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Energy Transfer in Organic Phosphors*

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A quantitative theory is developed of the photofluorescence and scintillation properties of organic materials. On this theory the intermolecular energy transfer occurs by photon emission and absorption; the molecular emission spectrum extends continuously from the ionization energy E_I down to the strong fluorescence band normally observed; the emission of primary photons $\sim E_I$ is excited by ionizing radiations; and the subsequent scintillation process consists of a photon cascade, through the emission spectrum. The theory is in agreement with the experimental data on the photofluorescence and scintillations from pure and mixed crystals, and on the scintillations from solutions. It is shown that, because of self-absorption, many of the existing data refer only to the technical fluorescence properties, and a preliminary assessment is made of the molecular properties of the more important organic phosphors.

1. INTRODUCTION

VARIOUS studies[1] of the photofluorescence and scintillation properties of different organic phosphor systems—pure and mixed crystals, liquid and solid solutions—have shown clearly that the observed fluorescence emission generally occurs from molecules other than those initially excited by the incident radiation. Several alternative theories, notably "exciton migration"[2] and "sensitized fluorescence,"[3] have been proposed to account for this intermolecular energy transfer. These have been discussed elsewhere by the author,[1] and they have been shown inadequate to explain the full range of experimental data now available. In particular these theories postulate *strong* electronic coupling either between neighboring or distant molecules, while spectral and other data show clearly that such coupling in organic crystals is so *weak* that the electronic structure of a molecule is practically unperturbed by its environment. It has therefore been proposed by the author[1] that the intermolecular energy transfer occurs by the simple process of *photon emission and absorption*.

In this paper the photon theory is developed further, and compared with the experimental results. It is shown that many of the previous observations on the photofluorescence and scintillation properties of organic materials refer only to the *technical* properties of the materials. Such observations, made on relatively thick specimens, give little direct information about the true *molecular* fluorescence, due to the strong self-absorption which occurs.

2. PHOTOFLUORESCENCE OF MIXED CRYSTALS

We consider initially the photofluorescence of mixed organic crystals (e.g., anthracene in naphthalene, naphthacene in anthracene). On the photon emission and absorption theory, the processes listed in Table I occur in a mixed crystal containing solute molecules Y in a solvent of molecules X. It is assumed for simplicity and clarity that the incident radiation is absorbed entirely by X, and that X is transparent to the fluorescence emission of Y. These conditions correspond to those normally obtaining in relatively dilute solid solutions. Square brackets indicate concentrations in molecules/solvent molecule (i.e., $[X]=1$), X^* and Y^* represent molecules of X and Y with the excitation energy, and $k(=1/t)$ represents the probability of a process of decay time t.

The *molecular* quantum efficiency q_{0X} of fluorescence by X is given by

$$q_{0X}=\frac{1}{1+(k_{iX}/k_{fX})},\tag{1}$$

as a result of the competitive processes (2) and (3). The quantum efficiency of the *escape* of the fluorescence of X from the crystal, i.e., the *technical* fluorescence quantum efficiency, is given by

$$q_{eX}=\frac{q_{0X}}{1+(k_X/k_{eX})+(k_Y/k_{eX})[Y]}+\frac{k_X}{k_{eX}}\left(\frac{q_{0X}}{1+(k_X/k_{eX})+(k_Y/k_{eX})[Y]}\right)^2+\left(\frac{k_X}{k_{eX}}\right)^2\left(\frac{q_{0X}}{1+(k_X/k_{eX})+(k_Y/k_{eX})[Y]}\right)^3+\cdots\tag{2}$$

$$=\frac{q_{0X}}{1+(1-q_{0X})(k_X/k_{eX})+(k_Y/k_{eX})[Y]}\tag{3}$$

due to the competitive processes (2), (3), (4), (5), and (9). Terms 1, 2, 3, $\cdots$ in (2) represent the escape of light from the crystal after 1, 2, 3, $\cdots$ molecular emissions.

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[1] J. B. Birks, *Scintillation Counters* (Pergamon Press, London; McGraw-Hill Book Company, Inc., New York, 1953).

[2] Bowen, Mikiewicz, and Smith, Proc. Phys. Soc. (London) **A62**, 26 (1949).

[3] J. Franck and R. Livingston, Revs. Modern Phys. **21**, 505 (1949).

TABLE I. Photon transfer processes.

