# **723.** *Photo- and Semi-conductance in Organic Crystals. Part IV.* Spectral Dependence of Photocurrents in Aromatic Hydrocarbon Crystals in Dry Air with Polarized Light.*

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A surface current, $I_{\rm S}$, may arise whenever light falls in an electronic absorption region of a crystal of an aromatic hydrocarbon. The polarization of the light affects $I_{\rm S}$ in a way similar to its effect on the extinction coefficient. Consequently conclusions can be drawn about electronic transitions in the crystal from measurements of $I_{\rm S}$. Observed polarizations are given for anthracene, chrysene, pyrene, and 1 : 2-5 : 6-dibenzanthracene, and their significance for the theory of electronic excited states is discussed.

The spectral dependance of the bulk current, $I_{\rm B}$, differs from that of $I_{\rm S}$. This is attributed to the fact that carriers liberated in the bulk are independent of a surface effect such as that which explains the curve of surface current against frequency.

THE surface photocurrent, $I_{\rm S}$, in anthracene and tetracene crystals [1-4] depends on the plane of polarization and upon the wavelength of the incident light in a way which makes the curve of surface current against frequency, ν, resemble the absorption spectrum of the crystal. This knowledge is now extended to the second main absorption system in anthracene and several other hydrocarbon crystals in polarized light, for which we had previously reported results only with unpolarized light.[5]

## EXPERIMENTAL AND RESULTS

Crystals were prepared and purified as previously.[6] Crystal structures and optical data [7] are known, naphthalene,[8] anthracene,[9] phenanthrene,[10] chrysene,[11] and pyrene [12] being monoclinic, and 1 : 2-5 : 6-dibenzanthracene [13] being either monoclinic or orthorhombic. For the monoclinic crystals, the *ab* plane was the well-developed cleavage face, but the *ac* plane was developed for dibenzanthracene. For surface currents, a sublimation flake was placed on a silica disc and extinction directions found and distinguished (under a Zeiss polarising microscope) conoscopically. For electrodes, " Alkadag " was painted parallel to a crystal optical direction. For bulk currents, the experimental arrangement was as before.[6] Light sources were a fan-cooled 1000 w projection lamp, a 12v/60 w tungsten filament, a high-pressure mercury lamp in quartz, and a " Vitreosil " hydrogen discharge. Light, dispersed by a Beckman monochromator, was polarized by a Wollaston prism unit. Two rectangular images (*ca.* 2 mm. × 10 mm. and separated by 2 mm.) of the exit slit were each plane-polarized mutually perpendicular. Careful alignment was necessary to ensure that the beams were symmetrically disposed so that, with one always masked, vertically and then horizontally polarized light could be placed on the crystal by rotation of the prism. The lamps were calibrated with a Schwarz linear thermopile of sensitivity 2·2 μv/μw at the exit slit for unpolarized and, in place of the crystal, for polarized light. The projector and mercury lamp were calibrated directly, then the latter used to calibrate a 1P28 photomultiplier which was then

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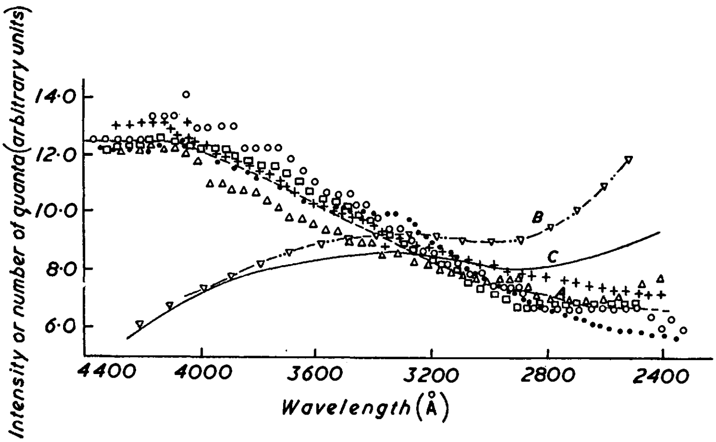
* Part III, preceding paper.

