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PHOTOGENERATION OF CHARGE CARRIERS IN ANTHRACENE THROUGH TWO PHOTON EXCITATION

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Onsager's theoretical description of the diffusive motion of a pair of oppositely charged particles in an applied field[1] appears to be satisfactory for describing the field dependence of carrier generation in low mobility materials.[2-5] This theory predicts also that the quantum efficiency of carrier generation is dependent upon the energy of excitation. Though this dependence is often not found in organic materials such as anthracene,[4,6-7] presumably due to internal conversion thermalization processes, it is found to hold for a-selenium.[5] The field dependence of the quantum efficiency in a-selenium was originally described within the framework of a Poole-Frenkel[8,9] effect, but more recent results from a two-photon excitation study showed Onsager's theory gave good agreement with experiment over a wider range of applied fields, particularly for low fields, because surface effects were eliminated.[5] Since Onsager's theory gives agreement with single photon experimental studies on anthracene when clean crystal surfaces are used,[2,4] (no surface effects), it was thought worthwhile to study two photon carrier generation also in anthracene as a function of applied field and excess photon energy.

Samples of a measured thickness, cleaved from highly purified single crystal anthracene, triplet lifetime ∿22 msec,

were mounted in a nitrogen cryostat between either two spring mounted electrodes both of indium tinoxide coated quartz, or with one electrode polished brass. First a series of temperature-current transient measurements were made with a pulsed nitrogen laser[10] as excitation. The mobilities of both electrons and holes were calculated from the current transient discontinuity, and they were equal to literature values[11] for the c' crystal direction at room temperature, $\sim$0.4 cm^2/Vsec and 0.8 cm^2/Vsec respectively, with only a slight temperature dependence. Some bulk trapping was seen for low applied fields. No space charge effects were seen. This same nitrogen laser was used to pump a dye laser, whose output was measured, and afterwards monitored, by a calibrated photodiode. The integrated photocurrent produced in the crystal by the dye laser pulse, together with the laser pulse monitor signal, were recorded on an oscilloscope. The general features of the photocurrent pulse were:- (1) that the current transient was triangular in shape with a rise time of less than 0.1 μsec, and a fall time which gave calculated mobilities almost equal to those from the single photon transients, (2) that the integrated current pulse was dependent upon the square of the dye laser intensity and also increased with the crystal thickness, over the measured temperature range. These results showed that surface effects and space charge effects were unimportant, and that carrier generation took place in the crystal bulk.[12] With an excitation wavelength of 6050 Å, it was found that photocurrent varied linearly with the applied field up to 10^6 V/m. Furthermore it was found that these results showed a slope/intercept value of $\sim 10^{-5}$ cm/V, with an extrapolation from results at reasonably low applied fields. Bulk trapping at low fields caused a departure from the high field linear dependence of the

current.[13] With the literature value of 10^{48} cm^4 sec photon^{-1} [14] for the two photon absorption coefficient, the quantum efficiency of generation at high field was calculated as $\sim 10^{-5}$. These results are the same as found in single photon studies.[2]

The measured photocurrents decreased as the temperature decreased. This temperature dependence was measured from ~200-300 K for six different excitation wavelengths between 4700 Å and 6050 Å. These wavelength limits were imposed by the observed laser intensity/photocurrent dependencies approaching a linear or cubic relationship respectively. Some typical results of the changing photocurrent, normalized to account for laser intensity changes, are shown in Figure 1 as log photocurrent vs T^{-1}.

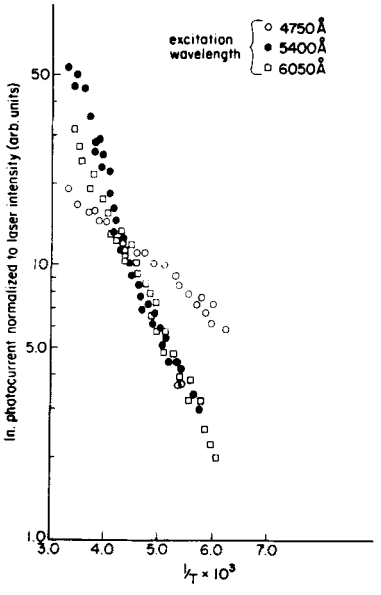

FIGURE 1 Change of the ℓn of the observed photocurrent normalized to dye laser excitation pulse power as a function of T^{-1}. The excitation and photocurrent are both in the anthracene crystal c' direction.

In the Onsager theory, the free carrier quantum yield ϕ can be written $\phi = \int\phi_0 g(r,\theta)f(r,\theta)dt$ where ϕ_0 represents the primary quantum yield of charge pairs, and $g(r,\theta)$ represents the initial spacial distribution of thermalized charge pairs. Substitution of the Onsager relation truncated at the linear field term into this expression for ϕ gives $\phi = A(T)[1+(e^3/2DK^2T^2)E]$ where $A(T) = 4\pi\int\phi_0 \exp(-e^2/DrkT)g(r)r^2dr$ if $g(r)$ has spherical symmetry and ϕ_0 is independent of E. D is the dielectric constant. This equation for ϕ predicts a linear quantum yield/field dependence and that the slope/intercept ratio is a constant, as has been experimentally shown. Furthermore if $g(r)$ is taken as a delta function, r_0, the thermalization length, can be calculated from a plot of log photocurrent vs 1/T, (ie Figure 1) though naturally quantum yield data would be better. $g(r)$ is assumed to be a delta function. From results as shown in Figure 1, with slopes calculated from a least squares fit, the value of r_0 is found to be constant in the excitation energy range 4-5 eV, and to monotonically increase with excitation energies 5→5.3 eV Figure 2. The same features have been found in single photon studies in these same energy regions.[4] The magnitude of r_0 calculated, ∿40 Å, is of questionable value for it is sensitive to the form of $g(r)$ taken, but its constant value indicates most that thermalization takes place not through numerous collisions within the lattice, but through internal conversion until a relatively long lived electronic state is reached.[2,6] This same final state could be reached by either one or two photon processes. Parity interconversion only requires the absorption/emission of a phonon of either parity, and it is to be expected that vibronic coupling would be reasonably large for these excited states.

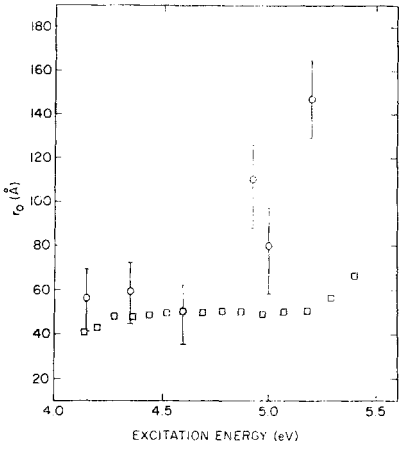

FIGURE 2 Variation of calculated $r_0(o)$ with 2x photon energy. Error bars show the extreme limits calculated from a least square fit of experimental results. For comparison, earlier results [□] for one-photon excitation are included.

In summary we have shown that the photocarrier generation characteristics of anthracene observed through two photon studies, where surfaces are unimportant, parallel those observed for single photon studies with clean or virgin crystal surfaces.

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