

A COMPARATIVE STUDY OF SINGLET → TRIPLET ABSORPTION IN SOME HALOGENATED TOLUENES IN THE VAPOUR AND LIQUID STATES*

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ABSTRACT. The absorption spectra in the near ultraviolet region due to singlet → triplet transition in the vapours of *o*-chlorotoluene, *p*-chlorotoluene, *m*-bromotoluene and *p*-bromotoluene at 24°C have been investigated using a path length of 18.9 metres at the respective saturation vapour pressures and these spectra have been compared with those for the equivalent path lengths of the liquids. It has been observed that the absorption due to singlet → triplet transition is of continuous nature and the long wavelength limit of maximum absorption in the liquid state is found to be at about 29000 cm⁻¹ for all the compounds, but in the case of the vapours the limit is shifted towards higher frequencies, the shift being smaller for the *para* compounds than for the *ortho* or *meta* compounds. It has been concluded that singlet → triplet transition is enhanced by the influence of heavy atoms of the surrounding molecules in the liquid state.

INTRODUCTION

Kasha (1952) reported that the very weak singlet → triplet absorption bands of α -chloronaphthalene is strengthened considerably in solution in ethyliodide, and he attributed this to an intermolecular spin-orbit perturbation due to the heavy iodine atom (*Z*-effect). Later, McClure *et al.* (1954) also observed the *Z*-effect in singlet → triplet absorption bands of halogen substituted benzenes and naphthalenes and put forward a simple theory to explain it. The dependence of intensity of continuous absorption due to singlet → triplet transition on the atomic number of the substituent atoms in the case of some halogenated toluenes in the liquid state was also studied by Roy (1960).

It was first shown by Evans (1956) that the discrete absorption bands around 3300 Å observed by previous workers in the spectra due to long absorption path of liquid benzene disappear when the dissolved atmospheric oxygen is removed from the liquid. He next studied (Evans, 1957a) the absorption spectra of solutions of benzene, fluorobenzene, diphenyl, styrene and fluorene in chloroform

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saturated with oxygen gas at high pressures and observed some discrete bands due to singlet→triplet absorption in most of the cases. He further observed that in the case of solution of α -bromonaphthalene there was only continuous absorption in the region 4000 Å—5000 Å, but when the solution was saturated with oxygen gas at a pressure of 76 atmospheres sharp bands appeared in this region without appreciable rise in the absorption coefficient. On the other hand, he observed that when a 0.9M solution of naphthalene in chloroform was saturated with oxygen gas at different pressures up to 100 atmospheres, the absorption coefficient increased proportionately with the increase in the pressure of the gas.

Robertson and Reynolds (1958) carried out an interesting experiment to prove the correctness of the theory of probability of singlet→triplet transition put forward by McClure (1949, 1952) and by Mizushima and Koide (1952). Kasha (1952) had suggested that the probability of singlet→triplet transition is enhanced when the molecules are surrounded by heavy atoms owing to the perturbation of the spin-orbital coupling by the heavy atoms. Since the spin-orbital coupling operator depends on the inverse third power of the distance between the π -electron and the heavy atom, Kasha (1952) suggested that hydrostatic pressure would increase the perturbation. Robertson and Reynolds (1958) subjected a mixture of α -chloronaphthalene and ethyl iodide to pressures ranging from 1 to 3644 atmospheres and observed that there was a two-fold increase in the singlet→triplet absorption with the increase of pressure mentioned above. In the case of pure α -chloronaphthalene, however, the singlet→triplet absorption was much weaker and no such pressure effect was observed.

The perturbation of the spin-orbital coupling by the magnetic field of surrounding paramagnetic molecules in the gaseous state was first observed by Evans (1957b). He introduced in the absorption cell containing vapours of either benzene or fluorobenzene at a pressure of 70 mm of Hg oxygen gas at pressures up to 130 atmospheres and observed intense absorption bands in the region 3000 Å—3400 Å. The influence of neighbouring molecules of the same kind on such singlet→triplet absorption was, however, not known and it was recently investigated by Sirkar and Roy (1960) using long absorbing paths of the vapour. It was observed by them that benzene vapour at a pressure of 120 mm and with path length 18.90 metres shows only very feeble continuous absorption in the region 3000 Å—3400 Å and an equivalent path length of liquid benzene shows very slightly stronger absorption in this region. In the case of *o*-bromotoluene vapour with similar path length, however, the continuous absorption in the region 3400 Å—3600 Å was observed to be much stronger and it increased considerably when an equivalent path length of the liquid was used. These results show that the spin-orbital coupling of the π -electron is perturbed by heavy atoms in surrounding molecules of the same kind. In order to find out whether such a general conclusion can be drawn from these results, the investigations have been extended

A Comparative Study of Singlet→Triplet Absorption, etc. 145

to a few other substituted benzene compounds and the results have been discussed in the present paper.

