Luminescent Emission from an Organic Solid with Traps

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On the basis of a nearest-neighbor random-walk model for exciton propagation, we calculate the time-dependent luminescent emission from an organic phosphor containing exciton traps. For the situation in which the traps themselves also emit a characteristic luminescence, we also calculate the time dependence of that luminescence. The results agree qualitatively with recent measurements of the time dependence of the fluorescence of tetracene-doped anthracene; detailed comparison yields reasonable values for the lifetime of each phosphor and for the time the anthracene singlet exciton spends on one site. There is no need to postulate a long-range energy-transfer mechanism.

SOME years ago, it was shown[1] that experiments involving the presence of traps[2] in luminescent organic materials provide a tool for studying the mechanism of energy transfer in these materials. In that experiment,[3] the material was anthracene and the traps were different chemical species, detailed nature unknown, introduced by damaging the solid with high-energy radiation prior to the luminescence measurement. Experimental results were found to be consistent with a localized model for radiation damage and a random-walk model for energy transfer. However, detailed calculations for the integrated luminescent emission from an organic solid with traps on the basis of a random-walk model were not completed until recently.[4] Recently, Powell and Kepler[5] have reported an experiment similar in principle to that of SEA, but more sophisticated in two ways: (a) The traps, rather than an unknown chemical species, are themselves molecules with a characteristic luminescence, viz., tetracene, and (b) the time-resolved rather than integrated, luminescence of both substances was measured. In view of these experimental results, a calculation of the time-dependent luminescence from both the host molecules and the traps on the basis of a random-walk model seems worthwhile. (The "diffusion" model for energy transfer mentioned by PK and others may, of course, be considered an approximation to the random-walk model.)

The detailed model is as follows: There are two kinds of sites, ordinary or "host" (H), and a fraction q of "traps" (T). An incident photon is absorbed at a host site and excites it; after time τ the excitation energy is transferred to one of its nearest neighbors unless, with a constant probability α per step, it is first emitted as

luminescence. If the newly stepped-on site is a host site, the process repeats itself; if it is a trap, the walk stops and emission of a distinguishable luminescence occurs later, with a constant probability β per time of one step (i.e., with a probability β/τ per unit time).

We first calculate the probability of observing host luminescence at step n of the random walk. In the absence of traps, this would be $(1-\alpha)^{n-1}\alpha$ ($n-1$ non-emissions followed by one emission); with traps present it is

$$(1-\alpha)^{n-1}\alpha(1-q)^{V_n}, \tag{1}$$

where V_n is the number of distinct sites visited before step n, and the last factor, therefore, is the probability that none of the sites visited before step n be traps. A basic result of random-walk theory[6] states that[7]

$$V_n \rightarrow (1-F)n. \tag{2}$$

F, though mathematically an interesting quantity, may be taken as a known constant for our purposes.[8] The (H) luminescence at the nth step is thus given by

$$I_n{}^{\mathrm{H}}=[\alpha/(1-\alpha)][(1-\alpha)(1-q)^{1-F}]^n. \tag{3}$$

The calculation of emission from a trap when the time for (precisely) n steps has elapsed[9] involves four rather than three steps: First, there are n_1 steps onto host sites, then, one step onto a trap,[10] then, a waiting period of $n-n_1$ steps before, finally, emission of trap

[1] H. B. Rosenstock and J. H. Schulman, J. Chem. Phys. **30**, 116 (1959).

[2] "Trap" is here defined as an exciton trap, a site capable of holding energy that, otherwise, propagates through the lattice. In the literature, such sites are sometimes called "poisons" if the trapping is permanent, and "activators" if delayed luminescence results. The word trap in some papers is reserved for traps of massive particles. We hope no confusion will result.

[3] J. H. Schulman, H. W. Etzel, and J. G. Allard, J. Appl. Phys. **28**, 792 (1957); referred to as SEA.

[4] H. B. Rosenstock, J. Chem. Phys. **48**, 532 (1968); referred to as R.

[5] R. C. Powell and R. G. Kepler, Phys. Rev. Letters **22**, 636 (1969); referred to as PK.

[6] F. Spitzer, *Principles of Random Walk*, (D. Van Nostrand, Inc., Princeton, N. J., 1964), p. 35 ff.

[7] This is valid asymptotically for large n. n is almost always large when q and α are both small, as is always the case in physical applications.

[8] F is defined as the probability that the walker eventually returns to the origin. Its values are 0.340537330 for the simple cubic, 0.256318237 for the face-centered cubic, and 0.282229985 for the body-centered cubic lattice [E. W. Montroll, J. Soc. Ind. Appl. Math. **4**, 241 (1956)]. It has not been calculated for the anthracene lattice, but will here be estimated as 0.3.

[9] We speak here of events at "the time for n steps" rather than at "the nth step" because, after trapping, the walk stops and no more "steps" occur. This is purely a linguistic, not a mathematical, difficulty.

