

498. The Intensity of Ultraviolet Light Absorption by Monocrystals. Part V.¹ Absorption by Naphthacene at 295 and 78°K of Plane-polarized Light of Wavelengths 1850—3200 Å

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Quantitative measurements of the absorption by naphthacene monocrystals of plane-polarised light are reported from 1850 to 3200 Å at 78 and 295°K. Five electronic transitions are detected. These are discussed in terms of the excited electronic states of the naphthacene molecule and assigned to symmetry species. The Davydov splitting of the intense $B_{2u} \leftarrow A_g$ transition at 4.5 eV in solution is observed in the crystal with components at 4.0 eV and 5.7 eV. Difficulties in the interpretation of the spectrum owing to the crystal being triclinic are noted.

PREVIOUS work¹⁻⁴ on the naphthacene crystal spectrum has been confined to the region below 42,000 cm^{-1} , and no low-temperature polarised crystal spectrum at energies above 30,000 cm^{-1} has been reported. Since Part IV was published,¹ the crystal structure of naphthacene has been more accurately determined,^{5,6} with some variations in certain calculations of Part IV, in which Walsh's⁷ analysis of the original crystallographic data of Sinclair⁸ and Hertel and Bergk were⁹ used. The analysis of the spectrum above 30,000 cm^{-1} is made in the light of more recent crystal data.

Lyons and Morris¹⁰ found that the intense second electronic molecular transition of anthracene (at 42,000 cm^{-1} in the vapour¹¹) was split in the crystal. *a*-polarised absorption appeared between 41,000 and 54,000 cm^{-1} as predicted by the theory of Davydov splitting.¹² A similar Davydov splitting is expected for the intense free molecule absorption of naphthacene.^{7,13} A reduction of the absorption intensity of the vapour at 38,850 cm^{-1} ,¹¹ to a small value in the crystal at the same energy position,¹ was observed, and taken to indicate that the naphthacene transition experienced a large factor group splitting in the crystal, similar to that with anthracene. This Paper reports, *inter al.*, the first measurement of this splitting. A preliminary report by one of us gave the spectrum without any discussion.¹⁴

EXPERIMENTAL

Naphthacene was an Eastman Kodak White Label sample. The best preparation of large thin crystals was by heating the naphthacene for 1½ hr. at 330°C, in an asbestos-lagged evaporating dish under an inverted filter funnel in an atmosphere of purified nitrogen. On cooling for 1 hr., crystals were formed on the side of the filter funnel. Crystals were mounted on fluorite, lithium fluoride, or Suprasil discs. Absorption measurements were performed on 15 crystals. Thicknesses determined with an Ehringhaus compensator range from 0.1 to 0.6 microns. The birefringence at the sodium D line was 0.194.¹

¹ Part IV, Bree and Lyons, *J.*, 1960, 5206.

² Borisov, *Trudy Inst. Fiz. Akad. Nauk S.S.R.*, 1953, **4**, 102.

³ Craig, Hobbins, and Walsh, *J. Chem. Phys.*, 1954, **22**, 1616.

⁴ Sidman, *J. Chem. Phys.*, 1956, **25**, 122.

⁵ Robertson, Sinclair, and Trotter, *Acta Cryst.*, 1961, **14**, 697.

⁶ Campbell, Robertson, and Trotter, *Acta Cryst.*, 1962, **15**, 289.

⁷ Walsh, Ph.D. Thesis, University of Sydney, 1958.

⁸ Sinclair, Ph.D. Thesis, University of Glasgow, 1955.

⁹ Hertel and Bergk, *Z. phys. Chem. (Leipzig)*, 1936, **B33**, 319.

¹⁰ Part III, Lyons and Morris, *J.*, 1959, 1551.

¹¹ Morris, Ph.D. Thesis, University of Sydney, 1959.

¹² Craig, *J.*, 1955, 2302.

¹³ Craig and Walmsley in "Physics and Chemistry of the Organic Solid State," vol. 1, ed. Fox, Labes, and Weissberger, Interscience Publ. New York, 1963, p. 585.

