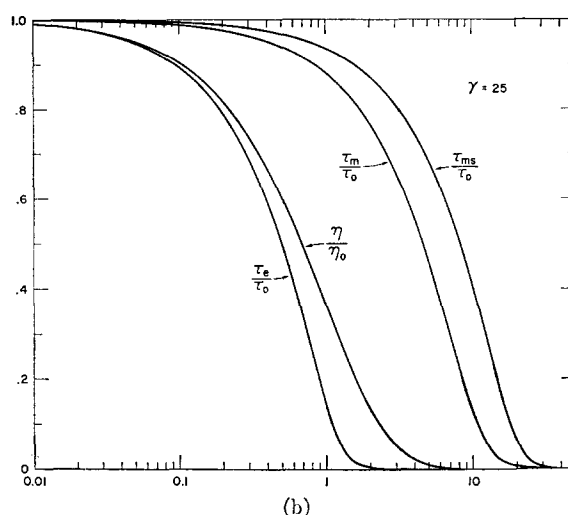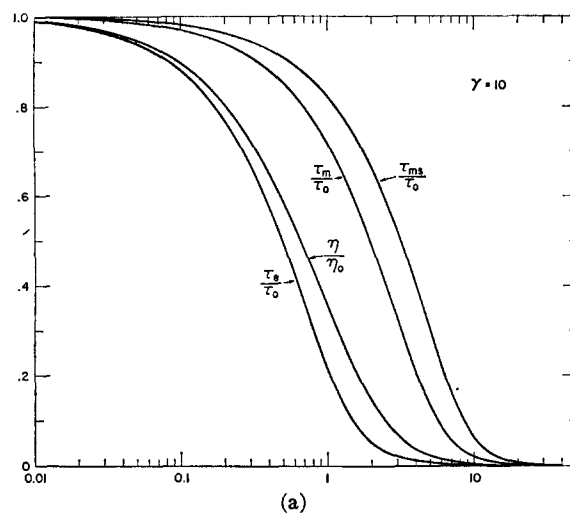

FIG. 1. The relative yield and the decay time as functions of the acceptor concentration. Figures 1(a), 1(b), and 1(c) refer to $\gamma = 10$, 25, and 50, respectively. The abscissa represents c/c_0 on a logarithmic scale, and the ordinate η/η_0, τ_m/τ_0, τ_{ms}/τ_0, and τ_e/τ_0.

III. NUMERICAL RESULTS AND DISCUSSION

The relative yield η/η_0 and the decay times τ_m/τ_0, τ_{ms}/τ_0, and τ_e/τ_0 as functions of c/c_0 for a number of values of γ were calculated on a computer. For evaluation of the integrals necessary in computing η/η_0, τ_m/τ_0, and τ_{ms}/τ_0, we used a subroutine which allows the programmer to prescribe a limit of error in numerical integration. The quantity τ_e/τ_0 was obtained by solving the transcendental equation (6) through a standard *regula falsi* method.

Table I shows some of our numerical results. The entries have been rounded off at the fifth decimal place so that the error is at most 5×10^{-5}. Figures 1(a), 1(b), and 1(c) are plots of η/η_0, τ_m/τ_0, τ_{ms}/τ_0, and τ_e/τ_0 as functions of c/c_0 for $\gamma=10, 25, 50$, respectively. One readily observes that the curves for τ_m/τ_0 and τ_{ms}/τ_0 are sensitive to the parameter γ and gradually shift towards high c/c_0 values with an increase in γ. The curves for η/η_0 and τ_e/τ_0 are less sensitive to γ. All of them differ considerably from the corresponding curves for dipole–dipole transfer, the difference becoming more and more pronounced with an increase in γ. (For a detailed comparison, the reader is referred to Ref. 29.) Figures 2 and 3 give another kind of representation, showing a plot of η/η_0 vs τ_m/τ_0 and τ_e/τ_0, and of η/η_0 vs τ_{ms}/τ_0, respectively, which we call $\eta-\tau$ plots. This representation is quite convenient for comparison with experiment, because one does not need to know a value of c_0. As γ increases, the dependence of the rate constant on the distance becomes stronger, and as ex-

FIG. 3. The relative yield vs the decay time for steady-state excitation. The abscissa represents τ_{ms}/τ_0 and the ordinate η/η_0. The numeral on a curve denotes the value of γ.

pected, the $\eta-\tau$ plot departs farther from that for the Stern–Volmer model and approaches that for the Perrin model. [See Eqs. (A3)–(A6) and (A10) in Appendix I.]

In order to understand the behavior of η/η_0 for a given γ as a function of c/c_0, it is helpful to introduce quantities α and β such that

$$\eta/\eta_0=\exp(-\alpha c/c_0),\qquad(30)$$

$$\eta/\eta_0=(1+\beta c/c_0)^{-1}.\qquad(31)$$

The right-hand sides of the above equations are of the forms derived from the Perrin model and the Stern–Volmer model, respectively, but modified with the factors α and β in front of c/c_0. (See Appendix I.) We can put our calculated value of η/η_0 in the left-hand sides and solve for α and β. The resulting α and β are functions of c/c_0. We have found that α indeed decreases with c/c_0 but that the change in α is not very significant for moderate c/c_0 values. For example, in the region $0.01\leq c/c_0\leq3$, α decreases from 1.1 to 0.9 for $\gamma=10$, from 1.02 to 0.98 for $\gamma=25$, and from 1.005 to 0.996 for $\gamma=50$. Thus we see that the relative yield η/η_0 for moderate c/c_0 values behaves approximately like the Perrin model with an accuracy increasing with γ. On the other hand, β increases rather steeply with c/c_0. For example, even in the smaller region $0.01\leq c/c_0\leq1$, β increases from 1.11 to 1.81 for $\gamma=10$, from 1.02 to 1.73 for $\gamma=25$, and from 1.01 to 1.72 for $\gamma=50$. In view of this large variation of β, approximation by the Stern–Volmer equation (31) with a constant β is less meaningful.

