

# Multiphoton processes of charge carrier generation in thianthrene crystals

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Photoconductivity in crystals of thianthrene has been studied by a standard dc method and by exciting with pulses of weakly absorbed light from a dye laser. The dc photoconductivity excited in the range 300–400 nm depends on the light intensity to the 1.5 power and is attributed to the interaction between singlet and triplet excitations. The  $S$ - $T$  interaction coefficient is estimated to be  $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . Pulsed photoconductivity in the range 450–640 nm, which follows a cubic light intensity dependence can be explained as arising from photoionization of two-photon produced singlet excitations. This hypothesis is corroborated by a comparison of the action spectrum of the two-photon absorption coefficient with that of the three-photon generation of charges. The photoionization cross section of a singlet excitation is found to be  $\sim 10^{-23} \text{ cm}^2$ . In the range 385–440 nm, the pulsed photocurrent depends on the square of the light intensity, where carrier generation occurs through the photoionization of triplets formed by a direct  $S_0$ - $T_1$  absorption or photoionization of singlets formed by absorption within the Urbach tail of the first absorption band.

## I. INTRODUCTION

Studies of charge carrier photogeneration in organic substances show, as a rule, that a variety of processes may be responsible for the formation of free charge carriers in these materials. It has been shown that an intrinsic photogeneration process is possible, at least for some substances, bearing some similarity to the band-band transition in semiconductors.<sup>1-3</sup> Alternatively, neutral molecular excitons may act as intermediates in the generation process, and then interactions with crystal defects, the surface or mutual exciton interactions become dominant. Most work concerning the mechanisms of such processes has been done on anthracene—the well-established model organic crystal. Nevertheless, results obtained for anthracene cannot be considered fully representative for the whole class of organic photoconductors. To enlarge the knowledge of the photoconductivity of organics, it is imperative that photogeneration studies be carried out on substances of different spectroscopic and molecular properties in order to find relations between the character of excited states of a substance and its photoconductive properties.

This paper presents results of the studies of photoconductivity of thianthrene—a sulphur analog of anthracene. Apart from measurements of the steady-state photoconductivity, we have also made measurements of pulsed photocurrents induced by a dye laser tuned within a wide frequency range. Such measurements allow one to study multiphoton photogeneration processes taking place in the crystal bulk, thus eliminating uncertainties due to possible surface effects.<sup>4-7</sup>

## II. EXPERIMENTAL

Thianthrene was carefully purified by chromatography, vacuum sublimation, and zone melting. The latter step was carried out in a "combination tube" and the purified material could thus be transferred to a

crystal growing vessel without a contact with the atmosphere. The crystal growth was accomplished by the Bridgman technique. Thianthrene samples used in the photoconductivity measurements were cleaved from crystals boules along the cleavage plane.

dc photocurrent measurements were carried out under nitrogen in a chamber provided with quartz windows. The sample in a sandwich configuration was illuminated through an ITO (indium-tin oxide) covered quartz electrode. A 2.5 kW xenon arc and a 1 m grating monochromator (Chromatix) were used to provide the monochromatic exciting light. The photocurrents were recorded with a Keithley electrometer and a chart recorder. The photocurrent usually stabilized  $\sim 2$  min. after switching on the exciting light, and this value was considered to be the steady-state photocurrent.

Pulse measurements were taken with a technique similar to that used by Bergman and Jortner.<sup>7</sup> A Molelectron DL-200 dye laser provided  $\sim 10$  ns single pulses of light, delivering up to 1.2 mJ per pulse. To obtain measurable values of the pulse photocurrent, it was found necessary to use thick parallelepiped-shaped thianthrene samples with electrodes placed at lateral surfaces. Typical dimensions of a sample were: height (along which the laser beam propagated)— $\sim 8$  mm; electrode distance—2–3 mm. The generated charge was measured with a high input impedance FET follower, which provided the intergrated photocurrent signals displayed and photographed from a Tectronics two-channel oscilloscope, the other channel of which was used to monitor the intensity of laser pulses measured with a calibrated photodiode.

