THE ELECTRICAL FIELD DEPENDENCE AND THE EFFECT OF CONTACTS OF PHOTOCONDUCTIVITY IN MOLECULAR CRYSTAL: ANTHRACENE

Riyad N. Ahmed-Bitar and Hisham Hidmi
University of Jordan, Physics Department, Amman, Jordan

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Abstract

Crystals sandwiched between metallic and liquid electric contact electrodes showed different electric field dependence of dark and photoconductivity. The crystal with metallic contact exhibit a slope to intercept ratio consistent with both Onsager's theory of geminate recombination and the reported results. The liquid contact electrodes showed better electrical conduction and a negative nonlinear term with the field. The intensity and spectral response dependence of the photocurrent is explained in terms of singlet and triplet exciton photoionization.

Introduction

Electrical properties of organic crystals have been extensively studied experimentally and theoretically [1-19]: transport properties [1-10], electrical switching and memory devices [11-19] and photoconductivity [1-5]. Despite this numerous experimental results, the theory of electrical transport phenomena in organic solids is yet not complete owing to the complication of the system, the many different energetic processes involved in the photogeneration of charge carriers and problems related to the electric contacts.

Bergman and Jortner [20] studied the processes involved in photon (s)-induced charge carrier in detail. Others studied the effect of dark injection of the contacts and conditions of illumination on the photocurrent spectra of tetracene and pentacene [21,30], and electric field dependence of the dark and photocurrent [22,23,24].

In this article, the dependence of the dark and photocurrent on electric fields up to 2 × 10^4 volts/cm was studied. Four lasing lines (λ = 514.5, 498.5, 476.5 and 459 nm) or cw argon ion laser were shined on an anthracene crystal sandwiched between either metallic contact or liquid contact electrodes. Short circuit photovoltaic measurements were also done.

These measurements will allow an evaluation of the effect of the electrical contacts on the electric field dependence of the current. They also allow for a comparison with recent results obtained on tetracene, pentacene [21,30], and anthracene [22,23,24] and a check on Onsager's theory of geminate recombination [26].

Experimental

The sample was prepared by the sublimation method in a 0.1 Torr of He atmosphere. Anthracene powder was evaporated on a cold finger to form planar monoclinic single crystals of approximately 8 x 8 mm with 0.1-0.5 mm thickness.

Two electric cells of anthracene single crystals were constructed by having two different electrode contacts with the crystal-metallic contacts and liquid contacts fixed perpendicular to the c'-axis of the crystal. Distilled water was used to make the liquid contact and silver wires were used to close the electric cell as can be seen in figure 1.

In the case of metallic contacts the crystal was sandwiched between soft indium and soft copper mesh to form metallic contact electrodes. Dissolved anthracene in dichloromethane was spread on the mesh to ensure good electric contact. The mesh was used for two reasons, the first is to establish planar equipotential surfaces normal to the c'-axis, and the second is to allow the laser beam to interact with the crystal.

Argon ion laser lines (λ=514.5, 496.5, 476.5, 459 nm) with intensity $I = 10^{23}$ photon cm^{-2} sec^{-1} were used to excite the crystal to the first singlet and triplet states. Dark and photocurrents were measured with a 600-B Keithley electrometer with fields varying from 0 up to 2×10^4 volts/cm.

Results and Discussion

A typical steady-state current-voltage (I-V) characteristic obtained for metallic contact electrodes of anthracene crystal (4 x 4 x 0.15 mm) is illustrated in figure 2. The curves labeled a, b, c, d, and e are those for dark and photocurrents when the crystal was illuminated with a laser beam at wavelengths 514.5, 496.5, 476.5 and 459 nm respectively. The vurves exhibit the following distinct features: first, forward increase in the current occurs with illumination of the crystal with laser light; second, the current increases with the increase in laser frequency; third, at low frequencies, the (I-V) characteristic is almost linear and ohmic as long as $V \angle 1000$ volts and at high frequency it shows a small quadratic term.

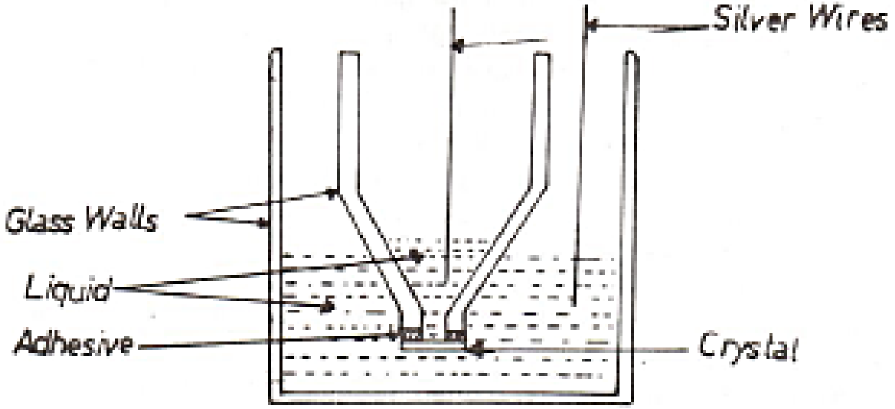

Figure 1: Liquid contact cell.

