1001. *Photo- and Semi-conductance in Organic Crystals. Part IX.* Photo-conductance in Anthracene and Naphthacene Irradiated in the Vacuum Region.*

By L. E. Lyons and G. C. Morris.

Photo-conductance has been found to occur when single crystals of anthracene and naphthacene are irradiated with light of energy 36,000—66,000 cm.$^{-1}$. The effect has been distinguished from photo-emission of electrons which also occurs. There is no marked change in the quantum efficiency of the production of electrons from that observed at lower energies. The effect is considered as essentially similar to that previously observed at lower energies, and trapping processes therefore are regarded as of great importance.

Whether or not photo-conductance would occur in the region of the spectrum in which photo-emission of electrons occurs has been an interesting question, answered only by some work on other insulators which has since been superseded.[1] Whether there would be any great change in photo-conductivity when light of higher energy was used was also a question previously unanswered. The present work was carried out in an attempt to answer these questions.

Experimental

Crystals of anthracene and naphthacene were grown by controlled sublimation in the dark in an atmosphere of carbon dioxide or nitrogen. Crystals were examined under a Zeiss polarizing microscope for visible flaws and for thickness measurements; those with obvious flaws were rejected. Most crystals used were between 1 and 5 microns thick, the other dimensions being kept as large as possible consistently with the size of the exit beam.

The usual crystal holder was a hollow brass cylinder, jacketed for temperature control. The light was admitted to the cell interior through a fluorite window on the front face. The cell could be evacuated. The mounting of the crystal was on a piece of thick Teflon. The electrical leads passed through the Teflon to preserve rigidity. The cell cylinder could be held at any desired potential, and the field across the crystal varied independently, the current flow through the crystal being measured. The crystals were either placed directly across the electrodes by using Aquadag to form the electrical connection between the platinum wires and the crystal, or first mounted upon a silica disc, the Aquadag being then painted over two opposite crystal edges in a surface cell arrangement. The disc could be held on the Teflon spacer in the cell.

An atmosphere of nitrogen surrounding the crystal was necessary when the dependence was sought of the current on the potential of an electrode used to collect photoemitted electrons, or when investigations of the photocurrent at different pressures independent of the spectrograph pressure were carried out.

The developed crystal face for both hydrocarbons was the (001) plane. Although it was not possible to use polarized light, since insufficient intensity was available, the crystal was held so that the field direction was parallel to an extinction direction. The light was monitored by the exit slit so that it just covered the crystal area in width. The spectral region of particular interest was above 40,000 cm.$^{-1}$.

Both surface and bulk currents are possible, depending upon the electrode arrangement, but the present work was confined to surface cells, *i.e.*, cells in which both electrodes were placed on the one surface of the crystal.

Electrode connections to the crystal were deemed good when the back-photocurrent, obtained by illumination when the field had been switched off, was negligible (cf. ref. **2**). Other connections were soldered to ensure good electrical contact. The field direction through the crystal was reversed to check for anharmonicities in the illumination which could result in

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* Part VIII, preceding paper.

[1] Taylor and Hartman, *Phys. Rev.*, 1959, **113**, 1421.

[2] Lyons and Morris, *J.*, 1957, 3648.

localized space-charges.[2] When a crystal was mounted on a silica disc, careful drying of the assembly by evacuation or a phosphoric oxide desiccant prevented leakage currents. When the crystal was placed directly across the electrodes, no trouble with leakage was experienced. The crystal usually clung to the silica disc which was electrostatically charged by rubbing. Then the electrode material was painted on the side from which the light was incident. This method meant that the electrode material was not totally confined to one side, but would make contact with the edge of the crystal. However, the electrode material did not flow between the crystal and the disc—the only electrical connection to the face not illuminated was along the crystal edge.

The reproducibility of the results involving both long- and short-time effects was always carefully checked by repetition of the results on one crystal and by the use of different crystals.

