299. *The Intensity of Ultraviolet Light Absorption by Monocrystals. Part III.*[1] *Absorption by Anthracene at* 295° K, 90° K, *and* 4° K *of Plane-polarised Light of Wavelengths* 1600—2750 Å.

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

Quantitative measurements of the absorption by anthracene monocrystals of plane-polarised light are reported from 1600 to 2750 Å at 4° K, 90° K, and 295° K. Five transitions are detected and these are discussed in terms of the excited electronic states of the anthracene molecule. The Davydov splitting of the molecular transition at 4·8 ev is confirmed by the measurement of the component polarised perpendicularly to the *b* crystal axis. The various upper states are assigned to symmetry species.

The interpretation of the spectrum [1] of the anthracene molecule has been greatly assisted by the study of crystal spectra with plane-polarised light. In the past, experimental difficulties have limited observations of intensity of absorption to the region below 48,000 cm.$^{-1}$. Although there have been one or two observations [2] of aromatic crystal spectra in the vacuum region with polarised light no work has been reported on anthracene except for a brief mention [3] of a qualitative experiment. No previous work at low temperatures with polarised radiation in the vacuum region is known to us. The region above 48,000 cm.$^{-1}$ is important to the understanding of the anthracene spectrum in several respects. One object of the present work was to test the prediction of the crystal splitting of the second main absorption system, found in solution near 40,000 cm.$^{-1}$. In Part II it was found that the *b* component of this transition had an extinction coefficient which agreed with the value predicted. The *a* component (polarised perpendicularly to the *b* crystal axis) could not be found below 46,000 cm.$^{-1}$ and was expected to lie at higher energies with a calculated molar extinction coefficient of 170,000, the molecular transition being polarised along the longer in-plane axis.

EXPERIMENTAL

Anthracene was chromatographed [cf. ref. 4]. Crystals were prepared by sublimation in carbon dioxide in the dark, transferred to polished fluorite or lithium fluoride discs and an appropriate section selected. Axes were determined by conoscopic investigation under a Zeiss polarising microscope, thicknesses being determined by use of an Ehringhaus compensator. The birefringence at 5461 Å was taken as 0·134.[5] The crystal holder allowed rotation of the crystal through known angles, as well as lateral and vertical movements. The light source was an Allen hydrogen arc [6] with a fluorite window attached by an O-ring seal to the metal casing and operated usually at 4 A, 60 V. Calibration arcs were a standard copper arc in a nitrogen stream, or a copper hollow-cathode tube with a sapphire window.

The light was condensed by a lithium fluoride lens on the crystal of which the requisite area was left unmasked. The emergent light was condensed to a beam about 1 mm. in diameter at the slit. The beam was analysed by a special Wollaston prism designed to fit inside the spectrograph and produce at the plate two beams polarised mutually perpendicularly about 1 mm. apart. With all optical components and crystals about 0·1 μ thick examination was possible to about 64,000 cm.$^{-1}$. The prism itself transmitted to about 67,000 cm.$^{-1}$. Crystals thicker than 0·3 μ were too thick for measurement above 50,000 cm.$^{-1}$.

The low-temperature runs were done in either a helium cryostat [7] fitted with fluorite windows

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[1] Part II, Bree and Lyons, *J.*, 1956, 2662; see also Craig, Hobbins, and Walsh, *J. Chem. Phys.*, 1954, **22**, 1616; Craig and Hobbins, *J.*, 1955, 539 and 2309; Sidman, *Phys. Rev.*, 1956, **102**, 96; Ferguson and Schneider, *J. Chem. Phys.*, 1958, **28**, 761; Perkampus, *Z. phys. Chem.* (*Frankfurt*), 1957, **13**, 278.

[2] Nelson and Simpson, *J. Chem. Phys.*, 1955, **6**, 1146; Romand and Vodar, *Compt. rend.*, 1951, **233**, 930.

[3] Dunn and Lyons, quoted by Lyons, *J. Chem. Phys.*, 1955, **23**, 1973.

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

[5] Obreimov, Prikhotjko, and Rodnikova, *Zhur. eksp. teor. Fiz.*, 1948, **18**, 409.

[6] Allen, *J. Opt. Soc. Amer.*, 1941, **31**, 268.

