257. *Perturbation of Singlet–Triplet Transitions of Aromatic Molecules by Oxygen under Pressure.*

By D. F. Evans.

The perturbing effect of oxygen on singlet–triplet absorption spectra has been studied quantitatively with a large number of aromatic hydrocarbons, and pressures of oxygen up to nearly 100 atm. In most cases well-defined absorption bands were observed, which disappeared on removal of the oxygen. The longest-wavelength band almost exactly coincides with the shortest-wavelength phosphorescence band in those cases where the phosphorescence emission has been studied. The only exception is 3 : 4-benzopyrene, for which the phosphorescence data may be in error. Solvent shifts of singlet–triplet transitions are very small. No comparable perturbation was observed with sulphur dioxide, and it is concluded that the effect is largely due to the paramagnetic nature of the oxygen molecule, although " charge transfer " may play some part. The nature of the stronger absorption at shorter wavelengths is also discussed.

It was recently shown [1] that the " singlet–triplet " absorption bands around 3300 Å observed for long path-lengths of liquid benzene by Sklar,[2] Lewis and Kasha,[3] and Pitts [4] disappear when the dissolved atmospheric oxygen is removed. Conversely, they appear much more strongly in benzene saturated with pure oxygen. This was attributed to a spin-orbit perturbation [5] [6] of the benzene triplet level by the inhomogeneous field of the paramagnetic oxygen molecule which effectively introduces a slight degree of singlet character into the triplet level (and, possibly, a slight degree of triplet character into the ground singlet level).

In the present work, the effect has been studied in detail for a large number of aromatic hydrocarbons, with pressures of oxygen up to nearly 100 atm.

Experimental

Apparatus and Procedure.—The high-pressure absorption cell consisted of a flanged brass tube fitted with two ¼ in. thick plate-glass windows, each bolted between two ⅛ in. thick polytetrafluoroethylene gaskets. The effective path length was 7·2 cm. The cell was connected, *via* a

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[1] Evans, *Nature*, 1956, **178**, 534.
[2] Sklar, *J. Chem. Phys.*, 1937, **5**, 669.
[3] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994.
[4] Pitts, *J. Chem. Phys.*, 1950, **18**, 1416.
[5] McClure, *ibid.*, 1949, **17**, 905.
[6] Yuster and Weissman, *ibid.*, p. 1182.

union to permit filling, to a small diaphragm valve, and the whole assembly could be fitted in the 10-cm. cell compartment of the Beckman D.U. spectrophotometer.

After the cell had been filled with solution, the absorption spectrum was first measured relative to air (or better, relative to two plate-glass windows cemented together with Silicone oil). This absorption was very small, except occasionally at the shortest wavelengths. The cell was then attached to a cylinder containing oxygen at a known pressure and shaken vigorously for about 5—6 min. Experiments showed that complete saturation was easily attained in this time. The diaphragm valve was closed, the cell disconnected, and its absorption remeasured. By subtraction the absorption spectrum resulting from the effect of the dissolved oxygen was obtained. It can be estimated from data of Horiuti[7] and Fischer and Pfleiderer[8] that the change in volume of the solution on saturation with oxygen at 75 atm. was only about 3%, and accordingly no correction was applied.

Except where otherwise stated, chloroform was used as the solvent. Chloroform is a very good solvent for aromatic hydrocarbons, and it was thought to be safer for routine use with high pressures of oxygen than such solvents as benzene or carbon disulphide. The absorption of oxygen dissolved in pure chloroform was almost negligible over the region studied (3500—8000 Å). In all cases the additional absorption observed in the presence of aromatic hydrocarbons remained constant during the period of measurement (1—2 hr.) and disappeared on removal of the oxygen.