¹⁴ Lyons in "Physics and Chemistry of the Organic Solid State," vol. 1, ed. Fox, Labes, and Weissberger, Interscience Publ. New York, 1963, p. 745.

Measurement of angles between edges confirmed⁹ the developed face as (001), and showed that the *b* crystal axis was within 2° of the slow extinction direction of the sublimation flake in the visible region. By analogy with naphthalene and anthracene, the principal axis of the indicatrix will be close to the *b* crystal axis, given as the trace of the (201) plane on the (001) plane. Vibration directions were determined by orthoscopic and conosopic investigation under a Zeiss polarising microscope.

The crystal holder allowed rotation of the crystal through known angles, lateral and vertical movements. The light source was an Allen hydrogen arc¹⁵ usually operated at 4 A, 60 v. Calibration arc was a standard copper arc in a nitrogen stream. Light was condensed by a lithium fluoride lens on to the requisite unmasked area of the crystal. The emergent light was condensed to a beam about 1 mm. in diameter at the slit. The beam was analysed inside the spectrograph by a Wollaston prism, designed to produce at the plate two beams polarised mutually perpendicularly and about 1 mm. apart. Oxygen was removed from the light path by a continuous stream of dry nitrogen. The slit was covered by a fluorite window.

The Hilger 3-metre normal incidence grating spectrograph was used in the 1st order (5.78 Å/mm. dispersion), operated at a pressure of 10⁻⁴ mm. or less, vapours being trapped by liquid air. Ilford Q₁ and Q₂ plates were used for photographic photometry. Comparison blanks were obtained by using neutral nickel gauze filters.¹⁶ Failure of the reciprocity law was negligible over the range of times (1—120 min.) considered. Plate blackening was measured on a Hilger recording microphotometer.

A 1P28 photomultiplier coated with sodium salicylate was used for photoelectric measurement, the output being measured on a Vibron electrometer. The incident and transmitted beams were examined alternately in each polarisation, similarly polarised beams always falling on the same area to avoid error.¹⁷ The wavelength setting calibrated by a mercury lamp was altered by rotating the grating and plate holder around the Rowland circle by means of an external handle.

RESULTS

In Figure 1, the crystal spectrum of naphthacene at 295°K is presented. Table 1 lists the band positions and molar extinction coefficients at maxima. Errors in wavelength depend on the band shape. Even at 78°K bands were not sharp. Errors in extinction coefficient

TABLE I

Band positions in naphthacene crystal spectrum at 295°K. Molar extinction coefficients, $\epsilon = \left(\frac{1}{cd}\right) \log_{10} \left(\frac{I_0}{I}\right)$ at maxima

Parallel to <i>b</i> direction			Parallel to <i>q</i> direction		
λ (Å)	ν (cm. ⁻¹)	ϵ_b	λ (Å)	ν (cm. ⁻¹)	ϵ_q
3120	32,050	750	3100	32,260	500
			2810	35,590	1700
2750	36,360	3300			
2640	37,880	2900	2680	37,310	1400
2307	43,350	12,000	2303	43,220	6000
2267	44,110	11,700	2266	44,130	6400
2248	44,480	12,000	2250	44,440	7000
2233	44,780	13,500			
2196	45,540	16,500	2190	45,660	9000
2160	46,300	21,000	2150	46,510	10,000
			2135	46,840	9500
			2123	47,100	8500
2113	47,280	16,200			
2013	49,680	7200	1932	51,760	4500
1935	51,680	6200	1890	51,910	4100
1901	52,600	6000	1860	52,760	3800
1870	53,470	5800			
1850	54,050	5600	1810	55,250	3600

¹⁵ Allen, *J. Opt. Soc. Amer.*, 1941, **31**, 268.

¹⁶ Sawyer and Vincent, *J. Opt. Soc. Amer.*, 1943, **33**, 247.

¹⁷ Norman and Kay, *J. Sci. Instr.*, 1952, **29**, 33.