EXPERIMENTAL

The substances selected for studying the absorption spectra due to singlet→triplet transition in the present investigation are orthochlorotoluene, parachlorotoluene, matabromotoluene and parabromotoluene. Chemically pure samples of *o*-chlorotoluene and *p*-chlorotoluene obtained from British Drug House, England, *p*-bromotoluene obtained from Fisher Scientific Company, U.S.A. and *m*-bromotoluene from City Chemical Corporation, New York, U.S.A. were distilled several times under reduced pressure before being used in the investigation.

The experimental arrangement was the same as that employed in an earlier investigation (Sirkar and Roy, 1960). The absorption spectra of the substances in the vapour state were photographed first by filling up the absorption cell, 18.90 metres long, with the vapours of the compounds at the saturation pressures at about 24°C. The pressure was measured carefully with a differential manometer and the short empty cell for the liquid was also placed in the path of light in order to take into account the loss of incident light during its passage through this empty cell. The pressure was found to be about 55 mm for the bromotoluenes and about 50mm for the chlorotoluenes. After photographing the absorption spectrum of the vapour of each of the compounds the long vapour cell was evacuated and the short cell of length 7 mm for the bromo compounds and 6.5 mm for the chloro-compounds was filled with the distilled liquid and the absorption spectrum of the liquid was photographed on the same film with the same time of exposure and under identical conditions. In order to test the genuineness of the absorption observed in case of the substances in the vapour state with a path length of 18.90 metres, the absorption spectra were also studied for shorter path lengths. Using a path length of 9.45 metres, the absorption spectrum of *p*-bromotoluene in the vapour state was, therefore, photographed and compared with the spectrum for a path length of 3.5 mm of the liquid. A Hilger medium quartz spectrograph and Agfa Isopan films were used to photograph the spectra. The time of exposure was about 10 hours in every case. Iron arc spectrum was photographed in each spectrogram as comparison. Microphotometric records of the spectrograms were obtained with a self-recording microphotometer supplied by Kipp and Zonen. The wavelengths in the continuous absorption spectra were measured by drawing a sharp line on the film in the position of a known iron line in the adjacent iron arc spectrum and comparing the microphotometric records of the iron arc and absorption spectra.

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra due to pure metabromotoluene and parabromotoluene in the liquid and vapour states are repro-

duced in Figs. 1(a)—1(d), respectively, and the absorption spectra due to pure orthochlorotoluene and parachlorotoluene in the liquid and vapour states are reproduced in Figs. 2(a)—2(d), respectively. Figs. 3(b) and 3(a) show the spectra due to path lengths of 9.45 metres of *p*-bromotoluene in the vapour state and 3.5 mm of the liquid respectively. The reference line in the records has the wavelength 4051 Å.

