Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: H. Baessler & G. Vaubel (1970): Detection of Photoemission of Electrons into Anthracene Crystals by Studying Recombination Radiation, Molecular Crystals and Liquid Crystals, 11:1, 25-34

To link to this article: http://dx.doi.org/10.1080/00268947008084925

Molecular Crystals and Liquid Crystals. 1970. Vol. 11, pp. 25–34

Printed in Great Britain

Detection of Photoemission of Electrons into Anthracene Crystals by Studying Recombination Radiation

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Received March 31, 1970; *in revised form May* 11, 1970

Abstract—Evidence for photoemission of electrons from a calcium contact into anthracene crystals is presented. It is based on the observation of recombination radiation resulting from mutual annihilation of photoinjected electrons with holes which are supplied by an ohmic counter-electrode. The method avoids spurious effects due to optical release of trapped electrons. The problem of photoemission of electrons from alkali-metals into anthracene crystals is discussed.

1. Introduction

The external photoelectric effect provides a useful and often applied technique for experimental determination of the barrier height for electron or hole injection across inorganic metal–insulator–junctions.(1–3) If χ denotes the barrier height and $h\nu$ the energy of the photons absorbed by metal electrons, photoinjection can occur if $h\nu > \chi$. The photoelectric yield defined by number of injected carriers per absorbed photon depends on the excess photon energy $h\nu - \chi$ and follows $\eta(h\nu) \sim (h\nu - \chi)^n$. In most cases $n = 2$ (Fowler relation(4)). This, however, requires that the insulator has empty conducting states in the energy range $0 \cdots (h\nu - \chi)$ above the bottom of the conduction band or below the top of the valence band. Because of strong interaction forces leading to broad and overlapping bands this condition is normally fulfilled with inorganic insulators in an energy range $h\nu - \chi$ of several eV.

Due to the weak intermolecular coupling forces in organic crystals

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like anthracene the width of the lowest valence and conduction bands is very small, numerically of the order 10^{-2} eV.(5) This is of major importance in photoemission studies: Since forbidden zones exist above the lowest conduction band and below the highest valence band the photoelectric yield η should approach a constant value for $h\nu - \chi > \delta$, where δ stands for the band-width, i.e. $\eta(h\nu)$ should resemble a step-function: $\eta = 0$ for $h\nu < \chi$ and $\eta = \text{const}$ for $h\nu > \chi + \delta$. Apart from this η might change when going from an inorganic to an organic insulator as a result of changes in the magnitude of electron–phonon interactions at the metal–insulator interface which are of importance for momentum conservation during the charge-transfer process. However, in organic crystals interaction between electrons and long-wavelength phonons is strong.(6) Therefore there is no apparent reason why photo-emission from a metal into an organic crystal should not be observable provided that no chemical reaction takes place at the interface forming a layer which inhibits the charge-transfer process.

Photoemission of holes from several metals into anthracene single crystals (Harshaw) has recently been established by Williams and Dresner.(7) On electron photoemission currents has first been reported by the present authors.(8) These results were experimentally confirmed by Dresner(9) and Donnini and Abetino.(10) There was, however, some discussion concerning the role of trapped electrons in those experiments. In particular, Mehl(11) and Many, Levinson and Teucher(12) have shown that alkali metals and amalgams of alkali and alkaline–earth metals which had been used in the previous studies form ohmic contacts for electron injection into anthracene in the absence of illumination. In this case any photocurrent must result from optical release of trapped carriers—a process which is well understood(12–14)—or at most from photoinjection of minority carriers from the positive counterelectrode. Several arguments have been presented(15) against the predominance of these effects in the investigations mentioned above(8): (1) In all cases the magnitude of the dark current was considerably below the level characteristic for space-charge-limited (SCL)-currents. (2) The threshold photon energies for the photocurrent increased with increasing work function of the contact metal (up to $\chi^- \approx 2.0$ eV in the case of Pb). (3) No time dependence of the current was observed. (4) At reversed polarity the photocurrents were negligible except in cases where photoemission of holes could occur. (5) The sum of the threshold energies for electron and hole emission from the same metal was independent of the particular metal and equal to the value of the band gap at the interface.(16) Furthermore Pott and Williams(17) have reported that alkali and alkaline-earth metals do not form ideally ohmic contacts with anthracene. Moreover the contact-behavior in the dark strongly depends on the presence of surface states (18) which seem to be sensitive to the method of crystal growing and electrode preparation.