The same dye laser was used for the measurements of the action spectrum of the two-photon induced fluorescence of thianthrene. In these measurements, the laser was pulsed repetitively (30 Hz), while being continuously scanned through the wavelength region of interest. Light emitted from the thick thianthrene sample was analyzed

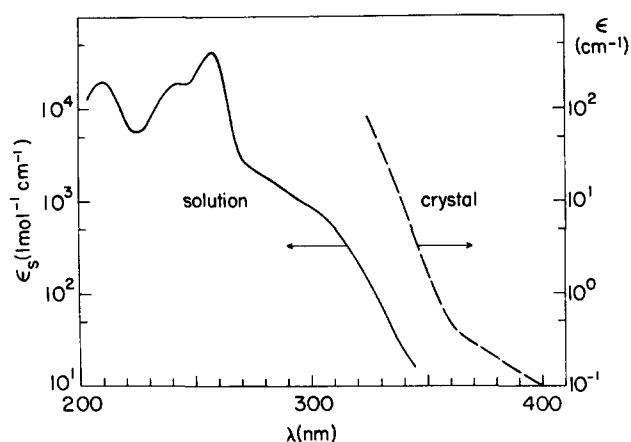


FIG. 1. The absorption spectrum of thianthrene solution and the absorption tail in the crystal.

with a 0.75 m grating monochromator (Spex) and monitored at a fixed selected wavelength within the fluorescence band (usually 420–450 nm) with a photomultiplier and photon-counting electronics (Ortec). The laser light intensity was at the same time monitored with a photodiode whose output was fed to a boxcar averager (Princeton).

### III. RESULTS

#### A. dc photoconductivity

Steady-state photocurrents were observed when thianthrene samples were irradiated with light of wavelengths shorter than  $\sim 400$  nm. The wavelength dependence of the photocurrent was studied in the region 300–400 nm, i. e., in the region of relatively weak absorption of thianthrene crystals (see Fig. 1). In order to construct an action spectrum of the photocurrent, it is always necessary to ascertain the light intensity dependence. A typical result of such a study is given in Fig. 2. As can be seen, the photocurrent is a super-

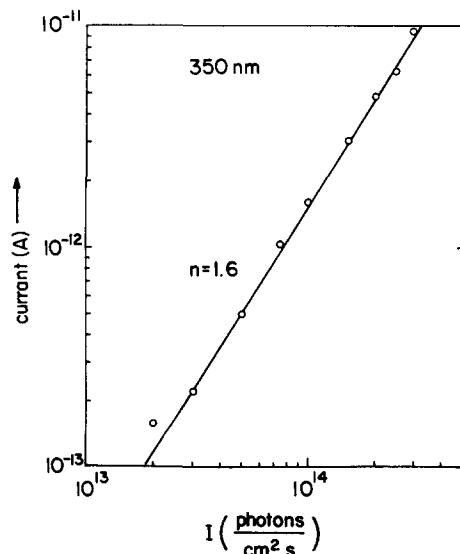


FIG. 2. A typical light intensity dependence of the steady-state photocurrent in thianthrene.

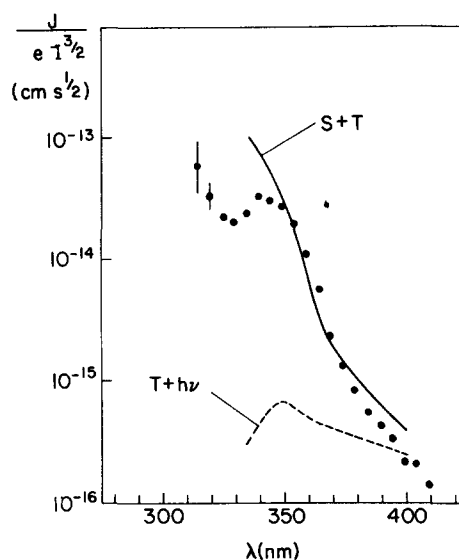


FIG. 3. dc photoconductivity action spectrum, normalized according to the  $3/2$  power intensity dependence. Circles denote experimental points. Full line and broken line show the wavelength dependences of the photogeneration efficiency expected for the singlet-triplet process and for the triplet photoionization process, respectively, calculated from the absorption coefficient data given in Fig. 1 and employing Eq. (8).

linear function of the light intensity, and, although some spread of the value of the slope of log-log photocurrent-light intensity dependences was observed, all results were reasonably well described by a  $3/2$  power dependence. Only at the shortest wavelengths used in this study could an onset of a photocurrent linearly dependent on the light intensity be seen. This feature is the source of a large spread of results near 300 nm in Fig. 3, which shows the photocurrent action spectrum normalized according to the  $3/2$  power dependence.

