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Abstract

Full Text

PHYSICS

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INDUCTIVE-RESONANCE ENERGY TRANSFER FROM AROMATIC MOLECULES IN THE TRIPLET STATE*

(Presented by Academician A. N. Terenin, November 5, 1962)

Earlier [1] the authors reported a new phenomenon of radiationless energy transfer from a triplet donor molecule to an unexcited acceptor molecule, with transfer of the latter into a singlet excited state (Fig. 1). In the present work we undertook a detailed investigation of this effect in order finally to clarify its mechanism. Radiationless intermolecular energy transfer from the triplet level to the singlet level was observed by us for a large number of combinations of various substances: simple aromatic compounds, dyes of different classes, biological pigments, and amino acids (see Table 1). The presence of energy transfer was established from the shortening of the phosphorescence decay time (τ_{phosph}) of the donor in the presence of the acceptor in a solid solution at 77 or 90° K, since this indicates the appearance, in the presence of the acceptor, of an additional probability of deactivation of the donor triplet molecule caused by radiationless energy transfer. For all combinations given in Table 1, except the last, a shortening of τ_{phosph} of the donor in the presence of the acceptor was observed. The phenomenon always occurs when the absorption spectrum of the acceptor overlaps the phosphorescence spectrum of the donor. The last pair in the table, for which there is no overlap of the spectra, also does not show a shortening of the donor τ_{phosph}.

Fig. 1. Scheme of the electronic levels of molecules, illustrating energy transfer

from the triplet level of the donor ($^3\Gamma_D$) to the singlet level of the acceptor ($^1\Gamma^*_A$). Solid arrows denote radiative transitions, wavy arrows—internal quenching; dashed arrows—transitions accompanying radiationless energy transfer.

The measurements were carried out in ethanol, dibutyl ether, and a mixture of water and ethanol at 77 or 90° K, with the donor concentration kept constant, which excludes shortening of τ_{phosph} due to diffusion processes and due to various concentration effects of the donor itself. We also investigated to what extent the molecules participating in the transfer were associated under the conditions of our experiments. The absorption spectra of acceptors were measured while varying their concentration from 10^{-5} to $1.5 \cdot 10^{-2}$ mole/l, and the phosphorescence spectra of donors while varying the concentration within the same limits. Neither the former nor the latter spectra changed with increasing concentration within the indicated limits. The exception is rhodamine B, whose absorption spectrum in ethanol at 77° K varied with concentration. It is also difficult to suppose that the transfer of energy for the pair N,N-dimethylaniline* + 9-methylanthracene can be caused by association (the asterisk denotes the energy donor).

The question arises as to the mechanism of the triplet-singlet transfer phenomenon we have observed. Earlier, in the works of A. N. Terenin and one of the authors (^{2}), it was shown that triplet-triplet energy transfer is due to exchange-resonance interactions.

Table 1

Combination of substances for which energy transfer from the triplet to the singlet level was studied

Donor	Acceptor	R_{exp}, Å	R_{theor}, Å
Triphenylamine	Rhizoidine	52	34
Tryptophan	Rhizoidine	46	25
n-Phenylbenzaldehyde	Rhizoidine	33	32
Triphenylamine	Chlorophyll a+b	54	33
Triphenylamine	Pheophytin a+b	52	36
Triphenylamine	Fuchsin	37	29
Fluorescein (cation)	Fuchsin	37	–
Triphenylamine	Rhodamine B	36	–
Triphenylamine	Fluorescein Na	35	–
2-Naphthyl methyl ketone	Fluorescein Na	43	–
N,N-Dimethylaniline	9-Methylanthracene	24	–
Tripaflavin	Fuchsin	31	–

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* The work was reported at the XI Conference on Luminescence in September 1962 in Minsk.

