999. *Photo- and Semi-conductance in Organic Crystals. Part VII.* Space-charge Effects in Anthracene.*

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Space-charge effects in the photo-conductance of anthracene crystals influence the spectral response in both sandwich and surface cells. The voltage- and time-dependence of the photocurrent also vary with the space-charge. Infrared radiation of wavelengths 1·5—2 μ is able to reduce the space-charge by releasing trapped charge.

A SPECTRAL response of photo-conduction in anthracene has been reported several times previously.[1-8] On a number of occasions, there has been observed a close similarity between the spectral dependence of the extinction coefficient, ε, and that of the photocurrent, I.[1-3,7] In various places types of spectral response differing from the general shape of the absorption spectrum have been reported.[4-6]

Recently, the spectral responses have been determined by Ferguson and Schneider [8] with new arrangements of the electrodes and a suggestion made which associated the similarity or dissimilarity between the absorption spectrum and the spectral response with whether the light beam fell on the same surface of the crystal as the electrodes (front illumination) or on the opposite " back " surface. We have obtained the spectral response under various conditions to test this and other theories.[5,9] Although Ferguson and Schneider's experimental results, *inter alia*, have been confirmed yet some of their conclusions must be changed. Alternative explanations in accord with general expectations for near-insulators are advanced to account for the results. These involve an emphasis upon the effects of space-charge.

EXPERIMENTAL

Surface currents were measured by means of the D.C. amplifier described previously.[4] Bulk currents were detected by means of a vibrating-reed electrometer capable of detecting less than 10^{-16} amp. Currents could be recorded continuously by means of a Varian G10 recorder. For the surface effect, anthracene crystals were grown by sublimation in an inert atmosphere. These crystals were generally transferred to a clean silica disc to which their developed *ab* face adhered strongly. Electrode material of " Alcadag " or silver was painted

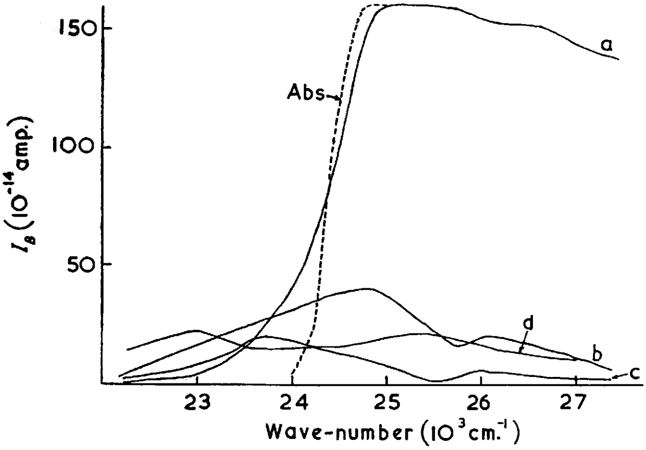
* Part VI, preceding paper.

1 Carswell, *J. Chem. Phys.*, 1953, **21**, 1890.
2 Part II, Carswell and Lyons, *J.*, 1955, 1734.
3 Lyons and Morris, *Proc. Phys. Soc.*, 1956, **69**, 1162.
4 Part III, Lyons and Morris, *J.*, 1957, 3648.
5 Compton, Schneider, and Waddington, *J. Chem. Phys.*, 1957, **27**, 160.
6 Kommandeur and Schneider, *J. Chem. Phys.*, 1958, **28**, 582.
7 Rosenberg, *J. Chem. Phys.*, 1958, **29**, 1108.
8 Ferguson and Schneider, *Canad. J. Chem.*, 1958, **36**, 1633.
9 Lyons, *J. Chem. Phys.*, 1955, **23**, 220.

on to the *ab* face by means of a fine brush, care being taken not to overlap the edges of the crystal with material when such a mounting was necessary. Electrical contact could then be effected by attaching the electrodes to thin platinum wires sealed into polystyrene. For the measurements on bulk photocurrents, sections 0·5—3·0 mm. thick were cut from a long cylindrical crystal. On one *ab* face a semi-transparent grid electrode of either silver or Alcadag was painted. On the opposite face was painted a guard ring together with the other electrode.