In conclusion, we may point out that our calculated results are in accord with the features (1) and (2) of Sec. I which summarize the observation of triplet–triplet energy transfer by Terenin and Ermolaev.
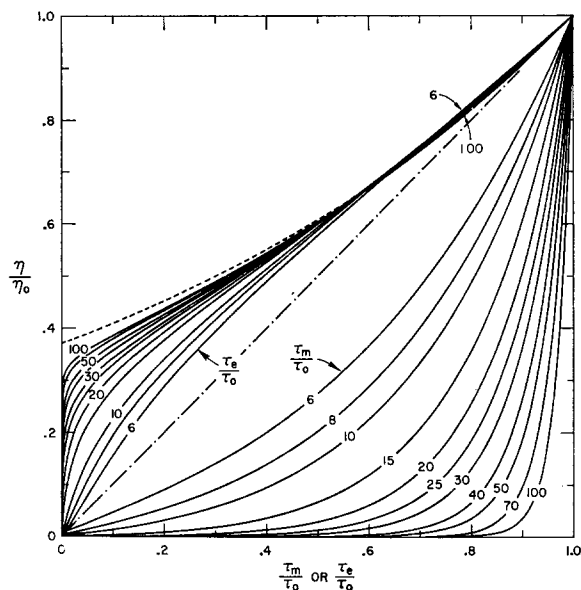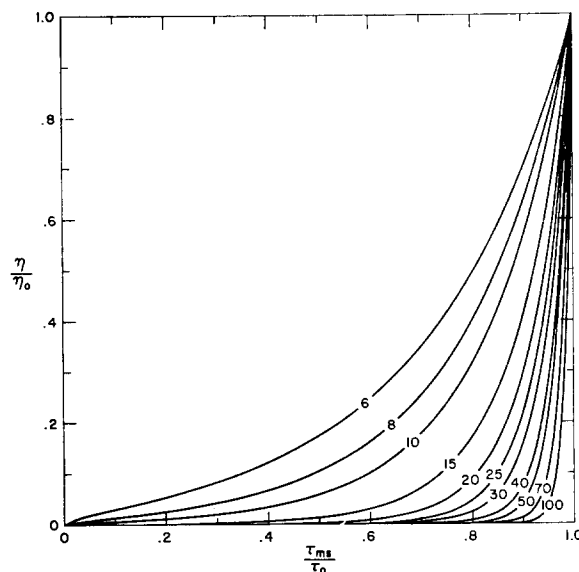

FIG. 2. The relative yield vs the decay time for flash excitation. The abscissa represents τ_m/τ_0 or τ_e/τ_0, and the ordinate η/η_0. The numeral on a curve denotes the value of γ. The Stern–Volmer model, for which $\eta/\eta_0=\tau_m/\tau_0=\tau_e/\tau_0$, gives the diagonal straight line. The Perrin model gives relations $\eta/\eta_0=\exp(\tau_e/\tau_0-1)$ and $\tau_m/\tau_0=1$ (for any η/η_0). The former is represented by the broken curve and the latter by the vertical straight line at the right side of the figure.

TABLE I. The relative yield and decay time of donor luminescence as functions of the acceptor concentration.

c/c_0	$\gamma=10$				$\gamma=15$			
	η/η_0	τ_m/τ_0	τ_{ms}/τ_0	τ_e/τ_0	η/η_0	τ_m/τ_0	τ_{ms}/τ_0	τ_e/τ_0
0.010	0.9891	0.9969	0.9982	0.9877	0.9896	0.9980	0.9989	0.9886
0.015	0.9837	0.9954	0.9972	0.9815	0.9845	0.9970	0.9983	0.9829
0.020	0.9783	0.9938	0.9963	0.9754	0.9793	0.9959	0.9977	0.9772
0.025	0.9729	0.9923	0.9954	0.9693	0.9743	0.9949	0.9971	0.9716
0.030	0.9676	0.9907	0.9945	0.9632	0.9692	0.9939	0.9966	0.9659
0.040	0.9571	0.9876	0.9926	0.9512	0.9591	0.9919	0.9954	0.9547
0.050	0.9467	0.9846	0.9908	0.9392	0.9492	0.9899	0.9943	0.9435
0.070	0.9263	0.9784	0.9871	0.9154	0.9297	0.9858	0.9920	0.9212
0.100	0.8965	0.9693	0.9816	0.8805	0.9011	0.9798	0.9885	0.8882
0.150	0.8493	0.9541	0.9724	0.8240	0.8556	0.9697	0.9828	0.8343
0.200	0.8047	0.9391	0.9633	0.7698	0.8125	0.9597	0.9771	0.7818
0.250	0.7628	0.9241	0.9542	0.7179	0.7717	0.9498	0.9714	0.7308
0.300	0.7233	0.9094	0.9452	0.6683	0.7330	0.9399	0.9657	0.6814
0.400	0.6509	0.8802	0.9272	0.5761	0.6617	0.9201	0.9544	0.5873
0.500	0.5865	0.8516	0.9094	0.4935	0.5977	0.9006	0.9431	0.5002
0.700	0.4781	0.7960	0.8742	0.3565	0.4885	0.8620	0.9207	0.3491
1.000	0.3554	0.7168	0.8227	0.2146	0.3627	0.8055	0.8873	0.1850
1.500	0.2225	0.5965	0.7402	0.0965	0.2236	0.7151	0.8326	0.0572
2.000	0.1441	0.4910	0.6622	0.0499	0.1402	0.6299	0.7791	0.0203
2.500	0.0964	0.4001	0.5890	0.0295	0.0894	0.5503	0.7269	0.0090
3.000	0.0666	0.3233	0.5207	0.0194	0.0581	0.4766	0.6761	0.0047
4.000	0.0348	0.2073	0.3997	0.0102	0.0260	0.3482	0.5790	0.0018
5.000	0.0202	0.1318	0.2999	0.0064	0.0125	0.2456	0.4886	0.0009
7.000	0.0088	0.0552	0.1608	0.0033	0.0037	0.1122	0.3310	0.0003
10.000	0.0038	0.0187	0.0613	0.0018	0.0010	0.0315	0.1613	0.0001
15.000	0.0016	0.0055	0.0159	0.0009	0.0002	0.0051	0.0373	0.0001
20.000	0.0009	0.0026	0.0061	0.0006	0.0001	0.0014	0.0088	0.0000
25.000	0.0006	0.0015	0.0031	0.0004	0.0000	0.0006	0.0027	0.0000
30.000	0.0005	0.0010	0.0019	0.0004	0.0000	0.0003	0.0011	0.0000
40.000	0.0003	0.0005	0.0009	0.0002	0.0000	0.0002	0.0003	0.0000
50.000	0.0002	0.0004	0.0005	0.0002	0.0000	0.0001	0.0001	0.0000
70.000	0.0001	0.0002	0.0003	0.0001	0.0000	0.0001	0.0001	0.0000