[1] Part II, Carswell and Lyons, *J.*, 1955, 1734.
[2] Lyons, *J. Chem. Phys.*, 1955, **23**, 220.
[3] Carswell, Ferguson, and Lyons, *Nature*, 1954, **173**, 736.
[4] Bree and Lyons, *J. Chem. Phys.*, 1954, **22**, 1630.
[5] Lyons and Morris, *Proc. Phys. Soc.*, 1956, **69**, 1162.
[6] *Idem*, preceding paper.
[7] Sundarajan, *Z. Krist.*, 1936, **93**, 238; Winchell, " Optical Properties of Organic Compounds," Univ. of Wisconsin Press, 1st Edn., 1943; Krishnan and Banerjee, *Z. Krist.*, 1936, **91**, 170.
[8] Abrahams, Robertson, and White, *Acta Cryst.*, 1949, **2**, 233.
[9] Mathieson, Robertson, and Sinclair, *Acta Cryst.*, 1950, **3**, 245.
[10] Basak, *Indian J. Phys.*, 1950, **24**, 309.
[11] Iball, *Proc. Roy. Soc.*, 1934, *A*, **146**, 140.
[12] Robertson and White, *J.*, 1947, 358.
[13] *Idem, ibid.*, p. 1001.

used to calibrate the hydrogen lamp. Variations in slit widths were avoided by the use of nickel gauze filters and lens diaphragms. Two different mercury lamps were each used with three photomultipliers, their spectral response curves being similar to those listed by the manufacturers. Fig. 1 shows the calibration curve for the hydrogen lamp. Thus, for this lamp we have (*a*) the number of photons and (*b*) energy distribution (in ergs) with fixed monochromator slits, (*c*) number of photons at exit slit with constant wave-number bandpass ($\Delta\nu$), (*d*) quantal distribution with variable entrance and exit slits and constant $\Delta\nu$. Stray light can cause spurious effects such as long-wavelength tails in the photocurve. Filters were used to check the presence of this stray light, and ensure that its intensity was insignificant. At lower wavelengths (*ca.* 2200 Å), its level reached undesirable proportions but no determinations of photocurrent were made below 2500 Å as photoelectric emission from the electrode assembly became noticeable. The ratio $I_x/I_y$ of the currents obtained with the light polarized in the directions $x$ and $y$ was obtained at any particular wavelength by taking successive current readings with horizontally and then vertically polarized light on the crystal. A standard (1 min.) build-up and decay time was chosen with repetition of current readings until constancy of the ratio ($\pm$0·02) was obtained. For photocurves the method was similar, readings also being repeated of peaks and minima in case the current values had increased with time.[6] The method of, and reasons for, altering slit widths at each wavelength has been discussed.[1] The correction for variation in lamp emission obtained from (*d*) (see Fig. 1) was the only correction necessary.

FIG. 1. *Intensity output of Vitreosil hydrogen lamp.*



*A*. At exit slit of Beckman monochromator with fixed entrance and exit slits.

△ Photomultiplier No. 1 calibrated by mercury lamp 1.
+ Photomultiplier No. 1 calibrated by mercury lamp 2.
○ Photomultiplier No. 2 calibrated by mercury lamp 1.
□ Photomultiplier No. 2 calibrated by mercury lamp 2.
● Photomultiplier No. 3 calibrated by mercury lamp 1.

*B*. Relative number of quanta emitted by Vitreosil hydrogen lamp at each wavelength setting used in determination of polarized photocurves.

Full line calculated from *A*.
▽ Experimentally determined.

*C*. Curve *B* corrected for absorption by Wollaston unit.

*Ratios* $I_b/I_a$.

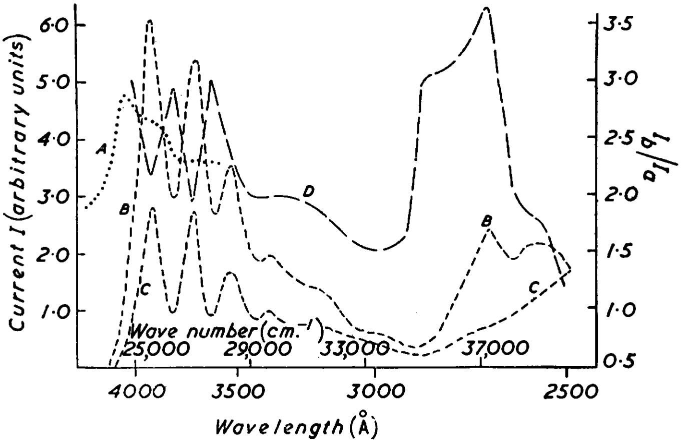
| Wavelength (Å) ............ | 3131 | 3021 | 2964 | 2803 | 2643 | 2560 |
|---|---|---|---|---|---|---|
| Frequency (cm.$^{-1}$) .................. | 31,939 | 33,102 | 33,738 | 35,676 | 37,836 | 39,063 |
| Naphthalene ........................ | 1·3 | 1·2 | 1·1 | 1·3 | 1·1 | 1·1 |
| Phenanthrene ..................... | 1·1 | — | — | — | — | — |