Spectral dependences were determined by using a Beckman D.U. spectrometer as a monochromator. The light source was a tungsten projector lamp whose radiation could be polarized by a polaroid sheet. By means of focusing the light from the exit slit of the monochromator on to a narrow variable slit, the effect of the geometry of the exciting light beam could be studied. Provision was also made for simultaneous background illumination of the crystal when required.

FIG. 1. *Spectral response in a " sandwich" cell for field strengths indicated; b polarization.* (*a*)—(*c*) *Positive electrode illuminated.* (*d*) *Negative electrode illuminated.* (*a*) 5000, (*b*) 3000, (*c*) 500, (*d*) 5000 v *cm.*$^{-1}$.



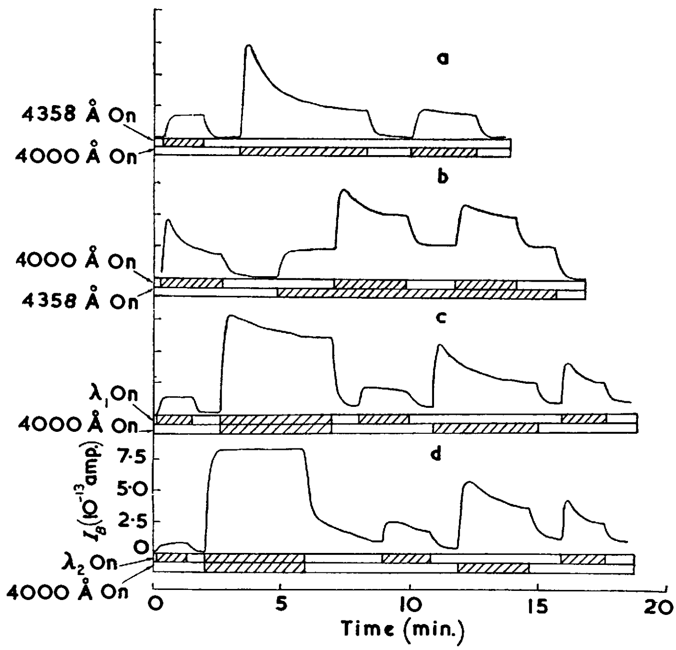


FIG. 2. *Photocurrent–time curves in a " sandwich " cell:* λ_1, *light between* 6000 *and* 15,000 Å; λ_2, *between* 6000 *and* 20,000 Å. *For a—d see text.*

RESULTS

Results for the sandwich cell are summarized in Figs. 1 and 2. In Fig. 1, the various curves show the relative magnitudes of the currents, those on curve (*a*) having been reduced to one-fifth of the original values. Only a slight variation in the results followed from the use of light polarized in the *a* crystal direction rather than the *b*.

Fig. 2 shows the variation of I_B, the current in the sandwich cell, with time, t, after the light had been switched on and off. The curves (*a*) show the effects of light of two different wavelengths. Light of wavelength 4000 Å gives a peak in the I_B–t curve, but that of wavelength 4358 Å does not. For (*b*), light of both wavelengths was combined in the ways shown in the Figure. Figs. (2)*c* and (*d*) show the effects of combining with light of λ 4000 Å two ranges of red and infrared radiation. The infrared light is shown to have a marked effect, which becomes greater when the range is extended from 15,000 to 20,000 Å.