Process	Relative rate	Description of process
1. $X+h\nu\rightarrow X^*$	1	Excitation by light
2. $X^*\rightarrow X+h\nu_X$	$k_{fX}[X^*]$	Fluorescence of X
3. $X^*\rightarrow X$	$k_{iX}[X^*]$	Internal quenching of X
4. $X+h\nu_X\rightarrow X^*$	$k_X k_{fX}[X^*]$	Self-absorption of X
5. $Y+h\nu_X\rightarrow Y^*$	$k_Y k_{fX}[X^*][Y]$	Absorption of Y
6. $Y^*\rightarrow Y+h\nu_Y$	$k_{fY}[Y^*]$	Fluorescence of Y
7. $Y^*\rightarrow Y$	$k_{iY}[Y^*]$	Internal quenching of Y
8. $Y+h\nu_Y\rightarrow Y^*$	$k_Y' k_{fY}[Y^*][Y]$	Self-absorption of Y
9. $h\nu_X\rightarrow$	$k_{eX} k_{fX}[X^*]$	Escape of $h\nu_X$
10. $h\nu_Y\rightarrow$	$k_{eY} k_{fY}[Y^*]$	Escape of $h\nu_Y$

In these relations (k_{iX}/k_{fX}) describes the internal quenching, which reduces the molecular quantum efficiency q_{0X} below unity. $(1-q_{0X})(k_X/k_{eX})$ represents the effect of self-absorption of X, which together with the internal quenching produces "self-quenching." $(k_Y/k_{eX})[Y]$ describes the relative probability of photon capture by Y, i.e., energy transfer from X to Y. In the absence of internal quenching $q_{0X}=1$, and (3) becomes

$$q_{eX}=\frac{1}{1+(k_Y[Y]/k_{eX})}. \tag{4}$$

The *molecular* fluorescence quantum efficiency q_{0Y} of Y is, similarly,

$$q_{0Y}=\frac{1}{1+(k_{iY}/k_{fY})}, \tag{5}$$

and the *technical* quantum efficiency q_{eY} of the escape of the fluorescence of Y is given by

$$q_{eY}=\frac{q_{eX}q_{0Y}(k_Y/k_{eX})[Y]}{1+(1-q_{0Y})(k_Y'/k_{eY})[Y]}. \tag{6}$$

(k_{iY}/k_{fY}) describes the internal quenching of Y. $(1-q_{0Y})(k_Y'/k_{eY})[Y]$ represents the effect of self-absorption, which together with the internal quenching produces "concentration quenching." In the absence of internal quenching, $q_{0X}=q_{0Y}=1$, and (6) becomes

$$q_{eY}=q_{eX}(k_Y/k_{eX})[Y]=1-q_{eX}. \tag{7}$$

The quantities k_{eX}, k_X, and $k_Y[Y]$ are not independent, but are related by

$$k_{eX}+k_X+k_Y[Y]=1. \tag{8}$$

Their magnitudes depend on the relative absorption coefficients of X and Y for the fluorescence of X, and on the size of the crystal. For a pure crystal ($[Y]=0$) of anthracene of thickness $\geqslant 1$ mm, values of $k_{eX}=0.2$, $k_X=0.8$ have been obtained from spectral measurements,[4] and similar observations on thick naphthalene crystals indicate that k_{eX} is even smaller for this material. The effect of this self-absorption of X is to increase the "energy transfer" parameter (k_Y/k_{eX}), since the molecules of Y may absorb not only the primary emission of X, but subsequent re-emissions following self-absorption. The observations of Bowen *et al.*[2] that the transfer effect disappears when the mixed crystals are dissolved in benzene are readily explained, since the effective concentration of Y for photon absorption should now be expressed in molecules/*benzene* molecule, so that $[Y]\rightarrow 0$ and $k_{eX}\rightarrow 1$.

A further factor contributing to the efficient $(X\rightarrow Y)$ energy transfer in the crystal is the directional alignment of the molecules of X and Y, and of the polarizations of the emission of X and the absorption of Y.[1] If the molecular alignment is destroyed, as in homogeneous mixed sols of X and Y, the effective absorption coefficient of Y for the emission of X will be reduced due to the random molecular orientation, by a factor

$$f=\frac{\int_0^{\frac{1}{2}\pi}\int_0^{\frac{1}{2}\pi}\cos^2\theta\,\cos^2\phi\, d\theta d\phi}{\int_0^{\frac{1}{2}\pi}\int_0^{\frac{1}{2}\pi} d\theta d\phi}=0.25, \tag{9}$$

relative to that for alignment of Y parallel to X. Bowen and Mikiewicz[5] have measured the intensities of the two fluorescence components L_X and L_Y for anthracene-naphthacene crystals, and for homogeneous anthracene-naphthacene sols. They find that $L_X=L_Y$ at a concentration of $\sim 1.8\times 10^{-5}$ g naphthacene/g anthracene in the crystals, and at a concentration of $\sim 9\times 10^{-5}$ g/g in the sols, giving $f\sim 0.2$ in agreement with (9).