To discuss the mechanism of the photogeneration process in thianthrene giving rise to these intensity dependences one should, first of all, note that the photogeneration seems to be a bulk process taking place even at relatively low values of the absorption coefficient. The photocurrent value was found to be the same for both voltage polarities, which indicates that the process is of an intrinsic nature.

A superlinear dependence of the photocurrent on the light intensity is usually taken as a proof of a multiphoton generation mechanism—taking place either via an exciton-exciton interaction and/or exciton photon interaction or via multiphoton absorption (see, e. g., Ref. 7, and references therein). It can be concluded that the energy of a single photon of a wavelength below 300 nm is not high enough to produce a pair of free charge carriers in thianthrene, or, in other words, is lower in energy than the band gap. Among the various multiphoton processes which have been postulated in the literature, one can select those which are inconsistent with the present experimental data and those which may provide a more or less consistent interpretation of the observed phenomena.

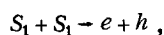
First of all, one can reject a mechanism based on a direct two-photon absorption leading to the formation of a geminate pair of charges or to a higher dissociative state (cf. Ref. 8). For light intensities used in this work ( $\sim 10^{14}$  photons/cm<sup>2</sup> s), one can estimate the rate of production of excited states from the equation

$$\frac{d[S_n]}{dt} = \sigma_2 NI^2, \quad (1)$$

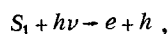
where  $\sigma_2$  is the two-photon absorption coefficient,  $N$  the density of molecules, and  $I$  is the light intensity. Assuming  $\sigma_2$  of the order of  $10^{-50}$  cm<sup>4</sup> s [as in anthracene (Ref. 9)] and taking the density of molecules as  $4 \times 10^{21}$  cm<sup>-3</sup>, one finds that  $d[S_n]/dt$  is as low as  $10^{-1}$  cm<sup>-3</sup> s<sup>-1</sup>, which would lead to current densities lower than  $10^{-20}$  A/cm<sup>2</sup>, i.e., very much smaller than observed.

Thus, one can assume that the initial step of the photo-generation mechanism is a one-photon absorption taking place in the tail of the first  $n\pi^*$  singlet absorption band of thianthrene, which gives rise to the shoulder at  $\sim 300$  nm in the absorption spectrum (Fig. 1). Obviously, such an exciton does not possess enough energy to freely dissociate into a pair of free charge carriers nor to generate free carriers upon interaction with crystal defects, since such processes should yield a linear light intensity dependence of the photocurrent. Super-linear intensity dependences may result from the following mechanisms:

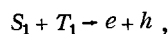
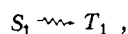
(i) collision ionization of two singlet excitons



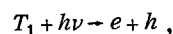
(ii) photoionization of a singlet exciton



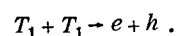
(iii) singlet-triplet interaction



(iv) photoionization of a triplet exciton



(v) triplet-triplet annihilation



Equations governing the kinetics of exciton population and the charge carrier production may then be written as

$$\frac{\partial[S]}{\partial t} = \epsilon I_0 \exp(-\epsilon x) - \frac{[S]}{\tau_S} - k_{IC}[S] + \psi_S \gamma [T]^2, \quad (2)$$

$$\frac{\partial[T]}{\partial t} = k_{IC}[S] - \frac{[T]}{\tau_T} - \gamma [T]^2, \quad (3)$$

$$\begin{aligned} \frac{\partial m}{\partial t} = & k_{SS}[S]^2 + \sigma_S [S] I_0 \exp(-\epsilon x) + k_{ST}[S][T] \\ & + \sigma_T [T] I_0 \exp(-\epsilon x) + \psi_m \gamma [T]^2 - \frac{m}{\tau_m}. \end{aligned} \quad (4)$$

