ELECTRONIC ENERGY TRANSFER

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THE energy of a molecule, E, may be considered for most purposes as the sum of electronic, vibrational, rotational, and translational contributions:

$$E = E_{\mathrm{el}} + E_{\mathrm{vib}} + E_{\mathrm{rot}} + E_{\mathrm{trans}}.$$

The separation between the various energy levels in any molecule is such that there are a series of vibrational levels associated with each electronic energy level, each vibrational level having in turn a series of rotational levels associated with it. Translational energy can be assumed to be continuous.

Transfer of energy can occur radiatively owing to emission and re-absorption of a photon or non-radiatively during a collision between two molecules when energy may be exchanged and possibly converted from one form into another. Energy transfer due to charge transfer and chemical reaction will not be discussed here.

A collision in which kinetic energy is conserved is known as an *elastic collision*. *Inelastic collisions* in which kinetic energy is converted into internal energy of one partner are known as *collisions of the first kind* and those in which the internal energy of one of the colliding molecules is reduced whether that of the other is increased or not, are called *collisions of the second kind.*

1. Different Types of Energy Transfer

It is convenient to classify ten different types of energy transfer which can occur in molecular collisions. There are four cases in which the energy remains substantially of the same kind and six cases where one kind of molecular energy is converted into another. This classification is useful even though it ignores the small energy discrepancies which often exist. Thus, in a collision involving the exchange of electronic excitation energy, which is classified as *electronic–electronic* energy transfer, partial interchange of other kinds of energy must occur in all cases except where there is an exact correspondence between the electronic excitation energies gained and lost.

From ultrasonic and shock-wave experiments we know that *translational–translational* energy transfer is very efficient and *rotational–translational* is only slightly less so. Typical values for Z_{rot}, the average number of collisions necessary to effect rotational–translational transfer are about 10 for oxygen and nitrogen at room temperature but for hydrogen $Z_{\mathrm{rot}} = 250$.[1] The much larger value for hydrogen is thought to be due to the large spacing between its rotational energy levels. A similar dependence

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[1] T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases", Butterworths, London, 1961.

of the efficiency of *vibrational–translational* energy transfer on the size of the quantum is apparent from a large number of experimental values. For oxygen and nitrogen values of Z_{1-0} the average number of collisions necessary for transfer of the lowest vibrational quantum at room temperature are *ca.* 10^7, but for bromine this falls to *ca* 5000.[1] Theoretical treatment of this type of transfer is well advanced and the Schwartz, Slawsky, and Herzfeld (S.S.H.) theory[2] can predict the probability of transfer to within an order of magnitude provided the molecules concerned have similar masses.

No definite result is available on *rotational–rotational* or *vibrational–rotational* energy transfer. However, there is an increasing amount of data on *vibrational–vibrational* energy transfer from ultrasonic, flash-spectroscopic, and fluorescence studies. For example, vibrational energy transfer from nitric oxide in its ground and excited states to nitrogen and other molecules have been studied and once again a reduction in efficiency is found when the energy discrepancy increases.[3] For large molecules vibrational-energy transfer takes place at almost every collision.

Complete conversion of electronic energy into translational or rotational energy is most unlikely. However, partial conversion of electronic energy into translational energy can occur. Those measurements which are available suggest that the possibility of *electronic–translational* energy transfers decreases rapidly with the increasing magnitude of the energy to be transferred.[3] Thus, the process

$$\mathrm{Na}(3^2P_{\frac{3}{2}}) + \mathrm{M} = \mathrm{Na}(3^2P_{\frac{1}{2}}) + \mathrm{M}$$

where M is an inert gas takes place at every collision because the energy discrepancy is very small, $\Delta E = -17$ cm.$^{-1}$. However, when the energy discrepancy is large as with $\mathrm{Hg}(6^3P_1)$ and $\mathrm{Hg}(6^3P_0)$, where $\Delta\mathrm{E} = -1767$ cm.$^{-1}$, inert gases have little quenching effect although quenching due to *electronic–vibrational* energy transfer from $\mathrm{Hg}(6^3P_1)$ takes place with high efficiency when the loss in electronic energy can be accommodated mainly as vibrational energy in the quenching molecule. Recently the quenching of $\mathrm{Hg}(6^3P_1)$ has been subjected to close scrutiny (for a discussion see ref. 3).

The tenth process, *electronic–electronic* energy transfer, is the subject of this Review. Much evidence has been obtained which illustrates that in favourable cases transfer of electronic excitation energy occurs at every collision and even over distances much greater than collision diameters (see later).

2. Experimental Technique

(a) Emission Spectroscopy.—We can represent the process of electronic energy transfer as

$$\mathrm{D}^* + \mathrm{A} \rightarrow \mathrm{A}^* + \mathrm{D}$$

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[2] R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, *J. Chem. Phys.*, 1952, **20**, 1591.
[3] A. B. Callear, *Appl. Optics.*, Suppl. 2, 1965, 145.

where D and A represent the energy donor and acceptor and an asterisk an electronically excited state. Many excited states show characteristic emission spectra. Energy transfer reduces emission from D* and sensitizes emission from A*. Most mechanisms of energy transfer also predict a decrease in the lifetime of the electronically excited state of the donor since transfer competes with other processes of decay. Information concerning electronic energy transfer can therefore be obtained by studying the intensity of emission of D* and/or A* as a function of the concentration of A or from kinetic measurements on the rate of decay of emission from the donor and/or the rate of build-up of emission from the acceptor.

Electronic excitation can be produced by many methods but the most convenient is by absorption of electromagnetic radiation. The absorption of monochromatic light is governed by the Beer–Lambert law

$$I = I_0 (1 - 10^{-\epsilon c l})$$

where I_0 is the intensity of incident light, I is the intensity of light absorbed, c is the concentration of the absorbing species, ϵ is its extinction coefficient at this wavelength, and l is the path length. It is often possible selectively to excite the donor in energy transfer experiments but if the absorption spectra of the donor and acceptor overlap at all wavelengths then the intensity of monochromatic light absorbed by the donor will be given by

$$I_{\mathrm{D}} = \frac{\epsilon_{\mathrm{D}} c_{\mathrm{D}}}{\epsilon_{\mathrm{A}} c_{\mathrm{A}} + \epsilon_{\mathrm{D}} c_{\mathrm{D}}} I_0 [1 - 10^{-(\epsilon_{\mathrm{A}} c_{\mathrm{A}} + \epsilon_{\mathrm{D}} c_{\mathrm{D}})}]$$

where subscripts D and A refer to the donor and acceptor respectively.

