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ON THE INVOLVEMENT OF TRIPLET EXCITONS IN A TWO PHOTON GENERATION OF CHARGE CARRIERS IN ANTHRACENE.§

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ABSTRACT: Two photon generation of carriers in anthracene has been studied using double pulses of a dye laser. The results indicate that photoionization of triplet excitons plays an important role in the photogeneration. The triplet exciton photoionization cross section is estimated to be of the order of 10^{-20}cm^2, in agreement with early results of Holzman et al.

The mechanism(s) by which charge carriers are generated in anthracene are complex and poorly understood, no matter if single photon generation or multiphoton generation is considered. There is however one fundamental difference between these two generation processes. For single photon generation, $h\nu \gtrsim 4$ eV, it can be envisaged that the primary CT state prepared before dissociation may be reached by a direct light absorption because it gains some transition strength from strongly allowed optical transitions to nearby singlet Frenkel exciton states.[1] There is no obvious parallel process which can occur for 2 or 3 photon generation $2(3)h\nu \gtrsim 4$ eV. Moreover, some confusion is evident in the literature with respect to the analysis of multiphoton generation with primary excitation of 600-650 nm. For example, Strome[2] observed a square dependence of carrier generation on light intensity at 525, 571 and 597 nm, and considered the process to be a direct band-band transition. He calculated the triplet exciton photoionization cross section as 5×10^{-22} cm^2, contradicting earlier results by Holzman et al.[3] who reported a cross section of 4×10^{-21}cm^2. According to Strome, this value should be increased fivefold due to incorrect estimation of the S_n-T_n crossing rate made by Holzman et al. Later a more detailed study by Bergman

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and Jortner[4] concluded that depending on excitation wavelength, two, three or four quantum processes may dominate carrier generation. They also contended that direct band-band two photon transitions are more important than triplet photoionization but assumed the magnitude of the triplet photoionization cross section was that calculated by Strome.

In view of these conflicting proposals, and the theoretical importance of understanding two phonon carrier generation itself, let alone its relevance in formulating a quantum mechanical description of the one photon process, we have studied laser induced photogeneration efficiencies in anthracene using a double pulse technique. The principle is similar to that used by Strome and by Holzman et al; a nitrogen pumped pulsed dye laser is made to pulse twice with a variable delay between pulses. The first pulse then can generate carriers and triplet excitons, which decay sufficiently slowly to be able to influence the generation efficiency of a second pulse if triplet excitons are of importance. A pumped dye laser (Molectron) provided double pulses of light with a delay between pulses of 17.5 to 50 ms. The integrated photocurrent signal was displayed on a scope together with the output of a photodiode monitoring the excitation light intensities. Preliminary measurements of wavelength and light intensity dependences of the photogeneration yield have shown that at very low light intensities a photocurrent signal directly proportional to light intensity was present, presumably due to charge detrapping. The presence of this phenomenon, when superimposed on third-power dependences which were observed at very high laser intensities could indeed give rise to erroneous determination of two photon generation coefficient K_2. Accordingly, the measurements were performed specifically in the wavelength and intensity range where these effects could be minimized. A wavelength of 610 nm was selected for the delayed pulse study. The K_2 vs. λ plot of Bergman and Jortner[4] exhibits a maximum at this wavelength, the K_2 value being ca 8×10^{-40} cm s^2. For our experiments, with photon densities of the order of 10^{23} cm^{-2} s^{-1} (10 ns pulses) carrier concentrations of $\sim 10^7$ cm^{-3} were obtained, giving with reasonable accuracy a similar value for the two photon generation constant K_2. However, when a second laser pulse hits the sample immediately after the first pulse, the resulting photogenerated charge is found to significantly exceed the charge expected calculated using the K_2 value given by Bergman and Jortner and also found in this work - ca 8×10^{-40} cm^2 s at 610 nm. K_2 is defined by relation $m = K_2 I^2$ where m is the carrier concentration (cm^{-3}) and I

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is the light intensity (cm^{-2} s^{-1}). Note that K_2 depends on pulse duration time - ca 10 ns in this work.

A plot of the excess charge vs the delay time between pulses (Fig. 1) shows a decay time corresponding to ca 8 ms. Detrapping of trapped charge by this second pulse could also account for these results, however calculating the trap photoionization cross section involved, assuming hole photodetrapping (measured hole trapping time was ∿40 μs in the crystal studied, trapping time of electrons was in excess of 1 ms) gives a value of $\sim 3 \times 10^{-15}$ cm^{-2} - almost three orders of magnitude higher than cross section reported by Schott and Berrehar[5]. Delayed fluorescence decay measurements showed triplet lifetimes of ca 15 ms. Therefore because the number of carriers which would be trapped and then detrapped under our pulsed laser conditions would be too small to account for the observed photocurrent we can interpret Fig. 1 as the photoionization of the residual triplet excitons formed by the first laser pulse. Assuming an S-T absorption coefficient of 7×10^{-4} cm^{-1} and an effective triplet lifetime of 8 ms, the calculated triplet photoionization cross section is $\sim 5 \times 10^{-20}$ cm^2. This value is close to Holzman's reported $2 \times 10^{-20} cm^2$; further circumstancial evidence that for these experiments triplet photoionization is the carrier generation dominant process. Indeed, the K_2 value calculated using the S-T absorption coefficient[6] and the triplet photoionization cross section given here, is $\sim 10^{-39} cm^2 s$, in agreement with the value reported.

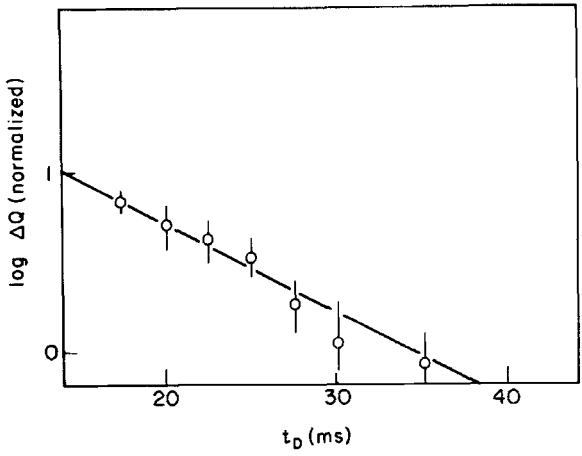

FIGURE 1. Dependence of the excess charge generated by the second pulse on the time elapsed between pulses.

Thus for the crystal and laser wavelengths used in these experiments, photoionization of triplet excitons gives rise to a significant component of the photocurrent. Therefore, in this case, a direct comparison of one and two photon carrier generation processes through the application of Onsager's theory is questionable. If exciton photoionization, or absorption of a second photon by this exciton is involved, then the states finally generated are not likely to be equivalent to those generated by single photon transitions, and furthermore their excess energy will also be less than twice the photon energy.

The data used earlier[7] to analyse two photon carrier generation in terms of Onsager's description of diffusive processes are not sufficiently accurate to show these differences.

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