The Phosphorescence Spectra of Naphthalene and Some Simple Derivatives.

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A photomultiplier technique has been used to measure the phosphorescence emission from naphthalene and some simple derivatives. The spectrum of naphthalene has been interpreted in terms of known vibration frequencies and an explanation advanced for the appearance of b_{1g} fundamentals. The reduction in the symmetry of the parent molecule brought about by simple substitution, causes marked changes in the spectrum, which are explained in some detail.

PREVIOUS methods of measuring the phosphorescence emission from naphthalene (Goldstein, *Phil. Mag.*, 1910, **20**, 619; Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100; Terenin and Ermolaev, *Akad. Nauk S.S.S.R. Pamyati S.I. Vavilov*, 1952, 137) employed photography. Because of the low light intensity this necessitated low-dispersion instruments and rather large slit widths with resultant loss of accuracy.

Photoelectron multipliers have made possible the quantitative measurement of very low light intensities (cf. S. Rodda, " Photoelectric Multipliers," Macdonald, London, 1953) and opened a wide field particularly in molecular spectroscopy. We used a photoelectron multiplier with a constant-deviation glass spectrometer to measure quickly and accurately the emission from naphthalene and simple derivatives.

At the low temperatures (77° K) at which phosphorescence is usually studied the initial state may be taken as the zero-point vibrational level of the lowest triplet state. All frequency differences in the spectrum will then be characteristic of the ground state. Herzberg and Teller (*Z. physikal. Chem.*, 1933, *B*, **21**, 410) established the principles that govern the vibrational structure of an electronic transition. If the symmetry of the nuclei is unchanged by the transition the vibrations most strongly excited will be totally symmetric. Furthermore for an aromatic molecule these vibrations will be predominantly carbon (skeletal) motions.

Dikun and Sveshnikar (*Zhur. Eksper. Teoret. Fiz.*, 1949, **19**, 1000; *Doklady Akad. Nauk*

S.S.S.R., 1949, **65**, 637) and Shull (*J. Chem. Phys.*, 1949, **17**, 295) have shown that the phosphorescent level in benzene (identified with a triplet spin configuration by Lewis and Kasha, *loc. cit.*) is either $^3B_{1u}$ or $^3B_{2u}$ (point group D_{6h}) and the resulting transition to the ground (singlet) state is symmetry-forbidden. (References to symmetry apply here to spatial symmetry, the spin prohibition being understood.)

As quantum-mechanical calculations (Craig, *Proc. Int. Congr. Pure Appl. Chem.*, 1947, **11**, 411) predict the ground triplet of naphthalene to be $^3B_{2u}$, the transition to the ground state should be symmetry-allowed. This behaviour, in contrast to that observed with benzene, presents several interesting possibilities.

Naphthalene belongs to the point group D_{2h} and (cf. Kohlrausch and Seka, *Chem. Ber.*, 1938, *B*, **71**, 1551) possesses nine totally symmetric (a_g) vibrational modes, of which five are skeletal vibrations.

If the triplet–singlet transition is symmetry-allowed the vibrational pattern will be governed by the considerations outlined above. The spectrum should contain only five vibration frequencies, either singly or in progressions. Their relative intensities will depend on the change in size of the nuclear framework of the two states and the way in which the particular modes are able to incorporate this difference into their motion.

It is possible by simple substitution (simple, as used here, refers to single-atom substituents, so that the number of atoms in the molecule is unchanged) to reduce the point-group symmetry of the naphthalene molecule through C_{2h} to C_s. The new point groups have fewer symmetry requirements and a number of vibrations that were described by non-totally symmetric representations in naphthalene symmetry now fall into the totally symmetric representations of the lower point groups :

Species of D_{2h}	Resolved into	
(No. of skeletal vibrations)	Species of C_{2h}	Species of C_s
A_g (5)	A_g (9)	A' (17)
B_{1g} (4)		
B_{2g} (1)	B_g (3)	A'' (7)
B_{3g} (2)		
A_u (2)	A_u (4)	
B_{1u} (2)		
B_{2u} (4)	B_u (8)	
B_{3u} (4)		

This suggests that the vibrational pattern in passing from naphthalene to, say, a monohalogenonaphthalene might become quite complex, because the latter possesses 17 totally symmetric skeletal vibrations. These purely symmetry requirements, however, must be augmented by considerations of the dynamics of the vibrational motions. Only those vibrations whose dynamics satisfy the difference in framework size and shape will be strongly excited.