Quantum yields of luminescence, ϕ, are defined as follows:

$$\phi = \frac{\text{Number of quanta emitted}}{\text{Number of quanta absorbed}}$$

These are most easily measured relative to some standard, *e.g.*, quinine bisulphate solution[4] but care must be taken to allow for refractive-index changes.[5] The rate of emission of fluorescence, F, due to the absorption of monochromatic light by a single species will be given by

$$F = \phi_{\mathrm{F}} I_0 (1 - 10^{-\epsilon c l})$$

where ϕ_{F} is the quantum yield of fluorescence. When excitation and observation of luminescence is at right angles the emitted light passes through a depth of reactant and allowance must be made for any reabsorption of the luminescence. This has been called the 'inner filter effect' and is an example of the radiative energy transfer process. In energy-transfer experiments the probability of radiative transfer should always be considered. Unlike non-radiative transfer, its efficiency depends on the volume of the reaction vessel.

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[4] W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229.

[5] J. J. Hermans and S. Levinson, *J. Opt. Soc. Amer.*, 1951, **41**, 460.

At very low concentrations when only a small fraction of the exciting light is absorbed ($< 5\%$), F may be taken as equal to $\phi_F I_0$ ($2{\cdot}3\epsilon cl$). Under these conditions reabsorption is usually low and can often be neglected. If it is necessary to work at high concentrations with high absorbance then excitation at and observation from the front face of the reaction vessel is preferable.

Emission spectra can be recorded by use of a spectrograph and photographic plates, or electrically with a photomultiplier in conjunction with a monochromator. In order to obtain absolute spectra, corrections must be applied for the variation in the sensitivity of the detector with wavelength. Characteristic excitation spectra can also be recorded, *i.e.*, spectra showing the intensity of the luminescence as a function of the exciting wavelength. For a single species with ϕ_F independent of wavelength, the excitation spectrum is identical with the absorption spectrum. Although intruments have been designed which present true excitation spectra directly,[6] spectra which are uncorrected for variation in the intensity of the exciting source with wavelength are more usually obtained. In mixtures showing sensitised luminescence the excitation spectra of the acceptor often shows an increase in wavelength regions where the donor absorbs.

Under most conditions luminescence decays exponentially following cut off of excitation. The most direct method of determining the mean lifetime of luminescence decay is to excite the luminescence with a light pulse of shorter duration and then observe the intensity of the emitted light as a function of time using a photomultiplier and oscillograph. Light pulses lasting less than 10^{-8} sec. have been used.[7] For determining very fast lifetimes, phase shift methods are also useful. The luminescence is excited with light modulated at a high frequency ($\omega/2\pi$ sec.$^{-1}$) using either Kerr cells pulsed between crossed Nicol prisms or by passing the light through a liquid subjected to ultrasonic waves. The difference in phase θ between the exciting and emitted light is determined and since tan θ equals $\omega\tau$, the mean lifetime, τ, is easily obtained. Modulation of the exciting light can also be made by use of rotating discs as in the Becquerel phosphoroscope and its various modifications (see ref. 8).

(b) Flash Photolysis.—Absorption spectra of excited states with lifetimes $>10^{-6}$ sec. can be studied by the technique of flash photolysis.[9] Since most singlet states have lifetimes shorter than this, the method has been applied only to triplet states. For energy-transfer studies the sensitised production of triplet–triplet absorption of the acceptor or the increase in the rate of decay of the triplet state absorption of the donor can be investigated. A short-duration flash is used to populate sufficient triplet states so that their absorption can be recorded on photographic plates

[6] C. A. Parker, *Nature*, 1958, **182**, 1002.

[7] S. S. Brody, *Rev. Sci. Instr.*, 1957, **28**, 1021.

[8] P. Pringsheim, "Fluorescence and Phosphorescence", Interscience Publishers, New York, 1949.

[9] G. Porter, *Proc. Roy. Soc.*, 1950, *A*, **200**, 284.

using a second spectroscopic flash fired after a short known delay. Alternatively the decay of the transient absorption can conveniently be measured by use of a continuous light source and recording the change in absorption at a set wavelength during and following the photolysis flash. A diagram of a typical flash-kinetic spectrophotometric apparatus is shown in Figure 1.

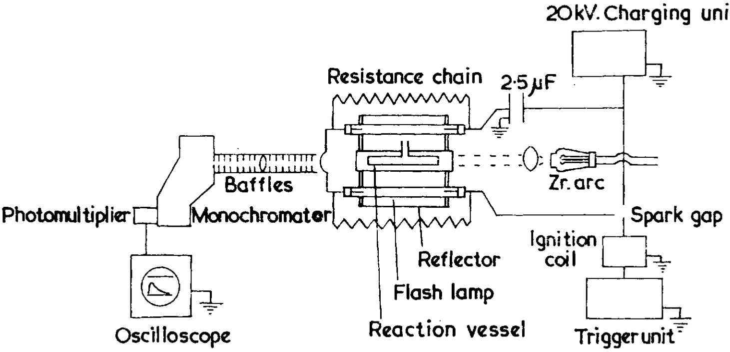

FIG. 1. *A flash kinetic spectrophotometer*

The flash duration limits the application of this method to metastable states. Porter has shown that in order to get detectable amounts of a transient with an extinction coefficient of 10^4 l.mole.$^{-1}$ cm.$^{-1}$ a reasonable energy requirement is 12 joules electrically stored.[10] The flash duration is inversely proportional to the energy dissipated. Most experiments have been made with flash energies of 100—1000 J which give flash lifetimes of 10^{-6}—10^{-5} sec. The gas-filled discharge lamps give a continuous reproducible output throughout the range 2000—10,000 Å but the reaction vessels may be surrounded with filters to ensure that only the donor absorbs exciting light.

(c) Chemical and Other Methods.—Electronic energy transfer can lead to inhibition of photoreactions of the donor and to photosensitised reactions of the acceptor. Hammond and his co-workers[11] have shown that *cis-trans* interconversion of piperylenes, stilbenes, 1,2-diphenylpropenes, and ethyl maleate–ethyl fumarate can be affected by many photosensitisers. The quantum yields of sensitised photoisomerisations and the $[cis]_S/[trans]_S$ ratio in the "photo stationary state" in the presence of sensitisers have been measured. The photostationary state refers to the time-independent situation reached after prolonged irradiation which is the same regardless of whether pure *cis* or pure *trans* isomer is the original reactant. The dependence of the ratio $[cis]_S/[trans]_S$ for stilbene solutions in benzene

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[10] G. Porter, *Z. Electrochem.*, 1960, **64**, 59.

