

point, where

$$x = x_c = \sqrt{2} - 1.$$

Near the critical point,  $I$  has a branch point:

$$I \cong [4(\sqrt{2} + 2)(x_c - x)]^{1/8}.$$

In Fig. 4,  $I$  is plotted against the temperature.

This work was completed in the summer of 1951 while the author was at the University of Illinois. He wishes to take this opportunity to thank the staff of the Department of Physics, University of Illinois for the hospitality extended him during his stay. He also wishes to thank Bruria Kaufman for many stimulating discussions.

## High Energy Induced Fluorescence in Organic Liquid Solutions (Energy Transport in Liquids). III\*†

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Experimental results on the fluorescence of a large number of efficient solutions under both gamma-ray and alpha-particle excitation are presented. These results are compared with the theory to be found in Part I, and very good agreement is obtained in almost all cases. The physical efficiencies of some of these solutions under gamma-ray excitation are found to be quite high when compared with an anthracene crystal. The light output for the same amount of absorbed energy is considerably less for alpha-particle excitation than for gamma-rays in all of the solutions. The experimental data are discussed in conjunction with the theoretical considerations, and the physical processes involved in the large fluorescence of the solutions are analyzed.

### A. EXPERIMENTAL RESULTS

SOME experimental and theoretical results on the fluorescence of organic liquid solutions using gamma-ray excitation have previously been reported.<sup>1-3</sup> This paper presents results under alpha-particle excitation in addition to further findings with gamma-ray bombardment. The light intensities of all the solutions were measured as a function of the solute concentrations, using mainly a RCA 1P28 photomultiplier with both types of excitation. In most cases, in order to minimize errors, the identical solutions were used for both excitations in comparing their effects. The light emission in the case of gamma-ray excitation is referred to the emission of an anthracene crystal of the same mass and in the same geometrical setting. Such relative fluorescence values at the optimum concentration are described here by the term relative physical efficiencies. These efficiencies differ somewhat from the practical efficiencies published previously,<sup>3</sup> as a consequence of the use of a nonreflecting container in the present measurements to minimize effects caused by different amounts of reflection at the walls of the container because of the spectral differences in the emission of the solutions. The values listed in Table I still depend to some extent on the spectral distribution of the emitted light because of the non-uniform spectral response of the photomultiplier. To determine the im-

portance of such effects, measurements were made using two photomultipliers with different spectral responses (RCA 1P28 and 1P21), after the emission spectra of many of the solutions were determined.<sup>2</sup> A measure of the importance of this spectral effect is given in the last column of Table I, where the ratios of the intensities in the two photomultipliers for the different solutions are presented. The gamma-ray results for all the solutions are referred to the same mass, which means approximately the same amount of absorbed gamma-ray energy since the number of electrons per gram is essentially the same for all these organic solutions (see below).

It is to be noted that some of the light emission efficiencies are quite high; this is particularly the case for *p*-terphenyl which in phenylcyclohexane and xylene has an efficiency about half as great as an anthracene crystal. Since an anthracene crystal converts about 15 percent of the absorbed energy into light (measurements on a naphthalene crystal show about 5 percent conversion and anthracene is better by a factor of about 3),<sup>4</sup> this indicates that with the solutions as much as about 7 percent of the absorbed gamma-energy may be transformed into light. Another feature to be noted is that fairly generally a solute showing a relatively high efficiency in one solvent exhibits a rather high light emission in the other efficient solvents.

For alpha-particles the values are also referred to a standard measurement with an anthracene crystal or a zinc sulfide powder. Here there is the difficulty that the anthracene crystal surface deteriorates rather quickly under the alpha-particle bombardment (a 10-mC

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† This is part of a dissertation (M.F.) in partial fulfillment of the requirements for the PhD degree at New York University.

<sup>1</sup> H. Kallmann and M. Furst, *Phys. Rev.* **79**, 857 (1950).

<sup>2</sup> H. Kallmann and M. Furst, *Phys. Rev.* **81**, 853 (1951).

<sup>3</sup> H. Kallmann and M. First, *Nucleonics* **8**, 32 (1951).

<sup>4</sup> Broser, Kallmann, and Martius, *Z. Naturforsch.* **4a**, 204 (1949).

TABLE I. Relative physical efficiencies of solutions.

	Xylene	Benzene	Cumene	<i>p</i> -Cymene	<i>p</i> -Dioxane	Phenetole	Phenyl cyclo- hexane	Phenyl ether	Toluene	Av. ratio 1P21/1P28 <sup>a</sup>
Anthracene	0.060	0.046	0.042	0.039	0.025	0.048	0.059	0.045	0.047	0.98
Anthranilic acid	0.15	0.11	0.10	0.12	0.082	0.13	0.16	0.13	0.13	0.97
Diphenylbutadiene	0.12	0.058	0.078	0.069	0.019	0.067	0.14	0.093	0.081	0.95
Diphenylhexatriene	0.14	0.11	0.090	0.064	0.042	0.12	0.21	0.091	0.13	0.95
Durene	0.048	0.078	...	...	...	...	0.12	0.044	...	0.39
Fluoranthene	0.075	0.070	0.080	0.073	0.057	0.061	0.079	0.078	0.070	0.97
Methyl <i>p</i> -aminobenzoate	0.062	0.049	0.039	0.036	0.022	0.051	0.059	0.054	0.051	0.88
Methyl anthranilic acid	0.13	0.085	0.086	0.089	0.097	0.11	0.11	0.10	0.11	0.97
Phenyl $\alpha$ -naphthylamine	0.23	0.20	0.17	0.12	0.091	0.20	0.28	0.24	0.22	0.97
<i>p</i> -Terphenyl	0.48	0.38	0.39	0.34	0.27	0.32	0.48	0.41	0.43	0.92
Carbazole	0.12	...	...	...	...	...	...	...	...	...
Fluorene	0.15	...	...	...	...	...	...	...	...	...
Naphthalene	0.032	0.029	...	...	...	...	...	...	...	...
$\alpha$ -Naphthylamine	0.17	...	...	...	...	...	...	...	...	...
$\beta$ -Naphthylamine	0.13	...	...	...	...	...	...	...	...	...
Pyrene	0.086	...	...	...	...	...	...	...	...	...
Stilbene	0.038	...	...	...	...	...	...	...	...	...
<i>m</i> -Terphenyl	0.20	...	...	...	...	...	...	...	...	...

<sup>a</sup> Ratio of anthracene crystal taken as 1.

polonium source was used). The crystal surface had to be renewed (by scraping or dissolving off the top layer) in order to obtain consistent measurements. The arrangement for the alpha-particle solution measurements is shown in Fig. 1; the instrumental portion is the same as for the gamma-ray measurements. A small amount of solution (0.7 cc) in a brass container with a quartz plate window was placed above the photographic shutter. The alpha-particle source was situated above the solution and separated from it by a very thin aluminum foil. This was necessary to avoid the light excited in the air in the vicinity of the alpha-particle source; this light was found to be comparable to the emission from the solution if the air gap was considerable.