[7] Walsh, Ph.D. Thesis, Sydney, 1958.

or else a conventional low-temperature apparatus. Oxygen was removed from the light path by blowing a continuous oxygen- and water-free stream of nitrogen between the components. A fluorite window covered the slit.

The Hilger 3 metre normal incidence vacuum grating spectrograph was used in the 1st order (5·78 Å/mm. dispersion) and operated at a pressure of 10^{-4} mm. Hg or less, vapours being trapped by liquid-air containers. Ilford Q_1 and Q_2 plates were developed in Ilford Developer 19b for 3 min. Ten exposures could be placed on a plate, comparison spectra being obtained by means of a diaphragm before the plate. Each wavelength setting gave a span of 1400 Å on the plate. Blackening was measured on a Hilger recording microphotometer, each spectrum being traced twice. The calibration arc was traced and then the spectrum to be measured, part of

FIG. 1. *Absorption spectra of anthracene.* . . . . *solution in* n-*heptane*; —— *b crystal spectrum with the electric vector of the light parallel to b crystal axis*; —·—·— *a crystal spectrum electric vector perpendicular to b in* (001) *plane.*

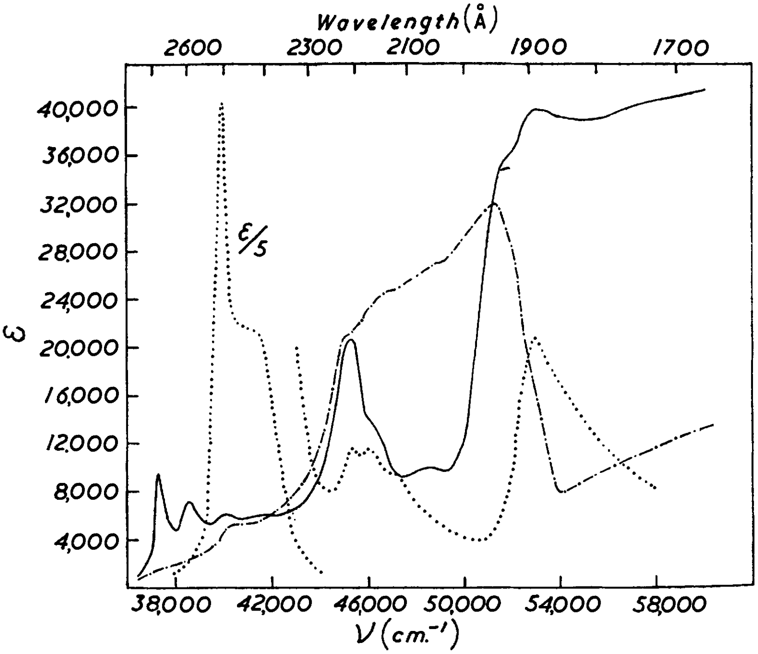

TABLE 1. *Extinction coefficients,* ε = (1/*cd*) log₁₀(*I*₀/*I*) *at turning points; room temperature.*

c, lowest wave-length observed with continuum.
l, observed with line source. s, shoulder.
* Maximum.

λ (Å)	ν (cm.$^{-1}$)	ε_b	λ (Å)	ν (cm.$^{-1}$)	ε_a
2680·5 *	37,315 *	9600			
2638	37,910	5000			
2595 *	38,530 *	7200			
2546	39,280	5400			
2490 *	40,160 *	6200	2500 ^{s}	40,000 ^{s}	5000
			2220 ^{s}	45,050 ^{s}	21,000
2210 *	45,250 *	20,800			
2170 ^{s}	46,080 ^{s}	14,000	2130 ^{s}	46,950 ^{s}	25,000
2110	47,390	9200			
2070 *	48,310 *	10,400	2050 ^{s}	48,780 ^{s}	27,200
2032	49,200	9600			
1930 ^{s}	51,810 ^{s}	36,000	1950 *	51,280 *	32,000
1890 *	52,910 *	40,000			
			1850	54,050	8000
1667 ^{c}	60,000 ^{c}	41,500	1667 ^{c}	60,000 ^{c}	13,400
1660 ^{1}	62,500 ^{1}	42,000	1600 ^{1}	62,500 ^{1}	15,000

the calibration arc being also traced at both ends of this spectrum. Exact superposition of corresponding arc lines at either end of the tracings was always possible. Wavelengths reduced to vacuum were calculated from the tracings. For photoelectric measurement, a 1P28 photomultiplier coated with sodium salicylate[8] was fitted inside the spectrograph, one or other polarised beam being cut off by a movable diaphragm. One of four pre-set slits mounted on the plate holder could be selected. The incident and transmitted beams were examined alternatively in each polarisation, similarly polarised beams always falling on the same area to avoid errors.[9] For the low-temperature work, the incident beam was examined after the