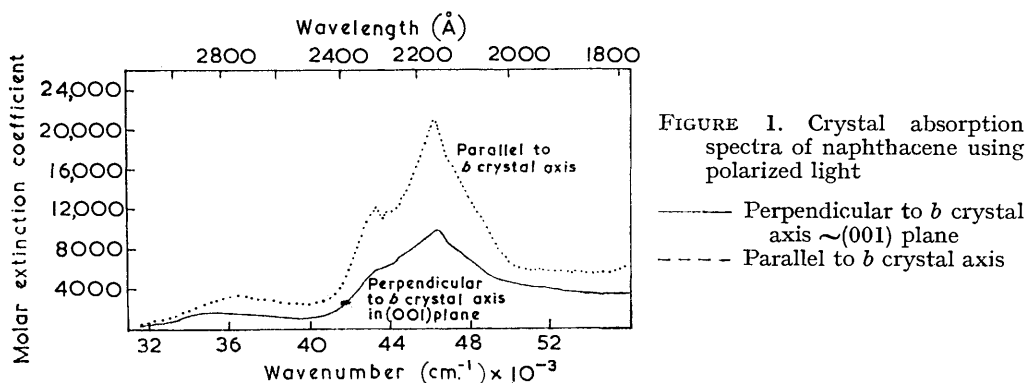


FIGURE 1. Crystal absorption spectra of naphthacene using polarized light

were about 10% at less than $50,000 \text{ cm}^{-1}$ and 20% at more than $50,000 \text{ cm}^{-1}$ for the photoelectric measurement, but about twice this for photographic measurement. The uncertainty in thickness measurements was a large source of error.

DISCUSSION

Crystal directions are related to the absorption directions of the naphthacene sublimation flake as follows: p is normal to the ab plane; q lies in the ab plane perpendicular to the b axis; b is the "slow" and q is the "fast" direction of the sublimation flake examined. Bree and Lyons¹ noted that the absorption directions altered with wavelength. With a vibration direction of the plane polarised light parallel to the b crystal axis and one parallel to the q direction, the alteration of the absorption direction with wavelength was

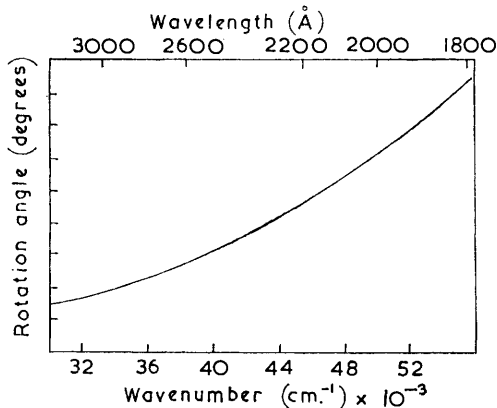


FIGURE 2. Rotation of the (001) crystal face about p -direction for maximum absorption along b direction. On the ordinate scale, each division represents four degrees

found by rotating the (001) plane to give maximum absorption along the slow direction. Figure 2 shows the dependence of the rotation angle upon wavenumber. Bree and Lyons found that a 2300 \AA , at 12° rotation was necessary for maximum absorption. Our result is slightly higher. The results of Figure 2 will be neglected to simplify the discussion, although such a neglect becomes more serious at higher energies. If the crystal is aligned for maximum absorption in the b -polarisation, there is a lessening of intensity in the q -direction. At higher energies, experimental f -values are changed by up to 25%.

The explanation of the spectrum will be confined to π - π transitions. Only the theoretically expected singlet upper states will be considered. No definite evidence was found in this region for triplet $2p\pi$ states, ionised states, and states involving atomic

orbitals with $n > 2$. These are expected to occur in view of our previous determination of the photoionisation threshold of crystalline naphthacene at $42,400 \text{ cm.}^{-1}$.¹⁸

The two molecules in the unit cell belong to crystallographically distinct sets. Transitions in the crystal are allowed along all three-crystal axes. Thus the transition moments to either an α or a β crystal level have projections along the *three* absorption directions p , b , and q . In Table 2, the intensities of crystal transitions arising from unit transition moments along the molecular axes are given. From the f -value in solution for each transition, the predicted intensities (f') from first-order theory can be obtained. Table 3 lists these. The f -values in solution refer to n-hexane as solvent.¹¹ It is preferable to use f -values rather than ϵ -values for predicted intensities as there is a marked redistribution of intensity in the band system when different solvents are used.¹¹