The results of the experiments are shown in Figs. 1—6 and the Table. For most substances the crystal spectrum is not available and there is shown in the diagrams a spectrum based on the solution spectrum but with approximate estimated corrections to allow for the shift of wavelength of absorption with change of phase. These corrections are based upon the shifts observed in going from the spectrum of the solution to the $I_S$–ν curve of the crystal.

The magnitude of the current was often so small that a very wide slit was used. Consequently the resolution is not as good as could be desired and therefore, for example, the value of $I_b/I_a$ is less than would be obtained otherwise. Lack of resolution should not affect the relative change of $I_b/I_a$ with ν. In interpreting the plots of $I_b/I_a$ against ν the emphasis should be on the way in which the ratio changes rather than upon its absolute value. As well as the effect of a wide slit in lowering $I_b/I_a$, there is another effect which is especially pronounced in substances like naphthalene, where the current is very small. The presence of a bulk current comparable in magnitude with $I_S$ is more likely with, say, naphthalene than with anthracene. As a result it is more difficult to draw conclusions about the absorption spectrum from currents in naphthalene than from those in anthracene.

The alteration of the polarization ratio due to a misalignment of 1° or 2° of the electrodes was calculated as negligible. No dependence of $I_b/I_a$ on field direction or on light intensity was found, but with non-uniform illumination of the crystal $I_b/I_a$ changed slightly with voltage.

FIG. 2. *Spectral dependence of the photocurrent from single crystals of anthracene.*



Curves have been corrected for quantal distribution of source.

*A*. Bulk current. Crystal 5 mm. thick. Field parallel to *c′*-axis. Voltage applied = 500 v.
*B*. Surface current when light is polarized along the *b*-axis of the crystal.
*C*. Surface current when light is polarized along *a*-axis of crystal.
For *B* and *C*, crystal is 2 μ thick, and field direction is along *b*-axis. Field = 1000 v/cm.
*D*. Current ratio $I_b/I_a$.
Current scale is same for *B* and *C*, but differs for *A*. Spectral bandpass 750 cm.$^{-1}$.

## DISCUSSION

Results with both unpolarized and polarized light show that $I_S$ arises whenever radiation falls within an absorption region of the crystal. The earlier conclusion [3] to this effect is accordingly substantiated.

*Anthracene.*—The spectral dependence has been discussed before [1,2] and a close relation between $I_S$ and ε (extinction coefficient) observed in the first absorption region. In the second region, with unpolarized light the linear relation of $I_S$ and ε did not hold well, as was to be expected; however, for ν >37,000 cm.$^{-1}$, $I_S$–ν and ε–ν curves were entirely different. This was puzzling but the great experimental difficulties in that region were thought to be responsible. More recently the crystal spectrum has been determined with polarized light.[14] Fig. 2 shows a determination of the $I_S$–ν curve recorded with polarized light for a constant number of incident quanta at each wavelength. Corrections have been applied to allow for the quantal distribution of the source and absorption by the

[14] Bree and Lyons, *J.*, 1956, 2662; Craig and Hobbins, *J.*, 1955, 539.