The effect of stray light was checked by the use of filters. Currents measured in the region above, say, 55,000 cm.$^{-1}$ could be checked by putting oxygen between the slit and the light source; no photocurrent should then be, or was, registered. The stray light was also shown by photography and by photomultiplier recording to be negligible. Since the photoconduction response did not alter very markedly with wavelength it was easier to determine the effect of scattered radiation than it was in the experiments on photo-emission.[3] The effects of photo-emission were carefully checked to see if the currents obtained could be accounted for as due to photo-emission or its accompanying effects. Carefully cutting the crystal and using an atmosphere of nitrogen to inhibit a photo-emission current reaching the electrode showed that some internal photocurrent was being registered. The properties of this current are presented in the results.

Current–Time Relation.—On both compounds in either a vacuum or a nitrogen atmosphere, this was similar to that found previously for light of lower energy. Over the first minute of illumination the current remained fairly steady unless bad electrode contacts were present or non-uniform illumination was used. A drop of the current value occurred when this happened and this drop was accompanied by the possibility of registering a back-photocurrent by illumination with the field switched off. Even with good contacts and uniform illumination, a gradual polarization of the electrodes occurred, giving rise to a slightly increasing current during some hours.

Standard conditions of illumination and dark time were used in the following experiments. After stabilization of the dark current, or the capacity-coupling surge accompanying application of a field on the crystal, light was allowed to fall upon the crystal for 30 sec. The steady maximum was reached within this time. The light was cut off for 30 sec., in which time the current decayed to zero. Repetition of this procedure gave a reasonably constant current at a particular wavelength, light intensity, and voltage.

Effect of Evacuation.—The photocurrent from naphthacene was unaffected by evacuation, or by evacuation simultaneous with illumination with the rather low light intensities used. Since oxygen strongly absorbs radiation above 54,000 cm.$^{-1}$, this result could be checked only below this energy. Nitrogen did not affect the photocurrent's magnitude and did not absorb radiation in the region of interest. It was used to provide an atmospheric pressure about the crystal to inhibit photo-emission electrons from migrating to the positive electrode.

The photocurrent from anthracene is affected by evacuation and illumination techniques. Previous workers agreed that oxygen increased the photocurrent upon illumination. The present work, utilizing both polychromatic and monochromatic radiation below 54,000 cm.$^{-1}$, showed four main results.

(*a*) When evacuation was used without continuous irradiation, the photocurrent was almost the same as that in air. (*b*) Continuous illumination whilst evacuation was in progress decreased the photocurrent to less than 1/20th of the current in air; this rate of decrease depended on the light intensity, and with the low light levels obtainable from monochromatic light it took hours for completion. (*c*) Continuous illumination in air restored the photocurrent in a vacuum to its original value in air. (*d*) When evacuation was effected in the dark, and an atmospheric pressure of dry purified nitrogen or hydrogen added, the photocurrent remained fairly steady upon illumination even with fairly intense polychromatic light. With the weaker monochromatic light, no alteration was noticed. This arrangement of nitrogen filling was useful for measuring the spectral response curves.

Current–Light Intensity Relation.—Monochromatic light to 67,000 cm.$^{-1}$ was used, different

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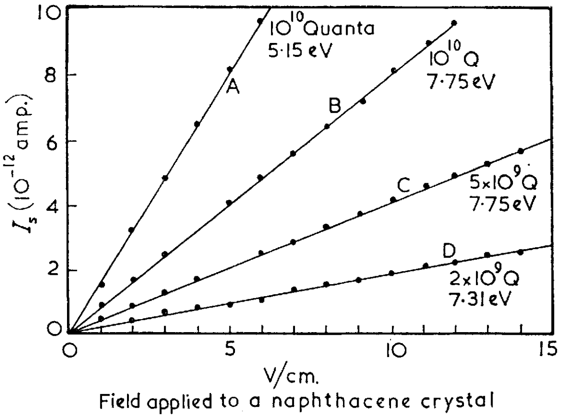
[3] Part VIII, preceding paper.

intensities being obtained by neutral calibrated filters. Only naphthacene was used, as the currents were too small with anthracene at low light levels. In the relation $I_s \approx L^n$ the exponent n was 1, but not strictly so when low field strengths were used. For example, with a field strength of about 100 v/cm., photon energy of 7·80 ev, and intensity varying over a 100-fold range up to 10^{10} quanta incident on the crystal, n was 0·93.

