772. *Magnetic Perturbation of Singlet–Triplet Transitions. Part II.**

By D. F. Evans.

Well-resolved singlet–triplet absorption bands have been observed with benzene and fluorobenzene vapours in the presence of high pressures of oxygen. The 0,0 band is relatively intense for benzene, although the transition is forbidden on symmetry grounds; an explanation is given.

The triplet level of pyridine in 2 : 2 : 4-trimethylpentane solution has been located at 29,650 ± 100 cm.$^{-1}$ (3·68 ev) by perturbation with oxygen under pressure, in excellent agreement with a recent theoretical value of 3·72$_3$ ev. The very small solvent shifts obtained with chloroform and ethyl alcohol indicate that the transition involved is π–π, and not n–π.

The weak absorption maxima of thiophen reported around 3150 Å, and provisionally assigned to a singlet–triplet transition, is almost certainly spurious.

Nitric oxide also perturbs the singlet–triplet bands of (liquid) benzene in a similar manner to oxygen. This agrees with the explanation previously given for the effect of oxygen.

Dissolved oxygen strongly induces the single–triplet transitions of aromatic molecules.[1, 2] This provides a useful method for locating their triplet levels. Further results are now reported. As the effect of oxygen was attributed to its paramagnetic nature, the spectrum of another simple paramagnetic molecule, nitric oxide, has been investigated in benzene.

Experimental

Apparatus.—A Unicam S.P. 500 spectrophotometer, normally fitted with the 10 cm. cell housing, was used. A quartz lens was necessary to focus the light beam when using a 50 cm. cell.

The high-pressure cell (built by Research and Industrial Instruments Co., London) is an improved version of that previously described.[2] Made of stainless steel, it has two fused silica windows (1 cm. thick) bolted between polytetrafluoroethylene gaskets. Its effective path length is 5·2 cm. The cell is connected, *via* an Ermeto coupling, to a stainless steel needle valve, and the whole assembly fits into the 10 cm. Unicam S.P. 500 (or Beckman DU) cell housings. The measurements on pyridine solutions were carried out as described previously.[2] The absorption of oxygen dissolved in the pure solvents was small.

In order to study perturbation in the gas phase, a drop of benzene or fluorobenzene was placed in the bottom of the high-pressure cell, and the spectra measured after equilibrium had been attained in the cell housing (care being taken to ensure that liquid had not condensed on the cell windows). The absorption of both benzene (or fluorobenzene) vapour and oxygen separately was found to be very small over the wavelength region studied. Measurements were also made with a known concentration of benzene vapour (in the absence of any liquid phase) by connecting the evacuated cell to a tube of benzene at a known temperature. The valve was closed, the cell removed, and after the blank absorption had been obtained, oxygen at a known pressure was allowed in. The inward rush of gas prevented appreciable back-diffusion of the benzene vapour.

The apparatus used for the nitric oxide experiment is shown in Fig. 1. A stream of oxygen-free nitrogen (chromous chloride bubblers) was passed successively through saturated sodium hydroxide solution, sodium hydroxide pellets, a trap maintained at about −130°, and a bubbler containing pure benzene. It was finally passed through the cell, which was frequently shaken, until all the oxygen present had been removed. The (small) absorption of the deoxygenated benzene was then measured in the region 2900—3700 Å. After again being flushed with

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* Part I is regarded as the paper by Evans, *J.*, 1957, 1351.

[1] Evans, *Nature*, 1956, **178**, 534.

[2] Evans, *J.*, 1957, 1351.

nitrogen, the benzene was saturated with nitric oxide from a cylinder (Matheson Co. Inc.) and purified as above, and its absorption remeasured. By subtraction the spectrum resulting from the effect of the dissolved nitric oxide was obtained. Finally, nitrogen was once more passed through the cell to ensure that the additional absorption disappeared on removal of the nitric oxide. No absorption was observed with gaseous nitric oxide at 1 atmosphere (0·042M).