c/c_0	$\gamma=20$				$\gamma=25$			
	η/η_0	τ_m/τ_0	τ_{ms}/τ_0	τ_e/τ_0	η/η_0	τ_m/τ_0	τ_{ms}/τ_0	τ_e/τ_0
0.010	0.9898	0.9985	0.9992	0.9890	0.9899	0.9988	0.9994	0.9892
0.015	0.9847	0.9977	0.9988	0.9835	0.9849	0.9982	0.9990	0.9838
0.020	0.9797	0.9970	0.9983	0.9780	0.9799	0.9976	0.9987	0.9785
0.025	0.9747	0.9962	0.9979	0.9726	0.9749	0.9970	0.9984	0.9731
0.030	0.9697	0.9955	0.9975	0.9671	0.9700	0.9964	0.9981	0.9678
0.040	0.9599	0.9940	0.9967	0.9562	0.9602	0.9952	0.9974	0.9571
0.050	0.9501	0.9925	0.9959	0.9453	0.9505	0.9940	0.9968	0.9464
0.070	0.9309	0.9894	0.9942	0.9237	0.9314	0.9916	0.9954	0.9251
0.100	0.9027	0.9849	0.9917	0.8916	0.9035	0.9880	0.9935	0.8935
0.150	0.8578	0.9774	0.9876	0.8389	0.8589	0.9820	0.9902	0.8414
0.200	0.8152	0.9699	0.9834	0.7871	0.8165	0.9760	0.9870	0.7901
0.250	0.7748	0.9624	0.9793	0.7365	0.7762	0.9700	0.9838	0.7396
0.300	0.7364	0.9550	0.9751	0.6870	0.7380	0.9640	0.9805	0.6901
0.400	0.6655	0.9401	0.9669	0.5918	0.6672	0.9521	0.9740	0.5941
0.500	0.6016	0.9253	0.9587	0.5021	0.6034	0.9402	0.9675	0.5026
0.700	0.4921	0.8959	0.9422	0.3421	0.4938	0.9165	0.9546	0.3366
1.000	0.3651	0.8524	0.9177	0.1627	0.3661	0.8813	0.9353	0.1457
1.500	0.2236	0.7817	0.8772	0.0334	0.2235	0.8235	0.9033	0.0192
2.000	0.1383	0.7131	0.8373	0.0078	0.1373	0.7669	0.8715	0.0029
2.500	0.0864	0.6470	0.7978	0.0026	0.0849	0.7115	0.8399	0.0007
3.000	0.0546	0.5836	0.7588	0.0011	0.0529	0.6575	0.8087	0.0002
4.000	0.0226	0.4659	0.6826	0.0003	0.0210	0.5542	0.7469	0.0001
5.000	0.0098	0.3619	0.6090	0.0001	0.0086	0.4581	0.6864	0.0000
7.000	0.0022	0.1993	0.4709	0.0000	0.0016	0.2927	0.5695	0.0000
10.000	0.0003	0.0668	0.2926	0.0000	0.0002	0.1234	0.4073	0.0000
15.000	0.0000	0.0088	0.0976	0.0000	0.0000	0.0188	0.1895	0.0000
20.000	0.0000	0.0016	0.0231	0.0000	0.0000	0.0029	0.0619	0.0000
25.000	0.0000	0.0005	0.0051	0.0000	0.0000	0.0007	0.0146	0.0000
30.000	0.0000	0.0003	0.0014	0.0000	0.0000	0.0003	0.0032	0.0000
40.000	0.0000	0.0001	0.0002	0.0000	0.0000	0.0001	0.0003	0.0000
50.000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0001	0.0001	0.0000
70.000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0001	0.0000	0.0000