The purpose of the present paper is to present direct experimental evidence for the occurrence of photoemission of electrons from a calcium contact into an anthracene crystal utilizing an electron counting technique based on recombination radiation. The crystal is provided with a semitransparent gold anode which forms a strongly hole-injecting contact.(19) The Ca-cathode injects an electron dark-current which is orders of magnitude less than the hole current. This means that the space charge stored in the crystal is almost exclusively built up by holes. All injected electrons must therefore recombine with holes within the crystal. Any enhancement of the electron injection rate by light must therefore lead to an increase in the intensity of recombination radiation.(20) On the other hand optical detrapping in the bulk cannot contribute to recombination radiation since it does not generate free electrons. The method has two further advantages: (1) Any ambiguity concerning the polarity of the injected carriers(21) is avoided since any photoinjection from the counterelectrode is masked by dark injection.(2) If the photon energy is below the singlet-triplet excitation energy of the crystal triplet excitons cannot be involved.(22)

2. Experimental

Anthracene single crystals were grown from solution. The solvent was a mixture of redistilled 1,2-symm dichloroethene, 1,2-transdichloroethylene and trichloroethylene in the volume ratio 1.0:0.9:0.1. Anthracene was purified by 30 zone passes. The crystal was contacted with a semitransparent gold layer. Afterwards it was mounted in a vacuum chamber in which the Ca-contact was deposited. Great care was taken to avoid photo-oxidation of the crystal surface during sample handling. All measurements were done in situ. Attempts which were undertaken to prepare air-resistive samples by covering the Ca-layer by a protective gold layer and an epoxy (or paraffin) layer gave unsatisfactory results.

A 1600 W Xe lamp was used for excitation. The incident beam passed through red filters (6 mm Schott RG 715 yielding a transmission of 10^{-5} at 680 nm and 0.5 at 720). Blue emission of the crystal was spectrally isolated by 6 mm Schott BG 23 filters and an appropriate solution of dyestuffs (" capri-blue " and crypto–cyanin in methanol). In order to achieve maximum sensitivity a set of light guides of fused quartz was employed in combination with a mirror of 50% transparency at 500 nm acting as a beam-splitter. The recording unit consisted of an RCA 6655A photomultiplier connected to a Keithley electrometer. Crystal currents were measured with Hewlett–Packard μAmmeter.

3. Results

Figure 1 shows $j(V)$-plots for the dark-current obtained with various electrode combinations. With Ca –, Au + the current follows $j \sim V^6$ indicating that it is probably space-charge-limited.(23) In order to check that the high current level results from hole injection from Au +, the gold anode was replaced by Pb. Since the threshold energies for electron or hole injection are $\chi_{\text{Ca}}^{-} = 1.05$ eV(18) and $\chi_{\text{Pb}}^{+} = 1.6$ eV(7) respectively the majority carriers must now be electrons. The dark-current is reduced by about four orders of magnitude. (For Pb –, Ca + the current is still lower.) This demonstrates (1) that Ca is only weakly electron injecting and (2) that in the Ca –, Au + combination no or only very little electron trapped space-charge can exist whereas the density of trapped holes is high.

The voltage dependence $I(V)$ of the intensity of the recombination radiation emitted from the crystal with the electrode combination Ca –, Au + in the absence of illumination closely resembles the $j(V)$-curve characterizing electron injection from Ca (see Fig. 1). The shift towards lower voltages results from field enhancement near the weakly injecting Ca contact due to positive spacecharge. This