The equations obtained on the photon theory are in general agreement with the available experimental data on mixed organic crystals[2,6,7] though further observations on the effect of crystal size are desirable. The theory gives a clear physical interpretation of the processes of "resonance energy transfer," self-quenching, and concentration quenching, for which several more complex and less satisfactory mechanisms have been proposed.[2,3,6–10]

3. SCINTILLATIONS FROM MIXED CRYSTALS AND SOLUTIONS

An extension of the photon theory has been proposed by the author[1] in considering the excitation of the fluorescence by ionizing radiation, i.e., scintillations. It is proposed that the ionization and excitation of the molecules by the ionizing particle cause the emission of photons whose energy is $\sim$ the molecular ionization energy. This primary photon emission is discussed in more detail later. The absorption coefficient for these

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

[5] E. J. Bowen and E. Mikiewicz, Nature **159**, 706 (1947).

[6] G. T. Wright, Ph.D. thesis, University of Birmingham, 1952 (unpublished).

[7] G. T. Wright, Proc. Phys. Soc. (London) **A66**, 777 (1953).

[8] P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, New York, 1949).

[9] H. Kallmann and M. Furst, Phys. Rev. **79**, 857 (1950).

[10] H. Kallmann and M. Furst, Phys. Rev. **81** 853 (1951).

primary photons is relatively low (molar extinction coefficient $\epsilon \sim 10^2$) and they are reabsorbed at $\sim 10^4$ molecular distances from the ionization column.

In a mixed crystal, or in a liquid solution of Y in a solvent X, the primary photons will excite the photofluorescence of X and Y. If p primary photons are produced and are completely absorbed within the phosphor, the number of fluorescence photons $h\nu_X$, $h\nu_Y$ escaping are given by pq_{eX} and pq_{eY}, respectively. Hence for mixed crystals it is to be expected that the relative intensities of the two fluorescence components will be independent of the manner of excitation. This has been confirmed experimentally for naphthalene-anthracene crystals by Wright[6,7] who compared the fluorescence excited by α rays and by 254-mμ ultraviolet radiation, and by the author,[1] who has compared the fluorescence excited by α rays and by the internal conversion electrons from In^{114}. In each case the ratio of the intensities of the naphthalene and anthracene components was found to be independent of the mode of excitation.

For liquid organic solution phosphors pq_{eX}, the solvent fluorescence, is small because of strong self-absorption and internal quenching. The solute fluorescence, which is observed, is given by

$$L_Y = pq_{eY} = \frac{pq_{0X}q_{0Y}(k_Y/k_{eX})[Y]}{[1+(1-q_{0X})(k_X/k_{eX})+(k_Y/k_{eX})[Y]][1+(1-q_{0Y})(k_Y'/k_{eY})[Y]]} \tag{10}$$

$$= \frac{P[Y]}{(Q+[Y])(R+[Y])}, \tag{11}$$

where P, Q, and R are parameters depending on the mode of excitation, and on the properties of the solvent and solution. Equation (11) is the empirical equation found by Furst and Kallman[11] to be in excellent agreement with their experimental observations on the dependence of relative scintillation efficiency L_Y on concentration $[Y]$ for a wide range of organic solutions, excited by γ rays or by α rays.

It should be noted however that (10) is derived from (6), which is based on the initial postulate that the incident radiations, in this case the p primary photons, are absorbed entirely by the solvent molecules X. If the absorption coefficient of Y for the primary photons is high compared with that of X, direct excitation of Y by the primary photons will also occur. It may be readily shown by a similar analysis to that in Sec. 2, that the additional fluorescence component is also of the form

$$L_Y' = \frac{P'[Y]}{(Q'+[Y])(R'+[Y])}, \tag{12}$$

the first term in the denominator representing the competition between absorption by X and by Y, and the second term the competition between concentration quenching and the escape of the fluorescence emission.

