

This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 17 February 2013, At: 06:00

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Molecular Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl15>

## On the Fluorescence Decay Curve of Anthracene

G. J. Dienes<sup>a</sup>

<sup>a</sup> Brookhaven National Laboratory, Upton, New York  
Version of record first published: 21 Mar 2007.

To cite this article: G. J. Dienes (1967): On the Fluorescence Decay Curve of Anthracene, *Molecular Crystals, Liquid Crystals*, 3:2, 293-296

To link to this article: <http://dx.doi.org/10.1080/15421406708083445>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# On the Fluorescence Decay Curve of Anthracene<sup>†</sup>

G. J. DIENES

Brookhaven National Laboratory, Upton, New York

Received July 12, 1967

Recent contributions in *Phys. Rev. Letters* indicate that the interpretation of fluorescence decay experiments in anthracene is by no means clear-cut.<sup>1,2</sup> The basic dilemma is how to reconcile the fluorescence experiments of Bergman *et al.*<sup>1</sup> with the photogeneration of free carriers experiments of Silver *et al.*<sup>3</sup> Bimolecular rate constants are derived from both of these experiments which differ by a factor of about 10<sup>4</sup>. Thus, if these experiments are measuring the same basic processes a serious discrepancy exists.

The purpose of this note is to outline a more careful kinetic analysis. It will be shown that fluorescence decay curves are not diagnostic of dissipative (i.e. non-fluorescent) processes, that at least two dissipative processes are needed to explain the available experimental data, and that the bimolecular rate constants measured by fluorescence decay and by carrier production are not the same.

The basic assumptions in all the treatments are that singlet excitons decay by fluorescence and also by forming an intermediate by a bimolecular process. The intermediate then may decay by producing free carriers,<sup>3</sup> by autoionization,<sup>2</sup> etc. These basic assumptions are retained. Further, interest here is focused on processes following pulse generation, and consequently generation terms are not considered,<sup>4</sup> i.e. at time zero the system contains a certain concentration of singlets. The various processes may be symbolized by the equations:



<sup>†</sup> Work supported by the U.S. Atomic Energy Commission.



where  $n$  = concentration of singlets

$n_2$  = concentration of intermediate

$q$  = concentration of light quanta

$P_1, P_2$  = products of dissipative processes

The differential rate equations corresponding to Eqs. (1-4) are

$$\frac{dn}{dt} = -\beta_s n - 2K_1 n^2 + 2K_2 n_2 \quad (5)$$

$$\frac{dn_2}{dt} = K_1 n^2 - K_2 n_2 - K_3 n_2 - K_4 n_2 \quad (6)$$

$$\frac{dP_1}{dt} = K_3 n_2 \quad (7)$$

$$\frac{dP_2}{dt} = K_4 n_2 \quad (8)$$

$$\frac{dq}{dt} = \beta_s n \quad (9)$$

The last equation simply states that the measured intensity of fluorescence, which is proportional to  $dq/dt$ , is proportional to the singlet concentration and hence measures  $n$  directly.

These coupled non-linear differential equations cannot be solved in closed form. The usual trick is to assume a steady state approximation. In the present case the interest is in the decay of  $n$  following a short pulse which produced a high concentration of  $n$ . It seems sensible then to assume that the intermediate,  $n_2$ , quickly reaches steady state. From Eq. (6), then, letting  $dn_2/dt = 0$ , one obtains

$$n_2 = K_1 n^2 / (K_2 + K_3 + K_4) \quad (10)$$

and substitution into (5) yields

$$\frac{dn}{dt} = -\beta_s n - 2K_1 n^2 [1 - K_2 / (K_2 + K_3 + K_4)]. \quad (11)$$

The bimolecular rate constant,  $\gamma_s$ , measured by Bergman *et al.*<sup>1</sup> may now be identified as

$$\gamma_s = 2K_1[1 - K_2/(K_2 + K_3 + K_4)] \quad (12)$$

If  $K_2$  is dominantly large,  $\gamma_s \cong 0$  and the quadratic term would not be observed; hence this case, which is the equilibrium approximation, can be eliminated. Experimentally  $\gamma_s$  is the large bimolecular rate constant and, therefore, it is sensible to make the quantity in the brackets in Eq. (12) approach one. Assume that  $K_4$  is dominantly large. Then,

$$n_2 \cong \frac{K_1}{K_4} n^2 \quad (13)$$

$$\gamma_s \cong 2K_1 \quad (14)$$

$$\frac{dP_1}{dt} \cong \frac{K_3 K_1}{K_4} n^2 \quad (15)$$

$$\frac{dP_2}{dt} \cong K_1 n^2 \quad (16)$$

The fast dissipative process,  $dP_2/dt$ , clearly measures the same rate constant (except for a factor of 2) as the fluorescence decay experiment ( $\gamma_s$ ). If one now identifies  $dP_1/dt$  with free carrier production then the rate constant measured by Silver *et al.*<sup>3</sup>  $\alpha$ , is

$$\alpha = \frac{2K_3 K_1}{K_4}, \quad (17)$$

which is a composite quantity. Experimentally,  $\gamma_s/\alpha \cong 10^4$ . What this means is that  $K_4 K_3 \cong 10^4$  consistent, of course, with the assumption that  $K_4$  is large. If only one dissipative process is present ( $K_3 = 0$  or  $K_4 = 0$ , or  $K_3 = K_4$ ), the same rate constant (within a factor of 2, or within a factor of 4 for  $K_3 = K_4$ ) will be measured by the decay of  $n$  and by measuring the product of the dissipative decay of  $n_2$  ( $P_2$  or  $P_1$ ). Thus, the difference between  $\gamma_s$  and  $\alpha$  can only be explained if there are at least two dissipative processes present characterized by different rate constants. Also, quite clearly,  $\gamma_s$  itself, and hence the fluorescence decay experiments, give no information about the dissipative processes.

Finally, a word of caution about using various approximations, including the steady state one, in solving non-linear rate equations. Computer studies<sup>5</sup> of such equations describing defect interactions and annealings have shown that the region of applicability, with respect to the magnitude of the constants involved, of various approximations<sup>6</sup> may be very limited. There are always time and concentration domains where such approximations are not valid, but only detailed computer calculations can define the regions of validity. If further experimental data warrant it, the above rate equations should be carefully studied by computer techniques.

## REFERENCES

1. Bergman, A., Levine, M. and Jortner, J., *Phys. Rev. Lett.* **18**, 593 (1967).
2. Sharma, R. D., *Phys. Rev. Lett.* **18**, 1139 (1937).
3. Silver, M., Olness, D., Swicord, M. and Jarnagin, R. C., *Phys. Rev. Lett.* **10**, 12 (1963).
4. For a discussion of generation terms see: Tolstoi, N. A. and Abramov, A. P., *Optics Spectrosc.* (Russ. Transl.) **20**, 273 (1966); *Sovj. Phys. Solid State* **9**, 255 (1967).
5. Damask, A. C. and Dienes, G. J., *Point Defects in Metals*, Gordon and Breach, New York, 1963, Chapter II.
6. Sharma<sup>2</sup> used the equilibrium approximation in his analysis. This is probably a poor approximation since, if consistently applied, it would eliminate all but the linear term in  $dn/dt$ .