Results and Analysis.—The assignment column in the tables refers to known vibration frequencies (Luther, *Z. Elektrochem.*, 1948, **52**, 210, and Ferguson and Werner, to be published). The probable assignment column signifies that vibrational data are incomplete or lacking.

Naphthalene and 1 : 5-*dideuteronaphthalene.* See Figs. 1 and 2 and Table. The spectrum of naphthalene presents a marked contrast to that of benzene where the features are those of a forbidden transition. The major part of the intensity is carried off by progressions and combinations of only three frequencies, *viz.*, 512, 1380, and 1575 cm.$^{-1}$. The 1575 cm.$^{-1}$ vibration, however, is unexpected as it has been assigned to a b_{1g} motion (Pimentel and McClellan, quoted by Barrow and McClellan, *J. Amer. Chem. Soc.*, 1951, **73**, 573; Luther, *loc. cit.*). The other two are well-known a_g skeletal vibrations observed in the fluorescence spectrum of naphthalene. It should also be noted that another b_{1g} mode plays a part, *viz.*, the 1146 cm.$^{-1}$, although to a much lesser extent than the others (see Fig. 1 and Table). As these assignments are too well established to be seriously doubted, the explanation must come from a change of equilibrium configuration symmetry between the lowest triplet and singlet states.

Band position, cm.$^{-1}$	Separation from 0,0	Assignment	Band position, cm.$^{-1}$	Separation from 0,0	Assignment	Band position, cm.$^{-1}$	Separation from 0,0	Assignment
Naphthalene								
21,246	—	0,0	19,856	1390	1380,0	18,820	2426	2 × 512 + + 1380,0
20,730	516	512,0	19,665	1581	1575,0			
20,200	1046	2 × 512,0	19,355	1891	512 + 1380,0	18,440	2806	2 × 1380,0
20,105	1141	1146,0	19,200	2046	512 + 1576,0	18,269	2987	1380 + 1576,0
1 : 5-*Dideuteronaphthalene*								
21,260	—	0,0	19,719	1541	1541,0	18,590	2670	1112 + 1541,0
20,760	500	500,0	19,390	1870	500 + 1386,0	18,480	2780	2 × 1386,0
20,148	1112	1112,0	19,185	2075	500 + 1541,0	18,315	2945	1386 + 1541,0
19,874	1386	1386,0	18,800	2460	1112 + 1380,0	18,700	3090	2 × 1541,0
α-*Fluoronaphthalene*								
21,062	—	0,0	19,474	1588	1576,0	18,500	2562	1153 + 1378,0
20,830	230	224,0	19,190	1872	526 + 1378,0	18,280	2782	2 × 1378,0
20,554	508	526,0	18,930	2132	526 + 1576,0	18,110	2952	1378 + 1576,0
19,900	1162	1153,0	18,730	2332	2 × 1153,0	17,890	3172	2 × 1576,0
19,684	1378	1378,0						
β-*Fluoronaphthalene*								
21,268	—	0,0	19,878	1390	1390,0	18,730	2538	1173 + 1390,0
20,804	464	464,0	19,682	1586	1586,0	18,500	2768	2 × 1930,0
20,500	768	768,0	19,425	1843	464 + 1390,0	18,285	2983	1390 + 1586,0
20,340	948	948,0	19,215	2053	464 + 1586,0	18,080	3188	2 × 1586,0
20,095	1173	1173,0						
α-*Chloronaphthalene*								
20,645	—	0,0	19,269	1376	1368,0	18,350	2295	2 × 1159,0
20,440	205	222,0	19,118	1527	1565,0	18,145	2500	1159 + 1380,0
20,125	520	515,0	18,760	1885	515 + 1368,0	17,930	2715	2 × 1380,0
19,710	935	954,0	18,585	2060	515 + 1565,0	17,725	2920	1368 + 1565,0
19,480	1165	1159,0						
β-*Chloronaphthalene*								
21,069	—	0,0	19,674	1395	1386,0	18,845	2224	1386 + 863,0
20,784	285	281,0	19,430	1639	1624,0	18,260	2809	1624 + 1153,0
20,558	511	516,0	19,182	1887	1386 + 516,0	18,030	3039	1624 + 1386,0
20,232	837	863,0	18,930	2139	1624 + 516,0	17,830	3239	2 × 1624,0
α-*Bromonaphthalene*								
20,652	—	0,0	19,610	1042	1055,0	18,530	2122	1363 + 731,0
20,495	157	176,0	19,300	1352	1363,0	18,340	2312	1559 + 731,0
20,330	322	304,0	19,116	1536	1559,0	17,945	2706	2 × 1363,0
20,138	514	511,0	18,740	1912	1363 + 511,0	17,740	2912	1559 + 1363,0
19,892	740	731,0						
β-*Bromonaphthalene*								
21,036	—	0,0	19,648	1388	1376,0	19,182	1854	1574 + 276,0
20,782	254	276,0	19,452	1584	1574,0	18,810	2226	1376 + 812,0
20,528	508	519,0	19,390	1646	1376 + 276,0	18,650	2386	1574 + 812,0
20,218	818	812,0						
1 : 5-*Dibromonaphthalene*								
20,086	—	0,0	18,960	1126	1126,0	18,010	2076	1536 + 494,0
19,592	494	494,0	18,720	1366	1366,0	17,780	2306	1536 + 758,0
19,328	758	758,0	18,550	1536	1536,0	17,300	2786	2 × 1366,0
19,140	946	946,0	18,240	1846	1366 + 494,0			
2 : 6-*Dibromonaphthalene*								
20,806	—	0,0	19,740	1066	1066,0	18,665	2141	1360 + 796,0
20,560	246	246,0	19,446	1360	1360,0	18,415	2391	1538 + 796,0
20,302	504	504,0	19,268	1538	1538,0	18,080	2726	2 × 1360,0
20,010	796	796,0	18,920	1886	1360 + 504,0	17,885	2921	1538 + 1360,0
19,820	986	986,0	18,730	2076	1538 + 504,0	17,690	3116	2 × 1538,0

