Photo- and Semi-conductance of Organic Crystals. Part II. Spectral Dependence, Quantum Efficiency, and a Relation between Semi- and Photo-effects in Anthracene.*

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Photoconductance in anthracene displays a spectral dependence which reproduces the maxima and minima of the ultraviolet absorption spectrum of the crystal. Such a dependence may be explained by the necessary participation of surface molecules to which absorbed energy must be transferred as excitons. There is a separate threshold of photoconductance for each electronic transition. The position of the transition to a molecular triplet level coincides with the activation energy determined by others for semiconductance. The quantum efficiency of photoconductance depends upon the applied field and is of the order of 10^{-4}. The introduction of 10^{-4}M-tetracene into anthracene increases the photocurrents, especially in the region of the second electronic transition (40,000 cm.$^{-1}$).

THE wavelength dependence of the photoconductance of anthracene has not been previously reported except in a preliminary way in connection with the present work. The threshold of photoconductance was found by Volmer to occur at about 4000 Å, and as this has been confirmed by Vartanyan (references in Part I *) and with considerable accompanying detail by us, it may be assumed that other values sometimes reported are in error. As is now shown, to talk of a simple threshold is not by any means a sufficient description of the phenomenon, since it is not true that light of all wavelengths below the " threshold " is equally effective in promoting photoconductance. This is true even if " threshold wavelength " were always perfectly defined. The term has been used to denote the wavelength at which a current either is just detectable or else reaches half its maximum value. The latter usage, although precise, refers to a quantity which varies with the experimental conditions. A better definition than either, if the term is retained, is the wavelength at which the current first reaches a maximum value, a usage analogous to that of $\lambda_{max.}$ in absorption spectroscopy. With anthracene and similar molecules, photoconductance is related closely to the absorption spectrum of the crystal and such an analogy is accordingly justified. We have suggested a rule (Carswell, Ferguson, and Lyons, *Nature*, 1954, **173**, 736) that wavelengths locating an electronic transition are those which give rise to photoconductance, and furthermore, that to every electronic transition of the vapour molecule there corresponds a region of photoconductance in the crystal. Evidence presented below is consistent with this rule, as is a more recent study on tetracene (Bree and Lyons, *J. Chem. Phys.*, 1954, **22**, 1610).

EXPERIMENTAL

A Beckman spectrophotometer (stripped of its photocell attachment and fitted with the specially made photoconductance cell and amplifier attachment as described in Part I, *loc. cit.*) was used as a monochromator in conjunction with the usual tungsten and 300-mA hydrogen discharge lamps. For the experiments with polarised radiation a piece of " Polaroid " was used, after its spectrum had shown it to be a perfectly satisfactory polariser for light in the anthracene long-wave absorption region; in such experiments a monochromator was not used but was replaced by a mercury-discharge lamp plus a filter to transmit the 3650 Å region. The exact transmission was checked spectrally and found to extend over about 700 Å. Complete " spectra " have since been obtained by Bree and Lyons (*loc. cit.*), using polarised radiation and a photoconductance method. In all the above-mentioned experiments a single crystal was suspended between two platinum electrodes and attached with " Aquadag," but in order to examine the optical directions in the crystal it was necessary to mount the crystal on a removable glass piece to which " Aquadag " contacts were made; the illumination was now through the glass. Markings on the glass were made to indicate directions of maximum and minimum current

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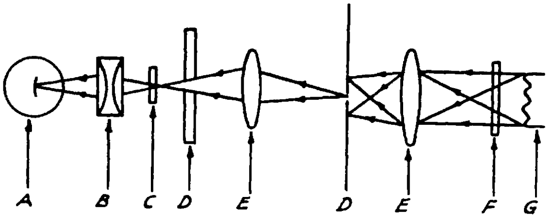
* Part I, preceding paper.

when plane-polarised light was used, and these were then correlated with optical directions with the aid of a polarising microscope. With a glass mount, somewhat unstable dark currents were introduced, and so there were now included a more intense light source and a less sensitive amplifier incorporating a ME1400 electrometer valve and a 10^{10} ohm grid resistor. In this way fluctuations in the dark current became of reduced importance.

