Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Z. Burshtein [a] , J. Levinson [a] & A. Many [a]

[a] The Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem, Israel

To cite this article: Z. Burshtein , J. Levinson & A. Many (1974): Determination of the Singlet-Triplet Absorption Coefficient in Anthracene, Molecular Crystals and Liquid Crystals, 25:1-2, 45-52

To link to this article: http://dx.doi.org/10.1080/15421407408083403

Mol. Cryst. Liq. Cryst., 1974, Vol. 25, pp. 45-52

Printed in Dordrecht, Holland

Determination of the Singlet-Triplet Absorption Coefficient in Anthracene[†]

Z. BURSHTEIN, J. LEVINSON and A. MANY

The Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem, Israel

(Received July 17, 1973)

Measurements of the delayed-fluorescence excitation spectrum in anthracene could so far yield only the relative variation of the singlet-triplet absorption coefficient α with wavelength. In the present work the absolute magnitude of α is derived from studies involving the interaction of photo-generated triplet excitons with trapped electrons introduced into the sample by contact injection. Such an interaction results in the liberation of trapped electrons on the one hand and in the quenching of the triplet-exciton lifetime on the other. The former process is studied by photocurrent measurements while the latter is monitored by triplet lifetime measurements. The value of α so determined is $(1.2, \pm 0.2) \times 10^{-3}$ cm^{-1} at the first singlet-triplet absorption peak (6780 A).

INTRODUCTION

The absolute magnitude of the singlet-triplet absorption coefficient in anthracene has not been determined so far. The difficulty in such determination lies in the fact that the singlet-triplet transition is forbidden to a first approximation by virtue of spin-orbit coupling and hence is very weak. Only the relative variation of the absorption could be obtained, through the measurement of the excitation spectrum for delayed fluorescence.[1,2] The delayed-fluorescence process results from the radiative decay of singlet excitons produced by the mutual annihilation of pairs of photo-generated triplet excitons.[1,2] The excitation spectrum for delayed fluorescence is thus proportional to the square of the singlet-triplet absorption coefficient α. However, not all triplet-triplet annihilation processes necessarily produce singlet excitons. This method can therefore yield only the

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[†] The research reported herein has been sponsored in part by the European Research Office, U.S. Army, London, England.

product $f\alpha$, where f is the fraction of triplet-triplet annihilation processes that lead to delayed fluorescence.

The measuerement of α described in this paper is based on the interaction of photo-generated triplet excitons with trapped electrons.[3] Under the proper conditions, such an interaction results in the liberation of trapped electrons on the one hand, and in the lowering of the triplet lifetime on the other. Combined measurements of the two effects yields α.

THEORETICAL CONSIDERATIONS

Electron trapping processes in anthracene have been studied in detail by Many et al.[3] These workers introduced trapped electrons into the anthracene sample by injection from an alkali or alkaline-earth metal contact. The photocurrents measured in the *reverse* polarity (non-injecting mode) were shown to arise from direct optical excitation of the trapped electrons at long wavelengths, while in the triplet absorption region ($\lambda \lessapprox 6900$A) de-trapping by interaction with photo-generated triplet excitons was found to play the dominant role. Moreover, in the samples studied the traps involved were sufficiently deep in energy so that the *thermal* release of trapped electrons within the measurement time was completely negligible. For sufficiently high reverse voltages, such that the electron Schubweg is large compared to the sample's thickness L, the saturated reverse photocurrent density is given by[3]

$$J = \tfrac{1}{2} qL\,(-\mathrm{d}n_t/\mathrm{d}t)\,, \tag{1}$$

where q is the electronic charge and n_t the density of trapped electrons. As de-trapping proceeds, the photocurrent decays until it vanishes when all the traps are emptied. For the present investigation, however, we are interested only in the *initial* photocurrent ($t = 0$), which monitors the number of trapped electrons injected during the prior application of the forward voltage. Accordingly, in Eq. (1), as well as in the following discussions, J will be taken to represent the initial photocurrent density.