[11] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, 1964, **86**, 3197.

on the triplet levels of the sensitisers is shown in Figure 2. The photostationary states have been shown to form a coherent pattern if energy transfer from the triplet state of the various donors to both spectroscopic and "non-spectroscopic" triplet states of these flexible acceptors is assumed. These measurements have revealed features concerning electronic energy transfer which have not so far become apparent from other methods of study.

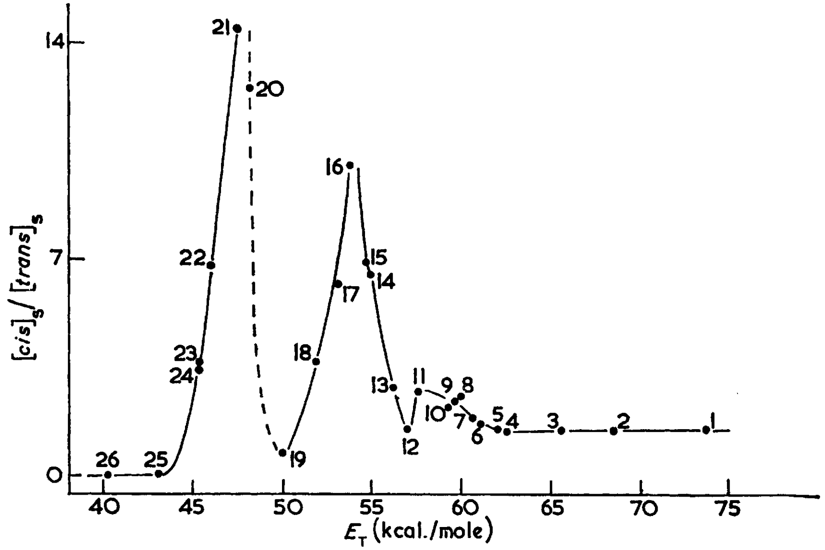

FIG. 2. *Photosensitised isomerisation of the stilbenes.* [Reproduced *by permission* from *J. Amer. Chem Soc.*, 1946, **86**, 3203].
1, Acetophenone. 2, Benzophenone. 3, Thioxanthone. 4, Anthraquinone. 5, Flavone. 6, Michler's ketone. 7, 4-Acetylbiphenyl. 8, 2-Naphthyl phenyl ketone. 9, 2-Naphthaldehyde. 10, 2-Acetonaphthone. 11, 1-Naphthyl phenyl ketone. 12, 1,4-Naphthaquinone. 13, 1-Naphthaldehyde. 14, Biacetyl. 15, Pentane-2,3-dione. 16, Benzil. 17, Fluorenone. 18, Duroquinone. 19, Benzoquinone. 20, Pyrene. 21, 1,2-Benzanthracene. 22, Benzanthrone. 23, Acridine. 24, 3-Acetylpyrene. 25, Eosin. 26, 9-10-Dibromoanthracene.

This example will serve to illustrate that useful information concerning energy transfer can be obtained from measurements on photosensitised reactions. It is important to note, however, that the physical process of electronic energy transfer is not the only one which can lead to sensitisation and inhibition of photochemical reactions.

Triplet states are paramagnetic and therefore show characteristic electron spin resonance spectra. Since the first e.s.r. spectrum of a triplet state was reported by Hutchinson and Mangum in 1958[12] several spectra have been obtained due to triplet states formed by irradiation of ground-state molecules in rigid or viscous media. The forbidden transition between

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[12] C. A. Hutchinson and B. W. Mangum, *J. Chem. Phys.*, 1958, **29**, 952.

the highest and lowest sublevels with $\Delta m = \pm 2$ is particularly strong and this has been used to detect triplet energy transfer.[13]

3. Electronic Energy Transfer between Atoms and Simple Molecules

Transfer between atoms constitutes the simplest case and it is therefore not surprising that the first demonstration of electronic energy transfer should have been between atoms. In 1923 Cario and Franck showed that in gaseous mixtures of mercury and thallium, light absorbed by mercury sensitises the emission of the thallium atoms.[14] Many other examples have been found (see ref. 15) but few quantitative results were available until the recent work arising from the interest in rare-gas lasers. It is customary to express the efficiency of energy transfer in the gas phase in terms of collisional cross sections which are estimated from simple kinetic theory. Javan, Bennett, and Herriott[16] have shown that the rate of decay of $He^*(2^3S_1)$ following a pulsed d.c. discharge increases in the presence of neon with a collisional cross section of $3{\cdot}7 \pm 0{\cdot}5 \times 10^{-17}$ cm.^{2}. Sensitised emission from neon showed that transfer from helium had occurred. Apparently four states are populated directly with similar efficiencies even though the energy discrepance ΔE increases from -314 to -1247 cm.$^{-1}$. The process can be represented as

$$He^*(2^3S_1) + Ne(2^1S_0) \rightarrow He(1^1S_0) + Ne^*(2s_{2,\,3,\,4,\text{ or }5})$$

The neon excited states are usually labelled as above using the Paschen notation since these states approach the *j–j* coupling limit. They are the four states arising from the electron configuration $1s^22s^22p^54s^1$. Transfer from $He^*(2^1S_0)$ to neon has also been investigated and the collisional cross section was found to be $\sim 4 \times 10^{-16}$ cm.^{2}. In this case transfer occurs almost predominately to the $3s_2$ state (Paschen notation):[17]

$$He^*(2^1S_0) + Ne(2^1S_0) \rightarrow He(1^1S_0) + Ne^*(3s_2)$$

These efficient energy-transfer processes cause population inversion in the helium–neon laser and give rise to laser action from the excited states of neon.

So far no evidence is available for long-range transfer between atoms and more measurements are needed to help establish a systematic theoretical treatment.

Mercury-photosensitised reactions have been studied in great detail. Many quenching cross sections have been published including those of

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[13] J. B. Farmer, C. L. Gardner, and C. A. McDowell, *J. Chem. Phys.*, 1961, **34**, 1058; B. Smaller, E. C. Avery, and J. R. Remko, *ibid.*, **43**, 922.

[14] G. Cario and J. Franck, *Z. Physik*, 1923, **17**, 202.

[15] K. J. Laidler, "The Chemical Kinetics of Excited States", Oxford University Press, 1955.

[16] A. Javan, W. R. Bennett, and D. R. Herriott, *Phys. Rev. Letters*, 1961, **6**, 106.

