# **101.** *Excited States of Benzene. Part VII. Description and Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of 1 : 3 : 5-Trideuterobenzene.*

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The ultraviolet fluorescence spectrum of 1 : 3 : 5-trideuterobenzene is described, and measurements of the frequencies of many bands are recorded. A complete vibrational analysis of the spectrum is given. A number of fundamental frequencies of both electronic states are recognised, and are assigned to vibrations.

(1) *Measurements.*—The 1 : 3 : 5-trideuterobenzene was a sample prepared by the trideuteration of aniline and subsequent deamination (Best and Wilson, *J.*, 1946, 239; cf. Part VI, Section 1). Its fluorescence spectrum was excited in a 25-cm. column of the vapour by means of the mercury resonance line, 2537 A. We used the spiral lamp and cell described previously (Ingold and Wilson, *J.*, 1936, 941). As heretofore, dilute acetic acid was employed as filter in order to keep out light of damagingly short wave-length, and any photochemical losses were made good by circulating the vapour through the cell between two reservoirs containing the liquid or solid material. The temperatures of the reservoirs controlled both the flow-rate and the pressure in the cell. The spectrograph was the same Littrow-pattern instrument as that used for the absorption measurements (Part VI, Section 1) : it was again maintained at 20·0°, but was now focused for the region 3150—2530 A. It is necessary to provide a pressure sufficient to quench the resonance spectrum, *i.e.*, to furnish, in sufficient frequency, the collisions which are needed to take away that excess of vibrational and rotational energy, above the thermally normal amount, which the newly excited molecule contains; so that it is not in an abnormally violent state of vibration and rotation when it fluoresces. The resonance spectrum was effectively quenched when the pure vapour of 1 : 3 : 5-trideuterobenzene was employed at 25 mm. At this pressure most of the fluorescence spectrum could be recorded in exposures ranging from 10 to 40 minutes.

Special measures had to be taken in order to deal with the spectral region in which the fluorescence band-system overlaps the absorption system; for in that region most of the fluorescence light is reabsorbed under the conditions described, with the result that the record is very incomplete. This difficulty was overcome following the general procedure devised by Cuthbertson and Kistiakowsky (*J. Chem. Physics*, 1936, **4**, 9) : first, the pressure of the 1 : 3 : 5-trideuterobenzene was reduced, with the result that, although the intensity of fluorescence was correspondingly diminished, the proportion of fluorescence light which became absorbed was also reduced, and, by the use of a sufficiently low pressure, could be made unimportant; then, the diminished photographic intensity was compensated by a suitable increase of exposure; and finally, the high collision frequency needed to quench the resonance spectrum was provided by the addition, to a sufficiently high pressure, of spectrally inert gas. A pressure of 1 : 3 : 5-trideuterobenzene amounting to 0·2 mm. was found to be sufficiently low : the resultant exposures, 24—48 hours, were not prohibitively long. For the quenching we employed nitrogen, which is less efficient for this purpose than 1 : 3 : 5-trideuterobenzene itself, so that a pressure of several hundred mm. was necessary. That being so, we introduced the nitrogen at atmospheric pressure for convenience. It was passed over the solid 1 : 3 : 5-trideuterobenzene at a controlled temperature, then through the fluorescence cell, and then through a tube cooled in liquid air for the recovery of the 1 : 3 : 5-trideuterobenzene.

The iron arc was employed for the production of comparison spectra. The spectrograms were evaluated in part directly by means of the microscope, but mainly in the form of microphotometer records, as described already for the absorption spectrum (Part VI, Section 1).

The general structure of the spectrum is like that of the fluorescence spectrum of benzene or hexadeuterobenzene (Part I, Section 4 and Fig. 1, p. 409), except for certain differences. The chief of these is that, just as in the absorption spectrum of 1 : 3 : 5-trideuterobenzene the successive members of the positively-running, totally symmetrical progressions show an increasing multiplicity as the upper-state quantum numbers increase (Part VI, Sections 1 and 2), so, in the fluoresecnce spectrum of this substance, the successive members of the negatively-running, totally symmetrical progressions exhibit increasing multiplicity as the lower-state quantum numbers increase. One observes the usual growth of complexity along the sequence due to *n*—*n* transitions of the low-frequency vibration (cf. Part II, Section 1; and following Parts). On the other hand, resonance phenomena do not produce such striking effects as are found in the fluorescence spectrum of benzene (Part III, Sections 2 and 6), and in this respect the present spectrum more closely resembles that of hexadeuterobenzene.

