525. *The Intensity of Ultraviolet Light Absorption by Monocrystals. Part II.* Absorption and Reflection by Anthracene of Plane-polarised Light.*

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Reflection and absorption spectra are reported, from 4000 to 2150 Å, for anthracene monocrystals, the thicknesses of which were measured by interferometry (Part I *). Oscillator strengths and extinction coefficients for two *b* polarised transition components (at 3930 and 2680 Å; $f = 0{\cdot}062$ and 0·047) and for an *a* polarised component (at 3930 Å; $f = 0{\cdot}025$) are reported as the result of direct absorption measurements. Oscillator strengths of a further *a* component (at 1700 ± 200 Å; $f = 0{\cdot}5$) and a *b* component at 2270 Å ($f = 0{\cdot}03$) were calculated from refractive indices derived from the reflection spectra. The results verify a number of existing theoretical predictions as to the polarisation ratio of System I, the reality of intermolecular intensity " stealing " in molecular crystals, and the magnitude of Davydov splitting of System II, as well as confirming the assignment of Systems I and II to B_{2u} and B_{3u} upper electronic states. Evidence is presented that System III records a B_{2u} upper state. A further weak transition, in *a* polarisation near 2570 Å, possibly denotes a theoretically expected B_{1g} upper state.

THE relatively few polarised ultraviolet absorption spectra recorded on organic monocrystals have not usually given information on the absolute intensity of absorption. An exception is the calculation, from refractive-index measurements, of oscillator strengths

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* Part I, preceding paper.

for the 3900 Å system in anthracene crystals.[1,2] This method, which is applied here to the third main absorption system of anthracene, has previously been used only for the first system, I. Other methods[3] used on anthracene were of much higher accuracy for relative intensities than for absolute values. The absorption in anthracene crystals at 2680 Å predominantly polarised in the *b* crystal direction, has been associated,[3] not with a vapour transition polarised along the shorter in-plane molecular axis, *y*, but with the weaker component of a transition polarised along the longer in-plane molecular axis, *x*. The stronger component was assumed to be separated from the weaker and displaced towards the violet by some 16,000 cm.$^{-1}$. This result was consistent with the absorption of the crystal in both the 2200 and the 1890 Å region being polarised in the *a* crystal direction.[4] The value[3] for ε_b (26,300) at 2680 Å was assumed[3] to confirm the *x* polarised nature of the transition because of the approximate agreement with ε_b (9100) calculated from the solution coefficient. The interferometric method has enabled us to test this assumption with considerably more precision than was obtained previously.

Experimental procedures involved the measurement of feeble light intensities since it proved almost impossible to handle crystals less than 0·18 μ thick (about 200 molecular layers). Increasing the light intensity, by focusing the light on to a small area of the crystal, was not permissible, since only parallel light was wanted. (It was shown that for the 3900 Å system a convergence of the light at the crystal produced a decrease in observed optical density, which is consistent with the transition's being short-axis polarised. This method of determining the polarisation of a crystal transition may be performed without any polarising prism in the optical path.)

The source was either a "Vitreosil" hydrogen discharge lamp or a 60/24 w tungsten filament. A Wollaston prism which could be rotated through 180° to interchange the two beams provided plane polarisation of the light. The crystal could be rotated by known amounts. The incident and the transmitted beam were examined alternately with a 1P28 photomultiplier placed behind the exit slit of a monochromator from a Beckman DU spectrophotometer. Errors[6] were avoided by comparing similarly polarised beams falling on the same area. The photomultiplier response was assumed directly proportional[7] to the light flux. The space around it and the grid resistor was desiccated with phosphoric oxide. The D.C. amplifier[5] was used as a null-point detector, whose sensitivity was controlled by shunts and a variable grid resistor. For the reflection spectrum the crystal was mounted on a fused silica disc and the intensity reflected from the anthracene was compared with that reflected from the disc. A parallel beam of light fell normally ($\pm 2°$) on the reflecting surface and passed through the polarising system before entering the monochromator. The reflection from the silica disc was calculated from the known refractive indices.[8]