Chemicals.—Chloroform (for analysis) was used directly, without removal of the ethyl alcohol inhibitor ($\sim$1%). Benzene (for molecular-weight determinations) was repeatedly shaken with concentrated sulphuric acid, washed, dried, and fractionally distilled. Successive fractions had almost identical ultraviolet absorption. Fluorobenzene was treated similarly. Naphthalene (for molecular-weight determinations) was once recrystallized from alcohol. Styrene, α-bromonaphthalene, and *cis*-stilbene were fractionally distilled *in vacuo*. The remaining compounds were all purified by chromatography (in benzene or light petroleum solution) through alumina or silica gel–alumina columns, and subsequent recrystallization. 9-Methylanthracene, prepared from anthrone and methylmagnesium iodide[9] and further purified *via* the picrate, had m. p. 80°. 9-Nitroanthracene, prepared as described in *Org. Synth.*,[10] had m. p. 146·5°.

RESULTS AND DISCUSSION

The results are shown in Figs. 1—5. It can be seen that the great majority of the hydrocarbons studied give well-defined absorption bands, in addition to the rapidly rising absorption at shorter wavelengths. The longest-wavelength band for each compound is given in Table 1, together with the shortest-wavelength phosphorescence band (where known), *i.e.*, the 0, 0 band of the triplet–singlet emission spectrum. The very close agreement shows quite clearly that these bands are, in fact, the (induced) singlet–triplet absorption bands of the aromatic hydrocarbons.

The only definite discrepancy is found with 3 : 4-benzopyrene. Ilina and Shpolskii[11] reported two phosphorescence bands at 5950 and 6340 Å for 3 : 4-benzopyrene in a boric acid glass, whereas the first absorption band is at 6817 Å (Table 1 and Fig. 4). However, the Russian workers were unable to observe any phosphorescence in a low-temperature glass, and it seems very likely that decomposition had occurred as a result of the high temperature involved in the preparation of a boric acid glass and that the reported bands were due to impurities. The featureless absorption shown by diphenyl, in contrast to the well-defined phosphorescence bands starting at 4390 Å,[12] can be attributed to the various configurations adopted under different conditions owing to rotation of the benzene rings about the central bond.

In general, however, perturbation with oxygen under pressure seems a useful method for locating and confirming the triplet levels of aromatic hydrocarbons. When compared

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[7] Horiuti, *Sci. Papers Inst. Phys. Chem. Res.* (*Tokyo*), 1931, **17**, No. 341, 125.

[8] Fischer and Pfleiderer, *Z. anorg. Chem.*, 1922, **124**, 61.

[9] Beckwith and Waters, *J.*, 1956, 1108.

[10] *Org. Synth.*, **31**, 77.

[11] Ilina and Shpolskii, *Izvest. Acad. Nauk S.S.S.R., Ser. Fiz.*, 1951, **15**, 585.

[12] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.

with the study of phosphorescence emission, it has the disadvantage that comparatively strong solutions (of the order of 1%) are required, but it is applicable in cases where no phosphorescence can be observed. The enhancement of the intensity of singlet-triplet absorption bands by oxygen seems greater (at least for unsubstituted hydrocarbons such as naphthalene) than that produced by solvents containing heavy atoms.[13]