Discussion

We are first concerned with the spectral response of I_B. The occurrence of space-charges in sandwich cell arrangements has been observed many times. Kallmann and Rosenberg[10] studied many light-induced polarization effects but did not discuss the spectral dependence of I_B. Compton, Schneider, and Waddington[5] and also Lyons and Morris[4] reported I_B–$\bar{\nu}$ (or λ) curves which showed a peak at frequencies less than that of the first peak of the ε–$\bar{\nu}$ curves. The Canadian authors explained the peak in terms of a greater recombination of carriers when the light was strongly absorbed. The others expected I_B to be independent of wavelength for a thick crystal which absorbs all the light, and attributed the observed peak to a double layer of charge at the electrode. In both cases space-charges and trapped carriers were recognized. Kommandeur and Schneider[6] later concluded that the main feature of the I_B–λ curves is that their maxima corresponded to minima in the ε–λ curves. These authors showed graphs in which $I_B \propto 1/\sqrt{\varepsilon}$, a result derived by them on the assumption that I_B was limited by recombination. Space-charges were recognised and used to explain a number of results, but the peak in the I_B–λ curve was explained in terms of recombination.

For illumination of the positive electrode, the present work shows [Fig. 1, curve (*a*)] that it is possible to find conditions of sufficiently high field under which I_B does become independent of $\bar{\nu}$ in regions of absorption. This is the result expected earlier[4] but not found. The drop in I_B at about $\bar{\nu}$ 24,900 cm.$^{-1}$ correlates fairly well with the drop in the absorption. In this case there is thus a similarity between the I_B–$\bar{\nu}$ and $L_{\text{abs.}}$–$\bar{\nu}$ curve measured on the same crystal ($L_{\text{abs.}}$ is the light absorbed). It is clear also that I_B is independent of the value of ε over a large range and therefore independent of the region in the crystal in which the carriers are formed (cf. ref. 11).

When the applied field, V, is reduced, the magnitude of I_B falls considerably more than even an $I_B \propto V^2$ relation would predict. At the same time maxima and minima appear in the I_B–$\bar{\nu}$ curve, but these do not coincide with the inflections in the ε–$\bar{\nu}$ curve, or even with each other. We now assume that both the reduction in the magnitude of I_B and the appearance of maxima and minima are due to the formation of space-charges. At sufficiently high values of the applied field the space-charge effect is minimised because the carriers are so strongly drawn to the electrodes. At lower fields the dependence on $\bar{\nu}$ arises from differing regions of formation of carriers with differing ε. The space-charge effect is most simply considered as a reduction in the field within the crystal.

The reason for the occurrence of a peak in the I_B–$\bar{\nu}$ curve is that, as ε increases, the space-charge effect increases and so I_B decreases. At lower values of $\bar{\nu}$, I_B decreases because of a fall-off in the light absorbed by the crystal. This fall-off has been discussed before (*e.g.*, ref. 6).

The variation of I_B with V^2 provides evidence for space-charges. In addition I_B–t curves (Fig. 2 and refs. 5—6) give further evidence. The variation of the I_B–t curves with $\bar{\nu}$ supports the above interpretation of the I_B–$\bar{\nu}$ curves. The curves in Fig. 2(*a*) show that space-charge occurs with light of λ 4000 Å but not of λ 4358 Å, when the carriers

[10] Kallmann and Rosenberg, *Phys. Rev.*, 1955, **97**, 1596.
[11] Goodman, *J. Appl. Phys.*, 1959, **30**, 144.

are produced more uniformly throughout the crystal. Curve (*b*) shows that space-charge is produced by light of λ 4000 Å even when illumination by 4358 Å light occurs simultaneously. The same thing is true, but to a much smaller extent, when λ_1 (6000—15,000 Å) is used instead of 4358 Å [curve (*c*)]. When λ_1 is used after the 4000 Å light has been switched off for 2 min., a maximum in the I_B–t curve is obtained [curve (*c*)]. A similar peak is not obtained with 4358 Å light instead of λ_1. The peak is attributed to the partial liberation by λ_1 of trapped carriers which absorb the red–infrared light. λ_2 shows a similar but more pronounced effect than λ_1. The difference between the effects of λ_1 and λ_2 is consistent with the liberation of the more deeply trapped carriers by quanta of energy, *ca.* 0·8 ev. Some earlier results of Goldsmith [12] may be explained along similar