The results quoted for ε in Tables 1 and 2 are all mean values with the exception of ε_b at 3930 and 3720 Å. In general the accuracy was such that all readings were within 5% of the mean. This error was attributed more to the spectrophotometry than to the thickness measurement. At wavelengths below 2900 Å the readings for ε might be low owing to stray light but the use of a filter between 2900 and 4000 Å removed all but a negligible amount of stray light, as is shown by the reproducibility of ε for various crystal thicknesses. However, at wavelengths at which absorption was very strong the effect of stray light again became important. No matter how thick the crystal used there appeared to be a limiting optical density (E) of about 3·4, which could only have been due to stray light. A plot of E_b against thickness for 3930, 3720, and 3530 Å is shown in Fig. 1. Since the origin must be a point on the graph the broken lines through the origin give minimum values for E_b. In the case of 3720 Å the line passes nearly through the points observed on the two thinnest crystals and consequently E_b observed on the thinnest must be very close to the true value,

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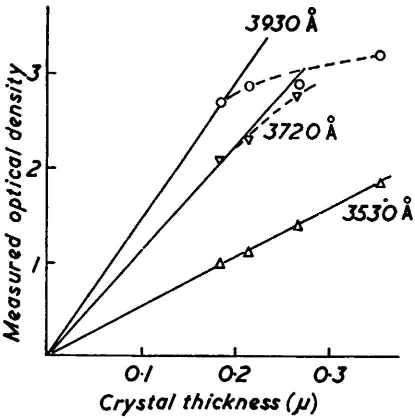
[1] Obreimov, Prikhotjko, and Rodnikova, *Zhur. eksp. teoret. Fiz.*, 1948, **18**, 409.
[2] Eichis, *ibid.*, 1950, **20**, 471.
[3] Craig and Hobbins, *J.*, 1955, 539.
[4] Lyons, *J. Chem. Phys.*, 1955, **23**, 1973.
[5] Ferguson, Iredale, and Taylor, *J.*, 1954, 3160.
[6] Normand and Kay, *J. Sci. Inst.*, 1952, **29**, 33; Clancy, *J. Opt. Soc. Amer.*, 1952, **42**, 357.
[7] Engstrom, *ibid.*, 1947, **37**, 420.
[8] Jenkins and White, "Fundamentals of Physical Optics," McGraw-Hill, New York, 1950, p. 514.

being if anything a little less. For 3930 Å, E_b for the thinnest crystal is given in Table 1. The true value must be as great as or greater than this. At 3530 Å all the points fall on a straight line which passes through the origin. It follows that, for the optical density range covered, scattered light was negligible. This indeed was the situation except when $E > 2{\cdot}2$.

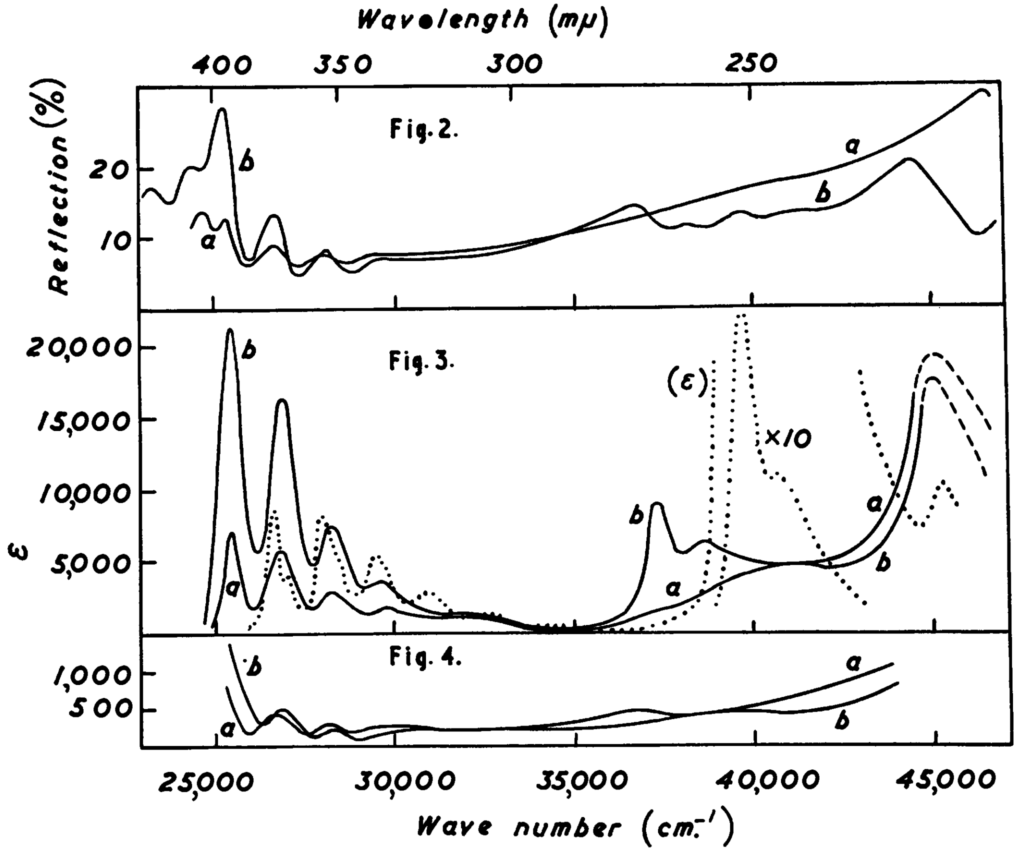
A variation of E with slit width was observed: the wider the slit the smaller was the optical density. This effect reduced an optical density from 2·6 to 2·5 when the slit was opened from 0·08 to 0·20 mm. but became of little importance for further opening. In all experiments the minimum slit width was used, but even so the very high extinction coefficients are again liable to a small correction. Where this applies the minimum value is shown in the Tables.