Current–Field Strength Relation.—This is shown in Fig. 1 for a naphthacene single crystal at different light intensities and with use of photon energies extending into the vacuum-ultraviolet region. The voltage settings were made in random order. No tendency for current saturation was noticed, but neither light intensity not field strength was very large. Anthracene gave a similar result, but a smaller range of voltages had to be used. The lower limit of field strength was set by the smaller quantum efficiency of photoconduction for anthracene. The upper limit was usually set by leakage currents, if the crystal was mounted on a silica disc, or, if not, it was governed by a discharge occurring at high field strengths when the crystal was surrounded by nitrogen.

FIG. 1. *Photocurrent, I_s, in a surface cell plotted against field strength, E.*



	A	B	C	D
Quanta	10^{10}	10^{10}	5×10^9	2×10^9
ev	5·15	7·75	7·75	7·31

Experiments using different voltages across the crystal and on the metal shield were also performed. The shield was placed at +300 v (giving a field strength of about 300 v/cm. for electrons photo-emitted from the crystal), and a potential of 10 v was put across a crystal with surface electrodes spaced 2 mm. apart. A photocurrent was registered as flowing in the crystal circuit upon illumunation. Further, the effect of the shield potential upon the current flow was checked to see what effect a voltage of +300 v had on the current flowing in the crystal when light of energy insufficient to cause photo-emission was used. The experiment of using the crystal as one plate of a condenser with a metal disc as the other plate has been described for anthracene.[4] The general result that the photocurrent was greater when the shield was negative was confirmed, but the results were complicated, as Bree has pointed out. However, the application of a potential of +300 v to the shield caused only a small decrease in the current value relative to that when the shield was at earth potential. Thus a current was registered even when any photo-emitted electrons would be attracted away from the positive electrode on the crystal surface.

Current–Photon Energy Relation.—Difficulty was encountered in extending measurements into the vacuum-ultraviolet region for two main reasons. (*a*) For anthracene, the current was very small owing to the small band-pass (*ca.* 100 cm.$^{-1}$) which had to be used. With naphthacene, this trouble was not experienced. (*b*) The effects of evacuation did not matter for naphthacene, but, as judged from the previous work, the spectral response of anthracene altered upon evacuation, losing its resemblance to the absorption spectrum; the current also

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[4] Compton, Schneider, and Waddington, *J. Chem. Phys.*, 1957, **27**, 160; Bree, Ph.D. Thesis, Sydney, 1958; Part VI, Bree and Lyons, *J.*, 1960, 5179.

markedly decreased. The cell containing the anthracene crystal was evacuated in the dark and then surrounded by an atmosphere of purified nitrogen. Such an arrangement gave a measurable current. For naphthacene, this arrangement was used as well as an evacuated assembly.

The steps used in taking a spectral response curve (" photocurve ") after alignment of the crystal and stabilization of the surge current attendant upon field application were as follows: (*a*) With the entrance and the exit slit of a fixed width, light of a chosen wavelength was passed on to the crystal for 30 sec. After this, the light was cut off from the crystal for 30 sec. (*b*) Light with wavelengths 100 Å apart was used with the same procedure, until the spectral range was spanned. (*c*) Light with wavelengths 20 Å apart was then used as above. (*d*) Any alteration of a photocurrent at a particular wavelength due to the time interval involved could be readily seen by this procedure, but was, indeed, slight. Corrections could easily be applied because (*b*) gave the general shape of the spectral response, whilst (*a*) gave the response curve accurately at closely situated wavelengths. Systematic errors were thus minimized. (*e*) The crystal was carefully cut down the middle so that approximately the same crystal area remained, but no current could flow through the crystal. The procedure (*a*)—(*d*) was then repeated. A small current was registered in the regions where the quantum efficiency of photo-emission was greatest, being up to 30% of the first current measured. (*f*) The current difference (*d*) — (*e*) was thus obtained. The value of this at each wavelength was corrected for the quantal distribution of the lamp, a band-pass of 100 cm.$^{-1}$ being used.