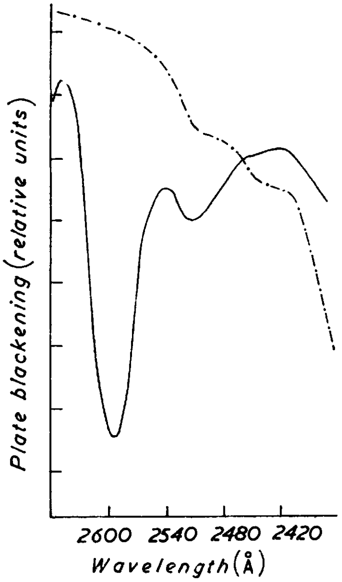

FIG. 2. *Microphotometer traces of b and a crystal spectra at* 90° K.

——— *electric vector parallel to b.*
—·—·— *a.*

TABLE 2. *Reduced oscillator strengths* ($f_{a,b} = 1{\cdot}44 \times 10^{-9}\int \varepsilon_{a,b}\, d\nu$) *in the crystal at room temperature.*

(abs., absorption spectrum; ref., reflection spectrum; r.i. refractive index); * Present work.

System	Range of ν (cm.$^{-1}$)	f_b	f_a	Method
I		0·033(?)	0·015	abs.[a]
		0·06	0·013	ref.[a]
	25,000—33,000	0·064	0·025	abs.[b]
		0·10	0·057	r.i.[c]
		0·057	0·013	r.i.[d]
		0·04	0·017	abs.[e]
II	37,000—41,000	0·047		abs.[b]
	37,000—41,000	0·035	(0·020)	abs.*
	41,000—54,000		0·368	abs.*
III		0·16		ref.[f]
		0·4		ref.[b]
		0·09		abs.[f]
	41,000—47,500	0·099		abs.*
IV	47,500—49,500	0·029		abs.*
V	49,500—60,000	$\geqslant$0·55		abs.*
	54,000—60,000		0·094	abs.*

[a] Borisov, *Trudy Inst. Fiz. Akad. Nauk Ukrain. S.S.R.*, 1953, 102. (See Technical Translation TT-613, 1956, Nat. Res. Council, Canada.) [b] Part II. [c] Ref. 5. [d] Eichis, *Z. exsp. teoret. Fiz.*, 1950, **20**, 471. [e] Brodin and Prikhotjko, *Optika i Spectroskopiya*, 1957, **2**, 448; Kharitonova, *ibid.*, 1958, **5**, 29. [f] Ref. 19.

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[8] Williams, Meharry, Maslen, and Falconer, *J. Opt. Soc. Amer.*, 1954, **44**, 654; Bolton and Williams, *Nature*, 1952, **169**, 325; *Brit. J. Appl. Phys.*, 1954, **4**, 6; Johnson, Watanabe, and Tousey, *J. Opt. Soc. Amer.*, 1951, **41**, 702.

[9] Norman and Kay, *J. Sci. Instr.*, 1952, **29**, 33; Clancy, *J. Opt. Soc. Amer.*, 1952, **42**, 357.

transmitted beam spectrum was obtained. The photomultipler response (assumed directly proportional[10] to the light flux) was measured on an Electronic Industries Ltd. Vibron electrometer model 33B. The wavelength setting calibrated by a mercury lamp could be altered by rotating the grating and plate holder around the Rowland circle by means of an external handle.

FIG. 3*a*.

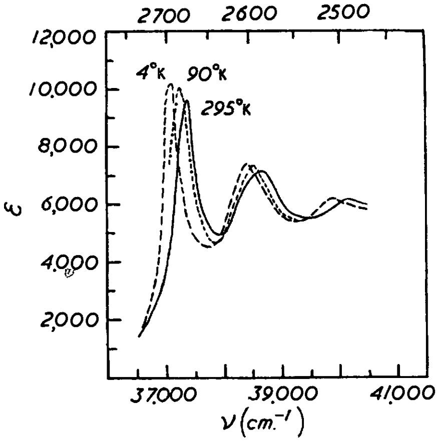

FIG. 3*b*.