Reflection of light from the front and the back surface of the crystal and from the surfaces of the silica disc was appreciable. It may easily be shown that the reflection correction to $E_{\text{obs.}}$ is given by $\log_{10}\gamma$ where γ denotes $[(1 - 1{\cdot}92R_s)/(1 - R_1)(1 - R_2)(1 - R_s)]$; R_s is the fractional reflection at an air–silica surface, R_1 that at an air–anthracene surface, and R_2 that at an anthracene–silica surface. $R_s = (\mu_s - 1)^2/(\mu_s + 1)^2$ where μ_s is the refractive index of silica. In an absorption region $R_1 = [(\mu - 1)^2 + k^2]/[(\mu + 1)^2 + k^2)]$ where μ is the refractive index of anthracene and k the extinction index, related to ε, the molar extinction coefficient, by the formula $k = 2{\cdot}303\ \lambda\varepsilon c/4\pi$ [λ, the wavelength in air; c, the molar concentration of anthracene in the crystal ($c = 7{\cdot}0\text{M}$)]. It follows that $k = 1{\cdot}28\lambda\varepsilon$. R_2 is given by a formula similar to that for R_1, except that μ_s replaces unity. Values of R_1 were obtained from measurements of the reflection from an anthracene crystal over the range 2200—4000 Å. Fig. 2 shows spectra of a crystal sufficiently thick for back-surface reflection to be negligible at wavelengths for which absorption occurred. R_1 being determined, μ, R_2, and γ were calculated in that order. The resulting corrections to ε are shown in Fig. 4. In Fig. 3 is shown the curve for ε (corrected) against ν, as well as the spectrum in a solution of *iso*octane.[16] Since the maximum refractive index near an absorption band occurs at a wavelength greater than that of the peak of the band, it follows that the maximum reflection will be at a wavelength greater than that of the band peak. Observation of the wavelength of the peak will therefore be slightly altered when allowance is made for reflection. Such a "reflection correction" will become important only when small wavelength intervals are of interest, as, for example, in studies on the Davydov shift in crystal spectra. Preliminary studies indicate that the reflection correction is of the order of 10 cm.$^{-1}$ for the 3920 Å peak in anthracene. Values for molar extinction coefficients, corrected for reflection losses, are listed in Tables 1 and 2 and for oscillator strengths in Table 3. Certain derived quantities are also shown. ε_b and ε_a, referring to electric vector vibrations along directions b and a, are defined by ε_b (or ε_a) $= (1/cd)\log_{10}(I_0/I)$ ($c = 7{\cdot}0$ moles/l.; d is the thickness in cm.,

FIG. 1.



