The Near-ultra-violet Absorption Spectra of Naphthalene and Its Monohalogen Derivatives in Solution.

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The near-ultra-violet absorption spectra of naphthalene and its monohalogeno-derivatives have been observed in rigid-glass solution at liquid-oxygen temperature. The spectra may be interpreted in favour of an ^1A_g–^1A_g assignment for the 2800—3200-Å region of the naphthalene spectrum. The perturbing vibration in the case of the α-compounds has been shown to be analogous to the 478-cm.$^{-1}$ perturbing vibration of naphthalene.

The spectra of the two isomers differ markedly in their vibrational structure. Whereas the α-derivatives shows a dual nature, *i.e.*, progressions built on both 0,0 and 0,1 bands,* the β-compounds are characterized by a simpler structure and all possess strong 0,0 transitions.

Very weak long-wave-length bands were discovered in the α-derivatives. The evidence for the existence of these bands is discussed, but no assignment can be made.

THE near-ultra-violet absorption spectrum of naphthalene has been the subject of much recent work and in particular it is of prime interest to fix the symmetry species of the first excited singlet level. Craig and Lyons (*J. Chem. Phys.*, 1952, **20**, 1499) have recently reviewed the experimental results and have assigned the first excited singlet level to the species A_g of the point group D_{2h}, of the molecule. The work of Schnepp and McClure (*ibid.*, p. 1375) on the vapour fluorescence of naphthalene also supports this assignment providing the perturbing vibration has the symmetry b_{2u}.

The assignment of the first excited singlet level as A_g is supported by theoretical calculations using the valence-bond method (Blumenfeld, *J. Phys. Chem., U.S.S.R.*, 1947, **21**, 529; Craig, Proc. Int. Congr. Pure Appl. Chem., 1947, **11**, 411). However, L.C.A.O. calculations make this level B_{2u}, while more recent calculations by Jacobs (*Proc. Phys. Soc.*, 1949, **62**, *A*, 710), with the inclusion of configuration interaction, show a near coincidence of two levels, B_{2u} and B_{3u}. The third assignment of this level as B_{3u} by Platt, from free electron model considerations (*J. Chem. Phys.*, 1949, **17**, 484; 1951, **19**, 1418), is supported by the spectral resemblances of the cata-condensed hydrocarbons as discussed by Klevens and Platt (*ibid.*, p. 470).

This paper reports a study of the effect of monohalogen substitution on the absorption spectrum of naphthalene. Interpretation of the spectra, in the absence of detailed knowledge of naphthalene itself, would appear to be too difficult. However, halogen substitution, in effect, applies a varying perturbation to the electronic terms of naphthalene, so that discussion of the spectra may settle some of the outstanding problems.

De Laszlo (*Proc. Roy. Soc.*, 1926, *A*, **111**, 355) described the absorption spectra of α- and β-chloro- and -bromo-naphthalene, both in the vapour and in solution. His measurements are not comprehensive enough for detailed treatment of the problem and the bands suffer from temperature broadening. The spectra were therefore measured at liquid-oxygen temperature. Because four of the compounds are liquids, the spectra were all measured in rigid glass solution, which permitted easy control of the region of the spectrum under observation by change of concentration. Although the solvent used consists of hydrocarbons, the molecular fields surrounding a solute molecule are sufficiently inhomogeneous to make the 0,0 band of naphthalene appear, in contrast to the vapour spectrum.

RESULTS

Naphthalene.—Schnepp and McClure (*loc. cit.*) explained the vapour fluorescence of naphthalene in terms of four totally symmetric ground-state frequencies 512,764, 1025, and 1380 cm.$^{-1}$.

* In the symbolism used in this paper the first number denotes the ground-state vibration and the second the excited-state vibration.

The spectrum of naphthalene found in this research agrees well with these figures (Table 1). It is seen that from band 2 we have intervals 473, 698, and 970 in the upper state. The 1380 ground-state fundamental does not appear to have a strong counterpart in the upper state.

