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Decay Times of Fluorescent Substances Excited by High-Energy Radiation*†

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Decay times of fluorescent light emitted by organic solutions and by organic and inorganic solids when excited by high-energy radiation are determined under various experimental conditions. The pulse-height ratios for alpha-particle and electron excitations are also found.

The probabilities for radiative and nonradiative transitions of the light emitting molecule are estimated and compared with values obtained from absorption measurements. The time required for energy transfer is estimated. The ratio of pulse heights obtained under alpha-particle excitation to those obtained under electron excitation are found to be roughly the same for all organic solutions and solids despite wide variations in lifetime; also no difference in lifetime between alpha-particle and electron excitations is found. This is not explained by present theories. A new theory to explain these facts is outlined.

INTRODUCTION

THIS paper presents results of decay-time measurements on organic compounds as solids and solutes, and on some inorganic substances; pulse-height ratios obtained with light flashes induced by alpha particles compared to those induced by electrons; an investigation of the influence of external conditions upon the decay time, and a discussion of the theory of the processes involved. The pulse ratio method[1] and the oscilloscope method[2] were used. It was found that the first method is good only for substances with decay times of 15 millimicroseconds or longer, while with the latter method decay times, almost an order of magnitude shorter, can be measured. Only results with the oscilloscope method are presented here because of greater accuracy in the region of measurements.

DESCRIPTION OF EXPERIMENTAL ARRANGEMENT

A 5819 photomultiplier was used with the solid samples directly coupled to the window by Duco cement or Silicone grease and the solutions placed in a glass beaker coupled to the photomultiplier in the same way. All measurements were made at room temperature using a solution depth of 15 mm for electrons and 4 mm for alpha particles. The current pulse from the photomultiplier was fed through a cathode follower into the vertical amplifier of a Tektronix 517 oscilloscope. The oscilloscope trace was photographed with a 35-millimeter camera. It was then traced on graph paper from the magnified image produced by a projection type comparator. Since the time constant of the electrical circuit was large compared to the anticipated lifetimes, one exponential curve was used to approximate the rise of the voltage pulse. The time taken to reach $(1-1/e)$ of its final value is taken as the decay time of the substance as is described below. The horizontal sweep time was calibrated by means of a 50-Mc/sec sinusoidal signal from a crystal-controlled oscillator.

Fast electrons were provided by strontium 90 and radium *E* and a Van de Graaff generator operating at a voltage of 1.1 Mev. The Van de Graaff arrangement had the advantage of supplying pulses almost homogeneous in height. Polonium 210 was the source of alpha particles.

RESULTS

The results of the decay-time measurements are presented in Table I. The time constants listed are decay times of individual substances including the spread of electron transit time in the photomultiplier. The measured rise times τ_0 of the scope trace are not true decay times of the flashes, but are longer as a consequence of the finite response time of the photomultiplier and scope amplifier. In order to determine the actual time constant τ_f of the flash from τ_0, use is made of the square-root rule,[3] $\tau_0=(\sum_i\tau_i^2+\tau_f^2)^{\frac{1}{2}}$, where each τ_i represents the time constant of a part of the apparatus. With the aid of a square-wave signal of a rise time of 0.5×10^{-9} second, τ_i was determined as 5×10^{-9} second from which a time-constant $\tau_c=[\tau_0^2-(5\times10^{-9})^2]^{\frac{1}{2}}$ was obtained. This value is presented in the tables. τ_c differs from τ_f because of the finite transit time spread τ_s of the photomultiplier. Since this was not measured, τ_c rather than τ_f values

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* Experimental work done at Evans Signal Laboratory, Fort Monmouth, New Jersey.

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[1] Broser, Kallmann, and Reuber, Z. Naturforsch. **5a**, 79 (1950); Bittmann, Furst, and Kallmann, Phys. Rev. **87**, 83 (1952).

[2] R. F. Post and H. S. Shiren, Phys. Rev. **78**, 80 (1950); G. G. Kelley and M. Goodrich, Phys. Rev. **77**, 138 (1950); J. S. Allen, Atomic Energy Commission Report, AECU-996, 1951 (unpublished); G. T. Wright, Proc. Phys. Soc. (London) **B69**, 358 (1956); R. K. Swank and W. L. Buck, Rev. Sci. Instr. **26**, 15 (1955); Liebson, Bishop, and Elliot, Phys. Rev. **80**, 907 (1950); Ravilious, Farrar, and Liebson, J. Opt. Soc. Am. **44**, 238 (1954); Schmillen, Schmillen, and Rohde, Z. Naturforsch. **8a**, 213 (1953); Cherkasov, Molchanov, Vember, and Voldakina, Doklady Akad. Nauk U.S.S.R. **109**, 292 (1956); R. C. Sangster and J. W. Irvine, Jr., J. Chem. Phys. **24**, 670 (1956). See Sangster for additional references on decay times.

[3] W. C. Elmore and Matthew Sands, *Electronics* (McGraw-Hill Book Company, Inc., New York, 1949), first edition, p. 139.

TABLE I. Decay times[a] and relative efficiencies for alpha- and beta-particle excitation.