In the above equations,  $[S]$  and  $[T]$  and  $m$  stand for the local concentrations of singlet and triplet excitons, and charge carriers, respectively;  $\epsilon$  is the absorption coefficient;  $\tau_S$  and  $\tau_T$  are the lifetimes of singlet and trip-

let excitons, respectively;  $I_0$  is the incident light intensity;  $\gamma$  is the triplet-triplet annihilation rate constants;  $k_{IC}$  stands for the rate constant of the intersystem crossing;  $\sigma_S$  and  $\sigma_T$  are the photoionization cross sections of a singlet and a triplet, respectively;  $k_{SS}$  and  $k_{ST}$  are the rate constants of the singlet-singlet and singlet-triplet collisions ionization; and  $\psi_S$  and  $\psi_m$  denote the fractions of triplet-triplet annihilations which lead to the formation of a singlet or of a pair of charge carriers, respectively.

Diffusion of excitons has been neglected in the above equations, which is justified for low absorption coefficients (i.e., small exciton concentration gradients), and also second-order recombination of charges has not been included. The carrier lifetime is taken to include all processes of free carrier removal from the sample region of interest, i.e., drift and trapping of carriers. Under the stationary illumination  $\partial[S]/\partial t = \partial[T]/\partial t = \partial m/\partial t = 0$ , and one can estimate the concentrations of excitons as

$$[S] = \tau'_S I_0 \exp(-\epsilon x) \quad (5)$$

and

$$[T] = \left( \frac{k_{IC}}{\gamma} \right)^{1/2} [\tau'_S \epsilon I_0 \exp(-\epsilon x)]^{1/2}, \quad (6a)$$

if  $\gamma [T]^2 \gg [T]/\epsilon_T$ , i.e., for high triplet density, or

$$[T] = \tau_T k_{IC} \tau'_S \epsilon I_0 \exp(-\epsilon x), \quad (6b)$$

if  $\gamma [T]^2 \ll [T]/\tau_T$ , i.e., for low triplet density.

In the above equations,  $\tau'_S = (\tau_S^{-1} + k_{IC})^{-1}$  stands for the effective singlet lifetime (including the rate of the intersystem crossing).

On inserting the expressions (5) and (6) into Eq. (4), it becomes evident that, while the charge carrier production rate by the processes (i) and (ii) should be described by square light intensity dependences, the processes in which triplet excitons contribute to the formation of charges may be described by intensity dependences with powers lower than two, provided that triplet densities are high enough to make the triplet annihilation prevail over the monomolecular triplet decay. In particular, singlet-triplet interactions and the triplet photoionization processes taking place at high triplet densities should result in a photocurrent which is proportional to the light intensity of a 3/2 power. This conclusion has already been presented in Ref. 10, where the photogeneration in crystals of *p*-terphenyl has been attributed to those two processes, although no distinction could be made between them.

On rewriting Eq. (4) in a form containing explicit expressions for exciton concentration and containing only the triplet-singlet and triplet-photon terms

$$\begin{aligned} \frac{\partial m}{\partial t} = & k_{ST} [\tau'_S \epsilon I_0 \exp(-\epsilon x)]^{3/2} \left( \frac{k_{IC}}{\gamma} \right)^{1/2} \\ & + \sigma_T (\tau'_S \epsilon)^{1/2} [I_0 \exp(-\epsilon x)]^{3/2} \left( \frac{k_{IC}}{\gamma} \right)^{1/2} \\ & - \frac{m}{\tau_m} = 0, \end{aligned} \quad (7)$$

one notes that the two terms contain a different dependence on the absorption coefficient, and this feature can be used to distinguish between them. For relatively weak absorption [ $\exp(-\epsilon x) \cong 1$ ], the singlet-triplet interaction is characterized by a  $\epsilon^{3/2}$  dependence, whereas the photoionization of triplets follows a  $\epsilon^{1/2}$  dependence. Assuming that the electric field applied to the sample is sufficiently large to collect all carriers which have escaped the geminate recombination, one can express the current density  $J$  as

$$J = ek_{ST}(\tau'_S \epsilon)^{3/2} \left( \frac{k_{IC}}{\gamma} \right)^{1/2} I_0^{3/2} \frac{2}{3} \frac{1 - \exp(-3/2L)}{\epsilon} + e\sigma_T(\tau'_S \epsilon)^{1/2} \left( \frac{k_{IC}}{\gamma} \right)^{1/2} I_0^{3/2} \frac{2}{3} \frac{1 - \exp(-3/2L)}{\epsilon} \quad (8)$$