The quantum efficiency of photoconductance, *i.e.*, the number of electrons entering the external circuit for each quantum of radiation absorbed, was determined with sufficient accuracy to ensure that the result was correct to within a power of ten. A new 931A photomultiplier tube with stabilised high-tension supply was used as a measuring device, and use was made of the manufacturer's published sensitivity characteristics : at 4000 Å, 1395; 3650 Å, 1316 μA/μw. The apparatus was set up as in Fig. 1 so that a narrow cone of nearly monochromatic (3650 Å) light was focused on to the crystal between the electrodes and the emergent light, collected by a large-aperture lens, and allowed to fall on the photocathode. With this arrangement it was shown that only a negligible amount of light penetrated an absorption band of the crystal. A small fraction, 2%, of the incident light intensity did indeed emerge from the crystal. This was attributed largely to fluorescence and so the intensity of the incident beam (measured with the crystal removed) was taken to give a satisfactory measure of the light absorbed. The photocurrent was measured with a field of about 600 v/cm.

FIG. 1. *Arrangement used for determining quantum yield.*
A, photomultiplier.
B, wide-aperture lens.
C, crystal.
D, screens with small openings.
E, lens.
F, filter.
G, lamp.



RESULTS AND DISCUSSION

The spectral dependence of the photocurrent, which may be studied in several ways, depends on the variation of slit width with wavelength. In the Beckman spectrophotometer the entrance and exit slits work together so that doubling the slit width gives, for sufficiently narrow widths, a quadrupling of the emergent intensity. The simplest method to determine the spectral dependence is with a constant slit width, but in addition either a constant wavelength interval or a constant wave-number (*i.e.*, frequency) interval may be used. All three methods were used and the results are shown in Fig. 2, labelled (*a*), (*b*), and (*c*), respectively. The wave-numbers of the maxima show that in each case there is a close

Frequencies $\bar{\nu}$ (cm.$^{-1}$) and wavelengths λ (Å) of maxima.

Photoconductance of crystal		Absorption spectrum			
		of crystal		of solution in *iso*octane	
λ	$\bar{\nu}$	$\bar{\nu}$ [1]	$\bar{\nu}$ [2]	$\bar{\nu}$ [3]	$\bar{\nu} - 1040$ †
First transition					
3915	25,550	25,580	25,540	26,640	25,600
3800 *	26,320	—	—	—	—
3700	27,030	27,030	26,990	28,090	27,050
3530	28,330	28,490	—	29,500	28,460
3420	29,240	—	—	—	—
3310	30,210	29,850	—	30,860	29,820
3140	31,850	—	—	—	—
3060	32,680	—	—	—	—
2960	33,780	—	—	—	—
Second transition					$\bar{\nu} - 2250$
2685	37,240	—	37,520	39,840	37,590
2590	38,610	—	—	—	38,570
2495	40,080	—	—	—	—
2370	42,190	—	43,480	—	—

[1] Kortum and Finckh, *Z. physikal. Chem.*, 1952, **52**, *B*, 263. [2] Craig and Hobbins, *J.*, 1955, **539**. [3] Catalog of Ultraviolet Spectrograms, A.P.I. Project 44 at N.B.S. * Probably due to a hydrogen line. † Values corrected by the amounts shown for the shift upon change of phase.

resemblance to the ordinary absorption spectrum of the crystal. The correspondence is shown clearly in Table 1 and is seen to apply not only to the first (low-energy) transition beginning at about 25,500 cm.$^{-1}$, but also to the second transition at about 37,240 cm.$^{-1}$. The greater amount of structure in (*b*) than in (*a*) is due to the use of a smaller slit width in (*b*), 0·13 mm. at 23,810 cm.$^{-1}$ compared with 2·0 mm. Since the curves were taken with a hydrogen lamp which emitted lines, there was the danger of recording false maxima in the photoconductance results although not to an equal extent in the absorption spectra, for the reasons discussed in Part I (*loc. cit.*). One maximum believed to be false is marked with an asterisk in the Table; it has no analogue in the absorption spectrum. The most pronounced maxima in the photoconductance curves occur at wavelengths which are in bold type in the Table. All of these have some recorded analogue in the absorption spectra. Of the maxima which are less pronounced in the photoconductance curves (in ordinary type in the Table) a number have no analogues in the absorption spectra, but, since there are no known hydrogen lines at the measured wave-numbers, there is no reason to doubt the genuineness of the maxima. Consequently, the photoconductance method is seen to supply information which supplements that already obtained by the more usual methods of absorption spectroscopy. Errors in the determination of the bold-face wavelengths might amount to ±5 Å (±40 cm.$^{-1}$) whilst errors in the other wavelengths might be somewhat greater.