The de-trapping rate can be expressed as

$$\mathrm{d}n_t/\mathrm{d}t = -(\sigma F n_t + R_t n_t T)\,, \tag{2}$$

where F is the photon flux, σ the cross section for direct photo-excitation out of the traps, T is the concentration of triplet excitons and R_t the rate constant characterizing the triplet-trapped electron interaction. The rate equation governing the triplet concentration is[2]

$$\mathrm{d}T/\mathrm{d}t = \alpha F - \beta T - \gamma_{\mathrm{tot}} T^2 \tag{3}$$

where β is the monomolecular decay-rate coefficient (reciprocal of the triplet lifetime τ) and γ_{tot} is the overall bimolecular annihilation rate constant.

The influence of the traps on the triplet lifetime provides a link between Eqs. (2) and (3). In Eq. (2), β is the decay-rate coefficient in the presence of a trap density n_t. If we denote by β_0 the coefficient in the absence of trapped electrons ($n_t = 0$) then[4,5]

$$\beta - \beta_0 = R_t n_t\,. \tag{4}$$

It is worth mentioning at this point that Weisz et al.[4] have verified the linear relation between $\beta - \beta_0$ and the number of triplet quenchers (created in their case by gamma irradiation) over more than two orders of magnitude.

Under steady-state conditions and for low photon fluxes such that $\gamma_{tot} T << \beta$, one obtains from Eq. (3) the steady-state triplet concentration as

$$T = \alpha F/\beta\,. \tag{5}$$

Steady-state conditions are obtained a few triplet lifetimes (20 - 25 msec) following the onset of illumination. This is considerably shorter than the decay time of the reverse photocurrent[3] (Eq. (1)). Thus the measured *initial* photocurrent corresponds to steady-state conditions as far as the triplet concentration is concerned.

Using Eqs. (2), (4) and (5) one obtains from Eq. (1)

$$J - J_D = \tfrac{1}{2} q\alpha F(\beta - \beta_0)/\beta\,. \tag{6}$$

where $J_D \equiv \frac{1}{2} qL\sigma F n_t$ is the contribution of direct photoexcitation to the total saturated reverse photocurrent. Eq. (6) can be re-written as

$$2(\eta - \eta_0)/L = \alpha(\beta - \beta_0)/\beta \tag{7}$$

where $\eta \equiv J/qF$ and $\eta_D \equiv J_D/qF$ are the quantum yields (electrons per incident photon) of the respective photocurrents. Experimentally, a plot of $(\eta - \eta_D)$ versus $(\beta - \beta_0)/\beta$ should thus yield the value of the singlet-triplet absorption coefficient α at the wavelength studied.

It should be noted that Eq. (7) is valid irrespective of the type and energy distribution of the traps present, provided all traps are sufficiently deep. For the case of several sets of traps, $R_t n_t$ should be replaced by a suitable summation but this leaves Eq. (7) unchanged.

EXPERIMENTAL

The measurements were carried out on single-crystal anthracene platelets grown in this laboratory from the vapour phase. The platelets, 50 – 100 μ in thickness, were enclosed in a sandwich-type cell. A transparent conducting glass served as one electrode while the other was an injecting contact consisting of a Hg-Na amalgam. The sample holder, the photocurrent measuring circuit and the optical system were similar to those described elsewhere.[3] For better spectral resolution, however, a Jarrel-Ash grating double monochromator has been introduced. Also, an RCA type IP-28A photomultiplier has been added for delayed-fluorescence measurements.

For exciting the delayed fluorescence, light from a 150 W Kondo projection lamp was focussed on the sample through a Corning C.S.3-67 filter which cuts off light below $\lambda \approx 5000$ A. The exciting light was chopped (at frequency of 70 Hz) by a perforated rotating disc. Care was taken to ensure a symmetrical waveform, with the duration of illumination equal to that of darkness. The delayed fluorescence from the anthracene sample ($\lambda_{\text{peak}} = 4200$ A) was isolated by means of a double Kodak Wratten filter No. 47 in series with a 2-cm thick filter of a saturated solution of $CuSO_4$ in water. The fluorescence signal detected by the photomultiplier was fed into a type HR-8 PAR lock-in amplifier tuned to the fundamental frequency (70 Hz). The exciting-light intensity was sufficiently low so that $\gamma_{\text{tot}}T \ll \beta$ (see Eq. (3)). Under these conditions the delayed-fluorescence intensity should be proportional to the square of the exciting light intensity,[1,2] a relation which was indeed verified experimentally.

