1029. *Luminescence from Zone-refined Anthracene at 4°K, and the Davydov Splitting.*

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The sharp-line fluorescence spectrum of a zone-refined anthracene mono-crystal has been recorded at 4°K with polarized light. The spectrum contains 96 lines, of which 52 have been assigned in terms of lattice vibrations and ground-state molecular vibrations of anthracene. The spectrum exhibits several clearly defined groups of bands; the strongest group is attributed to transitions from the lower free exciton level to vibronic levels of the ground state, and the remaining groups we attributed to crystal imperfections other than impurities which are removed by zone refining. The results show that the Davydov splitting of the first system in anthracene has the value 383 ± 9 cm.$^{-1}$, which is greater than values previously reported.

FOR many years the gap of nearly 500 cm.$^{-1}$ between the absorption and fluorescence maxima in the 25,000 cm.$^{-1}$ system of the anthracene crystal has not been clearly understood. The Davydov splitting between the *b*- and *ac*-polarized components of the absorption spectrum at 25,400 cm.$^{-1}$ was at first thought [1-3] to be of the order of 0—60 cm.$^{-1}$, whilst the fluorescence origin was thought [2] to be at *ca.* 24,900 cm.$^{-1}$. Wolf [4] observed a very broad peak in *b*-polarized absorption at 25,270 cm.$^{-1}$, and concluded that the splitting was 220 cm.$^{-1}$. Later work by Brodin [5] and by ourselves [6] showed that the Davydov splitting is still larger, and of the order of 300 cm.$^{-1}$. The splitting varied with the thickness of the crystal and an extrapolated value of 336 ± 25 cm.$^{-1}$ was quoted for zero crystal thickness,[6] the largest value observed in absorption being 278 cm.$^{-1}$ on a crystal 0.08μ thick.[7] Such large splittings pointed to the need to include multipole terms in theoretical calculations.[6] It was subsequently shown [8] that experiment and theory could be reconciled if octupole interactions were held responsible for the increased splitting. The larger value of the splitting indicated [6] that the free exciton level terminating a *b*-polarized transition in absorption lies at $25,150 \pm 25$ cm.$^{-1}$. This was partly confirmed by earlier work [9] in which it was shown that purification of anthracene by means of zone refining removed the impurity centres which acted as energy traps, and, as a result, the apparent fluorescence origin was found to occur at $25,040 \pm 50$ cm.$^{-1}$ instead of previously reported values of 24,908 [2] and 24,904 cm.$^{-1}$.[10]

This larger value of the Davydov splitting indicates that at low temperatures the fluorescence should originate from the lowest allowed level of the exciton band, which in this case is the *b*-polarized component, and should, therefore, appear to be predominantly *b* polarized. Experimentally this is the case.[2,11] The remaining discrepancy between the *b* origin predicted by absorption work at 25,150 cm.$^{-1}$ and the fluorescence origin observed at 25,040 cm.$^{-1}$ was attributed mainly to reabsorption. This discrepancy has been reconciled still further by recent Russian results [12] in which the origin for fluorescence has been placed at $25,100 \pm 10$ cm.$^{-1}$.

[1] Craig and Hobbins, *J.*, 1955, 2309.
[2] Sidman, *Phys. Rev.*, 1956, **102**, 96.
[3] Ferguson and Schneider, *J. Chem. Phys.*, 1958, **28**, 761.
[4] Wolf, *Z. Naturforsch*, 1958, **13***A*, 414.
[5] Brodin and Marisova, *Optics and Spectroscopy*, 1961, **10**, 242.
[6] Lacey and Lyons, *Proc. Chem. Soc.*, 1960, 414.
[7] Lacey and Lyons, unpublished results.
[8] Craig, Claxton, and Thirunamachandran, *J. Chem. Phys.*, 1961, **35**, 1525.
[9] Alexander, Lacey, and Lyons, *J. Chem. Phys.*, 1961, **34**, 2200.
[10] Prikhot'ko and Fugol, *Optika i Spectroskopiya*, 1958, **4**, 335; See also Ferguson and Schneider, *J. Chem. Phys.*, 1956, **25**, 780.
[11] Choudhury and Ganguly, *Proc. Roy. Soc.*, 1960, *A*, **259**, 419.
[12] Shpak and Sheremet, *Optics and Spectroscopy*, 1963, **14**, 433.

