**102.** *Excited States of Benzene. Part VIII. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of 1 : 4-Dideuterobenzene.*

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The ultraviolet absorption spectrum of 1 : 4-dideuterobenzene is described, and measurements of the frequencies of many bands are recorded. A complete vibrational analysis of the spectrum is given. The isotopic loading in this molecule produces a splitting into two distinct vibrations of each of those vibrations which are degenerate in the hexagonally symmetrical benzenes. Some spectral effects of the resolved degeneracies are pointed out. Eighteen fundamental frequencies of the upper electronic state and seven of the lower state are recognised, and all are assigned to their vibrations. Part of the theoretical basis of the assignments is given, the remainder being reserved for treatment in Part XI.

(1) *Measurements.*—The 1 : 4-dideuterobenzene was prepared from *p*-dibromobenzene in two stages by treatment of Grignard derivatives with deuterium oxide (Weldon and Wilson, *J.*, 1946, 235). The absorption spectrum of its vapour in the near-ultraviolet was recorded and evaluated exactly as described for 1 : 3 : 5-trideuterobenzene (Part VI, Section 1).

We shall first notice the general characteristics of the spectrum. Broadly, it is similar to that of benzene or hexadeuterobenzene, having the same four main series, involving positive progressions and negative sequences (cf. Part I, Section 4 and Fig. 1, p. 409). The notable effect, observed with 1 : 3 : 5-trideuterobenzene, of having two strongly progression-forming frequencies which together produce a rapidly developing complexity along the progressions, is not apparent in the absorption spectrum of 1 : 4-dideuterobenzene, because this has only one strong progression-forming frequency. However, this spectrum has its own particular complications, all of which arise from the splitting into two of certain vibrations which were doubly degenerate in benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene. The effect is to produce more complicated bands, as well as more bands, though this descriptive distinction is arbitrary from the point of view of analysis. The progressions are on the whole more complicated than those of benzene and hexadeuterobenzene, but it is the sequences, rather than the progressions, along which one observes a very rapidly developing complexity.

We may describe the last-mentioned peculiarities more fully. Part of the effect arises from the circumstance that the main perturbing vibration, on which spectral activity depends, is degenerate in benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene, and becomes replaced in 1 : 4-dideuterobenzene by two similar, but distinct vibrations, whose frequencies fall apart by a few wave-numbers both in the electronic ground state and in the excited state. The result is that some of the simplest bands in the spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene become replaced by doubled bands, whilst more complicated bands have their complexity increased, in the spectrum of 1 : 4-dideuterobenzene. Thus the bands of the main progressions of series A and B in the absorption spectrum of benzene and hexadeuterobenzene are simply constituted : they involve the excitation, in one or other of the combining states, of only a single quantum of the degenerate perturbing vibration, and, otherwise, only one or more quanta of the totally symmetrical, progression-forming vibration : such bands, at our degree of resolution, appear more or less smoothly shaded to red from a single outstanding head on the short-wave side. In the absorption spectrum of 1 : 4-dideuterobenzene, each such band is replaced by two bands so strongly overlapped as to produce the appearance of a single band with two equal heads a few wave-numbers apart on the short-wave side. Fig. 1 illustrates the character described. It is merely for convenience, and particularly for the sake of reducing the total number of equations

FIG. 1.

*Reproduction of part of a microphotometric record of the absorption spectrum of 1 : 4-dideuterobenzene, showing the double-headed bands.*



$$\nu \qquad B_0^o \qquad D_0^o$$
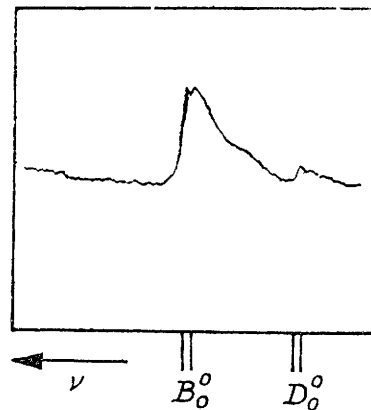
*The original record had to be rephotographed and intensified several times in order to obtain a line thick enough for the preparation of a block. The very fine line of the original record resolved the band heads much more clearly than does the reproduction. The region depicted runs from about 37430 cm.$^{-1}$ to 37670 cm.$^{-1}$.*

necessary to represent the spectrum, that we give such double-headed bands a single label, even though we know that their two intensity maxima are produced by vibrationally distinct transitions.

A second perturbing vibration is that which produces band-series E in the absorption spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene. This vibration is also degenerate, and in 1 : 4-dideuterobenzene its place is taken by two vibrations, whose frequencies, in either electronic state, fall apart by about 20 cm.$^{-1}$. The result is that each of the E bands of benzene, hexadeuterobenzene, or 1 : 3 : 5-trideuterobenzene becomes replaced in the absorption spectrum of 1 : 4-dideuterobenzene by two neighbouring bands. To these more widely separated bands we have given distinctive names : the lower-frequency members of the band-pairs we collectively call series E, whilst the remaining members form our series E'.

A similar duplication may arise in the case of those series which, in benzene, hexadeutero-benzene, and 1 : 3 : 5-dideuterobenzene, involve, besides the primary activating vibration, an excitation, in either electronic state, of the first overtone of a degenerate vibration. Series G, for example, is characterised by the excitation, additionally to the main perturbing vibration, of a degenerate first overtone in the upper electronic state. In 1 : 4-dideuterobenzene the vibration, which is thus excited as its overtone, becomes split into two vibrations, whose overtones in the upper electronic state lie 44 cm.$^{-1}$ apart. Thus, corresponding to each G band, we find two bands separated by this interval. We call the lower-frequency members of the band-pairs series G, and the upper-frequency members series G'.

Some of the most striking effects of the loss of degeneracy appear in the sequences; for the chief sequence-forming vibration of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene is degenerate, and in 1 : 4-dideuterobenzene becomes replaced by two sequence-forming vibrations, whose frequencies, in either electronic state, are fairly well separated. One result of this duplexity arises in those sequences which start from bands, such as those of the main progressions A and B, which owe their spectral activity to an independent perturbing vibration. In such cases the stronger bands, indeed all the observed bands, constitute what we call a " simply branching " sequence, that is, one formed under the restriction that the same sequence-forming vibrations are present with the same quantum numbers in the upper and the lower electronic states. There are two one-quantum bands, three two-quantum bands, and so on, in such a sequence, because one quantum of a sequence-forming vibration can be supplied in two ways, and two quanta of such vibrations in three ways, and so on ; and because the two combining states are identically constituted with respect to such vibrations.

More complicated effects appear where the main cause of spectral activity is the presence in the combining states of the sequence-forming quanta themselves. In benzene, hexadeutero-benzene, and 1 : 3 : 5-trideuterobenzene the degenerate sequence-forming vibration itself produces a series called J, which appears when, in the absence of other non-totally symmetrical vibrations, equal numbers of quanta of this vibration are present in the two combining states. In 1 : 4-dideuterobenzene there are two sequence-forming vibrations, and all that matters, in order that they should produce the type of spectral activity which we associate with series J, is that the two vibrations between them should furnish the same total number of quanta to each of the combining states : it is unnecessary that each vibration separately should supply the same number of quanta to each state : whether they do or do not, the intensities are comparable. Thus the simple sequences of series J in the spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene become replaced in the spectrum of 1 : 4-dideuterobenzene by a sequence exhibiting what we call " complex branching ". There are now four one-quantum bands, nine two-quantum bands, and so on; because one quantum can be supplied in two ways to each of the combining states, and the alternatives are independent of each other; whilst two quanta can be supplied in three ways to each state, independently; and so on. The qualitative result is that, in place of the few, well-spaced, relatively strong bands of series J, as seen in the absorption spectrum of benzene, hexadeuterobenzene, or 1 : 3 : 5-trideuterobenzene, we find in the spectrum of 1 : 4-dideuterobenzene the total intensity distributed in a close array of many weaker bands.

Our detailed observations are recorded in Table I. Frequencies (corrected to vacuum) and intensities are expressed with the conventions used previously (cf. Part VI, Section 1). The vapour pressures corresponding to the temperatures mentioned in the column of intensities are computed to be approximately as follows : at 20°, 74 mm.; at − 10°, 15 mm.; at − 30°, 4 mm.