Some typical results are reproduced in Figs. 2 to 6, where the indicated points give the experimental values and the drawn lines represent the curves which are calculated to fit the experimental points closely by means of the three parameters occurring in our theory<sup>1,2</sup> (see below). All of the experimental results of light intensity as a function of concentration are presented in summary form in Tables II to X by means of these parameters.† From the measured intensities no direct comparison can be made between the relative light efficiencies of gamma-rays and alpha-particles. They represent the readings of the measuring instrument with quite different exciting energies. It is, however, possible to refer these readings to the same amount of absorbed energy by calculation. It is then found that the light efficiencies under alpha-particle excitation are smaller than those under gamma-ray excitation by a factor of about 40 when comparing the maximum light emission

† Note: These values are calculated for concentrations in grams per liter. It would be somewhat more meaningful to use moles per liter. The relative *P*, *Q*, and *R* values would then be somewhat increased for the lighter solute molecules. The *P/R* values would remain unchanged.

from solutions of terphenyl in xylene. From this value all the alpha-particle intensities obtained from the parameters can be referred to the gamma-ray intensities. This value coincides in order of magnitude with the values given by Broser, Kallmann, and Martius<sup>4</sup> for the ratio between the gamma-ray and alpha-particle excitation efficiencies of organic crystals.

The curves and tables show a further difference in the effect of gamma-ray and alpha-particle excitation. All the alpha-particle curves have their maxima shifted to larger concentrations than the gamma-ray maxima. The degree of shift is not the same for all the solutions, but quite definite differences occur with the different solutions. A tentative explanation for such a behavior will be given below.

## B. THEORETICAL CONSIDERATIONS

To explain the observed variations light with concentration variations and the large amount of light

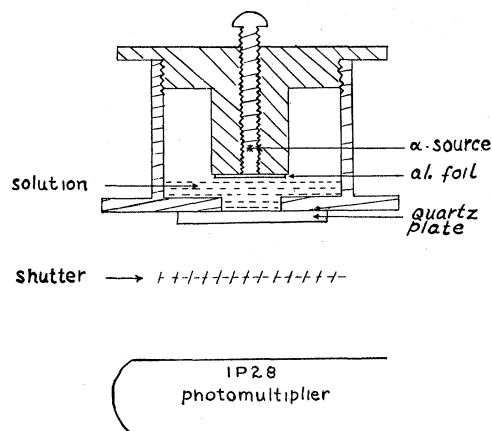


Fig. 1. Arrangement where an alpha-particle source excites a solution which emits light through a quartz window to a photomultiplier.

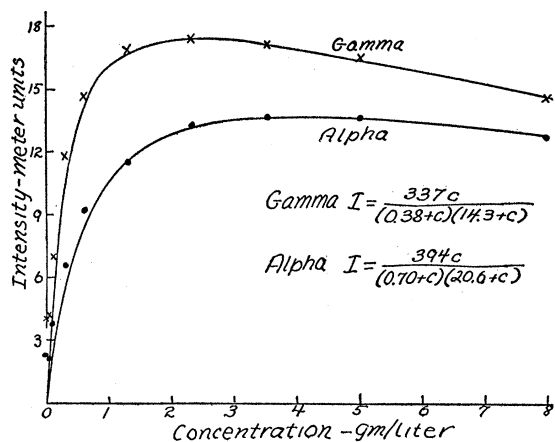


FIG. 2. Variation of emitted light intensity for various concentrations of diphenylbutadiene in benzene showing the experimental points and the agreement of the theory (curve) for both gamma-ray and alpha-particle excitations.

emission under high energy radiation, a theory has been proposed by us<sup>1</sup> which describes the light intensity  $I$  for a concentration  $c$ , by the equation

$$I = Pc / [(Q+c)(R+c)]. \quad (1)$$

The theory assumes that there is a transfer of energy from the excited solvent molecules to the solute, where this energy is trapped. The probability of this transfer and trapping is measured by  $\alpha c$ . The energy transfer is counteracted by a quenching in the solvent molecules, the probability of which per unit time is described by  $1/\tau_q$ . The constant  $Q$  in the above formula is then given by

$$Q = 1/(\alpha\tau_q). \quad (2)$$

After the excitation energy has been transferred to the solute and localized there, it is no longer exposed to the internal quenching in the solvent. In the solute the energy may then be subjected to three processes which must be considered: (1) The process of light emission; the probability of this per unit time is  $1/\tau_e$ . (2) The

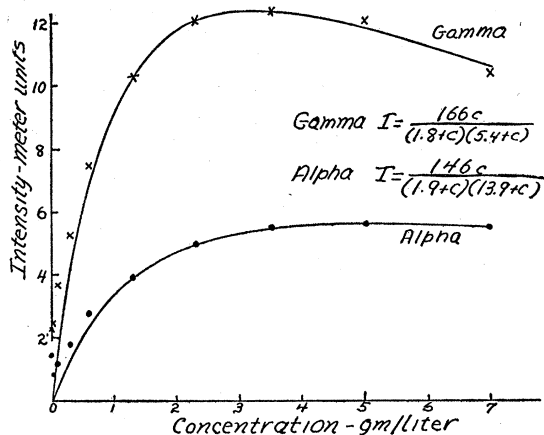


FIG. 3. Same as Fig. 2 except diphenylhexatriene in *p*-dioxane.

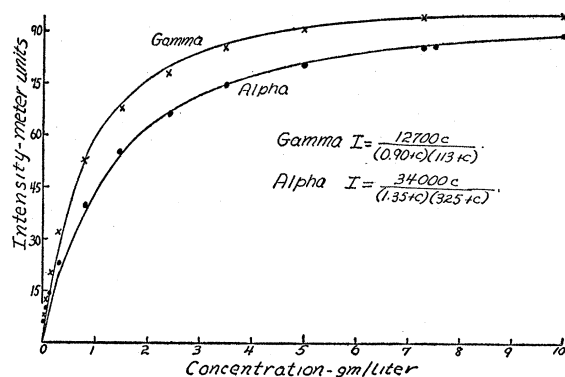


FIG. 4. Same as Fig. 2 except terphenyl in phenetole.

light energy process is counteracted by an internal quenching process in the solute, the probability of which is denoted by  $1/\tau_i$ . (3) There is also another process which competes with the light emission described in the literature by self-quenching which only occurs at higher concentrations; the probability of this per unit time is described by  $\beta c$ . From these, the parameters  $P$  and  $R$  are, respectively,

$$P = \eta_e \delta / \beta \tau_e \quad (3)$$

and

$$R = (1/\beta)(1/\tau_i + 1/\tau_e), \quad (4)$$

where  $\eta_e$  describes the number of electrons of the solvent excited per unit time which are capable of transferring their energy to the solute, and  $\delta$  is a constant which transforms the number of emitted quanta into meter units. The result, that mainly solutions made with solvents containing double bonds are the ones which have large fluorescent intensities under high energy radiation, suggests that the energy transfer is connected mainly with the electrons in these double bonds. The maximum intensity emitted by a solution measured in meter units and the maximum concentration in grams per liter can be calculated, respectively, from the values

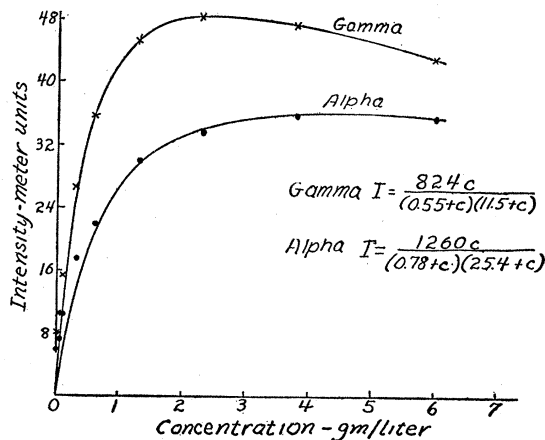


FIG. 5. Same as Fig. 2 except anthranilic acid in phenylcyclohexane.