					Relative peak heights[c]		
Substance	Conc. (g/l)	Solvent[b]	τ_c (alpha)	τ_c (beta)	Eff.[d] (alpha)	Eff.[e] (beta)	Beta[f] Alpha
Acenaphthene	3	*X*	...	10.6±2.9	1.3	14	11
Acenaphthene	3	*P*	...	20.7±4.6	1.6	14	9
α,α′-binaphthyl	3	*X*	5.9± 1.4	6.0±2.5	3.6	29	8
α,α′-binaphthyl	5	*BPN*	...	11.4±2.0	2.4	19	8
α,α′-binaphthyl	5	*BPD*	...	10.0±2.8	...	...	...
9,10-diphenylanthracene	4	*X*	11.5± 1.8	8.9±2.3	3.4	27	8
9,10-diphenylanthracene	5	*P*	11.4± 2.0	10.8±1.9	2.2	29	13
9,10-diphenylanthracene	3	*PE*	12.6± 1.6	12.9±1.9	1.7	14	8
9,10-diphenylanthracene	4	*XP*	10.2± 1.4	10.2±1.6	2.1	23	11
9,10-diphenylanthracene	3	*T*	9.5± 1.5	9.4±1.5	3.9	27	7
9,10-diphenylanthracene	1	*BPN*	...	15.8±3.1	2.2	18	8
Diphenylhexatriene	3	*X*	6.3± 1.4	6.9±1.3	2.4	29	12
Diphenylhexatriene	3	*P*	9.1± 1.2	9.1±1.2	3.0	27	9
2,5-diphenyloxazole	4	*X*	6.4± 1.4	4.8±1.5	4.4	35	8
2,5-diphenyloxazole	4	*P*	6.2± 1.4	5.8±1.3	3.5	35	10
2,5-diphenyloxazole	5	*BPN*	...	8.2±2.4	2.6	26	10
2,5-diphenyloxazole	5	*BPN*	...	5.3±0.8	...	...	...
Fluoranthene	5	*X*	...	24.0±2.3	...	...	...
Naphthalene	10	*P*	...	33.9±6.6	...	...	...
α-naphthyl phenyloxazole	4	*X*	...	5.3±0.8	...	...	...
α-naphthyl phenyloxazole	3	*BPN*	...	7.9±1.5	...	...	...
m-terphenyl	20	*X*	10.5± 0.8	8.5±1.4	1.8	18	10
m-terphenyl	20	*P*	11.4± 1.9	11.3+1.7	1.8	14	8
p-terphenyl	4	*X*	7.3± 1.6	4.7±2.0	4.0	28	7
p-terphenyl	4	*P*	6.0± 1.3	6.6±1.8	3.5	28	8
Anthracene	...	...	24.2± 2.7	21.5±2.8	10.0	100	10
Chrysene	...	...	22.0± 2.6	22.0±2.6	4.7	70	15
Diphenylacetyle	...	...	5.1± 1.3	5.1±1.3	6.2	...	...
Naphthalene	...	...	74.2±10.7	76.2±9.2	2.6	27	10
Pyrene	...	...	44.1± 3.7	39.1±9.8	2.3	35	15
Stilbene	...	...	4.2± 1.7	4.7±2.3	7.0	70	10
Plastic scintillator	...	...	3.5± 2.0	3.5±2.3	5.2	70	13
Calcium fluoride	...	...	740	640	2.4	18	8
Calcium tungstate	...	...	3100	3200	4.3	33	8
Cesium bromide (Tl)	...	...	1900	2100	12.0	36	3
Sodium chloride (5% AgCl)	...	...	3900	...	2.0	10	5
Potassium bromide (0.5% TlBr)	...	...	180	...	2.6	10	4

[a] All decay times, τ_c, are expressed in millimicroseconds (10^{-9} sec).

[b] *X*—xylene; *P*—phenylcyclohexane; *XP*—xylene plus 30% paraffin oil; *T*—toluene; *BPN*—*n*-butyl phosphate plus 300 grams per liter naphthalene; *BPD*—*n*-butyl phosphate plus 200 grams per liter biphenyl; *PE*—phenyl ether.

[c] The relative peak heights are only approximate values and are lower than those obtained by other investigators. This can be attributed to the fact that peak pulse-height measurements were used to obtain the efficiencies rather than integrated current measurements.

[d] The efficiency for alpha excitation relative to anthracene was taken as 10 and was corrected for unit absorbed energy, but not for the photomultiplier spectral response.

[e] The efficiency for beta excitation relative to solid anthracene was taken as 100 and was corrected for equal absorbed energy, but not for the photomultiplier's spectral response.

[f] Ratio of beta to alpha efficiency per unit absorbed energy.

are given. These are connected by the formula:

$$\tau_f=(\tau_c^2-\tau_s^2)^{\frac{1}{2}}. \tag{1}$$

This is of importance only for fast substances since τ_s is about 3 to 4×10^{-9} second. Upon using such a value, the true decay time of, for example, *p*-terphenyl in xylene is calculated to be 3×10^{-9} second. This is in agreement with results reported in the literature.[4] For the shortest occurring time constants, τ_f of about 2×10^{-9} second, the oscilloscope method is not precise, but its precision increases with increasing time constant. Nevertheless the measurements on fast substances are useful since they provide an upper limit for the effect of the solvent on time constants (see below).

The accuracy of the results is further limited by the statistical nature of the measurement. When one-Mev electrons are totally absorbed by an anthracene crystal, only 500 primary photocathode electrons result from the initial light pulse using the best geometry, and the expected fluctuation is five percent. The measurement of the decay time actually can utilize only a fraction of this number (it determines the number of electrons produced up to various periods of time), so that even larger uncertainties are to be expected. The situation is even worse for solutions since some of these have efficiencies only twenty percent of that of crystalline anthracene.

The various efficiencies were obtained by comparing the respective deflections on the oscilloscope to those obtained with anthracene under alpha-particle and electron excitations.

An inspection of Table I discloses the following: (1) The observed decay times of organic solids as well as solutes cover a range of more than one order of magnitude. Some substances have long decay times as

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[4] S. H. Liebson, Nucleonics **10**, No. 7, 42 (1952).