I_0, I, are the intensities of incident and transmitted light). The quantity $\varepsilon_u = (1/cd) \log_{10} (I_0/I)$ is not a true extinction coefficient when unpolarised light is used. It is easily shown that $\varepsilon_u = (1/cd) [\log_{10} 2 - \log_{10} (10^{-\varepsilon_a cd} + 10^{-\varepsilon_b cd})]$. As d increases, the term in ε_a becomes increasingly more important than that in ε_b, provided $\varepsilon_a < \varepsilon_b$. Also, as d increases the term $(1/cd) \log 2$ decreases. Consequently, ε_u will approach ε_a for large d, when $\varepsilon_a < \varepsilon_b$. That this is consistent with experimental results is shown in Fig. 5. Such a variation in ε_u represents a failure of Lambert's law for such crystals in unpolarised light. If it happens that $\varepsilon_b = \varepsilon_a$ at any wavelength, then $\varepsilon_u = \varepsilon_a (= \varepsilon_b)$ also. Such a point occurs in the anthracene crystal spectrum at about 2430 Å. In Tables 1 and 2 there are given * ε_a, ε_b (observed) and ε'_a, ε'_b [calculated from ε (solution), an oriented-gas model being assumed and the known orientations of the molecules in the anthracene crystal being used[9]]. Values of ε', calculated for transition moments along both the x (longer) and the y (shorter) axis in the molecular plane, are given. (Polarisation perpendicular to the molecular plane is of no importance in π–π transitions.)



FIGS. 2—4. *b*, *a*, refer to anthracene crystals examined in light plane-polarised parallel and perpendicular to the *b* crystal axis. Broken lines refer to values in *iso*octane solution.

Oscillator strengths, f, are given by $f = 4{\cdot}31 \times 10^{-9} \int \varepsilon \mathrm{d}\nu$ for a solution or gas where ν is the wave number in cm.$^{-1}$, but for plane-polarised light on an anthracene crystal, $f_{a,b,p} = 1{\cdot}44 \times 10^{-9} \int \varepsilon_{a,b,p} \, \mathrm{d}\nu$, where p is a crystal direction perpendicular to both a and b.

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* For the remainder of this paper primes will be used to denote calculated values as opposed to unprimed letters for observed values.

[9] Mathieson, Robertson, and Sinclair, *Acta Cryst.*, 1950, **3**, 245, 251.

It is implied that $f = f_a + f_b + f_p$. In terms of extinction coefficients as defined above, the solution value, ε, is given by $\varepsilon = (1/3)(\varepsilon_a + \varepsilon_b + \varepsilon_p)$. Such a comparison between solution and crystal coefficients is valid only when the crystal bands actually correspond to the solution band. If there is splitting in the crystal all measurements must be taken at the actual band positions. The comparison in any event becomes invalid to the extent that intermolecular interactions in the crystal increase the intensity of one absorption system as a result of the presence of another (" intensity stealing "), the second-order perturbation effect.[10] Further errors may arise if there is a different vibrational structure of the band system in the crystal from that of the solution. Despite these difficulties it is possible to arrive at valuable conclusions when the two last-mentioned are neglected.

System I of the molecular absorption (cf. Tables 1 and 3) occurs in solution with peaks at 26,680, 28,130, 29,520, and 30,940 cm.$^{-1}$, having $v = 0,1,2,3$ (v is the number of quanta of the totally symmetric vibration excited in the upper state). In the crystal the peaks appear, with a slight splitting which is neglected here, in both b and a polarisations, but displaced to 25,450, 26,880, 28,330, and 29,760 cm.$^{-1}$. (The measured splitting[3] should be subjected to the " reflection correction " as indicated above.) It is possible to deduce that the molecular transition is $A_g - B_{2u}$ (y polarised) by comparing the extinctions ($\varepsilon_{a,b}$) measured in the crystal with those ($\varepsilon'_{a,b}$) calculated from the value in solution, since the values of $\varepsilon'_{a,b}$ depend on the molecular direction in which the transition is polarised. If the transition is x (long-axis) polarised there is quite good agreement between ε'_a and ε_a (Table 1) for the various peaks, but no agreement at all between ε'_b and ε_b. However, for a y polarised transition, agreement is obtained between ε'_b and ε_b and also between ε'_a and ε_a (to within a factor of 2—3). The same conclusion holds when oscillator strengths are considered: there is agreement between f_b and f'_b and also between f_a and f'_a, if the transition is y polarised, but no agreement between f_b and f'_b if the transition is x polarised. It follows that the transition is y polarised. If the oriented-gas model were completely satisfactory as a description of the crystalline state of anthracene the ratio of the absorption intensities in the two directions (f'_b/f'_a) would be greater than 7 : 1. The experimental ratio (f_b/f_a) is about 2·5 : 1 and certainly not greater than 4 : 1. Such a lowering has been expected[10] on theoretical grounds. In fluorescence the corresponding ratio has been observed[11] as 3 : 1. This shows that the presence of intermolecular forces affects the spectrum. Table 3 allows the theoretical explanation to be put to a further test than that involving only the ratio of f_b to f_a, for it is now possible to compare f_a with f'_a and f_b with f'_b and so to discuss in a quantitative way the phenomenon of " intensity stealing."