optics (see Fig. 1). It is now clear that a resemblance between the $I_S$–$\nu$ and the $\varepsilon$–$\nu$ curves exists even in this second absorption region. At still higher energies the resemblance should decrease because of photoelectric emission from the surface of the crystal. A plot of $\varepsilon$ against $\nu$ is shown in Fig. 3. For the lower values of $\varepsilon$ the relation is approximately linear and thus supports the earlier theory,[2] *i.e.*, the excitation energy regains the surface and then liberates carriers. The further into the crystal the photon penetrates the less chance does it have of regaining the surface. It is not necessary[6] to assume that the liberation of carriers is greater at the surface than in the bulk; this may still be true, but a varying mobility of carriers between bulk and surface must also be considered. In any event, the main point of the theory is preserved—the excitation or the carrier regains the surface. The surface effect is expected to be less important for a large single crystal in a sandwich cell and the resemblance to the absorption spectrum therefore should be lost. Fig. 2, *A* shows the spectral dependence of the bulk photocurrent for a crystal several millimetres thick. For measurable values of $I_B$ a tungsten source was necessary, so only part of the first transition is observed. This curve differs markedly from that for the surface current $I_S$, and to a certain extent, therefore, the " surface theory " for $I_S$–$\nu$ curves is confirmed. Further points in favour of the theory are: (i) $I_B$ is much less affected by changes in the surrounding atmosphere than is $I_S$;[6] (ii) the ratio of $I_b/I_a$ for the above crystal is unity at 4000 Å and in the absorption region. A current up to wavelengths of about 4400 Å for a crystal 5 mm. thick is explicable without additional assumptions if the absorption is regarded as taking place from a ground level which contains vibrationally excited molecules. For a thick crystal which absorbs all light incident at any wavelength the current is expected (all surface effects being neglected) to be independent of $\nu$. The existence of a peak in the $I_B$–$\nu$ curve appears therefore to be due in some way to the double layer which is known to exist at the electrode.[6]

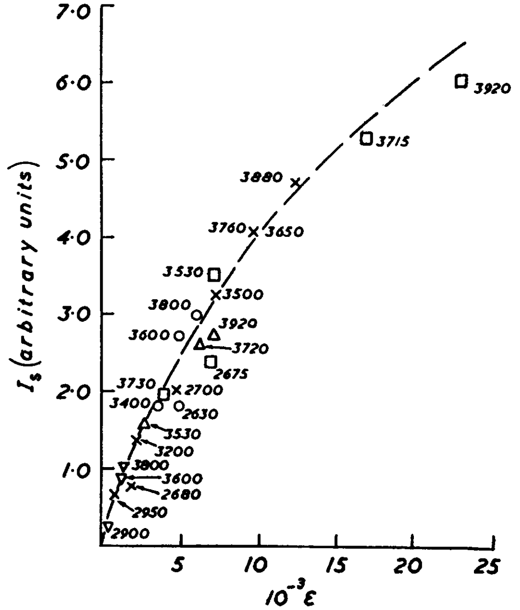


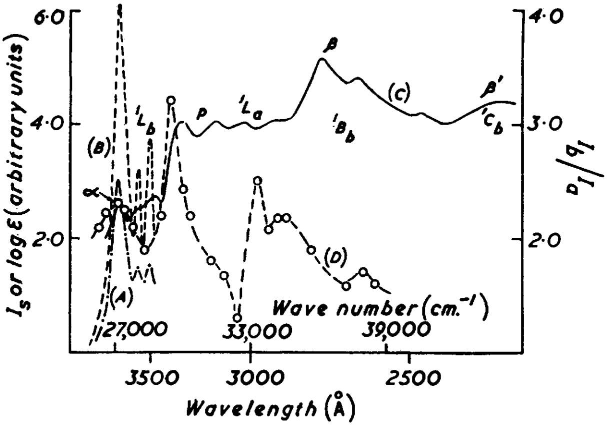
FIG. 3. *Surface current* ($I_S$) *plotted against extinction coefficient* ($\varepsilon$) *for a single crystal of anthracene* (*cf. Fig.* 2).

□ $I_b$ maxima.
○ $I_b$ minima.
△ $I_a$ maxima.
▽ $I_a$ minima.
× $I_b$ random points.

Extinction coefficients are from Bree and Lyons, *J.*, 1956, 2662. Wavelengths (Å) are stated beside points.