[17] E. E. Benton, E. E. Ferguson, F. A. Matsen, and W. W. Robertson, *Phys. Rev.*, 1962, **128**, 206; A. B. White and E. T. Gordon, *Appl. Phys. Letters*, 1963, **3**, 197.

molecules which cannot quench by accepting electronic energy because they have no suitable electronic energy levels. Although little success at correlating the efficiencies had been achieved it was considered until recently that the excited atom acted primarily as an energy carrier. However, in a recent review Gunning and Strausz[18] stress the similarity in chemical nature of O(^3P) and Hg(^3P) and point out that quenching cross sections tend to increase with the electron-donating character of the quenching species, which suggests either charge transfer or chemical-bond formation during collision. With strong interactions the quenching molecule loses its identity and the energy transfer process may be intramolecular rather than intermolecular. It is noteworthy that quenching cross sections for deactivation of Hg(6^3P_0) are much smaller than those of Hg(6^3P_1).

4. Electronic Energy Transfer of Large Molecules

Many quantitative data on electronic energy transfer between complex molecules are available, allowing theoretical treatments to be tested. Energy transfer from large molecules is greatly simplified because radiationless processes are so efficient, especially in solution, that the lowest excited singlet and triplet states are reached rapidly and usually transfer occurs only from these two states. This is not true at very low pressures in the gas phase where *resonance fluorescence*, which in large molecules is generally taken to include all emission from the originally excited energy level, may be observed.

The remainder of this Review will deal exclusively with molecules in fluid or rigid solution or in the gas phase at pressures greater than a few centimetres of Hg. It will not be concerned with very low pressures or with molecular aggregates or crystals.

(a) Intramolecular Energy Transfer.—Figure 3 shows intramolecular radiative and non-radiative transitions for a typical aromatic molecule. The intensity of singlet–singlet absorption varies from very strong to weak, *e.g.*, ϵ_{max} is *ca.* 10^4 l. mole^{-1} cm.$^{-1}$ for allowed $\pi \rightarrow \pi^*$ transitions but only *ca.* 10^2 l. mole^{-1} cm.$^{-1}$ for many $n \rightarrow \pi^*$ transitions. Other transitions need not concern us here. Only a few values of ϵ_{max} for triplet–triplet absorption have been measured[19] but it seems likely that a similar range of values exists. Singlet–triplet absorption involves a spin change and is therefore very weak except where the molecule contains a very heavy atom.[20]

For many molecules the only strong emission observed in fluid solution and in the gas phase at pressures greater than a few cm. of Hg. is *fluorescence, i.e.*, emission from the thermally relaxed lowest excited singlet state. Thus, in Figure 3 fluorescence is shown arising from the lowest vibrational level of the lowest excited singlet state. The radiative lifetime of a (π, π^*) state is *ca.* 10^{-8} sec., and since the quantum yield of fluorescence

[18] H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, 1963, **1**, 209.
[19] R. A. Keller and S. G. Hadley, *J. Chem. Phys.*, 1955, **42**, 2382.
[20] M. Kasha, *J. Chem. Phys.*, 1952, **20**, 71.

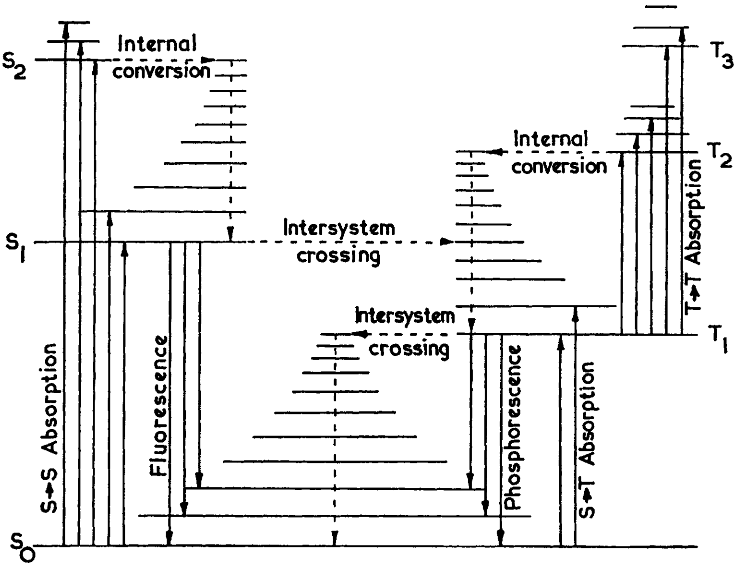

FIG. 3. *Schematic diagram showing radiative and non-radiative transitions (continuous and broken lines respectively) between singlet* (S) *and triplet* (T) *states of a typical organic molecule.*

is generally less than unity the decay of fluorescence is somewhat faster than this. When the lowest excited singlet state is (n, π^*) the radiative lifetime is *ca.* 10^{-6} sec., and fluorescence from such states is generally either weak or absent.

Delayed fluorescence has a lifetime much greater than 10^{-8} sec., but this is due to different mechanisms of production of the fluorescent state and not to a change in the transition probability. Temperature-dependent delayed fluorescence arises as a result of thermal excitation from the lowest triplet state to the lowest excited singlet state. This emission was originally known as α-phosphorescence.[21] Intermolecular mechanisms for delayed fluorescence are also well established (see later).

Phosphorescence is emission from the lowest excited triplet state in thermal equilibrium with its surroundings. The radiative lifetime in molecules containing no atom heavier than oxygen is *ca.* 10^{-3} and *ca.* 10 sec. for (n, π^*) and (π, π^*) states respectively. Phosphorescence yields are very low except in rigid solutions.

Non-radiative processes which result in intramolecular energy transfer compete with radiative transitions and since the quantum yield of fluorescence of many molecules is constant irrespective of which state is initially excited, and since emission from higher excited states is not usually detectable we can estimate rates for the radiationless transitions. The iso-

[21] G. N. Lewis, D. Lipkin, and T. Magel, *J. Amer. Chem. Soc.*, 1941, 63, 3005.

energetic non-radiative transitions between different electronic states with and without change of spin are known as *intersystem crossings* and *internal conversions* respectively.[22] These are followed by very efficient conversion of the excess of vibrational and rotational energy of the lower electronic state into heat.

(i) *Internal conversion.* Internal conversion between higher excited states is very efficient indeed. Thus, emission from higher singlet states has been reported in only a very few cases, *e.g.*, azulene,[23] and triplet–triplet emission has never been established. The reasons for the lack of efficiency of internal conversion to the ground state are still not fully understood. Various theoretical approaches to this problem have been made and these were reviewed recently.[24] The explanation given by Franck and Sponer[25] who suggest that radiationless transitions may be intramolecular resonance transfer processes, analogous to the well established intermolecular resonance transfer processes has not received as much attention as it merits.