The present work leaves little doubt as to the positions of the two Davydov components of the exciton band, and furthermore confirms the large value of the Davydov splitting predicted by earlier absorption work.

<div align="center">EXPERIMENTAL</div>

The anthracene was purified by means of zone refining, the column being subjected to 254 passes of the zone heater.[13]

Crystals were then prepared by subliming the anthracene in the dark in an inert atmosphere. The thickness and extinction directions of the crystal were then determined with the aid of a polarizing microscope. For the low-temperature spectra the crystal was mounted on a copper disc with G.E. 7031 (General Electric adhesive), the disc then being fitted into the helium cryostat.

The fluorescence was excited by the 3660 Å line of a high-pressure 250-w Mazda mercury lamp, using a Hilger D-292 monochromator, and was recorded on a Hilger Littrow mounting quartz spectrograph, using a 50-μ slit-width.

<div align="center">RESULTS</div>

The polarized fluorescence spectrum of a 10·7-μ crystal of zone-refined anthracene, photographed at 4°K, showed a sharp-line spectrum extending from 25,076 cm.$^{-1}$, in the *b* polarization, to 20,827 cm.$^{-1}$, in the *ac* polarization (Fig. 1).
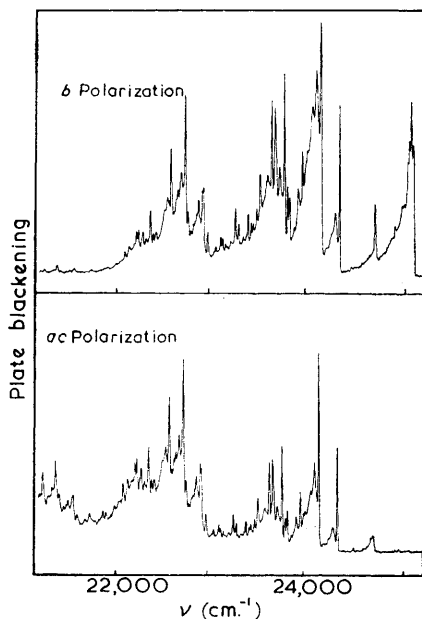

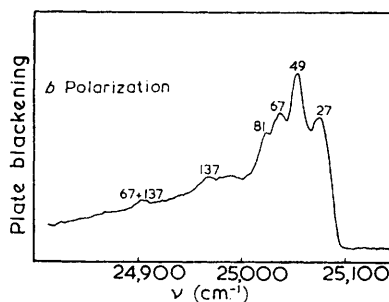FIG. 1.   Microdensitometer traces of luminescence of crystalline anthracene recorded at 4°K.

FIG. 2.   Expanded microdensitometer trace of the origin region in the *b*-polarization luminescence of anthracene at 4°K.

The region of the origin, which was missing entirely in the *ac* polarization, consisted of four sharp lines in a space of 50 cm.$^{-1}$, beginning with 25,076 cm.$^{-1}$, and two weaker lines slightly to lower energy. This can be seen clearly in the microphotometer tracing (Fig. 2); the lines appearing as shoulders in the tracing are seen as discrete lines on the actual plate.

The remaining lines to the red of the origin region occur, within experimental error (± 5 cm.$^{-1}$), at the same frequency in both polarizations, but with the intensity in the *b* polarization several times that in the *ac*. In the 22,000—21,000 cm.$^{-1}$ region, the number of lines in the *ac* polarization exceeds that in the *b*. This is attributed, in part, to the optics of the spectrograph, which are found to favour one polarization more than the other because of the angle of inclination of the plate to the optic axis of the spectrograph. As a result, only the more-intense lines in this region were detected in the *b* polarization.