Table I contains our measured frequencies, corrected to vacuum, and visually estimated intensities. Assignments are given in terms of a literal notation, the key to which is in Tables II and III. The letter-symbols by which the various series of bands are denoted have been made to correspond as far as possible to those used to designate the band-series of the absorption spectrum. Series A, B, C, D, H, I, J, j, L, l', M, N, Q, and v, are identical in the two spectra, except that totally symmetrical progressions run mainly in the positive direction in absorption, but mainly in the negative direction in fluorescence.

TABLE I.

*Fluorescence Spectrum of* 1 : 3 : 5-*Trideuterobenzene. Frequencies, Intensities, and Assignments* (*cf. Tables II and III*).

| Freq. (cm.$^{-1}$). | Inty. | Assgnt. | Freq. (cm.$^{-1}$). | Inty. | Assgnt. | Freq. (cm.$^{-1}$). | Inty. | Assgnt. |
|---|---|---|---|---|---|---|---|---|
| 38697·4 | ms | $A^{0}_{0}$ | 36781·1 | ms | $A^{0}_{-2}$ | 35334 | w | $B^{2}_{-1-1'}$ |
| 613·4 | mw | $C^{0}_{0}$ | 735 | w | $A^{0}_{-1-1'}$ | 316 | ww | $N^{1}_{-2}$ |
| 582 | ww | $L^{0}_{0}$ | 705·8 | mw | $C^{0}_{-2}$ | 299 | ww | $D^{2}_{-2}$ |
| 567 | ww | $B^{0}_{1'}$ | 698·0 | ww | $B^{6}_{0}$ | 245 | ww | $D^{2}_{-1-1'}$ |
| 544·6 | m | $A^{1}_{0}$ | 686·0 | ww | $A^{0}_{-2'}$ | 233·2 | w | $B^{3}_{-2}$ |
| 480·0 | mw | $B^{0}_{1}$, $M^{0}_{0}$ | 638·2 | ss | $B^{0}_{-1}$ | 223 | ww | |
| 468·0 | mw | $C^{1}_{0}$ | 586·9 | ms | $B^{0}_{-1'}$ | 184 | ww | $B^{3}_{-1-1'}$ |
| 454 | w | | 555·1 | ms | $D^{0}_{-1}$ | 166 | ww | $N^{2}_{-2}$ |
| 401·6 | w | $D^{0}_{1}$ | 502 | mw | $D^{0}_{-1}$ | 148 | ww | $D^{3}_{-2}$ |
| 394 | mw | $A^{2}_{0}$ | 487·8 | s | $B^{1}_{-1}$ | 126 | ww | $B^{3}_{-2'}$ |
| 330 | w | $B^{1}_{1}$, $M^{1}_{0}$ | 438·0 | ms | $B^{1}_{-1'}$ | 104 | ww | $X_{0}'$ |
| 323 | w | $C^{2}_{0}$ | 424 | w | $N^{0}_{-1}$ | 079 | ww | $B^{4}_{-2}$ |
| 254 | ww | $D^{1}_{1}$ | 403·7 | mw | $D^{1}_{-1}$ | 072 | ww | |
| 246 | w | $A^{3}_{0}$ | 348 | ww | $D^{1}_{-1'}$ | 036 | ww | $B^{4}_{-1-1'}$ |
| 240 | w | | 337·6 | ms | $B^{2}_{-1}$ | 016 | ww | $N^{3}_{-2}$ |
| 184 | w | $B^{2}_{1}$, $M^{2}_{0}$ | 289 | mw | $B^{2}_{-1'}$ | 011 | ww | |
| 176 | ww | | 281 | w | $N^{1}_{-1}$ | 34996 | ww | $D^{4}_{-2}$ |
| 105 | ww | $j^{0}_{0}$ | 268 | w | | 940 | ww | $X^{0}_{-1}$ |
| 036 | mw | $H^{0}_{0}$ | 252 | w | $D^{2}_{-1}$ | 933 | ww | $B^{5}_{-2}$ |
| 033 | mw | $J^{1}_{0}$ | 198 | ww | $D^{2}_{-1'}$ | 866·3 | w | $A^{0}_{-4}$ |
| 37986 | ww | l′ | 187·8 | m | $B^{3}_{-1}$ | 856 | ww | |
| 968 | w | $Q^{0}_{0}$ | 177·0 | w | | 817 | ww | $A^{0}_{-3-1'}$ |
