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Energy Transfer by Means of Collision in Liquid Organic Solutions under High Energy and Ultraviolet Excitations*

MILTON FURST AND HARTMUT KALLMANN

Physics Department, New York University, Washington Square, New York, New York

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Experiments are described which show that energy transfer by means of "collisions" occurs when a liquid organic solution is excited by ultraviolet light as well by high-energy radiation. With light excitation the possibility of any transfer by ionization and/or by hidden radiation could be completely eliminated. It was found that energy transfer by way of collision between various molecules under excitation by light is of the same magnitude as with high-energy radiation excitation. Energy transfer by way of absorption and subsequent re-emission occurs only in complex solutions containing at least two kinds of efficient fluorescent molecules. Basically the technique of the experiments with light consisted of irradiating different solutions with various wavelengths, thereby selectively exciting various components of the solutions, and of observing the corresponding effects on the fluorescent light output. The solutions measured in this investigation used xylene and cyclohexane as solvents; anthracene, p-terphenyl, and 9,10-diphenylanthracene as fluorescent solutes; and additional naphthalene which in some respects behaves like a solvent when present in large concentrations. In complete agreement with results under gamma-ray excitation, energy transfer under light excitation takes place from naphthalene to anthracene and diphenylanthracene, and from xylene to terphenyl, while none occurs from naphthalene to terphenyl.

INVESTIGATIONS of the fluorescence of dilute liquid organic solutions under high-energy radiation have shown that energy is transferred from the solvent molecules to those of the solute.[1,2] The primary radiation is certainly absorbed mostly by the solvent which makes up the bulk of the solution; nevertheless, the outcoming fluorescence from "effective" solutions with a single solute is invariably associated with the spectral characteristics of the solute rather than of the solvent. With complex solutions containing more than one solute, the energy transfer has even been traced from one type of solute molecule to the other.[2,3]

In the earlier papers this energy transfer was attributed to a migration of excitation energy[4-6] from one solvent molecule to another until it is eventually trapped by a solute molecule; the emission then takes place from the solute. Another possible type of energy transfer, that by means of absorption, was also studied.[2-8] In this type of transfer, a light quantum is emitted by one type of molecule and reabsorbed by by another, and then the fluorescent emission occurs. Such transfer was observed to take place in complex solutions containing several fluorescent solutes from one kind of solute molecule to the other but not ordinarily from the solvent molecule to that of the solute. Generally a considerable decrease in emitted energy accompanies transfer via radiation because of the internal quenching of the absorbing solute. The transfer can occur only if the transferring material emits radiation; since, however, almost all of the pure solvents used in fluorescent work (e.g., xylene, p-dioxane, etc.) emit only small amounts of radiation, it was concluded that the energy transfer from an excited solvent occurs almost entirely by way of collision. There is also the possibility that the fluorescence of a solution excited by high-energy radiation is due to the ionization of the solvent (rather than excitation) and to the transfer

[1] H. Kallmann and M. Furst, Phys. Rev. **79**, 857 (1950); M. Furst and H. Kallmann, Phys. Rev. **85**, 816 (1952).
[2] H. Kallmann and M. Furst, Phys. Rev. **81**, 853 (1951).
[3] M. Furst and H. Kallmann, Phys. Rev. **89**, 912 (1953).
[4] S. I. Weissman, J. Chem. Phys. **10**, 214 (1942).
[5] Bowen, Mikiewicz, and Smith, Proc. Phys. Soc. (London) **A62**, 26 (1949).
[6] E. J. Bowen and P. D. Lawley, Nature **164**, 572 (1949).
[7] E. J. Bowen, Symposia Soc. Exptl. Biol. **5**, 152 (1951).
[8] J. B. Birks, *Scintillation Counters* (McGraw-Hill Book Company, Inc., New York, 1953), p. 68.

