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Triplet–Triplet Energy Transfer between the Same Molecular Species

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A method for obtaining the rate constants for triplet–triplet energy transfer between the same molecular species is presented. It is an improvement on a previously proposed method and comprises an analysis of the phosphorescence decay curve of a mixture of an organic substance and its deuterated homolog. It has been found that the new method gives a good fit to experimental decay curves at 77 and 4.2 K. It was also found that the critical transfer distance between similar molecules is usually smaller than that between differrent molecules.

So far, very few investigations have been reported on the triplet–triplet energy transfer between the same molecular species. Photoselection1) (or magnetophotoselection2)), which consists of the measurement of the concentration depolarization of phosphorescence, has been the only investigative method until 1975. These methods, however, had a fatal drawback in that results could not evade the effect of a singlet–singlet transfer whenever it took place.3)

The isotopic mixture method4,5) and the ODMR method6) were developed by one of the authors. The former method was based on the fact that some kinds of organic molecules (H) and their deuterated homologs (D) are quite similar in electronic structures, but are quite different regarding their phosphorescence lifetimes. It consists of analyzing the phosphorescence decay profile of a mixed solution of H and D, where the decay form tends to deviate from a mere superposition of each decay curve when an energy transfer takes place. This method is almost free from the effects of a singlet–singlet transfer since the extent of the initial triplet population is not important in the treatment. However, the analysis is inevitably crude due to the presence of a back transfer which precludes an exact statistical treatment. The latter method makes use of the fact that spin angular momentum must be conserved during an energy transfer. However, the spin-lattice relaxation taking place in a glassy solvent greatly affected the population of each spin sublevel, making a quantitative discussion almost impossible.

The present paper concerns an improvement in the isotopic-mixture method. First, in order to completely exclude any effect due to a singlet–singlet transfer, benzophenone was used as a sensitizer for initial pumping. Second, the experimental decay curves were analyzed by a computer-simulation method, rather than by seeking a solution to the rate equations in a closed form. Thus a more exact statistical treatment is now possible. Moreover, we have taken into account not only the D→H and H→D energy transfers, but also the D→D transfer. The last process may increase the possibility that the exitation on D happens to encounter an H molecule7,8). Inhomogeneous widths of the T_1 levels were also taken into consideration in order to account for the temperature dependence of energy-transfer efficiency.

Experimental

The samples used were naphthalene, phenanthrene, and biphenyl (H) together with their perdeuterated homologs (D). Equal molar amounts of H and D were dissolved in methyl methacrylate and deoxygenated by several freeze-thaw cycles. The sample solutions were polymerized at 100 °C for 48 h without an initiator and then annealed at 40 °C for 24 h. The initial concentration was 0.20, 0.15, 0.10 or 0.075 mol dm^{-3} for each component. In each case, benzophenone (0.20 mol dm^{-3}) was added as a sensitizer. The volume contraction according to polymerization was 1/1.27 and contraction by cooling was only a few percent; hence the latter effect was disregarded.

Samples were irradiated at 340 or 350 nm for 20 s using two shutters to excite only the benzophenone, and the total decays of the ensuing phosphorescence, containing H and D components simultaneously, were observed at 77 and 4.2 K. The output signals were accumulated 10—20 times to improve the S/N ratio.

Simulation

Simulation was carried out upon the following assumptions.

1) Solute molecules are randomly distributed in poly(methyl methacrylate) (PMMA); thus, the distribution of the nearest-neighbor distance (R) is9)

$$\rho(R) = \rho(R,\ C) = 4\pi CR^2 \exp(-4\pi CR^3/3), \tag{1}$$

where C is the concentration of the solute.

2) The distribution of the mutual orientation is also random; thus, the effect of the orientation on the transfer rate can be ignored.

3) Energy is transferred only to the nearest-neighbor molecule.

4) The sensitization efficiency of benzophenone is the same for H and D.