TABLE 1. *Naphthalene.*

Band no.	Position ($cm.^{-1}$)	Distance from 0,0	Assignment	Band no.	Position ($cm.^{-1}$)	Distance from 0,0	Assignment
1	31,736	—	0,0	6	33,162	1420	0,455 + 970
2	32,191	455	0,455	7	33,358	1622	0,455 + 473 + 698
3	32,455	719	0,698	8	33,638	1902	0,455 + 473 + 970
4	32,664	928	0,455 + 473	9	33,859	2123	0,455 + 698 + 970
5	32,889	1153	0,455 + 698				

Band 1 is the 0,0 and it appears because of solvent perturbations. Band 3, also weak, is due to the excitation of the fundamental 698 $cm.^{-1}$ of the upper state. The interval between the

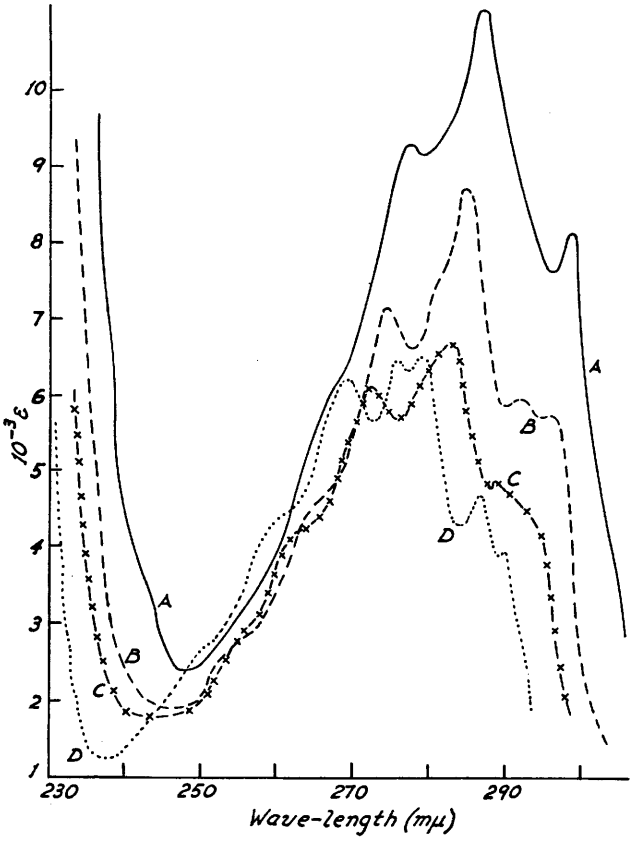


FIG. 1. *Absorption curves for the second transition of the α-compounds.*

A, α-Iodo-, B, α-bromo-, C, α-chloro-, and D, α-fluoronaphthalene.

0,0 and band 2, *i.e.*, the value of the perturbing vibration in the upper state, is 455 $cm.^{-1}$ and is, within the experimental limits, the same as that (464 $cm.^{-1}$) found by Schnepp and McClure.

As it was not possible to make microphotometer tracings of the plates, line diagrams showing the positions and approximate visual intensities of the bands are included. The naphthalene spectrum is shown in Figs. 2 and 4.

α-Substituted Halogenonaphthalenes.—The absorption curves for the second transition of these compounds are shown in Fig. 1. The effect of α-halogen on the second transition of naphthalene (as regards red shift and intensification) parallels the effect, as noted by Ferguson and Iredale (*J.*, 1953, 2959), on the second transition of benzene.

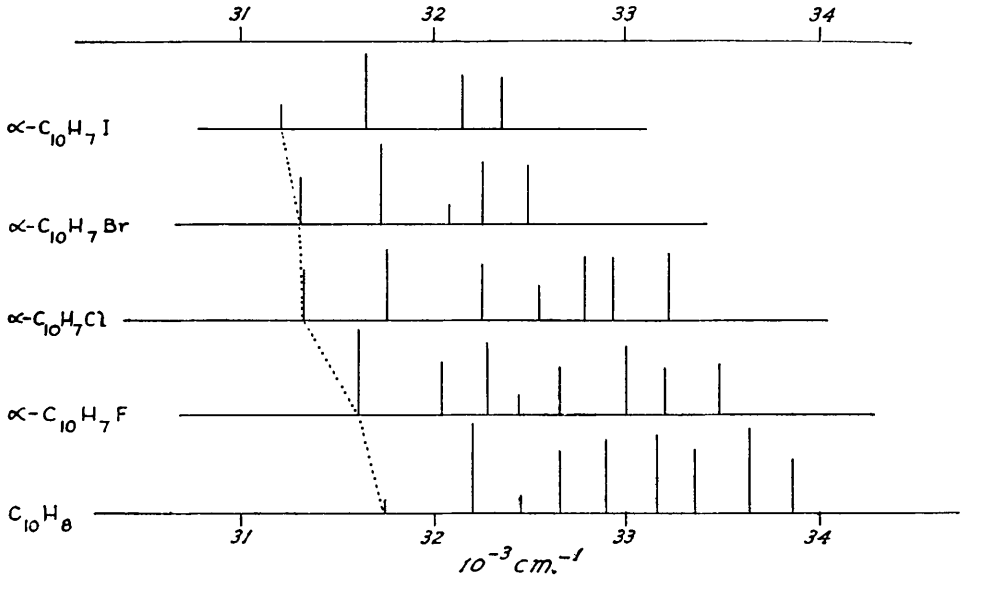
The effect of α-substitution on the weak system of naphthalene produces a gradual change in the spectrum as we pass from iodine to fluorine. A temperature-dependent band was found in the iodo-compound; but this was not evident for the other derivatives, either because the

