

DISCUSSIONS OF THE FARADAY SOCIETY
NO. 27, 1959

ENERGY TRANSFER
WITH SPECIAL
REFERENCE TO
BIOLOGICAL SYSTEMS

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THE FARADAY SOCIETY

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A GENERAL DISCUSSION
ON
ENERGY TRANSFER WITH SPECIAL
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14th-16th April, 1959

A GENERAL DISCUSSION on Energy Transfer with Special Reference to Biological Systems was held at Nottingham University on the 14th, 15th and 16th April 1959. The President, Dr. E. W. R. Steacie, O.B.E., D.Sc., LL.D., F.R.S., was in the Chair and over 200 members and visitors were present.

Among the distinguished overseas members and guests welcomed by the President were the following:

Dr. S. J. Adelstein (Harvard), Mr. J. Ames (Leiden), Prof. W. Berends (University of Delft), Dr. R. Braams (Utrecht), Prof. Milton Burton (University of Notre Dame), Prof. Britton Chance (Philadelphia), Dr. J. J. Chang (Bethesda), Prof. S. Claesson (University of Uppsala), Prof. M. Dole (Northwestern University), Dr. L. N. M. Duysens (Leiden), Dr. H. Feilchenfeld (Hebrew University), Prof. Th. Förster (Stuttgart), Dr. M. Furst (Washington Square College), Dr. H. R. Gersmann (Amsterdam), Dr. Z. R. Grabowski (University of Warsaw), Dr. W. A. Hagins (Bethesda), Dr. B. Hargitay (Bruxelles), Prof. R. Havemann (Humboldt University), Dr. J. Higgins (Free University of Brussels), Prof. and Mrs. F. H. Johnson (Princeton University), Dr. J. de Jonge (Eindhoven), Prof. H. Kallmann (Washington Square College), Dr. Tsao E. King (Oregon State College), Dr. J. Kratochvil (University of Zagreb), Prof. R. L. Livingston (University of Minnesota), Dr. W. Looney (M.I.T.), Prof. R. Lumry (University of Minnesota), Dr. K. Minnaert (Amsterdam), Prof. W. J. Moore (Indiana University), Dr. A. Müller (Karlsruhe), Dr. J. Olin (Zurich), Dr. L. Paoloni (Rome), Dr. H. Pietsch (Humboldt University), Prof. E. Rabinowitch (University of Illinois), Dr. M. P. Reddy (Saclay), Prof. R. A. Robinson (University of Malaya), Dr. B. Rosenberg (New York University), Mr. K. Rosengren (University of Lund), Prof. M. Schoen (Munich), Dr. D. Schulte-Frohlinde (Heidelberg), Prof. H. Shull (Indiana University), Mr. J. W. Steketee (Eindhoven), Prof. Stig. Sunner (University of Lund), Dr. G. Szasz (Zurich), Dr. A. Szent-Györgyi (Woods Hole, Mass.), Mr. P. Taylor (Philadelphia), Prof. A. Terenin (Leningrad), Mr. D. Timm (University of Lund), Dr. A. R. van Dyken (Washington), Dr. I. Wadsö (University of Lund), Dr. B. E. Wahler (Berlin), Dr. A. Weller (Stuttgart), Dr. and Mrs. G. M. Wyman (Frankfurt).

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10TH SPIERS MEMORIAL LECTURE

TRANSFER MECHANISMS OF ELECTRONIC EXCITATION

BY TH. FÖRSTER

Laboratory of Physical Chemistry, Technische Hochschule, Stuttgart

Received 14th April, 1959

Let me say at the beginning that I feel extremely honoured by the invitation to deliver the 10th Spiers Memorial Lecture. Though I never had the pleasure of meeting Mr. Spiers, whose death occurred before I began my own studies, I am well aware of his contributions to the development of your Society. There is no doubt that he has determined essentially the character of these Discussions by which the Faraday Society has become famous throughout the world.

When I was informed that your Society planned to devote this Discussion to the subject of Energy Transfer, I felt fascinated. Twelve years ago, when I began to occupy myself with this subject, it was a very neglected one. In the meantime, many people have become interested in it, and its applications range from radiation physics to biology.

While the Discussion is concerned with energy transfer of any possible mechanism, I should like to restrict this Introductory Lecture to a more specific mechanism of energy transfer. This is the transfer of electronic excitation energy between otherwise well-separated atomic or molecular electronic systems. The most simple case is that of two distinct atoms in the empty space where electronic excitation of one atom may result in excitation of the other one. Similar cases are of atoms or molecules in solution or in crystalline environment, provided this environment does not allow electronic transfer from one to the other.