The decay of the donor luminescence after flash excitation is described by $\phi(t)$ of Eq. (23). The solid curves in Figs. 4(a), 4(b), and 4(c) show a plot of $\log_{10}\phi(t)$ against t/τ_0 for several c/c_0 values, corresponding to $\gamma = 10$, 25, and 50, respectively. The nonexponentiality is obviously more pronounced for larger c/c_0 values. As γ increases, the curves tend to show an increasingly rapid initial drop followed by a nearly exponential decay. The function $\phi_s(t)$, which represents the decay of the donor luminescence after steady-state excitation, is calculated by putting (23) into (7). The dashed curves in Figs. 4(a), 4(b), and 4(c) show the functions $\phi_s(t)$. One readily sees that $\phi_s(t)$ decays more slowly and thus exhibits less distinctive nonexponentiality than $\phi(t)$, in agreement with an observed result.[19]

IV. ANALYSIS OF EXPERIMENTAL DATA

Here we show a procedure for analyzing experimental data on energy transfer by the exchange mecha-

TABLE I (*Continued*)

	γ=30					γ=40		
0.010	0.9899	0.9990	0.9995	0.9894	0.9900	0.9992	0.9996	0.9895
0.015	0.9849	0.9985	0.9992	0.9841	0.9850	0.9989	0.9994	0.9843
0.020	0.9800	0.9980	0.9989	0.9788	0.9801	0.9985	0.9992	0.9791
0.025	0.9750	0.9975	0.9987	0.9735	0.9752	0.9981	0.9990	0.9739
0.030	0.9701	0.9970	0.9984	0.9682	0.9703	0.9977	0.9988	0.9687
0.040	0.9604	0.9960	0.9979	0.9576	0.9606	0.9970	0.9984	0.9582
0.050	0.9507	0.9950	0.9973	0.9471	0.9509	0.9962	0.9980	0.9479
0.070	0.9317	0.9930	0.9963	0.9260	0.9320	0.9947	0.9972	0.9271
0.100	0.9039	0.9900	0.9947	0.8947	0.9043	0.9925	0.9961	0.8961
0.150	0.8594	0.9850	0.9920	0.8430	0.8600	0.9887	0.9941	0.8449
0.200	0.8172	0.9800	0.9893	0.7919	0.8178	0.9850	0.9921	0.7941
0.250	0.7770	0.9750	0.9866	0.7416	0.7778	0.9813	0.9901	0.7439
0.300	0.7389	0.9700	0.9840	0.6920	0.7397	0.9775	0.9882	0.6943
0.400	0.6682	0.9600	0.9786	0.5954	0.6691	0.9700	0.9842	0.5969
0.500	0.6043	0.9501	0.9733	0.5027	0.6053	0.9626	0.9803	0.5026
0.700	0.4946	0.9303	0.9627	0.3323	0.4955	0.9477	0.9724	0.3260
1.000	0.3667	0.9008	0.9467	0.1324	0.3672	0.9254	0.9606	0.1127
1.500	0.2234	0.8521	0.9203	0.0108	0.2233	0.8885	0.9410	0.0033
2.000	0.1367	0.8041	0.8939	0.0011	0.1361	0.8518	0.9215	0.0001
2.500	0.0840	0.7567	0.8677	0.0002	0.0832	0.8155	0.9020	0.0000
3.000	0.0519	0.7102	0.8417	0.0001	0.0510	0.7794	0.8825	0.0000
4.000	0.0201	0.6198	0.7901	0.0000	0.0193	0.7084	0.8439	0.0000
5.000	0.0080	0.5336	0.7391	0.0000	0.0074	0.6390	0.8054	0.0000
7.000	0.0014	0.3767	0.6393	0.0000	0.0011	0.5064	0.7293	0.0000
10.000	0.0001	0.1922	0.4965	0.0000	0.0001	0.3290	0.6176	0.0000
15.000	0.0000	0.0412	0.2853	0.0000	0.0000	0.1187	0.4402	0.0000
20.000	0.0000	0.0063	0.1272	0.0000	0.0000	0.0298	0.2800	0.0000
25.000	0.0000	0.0013	0.0403	0.0000	0.0000	0.0057	0.1487	0.0000
30.000	0.0000	0.0004	0.0095	0.0000	0.0000	0.0013	0.0607	0.0000
40.000	0.0000	0.0001	0.0006	0.0000	0.0000	0.0002	0.0046	0.0000
50.000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0001	0.0004	0.0000
70.000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0001	0.0001	0.0000