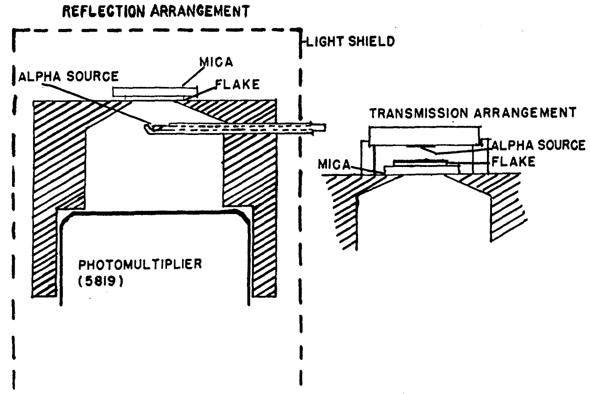

FIG. 1. Experimental arrangement for the decay-time measurements of the transmitted and reflected light from thin and thick samples of anthracene when excited by alpha particles.

solutes and as solids; e.g., fluoranthene and naphthalene. The large variation of decay times is noteworthy because it results from two quite different and competing processes, the light-emitting process and the quenching process; the large spread of both indicates some correlation between the two processes (see below). The relative difference between the actual decay times is even more pronounced if one considers that τ_c given in the table is larger than the actual τ_f (discussed above). (2) The decay time seems to depend on the solvent used. Thus solutions in solvents consisting of a liquid component to which naphthalene or biphenyl has been added seem to have longer decay times than those in a simple solvent, e.g., xylene. (3) No difference between decay times of organic scintillators produced by alpha particles or produced by fast electrons was found. This is also true of the inorganic phosphors investigated. (4) The ratio between peak heights due to alpha particle and electron excitations is almost the same for all organic compounds investigated whether they are solid or in solution although they have quite different decay times and efficiencies. These findings are interpreted in the theoretical section below.

Investigations by Birks[5] have shown that the decay time of an organic scintillator depends on specimen thickness and this dependence was attributed by him to self-absorption within the sample. Thus, the fluorescence which is initially emitted is partially reabsorbed and then re-emitted and this may take place a number of times until the emission consists of long enough wavelengths so that no absorption occurs; then the light escapes from the crystal. In order to study this effect further, a series of measurements of the decay times of very thin and thick specimens of both anthracene and naphthalene were made. Thin specimens were obtained by heating anthracene or naphthalene powder and then allowing slow cooling and crystallization in a closed vessel. The flakes obtained by this method were found to be between 0.01 and 0.02 millimeter thick. They were mounted on thin sheets of mica so that they could be handled. A one-half inch anthracene cube[6] and a naphthalene crystal 2.1 millimeters thick were used as the thick specimens. Alpha-particle excitation was provided by a polonium source placed above the flake or thick sample. The anthracene measurements were made with both the 5819 and the 1*P*21 photomultipliers in an arrangement as shown in Fig. 1. The results are presented in Table II. The results were essentially the same although a number of different flakes from various sources[7] of anthracene were measured. The difference in the decay time of the thin and thick specimens of anthracene is about 8 millimicroseconds for both photomultipliers. The difference between the thin and thick values in the case of naphthalene is percentagewise much smaller. This is expected if the difference in decay time is attributed to a re-emission process since naphthalene has a much smaller absorption than anthracene and is about one-third as efficient as anthracene. Thus, there is only small probability that the light which is absorbed is re-emitted.

TABLE II. Decay times[a] of thin and thick samples for alpha-particle excitation.

Substance	τ_c (thin sample)	τ_c (thick sample)
Anthracene (1*P*21)	12.4±3.3	19.2±3.2
Anthracene (5819)	12.0±2.7	20.4±1.0
Naphthalene (5819)	64.7±5.4	79.8±7.7

[a] All decay times, τ_c, are expressed in millimicroseconds (10^{-9} sec).

Additional evidence about the reality of the difference of time constant between thin and thick specimens was obtained by the following experiment: The decay times for five different arrangements using a thin and a thick specimen of anthracene were determined. The thick sample was a disk[8] about 5 millimeters thick. A polonium alpha-particle source was used in an arrangement in which excitation of the samples took place from the top. The filter referred to in Table III cut out wavelengths up to 4000 A. Arrangements (1) and (2) were used to check the influence of the filter on the decay time of the flakes; no influence was found. The filter also does not influence τ when interposed between flake and disk since the ultraviolet part of the fluorescent radiation, the reabsorption of which lengthens the decay time, is removed before reaching the disk. The disk then acts as a completely transparent window for the finally transmitted radiation. But in arrangement (4) τ is considerably lengthened because here the uv part hits the disk where it can be reabsorbed. Thus (4)

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[5] J. B. Birks and W. A. Little, Proc. Phys. Soc. (London) **A66**, 921 (1953).

[6] Obtained from Harshaw Chemical Company.

[7] Reilley Tar and Chemical Company, Harshaw Chemical Company, and Fisher Scientific.

[8] Obtained from National Radiac Company.

gives about the same change in τ as does the disk alone in (5). Arrangement (3) shows further that light of longer wavelengths is emitted with the same time constant as that of shorter wavelengths. This indicates that the τ observed with the thin flake is the intrinsic time constant of anthracene and that no further reduction can be accomplished by the use of still thinner flakes; otherwise a difference in time constant between the total emission and the long-wavelength emission would have been found.

The experiments described up to now only involve measurements of transmitted light. Similar time constants are obtained when reflected light is measured. The arrangement of Fig. 1 was used for this purpose. The jig permitted the specimen to be irradiated by alpha particles from above or below, and thus either transmitted or reflected light could be measured. A measurement of two flakes laid one upon the other was also carried out.