Experimental evidence has been presented which suggests that direct internal conversion to the ground state is negligible for benzene[26] and biacetyl[27] in the gas phase, for certain anthracene derivatives in solution[28] and for 1-halogenonaphthalenes in rigid solution at low temperatures.[29] A similar conclusion has been reached by Lim and his co-workers[30] for many hydrocarbons in solution based on their observation that perdeuterated and perprotonated hydrocarbons have almost identical fluorescence yields and lifetimes. If a radiationless transition $S_1 \rightarrow S_0$ were occurring a large change would be expected (see later).

(ii) *Intersystem crossing.* Intersystem crossing from the lowest excited singlet state is an efficient process since it is responsible for triplet-state production following singlet–singlet absorption. The quantum yields of triplet production, ϕ_t, must be at least as high as the quantum yield of phosphorescence, which in rigid media can approach unity. Recently ϕ_t values have been reported in solution[28,31] and a range of values, some equal to unity, have been observed. Intersystem crossings from higher excited singlet states do not normally occur presumably because they compete with the very efficient internal conversion processes and not because they are any less efficient than those from the lowest excited singlet state. 9,10-

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[22] M. Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.
[23] M. Beer and H. C. Longuet-Higgins, *J. Chem. Phys.*, 1955, **23**, 1390.
[24] P. Seybold and M. Gouterman, *Chem. Rev.*, 1965, **65**, 413.
[25] J. Franck and H. Sponer, *J. Chem. Phys.*, 1956, **25**, 172.
[26] G. B. Porter, *J. Chem. Phys.*, 1960, **32**, 1587.
[27] H. Ishikawa and W. A. Noyes, *J. Chem. Phys.*, 1962, **37**, 583.
[28] T. Medinger and F. Wilkinson, *Trans. Faraday. Soc.*, 1965, **61**, 620.
[29] V. L. Ermolaev and E. B. Sveshnikova, *Optics and Spectroscopy*, 1964, **16**, 320.
[30] E. C. Lim and J. D. Laposa, *J. Chem. Phys.*, 1964, **41**, 3257; J. D. Laposa, E. C. Lim, and R. A. Keller, *ibid.*, 1965, **42**, 3025.
[31] A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1965, **87**, 2322.

Dibromoanthracene may be an exception to this rule.[32] Intersystem crossing from the lowest excited triplet state to the ground state is a very inefficient process. Substitution of deuterium for hydrogen in various hydrocarbons leads to an increase in the phosphorescence lifetime. Robinson and Frosch have interpreted this as being due to a reduction in Franck–Condon vibrational overlap which is larger for C–H vibrations than for C–D, resulting in less intersystem crossing in the deuterium compounds.[33] The greater rates for intersystem crossing from S_1 may be due in many cases to higher triplet levels lying between S_1 and T_1. The intersystem crossing would then be from S_1 to T_2 or T_3, etc. This would explain the lack of any effect on the fluorescence when deuterium is substituted for hydrogen since in anthracene, for example, the energy difference $S_1 - T_1$ and $T_1 - S_0$ are 11,000 and 14,700 cm.$^{-1}$ respectively. In this explanation it is also necessary to assume that non-radiative transfer $S_1 \rightarrow S_0$ does not occur.

In fluid solution the decay of the triplet state has been much investigated. An all-inclusive equation for triplet-state decay is given below.

$$\frac{-\mathrm{d}[\mathrm{T}]}{\mathrm{d}t} = k_r[\mathrm{T}] + k_1[\mathrm{T}] + k_2[\mathrm{T}]^2 + k_3[\mathrm{T}][\mathrm{G}] + \Sigma k_q[\mathrm{T}][\mathrm{Q}]$$

where T and G represent the triplet and ground states and k_r, k_1, k_2, k_3, and k_q, the rate constants for radiative, non radiative, triplet–triplet quenching, self-quenching by the ground state, and quenching by the quencher Q respectively. Most early values of the first order rate constants for triplet-state decay in solution were viscosity-dependent but were not true values of k_1 because they included effects due to the various k_q [Q] terms. In a recent paper Hoffman and Porter[34] claim to have measured k_1 for many anthracene derivatives in liquid paraffin. For 9,10-dibromoanthracene these authors found k_1 to be independent of a 170-fold change in viscosity.

Substitution of heavy atoms into large molecules leads to an increase in the probability of intersystem crossing. It also increases the probability of radiative transitions between singlet and triplet states.

(iii) *Special compounds.* The efficiency of intramolecular energy transfer has been studied in certain molecules consisting of more than one characteristic group[35] sometimes separated by up to three saturated carbon atoms.[36] Only the lowest state of any multiplicity is found to emit and it appears these molecules behave similarly to the more simple examples.

Intramolecular energy transfer in rare-earth chelates has been much investigated. Crosby and his co-workers[37] have shown that the efficiency of transfer from the ligand to the central ion is a sensitive function of the

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[32] J. Ferguson, *J. Mol. Spectroscopy*, 1959, **3**, 177.

[33] G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 1962, **37**, 1962; 1963, **38**, 1187.

[34] M. Z. Hoffman and G. Porter, *Proc. Roy. Soc.*, 1962, *A*, **268**, 46.

[35] V. Ermolaev and A. Terenin, *J. Chim. phys.*, 1958, **55**, 698; A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1965, **87**, 2322.

[36] O. Schnepp and M. Levy, *J. Amer. Chem. Soc.*, 1962, **84**, 172.

[37] G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Chem. Phys.*, 1961, **34**, 743.

relative position of the resonance energy levels in the ion and the triplet states of the ligands. Laser action from rare-earth chelates has been obtained[38] and much work is at present in progress in this field.

