# **840.** *Absorption and Emission Spectra of Aromatic Radicals. Part I. Absorption and Emission Spectrum of the Benzyl Radical in the Visible Region.*

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The V-spectrum from a toluene discharge has been re-examined under more vigorous conditions with a view to obtaining the vibrational frequencies ($\omega'$) of the excited state. A comparative vibrational frequency analysis has been made of the $\omega'$-values of the radicals from toluene and $\alpha\alpha\alpha$-trideuterotoluene discharges, and six corresponding $\omega'$-values have been determined. These six values of the radical from the toluene discharge have been employed to interpret the visible-absorption spectrum of the benzyl radical at −196°, thus establishing a common upper electronic state of the absorber and the emitter. The work shows that the benzyl radical is the V-spectrum emitter. In addition, it establishes that the furthermost red band of the absorption system is the (O,O)-band.

Several investigations[1] have been made with a view to identifying the emitter of a band system in the 4400—5000 Å region (known as the V-spectrum) which results from the decomposition of certain monosubstituted benzene derivatives in a discharge at low current

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[1] Marsh, McVicker, and Stewart, *J.*, 1924, 1743; Schüler and Reinebeck, *Z. Naturforsch.*, 1949, **4a**, 577; Schüler, Reinebeck, and Köberle, *ibid.*, 1952, **7a**, 421, 428; Schüler and Michel, *ibid.*, 1955, **10a**, 439; Walker and Barrow, *Trans. Faraday Soc.*, 1954, **50**, 541.

density. Schüler and Stockburger [2] identified the benzyl radical in such a discharge by means of its absorption spectrum from the ground state to the second excited electronic state. The absorption frequencies corresponded with those obtained by Porter and Wright [3] for the benzyl radical in a flash-photolysis approach. Although this left no doubt as to the presence of the benzyl radical in such a discharge, it did not prove that this radical was the emitter of the V-spectrum since Schüler and Degenhart [4] obtained a variety of products from these discharges.

Bindley and Walker,[5] from a discharge study of monoalkyl benzenes, identified the benzyl radical as the V-spectrum emitter. This was based on the isotopic shift obtained from the radicals from $C_6H_5{\cdot}CD_3$ compared with $C_6H_5{\cdot}CH_3$ and an empirical approach which depended on the sensitivity of the 6a mode vibrational frequency to the mass of the alkyl substituent.

Porter and Strachan [6] obtained the absorption spectrum, in the visible region, of the benzyl radical trapped in a rigid matrix. This consisted of seven bands extending from 4220 to 4635 Å. As they pointed out, there is some uncertainty as to whether the furthermost red band (4635 Å) or the nearest adjacent band at 4527 Å is here the (O,O)-band. The (O,O)-band of the V-spectrum emitter is at 4477 Å. In solutions a shift of 50 Å is the order of the normal solvent effect.

The present work has as objectives to obtain a more secure identification of the V-spectrum emitter and to determine whether the furthermost red band in the visible-absorption spectrum of the benzyl radical is the (O,O)-band. This information is required for analysis of the absorption spectra of aromatic radicals (see Part II).

## EXPERIMENTAL AND RESULTS

Toluene was purified by shaking it with several batches of sulphuric acid (*d* 1·84) until no darkening occurred. After traces of acid had been neutralised the toluene was washed with distilled water, dried (KOH), refluxed over sodium, and fractionally distilled. Trideuterotoluene was purchased from the Volk Radio-Chemical Co., Chicago, and was, at least, 98% pure.

The vapour of the compound, under very low pressure, was allowed to flow along a horizontal glass tube (about 4 cm. in diameter) round which were wrapped two external copper-foil electrodes, connected to a radio-frequency oscillator working at ~6 Mc./sec. and maximum power. The vapour was drawn from a container through an inlet tap by an Edwards oil diffusion pump backed by a rotary oil pump, and condensed by a liquid-nitrogen trap in front of the former pump. Spectra were recorded by means of an F/4 spectrograph with glass optics. For wavelength calibration iron arc lines were superposed, and the wavelengths were determined from two microdensitometer traces. Band maxima are recorded in the Tables. The relative intensities were obtained mainly by visual estimation on a 1 : 10 scale.

*Results.*—The emission bands to the red side of the (O,O)-band for the radicals from toluene and trideuterotoluene have been reported and a vibrational analysis carried out.[5] By the use of more vigorous discharge conditions additional bands on the violet side were obtained.

In addition, since a higher-powered discharge was used, the possibility that some of the bands to the violet side of the (O,O)-band were due to an impurity or a further decomposition product was increased. To minimise this, trideuterotoluene was examined under similar conditions, and a comparative vibrational-frequency analysis of the bands from the resulting radicals is made in Table 1. An added advantage of such an analysis is that the fundamentals can be fixed with greater certainty.