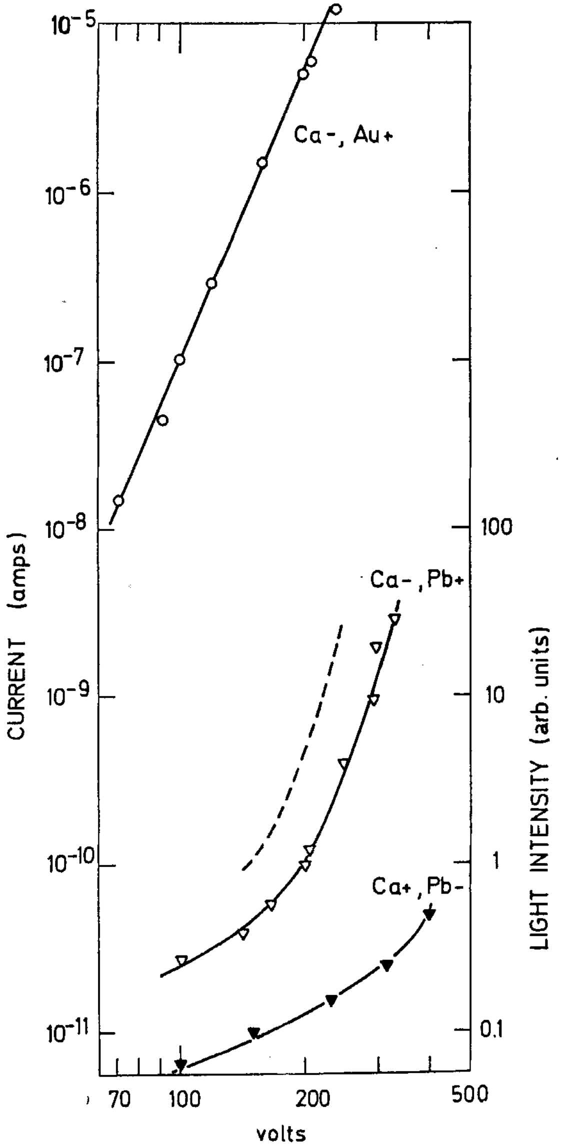

Figure 1. Dependence of the crystal-dark-current on the applied voltage for various electrode combinations. Crystal thickness: 40 μ, electrode area: 0.1 cm^2. All curves are taken at room-temperature. The dashed curve represents the intensity of recombination radiation (in arbitrary units) observed with the electrode combination Au +, Ca – in the absence of illumination.

agreement justifies the method of electron counting by measuring the recombination radiation. The dependence of the emission intensity I on the crystal current is plotted in Fig. 2. The departure from linearity arises from the fact that electron injection from Ca rises faster with the voltage than the hole current.

Upon illumination of the Ca cathode with light of a photon energy $h\nu \leqslant 1.7$ eV the intensity of recombination radiation emitted by the

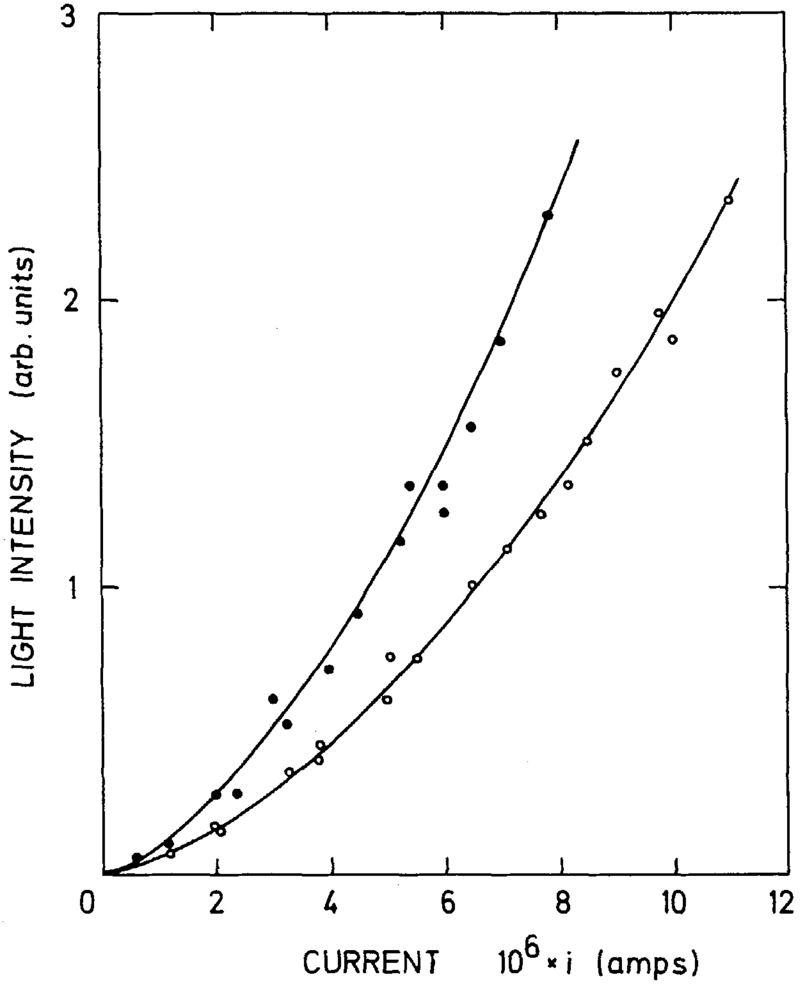

Figure 2. Relationship between intensity of the recombination radiation and crystal current. Open circles: without illumination; closed circles: Calcium contact illuminated with photons of $h\nu \leqslant 1.7$ eV.

crystal increases by about a factor of 2 (see Fig. 2). With various samples the relative magnitude of the effect is reproducible within ±100%. Most likely minor changes in the contact properties, which are difficult to control, are the reason for these uncertainties. The risetime of the light-stimulated recombination radiation is determined by the time-constant of the electrometer ($\approx$1 sec) '(see Fig. 3). The absence of any significant time dependence strongly argues against a trivial heating effect. The intensity of light-stimulated recombination radiation is proportional to the emission intensity in the absence of illumination (Fig. 2). This means that the field dependence is the same for thermally and optically stimulated electron injection. This point is confirmed by direct measure-