(b) Intermolecular Transfer from Singlet States.—(i) *Collisional transfer.* Singlet–singlet energy transfer between organic molecules, *i.e.* the process,

$$\mathrm{D}^*(S_1) + \mathrm{A}(S_0) \rightarrow \mathrm{D}(S_0) + \mathrm{A}^*(S_1)$$

has been known for many years to occur in both the gas phase[39] and in solution[40] but, until recently, few quantitative results were available. Dubois and his co-workers have shown that biacetyl accepts electronic energy from many excited donor molecules in fluid solution at rates which are consistent with a diffusion-controlled process.[41] In these experiments, both quenching of the donor fluorescence and sensitisation of biacetyl fluorescence were measured. The transfer rate constants k_t are shown in Table 1. These values are close to those predicted from the equation

$$k_t = \frac{8\boldsymbol{RT}}{2000\eta} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

TABLE 1. *Rate constants for singlet–singlet energy transfer to biacetyl in ærated hexane solution at 28°.*

Donor	Quenching const.[a] K_Q(l.mole^{-1})	Mean life-time[b] $10^9\tau_D$(sec.)	k_t(l.mole^{-1} sec.$^{-1}$)
Benzene	214	5·7	$3{\cdot}8 \times 10^{10}$
Toluene	214	5·8	$3{\cdot}7 \times 10^{10}$
o-Xylene	208	6·0	$3{\cdot}5 \times 10^{10}$
m-Xylene	200	6·0	$3{\cdot}3 \times 10^{10}$
p-Xylene	210	6·1	$3{\cdot}4 \times 10^{10}$
Ethylbenzene	208	5·7	$3{\cdot}6 \times 10^{10}$
Cumene	204	6·0	$3{\cdot}4 \times 10^{10}$
Pentamethylbenzene	177	3·9	$4{\cdot}5 \times 10^{10}$
n-Propylbenzene	217	5·2	$4{\cdot}2 \times 10^{10}$
n-Butylbenzene	214	6·8	$3{\cdot}2 \times 10^{10}$
Hexamethylbenzene	80	2·0	$4{\cdot}0 \times 10^{10}$
Naphthalene	186	8·3	$2{\cdot}2 \times 10^{10}$

[a] J. T. Dubois and R. L. Van Hemert, *J. Chem. Phys.*, 1964, **40**, 923.
[b] T. V. Ivanova, P. I. Kudriashov, and B.Ya. Sveshnikov, *Doklady Akad. Nauk S.S.S.R.*, 1961, **138**, 572.

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[38] H. Samelson, A. Lempicki, V. A. Brophy, and C. Brecher, *J. Chem. Phys.*, 1964, **40**, 2547; H. Samelson, A. Lempicki, and C. Brecher, *ibid.*, 1964, **40**, 2553.

[39] A. N. Terenin and A. Karyakin, *Izvest. Akad. Nauk S.S.S.R.*, *Ser. Fiz.*, 1951, **15**, 550.

[40] J. Perrin and (Mlle) Choucroun, *Compt. rend.*, 1929, **189**, 1213.

[41] J. T. Dubois and B. Stevens, "Luminescence of Organic and Inorganic Molecules", Wiley, New York, 1962, p. 115; J. T. Dubois and M. Cox, *J. Chem. Phys.*, 1963, **38**, 2536; J. T. Dubois and R. L. Van Hemert, *ibid.*, 1964, **40**, 923.

which gives at 28°C $k_t = 3{\cdot}5 \times 10^{10}$ l. mole^{-1} sec.$^{-1}$ for hexane. Osborne and Porter[42] have shown that for diffusion-controlled reactions this equation gives good agreement with experiment.

Few quantitative measurements of energy transfer from singlet states have been made in the gas phase although Stevens[43] has shown that energy transfer from benzene to anthracene occurs with unit collisional efficiency at normal collisional distances.

(ii) *Long-range single-step transfer.* Singlet–singlet transfer is also possible over distances much greater than normal collisional diameters. For efficient transfer close resonance between the initial and final state is required. This is possible if vibrations are included even if there is an electronic energy difference ΔE (Figure 4). This resonance transfer at large distances is mainly due to non-radiative coupling between the transition dipoles of the states concerned. Förster[44] has given the process a quantum-mechanical treatment considering only dipole–dipole interactions and has

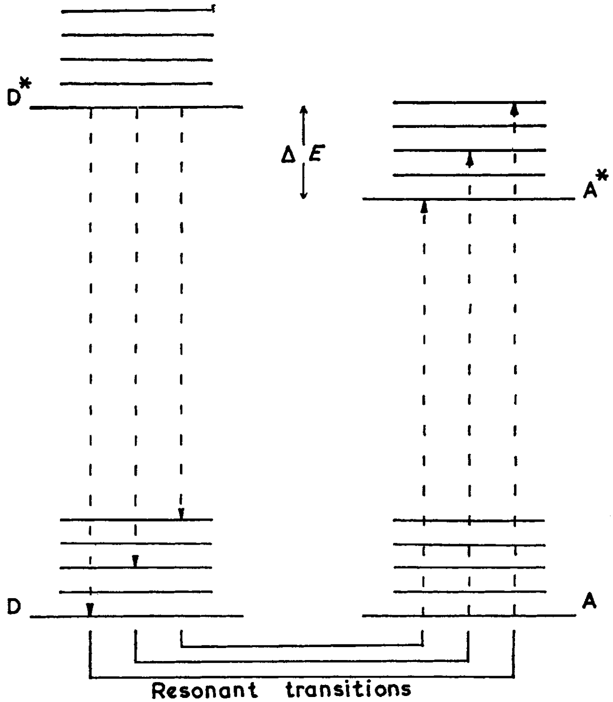

FIG. 4. *Energy-level diagram for a donor* D *and acceptor* A *with an electronic energy difference* ΔE.

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[42] A. D. Osborne and G. Porter, *Proc. Roy. Soc.*, 1965, *A*, **284**, 9.
[43] B. Stevens, *Discuss. Faraday Soc.*, 1959, **27**, 34.
[44] Th. Förster, *Discuss. Faraday Soc.*, 1959, **27**, 7.

obtained the following equation for the rate constant for transfer $k_{\mathrm{D}^*\rightarrow\mathrm{A}^*}$

$$k_{\mathrm{D}^*\rightarrow\mathrm{A}^*} = \frac{9000(\ln 10)\kappa^2\eta_{\mathrm{D}}}{128\pi^5\, n^4 N\tau_{\mathrm{D}}R^6}\int_0^\infty f_{\mathrm{D}}(v)\,\epsilon_{\mathrm{A}}(v)\,\frac{dv}{v^4}$$

where $\epsilon_{\mathrm{A}}(v)$ is the molar decadic extinction coefficient of the acceptor at wavenumber v, $f_{\mathrm{D}}(v)$ the spectral distribution of the fluorescence of the donor (measured in quanta and normalised to unity on a wavenumber scale), N is Avogadro's number, τ_{D} is the mean lifetime of the excited state, and η_{D} the quantum yield of fluorescence of the donor, n is the refractive index of the solvent, R is the distance between the molecules and κ is an orientative factor which for a random distribution equals $(\frac{2}{3})^{\frac{1}{2}}$.