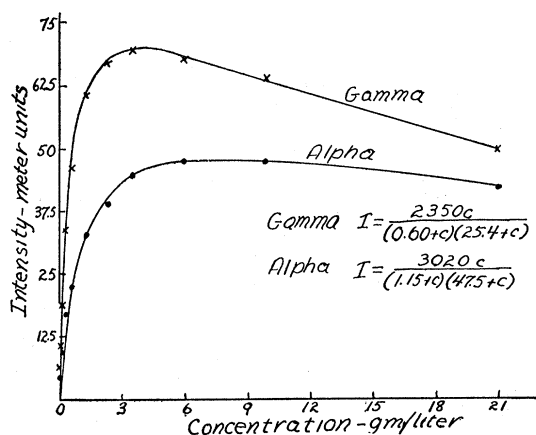


FIG. 6. Same as Fig. 2 except phenyl  $\alpha$ -naphthylamine in xylene.

listed in Tables II to X by the formulas

$$I_{\max} = P / (Q^{\frac{1}{2}} + R^{\frac{1}{2}})^2 \quad (5)$$

and

$$C_{\max} = (QR)^{\frac{1}{2}} \quad (6)$$

In these meter units, an anthracene crystal of the same mass as the solutions has a reading of 300 for gamma-ray excitation.

The curves of Figs. 2-6 show that on the whole the proposed theory fits the experimental results very well. There are definite systematic variations at low concen-

TABLE II. Solution parameters—solvent: benzene.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene 1 <sup>a</sup>	106	0.40	4.6	23
Anthracene 2	87	0.42	3.7	24
Anthranilic acid 1 <sup>a</sup>	467	0.45	9.4	50
Anthranilic acid 2	450	0.52	9.5	47
Diphenylbutadiene	337	0.38	14.3	24
Diphenylhexatriene	225	0.55	3.55	63
Durene 1 <sup>a</sup>	3000	0.75	133	23
Durene 2	6900	0.85	265	26
Fluoranthene 1 <sup>a</sup>	9020	0.45	405	22
Fluoranthene 2	8570	0.42	402	21
Methyl anthranilic acid	1235	0.55	38.4	32
Methyl <i>p</i> -aminobenzoate	63	0.38	2.08	30
Phenyl $\alpha$ -naphthylamine 1 <sup>a</sup>	1760	0.44	23.3	76
Phenyl $\alpha$ -naphthylamine 2 <sup>b</sup>	1975	0.40	28.9	68
Phenyl $\alpha$ -naphthylamine 3 <sup>b</sup>	2950	0.48	40.3	73
<i>p</i> -Terphenyl 1 <sup>a</sup>	5610	0.57	41	137
<i>p</i> -Terphenyl 2	7100	0.61	51	139
Alpha-excitation:				
Anthracene 2	257	0.75	19.3	13
Anthranilic acid 2	375	0.75	13.7	27
Diphenylbutadiene	394	0.70	20.6	19
Diphenylhexatriene	141	0.65	5.0	28
Durene 2	19100	1.6	1270	15
Fluoranthene	10800	1.0	730	15
Methyl <i>p</i> -aminobenzoate	56.7	0.80	3.0	19
Methylanthranilic acid	540	0.90	26.4	20
Phenyl $\alpha$ -naphthylamine 2	3480	0.77	91.5	38
Phenyl $\alpha$ -naphthylamine 3	3875	0.81	85	45
<i>p</i> -Terphenyl	10250	1.8	80	128

<sup>a</sup> No corresponding alpha-curve.  
<sup>b</sup> Especially purified.

TABLE III. Solution parameters—solvent: cumene.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene 1 <sup>a</sup>	109	0.75	4.3	25
Anthracene 2 <sup>b</sup>	109	0.70	5.4	20
Anthranilic acid	542	1.1	10.2	53
Diphenylbutadiene	452	1.25	10.7	42
Diphenylhexatriene	173	0.95	2.43	71
Fluoranthene 1 <sup>a</sup>	7570	0.85	301	25
Fluoranthene 2 <sup>b</sup>	22800	1.55	885	26
Methyl <i>p</i> -aminobenzoate	75	0.80	2.81	27
Methylanthranilic acid	1413	1.05	40.2	35
Phenyl $\alpha$ -naphthylamine 1 <sup>a</sup>	1603	1.0	20.7	77
Phenyl $\alpha$ -naphthylamine 2 <sup>b</sup>	1550	1.9	21.6	72
Phenyl $\alpha$ -naphthylamine 3 <sup>b</sup>	1250	1.3	19.2	65
Terphenyl 1 <sup>a</sup>	5700	1.3	34.5	165
Terphenyl 2 <sup>b</sup>	4010	1.2	33.1	121
Alpha-excitation:				
Anthracene 2	239	0.7	17.5	14
Anthranilic acid	615	1.5	18.8	33
Diphenylbutadiene	583	1.18	19.7	30
Diphenylhexatriene	127	1.3	2.79	46
Fluoranthene 2	20100	2.7	1245	16
Methyl <i>p</i> -aminobenzoate	159	0.9	7.2	22
Methylanthranilic acid	970	1.2	44.3	22
Phenyl $\alpha$ -naphthylamine 2	2483	1.95	47.7	49
Terphenyl 2	4060	2.4	31.2	130

<sup>a</sup> No corresponding alpha-curve.