The data are presented in Table IV. Single flakes give the same short τ in both the reflection and transmission arrangements, indicating once more that the intrinsic time constant is reached. The double flake has a slightly longer τ value in the transmission arrangement compared to that using reflection, and the disk has only a slightly higher τ value than the flake when reflection is used but gives a longer τ in the transmission arrangement. Smaller pulses are obtained under transmission than under reflection; with a disk the difference is about 40%. In the single-flake experiments this is due to a geometry effect; the alpha-particle track in the flake is longer in the reflection measurement than in the one with transmission. In the disk experiments it is due to the backscattering of the blue light. These experiments are in agreement with the assumption of Birks that the blue part of the emitted light is reabsorbed and re-emitted. It may be mentioned that for such flakes the radiation may be partially imprisoned in the flake because of total reflections; this may lengthen the light path considerably and thereby increase the absorption.

Next to be considered is the influence in solutions of reabsorption effects upon the time constants. In the experiments using alpha particles the depth of the solution was so small that absorption in the solute was less than in the thin flakes; time constants measured in this way can therefore be considered as intrinsic. In the case of beta-particle excitation the thickness was greater and was equivalent to about two flakes. The lengthening of the time constants in these solutions is, however, smaller than in flakes for these reasons: Not all photons of the emitted light penetrate the whole solution, and the efficiency is less than one, reducing the probability of re-emission, as described, for naphthalene. Thus it can be assumed that the time constants of solutions represent intrinsic values rather well under both types of excitation.

TABLE III. Influence of ultraviolet part of anthracene's emission spectrum on the decay time[a] for alpha-particle excitation.

Arrangement	τ_c
(1) flake+5819	11.1±1.3
(2) flake+filter+5819	12.2±2.0
(3) flake+filter+disk+5819	11.6±2.1
(4) flake+disk+5819	19.7±2.9
(5) disk+5819	22.8±3.4

[a] All decay times, τ_c, are expressed in millimicroseconds (10^{-9} sec).

After the termination of these experiments a paper by Wright was published.[2] He reports that alpha-particle pulses have longer time constants than those induced by electrons. He uses a method which is essentially equivalent to the pulse ratio method[1] except that the power output is measured as a function of the input resistance. We came to the conclusion that the pulse ratio method is not so accurate as single time-constant measurements in the oscilloscope method. In Wright's method the effect of many pulses is observed, whereas in the method used here a single pulse is measured. We cannot explain the difference between our results and those obtained by Wright. The theory which is proposed later shows that alpha-particle-induced light flashes may have a longer tail of light emission than beta-particle-induced flashes.

DISCUSSION OF THE RESULTS

The measured decay times of a solute can be considered as composed of two components: one due to the time required for transferring the excitation energies from solvent to solute, and a second due to the actual decay time τ_m of the excited fluorescent molecule; this latter decay time should be the same as that observed under light excitation.

A. Probability of Light Emission and of Quenching

If one assumes the transfer time to be small (as will be shown later it is of only minor importance), τ_m is essentially the measured time constant. Then for τ_m

TABLE IV. Comparison of decay time[a] of the reflected and transmitted light from anthracene for alpha particle excitation.

Arrangement	τ_c	Pulse height[b]
flake by reflection	11.0±1.3	44
flake by transmission	12.1±2.2	34
double flake by reflection	11.5±1.0	26
double flake by transmission	14.0±3.0	22
disk by reflection	16.0±2.6	25
disk by transmission	23.8±1.1	15

[a] All decay times, τ_c, are expressed in millimicroseconds (10^{-9} sec).

[b] Pulse heights are expressed in arbitrary units and have been corrected for unit absorbed energy.

the following well-known equations hold:

$$\frac{1}{\tau_m}=\frac{1}{\tau_r}+\frac{1}{\tau_{rl}}, \tag{2}$$

$$\tau_r=\frac{\tau_m}{f}, \quad \tau_{rl}=\frac{\tau_m}{1-f}, \quad \text{where} \quad f=\frac{\tau_{rl}}{\tau_r+\tau_{rl}}, \tag{3}$$

$$\frac{1}{\tau_r}\sim\nu^2\int\epsilon_\nu d\nu, \tag{4}$$

where f = quantum efficiency of light emission, $1/\tau_r$ and $1/\tau_{rl}$ are, respectively, the probabilities per unit time that the excited molecule returns to the ground state via a radiative or a radiationless transition, and ϵ_ν is the extinction coefficient of the solute for a frequency ν. Equation (4) holds only for solutes since in a solid the emission process, and thus the probability of emission $1/\tau_r$, may be due to a cooperation of many molecules so that the value may be different from that of single molecules.

Since the efficiencies of many solutes and solids are experimentally known[9] (relative efficiencies measured under gamma excitation are closely correlated to those observed with light), one can calculate τ_r and τ_{rl} separately from the τ_m which is equal to the observed lifetime to a first approximation (see next section). Anthracene was not measured as a solute in this investigation, but it may be included in our discussion. Its time constant τ_m is reported to be 2×10^{-9} second,[4] giving 12×10^{-9} and 2×10^{-9} second, respectively, for τ_r and τ_{rl} according to Eq. (3) with f equal to 15%. If the probability of the radiationless transition for the various molecules is calculated in this way, it is found that anthracene in solution is one of the most unstable excited molecules with a τ_{rl} of only 2×10^{-9} second (p-terphenyl has a τ_{rl} of 7.5×10^{-9} second); solutes with rather small efficiencies such as fluoranthene and naphthalene have much higher τ_{rl} values of about 30 to 40×10^{-9} second. Values of τ_m for these compounds are mostly due to the time in which the substances are quenched because the probability of light emission is small. It is rather susprising that substances with large τ_r show any noticeable efficiency. If it were assumed that quenching of an excited molecule by interaction with the surroundings is of the same order of magnitude for most of the solutes, it would follow that molecules with long τ_r would show only a small efficiency. The results show that this is not the case, indicating that the probability of quenching and of light emission are correlated with each other. For instance, solutes with a small probability of light emission (small transition dipole) are also less subject to the influence of quenching interaction.