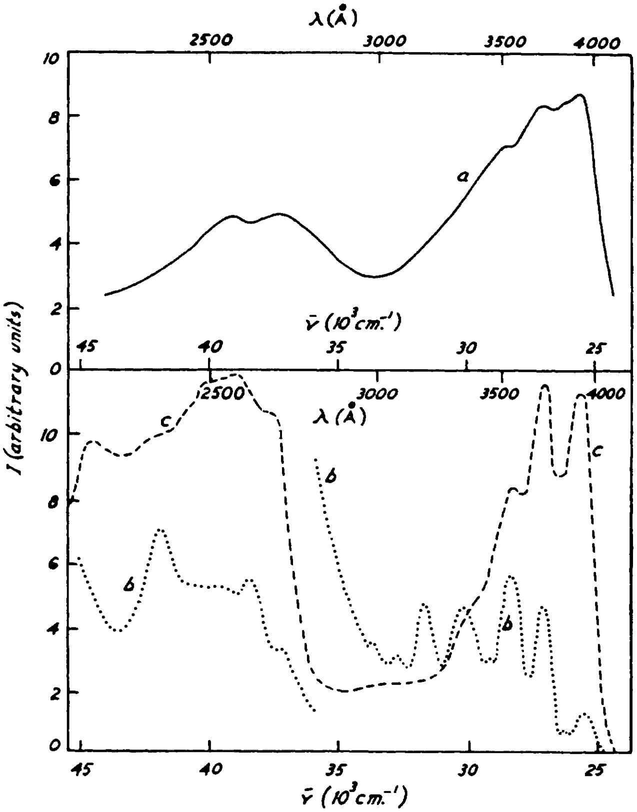


FIG. 2. *Observed spectral dependence of the photocurrent in anthracene crystals in air.*

(*a*) *With a constant* (2 *mm.*) *monochromator slit width.*

(*b*) *With slit giving a constant* $\Delta\lambda$ (25 Å) *on to crystal.*

(*c*) *With slit giving a constant* $\Delta\bar{\nu}$ (750 *cm.*$^{-1}$) *on to crystal.*

The magnitude of the current at different wave-numbers is of considerable interest. The main conclusion from the curves in Fig. 2 is that the current is greatest in the two regions where the crystal absorbs, and falls to a minimum between the absorbing regions. This is true of all three curves (*a*), (*b*), and (*c*) but is more easily seen in (*a*) and (*c*) than in (*b*). Whilst curves (*a*) and (*c*) are actual experimental curves, each made on a particular crystal, it proved impossible to obtain a curve of type (*b*) with a single crystal, owing to the great increase of current at the higher wave-numbers which resulted from the necessary 14-fold increase in slit width. In Fig. 2(*b*) the curve is composite, the part at lower wave-numbers being recorded under different conditions from that at higher. The effect of this is to reduce the height of the higher wave-number part relatively to the remainder. Comparison of the magnitudes of I at different wave-numbers is not a simple matter unless either the difference in the I values is very great or that in the wave-number values is small. There is no doubt from Fig. 2 that there is a general resemblance to the crystal absorption spectrum, or that I at a peak is greater than I at immediately neighbouring wave-numbers. But it is not at all clear whether I reaches a greater value in the first absorption region or in the second. Such comparison of I values at widely differing wave-numbers is improved if the curves are corrected first for the variation in the output of the lamp with wave-number, and secondly, for the alteration in the entrance slit with wave-number. The second correction is not necessary with curve (*a*), since both the entrance and exit slits of the monochromator were held constant. The first correction may be made in one of two ways depending on whether a curve is desired which represents a constant quantal output or a constant energy output from the lamp. (By constant quantal output is meant that the number of quanta at the entrance slit is constant with wave-number.) Allowance must also be made where necessary either for the varying dispersion of the monochromator or for variation in the exit slit.