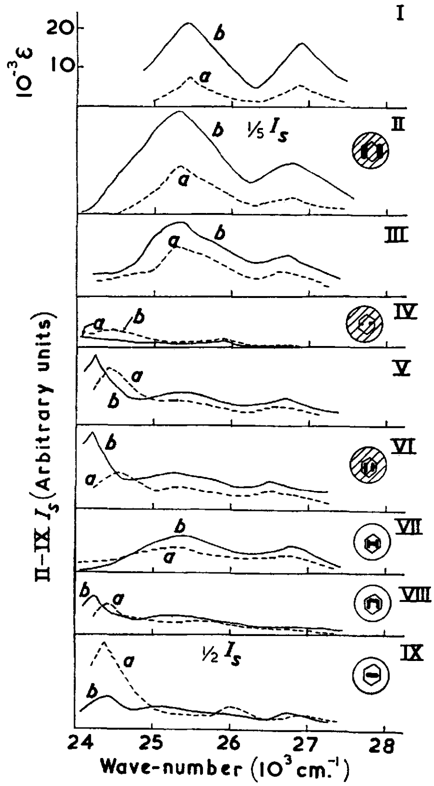


FIG. 3. (i) *Polarized absorption spectrum of crystal* (Bree and Lyons, *J.*, 1956, 2663). (ii)—(ix) *Spectral responses of photoconductance in the surface cells indicated*: (ii), (iv), (vi)—(ix), *front illumination*; (iii), (v), *back illumination.*

b,a refer to electric vectors of the light which are parallel and perpendicular to the b crystal axis. The current scale is only approximately constant in the various cases (ii)—(ix).

lines. Traps are possibly anthracene molecules or negative anthracene ions (cf. refs. 4, 13).

The near-infrared absorption spectrum of a 1·0 mm. thick anthracene crystal was measured. Besides the presence of vibrational bands, overall absorption of extinction coefficient about 0·5 occurs in the region 10,000—20,000 Å. Thus such a crystal transmits a considerable fraction of incident red–infrared radiation.

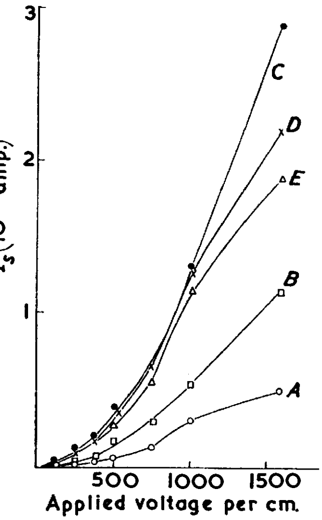
The results for the surface cell are shown in Figs. 3—7. The observed spectral response was corrected to equal amounts of absorbed energy, reflection losses being neglected. Fig. 3 shows the effect of varying arrangements of the electrodes and the light beam. The chief result is that when light fell over the entire area between two elongated and parallel electrodes [Fig. 3(ii) and (iii)] the current was much larger than in any other case and also the I_s–$\bar{\nu}$ curve resembled the ε–$\bar{\nu}$ curve. The same result was obtained whether the light fell on the front or the back surface. Ferguson and Schneider [8] made no mention

[12] Goldsmith, Ph.D. Thesis, Purdue, 1955.
[13] Bryant, Bree, Fielding, and Schneider, *Discuss. Faraday Soc.*, 1959, **28**, 48.

of the relative magnitudes of I_s with different electrode arrangements but observed the resemblance between the I_s and the ε dependences upon $\bar{\nu}$, as had earlier workers [1-3] with similar electrode arrangements to that used in Fig. 3, (ii) and (iii). With other electrode arrangements Ferguson and Schneider obtained different I_s–$\bar{\nu}$ curves and attributed the differences to whether the light fell on the front or the back surface. In Fig. 3 curves (iv)—(vi) show that the I_s–$\bar{\nu}$ curve varies with the arrangement of the electrodes whilst the light covers the crystal. Curves (vii)—(ix) show results obtained when the light fell only on a restricted area, as indicated in the diagrams.