The triplet lifetime in the presence of different trapped-electron concentrations was derived by the phase shift method.[6] It can readily be shown that for

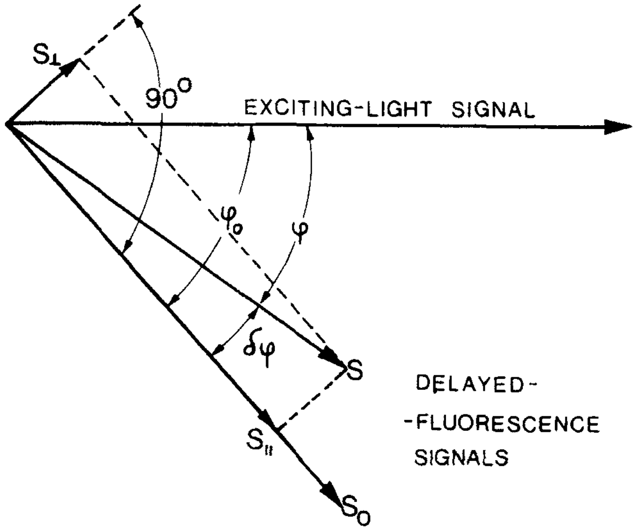

FIGURE 1 Vector diagram of signals fed into lock-in amplifier. S_0 and S are the delayed-fluorescence signals before and after application of injecting voltage, ϕ_0 and ϕ – their phase angles with respect to the exciting-light signal. The phase difference $\delta\phi$ obtained from measurement of the in-phase component $S_{\parallel}$ (along S_0) and the 90°-out-of-phase component ($S_\perp$).

the symmetrical waveform of the exciting light used, the phase angle ϕ by which the fundamental component of the delayed fluorescence (angular frequency ω) lags behind that of the exciting light, is related to the triplet lifetime $\tau(=1/\beta)$ by the relation $\tan\phi = \omega\tau$. The phase angle ϕ is read off the phase dial of the lock-in amplifier.

The accuracy in the measurement of ϕ is about 1°, which is adequate for the determination of β and β_0. It is not sufficient, however, for deriving the difference $\beta - \beta_0$, which is usually small compared to β_0 and is of primary importance in obtaining α (see Eq. (7)). Accordingly, the procedure illustrated by the vector diagram of Figure 1 was employed. First the phase angle ϕ_0 (and hence β_0) corresponding to no applied voltage across the sample is determined. In this process the phase angle of the delayed-fluorescence signal (vector $\mathbf{S}_0$) has been rotated by ϕ_0 so as to give maximum signal at the amplifier meter (and zero reading 90° off this angle). With the phase dial set in this position, an injecting voltage is now applied. As a result the triplet lifetime is decreased and the delayed-fluorescence signal (vector **S**) assumes a new angle ϕ. The small change $\delta\phi$ is obtained by measuring (on the amplifier meter) the in-phase ($S_{\parallel}$) and the 90°-out-of-phase ($S_{\perp}$) components of **S**, it being given by the relation $\tan(\delta\phi) = S_{\perp}/S_{\parallel}$. This leads to a rather accurate determination of $\delta\phi(\pm 0.05°)$ and hence of the change $\beta - \beta_0$ brought about by the injecting voltage.