| 957 | ww | $j^{1}_{0}$ | 142 | w | $B^{3}_{-1'}$ | 805 | ww | $V^{0}_{-1}$ |
| 937 | w | $I^{0}_{0}$ | 129 | ww | $N^{2}_{-1}$ | 792 | ww | $C^{0}_{-}$ |
| 889 | mw | $H^{1}_{0}$ | 118 | ww | | 770 | ww | $A^{0}_{-2-2'}$ |
| 879 | mw | $J^{2}_{0}$ | 101 | ww | $D^{3}_{-1}$ | 730·4 | mw | $B^{0}_{-3}$ |
| 805 | ww | $j^{2}_{0}$ | 096 | ww | | 678·0 | w | $B^{0}_{-2-1}$ |
| 800 | ww | | 051 | ww | $D^{3}_{-1'}$ | 652·0 | ww | $D^{0}_{-3}$ |
| 785 | ww | $I^{1}_{0}$ | 035 | w | $B^{4}_{-1}$ | 628 | ww | $B^{0}_{-1-2'}$ |
| 740·0 | ms | $A^{0}_{-1}$ | 023 | ww | | 597 | ww | $D^{0}_{-2-1'}$ |
| 637 | ww | $I^{2}_{0}$ | 35971 | ww | $N^{3}_{-1}$ | 578·0 | w | $B^{1}_{-3}$ |
| 590·3 | ss | $B^{0}_{0}$ | 966 | ww | | 528 | ww | $B^{1}_{-2-1'}$ |
| 507·9 | ms | $D^{0}_{0}$ | 957 | ww | $D^{4}_{-1}$ | 517 | ww | $N^{0}_{-3}$ |
| 443·5 | s | $B^{1}_{0}$ | 947 | ww | | 477 | ww | $B^{1}_{-1-2'}$ |
| 389 | w | $v^{0}_{0}$ | 894 | w | $X^{0}_{0}$ | 426·0 | w | $B^{2}_{-3}$ |
| 377·7 | mw | $N^{0}_{0}$ | 887 | ww | $B^{0}_{-1}$ | 378 | ww | $B^{2}_{-2-1}$ |
| 356·4 | m | $D^{1}_{0}$ | 877 | ww | | 366 | ww | $N^{1}_{3}$ |
| 348 | mw | | 822·6 | m | $A^{0}_{-3}$ | 349 | ww | $D^{2}_{-3}$ |
| 295·3 | ms | $B^{2}_{0}$ | 812·4 | w | | 329 | ww | $B^{2}_{-1-2'}$ |
| 284·1 | m | | 775·6 | w | $A^{0}_{-2-1'}$ | 290 | ww | $D^{2}_{-2-1'}$ |
| 236 | ww | $v^{1}_{0}$ | 759 | w | $V^{0}_{0}$ | 267·9 | w | $B^{3}_{-3}$ |
| 222·8 | mw | $N^{1}_{0}$ | 746·4 | w | $C^{0}_{-3}$ | 260·7 | ww | |
| 205·3 | mw | $D^{2}_{0}$ | 737 | ww | $B^{6}_{-1}$ | 231 | ww | $B^{3}_{-2-1'}$ |
| 146·0 | m | $B^{3}_{0}$ | 730 | ww | $A^{0}_{-1-2'}$ | 212 | ww | $B^{3}_{-2-1'}$<br>$N^{2}_{3}$ |
| 134 | mw | | 684·0 | s | $B^{0}_{-2}$ | 209 | ww | |
| 084 | ww | $v^{2}_{0}$ | 632·3 | m | $B^{0}_{-1-1'}$ | 201 | ww | $D^{3}_{-3}$ |
| 075·4 | mw | $N^{2}_{0}$ | 603·6 | mw | $D^{0}_{-2}$ | 190 | ww | |
| 057·9 | mw | $D^{3}_{0}$ | 581·5 | w | $B^{0}_{-2'}$ | 164 | ww | $B^{3}_{-1-2'}$ |
| 36996·6 | mw | $B^{4}_{0}$ | 550·0 | w | $D^{0}_{-1-1'}$ | 125 | ww | $B^{4}_{-3}$ |
| 990 | w | | 533·4 | m | $B^{1}_{-2}$ | 070 | ww | $B^{4}_{-2-1'}$ |
| 983 | w | | 483·3 | mw | $B^{1}_{-1-1'}$ | 042 | ww | $D^{4}_{-3}$ |
| 926 | mw | $N^{3}_{0}$ | 469·3 | w | $N^{0}_{-2}$ | 33981 | ww | $B^{5}_{-3}$ |
| 907 | w | $D^{4}_{0}$ | 451 | w | $D^{1}_{-2}$ | 913·6 | w | $A^{0}_{-5}$ |
| 852 | mw | $B^{5}_{0}$ | 433 | w | $B^{1}_{-2'}$ | 861·0 | ww | $A^{0}_{-4-1'}$ |
| 844 | w | | 398 | ww | $D_{-1-1'}$ | 839 | ww | $C^{0}_{-5}$ |
| 835 | w | | 383·3 | mw | $B^{2}_{-2}$ | 832 | ww | |