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of the positive charge from the solvent molecule to that of the solute. This type of transfer seems, however, also to be of only minor importance since it could not account for the high efficiency observed with some solutions and for the almost complete lack of fluorescence under high-energy radiation in many organic solutions which exhibit strong fluorescence under light excitation. A change of the solvent often results in a considerable decrease of the high-energy-induced fluorescence without any decrease of the light-induced fluorescence, which is very difficult to understand if the transfer occurs by means of ions.

Some authors, nevertheless, assume that in solutions containing only one solute the energy transfer

TABLE I. Effects of addition of naphthalene on the fluorescence of various xylene solutions under γ-ray and uv excitations.

(a) Miscellaneous solutes

				Fluorescent intensity[a]			
				γ-ray excitation		Light (3130A) excitation	
Solute	g/l	Additional solute	g/l	No Filter	0-52 Filter[b]	No Filter	0-52 Filter[b]
...	...	...	...	0.025	0.005	0.03	0.003
Naphthalene	70	...	...	0.04	0.012	0.07	0.01
Terphenyl	0.5	...	...	0.29	0.10	1.0	0.30
Terphenyl	0.5	Anthracene	0.05	0.12	0.085	0.26	0.18
Terphenyl	0.5	Anthracene	0.3	0.09	0.077	0.18	0.155

(b) Anthracene as fluorescent solute

Anthracene	0.3	Naphthalene	0	0.06	0.05	0.19	0.15
Anthracene	0.3	Naphthalene	1	0.06	0.05	0.16	0.13
Anthracene	0.3	Naphthalene	10	0.06	0.05	0.11	0.09
Anthracene	0.3	Naphthalene	40	0.06	0.05	0.11	0.09
Anthracene	0.3	Naphthalene	70	0.06	0.05	0.11	0.09
Anthracene	0.3	Naphthalene	100	...	...	0.11	0.09
Anthracene	0.3	Naphthalene	200	0.06	...	0.10	0.08

(c) Terphenyl as fluorescent solute

Terphenyl	4	Naphthalene	0	0.5	0.16	1.0	0.28
Terphenyl	0.5	Naphthalene	0	0.29	...	0.97	0.25
Terphenyl	0.5	Naphthalene	0.5	0.20	..	0.92	0.23
Terphenyl	0.5	Naphthalene	10	0.085	...	0.35	0.08
Terphenyl	0.5	Naphthalene	70	0.046	...	0.09	0.02

(d) Diphenylanthracene as fluorescent solute

9,10-Diphenyl-anthracene	0.5	Naphthalene	0	0.17	0.14	0.47	0.44
9,10-Diphenyl-anthracene	0.5	Naphthalene	0.5	0.15	0.13	0.33	0.30
9,10-Diphenyl-anthracene	0.5	Naphthalene	1	0.13	0.12	0.28	0.25
9,10-Diphenyl-anthracene	0.5	Naphthalene	5	0.13	0.12	0.22	0.19
9,10-Diphenyl-anthracene	0.5	Naphthalene	10	0.13	0.12	0.20	0.17
9,10-Diphenyl-anthracene	0.5	Naphthalene	20	0.14	0.13	0.21	0.18
9,10-Diphenyl-anthracene	0.5	Naphthalene	40	0.14	0.13	0.20	0.17
9,10-Diphenyl-anthracene	0.5	Naphthalene	70	0.15	0.14	0.20	0.17
9,10-Diphenyl-anthracene	0.5	Naphthalene	100	0.17	0.16	0.21	0.18

(e) Terphenyl as solute—3340-A exciting light

...	...	...	...	0.025	0.005	0.17	0.01
Naphthalene	70	...	...	0.04	0.01	0.18	0.02
Terphenyl	2	Naphthalene	0	0.49	0.16	1	0.33
Terphenyl	2	Naphthalene	1	0.36	0.12	1	0.33
Terphenyl	2	Naphthalene	10	0.21	0.07	0.9	0.30
Terphenyl	2	Naphthalene	70	0.09	0.03	0.6	0.23

[a] All gamma-ray intensity values are referred to anthracene crystal of the same mass without any filters present as 1, the light excitation values for 3130A refer to the value of terphenyl (4 g/l) in xylene as 1, without filters being present; and the intensity values for 3340A refer to xylene and terphenyl 2 g/l as 1 with no filters present.