<sup>b</sup> Change in solvent properties probably caused by absorption of oxygen.

trations. These deviations arise from the fact that in our theory it is assumed that the solvent shows no emission, whereas in reality the solvents do fluoresce to an extent comparable with the emission intensities of the efficient solutions at very low concentrations. One might attempt to deduct these solvent emission values

TABLE IV. Solution parameters—solvent: *p*-cymene.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene	118	1.15	4.2	28
Anthranilic acid 1 <sup>a</sup>	558	2.7	5.4	104
Anthranilic acid 2 <sup>b</sup>	467	3.6	9.3	50
Diphenylbutadiene	496	2.6	10.4	48
Diphenylhexatriene 1 <sup>a</sup>	243	1.9	2.12	115
Diphenylhexatriene 2 <sup>b</sup>	209	2.5	2.3	75
Fluoranthene 1 <sup>a</sup>	7300	0.85	320	23
Fluoranthene 2 <sup>b,c</sup>	7950	1.5	308	26
Methyl <i>p</i> -aminobenzoate	88	1.0	3.24	27
Methylanthranilic acid	1380	1.4	35	40
Phenyl $\alpha$ -naphthylamine 1 <sup>a</sup>	1068	1.3	17.0	63
Phenyl $\alpha$ -naphthylamine 2 <sup>b</sup>	715	3.0	12.4	57
<i>p</i> -Terphenyl 1 <sup>a</sup>	5550	1.3	37.5	148
<i>p</i> -Terphenyl 2 <sup>b</sup>	3620	2.1	25.0	145
Alpha-excitation:				
Anthracene	123	1.5	6.0	21
Anthranilic acid 2	503	4.0	14.0	36
Diphenylbutadiene	482	2.7	13.3	36
Diphenylhexatriene 2	192	2.5	4.5	43
Fluoranthene 2	12930	2.0	800	16
Methyl <i>p</i> -aminobenzoate	199	0.9	9.4	21
Methylanthranilic acid	1275	1.4	52	24
Phenyl $\alpha$ -naphthylamine 2	1230	2.4	35	35
<i>p</i> -Terphenyl 2	8050	2.65	74	109

<sup>a</sup> No corresponding alpha-curve.

<sup>b</sup> Greater purification.

<sup>c</sup> Change in solvent properties probably caused by oxygen absorption.

TABLE V. Solution parameters—solvent *p*-dioxane.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene 1 <sup>a</sup>	91	2.0	6.85	13
Anthracene 2	108	2.0	5.8	19
Anthranilic acid 1 <sup>a</sup>	1370	1.8	37	37
Anthranilic acid 2	1565	1.8	47	33
Diphenylbutadiene 1 <sup>a</sup>	385	2.5	44	9
Diphenylbutadiene 2	300	2.3	40	8
Diphenylhexatriene 1 <sup>a</sup>	158	2.0	6.1	26
Diphenylhexatriene 2	166	1.8	5.4	32
Fluoranthene 1 <sup>a</sup>	11080	4.3	704	16
Fluoranthene 2 <sup>b</sup>	15900	4.5	800	20
Methyl <i>p</i> -aminobenzoate	102	0.8	9.1	11
Methylanthranilic acid	4030	2.45	104	39
Phenyl $\alpha$ -naphthylamine 1 <sup>a</sup>	1760	3.8	44.5	40
Phenyl $\alpha$ -naphthylamine 2	1650	4.0	33	50
<i>p</i> -Terphenyl 1 <sup>a</sup>	11400	6.0	113	101
<i>p</i> -Terphenyl 2	15700	5.5	132	119
Alpha-excitation:				
Anthracene 2	123	2.1	11.4	11
Anthranilic acid <sup>c</sup>	2150	2.6	118	18
Anthranilic acid 2	2140	2.4	127	17
Diphenylbutadiene 2	268	4.5	38	7
Diphenylhexatriene 2	146	1.9	13.9	10
Fluoranthene 2	19400	7.0	2060	9
Methyl <i>p</i> -aminobenzoate	600	0.4	73	8
Methylanthranilic acid	3190	4.5	150	21
Phenyl $\alpha$ -naphthylamine <sup>c</sup>	3800	5.3	159	24
Phenyl $\alpha$ -naphthylamine 2	2980	5.2	125	24
Terphenyl <sup>c</sup>	11950	6.5	222	54
Terphenyl 2	12800	5.8	236	54

<sup>a</sup> No corresponding alpha-curve.<sup>b</sup> Further purified.<sup>c</sup> No corresponding gamma-curve.

from the intensities of the solutions; but this cannot be done unambiguously since the emission of the solvent already very likely originates in tiny amounts of fluorescent impurities,<sup>1</sup> and since it was also found that in solutions containing several fluorescent solutes the intensity of one solute may be changed by tiny amounts of the other solutes.<sup>2</sup> There are a small number of rather efficient solutes such as fluorene, pyrene, and

TABLE VI. Solution parameter—solvent: phenetole.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene	129	0.85	4.38	29
Anthranilic acid	563	0.60	9.6	59
Diphenylbutadiene	362	0.45	13	28
Diphenylhexatriene	249	0.65	2.9	86
Fluoranthene	7650	0.48	390	20
Methyl <i>p</i> -aminobenzoate	158	0.38	6.8	23
Methylanthranilic acid	732	0.45	16.2	45
Phenyl $\alpha$ -naphthylamine	2320	0.68	28.4	82
<i>p</i> -Terphenyl	12700	0.90	113	112
Alpha-excitation:				
Anthracene	189	0.90	11.4	17
Anthranilic acid	630	0.68	20.0	32
Diphenylhexatriene	197	0.95	4.0	49
Diphenylbutadiene	545	0.60	24	23
Fluoranthene	8780	0.85	795	11
Methyl <i>p</i> -aminobenzoate	377	0.38	19.2	20
Methylanthranilic acid	675	0.67	22.7	30
Phenyl $\alpha$ -naphthylamine	2360	0.90	52.8	45
<i>p</i> -Terphenyl	34000	1.35	325	105

TABLE VII. Solution parameters—solvent: phenylcyclohexane.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene	154	0.50	5.13	30
Anthranilic acid 1 <sup>a</sup>	627	0.65	8.2	77
Anthranilic acid 2	824	0.55	11.5	72
Anthranilic acid 3	860	0.57	11.9	72
Diphenylbutadiene 1 <sup>a</sup>	953	0.38	16.5	58
Diphenylbutadiene 2	632	0.40	11.5	55
Diphenylbutadiene 3	726	0.40	13.2	55
Diphenylhexatriene 1 <sup>a</sup>	254	1.0	1.7	150
Diphenylhexatriene 2	428	0.90	2.8	144
Durene 1 <sup>a</sup>	6340	1.25	205	31
Durene 2	10430	1.15	250	42
Fluoranthene 1 <sup>a</sup>	2580	0.37	104	25
Fluoranthene 2	3700	0.35	140	26
Methyl <i>p</i> -aminobenzoate	94	0.42	2.72	35
Methylanthranilic acid	576	0.50	12.5	46
Phenyl $\alpha$ -naphthylamine 1 <sup>a</sup>	2100	0.50	22.4	94
Phenyl $\alpha$ -naphthylamine 2 <sup>b</sup>	2840	0.55	25.5	111
Phenyl $\alpha$ -naphthylamine 3 <sup>b</sup>	3010	0.45	28	107
<i>p</i> -Terphenyl 1 <sup>a</sup>	6000	0.53	33	182
<i>p</i> -Terphenyl 2	5300	0.55	29.2	182
Alpha-excitation				
Anthracene	327	0.60	16	20
Anthranilic acid 2	1260	0.77	25.4	50
Anthranilic acid 3	1230	0.80	26.4	47
Diphenylbutadiene 2	455	0.75	9.7	47
Diphenylbutadiene 3	666	0.70	14.2	47
Diphenylhexatriene <sup>c</sup>	243	0.90	3.6	68
Diphenylhexatriene 2	308	0.90	3.85	80
Durene 2	11230	1.3	445	25
Fluoranthene 2	16600	0.50	880	19
Methyl <i>p</i> -aminobenzoate	123	0.45	5.3	23
Methylanthranilic acid	1120	0.80	30	37
Phenyl $\alpha$ -naphthylamine 2	3890	1.35	38.4	100
Phenyl $\alpha$ -naphthylamine 3	4200	1.15	40	105
<i>p</i> -Terphenyl 2	15950	1.10	100	160

<sup>a</sup> No corresponding alpha-curve.<sup>b</sup> Further purified.<sup>c</sup> No corresponding gamma-curve.