	γ=50					γ=70		
0.010	0.9900	0.9994	0.9997	0.9896	0.9900	0.9996	0.9998	0.9897
0.015	0.9850	0.9991	0.9995	0.9845	0.9851	0.9994	0.9997	0.9846
0.020	0.9801	0.9988	0.9994	0.9793	0.9802	0.9991	0.9996	0.9795
0.025	0.9752	0.9985	0.9992	0.9741	0.9753	0.9989	0.9995	0.9744
0.030	0.9703	0.9982	0.9991	0.9689	0.9704	0.9987	0.9993	0.9693
0.040	0.9606	0.9976	0.9988	0.9586	0.9607	0.9983	0.9991	0.9590
0.050	0.9510	0.9970	0.9984	0.9483	0.9511	0.9979	0.9989	0.9488
0.070	0.9321	0.9958	0.9978	0.9277	0.9323	0.9970	0.9985	0.9284
0.100	0.9045	0.9940	0.9969	0.8970	0.9047	0.9957	0.9978	0.8979
0.150	0.8602	0.9910	0.9953	0.8460	0.8605	0.9936	0.9967	0.8472
0.200	0.8182	0.9880	0.9938	0.7954	0.8184	0.9914	0.9956	0.7968
0.250	0.7782	0.9850	0.9922	0.7452	0.7785	0.9893	0.9945	0.7467
0.300	0.7401	0.9820	0.9906	0.6955	0.7405	0.9872	0.9934	0.6969
0.400	0.6695	0.9760	0.9875	0.5977	0.6699	0.9829	0.9912	0.5985
0.500	0.6057	0.9700	0.9844	0.5023	0.6061	0.9786	0.9890	0.5019
0.700	0.4959	0.9581	0.9782	0.3217	0.4962	0.9701	0.9846	0.3164
1.000	0.3675	0.9402	0.9688	0.0988	0.3677	0.9573	0.9780	0.0801
1.500	0.2232	0.9106	0.9533	0.0010	0.2232	0.9360	0.9670	0.0001
2.000	0.1358	0.8810	0.9377	0.0000	0.1356	0.9147	0.9560	0.0000
2.500	0.0828	0.8516	0.9222	0.0000	0.0824	0.8935	0.9450	0.0000
3.000	0.0505	0.8224	0.9067	0.0000	0.0502	0.8724	0.9340	0.0000
4.000	0.0189	0.7644	0.8759	0.0000	0.0186	0.8303	0.9121	0.0000
5.000	0.0071	0.7072	0.8451	0.0000	0.0069	0.7884	0.8902	0.0000
7.000	0.0010	0.5957	0.7840	0.0000	0.0010	0.7057	0.8465	0.0000
10.000	0.0001	0.4384	0.6935	0.0000	0.0001	0.5846	0.7814	0.0000
15.000	0.0000	0.2199	0.5463	0.0000	0.0000	0.3955	0.6740	0.0000
20.000	0.0000	0.0817	0.4059	0.0000	0.0000	0.2345	0.5684	0.0000
25.000	0.0000	0.0238	0.2761	0.0000	0.0000	0.1155	0.4651	0.0000
30.000	0.0000	0.0054	0.1643	0.0000	0.0000	0.0480	0.3654	0.0000
40.000	0.0000	0.0005	0.0310	0.0000	0.0000	0.0053	0.1850	0.0000
50.000	0.0000	0.0002	0.0027	0.0000	0.0000	0.0008	0.0590	0.0000
70.000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0001	0.0013	0.0000

nism in terms of our theoretical results. It should be understood, first of all, that the system under study is supposed to comply with the basic assumptions (a), (b), and (c) of Sec. II. The objective of the analysis is to decide whether the theory is capable of reproducing a set of experimental data with satisfactory agreement, and, if this is the case, further to determine an optimum set of parameters γ and c_0. These parameters can be readily converted into L by (15) and (25) and information is thereby obtained concerning the asymp-totic behavior of the exchange integral for the donor–acceptor pair in question, and also concerning the tail of the molecular wavefunctions. If the spectral overlap between the donor emission and the acceptor absorption is known, an absolute value of the exchange integral is determined.

Measurements of both η/η_0 and of τ_m/τ_0 and/or τ_{ms}/τ_0 over a fairly large range of the acceptor concentration c is essential for the analysis. The quantity τ_e/τ_0 is helpful but less important, because it is relatively in-
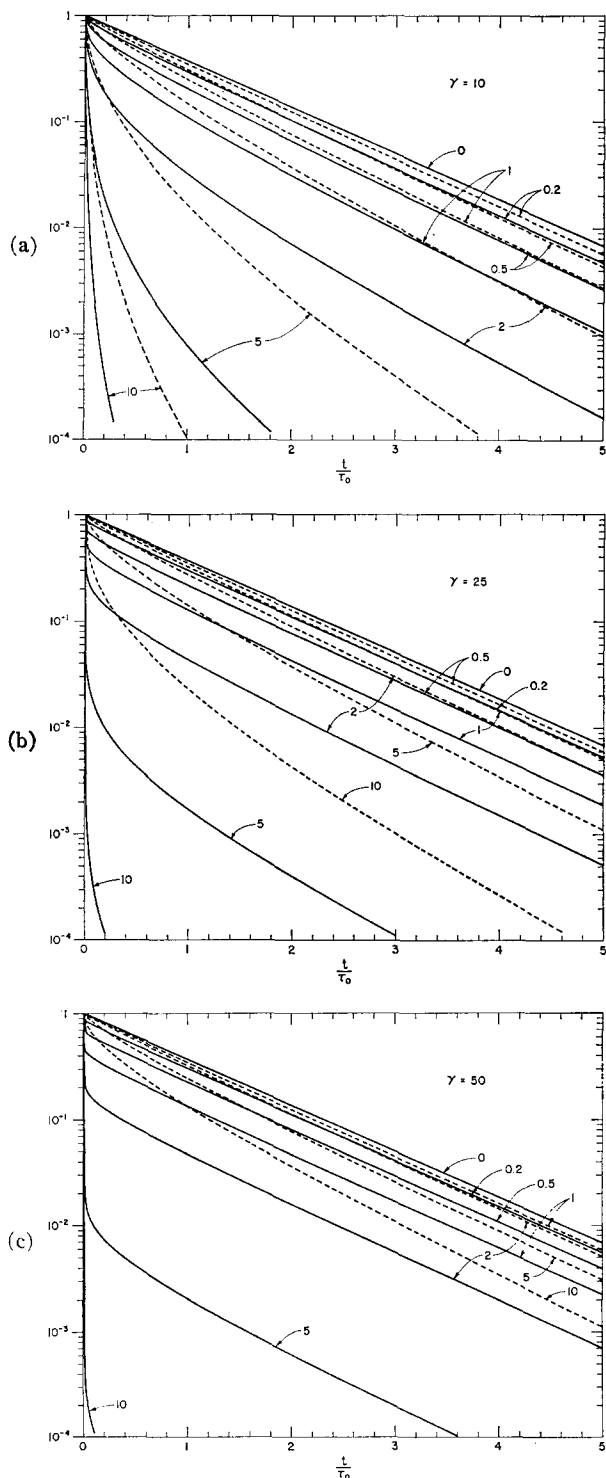
FIG. 4. The decay of donor luminescence under the influence of energy transfer by the exchange mechanism. The figures 4(a), 4(b), and 4(c) refer to $\gamma=10$, 25, and 50, respectively. The abscissa represents t/τ_0, i.e., the time after excitation measured in units of the decay time τ_0 of spontaneous deactivation in the donor. The solid curve represents the decay function $\phi(t)$ after flash excitation, and the broken curve the decay function $\phi_s(t)$ after steady-state excitation. The numeral on a curve denotes the value of c/c_0.