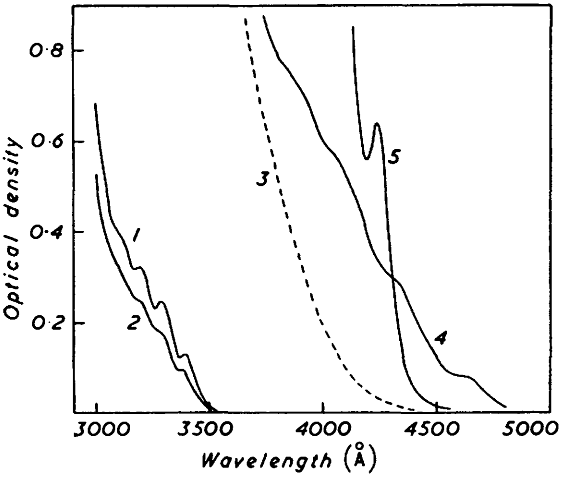

FIG. 1. 1, *Benzene, pure liquid,* 11·3M, 5-*cm. cell,* 0·89 *atm.* [*max.* (*cm.*$^{-1}$) 29,440, 30,350, 31,250, ~32,100 i]. 2, *Fluorobenzene, pure liquid,* 10·7M, 5-*cm. cell,* 0·91 *atm.* (29,500, ~30,500 i). 3, *Diphenyl,* 0·90M, ~45 *atm.* 4, *Styrene,* 0·89M, 76 *atm.* (21,600, ~23,100 i, ~24,400 i, ~25,900 i). 5, *Fluorene,* 0·90M, 76 *atm.* (23,580). *Unless otherwise stated, measurements shown in Figs.* 1—5 *were made on* $CHCl_3$ *solutions in a* 7·2-*cm. cell. Chloroform saturated at* 76 *atm. is approximately* 0·7M *with respect to oxygen.*[8]

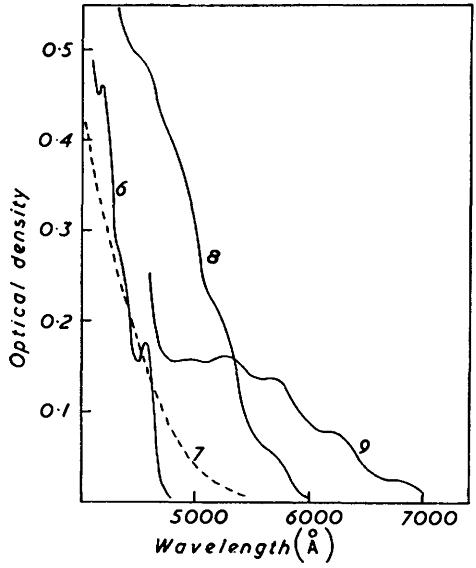

FIG. 2. 6, *Diphenylacetylene,* 0·62M, 75 *atm.* (21,860, 23,890). 7, cis-*Stilbene,* 0·53M, 76 *atm.* 8, trans-*Stilbene,* 0·72M, 76 *atm.* (17,750 i, ~19,100 i, ~20,600 i, ~22,200 i). 9, *Diphenylbutadiene,* 0·25M, 76 *atm.* [~14,700 (?), 16,180, 17,670, 18,960, 20,260].

Intensities.—The dependence of the intensity of absorption on both the oxygen pressure and the concentration of hydrocarbon was studied with naphthalene. Measurements at various pressures showed that the shape of the curve was independent of the oxygen pressure (within ±1%), and accordingly only the results for the shortest-wavelength naphthalene band at 4160 Å are plotted in Fig. 6. The optical density is approximately proportional to the oxygen pressure, although there seems to be a slight falling off at the higher pressures. This effect is, however, little greater than the experimental errors. The optical density is also directly proportional to the concentration of naphthalene (Table 2). The results for a 0·9M-solution of naphthalene are also in agreement, although a slight change in the solubility of the oxygen might be expected.

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[13] Kasha, *J. Chem. Phys.*, 1952, **20**, 71.

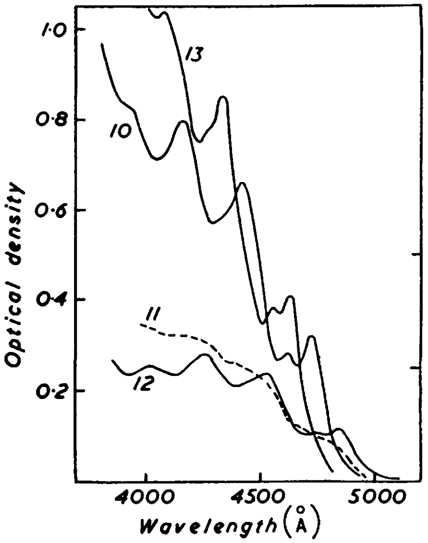

Fig. 3. 10, *Naphthalene*, 0·90M, 76 *atm.* (21,180, 21,670, 22,600, 24,020). 11, *α-Bromonaphthalene*, 2·5M, *no* O_2, 10-*cm. cell.* 12, *α-Bromonaphthalene*, 0·50M, 75 *atm.* (20,650, 21,110, 22,100, 23,470, 24,810). 13, *Phenanthrene*, 1·01M, ~47 *atm.* (21,600, 21,970, 23,040, 24,500). (The numerals on the right-hand sign are $10^2\varepsilon$ for the broken curve.)