Assignments are expressed, as usual, by means of a literal notation. The letter-symbols are furnished with subscripts and superscripts, which represent the quantum numbers, in either electronic state, of the vibrations $A_g(C)$, $A_u(C)$, and $B_{1u}(C)$, as explained in the Note beneath

Table I. The letters themselves distinguish those vibrational changes which are peculiar to the different band-series : they are defined by the equations of Table II, which also records the observed ranges of the above-mentioned quantum numbers. The vibration frequencies contained in the equations of Table II are assigned to vibrations in Table III. The meanings of the

### TABLE I.

*Absorption Spectrum of* 1 : 4-*Dideuterobenzene. Frequencies, Intensities, and Assignments.*
(*cf. Tables II and III*).

| Freq. (cm.⁻¹). | Inty. (20°). | Assgnt. | Freq. (cm.⁻¹). | Inty. (−10°). | Assgnt. | Freq. (cm.⁻¹). | Inty. (−30°). | Assgnt. |
|---|---|---|---|---|---|---|---|---|
| 36582 | ew | $B_{-1}^{0-0}$ | 37924 | ew | $j_0^{1-1}$ | 38988·2 | mw | $G_0'^{1'-1'}$ |
| 586 | ew | $F_0^{0-0}$ | 953·6 | w | $j_0^{1'-1}$ | 998 | w | $G_0'^{1-1}$ |
| | *Inty.* | | 971 | w | $J_0^{1-1'}$ | 39016·4 | w | |
| | *(−10°).* | | 994·5 | w | $J_0^{1'-1'}$ | 045·4 | w | $S_0^{0-0}$ |
| 37109 | w | $B_0^{21'-21'}$ | 38015 | w | $J_0^{1-1}$ | 066·0 | w | |
| 129·3 | vw | $B_0^{3-3}$ | 033·6 | w | $J_0^{1'-1}$ | 084·5 | mw | |
| 166·8 | w | $D_0^{11'-11'}$ | 052 | vw | $H_0'^{0-0}$ | 098·8 | mw | $G_0^{0-0}$ |
| 184 | w | $D_0^{2-2}$ | 098·2 | mw | $M_0^{11'-11'}$ | 108·8 | mw | |
| 240·1 | mw | $B_0^{2'-2'}$ | 103 | mw | | 138·0 | mw | |
| 252·7 | mw | $B_0^{11'-11'}$ | | *Inty.* | | 142·5 | mw | $G_0'^{0-0}$ |
| 263 | mw | $B_0^{2-2}$ | | *(−30°).* | | 148·2 | mw | |
| 270 | mw | | 241·5 | vw | $M_0^{1'-1'}$ | 154·2 | mw | |
| 292·7 | w | $N_0^{0-0}$ | 279·2 | vw | $C_0^{11'-11'}$ | 182·4 | vw | $U_0^{0-0}$ |
| 309 | w | $D_0^{1'-1'}$ | 353 | w | $A_0^{2'-2'}$ | 187·1 | vw | |
| 318·2 | w | | 367·6 | ms | $A_0^{11'-11'}$ | 198·5 | w | $T_0^{0-0}$ |
| 326·3 | w | $D_0^{1-1}$ | 382·1 | ms | $A_0^{2-2}$ | 207·7 | vw | $C_1^{2-2}$ |
| 336 | vw | | 405·4 | w | $M_0^{0-0}$ | 218·5 | vw | $B_2^{1'-1'}$ |
| 393·7 | ms | $B_0^{1'-1}$ | 426·4 | mw | $C_0^{1'-1'}$ | 229·1 | vw | $B_2^{1-1}$ |
| 399·6 | ms | | 434 | w | | 236·8 | vw | |
| 408·3 | ms | $B_0^{1-1}$ | 449 | vw | $C_0^{1-1}$ | 268·8 | mw | $A_1^{11'-11'}$ |
| 413·5 | ms | | 466·6 | w | $B_1^{0-0}$ | 281·2 | mw | $A_1^{2-2}$ |
| 419·2 | vw | $B_0^{1'-1}$ | 511·1 | s | $A_0^{1'-1'}$ | 288·8 | mw | |
| 425·0 | w | | 519·5 | ms | $A_0^{1-1}$ | 295·6 | w | $R_0^{2-2}$ |
| 467·3 | ms | $D_0^{0-0}$ | 526·3 | ms | | 316·3 | w | $M_1^{0-0}$ |
| 472·8 | ms | | 580 | ms | $C_0^{0-0}$ | 323·4 | w | $C_1^{1'-1'}$ |
| 552·6 | s | $B_0^{0-0}$ | 586·0 | ms | | 339·5 | w | |
| 558·1 | s | | 665·0 | vs | $A_0^{0-0}$ | 355·5 | w | $C_1^{1-1}$ |
| 597 | w | $C_{-1}^{0-0}$ | 670·7 | vs | | 377·9 | w | $B_2^{0-0}$ |
| 612 | w | | 701·5 | vw | $\omega_0^{0-0}$ | 385 | vw | $Q_0^{0-0}$ |
| 685·7 | ms | $A_{-1}^{0-0}$ | 722 | ew | $P_0^{0-0}$ | 412·6 | s | $A_1^{1'-1'}$ |
| 692·6 | ms | | 728 | ew | | 427·0 | s | $A_1^{1-1}$ |
| 701 | vw | $J_0^{21'-21'}$ | 754 | ew | $G_0^{2'-2'}$ | 433·5 | s | |
| 710 | ew | $j_0^{2-2'}$ | 764 | ew | | 441·7 | m | $R_0^{1-1}$ |
| 727 | vw | $J_0^{3-3}$ | 776·1 | vw. | | 449·0 | w | $E_0^{1'-1'}$ |
| 738 | ew | $j_0^{2-11'}$ | 783 | vw | $G_0^{11'-11'}$ | 466·6 | w | |
| 744 | ew | $J_0^{21-3}$ | 795 | ew | | 485 | ms | $C_1^{0-0}$ |
| 762 | vw | $J_0^{12-3}$ | 802 | ew | $G_0^{2-2}$ | 494·3 | ms | |
| 770·6 | vw | $j_0^{2-2}$ | 806 | ew | | 501·4 | m | $E_0'^{1-1}$ |
| 785· | vw | $J_0^{3-3}$ | 815 | ew | | 525·8 | mw | |
| 795·3 | vw | $J_0^{2-2'}$ | 828·0 | vw | $G_0'^{2'-2'}$ | 536·0 | w | $K_0^{0-0}$ |
| 808·8 | vw | $J_0^{11'-2'}$ | 839 | ew | $G_0'^{11'-11'}$ | 573·9 | vs | $A_1^{0-0}$ |
| 825·6 | vw | $J_0^{2-11'}$ | 848 | ew | | 579·6 | vs | |
| 834·6 | vw | $J_0^{2'-2'}$ | 866 | ew | $G_0'^{2-2}$ | 587·5 | m | $R_0^{0-0}$ |
| 845 | ew | $J_0^{11'-11'}$ | 872 | ew | | 605 | vw | $\omega_1^{0-0}$ |
| 865·5 | w | $J_0^{2-2}$ | 914·9 | w | $G_0^{1'-1'}$ | 623·5 | mw | $E_0^{0-0}$ |
| 873·4 | w | $J_0^{2'-11'}$ | 930·2 | w | | 632·7 | mw | |
| 887·4 | w | $J_0^{11'-2}$ | 939 | w | | 642·6 | m | $E_0'^{0-0}$ |
| 902·6 | vw | $j_0^{1'-1'}$ | 947·0 | w | $G_0^{1-1}$ | 662·3 | m | |
| 912·5 | w | $J_0^{2'-2}$ | 958 | w | | 696 | vw | $O_0^{1-1}$ |