Analysis of the spectrum shows that, as well as the lines due to normal molecular vibrations

[13] Lacey and Lyons, *Rev. Sci. Instr.*, 1963, **34**, 309.

TABLE 1.

Intramolecular vibrational frequencies (in cm.⁻¹) in anthracene.

Fluorescence						Phosphorescence Rigid solution 77°K g	Raman		
Crystal 14°K a	Crystal 4°K b	Crystal 20°K c	In naphthalene 20°K d	In n-heptane 77°K e	In n-heptane 77°K f		Crystal h	Solution h	Solution i
319w									
367s	371								
			398w						
398m		394	403vs	398	390, a_g	409	397, b_{3g}	400, b_{3g}	388 (1)
419s	415, a_g								
445m									
500vs	497						475, a_g	474, a_g	
559s							522, a_g	522, a_g	521 (0)
								577	
				627			606, a_g		
							655, b_{3g}	652, b_{3g}	
752w			752w	763			749, a_g	745, a_g	751, ($\frac{1}{2}$)
								852	
	1003, a_g		1003vw	1021			1009, b_{3g}	1012, b_{3g}	1007 ($\frac{1}{2}$)
				1044				1130	
1167s	1163, a_g	1167	1165s	1169	1165, a_g		1165, a_g		1161 ($\frac{1}{2}$)
							1175	1178	1178 ($\frac{1}{2}$)
				1194			1188, b_{3g}		
1266vs	1264, a_g	1262	1264s	1267	1265, a_g	1268	1261, a_g	1262, a_g	1262 (1)
								1324	
							1403, a_g	1397, a_g	1400 (8)
1411vvs	1407, a_g	1402	1416vvs	1413	1407, a_g	1410	1413, a_g		
							1439, b_{3g}	1444, b_{3g}	
							1481, b_{3g}	1481, b_{3g}	1478 ($\frac{1}{2}$)
								1520	
1559s	1559, a_g	1558	1567 (1165 + 403) vs	1568	1567, a_g	1556	1555, a_g	1551, a_g	1558 (3$\frac{1}{2}$)
							1603	1603	
1638s		1644	1645	1643	1645, a_g		1632, b_{3g}	1631, b_{3g}	1631 (3)

(a) Pesteil and Barbaron, *J. Phys. Radium*, 1954, **15**, 92. (b) Sidman, *Phys. Rev.*, 1956, **102**, 96. (c) Shpak and Sheremet, *Optics and Spectroscopy*, 1963, **14**, 433. (d) Sidman, *J. Chem. Phys.*, 1956, **25**, 115. (e) Bree, personal communication. (f) Bolotnikova. *Izvest. Akad. Nauk S.S.S.R., Ser. fiz.*, 1959, **23**, 29. (g) Padhye, McGlynn, and Kasha, *J. Chem. Phys.*, 1956, **24**, 588. (h) Colombo and Mathieu, *Bull. Soc. franc. Mineral Crist.*, 1960, **83**, 250. (i) Manzoni-Ansidei, *Gazzetta*, 1937, **67**, 790.

and their multiples and combinations, there are also very strong sharp lines which appear to be origins for progressions involving one and two quanta of a 1410 cm.⁻¹ vibration.

The *b* origin used for the analysis was placed at 25,103 cm.⁻¹, for the following reasons. In the literature there are many varying values quoted for the fundamental molecular vibrations in anthracene (see Table 1). Consequently, there was some doubt as to which values should be used, in conjunction with the strongest lines in the spectrum, to determine the origin. (Considering the thickness of the crystal, the 0–0 band must have been at least partially reabsorbed.) Accordingly, the various literature values for the most common vibrational frequencies (in italics in Table 2) were added in turn to the corresponding lines in the present spectrum (namely, *b* and *ac*: 24,705—6; 23,933—3; 23,844—5; 23,693—6; 23,541—2; 23,472—2 cm.⁻¹). Averaging of the values so obtained gave a value of 25,103 ± 2 cm.⁻¹ for the position of the origin.