System II.—This was assigned by Bree and Lyons as $B_{2u} \leftarrow A_g$, long-axis polarised, y , but they noted the difficulties of such an assignment in terms of the existing theories of molecular levels. The transition occurs at $35,030 \text{ cm.}^{-1}$ (vapour¹¹); $34,150 \text{ cm.}^{-1}$ (solution); $36,000 \text{ cm.}^{-1}$ (crystal). Evidence for a hidden transition in anthracene has been presented elsewhere.^{10,19} The presence of such a transition in naphthacene strengthens the previous arguments. The experimental f -values from $31,000$ — $40,000 \text{ cm.}^{-1}$ are $f_b = 2.8 \times 10^{-2}$, $f_q = 1.5 \times 10^{-2}$. If system III marks a B_{2u} upper state of which the α -crystal component is sent to higher energies and the β -crystal component to lower energies, some of the intensity in this region is due to the displaced β -crystal component. For this β -component, $f'_b = 4.6 \times 10^{-3}$, $f'_q = 1.2 \times 10^{-3}$. The experimental f -values for system II should thus be little affected by the presence of system III's β -crystal component. If a first-order approximation were sufficient for system II a B_{1u} molecular state would have $f'_b = 7.8 \times 10^{-2}$, $f'_q = 1.5 \times 10^{-2}$; a B_{2u} molecular state would have $f'_b = 6.6 \times 10^{-3}$, $f'_q = 7.3 \times 10^{-3}$. Polarisation considerations lead to the assignment B_{1u} . Walsh⁷ used second-order considerations to calculate that the splitting of the crystal bands is negligible

TABLE 2

Intensities of the crystal transitions arising from unit transition moments along the molecules axes

	Long	Short	Normal
α -Crystal component			
$(m.q)^2$	7.3×10^{-2}	1.4×10^{-3}	7.7×10^{-1}
$(m.b)^2$	6.3×10^{-2}	7.8×10^{-1}	5.8×10^{-4}
$(m.p)^2$	8.6×10^{-1}	4.9×10^{-2}	5.8×10^{-2}
β -Crystal component			
$(m.q)^2$	6.8×10^{-4}	1.5×10^{-1}	2.8×10^{-4}
$(m.b)^2$	2.6×10^{-3}	2.8×10^{-4}	1.6×10^{-1}
$(m.p)^2$	3.0×10^{-5}	1.8×10^{-2}	1.0×10^{-2}
$\alpha + \beta$ Crystal component			
$(m.q)^2$	7.3×10^{-2}	1.6×10^{-1}	7.7×10^{-1}
$(m.b)^2$	6.6×10^{-2}	7.8×10^{-1}	1.6×10^{-1}
$(m.p)^2$	8.6×10^{-1}	6.9×10^{-2}	6.8×10^{-2}

($m.b$) denotes the cosine of the angle between a molecular axis and the b crystal direction

and that a shift of about 600 cm.^{-1} to higher energies would be obtained for a B_{1u} state. The observed shift is 900 cm.^{-1} to higher energies. The assignment B_{1u} (short-axis polarised) agrees with Pariser's²⁰ ${}^1B_{1u}^+$ state at 4.7 eV with intensity of 0.16 and Ham and Ruedenberg's²¹ 1L_a state. Neither Moffitt²² nor Kleven and Platt²³ recognise the transition. Hummel and Ruedenberg²⁴ predict a short axis transition at $33,932 \text{ cm.}^{-1}$

¹⁸ Lyons and Morris, *J.*, 1960, 5192.

¹⁹ Lyons and Morris, *J. Mol. Spectroscopy*, 1960, 4, 480.

²⁰ Pariser, *J. Chem. Phys.*, 1956, 24, 250.

²¹ Ham and Ruedenberg, *J. Chem. Phys.*, 1956, 25, 1.

²² Moffitt, *J. Chem. Phys.*, 1954, 22, 320, 1820.