[b] Corning 0-52 filter cuts off all radiation below 3400A and has a transmission of greater than 50 percent for wavelengths above 3600A. The filter is placed in front of the photomultiplier.

takes place essentially by way of transfer of hidden radiation (1000A$-$2000A). In order to further clarify this situation and to trace more directly the energy transfer by the described migration of excitation energy and its final trapping by a solute molecule, experiments employing excitation by light were performed where excitation and transfer by means of hidden radiation is impossible. These experiments (described below) also show that collision transfer occurs with considerable probability.

The light-excitation experiments have been carried out by using ultraviolet light of various wavelengths in different kinds of solutions. For this purpose a Bausch and Lomb monochromator employing a mercury arc lamp as light source was used. The light from this instrument was directly incident on the surface of a solution placed in a glass or quartz beaker. The fluorescent light was viewed by a 1P28 photomultiplier in a direction perpendicular to the incident light.

Of particular interest in relation to the energy transfer were effects observed when naphthalene was added to various xylene solutions while excited by gamma radiation. Naphthalene solutions without additional solutes fluoresce only slightly under high energy or light excitation. The addition of large amounts of naphthalene into anthracene solutions (up to 200 g/l of naphthalene to 0.3 g/l of anthracene) produces practically no change in the fluorescent light output (see Table I). When a similar experiment is carried out, however, with p-terphenyl as the fluorescent solute, the addition of naphthalene results in a strong decrease in the fluorescent output. These findings were explained by assuming that the energy which is primarily absorbed in the xylene (greater than 75 percent even with 200 g/l of naphthalene) is first transferred mainly to the naphthalene because of its large excess in concentration and subsequently from it to the fluorescent solute. In the case of anthracene, the lowest excitation energy of the anthracene molecule is sufficiently below that of the naphthalene molecule that a transfer of energy from the naphthalene to the anthracene can occur rather easily. This transfer takes place almost entirely by means of collisions rather than by means of radiation since the light output of naphthalene is relatively weak. On the other hand, with p-terphenyl the excitation levels of both solutes are close to each other as shown by the similarities in the absorption ranges. Consequently, the energy transfer is expected to be much less probable from the naphthalene to terphenyl than to the anthracene if it occurs at all. The excitation energy of the naphthalene is therefore quenched before it has a chance to go over to the terphenyl; thus the final outcome is a decrease in the light output when the amount of naphthalene is increased. Such a difference in behavior as that found between anthracene and terphenyl solutions could perhaps also be explained by assuming that no energy transfer at all occurs to naphthalene; the decrease of the terphenyl fluorescence

would then be attributed to a special quenching of terphenyl fluorescence by the naphthalene. However, the light experiments described below reject this possibility.

A behavior somewhat similar to that of anthracene was also displayed by 9,10-diphenylanthracene,
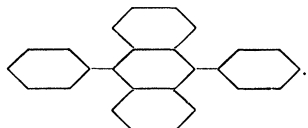
This molecule has a fluorescent spectral range similar to that of anthracene and its state of lowest excitation energy is therefore assumed to be close to that of anthracene. Its fluorescent light output in xylene solutions is, however, considerably larger than that of anthracene and is almost as great as that of p-terphenyl. Under gamma rays, the addition of small amounts of naphthalene to this substance produces a small decrease in light output which is not found with anthracene; increasing the concentration of naphthalene, however, here results in an increase in light output. The initial decrease may be due to a small quenching of diphenylanthracene by naphthalene (possibly because of impurities). The later rise is attributed to the better energy transfer (by collisions) from naphthalene to diphenylanthracene than that from xylene to diphenylanthracene.