The frequencies of all the lines observed in the fluorescence spectrum of the 10·7-μ crystal are recorded with their respective intensities and tentative assignments in Table 2. The intensity distribution over the lines appeared to be approximately equal in the two polarizations, except for the last four lines in the *b* polarization (Table 2). These were affected by the optics of the spectrograph.

Of the ninety-six lines observed, tentative assignments are given for fifty-two, some of which can be assigned in more than one way.

DISCUSSION

The results obtained at 4°K are in many aspects similar to those obtained recently at 20·4°K by Shpak and Sheremet,[12] but there are some points of difference.

TABLE 2.

Anthracene fluorescence at 4°K.

Band no.	Observed ν (cm.⁻¹ ± 5 cm.⁻¹) Polarisation		Differences from 25,103 (cm.⁻¹):	Possible assignments (cm.⁻¹)	Δν (assigned − observed) (cm.⁻¹)
	b	ac	b or ac		
	(25,103)			Origin assumed	
1	25,076s		27	27, lattice	0
2	25,054vs		49	45 or 49, lattice	−4, 0
3	25,036ms		67	67, lattice	0
4	25,022w		81	81, lattice	0
5	24,966vw		137	137, lattice	0
6	24,903w		200	67 + 137	4
7	24,705vs	24,706	398	398	0
8	24,472vw		631	*631* (627 *)	0, −4
9	24,350vs	24,350	753	753	0
10	24,310w, br	24,310	793	2 × 398, 753 + 45	3, 5
11	24,263vw, br	24,264	840	*840*	0
12	24,163vs	24,163	940	940	0
13	24,119s	24,119	984	940 + 45	1
14	24,073ms, br	24,074	1030	*1030* (1021 *)	0, −9
15	24,024vw	24,025	1079		
16	24,012vw	24,010	1091		
17	23,976s	23,976	1127	*1127* (1130 †)	0, 3
18	23,933ms	23,933	1170	1170, *1127* + 45	0, 2
19	23,890vw	23,892	1213		
20	23,844ms	23,845	1259	1259	0
21	23,823s	23,824	1280	1259 + 27	6
22	23,789vs	23,789	1314	*1314* (1324 †)	0, 10
23	23,744ms	23,744	1359	*1314* + 45	0
24	23,711w	23,709	1392	*1392* (1403 †)	0, 11
25	23,693s	23,696	1410	1410	0
26	23,658vs	23,659	1445	*1445*, 1410 + 27 (1439 †)	0, −8, −6
27	23,614vw, br	23,614	1489	*1489*, 1410 + 81 (1481 †)	0, +2, −8
28	23,601vvw	23,601	1502	2 × 753	4
29	23,541s	23,542	1562	1562	0
30	23,507ms	23,507	1596	1562 + 27 (1603 †)	−7, 7
31	23,472w	23,472	1631	1631, 1562 + 67	0, 2
32	23,452w	23,452	1651	1259 + 398, 1562 + 81	6, −8
33	23,418s	23,418	1685		
34	23,404vvw	23,404	1699	1562 + 137	0
35	23,371vw	23,372	1732		
36	23,320ms	23,321	1783		
37	23,302vw	23,303	1801	1410 + 398	7
38	23,286s	23,287	1817		
39	23,241vvw, br	23,240	1862		
40	23,184mw	23,185	1919		
41	23,154ms	23,155	1949		
42	23,133ms	23,134	1970	1562 + 398	−10
43	23,081w	23,082	2022	1631 + 398	7
44	23,063vvw	23,062	2040	*631* + 1410	1
45	22,994ms	22,996	2109		
46	22,947s	22,949	2156		
47	22,935s	22,936	2168	753 + 1410	−5
48	22,894ms	22,896	2209	753 + 1410 + 45	−1
49	22,878w	22,878	2225		
50	22,857vvw	22,862	2246		
51	22,839vvw	22,839	2264	3 × 753	−5
52	22,813vvw	22,815	2290		
53	22,784w	22,785	2319		
54	22,763w	22,762	2340	2 × 1170	0
55	22,749vs	22,748	2354	940 + 1410	−4
56	22,706s, br	22,708	2397	940 + 1410 + 45	−2
57	22,672ms	22,672	2431	1170 + 1259	−2
58	22,652ms	22,652	2451		
59	22,625w	22,627	2478		
60	22,596s	22,597	2507		
61	22,575w, br	22,576	2528		
62	22,560w, br	22,561	2543	*1127* + 1410	−6
63		22,528w, br	2575	1170 + 1410, *1127* + 1410 + 45	5, 7
64	22,437w	22,438	2666	1259 + 1410	3