*Chrysene.—At wave numbers* 26,000—29,000 *cm.* $^{1}$. Fig. 4 shows clearly that there is a general resemblance to the absorption spectrum in this region. The wavelength shift from the solution spectrum in 95% ethanol to the crystal $I_S$–$\nu$ curve is 420 cm.$^{-1}$ for the first transition and rather greater, *ca.* 1350 cm.$^{-1}$, for the component of the second transition observed near 30,000 cm.$^{-1}$ in the crystal. If the resemblance between $I_S$ and $\varepsilon$ curves be accepted then it is clear that in the first transition absorption is stronger in the *b* crystal direction than in the *a*. On Platt's theory [15] this transition should be long-axis polarized. The band is analogous to the 31,642—31,476 cm.$^{-1}$ system in a naphthalene crystal and a similar explanation should exist for both naphthalene and chrysene long-wavelength systems. If therefore the naphthalene upper state is assigned as $B_{3u}$ (in $D_{2h}$),$^1L_b$, then the chrysene is also $^1L_b$—long-axis polarized. Strictly speaking, the chrysene molecule is of a lower symmetry than naphthalene, being $C_{2h}$ instead of $D_{2h}$. Consequently the $x$ (longer) and $y$ (shorter) in-plane directions both belong to the same irreducible $B_u$ representation of the symmetry group. The effect of this on the spectrum should be to mix the $B_{2u}$ and $B_{3u}$ upper states. Hence in chrysene the intensity of the $^1L_b$ transition should be rather more than in, say, naphthalene. This is actually the case. For chrysene $f = 0{\cdot}005$; for naphthalene $f = 0{\cdot}002$; however the different size of the molecules is another factor which has to be considered. The $^1L_b$ transition has not been measured in absorption in tetracene and anthracene which are closer in size to chrysene than is naphthalene.

FIG. 4. *Spectral dependence of the photocurrent from single crystals of chrysene.*



Curves have been corrected for quantal distribution of source.

*A*. Surface current when light is polarized along the *a*-axis of crystal.
*B*. Surface current when light is polarized along *b*-axis of crystal.
*C*. Absorption spectra of solutions (from Friedel and Orchin, "Ultraviolet spectra of aromatic compounds," Wiley, New York, 1951) shifted to allow for effect of change of phase. For 1st transition shift is 420 cm.$^{-1}$, for 2nd transition 1350 cm.$^{-1}$. The 3rd and 4th systems are likewise moved 1350 cm.$^{-1}$ although the actual shift might be expected to be greater.
*D*. Current ratio $I_b/I_a$. Spectral bandpass for (*A*), (*B*) and (*D*) is *ca.* 750 cm.$^{-1}$.
Crystal thickness 2·5 μ. Field direction along *b* axis. Field 750 v/cm.

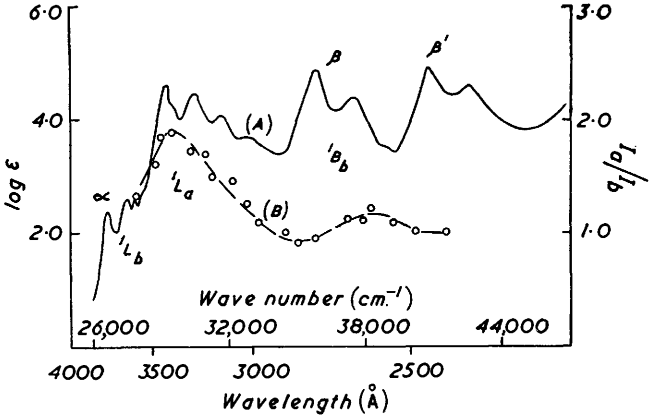
The only justification for speaking of " long-" and " short-axis " transitions in chrysene molecules is that the analogy with the linear polyacenes is preserved, *e.g.*, in the crystal structure and in the solution spectra. A long-axis transition in chrysene on the oriented-gas model will probably give rise to a greater absorption in the *a* crystal direction than in the *b*. (A comparison of the unit-cell dimensions of naphthalene, anthracene, and chrysene shows that the long axis of the chrysene molecules lies nearest to the *c* crystal direction, a situation which results, for both naphthalene and anthracene, in a greater component along *a* than along *b*. If it happens that the reverse is true with chrysene, the observed $I_b/I_a$ ratio is directly explicable.) The explanation of $I_b/I_a$ being greater than unity when the transition is long-axis polarized may be given in terms of intensity stolen from the *a* component of the next (stronger) transition and added to the weaker component of this transition, thus reversing the expected polarization ratio. Such is the theory given [16] for the long-wavelength naphthalene system and a similar situation must be presumed in

[15] Platt, *J. Chem. Phys.*, 1949, **17**, 484.
[16] McClure, *ibid.*, 1954, **22**, 1668.

chrysene. Intensity stealing by a crystal mechanism has been measured [14] in anthracene. The transition can therefore be assigned to a $^1L_a$ upper state even though the $I_b/I_a$ ratio is greater than unity.