Experiments analogous to those with gamma radiation have also been performed with light. The advantage of using light consists essentially in the possibility of primarily exciting only a single constituent of the solution such as one of the solutes or the solvent by appropriate choice of the wavelength. In particular, with light as the exciting agent, the excitation may be localized in the solute molecules, thus by-passing the solvent if it is transparent to the exciting radiation. First xylene-anthracene solutions with various amounts of additional naphthalene were excited by light of 3130A. For this wavelength xylene is essentially transparent, though the solutes (anthracene, diphenylanthracene, naphthalene, and terphenyl) show considerable absorption. If the absorption coefficient of the naphthalene molecule at this wavelength is arbitrarily taken as 1, the absorptions of anthracene and p-terphenyl molecules are about 5 and 32, respectively;[9] with 10 g/l of additional naphthalene 90 percent of the light is absorbed by naphthalene, and with 100 g/l about 99 percent. The absorption of 9,10-diphenylanthracene is also in this range of values. The depth of the solution was such that in any event the light was "completely" absorbed either by the fluorescent solute or by the naphthalene.

Examination of Table I shows that the fluorescence of pure xylene is rather weak under light as well as

under gamma radiation, and the addition of 70 g/l of naphthalene produces only a relatively small increase of light output. It reveals further that the emitted light, even with large amounts of naphthalene present, occurs mostly at wavelengths below about 3500A. The addition of naphthalene to the anthracene solution brings about a decrease in fluorescence of about 47 percent; the light output is characteristic of anthracene though almost all of the incident radiation is absorbed by the naphthalene. The light output is almost constant beyond 10 g/l of naphthalene (90 percent absorption by naphthalene).

These experiments demonstrate the energy transfer from naphthalene to the anthracene by collision. Energy transfer by ions is excluded since the exciting radiation is not energetic enough to produce ionization. Energy transfer by absorption of radiation is also excluded since, because of quenching in the anthracene molecule when in solution, the observed anthracene radiation should be five times smaller than the original naphthalene radiation if transfer occurred by way of radiation. Since the anthracene radiation is even larger than that of the naphthalene radiation, the energy transfer must take place by way of "collision." The reason that energy transfer by absorption is always connected with a decrease in light output is the fact that the quantum yield of most solutes is smaller than one (as crystals the quantum efficiency may be of the order of 1). This means that considerably less light is re-emitted than absorbed. In the case of anthracene in solution, the quantum yield is of the order of 20 percent; thus a decrease in light output by a factor of about five is to be expected. This is also demonstrated by the values in the first portion of Table I where the light output for 0.5 g/l of p-terphenyl in xylene without naphthalene is described for both 0.05 g/l and 0.3 g/l of additional anthracene. Small amounts of anthracene are sufficient to absorb most of the terphenyl radiation. Consequently, a clear indication that there is energy transfer by collision is given by the result that when 200 g/l of naphthalene are present, 53 percent of the anthracene light output is obtained compared to that when no naphthalene is present, and the fact that this light emission is 1.5 times larger than that of naphthalene (but in the spectral region of anthracene). The decrease in light emission of anthracene because of the addition of naphthalene is explained as follows: at the higher naphthalene concentrations all light is absorbed by the naphthalene, but only 53 percent of this energy is transferred by collisions to anthracene at anthracene concentrations of 0.3 g/l. This value is in fair agreement with the calculated energy transfer from gamma radiation (see below).