²³ Kleven and Platt, *J. Chem. Phys.*, 1949, 17, 471; Platt, *ibid.*, p. 484.

²⁴ Hummel and Ruedenberg, *J. Phys. Chem.*, 1962, 66, 2334.

($f = 0.036$) (tight bonding approximation) and by inter-ring bonding approximation a short axis transition at $36,758 \text{ cm}^{-1}$ ($f = 0.043$).

TABLE 3

Predicted intensities of crystal transitions from first-order perturbation theory arising from transition moments along molecular axes

Solution ν (cm^{-1})	Molecular axis	α -Crystal component			β -Crystal component			
		$(m.q)^2$	$(m.b)^2$	$(m.p)^2$	$(m.q)^2$	$(m.b)^2$	$(m.p)^2$	
34,000	0.10	Long	7.3×10^{-3}	6.3×10^{-3}	8.6×10^{-2}	6.8×10^{-5}	2.6×10^{-4}	3.0×10^{-6}
		Short	1.4×10^{-4}	7.8×10^{-2}	4.9×10^{-3}	1.5×10^{-2}	2.8×10^{-5}	1.8×10^{-3}
		Normal	7.7×10^{-2}	5.8×10^{-5}	5.8×10^{-3}	2.8×10^{-5}	1.6×10^{-2}	1.0×10^{-3}
36,500	1.75	Long	1.3×10^{-1}	1.1×10^{-1}	1.5	1.2×10^{-3}	4.6×10^{-3}	5.3×10^{-5}
		Short	2.5×10^{-3}	1.4	8.6×10^{-2}	2.6×10^{-1}	4.9×10^{-4}	3.2×10^{-2}
		Normal	1.3	1.0×10^{-3}	1.0×10^{-1}	4.9×10^{-4}	2.8×10^{-1}	1.8×10^{-2}
44,000	0.16	Long	1.2×10^{-2}	1.0×10^{-2}	1.4×10^{-1}	1.1×10^{-4}	4.2×10^{-4}	4.8×10^{-6}
		Short	2.2×10^{-4}	1.2×10^{-1}	7.8×10^{-3}	2.4×10^{-2}	4.5×10^{-5}	2.9×10^{-3}
		Normal	1.2×10^{-1}	9.3×10^{-5}	9.3×10^{-3}	4.5×10^{-5}	2.6×10^{-2}	1.6×10^{-3}
47,500	0.43	Long	3.2×10^{-2}	2.7×10^{-2}	3.7×10^{-1}	2.9×10^{-4}	1.1×10^{-3}	1.3×10^{-5}
		Short	6.0×10^{-4}	3.4×10^{-1}	2.1×10^{-2}	6.5×10^{-2}	1.2×10^{-4}	7.7×10^{-3}
		Normal	3.3×10^{-1}	2.5×10^{-4}	2.5×10^{-2}	1.2×10^{-4}	6.9×10^{-2}	4.3×10^{-3}
53,500	0.27	Long	2.0×10^{-2}	1.7×10^{-2}	2.3×10^{-2}	1.8×10^{-4}	7.0×10^{-4}	8.1×10^{-6}
		Short	3.8×10^{-4}	2.1×10^{-1}	1.3×10^{-3}	4.1×10^{-2}	7.6×10^{-5}	4.9×10^{-3}
		Normal	2.1×10^{-1}	1.6×10^{-4}	1.6×10^{-2}	7.6×10^{-5}	4.3×10^{-2}	2.7×10^{-3}