R_0, the distance at which transfer and spontaneous decay of the excited donor are equally probable, is given by

$$R_0^6 \approx \frac{9000 \ln 10\ \kappa^2\eta_{\mathrm{D}}}{128\pi^5\ n^4 N v^4}\int_0^\infty f_{\mathrm{D}}(v)\,\epsilon_{\mathrm{A}}(v)\,\mathrm{d}v$$

When the transitions in both the donor and the acceptor are fully allowed and there is good overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor, R_0 values of 50—100 Å are predicted from this equation,[44] and the rate constants for energy transfer due to coulombic interactions are much greater than those calculated for diffusion-controlled reactions.

Experimental values have been obtained which give striking agreement with these theoretical predictions. For example, Bowen and his co-workers,[45] using 1-chloroanthracene as sensitiser and perylene as acceptor, obtained the following transfer rate constants: 1·6, 2·0, 1·4, and 1·5 × 10^{11} l. mole^{-1} sec.$^{-1}$ in benzene, chloroform, liquid paraffin at room temperature, and in a rigid glass of tetra- and penta-chloroethanes at 77°K respectively. These rates are obviously viscosity-independent and much greater than those expected for diffusion controlled reactions. They represent transfer over distances greater than 40 Å in each case. A comparison of experimental and theoretical values for a number of donor–acceptor pairs is given in Table 2.

Energy transfer between like molecules does not, of course, lead to detectable sensitised fluorescence but evidence for transfer has come from fluorescence studies using polarised excitation. The fluorescence is also polarised and the extent of polarisation of the fluorescence decreases with increasing concentration of the fluorescent substance. For some compounds this effect is very efficient even in viscous solutions. The first suggestion of long-range transfer was made by Perrin[46] to explain this concentration depolarisation.

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[45] E. J. Bowen and B. Brocklehurst, *Trans. Faraday Soc.*, 1953, **49**, 1131; 1955, **51**, 774; E. J. Bowen and R. Livingston, *J. Amer. Chem. Soc.*, 1954, **46**, 6300.

[46] J. Perrin, "2 me conseil de Chimie Solvay," Gauthier and Villar, Paris, 1925, p. 322.

TABLE 2. *Long-range transfer distances for singlet–singlet energy transfer*

Donor	Acceptor	R_0(Å) Calc.	R_0(Å) Found
Anthracene	Perylene	31	54[a]
Perylene	Rubrene	38	65[a]
9,10-Dichloroanthracene	Perylene	40	67[a]
Anthracene	Rubrene	23	39[a]
9,10-Dichloroanthracene	Rubrene	32	49[a]
Fluorescein	Fluorescein	50	26[b]
Rhodamine-B	Rhodamine-B	55	30[b]
Chlorophyll-*a*	Chlorophyll-*a*	80	36[b]
Chlorophyll-*a*	Copper pheophytin-*a*	38—41	40[c]
Bis(hydroxyethyl)-2,6-naphthalenedicarboxylate	Sevron yellow G.L.	26	27[d]
Pyrene	Sevron yellow L.	39	40—46[d]

[a] W. R. Ware, *J. Amer. Chem. Soc.*, 1961, **83**, 4374.
[b] G. Weber, *Trans. Faraday Soc.*, 1964, **50**, 552.
[c] A. G. Tweet, W. D. Bellamy, and G. L. Gaines, *J. Chem. Phys.*, 1964, **41**, 2068.
[d] R. G. Bennett, *J. Chem. Phys.*, 1964, **41**, 3037.

Long-range transfer is also possible from an excited singlet state to an excited triplet state. The process may be represented as

$$D^*(S_1) + A^*(T_1) \rightarrow D(S_0) + A^*(T_2)$$

If the transitions in the donor and the acceptor are fully allowed and if there is good overlap between the fluorescence spectrum of the donor and the triplet–triplet absorption spectrum of the acceptor, then transfer over large distances is predicted. Bennett[47] has shown that this process occurs in a cellulose acetate film at 77°K, leading to quenching of perylene fluorescence in the presence of high concentrations of triplet [$^2H_{10}$]phenanthrene.

(iii) *Concentration quenching of fluorescence.* The quantum yield of fluorescence of many compounds decreases with increasing concentration. In some cases, *e.g.*, with aqueous solutions of thionine and methylene blue, this self-quenching is due to the formation of ground-state dimers. In other cases, the lowest excited singlet state collides with and associates with a ground-state molecule to give an excited dimer. Colpa[48] has suggested that this dimer could be converted into a second singlet dimer which corresponds to two triplet states associated so that the total spin quantum number is zero. The second dimer could then dissociate to give two triplet states, the overall reaction being:

$$M^*(S_1) + M(S_0) \rightarrow M_2^*(S_x) \rightleftharpoons M_2^*(S_y) \rightarrow M^*(T_1) + M^*(T_1)$$

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[47] R. G. Bennett, *J. Chem. Phys.*, 1964, **41**, 3048.

[48] J. P. Colpa, Paper presented at the Fifth Congress on Molecular Spectroscopy, Amsterdam 1961.

This process, the reverse of which is well established, leads to the transfer of the energy of one excited singlet state to give two excited triplet states. Recent work in our laboratories[49] has shown that the excited dimer of pyrene formed by association of excited and ground-state molecules undergoes some dissociation to produce triplet monomers, but it is not known whether one or two triplet states are produced from each excited dimer.

Stevens[50] has termed excited dimers which are dissociative in the ground state as *excimers*. The properties of excimers have been subjected to much recent study. It seems very likely that excimers will be capable of transferring energy themselves and thus prove to be intermediates in energy transfer processes at high concentrations.

(c) Intermolecular Transfer from Triplet States.—(i) *Collision transfer.* The process,

$$D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(T_1)$$

has become known as triplet–triplet energy transfer. It was first observed in rigid media by Terenin and Ermolaev who studied quenching of donor phosphorescence and sensitisation of the acceptor phosphorescence.[51] Using biacetyl, one of the few compounds that phosphoresce in solution, Bäckström and Sandros showed that this phosphorescence was quenched by acceptor molecules with lower triplet levels at every collision in benzene solution and that molecules with higher triplet levels sensitised the biacetyl phosphorescence.[52] Porter and Wilkinson, using the technique of flash photolysis, demonstrated that triplet–triplet energy transfer between various pairs of molecules occurs with unit collisional efficiency in fluid solution at normal collisional distances, provided the triplet level of the donor is at least 1000 cm.$^{-1}$ higher than that of the acceptor.[53] Sandros has shown that when the triplet levels are close together, back-transfer occurs with a rate given by

$$k_b = k_f \exp\left(-\frac{\Delta E_t}{RT}\right)$$

where ΔE_t is equal to the difference in triplet energy levels and k_f and k_b are the rate constant for forward and back transfer.[54]

Triplet-energy transfer is responsible for inhibiting a number of photoreactions[55] and for sensitising other reactions in solution.[56] It has also been

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[49] T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, 1966, **62**, 1785.