Similar types of light excitation experiments were carried out with p-terphenyl and 9,10-diphenylanthracene which further bear out these conclusions. With p-terphenyl, the addition of naphthalene produces a strong decrease in light output. Thus when the molecular ratio of naphthalene to terphenyl is 250 to 1, which

[9] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds* (John Wiley and Sons, Inc., New York, 1951).
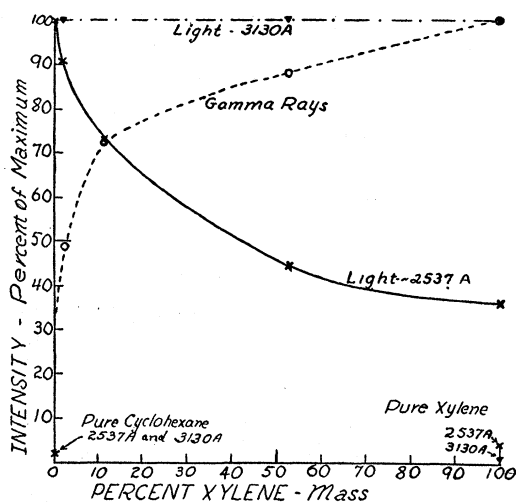
FIG. 1. Fluorescence of p-terphenyl in mixtures
of cyclohexane and xylene.

means a light absorption ratio of 8 to 1 in favor of naphthalene, there is a decrease of intensity of about 90 percent, almost down to the value of naphthalene without terphenyl. Most of the decrease in intensity is here accounted for by the absorption of the incident energy by naphthalene and the lack of transfer to the terphenyl either by collision or otherwise.

Experiments with 9,10-diphenylanthracene yield results similar to those with anthracene, as is to be expected from the emission spectrum of this substance; its fluorescent efficiency under light excitation is about one-half that of terphenyl. Addition of naphthalene to such solutions produces (as in anthracene) a decrease of the fluorescence, here of about 55 percent. Again the results are attributed to the absorption by naphthalene of the incident radiation and an energy transfer to diphenylanthracene by collisions. The essential difference compared to anthracene is the almost three times larger emitted intensity due to smaller internal quenching. The experiments show again that no energy transfer by way of absorption occurs, since this would again result in an eventual light output smaller than that of naphthalene.

One further point to be cleared up is the strong decrease of radiation when naphthalene is added to p-terphenyl. This is certainly associated with the increased amount of absorption by the naphthalene; but it might be argued that this decrease is not due to a lack of energy transfer by collisions from naphthalene to terphenyl, but rather to a special quenching of the excited terphenyl molecule by naphthalene. In order to make a decision between these possibilities, experiments were performed with light of 3340A. This radiation is scarcely absorbed by naphthalene, though it is still comparitively strongly absorbed by terphenyl and excites it. The results are described in the last portion of the Table I. Additional naphthalene here produced

only a small drop in fluorescent intensity compared to that observed with 3130A, very little change in intensity taking place with molecular ratios up to about 9 to 1 (10 g/l naphthalene). Thus, whereas under excitation by gamma rays or light of 3130A wavelength, a decrease in fluorescence by a factor of 2.5 or 3 is found the decrease in fluorescence under the light of 3340A wavelength amounts to only 10 percent, indicating that the quenching of the excited terphenyl molecules by naphthalene is small if present at all. This supports our earlier contention that the decrease in the terphenyl-naphthalene radiation occurs because there is no energy transfer from naphthalene to terphenyl, and only a relatively small special quenching of the terphenyl radiation by naphthalene.