transition is becoming more allowed or because the appearance of new bands in this region obscures it.

As with benzene the red shift is greatest for the iodo-compound. It is interesting that the values of the ratio of red shift of 0,0 of β- to α-isomer for the fluoro-, chloro-, and iodo-compounds are 1·61, 1·63, and 1·58 respectively.

α-Iodonaphthalene.—The spectrum of the 3200-Å region is shown in Fig. 2. Table 2 contains the positions of the bands of the weak system. In this compound the second transition largely obscures the first, owing to substitution of iodine in the α-position, as can be seen from Fig. 1. This overlap is increased at low temperatures and allows us to fix only four bands of the weak system.

FIG. 2.



The 0,0's are connected by broken lines.

Like naphthalene this compound has a temperature-dependent band (not band 1), but its position cannot be fixed with certainty. A comparison of plates, taken at room temperature, of α-iodonaphthalene and naphthalene shows that the intervals between the 1,0 and 0,1 bands * of both compounds are practically the same, but it is impossible to make accurate measurements

TABLE 2. *α-Iodonaphthalene.*

Band no.	Position (cm.$^{-1}$)	Distance from 0,0	Assignment	Band no.	Position (cm.$^{-1}$)	Distance from 0,0	Assignment
1	30,936	—	—	4	32,144	923	0,428 + 495
2	31,221	—	0,0	5	32,359	1138	0,428 + 710
3	31,649	428	0,428				

TABLE 3. *α-Bromonaphthalene.*

Band no.	Position (cm.$^{-1}$)	Assignment	Band no.	Position (cm.$^{-1}$)	Distance from 0,0	Assignment
1	30,623	—	5	31,736	420	0,420
2	30,828	—	6	32,074	760	0,760
3	31,133	—	7	32,248	934	0,420 + 514
4	31,314	0,0	8	32,500	1186	0,420 + 760

of these intervals at room temperature. The value of the perturbing vibration appears to have dropped slightly to about 430 cm.$^{-1}$.

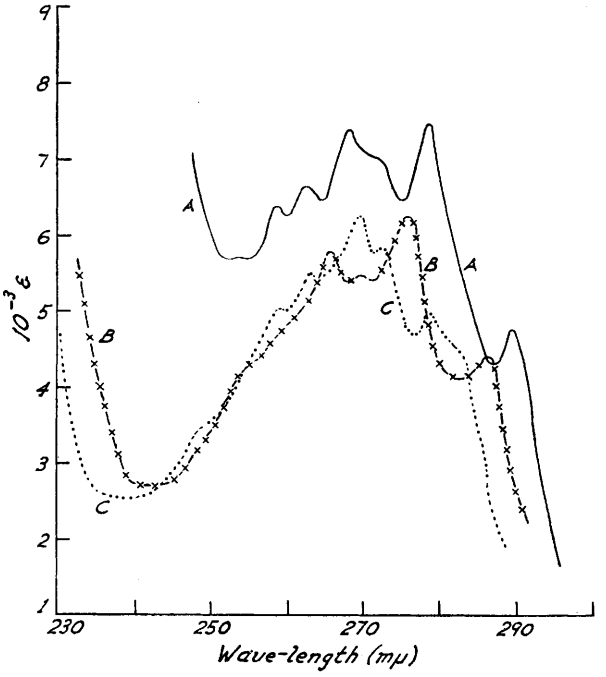
The system is very similar in structure and intensity to that of naphthalene, with the

* For symbolism see footnote, p. 304.

exception of band 1, which is to be linked with the weak bands found in α-chloronaphthalene and is not due to an impurity.