This change of symmetry can come about in either or both of two ways. The triplet state may be inherently distorted or else the presence of the solvent introduces a perturbation sufficiently strong to distort one of the states slightly more than the other. To test these explanations we used 1 : 5-dideuteronaphthalene which has the point-group symmetry C_{2h} in the ground state, and in which the four skeletal b_{1g} vibrations of naphthalene become totally symmetric in the new point group (see Table). The substitution of deuterium for hydrogen will not significantly alter the configuration of the carbon framework, so that comparison of its phosphorescence with that of naphthalene should show how b_{1g} fundamentals become active in the naphthalene spectrum.

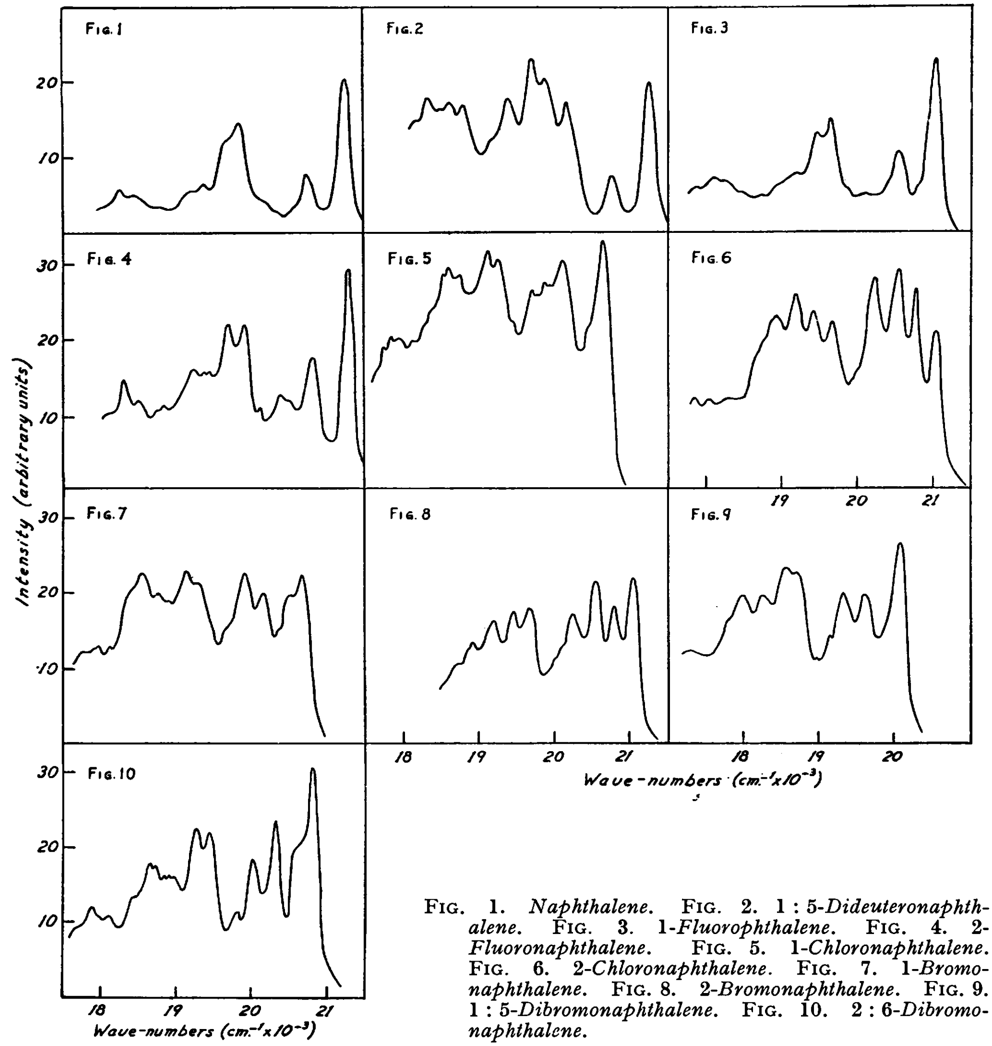

FIG. 1. *Naphthalene.* FIG. 2. 1 : 5-*Dideuteronaphthalene.* FIG. 3. 1-*Fluorophthalene.* FIG. 4. 2-*Fluoronaphthalene.* FIG. 5. 1-*Chloronaphthalene.* FIG. 6. 2-*Chloronaphthalene.* FIG. 7. 1-*Bromonaphthalene.* FIG. 8. 2-*Bromonaphthalene.* FIG. 9. 1 : 5-*Dibromonaphthalene.* FIG. 10. 2 : 6-*Dibromonaphthalene.*

As can be seen from Fig. 2, the contribution to the intensity distribution made by the 1575 and 1146 cm.$^{-1}$ b_{1g} modes of naphthalene increases greatly relative to that of the naphthalene a_g fundamentals. This then points to the distortion of the molecule by solvent perturbations as the explanation for the appearance of b_{1g} fundamentals in naphthalene.

The appearance of b_{1g} fundamentals by perturbation of an appropriate electronic state was considered improbable in view of the large increase of their intensity in the dideuterocompound. If they were stealing intensity from another level then substitution by deuterium would not affect it to the degree observed. The 1575 cm.$^{-1}$ fundamental, from observation with the substituted naphthalenes, is particularly suitable for excitation in this transition and it seems likely that even a small perturbation of the molecule enables it to appear.