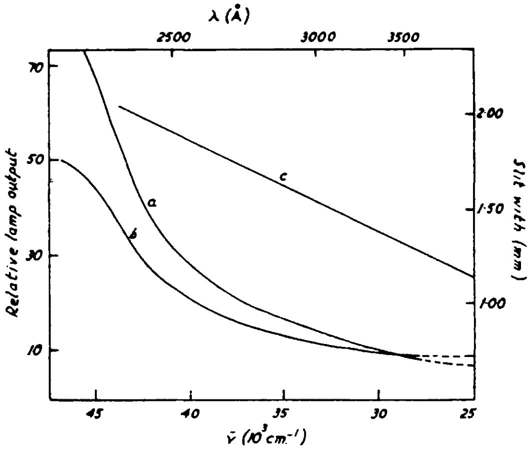


FIG. 3. *Variation in hydrogen lamp relative output with wave-number; and variation in slit to give a constant* $\Delta\bar{\nu}$ = 750 *cm.*$^{-1}$.

(*a*) *Lamp energy output.*
(*b*) *Lamp quantal output.*
(*c*) *Slit width.*

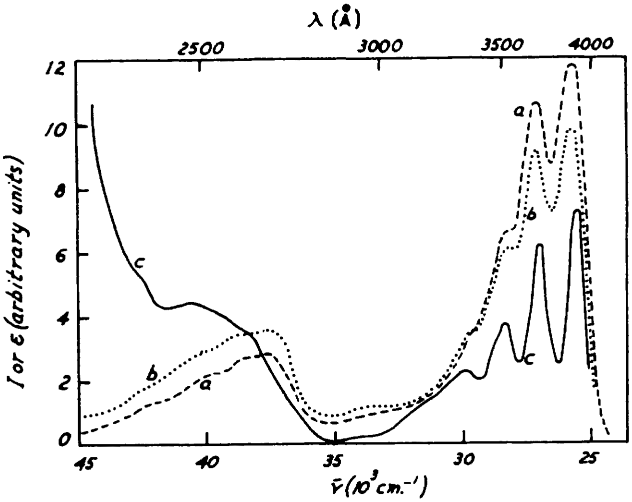


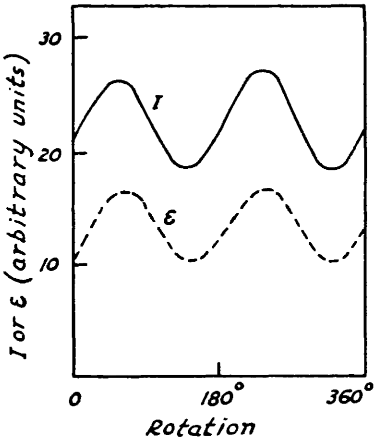
FIG. 4. *Curve* (*c*) *of* FIG. 2 *corrected for entrance slit variation with wave-number.*

(*a*) *Constant energy incident on crystal.*
(*b*) *Constant number of quanta incident.*
(*c*) *Absorption spectrum of crystal.*

Two curves, shown in Fig. 4, are of considerable significance: (i) curve 2(*c*) corrected first to give a constant entrance slit and secondly to give a constant energy output from the lamp, and (ii) curve 2(*c*) corrected to give constant entrance slit and constant quantal output from the lamp. Fig. 3 shows curves used in making the corrections and gives the lamp output as a function of wave-number as well as the variation in exit slit necessary to pass a constant band of $\Delta\bar{\nu} = 750$ cm.$^{-1}$. The lamp-output curve, which is not in absolute units, is based upon the maker's curve for a Hilger–Flood lamp similar to the lamp actually used. Extrapolation without regard to the presence of hydrogen lines, the effect of which was discussed in Part I, was done in accordance with Allen's curve for a hydrogen arc (*J. Opt. Soc. Amer.*, 1941, **31**, 2681) and can be very little in error, since the curve is almost parallel to the abscissa at the relevant wavelengths. The curve giving the relative numbers of quanta was calculated from that giving the energy.