5) The environment of each molecule was assumed

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to be statistically equivalent; that is, a correlation of environments for donor and acceptor molecules was disregarded.[7)]

6) The rate constant for energy transfer can be expressed as a product of two terms,

$$k_{\mathrm{ET}}(R,\ \Delta E) = k_1(R)\cdot k_2(\Delta E) \tag{2}$$

$k_1(R)$ is approximated[10)] as

$$k_1(R) = k_{\mathrm{D}}\exp(\gamma(1-R/R_0)), \tag{3}$$

where k_{D} is the phosphorescence decay constant of D and γ and R_0 (critical transfer distance) are parameters to be determined. The use of k_{D} is perfectly arbitrary. k_{H} (decay constant of H) or any other reference value may be employed instead, whereupon the critical distance changes according to the reference value. However, because of the strong R-dependent nature of the transfer rate, the obtained values of γ and R_0 are not very sensitive to the reference value. $k_2(\Delta E)$ is a function of the triplet energy difference in a donor (excited molecule)-acceptor (nearest-neighbor molecule) pair, $\Delta E=E_{\mathrm{donor}}-E_{\mathrm{acceptor}}$. It does not depend on whether the molecules are H or D, and can be expressed as

$$\begin{aligned} k_2(\Delta E) &= \exp(\Delta E/kT) && \text{if } \Delta E\leq 0,\\ &\quad 1 && \text{if } \Delta E\geq 0. \end{aligned} \tag{4}$$

7) The triplet energy of the solute molecule differs from site to site. Its distribution, $\sigma(E)$, is assumed to follow the spectral form of the 0-0 phosphorescence band (*vide infra*).

Since energy is transferred from molecule to molecule while being dissipated by intramolecular processes, the decay of a D molecule is expressed as

$$f_{\mathrm{D}}(t,\ R,\ \Delta E) = \exp[-(k_{\mathrm{D}}+k_{\mathrm{ET}}(R,\ \Delta E))t]. \tag{5}$$

Similarly, the decay of an H molecule is given by

$$f_{\mathrm{H}}(t,\ R,\ \Delta E) = \exp[-(k_{\mathrm{H}}+k_{\mathrm{ET}}(R,\ \Delta E))t]. \tag{6}$$

In the following, superfix 0 stands for a group of molecules which are excited by a transfer from benzophenone. Superfix n is for those molecules which are excited by a transfer from group $n-1$.

Decay of the group 0 is

$$\begin{aligned} f_{\mathrm{D}}^{0}(t) &= \int \mathrm{d}R\rho(R)\\ &\quad\times \int \mathrm{d}\Delta E[\xi_{\mathrm{DD}}(\Delta E)+\xi_{\mathrm{DH}}(\Delta E)]f_{\mathrm{D}}(t,\ R,\ \Delta E)/2, \end{aligned} \tag{7}$$

$$f_{\mathrm{H}}^{0}(t) = \int \mathrm{d}R\rho_{\mathrm{D}}(R)\int \mathrm{d}\Delta E\xi_{\mathrm{HD}}(\Delta E)f_{\mathrm{H}}(t,\ R,\ \Delta E), \tag{8}$$

where $\xi_{\mathrm{DD}}(\Delta E)$, $\xi_{\mathrm{DH}}(\Delta E)$, and $\xi_{\mathrm{HD}}(\Delta E)$ are the distributions of ΔE for D→D, D→H, and H→D donor-acceptor pairs, respectively, and are

$$\xi_{\mathrm{AB}}(\Delta E) = \int \sigma_{\mathrm{A}}(E)\sigma_{\mathrm{B}}(E-\Delta E)\mathrm{d}E. \tag{9}$$

$\rho(R)$ is the distribution of the distance to the nearest-neighbor molecule, irrespective of whether it is H or D. $\rho_{\mathrm{D}}(R)$ is the distribution of the distance to the nearest-neighbor D molecule, so that

$$\left.\begin{aligned} \rho(R) &= \rho(R,\ C)\\ \rho_{\mathrm{D}}(R) &= \rho(R,\ C/2) \end{aligned}\right\}, \tag{10}$$

where C is the total concentration. The transfer H→H is disregarded, since the lifetime of H is short; however, it is partly taken into account by using the above ρ_{D} expression rather than $\rho_{\mathrm{D}}=\rho/2$. We took the arithmetic mean of ξ_{DD} and ξ_{DH} because the probability that the nearest-neighbor molecule is H or D is the same.