TABLE 2. (*Continued.*)

Band no.	Observed ν (cm.⁻¹ ± 5 cm.⁻¹) Polarisation b	ac	Differences from 25,103 (cm.⁻¹): b or ac	Possible assignments (cm.⁻¹)	Δν (assigned − observed) (cm.⁻¹)
65	22,411ms	22,411	2692	Origin assumed	
66	22,391vw	22,391	2712		
67	22,375s	22,377	2728	1170 + 1562, *1314* + 1410	4, −4
68	22,335w	22,335	2768	*1314* + 1410 + 45	1
69	22,294mw	22,294	2809	2 × 1410	11
70	22,258vw	22,259	2845		
71	22,243ms	22,245	2860		
72	22,223ms	22,226	2880		
73	22,141w	22,143	2962	1410 + 1562	10
74	22,092w	22,095	3011		
75	21,998vvw	22,002	3105		
76		21,908w	3195	1562 + 1631	−2
77		21,873w	3230		
78		21,719w	3384		
79		21,679vw, br	3424		
80		21,585mw, br	3518		
81	21,532vvw	21,533w, br	3571	753 + 2 × 1410	2
82		21,482w	3621	753 + 2 × 1410 + 45	−3
83		21,460vw	3643		
84		21,433vw, br	3670		
85	21,382vvw	21,381s, br	3721		
86	21,336w	21,338s	3767	940 + 2 × 1410	−7
87		21,295vvw, br	3808	940 + 2 × 1410 + 45	−3
88		21,253vvw, br	3850		
89	21,191w	21,191s	3912		
90		21,145vvw, br	3958	*1127* + 2 × 1410	−11
91		21,105w	3998	*1127* + 2 × 1410 + 45	−6
92		21,034mw, br	4069		
93		21,000vvw	4103		
94		20,961mw	4142	*1314* + 2 × 1410	−8
95		20,885vw, br	4218	3 × 1410	12
96		20,827vvw, br	4276		

* Observed by Bree, personal communication.   † Observed by Colombo and Mathieu in Raman Spectrum of crystal; see Table 1, ref. (*h*).

Origin Region.—In the Russian work, the *b* component of the luminescence began with a broad (Δν ≃ 60 cm.⁻¹) intense band at 25,005 cm.⁻¹, with a sharp violet edge in the 25,090 cm.⁻¹ region and a weak background reaching to 25,103 cm.⁻¹. This band was also weakly present in the *ac* polarization; with equal exposures for both polarizations, there was slight blackening of the plate at 25,040 cm.⁻¹ in the *ac* polarization. In our work, the broad band observed by Shpak and Sheremet [12] was resolved into four sharp lines, having maxima at 25,076, 25,054, 25,036, and 25,022 cm.⁻¹. The 25,076 cm.⁻¹ line showed a sharp violet edge at 25,097 cm.⁻¹. Although the exposure for the *ac* polarization was three times longer than that for the *b* polarization, it was not possible to detect even the slightest presence of the *b*-component origin bands in the *ac* polarization. The first band observable in the *ac* polarization was at 24,706 cm.⁻¹, which is at a distance from the (*b*) origin of 398 cm.⁻¹, equal to that of the first molecular ground-state vibrational frequency. This absence of origin bands in the *ac* polarization at low temperature is expected from theoretical considerations, an allowed electronic level of the isolated molecule being split into two optically accessible (vibrationless) exciton states in the crystal, the separation of which, in energy, is termed the Davydov splitting. In the present case, an absorption transition to the lower energy level is *b* polarized. The emission spectrum is not entirely *b* polarized, because of the effects [14] of molecular vibrations in the ground electronic state. Whilst the vibrationless transition will be entirely *b* polarized, vibronic transitions will have components along the *b* axis and in the *ac* plane, the ratio of *b*- to *ac*-polarized intensity in the vibronic transitions being simply the polarization ratio in absorption.