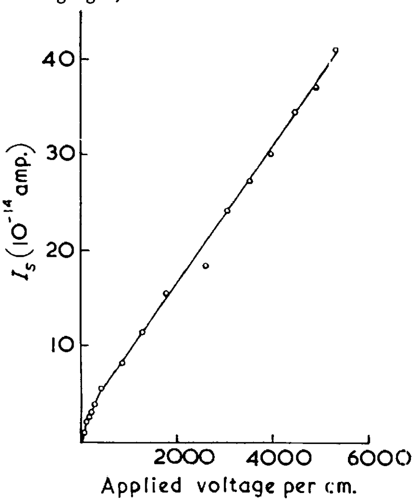
The resemblance to the ε–$\bar{\nu}$ curve is most pronounced in curve (vii), in which both the light and the electrodes were entirely on the front surface. Such a resemblance cannot therefore be attributed to illumination of the back surface, as was done previously. The

FIG. 4. *Photocurrent–applied voltage/cm. curves for wavelengths indicated in surface cell of Fig.* 3 (vi), *b polarization.*



A, 4200 Å; *B*, 4100 Å; *C*, 4000 Å; *D*, 3930 Å; *E*, 3900 Å.

FIG. 5. *Photocurrent–applied voltage/cm. curves for surface cell of Fig.* 3(iv); *b polarization. Exciting light,* 4000 Å.



more nearly did the light fall on an area of homogeneous field the more the similarity to the absorption spectrum was evident. In both the bulk and the surface cells those experiments in which I was reduced by the arrangement employed were also those in which the I–$\bar{\nu}$ curve was varied. In both cases the variation resulted in the appearance of a peak in the I–$\bar{\nu}$ curve at values of $\bar{\nu}$ below the value at which ε is a maximum. The similarity of this behaviour leads to the enquiry as to whether the cause is not also similar. Fig. 4 shows that, with certain electrode arrangements corresponding to curve (vi) of Fig. 3, the I_s–V curve is not linear but tends to become so at higher fields. The variation is towards an I_s–V^2 relation and suggests that space-charges may indeed be influencing the result. The result holds for various wavelengths. However, with the dot electrodes, corresponding to curve (iv) of Fig. 3, a linear relation holds at all but low fields (Fig. 5). In this case of considerable inhomogeneity of field it is hard to predict the voltage-dependence expected in the presence of space-charge.

Further evidence of space-charges was obtained from I_s–t curves (Fig. 6). When $\lambda = 4000$ Å a small but definite decrease in I_s from its maximum value occurred with time. Subsequent illumination with λ_2 in the absence of 4000 Å light gave a maximum in I_s although irradiation with λ_2 without the previous use of 4000 Å gave no detectable current. The simultaneous use of λ_2 with 4000 Å light removed the fall-off in I_s from its maximum value and also reduced the current caused by subsequent irradiation with λ_2. We attribute the fall-off in the first case to the formation of space-charge, and the current caused by λ_2 to the liberation of trapped charge, which also removed the fall-off in I_s during simultaneous illumination. Fig. 6 also shows the effect of a strong field. I_s now gradually rises so that it appears that a space-charge forms initially but is gradually reduced with time. λ_2 employed subsequently produced a current showing that the high field had not removed all the space-charge.

The effect of λ_2 was also seen on the I_s–$\bar{\nu}$ curves. The theory is advanced in this paper that the departure of the I_s–$\bar{\nu}$ curve from the ε–$^-$ curve is due to space-charge. Since λ_2

FIG. 6. *Photocurrent–time curves for surface cell of Fig.* 3(iv).