Donor	Acceptor	R_{exp}, Å	R_{theor}, Å
Tripaflavin	Rhodamine B	46	–
Tripaflavin	Rhizoidine	No effect	No effect

In the case of energy transfer between singlet levels, the mechanism of interaction is inductive-resonance (^{3}, ^{4}). The theory of inductive-resonance transfer was developed by Förster (^{3}), M. D. Galanin (^{4}), and Dexter (^{5}). However, with regard to the possibility of transfer from a triplet level to a singlet one, Förster and Dexter came to different conclusions. Dexter (^{5}) considered that such transfer could be neglected, since its probability is small. On the other hand, Förster (^{6}) indicates that triplet-singlet transfer should occur at distances close to those for singlet-singlet transfer. Indeed, although the probability of triplet-singlet transfer is very small, the probability of deactivation of a triplet molecule by emission of phosphorescence is also small, since both processes—emission of phosphorescence and transfer of energy to the singlet level of the acceptor—are intercombination-forbidden and therefore compete successfully with one another. The possibility of an effect consisting in the shortening of τ_{phosph} in the presence of phosphorescence-quenching light absorbers also follows from the classical theory of energy transfer of M. D. Galanin and I. M. Frank (^{7}).

Despite the fact that the effect of transfer from the triplet level to the singlet level is predicted by the theory of inductive-resonance transfer, it is of interest to verify the agreement of the consequences of this theory with the quantitative regularities of the new effect. First of all, we compared the experimental values of the critical transfer distance (R_{exp}), determined from the formula

$$R_{\text{exp}} = 7.35/\sqrt[3]{C_{1/2}}, \tag{1}$$

where $C_{1/2}$ is the concentration of the acceptor in moles per liter at which τ_{phosph} of the donor is reduced by half, with R_{theor}, calculated from the formula

$$R_{\text{theor}} = \left[\frac{9\ln 10\,\chi^2}{128\pi^6 n^4 N' g}\int_0^\infty Ph_Q^D(\nu)\,\varepsilon^A(\nu)\,\frac{d\nu}{\nu^4}\right]^{1/6}, \tag{2}$$

where $\chi^2 = {}^2/_3$; n is the refractive index of the medium; $N' = 6.02\cdot 10^{20}$; $Ph_Q^D(\nu)$ and $\varepsilon^A(\nu)$ are the intensity distributions in the spectra of phosphorescence of the donor and absorption of the acceptor; ν is the wave number in reciprocal centimeters. The values of R_{exp} and R_{theor} given in Table 1 are of the same order, which confirms the inductive-resonance character of the transfer in this case. The obtained values of R_{exp} are significantly greater than the transfer distances for triplet levels (^{8}). The smaller values of R_{theor} in comparison with R_{exp}, it seems to us, may be attributed to the approximate nature of formulas (1) and (2).

Fig. 2

Figure 2: Fig. 2

Data on the mechanism of transfer can also be obtained by comparing the course of the decay curves for the yield q and the donor luminescence τ with increasing acceptor concentration. According to Galanin' s theory (^{9}), for inductive-resonance transfer in the case of viscous and solid solutions, the ratio of the tangent of the angle of inclination of the q/q_0 curve to the abscissa axis to the tangent of the τ/τ_0 curve is equal to 2 as $C \to 0$ (C is the acceptor concentration). In the case of exchange-resonance transfer, however, the ratio $(\operatorname{tg} q/q_0) \cdot (\operatorname{tg} \tau/\tau_0)^{-1}$ as $C \to 0$ is considerably greater than 2 (^{2}). We studied the decrease in the phosphorescence yield of the donor as the acceptor concentration increased, using the combinations: triphenylamine* + chrysoidine and 2-naphthyl methyl ketone* + fluorescein Na. Excitation was carried out at $\lambda 3130$ Å; the work was conducted under conditions of complete absorption and observation from the excitation side, at a constant ratio of donor and acceptor concentrations. Fig. 2 shows the curve for the decrease in the phosphorescence yield of triphenylamine in the presence of chrysoidine at various concentrations*. The relative yield of the unquenched solutions was obtained by extrapolating the constructed curve to zero quencher concentration. The accuracy of the extrapolation is sufficient, since we were able to reach the region of low chrysoidine concentrations ($C_{\text{chr}} = 2 \cdot 10^{-4}$ mol/l).