The height of the peak representing one quantum of the 512 cm.$^{-1}$ a_g vibration of naphthalene bears the same ratio to that of the 0,0 band for both compounds.

Substituted naphthalenes. The point-group symmetry for single-atom monosubstituted naphthalenes is C_s; for symmetrical disubstitution it is C_{2h}. The spectra should be, and are, more complex than those of the parent compound because of this reduction in symmetry. When substitution by halogen is considered, a more important change than that experienced with deuterium is found. Halogen atoms substituted into the ring possess non-bonding electrons which are capable of interacting with the π-electrons of the aromatic ring. It is impossible, however, to predict how the structure of the band system will be affected by these perturbations.

Fluoronaphthalenes. See Figs. 3 and 4 and Table. These spectra, unlike those of the other halogen derivatives, are very similar to that of naphthalene. The 0,0 band of the spectrum of the β-compound is practically unchanged with respect to that of naphthalene, but the spectrum of the α-compound suffers a slight red shift (about 200 cm.$^{-1}$). The spectrum of the α-compound can be analysed quite simply in terms of known vibration frequencies, but no Raman data are available for comparison with the spectrum of the β-compound.

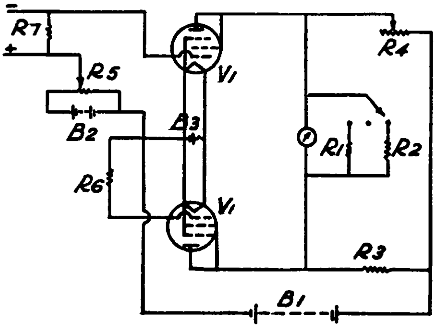

FIG. 11.

R_1 = 10 Ω.
R_2 = 170 Ω.
R_3 = 15,000 Ω.
R_4 = 17,000 Ω.
R_5 = 1 megohm.
R_6 = 10 megohm.
R_7 = 130 megohm.
B_1 = 67½ v.
B_2 = 7½ v.
B_3 = 1½ v.
V_1 = IT4.

