Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 04 Oct 2006.

To cite this article: A. Kurabayashi & M. Kotani (1990): Charge Carrier Generation in Phenothiazine Crystal, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 183:1, 193-196

To link to this article: http://dx.doi.org/10.1080/15421409008047456

Mol. Cryst. Liq. Cryst., 1990, vol. 183, pp. 193–196
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Printed in the United States of America

CHARGE CARRIER GENERATION IN PHENOTHIAZINE CRYSTAL

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Abstract Photo-carrier generation in phenothiazine crystal was studied with two-color, two-step excitation. The results indicate the presence of an intermediate state with a lifetime of ~60μs, which seems to be the CT state already inferred from the electro-absorption spectroscopy and was expected to be long-lived.

A CT state may play an important role in charge separation by the action of light, such as photo-carrier generation in photoconductors, primary step in photo-redox reactions and photosynthesis. A CT transition in a single component crystal is difficult to detect, since it is very often buried in much stronger transitions of the component compounds. We have already reported that phenothiazine (PTZ) is unique in that a CT transition can be observed outside the strong local excitation region in the spectrum[1] (Fig. 1). The transition is sensitive to the electric field. The photoconduction action spectrum has also a large peak at

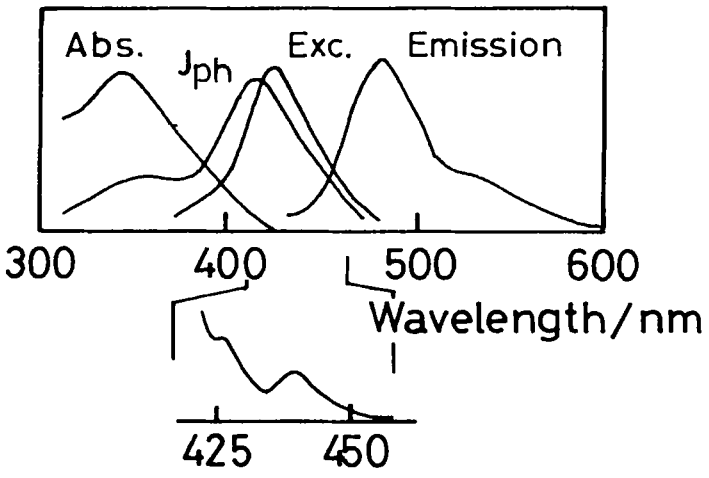

FIGURE 1 Absorption spectrum, emission spectrum (Exc. is its excitation spectrum) and the action spectrum for photo-conduction (J_{ph}). Two small peaks in the 410-440 nm region are transitions to CT exciton states.

this energy. It has been discussed that the CT state can have a long lifetime, since it is the lowest-lying excited singlet state and the radiationless transition to the ground state may be slow, due to a very unfavourable Franck-Condon factor.

Here will be reported a study of charge carrier generation in PTZ crystal with two-color, two-step excitation, a technique which has been successfully applied to naphthalene, p-terphenyl and anthracene.[2] It has been found that the state generated by the CT transition has indeed a long lifetime and is involved in the generation of charge carriers.

PTZ was purified by extensive zone-refining. Single crystals were grown from the melt by the Bridgman method. Care was taken not to expose the material to the ambient atmosphere during the final stage of the purification process. Transfer of the zone-refined material to a Bridgman ampoule was done in a sealed glass tube using the breakable seal technique. Electrical measurements were made with the standard time-of-flight method.[3] A thin platelet, typically 0.2 mm thick, obtained by cleaving an ingot, was sandwiched between a stainless steel electrode and a SnO_2-coated quartz plate. The

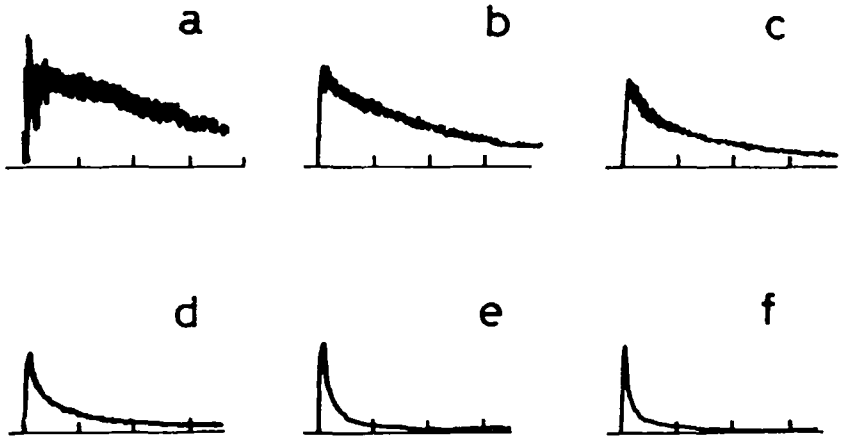

FIGURE 2 Photocurrent waveforms with various excitation intensities (λ=420 nm). The rise (not seen with this time scale) and the decay of the signal become faster with increasing excitation intensity (a → f). The time scale is 200 μs/div.