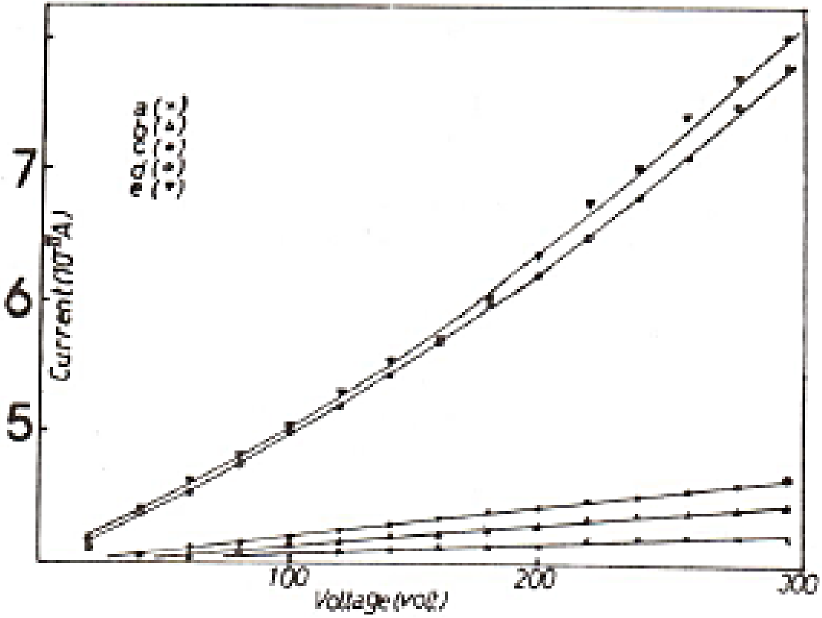

Figure 2: I-V characteristics (Metallic contact). Plots a,b,c,d and e curves correspond to anthracene crystal in dark, and illuminated with laser light; wave length 514.5, 497.5, 479.5, 459 nm respectively, laser power in 0.2 w, for all wavelengths.

To understand these features, it is important to notice that the direct threshold to the conduction band Eg relative to the ground state of the crystal is 4 ev [20]. The processes involved in the generation of charge carriers depends on the wavelength (summarized in ref. 20) e.g. illumination with λ = 459 nm produces one photon excitation of singlet excitons. Charge carriers then originate form either singlet exciton photoionization or collision of excitons. The photons of λ = 514.5, 496.5 and 476.5 nm produce one photon excitation of triplet excitons. Charge carriers then originate from triplet exciton photoionization. This model is not adequate to account for the sharp increase in photocurrent at λ = 476 nm relative to 496.5 and 514 nm. This inconsistency can be removed, if we assume that laser light with λ = 476.5 produces also singlet excitons through one photon excitation into the Urbach type exponential absorption tail. Also we cannot discard the generation of charge carriers through the absorption of a photon by a trapped carrier (by defects or impurities) and thereby undergo a transition to a conduction state.

The (I-V) curves confirm a linear field dependence and a small quadratic term in the case of λ = 476.5 and 459 nm. This is in agreement with Onsager's theory of geminate recombination [26]. The probability f (r,θ) that an isolated, thermalized pair with initial separation r and orientation θ relative to the applied field E will escape geminate recombination expanded through quadratic terms in E is

$$f(r,\theta) = \exp(-2q/r)\,[1+\beta q(1+\cos\theta) + \beta^2 q(q-r)\,(1+\cos\theta)^2]$$

where $q = e^2/2DKT$, $\beta = eE/2KT$, and D is the dielectric constant. Our results gave a ratio of the slope to intercept of 3.5×10^{-5} which is in agreement with the results of Batt et al. [24], Chance et al., [23] and Zhukov et al [30]. These results can weakly be compared with the recent results obtained on tetracene thin films [21] due to the fact that the excitation intensities ($I \sim 10^{12}$ cm^{-2} sec^{-1})are much weaker than ours($I \sim 10^{23}$ cm^{-2} sec^{-1}). The quadratic small term (for λ= 476.5 and 459 nm) is due to the space charge limited current [27].