Furthermore, we should exclude the trivial case of an excitation transfer that consists in the emission of one quantum of light by the first atom or molecule followed by re-absorption by the second one. This mechanism can be understood easily by the familiar laws of optics and, is, therefore, of not much interest, even if it may contribute to transfer in special cases. It is only the non-radiative transfer of excitation occurring during the short lifetimes of excited electronic systems which we shall consider here.

Although this mechanism is a very specific one, it seems to be of general occurrence. It is responsible for the phenomenon of sensitized fluorescence of atoms and molecules which has been observed in the vapour phase as well as in solution and in the crystalline state. It leads to the so-called *concentration depolarization* of fluorescence and sometimes contributes to concentration quenching. Moreover, it plays an essential part in the properties of organic scintillators and of certain types of inorganic crystalline phosphors. Finally, it contributes to reactions observed in radiation chemistry and in the photochemistry of biological systems, and it is considered today even in connection with other biological processes.

The first observation of energy transfer was made by Cario and Franck (1922) in their classical experiments on sensitized fluorescence of atoms in the vapour phase. A mixture of mercury and thallium vapour, when irradiated with the light of the mercury resonance line, shows the emission spectra of both atoms. Since thallium atoms do not absorb the exciting light, they can get excited only indirectly by an excitation transfer from mercury atoms. A transfer by re-absorption is impossible here. Therefore, this transfer must be a non-radiative one with a mercury atom as the *donor* or *sensitizer* and the thallium atom as the

acceptor. Unfortunately, in this case it cannot be decided whether the transfer occurs between distant atoms or during a normal collision or even in a labile molecule formed as an intermediate. This decision, however, was possible in similar cases, as in the mercury-sensitized fluorescence of sodium and in the mutual sensitization of the fluorescence of different mercury isotopes. In these cases, the transfer occurs over distances very much larger than those in normal collisional separations. A more complete discussion of these and similar cases has recently been given by Livingston.²

Similar observations of sensitized fluorescence have been made with molecular vapours. The experiments of Terenin and Karyakin³ with naphthalene as sensitizer and acridine as acceptor may be mentioned as an example. Another case will be reported later by Dr. Stevens.⁴ More numerous are the investigations on sensitized fluorescence in solution, some examples of which are presented in table 1. Only such cases are considered here, where both sensitizer and acceptor are at low concentrations in an inert solvent. Without exception, the transfer takes place from a sensitizer absorbing at lower wavelengths to an acceptor absorbing at higher ones, because a transfer in the opposite direction would be impossible for energetic reasons. As we shall see later, a moderate red shift is favourable to this kind of transfer.

TABLE 1.—SENSITIZED FLUORESCENCE IN SOLUTIONS

sensitizer	acceptor	remarks	ref.
phenosafranine	tetrabromresorufin	qualitatively	5
tryptaflavine	rhodamine-B	only sensitizer	6, 7
		quenching quantitatively	
benzoflavine	rhodamine-B	sensitizer life-time	8
and many other systems		measured	
chlorophyll- <i>b</i>	chlorophyll- <i>a</i>	both components	9
1-chloroanthracene	perylene	quantitatively	10, 11, 12

The first observations of sensitized fluorescence in solution, though of a more qualitative nature, were made very early by J. Perrin and Choucrun.⁵ In our own first experiments with tryptaflavine and rhodamine,^{6, 7} only the quenching in sensitizer fluorescence resulting from excitation transfer could be followed quantitatively. Nevertheless, transfer over a separation of 70 Å was established and the non-trivial kind of this transfer recognized by quenching experiments which indicated a decrease in lifetime of the excited sensitizer. Similar results were obtained by Galanin and Levshin⁸ for a large number of similar systems, where the decrease in sensitizer lifetime was measured directly. The first measurements where the intensities of both fluorescence components could be followed quantitatively were those of Watson and Livingston⁹ with both chlorophylls. Of special importance are the experiments of Bowen, Brocklehurst and Livingston¹⁰⁻¹² with 1-chloroanthracene and perylene where any possible trivial mechanism was excluded with special care. Some of their results are reported in fig. 1.

With a constant ratio of both components, sensitizer and acceptor absorb constant fractions of the exciting light. The increase in perylene fluorescence with increasing concentration must, therefore, result from energy transfer by chloroanthracene. At the same concentrations, a decrease in chloroanthracene fluorescence due to this transfer is observed. Furthermore, the total quantum yield of fluorescence increases with concentration. This results from the fact that chloroanthracene by itself has low fluorescence efficiency due to internal quenching. This internal quenching is diminished when the lifetime of the excited chloroanthracene molecule is decreased by excitation transfer to perylene. A trivial re-absorption process would not shorten the lifetime of the sensitizer and, therefore, not increase the total fluorescence yield.