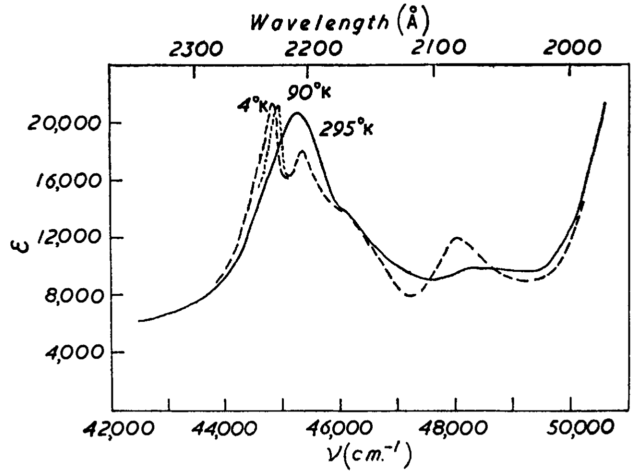

FIG. 3. *Effect of lowering the temperature from* 295° K *to* 90° K *and* 4° K (*b polarisation*).
(*a*) 37,000 cm.$^{-1}$ region; (*b*) 46,000 cm.$^{-1}$ region.

Molar extinction coefficients were obtained by both photographic photometry and photoelectric methods. For the former, light filters of nickel gauze,[11] neutral as calibrated on a Uvispek spectrophotometer to 45,500 cm.$^{-1}$, were assumed neutral to 62,500 cm.$^{-1}$. This assumption was later proved correct by photomultiplier measurement of their optical density. Eight filters of optical densities from 0·16 to 1·14 were used. Failure of the reciprocity law was negligible over the range of times considered (less than six-fold). Exposure times varied between 1 min. and 1½ hr. It was preferable to cut down exposure time by opening the slit to as much as a 3 Å band-pass (after ascertaining that no fine structure was present) in order to reduce the effect of stray light which rendered the photometry above 55,500 cm.$^{-1}$ difficult.

[10] Engstrom, *J. Opt. Soc. Amer.*, 1947, **37**, 420.
[11] Sawyer and Vincent, *J. Opt. Soc. Amer.*, 1943, **33**, 247.

The photomultiplier method was the more accurate for extinction coefficients, but the signal : noise ratio was too small for high accuracy above 55,000 cm.$^{-1}$. Wavelength measurements were best done photographically. The lamp, provided it was vacuum-tight, needed no stabilisation for reproducibility.

The solution spectrum was obtained in 1 mm. " Ultrasil " cells with *n*-hexane as solvent on both the vacuum instrument and a " Spectracord " double-beam recording spectrophotometer.

The results are shown in Figs. 1—3 and Tables 1—5. The errors in wavelengths depend on the band shape, sharper bands being accurate to 2 Å. The errors in extinction coefficient were about 15% ($<$50,000 cm.$^{-1}$) or 30% ($>$50,000 cm.$^{-1}$) with the photographic method, but about 10% and 20% with the photomultipler; the main error lay in the measurement of the crystal thicknesses. Errors in oscillator strengths arise mainly from determining the exact wavenumber spread of the transition but, with $\Delta\nu$ as stated in the Tables, the errors in f correspond to those in ε. A further error may arise from surface effects.[12] Whilst these may alter the bulk spectrum to a certain extent, no evidence of this was seen.

The " reduced " oscillator strength is convenient in the consideration of crystal transitions and may be defined so that $f_a + f_b + f_p$ approximates to f for a solution. The Russian workers calculate oscillator strengths for the crystal which are three times as great as f_a or f_b, so their results have been divided by three in Table 2.

TABLE 3. *Oscillator strengths*, $f = 4{\cdot}31 \times 10^{-9} \int \varepsilon \, d\nu$.