Chloronaphthalenes. See Figs. 5 and 6 and Table. As before, the spectrum of the α-compound is shifted more towards the red, compared with naphthalene, than is the spectrum of the β-compound. The systems can be analysed in terms of known vibration frequencies. The greater complexity of the spectrum of the α-compound is apparent from the Figures.

Bromonaphthalenes. See Figs. 7 and 8 and Table. These spectra follow closely in structure, position, and intensity the corresponding chloro-derivatives.

Dibromonaphthalenes. See Figs. 9 and 10 and Table. The difference between these spectra is very much the same as that between α- and β-substituted derivatives. The red shift of the 0,0 band in the case of the 2 : 6-compound is nearly twice as great as the shift for the β-mono-derivative and is much less than the shift for the 1 : 5-compound, which again is nearly twice as great as the shift for the α-mono-derivative.

As in the monochloro- and -bromo-derivatives a low vibration becomes quite prominent in the spectrum of the 2 : 6-derivative. Although this vibration does not appear in the spectrum of the 1 : 5-derivative, the asymmetry of the first band suggests that it might be concealed under it.

No Raman data are available to verify assignments.

Conclusions.—The phosphorescence emission of naphthalene is unique in that its vibrational pattern is strongly dependent on the point-group symmetry of the molecule. Although naphthalene possesses 48 different vibrational modes, the requirements enforced by symmetry and the nature of the electronic states involved in the transition are such that the spectrum is extremely simple and can be interpreted in terms of a few characteristic frequencies. These frequencies still predominate in the spectra of the substituted naphthalenes, but the appearance of new vibrations, particularly low-frequency modes, makes their pattern quite complex, although still interpretable with known vibration frequencies.

The 1575 cm.$^{-1}$ b_{1g} mode of naphthalene, probably because of its mechanics, is particularly suitable for excitation in the spectrum and it appears even in the naphthalene spectrum because of solvent perturbations.

The phosphorescence emission of naphthalene therefore records a characteristically allowed transition from the ground-triplet to the ground-singlet state. From theoretical calculations this level probably has the symmetry classification $^3B_{2u}$.

EXPERIMENTAL

Apparatus.—The photoelectron multiplier used was a R.C.A. type 1P21. The spectrograph was a Hilger, glass-prism, constant-deviation type, with a dispersion of about 20 Å/mm. at 4350 Å and about 60 Å/mm. at 5790 Å. The multiplier was fixed and the prism rotated to record the spectrum.

The high, stable, D.C. voltage required by the photomultiplier was provided by a slight adaption of Zimm's circuit (*J. Chem. Phys.*, 1948, **16**, 1102). As the D.C. amplifier was very efficient and stable the circuit is shown in Fig. 11. It includes a low-voltage supply to compensate for the dark current of the phototube. This had to be balanced before each reading but changed little.

Calibration for spectral sensitivity was made with a tungsten lamp standardized by the National Standards Laboratory, Sydney. By use of Planck's equation for a black-body radiator and making allowance for the change in dispersion of the spectrograph, correction factors were determined so that the curves finally obtained give the energy emitted as a function of wave number for equal band width in Ångström units. All readings were taken with the spectrograph slit at 0·14 mm. and the slit before the photocathode at 0·2 mm. The estimated accuracy for sharp peaks is ±15 cm.$^{-1}$.

Solvent.—The solvent was light petroleum, purified by being repeatedly stirred with a concentrated sulphuric acid–oleum mixture until no further coloration occurred, washed, dried, and distilled, the fraction boiling at 58—60° being collected. It freezes easily to a clear, rigid, glass without cracking and keeps free from phosphorescent impurities even on long storage. We found it much more convenient to use than the more generally known E.P.A. mixture.

Compounds.—We thank Miss B. J. Russell for the sample of 1 : 5-dideuteronaphthalene, which was analysed as 94% of dideuteronaphthlaene and 6% of monodeuteronaphthalene. For the dibromo-compounds we thank Miss Russell and Mr. Hunt. The physical constants are as follows : m. p. naphthalene, 80°, 1 : 5-dideutero-, 79·8°, β-fluoro-, 60°, β-chloro-, 62°, β-bromo-, 59°, 1 : 5-dibromo-, 129°, and 2 : 6-dibromo-naphthalene, 160°. B. p. α-fluoro-, 48°/0·6 mm., α-chloro-, 73°/0·2 mm., and α-bromo-naphthalene, 101°/1·5 mm.

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