TABLE I—*contd.*

| Freq. (cm.⁻¹). | Inty. (−30°). | Assgnt. |
|---|---|---|
| 39705·7 | w | $W_0^{0-0}$ |
| 728·2 | vw | $z_0^{0-0}$ |
| 829·4 | mw | $O_0^{0-0}$ |
| 836·8 | mw | |
| 855·3 | vw | $G_1'^{1-1}$ |
| 862·1 | vw | $G_1^{1-1}$ |
| 875·0 | vw | |
| 899·1 | vw | $G_1'^{1'-1'}$ |
| 904·7 | vw | |
| 967 | vw | $S_1^{0-0}$ |
| 976·1 | w | $L_0^{0-0}$ |
| 992·5 | vw | $G_1^{0-0}$ |
| 40017·5 | w | |
| 050·1 | w | $G_1'^{0-0}$ |
| 053·0 | w | |
| 065·3 | w | |
| 075 | ew | $I_0^{0-0}$ |
| 082 | ew | |
| 092 | ew | $U_1^{0-0}$ |
| 096 | ew | |
| 107·0 | w | $T_1^{0-0}$ |
| 128·6 | vw | $B_3^{1'-1}$ |
| 149 | ew | $B_3^{1-1}$ |
| 185·3 | mw | $A_2^{2-2}$ |
| 190·3 | mw | |
| 212·7 | mw | $V_0^{0-0}$ |
| 224·8 | vw | $M_2^{0-0}$ |
| 257 | vw | $C_2^{1-1}$ |
| 260·2 | vw | |
| 285·6 | w | $B_3^{0-0}$ |
| 326·1 | ms | $A_2^{1'-1'}$ |
| 331·3 | s | |
| 342·6 | ms | $A_2^{1-1}$ |
| 346·6 | s | |
| 358·3 | m | $E_1'^{1'-1'}$ |
| 374 | w | |
| 403·0 | vw | $C_2^{0-0}$ |
| 407·0 | vw | |
| 415·3 | vw | $E_1'^{1-1}$ |
| 418·4 | vw | |
| 441 | vw | $K_1^{0-0}$ |
| 40480·1 | vs | $A_2^{0-0}$ |
| 490·8 | vs | |
| 507·9 | m | $X_0^{0-0}$ |
| 523 | ew | $\omega_2^{0-0}$ |
| 530·8 | mw | $E_1^{0-0}$ |
| 544·3 | mw | |
| 549·8 | m | $E_1'^{0-0}$ |
| 570·0 | m | |
| 599 | vw | $O_1^{1-1}$ |
| 617·2 | w | $W_1^{0-0}$ |
| 637·4 | vw | $z_1^{0-0}$ |
| 641·4 | vw | |
| 731·1 | mw | $O_1^{0-0}$ |
| 735·5 | mw | |
| 743·7 | mw | |
| 754·6 | vw | $G_2^{1'-1'}$ |
| 770 | ew | $G_2^{1-1}$ |
| 789·6 | vw | |
| 868·6 | vw | $S_2^{0-0}$ |
| 881·1 | w | $L_1^{0-0}$ |
| 890·5 | w | |
| 918·8 | w | $G_2^{0-0}$ |
| 930·4 | w | |
| 964 | vw | $G_2'^{0-0}$ |
| 970·4 | vw | |
| 977 | vw | |
| 41010 | w | $T_2^{0-0}$ |
| 028 | vw | $Y_0^{0-0}$ |
| 125 | vw | $V_1^{0-0}$ |
| 229·4 | mw | $X_0'^{0-0}$ |
| 240 | mw | $A_3^{1'-1'}$ |
| 258·7 | mw | $A_3^{1-1}$ |
| 271·8 | w | $E_2^{1'-1'}$ |
| 283 | w | |
| 354 | w | $K_2^{0-0}$ |
| 386 | s | $A_3^{0-0}$ |
| 393 | s | |
| 405 | m | $X_1^{0-0}$ |
| 428·5 | vw | $\omega_3^{0-0}$ |
| 443·5 | w | $E_2^{0-0}$ |
| 448·1 | w | |
| 41458 | w | $E_2'^{0-0}$ |
| 479·2 | w | |
| 492·0 | vw | $O_2^{1-1}$ |
| 501 | vw | |
| 530 | vw | $W_2^{0-0}$ |
| 545·4 | vw | $z_2^{0-0}$ |
| 636 | mw | $O_2^{0-0}$ |
| 641·8 | mw | |
| 653·6 | mw | |
| 782·4 | w | $L_2^{0-0}$ |
| 796 | mw | $Y_0''^{0-0}$ |
| 803·1 | mw | |
| 843 | vw | $G_3^{0-0}$ |
| 853 | vw | $G_3'^{0-0}$ |
| 867 | w | |
| 914 | vw | $T_3^{0-0}$ |
| 985·3 | w | $A_4^{11'-11'}$ |
| 997·4 | w | |
| 42009·6 | vw | $A_4^{2-2}$ |
| 132·7 | mw | $X_1'^{0-0}$ |
| 141 | mw | $A_4^{1'-1'}$ |
| 146 | mw | |
| 154·8 | w | $A_4^{1-1}$ |
| 256 | w | $K_3^{0-0}$ |
| 297·5 | m | $A_4^{0-0}$ |
| 305 | m | |
| 548·5 | w | $O_3^{0-0}$ |
| 556·1 | w | |
| 700·3 | w | $Y_1''^{0-0}$ |
| 713·5 | w | |
| 754·6 | vw | $G_4^{0-0}$ |
| 768 | vw | $G_4'^{0-0}$ |
| 784·6 | vw | |
| 43049·0 | mw | $A_5^{1'-1'}$ |
| 060 | w | $A_5^{1-1}$ |
| 068 | w | |
| 171 | w | $K_4^{0-0}$ |
| 200 | mw | $A_5^{0-0}$ |
| 211 | mw | |

*Note :* In the assignment column, the quantum numbers of the progression-forming, $A_g$(C), vibration are shown as subscripts, an implied positive sign referring to the upper electronic state, and a negative sign to the ground state. These upper- and lower-state quantum numbers are called $p'$ and $p''$, respectively, in Table II. The quantum numbers of the two sequence-forming vibrations, $B_{1u}$(C) and $A_u$(C), are shown as superscripts, the former without dashes, and the latter with dashes, an implied positive sign again referring to the upper electronic state, and a negative sign to the lower state. These quantum numbers are expressed by a contracted notation in Table II. The common number of quanta of the vibration $B_{1u}$(C) in both states is called $s$, whilst the common number of quanta of the vibration $A_u$(C) in both states is called $t$; and a common number of quanta referring to the vibration $A_u$(C) in the upper state and $B_{1u}$(C) in the lower is termed $u$, whilst a common number of quanta with the reverse distribution of vibrations is termed $v$. In series J, $s$, $t$, $u$, and $v$ cannot *all* be zero simultaneously, since $J_0^{0-0}$ is forbidden.

vibration symbols in this Table will be made clear by reference to Part I, Section 7, especially to Table V in that Section (p. 415). (For diagrams of the vibrations, see *J.*, 1946, pp. 278—299.)

The band-series A—E, G, H, J, M, and N correspond as closely as the different symmetries of the molecules allow to the identically named series of the absorption spectra of benzene,

hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene. Where, in the spectrum of 1 : 4-dideutero-benzene, two similar series arise from a resolved degeneracy, the one with the higher frequencies is distinguished by means of a dash : E, E′ and G, G′. Certain other series have been named to correspond as closely as possible to identically named series in the absorption spectrum of benzene. These are series F, O, P, and U : corresponding series are not observed in the spectrum of hexadeuterobenzene (cf. Parts II, IV, and VI).

<div align="center">TABLE II.</div>

*Absorption Spectrum of 1 : 4-Dideuterobenzene. Key to Assignments (cf. Table I).*

| | Freq. (cm.⁻¹.) | $p'$. | $p''$. | $s$. | $t$. | $u$. | $v$. |
|---|---|---|---|---|---|---|---|
| A | $= 38154 + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 909p' - 978p'' - 143s - 161t$ | 0—5 | 0, 1 | 0—2 | 0—2 | | |
| B | $= \,,\quad - \begin{Bmatrix}596 \\ 601 \cdot 5\end{Bmatrix} + 909p' - 978p'' - 143s - 161t$ | 0—3 | 0, 1 | 0—3 | 0—2 | | |
| C | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + \begin{Bmatrix}(511-596) \\ (516 \cdot 5 - 601 \cdot 5)\end{Bmatrix} + 909p'$ $- 978p'' - 143s - 161t$ | 0—2 | 0, 1 | 0—2 | 0, 1 | | |
| D | $= \,,\quad + \begin{Bmatrix}(511-596) \\ (516 \cdot 56 - 01 \cdot 5)\end{Bmatrix} - \begin{Bmatrix}596 \\ 601 \cdot 5\end{Bmatrix} - 143s - 161t$ | | | 0—2 | 0, 1 | | |
| E | $= \,,\quad + 1469 + 909p' - 161t$ | 0—2 | | | 0, 1 | | |
| E′ | $= \,,\quad + 1489 + 909p' - 143s$ | 0—2 | | 0, 1 | | | |
| F | $= \,,\quad - 1568$ | | | | | | |
| G | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 222 + 909p' - 143s - 161t$ | 0—4 | | 0—2 | 0—2 | | |
| G′ | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 243 + 909p' - 143s - 161t$ | 0—4 | | 0—2 | 0—2 | | |
| H′ | $= \,,\quad - \begin{Bmatrix}596 \\ 601 \cdot 5\end{Bmatrix} + 2 \times 243$ | | | | | | |
| J | $= \,,\quad - 143s - 161t - 122u - 182v$ | | | 0—3 | 0—2 | 0—22 | 0—2 |
| j | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} - \begin{Bmatrix}596 \\ 601 \cdot 5\end{Bmatrix} - 143s - 161t - 122u$ | | | 0—2 | 0, 1 | 0, 1 | |
| K | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 435 + 909p'$ | 0—4 | | | | | |
| L | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 655 + 909p'$ | 0—2 | | | | | |
| l | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 706$ | | | | | | |
| M | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} - 265 + 909p' - 143s - 161t$ | 0—2 | | 0, 1 | 0, 1 | | |
| N | $= \,,\quad - \begin{Bmatrix}596 \\ 601 \cdot 5\end{Bmatrix} - 265$ | | | | | | |
| O | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 585 + 909p' - 143s$ | 0—3 | | 0, 1 | | | |
| P | $= \,,\quad - \begin{Bmatrix}596 \\ 601 \cdot 5\end{Bmatrix} + 2 \times 585$ | | | | | | |
| Q | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 357$ | | | | | | |
| R | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 457 - 143s$ | | | 0—2 | | | |
| S | $= \,,\quad + 2 \times 457 + 909p'$ | 0—2 | | | | | |
| T | $= \,,\quad + 457 + 585 + 909p'$ | 0—3 | | | | | |
| U | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 909p'$ | 0, 1 | | | | | |
| V | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2 \times 775 + 909p'$ | 0, 1 | | | | | |
| W | $= \,,\quad + 2 \times 775 + 909p'$ | 0—2 | | | | | |
| ω | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 775 - 736 + 909p'$ | 0—3 | | | | | |
| X | $= \,,\quad + 2355 + 909p'$ | 0, 1 | | | | | |
| X′ | $= \,,\quad + 3075 + 909p'$ | 0, 1 | | | | | |
| Y | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 2355$ | | | | | | |
| Y″ | $= \,,\quad + \begin{Bmatrix}511 \\ 516 \cdot 5\end{Bmatrix} + 3132 + 909p'$ | 0, 1 | | | | | |
| z | $= \,,\quad + 2 \times 787 + 909p'$ | 0—2 | | | | | |

*Note :* The frequency 38154 cm.⁻¹ is that of the electronic origin. The other frequencies are vibration frequencies, which are assigned to vibrations in Table III, and in the Note thereunder. The frequencies in braces are to be read alternatively. The symbols for quantum numbers are defined in the Note beneath Table I.