Let A^0 be the amount of energy transferred to other molecules in the course of decay (7) and (8), so that

$$\begin{aligned} A_{\mathrm{DD}}^{0}(t) &= \int \mathrm{d}R\rho(R)\\ &\quad\times \int \mathrm{d}\Delta E\xi_{\mathrm{DD}}(\Delta E)k_{\mathrm{ET}}(R,\ \Delta E)f_{\mathrm{D}}(t,\ R,\ \Delta E)/2, \end{aligned} \tag{11}$$

$$\begin{aligned} A_{\mathrm{DH}}^{0}(t) &= \int \mathrm{d}R\rho(R)\\ &\quad\times \int \mathrm{d}\Delta E\xi_{\mathrm{DH}}(\Delta E)k_{\mathrm{ET}}(R,\ \Delta E)f_{\mathrm{D}}(t,\ R,\ \Delta E)/2, \end{aligned} \tag{12}$$

$$\begin{aligned} A_{\mathrm{HD}}^{0}(t) &= \int \mathrm{d}R\rho_{\mathrm{D}}(R)\\ &\quad\times \int \mathrm{d}\Delta E\xi_{\mathrm{HD}}(\Delta E)k_{\mathrm{ET}}(R,\ \Delta E)f_{\mathrm{H}}(t,\ R,\ \Delta E). \end{aligned} \tag{13}$$

In the course of a successive transfer of energy, the decay of group n becomes,

$$f_{\mathrm{D}}^{n}(t) = [A_{\mathrm{DD}}^{n-1}(t) + A_{\mathrm{HD}}^{n-1}(t)]*f_{\mathrm{D}}^{0}(t), \tag{14}$$

$$f_{\mathrm{H}}^{n}(t) = A_{\mathrm{DH}}^{n-1}(t)*f_{\mathrm{H}}^{0}(t), \tag{15}$$

where

$$A_{\mathrm{DD}}^{n}(t) = [A_{\mathrm{DD}}^{n-1}(t) + A_{\mathrm{HD}}^{n-1}(t)]*A_{\mathrm{DD}}^{0}(t), \tag{16}$$

$$A_{\mathrm{DH}}^{n}(t) = [A_{\mathrm{DD}}^{n-1}(t) + A_{\mathrm{HD}}^{n-1}(t)]*A_{\mathrm{DH}}^{0}(t), \tag{17}$$

$$A_{\mathrm{HD}}^{n}(t) = A_{\mathrm{DH}}^{n-1}(t)*A_{\mathrm{HD}}^{0}(t). \tag{18}$$

The asterisk $*$ denotes a convolution. The total phosphorescence decay is, then,

$$F(t) = \sum_{n=0}^{\infty}[k_{\mathrm{D}}^{\mathrm{r}}f_{\mathrm{D}}^{n}(t) + k_{\mathrm{H}}^{\mathrm{r}}f_{\mathrm{H}}^{n}(t)], \tag{19}$$

where $k_{\mathrm{D}}^{\mathrm{r}}$ and $k_{\mathrm{H}}^{\mathrm{r}}$ are the radiative rate constants of D and H, respectively. Finally, we convolute $F(t)$ with the 20 s square form of the light-sourse intensity $I(t)$

$$G(t) = I(t)*F(t) \tag{20}$$

and then normalize $G(t)$ with respect to the integrated area.