Further experiments have shown that in this case the transfer occurs not over collisional distances but over the mean intermolecular distances of sensitizer and acceptor, corresponding to a concentration of 10^{-3} to 10^{-2} M. This is demonstrated by the fact that sensitization occurs with similar half-value concentrations in solution of very different viscosities and even in organic glasses at low temperature. The possibility of the formation of a complex between sensitizer and acceptor molecules was excluded by the additivity of the absorption spectra and the different dependence on concentration to be expected in this case. It must be concluded, therefore, that excitation transfer of a non-trivial nature occurs over the mean distances between statistically distributed molecules which are about 40 \AA in this case.

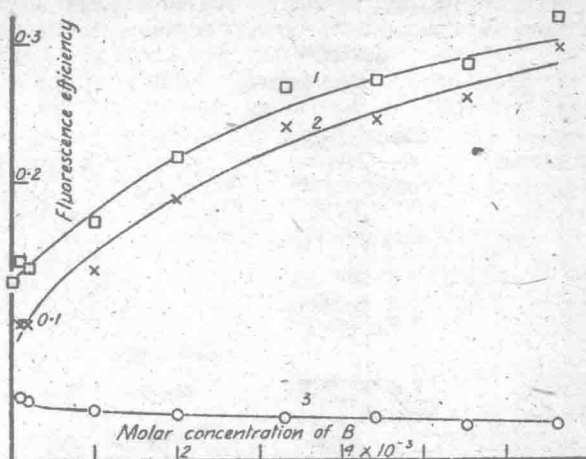


FIG. 1.—Fluorescence of mixed solutions in benzene of 1-chloroanthracene and perylene in 5:1 molar ratio (taken from Bowen and Brocklehurst¹⁰).

Table 2 summarizes some qualitative features of this kind of long-range transfer and of some more or less trivial mechanisms. The non-trivial transfer differs from re-absorption transfer by its independence of the volume of the solution, by the decrease in sensitizer fluorescence lifetime, and by the invariability of the

TABLE 2.—CHARACTERISTIC PROPERTIES OF TRANSFER MECHANISMS

	non-trivial transfer	reabsorption	complexing	encounter
dependence on volume	none	increase	none	none
dependence on viscosity	none	none	none	decrease
sensitizer lifetime	decreased	unchanged	unchanged	decreased
sensitizer fluorescence spectrum	unchanged	changed	unchanged	unchanged
absorption spectra	unchanged	unchanged	changed	unchanged

sensitizer fluorescence spectrum. It differs from short-distance collisional transfer by its independence of solvent viscosity and from transfer within a molecular complex by the constancy of absorption spectra and the decrease in sensitizer fluorescence lifetime. In most cases, some of these different properties allow a decision between trivial and non-trivial transfer mechanisms. Further discriminations may be made by quantitative studies of these properties.

Let us now consider the mechanism of this long-range excitation transfer in more detail. It may be astonishing that such a transfer is possible at all during the short lifetimes of excited molecules which usually are of the order of 10^{-8} sec. One should consider, however, that this is actually a long time for electronic systems, where orbital motions occur during 10^{-15} sec. Therefore, the comparatively weak interaction between distant atoms or molecules may be sufficient for excitation transfer, provided some kind of *resonance condition* is fulfilled.

This was recognized already by J. Perrin^{13,14} who formulated a first theory of excitation transfer between molecules in solution based on the principles of classical physics. This theory, as well as its later quantum-mechanical refinement by F. Perrin¹⁵ predicted transfer distances of more than 100 Å but was insufficient quantitatively. The simpler case of energy transfer between atoms has been treated by Kallmann and London¹⁶ who arrived at similar transfer distances.

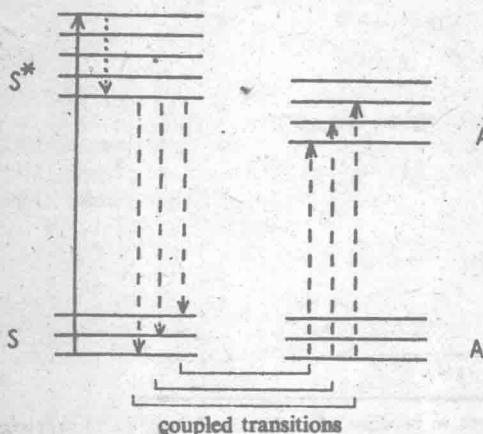


FIG. 2.—Simplified energy level diagram of sensitizer (S) and acceptor (A).