System III.—There seems little doubt that this marks a B_{2u} molecular transition. The absence of a strong crystal band at the solution absorption maximum has been noted before.¹ By analogy with anthracene,¹⁰ the α -crystal component should be sent to higher energies and have high intensity ($f'_q = 1.3 \times 10^{-1}$, $f'_b = 1.1 \times 10^{-1}$). We associate the strong absorption near $46,300 \text{ cm}^{-1}$ with the displaced α -crystal component of the $39,000 \text{ cm}^{-1}$ molecular transition. Interpretation of the spectrum is complicated by the presence of other π — π absorption in this region along both the b and q directions. For reasons considered later the region $41,000$ to *ca.* $45,000 \text{ cm}^{-1}$ marks a separate electronic transition. This region will be neglected for the present. For the region $43,500$ — $51,000 \text{ cm}^{-1}$ (both extrapolated), $f_b = 1.2 \times 10^{-1}$, $f_q = 7.0 \times 10^{-2}$. For a B_{2u} polarised transition, the α -crystal component would have $f'_b = 1.1 \times 10^{-1}$, $f'_q = 1.3 \times 10^{-1}$. The presence of the free molecule transition near $47,500 \text{ cm}^{-1}$ in solution and its polarisation along the short molecular axis (see later) is probably the reason for f_b being greater than f_q although the opposite is expected.

The Davydov splitting is some $10,000 \text{ cm}^{-1}$, if the β -crystal component is at $36,000 \text{ cm}^{-1}$. Walsh⁷ has calculated for a B_{2u} molecular transition that the α -crystal component is displaced $18,689 \text{ cm}^{-1}$ to higher energies relative to the free molecule level and the β -crystal component displaced 7789 cm^{-1} to lower energies. The Davydov splitting was $13,239 \text{ cm}^{-1}$ and the energy shift 5450 cm^{-1} to higher energies. Although some revision of these values is needed because of the revised crystal data and of the position of the free molecule absorption in the vapour (not solution), it is seen that Davydov's theory can be used to give approximate agreement with experiment (cf. ref. 13). It is possible that the bands which appear at $32,050 \text{ cm}^{-1}$ (b -direction) and $32,260 \text{ cm}^{-1}$ (q -direction) are the β -crystal components of bands corresponding to the $39,000 \text{ cm}^{-1}$ vapour band and having predicted intensities $f'_b = 4.6 \times 10^{-3}$ and $f'_q = 1.2 \times 10^{-3}$. The bands are not "hot" bands to be associated with the absorption near $36,000 \text{ cm}^{-1}$ as is shown from both intensity considerations and their sharpening at 78°K . They must arise from some electronic transition in the molecule. The f -values from *ca.* $31,000$ to *ca.* $33,000 \text{ cm}^{-1}$ (extrapolated) are $f_b = 1.2 \times 10^{-3}$; $f_q = 8.0 \times 10^{-4}$; which agree in both polarisation and intensity with the values expected for the β -component. However, the possibility of this marking the short-axis polarised transition predicted²⁴ at $33,932 \text{ cm}^{-1}$ with intensity 3.6×10^{-2} should not be forgotten.

System IV.—This occurs both in the vapour and in the crystal near 43,400 cm.⁻¹. It is most clearly seen at 78°K when much of the vibrational structure to the red of the 46,300 cm.⁻¹ peak disappears. The peaks at 43,350, 44,110, 44,480, and 44,780 cm.⁻¹ (*b*-direction) and 43,270, 44,130, and 44,440 cm.⁻¹ (*q*-direction) are probably associated with this system. In solution in *n*-hexane, peaks at 43,950, 44,750, and 45,660 cm.⁻¹ probably correspond to this system in the crystal. The ϵ -value in solution is about 7000 for the first peak which could correspond to the crystal absorption peak at 43,350 cm.⁻¹ ($\epsilon_b = 12,000$, $\epsilon_q = 6000$). For a long-axis polarised transition $\epsilon'_b = 1380$, $\epsilon'_q = 1540$. For a short axis transition, $\epsilon'_b = 16,500$, $\epsilon'_q = 3300$. Only the short axis transition gives $\epsilon'_b > \epsilon'_q$ and of the expected magnitude. An assignment $B_{1u} \leftarrow A_g$ *z*-polarised transition in the molecule seems likely. This could correspond to the B_{1u} state suggested by Hummel and Ruedenberg²⁴ at 42,522 cm.⁻¹ with intensity 7.9×10^{-2} , or Pariser's B_{1u}^+ state at 6.5 eV.