RESULTS AND DISCUSSION

The experimental procedure consists of the following steps. First the triplet lifetime τ_0 (and thus $\beta_0 = 1/\tau_0$) is measured in the absence of an applied voltage. Next a forward, injecting voltage of a given magnitude is applied and the reduction in lifetime (i.e. $\beta - \beta_0$) caused by the trapped electrons introduced by injection is determined. The voltage polarity is then reversed and the saturated reverse photocurrent J at the onset ($t = 0$) of a known photon flux F is measured. This sequence of measurements provides one experimental point in the plot of the quantum yield $\eta(=J/qF)$ versus $(\beta - \beta_0)/\beta$ (Eq. (7)). The sequence is repeated for various injecting voltages. The reason why $\beta - \beta_0$ and J are not determined simultaneously (during the application of the reverse voltage) is that for the light intensities used in measuring the triplet lifetime, optical bleaching of the traps is too rapid to permit such a maesurement. In the forward polarity, on the other hand, the traps are continuously being replenished by injection and the trapped-electron content which the triplet lifetime monitors is fixed and determined by the applied voltage. The justification for this procedure lies in the fact that the traps involved are stable thermally[3] so that the same density of trapped electrons exists in the forward polarity (when $\beta - \beta_0$ is measured) and in the reverse polarity (when J is measured). In principle, one should also consider the effect on β of the *free* electrons which are present during the lifetime measurement. For injecting voltages below the trapped-filled limit,[3] however, the free electron densities (estimated from the photocurrents *during* the lifetime measurement) were always six to seven orders of magnitude smaller than the total density of injected (trapped) space charge. Thus, even though the interaction rate constant of triplets with free electrons is larger than that with trapped electrons[5,7] (10^{-9} compared to $3\times10^{-11}\,\mathrm{cm}^3\,\mathrm{sec}^{-1}$), the contribution of free electrons to the triplet-exciton quenching process can safely be neglected.

An interesting effect has been observed in the course of the measurements. Immediately following the application of the Hg-Na contact, a four-fold increase in the delayed fluorescence took place while the phase angle and hence the triplet lifetime remained unchanged. This means that the exciting light intensity has been doubled, most probably due to the almost complete reflection of the incident light at the amalgam/anthracene interface. After about 15 minutes, however, the fluorescence signal decreased to its original level (prior to the application of the contact), indicating that the reflectivity of the interface has

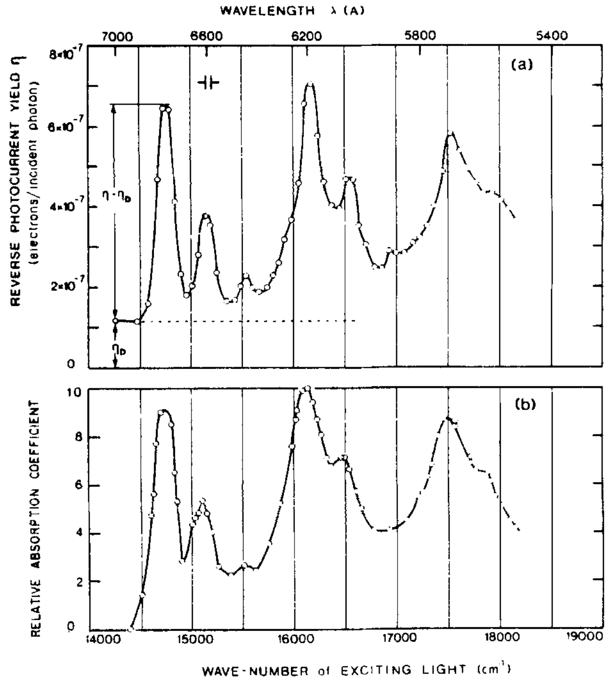

FIGURE 2 (a) Spectral yield η of saturated reverse photocurrent. Sample thickness 110μ; injecting voltage applied prior to photocurrent measurement 600 V. (b) Relative variation of singlet-triplet absorption coefficient obtained by taking the square root of the delayed-fluorescence excitation spectra measured by Avakian et al.[1]