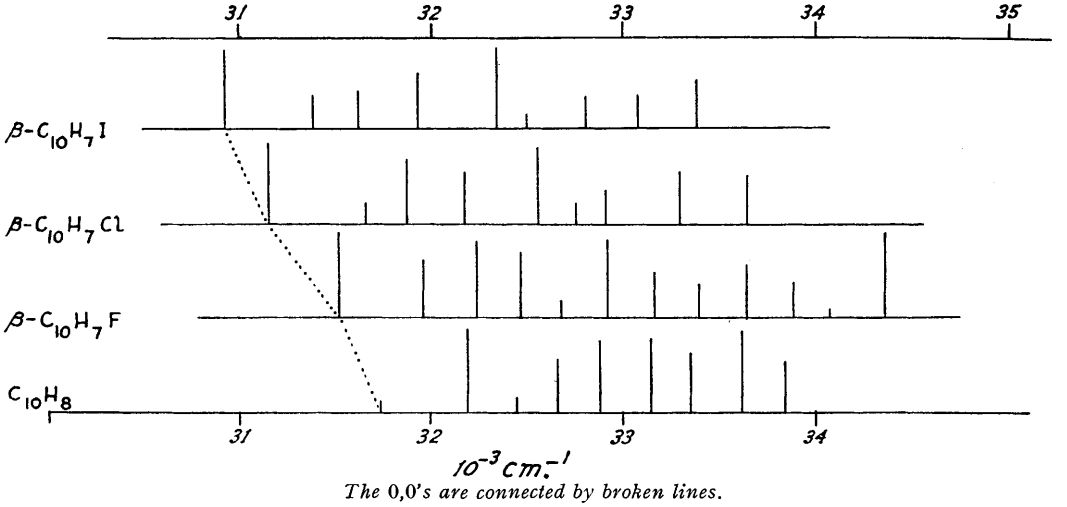
α-*Bromonaphthalene.*—The spectrum of the weak system is shown in Fig. 2 and the positions

FIG. 3. *Absorption curves for the second transition of the β-compounds.*



A, β-*Iodo-*, *B*, β-*chloro-*, *and C*, β-*fluoro-naphthalene.*

FIG. 4.



The 0,0's are connected by broken lines.

of the bands are given in Table 3. The spectrum has almost the same pattern as in naphthalene; the exception is that the 0,0 band is more intense.

Although band 4 has been assigned as the 0,0 we find the presence of three very weak bands to the long-wave-length side of band 4. These are not temperature-dependent and cannot belong to the system originating at band 4.

α-Chloronaphthalene.—See Fig. 2 and Table 4. Band 6 is assigned as 0,0 and the pattern of the system is similar to the other derivatives. However, very weak bands appear on the long-wave-length side of this system. An impurity was suspected and the compound was carefully re-purified by passage through a chromatographic column and by vacuum-distillation, but the bands persisted.

TABLE 4. *α-Chloronaphthalene.*

Band no.	Position ($cm.^{-1}$)	Assignment	Band no.	Position ($cm.^{-1}$)	Distance from 0,0	Assignment
1	30,257	—	6	31,319	—	0,0
2	30,441	—	7	31,763	444	0,444
3	30,668	—	8	32,251	932	0,444 + 488
4	30,840	—	9	32,570	1151	0,444 + 707
5	31,158	—	10	32,790	1471	0,444 + 1027
			11	32,930	1611	0,444 + 488 + 707
			12	33,227	1908	0,444 + 1464

As a further check a photograph of the phosphorescence spectrum was taken and found to agree with that published by Lewis and Kasha (*J. Amer. Chem. Soc.*, 1944, **66**, 2100). Further, on examination of the "excitation spectrum" (P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publ., New York, 1949, p. 306), with the Beckman spectrophotometer as monochromator, these bands excited phosphorescence which was apparently the same as that produced by irradiation at lower wave-lengths. The efficiency of these bands in exciting phosphorescence is as yet not known.

The present results are compared with de Laszlo's (*loc. cit.*) in Table 5. The solvents were slightly different (hexane and light petroleum), and de Laszlo's measurements were made at room temperature.