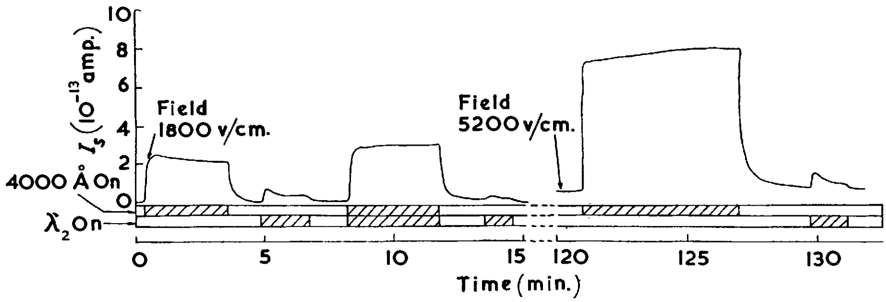
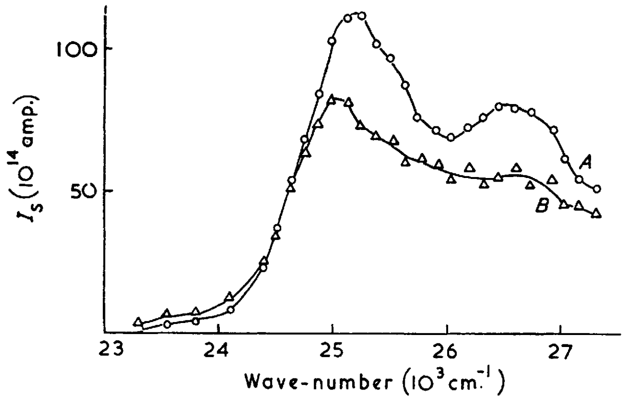


FIG. 7. *Spectral response of the surface cell of Fig.* 3(iv).



A, In presence of red–infrared radiation; B, without red–infrared irradiation.

removed space-charge, then the use of λ_2 together with other radiation which produced space-charge should change the I_s–$\bar{\nu}$ curve and make it more closely resemble the ε–$\bar{\nu}$ curve. Fig. 7 shows that this is in fact the case. Not only do the maxima in the resultant curve appear nearer to those in the ε–$\bar{\nu}$ curve, but also the magnitude of I_s increases in the regions of high absorption, thus providing further evidence that space-charge was being removed by λ_2.

The existence of space-charges in the dark has been recognised previously by Goldsmith,[12] by Kallmann and Rosenberg,[10] and by Kommandeur and Schneider.[6] A survey of the literature shows that there is considerable evidence that all the values reported for the dark conductivity of anthracene have been limited by space-charge. A similar conclusion applies to many values reported for other organic materials. The evidence is of two types: (i) the current–time curve after the field had been switched on and off, and (ii) the current–voltage relationship. Type (i) has been discussed briefly before.[6]

Type (ii) for anthracene can be found in the work of Mette and Pick [14] and of Riehl,[15] Northrop and Simpson,[16] and Inokuchi.[17] All these workers report an ohmic relation at fields up to about 3500 v cm.$^{-1}$. At higher fields the currents are relatively greater. This can be associated with the decreasing importance of the space-charge. The fact that an ohmic relation is obtained at lower fields does not mean that space-charge is absent; it merely means that the polarization is proportional to the applied voltage. Kallman and Rosenberg [10] have shown that such a proportionality does in fact exist. It is possible, but by no means certain, that the temperature coefficient of semiconduction will remain unchanged when the effects of space-charge are allowed for. Some of the conflict in the existing [14-17] results in the temperature coefficients might well be removed. The increase of the current above the ohmic relation commences at lower fields when the temperature is raised.[17] This again is consistent with a space-charge interpretation of the results.

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[14] Mette and Pick, *Z. Physik,* 1953, **134**, 566.
[15] Riehl, *Zhur. Fiz. Khim.,* 1955, **29**, 959.
[16] Northrop and Simpson, *Proc. Roy. Soc.,* 1956, *A*, **234**, 124.
[17] Inokuchi, *Bull. Chem. Soc. Japan,* 1956, **29**, 131.