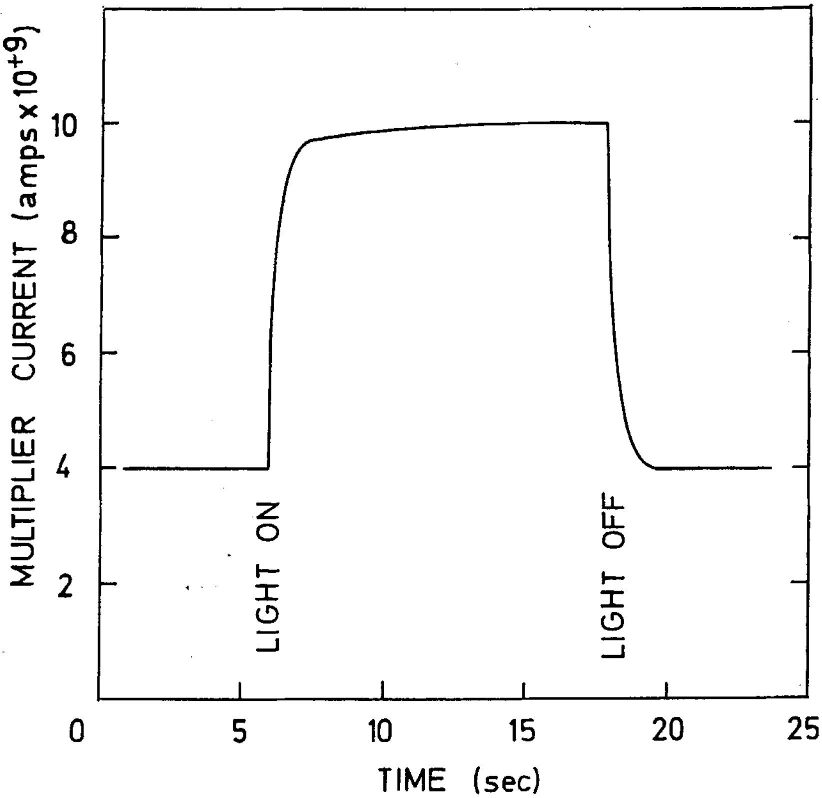

Figure 3. Time-dependence of the recombination radiation stimulated by illumination of the Ca-contact. The multiplier-darkcurrent has been subtracted.

ments of the photoemission current originating from a Ca cathode: With the electrode system Ca −, Pb + the current increases by about a factor of 2, independent of the voltage, upon illumination with a photon energy of $h\nu \leqslant 1.7$ eV which is insufficient to cause appreciable hole injection from Pb +.

The influence of the illumination on the crystal current under the electrode condition Ca −, Au + is almost negligible and unreproducible with various samples. Occasionally even a slight decrease was observed. This is somewhat surprising since optical detrapping of holes in the bulk might be expected leading to an increase of the SCL current.(12–14) However, in a photon energy range below the energy of triplet excitons optical detrapping proceeds with a very low quantum yield via direct transitions between filled traps and conducting states. The effect is masked if the rate of recombination between trapped holes and injected electrons exceeds optical release of holes. This is probably the case with the electrode combination Ca −, Au +. On the other hand the absence of any significant influence of illumination on the current level confirms the interpretation that the observed stimulated recombination radiation is due to photoinjection of minority carriers, i.e. electrons.

4. Discussion

The experiments reported herein demonstrate the occurrence of photoemission of electrons across a Ca-anthracene interface. They cannot yield information concerning details of the process, in particular, whether the injected electrons originate from the metal or from an interfacial layer formed by chemical reaction between Ca and anthracene. The latter possibility, however, is unlikely: As has been pointed out earlier,(8,15) the spectral response curves for the photoemission current are in agreement with theoretical predictions for photoemission into a vibronically split narrow band and into a broad upper conduction band. Furthermore the photoelectric yield does not decrease with increasing metal work-function whereas the reactivity of alkali and alkaline–earth metals towards anthracene is greatly reduced with increasing ϕ.

A concluding remark shall be made concerning photoemission of electrons from Na into anthracene. Attempts to detect light-stimulated recombination radiation with the combination Na –, Au + failed, presumably as a result of high electron injection from Na in the dark. In previous experiments using Harshaw crystals, however, dark injection from Na – was low enough to observe photoinjection. Apparently solution grown crystals as used in course of the present work contain a smaller amount of surface states.(24) No additional surface potential is then built up.(18) The answer to the question whether or not photoemission of electrons from alkali metals into anthracene is observable depends on the experimental technique employed. A similar situation seems to be present with the Au-anthracene contact: With solution grown crystals Au forms a strongly hole injecting contact. This is not true for Harshaw crystals where a threshold energy for photoemission of holes of $\chi_{\mathrm{Au}}^{+} = 1.17$ eV has been found.(7)

Acknowledgement

We wish to thank Professor N. Riehl for his interest in this work. Financial support by the " Deutsche Forschungsgemeinschaft " is gratefully acknowledged.

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