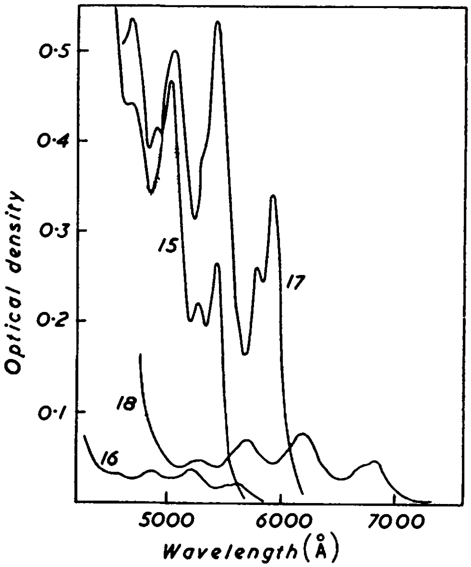

Fig. 4. 15, *Fluoranthene*, 0·91M, 76 *atm.* (18,450, 19,010, 19,940, 20,410, 21,420). 16, 1 : 2-3 : 4-*Dibenzanthracene*, 0·075M, 76 *atm.* (17,790, 19,180, 20,510, ~21,980). 17, *Pyrene*, 0·89M, ~50 *atm.* (16,930, 17,280, 18,470. 19,820, 21,370). 18, 3 : 4-*Benzopyrene*, 0·103M, 76 *atm.* (14,670, 16,190, 17,540, 18,960).

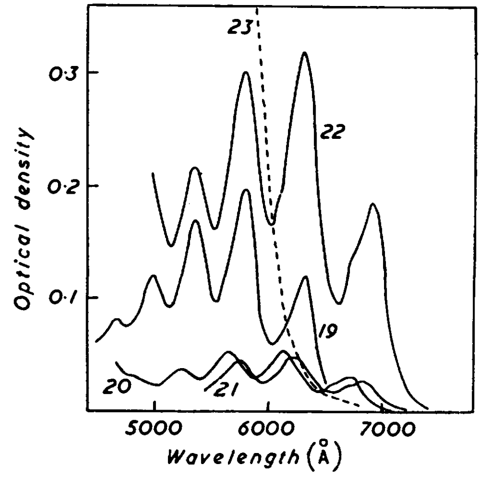

Fig. 5. 19, *Acridine*, 0·90M, ~75 *atm.* (15,840, 17,240, 18,640, 20,040, 21,430). 20, *Anthracene*, 0·087M, ~93 *atm.* (14,870, ~15,250 i, 16,300, 17,690, 19,080). 21, 9-*Nitroanthracene*, 0·25M, 75 *atm.* (14,630, 16,000, 17,360). 22, 9-*Methylanthracene*, 0·69M, 76 atm. (14,460, ~14,850 i, 15,840, 17,250, 18,660). 23 (– – – –), 9-*Methylanthracene*, 0·70M, 0·65M-SO_2, 10-*cm. cell.*

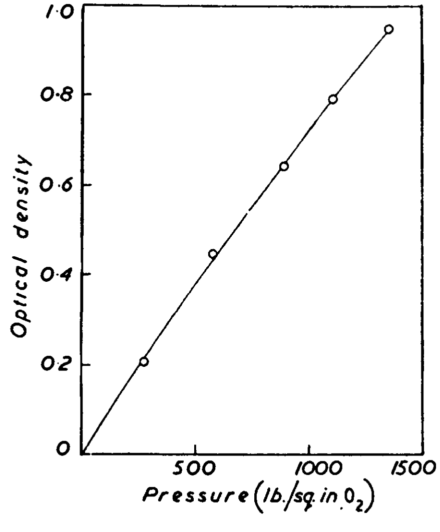

Fig. 6. *Dependence of absorption on oxygen pressure.* 0·9M-*Solution of naphthalene in chloroform ;* 4160 Å *peak.*