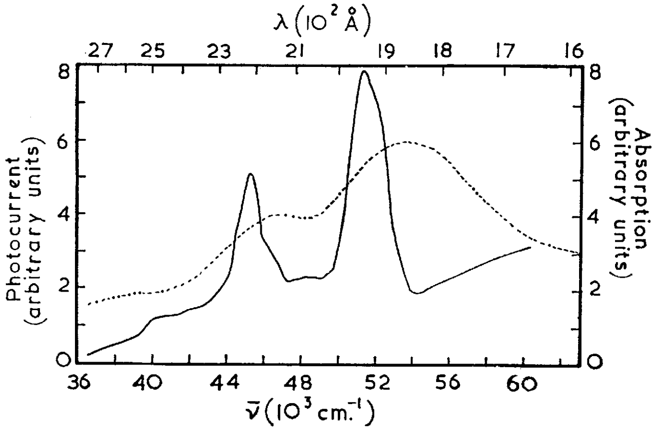

FIG. 2. *Spectral dependence of the photocurrent in anthracene.*

— · — *Photocurrent.*

···· · *Absorption of unpolarized light.*

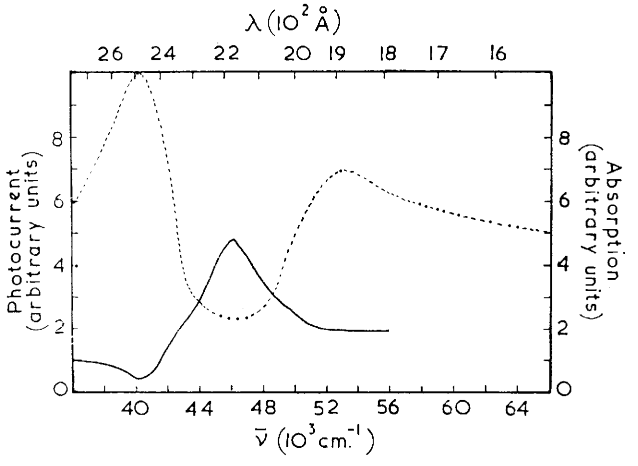

FIG. 3. *Spectral dependence of the photocurrent in naphthacene.*

- - - *Photocurrent.*

—— *Absorption of unpolarized light.*

Fig. 2 gives the photocurrent spectral response for anthracene single crystals obtained by the above means. Also included on the graph is the absorption spectrum of an anthracene crystal in unpolarized light obtained from the polarized spectra by assuming that the incident light is polarized 50% along the *b*-crystal axis, and 50% in the *ac* plane, and using a crystal thickness of 10 μ.

The accuracy of current magnitudes in the photocurve is only about 50% owing to the small currents. Fig. 3 gives the spectral response of the photocurrent for single crystals of naphthacene. Also given is the absorption spectrum of a 10 μ single crystal of naphthacene, unpolarized light being used. The accuracy of the current values is about 10% for a particular crystal, but variations from crystal to crystal were found. This has been discussed elsewhere for anthracene.[3] The same shape of the photocurve, however, was obtained for the several crystals used. Further, it did not vary when the photocurve was obtained in air (below 50,000 cm.$^{-1}$), in a vacuum, and in nitrogen.

Differentiation of Photoconduction from Photo-emission.—For some substances other than hydrocarbons investigators have tried to measure photoconductivity in a region where photoemission occurs and have concluded that it is not possible. Thus, Spicer [5] writes: " If external photoelectrons are created, these are attracted to the positive electrode and form a current which masks the internal photocurrent. This makes it impossible to extend the photoconductive measurements much beyond the photoemissive threshold." Also, careful work by Taylor and Hartman [1] on pure alkali halides led them to conclude that no true photocurrent exists in these substances. Pseudo-photocurrents can be easily registered owing to the effects of photoemission. As stated earlier, the photocurrent commences at photon energies more than 3 ev below the photoemission threshold for the hydrocarbons. In this respect, of course, they differ markedly from the compounds considered by Spicer.