For naphthalene and phenanthrene, the values of

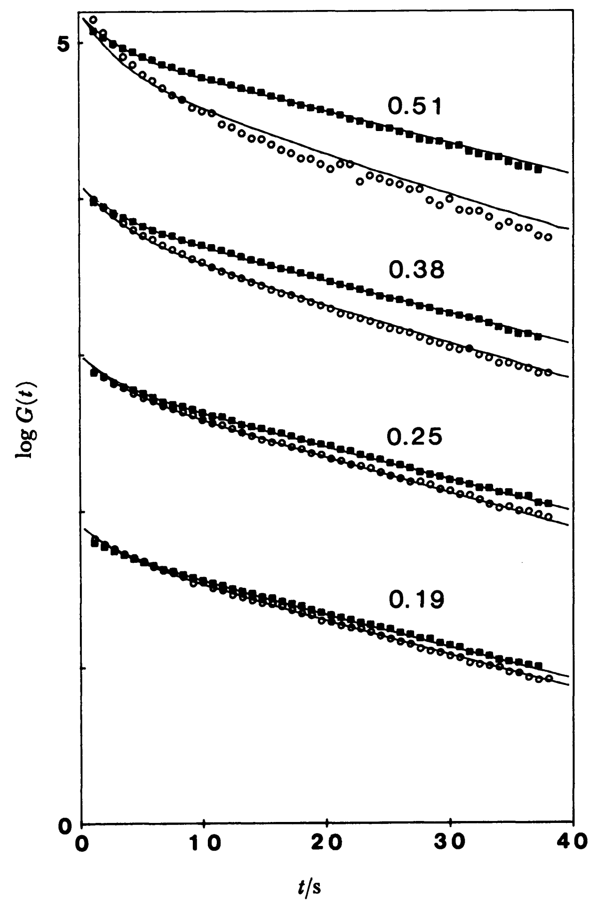

Fig. 1. Decay of naphthalene phosphorescence at 77 K (lower curves) and 4.2 K (upper curves). Total concentrations (mol dm^{-3}) are indicated. Solid lines: calculated ($\gamma = 15$, $R_0 = 13.0$ Å); ○ and ■: experimental.

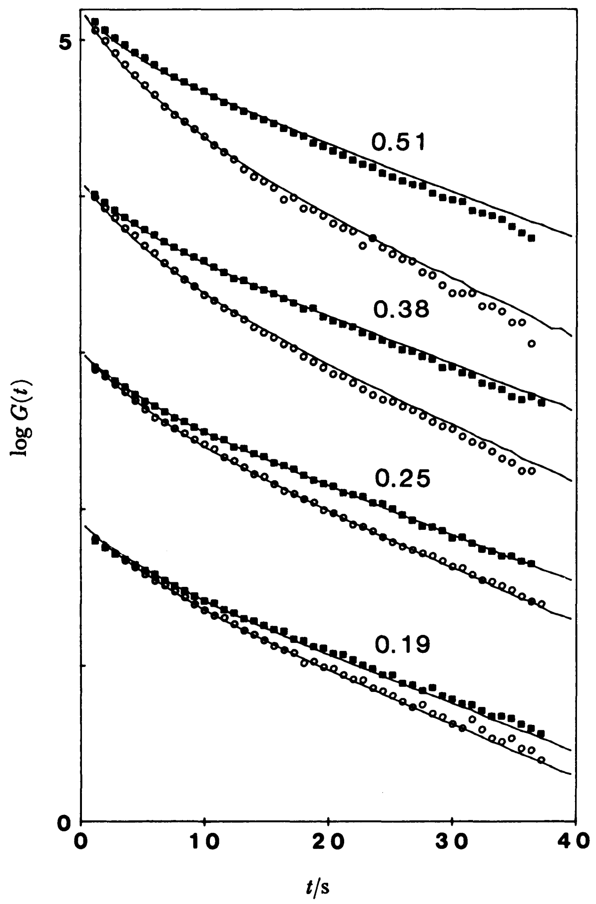

Fig. 2. Decay of phenanthrene phosphorescence at 77 K (lower curves) and 4.2 K (upper curves). Total concentrations (mol dm^{-3}) are indicated. Solid lines: calculated ($\gamma = 10$, $R_0 = 14.5$ Å); ○ and ■: experimental.