The reproducibility of, say, curve 2(*c*) was excellent as regards wave-number of the peaks but not so good, ±15%, as regards the ratio of the currents under given conditions at 40,000 and 27,030 cm.$^{-1}$. Such accuracy is comparable, however, with that obtainable in the measurement of crystal absorption spectra, as we have found. The accuracy may therefore be considered satisfactory at present.

FIG. 5.

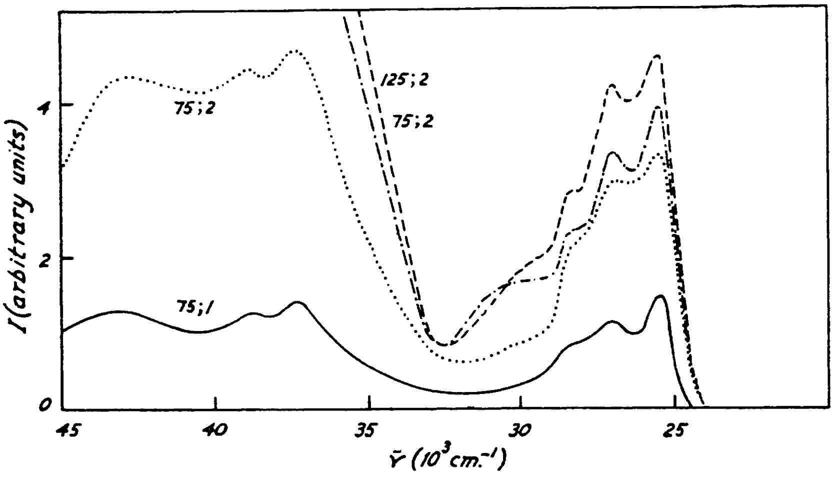


It is seen that removal of variation over the spectral range which was due to the lamp emission, the entrance slit, and the monochromator dispersion makes a great difference to the curve in Fig. 2(*c*). Curves (*a*) and (*b*) in Fig. 4, which result, are alike in showing a greatly reduced current in the higher energy system. However, the overall resemblance to the absorption spectrum is preserved, and from this similarity (shown in Fig. 4 by an absorption curve due to Bree and Lyons, unpublished) the conclusion most important in considerations of the mechanism of the process may be drawn. It is clear that the primary process in the photoconductance is the absorption of light by the anthracene crystal, and not, as is the case with a number of inorganic photoconductors, by some impurities in the bulk crystal. This is not to say that the presence of non-anthracene molecules is not at all necessary; indeed, the opposite is the case at least in regard to the surface layers, for the work of Vartanyan (*Doklady Akad. Nauk S.S.S.R.*, 1950, **71**, 641) and of ourselves (Carswell, Ph.D. Thesis, University of Sydney, 1954; Part I, *loc. cit.*) has been confirmed by Chynoweth (*J. Chem. Phys.*, 1954, **22**, 1029), and it is now established that oxygen increases the photoconductance above its vacuum value in a way that other gases such as nitrogen do not, and it is likely that some compound between the oxygen and the surface anthracene facilitates the process. Lyons (*J. Chem. Phys.*, in the press) has shown that the spectral dependence may be explained upon the assumption that exciton migration from the absorption site to the surface is the necessary second step in the mechanism. The following steps, however, are very much less clear. The possibility of ionisation of the surface anthracene is hard to determine but certainly must be considered in the absorption region if the effective dielectric constant is anything like the macroscopic value. However, it is plain that it is necessary first to produce an excited electronic state of the anthracene in the crystal surface. There is some evidence (Carswell, Ferguson, and Lyons, *loc. cit.*) that not only states corresponding to singlet excited states in the vapour but also those corresponding to triplet excited states are effective in giving rise to conduction. In this way a connection has been seen between photo- and semi-conduction. It is therefore of interest to compare the relevant energy quantities: Eley, Parfitt, Parry, and Taysum (*Trans. Faraday Soc.*, 1953, **49**, 79) and Mette and Pick (*Z. Physik*, 1953, **134**, 566) are in agreement that the activation energy of semiconductance in anthracene crystals is 1·65 ev (13,400 cm.$^{-1}$). This is interpretable if it corresponds to the height of the first "triplet" level above the ground state, 14,700 cm.$^{-1}$ in the vapour (Kasha and McGlynn, *Ohio State University Symposium on Molecular Structure and Spectroscopy*, June, 1954). Experimental work on photoconduction is difficult in this region, but on the above theory there should be a very weak photoconductance effect produced by very near infrared radiation. One " threshold " of photoconduction would accordingly be in the infrared region at a much lower energy than that of the threshold observed by us at 25,550 cm.$^{-1}$ (3915 Å) if the maximum is taken, or at about 24,400 cm.$^{-1}$ (4100 Å) if the point of first current detection is taken.