TABLE III.

*Absorption Spectra of* 1 : 4-*Dideuterobenzene.   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. |
|---|---|---|---|
| 909 | 978 | 69 | $A_g(C)$ |
| 511 | 596 | 85 | $A_g(C\ 1)$ |
| 1489 | — | — | $A_g(C\ 2)$ |
| 2355 | — | — | $A_g(H\ 1)$ |
| 3132 | — | — | $A_g(H\ 2)$ |
| 243 | — | 161 | $A_u(C)$ |
| 706 | — | — | $A_u(H)$ |
| 516·5 | 601·5 | 85 | $B_{1g}(C\ 1)$ |
| 1469 | 1568 | — | $B_{1g}(C\ 2)$ |
| 3075 | — | — | $B_{1g}(H\ 2)$ |
| 222 | — | 143 | $B_{1u}(C)$ |
| 435 | — | — | $B_{1u}(H\ 1)$ |
| 655 | — | — | $B_{1u}(H\ 2)$ |
| 585 | — | 265 | $B_{2g}(H)$ |
| 357 | — | — | $B_{3g}(C)$ |
| 457 | — | — | $B_{3g}(H\ 1)$ |
| 775 | — | — | $B_{3g}(H\ 2)$ |
| 787 | — | — | $B_{3u}(H\ 1)$ |

*Note :*  By the addition of one-quantum of the $A_g(C\ 1)$ vibration to one, and one of the $B_{1g}(C\ 1)$ vibrations to the other of the two combining states, differences of 80 cm.$^{-1}$ and 90 cm.$^{-1}$ may arise. Similarly, by the addition of one quantum of the $A_u(C)$ vibration to one state, and one of the $B_{1u}(C)$ vibration to the other, differences of 122 cm.$^{-1}$ and 182 cm.$^{-1}$ follow, which appear explicitly in equations J and j of Table II.   Concerning the frequency 787 cm.$^{-1}$, see the text (Section 9).

(2) *Band Series* A—D.—As with the spectra described in the preceding papers, so also with the present spectrum, the four band series A—D provide the main structure (Part I, Section 4). Here, band series A and B involve 0—1 and 1—0 transitions, respectively, in either of the two distinct, but similar, planar, ring-bending vibrations, $A_g(C\ 1)$ and $B_{1g}(C\ 1)$; whilst series C and D depend on 1—2 and 2—1 transitions, respectively, of the same vibrations (Part I, Section 7). These transitions directly produce the four active origins $A_0^{0-0}$, $B_0^{0-0}$, $C_0^{0-0}$, $D_0^{0-0}$.   From these origins progressions in the totally symmetrical vibration $A_g(C)$ proceed, mainly in the positive direction, although some one-quantum members of corresponding negative progressions can be seen, much weakened by their Boltzmann factors.   From the stronger bands of these progressions run " simply branching " sequences (cf. Section 1), always in the negative direction : they are due to *n*—*n* transitions in either of the distinct but similar, out-of-plane vibrations $A_u(C)$ and $B_{1u}(C)$.
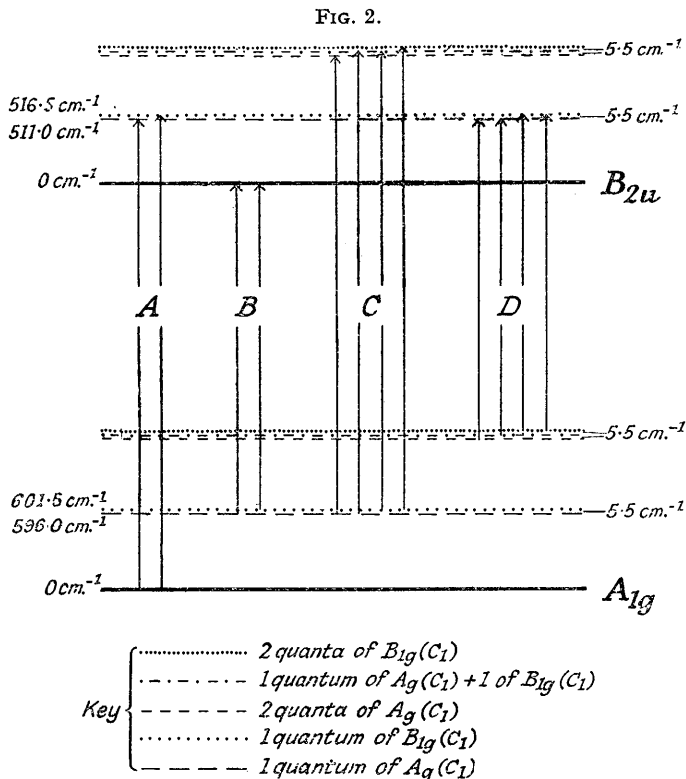
We may first consider the effect of the duplexity of the origin-forming vibrations.   All those bands of series A and B which are suitable for detailed observation can be seen as close doublets (cf. Fig. 1).   The doublet separation in series A will represent the difference between the fundamental frequencies of the vibrations $A_g(C\ 1)$ and $B_{1g}(C\ 1)$ in the upper electronic state; and the separation in series B will represent the corresponding separation in the electronic ground state (cf. Fig. 2).

The bands of series C and D also appear as doublets, although they could in principle (cf. Part I, Section 7) be sextets, since two vibrational levels in one state are available to combine each with each of three vibrational levels of the other state (cf. Fig. 2).   There are two reasons for the observed simplification.   One is that those transitions which are strong enough for our observation always proceed by the simple loss or gain of an $A_g(C\ 1)$ or $B_{1g}(C\ 1)$ quantum, and not by the substitution of a pre-excited quantum of either kind by one of the other kind.   This restriction reduces the six possible transitions to four (cf. Fig. 2).   The further reason is that the separation between the $A_g(C\ 1)$ and $B_{1g}(C\ 1)$ frequencies in the upper electronic state happens to be identical with their separation in the lower state to within the errors of observation, with the result that the four transition frequencies coincide in pairs.   This will be clear from Fig. 2.

Our value for the frequency separation of the $A_g(C\ 1)$ and $B_{1g}(C\ 1)$ vibrations, alike in the upper state and in the ground state, is 5·5 cm.$^{-1}$; and so sharp are the heads of the best doublet bands that this figure is likely to be reliable to within a few tenths of a wave-number.   Now Herzfeld, Hobden, Ingold, and Poole attempted to estimate this frequency separation for the electronic ground state by resolution of the corresponding doublet Raman line (*J*., 1946, 276).

Their value was 4·3 cm.$^{-1}$ (cf. Poole, *J.*, 1946, 245, and especially Fig. 1 of his paper); but they remarked (*loc. cit.*, p. 276, footnote) that this estimate was likely to be low, because the overlap of the components of the doublet was large in relation to the spectral width of each component. The present work confirms that the error was in the anticipated direction, and gives an indication of its magnitude.

Discussing vibrations in the electronic ground state, Herzfeld, Hobden, Ingold, and Poole (*loc. cit.*) gave three reasons for assigning the lower of the Raman doublet frequencies to the $A_g$(C 1) vibration, and the upper one to the $B_{1g}$(C 1) vibration. One of these reasons, that which was based on the forms of the normal co-ordinates, applies equally well to the electronically excited state. In any case it would seem that the dynamical factors which separate the frequencies, when the benzene molecule is loaded as it is in 1 : 4-dideuterobenzene, are likely to work the same way in both states. Accordingly, we assume that the lower of the fundamental

FIG. 2.



Key {
······················ *2 quanta of $B_{1g}(C_1)$*
·—·—·—·— *1 quantum of $A_g(C_1)$ +1 of $B_{1g}(C_1)$*
— — — — — *2 quanta of $A_g(C_1)$*
············ *1 quantum of $B_{1g}(C_1)$*
— — — — — *1 quantum of $A_g(C_1)$*
}

*Scheme of energy levels and transitions, illustrating the doublet structure of the main bands of Series A—D in the absorption spectrum of 1 : 4-dideuterobenzene. (Not to scale.)*

doublet frequencies of the upper electronic state belongs to the $A_g$(C 1) vibration, whilst the upper doublet frequency belongs to the $B_{1g}$(C 1) vibration.
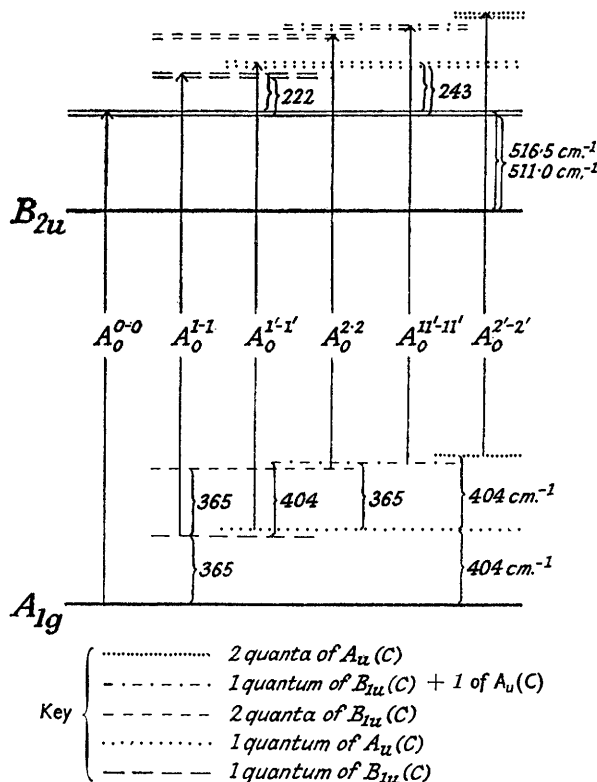
The progressions in the totally symmetrical frequencies, $A_g$(C), require no special comment : except for the fact that they maintain the doublet character described, they are as simple as for benzene or hexadeuterobenzene. For positive progressions the repeating interval is 909 cm.$^{-1}$; for negative progressions the interval is 978 cm.$^{-1}$.