The I-V characteristic curves for anthracene with liquid contact electrodes is shown in fig. 3. The curves have both negative quadratic term. This is indicative of the importance of the contact on the conduction mechanism. Therefore one should consider the whole electrical cell (crystal plus contact) for the obtained results. This effect may be due to diffusion current of some ions through the crystal, the injection of charge carriers at the interface [27], and the polarization field produced by the contact material. Our results are in disagreement with the results obtained by Mark and Hellfrich [8] on 50 um anthracene crystal with NaI liquid contact. They observed the current varies with the third power of the bias at low voltages and linear at high voltages. This disagreement can

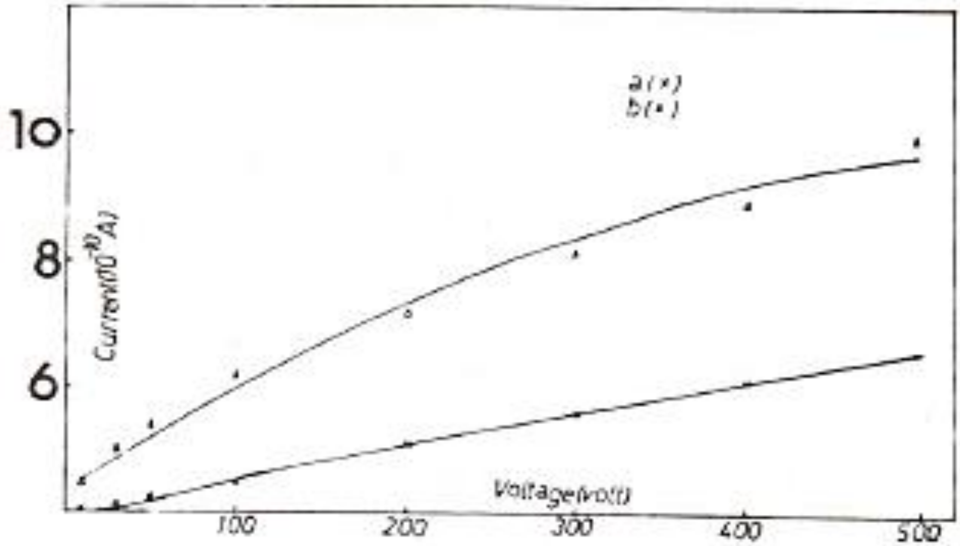

Figure 3: I-V characteristics (liquid contact). Plots a and b curves correspond to dark and photo current respectively. Laser light is λ = 496.5 nm and power = 0.2 w.

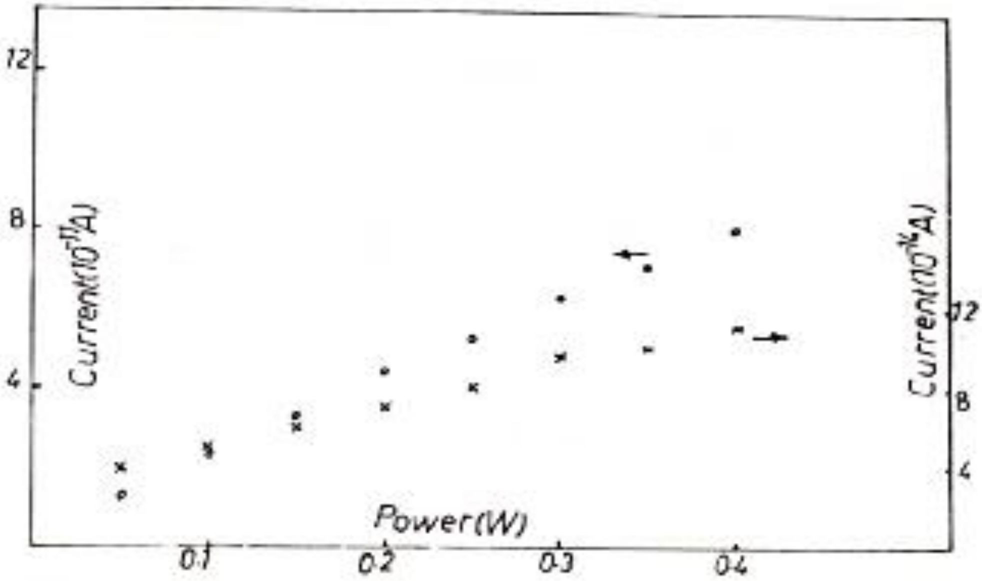

Figure 4: Powere - current characteristics
a- high bias voltage
b- low bias voltage.

be expected since NaI is a reactive materials and ions (Na^+ and I^-) may defuse in the crystal.