TABLE 5.

de Laszlo		This work		de Laszlo		This work	
Band	Position ($cm.^{-1}$)	Band	Position ($cm.^{-1}$)	Band	Position ($cm.^{-1}$)	Band	Position ($cm.^{-1}$)
IA	30,845	4	30,840	III	32,240	8	32,251
IB	31,260	5, 6 } Mean	31,288	IV	32,810	10	32,790
				V	33,210	12	33,227
II	31,720	7	31,763				

De Laszlo's band IB (which corresponds to the mean of bands 5 and 6 of this work) is split at low temperatures, and the higher-frequency component is assigned here as the 0,0. His band IA corresponds to one of the "strong" weak bands found at low temperature.

α-Fluoronaphthalene.—See Fig. 2 and Table 6. As in benzene, fluorine causes more disturbance than do the other halogens. The system is characterized by the appearance of a strong 0,0 but the vibrational structure is more complex and is not simply related to the other spectra, except in the interval 430 $cm.^{-1}$ between the 0,0 and band 2.

TABLE 6. *α-Fluoronaphthalene.*

Band no.	Position ($cm.^{-1}$)	Distance from 0,0	Assignment	Band no.	Position ($cm.^{-1}$)	Distance from 0,0	Assignment
1	31,598	—	0,0	5	32,658	1060	0, ?
2	32,031	433	0,433	6	32,998	1400	0, ?
3	32,277	679	0,679	7	33,206	1608	0, ?
4	32,455	857	0, ?	8	33,490	1892	0, ?

Bands corresponding to the very weak ones found in the other derivatives were looked for but only one extremely weak band removed about 100—200 $cm.^{-1}$ to long-wave-length of the 0,0 was found.

Summary for α-Halogenonaphthalenes.—α-Substitution by halogen causes a steady increase in intensity of the 0,0 and thereby a more allowed nature of the transition as we go from iodine to fluorine. A striking feature is the similarity in the 0,0—0,1 interval in all these compounds. It is only in α-iodonaphthalene that we can positively identify a temperature-dependent band, but the other compounds show such an excellent correspondence that their interpretation follows immediately.

It appears, in contrast to the β-compounds, that there are many fundamentals excited

strongly in the upper state, so that the vibrational pattern becomes quite complex (see α-fluoronaphthalene). The complexity is also enhanced by the dual nature of the transition, *i.e.*, vibrations are built on both the 0,0 and the 0,1 band.

The infra-red and Raman spectra of these compounds (measured by Mr. R. Werner, unpublished) contain an infra-red-active vibration of frequency about 470 cm.$^{-1}$ in all of these compounds, related it seems certain to the fundamental 478 cm.$^{-1}$ frequency of naphthalene. The vibration is remarkably unaffected by any of the halogens in either position of the ring. This vibration is to be linked with the approximately constant interval found in the upper state of the α-compounds. These results further confirm that the 478-cm.$^{-1}$ fundamental is the perturbing one in naphthalene.

A vibration of frequency about 490 cm.$^{-1}$ in the upper state of these compounds corresponds to the Raman-active vibration of frequency about 520 cm.$^{-1}$ in the ground state. It is remarkable that although the totally symmetric mode 1380 cm.$^{-1}$ in naphthalene does not alter markedly in the α-derivatives, it does not appear as a strong fundamental in the upper state.

It is not possible at present to decide the nature of the very weak bands found in the α-derivatives (the strongest—for α-chloronaphthalene—has an extinction coefficient of about 70, and the others are very much weaker). That they were only found in the α-derivatives suggests that they are due to a long-axis perturbation. Their assignment to a singlet level is extremely improbable, whilst a triplet assignment also meets with difficulties.

β-*Halogenonaphthalenes.*—The absorption curves for the second transition (Fig. 3) disclose a big difference between the effects of α- and β-substitution. Whereas α-substitution shifts the second transition to the red, β-substitution has less effect, and it is the first transition that is influenced more strongly by this substitution. The red shift of the weak transition is in the same order as for α-substitution but is greater.

The relevant results are in Fig. 4 and Table 7. The spectra are each characterized by the appearance of a strong 0,0. The smaller overlap by the second transition allows more structure to be seen than with the corresponding α-compounds, this being particularly noticeable in the case of β-fluoronaphthalene.