TABLE 1. *Triplet levels (cm.$^{-1}$) of aromatic molecules obtained from oxygen perturbation and phosphorescence spectra respectively.*

Compound	Oxygen perturbation ($CHCl_3$ soln.*)	Phosphorescence (low-temp. glass)
Benzene	29,440	29,470 [a]
Fluorene	23,580	23,750 [5]
Phenanthrene	21,600	21,600 [5]
Naphthalene	21,180	21,246 [b]
Fluoranthene	18,450	—
1 : 2-3 : 4-Dibenzanthracene	17,790	—
Pyrene	16,930	16,940,[11] 16,800 [5]
Anthracene	14,870	14,927 [c]
3 : 4-Benzopyrene	14,670	(16,810 [11] †)
Acridine	15,840	—
Styrene	21,600	—
trans-Stilbene	17,750	—
Diphenylacetylene	21,860	—
Fluorobenzene	29,500	—
α-Bromonaphthalene	20,650	20,700 [12]
9-Nitroanthracene	14,630	—
9-Methylanthracene	14,460	—

* Accuracy probably about 50 cm.$^{-1}$ for the condensed-ring hydrocarbons (and diphenylacetylene), and about 100—200 cm.$^{-1}$ for the other hydrocarbons.

† In boric acid glass, see text.

[a] Shull, *J. Chem. Phys.*, 1949, **17**, 295. [b] Ferguson, Iredale, and Taylor, *J.*, 1954, 3160. [c] Padhye, McGlynn, and Kasha, *J. Chem. Phys.*, 1956, **24**, 588.

TABLE 2. *Effect of concentration of naphthalene on absorption.*

Wavelength (Å)		4723	4614	4424	4164	4000
Optical density (1120 lb./sq. in. O_2)	0·25M	$0{\cdot}175_5$	$0{\cdot}153_5$	$0{\cdot}358_5$	0·436	$0{\cdot}409_5$
	0·50M	$0{\cdot}091_5$	0·081	0·183	0·224	0·212
Ratio		1·95	$1{\cdot}95_5$	1·99	2·01	2·02

These results show that experiments made under different conditions of oxygen pressure and hydrocarbon concentration can be compared (after correction) with fair accuracy. Then, when any necessary allowance is made for the background, non-triplet, absorption, it is found that the induced triplet bands of all the unsubstituted condensed-ring hydrocarbons studied differ only slightly in intensity (by a factor of about two).

As a result of the perturbing effect of the heavy bromine atom in α-bromonaphthalene, very weak singlet–triplet bands can be detected in the absence of oxygen (Fig. 3; cf. McClure, Blake, and Hanst [14]). In spite of this, the effect of dissolved oxygen is less than with naphthalene, indicating that the two types of perturbation do not particularly reinforce each other. It is also noteworthy that acridine and 9-nitroanthracene give much weaker bands than anthracene or 9-methylanthracene.

Solvent Shifts of Triplet Bands.—Since the triplet bands are normally very sharp, it is possible, with the aid of oxygen perturbation, to study accurately the effect of various solvents on their position. This has been done with naphthalene, in four solvents of widely differing refractive indices, *n*-hexane (n_D 1·38), chloroform (n_D 1·45), benzene (n_D 1·50), and carbon disulphide (n_D 1·63). (The refractive indices of the 0·9M-solutions used will be slightly different.) The results are in Table 3.

These solvent shifts are very small, appreciably smaller in fact than the usual shifts for singlet–singlet transitions, even those of comparatively low intensity.[15] That the energies of singlet–triplet transitions are relatively independent of external conditions is further indicated by the close agreement between the two columns in Table 1.

Vibrational Structure.—The triplet-state vibrational frequencies which appear (as progressions or combination frequencies) in the singlet–triplet absorption spectra are determined by symmetry conditions, and the change of molecular geometry on excitation.[16]

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[14] McClure, Blake, and Hanst, *J. Chem. Phys.*, 1954, **22**, 555.

[15] Coggeshall and Pozefsky, *ibid.*, 1951, **19**, 980; Bayliss and Hulme, *Austral. J. Chem.*, 1953, **6**, 257.