4051 Å

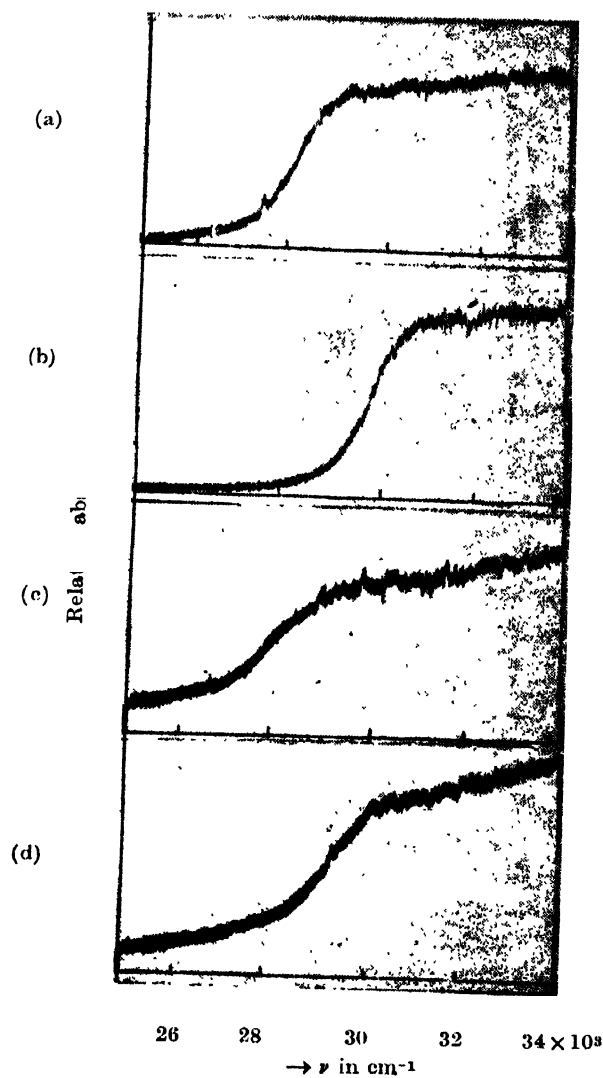


Fig. 1. (a) *m*-Bromotoluene (liquid);
 (b) " (vapour)
 (c) *p*-Bromotoluene (liquid)
 (d) " (vapour)

A Comparative Study of Singlet→Triplet Absorption, etc. 147

The microphotometric records of the absorption spectra reproduced in Figs. 1 and 2 show that in the cases of all the four compounds the absorption spectrum due to the liquid is displaced towards red with respect to that due to the vapour phase. This shift is however, different for the different compounds.

4051 Å

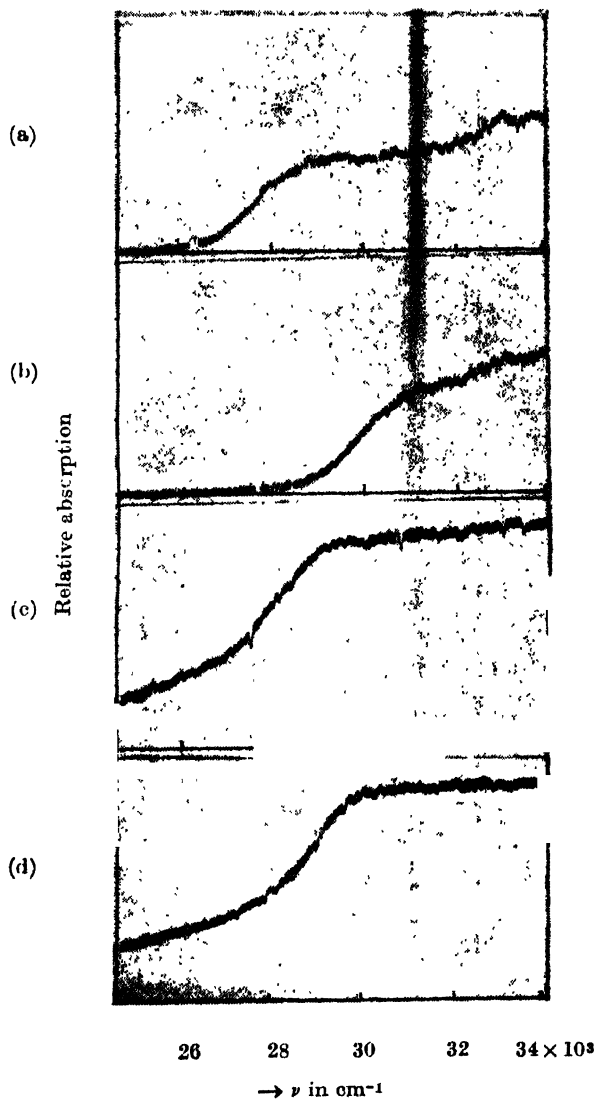


Fig. 2. (a) *o*-Chlorotoluene (liquid)
(b) " (vapour)
(c) *p*-Chlorotoluene (liquid)
(d) " (vapour)

A comparison of the curves in Fig. 1 shows that the spectrum due to the parachlorotoluene in the vapour state is shifted towards red by about 1000 cm^{-1} with respect to that due to the ortho compound in the vapour state. Similarly, Fig. 2, shows that the spectrum due to *p*-bromotoluene in the vapour state is shifted towards red by about 500 cm^{-1} with respect to that due to the meta compound. When the vapours are liquefied there is further shift of the spectrum towards red, but although in the case of *o*-chlorotoluene the position of maximum absorption on the long wavelength side shifts from 31000 cm^{-1} to 29000 cm^{-1} with the liquefaction of the vapour, such shift is from 29600 cm^{-1} to 29000 cm^{-1} in the case of *p*-chlorotoluene. In the case of *p*-bromotoluene, on the other hand, such shift is from 30000 cm^{-1} to 29000 cm^{-1} and in the case of *m*-bromotoluene the shift is a little more, being from 30500 cm^{-1} to 29000 cm^{-1} . As the 0,0 band due to singlet→singlet transition occurs in the neighbourhood of 36000 cm^{-1} (Roy, 1956) in all these cases, the absorption in the region of 30000 cm^{-1} cannot