The I-V characteristic is fitted to a quadratic equatin: $I = G_0+G_1V+G_2V^2$, where G_0 is the intercept at zero field G_1 represents the conductance and G_2 represents the off linearily term. The dark and photoconductivity constants are calculated in order to draw certan conclusions. The values obtained are listed in table 1 and 2.

The errors sighted in the tables reflect root mean square deviation from the fit. Reproducibility though was found to be better than 10% over one week. Also we checked the different sources of current which would contribute to the measurements by removing the crystal and measuring through air and plexiglass sample. This check gave currents which are two orders of magnitude smaller and very weak response to laser light.

Conductivity constants of anthracene crystals for liquid contact σ-L and metallic contact σ-M are shown in table 1 and 2. It is clear that σ-L deduced from measurements on liquid contact cel is approximately a factor of 100 times larger than the corresponding σ-M for metallic contact cell. This may be attributed to three reasons, the first is that the liquid contact makes the best electric contact between insulatore and conductor; the second is that the liquid contact can be unblocking to the exchange of ions. The third is that themesh reduces the surface area of the electric contact and scatters part of the laser light which were not considered n the calculation. But still the ratio of σ^L_D / σ^L_P (the dark conductivity to the photo conductivity for liquid contact cells) are approximately the same as σ^M_D / σ^M_P for metallic contact.

For $2h\nu \sim E_g$ 4ev, the increase in σ'_P over σ'_D is interpreted by producing free charge carriers via two processes either singlet exciton photo ionization or triplet exciton photoionization [20]. Bergman and Jorther [20] argued that the exciton collision ionization process can not take place with intensities $I < 10^{27}$ cm^{-2} sec^{-1}.

Table 1 also shows the dependence of photoconduction current on the laser frequency. The sharp increase in photocurrent at high laser frequencies is due to the difference in the value of cross sections of photoionization of singlet to triplet excitons. σ'_p (λ= 476.5 and 459 nm) is found a factor of 5.4 larger than σ_p (λ= 496.5 and 514.5 nm). This result lies between the values found for the ratio of the cross section of singlet and triplet exciton photoionization by Strome [28], Holzman et al., [29] and Samoc et al. [25].

Finally the conduction current was studied as a function of laser power illustrated in figure 4. The cell was biased with high/low voltage ~ 300/1 volt in a short circuit configuration. In both cases the current increases linearly with a slope of 1.9 x 10^{10} and 2 x 10^{13}amp/w^{-1} for high and low bias respectively. The crystal acts as a photovoltaic high impedance device with 2.5 volts/watt in the low bias case. This behavior of conduction current with intensity is consistent with the assumption of exciton photoionization.

Conclusion

The conclusions can be summarized as sollows:

1. The dependence of the current on the electric field agrees with both the reported results and the Onsager's theory of geminate recombination. The nonlinear term is interpreted in terms of space charge limited current.
2. Electric contacts to the crystal have to be evaluated for electric measurements. To understand the effect of the contact relative to the bulk, we suggest that the measurements of impedance and phase angle produced by the whole cell should give relaxation times for the different conduction mechanisms (bulk conduction, and interfacial conduction) in the cell.
3. The dependence of photocurrent on the laser frequency is interpreted in terms of singlet and triplet exciton photoionization. The ratio f the cross section of singlet to triplet photoionization is found to be in agreement with the reported results [25,28,29]. Photocurrent generated by a trapped carrier cannot be disregarded.
4. The dependence of photocurrent on laser power confirms the conclusion in point 3 above.

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Table 1: Effective Dark/Photo Conductivity Constent for Metalic Contact Anthracene Crystal. Units are in MKS-System

Constants	Dark	Photo			
		514 nm	497 nm	479 nm	459 nm
10^{-13} G_1	0.082 ±0.004	0.155 ±0.006	0.238 ±0.002	0.818 ±0.031	0.848 ±0.053
10^{-17} G_2	0.139 ±0.000	0.422 ±0.000	0	14.80 ±0.01	16.53 ±0.02
10^{-14} σ	7.7 ±0.5	14.5 ±0.9	22 ± 1	77 ± 5	79 ± 5

Table 2: Effective Dark/Photo Conductivity Constant for Liquid Contact Anthracene Crystal. Units are in MKS-System

Constants	Dark	Photo
10^{-12} G_1	0.555 ± 0.010	1.812 ± 0.13
10^{-16} G_2	− 0.582 ± 0.020	− 14.4 ± 2.9
10^{-12} σ	6.6 ± 0.3	21.6 ± 0.8