All the efficient solvents used (e.g., xylene, toluene, benzene) possess molecules which fluoresce in dilute solution, although this fluorescence is not normally observed from the bulk liquid due to "self-quenching." This association of solvent molecular fluorescence with scintillation efficiency suggests that the main process in liquid phosphors is the initial excitation of the solvent molecules leading to fluorescence emission, which is absorbed and re-emitted by the solute molecules, as described by (10) and (11). The much lower scintillation efficiency[9] of solutions of terphenyl in "nonfluorescent" solvents (paraffin oil, hexane, etc.) is attributable to the fact that the solute fluorescence will only be excited directly by primary photon absorption, as described by (12). Since the scintillation efficiency of terphenyl in a nonfluorescent solvent is only about 15 percent of that from a terphenyl solution in a fluorescent solvent, it appears that about 85 percent of the solute emission in the latter case is excited by the solvent emission. The alternative possibility, that the differences between the two classes of solvent are due to differences in the primary photon emission efficiency (which may be associated with the fluorescence efficiency) and in the absorption coefficients for these primary photons [P' and Q' in (12)], cannot however be discarded on the existing experimental evidence.

4. PHOTOFLUORESCENCE OF PURE CRYSTALS

In pure crystal phosphors only processes (1), (2), (3), (4), and (9) in Table I are operative. The molecular quantum efficiency q_0 (suffix X will be omitted since only one molecular species is present) is given by (1) as before, but the technical quantum efficiency q_e from (2) becomes

$$q_e = \frac{q_0}{1+(1-q_0)(k/k_e)} = \frac{1}{1+(k_i/k_ek_f)}, \tag{13}$$

since $(k+k_e)=1$.

In the absence of internal quenching, the molecular photofluorescence decay time $(t_f)_{00} = 1/k_f$. Due to internal quenching, the actual *molecular* decay time $(t_f)_0$ is reduced to

$$(t_f)_0 = \frac{(t_f)_{00}}{1+[(t_f)_{00}/t_i]} = q_0(t_f)_{00}. \tag{14}$$

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[11] M. Furst and H. Kallmann, Phys. Rev. **85**, 816 (1952).

The *technical* photofluorescence decay time t_f of a thick crystal is increased,[4] due to the self-absorption, to

$$t_f=\frac{(t_f)_{00}}{k_e+[(t_f)_{00}/t_i]}. \tag{15}$$

If the internal quenching is small, i.e., $(t_f)_{00}\ll t_i$, then (15) and (13) may be approximated to

$$t_f=n(t_f)_0, \tag{16}$$

$$q_e=(q_0)^n, \tag{17}$$

where

$$n=1/k_e \tag{18}$$

represents the average number of molecular fluorescence emissions of decay time $(t_f)_0$, quantum efficiency q_0, that occur prior to the escape of the fluorescence from the crystal. These approximate relations provide a simple physical model of the photon cascade process that occurs.

For anthracene at room temperature, values of $q_0=0.9$ and $(t_f)_0=3.5\pm1.0$ mμ sec have been observed for microcrystalline specimens, $t_f=14\pm2$ mμ sec has been measured for a thick crystal, and $k_e=0.2$ has been obtained from the ratio of the areas under the thick crystal (technical) and micro-crystalline (molecular) fluorescence spectra.[4] Substitution in (13)–(15) gives $(t_f)_{00}=3.9\pm1.2$ mμ sec, $t_i=35\pm10$ mμ sec, $q_e=0.58$ and $t_f=12.6\pm3.5$ mμ sec, this last value agreeing within the experimental error with that observed directly. The approximate Eqs. (16)–(18) give $n=5$, $t_f=17.5\pm5.0$ mμ sec and $q_e=0.59$.

The photofluorescence quantum efficiency q_0 is practically independent of the excitation wavelength down to at least 250 mμ, i.e., into the second and higher electronic absorption bands. This effect has been interpreted previously[8] as due to internal conversion with 100 percent efficiency from the higher electronic states into the first electronic excited state, from which the observed emission occurs. This explanation is not completely satisfactory, since it fails to explain why the absorption from the ground state into the higher electronic states should be highly "allowed" ($\epsilon\sim10^4-10^5$) while the reverse transition, corresponding to emission, should be completely "forbidden." The photon theory suggests a simple alternative description of the effect. Fluorescence emission from these higher electronic states may occur with an ultra-short decay time $\sim10^{-11}$ sec, since the oscillator strengths are $\sim10^2-10^3$ that of the normal photofluorescence emission corresponding to the 1st electronic absorption band ($\epsilon\sim10^2$). The internal quenching will be negligible, owing to the very short lifetime of the excited state compared with $t_i\sim35$ mμ sec, and the quantum efficiency will be practically 100 percent. Such emitted photons will be very strongly reabsorbed by neighboring molecules, and after several repetitions of the process, during which thermal degradation of the excess energy occurs, the normal fluorescence from the 1st excited state will be observed.