[10] A more complex theory results from the assumption that the probability of stepping on an adjacent trap differs from the probability for stepping on an adjacent host site. A heuristic way of introducing this into the present formalism is to replace q by $q_{\mathrm{eff}}=q\tau_{\mathrm{TH}}/\tau_{\mathrm{HH}}$, where τ_{TH} and $\tau_{\mathrm{HH}}=\tau$ are physically related to the wave-function overlaps between H and T and between H and H.

luminescence; this must be summed over all n_1. The first of these probabilities is $(1-\alpha)^{n_1}$, as before, and similarly the third probability is $(1-\beta)^{n-n_1-1}$, and the fourth is simply β; the second probability is found by subtracting

P (trapping before or at n_1) $-P$ (trapping before n_1)
$\quad = 1-P$ (no trapping before or at n_1)
$\qquad\qquad -[1-P$ (no trapping before n_1)$]$
$\quad = 1-(1-q)^{(1-F)n_1}-[1-(1-q)^{(1-F)(n_1-1)}]$
$\quad = (1-F)q(1-q)^{(1-F)n_1},$

where we have utilized $(1-q)^{1-F}\cong 1-(1-F)q$, valid[11] for small q. Thus, altogether, the (T) luminescence at step n is

$$I_n{}^T = \frac{\beta(1-F)q}{(1-\alpha)(1-\beta)}(1-\beta)^n \sum_{n_1=1}^{n}\left[\frac{(1-\alpha)(1-q)^{1-F}}{1-\beta}\right]^{n_1},$$

which sums to

$$I_n{}^T = \frac{\beta(1-F)q(1-q)^{1-F}}{(1-\beta)[\alpha-\beta+(1-F)q]}$$
$$\times\{(1-\beta)^n-[(1-\alpha)(1-q)^{1-F}]^n\}. \quad (4)$$

It is convenient to introduce quantities a, b, and c defined by

$$e^{-a}=(1-\alpha),\quad e^{-b}=(1-\beta),\quad e^{-c}=(1-q) \quad (5)$$

which, whenever α, β, and q are small, as they usually are in physical applications, are essentially equal to them, and to denote time by $t=n\tau$. Then, Eqs. (3) and (4) become

$$I^H(t)=[a/(1-a)]e^{-[a+(1-F)c]t/\tau}, \quad (6)$$

$$I^T(t)=\frac{b}{1+[(a-b)/(1-F)c]}$$
$$\times(e^{-bt/\tau}-e^{-[a+(1-F)c]t/\tau}). \quad (7)$$

Equations (6) and (7) are the solutions to our problem. a/τ and b/τ have simple physical meanings; they are the probabilities per unit time, or inverse lifetime, of host and trap luminescence. For comparison with experiment, we must include the effect of the time dependence of the light pulse; if this is $G(t_0)$, the observed luminescence will be

$$\int_0^t G(t_0)I(t-t_0)dt_0.$$

If we deal with a square pulse[12] of duration t^*, we find that for $t>t^*$ the simple exponential time dependence
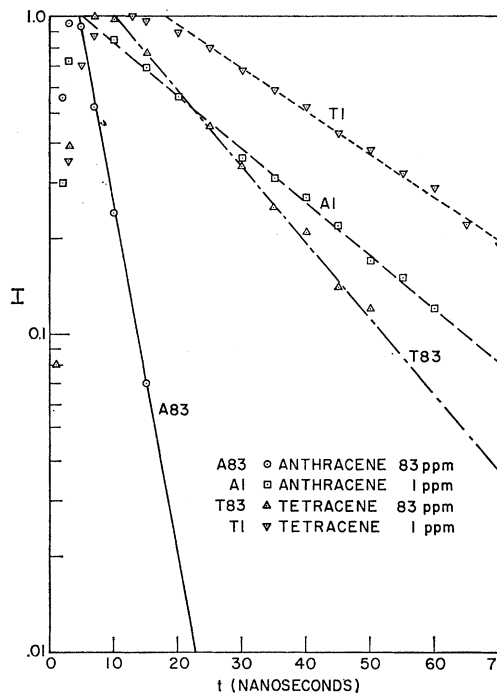

FIG. 1. Characteristic luminescence of anthracene (A) and of tetracene (T) from solid anthracene doped with 1 ppm and with 83 ppm of tetracene. From PK, Ref. 5. Each curve is separately normalized.

of the luminescence is not changed, although in (7) each term will be multiplied by a different constant factor. This suggests that for other reasonable pulse shapes the qualitative form of the luminescence for $t\gg t^*$ will also be unaffected.

In view of the simple exponential time dependence of (6) and (7), we have replotted the points from all of PK's figures on a semilogarithmic scale in our Fig. 1. This shows luminescence of both the host, anthracene, and the traps, tetracene, each for concentrations c of 1×10^{-6} and 83×10^{-6} of traps. Within experimental error, straight-line (exponential) behavior is found,[13] as required by (6) and (7). A semiquantitative analysis of Fig. 1 now enables us to roughly calculate the values of some of the parameters in (6) and (7).