sensitive to γ. We need not comment about the measurement of η/η_0 except to mention that care must be taken to check the possible occurrence of singlet–singlet transfer in the energy range of observation.

A procedure for the analysis may be as follows:

(1) Determine τ_m and/or τ_{ms} from a decay curve by numerical or graphical integration. Otherwise, use a phase fluorometer to obtain τ_m directly.[31–36]

(2) Make an $\eta - \tau$ plot like Fig. 2 and estimate an approximate value of γ by comparison with the theoretical curves in Fig. 2 or Fig. 3.

(3) Plot η/η_0, τ_m/τ_0, and/or τ_{ms}/τ_0 vs $\log_{10}c$. The acceptor concentration c must have been corrected for the shrinkage of the solution upon freezing. (The shrinkage in volume amounts to about 20% for the case of EPA solutions.[41])

(4) Compare the experimental points plotted as above with the theoretical curve for a value of γ in the neighborhood of the approximate estimate at Step (2). Determine a value of c_0 by shifting the experimental plot horizontally on the abscissa until the best fit is obtained. Repeat this for a series of values of γ and determine the optimum value of γ. The value of c_0 should turn out to be reasonably stable with respect to a small change in γ, if the theory agrees with experiment. An equivalent process can be carried out on a computer with a least-squares fit criterion.

Once the parameters c_0 and γ are determined, comparison of the theoretical decay functions, $\phi(t)$ and/or $\phi_s(t)$, at a definite acceptor concentration is feasible. A satisfactory agreement here establishes consistency of the analysis.

As an illustration, we have analyzed two sets of data published by Ermolaev and Terenin. They dispersed the donor, benzophenone, and the acceptor, either naphthalene or 1-bromonaphthalene, in an alcohol–ether solution and studied the phosphorescence of the donor at $-195°C$. We have read experimental points from Fig. 1 of Ref. 15 and computed the relative yield η/η_0 and the decay time τ/τ_0 of the donor phosphorescence. Although Ermolaev and Terenin do not make a clear statement of a definition of their decay time τ, except that they measured it by an oscillographic phosphoroscope, we presume here that their τ corresponds to our τ_m defined by (5). We also assume that the shrinkage of the solution upon freezing has been taken into account in their original data.

At Step (2) of our procedure, we have found that theoretical curves for $\gamma \approx 20$ give a reasonable fit with the experimental $\eta - \tau$ plot. Then, at Step (4), we have concluded that the best fit is obtained with the values of γ and c_0 in the first two lines of Table II when all the experimental points are treated with equal weight.

[41] D. S. McClure, J. Chem. Phys. **19**, 670 (1951).

Figure 5 illustrates both the experimental values (points, referring to the abscissa above) and the theoretical curves (solid curves, referring to the abscissa below) for $\gamma = 19.5$. The agreement of theory with experiment is satisfactory, and particularly good for the case of 1-bromonaphthalene. The theoretical curves for $\gamma = 18.0$ which fit best with the data for naphthalene are only slightly displaced from the solid curves in Fig. 5 and are not shown there. From the set of values of γ and c_0, we can reasily calculate R_0 and L by (15) and (25), the result being included in Table II. The value of L, about 1.3–1.4 Å, is the order of magnitude which one would expect from the size of the electronic cloud of a benzene ring.

V. SUMMARY

The decay of donor luminescence under the influence of energy transfer by the exchange mechanism has been shown to be amenable to quantitive analysis. From a set of observed data on the yield and decay time, one can determine the rate constant for energy transfer and hence deduce information about the intermolecular exchange interaction, which is not otherwise readily accessible. It should be emphasized that careful measurement of a well-defined decay time and/or decay curve is very important for the proposed method of analysis.
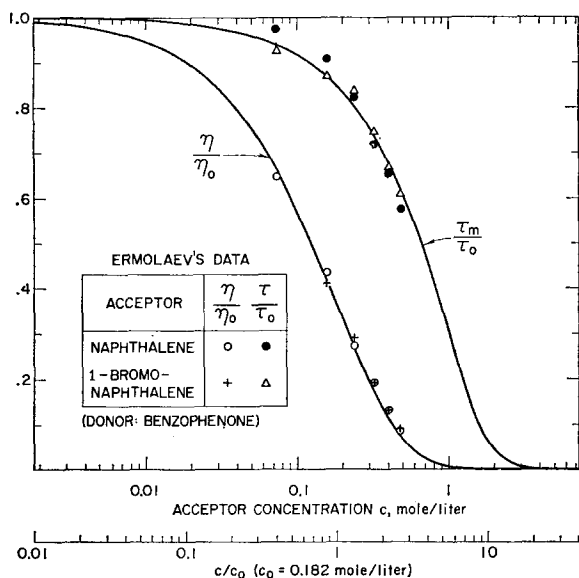