Our work indicates that photo-conduction does not die away when photo-emission occurs, but continues throughout the same spectral region. The two types of current are distinguishable to 68,000 cm.$^{-1}$ for naphthacene and to 63,000 cm.$^{-1}$ for anthracene. For naphthacene, the quantum efficiency of photo-conduction is *ca.* $5 \times 10^{-6}\ eQ^{-1}E^{-1}$. Thus, with a field strength of 1000 v/cm. (and even larger could be used) each incident quantum of radiation would give 5×10^{-3} electrons in the external circuit. If this value is compared with the ordinate of Fig. 4 of Part VIII it is seen that only above 64,000 cm.$^{-1}$ does the photo-emission yield become larger than the photo-conduction yield. Thus I_s was not swamped by I_e below this value, and indeed the effect of I_e can be readily allowed for as discussed below. However, the position was not so satisfactory for anthracene. A field strength of 1000 v/cm. enabled photocurrents to *ca.* 50,000 cm.$^{-1}$ to be read without fear of photo-emission currents swamping them, but to extend the results above this region was more difficult.

The effect of introducing an atmosphere of gas (nitrogen) about the crystal must be considered. Brode's work [6] has shown the probability of an electron's being collected after emission as a function of pressure for different gases. When an atmospheric pressure of gas is used, the electron's mean free path is very small, and the probability of its reaching the positive electrode low. In this work, no direct determination of the influence of an atmosphere of gas on I_e was made. It was made indirectly, however, when the crystal was cut and the excitation spectrum re-measured to determine the contribution of I_e to the measured current. I_e did not become comparable with I_s until *ca.* 68,000 cm.$^{-1}$ for naphthacene and *ca.* 63,000 cm.$^{-1}$ for anthracene.

When considering this apparent drop in emission yield two points must be remembered: (i) The electrons may be photo-emitted from the crystal in the same quantity, but the mean free path, being approximately inversely proportional to the pressure, would be much smaller. Thus many of the emitted electrons may not reach the electrode. (ii) Some of the electrons may be prevented from leaving the crystal because the potential barrier at the crystal–nitrogen interface is larger than at the crystal–vacuum interface. However, the electrons are still released in the crystal, so that if drawn across the potential barrier, they could contribute to I_e, unless quenching processes prevent this.

A difficulty then presents itself: for, if the electrons are released but cannot surmount the energy barrier at the crystal–nitrogen surface, they, and/or the holes they leave free, should be able to contribute to the photo-conductivity. Hence, in addition to the conductivity produced as a result of illumination in the exciton band region, there should be this additional

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[5] Spicer, *Phys. Rev.*, 1958, **112**, 114.

[6] Brode, *Rev. Mod. Phys.*, 1933, **5**, 257.

contribution due to the released electrons and/or holes. That the quantum efficiency of photo-conduction is almost unchanged (after allowance, of course, for change in extinction coefficient with frequency) from the region of the first exciton level until *ca.* 60,000 cm.$^{-1}$ suggests that these released electrons and/or holes play little part in the value of I_s. One possible objection to this statement is that the true I_s value actually decreased, but the electrons released in the crystal for photoemission provide further carriers to keep the measured I_s at a value consistent with a constant quantum efficiency. However, there seems little reason for the photocurrent to die away when these free electrons and/or holes are produced. The most plausible hypothesis is that the latter do not contribute much to the I_s value.

The effect of the positive charge possibly left on the crystal surface after electrons are emitted must be considered, for such a charge would reveal itself in an increase of conductivity beyond what would normally be attributable to I_s. In regard to this, there are three important considerations.

(i) The hydrocarbons have a high resistivity. Values of the resistivity have been obtained by several authors.[7] For anthracene the results vary between 10^{12} ohm cm.$^{-1}$ to 10^{21} ohm cm.$^{-1}$. It would be interesting to see if any change in the resistivity occurred when thoroughly outgassed single crystals were used in a definite crystallographic direction and under vacuum conditions (cf. ref. 8). In any case, the results indicate what good insulators these hydrocarbons are, but they may also indicate a difference in purity of the samples used by the various workers, as well as differences due to space-charge effects.[9] Charges isolated on the surface may be expected to remain for some time unless trapping and recombination processes occur. (ii) The measured current–time relation does not show any decrease of current with time. If that does happen, it occurs in a time shorter than the time constant of the apparatus, *i.e.*, equilibrium between charges formed and charges neutralized by electrons flowing out of the electrode into the crystal occurs in less than 3 sec. The electrode separation was usually 1—2 mm. Thus, if electrons were to flow into the crystal to neutralize the charges, they would have to flow for a comparatively large distance. This is linked with the I_e–t relationship when thick crystals are used, although the carriers do move along different crystallographic planes. In this case I_e decreased with time until a steady state was reached. Assuming that the carrier mobilities are not very different in the bulk and on the surface, one would expect a decrease of the measured current with time if I_e were contributing to the current. (iii) A continual building-up of charge on the crystal surface does not occur, but an equilibrium is reached. Even with different thicknesses, I_e is reasonably constant, irrespective of whether one measures the number of electrons flowing out of the electrode to which the emitter was attached or the number of electrons reaching the collector in vacuum conditions.