The τ_r computed from (3) can be compared, at least for solutes, with those obtained from Eq. (4). Although such a comparison is very crude because published absorption curves are often not accurate enough for studying special excited states, one should expect that these τ_r values are proportional to the respective absorption areas. One finds indeed that this is fairly well the case in many instances. There are two important exceptions: m-terphenyl and fluoranthene. Since the absorption curve of m-terphenyl does not differ greatly from that of p-terphenyl, both substances should have the same τ_r but different τ_m. The τ_m of m-terphenyl should be smaller than that of p-terphenyl because of the smaller efficiency of m-terphenyl. This is contrary to the result in Table I. A similar inconsistency is found with fluoranthene which has an absorption spectrum similar to that of anthracene, but has a τ_m about 10 times as large as that of anthracene. It is difficult to state the true reason for these apparent discrepancies. There is always the possibility, however, that the absorption band due to a low-lying state of excitation is so weak that it is overshadowed by the stronger absorption band due to higher states so that the true absorption band of the state of lowest excitation is much smaller than the measured absorption. A low-lying excited state of this type with weak absorption is well known in naphthalene.

A correlation between the τ_r of solids and of solutes also seems to exist. Thus the τ_m of solid naphthalene is about 80×10^{-9} second, and that of the solute is 34×10^{-9} second, but their τ_r's are both of the order of 300×10^{-9} second. This long decay time is attributed to the small transition probability mentioned above of the lowest excited state of naphthalene. The respective values of τ_r for solid and solute fluoranthene are both relatively long, namely 113 and 214×10^{-9} sec, respectively. Similar correlations exist for anthracene, diphenylhexatriene, and quaterphenyl, but it is doubtful whether such correlation exists in all cases.

B. Evaluation of the Transfer Time

An upper limit for the lengthening of the decay time τ_f of the flash due to the transfer of energy from the solvent to the solute can be obtained in the following way. If one assumes that a high-energy particle mainly excites the solvent (because of its greater abundance), the following differential equations hold for the number of excited solvent molecules n_s, and the number of excited solute molecules n_m:

$$\frac{dn_s}{dt}=-n_s\left(\frac{1}{\tau_q}+\frac{1}{\tau_t}\right)\equiv-\frac{n_s}{\tau_v}; \quad \frac{1}{\tau_t}=Y\sigma c, \tag{5}$$

$$\frac{dn_m}{dt}=\frac{n_s}{\tau_t}-\frac{n_m}{\tau_m}, \tag{6}$$

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[9] Kallman, Furst, and Brown, *Proceedings of the International Conference on Fluorescence and Phosphorescence at Garmisch-Partenkierchen, August, 1956* [Friedrich Vieweg und Sohn (to be published)].

where $1/\tau_t$ is the probability per unit time that the excitation energy is transferred from an excited solvent molecule to a solute molecule. τ_v corresponds to the solvent lifetime and is defined by Eq. (5). σ is the cross section of this reaction, Y a collision factor,[9] and c the concentration of the solute; $1/\tau_q$ is the probability that the excited solvent molecules return to the ground state without having transferred energy to the solute, and τ_m is the true lifetime of the excited solute molecules used in Eqs. (2) to (4). The τ_q and τ_m are intrinsic to the solvent and solute, respectively, but may be influenced by their surroundings. The parameter Q previously introduced in the theory of energy transfer is connected with τ_t and τ_q by the following relations:

$$Q=[Y\sigma\tau_q]^{-1}. \tag{7}$$

Under the initial conditions $n_s=n_0$, $n_m=0$, one has the following solutions:

$$n_s=n_0e^{-t/\tau_v}, \tag{8}$$

$$n_m=\frac{n_0\tau_v\tau_m}{\tau_t(\tau_v-\tau_m)}(e^{-t/\tau_v}-e^{-t/\tau_m}). \tag{9}$$

From this formula it follows immediately that good energy transfer still occurs if τ_t becomes smaller than τ_q when τ_v/τ_t is about 1. The number of quanta emitted within dt is equal to $(n_m/\tau_r)dt$ [from Eqs. (2) to (4)]. If $\tau_v\ll\tau_m$, Eq. (9) represents the usual shape of the light flash (very sharp rise) and an exponential decay with time constant τ_m if $\tau_v\sim\tau_m$ the flash has a finite rise time, given by the smaller of the values of τ_v and τ_m; the decay time is determined by the longer one. This makes the measured duration of the flash longer than the solute time constant τ_m roughly by τ_v. The latter is different from τ_t and always smaller than both τ_t and τ_q [see Eq. (5)]. For small solute concentrations c, τ_v is largest and equal to τ_q; with increasing c, τ_v becomes smaller and at a solute concentration where half of the total energy is transferred to the solute, τ_v is, equal to one-half of τ_q. This is often roughly the concentration at which the maximum light emission occurs, as can be determined from an analysis of intensity *versus* concentration curves. Thus one would expect a dependence of τ_f upon concentration only if τ_q is comparable with τ_m.