TABLE VIII. Solution parameters—solvent: phenyl ether.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene 1 <sup>a</sup>	214	0.55	10.5	20
Anthracene 2	214	0.55	10.5	20
Anthranilic acid <sup>a</sup>	1060	0.60	19.3	55
Diphenylbutadiene	645	0.70	15.8	41
Diphenylhexatriene 1 <sup>a</sup>	544	0.90	5.62	97
Diphenylhexatriene 2	409	0.82	4.05	101
Fluoranthene	5550	0.70	206	27
Methyl <i>p</i> -aminobenzoate	232	0.48	9.6	24
Methylanthranilic acid	1315	0.60	33.7	39
Phenyl $\alpha$ -naphthylamine 1 <sup>a</sup>	2930	0.72	33.4	88
Phenyl $\alpha$ -naphthylamine 2 <sup>b</sup>	4100	0.73	44.5	92
<i>p</i> -Terphenyl 1 <sup>a</sup>	19800	1.1	142	140
<i>p</i> -Terphenyl 2	21900	1.15	152	144
Alpha-excitation:				
Anthracene 2	458	0.80	21	22
Anthranilic acid <sup>c</sup>	1212	0.80	31	39
Diphenylbutadiene	619	0.75	22.5	28
Diphenylhexatriene 2	347	0.80	5.65	61
Fluoranthene	24200	1.05	1170	21
Methyl <i>p</i> -aminobenzoate	477	0.55	23.4	20
Methylanthranilic acid	875	1.25	30	29
Phenyl $\alpha$ -naphthylamine 2	4880	1.3	64	76
<i>p</i> -Terphenyl 2	44850	1.7	340	132

<sup>a</sup> No corresponding alpha-curve.<sup>b</sup> Further purified.<sup>c</sup> No corresponding gamma-curve.

*m*-terphenyl where the agreement between theory and experiment is not so good. In some of these cases, additional purifications have corroborated the idea that at least part of the discrepancy is due to small amounts of impurity which may become quite effective, especially at higher concentrations. For pyrene, however, impurities are not responsible for the deviations, but rather its weak fluorescence which reaches a maximum at such high concentrations (because self-quenching is very weak) that other effects such as the direct excitation of the solute molecules by the incident radiation must be taken into account.

After our theory on solutions was published, a somewhat different theory proposed originally for crystals was applied to some of our results with solutions.<sup>5</sup> It is not felt that this other theory gives any better fit in view of the circumstance that the underlying physical ideas seem to be inapplicable to solutions.

An informative extrapolation can be made from the knowledge of the parameters. Thus the light intensity which a solution would emit if self-quenching would not reduce the light emission at higher concentrations, can be calculated by letting  $\beta$  approach zero. Then the asymptotic intensity that would be reached at infinite concentration is given by

$$I_{\text{ext}} = P/R = \delta\eta_e / [1 + (\tau_e/\tau_i)]; \quad (7)$$

in this expression the value of  $\beta$  no longer appears.

The values of the parameters show that  $I_{\text{ext}}$  of some of the solutions compared to an anthracene crystal are as high as 0.6 for terphenyl in xylene;  $I_{\text{max}}$  in this case was 0.48. For diphenylhexatriene in phenylcyclohexane there is a particularly large increase of  $I_{\text{ext}}$  over  $I_{\text{max}}$  from 0.21 to 0.5. If these extrapolated intensities are

TABLE IX. Solution parameters—solvent: toluene.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene	99.5	0.56	3.65	27
Anthranilic acid	655	0.60	11.3	58
Diphenylbutadiene	327	0.47	8.9	37
Diphenylhexatriene	231	0.53	3.0	77
Fluoranthene	5300	0.45	231 †	23
Methyl <i>p</i> -aminobenzoate	77.9	0.40	2.6	30
Methylanthranilic acid	866	1.15	16.0	54
Phenyl $\alpha$ -naphthylamine	1810	0.49	20.9	87
<i>p</i> -Terphenyl 1	5680	0.72	33.3	171
<i>p</i> -Terphenyl 2	6050	0.85	36.0	168
Alpha-excitation:				
Anthracene	183	0.65	11.2	16
Anthranilic acid	842	0.65	32.6	26
Diphenylbutadiene	407	0.60	18.7	22
Diphenylhexatriene	140	0.70	3.9	36
Fluoranthene	6180	1.0	400	15
Methyl <i>p</i> -aminobenzoate	95.5	0.55	5.25	18
Methylanthranilic acid	577	1.75	15.5	37
Phenyl $\alpha$ -naphthylamine	2105	0.83	42.2	50
Terphenyl 1	7110	1.30	57	125
Terphenyl 2	7980	1.35	62.7	127

<sup>5</sup> P. D. Johnson and F. E. Williams, Phys. Rev. 81, 146 (1951).

TABLE X. Solution parameters—solvent: xylene.