TABLE 1. PHOSPHORESCENCE LIFETIMES (s)

Sample	77 K	4.2 K
Naphthalene-d_0	2.3	2.4
Naphthalene-d_8	21.0	21.5
Phenanthrene-d_0	3.3	3.4
Phenanthrene-d_{10}	14.5	14.5
Biphenyl-d_0	3.7	4.4
Biphenyl-d_{10}	10.0	11.2

k^r_D and k^r_H were borrowed from the results of Fischer and Lim[11] (0.0163 s^{-1} and 0.0276 s^{-1} for naphthalene and 0.0215 s^{-1} and 0.0311 s^{-1} for phenanthrene, respectively). Since the values for biphenyl H and D were not available, they were assumed to be equal to each other.

Values of k_H and k_D were measured separately, as displayed in Table 1. They were constant over the whole range of concentrations. For naphthalene and phenanthrene, they were essentially unaffected by the temperature. For biphenyl, on the contrary, both of them increased when the temperature was lowered.

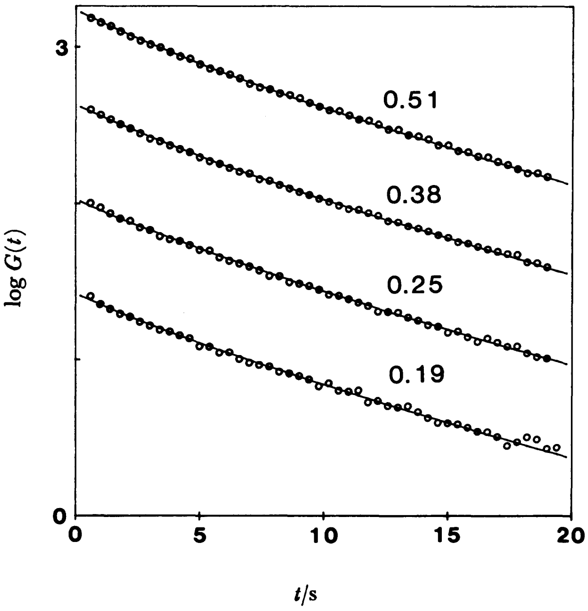

Fig. 3. Decay of biphenyl phosphorescence at 77 K. Total concentrations (mol dm^{-3}) are indicated. Solid lines: calculated ($\gamma = 25$, $R_0 = 8.5$ Å); ○: experimental.

This may be attributed to the structural change which often takes place in labile molecules. Hence, only the curves at 77 K were simulated.

Calculations were carried out up to n=20. The inclusion of higher terms was found to be unnecessary. The results are compared with experiments in Figs. 1—3.

Results and Discussion

Calculations were carrried out by changing γ and R_0 to seek for the best fits to the experimental curves at 77 K. The best fits were obtained by minimizing the square sums of the residuals and, also, by inspecting the uniformity of the distribution of the residuals. Optimal R_0 values are not very sensitive to γ. Changing the latter from 25 to 10 causes a change in the former by only 1.0 Å for naphthalene and no change for phenanthrene (Table 2). A calculation was also carried out by taking account of the exclusion volume for the neighboring molecule within the van der Waals radii, with essentially no effect. This is reasonable since the distribution of R falls off rapidly with decreasing R, whereas the effect of γ has just the reverse trend. However, the distribution of residuals is fairly sensitive to γ; thus, the best values of γ could be obtained and are displayed in Figs. 1—3 and in Table 2.[12]