[16] McClure, *J. Chem. Phys.*, 1956, **24**, 1; also refs. *a* and *b* of Table 1.

Two such frequencies (of ~1400 and ~400—500 cm.$^{-1}$) are normally observed with the condensed-ring hydrocarbons studied, the former being especially prominent. Similar frequencies are also prominent in the phosphorescence spectra [12, 17] and in many of the singlet–singlet absorption spectra.[16] [18] Low-temperature measurements of singlet–triplet spectra perturbed by oxygen might be of interest, since the vibrational structure would almost certainly be better resolved, but involve appreciable experimental difficulties.

TABLE 3. *Solvent shifts* (*cm.*$^{-1}$) *of naphthalene bands* (*to lower frequencies*) *relatively to* n-*hexane.*

Band position (*n*-hexane)	Shifts		
	Chloroform	Benzene	CS_2
21,190	20	40	120
21,690	10	30	110
22,600	0	20	100
24,020	0	10	—

For hydrocarbons having low-lying triplet levels, where the background non-triplet absorption is small, the second band is normally the most intense, and the maximum absorption (with smoothed-out vibrational structure) lies at a frequency about 2000 cm.$^{-1}$ greater than that of the first (0, 0) band.

Positions of Triplet Levels.—The triplet levels of anthracene and its derivatives as found by oxygen perturbation are in complete agreement with the recent work of Padhye, McGlynn, and Kasha.[19] These workers showed that the earlier results of Lewis and Kasha on the phosphorescence of anthracene,[12] which had been called into question by Reid,[20] were in fact correct. However, one rather puzzling discrepancy was found. Padhye, McGlynn, and Kasha claimed that the absorption spectra of anthracene (0·084M in CS_2; 20-cm. cell) showed weak singlet–triplet absorption bands. In an attempt to check this, since a 20-cm. cell was not available, a (deoxygenated) 2·3M-solution of 9-methylanthracene in purified carbon disulphide was examined in a 10-cm. cell. In spite of the 13-fold increase in (concentration × path length) no bands were observed, and the weak absorption obtained, which may be partly due to impurities, was only about one-third of that recorded for anthracene (ε of 9-methylanthracene: 0·0004, 14,500 cm.$^{-1}$; 0·0007$_6$, 15,500 cm.$^{-1}$; 0·0013, 16,500 cm.$^{-1}$; 0·0017, 17,500 cm.$^{-1}$). Since 9-methylanthracene perturbed by oxygen gives very well-defined triplet bands, and the unperturbed singlet–triplet absorption should be very similar to that of anthracene, it seems likely that the anthracene bands do not represent the true singlet–triplet absorption intensity. The life-time of the anthracene triplet state [21] in a rigid glass is less than 0·1 sec., but the intrinsic life-time in the absence of any competing radiationless processes is probably considerably greater (cf. Gilmore, Gibson, and McClure [22]).

Although the two lowest singlet states of anthracene and acridine are almost identical in energy,[23] it may be noted that the triplet bands of acridine lie at considerably shorter wavelengths than those of anthracene (Fig. 5).

The observed triplet level for 1 : 2-3 : 4-dibenzanthracene is in quite good agreement with that calculated by Hall [24] (obs. 17,790 cm.$^{-1}$; calc. 18,250 cm.$^{-1}$).

Mechanism of "Oxygen" Effect.—As mentioned in the introduction, this effect has been attributed to the paramagnetism of the oxygen molecule. However, Reid [20, 25] has

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[17] Ref. *b* of Table 1.

[18] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, New York, 1951.

[19] Ref. *c* of Table 1.

[20] Reid, *J. Chem. Phys.*, 1952, **20**, 1212, 1214.

[21] Craig and Ross, *J.*, 1954, 1589.

[22] Gilmore, Gibson, and McClure, *J. Chem. Phys.*, 1952, **20**, 829.

[23] Badger, Pearce, and Pettit, *J.*, 1951, 3199.

[24] Hall, *Proc. Roy. Soc.*, 1952, *A*, **213**, 113.