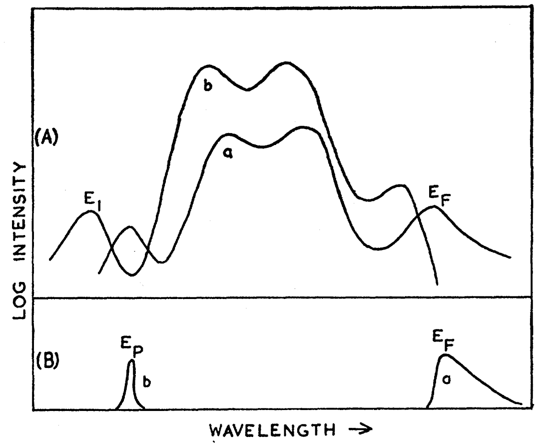

FIG. 1 (A). Molecular spectrum; (*a*) fluorescence, (*b*) absorption. (B). Technical fluorescence spectrum of crystal of a few μ thickness; (*a*) normal emission, (*b*) primary photon emission.

It is proposed therefore that the *complete* molecular fluorescence spectrum corresponds to the *complete* absorption spectrum, and not just to the first electronic band, which is all that has been observed previously. This failure to observe the complete emission spectrum may be due to various causes: (a) the use of relatively thick crystals or solutions, (b) inadequate exposure times or detection sensitivity, and (c) excitation of the fluorescence by irradiation in the first electronic absorption band (e.g., by 365-mμ radiation). Each emission band would be expected to be approximately the mirror image of the corresponding absorption band, but with its maximum intensity shifted by about 50 mμ towards longer wavelengths. A schematic diagram of the proposed *molecular* fluorescence and absorption spectrum is shown in Fig. 1(A). Both spectra extend from about the molecular ionization energy E_I down to the energy E_F of the first electronic transition. Measurements on the molecular spectra of microcrystalline fluorescent organic compounds are in progress in the author's laboratory.

Because of the overlap of the molecular absorption and emission spectra, the *technical* fluorescence from a relatively thick specimen ($>1\mu$) will only be observed in spectral regions of low absorption. Apart from the region near E_F, where the normal technical fluorescence is observed, there is a further region of low absorption ($\epsilon\leqslant10^2$) in the vacuum ultraviolet[12] near E_I. Photons emitted in this region have a relatively long mean free path $\sim7\mu$ in the crystal, so that when near the crystal surface they are able to escape without reabsorption. These are the primary photons of energy E_P, whose emission is excited by ionizing radiation, according to the theory.[1] The decrease of specific fluorescence near the phosphor surface[13] is attributed to the escape of the primary photons.[14,1] The *technical* fluorescence spectrum

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[12] H. B. Klevens and J. R. Platt, J. Chem. Phys. **17**, 470 (1949).

[13] J. W. King and J. B. Birks, Phys. Rev. **86**, 568 (1952).

[14] J. B. Birks, Phys. Rev. **86**, 569 (1952).

of a crystal a few microns thick is shown schematically in Fig. 1(B). It will be noted that there are *two* main regions of emission, E_P and E_F.

5. SCINTILLATIONS FROM PURE CRYSTALS

In a thicker crystal, excited by ionizing radiation, the emission E_P is unable to escape. The scintillation process corresponds to the reabsorption of the primary photons E_P, followed by a cascade of photon emissions and absorptions, culminating in the normal emission E_F which ultimately escapes from the crystal. For excitation by fast electrons, the ion pairs are produced ~100 molecular distances apart, so that quenching in the ionization column is negligible. Under these conditions the decay of the scintillation pulses has been observed to be exponential and of technical scintillation decay time t_I. We may therefore, by analogy with the previous photofluorescence results, take

$$t_I = t_P + t_f, \tag{19}$$

where t_f is the technical photofluorescence decay time, and t_P the technical decay time of the primary photon emission. The decay times of the emission in the intermediate region of high absorption are negligible, compared with t_f and t_P. Liebson, Bishop, and Elliot[15] have measured t_I for γ-ray excitation and for several organic phosphors, and they find in general that $t_I > t_f$ in accordance with (19). Typical values of t_f and t_P obtained from their results, using (19), are listed in Table II.