TABLE I—*contd.*

| Freq. (cm.$^{-1}$). | Inty. | Assgnt. | Freq. (cm.$^{-1}$). | Inty. | Assgnt. | Freq. (cm.$^{-1}$). | Inty. | Assgnt. |
|---|---|---|---|---|---|---|---|---|
| 33780·0 | w | $B^0_{-4}$ | 33542 | ww | $D^1_{-4}$ | 32960·9 | ww | $A^0_{-6}$ |
| 725·4 | w | $B^0_{-3-1'}$ | 524·6 | ww | $B^1_{-2-2'}$ | 907·9 | ww | $A^0_{-5-1'}$ |
| 702 | ww | $D^0_{-4}$ | 474·6 | ww | $B^2_{-4}$ | 833·7 | ww | $B^0_{-5}$ |
| 673 | ww | $B^0_{-2-2'}$ | 423 | ww | $B^2_{-3-1'}$ | 773 | ww | $B^0_{-4-1'}$ |
| 627·0 | w | $B^1_{-4}$ | 415 | ww | $N^1_{-4}$ | 687 | ww | $B^1_{-5}$ |
| 575·3 | ww | $B^1_{-3-1'}$ | 326 | ww | $B^3_{-4}$ | 623 | ww | $B^1_{-4-1'}$ |
| 566·7 | ww | $N^0_{-4}$ | 176 | ww | $B^4_{-4}$ | | | |

*Note :* The intensity symbols, and the numerical parts of the assignment symbols, are explained in the first Note beneath Table I of Part III, and in the Note under Table I of Part VI. The letter-symbols here used are defined in the following Tables.

TABLE II.

*Fluorescence Spectrum of* 1 : 3 : 5-*Trideuterobenzene. Key to Assignments* (*cf. Table I*).