The following general conclusions may be drawn:

1. An upper limit for τ_q can be obtained from the τ_f of a solute with shortest lifetime; τ_v being smaller than τ_f, and τ_v being roughly $\frac{1}{2}\tau_q$ at maximum light output, it follows that $\tau_q<2\tau_f$. With $\tau_f\sim2.5\times10^{-9}$ sec, τ_q should be smaller than 5×10^{-9} second for efficient solvents such as xylene, phenylcyclohexane, and phenylether. τ_q can also be estimated from the solute concentration at which considerable energy transfer takes place or from the quencher concentration at which the excited solvent molecule is quenched to half of its original value, for instance, by carbon tetrachloride. Under reasonable assumptions for the migration of energy[10] in the solvent, one obtains a value of the magnitude of 10^{-9} sec for τ_q.

2. A particularly large Q value for special solutes such as *m*-terphenyl probably means a small cross section σ in (7) which means that comparatively large solute concentrations are required to make τ_t about equal to τ_q so that good energy transfer can be obtained.

3. Indications in Table I that the time constants in solutions with a combination of materials as the solvent, such as those containing naphthalene or biphenyl, are longer than those in xylene, may be due to a long transfer time from the intermediate solvent (naphthalene or biphenyl) to the solute. For instance in *n*-butylphosphate as solvent, without additional naphthalene, 2,5-diphenyloxazole at a concentration of 5 g/l exhibits only very small high-energy induced fluorescence. This can be explained by the assumption that the quenching time τ_q of butylphosphate and thus τ_v is extremely short so that only very rarely do "collisions" [11] occur between an excited butylphosphate molecule and a solute molecule during the short lifetime of the excited butylphosphate. It might instead be assumed that τ_q is not short but that the probability of energy transfer at a collision of an excited butylphosphate molecule with a solute molecule is small (small cross section for this reaction). Since energy transfer by butyl phosphate is small for all solutes, it seems more reasonable to assume that the reason for this lack of energy transfer is the result of a short τ_q. This would mean that τ_v from butylphosphate to the solute and thus also to naphthalene is always short. Thus longer time constants observed in mixed solvent solutions may then not be due to a longer transfer time from the main solvent (butylphosphate) to naphthalene but instead be due to a longer time of transfer from naphthalene to the solute. According to Table I the excited naphthalene molecule in a xylene solution has a comparatively long lifetime, at least for concentrations of about 10 g/l of naphthalene. It is possible that the transfer time τ_t from naphthalene to the solute is also relatively long because of small transfer cross sections. It would then follow that, for all solutions made in a combination of naphthalene and a liquid solvent, the shortest decay times observed should be longer than in xylene. The present measurements are not accurate enough to ascertain whether this is really the case.

4. It is known that Q values for transfer from naph-

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[10] H. Kallmann and M. Furst, Phys. Rev. **79**, 857 (1950); 81, 853 (1951); Nucleonics **8**, No. 3, 32 (1951).

[11] The term "collision" is not meant to indicate that energy transfer is necessarily due to motion of the excited molecule; it may equally well be that transfer is due to a migration (jump) of excitation energy through the solvent.[10] With respect to transfer to the emitting solute, "collision" does not necessarily mean that the specific solvent molecule carrying the excitation energy at the instant of transfer is in close contact with the solute molecule which takes over the energy, i.e., this transfer may occur with a greater probability than determined by the geometric cross section of the molecules.[10] Neither type of transfer, however, occurs by means of light emission and absorption.

thalene and those for transfer from xylene to various solutes are nearly the same. (The naphthalene value is possibly slightly smaller than that of xylene.) This Q value is connected to τ_q according to Eq. (7). Since the respective Q values are almost equal, it is necessary to assume either that naphthalene and xylene both have about the same τ_q and the same cross section σ, or that these substances have different τ_q and different cross sections but that the product $\tau_q\sigma$ of both substances is nearly the same.

C. Dependence of Lifetime and Efficiency upon Density of Excitation

Next to be discussed is the well-known large difference in light efficiency between electron and alpha particle excitation and the lack of difference in time constants under these excitations which is reported in this paper. When the effect of decreased alpha-particle efficiency was observed,[12] it was attributed to a quenching between excited molecules due to the high density of excitation in the wake of an alpha particle. The quantitative formulation of this idea was given by Wright and Birks.[13] It will be shown here that this formulation of the theory is not adequate for explaining all the observed effects of alpha particle and electron excitations. First some of the results of Birks and Wright will be reviewed; they are rewritten for convenience in the later discussion. When there are n excited molecules, Eq. (10) is the basic differential equation which characterizes the dependence of n upon time:

$$\frac{dn}{dt}=-\frac{n}{\tau_m}-\delta n\left(\frac{n}{V}\right). \tag{10}$$

Here τ_m has the same meaning as that defined in Eq. (3) and is intrinsic to the excited molecule. δ is a parameter which is associated with the mutual quenching of excited molecules; this quenching effect in the derivation by Birks and Wright is assumed to be due to bimolecular action described by the dependence upon n^2. The parameter δ depends upon the cross section of this quenching and does not depend essentially upon τ_m. The excitation takes place in a volume V so that n/V is the density of excitation. If there are Δn_0 originally excited molecules produced by a fast particle along a path of length Δl and a cross sectional area A, the light emission ΔI is given by

$$\Delta I=\int_0^\infty\frac{\Delta n}{\tau_r}dt=-\frac{\tau_m}{\tau_r}\int_{\Delta n_0}^{0}\frac{d(\Delta n)}{[1+\tau_mK(dn_0/dl)(\Delta n/\Delta n_0)]}$$
$$=\frac{\Delta n_0\tau_m}{\tau_r}\left(\frac{\ln(1+X_0)}{X_0}\right), \tag{11}$$