Fig. 2. Change in the relative fluorescence yield $q_{\text{fl}}/q^0_{\text{fl}}$ (1), phosphorescence yield $q_{\text{phosph}}/q^0_{\text{phosph}}$ (2), and relative phosphorescence decay time $\tau_{\text{phosph}}/\tau^0_{\text{phosph}}$ (3) of triphenylamine as a function of the concentration of chrysoidine. Solvent—ethanol, 90° K

Observation of transfer from the triplet level of triphenylamine to the singlet excited level of chrysoidine is complicated by the fact that energy transfer from the fluorescent level of triphenylamine to chrysoidine takes place simultaneously. Therefore we separately measured the quenching of the fluorescence of triphenylamine. The quenching curve is shown in Fig. 2. The small magnitude of quenching is consistent with the slight overlap of the fluorescence spectrum of triphenylamine with the absorption spectrum of chrysoidine. It is seen from Fig. 2 that the ratio $\operatorname{tg} q/q_0$ to $\operatorname{tg} \tau/\tau_0$ is equal to 2 as $C_A \to 0$, which once again confirms the inductive-resonance mechanism of the transfer phenomenon under study.

The shortening of the decay time and the quenching of donor phosphorescence as the acceptor concentration increases convincingly shows the presence of non-radiative energy transfer from the triplet level. It is assumed that as a result of such energy transfer the singlet level of the acceptor is excited. To obtain more direct evidence of this, we investigated the appearance of sensitized afterglow of the acceptor. The phenomenon was studied for the combination of the donor 2-naphthyl methyl ketone with the acceptor fluorescein Na. Fluorescein Na (the

Figure 3

Figure 3: Figure 3

dianion of fluorescein) in ethanol at 77° K has green fluorescence with a quantum yield close to 1 and exhibits no phosphorescence (10). 2-Naphthyl methyl ketone, on the contrary, exhibits only phosphorescence with a low yield ~ 0.05 (11). The combination 2-naphthyl methyl ketone* + fluorescein Na, when observed through a phosphoroscope, in addition to the weak phosphorescence of the ketone, reveals a bright afterglow of fluorescein Na, spectrally coinciding with the fluorescence spectrum of the acceptor excited directly. In Fig. 3 we have plotted the dependences on acceptor concentration of the quantum yields of the phosphorescence of 2-naphthyl methyl ketone and of the sensitized afterglow of fluorescein Na, taking into account the concentration quenching of the latter. It is seen from Fig. 3 that simultaneously with the decrease in the yield of 2-naphthyl methyl ketone, the yield sharply increases of fluorescein Na luminescence, with the quantum yield of fluorescein increasing many times faster than the yield of 2-naphthyl methyl ketone falls. The relative quantum yield of nonradiative energy transfer ($\gamma = q_{\text{s.p.A}}/(q_{0D} - q_D)$), i.e., the ratio of the number of quanta of sensitized afterglow to the number of quenched quanta of donor phosphorescence, calculated for different acceptor concentrations C with the introduction of a correction for concentration quenching of fluorescein Na, remains constant within the limits of measurement error and is equal to 33. The latter unambiguously indicates that the effect cannot be caused by reabsorption and secondary luminescence. The phenomenon can be explained if, by analogy with work (12), it is assumed that strong quenching occurs at the triplet level and that energy transfer competes not only with emission but also with quenching at the donor triplet level. Thus, the phenomenon of energy transfer from the triplet to the singlet level can be used to study quenching in donor molecules.

Fig. 3. Changes in the phosphorescence yield q_D of the donor—2-naphthyl methyl ketone (1)—and the yield of sensitized afterglow of fluorescein $q_{\text{s.p.A}}$ (2) as a function of the concentration of the acceptor—fluorescein. A correction has been introduced for concentration quenching of the latter (3). Solvent: ethanol, 77° K. Observation from the side of excitation; $C_D : C_A = \text{const}$.

It was of interest to investigate a new type of energy transfer on such biologically important objects as chlorophyll, pheophytin, and tryptophan. We studied the combinations triphenylamine* + chlorophyll $a + b$, triphenylamine* + pheophytin $a + b$, and tryptophan d, t^* + chrysoidine. In all three cases the overlap of the phosphorescence spectra of the donors and the absorption spectra of the acceptors was large, and transfer proceeded with high probability. In the case

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* The phosphorescence yield of triphenylamine does not depend on concentration.

of the combinations triphenylamine* + chlorophyll and triphenylamine* + pheophytin, energy transfer should occur to the second excited singlet level, since the phosphorescence spectrum of triphenylamine overlaps with the corresponding absorption bands of the pigments.

In conclusion, we consider it our pleasant duty to express our deep gratitude to Academician A. N. Terenin for his attention to this work and to A. V. Aristov for providing the apparatus for measuring phosphorescence decay.

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