Gamma-excitation: Solute	P	Q	R	P/R
Anthracene 1 <sup>a</sup>	106	0.55	3.15	34
Anthracene 2	130	0.53	3.7	35
Anthranilic acid 1 <sup>a</sup>	646	0.80	8.6	75
Anthranilic acid 2	595	0.75	9.0	66
Carbazole	342	0.55	5.6	61
Diphenylbutadiene 1 <sup>a</sup>	630	0.45	14.0	45
Diphenylbutadiene 2	480	0.63	8.4	57
Diphenylhexatriene 1 <sup>a</sup>	240	0.80	2.2	109
Diphenylhexatriene 2	218	0.75	2.1	104
Fluoranthene 1 <sup>a</sup>	4770	0.35	206	24
Fluoranthene 2	6700	0.40	275	24
Fluorene 1 <sup>b</sup>	155	0.80	1.8	86
Fluorene 2 <sup>b,c</sup>	577	0.35	8.7	66
Methyl <i>p</i> -aminobenzoate	76	0.55	1.64	46
Methylanthranilic acid	972	1.1	16.0	61
$\alpha$ -naphthylamine	567	0.60	6.7	78
$\beta$ -naphthylamine	1048	0.36	21.5	49
Phenyl $\alpha$ -naphthylamine 1 <sup>a</sup>	1780	0.75	18.2	98
Phenyl $\alpha$ -naphthylamine 2 <sup>c</sup>	2350	0.60	25.4	93
Pyrene <sup>b</sup>	105200	2.6	3850	27
Stilbene	838	0.38	63	13
<i>p</i> -Terphenyl 1 <sup>a</sup>	7900	0.58	44.8	176
<i>p</i> -Terphenyl 2 <sup>a</sup>	7870	0.60	43.3	182
<i>p</i> -Terphenyl 3	8050	0.55	45.5	177
Alpha-excitation:				
Anthracene <sup>d</sup>	123	0.65	7.6	16
Anthracene 2	134	0.70	6.2	22
Anthranilic acid 2	685	0.70	21.7	32
Carbazole	1840	0.55	77	24
Diphenylbutadiene	600	0.70	16	38
Diphenylhexatriene <sup>d</sup>	148	0.90	3.6	41
Diphenylhexatriene 2	191	0.95	4.0	48
Fluoranthene 2	18100	0.80	1130	16
Fluorene 1 <sup>b</sup>	197	1.0	3.6	55
Fluorene 2 <sup>b</sup>	6900	0.60	17.1	40
Methyl <i>p</i> -aminobenzoate	98.5	0.75	3.4	29
Methylanthranilic acid	3020	1.05	115	29
$\alpha$ -naphthylamine	770	0.70	19.5	39
$\beta$ -naphthylamine	2470	0.48	85	29
Phenyl $\alpha$ -naphthylamine <sup>d</sup>	1885	1.3	31.5	60
Phenyl $\alpha$ -naphthylamine 2	3020	1.15	47.5	64
Pyrene <sup>b</sup>	159500	6.0	8000	20
Stilbene	5290	0.53	570	9
Terphenyl 3	9550	1.2	70.5	135

<sup>a</sup> No corresponding alpha-curve.

<sup>b</sup> Poor over-all fit.

<sup>c</sup> Further purified.

<sup>d</sup> No corresponding gamma-curve.

calculated for the same number of double bonds per gram of solvent (these may be mostly responsible as remarked above, for the energy transfer and fluorescence) rather than for the same mass, the extrapolated intensities relative to an anthracene crystal are considerably larger for phenylcyclohexane solutions; and for a solution of terphenyl in phenylcyclohexane, in particular, this intensity is greater than that of an anthracene crystal (see also below).

There is another point which requires discussion. From the analysis of the experimental curves, two parameter values are obtained which are identified with  $Q$  and  $R$ . Since, however, these values occur symmetrically in Eq. (1), there is ambiguity as to which value should be ascribed to  $R$  and which to  $Q$ . We have always, however, identified the larger of these constants with  $R$  for the following reasons. For some solutions the

constant thus identified as  $R$  is found to be very large; nevertheless, the value  $P/R$  lies in the normal range of intensities. If, however, the identification were interchanged, the extrapolated intensities for vanishing self-quenching would be far too large and would in some cases give an energy larger than the energy absorbed. Therefore in a considerable number of cases our identification is certainly without ambiguity. Since now the values identified as  $Q$  (these are always the smaller ones) group around a certain value with relatively small variation when different solutes are put into the same solvent and  $Q$  is associated mainly with the solvent; it is felt that our identification is the correct one in all cases.

The values obtained for the parameters give some information about the magnitudes of the physical quantities occurring in the theory. Consider  $P/R$  which according to (7) depends only on the number of excited solvent electrons or perhaps mainly on those associated with the double bonds, and the ratio of  $\tau_i/\tau_e$ . If now the  $P/R$  ratios for a given solvent using different solutes are compared, the relative values of  $\tau_i/\tau_e$  for the different solutes may be obtained. And if the assumption that the number of effective excited electrons either is constant for a given mass or is proportional to the number of double bonds in that mass is valid, information may be gained about the dependence on the solvent of  $\tau_i/\tau_e$  by comparing the  $P/R$  values of a given solute in different solvents. The values for  $Q$  give the ratio between the internal quenching in the solvent and the probability of energy transfer (trapping) per unit concentration. For a given solvent they are surprisingly constant for different solutes, which indicates that the mechanism of energy transfer is essentially similar for all the solutes. For durene, which has a fair fluorescence within the solvents benzene and phenylcyclohexane but only a poor fluorescence with the other solvents, the explanation is certainly associated with the emission spectrum of this substance which extends relatively far into the ultraviolet. On the other hand, the values of  $Q$  looked upon as a function of the solvent show considerably more variation. Thus values of  $Q$  for cumene, *p*-cymene, and especially for dioxane are considerably greater with all solutes than they are for the other solvents listed in the tables. In some cases the  $Q$  values for a solute in *p*-dioxane are as much as 10 times larger than for an example in benzene. This indicates that the internal quenching ( $1/\tau_q$ ) of this solvent is larger than for any of the others.

The  $P$  and  $R$  values are quite erratic and change considerably for the same solute in different solvents, sometimes by a factor of 5. If  $P$  and  $R$  are considered as a function of the solute, however, the variations are very much larger (in some cases they vary by a factor of 500). This indicates that these parameters are chiefly a property of the solute which is, however, to some extent influenced by the solvent. These strong changes from solute to solute are due mainly to variations in the

self-quenching coefficient  $\beta$ ; without a detailed theory of self-quenching, however, no conclusions can be made about these variations. According to Eq. (3)  $P$  depends upon  $\eta_e$ ,  $\beta$ , and  $\tau_e$ . Now  $\eta_e$  does not change very much, as can be seen from the  $P/R$  values;  $\tau_e$  can be evaluated theoretically<sup>6</sup> and certainly does not change so drastically as  $P$ . Thus the large variation in  $P$  must be attributed to variations in  $\beta$ .

There is another source of information on the magnitudes of  $\tau_e$  and  $\tau_i$ . This is the measurement of the decay time  $\tau$  of the light flashes which is given for dilute solutions and organic crystals by

$$1/\tau = (1/\tau_i) + (1/\tau_e). \quad (8)$$

These lifetimes  $\tau$  have been measured to be of the order of 3 to  $5 \times 10^{-9}$  sec for the solutions; for crystals the lifetimes are mostly considerably longer.<sup>7,8</sup> If now the lifetime and the relative light emission [proportional to  $1/(1 + \tau_e/\tau_i)$ ] are known the time constants  $\tau_i$  and  $\tau_e$  can be individually evaluated. In an anthracene crystal, the absolute efficiency of converting the absorbed gamma-ray energy into light is so high that the internal quenching must be small, which means that  $\tau_i$  may be assumed to be probably larger than or about the same as  $\tau_e$ . For the best solutes it may then be assumed that  $\tau_i$  is also about the same as  $\tau_e$  since their efficiencies in certain solutions are close to that of anthracene. The measurements of  $\tau$  for crystals then indicate that in the crystal both  $\tau_i$  and  $\tau_e$  are greater than for solutions, since  $1/\tau$  is smaller and essentially determined in such a case by  $1/\tau_e$ . For  $\tau_i$  such an increase in crystals seems reasonable because the smaller interaction between neighboring molecules will most likely have the effect of decreasing the internal quenching. The fact that  $\tau_e$  is larger in a crystal than for the relatively isolated solute molecules in a dilute solution shows that this emission time is prolonged in crystals, probably because of interference of the excited wave functions. Another suggestion that  $\tau_e$  may be larger for crystals is obtained from considering the fluorescent emission of a naphthalene crystal excited by gamma-rays. Its efficiency is about  $\frac{1}{3}$  that of anthracene, but the decay time is 3 times as long. This means that the observed  $\tau$  is given practically by  $\tau_i$  and is of the order of  $6 \times 10^{-8}$  sec<sup>8</sup> and that  $\tau_e$  as calculated from the smaller efficiency is of the order of  $1 \times 10^{-7}$  sec; whereas for the best solution (terphenyl in phenylcyclohexane)  $\tau_e$  is of the order of  $5 \times 10^{-9}$  sec. This may indicate that perhaps in perfect crystals  $\tau_e$  would tend to still higher values and only the distortions in the lattice produce these smaller lifetimes of  $1 \times 10^{-7}$  sec in naphthalene and  $2 \times 10^{-8}$  sec in anthracene.