[14] *E.g.*, Hochstrasser, " The Luminescence of Organic Molecular Crystals," Florida State University, March 1961; McRae, *Austral. J. Chem.*, 1961, **14**, 329, and later Papers.

The possibility of the 0–0 *ac*-polarized band appearing, because of thermal population of the higher energy exciton level, is negligible at 4°K because of the large energy-separation of the two levels (*ca.* 300—400 cm.$^{-1}$). It should be possible, however, to populate the upper level at higher temperatures, and so to cause the 0–0 region to lose its unique polarization.

This has been observed by Shpak and Sheremet,[12] who observed a weak band at 25,200 cm.$^{-1}$ tailing to 25,300 ± 20 cm.$^{-1}$ in the *ac* polarization when the temperature was raised to 77°K. In the present work, we have observed no band near 25,200 cm.$^{-1}$ in the *ac* polarization at 80°K, but this is no doubt because the length of the exposure ($4\frac{1}{2}$ hr.) was adjusted to give a clear spectrum of the main fluorescence and was, therefore, not sufficient to allow detection of the very weak band.

Lattice Vibrations.—The assignment of the first five lines (excluding the assumed origin) in the 0–0 region of the *b* polarization to superposed lattice vibrations agrees, within the order of accuracy of measurement, with other values for lattice frequencies of anthracene obtained by various workers using fluorescence, *X*-ray, and Raman methods (see Table 3).

TABLE 3.

Lattice vibrational frequencies.

Anthracene					Naphthalene		
Fluor., crystal 4°K [a]	Fluor., crystal 14°K [b]	Fluor., crystal 4°K [c]	X-Ray, crystal [d]	Raman, crystal [e]	Fluor., anthracene in naphthalene 20°K [f]	Raman [g]	Raman [h]
27 ± 5					30		
45—49	42	37 ± 5	42	48 ± 4	50	45	45
67			64	68 ± 5	81	75	73
					(30 + 50)		
81			83			107	109
137	114	114		120 ± 8		121	124

(a) This Paper.   (b) Pesteil and Barbaron, *J. Phys. Radium*, 1954, **15**, 92.   (c) Sidman, *Phys. Rev.*, 1956, **102**, 96.   (d) Cruickshank, *Rev. Mod. Phys.*, 1958, **30**, 163.   (e) Fruhling, *Ann. Physique*, 1951, **6**, 401.   (f) Sidman, *J. Phys. Chem.*, 1956, **25**, 115.   (g) Nedungadi, *Proc. Indian Acad. Sci.*, 1941, **13**.*A*, 161.   (h) Bhagavantam, *Proc. Indian Acad. Sci.*, 1941, **13**, *A*, 543.

The similarity of the values for anthracene and naphthalene, which has been studied extensively by Nedungadi[15] and by Bhagavantam,[16] substantiates the values for anthracene.