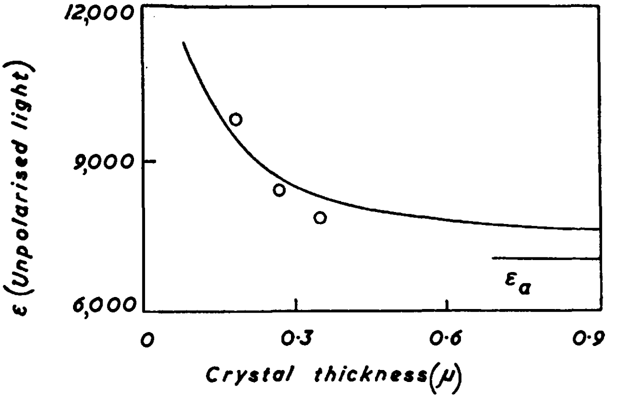

FIG. 5. *Failure of Lambert's law for an anthracene crystal in unpolarised light.*

The full curve shows the value of ε (unpolarised light), calculated from ε_b and ε_a.

There are two types of intensity stealing, one of which is intramolecular[12] and the other intermolecular. Both occur in crystals. We consider the present measurements only in

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[10] Craig, *J.*, 1955, 2302.

[11] Ganguly and Chaudhuri, *J. Chem. Phys.*, 1951, **19**, 617.

[12] Herzberg and Teller, *Z. phys. Chem.*, 1933, *B*, **24**, 410; Craig, *J.*, 1950, 59; Craig and Lyons: Lyons, Ph.D. Thesis, London, 1952.

TABLE 1. *Molar extinction coefficients at turning-points in the first main absorption system, I, of anthracene.*

Solution			Crystal						
λ (Å)	ν (cm.$^{-1}$)	ε (obs.)[16]	λ (Å)	ν (cm.$^{-1}$)	Polarisation †	ε′ calc.† for x transition	ε′ calc.† for y transition	ε ‡	$\varepsilon_b/\varepsilon_a$
3760 *	26,680	8380	3930 *	25,450	*b*	390	20,500	≥21,300 *	≥3·0
					a	6250	2600	7040 *	
			3800	26,320	*b*	—	—	5300	—
					a			1440	
3570 *	28,130	8260	3720 *	26,880	*b*	390	20,000	≥16,400 *	≥2·8
					a	6200	2600	5820 *	
			3600	27,780	*b*	—	—	4300	—
					a			1510	
3390 *	29,520	5450	3530 *	28,330	*b*	260	13,000	7460 *	2·6
					a	4000	1700	2820 *	
			3430	29,150	*b*	—	—	2950	—
					a			1300	
3230 *	30,940	2860	3360 *	29,760	*b*	130	6900	3360 *	1·9
					a	2100	900	1730 *	

Values marked * are maxima.

† *b* and *a* indicate polarisation parallel and perpendicular to the *b* crystal axis respectively; x is the longer and y the shorter molecular axis.

‡ Corrected for reflection losses.