These experiments show principally that there is an energy transfer from atom to atom by way of collision in liquid systems. In these light experiments, the naphthalene can be considered as playing to some extent the role of the bulk material from which the energy is transferred to other solutes. Xylene is essentially inactive in these light excitation experiments and has the purpose of making the systems liquid. Some experiments with light excitation in which xylene has the function of the bulk material for primary excitation have also been performed. First the fluorescent efficiency of p-terphenyl excited by a wavelength of 3130A was determined for xylene and cyclohexane as solvents; this wavelength is absorbed almost entirely by the terphenyl and not by either of these solvents. This experiment was carried out to determine the difference in quenching of terphenyl in both solvents; practically no difference was found. Then this experiment was repeated with wavelengths of about 2537A which are absorbed considerably by xylene but scarcely at all by cyclohexane, as well as with gamma rays for comparison; the results are shown in Fig. 1. For comparison, the light-induced intensities for the pure solvents without terphenyl are also indicated. In these experiments the relative amounts of xylene and cyclohexane were varied while the amount of terphenyl was kept unchanged. For 3130A, the fluorescent output is found to be practically constant for all the solvent ratios (straight line of Fig. 1). For the shorter wavelengths, the fluorescent intensity of terphenyl is greatest with pure cyclohexane and registers only 36 percent of this value for pure xylene. Under gamma radiation, in contrast, an increase by a factor of 3 was found when varying from pure cyclohexane to pure xylene. This decrease of fluorescent output with ~2537A light, and no change with 3130A light, is certainly due to the absorption of the ~2537A light by the xylene. With 2537A light in 100 percent xylene, the relative absorption ratio between xylene and 1 g/l of terphenyl is about 20 to 1 when the available data (for toluene) are used.[9] Since pure xylene without terphenyl has only a very small fluorescent emission, one would also expect a very weak fluorescent intensity for xylene and 1 g/l

terphenyl from these absorption values, since all radiation is practically absorbed by xylene. Thus the fluorescent intensity of these terphenyl solutions should drop by a factor of about 20 when cyclohexane is replaced by xylene. Instead only a drop by a factor of 2.8 is observed. This result can again be explained by assuming that the energy is transferred from xylene to terphenyl by collisions just as in the experiments with gamma radiation.

If the energy transfer calculated from these light experiments is compared with that computed from gamma-ray results, it is found that the transfer with light excitation is about half of that with gamma radiation and of the same order as that found in the alpha particles.[1] This may be associated with the large density of excitation present with the light intensities employed. Preliminary experiments indicate that with lower incident light intensities, higher efficiencies of energy transfer are obtained. The smaller efficiency under gamma rays in cyclohexane compared to that in xylene, although both solvents are found to have roughly the same quantum yield (as shown in experiments with 3130A), is due to the fact that the energy transfer in cyclohexane is considerably weaker than that in xylene.

The correlation of the gamma-ray excitation results with those obtained with ultraviolet excitation in all of the above experiments can be taken as very strong evidence in favor of transfer of excitation energy by means of collisions and against any essential contribution by ionization to any of the mechanisms for high-energy organic liquid fluorescence which are found in the literature. The energy transfer that takes place from solvent to solute or from one solute to another in these experiments under light excitation as well as under high-energy radiation has been shown to be due in large part of a "collision" mechanism[†] and certainly cannot be completely attributed to radiation absorption and re-emission (photon exchange) as is claimed by Birks.[4] It may be mentioned that if photon exchange did occur, it should be more pronounced for terphenyl than for anthracene because of its larger absorption coefficient. In this case the experiments described above could not be explained. Finally, it may be remarked that any energy transfer by means of absorption of radiation with wavelengths shorter than that of the absorption edge of naphthalene (~3250A) is also excluded by the fact that in this range p-terphenyl has a larger absorption coefficient than anthracene or diphenylanthracene. If such a transfer by absorption did occur, then terphenyl solutions should behave like anthracene or diphenylanthracene since no special quenching of terphenyl radiation by naphthalene occurs. Instead, the addition of naphthalene produced a large decrease in the light output of terphenyl solutions. Energy transfer by absorption of radiation with wavelengths greater than 3250A is excluded because such radiation, if present, would not have escaped detection in our arrangement.

The energy transfer described here for liquid systems is essentially similar to that observed by Bowen in solid solutions of organic materials.[5,6] These experiments also support the previously reported idea that energy transfer and subsequent fluorescence can occur only if the energy difference between the excited levels of the two types of molecules concerned is great enough so that the energy can be trapped and not returned to the transferring molecule. At the same time they show, as noted above, that no interaction of the self-quenching type occurs between these different types of molecules.

† *Note added in proof.*—Similar conclusions were also reached from analogous experiments by S. G. Cohen and A. Weinreb, Phys. Rev. **93**, 1117 (1954).