The negative sequences of series A—D involve two sequence intervals, each of which may either repeat itself, or add itself to the other, to form a " simply branching " sequence, the bands of which are doublets for the reasons already given. The structure of such sequences is illustrated, for the case of a sequence of series A, in Fig. 3.

The two sequence intervals are 161 cm.$^{-1}$ and 143 cm.$^{-1}$. Each represents the difference between the fundamental frequencies of a vibration in the lower and the upper electronic states. Each belongs to one of the vibrations, $A_u$(C) and $B_{1u}$(C), into which the main sequence-forming vibration of benzene, hexadeuterobenzene, or 1 : 3 : 5-trideuterobenzene splits when its degeneracy

is broken down by the particular form of isotopic loading which is present in 1 : 4-dideutero-benzene (Part I, Section 7). Now it is not an accident that the upper sequence interval, 161 cm.$^{-1}$,

FIG. 3.



$$Key \begin{cases} \text{.............} & \textit{2 quanta of } A_u \text{ (C)} \\ \text{– · – · – · –} & \textit{1 quantum of } B_{1u}\text{(C)} + \textit{1 of } A_u\text{(C)} \\ \text{– – – – –} & \textit{2 quanta of } B_{1u} \text{ (C)} \\ \text{············} & \textit{1 quantum of } A_u \text{ (C)} \\ \text{— — — —} & \textit{1 quantum of } B_{1u}\text{(C)} \end{cases}$$

*Scheme of energy levels and transitions, illustrating the development of a simply branching doublet sequence in Series A of the absorption spectrum of 1 : 4-dideuterobenzene. (Not to scale.)*

is identical with the sequence interval for benzene. For, as Bailey, Carson, Gordon, and Ingold explained in relation to the electronic ground state, one form of the $E_u^+$(C) vibration of benzene is identical with the $A_u$(C) vibration of 1 : 4-dideuterobenzene : in these vibrations, the atoms which differ in the two molecules do not move (*J.*, 1946, 298, cf. diagram XIV, p. 299). Of course, the same is true for the electronically excited state, and thus we can at once identify the difference frequency, 161 cm.$^{-1}$, as belonging to the $A_u$(C) vibration. The other difference frequency, 144 cm.$^{-1}$, must belong to the $B_{1u}$(C) vibration. One should expect this to be lower, because, whilst in the $A_u$(C) vibration all the hydrogen motion is in the light hydrogen atoms, in the $B_{1u}$(C) vibration much of it is in the heavy hydrogen atoms; this will reduce, in similar proportion, the fundamental frequencies of the latter vibration in both electronic states, and therefore, also the corresponding frequency difference.

The above-discussed series determine the position of the forbidden electronic origin,

$$J_0^{0-0} = 38154 \pm 1 \text{ cm.}^{-1}$$

and the following fundamental vibration frequencies,

$$\begin{aligned} A_g(\text{C 1})_{\text{ground}} &= 596 \text{ cm.}^{-1} & A_g(\text{C 1})_{\text{excited}} &= 511 \text{ cm.}^{-1} \\ B_{1g}(\text{C 1})_{\text{ground}} &= 601.5 \text{ cm.}^{-1} & B_{1g}(\text{C 1})_{\text{excited}} &= 516.5 \text{ cm.}^{-1} \\ A_g(\text{C})_{\text{ground}} &= 978 \text{ cm.}^{-1} & A_g(\text{C})_{\text{excited}} &= 909 \text{ cm.}^{-1} \end{aligned}$$

The ground-state frequencies as found in the Raman spectrum of liquid 1 : 4-dideuterobenzene are as follows : $A_g$(C 1) = 596.6 cm.$^{-1}$, $B_{1g}$(C 1) = 600.9 cm.$^{-1}$, $A_g$(C) = 978.0 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *J.*, 1946, 272).

(3) *Band Series* E, E', *and* F.—The band series E and E' are similar to the E bands of the absorption spectra of the three benzenes already studied (Parts II, IV, and VI). They lie just above the bands of the main progression, starting with the second member. As usual, they are double bands, the component of lower frequency being the stronger. In the present spectrum, however, we find twice the accustomed number of such bands, and they occur in pairs, overlapping slightly. They do not exhibit the narrow doublet splitting (5·5 cm.$^{-1}$) shown by the bands of series A—D, indeed, by most of the series in this spectrum.

We assume these band-pairs to be formed in 0—1 transitions of the two distinct, but closely similar vibrations, $B_{1g}$(C 2) and $A_g$(C 2), into which the degenerate carbon stretching vibration of benzene, hexadeuterobenzene, or 1 : 3 : 5-trideuterobenzene splits up when deuterium atoms are arranged as in 1 : 4-dideuterobenzene (Part I, Section 7). We assume also that, just as with the E bands of other absorption spectra, all the present E and E' bands gain most of their intensity by resonance with the neighbouring A bands; and that they probably suffer an upward frequency-displacement as a result of the resonance (cf. Part II, Section 3). For this reason, we take, as heretofore, the lower and stronger intensity maximum of each band as giving the better approximation to the unperturbed position of its vibrational origin.

The lower frequency members of the pairs of bands form series E, the parent band of which, $E_0^{0-0}$, lies 1469 cm.$^{-1}$ above the electronic origin. The remaining members form series E', the parent of which, $E_0'^{0-0}$, is found 1489 cm.$^{-1}$ above the origin. We tentatively assign the former series to the $B_{1g}$(C 2) vibration and the latter to the $A_g$(C) vibration. The reason for this choice is the same as that which Herzfeld, Hobden, Ingold, and Poole gave in relation to the electronic ground state (*loc. cit.*), *viz.*, that we should expect the $B_{1g}$(C 2) vibration to have the lower frequency since much of the motion is in the CD-groups, whereas in the $A_g$(C 2) vibration the motion is largely concentrated in the CH-groups. We take it that the same applies to the upper electronic state, in which the vibrations have the frequencies given by the frequency intervals quoted. However, this argument neglects the possibility of disturbance by assumed resonance displacements, and is therefore uncertain in its application to the electronically excited state.

Since the assignment, first proposed by Sponer and her collaborators, of the E bands of benzene to 0—1 transitions of the vibration $E_g^+$(C 2), was later considered doubtful by her (cf. Part II, Section 3), it seems worth noting that the duplication of this series, which we observe in the absorption spectrum of 1 : 4-dideuterobenzene (and, as we shall see later, in the spectrum of monodeuterobenzene), is strong evidence in favour of the original assignment; especially as the separation of the frequencies, into which the upper-state $E_g^+$(C 2) frequency must be assumed to split in 1 : 4-dideuterobenzene and monodeuterobenzene, is just of the sort of magnitude which we should expect on the basis of the known splitting which these frequencies suffer in the electronic ground state.

The extremely weak band $F_0^{0-0}$, found at the long-wave end of the spectrum, 1568 cm.$^{-1}$ below the electronic origin, is assigned to a 1—0 transition of the vibration $B_{1g}$(C 2). Its weakness must be associated with its very small Boltzmann factor. A band $F_0'^{0-0}$, due to a 1—1 transition of the vibration $A_g$(C 2), which is expected to appear about 1587 cm.$^{-1}$ below the origin, is probably present, but it was not measured, because it could not with certainty be distinguished from the tail of another very weak, long-wave band, $B_1^{0-0}$.