Since the concentration c of traps is known,[14] comparison of the slopes of the two anthracene curves enables us to evaluate a and τ. We find

$$\tau/a=28\times10^{-9} \text{ sec} \quad (8)$$

for the lifetime of the luminescence of anthracene,[15]

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[11] We note that the two-term binomial expansion would not be valid for the factor of $(1-q)^{(1-F)n_1}$, as n_1 can be large.

[12] PK attribute a duration of about 6 nsec to their pulse, but do not report its exact shape.

[13] The A83 curve is less reliable than the other three. It is based on three points only, and also suffers from special experimental difficulties mentioned by PK.

[14] We take it that ppm in PK refers to molecular, rather than weight concentrations.

[15] This is in good agreement with the value of 26 nsec given by J. B. Birks, T. A. King, and I. H. Munro, Proc. Phys. Soc. (London) (L) **80**, 355 (1962). Many earlier reported values are analyzed by J. B. Birks, *ibid.* **79**, 494 (1962).

and, with[8] $F=0.3$,

$$\tau=0.2\times10^{-12}\ \text{sec} \tag{9}$$

for the mean time an anthracene singlet exciton spends on one site. Of these two numbers, the latter is much more strongly dependent on the experimentally questionable A83 curve[13] and, hence, less reliable.[16] Next, we note that the A1 and T1 curves have nearly the same slope. This suggests that for that 1 ppm, the second exponential in (7) must be the dominant one. By contrast, the T83 curve has a different, yet reasonably constant, slope; this indicates that for 83 ppm the first term dominates in (7). Neglecting the second term in (7), we then find from the T83 curve

$$\tau/b=18\times10^{-9}\ \text{sec} \tag{10}$$

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[16] On the other hand, it should be better than the value 1.3×10^{-12} sec previously reported by R on the basis of time-

for the lifetime of the tetracene luminescence. In view of the uncertainty of the data, the absence of absolute (rather than normalized) values of luminescence, the unknown shape of the exciting light pulse, and the not exactly calculated value of F for the anthracene lattice, as well as other complexities,[15] a more detailed analysis of experiment would not be worthwhile now.

In summary, though we would not attribute great precision to our quantitative estimates (8)–(10), we feel that the agreement of experiment with (6) and (7) provides support for the random-walk model for exciton propagation in organic solids. Postulation of a long-range energy-transfer mechanism[5] appears not to be necessary.

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integrated measurements and very poorly known trap concentrations.

A Quantum Dissipation Theory of Anharmonic Crystals. II. Polaritons

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In an earlier paper a quantum-mechanical dissipation theory was used to deduce the effect of anharmonicity on crystal vibration modes. These modes interacting with electromagnetic radiation form a new system which is now investigated in a similar way. The coupled radiation-vibration, or polariton, modes experience damping and frequency shifts which are expressed, for alkali halides, in terms of the corresponding phonon quantities. The expressions for phonons are multiplied by a momentum-dependent factor corresponding in magnitude to the polariton's degree of phononlike character and ranging from zero to unity. Results for the example of potassium bromide are presented. Other excitations interacting with phonons are discussed with regard to such a treatment.

I. INTRODUCTION

IN an earlier paper[1] the quantum dissipation theory developed by Senitzky[2] was used to investigate the damping and frequency shifts of crystal vibration modes through anharmonic interactions. In quasiparticle terms, the phonons which occupy these modes are thought of as decaying by collisions with others. Apart from phonons, however, other excitations may exist within the volume of a crystal. Photons, excitons, magnons, and plasmons may also carry energy and, according to certain selection rules, interchange it amongst themselves and with the phonons. When two of these elementary excitations coexist in a crystal, it is often easier to think of them jointly as a new type of excitation whose energy spectrum has two branches. The case to be given special consideration in this paper is the photon-phonon combination, which is termed[3] the polariton.

The theory of elementary excitations is based on the harmonic approximation wherein only terms quadratic in the relevant coordinate are retained in the Hamiltonian. When higher than quadratic (anharmonic) terms are included, the mode damping and frequency shifts referred to above occur. This behavior was investigated for phonons in I and is here extended to polaritons. For polaritons, whose creation and annihilation operators are linear combinations of those of phonons and photons, the damping and shift expressions will depend on the proportional phonon contribution to the mixed excitation. That is, the damping-constant and frequency-shift expressions for phonons are multiplied by a momentum-dependent factor corresponding in magnitude to the polariton's degree of phononlike character and ranging from zero to unity.

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[1] A. H. Opie, Phys. Rev. **172**, 640 (1968), hereafter referred to as I.

[2] I. R. Senitzky, Phys. Rev. **119**, 670 (1960).

[3] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).