<sup>6</sup> R. S. Mulliken, *J. Chem. Phys.* **7**, 14, 121 (1939).

<sup>7</sup> G. B. Collins, *Phys. Rev.* **74**, 1543 (1948); C. G. Kelley and M. Goodrich, *Phys. Rev.* **77**, 138 (1950); R. F. Post and N. S. Shiren, *Phys. Rev.* **78**, 80 (1950).

<sup>8</sup> See Annual Report (May 1951) of U. S. Signal Corps, Contract No. DA 36-039 sc-35; these measurements were made by L. Bittman.

TABLE XI. (*P/R*) values for same mass/or same number of double bonds per gram.<sup>a</sup>

Gamma-excitation:	Benzene	Cumene	Cymene	Dioxane	Phenetole	Phenyl cyclohexane	Phenyl ether	Toluene	Xylene
Anthracene	24	20	28	19	29	30	20	27	35
	24	31	48	—	45	62	22	32	48
Anthranilic acid	47	53	50	33	59	72	55	58	66
	47	82	86	—	92	148	60	68	90
Diphenylbutadiene	24	42	48	8	28	58	41	37	57
	24	65	83	—	44	119	45	44	78
Diphenylhexatriene	63	71	75	31	86	153	101	77	104
	63	109	129	—	135	310	110	91	142
Durene	26	...	...	...	...	42	...	...	...
	26					86			
Fluoranthene	21	26	26	20	20	26	27	23	24
	21	40	45	—	31	53	30	27	33
Methyl <i>p</i> -aminobenzoate	30	27	27	11	23	35	24	54	46
	30	42	47	—	36	72	26	64	63
Methylanthranilic acid	32	35	40	39	45	46	39	30	61
	32	54	69	—	70	94	43	35	83
Phenyl $\alpha$ -naphthylamine	73	77	57	50	82	111	92	87	93
	73	119	98	—	128	228	101	103	127
<i>p</i> -Terphenyl	139	121	145	119	112	182	144	171	177
	139	187	250	—	175	374	157	202	241
Alpha-excitation:									
Anthracene	13	14	21	11	17	20	22	16	22
	13	22	36	—	27	41	24	19	30
Anthranilic acid	27	33	36	17	32	50	39	26	32
	27	51	62	—	50	103	43	31	44
Diphenylbutadiene	19	30	36	7	23	47	28	22	38
	19	46	62	—	36	97	31	26	52
Diphenylhexatriene	28	46	43	10	49	80	61	36	48
	28	71	74	—	77	164	67	42	65
Durene	15	...	...	...	...	25	...	...	...
	15					51			
Fluoranthene	15	16	16	9	11	19	21	15	16
	15	25	28	—	17	39	23	18	22
Methyl <i>p</i> -aminobenzoate	19	22	21	8	20	37	29	18	29
	19	34	36	—	31	76	32	21	40
Methylanthranilic acid	20	22	24	21	30	23	20	37	29
	20	34	41	—	47	47	22	44	40
Phenyl $\alpha$ -naphthylamine	45	49	35	24	45	100	76	50	64
	45	76	60	—	70	206	83	59	87
<i>p</i> -Terphenyl	128	130	109	54	105	160	132	125	135
	128	200	188	—	164	330	144	147	184

<sup>a</sup> Relative to the number of double bonds per gram of anthracene.



Considering now the solutions, the lifetimes in these are mostly given by  $\tau_i$  if the solution is not of the highest efficiency. (Though in the case of *p*-terphenyl solutions the measured  $\tau$  may be practically given by  $\tau_e$ .) It would be interesting if such an effect of decreasing lifetimes in the less efficient solutions could be observed. The lifetime of emission can be roughly calculated from theory or obtained from the absorption coefficients of these solute molecules in different solvents. The absorption coefficients increase in some instances nearly linearly with the number of double bonds,<sup>9</sup> and thus the lifetime  $\tau_e$  decreases with the increasing number of double bonds.

If the  $P/R$  values are now considered more fully (Table XI), some further information about  $\tau_e/\tau_i$  may be obtained. Thus for different solutes in a given solvent, a strong variation is found which indicates that  $\tau_e/\tau_i$ , which is essentially the internal quenching, is smallest for terphenyl, phenyl  $\alpha$ -naphthylamine, and diphenylhexatriene; but for anthracene solutions it is relatively large, although in the anthracene crystal,  $\tau_e/\tau_i$  must be small as is shown by the large light emission. If, instead, the  $P/R$  values for the same solute but varying solvents are considered, it is found that in some cases they are quite similar; however, in others there are noticeable differences in this ratio. Thus, for instance, the  $P/R$  values of terphenyl in different solvents for gamma-ray excitation are rather constant, whereas those for diphenylhexatriene are not. If the ratios for terphenyl and diphenylhexatriene are formed, it is found that in benzene it is 2.2, in phenylcyclohexane it is 1.2, in phenyl ether it is 1.4, in xylene 1.7, and in *p*-dioxane 3.8. This shows clearly that the internal quenching depends to some extent on the solvent. It may be emphasized that in this respect *p*-dioxane always behaved somewhat erratically, as can be seen for instance by comparing the values for diphenylbutadiene in benzene, dioxane, and phenylcyclohexane. A better insight into this situation could be obtained from the comparison of the  $P/R$  values for one solute in different solvents, but here the method of determining the variation of  $\eta_e$  from solvent to solvent is uncertain. The upper figures in Table XI are calculated by assuming that these numbers of excited electrons available for energy transfer are proportional to the mass of the solvent being excited. For the lower figures it is assumed that  $\eta_e$  is proportional to the number of double bonds per gram of solvent. This latter assumption was suggested by the observation that mostly dilute solutions with solvents containing double bonds exhibit large fluorescence under gamma excitation. There are solvents like hexane and paraffin oil with no double bonds which show some energy transfer, though very much smaller than the efficient solvents. The only exception found is *p*-dioxane, which is a rather efficient solvent though it contains no double bonds; it does, however, contain a ring structure.