These bands provide the following fundamental frequencies :

$$A_g(\text{C 2})_{\text{ground}} = (1587 \text{ cm.}^{-1}) \qquad A_g(\text{C 2})_{\text{excited}} = 1489 \text{ cm.}^{-1}$$
$$B_{1g}(\text{C 2})_{\text{ground}} = 1568 \text{ cm.}^{-1} \qquad B_{1g}(\text{C 2})_{\text{excited}} = 1469 \text{ cm.}^{-1}$$

The frequency in parenthesis, not satisfactorily observed in the absorption spectrum, is derived from the Raman spectrum of liquid 1 : 4-dideuterobenzene. The other ground-state frequency, as given by the Raman spectrum, is 1569 cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *loc. cit.*), in good agreement with the value now recorded. The higher of the pair of excited-state frequencies lies above the corresponding frequency for benzene (1470 cm.$^{-1}$), but this irregularity may be due to the postulated resonance displacements, as suggested in Part II, Section 3.
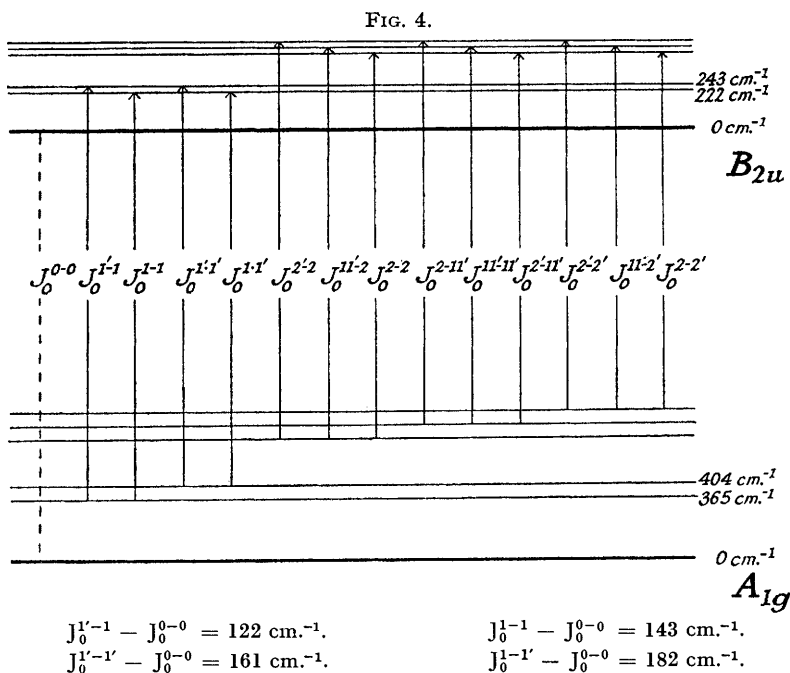
(4) *Band Series* G, G', H', J, *and* j.—The bands of series G and G' resemble the G bands of the absorption spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene (Parts II, IV, and VI). They have a similar, characteristically complex, shape : and they probably reproduce the doublet structure of A bands, superposed on their own special contours. They appear, as usual, between 400 cm.$^{-1}$ and 500 cm.$^{-1}$ above the stronger A bands ; but now we find twice the accustomed number of them, and they occur as adjacent pairs. The lower-frequency members of the pairs form series G, and the others, series G'.

The G bands of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene are explained by the assumption of an upward 0—2 transition of the degenerate, low-frequency vibration, superposed on those electronic and vibrational transitions which characterise the bands of series A. Analogously, we explain the bands of the present series G and G' by assuming, in similar combination, upward 0—2 transitions of each of the vibrations, $B_{1u}(C)$ and $A_u(C)$, into which the degenerate low-frequency vibration splits, when deuterium atoms are disposed in the molecule as in 1 : 4-dideuterobenzene (cf. Part I, Section 7).

The bands of series G are situated approximately 445 cm.$^{-1}$ above, and those of series G' about 485 cm.$^{-1}$ above, the related bands of series A. The two intervals represent overtone frequencies in the upper electronic state, one of the vibration $B_{1u}(C)$ and the other of the vibration $A_u(C)$. The larger interval is identical with the separation between G and A bands in the absorption spectrum of benzene. Accordingly we connect series G' with the overtone of the vibration $A_u(C)$, which, as we have already noted (Section 2), is identical with one form of the degenerate vibration, $E_u(C)$, of benzene. The other series, G, is connected with the overtone of the vibration $B_{1u}(C)$, which should have the lower fundamental frequency (Section 2), and therefore the lower overtone frequency.

The single band $H_0'^{0-0}$ probably marks the beginning of a double series, H, H', related to B bands, as the double series G, G' is to A bands. But no more of this assumed series can be seen, probably because, just below $H_0'^{0-0}$, the J series commences, the numerous bands of which nearly fill the spectrum for the next 300 cm.$^{-1}$ downward.

In the absorption spectra of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene, the J series consists of a simple $n$—$n$ sequence in the low-frequency, degenerate vibration. It runs negatively as if from the electronic origin except that the 0—0 band is absent, and may possibly be repeated after an interval corresponding to the upper-state frequency of the totally symmetrical vibration. In the corresponding series, J, of 1 : 4-dideuterobenzene, we have two vibrations, $A_u(C)$ and $B_{1u}(C)$, together taking the place of the degenerate vibration (Part I, Section 7). All possible pairs of their quanta are of comparable importance for the production of spectral activity, and therefore the J sequence is not dominated by the totally symmetrical combinations, as in general are sequences that start from a spectrally active origin. Accordingly, series J

Fig. 4.



$$J_0'^{1-1} - J_0^{0-0} = 122 \text{ cm.}^{-1}. \qquad J_0^{1-1} - J_0^{0-0} = 143 \text{ cm.}^{-1}.$$
$$J_0'^{1-1'} - J_0^{0-0} = 161 \text{ cm.}^{-1}. \qquad J_0^{1-1'} - J_0^{0-0} = 182 \text{ cm.}^{-1}.$$

*Scheme of energy levels and transitions, illustrating the development of the complex branching sequence J of the absorption spectrum of 1 : 4-dideuterobenzene. (Not to scale.)*

is not a simply branching sequence : it is a " complex branching " sequence, the mode of development of which can be followed with the aid of Fig. 4. The two vibrations in the two electronic

states produce four sequence intervals, as shown below the diagram, and these can be repeated or superposed on one another in every possible way. In Table I we mark all the four one-quantum bands, all the nine two-quantum bands, and five of the sixteen possible three-quantum bands, the series disappearing only as it runs beneath a rather strong band of series A. It may be noted that, unlike the majority of the bands in this spectrum, the bands of series J appear single-headed—as they well might, since they do not involve excitations of the doublet-forming vibrations, $A_g$(C 1) and $B_{1g}$(C 1).

A second complex branching sequence is present, but cannot be traced so fully. This is series j, to which we assign a constitution similar to that of series J except for the presence, additionally, of one quantum of one of the vibrations $A_g$(C 1) and $B_{1g}$(C 1) in each of the combining states. Thus series j is related to series J, just as C is to A, or as D is to B. Theoretically, series j starts from an active origin, but the 0—0 band, which would have only $A_g$(C 1) and $B_{1g}$(C 1) quanta, and not $A_u$(C) or $B_{1u}$(C) quanta, in its combining states, cannot be seen; so it is evident that the spectral activity of the series comes essentially, not from the single $A_g$(C 1) and $B_{1g}$(C 1) quanta, but from the repeating $A_u$(C) and $B_{1u}$(C) quanta, as it does in series J. We can therefore understand why totally symmetrical combinations of these quanta do not dominate the series, and why, accordingly, it shows " complex branching ", just as does the J series.

The upper-state overtone frequencies given by series G and G', and the various difference frequencies of series J, and of sequences within other series (cf. Section 2), provide us with the following fundamental vibration frequencies :

$$A_u(C)_{\text{ground}} = 404 \text{ cm.}^{-1} \qquad A_u(C)_{\text{excited}} = 243 \text{ cm.}^{-1}$$
$$B_{1u}(C)_{\text{ground}} = 365 \text{ cm.}^{-1} \qquad B_{1u}(C)_{\text{excited}} = 222 \text{ cm.}^{-1}$$

The two $A_u$(C) frequencies agree with the $E_u^+$(C) frequencies for benzene, as determined in Part II. The two ground-state frequencies agree satisfactorily with previous estimates : Herzfeld, Ingold, and Poole's indirect estimate of the $A_u$(C) frequency was 405 cm.$^{-1}$ (*J.*, 1946, 319); whilst Bailey, Carson, Gordon, and Ingold's study of the infra-red fundamental band, $B_{1u}$(C), gave the frequency 367 cm.$^{-1}$, this value being necessarily rather rough, because part of the band was outside the long-wave limit of their apparatus (*J.*, 1946, 288).

(5) *Band Series* K, L, *and* l.—We deal with these three series next, because, according to our interpretations, they are connected with the remaining vibrations of the out-of-plane classes $B_{1u}$ and $A_u$.

The bands of the main progression A, starting with the second member, are persistently accompanied on the low-frequency side by satellite bands, which collectively we call series K. Evidently the bands of series K are deriving their considerable intensity by resonance with the neighbouring A bands. This shows that their transitions, like those of the A bands, must start from the " vibrationless " ground state. We can explain such bands by assuming either the excitation of an upper-state frequency 870 cm.$^{-1}$, in combination with transitions of series A, or the excitation of an upper-state frequency 1385 cm.$^{-1}$ in combination with the electronic transition only. Taking account of the selection rules (Part I, Section 7), and making comparisons with other absorption spectra, especially with that of benzene itself (Part XI), we choose the former alternative, assigning the frequency 870 cm.$^{-1}$ as the first overtone of the vibration $B_{1u}$(H 1). Its nearest analogue in benzene is the hexagonal, out-of-plane, hydrogen vibration $A_{2u}$(H), which produces a very similar overtone series, also called K, in the absorption spectrum. It is natural to look for the 1—1 sequence bands of any vibration of rather low frequency, but such sequence bands of the $B_{1u}$(H 1) vibration would have the difference-frequency 162 cm.$^{-1}$, and would coincide with the prominent 1—1 bands of the vibration $A_u$(C) just as with benzene the $A_{2u}$(H) sequence bands cannot be observed since they coincide with those of the analogous vibration, $E_u^+$(C).