—: radiative transitions
: non-radiative transitions
 ----: transfer transitions.

We shall here consider the molecular case only, where the superposition of electronic and nuclear vibrational levels is essential. Fig. 2 represents the simplified energy level diagram of both molecules. During the absorption process, the sensitizer is excited to one higher vibrational level of its first electronic excitation state. From there it is converted to lower vibrational levels of the same electronic state by obtaining thermal equilibrium with the surrounding medium. In solution or in other condensed systems, this thermal relaxation takes place during 10^{-13} – 10^{-12} sec. It may be assumed for simplicity that the temperature is low enough for the excited molecule to remain in its lowest vibrational level for the rest of its lifetime of about 10^{-8} sec duration. After this time-interval it returns to the ground state by spontaneous radiative or non-radiative processes.

Let us now suppose that the energy difference for one of these possible deactivating processes in the sensitizer molecule corresponds exactly to that for a possible absorption transition in a nearby acceptor molecule. Then, with sufficient energetic coupling between these molecules, both processes may occur simultaneously, resulting in a transfer of excitation from sensitizer to acceptor. With the broad spectra of polyatomic molecules in solution, there is always sufficient coincidence between sensitizer and acceptor transitions, if the absorption spectrum of the acceptor overlaps the fluorescence spectrum of the sensitizer. Therefore, a moderate red shift of the acceptor spectra towards those of the sensitizer is favourable to this kind of transfer. With regard to this condition, this kind of energy transfer is often called "resonance transfer" or "transfer by inductive resonance". This peculiar kind of resonance condition results from thermal relaxation together with the Franck-Condon principle which act here essentially in the same manner as in producing the common Stokes shift.

It may be somewhat confusing that this condition is similar to that for re-absorption of the sensitizer fluorescence by the acceptor. Nevertheless, the mechanism of the non-trivial process is an entirely different one, leading to transfer before the emission of sensitizer fluorescence takes place. Also it needs some amount of mutual coupling between the electronic systems of both molecules and can, therefore, take place only over limited distances.

This coupling is strongest if the corresponding optical transitions in both molecules are allowed for electric dipole radiation. Then these transitions are coupled not only to the radiation field but also to each other. Naturally, the interaction energy is of a dipole-dipole nature, depending on an inverse proportionality to the third power of the molecular distance. The probability of energy transfer is then proportional to the square of this interaction energy and decreases, therefore, with the sixth power of the distance.¹⁷ A quantitative treatment leads to the following expression for the rate constant of the transfer process:

$$n_{S^* \rightarrow A^*} = \frac{9000 \ln 10 \kappa^2}{128 \pi^6 n^4 N \tau_S^0 R^6} \int_0^\infty f_S(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4} \quad (1)$$

Here ν is the wave number, $\epsilon(\nu)$ the molar decadic extinction coefficient, $f(\nu)$ the spectral distribution of fluorescence (measured in quanta and normalized to unity on a wave number scale), N Avogadro's number and τ_S^0 the intrinsic or radiative lifetime of the excited sensitizer. n is the refractive index of the solvent, R the mutual distance between both molecules and κ an orientation factor. More specifically, this is

$$\kappa = \cos \phi_{SA} - 3 \cos \phi_S \cdot \cos \phi_A$$

where ϕ_{SA} is the angle between the transition moment vectors of both molecules while ϕ_S and ϕ_A are the angles between these respective vectors and the direction $S \rightarrow A$. The average value for a random directional distribution is¹⁹ $\kappa^2 = \frac{2}{3}$.

Eqn. (1) may be rewritten more conveniently as

$$n_{S^* \rightarrow A^*} = \frac{1}{\tau_S} \left(\frac{R_0}{R} \right)^6 \quad (2)$$

Here τ_S is the actual mean lifetime of the excited sensitizer. It is connected to τ_S^0 and to the quantum yield η_S^0 of the sensitizer fluorescence (without transfer) by

$$\tau_S = \eta_S^0 \cdot \tau_S^0 \quad (3)$$

Obviously R_0 is the critical transfer distance for which excitation transfer and spontaneous deactivation of the sensitizer are of equal probability. From eqn. (1) to (3) one gets

$$R_0^6 = \frac{9000 \ln 10 \kappa^2 \eta_S^0}{128 \pi^6 n^4 N} \int_0^\infty f_S(\nu) \epsilon_A(\nu) \frac{d\nu}{\nu^4} \sim \frac{9000 \ln 10 \kappa^2 \eta_S^0}{128 \pi^6 n^4 N \bar{\nu}^4} \int_0^\infty f_S(\nu) \epsilon_S(\nu) d\nu \quad (4)$$

This is valid for any thermal equilibrium distribution over the vibrational levels of both molecules, provided the spectra are taken at the corresponding temperature. The transfer probability is independent of the exciting wavelength even if higher electronic states of the sensitizer are involved. As is to be expected, R_0 increases with the quantum yield of the sensitizer and with the overlap of the spectra. In typical cases, R_0 -values from 50 to 100 Å have been calculated.