Lattice vibrations in crystals like anthracene have been classified by various workers as either rotatory or translatory. All translatory vibrations are Raman-inactive.[16] The 73 cm.$^{-1}$ vibration in a naphthalene crystal has been identified by Bhagavantam[16] as being " due to rotatory movements about the *b* axis on the basis of its high intensity and the fact that the largest optical anisotropy of naphthalene is in the *ac* plane." We assume that a similar assignment can be given to the 67 cm.$^{-1}$ vibration in anthracene, which is also present in the Raman spectrum of the crystal (Table 3). The most commonly recurring lattice vibration throughout the spectrum is the 45 cm.$^{-1}$ vibration. As well as being built on the origin, it is built on four other vibrations which may or may not be molecular ground-state frequencies (see following Section). It is also built on the combinations of these frequencies with one and two quanta of a 1410 cm.$^{-1}$ vibration. This lattice vibration is given two values in Table 2, since, although 45 cm.$^{-1}$ is the value which best fits the frequencies in the Table, the difference from the origin is 49 cm.$^{-1}$.

The region (Fig. 3) displaced from the origin by one quantum of a 1410 cm.$^{-1}$ vibration reveals a band structure somewhat similar to that of the origin, except that the 23,693 cm.$^{-1}$ (origin + 1410 cm.$^{-1}$) line does not suffer reabsorption. Here again are the lattice frequencies 27 and 81 cm.$^{-1}$, but the other lattice vibrations are not observed, perhaps because of decreasing dispersion and an increasing background fluorescence.

[15] Nedungadi, *Proc. Indian Acad. Sci.*, 1941, **13**, *A*, 161.
[16] Bhagavantam, *Proc. Indian Acad. Sci.*, 1941, **13**, *A*, 543.

Band Groups.—The remainder of the spectrum shows several clearly defined band groups. The group consisting of the strongest bands can be attributed to transitions from the lower free-exciton level to vibronic levels of the ground state. Taking the origin of the lower exciton level to be at 25,103 cm.$^{-1}$, we obtain the following intervals for the ground-state molecular vibrations in anthracene: 398; *631*; 753; *840*; *1030, 1127*; 1170; 1259; *1314*; *1392*; 1410; *1445*; *1489*; 1562; and 1631 cm.$^{-1}$, in good agreement with the averages of values obtained by other authors (Table 1). The agreement confirms that the *b* origin lies at 25,103 cm.$^{-1}$. In the region 350—1650 cm.$^{-1}$, one can predict, from symmetry considerations, that there should be 9 × a_g vibrations (5 × CC stretch, 2 × CC bend, 2 × CH bend) and 9 × b_{3g} vibrations (3 × CC stretch, 3 × CC bend, 3 × CH bend), but the CH-bending vibrations in each case will be extremely weak and possibly will not appear in the spectrum. It is therefore likely that the seven most-common frequencies observed in the spectrum are those with a_g symmetry.

However, it is somewhat doubtful whether the frequencies listed in italics are true molecular vibrations, mainly because of the lack of evidence of their existence in work by previous authors (Table 1). The frequencies at *631* and *1030* cm.$^{-1}$ have been observed

Fig. 3. Expanded microdensitometer trace of the *b*-polarization luminescence of anthracene at $4°$K, displaced 1410 cm.$^{-1}$ from the origin.
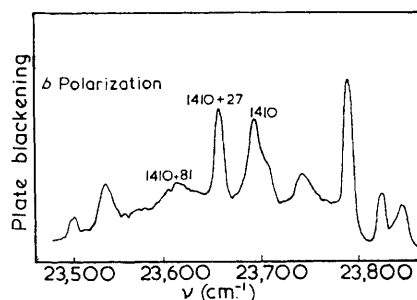
only by Bree [17] in n-heptane at $77°$K, while the *840, 1127*, and *1314* cm.$^{-1}$ frequencies have been observed by Colombo and Mathieu [18] in solution (Raman spectrum), but they did not give them any symmetry assignment. On the other hand, Colombo and Mathieu did observe the *1392, 1445*, and *1489* cm.$^{-1}$ frequencies in the crystal (Raman spectrum), and assigned them as a_g, b_{3g}, and b_{3g}, respectively. However, more work needs to be done on this point before any definite conclusion can be drawn. The possibility of these lines being associated with crystal imperfections is not excluded. Prikhot'ko and Fugol, in 1958,[10] suggested that the fluorescence of anthracene arose from imperfections. Later work [19] has shown that this view was broadly correct. Some crystal imperfections, associated with the presence of impurities, are able to interfere with the transfer of energy in exciton bands, especially at low temperature, and so alter the fluorescence spectrum. Zone refining removes a number of such effects, but certainly not all, as indeed is evident from the present spectrum.