Calculations of wavelength dependences of both terms, performed using the values of the absorption coefficient from Fig. 1, show that the singlet-triplet interaction is a more likely explanation of the experimental data (see Fig. 3). The data from Fig. 3 may be thus used to calculate the rate constant of the collision ionization of a singlet-triplet pair. At 350 nm,  $\epsilon = 2 \text{ cm}^{-1}$  and  $J/eI_0^{3/2} = 3 \times 10^{14} \text{ cm s}^{-1}$ . The intersystem crossing rate in thianthrene is known to be  $\sim 3 \times 7 \text{ s}^{-11,12}$ . We assume other parameters (i. e.,  $\tau'_S$  and  $\gamma$ ) to be of the same order of magnitude as in anthracene (i. e.,  $\tau'_S = 10^{-8}$  and  $\gamma = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ). The calculation yields  $k_{ST} = 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . This value may be compared with  $1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , obtained for an analogous process in *p*-terphenyl.<sup>10</sup>

### B. Pulsed photoconductivity induced by a tunable dye laser

Measurements of the magnitude of charge generated by 10 ns pulses of a dye laser were carried out within the wavelength region of very weak absorption, i. e., 420–640 nm, and within the singlet absorption tail at 385 nm. It was found that the high intensity pulses lead to the generation of charge whose magnitude depends on the light intensity to a power which varies with the wavelength. Figure 4 shows results of the studies of the intensity dependences plotted in double log co-

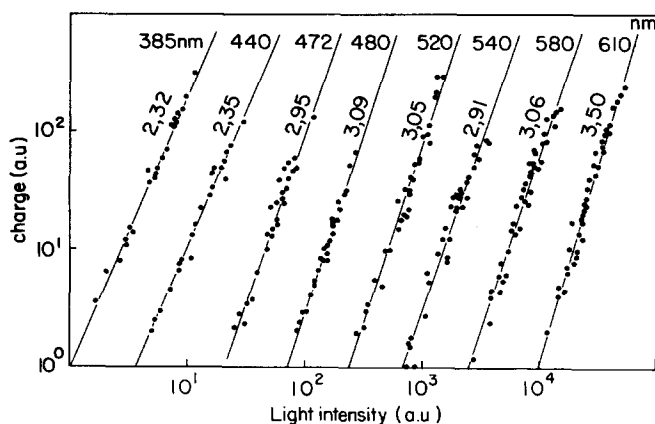


FIG. 4. A set of intensity dependences of the magnitude of charge generated by dye laser pulses. Wavelengths and least-square slopes of the straight lines are given in the figure. The light intensities used are in the range  $10^{22}$ – $10^{24}$  photons/ $\text{cm}^2 \text{ s}$ .

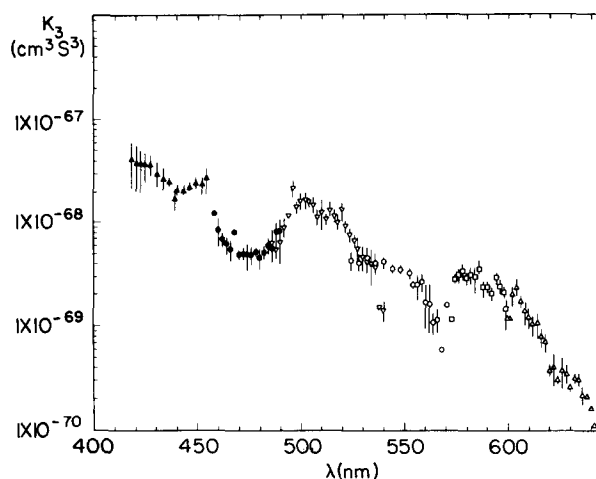


FIG. 5. Action spectrum of the three-photon generation of charges. Different symbols correspond to different dyes used. Vertical sections denote the spread of the results.

ordinates. Least square slopes of the lines drawn through experimental points are given in the figure. It can be seen that, within a wide wavelength range, the magnitude of the photogenerated charge follows a distinct  $I^3$  dependence. The slopes become lower at shorter wavelengths and, below 440 nm, one can assume that a square intensity dependence is fulfilled.