| | Freq. (cm.$^{-1}$). | $p', p''$. | $q', q''$. | $s$. |
|---|---|---|---|---|
| A | $= 38184 + 513 - 956p'' - 1005q'' - 150s$ | 0—6 | 0—2 | 0—3 |
| B | = ,, $-594\left\{\begin{matrix}+893p' + 988q' \\ -956p'' - 1005q''\end{matrix}\right\} - 150s$ | $\left\{\begin{matrix}0, 1 \\ 0\text{—}5\end{matrix}\right.$ | 0, 1<br>0—2 | $\left.\begin{matrix} \\ \end{matrix}\right\}$ 0—6 |
| C | = ,, $+ 2 \times 513 - 594 - 956p'' - 150s$ | 0—5 | | 0—2 |
| D | = ,, $+ 513 - 2 \times 594\left\{\begin{matrix}+893p' \\ -956p'' - 1005q''\end{matrix}\right\} - 150s$ | $\left\{\begin{matrix}0, 1 \\ 0\text{—}4\end{matrix}\right.$ | 0, 1 | $\left.\begin{matrix} \\ \end{matrix}\right\}$ 0—4 |
| H | = ,, $- 594 + 2 \times 223 - 150s$ | | | 0, 1 |
| I | = ,, $+ 513 - 2 \times 373 - 150s$ | | | 0—2 |
| J | = ,, $- 150s$ | | | 1, 2 |
| j | = ,, $+ 513 - 594 - 150s$ | | | 0—2 |
| L | = ,, $- 594 + 2 \times 495$ | | | |
| l′ | = ,, $+ 513 - 710$ | | | |
| M | = ,, $+ 513 - 215 - 150s$ | | | 0—2 |
| N | = ,, $- 594 - 215 - 956p'' - 150s$ | 0—3 | | 0—3 |
| Q | = ,, $- 215$ | | | |
| V | = ,, $- 594 - 2 \times 915 - 956p''$ | 0, 1 | | |
| v | = ,, $- 594 - 200 - 150s$ | | | 0—2 |
| X | = ,, $- 2290$ | | | |
| X′ | = ,, $- 3080$ | | | |

TABLE III.

*Fluorescence Spectrum of* 1 : 3 : 5-*Trideuterobenzene. Assignment to Vibrations of the Vibration Frequencies* (*cm.*$^{-1}$) *contained in Table II.*

| Upper-state fundamental frequencies (+). | Lower-state fundamental frequencies (—). | Diffs. of upper- and lower-state fundamentals (—) | Vibration. |
|---|---|---|---|
| 593 | 956 | — | $A_1'$(C) |
| 988 | 1005 | — | $A_1'$(C′) |
| — | 915 | 200 | $A_2''$(H 2) |
| 513 | 594 | 81 | $E'$(C 1) |
| — | 2290 | — | $E'$(H 1) |
| — | 3080 | — | $E'$(H′ 1) |
| 223 | 373 | 150 | $E''$(C) |
| 495 | 710 | 215 | $E''$(H 1) |

(2) *Band Series* A, B, C, *and* D.—As usual, these four series constitute the main frame of the spectrum (Part I, Section 4). The form of development of the branching negative progression is much more immediately obvious than is that of the positive progressions of the absorption spectrum (Part VI, Section 2). One reason for this is that the progression frequencies of the electronic ground state (956 and 1005 cm.$^{-1}$), which are of main importance for fluorescence, lie closer together than do the corresponding frequencies of the excited state (893 and 988 cm.$^{-1}$), which have the same importance for absorption; and thus, in the fluorescence spectrum, the multiplets arising in the progressions are less interleaved with other systems than are the multiplets of the absorption spectrum. A second reason is that the fluorescence spectrum contains nothing corresponding to the E series of the absorption spectrum; in general, the fluorescence spectrum exhibits no particularly marked resonance effects.

These series confirm the already given values (Part VI, Section 2) for the frequency of the forbidden electronic origin, and for the frequencies of the fundamental vibrations $E'$(C 1), $A_1'$(C) and $A_1'$(C′) in both upper and lower electronic states.

(3) *Band Series* H, I, J, *and* j.—These series correspond closely to the identically named series of the absorption spectrum; and they contribute along with the absorption series to the

determination of the lower- and upper-state fundamental frequencies, 373 and 223 cm.$^{-1}$, of the vibration $E''$(C), as already noted in Part VI, Section 4.

Series H consists of a negative sequence in 150 cm.$^{-1}$, running from a band $H_0^0$, lying 446 cm.$^{-1}$ above $B_0^0$. The transitions are from the second and higher quantum levels of the $E''$ (C) vibration of the upper electronic state, two such quanta being lost, whilst an $E'$(C 1) quantum of the lower electronic state is gained. The band $I_0^0$, situated 760 cm.$^{-1}$ below $A_0^0$, the parent of series I, is assumed to involve the loss of an $E'$(C 1) quantum in the upper state, and the acquisition of two $E''$(C) quanta in the lower state. Series J consists of a sequence in 150 cm.$^{-1}$ running negatively as if from the electronic origin, except that no band in this position appears. As usual, we assume 1—1, 2—2, . . . transitions of the vibration $E''$(C). Series j is another negative sequence in 150 cm.$^{-1}$, which runs from a band $j_0^0$ situated 79 cm.$^{-1}$ below the electronic origin. Here we assume 1—1, 2—2, . . . , transitions of the vibration E''(C), superposed on 1—1 transitions of the vibration $E'$(C 1).