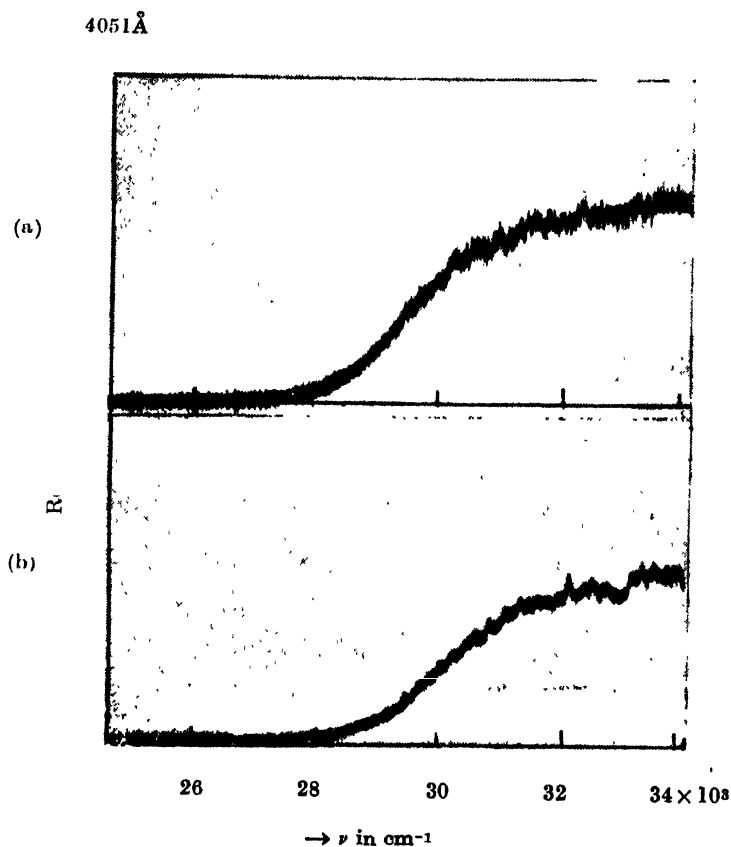


Fig. 3. (a) *p*-Bromotoluene (liquid)
(b) (vapour)

A Comparative Study of Singlet→Triplet Absorption, etc. 149

be due to an extension of the singlet→singlet absorption towards longer wavelengths, and therefore, it is due to singlet→triplet transition. A comparison of Fig. 1(d) with Fig. 3(b), further shows that when the path length of the vapour is halved, the absorption in the region from 30000 cm^{-1} to 31000 cm^{-1} diminishes considerably. This shows the genuineness of the absorption due to the longer path of the vapour.

It is evident from the above results that probability of such transition is enhanced much more in the case of ortho or meta halogen substituted toluenes than in the case of the para compounds, when the vapours are liquefied. It is to be pointed out further, that the wavelength limit of maximum absorption in the liquid state is almost at the same position (about 29000 cm^{-1}) in all the four cases. It is evident from these results that the enhancement of singlet→triplet absorption with the liquefaction of the vapour is due to the influence of the substituent halogen atoms in the surrounding molecules in the liquid state, because in the case of benzene such enhancement is extremely small (Sirkar and Roy, 1960). The difference observed in the case of the para compound and that in the case of ortho or meta compound can be explained on the hypothesis that as in the case of the para compound the halogen atom is far away from the CH_3 group it acts as a better shield against the interaction between the π -electrons of the ring and the halogen atom of the neighbouring molecule than in the case of the ortho or meta compound. In the ortho compound, the π -electrons in consecutive four carbon atoms being exposed to the influence of the halogen atom in the neighbouring molecule, there may be greater chance of the perturbation of the spin-orbital coupling than in the case of the para compound.

It can be seen from the curves in Figs. 1 and 2 that the absorption spectrum due to singlet→triplet transition is of continuous nature. As mentioned earlier, some previous workers observed discrete bands due to singlet→triplet transition induced by the influence of paramagnetic molecules on the π -electrons. It is highly probable that some preferentially orientated magnetic field due to the paramagnetic molecules produces such quantised new levels of the π -electrons while in the field of surrounding heavy atoms, such field has only random orientation giving rise to very broad perturbed levels.

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