TABLE 2. *Molar extinction coefficinets, ε, at points in the second main absorption system, II, of anthracene.*

Solution			Crystal					
λ (Å)	ν (cm.$^{-1}$)	ε (obs.)[16]	λ (Å)	ν (cm.$^{-1}$)	Polarisation	ε′ calc. for x transition	ε′ calc. for y transition	ε ‡
2520 *	39,680	232,000	2680 *	37,310	*b*	9100	480,000	9000 *
					a	170,000	72,000	1900
			2635	37,950	*b*	—	—	5250
					a			2300
2450 *	40,820	96,000	2590 *	38,610	*b*	3800	240,000	6620 *
					a	71,000	30,000	3200
			2520	39,680	*b*	—	—	5170
					a			4300
			2480	40,320	*b*	—	—	5070
					a			4800
			2440	40,980	*b*	—	—	4770
					a			5200
			2400	41,670	*b*	—	—	4630
					a			5700

For notes, see Table 1.

TABLE 3. *Oscillator strengths in solution and crystal, and derived quantities, for Systems I and II and for sections of System I.*

	System I					
v *	0	1	2	3		
$\lambda_{\text{max.}}$ (Å)	3930	3720	3530	3360	Total	System II
Crystal †						
f_b	≥0·023	≥0·021	0·011	<0·008	0·062	0·047
f'_b	0·017	0·024	0·018	0·011	0·078	0·035
f_a	0·0056	0·008	0·004	<0·007	0·025	
f'_a	0·0022	0·0032	0·0024	0·0014	0·010	0·57
f_b/f_a	≥4·1	≥2·62	2·75	—	2·48	
f_b/f'_b	≥1·4	≥0·9	0·6	—	0·8	
f_a/f'_a	2·5	2·5	1·7	—	2·5	
$f_a + f_b$	≥0·029	≥0·029	0·015	—	0·087	
Solution [16]						
f	0·022	0·031	0·023	0·013	0·099	2·3

* v, Quanta of totally symmetric vibration.

† f' calculated from value of f in solution by first-order theory for y transition.

relation to intermolecular stealing. The quantity $f_a/f'_a > 1$ indicates that the *a* component has been strengthened in the crystal. The observed ratio of 2·5 : 1 agrees well with that estimated theoretically to the second-order approximation. The ratio $f_b/f'_b < 1$ and so it must be concluded that, in the crystal, " intensity stealing " is in the opposite sense for the *b* and *a* polarisations. This result is predicted theoretically but has not previously found experimental verification.

As a measure of the relative intensities in the two polarisations the quantities f_b/f_a and $\varepsilon_b/\varepsilon_a$ are the simplest. Craig and Hobbins [3] introduce a polarisation ratio which, for systems like I, in which the Davydov splitting is small, has very nearly the same value as f_b/f_a. In Table 3 values of f_b/f_a are given. These are comparable with Craig and Hobbins's theoretically calculated ratios and their experimental results. The three values (for the peaks with $v = 0,1,2$) are respectively $\geqslant 4·1$ (3·0, 2·0); $\geqslant 2·6$ (2·8, 1·7); $= 2·75$ (2·6, 1·5). Our results show fairly good agreement with the theory and therefore support it. The observed decrease in the ratio, as *v* increases from 0 to 1, is more pronounced experimentally than the theory predicts. The ratio $\varepsilon_b/\varepsilon_a$ varies more regularly with *v* than f_b/f_a, probably as a result of a vibrational distribution in the crystal different from that in solution. In particular, the unexpectedly high value of f_b for $v = 0$ may be partly due to the band's covering a number of crystal vibrations, but ε_b for $v = 0$ is also high. Present theory has not predicted this. It could perhaps be due to a Franck–Condon effect, the size of the excited state in the crystal being slightly smaller than that in solution, but the results for the *a* polarisation then remain a difficulty.