(4) *Band Series* L, l', M, N, *and* Q.—These series correspond closely to the identically named series of the absorption spectrum (Part VI, Section 5). They all involve an excitation of the vibration $E''$(H 1) in either or both electronic states; and they contribute, together with the absorption series, to the determination of the fundamental frequencies, 710 and 495 cm.$^{-1}$, of this vibration in the ground and excited electronic states.

The band $L_0^0$, which is found 992 cm.$^{-1}$ above $B_0^0$, is explained by the assumption of a downward 2—0 transition of this vibration, combined with a downward 0—1 transition of the vibration $E'$(C 1). The very weak band l', situated 711 cm.$^{-1}$ below $A_0^0$, is assumed to involve a downward 0—1 transition of the vibration $E''$(H 1) in association with a downward 1—0 transition of the vibration $E'$(C 1). Series M and N consist of bands negatively displaced by 215 cm.$^{-1}$ from the stronger bands of series A and B respectively. They are explained by assuming 1—1 transitions of the vibration $E''$(H 1), in combination with the electronic and vibrational transitions which characterise the bands of series A and B. The band $Q_0^0$, which lies 216 cm.$^{-1}$ below the electronic origin, is considered to arise from a 1—1 transition of the vibration $E''$(H 1) between states in which no other vibration is excited.

(5) *Band Series* V *and* v.—The progression V starts with a band $V_0^0$ lying 1831 cm.$^{-1}$ below the main active origin $B_0^0$. We interpret the interval as the first overtone of the vibration $A_2''$(H 2), the fundamental frequency of which is known, from the infra-red spectrum, to be 915 cm.$^{-1}$ (Bailey *et al.*, *J.*, 1946, 255). Thus the band $V_0^0$ is assumed to be formed in a downward 0—2 transition of this vibration, in association with a 0—1 transition of the vibration $E'$(C 1).

The series labelled v consists of a number of weak bands lying 200 cm.$^{-1}$ below some of the strongest bands of series B. The parent band, $v_0^0$, of series v is also found in the absorption spectrum. For reasons explained in Part VI, Section 7, we regard the v bands as involving 1—1 transitions of the vibration $A_2''$(H 2), in combination with the transitions of the associated B bands. The interval, 200 cm.$^{-1}$, thus represents the difference between the fundamental frequencies of this vibration in the ground and the excited electronic states.

Thus, series V and v, taken together, provide the values already quoted in Part VI, Section 7, for the fundamental frequencies of the vibration $A_2''$(H 2) in the two electronic states, *viz.*, the frequencies 915 and 715 cm.$^{-1}$.

(6) *Band Series* X *and* X'.—The hydrogen-stretching vibrations appear to be excited only very weakly in this spectrum. We might expect the excitation, in the lower electronic state, of the totally symmetrical deuterium- and protium-stretching vibrations to be signalised by bands displaced by their known fundamental frequencies below the main active origin $B_0^0$. Actually, weak bands appear very close to these positions, but they can be interpreted as belonging to other series, and are therefore so assigned.

The excitation, in the lower electronic state, of the degenerate deuterium- and protium-stretching vibrations of the class $E'$ is, however, represented by the distinct, though weak, bands of series X and X'. The bands $X_0^0$ and $X_0'$ are found 2290 and 3080 cm.$^{-1}$, respectively, below the electronic origin. We assume that they arise in transitions from the " vibrationless " level of the electronically excited state to the fundamental levels of the vibrations $E'$(H 1) and $E'$(H 1'), respectively, in the lower electronic state. The intervals 2290 and 3080 cm.$^{-1}$ are thus interpreted as the fundamental frequencies of these two vibrations. The values given by Herzfeld, Ingold, and Poole (*J.*, 1946, 332), partly on the evidence of the Raman spectrum of the liquid, and partly on that of the infra-red spectrum of the vapour, were 2292 and 3084 cm.$^{-1}$ (cf. Part VI, Section 8).

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[*Received, April* 30*th*, 1947.]