	I	II	III	V
Vapour	0·11 [a]; 0·02 [b]	0·93 [b]		
Solution	0·10 [c]	1·56 [b]; 1·9 [c]; 2·3 [d] 1·6 *	$\leqslant$0·28 [d]; 0·22 [e] 0·21 *	0·6 [d]; 0·5 [e] 0·41 *

[a] Brodin and Prikhotjko, *Optika i Spectroskopiya*, 1957, **2**, 448; Kharitonova, *ibid.*, 1958, **5**, 29. [b] Ferguson and Schneider, *Canad. J. Chem.*, 1957, **35**, 1117. [c] Calc. from " Catalog of Ultraviolet Spectrograms," Amer. Petroleum Inst., Project 44 at Nat. Bur. Stand., Nos. 91 and 170. [d] Klevens and Platt, *J. Chem. Phys.*, 1949, **17**, 470. [e] Ref. 21. * Present work.

DISCUSSION

We now attempt to explain the main features of the observed spectrum in terms of π–π transitions. Only the theoretically expected singlet upper states are considered. It must be realised that triplet $2p\pi$ states and other states expected in the crystal such as ionised states and states involving atomic orbitals with $n \geqslant 3$ may possibly occur in this spectral region. A feature of the crystal spectrum is that there are no Rydberg bands clearly visible in the region in which they occur in the vapour. This agrees with the theory that such bands in the vapour are removed to much lower energies in the crystal. The ionisation and the photoelectric properties of the crystal in this region will be discussed in a subsequent paper.

The group-theory notation is that recommended [13] in 1955 and differs from that used in Part II. Throughout the discussion " *a* " refers to a direction perpendicular to the *b* crystal axis and lying in the (001) plane.

System I has been studied previously by a number of workers whose results are included for comparison. Table 2 shows that even for this most accessible system there is a large variation in the experimentally determined oscillator strengths. Nonetheless, there is clear confirmation of the *z* (short molecular axis) polarisation of the transition and of the $^1L_a : B_{1u}{}^+$ nature of the excited electronic state. Here Platt's symbol precedes the result calculated by Pariser.[14]

From the results for crystal and solution it follows that Obreimov, Prikhotjko, and Rodnikova's [5] f values for the crystal are high. Calculation of $f_p = 0{\cdot}01$ by the difference between $f_a + f_p$ and $f_{\text{soln.}}$ agrees with the value calculated by first-order theory which

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[12] Ferguson and Schneider, *J. Chem. Phys.*, 1958, **28**, 761.

[13] Mulliken, *J. Chem. Phys.*, 1955, **23**, 1997.

[14] Pariser, *J. Chem. Phys.*, 1956, **24**, 250.

gives $f_p' = 0{\cdot}01$ (see Part II). The transition to the low-lying $^1L_b : {^1B_{2u}}^-$ state is expected by Pariser and by Ham and Rudenberg [15] to be weak and to be buried beneath System I.

System II was observed in *b* polarisation both earlier (Part II) and in the present work which gives a slightly lower value for f_b but about the same value for ε_b. The general discussion of Part II is confirmed, as is the assignment of the polarisation as *y* (long molecular axis). The earlier work, however, could not investigate the *a* polarised absorption expected (on the basis of the reflection spectra taken at less than 45,000 cm.$^{-1}$) to appear between 52,000 and 66,000 cm.$^{-1}$ with a predicted f_a of 0·5. In the present work strong absorption was found to extend over the interval 41,000—54,000 cm.$^{-1}$ with an observed f_a of 0·37. This absorption is therefore taken to arise chiefly from System II of the molecular spectrum. There could be some absorption arising from other molecular systems. For example the *a* components of Systems III and IV are both likely to appear in this region. Both components of System II have now been measured in the crystal and the earlier result [3] is confirmed and made quantitative. The observed spectrum therefore confirms the theory [16] of the Davydov splitting of System II. The upper state of System II is identified as ^1B_b by Platt [17] and by Ham and Rudenberg. Pariser identifies the upper state of the very strong transition as ${^1B_{2u}}^+$. Both assignments are consistent with the observed spectrum.