It is seen that in general $t_P \sim t_f$. It is of importance to note that t_P is a property of the phosphor, similar to t_f. This suggests strongly that the primary photon emission is not due simply to ion recombination, which should take about the same time in similar organic materials, but that it is due to a definite electronic transition of the molecule, as proposed above. The similarity of t_P and t_f is attributable to the similarity of the extinction coefficients and oscillator strengths of the absorption bands E_P and E_F associated with the two transitions. We may therefore take as a working approximation, that

$$(t_P)_0 = (t_f)_0, \tag{20}$$

where $(t_P)_0$ is the molecular decay time of the primary photon emission. Hence, provided t_i, the internal quenching decay time, does not differ appreciably for the two excited states, corresponding to E_P and E_F, the molecular quantum efficiency of the primary photon emission will also be equal to q_0.

By analogy with (16),

$$t_I = m(t_f)_0, \tag{21}$$

where m is the average number of photon emissions of molecular decay time $(t_f)_0$, molecular quantum efficiency q_0, occurring in the photon cascade. Hence the technical scintillation quantum efficiency is

$$q_I = (q_0)^m, \tag{22}$$

expressed as the number of escaping fluorescence photons per initial primary photon.

TABLE II. Decay time components.

	Anthracene	Carbazole	Stilbene	Quaterphenyl	Diphenyl-acetylene
t_f ($m\mu$ sec)	17	7	3.1	3.8	2.5
t_P ($m\mu$ sec)	13	6	4.9	3.2	1.5

The energy expenditure per ion pair in gaseous organic materials (e.g., ethylene, methane) is $E_z = 30$ ev/ion pair. It is a reasonable assumption that one primary photon is produced per ion pair (in the absence of quenching in the ionization column) so that $E_z = 30$ ev/primary photon. These primary photons are absorbed and ultimately emitted as the technical fluorescence emission, of mean photon energy E_F, with an over-all technical quantum efficiency of q_I. Hence for excitation by radiation of low specific ionization the over-all technical energy conversion efficiency,

$$C_{IF} = E_F q_I / E_z. \tag{23}$$

Expressed alternatively, the energy expenditure per emitted photon is

$$E_{IF} = E_z / q_I. \tag{24}$$

6. DISCUSSION OF THE ORGANIC PHOSPHORS

For anthracene crystals at room temperature, values of $t_I = 27$ $m\mu$ sec, $(t_f)_0 = 3.5$ $m\mu$ sec and $q_0 = 0.9$ have been observed. Hence from (21) and (22), $m = 7.7$ and $q_I = 0.44$. The mean wavelength[16,17] of the technical emission spectrum is 469 $m\mu$, corresponding to a mean photon energy $E_F = 2.65$ ev. Hence from (23) and (24), $C_{IF} = 4.0$ percent, $E_{IF} = 68$ ev/photon. This value for the absolute scintillation efficiency of anthracene at room temperature is in excellent agreement with the experimental values of 65 ev/photon measured by Harrison,[17] and of 70.5 ev/photon measured by Birks and Szendrei.[16]

The technical scintillation efficiency q_I is increased by reducing the crystal thickness. For anthracene microcrystals m tends to 2, corresponding to one primary photon emission and one photofluorescence emission, and E_{IF} tends to a lower limit of 36 ev/photon. Because of the surface escape of primary photons this optimum efficiency cannot be attained, but thin anthracene flakes have a higher scintillation efficiency than thick crystals, tending towards this value. The effect has been observed in this laboratory.

Reduction of the temperature also causes an increase in q_I due to (a) the reduced overlap of the absorption and emission spectra, giving a decrease in m, and (b) the decrease in the internal quenching so that q_0

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[15] Liebson, Bishop, and Elliot, Phys. Rev. **80**, 907 (1950).

[16] J. B. Birks and M. E. Szendrei, Phys. Rev. **91**, 197 (1953).