FIG. 5. Comparison of Ermolaev's data with theory. Ermolaev's data for triplet-triplet energy transfer from benzophenone to naphthalene or to 1-bromonaphthalene are represented by the symbols explained in the inserted table in reference to the abscissa above, which gives the acceptor concentration c in units of mole/liter. The calculated values of η/η_0 and τ_m/τ_0 for $\gamma = 19.5$ are represented by the solid curves in reference to the abscissa below, which gives c/c_0. The optimum value of $c_0 = 0.182$ mole/liter has been found for best fit of the experimental data for the case of 1-bromonaphthalene.

TABLE II. Result of analysis of Ermolaev's data.

	Naphthalene	1-Bromo naphthalene
γ	18.0	19.5
c_0 (mole/liter)	0.186	0.182
R_0 (Å)	12.9	13.0
L (Å)	1.43	1.33

ACKNOWLEDGMENTS

APPENDIX I. SOME SIMPLE MODELS

We apply the general equation for the decay function (4) to some simple models for the purpose of illustration and comparison with energy transfer by the exchange mechanism.

1. Perrin Model

If we consider an "active sphere" with radius R_0 as proposed by Perrin,[42] the rate constant $n(R)$ is

$$n(R) = \begin{cases} \infty, & R < R_0, \\ 0, & R_0 < R. \end{cases} \qquad (A1)$$

Substitution of this into (4) gives

$$\phi(t) = \begin{cases} 1, & t = 0, \\ \exp(-t/\tau_0 - c/c_0), & t > 0. \end{cases} \qquad (A2)$$

where use has been made of (24) and (25). The relative yield and the decay times are given as follows:

$$\eta/\eta_0 = \exp(-c/c_0), \qquad (A3)$$

$$\tau_m/\tau_0 = 1, \qquad (A4)$$

$$\tau_{ms}/\tau_0 = 1, \qquad (A5)$$

$$\tau_e/\tau_0 = 1 - c/c_0, \qquad (1 \geq c/c_0). \qquad (A6)$$

2. Stern–Volmer Model

If the rate constant is independent of the distance, i.e.,

$$n(R) = n = \text{const.}, \qquad (A7)$$
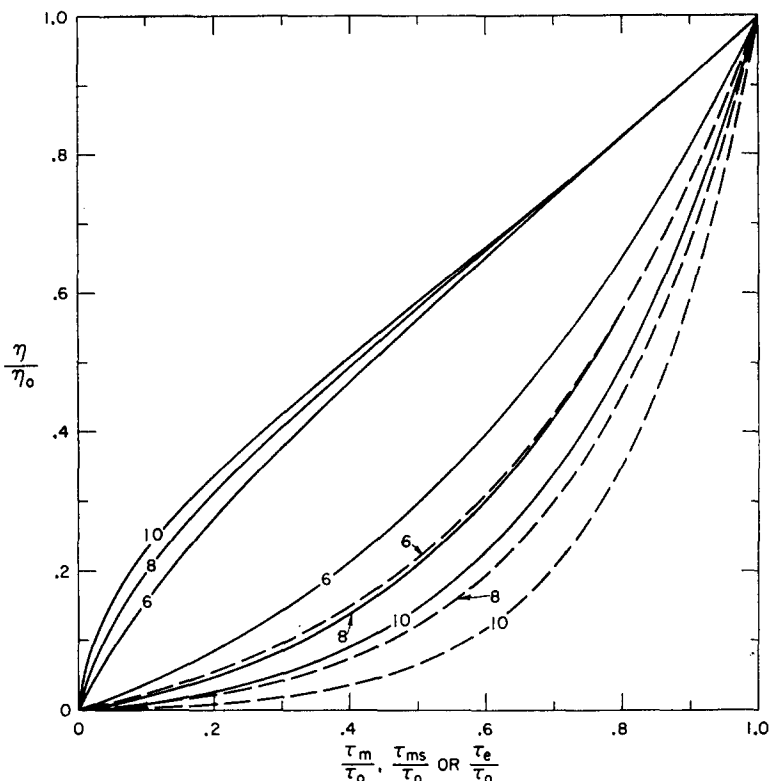
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[42] F. Perrin, Compt. Rend. **178**, 1978 (1924).

FIG. 6. The relative field η/η_0 vs the decay times τ_m/τ_0, τ_{ms}/τ_0, and τ_e/τ_0 for the inverse-power rate model. The abscissa represents τ_m/τ_0, τ_{ms}/τ_0, or τ_e/τ_0, and the ordinate η/η_0. The upper three solid curves (concave upwards) correspond to τ_e/τ_0, the lower three solid curves to τ_m/τ_0, and the broken curves to τ_{ms}/τ_0. The numeral on a curve denotes the value of s, the power in the expression for the transfer rate. Thus $s=6, 8$, and 10 correspond to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interaction, respectively.