That the additional bands may be attributed to the same emitter as those to the red of the (O,O)-band and to the same band system is confirmed by the vibrational analyses of the radicals in Table 1 and the reasonable correspondence of the $\omega'$- and $\omega''$-values of these radicals with

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[2] Schüler and Stockburger, *Spectrochim. Acta*, 1959, **13**, 841.
[3] Porter and Wright, *Trans. Faraday Soc.*, 1955, **51**, 1469.
[4] Schüler and Degenhart, *Z. Naturforsch.*, 1952, **7a**, 753.
[5] Bindley and Walker, *Trans. Faraday Soc.*, 1962, **58**, 217.
[6] Porter and Strachan, *Spectrochim. Acta*, 1958, **12**, 299.

TABLE 1.

Comparative vibrational frequency assignments for the radicals from toluene and trideuterotoluene based on (O,O)-values of 22324 and 22300 cm.$^{-1}$ (vac.), respectively, of intensity 10. Only the bands to the violet side of the (O,O)-band are taken into account.

| Radical from toluene | | | Radical from trideuterotoluene | | |
|---|---|---|---|---|---|
| Displacement from (O,O) | Intensity | Assignment * | Displacement from (O,O) | Intensity | Assignment * |
| 55 | 8 | 0 + 55 | 50 | 8 | 0 + 50 |
| 111 | 6 | 0 + 711 − 610(+10)<br>0 + 111? | 91 | 5 | 0 + 711 − 614(−6)<br>0 + 91? |
| 141 | 1 | 0 + 141 | 150 | 1 | 0 + 150 |
| 222 | 2 | 0 + 222 | 236 | 1 | 0 + 236 |
| 288 | 4 | 0 + 288 | 274 | 2 | 0 + 274 |
| 438 | 2 | 0 + 288 + 141(+9)<br>0 + 222 + 2 × 111(−6) | 420 | 1 | 0 + 274 + 150(−4)<br>0 + 236 + 2 × 91(+2) |
| 459 | 1 | 0 + 459 | 458 | 3 | 0 + 455(+3) |
| 505 | 1 | 0 + 503(+2) | 502 | 1 | 0 + 502 |
| 558 | 4 | 0 + 503 + 55(0) | 552 | 2 | 0 + 502 + 50(0) |
| 595 | 1 | 0 + 459 + 141(−5)<br>0 + 933 − 333(−5) | 599 | 1 | 0 + 455 + 150(−6)<br>0 + 930 − 330(−1) |
| 663 | 3 | 0 + 459 + 141 + 55(+8) | 662 | 1 | 0 + 445 + 150 + 50(+7) |
| 711 | 2 | 0 + 711 | 711 | 1 | 0 + 711 |
| 780 | 4 | 0 + 503 + 2 × 141(−5)<br>0 + 1177 − 386(−11) | 806 | 2 | 0 + 502 + 2 × 150(+4)<br>0 + 1187 − 386(+5) |
| 936 | 1 | 0 + 933(+3) | 930 | 2 | 0 + 930 |
| 1001 | 1 | 0 + 711 + 288(+2) | 986 | 2 | 0 + 711 + 274(+1) |
| 1131 | 2 | 0 + 933 + 141 + 55(+2) | 1124 | 2 | 0 + 930 + 150 + 50(−6) |
| 1171 | 1 | 0 + 1177(−6) | 1187 | 2 | 0 + 1187 |
| 1271 | 1 | 0 + 933 + 288 + 55(−5) | 1252 | 2 | 0 + 930 + 274 + 50(−2) |
| 1305 | 1 | 0 + 711 + 459 + 141(−6) | 1308 | 2 | 0 + 711 + 455 + 150(−8) |
| 1338 | 1 | 0 + 933 + 288 + 2 × 55(+7) | 1294 | 2 | 0 + 930 + 274 + 2 × 50(−1) |
| 2048 | 1 | 0 + 2 × 1177 − 2 × 151(−4) | 2055 | 1 | 0 + 2 × 1187 − 2 × 155(−9) |
| 2084 | 1 | 0 + 2 × 933 + 222(−4) | 2091 | 1 | 0 + 2 × 930 + 236(−5) |
| 2156 | 1 | 0 + 2 × 933 + 288(+2)<br>0 + 933 + 711 + 503(+9) | 2145 | 1 | 0 + 2 × 930 + 274(+11)<br>0 + 930 + 711 + 502(+2) |
| 2222 | 3 | 0 + 1177 + 933 + 2 × 55(+2) | 2205 | 1 | 0 + 1187 + 930 + 2×50(−12) |
| 2240 | 3 | 0 + 1177 + 933 + 141(−11) | 2259 | 1 | 0 + 1187 + 930 + 150(−8) |
| 2349 | 1 | 0 + 2 × 1177(−5) | 2374 | 1 | 0 + 2 × 1187(0) |

* The figures in parentheses are the experimental minus the calculated wave-number.

TABLE 2.