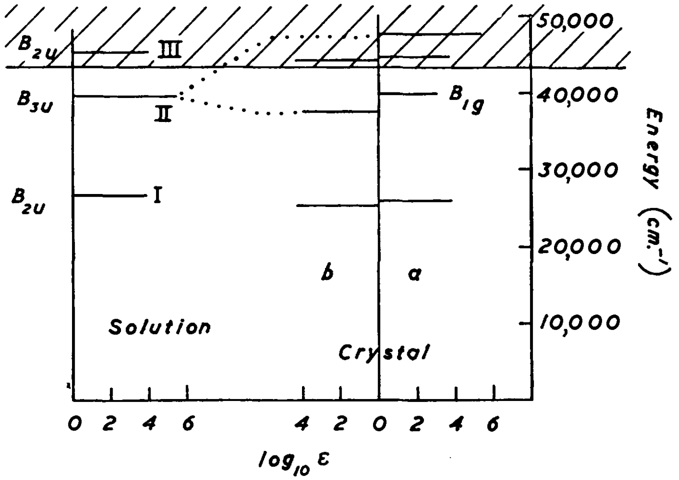
The absolute values of oscillator strengths for the complete system were calculated [2] from refractive-index measurements as $f_b = 0·13$ and $f_a = 0·04$. The earlier Russian work had yielded very much higher figures. Our results of 0·06 and 0·025 are lower again. The extrapolation of refractive-index figures is a procedure liable to appreciable error and the difference in the two sets of values is possibly so explained. It is clear that $f_a + f_b$ accounts for 0·09 of the total solution value of 0·10. By difference, f_p is expected to be about 0·01. From the solution value, on first-order theory, f'_p is calculated at 0·01. Since f'_p and f_p agree it is again clear that the transition is not long-axis polarised, since an *x* polarised transition would have f_p greater than f_a and f_b.

The reflection spectra obviously confirm that the absorption is *b* polarised, but the heights of the reflection peaks are of little quantitative value, since they depend on the refractive as well as the extinction index. (The peaks above 4000 Å in Fig. 2 are due to interference effects, which were negligible in regions of strong absorption.)

System II cannot be discussed in as much detail as System I since the *a* component appears chiefly at lower wavelengths.[10] The agreement (Table 3) between f'_b and f_b confirms the assignment of the 2680 Å absorption to the *b* component of System II (*x* polarised). Comparison of extinction coefficients (Table 2) is in this case better than the use of oscillator strengths, since the error in determining f_b is greatly increased by the onset of the next transition. For System II, $\varepsilon_b = 9000$ and $\varepsilon_b' = 9100$ (Table 2). Since the error in ε'_b is about 3% and in ε_b about 5% the agreement between ε_b and ε'_b is as good as could be expected. The agreement between calculated and experimental results obtained by Craig and Hobbins [3] was satisfactory to within a factor of three. Their conclusion that such a discrepancy was due to the experimental methods used rather than to a deficiency in the theory is seen therefore to be justified. The present results for ε_b accordingly provide a remarkable confirmation of the basic theoretical idea that Davydov splitting is responsible for removing the strong *a* component to another part of the spectrum (into the vacuum region). Such a removal furthermore explains why there is no agreement between the values of ε_a and ε'_a at about 2680 Å. At the same time, $\varepsilon'_a = 170,000$ is predicted for the intensity of the *a* component at lower wavelengths. System II is found also in the reflection *b* polarised spectrum with inflections at 2675, 2590, and 2490 Å. Such inflections are not paralleled in the *a* polarisation. However, the general rise in the reflection of *a* polarised light as the wavelength decreases indicates a very strong *a* polarised transition below our experimental limit. The *b* polarised inflections near 2675, 2590, and 2490 Å are all presumably associated with the one electronic origin and correspond to the absorption peaks at 2680 and 2590 Å. In the *a* polarised reflection spectrum there is a slight and almost imperceptible hump between 2500 and 2600 Å. That this has a basis in reality, although it is only of the same order as the experimental error, is suggested by the occurrence of a broad peak in the absorption spectrum between 2400 and 2690 Å. This was investigated carefully on a number of crystals and appeared in every case.

There are several possible explanations of this *a* absorption: (i) The *a* absorption appears because of crystal strain, misalignment, or imperfect crystal structure. (ii) If System II were not greatly split, the *a* absorption could be the component of a transition to a B_{2u} upper state. In this case the splitting might be explicable but all the intensity measurements calculated from the solution extinction would be low by a factor of 1/60. Molecular-orbital theory (LCAO) [13] also disagrees with such an assignment, as does the free-electron result.[14] (iii) The *a* absorption is a long-wavelength tail of the strong *a* component which has its origin at shorter wavelengths. But the intensity seems too great for this. (iv) The absorption is interpretable as a separate electronic transition. There is predicted [13] a B_{1g} upper state having the same energy as the B_{3u} state terminating System II. Transitions to this are electronically forbidden but could appear, as does the 2600 Å transition in benzene, through the action of vibrations. Such a transition would not be observed in solution beneath the very intense B_{3u} system.