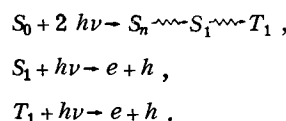
Results obtained at different wavelengths, using various dyes in the dye laser cell, allow one to construct an "action spectrum" of the apparent three-photon generation process by plotting the wavelength dependence of the generation coefficient  $K_3$  defined by the relation<sup>7</sup>

$$m = K_3 I^3, \quad (9)$$

where  $m$  is the concentration of charges generated by a laser pulse of the average intensity  $I$  (photons/ $\text{cm}^2 \text{ s}$ ). Figure 5 shows the spectrum obtained in such a manner. In spite of a considerable spread of the results, some structure is evident in the action spectrum.

To discuss the mechanism of the photogeneration by the three-photon process, we recall firstly the argument of Bergman and Jortner<sup>7</sup> that a direct three-photon absorption can be considered negligible as compared with three-photon processes with an intermediate exciton state. Thus, the most plausible mechanism is that of a two-photon formation of a singlet exciton and its subsequent photoionization. Since the intersystem crossing rate in thianthrene is rather high, one can also take into account photoionization of triplets produced from singlets by the spin conversion. Thus, because  $k_{IC}^1$  is of the same order of magnitude as the duration of the laser pulse, one can calculate that  $\sim 0.25$  of initially produced singlets will be converted to triplets during the pulse.

A mechanism involving both processes may be written as follows:



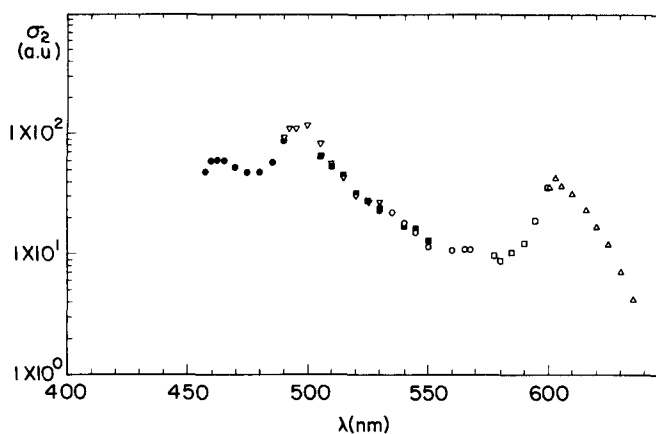


FIG. 6. Action spectrum of the two-photon induced fluorescence of thianthrene crystals.

Singlet-singlet or singlet-triplet interactions may probably be excluded from consideration since these two processes would lead to a fourth-power intensity dependence.

The kinetics of the photoionization processes may then be expressed as follows:

$$\frac{d[S]}{dt} = \sigma_2 N I(t)^2 - \frac{[S]}{\tau_S} - k_{IC}[S], \quad (10)$$

$$\frac{d[T]}{dt} = k_{IC}[S] - \frac{[T]}{\tau_T}, \quad (11)$$

$$\frac{dm}{dt} = \sigma_S [S] I(t) + \sigma_T [T] I(t), \quad (12)$$

where bimolecular processes have been neglected. The symbol nomenclature is as in Eqs. (1)–(4). The above equations can, in principle, be solved for a given laser pulse shape  $I(t)$  to give the number of carriers generated by the pulse. Since such a solution would demand exact data on both the pulse shape and exciton lifetimes and would involve numerical calculations (cf. Ref. 13), we shall, instead, adopt a simplified expression<sup>7</sup>