Materials.—Benzene was shaken several times with concentrated sulphuric acid, washed, dried, and repeatedly fractionally frozen to a constant freezing point of 5·54 ± 0·05°. It was finally fractionally distilled through a 1 m. column packed with glass helices (reflux ratio ≏ 20 : 1). Fluorobenzene was fractionally distilled. Pyridine was treated with a slight excess of dilute sulphuric acid, and the non-basic impurities distilled off.[3] The pyridine was liberated with alkali, fractionally distilled as the azeotrope with water through the 1 m. column to remove pyrazine,[4] dried, and again distilled. Thiophen was purified *via* the mercuric acetate derivative [5] and finally fractionally distilled.

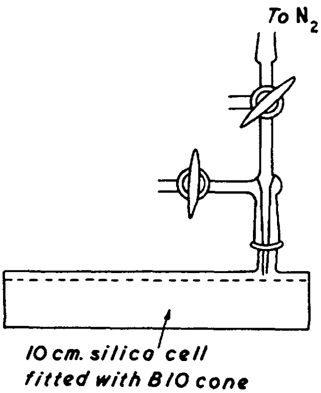

FIG. 1. *Light-absorption cell.*

RESULTS AND DISCUSSION

Singlet–Triplet Transitions in the Gas Phase.—The singlet–triplet bands of benzene perturbed by oxygen can be observed in a 5 cm. length of liquid benzene saturated with oxygen at *ca.* 0·2 atm.[1, 2] It was therefore thought that they might also be found with benzene (and fluorobenzene) vapour in the presence of oxygen at high pressure, and the results obtained in this way are shown in Fig. 2. The concentration of benzene and fluorobenzene in the vapour phase was considerably increased by the high pressure of oxygen. The bands were also observed with benzene vapour at *ca.* 70 mm. pressure (in the absence of any liquid phase), and oxygen at *ca.* 100 atm., but were much weaker (maximum optical density *ca.* 0·01).

As expected, the bands are much better resolved than with liquid benzene or fluorobenzene, partly because the background absorption [2] is shifted to considerably shorter wavelengths. This is another argument in favour of the assignment of this more intense background absorption to a charge-transfer transition, since such transitions are considerably shifted by solvents.[6] Although there will be very considerable pressure broadening of the bands by the high pressure of oxygen, any perturbation of the energy levels will be small since the refractive index of oxygen at 130 atm. around 3300 Å is only 1·035.[7] The close agreement between the positions of the bands in the gaseous and the liquid phase further illustrates the insensitivity of singlet–triplet transition energies to the external conditions (see Table). The longest-wavelength absorption band of benzene is of comparatively high intensity, even in the vapour phase. There can be little doubt that this band is the 0,0 band. The close agreement between its position and that of the

Triplet levels ($cm.^{-1}$).

	Vapour	Liquid	Low-temp. glass
Benzene	29,510	29,440 [2] (29,400,[8] 29,410 [9])	29,470,[10] 29,515 [11]
Fluorobenzene	29,530	29,500 [2]	—

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[3] Biddiscombe, Coulson, Handley, and Herington, *J.*, 1954, 1957.
[4] Brealey, *J. Chem. Phys.*, 1956, **24**, 571.
[5] Dimroth, *Ber.*, 1899, **32**, 758.
[6] Ham, *J. Amer. Chem. Soc.*, 1954, **76**, 3881.
[7] International Critical Tables, McGraw-Hill Book Company, Inc., New York, 1928, Vol. 7, p. 8.
[8] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994.
[9] Pitts, *J. Chem. Phys.*, 1950, **18**, 1416.
[10] Shull, *J. Chem. Phys.*, 1949, **17**, 295.
[11] Dikun and Sveshnikov, *Doklady Akad. Nauk S.S.S.R.*, 1949, **65**, 637.

shortest-wavelength phosphorescence band can hardly be coincidental, since a similar state of affairs is also found with other aromatic hydrocarbons.[2] Although there has been controversy as to the symmetry of the lowest triplet level of benzene, it is almost certainly either $^3B_{1u}$ or $^3B_{2u}$ (probably the former).[10, 12, 13, 14] On either assignment the singlet–triplet transition is forbidden on symmetry grounds, and hence the 0,0 band should be missing.* (Transitions can, however, occur together with a one-quantum change of an E_g vibration, as in the well-known 2600 Å system of benzene.[15]) Since the 0,0 band is relatively just as intense in the vapour phase as in liquid benzene, its appearance cannot be due to solvent perturbation, and the most likely explanation is that it occurs as a result of the reduction in symmetry of the system caused by the perturbing oxygen molecule. The very close agreement between the results for benzene and for fluorobenzene agrees with this, since the 0,0 band is allowed with fluorobenzene.