[25] Moodie and Reid, *J. Chem. Phys.*, 1954, **22**, 252.

shown that the emission spectra of trinitrobenzene–aromatic hydrocarbon complexes closely resemble the phosphorescence spectra of the parent aromatic hydrocarbons,* but have much shorter lifetimes. This reduction in life-time was attributed to the effect of "charge transfer" in the complex on the symmetry of the π-electrons of the aromatic hydrocarbon. Since there is evidence for charge-transfer complex formation between oxygen and organic compounds,[26, 27] the effect of sulphur dioxide on 9-methylanthracene was studied. Although sulphur dioxide almost certainly forms stronger complexes with aromatic hydrocarbons than does oxygen,[28] no singlet–triplet bands were observed and the absorption in the region of the first triplet band of 9-methylanthracene was very small (Fig. 5). It therefore seems very likely that the most important feature of the oxygen molecule responsible for the perturbation of singlet–triplet transitions is in fact its paramagnetic nature.

This does not necessarily mean that charge-transfer effects play no part at all. Thus, as mentioned above, the induced triplet bands are much less intense with 9-nitroanthracene and acridine than with anthracene or 9-methylanthracene. The substitution of a nitro-group, or of $\cdot\ddot{N}$ for $\cdot\ddot{C}H$, will considerably reduce the π-donor characteristics of the anthracene molecule. Further, the perturbing effect of oxygen seems greater than would be expected from its magnetic moment, when compared with the effect of the Gd^{3+} ion (as obtained from the phosphorescence life-times of the gadolinium, lanthanum, and lutecium complexes of dibenzoylmethane).[6] It is significant that two (triplet) oxygen molecules interact to form a very weak O_4 complex, which is either diamagnetic or very feebly paramagnetic.[29] Simultaneously, the extremely weak $^3\Sigma$–$^1\Sigma$ and $^3\Sigma$–$^1\Delta$ transitions are greatly enhanced in intensity.[30] A study of the perturbing effect of other paramagnetic substances on the singlet–triplet absorption bands of aromatic molecules might prove of interest.

In the presence of oxygen under pressure, the majority of aromatic hydrocarbons studied give rise to strong absorption at wavelengths shorter than the singlet–triplet absorption bands. This absorption was previously observed with a variety of aromatic compounds and oxygen at atmospheric pressure,[26] and is also found (at still shorter wavelengths) with non-aromatic compounds such as saturated hydrocarbons, alcohols, and ethers.[26, 27] Although it is possible that this more intense absorption is due to a magnetic perturbation of a higher triplet level of the organic molecule,[1] it seems much more likely that a charge-transfer transition is involved. It is not certain whether definite oxygen complexes are present, or whether the charge-transfer transition occurs between two adjacent molecules in the absence of complex formation (cf. Evans,[31] Mulliken [32]). General considerations, and a comparison of the solubilities of oxygen and nitrogen in organic solvents,[33] indicate that the latter view is probably correct for compounds such as the saturated hydrocarbons, and possibly even for many aromatic substances. The quantitative measurements on naphthalene described above, and those of Munck and Scott [27] on *cyclo*hexane (which were interpreted in terms of complex formation) are consistent with this.

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* This is not, however, true for anthracene.[19]

[26] Evans, *J.*, 1953, 345.

[27] Munck and Scott, *Nature*, 1956, **177**, 587.

[28] Andrews and Keefer, *J. Amer. Chem. Soc.*, 1951, **73**, 4169.

[29] Lewis, *ibid.*, 1924, **56**, 2027.

[30] Ellis and Kneser, *Z. Physik*, 1933, **86**, 583.

[31] Evans, *J. Chem. Phys.*, 1955, **23**, 1424.

[32] Mulliken, *Rec. Trav. chim.*, 1956, **75**, 845.

[33] Seidell, "Solubility of Inorganic and Metal Organic Compounds," Van Nostrand, 1940; Supplement, 1952; McKeown and Hibbard, *Analyt. Chem.*, 1956, **28**, 1490; Glendinning and Bedwell, Royal Aircraft Establishment, Chem. Rept. 477, 1951.