TABLE 7.

Band no.	Position (cm.$^{-1}$)	Distance from 0,0	Assignment	Band no.	Position (cm.$^{-1}$)	Distance from 0,0	Assignment
			β-Iodonaphthalene.				
1	30,926	—	0,0	6	32,510?	1584	0,?
2	31,398	472	0,472	7	32,808	1882	0,1418 + 472
3	31,642	716	0,716	8	33,100	2174	0,1418 + 716
4	31,931	1005	0,1005	9	33,400	2474	0,1418 + 1005
5	32,344	1418	0,1418				
			β-Chloronaphthalene.				
1	31,153	—	0,0	6	32,765?	1612	0,?
2	31,648	495	0,495	7	32,919	1766	0,1025 + 720
3	31,873	720	0,720	8	33,302	2149	0,1418 + 720
4	32,178	1025	0,1025	9	33,660	2507	0,1418 + 1025?
5	32,571	1418	0,1418				
			β-Fluoronaphthalene.				
1	31,514	—	0,0	7	33,176	1662	0,721 + 972
2	31,969	455	0,455	8	33,397	1883	0,455 + 1419
3	32,235	721	0,721	9	33,647	2133	0,721 + 1419
4	32,486	972	0,972	10	33,910	2396	0,972 + 1419
5	32,690	1176	0,455 + 721	11	34,095	2581	0,455 + 721 + 1419
6	32,933	1419	0,1419	12	34,386	2872	0,1419 + 1419

The three have common vibrational intervals superimposed on the 0,0. Four frequencies of the order 470, 700, 1000, and 1420 cm.$^{-1}$, respectively, appear in each spectrum, the values of these intervals being most accurately obtained in the fluoro-derivative because of the clarity of its spectrum.

As these compounds all possess strong 0,0's, it is most probably that the fundamental of value about 470 cm.$^{-1}$ is to be linked with the Raman frequency of about 520 cm.$^{-1}$ in these

compounds. This frequency corresponds to the totally symmetric mode of 512 cm.$^{-1}$ found in naphthalene. It appears therefore that the vibration that figures mainly in the spectra of the α-derivatives, *i.e.*, the infra-red 470 cm.$^{-1}$ of the ground state, is not excited strongly in the β-compounds and the transition is completely allowed. It is most interesting that, although all of these spectra have an allowed structure, they are not much more intense than those of the α-derivatives.

Discussion

The controversy over the assignment ^1A_g–^1A_g for the weak transition of naphthalene rests mainly on the following points: (1) The spectral resemblances of the cata-condensed hydrocarbons suggest that the weak system of naphthalene corresponds to the 2600-Å transition of benzene and, as such, as predicted by molecular-orbital theory, must be $g \rightarrow u$. (2) The system may be composite, *i.e.*, the bands 32,454 cm.$^{-1}$ and 31,513 cm.$^{-1}$ of the vapour spectrum correspond to 0,0's of separate electronic transitions, or else the appearance of a triplet level in this region complicates the spectrum, making analysis difficult. (3) Granted that the vibration 478 cm.$^{-1}$, in the ground state, is the perturbing one, its symmetry may be, not b_{2u}, but b_{3u}. (4) Symmetrical disubstitution, *i.e.*, 1 : 5- or 2 : 6-, should present the prohibition $g \rightarrow g$, so that the transition should be forbidden, whereas, in fact, it becomes allowed.

At first sight the spectral-resemblance objection to the A_g–A_g assignment appears to be strong, as it presents a relation between the cata-condensed hydrocarbons of an extremely simple nature. It meets with difficulties, however, in predicting the effect of halogen substitution on the naphthalene spectrum. α-Substitution produces an effect similar to that observed in benzene, but β-substitution shows no correlative effect with that of benzene.

We must therefore treat with care any superficial resemblances between the cata-condensed hydrocarbons, until more comprehensive data are available to decide whether the analogy can be carried so far as to identify completely the nature of any electronic level.

The experimental method of measuring the bands is justified by the results for the naphthalene spectrum. It should be noted that the method can give accurate results only if the vibrational structure of an electronic transition is characterized by the strong appearance of a few fundamentals in the excited state. That intervals similar to those found by Prikhojko (*Izvest. Akad. Nauk S.S.S.R.*, Ser. Fiz., 1948, **12**, 499) superimposed on the band 32,454 cm.$^{-1}$ in the vapour spectrum have been found in this research suggests strongly that this band is to be associated with the 0,1 band of a forbidden transition.