where

$$X\equiv\tau_mK\frac{dn_0}{dl}\frac{\Delta n}{\Delta n_0},$$

$K=\delta/A$, Δn is the number of excited molecules at time t, and $(dn_0/dl)=\omega(dE/dl)$, (dE/dl) being the energy loss per unit length and ω a constant. Since the dn_0/dl varies along the path of the alpha particles, only a small length of the total track is considered; when the total path is considered, an integration must be performed. When fast electrons are used, δ and thus K is small, and the expression becomes $\Delta I_e=\tau_m\Delta n_0/\tau_r$. The ratio R between alpha particle and electron light emission is then given for alpha particles by the following equation:

$$R=\frac{\Delta I_\alpha}{\Delta I_e}=\frac{\ln(1+X_0)}{X_0};\quad X_0=\tau_mK\frac{dn_0}{dl}. \tag{12}$$

For the total path a suitable average must be used to replace dn_0/dl.

Equation (12) is essentially Wright's formula but written differently. This formula is found to agree rather well with experimentally determined efficiencies of organic substances when excited by various particles and energies if the constant K is determined for one density of excitation. However, in other respects these formulas do not represent experimental observations correctly because the formulas depend upon time constants. According to (12), X_0 is about 35 when computed from the experimentally observed efficiency of polonium alpha particles, and it is not very different for many organic molecules although the τ_m values vary considerably. Since X_0 contains the product τ_mK (with K independent of τ_m), one would expect R and thus X_0 to vary from substance to substance because of differences in τ_m. This is not found although τ_m varies by a factor of 30 from *p*-terphenyl in solution to naphthalene; R is rather constant as Table I shows. To account for this, one must assume either that K is inversely proportional to τ_m which is difficult to understand theoretically, or that the theory omits some essential features of the quenching process. The experimental results seem to indicate that quenching due to high excitation density is actually a very fast process, of much shorter lifetime than the lifetime of the shortest of the investigated organic emitters. The consideration of the lifetimes of light flashes produced by highly ionizing particles leads to a similar conclusion. The table shows that the time constants for alpha-particle-induced and electron-induced light flashes are practically the same. Any quenching process, however, results in a decrease in lifetime of the excited molecule. Therefore a considerable decrease in lifetime under alpha-particle irradiation would be expected because of quenching of the excited molecule (by a factor of 10) resulting from the high density of excitation. Experience, however, shows that this is not the case. It appears once more as though the main part of quenching

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[12] L. Herforth and H. Kallmann, Ann. Physik 4, 231 (1949).

[13] G. T. Wright, Phys. Rev. **91**, 1282 (1953); J. B. Birks, Proc. Phys. Soc. (London) **A64**, 824 (1951).

is finished before any appreciable amount of light is emitted. The difference in lifetime when the light flash is produced by highly ionizing particles rather than by electrons can be calculated from the above equation, and from Eq. (10) the variation of Δn, and thus of X, as a function of t can be determined. It is given by

$$\frac{X}{1+X}=\frac{X_0}{1+X_0}e^{-t/\tau_m}. \tag{13}$$

The value of X at the time $t_{\frac{1}{2}}$ at which just half the light is emitted is defined as $X_{\frac{1}{2}}$ and is given by

$$\frac{\ln(1+X_{\frac{1}{2}})}{\ln(1+X_0)}=\tfrac{1}{2}. \tag{14}$$

From (13) and (14), $t_{\frac{1}{2}}$ can be obtained. When $X_0=35$ as above, a value of $X_{\frac{1}{2}}=5$ results and for $t_{\frac{1}{2}}$, a value of $0.16\tau_m$ results instead of $0.69\tau_m$ which is the value for electron excitation. This leads to time constants for alpha particles about one fourth as great as those for electrons under the assumption that the efficiencies for alpha particles and electrons are determined correctly. However, as pointed out earlier, the experiments give no indication of such a difference in time constants. In the bimolecular case no special assumption about the interaction constant δ can remove the discrepancy between theory and the experimental findings.

These results are not unexpected from a theoretical viewpoint. Alpha particles produce a total excitation density (consisting of different types of excitation) of about 10^{20} molecules per cm^3 in a channel having a main cross sectional area of the order of 10^{-12} cm^2. (This follows from normal energy-loss calculation.) There is a strong interaction among such excited molecules which results in a large degradation of electronic excitation energy through nonradiative means (quenching). The discussion in the previous paragraphs shows that this quenching dies away in a time shorter than the lifetimes of isolated molecules excited in their lowest excited state. The bimolecular term of Eq. (10) does not adequately account for the strong quenching. The addition of a term in the equation which describes the quenching as a collective interaction of the entire excited volume gives the following form:

$$\frac{dn}{dt}=-\frac{n}{\tau}\left[1+\tau\delta\left(\frac{n}{V}\right)+\tau\lambda\left(\frac{n}{V}\right)^m\right], \tag{15}$$

in which the term of power m represents the collective interaction (multiple collisions). This equation removes the difficulty concerning time constants in the bimolecular theory which has been discussed (see Table V). Fair agreement with experiments is already obtained when $m=4$ if λ is appropriately chosen. It is difficult, however, to give a physical mechanism explaining the additional term since the magntiude of the parameter λ necessary for agreement with experiment comes out too large to be produced by multiple collisions.