*At wave numbers* 29,000—33,000 *cm.*$^{-1}$. This region corresponds to the second main absorption system, Clar's "*p*" band,[17] assigned by Platt to a $^1A$–$^1L_a$ transition, short-axis polarized, analogous to the transition to a $B_{2u}$ upper state in naphthalene, anthracene, and tetracene. In the naphthalene $A_g$–$B_{2u}$ transition, the splitting was calculated [18] as 100 cm.$^{-1}$ by a method which used the known intensity of the transition instead of an explicit form for the one-electron wave functions. The other method may have given a larger answer as the result [19] obtained for an $A_g$–$B_{1u}$ transition ($f = 0{\cdot}1$) in benzene, explicit wave functions being used, was 540 cm.$^{-1}$. If it is correct with chrysene to identify the low $I_b/I_a$ value at 32,600 cm.$^{-1}$ as due to the presence of an *a* component of the second transition, then the splitting between the *b* and *a* components is over 540 cm.$^{-1}$. This high value may be due to what differences exist in the somewhat similar crystals structures of chrysene ($I2/c$) and naphthalene ($P2_1/a$). There should be in chrysene four split components compared with the two in naphthalene. However, with the crystal orientation examined, only two are observed.

FIG. 5. *Spectral dependence of the photocurrent from single crystals of pyrene.*



*A*. Absorption spectra of solutions (from same source and shifted as for Fig. 4, *C*).
*B*. Current ratio $I_b/I_a$. Spectral bandpass is *ca.* 750 cm.$^{-1}$. Crystal thickness *ca.* 3·0 μ. Field direction along *a* axis. Field 600 v/cm.

Over the whole region $I_a/I_b$ is greater than unity. It follows, therefore, by analogy with the absorption spectrum, that the transition is short-axis polarized and the $^1L_a$ assignment is confirmed.

*At wave numbers* 33,000—39,000 *cm.*$^{-1}$. This region corresponds to a *b* polarized component of the most intense (Clar's β) transition to a $^1B_b$–$B_u$ upper state, analogous to the $B_{3u}$ upper state 40,000 cm.$^{-1}$ in anthracene and 45,000 cm.$^{-1}$ in naphthalene (solutions). Such a transition is long-axis polarized, but the splitting would be sufficient to remove one component to the vacuum-ultraviolet region. In anthracene [14] the *a* component is removed and the *b* component remains in the crystal at about 37,000 cm.$^{-1}$. A similar phenomenon appears to occur in chrysene and the observed polarization is again *b* (from the $I_b/I_a$ ratio). The electronic transition is accordingly to be assigned to $^1B_b$ after Platt, but considered to be split so that between 33,000 and 36,000 cm.$^{-1}$ only the *b* component appears in the crystal spectrum.

*Pyrene.*—The long axis runs through four carbon atoms, including the two central

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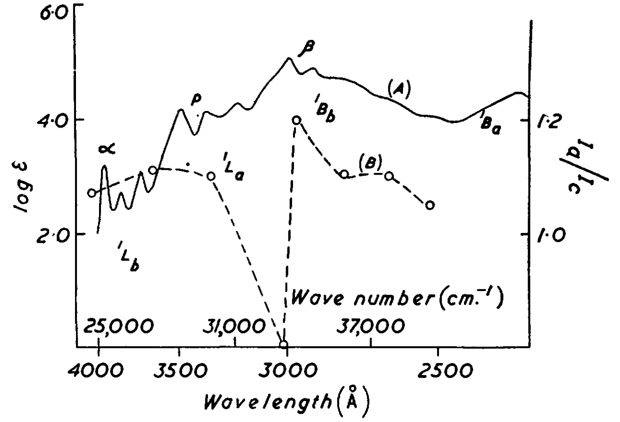
[17] Clar, "Aromatische Kohlenwasserstoffe," Springer, Berlin, 1952, 2nd edn.
[18] Craig and Walsh, *J. Chem. Phys.*, 1956, **24**, 471.
[19] Fox and Schnepp, *ibid.*, 1955, **23**, 767.