<sup>9</sup> Hausser, Kuhn, and Seitz, *Z. physik. Chem.* **B29**, 397 (1935).

On the assumption that double bonds are mostly responsible for the fluorescence, the values of Table XI show that  $\tau_e/\tau_i$  changes by a factor of 5 between different solvents. From a theoretical point of view one would assume that this change comes about by a change of  $\tau_i$  and not  $\tau_e$ . One could try to go still further and assume that the light emission of the most efficient solution, namely, *p*-terphenyl in phenylcyclohexane, is practically unquenched. In such a case  $\tau_e$  would be identical with the  $\tau$  measured from the decay of light flashes to be  $4 \times 10^{-9}$  sec. Once  $\tau_e$  is determined,  $\tau_i$  can be calculated for other substances from the  $P/R$  values in the table by assuming that  $\eta_e$  is proportional to either the mass or the double bonds and evaluating the relative values of  $\tau_e$  for the other substances from known absorption coefficients. Such a method of treatment could most easily be accomplished if  $P/R$  values in chemically similar molecules are considered; as for example, in the series of diphenylpolyenes consisting of stilbene, diphenylbutadiene, diphenylhexatriene, and diphenyloctatetraene. In this series  $\tau_e$  decreases with increasing number of double bonds fairly linearly,<sup>9</sup> and the  $P/R$  values and thus  $\tau_i/\tau_e$  increase with the number of double bonds in the line up to three; then  $\tau_i/\tau_e$  begins to decrease (diphenyloctatetraene is worse than diphenylhexatriene). It is therefore concluded that for larger numbers of double bonds the internal quenching is increased. A similar conclusion can be made by considering the series benzene, naphthalene, anthracene, and naphthacene; and the series benzene, diphenyl, terphenyl, and quaterphenyl. Again, in these series the  $\tau_e$  decreases with the number of double bonds, but the  $P/R$  values increase up to three rings and then decrease. (The measurements show that for quaterphenyl and naphthacene  $I_{\max}$  are definitely smaller than for terphenyl and anthracene, respectively, though the actual  $P/R$  values have not been calculated.) This is only a tentative preliminary approach to unveil the underlying processes, and it is to be noted that for crystals such a relationship does not hold, since, for example, solid stilbene is considerably better for high energy fluorescence than diphenylhexatriene.

These conclusions with respect to internal quenching could be checked by optical measurements if the absolute quantum efficiency of these solute materials when optically excited were determined. Up to now there is only a small amount known in this field.<sup>10</sup> Some of our measurements on absorption inside of the solution further support the above conclusions. For instance, small amounts of anthracene are found to absorb the *p*-terphenyl radiation and then quench it; this occurs because the internal quenching of anthracene in xylene is much higher than that of *p*-terphenyl. Diphenylhexatriene, which also absorbs the terphenyl radiation, however, quenches the radiation energy from the terphenyl molecules only slightly, especially in phenyl-

<sup>10</sup> P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949).

cyclohexane, in agreement with the results that the  $P/R$  values of diphenylhexatriene in phenylcyclohexane are close to those of terphenyl. If the above mentioned optical experiments could be performed, they would provide another method of determining  $\tau_i/\tau_e$ , and then it would be possible to determine the relative  $\eta_e$  values from our  $P/R$  values.

If the relative physical efficiencies (essentially maximum intensities) are looked at, the influence of  $Q$  is also present [see Eq. (5)]. However, the variations of these values stem in many instances mostly from changes in  $P/R$ . For example, the difference between the efficiencies of diphenylhexatriene in benzene and xylene come mainly from the smaller internal quenching of this substance in xylene. There is another outstanding effect which may be noted: it is the fluorescent behavior of *p*-, *m*-, and *o*-terphenyl solutions. Of these *p*-terphenyl is the most efficient, *m*-terphenyl has a relative physical efficiency compared to *p*-terphenyl of about 40 percent and *o*-terphenyl has practically zero efficiency. These differences are most probably due to an increase of internal quenching from *p* to *m* to *o*, since all three molecules have essentially the same absorption coefficient and thus the same  $\tau_e$ , and the self-quenching is less in *m* and probably *o*-terphenyl. It may be that this change in internal quenching is correlated with the change in angular orientation of the benzene rings; in *p*-terphenyl the rings lie in a straight line in one plane while in *m*- and *o*- there is a successive increase in angle with this line and the rings are not situated in the same plane.

If analogous considerations are made for the  $P$ ,  $Q$ , and  $R$  parameters with alpha-particle excitation, many similarities (though some differences) are found in the relative behavior of the different solutions. Thus, for instance, if the  $P/R$  values for a certain solution are arbitrarily set equal for alpha-particle and gamma-ray excitation, all the others essentially coincide; whereas the  $Q$  and  $R$  values are both increased in almost all cases, the  $R$  values showing greater relative increases in most instances. Some deviations from this latter rule appear to be the result of detrimental changes in solvent properties produced by chemical reaction of the solvents with the air.

The most notable feature of the alpha-particle experiments is, however, the lower efficiency of the conversion of the absorbed energy into light emission by a factor

of certainly more than 10. The explanation for this smaller efficiency is believed to lie in the much higher density of excitation with the alpha-particles. Inside the channel where an alpha-particle excites the solvent, the density of excited solvent molecules is so high (of the order of  $10^{20}$  molecules/cm<sup>3</sup>) that there exists a high probability that one excited molecule "collides" with another excited molecule before the energy transfer (described above) or light emission has occurred. If one assumes that each such collision leads to a quenching of excitation energy, then the strong decrease in the alpha-particle excited efficiency compared to that of gamma-rays can be understood, not only for the solutions but also for organic crystals where a similar decrease in alpha-particle efficiency is found. In the crystals the interaction between two excited molecules may come about by means of a migration of the excitation energy through the crystal; in the solutions, in addition to such a migration of excitation energy, the motion of the excited molecules may be important. See also reference 1. The question now arises as to the reason why this large quenching does not show up so strongly in the  $Q$  values because of changes in the  $1/\tau_q$  values. The answer lies in the fact that the strong quenching coefficient produced by the high excitation density of a single alpha-particle is a function of time, and thus quenching decreases progressively with the decrease of the density of the excited molecules. After most of the excited molecules have decayed, the quenching coefficient becomes quite normal and only comparatively slightly increased compared to gammas.

The fact that the  $R$  values are also increased can perhaps be explained as follows: The  $R$  values give the ratio between the internal quenching and light emission probabilities, and the self-quenching coefficient. Since the  $\tau_i/\tau_e$  values are not changed very much, as can be concluded from the small change in the relative  $P/R$  values for  $\alpha$ -particles as compared to gamma-rays, this change in  $R$  must be due to variations in self-quenching. Here the same considerations of the increased density of excitation may help in the understanding. The density of excitation, even after most of the excitation has decayed, is still high enough inside the channel<sup>10</sup> of excitation has decayed, is still high enough inside the channel of excitation so that many of the solute molecules are excited. Thus the number of unexcited solute molecules which are responsible for the self-quenching is decreased, and this shows up as an increase in  $R$ .