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: Ryuzi Katoh & Masahiro Kotani (1990): Photoionization of Singlet Excitation in Anthracene Single Crystal, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 183:1, 447-450

To link to this article: http://dx.doi.org/10.1080/15421409008047483

Mol. Cryst. Liq. Cryst., 1990, vol. 183, pp. 447–450
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Printed in the United States of America

PHOTOIONIZATION OF SINGLET EXCITON IN ANTHRACENE SINGLE CRYSTAL

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ABSTRUCI Photoionization of singlet exciton in anthracene single crystal by 2-color, 2-step excitation has been studied. Sn-S1 absorption spectrum were also measured. The ionization efficiency is discussed based on the experimental results.

INTRODUCTION

Recently, multi-photon and multi-step excitations have been applied to study excited state dynamics of molecules in the gas phase as well as in the solution. However, not many experiments have been done on organic solids. This is because of the difficulties such as possible sample damage by intense exciting light and the high density excitation effect which may complicate the interpretation of the results. We have proposed a 2-color 2-step excitation method which allows to avoid such difficulties encountered in organic crystals[1,2] Here will be reported an experiment in which this technique is applied to anthracene single crystal.

EXPERIMENTAL

Purification and crystal growth of anthracene crystal have been described in Ref.3. Photocurrent was measured by the time-of-flight (Kepler-LeBlanc) method. Transient absorption by singlet exciton was measured by a pump-probe method using nano-second laser pulses from an excimer laser / dye laser system. Details of these experiment will be reported elsewhere[4].

RESULTS AND DISCUSSION

When an anthracene crystal is excited with a 420nm photon in the absorption edge, charge carrier generation occurs by a two-photon process (Fig. 1, lower trace). There are two possible mechanisms. One is the ionization through singlet exciton annihilation, and the other is the photoionization of singlet excitons. From the analysis of the exciting light intensity dependence, we could show that photoionization of singlet exciton dominates under this condition[3].

With simultaneous irradiation with two pulses, one of 420nm and the other in the visible (480-600nm), an enhancement of the photocurrent is observed (Fig.1, upper trace) which is proportional to the visible light intensity. No detectable photo-response could be obtained with a 580nm pulse only. The increment decays with the time constant of 25ns. These observations clearly indicate that photoionization of singlet excitons occurs by visible light irradiation.

The spectrum of photoionization of singlet exciton (PI) and of transient absorption by singlet exciton (Abs) are shown in Fig.2. Ionization efficiency Φ is also shown in the Figure. Φ is given by

$$\Phi=\sigma_{PI}/\sigma_{A} \qquad (1)$$

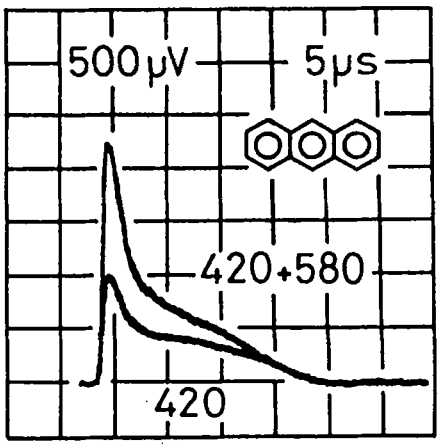

FIGURE 1 Photocurrent waveforms. Excitation with 420nm only (lower trace). Excitation with 420+580nm simultaneously (upper trace).

where σ_{PI} is the cross section for the photoionization of the singlet exciton and σ_A is the cross section for S_n-S_1 absorption. It may be seen that the excitation energy dependence of Φ is constant below 5.5eV and above that energy it increases with excitation photon energy. This indicates that below 5.5eV auto-ionization occurs after a rapid relaxation from various optically excited state to a common auto-ionizing state. On the other hand, another ionization channel seems to be opened above 5.5eV (for example; direct band-to-band transition).

Figure 3 shows the temperature dependence of the number of charge carriers generated by photoionization from singlet excited state with 580nm photon. According to the Onsager model the ionization efficiency Φ is given by, at low electric field[5],

$$\Phi=\Phi_{GP} \exp(-r_c/r_0)\{1+(e\, r_c/2kT)E\} \qquad (2)$$

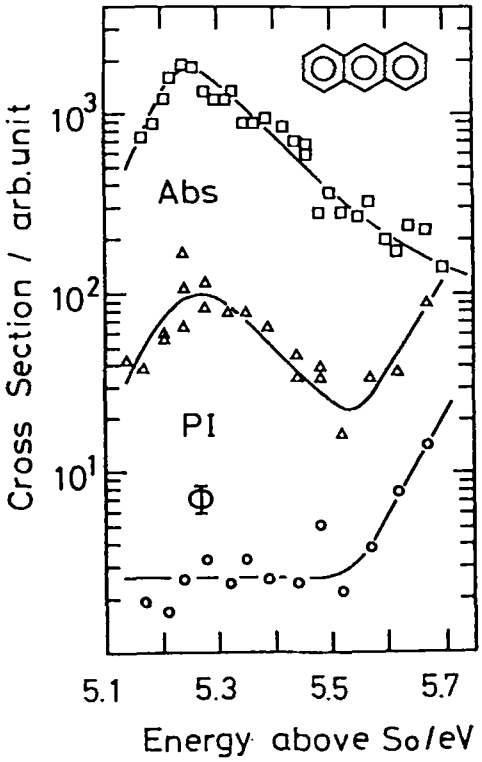

FIGURE 2 Absorption spectrum (Abs), photoionization spectrum (PI) and ionization efficiency (Φ) of singlet exciton.

where $r_c=e^2/4\pi\varepsilon\varepsilon_0 kT$, Φ_{GP} is the yield of the geminate ion pair and r_0 is the Onsager length (thermalization length). With electric field $E=1.5\times10^4$ V/cm, and $\varepsilon=3.2$ the result in Fig.3 is fitted with eq.(2). The Onsager length r_0 is found to be 25±5Å. A separate experiment with 1 color 2 step excitation with a 420nm photon yields r_0=36Å. This increase of Φ above 5.5eV is consistent with the general expectation that the ionization efficiency Φ may increase with the Onsager length r_0.

To obtain more information on carrier generation through such an experiment, measurements of polarized spectra and of absolute values of the cross sections may be helpful. Such measurements are under way and will be reported elsewhere[4].

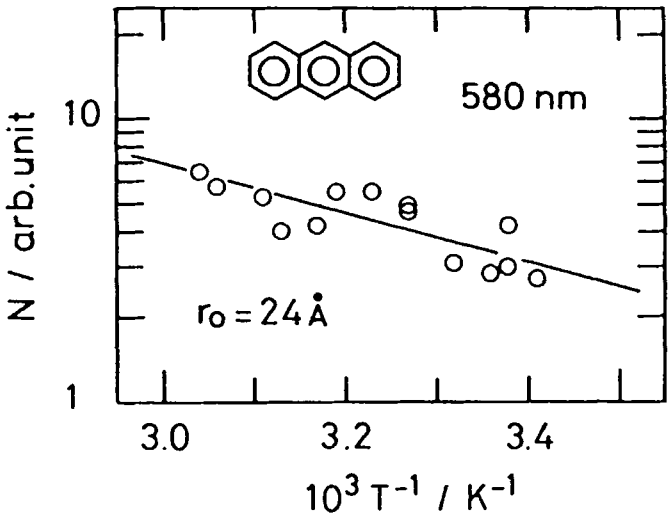

FIGURE 3 Number of charge carriers (N) vs. reciprocal temperature (580nm excitation).

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