[17] F. B. Harrison, Nucleonics **10**, No. 6, 40 (1952).

tends to unity, as the temperature approaches absolute zero. For thick anthracene crystals (a) is the major effect, since q_0 only increases from 0.9 towards 1.0, while m decreases from 7.7 towards 2. Liebson[18] has observed that t_I for anthracene decreases by about 56 percent in cooling from 10°C to -70°C. Neglecting the small change in q_0, we obtain from (21) and (22) that at -70°C $m=4.3$, $q_I=0.64$, corresponding to a 44 percent increase over the scintillation efficiency at 10°C. Sangster[19] has observed directly that the scintillation efficiency increases by 40 percent in cooling over this temperature range.

Anthracene is the most efficient of the known organic scintillators at room temperature. It is of interest therefore to consider the reasons for the inferiority of the other organic phosphors. If we denote the properties of anthracene by $(q_I)_A$, $(q_0)_A$, and m_A, the other phosphors may be divided into 4 possible categories:

$$\text{(A)}\ q_0\sim(q_0)_A,\quad m>m_A,\quad q_I<(q_I)_A;$$
$$\text{(B)}\ q_0<(q_0)_A,\quad m<m_A,\quad q_I<(q_I)_A;$$
$$\text{(C)}\ q_0<(q_0)_A,\quad m>m_A,\quad q_I<(q_I)_A;$$
$$\text{(D)}\ q_0\sim(q_0)_A,\quad m<m_A,\quad q_I>(q_I)_A.$$

Examples of each of the first 3 categories are known. So far no organic members of the desirable category (D) have been identified, although sodium iodide (thallium) is an inorganic member of this class.

Naphthalene probably belongs to class (A). Taking $q_0=0.9$, $(t_f)_0=3.5$ mμ sec, by analogy with anthracene, and combining these with the experimental values of $t_I=80$ mμ sec and $E_F=3.6$ ev, we obtain $m=23$, $q_I=0.09$, $C_{IF}=1.0$ percent, and $E_{IF}=341$ ev/photon, in excellent agreement with the direct experimental value[17] of $E_{IF}=350$ ev/photon. The major difference between the technical and microcrystalline emission spectra of naphthalene, due to the self-absorption associated with the high value of m, has been observed.[20] It is to be expected that a major increase in q_I for naphthalene will be produced by reducing the thickness or the temperature. The former effect has been observed for naphthalene flakes by the author, and has previously been reported by Kallmann.[21] The temperature effect, which is pronounced, has been observed by Liebson.[18] At low temperatures the scintillation efficiency of naphthalene approaches that of anthracene.

Stilbene, terphenyl, diphenylacetylene, and quaterphenyl belong to class (B). The reduced overlap of the absorption and emission spectra $(m<m_A)$ accounts for their low scintillation decay time t_I of 6 to 10 mμ sec, since their molecular decay time $(t_f)_0$ is similar to anthracene.[4] Although the experimental data for stilbene are less comprehensive than for anthracene, they may be used to estimate the other properties of the material. Birks and Little[4] have observed $(t_f)_0=1.7$ mμ sec, $t_f=3.0$ mμ sec, and Post and Shiren[22] and Lundby[23] have observed $t_I=6.0$ mμ sec, so that $m\sim3.5$. Sangster[19] has observed that C_{IF} for stilbene at room temperature is 0.45 that of anthracene, giving $C_{IF}=1.8$ percent, and that the mean wavelength of the technical emission spectrum is 410 mμ, so that $E_F=3.0$ ev. These values substituted in the appropriate equations give $q_I\sim0.18$, $q_0\sim0.6$, $(t_f)_{00}\sim3$ mμ sec. Different values of t_I and C_{IF} have been reported by other observers, and it is hoped to obtain more accurate data by observations of the main parameters for single specimens. It is to be expected that the decay time and scintillation efficiency of stilbene would show a smaller variation with temperature than anthracene, due to the smaller value of m, and this has been observed experimentally.[18,19,22]

Terphenyl and diphenylacetylene have rather similar properties to stilbene, but data on $(t_f)_0$ are not yet available so that q_0 cannot be evaluated. Quaterphenyl is of interest, as C_{IF} is 0.83 that of anthracene, while t_I is only 8.5 mμ sec.[19] The very slight increase[19] of only 7 percent in C_{IF} in cooling from 30°C to -70°C suggests that the self-absorption is negligible, and hence the experimental value[15] of $t_f=3.8$ mμ sec may be taken as approximately equal to $(t_f)_0$. Hence $m\sim2.2$, $q_I\sim0.38$, giving $q_0\sim0.65$. If q_0 increases with molecular chain length while m remains small, then the higher compounds quinquephenyl and sexiphenyl may have a higher scintillation efficiencies than anthracene as suggested by Sangster,[19] and hence belong to category (D). The existing experimental evidence suggests, however, that at room temperature $q_0\sim0.6$ for the polyphenyl compounds, compared with $q_0\sim0.9$ for the polycyclic compounds like naphthalene and anthracene.