R_0 of biphenyl is very small. We also measured several donor-acceptor systems, such as carbazole-naphthalene, carbazole-quinoline and carbazole-biphenyl. The values of R_0 were determined to be 16.5, 15.5, and 13.0 Å, respectively. We see that the value for biphenyl is also very small compared to the first two, which are in good agreement with those by Strambini and Galley[13] and by Oginets.[14] Thus, the acceptor property of biphenyl seems to be always poor. Gustav *et al.*[15] have calculated the structure of biphenyl by geometry optimization and have claimed that the molecule is twisted in the ground state by 22.9° about the central bond and is coplanar in the excited singlet and triplet states. If this is the case, the relaxed (planar) triplet biphenyl molecule must transfer its energy to the twisted acceptor molecule in the ground state. This requires an excess energy and renders the transfer less efficient. This may account for the small R_0 value.

It is interesting that the R_0 values for similar molecules are smaller than for different molecules. This may reflect a possible requirement that the sum of the Franck-Condon products, corresponding, apart from normalization factors, to the overlap of the S-T absorption spectrum of the acceptor and phosphorescence spectrum of the donor in the treatment of Dexter,[16] should be small due to the small energy difference between the donor molecule and the acceptor molecule.

TABLE 2. VALUES OF R_0 (Å)

Sample γ=	10	15	25	35
Naphthalene	12.5	$\underline{13.0}$	13.5	14.0
Phenanthrene	$\underline{14.5}$	14.5	14.5	15.0
Biphenyl	8.0	8.5	$\underline{8.5}$	9.0

The best values are underlined.

The fit is somewhat bad for curves of higher concentrations. This may be due to a failure of the assumptions, especially for 5, to hold at high concentrations.

In previous papers,[4,5] the triplet energy difference of H and D had been taken to be equal to the difference of the peak positions of their phosphorescence 0-0 bands; thus only the H→D back transfer had been assumed to be phonon-assisted. If this is true, the phosphorescence decay curves of the mixtures should be steeper at 4.2 K than at 77 K, since transfers to molecules with longer lifetime tend to be inhibited. This contradicted the present experiments and, thus, we have been forced to assume that the phonon-assisted energy transfer takes place in either direction. The phosphorescence spectra of the solutes in PMMA were broad and their band widths did not change even when the temperature was lowered to 4.2 K. Therefore, the widths of the 0-0 bands could be regarded as the inhomogeneous widths of the T_1 levels due to solvation. The Gaussian forms of the bands were regarded to be the distributions functions $\sigma(E)$ of T_1 energies in PMMA. Differences in the peak positions of H and D (that of D is always higher) is $110\,\text{cm}^{-1}$ for naphthalene, $60\,\text{cm}^{-1}$ for phenanthrene and $110\,\text{cm}^{-1}$ for biphenyl. These are smaller than their widths; thus the signs and the values of ΔE differ from site to site and do not depend much on the types of molecules. At 4.2 K, the energy is transferred mainly to sites with lower energies and the effect of temperature is to scramble the transfer sequences. The importance of the energy distribution has recently been stressed with regard to somewhat different aspects of the energy transfer.[17–19]

The values of γ and R_0 obtained from curves at 77 K were used to reproduce curves at 4.2 K. The fits are good, as can be seen from Figs. 1—2; thus, the present method has proven to be of use. In the above-metioned donor-acceptor systems of carbazole-naphthalene, carbazole-quinoline and carbazole-biphenyl, of which the energy differences were larger than their spectral widths, no change was observed in the donor phosphorescence decay curves when the temperature was changed from 77 to 4.2 K. This fact might strongly support our mechanism.

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$$k_1(R)=k_D(R_0/R)^m,$$

instead of the exponential function. We have calculated for naphthalene with m varying from 8 to 20. The fit was good with quite acceptable values of m=12—16 and R_0= 12.5—13.0 Å.

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