The progression of weak but moderately sharp bands, which constitute series L, starts with a band situated 1820 cm.$^{-1}$ above the electronic origin, or 1310 cm.$^{-1}$ above the main active origin $A_0^{0-0}$. One possible explanation would treat the separation from the electronic origin as the upper-state overtone frequency of the vibration $A_g$(C). Although the strict selection rules would allow this interpretation, we reject it on the ground that the fundamental frequencies of the $A_g$(C) vibration, taken in relation to the frequencies of the $A_{1g}$(C) vibration of benzene and hexadeuterobenzene, show that the former vibration must have very nearly perfect hexagonal symmetry, both in the ground and in the excited electronic states of 1 : 4-dideuterobenzene; so that it should not be excited to any appreciable extent in the absence of a suitable deforming vibration. Therefore we take the displacement from $A_0^{0-0}$ as the characteristic upper-state

frequency of series L, supposing this frequency to be excited in combination with the transitions of series A. Comparisons with other spectra, especially with the absorption spectrum of benzene (Part XI), lead us to assign this frequency as the upper-state first overtone of the vibration $B_{1u}(\text{H } 2)$. Its nearest analogue in benzene is the vibration $E_u^+(\text{H})$, the upper-state overtone of which also records itself in the absorption spectrum. Any 1—1 sequence bands of the 1 : 4-dideuterobenzene vibration $B_{1u}(\text{H } 2)$ could only be very weak, and would occur in positions in which they cannot be verified because of overlapping by stronger bands.

The following fundamental frequencies result from these assignments :

$$B_{1u}(\text{H } 1)_{\text{excited}} = 435 \text{ cm.}^{-1} \qquad B_{1u}(\text{H } 2)_{\text{excited}} = 655 \text{ cm.}^{-1}$$

As will be shown in Part XI, these values agree with the product rule. The corresponding ground-state frequencies are known from observations in the infra-red (Bailey, Carson, Gordon, and Ingold, *loc. cit.*) ; and they are as follows : $B_{1u}(\text{H } 1) = 597 \text{ cm.}^{-1}$; $B_{1u}(\text{H } 2) = 876 \text{ cm.}^{-1}$.

The single weak band $1_0^{0-0}$, lying 1411 cm.$^{-1}$ above $A_0^{0-0}$, is assumed to arise by excitation, in the upper electronic state, of the first overtone of the vibration $A_u(\text{H})$, in combination with those electronic and vibrational transitions which characterise $A_0^{0-0}$. This assignment is based on the position of the band. A band in the same position, relatively to the active origin $A_0^0$, was found in the absorption spectrum of benzene, and was considered to involve, in combination with the transitions of $A_0^0$, an excitation in the upper state of the first overtone of the vibration $E_u^+(\text{H})$ (Part II, Section 8). Now, as Bailey, Carson, Gordon, and Ingold explained, with reference to the electronic ground state, one of the normal co-ordinates of the vibration $E_u^+(\text{H})$ of benzene is identical with the normal co-ordinate of the vibration $A_u(\text{H})$ of the 1 : 4-dideuterobenzene, and therefore the frequencies of the two vibrations are exactly equal (*J.*, 1946, 298; diagram XV, p. 299). The same is equally true for the electronically excited state; and therefore the assignment of the 1 : 4-dideuterobenzene band follows from that of the benzene band. Thus we arrive at another fundamental frequency of the upper state :

$$A_u(\text{H})_{\text{excited}} = 706 \text{ cm.}^{-1}$$

The corresponding ground-state frequency is, of course, the same as that of the ground-state $E_u^+(\text{H})$ frequency of benzene, *viz.*, 970 cm.$^{-1}$, as estimated by Herzfeld, Ingold, and Poole from Raman and infra-red combination tones (*loc. cit.*).

(6) *Band Series* M, N, O, *and* P.—Series M consists of a number of prominent bands negatively displaced from A bands by the uniform interval 265 cm.$^{-1}$. Series N consists of a single band similarly displaced from the parent band of series B. We assume these M and N bands to arise from 1—1 transitions of the out-of-plane hydrogen vibration $B_{2g}(\text{H})$, in combination with the electronic and vibrational transitions of the related A and B bands.

Series, also called M and N, which are very closely similar to these, and have identically the same displacement, 265 cm.$^{-1}$, from series A and B, were found in the absorption, and the fluorescence, spectra of benzene. The identity of the frequency displacement in the absorption and fluorescence spectra proved the presence of 1—1 transitions; and, years before we had seen the absorption spectra of any partly deuterated benzene, we had assigned these transitions to the out-of-plane, hydrogen vibration $E_g^-(\text{H})$—mainly on the basis of the isotope shift of series M and N in hexadeuterobenzene. It was satisfactory, therefore, that these series should appear again in the absorption spectrum of 1 : 4-dideuterobenzene, and yet again, as we shall see in Part X, in that of monodeuterobenzene, in both cases in exactly the same relative positions as those in which they occur in the spectra of benzene. Only three of the thirty vibrational degrees of freedom of a benzene molecule are completely identical in benzene, monodeutero-benzene, and 1 : 4-dideuterobenzene : the vibration we had chosen is one of them. The chosen vibration, called $E_g^-(\text{H})$ in benzene, $A_2(\text{H}')$ in monodeuterobenzene, and $B_{2g}(\text{H})$ in 1 : 4-dideutero-benzene, involves counter-rotatory motions of the carbon and hydrogen hexagons about a para-axis, so selected that it will contain any deuterium atoms (cf. *J.*, 1946, 285, diagram XII).

Series O consists of a number of prominent bands positively displaced from A bands by the interval 1170 cm.$^{-1}$. Series P consists of a single band similarly displaced from the parent band of series B. We suppose these O and P bands to arise from upward 0—2 transitions of the vibration $B_{2g}(\text{H})$, in combination with the electronic and vibrational transitions of the correlated A and B bands.

Closely similar series, also called O and P, with just the same displacement from series A and B, were found in the absorption spectrum of benzene. They were assigned to upward 0—2 transitions of the vibration $E_g^-(\text{H})$, in combination with the electronic and vibrational transitions

of series A and B, respectively. It is consistent that we find the same two series in the absorption spectrum of 1 : 4-dideuterobenzene, and again, as we shall see in Part X, in that of monodeutero-benzene : the common displacement, 1170 cm.$^{-1}$, is evidently the upper-state overtone frequency of a vibration which is identical in all three benzenes. This justifies our assignment. It is of interest that the O bands of 1 : 4-dideuterobenzene are on the whole distinctly narrower than are the O bands of benzene, even though the former have cause to be 5·5 cm.$^{-1}$ wider since they must include the doublet separation of series A. The difference bears out our interpretation (Part II, Section 6) of the considerable breadth of the benzene bands, which we assumed to be due, at least in part, to the splitting by anharmonicity of the higher-order degeneracy involved in the overtone of a degenerate vibration. The vibration of 1 : 4-dideuterobenzene is, of course, not degenerate.

These assignments* lead to the following fundamental frequencies :

$$B_{2g}(H)_{ground} = 850 \text{ cm.}^{-1} \qquad B_{2g}(H)_{excited} = 585 \text{ cm.}^{-1}$$

The ground-state frequency, as found in the Raman spectrum of liquid 1 : 4-dideuterobenzene is 849·5 cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *loc. cit.*).

(7) *Band Series* Q, R, S, T, V, W, *and* $\omega$.—We group these series together because, according to our interpretations, they are all connected, in one way or another, with one of the three vibrations of the out-of-plane symmetry class $B_{3g}$.

The single weak band, $Q_0^{0-0}$, lies 714 cm.$^{-1}$ above the main active origin $A_0^{0-0}$. We assign the interval as the upper-state first overtone of the carbon vibration $B_{3g}(C)$. The assignment is based on comparisons with other benzenes (cf. Part XI).

Series R commences with a band $R_0^{0-0}$ situated 914 cm.$^{-1}$ above $A_0^{0-0}$. Progression S starts with a band $S_0^{0-0}$ lying 914 cm.$^{-1}$ above the electronic origin. Comparisons with the spectra of other benzenes (Part XI) suggest that the common interval is the upper-state first overtone of the hydrogen vibration, $B_{3g}(H\ 1)$. We recognise its fundamental frequency, 457 cm.$^{-1}$, again in the upper-state combination frequency $457 + 585 = 1042$ cm.$^{-1}$, by which the initial band progression T is displaced above the electronic origin. These assignments are in accordance with the selection rules (Part I, Section 7). Series S and T are assumed to involve the excitation, without an activating vibration of the $A_g$ or $B_{1g}$ class, either of two quanta of the vibration $B_{3g}(H\ 1)$, or of one quantum of this vibration and one of the vibration $B_{2g}(H)$. Both these vibrations derive from the degenerate benzene vibration $E_g^-(H)$, the excitation, without other vibrations, of the first overtone of which cannot be observed in the absorption spectrum of benzene because of overlapping, but is observed in the spectrum of hexadeuterobenzene, as also is the overtone of the analogous vibration, $E''(H\ 1)$, in the spectrum of 1 : 3 : 5-trideuterobenzene.