The strong narrow lines at 24,350 and 24,163 cm.$^{-1}$, which were also observed by Shpak and Sheremet,[12] were thought by them to be the start of strong sequences which they attributed to the presence of some impurity, but there seems little doubt that the 24,350 cm.$^{-1}$ line is the 753 cm.$^{-1}$ molecular vibration also observed by numerous other authors (see Table 1). The strong sequence beginning with 24,163 cm.$^{-1}$ cannot be interpreted quite so readily. In our work, the anthracene was subjected to extensive zone refining in the absence of light and oxygen, and it could well be that this sequence is associated with some crystal imperfection other than that associated with impurities removable by zone refining. (One such example is the inability of zone refining to remove small traces of

[17] Bree, personal communication.
[18] Colombo and Mathieu, *Bull. Soc. franc. Mineral. Crist.*, 1960, **83**, 250.
[19] Lacey, Lyons, and White, *J.*, 1963, 3670.

2-methylnaphthalene from naphthalene,[20] although it is worth noting that, recently, 2-methylnaphthalene has been completely removed from naphthalene by a process involving zone refining followed by chemical purification, sublimation, and further zone refining, resulting in the complete absence of the 2-methylnaphthalene, 31,062 cm.$^{-1}$ line in absorption and emission of the naphthalene [21].)

The line at 24,903 cm.$^{-1}$ was identified by Shpak and Sheremet [12] as beginning a very weak sequence which they found to coincide with the spectra which Prikhot'ko and Fugol [10] had attributed to transitions " from localised levels arising as a result of various lattice defects." The defects at the time were thought to be " unfilled molecular sites in the unit cell, *i.e.*, molecules in interstitial positions and so-forth, which, in luminescence, may play a similar role to impurity centres, being able to intercept excitation and also to act as emission centres." We did not detect any sequence built on the 24,903 cm.$^{-1}$ line. It seems possible, however, that this line could arise from a combination of the 67 and 137 cm.$^{-1}$ lattice vibrations.

Davydov Splitting.—Polarized-absorption spectra [6] of numerous crystals of varying thickness showed that the maximum of the *ac* polarization occurred at 25,486 $\pm$ 7 cm.$^{-1}$ in all cases. This value agrees with those of Craig and Hobbins (25,497 $\pm$ 7 cm.$^{-1}$) [1] and Wolf (25,490 cm.$^{-1}$),[4] but does not agree with those of Sidman (25,400 $\pm$ 20 cm.$^{-1}$) [2] and Brodin and Marisova (25,432 cm.$^{-1}$).[5] We cannot explain the discrepancy. Using the value 25,486 cm.$^{-1}$, we find that the Davydov splitting is (25,486—25,103) = 383 $\pm$ 9 cm.$^{-1}$, which we believe is the most accurate assessment yet obtained. The value 383 cm.$^{-1}$ is close to that expected from our prediction [6] that the *b* origin lies at 25,150 $\pm$ 25 cm.$^{-1}$. This value of the 0–0 band splitting is larger than would be expected on the basis of the theoretical crystal splitting (380 cm.$^{-1}$) calculated by McRae.[22]

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[20] *E.g.*, Shpak and Sheka, *Optics and Spectroscopy*, 1960, **9**, 29, and references contained therein; Wolf, *Naturwiss.*, 1961, **48**, 43.
[21] Sternlicht, Nieman, and Robinson, *J. Chem. Phys.*, 1963, **38**, 1326.
[22] McRae, *Austral. J. Chem.*, 1963, **16**, 315.