The current–voltage relation (Fig. 1) supports the idea that I_e contributes little to the measured current for naphthacene up to incident photon energies of 7·75 ev. The current values were smaller for anthracene and the I_s–E relation was obtained only over a small range of large voltages. One would not expect a linear dependence of the current upon field strength if I_e were contributing a significant proportion of the current. Confirmation of this idea was forthcoming with field strengths near 20 v/cm. and light of energy of 7·75 ev. The I_s–E curves became non-linear, probably showing the contribution of I_e. Thus Fig. 1 strongly supports the contention that the currents measured are not due to emitted electrons pulled to the positive electrode.

However, the possibility still exists that any positive charge left on the surface by emitted electrons can produce a linear I_s–E relation by allowing the positive charge to hop from molecule to molecule or electrons to migrate from electrodes. Such an action should have a linear field-dependence and so contribute to the measured current.

Certain experiments with the metal case held at various potentials support the idea that I_e contributed very little to the measured current. They do not, however, preclude the possibility that any positive charge left on the crystal can contribute to the current.

Thus the evidence points to a continuation of photo-conduction into the region where

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[7] Mette and Pick, *Z. Physik*, 1953, **134**, 566; Eley, Parfitt, Perry, and Taysum, *Trans. Faraday Soc.*, 1953, **49**, 79; Goldsmith, Ph.D. Thesis, Purdue, 1955; Northrop and Simpson, *Proc. Roy. Soc.*, 1956, *A*, **234**, 124; Inokuchi, *Bull. Chem. Soc. Japan*, 1956, **29**, 131; Riehl, *Zhur. Fiz. Khim.*, 1955, **29**, 959, 1152; *Ann. Physik*, 1957, **20**, 193.

[8] Pick and Wissmann, *Z. Physik*, 1954, **138**, 436.

[9] Part VII, *J.*, 1960, 5186.

photo-emission occurs. The internal photocurrent can be distinguished from the external current, but the effects accompanying an external photocurrent cannot be differentiated, although they are most likely small.

Current–Photon Energy Relation.—A comparison of the excitation spectra of both I_s and I_e shows but little correlation. For anthracene, the peak in I_e near 54,000 cm.$^{-1}$ could correspond to the peak in I_s in the same region. For naphthacene, the peak in I_e near 49,000 cm.$^{-1}$ has no analogue in I_s, although I_s is rising in this region to a peak near 53,000 cm.$^{-1}$.

A comparison of the I_s–ν curves (Figs. 2, 3) with the ε–ν curves shows some correlation (ε is the molecular extinction coefficient). For anthracene the curves are roughly similar, the photocurve being somewhat broadened and with less resolution. The dependence of I_s upon ε, found to hold to 40,000 cm.$^{-1}$, holds roughly throughout this region. However, it must be remembered that ε varies with thickness when unpolarized light is used, so the relation of Is and ε would vary with thickness. This effect may be neglected within the limits of accuracy of this work. For naphthacene I_s does not follow the absorption spectrum. It appears that the inverse of the absorption is being obtained. Bree and Lyons [4] obtained a photocurve which does resemble the absorption spectrum. Their curve 3 and our results should correspond, but are not closely similar. Each of several crystals in vacuum, nitrogen, or air (to 50,000 cm.$^{-1}$) gave the same result. The mounting technique did not differ from that used in obtaining previous photocurves,[3] so the result is thought to be a true effect. Further work may answer this question.

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THE UNIVERSITY OF SYDNEY, SYDNEY, N.S.W., AUSTRALIA. [*Received, April 11th,* 1960.]