FIG. 2.

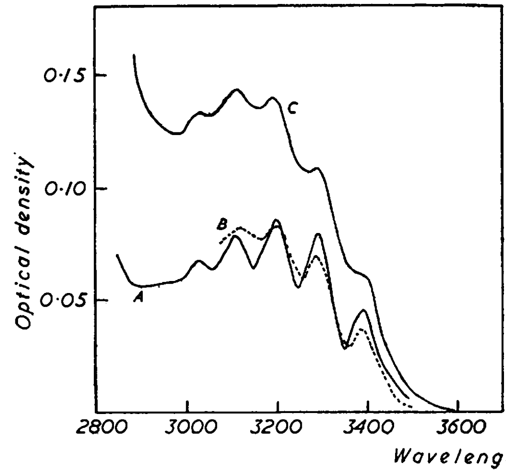

FIG. 3.

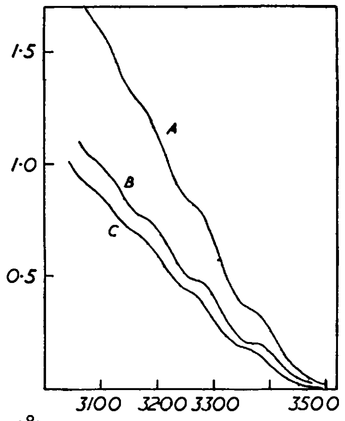

FIG. 2. *Absorption spectra.*

A, Benzene vapour in presence of oxygen at high pressure in the 5·2 cm. cell at *ca.* 20° and 130 atm. of oxygen. Max. at 29,510, 30,420, 31,300, 32,110, and 32,980 cm.$^{-1}$.

B, Fluorobenzene vapour in presence of oxygen at high pressure in the 5·2 cm. cell at *ca.* 22° and 140 atm. of oxygen. Max. at 29,530, 30,420, 31,270, and 32,080 cm.$^{-1}$.

C, Nitric oxide dissolved in benzene at 0·89 atm. (*ca.* 0·012M) in the 10 cm. cell. Max. at 29,450, 30,400, 31,300, 32,150, and 33,050 cm.$^{-1}$.

FIG. 3. *Absorption of oxygen in pyridine solutions in the* 5·2 *cm. cell.*

A, 1·1M-Pyridine in chloroform, oxygen pressure *ca.* 135 atm.

B, 0·50M-Pyridine in 2 : 2 : 4-trimethylpentane, oxygen pressure *ca.* 90 atm.

C, 0·60M-Pyridine in ethyl alcohol, oxygen pressure *ca.* 135 atm.

If the above interpretation is correct, the *unperturbed* singlet–triplet bands of benzene should differ markedly from those obtained in the presence of oxygen or nitric oxide. (This will not, in general, be so for other aromatic hydrocarbons such as naphthalene.) An unsuccessful attempt was made to detect these unperturbed bands by using a 50-cm. path of deoxygenated benzene, and they are obviously excessively weak. The (corrected) lifetime of the benzene triplet level obtained from phosphorescence data is 21 sec.,[16] but the

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* Although the 0,0 band appears in the phosphorescence spectrum it is extremely weak.[10, 11] This indicates that any atmospheric oxygen in the frozen glasses does not appreciably perturb the triplet–singlet transition, probably owing, at least in part, to the absence of molecular collisions. The unexpected character of the singlet–triplet absorption bands of benzene was commented on by Craig.[14]

[12] Craig, *J. Chem. Phys.*, 1950, **18**, 236.

[13] Pariser, *J. Chem. Phys.*, 1956, **24**, 250.

[14] Craig, *Rev. Pure Appl. Chem.*, 1953, **3**, 207.

[15] Sponer, Nordheim, Sklar, and Teller, *J. Chem. Phys.*, 1939, **7**, 207.