These formulae become invalid when energy transfer occurs before thermal equilibrium is established. This would be expected for gases under low pressure where thermal relaxation is slow, but also in liquid or solid medium when, due to strong interaction, the transfer is very rapid. In these cases, the transfer may take place from the vibrational level obtained by excitation directly and depend, therefore, on the exciting wavelength. This stands in some analogy to the phenomenon of resonance fluorescence of molecular vapours where the emission spectra show such a dependence.

Under extremely strong interaction, the transfer may even be faster than molecular vibrations. In this case the absorption spectra are no longer additive and it would be difficult to consider the excitation even temporarily localized at one molecule or the other. This is realized in some cases of molecular aggregation, preferably of alike molecules,²⁰⁻²² and will not be considered further.

Let us return again to energy transfer under conditions of thermal equilibrium in the vibrational levels. Even in this case, eqn. (1) to (4) are not generally valid because they refer to dipole-dipole interaction only. Therefore, eqn. (1) is rather the first term of an expansion in powers of R^{-1} . Other terms must be considered when the transfer occurs over small distances or when dipole-dipole interaction is weak because of forbidden optical transitions in sensitizer or acceptor.

Such forbiddenness may result from molecular symmetry or from spin intercombination (e.g. for transitions between singlet ground states and triplet excited states). In both cases, it must be considered first that transitions of this kind are never strictly forbidden. Symmetry-forbidden transitions²³ become partially allowed in combination with certain molecular vibrations, intercombination transitions by mixing of states with different multiplicities, especially in the presence of atoms with higher nuclear charges. Such transitions occur, therefore, in absorption as well as in emission. Naturally, the extinction is low and the emission delayed, being a typical phosphorescence in the case of intercombination transitions. Eqn. (1) to (4) should represent, at least approximately, even then the inverse sixth power term of our expansion.

If the optical transition is forbidden in the sensitizer but allowed in the acceptor, eqn. (4) still predicts large transfer distances in as far as the fluorescence (or phosphorescence) yield η_s is high. This results from the fact that the slower transfer rate calculated from eqn. (1) is compensated by a longer lifetime of the excited sensitizer, in as far as deactivation does not occur mainly by non-radiative processes. According to these considerations, long-range excitation transfer should be possible under suitable conditions even from the triplet state of a sensitizer to the singlet state of an acceptor.

On the other hand, a forbidden transition on the acceptor side results in low $\epsilon_A(\nu)$ so that eqn. (4) predicts only short transfer distance. Actually, this may be somewhat larger due to higher-order terms. For a symmetry-forbidden transition where dipole-dipole interaction is small, the transfer might be determined by dipole-quadrupole interaction and show an inverse 8th power dependence. As Dexter²³ has demonstrated, the transfer occurs over distances larger than those of molecular contact even in that case.

Finally, at small distances, exchange terms in the interaction operator must be considered.²³ These are essential if the transition is intercombination forbidden in the acceptor so that neither dipole-dipole nor higher multipole interaction leads to strong coupling. Electron-exchange interaction allows transfer only under conservation of the total multiplicity of the system, e.g. between triplet states of both sensitizer and acceptor. It needs some overlap of the electronic clouds of both molecules and occurs, therefore, at shorter distances only. Since resonance transfer does not need strong interaction, the transfer distances should be somewhat larger than contact separations. So even then transfer may occur between molecules otherwise considered as independent of each other.

The occurrence of energy transfer between triplet states has been demonstrated by Terenin and Ermolaev²⁴⁻²⁷ with solid solutions of benzophenone or benzaldehyde as sensitizers and substituted naphthalenes as acceptors. The transfer distances are about 14 Å which is much larger than calculated from eqn. (4) for dipole-dipole interaction in these cases. As already stated by the authors, an exchange mechanism as described before should be considered here.

It is quite natural that excitation transfer may not only occur between different molecules but also between separate electronic systems of the same molecule. Weissman,²⁸ Sevchenko and co-workers,^{29, 30} and also Crosby and Kasha³¹ have