we obtain from (4)

$$\phi(t) = \exp(-t/\tau_0) \lim_{N\to\infty} \exp(-Nnt). \qquad (A8)$$

The factor Nn in the exponent is proportional to the acceptor concentration c. On taking the limit $N\to\infty$, we must let n become vanishingly small so that Nn is finite; otherwise, the resulting decay function vanishes. We put the result in the form

$$\phi(t) = \exp\left[-\frac{(1+c/c_0)t}{\tau_0}\right], \qquad (A9)$$

using an arbitrary reference concentration c_0. Notice that the concept of a "critical transfer concentration" is not at all applicable to this model. The yield and the decay times all have the so-called Stern–Volmer concentration dependence[43]:

$$\frac{\eta}{\eta_0} = \frac{\tau_m}{\tau_0} = \frac{\tau_{ms}}{\tau_0} = \frac{\tau_e}{\tau_0} = \left(1+\frac{c}{c_0}\right)^{-1}. \qquad (A10)$$

3. Inverse-Power Rate Model

Consider the case where the rate constant is proportional to an inverse power of the distance. Then $n(R)$ may be written as

$$n(R) = \frac{(R_0/R)^s}{\tau_0}, \qquad (A11)$$

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[43] O. Stern and M. Volmer, Physik. Z. **20**, 183 (1919).

where s is a positive number and R_0 is a critical transfer distance. This model covers several important cases. It corresponds to electric-dipole–dipole interaction for $s=6$, dipole–quadrupole interaction for $s=8$, and quadrupole–quadrupole interaction for $s=10$.

Putting (A11) into (4) and changing integration variables, we have

$$\phi(t) = \exp\left(\frac{-t}{\tau_0}\right) \lim_{N\to\infty, R_V\to\infty} \left[\frac{3}{s}Z_V^{3/s} \int_{Z_V}^{\infty} Z^{-1-3/s}e^{-Z}dZ\right]^N, \qquad (A12)$$

where

$$Z_V = (t/\tau_0)(R_0/R_V)^s. \qquad (A13)$$

As long as we restrict ourselves to cases $s>3$, the integral in (A12) converges for any positive Z_V. Since $Z_V\to 0$ for $R_V\to\infty$, we use an expansion

$$\int_{Z_V}^{\infty} e^{-Z}Z^{-1-3/s}dZ = \left(\frac{s}{3}\right)\left[Z_V^{-3/s}\exp(-Z_V) - \Gamma\left(1-\frac{3}{s}\right)\right.$$

$$\left. + s/(s-3)Z_V^{1-3/s} + O(Z_V^{2-3/s})\right] \qquad (A14)$$

in evaluating the right-hand side of (A12). The result is conveniently expressed in terms of the acceptor concentration c and the critical transfer concentration c_0

defined by (25) as

$$\phi(t) = \exp\left[\frac{-t}{\tau_0} - \Gamma\left(1 - \frac{3}{s}\right)\frac{c}{c_0}\left(\frac{t}{\tau_0}\right)^{3/s}\right].$$ (A15)

Substitution of (A15) into (5), (6), (9), and (10) gives η/η_0, τ_m/τ_0, τ_{ms}/τ_0, and τ_e/τ_0 as functions of c/c_0. Actual evaluation requires numerical work. For a particular case $s=6$, η/η_0 and τ_m/τ_0 can be written in terms of the error function, as has been found by Förster[7] and Galanin.[8]

We summarize our numerical results in Fig. 6, again reserving an extensive tabulation for another report.[29]

A parenthetical remark may be made concerning dipole–dipole transfer. The theory of Förster and Dexter, which leads to a rate constant proportional to R^{-6}, has certain limitations as to its applicability, as has been pointed out, for example, by Robinson and Frosch.[44] Thus, a "phenomenological" rate constant including effects neglected in the theory may very well have a different dependence on R under certain circumstances. It is worth attempting to analyze a set of carefully controlled experimental data for a supposedly dipole-dipole case in terms of our theoretical results[29] for the inverse power-rate model and to determine an optimum value of the power s by a procedure similar to that described in Sec. IV. The resulting value of s may be larger or smaller than 6 depending on whether the phenomenological rate constant is effectively of shorter or longer range.

[44] G. W. Robinson and R. P. Frosch, J. Chem. Phys. **38**, 1187 (1963).

APPENDIX II. DERIVATION OF EQ. (28)

Changing the integration variable in (21) by $u=zy$, we have

$$g(z) = \int_0^z e^{-u}\left(\ln\frac{z}{u}\right)^3 du$$

$$= (\ln z)^3 H_0(z) + (\ln z)^2 H_1(z) + \ln z H_2(z) + H_3(z),$$ (A16)

where

$$H_k(z) = (-1)^k \binom{3}{k} \int_0^z e^{-u}(\ln u)^k du, \qquad k = 0, 1, 2, 3.$$ (A17)

The integrals in (A17) are expressed as

$$\int_0^z e^{-u}(\ln u)^k du = \Gamma^{(k)}(1) - \int_z^\infty e^{-u}(\ln u)^k du,$$ (A18)

where $\Gamma^{(k)}(1)$ is the kth derivative of the gamma function of argument unity. The order of magnitude of the second term in (A18), which is small as long as z is sufficiently large, can be determined by repeated partial integration. Putting the result into (A16), we find that the contributions from the second term in (A18) are only of the order of $e^{-z}(\ln z)^3 z^{-2}$. The terms of lower order all cancel out in (A16).

Numerical values of the coefficients h_1, h_2, and h_3 in (29) have been computed from the polygamma functions tabulated by Davis.[45]

[45] H. T. Davis, *Tables of the Higher Mathematical Functions* (Principia Press, Inc., Bloomington, Indiana, 1935), Vol. 2.