$$\frac{dm}{dt} = \sigma_S \sigma_2 N \tau_S' I^2 = \frac{K_3}{\tau_p} I^3, \quad (13)$$

where the contribution of the triplet photoionization has been completely neglected.  $I$  stands here for the average light intensity and  $\tau_p$  is the pulse duration. The  $K_3$  value may be thus considered to involve a product of the two-photon absorption coefficient  $\sigma_2$  and the photoionization cross section of a singlet exciton  $\sigma_S$ . Both parameters may be functions of the wavelength but one can suppose that the  $K_3$  vs  $\lambda$  dependence should show the same features as the two-photon absorption coefficient spectrum.

To further identify this concept, we have measured the action spectrum of the two-photon excited luminescence. It was checked that the intensity of the blue emission monitored at a fixed wavelength (say, 430 nm) was a square function of the intensity of exciting laser pulses (in the range 460–640 nm). The spectrum of  $\sigma_2$ , calculated as the intensity of the luminescence divided by the square of the laser light intensity, is shown in

Fig. 6. A comparison with Fig. 5 shows that, indeed, maxima in the photogeneration coefficient  $K_3$  are most probably due to the maxima in the two-photon absorption, although some dependence of  $\sigma_S$  on  $\lambda$  should also be taken into account. Data from Fig. 5 allow one to estimate the product  $\sigma_2 \sigma_S$  as around  $10^{-73} \text{ cm}^6 \text{ s}$ , which, assuming  $\sigma_2$  to be  $\sim 10^{-50} \text{ cm}^4 \text{ s}$ , gives an estimate of the photoionization cross section of a singlet exciton as  $\sim 10^{-23} \text{ cm}^2$ . This value is lower than the corresponding parameter for anthracene ( $\sim 10^{-20} \text{ cm}^2$ ; see Ref. 7, and references therein). However, in the light of uncertainties in the determination of the absolute value of  $K_3$  and approximations made in Eq. (13), this difference cannot be considered quantitative.

An important problem is also that of the mechanism of the photogeneration of charges at wavelengths shorter than 440 nm where, apparently, a two-photon process is operative. Phosphorescence spectra of thianthrene<sup>12</sup> show that the position of the first triplet level should be  $\sim 430 \text{ nm}$  (deduced from the threshold of phosphorescence of thianthrene solutions). This corresponds well with the onset of the two-photon process observed in the generation of charge carriers. Taking into account this coincidence, it is logical to assume that photoionization of triplets formed by a one-photon (forbidden) absorption is a dominant process at wavelengths between 400 and 440 nm. It may be recalled that such a mechanism was postulated for anthracene<sup>14</sup> as an alternative to the<sup>7,8</sup> direct two-photon band-band transition.

When thianthrene is excited at 385 nm, the efficiency of the two-photon generation becomes about two orders of magnitude higher than that at 440 nm. This increase may be attributed to the fact that, at 385 nm, direct absorption within the Urbach tail of the first singlet band becomes competitive and both singlets and triplets formed by intersystem crossing may be photoionized. However, since no data on the absorption coefficient of the forbidden  $S_0-T_1$  absorption in thianthrene are available, it is impossible to calculate and compare the photoionization cross sections of singlets and triplets.

#### IV. CONCLUDING REMARKS

Results obtained in this work indicate the importance of various exciton interaction processes as photogeneration pathways in crystalline thianthrene. One can anticipate that an extension of the studies of the steady-state photoconductivity to shorter wavelengths may lead to the detection of a direct one-photon generation process of the type encountered in, e.g., anthracene. This process is probably superimposed on multiphoton processes operative at longer wavelengths. Nevertheless, experiments with dye laser excitations do not show a hint of a two-quantum process which might be considered to originate from a two-photon transition to delocalized states in the conduction band, as has been postulated for anthracene.<sup>7,8</sup>

For thianthrene, the importance of various photogeneration paths may be supposed to be slightly different from those on anthracene, due to a different character of excited states ( $n\pi^*$  transition in thianthrene and efficient intersystem crossing). Nevertheless, esti-

mated rate parameters of exciton interactions fall in range of similar parameters calculated for other molecular crystals.

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