The suggestion that the bands 32,454 and 31,513 cm.$^{-1}$ of the vapour spectrum correspond to 0,0's of separate electronic transitions is seen to be incompatible with the results obtained here. Indeed the internal consistency between the spectra of the halogeno-naphthalenes and naphthalene points to the possibility of only one electronic transition in the region 2800—3200 Å of the naphthalene spectrum.

There is extremely little probability that a triplet level in this region has sufficient strength to complicate the spectrum. A triplet level would be sensitive to changes in atomic number of the halogen substituent, but no such effect was noticed. The weak bands found in the α-derivatives may possibly belong to a triplet level, but they would in no way interfere with the system in the region 2800—3200 Å of naphthalene.

There seems to be some doubt about the symmetry of the perturbing vibration responsible for the appearance of the spectrum (personal communication from G. C. Pimentel, mentioned by Schnepp and McClure, *loc. cit.*). Pictures of "mesomeric structures" (see, *e.g.*, Dewar, "The Electronic Theory of Organic Chemistry," Oxford, Clarendon Press, 1949, p. 175) show that α-substitution by halogen causes by far the most disturbance in the 2- and the 4-position, while β-substitution affects mainly the 1-position. We would therefore expect that α-substitution by halogen would, in effect, produce a perturbation to the electronic levels of naphthalene which is directed along both axes of the molecular plane. This perturbation, for fluorine, should be stronger along the

short axis, and, for iodine, stronger along the long axis (by analogy with the case of the halogenobenzenes (L. N. Ferguson, *Chem. Reviews*, 1952, **50**, 47). β-Substitution by halogen should produce a perturbation along the short axis only. That the observed results are in agreement suggests that a perturbation of symmetry B_{2u} is needed for the appearance of the transition. As the transition in naphthalene is polarized along the short axis, this is compatible with the assignment A_g–A_g.

De Laszlo has examined three symmetrical disubstituted naphthalenes, *viz.*, 2 : 6- and 1 : 5-dichloro- (*J. Amer. Chem. Soc.*, 1926, **50**, 982) and 2 : 6-dimethyl-naphthalene (*Z. physikal. Chem.*, 1925, **118**, 369), the last in the vapour as well as in solution. His results, viewed in the light of the results here, show that these compounds are all characterized by relatively strong 0,0's, this being particularly true for the 2 : 6-compounds.

Although this result opposes a *g*–*g* assignment the weight of other evidence supports the assignment A_g–A_g.

[*Added, December* 1*st*, 1953]: McClure and McConnell (*J. Chem. Phys.*, 1953, **21**, 1296) have recently published measurements on naphthalene and β-methylnaphthalene. Their results are contrary to those reported above in that they identify the ground-state frequency of 512 cm.$^{-1}$ with the value 430 cm.$^{-1}$ in the upper state. The author thanks Dr. L. E. Lyons for a suggestion that the interval 970 measured in naphthalene may be the mean of two intervals, namely, 2 × 473 and 1000. This would then make the band system very similar to that of the vapour spectrum.

Experimental

The absorption spectra were taken with a Hilger medium quartz spectrograph. An iron arc was used for comparison purposes. The low-temperature apparatus has been described previously (Ferguson and Iredale, *loc. cit.*). The solvent was light petroleum, b. p. 58—61°.

Measurement of Bands.—A representative plate was enlarged on to another plate, this plate was placed in the projection enlarger, and the spectrum focused on to a sheet of white paper (effective magnification, about 40). The centres of the bands were determined visually and referred to the accompaning iron spectrum. Accuracy is lost if two bands are overlapping but for most bands measured the accuracy is ±10—20 cm.$^{-1}$.

Materials.—The compounds, except α-chloro- and α-bromo-naphthalene and naphthalene, were all prepared by standard methods. All were purified by vacuum-sublimation or vacuum-distillation. B. p. were α-iodo-, 111°/1 mm., α-bromo-, 101°/1·5 mm., α-chloro-, 73°/0·2 mm., and α-fluoro-naphthalene 48°/0·6 mm. M. p. were β-iodo-, 53°, β-chloro-, 61°, and β-fluoro-naphthalene, 60°.

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