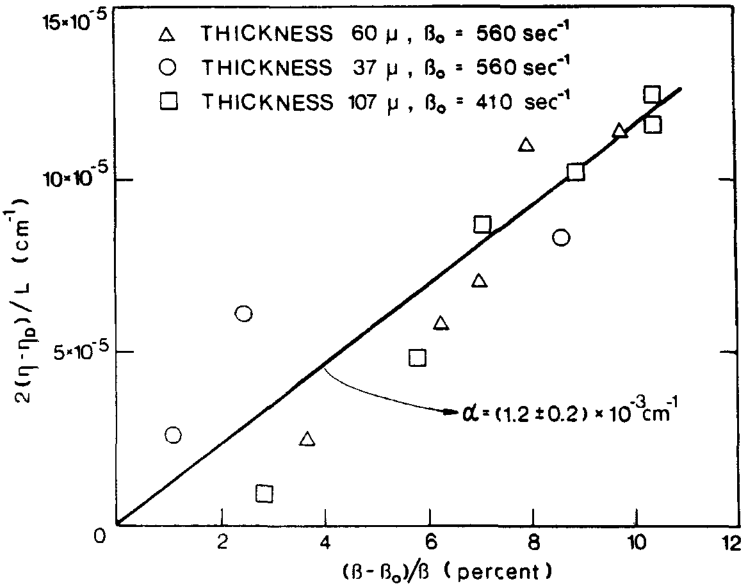

FIGURE 3 Plot of $2(\eta - \eta_D)/L$ against $(\beta - \beta_0)/\beta$ for three different samples. The different points for each sample correspond to different injecting voltages.

become as small as that of the free surface. This effect is very likely due to some chemical reaction between sodium and anthracene. In any case, since all measuremts of the reverse photocurrent were carried out well after the application of the amalgam contact, the photon flux F used in deriving the photocurrent yield η (Figures 2 and 3) was taken as the measured *incident* flux.

The relative magnitudes of the quantum yield for de-trapping by direct optical excitation (η_D) and through interaction with triplet excitions ($\eta - \eta_D$) can be assessed from spectral yield of the saturated reverse-photocurrent shown in Figure 2(a). The forward, injecting voltage used in filling up the traps prior to the measurement was 600 V. The yield values correspond to the *initial* reverse photocurrents, before significant optical bleaching of the traps takes place. The light intensities used were sufficiently low such that several points (covering part of the spectrum) could be taken without appreciable bleaching. Re-filling of the traps by injection was necessary in order to cover the entire spectrum. For comparison we have reproduced in Figure 2(b) the delayed-fluorescence excitation spectrum obtained by Avakian et al.[1] Actually, the ordinate here represents the square root of the fluorescence intensity so that the curve shown depicts the relative variation of the absorption coefficient of the singlet-triplet transition. It is seen that the two spectra are very similar, except that in the case of the reverse photocurrent there is a small additional contribution (η_D) due to de-trapping by direct photoexcitation. The variation of η_D with wavelength cannot be derived from the data of Figure 2(a). However, η_D is seen to be small compared to the overall yield at the absorption peaks, so that even a rough estimate of its magnitude does not introduce a large error in $\eta - \eta_D$. In particular, the measurement of α described below refers to the first absorption peak (6780 A) for which η_D must lie between 10^{-7} and $2\text{x}10^{-7}$, the yield values just below and beyond the peak. That η_D varies slowly in this range is evidenced also by the data of Weisz et al[5] who studied electron de-trapping processes by employing light pulses short compared to the triplet lifetime. Under these conditions the contribution of the triplets could be neglected so that the photocurrent reflected the direct photoexcitatin process only (η_D).

Figure 3 displays the results obtained at the first triplet absorption peak (6780 A) for $2(\eta - \eta_D)/L$ versus $(\beta - \beta_0)/\beta$. The three sets of points correspond to three different samples. In each sample the trapped-electron density, and hence η and β, were changed by varying the injecting voltage. In all cases, however, the injecting voltages were kept below the trapped-filled limit so as to eliminate the presence of a significant density of free electrons. The spread of the points near the origin is rather large because of the relatively large error involved in the measurement of small changes in triplet lifetime $(\beta - \beta_0)$. Nevertheless, the points, especially those away from the origin, provide a reasonably accurate estimate for the slope of the straight line. According to Eq. (7), this slope should be equal to the singlet-triplet absorption coefficient α. The value so obtained is $\alpha(6780\text{ A}) = (1.2 \pm 0.2) \times 10^{-3}\text{cm}^{-1}$.

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