The following tentative allocations are suggested for other phosphors for which data on q_I and t_I are available:[19] phenanthrene (B), chrysene (C), pyrene (A), fluoranthene (C), or (A), fluorene (C), carbazole (B), diphenylene oxide (B), bibenzyl (B), diphenylbutadiene (B).

7. CONCLUSION

The discussion above, based on existing experimental data, represents a preliminary attempt to compare the *molecular* properties of the different compounds. Now that these can be differentiated from the technical data reported hitherto, it is hoped to correlate the fluorescence properties of the organic molecules with their π-electron configurations.

The molecular properties $(t_f)_0$ and q_0 can be obtained from measurements on microcrystalline specimens, and from these $(t_f)_{00}$ and t_i can be deduced. The technical photofluorescence properties t_f and q_e can be obtained

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from similar measurements on thick crystals, and by comparison with the molecular properties, $n=1/k_e$ can be found. n may also be determined from a comparison of the molecular and technical photofluorescence spectra. The technical scintillation properties t_I and q_I can also be observed directly, and the related quantities m, t_P, and $(t_P)_0$ deduced. The direct measurement of these latter parameters is difficult. An experimental investigation is in progress to determine the main properties of interest for a large group of related organic fluorescent compounds.

The photon cascade theory provides a quantitative description of the fluorescence and scintillation properties of organic phosphors which is in excellent agreement with experiment. When considered in conjunction with the other experimental data discussed elsewhere,[1] the results provide strong evidence of the validity of the photon theory of energy transfer.

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Moduli and Internal Friction of Magnetite as Affected by the Low-Temperature Transformation

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The low-temperature ordering transformation in magnetite is the source of large nonelastic effects. For example, Young's modulus for the ⟨111⟩ direction at 108°K is 30 percent lower than the value one would estimate from higher-temperature measurements; an internal friction peak occurs near 95°K. We have attributed the nonelastic effects to stress-induced ordering of Fe^{++} and Fe^{+++} among the octahedral sites in the lattice.

A SECOND-ORDER transformation with critical temperature near 115°K occurs in magnetite[1–14] and has been attributed to ordering[2,3] of Fe^{++} and Fe^{+++} among the octahedral sites of the magnetite structure (spinel type). The symmetry changes from cubic to orthorhombic on cooling.[5] In certain crystallographic directions this transformation, we find, is accompanied by large effects in the moduli and internal friction. Stress-induced ordering is proposed as the explanation.

For our measurements two rods were prepared from a natural occurring magnetite single crystal containing 20.7 percent Fe^{++} and, as an impurity, 1.2 percent Zn (stochiometric Fe_3O_4 has 24.2 percent Fe^{++}). The long direction of one rod was parallel to a ⟨100⟩ direction; the long direction of the other was parallel to a ⟨111⟩ direction. Young's modulus of ⟨111⟩ and ⟨100⟩, the torsion modulus of ⟨100⟩, and the internal friction in each case were determined as functions of temperature and external magnetic field by the resonant vibration method. Both electromagnetic[15,16] and piezoelectric[17,18] excitation and detection of vibrations were employed. The strain amplitudes were approximately 10^{-7}, the frequency range, 50 to 130 kc/sec.

DATA AND INTERPRETATION

The moduli of crystalline solids are expected to increase on cooling approaching asymptotically a maximum value at very low temperatures, provided there is no change of state and all of the strains are elastic. Magnetite has a transformation. Furthermore, two sources of nonelastic strain are probably present, stress-induced domain motion (magnetostriction)[19,20] and stress-induced ordering of Fe^{++} and Fe^{+++} among the octahedral sites. Thus, for a given applied stress (σ), the total strain (ϵ) is given by (1).

$$\epsilon=\epsilon_{\text{elastic}}+\epsilon_{\text{domain-motion}}+\epsilon_{\text{ordering}}=\epsilon_1+\epsilon_2+\epsilon_3. \tag{1}$$

The observed modulus,

$$M=\frac{\sigma}{\epsilon}=\frac{\sigma}{\epsilon_1+\epsilon_2+\epsilon_3}, \tag{2}$$

is thus less than the truly elastic value.

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