FIG. 6. *Anthracene: energy levels and symmetry assignments in solution and crystal.*



Cross-hatching indicates a region of experimental uncertainty. Dotted lines show correlations between solution and crystal.

Strong *a* absorption observed at low wavelengths could be the beginning of either the next transition or else the *a* component of System II, in which case it is at rather higher wavelengths than expected from theory.

System III was observed plainly only in the *b* reflection spectrum. The absorption spectrum showed a peak at 2220 Å but this estimate of $\lambda_{\max.}$ could well need correction because of the presence of stray light. In the reflection measurements the stray light was less important. The inflection in the *b* reflection spectrum has a centre at about 2200 Å and certainly indicates a *b* polarised optical transition near this point. From the *b* refractive indices observed as 2·59 (2280 Å), 2·46 (2290 Å), 2·33 (2310 Å), and 2·24 (2330 Å) the band origin was estimated as 2270 Å and the oscillator strength f as 0·4. In solution there is a transition [15] with $f = 0{\cdot}28$ but this apparently includes some intensity from the overlapping very intense neighbouring system. Extinction coefficients gave rise to a

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[13] Coulson, *Proc. Phys. Soc.*, 1948, **60**, 257.

[14] Platt, *J. Chem. Phys.*, 1950, **18**, 1168.

[15] Klevens and Platt, *J. Chem. Phys.*, 1949, **17**, 470.

[16] American Petroleum Inst., " Catalog of U.V. Spectrograms," Project No. 44 at N.B.S., Nos. 91 and 170.

more conclusive argument. From the absorption spectrum (Fig. 3) it is clear that ε_b at about 44,500 cm.$^{-1}$ (2250 Å) definitely exceeds the peak solution value. Errors due to stray light would increase the crystal value and thus make the difference more pronounced. Now the only one of the three possible molecular transition polarisations which will make ε_b (crystal) greater than ε (solution) is the y direction. In this case $\varepsilon'_b = 2{\cdot}4\varepsilon$ (solution). A z transition (polarised normal to the molecular plane) would give $\varepsilon'_b = 0{\cdot}56\varepsilon$ (solution) and an x transition $\varepsilon'_b = 0{\cdot}045\varepsilon$ (solution). The presence of second-order effects will modify these figures somewhat, but it seems unlikely that the difference in $\varepsilon_b/\varepsilon$ (solution) between the y and either the x or the z direction will be upset. Consequently the intensity measurements show that System III is y polarised and the upper state concerned is of symmetry B_{2u}. The *a* component is expected to occur at only slightly shorter wavelengths than the *b*, since the total transition intensity is not great. Also the *a* component is expected to be rather weaker in intensity than the *b*, having $\varepsilon'_a = 1000$, on first-order theory. Intensity stealing from the exceedingly intense *a* component of System II would increase the value of ε_a. The observed absorption in the *a* polarisation is greater than in the *b* at about 44,500 cm.$^{-1}$. This is in accord with earlier observations [3,4] and may be explained as being due not only to an enhanced *a* component of System III but to the onset of the intense *a* component of System II. The reflection spectra support this view.

The assignment of System III as B_{2u} is supported by LCAO molecular-orbital theory. Coulson [13] calculated the energy of the third excited state which terminated an allowed transition as being 1·78 times as much above the ground state as was the first excited state. The spectrally observed ratio of the third to the first state's energy is 1·74. Theoretically, the symmetry of the third excited state was determined as B_{2u}, thus supporting our experimentally based conclusion. However, theoretical methods are still inconclusive. The present experimental position is summarised in Fig. 6, with the assignments and correlations between solution and crystal spectra which have been discussed above.

We are indebted to the Commonwealth Research Fund for financial support (to A. B.), and to Professor D. P. Craig and Mr. J. Ferguson for helpful discussions, to Professor Craig for reading the manuscript, and to Dr. C. K. Coogan for advice on reflection spectroscopy.

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[*Received, November 7th,* 1955.]