Progression V begins with a band situated 1550 cm.$^{-1}$ above the active origin $A_0^{0-0}$. We ascribe it to a transition, like that of $A_0^{0-0}$, but with a superposed excitation of the upper-state frequency 1550 cm.$^{-1}$. Progression W starts with a band lying 1550 cm.$^{-1}$ above the electronic origin $J_0^{0-0}$. These bands are very sharp, a fact which is consistent with our assumption that the frequency of the characteristic upper-state vibration is to be measured by the displacement from the electronic origin, $J_0^{0-0}$, rather than from the doublet band $A_0^{0-0}$. For reasons based essentially on comparisons with other spectra (Part XI), we regard the common interval, 1550 cm.$^{-1}$, as the first overtone, in the upper electronic state, of the remaining $B_{3g}$ vibration, *viz.*, $B_{3g}(H\ 2)$. Tentatively, we suggest that one quantum of this upper-state vibration, and one of the lower-state vibration $B_{3g}(H\ 1)$, are together involved in the production of the small positive interval which separates the very weak bands of series $\omega$ from the strongest bands of series A.

The above assignments lead to the following fundamental frequencies :

$$B_{3g}(C)_{excited} = 357 \text{ cm.}^{-1} \qquad B_{3g}(H\ 1)_{excited} = 457 \text{ cm.}^{-1}$$
$$B_{3g}(H\ 2)_{excited} = 775 \text{ cm.}^{-1}$$

The values are in accordance with the product theorem. The corresponding ground-state frequencies have been measured in the Raman spectrum of liquid 1 : 4-dideuterobenzene ; and

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* We consider the main part of the intensity of series M and N to be due to 1—1 transitions of the vibration $B_{2g}(H)$, rather than of the vibration $A_u(H)$, which has the same difference frequency, first, because the Boltzmann factor of the former vibration is larger, and secondly, because in all these spectra one notices a general correlation of transition probabilities between overtone series and sequences, and the overtone series, O and P, of the vibration $B_{2g}(H)$ are so much stronger than is the overtone series, l, of the vibration $A_u(H)$. It is not excluded that a minor part of the intensity of series M and N comes from 1—1 transitions of the vibration $A_u(H)$.

they are as follows : $B_{3g}(C) = 634 \cdot 1$ cm.$^{-1}$; $B_{3g}(H\ 1) = 736$ cm.$^{-1}$; $B_{3g}(H\ 2) = 967$ cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *loc. cit.*).

(8) *Band Series* X, X', Y, *and* Y''.—These are the series involving the deuterium- and protium-stretching vibrations of the electronically excited state. The selection rules (Part I, Section 7) allow three such fundamental vibrations to appear, *viz.*, a deuterium and a protium vibration of the $A_g$ class, and a second protium vibration belonging to the $B_{1g}$ class. It follows also from the selection rules that either these vibrations may be excited alone, or their excitation may be superposed on that of either of the more usual perturbing vibrations.

The excitation of the deuterium vibration, $A_g(H\ 1)$, alone can be seen in series X, which starts with a band situated 2355 cm.$^{-1}$ above the electronic origin. The bands of this progression are very sharp, as suits our assumption that they do not involve the perturbing vibrations of series A or B, and therefore do not contain a corresponding doublet separation. The upper-state frequency to which we are led agrees well with the upper-state deuterium-stretching frequencies of hexadeuterobenzene and 1 : 3 : 5-trideuterobenzene as determined in Parts IV and VI.

The excitation of one of the protium vibrations alone—we identify it as the vibration $B_{1g}(H\ 2)$—is seen in the parent band series X', which lies 3075 cm.$^{-1}$ above the electronic origin, and starts a two-membered progression. The bands of this progression are also very sharp, doubtless for the reason mentioned above. The existence of a band arising from the excitation alone of the other protium-stretching vibration, $A_g(H\ 2)$, cannot be verified, since it would coincide with a band of series E.

The deuterium-stretching vibration, $A_g(H\ 1)$, appears again in the assignment of a band $Y_0^{0-0}$ situated 2355 cm.$^{-1}$ above the active origin $A_0^{0-0}$. We explain this band by assuming the excitation, in the upper electronic state, of the fundamental vibration, $A_g(H\ 1)$, in combination with the electronic and vibrational transitions of $A_0^{0-0}$.

The $B_{1g}(H\ 2)$ frequency 3075 cm.$^{-1}$ cannot be found in the form of a band displaced by this amount above $A_0^{0-0}$; for such a band would be overlaid by the prominent band $O_2^{0-0}$. On the other hand, the second protium-stretching vibration, $A_g(H\ 2)$, is recognised in the assignment of the remaining high-frequency series, Y''. The parent band, $Y_0''^{0-0}$, is situated 3132 cm.$^{-1}$ above $A_0^{0-0}$, and starts a two-membered progression, the bands of which, though moderately sharp, appear to have a doublet structure similar to that of $A_0^{0-0}$. This is consistent with the view that the band $Y_0''^{0-0}$ involves an excitation, in the upper electronic state, of the vibration $A_g(H\ 2)$, in combination with the electronic and vibrational transitions of the $A_0^{0-0}$ doublet. The two upper-state protium-stretching frequencies, to which these assignments lead, are obviously in general agreement with the protium-stretching frequencies of benzene and 1 : 3 : 5-trideuterobenzene as determined in Parts II and VI.

It remains to be explained why we assign the upper of the two protium-stretching frequencies to the $A_g$ vibration, and the lower to the $B_{1g}$ vibration. There are two reasons. The first is the empirical analogy with the electronic ground state, in which the two corresponding frequencies stand in this order : these frequencies can be individually identified simply and with certainty by their polarisation in the Raman effect. The other reason is based on the theoretical consideration that the normal co-ordinate of the $B_{1g}$ protium-stretching vibration (cf. *J.*, 1946, 284, diagram IX) is identical with one normal co-ordinate of the $E_g^+$ protium-stretching vibration of benzene—not exactly and of mathematical principle, as with some normal co-ordinates which have been discussed above, but to a degree of approximation which is made very close by the high frequency and weak coupling of protium-stretching vibrations. In confirmation we find that, in the electronic ground state, the $B_{1g}$ protium-stretching frequency of 1 : 4-dideutero-benzene lies within five wave-numbers of the $E_g^+$ protium-stretching frequency of benzene. Now in the absorption spectrum of benzene we find both the $A_{1g}$ and the $E_g^+$ protium-stretching frequencies of the electronically excited state; but there is a clear distinction between them, inasmuch as the latter only can be excited without an accompanying perturbing vibration. In this way we know that the $E_g^+$ protium-stretching frequency of the excited state of benzene is 3080 cm.$^{-1}$. Our frequency, 3075 cm.$^{-1}$, of the excited state of 1 : 4-dideuterobenzene is 5 cm.$^{-1}$ below this, just as the $B_{1g}$ frequency of the ground state of 1 : 4-dideuterobenzene, 3042 cm.$^{-1}$, is 5 cm.$^{-1}$ below the $E_g^+$ frequency of the ground state of benzene, 3047 cm.$^{-1}$.

We may recapitulate these fundamental frequencies of the upper electronic state of 1 : 4-dideuterobenzene :

$$A_g(H\ 1)_{\text{excited}} = 2355 \text{ cm.}^{-1} \qquad A_g(H\ 2)_{\text{excited}} = 3132 \text{ cm.}^{-1}$$
$$B_{1g}(H\ 2)_{\text{excited}} = 3075 \text{ cm.}^{-1}$$

The corresponding ground-state frequencies, as determined in the Raman spectrum of liquid 1 : 4-dideuterobenzene, are as follows : $A_g(\text{H } 1) = 2280 \cdot 0$ cm.$^{-1}$; $A_g(\text{H } 2) = 3055 \cdot 0$ cm.$^{-1}$; $B_{1g}(\text{H } 2) = 3042$ cm.$^{-1}$ (Herzfeld, Hobden, Ingold, and Poole, *loc. cit.*). It will be noted that all the upper-state frequencies are higher than the corresponding ground-state frequencies, as we have already found for the hydrogen-stretching vibrations of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene (Parts II, IV, and VI).

(9) *Band Series* U *and* z.—Two band series remain, of which the first, U, has a counterpart in the absorption spectrum of benzene. It involves excitation in the upper electronic state of *two* quanta of the main perturbing vibration, $A_g(\text{C } 1)$ and $B_{1g}(\text{C } 1)$. Such even-quantum excitations should produce only weak spectral activity, and in fact the intensities of the bands of series U are very low.

The last series z can only tentatively be assigned. It is a three-membered progression of very weak bands, the first of which lies 1574 cm.$^{-1}$ above the electronic origin. It is not certain that these bands do not belong to series G, but they seem not to have the usual appearance of G bands nor the right intensity variation. If they are distinct, they cannot be explained solely in terms of independently determined frequencies, and thus must involve some additional upper-state frequency. Provisionally we may suggest the existence of an upper-state frequency, 787 cm.$^{-1}$, belonging to the planar deuterium-bending vibration, $B_{3u}(\text{H } 1)$, the ground-state frequency of which is 814 cm.$^{-1}$ (Bailey, Carson, Gordon, and Ingold, *loc. cit.*). An excitation in the upper state of the first overtone of this vibration might be held responsible for the production of series z.

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