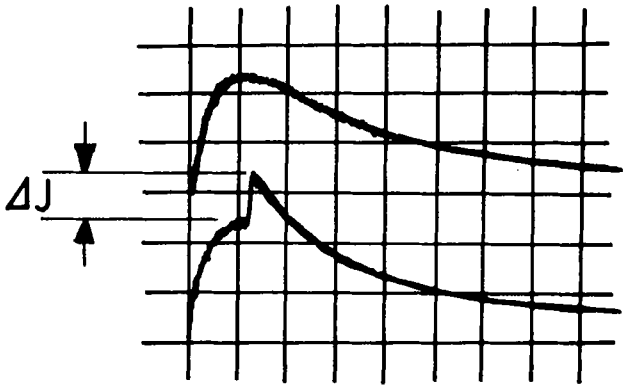

FIGURE 3 Photocurrent waveforms with 420 nm excitation (upper trace) and with 420 nm + 460 nm excitation (lower trace). The spike at t=2.5 μs is due to the photoionization of the excited state by a 460 nm pulse. Time scale is 2 μs/div.

light source was an excimer laser-pumped dye laser. In experiments in which two light pulses were necessary another dye laser pumped with a nitrogen laser was used. A pulse generator triggered both lasers, with or without a delay between them. The photocurrent was measured on an oscilloscope.

At 420 nm the absorption is weak and the crystal is excited homogeneously. This can be seen from the photocurrent waveform which is triangular when the excitation is weak. With increasing excitation

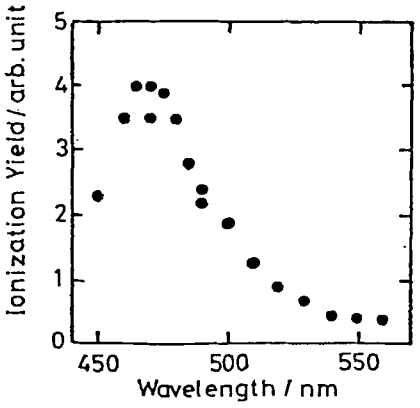

FIGURE 4 Photoionization spectrum of the intermediate state. The increment of the photocurrent (ΔJ in Fig. 3) is plotted as a function of the wavelength of the second pulse.

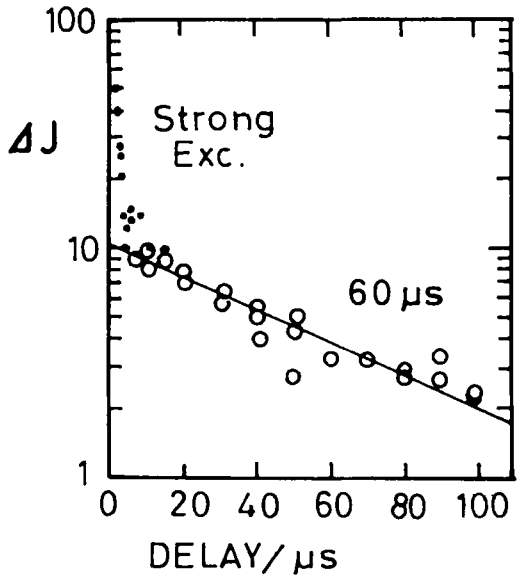

FIGURE 5 Decay of ΔJ (see Fig. 3) as a function of the delay between the 420 nm pulse and the 460 nm pulse, showing that the lifetime of the intermediate state is 60 μs. With strong excitation the first part of the decay is much faster, indicating the presence of a bimolecular process.

intensity the rise, and also the decay, of the photocurrent pulse becomes progressively faster (Fig. 2). This indicates the presence of bimolecular processes in the generation and decay of charge carriers. The involvement of an intermediate state could be most clearly seen in Fig. 3. The rise of the photocurrent is remarkably slow. This slow rise is observed only with excitations in the CT absorption region. The intermediate state can be photoionized by another light pulse (The lower trace in Fig. 3). By changing the wavelength of the second pulse the spectrum of photoionization could be obtained (Fig. 4). By an experiment in which the delay between the two pulses was varied the lifetime of the intermediate state could be also measured, which turned out to be indeed long, as expected.[1]

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