TABLE V. Ratio of light emitted by substance under alpha-particle excitation compared to electron excitation for various excited molecule interactions.

m	X_0	R	$t_{\frac{1}{2}}$
1 (bimolecular)	$\tau_m K'(dn_0/dL)$	$[\ln(1+X_0)]/X_0$	$0.16\tau_m$
4	$(\tau_m\lambda')^{\frac{1}{4}}(dn_0/dL)$	$\frac{1}{2\sqrt{2}X_0}\left\{\ln\frac{1}{2}\left(\frac{1+\sqrt{2}X_0+X_0^2}{1-\sqrt{2}X_0+X_0^2}\right)+\arctan\left(\frac{\sqrt{2}X_0}{1-X_0^2}\right)\right\}$	$0.64\tau_m$
∞	dn_0/dL	$1/X_0,\quad X_0>1$ $1,\quad X_0<1$	$0.69\tau_m$

Another way of evaluating the effect of this collective quenching is the following extension of Wright's ideas. The quenching occurs as a result of the high density of excitation in a small volume of radius about 10^{-6} cm. Various electronic excitation levels, intra- and interatomic vibrations, dissociations, formations of free radicals, free electrons, and a considerable electric field are produced in this channel volume. If this energy were to consist entirely of atomic vibrations concentrated in a volume of 10^{-15} cm^3 in a substance like anthracene (this is the total volume of the main excitation channel produced by a polonium alpha particle if the channel radius is assumed to be 0.5×10^{-6} cm), then the temperature of this volume would be raised to about 1000°C. The local rise in temperature, however, is not the only factor responsible for quenching since considerable quenching (although to a lesser extent than with alpha particles) is already found under proton and slow-electron excitations where the temperature rise is much smaller. It is known, however, from experiments that such a rise in temperature quenches excitation energy only slightly and in comparatively long times; in 10^{-9} sec this type of quenching would be entirely negligible. Thus it is likely that many and perhaps most of the enumerated excitation phenomena cooperate in the quenching process. Their effects must disappear in a time of about or less than 10^{-9} second in order to account for the strong quenching of short-lived fluorescent solutes. There are two apparent mechanisms for this: (1) the quenching "agents" may diffuse out of the critical volume, thereby decreasing the density of excitation (but not the total excitation), and produce a diminished quenching; or (2) the electronic excitation energy (essential for the fluorescence) may migrate out of this volume and not be subject to quenching. The latter process is probably the faster one, and dilution of the quenching agent may be neglected in an estimation.

The migration of the excitation energy can be described by a diffusion coefficient D_{esc} which is of the order of 5×10^{-4}. This value and a channel radius of 0.5×10^{-6} cm leads to a time of escape τ_{esc}, smaller than 10^{-9} sec. The change per unit time of the number n of electronic excitations inside the channel while this escape is taking place is:

$$\frac{dn}{dt}=-\frac{n}{\tau_{\text{esc}}}-\frac{n}{\tau_q}, \tag{16}$$

where $1/\tau_q$ is the probability of quenching inside the channel which is assumed to be proportional to the total density X of excitation assumed to be constant during this time, thus $(1/\tau_q)=\kappa X$. The total amount of light emission is assumed to be small during this time of quenching and is thus neglected in (16). The number of dn_{esc} of electronic excitations which escape in the time interval dt, is

$$dn_{\text{esc}}=\frac{n}{\tau_{\text{esc}}}dt, \tag{17}$$

where n follows from (16). By integrating (17), one obtains for n_{esc}, the number of the electronic excitations which eventually escape quenching (in the critical volume), the formula

$$n_{\text{esc}}=\frac{N_0\tau_q}{\tau_{\text{esc}}+\tau_q}=\frac{N_0}{1+\kappa X\tau_{\text{esc}}}, \tag{18}$$

where N_0 is the initial number of electronic excitations, and n_{esc} is the number which are finally available for light emission and ordinary quenching processes. For the ratio of light emission under alpha-particle excitation to that under electron excitation, we get

$$\frac{I}{I_0}=\frac{1}{1+aX}, \tag{19}$$

where $a=\kappa\tau_{\text{esc}}$. The values obtained from Eq. (19) are not very different from those given by the bimolecular theory. However, the time constants are independent of the type of excitation and also independent of the time constant the fluorescent material has, since the escape process is always fast for the usual values of D_{esc} and radius of the channel. For values of I/I_0 between 1 and 1/10, the bimolecular formula and (19) give rather similar results.

For very high excitation densities (e.g., higher than in the alpha-particle channel of polonium), the formula does not hold very well. One must bear in mind that it is derived under the assumption that practically all excitations occur in the channel volume where they will be de-excited as already described so that only a small portion escapes. This escaping portion decreases as $1/(1+aX)$ with the density of excitation. On the other hand, a small part of the excitation is also produced outside of the main channel volume; much less quenching occurs with this part. At very strong density of excitation, this latter portion may eventually become larger than the portion which escapes from the inner channel and emission may be larger than according to Eq. (19) for such high densities of excitations.

The final question is that of the possible existence of a long-time-constant tail in the light emission produced by an alpha particle. According to our measurements, the main light emission has the same characteristics for alpha particles and fast electrons except that for alpha particles the intensity is reduced by a considerable factor. Now it may be that after the main emission, some further emission occurs. This could be due to the recombination of free electrons and positive charges. Since the latter are certainly less quenched by the quenching agents than excited molecules, this tail may be more pronounced with alpha-particle excitation than with electrons. The amount of light emission in the tail may be the same for alpha-particle and electron excitation; but since under alpha particles the main light emission is quenched to a greater extent than is the emission in the tail, the ratio between the tail and main emission may be more pronounced for alpha particles. It would be very interesting to investigate whether the effects observed by Wright are due to such a delayed type of excitation.

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