[16] Gilmore, Gibson, and McClure, *J. Chem. Phys.*, 1955, **23**, 399.

derivation of this value involves considerable uncertainties. A recent theoretical calculation[17] predicts a lifetime of 260 sec. for a $^3B_{2u}$ level, and 2100 sec. for a $^3B_{1u}$ level.

Triplet Level of Pyridine.—Brealey[4] has recently shown the singlet–triplet absorption and emission bands previously reported[18] for pyridine are actually due to pyrazine present as an impurity. Since this leaves the lowest triplet level of pyridine unassigned, the problem has been investigated by the oxygen perturbation method. The results for pyridine dissolved in three different solvents are shown in Fig. 3. Absorption bands very similar to those observed with benzene are obtained. The longest-wavelength band is at 29,650 ± 100 cm.$^{-1}$ (2 : 2 : 4-trimethylpentane solution), and hence the lowest triplet level of pyridine is located at 3·68 ev, in excellent agreement with a recent theoretical value of $3{\cdot}72_3$ ev,[19] and very different from the previous erroneous value of 3·25 ev.

The very small solvent shifts found with chloroform and ethyl alcohol indicate that the singlet–triplet transition is π–π and not n–π. (This method of distinguishing between the two types of transition is now well established for singlet–singlet transitions.[20]) In agreement with this, the vibrational spacing of the bands (~900 cm.$^{-1}$) is very similar to that found with benzene.

Another molecule which is very similar in many respects to benzene is thiophen. No triplet bands could be detected down to about 2700 Å with the technique used for pyridine, although they were possibly obscured by the strong charge-transfer absorption observed at short wavelengths. Padhye and Desai[21] studied the absorption spectrum of thiophen in hexane and observed a weak maximum ($\varepsilon = 0{\cdot}048$), having two peaks at 3130 Å and 3180 Å, which was provisionally assigned to a singlet–triplet transition. However, our thiophen showed no such bands in 2 : 2 : 4-trimethylpentane solution, and the very weak absorption obtained (which may be partly due to impurities) was an order of magnitude less than that found by the Indian workers ($\varepsilon_{3150} = 0{\cdot}0035$). There thus seems to be no evidence for a singlet–triplet transition of thiophen in this region. This further illustrates the difficulties involved in observing *unperturbed* singlet–triplet absorption bands.

Nitric Oxide Perturbation.—The absorption spectrum of nitric oxide dissolved in benzene is shown in Fig. 2. The well-defined maxima occur at wavelengths almost exactly the same (within experimental error) as those previously observed with oxygen.[2, 8, 9] There can thus be little doubt that they are, in fact, due to a magnetically perturbed singlet–triplet transition of the benzene molecule. More bands are observed than with oxygen (although the intensity is less), since the background (non-triplet) absorption[2] is shifted to considerably shorter wavelengths.

Ross and Kasha[22] originally studied the ultraviolet absorption of nitric oxide in dimethylaniline and anisole. The absorption tails observed in the region 3000—4000 Å were regarded as arising from a perturbed singlet–triplet transition. However, it seems much more likely that these spectra, like the *strong* absorption with oxygen, are actually charge-transfer spectra, on the basis of the comparatively very high intensity, lack of fine structure which can be correlated with known triplet levels, and similarity to the spectra obtained with acceptor molecules such as sulphur dioxide, trinitrobenzene, and iodine.[23] In other words, oxygen and nitric oxide have a dual function, being both paramagnetic and electron accepting.

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[17] Hameka, Thesis, Leiden, 1956.

[18] Reid, *J. Chem. Phys.*, 1950, **18**, 1673; Kasha and Reid, unpublished work.

[19] McWeeny and Peacock, *Proc. Phys. Soc.*, 1957, **70**, *A*, 41; personal communication from Dr. McWeeny.

[20] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14; Halverson and Hirt, *J. Chem. Phys.*, 1951, **19**, 711; Stephenson, *ibid.*, 1954, **22**, 1077.

[21] Padhye and Desai, *Proc. Phys. Soc.*, 1952, **65**, *A*, 298.

[22] Ross and Kasha, unpublished work.

[23] Orgel, *Quart. Reviews*, 1954, **8**, 422.