At wave-numbers above 37,000 cm.$^{-1}$ the resemblance between photoconductance curve and absorption spectrum apparently ceases. This could conceivably be due to some experimental failure in the region, which is the most difficult of all to work in, or else could mean that some modification to the simple theory is necessary. This point is being investigated further.

A further point of similarity between photoconductance and the absorption spectrum was found in the effect of linearly polarising the radiation incident upon the crystal. As the plane of polarisation of the radiation was rotated, the current varied as shown in Fig. 5, in which also is shown the variation in extinction coefficient, ε, of the crystal. The crystal direction coinciding with the maximum value of I was determined by the polarising microscope to be exactly that of the b crystal axis, which is known to be also the direction for maximum absorption. The ratio of I due to light with the electric vector vibrating parallel to b to that perpendicular to b was determined as 1·5 : 1, in good agreement with the ratio of absorption coefficients 1·8 : 1 (Bree and Lyons, unpublished; Craig and Hobbins, *loc. cit.*).

FIG. 6.



The absolute quantum efficiency was not expected to be very high in view of the fact that for anthracene crystals the quantum yield of fluorescence is about 0·9 (Bowen, *Trans. Faraday Soc.*, 1939, **35**, 15). These determinations were in agreement in showing that at 3650 Å almost 10,000 quanta were necessary to produce one electron in the external circuit. Obviously, most absorbed energy is re-emitted. The quantum efficiency varies directly with the applied field, as was shown in Part I, and this figure gives only the order of magnitude at a field of approximately 600 v/cm.

Mixed Crystals.—Since in many inorganic substances the introduction of impurities is able to modify the photoconductance, tetracene was deliberately introduced into anthracene in a way similar to that used by Lipsett and Dekker for other studies (*Canad. J. Phys.*, 1952, **30**, 165). At concentrations above about 10^{-3}M tetracene ceases to form a solid solution and forms separate layers in the " crystal." The lower concentrations which were necessary to maintain homogeneity have so far prevented us from examining any photoconductance arising from absorption by the tetracene below 25,000 cm.$^{-1}$. The curves shown in Fig. 6 are the result of absorption by the anthracene and maintain a resemblance to the results on the tetracene-free samples. However, currents are greater in the higher than in the lower energy region when tetracene is present, as can be seen by comparing Fig. 6 with 2(*a*). With pure tetracene, currents are much higher than with pure anthracene (Bree and Lyons, *loc. cit.*), and this is consistent with the increased current in the mixed crystal arising from the relatively few tetracene molecules present. Some crystals gave exceptionally large and unstable currents in the higher energy region, and in all cases in both regions smaller potentials than with pure anthracene gave rise to instability.

The Vacuum Oil Co. and the Commonwealth Research Fund are again to be thanked, as is Mr. Bree for checking certain of the results and for allowing us to reproduce the absorption spectrum of anthracene crystals, and Mr. Ferguson for unpublished information on anthracene crystals containing tetracene in concentration greater than 10^{-3}M.

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