System II has $f = 1{\cdot}6$ in solution but $f_a + f_b = 0{\cdot}43$ only. This reduction in intensity is expected for a transition polarised along the longer molecular axis. The values calculated by first-order theory are $f_a' = 0{\cdot}48$ and $f_b' = 0{\cdot}04$. Consideration of intensity therefore confirms the polarisation of the transition deduced previously and also shows that the major factor causing the apparent great reduction in intensity on going from solution to crystal is simply the geometry of the molecular arrangement. The peculiar shape of the *a* component of II seems likely to be due to the presence of three close-lying *a* components from systems II, III, and IV. Three such upper states must mix greatly with each other in the crystal. There is predicted a further transition near system II which marks a ${^1B_{1u}}^+$ level according to Pariser and a second ^1L_a state according to Ham and Rudenberg. In both cases the molecular polarisation would be short-axis. In both Part II and the present work there was observed a weak extra absorption (system II′) at 40,000 cm.$^{-1}$.

At low temperatures a vibrational interval of about 980 cm.$^{-1}$ appeared in the *a* polarisation (Fig. 2). System II′, although possibly due to disoriented molecules, could conceivably mark a level expected by theory. Previously the B_{3g} level predicted by Coulson [18] was regarded as possibly present. The more recent theories make alternative assignments more likely than B_{3g}. Platt's original symbolism allowed for only one state of type ^1L_a. Ham and Rudenberg make no calculations for the second ^1L_a state but use the symbolism to indicate the empirical similarity between a pair of levels over a range of compounds.

System III was measured in Part II in *b* polarisation both by absorption ($f_b = 0{\cdot}09$) and reflection ($f_b = 0{\cdot}16$). The result deduced in Part II for f_b, also based on reflection measurements, was $f_b = 0{\cdot}43$. (In the summary of Part II the value is given incorrectly.) Bree's result [19] of 0·16 was based on later and fuller work than that reported in Part II and we consider it the more reliable of the two reflection results. In the present work f_b was found to be 0·10. Therefore the conclusion of Part II is confirmed and System III marks a *z* polarised molecular transition. If this transition marks Platt's ^1C_b state then it is electronically forbidden in the free molecule. The observed intensity is then to be explained by intra- and/or inter-molecular stealing from neighbouring bands of similar crystal symmetry. Ham and Rudenberg differ from Platt and assign the upper state as

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[15] Ham and Rudenberg, *J. Chem. Phys.*, 1956, **25**, 1.
[16] Craig, *J.*, 1955, 2302.
[17] Platt, *J. Chem. Phys.*, 1949, **17**, 481.
[18] Coulson, *Proc. Roy. Soc.*, 1948, **60**, 257.
[19] Bree, Ph.D. Thesis, Sydney, 1958.

^1B_a. This agrees with the observed polarisation, but Platt's assignment cannot be ruled out on these grounds. The consideration of f_b values (calculated as 0·005 for long-axis polarisation and 0·2 for for short-axis) confirms the short-axis assignment especially when it is remembered that the f value for the solution is likely to be high owing to the overlap with the next transition. Because ε_a was greater than ε_b in this region Craig[20] came to the opposite conclusion about this polarisation. At that time however Craig had not proposed the theory of the Davydov splitting of System II and so did not associate the larger *a* absorption with System II. The predicted splitting of 16,000 cm.$^{-1}$ compares with the present observed splitting of 8000—15,000 cm.$^{-1}$ (Fig. 1). The short-axis polarisation now confirmed agrees with Pariser's identification of the upper state as B_{1u}^+ although both his calculated energy and oscillator strength are higher than those observed. The Davydov splitting expected for System III is likely to be very much less than for System II and therefore the previous agreement is unlikely to be upset by such considerations. Nor could intensity stealing by an intermolecular mechanism in the crystal (which would have increased the *a* absorption more than the *b*) have reversed the polarisation.

System IV has not previously been discussed either in solution or in crystal and here was observed definitely only in *b* polarisation. It is weak ($f_b = 0{\cdot}029$). It is not a " hot " band associated with the strong *b* transition at 50,000 cm.$^{-1}$ since it appears even more definitely at 90° K and at 4° K (Fig. 3). The corresponding *a* component could well be buried beneath the strong *a* absorption at similar frequencies. In the solution spectrum[21] there is no region of absorption near 48,000 cm.$^{-1}$ which clearly marks a separate electronic transition. In phenanthrene, however, an " extra " band is probably present. Pariser predicts a $^1B_{2u}^+$ level at 7·2 ev, a transition to which is of appropriate intensity and is long-axis polarised. Ham and Rudenberg's second ^1L_b state is also a possibility in this instance in view of the fact that System V, which they assigned as the second ^1L_b, has the wrong polarisation property. Because of the lack of clear observation of the *a* component it is impossible to conclude what is the polarisation of System IV, especially as intermolecular intensity stealing from System V could well have augmented the f_b value of IV. There is no argument against the $^1B_{2u}^+$ assignment.