System V.—This occurs in solution near 47,500 cm.⁻¹ extending over some 6000 cm.⁻¹ with an *f*-value of 0.43. The transition may be expected in the crystal spectrum close to this region. System III probably has its α -crystal component in this region. The oriented-gas model predicts equal *b* and *q* polarised components for System III. That $f_b > f_q$ in this region indicates that the stronger *b*-absorption could arise from System V. This would occur only for a short-axis polarised transition, *i.e.*, $B_{1u} \leftarrow A_g$. The situation is complicated by other factors. The transition moment is about 0.92 Å. From the intermolecular dipole sums, the α -component of a B_{2u} transition would be 3400 cm.⁻¹ above and the β -component 1400 cm.⁻¹ below the transition energy of the free molecule absorption. The transition energy gauged from the solution spectrum (allowing a shift of about 1500 cm.⁻¹ to higher energies for solvent effects, based on a comparison with shifts for the other transition from free molecule to solution) would be near 49,000 cm.⁻¹. The vapour spectrum does indicate a stronger absorption beginning near this value. On this reasoning, the α -crystal component would occur near 52,000 cm.⁻¹ and the β -crystal component near 48,000 cm.⁻¹. The β -crystal component would contribute negligible intensity ($f'_q = 2.9 \times 10^{-4}$, $f'_b = 1.1 \times 10^{-3}$) to the absorption in this region. The α -component would have reasonable intensity along both directions ($f'_q = 3.2 \times 10^{-2}$, $f'_b = 2.7 \times 10^{-2}$). For a $B_{1u} \leftarrow A_g$ transition, both α and β crystal components of System V would be sent about 800 cm.⁻¹ to lower energies. They should both occur near 48,000 cm.⁻¹ with a total $f'_q = 6.5 \times 10^{-2}$ and $f'_b = 3.4 \times 10^{-1}$. If one accepts the near equality of f'_b and f'_q values of the α -component of System III occurring in this region the upper-state symmetry is probably B_{1u} . Platt,²³ Pariser,²⁰ and Hummel and Ruedenberg²⁴ assign the system to this symmetry species. The latter authors expect a short axis polarised transition at both 49,544 cm.⁻¹ (intensity = 0.067) and at 53,438 cm.⁻¹ (intensity = 0.952). It is likely that the first corresponds to this experimental transition.

In this region note that for System V, $f'_q = 6.5 \times 10^{-2}$, $f'_b = 3.4 \times 10^{-1}$ and for System III α -component $f'_q = 1.3 \times 10^{-1}$, $f'_b = 1.1 \times 10^{-1}$, *i.e.* the total f'_b is approximately twice total f'_q . Also, System III should provide half the total intensity. Experimental *f*-values in this region could then be divided as follows: System III: $f_b = 3.0 \times 10^{-2}$, $f_q = 4.6 \times 10^{-2}$. System V: $f_b = 9.0 \times 10^{-2}$, $f_q = 2.3 \times 10^{-2}$. This provides $f_q > f_b$ for System III as is expected in a B_{2u} polarised transition and $f_b \geq f_q$ for System V as is expected in a transition to a B_{1u} state.

At low temperatures, the bands near 46,300 cm.⁻¹ undergo a redistribution of intensity. Bands further than 300 cm.⁻¹ to the red of the peak could not be "hot" bands because of their intensity at 78°K. Peaks in both *b* and *q* polarisation moved about 100 cm.⁻¹ to lower energies, but because of the band's diffuseness at 295°K, exact measurement of the shifts was not possible.

System VI.—Above 51,000 cm.⁻¹ there is still strong absorption. A solution maximum occurs at 53,000 cm.⁻¹. In the crystal observed *f*-values to 56,000 cm.⁻¹ are $f_b = 5.6 \times 10^{-2}$, $f_q = 2.9 \times 10^{-2}$. It is doubtful whether these arise only from the crystal absorption