Comparison of the ground- and excited-state vibrational frequencies of the radicals from toluene and trideuterotoluene obtained from the visible-emission system with those of the ultraviolet-emission system of toluene.[5,7,8] The Pitzer–Scott notation [9] has been applied to classify the toluene frequencies.

| Symmetry type | Toluene | | Radical from toluene | | Radical from trideuterotoluene | |
|---|---|---|---|---|---|---|
| | $\omega'$ | $\omega''$ | $\omega'$ | $\omega''$ | $\omega'$ | $\omega''$ |
| Symmetry $A_1$ | | | | | | |
| 1 | 932 | 1003 | 933 | 993 | 930 | 1008 |
| 7*a* | 1189 | 1212 | 1177 | 1232 | 1187 | 1210 |
| 9*a* | — | 1180 | — | 1181 | — | 1172 |
| 12 | 751 | 781 | 711 | 756 | 711 | 746 |
| Symmetry $B_1$ | | | | | | |
| 6*a* | 456 | 519 | 459 | 528 | 455 | 511 |
| 6*b* | 528 | 620 | 503 | 610 | 502 | 614 |
| 18*b* | 281 | 347 | 288 | 333 | 274 | 330 |
| Symmetry $A_2$ | | | | | | |
| 16*a* | 227 | 405 | 222 | 386 | 236 | 386 |

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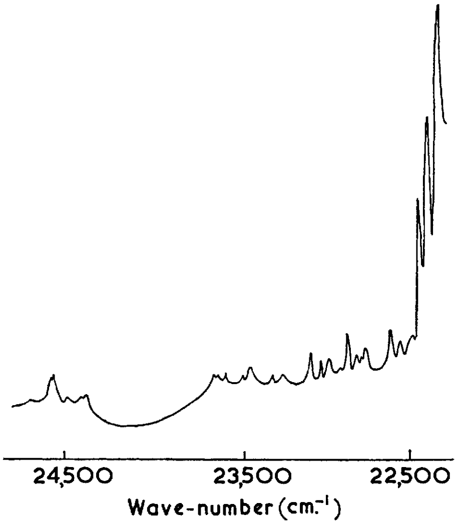
[7] Kahane-Paillous and Leach, *J. Chim. phys.*, 1958, **55**, 439.

[8] Bass, *J. Chem. Phys.*, 1950, **18**, 1403.

[9] Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803.

those from toluene for the ultraviolet system (see Table 2) which, of course, involves a higher electronic state than that of the visible-emission system of the radicals.

A microdensitometer trace for the benzyl radical of the bands to the violet side of the (O,O)-band is given in the Figure.



Microdensitometer trace of the bands to the violet side of the (O,O)-band for the radical from toluene. The 4315 Å CH band, and hydrogen bands and lines, have been deleted.

## DISCUSSION

From the comparative analysis of the radicals from toluene and trideuterotoluene the following points emerge: (i) Similar vibrational frequency assignments may be made for each species. (ii) The majority of the bands on the violet side of the (O,O)-band may be interpreted in terms of the ω'-values. The ω'-values required to interpret the radical spectra are of the same order as those of toluene. (iii) Of the six fundamental frequencies required for the analyses three of these vibrations (1, 7*a*, and 12) are total symmetric ones. Further, for each of these ω'-values a corresponding ω''-value was obtained in the analysis of the bands to the red side of the (O,O)-band (see Table 2). We shall now use the ω'-values to interpret the visible-absorption spectrum of the benzyl radical obtained by Porter and Strachan.[6] Since their work was carried out at the temperature of liquid nitrogen, it might be expected that, if their spectrum can be analysed in terms of the vibrational frequency values of the radical from toluene in Table 2, then ω' would be required. Such an analysis is carried out in Table 3, by using ω'-values required for the interpretation of the visible-emission spectrum. It may be concluded that the same radical is concerned in both the absorption and the emission system. It follows that the benzyl radical is

TABLE 3.

Vibrational analysis of the visible-absorption system of the benzyl radical based on a (O,O)-band value of 4635 Å.

| Wave-length (Å) | Wave-number displace-ment from 4635 Å | Assignment | Wave-length (Å) | Wave-number displace-ment from 4653 Å | Assignment |
|---|---|---|---|---|---|
| 4635m | 0 | (O,O)-band | 4330m | 1510 | 0 + 933 + 2 × 288(+1) |
| 4527vs | 510 | 0 + 503(+7) | | | 0 + 933 + 459 + 2 × 55(+8) |
| | | 0 + 459 + 55(−4)? | 4245w | 1970 | 0 + 2 × 933 + 2 × 55(−6) |
| 4460m | 840 | 0 + 503 + 288 + 55(−6) | | | 0 + 933 + 459 + 2 × 288(+2) |
| 4375s | 1270 | 0 + 711 + 503 + 55(+1) | 4220w | 2120 | 0 + 2 × 933 + 141 + 2 × 55(+3) |
| | | 0 + 933 + 288 + 55(−6) | | | 0 + 1177 + 933(+10) |

the emitter of the V-spectrum. In addition, it shows that the furthermost red band (at 4635 Å) of the visible absorption system is the (O,O)-band.

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