[50] B. Stevens, *Nature*, 1961, **192**, 725.

[51] A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, 1956, **52**, 1042.

[52] H. L. J. Bäckström and K. Sandros, *Acta. Chem. Scand.*, 1958, **12**, 823; 1960, **14**, 48.

[53] G. Porter and F. Wilkinson, *Proc. Roy. Soc.*, 1961, *A*, **264**, 1.

[54] K. Sandros, *Acta. Chem. Scand.*, 1964, **18**, 2355.

[55] F. Wilkinson, *J. Phys. Chem.*, 1962, **66**, 2569; G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, 1961, **57**, 1686.

[56] G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, 1961, **83**, 2395; K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, 1961, **83**, 2397.

observed to occur with high efficiency in the gas phase.[57]

Triplet–triplet transfer would not be expected to occur over large distances since the transitions in both the donor and acceptor are spin-forbidden. However, when collisions take place, orbitals overlap and an exchange mechanism may operate. The system will then be subject to Wigner's spin rule.[58] If S_a and S_b are the initial spin quantum numbers of the colliding molecules, the resultant spin quantum number of the two species taken together must have one of the values

$$S_a + S_b, S_a + S_b - 1, S_a + S_b - 2, \ldots\ldots |S_a - S_b|$$

It follows that the spin quantum numbers of the resulting species can only have values S_c and S_d, if at least one of the values

$$S_c + S_d, S_c + S_d - 1, S_c + S_d - 2, \ldots\ldots |S_c - S_d|$$

is common to the series above. Thus, the process,

$$D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(T_1)$$

is spin-allowed by an exchange mechanism and this is the mechanism which is thought to operate.

(ii) *Long-range transfer.* When the forbidden nature of a transition in the donor results in a corresponding increase in the lifetime of the excited state of the donor, as is the case for the triplet states of many molecules in rigid media, the probability of energy transfer relative to spontaneous decay can still be high, *e.g.*, coloumbic interaction for the process

$$D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(S_1)$$

results in equally large distances for transfer provided there is good overlap of the spectra concerned.[59] Bennett, Schwenker, and Kellogg have shown that the Föster theory quantitatively describes energy transfer from triplet [$^2H_{10}$]phenanthrene to the lowest excited singlet state of rhodamine-B over large distances in a cellulose acetate film at 77°K.[60]

(iii) *Triplet–triplet annihilation.* In fluid solution[61] and in the gas phase[62] bimolecular collisions of triplet states lead to quenching by a diffusion-controlled process. Parker[63] has recently illustrated that delayed fluorescence from solutions of compounds such as pyrene,

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[57] H. Ishikawa and W. A. Noyes, *J. Amer. Chem. Soc.*, 1962, **84**, 1502; R. E. Rebbert and W. A. Noyes, *J. Amer. Chem. Soc.*, 1962, **84**, 1502; R. E. Rebbert and P. Ausloss, *ibid.*, 1965, **87**, 1847.

[58] E. Wigner, *Nachr. Ges. Wiss. Gottingen Math. Physik Kl.*, 1927, p. 375.

[59] V. L. Ermolaev and E. B. Sveshnikova, *Doklady Akad. Nauk S.S.S.R.*, 1963, **149**, 1295.

[60] R. G. Bennett, R. P. Schwenker, and R. E. Kellogg, *J. Chem. Phys.*, 1964, **41**, 3040.

[61] G. Porter and M. R. Wright, *Discuss. Faraday Soc.*, 1959, **27**, 18.

[62] G. Porter and P. West, *Proc. Roy. Soc.*, 1964, *A*, **279**, 302.

[63] C. A. Parker, *Adv. Photochem.*, 1964, **2**, 305.

naphthalene, anthracene, etc., is due to the following process which is spin-allowed by an exchange mechanism.

$$D^*(T_1) + A^*(T_1) \rightarrow D(S_0) + A^*(S_1)$$

where D and A may be the same or different species. This reaction often takes place *via* stable excited dimers as represented below. Parker has also shown that triplet–triplet energy transfer followed by triplet–triplet annihilation can lead to sensitised delayed anti-Stokes fluorescence. Thus, for phenanthrene (Pn) and naphthalene (Np) the suggested mechanism is

$$\begin{aligned}
&Pn(S_0) + h\nu \rightarrow Pn^*(S_1) \rightarrow Pn^*(T_1)\\
&Pn^*(T_1) + Np(S_0) \rightarrow Pn(S_0) + Np^*(T_1)\\
&2Np^*(T_1) \rightarrow Np_2{}^*(Sy) \rightarrow Np^*{}_2(S_x) \rightarrow Np^*(S_1) + Np(S_0)\\
&Np^*(S_1) \rightarrow Np(S_0) + h\nu'
\end{aligned}$$

where $h\nu' > h\nu$. Delayed fluorescence in the gas phase[64] could also be due to triplet–triplet annihilation.

In a recent paper, Kellogg has obtained evidence for triplet–triplet annihilation in rigid media over large distances, using [$^2H_{10}$]phenanthrene in a cellulose acetate film at 77°K.[65] He suggests that the process

$$D^*(T_1) + A^*(T_1) \rightarrow D(S_0) + A^*(T_2)$$

is taking place by a coulombic mechanism and points out that there is good overlap of the phosphorescence with the triplet–triplet absorption spectra. As explained in the previous section, this is quite feasible, provided the phosphorescence yield is fairly high. In solution, there should be a fall in the probability of energy transfer as the phosphorescence yield decreases. However, this process is also allowed by an exchange mechanism so that the bimolecular quenching of triplet phenanthrene in solution may involve this process at normal collisional distances.

(d) Concentration Quenching of Triplet States.—Most triplet states in solution show very slight quenching by ground state molecules of the same species. However, this is not always the case; *e.g.*, for chlorophyll in benzene[66] the ground-state quenching-rate constant is 5×10^7 l. mole^{-1} sec.$^{-1}$. In rigid solution, measurement of concentration depolarisation of phosphorescence has been attempted but the transfer distance was found to be much smaller than that found for concentration depolarisation of fluorescence.[67]

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[64] R. Williams, *J. Chem. Phys.*, 1958, **28**, 577.

[65] R. E. Kellogg, *J. Chem. Phys.*, 1964, **41**, 3046.

[66] H. Linschitz and K. Sarkanen, *J. Amer. Chem. Soc.*, 1958, **80**, 4826.

[67] P. I. Kudriashov and B. Ya. Sveshnikov, *Optics and Spectroscopy*, 1960, **8**, 344.