TABLE 4
Some electronic states of naphthacene observed and calculated

System	Observed in soln.		Pol.	Observed in crystal			Pariser			Platt Assignment
	ev	<i>f</i>		ev	<i>f_b</i>	<i>f_q</i>	Assignment	Calc. <i>f</i>	Calc. ev	
II	4.2	0.10	<i>z</i>	4.4	0.028	0.015	<i>z</i> ¹ B _{1u} ⁺	0.16	4.7	
III	4.5	1.75	<i>y</i>	4.0	0.06	0.057	<i>y</i> ¹ B _{2u} ⁺	3.78	5.1	<i>y</i> ¹ B _b
IV	5.4	0.16	<i>z</i>	5.4	0.04	0.02	<i>z</i> ¹ B _{1u} ⁺	0.00	6.5	Forb. ¹ C _b
V	5.9	0.43	<i>z</i>	ca. 6.0	0.06	0.013				<i>z</i> ¹ B _a
VI	6.6	0.27	<i>z</i>	ca. 6.5	0.056	0.03				¹ C _a
VII										

System	Ham and Ruedenberg			Hummel and Ruedenberg (T.B.M.)			Hummel and Ruedenberg (I.R.M.)		
	Assignment	Calc. <i>f</i>	Calc. ev	Assignment	Calc. <i>f</i>	Calc. ev	Assignment	Calc. <i>f</i>	Calc. ev
II	<i>z</i> ¹ L _a			<i>z</i>	0.036	4.2	<i>z</i>	0.04	4.6
III	<i>y</i> ¹ B _b	3.97	4.9	<i>y</i>	3.28	5.0	<i>y</i>	4.58	5.0
IV	<i>z</i> ¹ B _a	0.75	5.4	<i>y</i>	0.51	5.2	<i>z</i>	0.03	5.1
V	<i>y</i> ¹ L _b		ca. 6.0	<i>y</i>	0.079	5.3	<i>y</i>	0.016	5.8
VI				<i>z</i>	0.057	5.7	<i>z</i>	0.036	6.0
VII				<i>z</i>	0.067	6.2	<i>z</i>	0.872	6.5
				<i>z</i>	0.952	6.7	<i>z</i>	0.664	7.0
				<i>z</i>	0.49	6.8	<i>z</i>		

corresponding to system VI in solution. The interpretation of the crystal spectrum in terms of molecular properties must therefore be made with reservations. For a short axis polarisation, $f'_q = 4.1 \times 10^{-2}$, $f'_b = 2.1 \times 10^{-1}$. For a long-axis polarisation, $f'_q = 2.0 \times 10^{-2}$, $f'_b = 1.7 \times 10^{-2}$. Since the intensity of *b*-polarisation is greater, a short axis polarisation is indicated. Pariser has a B_{2u}^+ state at 7.19 eV with intensity 0.086. However, the assignment of this band could be Pariser's B_{1u}^+ at 6.942 eV with intensity 1.203, in which case system V would be B_{1u}^+ at 6.541 eV of intensity 0.000 and the predicted band at 7.19 eV hidden under the broad absorption near 54,000 cm^{-1} . Hummel and Ruedenberg expect short-axis polarised bands at 53,438 cm^{-1} ($f = 0.952$) and at 56,672 cm^{-1} ($f = 0.664$). These assignments are consistent with the experimental results in both polarisation and position.

Table 4 summarises the observed and calculated spectral properties of naphthacene.

On the whole, the theories of electronic spectra account for the observed results. The Hummel and Ruedenberg approach based on L.C.A.O. molecular orbitals with neglect of σ -electron interactions, and using extensive configuration interaction gives the best results. For the alternative approximations for the small elements of the overlap and one electron energy matrices—the T.B.M. (tight-bonding approximation) and I.R.M. (intra-ring approximation), the most significant difference for naphthacene is the expectation from T.B.M. of a long-axis polarised transition of reasonable intensity (0.51) at 41,688 cm^{-1} close to the expected long-axis polarised transition at 5.0 eV (intensity = 3.28). A band of intensity 0.51 should be shown in the crystal spectrum, with $f'_q = 3.7 \times 10^{-2}$, $f'_b = 4.3 \times 10^{-1}$. The crystal spectrum near 40,000 cm^{-1} (allowing for free molecule to solid shift) does not give evidence of such a transition. The I.R.M. seems to have better predictive possibilities in this case.

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