System V is intense in solution ($f = 0{\cdot}4$) and presumably a large amount of the crystal absorption in *b* polarisation between 50,000 and 60,000 cm.$^{-1}$ is derived from this molecular system. If this is so then the fact that f_b is comparable with $f_{\text{soln.}}$ indicates that the transition is z polarised. The corresponding *a* absorption between 54,000 and 60,000 cm.$^{-1}$ and beyond may correspond wholly or in part to the *b* component between 50,000 and 60,000 cm.$^{-1}$. The value of f_a is in this case again in fair agreement with that expected for a z-polarised molecular transition. In this region, however, crystal effects are likely to be relatively more important than at lower energies. The interpretation of the crystal spectrum in terms of molecular properties must therefore be made with reservations.

The effect on the spectrum of lowering the temperature to 90° K and to 4° K was examined. Results were as follow: (i) In System II the *b*-polarised peaks became sharper and moved to lower energies (see Table 4 and Fig. 3); the extinction coefficients at the peaks became greater. (ii) In System II the *b*-polarised peak split into two with a separation of 630 cm.$^{-1}$ at 4° K. This presumably indicates a totally symmetric vibration in the third B_{1u}^+ excited state. (iii) In *a* polarisation shoulders appeared at 39,950, 40,900, 43,977, 46,080, 48,080, 48,780, 49,260, 49,580, and 49,930 cm.$^{-1}$. (iv) The peak in System IV was sharpened, increased in height, and moved to slightly lower energies.

The general lack of structure in the anthracene spectrum compared, for example, with that[7] in the naphthalene band at 32,000 cm.$^{-1}$ continues in the vacuum region. This diffuseness is attributable to the influence of lattice vibrations[22] and any mixing of the upper levels with conduction levels.

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[20] Craig, *Rev. Pure Appl. Chem.* (*Australia*), 1953, **4**, 207.

[21] Jones and Taylor, *Analyt. Chem.*, 1955, **27**, 228.

[22] Moffitt, personal communication.

TABLE 4. *Variation in positions of band maxima* (*cm.*$^{-1}$) *with temperature.*

T (°K) =						
295	37,320	38,530		45,250	46,080	48,310
90	37,210	38,510	44,840	45,290	46,080	48,080
4	37,110	38,420	44,700	45,330	46,020	48,010

On the whole lowering the temperature added little new knowledge of the spectrum beyond establishing that the ground state of System IV was not vibronic.

TABLE 5. *Some electronic states of anthracene observed and calculated.*

	Obs. in solution		Obs. in crystal				Platt[a]	Ham and Rudenberg[b]		Moffitt[c]	Pariser[d]		
	ev	f	ev	f_a	f_b	pol.	Assignment	Assignment	Calc. ev	Calc. f	Assignment	Calc. ev	f
I	3·4	0·1	3·1	0·02	0·06	z	z ^1L_a	z ^1L_a	3·6	0·11	z B_{1u}^+	3·6	0·4
							y ^1L_b	y ^1L_b	3·2	0·0005	y B_{2u}^-		
II	4·8	1·6	4·6, 5·7	0·4	0·04	y	y ^1B_b	y ^1B_b	5·2	1·45 >	y B_{2u}^+	5·5	3·2
								z ^1L_a			z B_{1u}^+	5·25	0·1
II′			5·0	0·01		?							
III	5·6	0·2	5·5		0·1	z	forb. ^1C_b	z ^1B_a	5·4		z B_{1u}^+	6·6	0·6
IV			6·0		0·03	?					y B_{2u}^+	7·2	0·1
V	6·7	0·4	6·3	⩾0·1	⩾0·6	z	z ^1B_a	y ^1L_b			z B_{1u}^+	7·8	

[a] Ref. 17. [b] Ref. 15. [c] Moffitt, *J. Chem. Phys.*, 1954, **22**, 320. [d] Ref. 14.

Table 5 summarises the experimental and theoretical conclusions.

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