atoms of this *peri*-condensed hydrocarbon. The crystal structure differs from that of anthracene, etc., in that the pyrene molecules occur in parallel pairs in the crystal. Such an arrangement of the molecules must cause a marked change in the Davydov splitting behaviour from that observed in the anthracene type crystal. If splitting is neglected, the oriented-gas model of the crystal predicts that in the (001) plane transitions polarized along the long molecular axis will give rise to $\varepsilon_a/\varepsilon_b = 5{\cdot}2$ : short-axis transitions yield $\varepsilon_a/\varepsilon_b = 1{\cdot}0$ ($\varepsilon_a, \varepsilon_b$ denote extinction coefficients for light plane-polarized in *a*, *b* crystal directions); $I_a/I_b$ is observed to be mostly greater than or equal to unity (Fig. 5) and this behaviour is therefore understandable in terms of the absorption spectrum. The first transition (Clar's α band) at 26,000 cm.$^{-1}$ has $I_a/I_b \approx 0{\cdot}8$, and the transition is therefore polarized along the shorter molecular axis. In terms of Platt's symbols, α bands are usually classed as $^1A$–$^1L_b$, a transition which is [20] short-axis polarized in pyrene although long-axis in anthracene. (Pyrene and similar molecules are in a way a special case, as is indicated [21] by measurements of fluorescence polarization which give the same result for the first two transitions, a result not expected on the free-electron theory.)

FIG. 6. *Spectral dependence of the photocurrent from single crystals of* 1 : 2-5 : 6-*dibenzanthracene.*



*A*. Absorption spectra of solutions (as for Fig. 4, *C*, but without shift for change of phase).
*B*. Current ratio $I_a/I_c$. Spectral bandpass *ca.* 750 cm.$^{-1}$. Field direction along *c* axis. Field 1000 v/cm.

In the second transition (*p*-band) $I_a/I_b$ shows an increase which may be explained by the presence of an *a* polarized region of absorption. As there is no evidence in the plot of $I_a/I_b$ against frequency of a large splitting, the most likely explanation is that the *p*-band is polarized along the longer molecular axis. A transition to a $^1L_a$ state is [20] long-axis polarized in pyrene, although short-axis in anthracene, etc. Thus our result is compatible with free-electron theory, although it should be noted that since the increase in $I_a/I_b$ is small, this transition could conceivably, like the first, be short-axis polarized.

In the region of the third transition (β band) and possibly also that of the fourth (β′ band), $I_a/I_b$ is about unity, indicating a short-axis transition. A transition to a $^1B_b$ state is [20] long-axis polarized in pyrene.

In each of the first three transitions, therefore, the results are consistent with free-electron theory. The first transition is, however, only doubtfully so.

1 : 2-5 : 6-*Dibenzanthracene.*—The molecular symmetry is $C_{2h}$ as in chrysene. Again, despite the lowering of symmetry, the α, *p*, β, and β′ bands appear, a fact which seems extraordinary on molecular-orbital theory, in which the upper states should all mix with a subsequent evening of intensity throughout the spectrum. This point has been discussed

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[20] Ham and Ruedenberg, *J. Chem. Phys.*, 1956, **25**, 1.
[21] Williams, *J. Chem. Phys.*, 1957, **26**, 1186.

by Moffitt.[22] On the oriented-gas model (no splitting) the crystal spectrum should show $\varepsilon_a/\varepsilon_c = 0{\cdot}001$ for a " long-axis " transition and $\varepsilon_a/\varepsilon_c = 4{\cdot}1$ for a " short-axis transition." For reasons given for chrysene, the $x$ and $y$ directions are degenerate; thus the terms " long-" and " short-axis " transition lose significance to an extent which seems greater in dibenzanthracene than in chrysene. This may well explain why $I_a/I_c$ is moderately constant with frequency (Fig. 4). Owing to the difficulty of obtaining suitable sublimation flakes, experimental data were not extensive and are incomplete. The most that can be said is that there is a slight emphasis on a " short-axis " component about 34,300 cm.$^{-1}$.

*Naphthalene and Phenanthrene.*—These gave very small currents (see Table 1 of ref. 6). $I_b/I_a$ is near to unity, possibly for the reason given earlier, although in the case of phenanthrene this ratio is near that of $\varepsilon_b/\varepsilon_a$.[23]

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[22] Moffitt, *J. Chem. Phys.*, 1954, **22**, 320.
[23] McClure, *ibid.*, 1956, **25**, 481.