# 63. *Structure of Benzene. Part XIX. The Infra-red Spectra of* 1 : 4-*Dideuterobenzene and* 1 : 2 : 4 : 5-*Tetradeuterobenzene : Description and Analysis.*

By C. R. Bailey, S. C. Carson, R. R. Gordon, and C. K. Ingold.

The infra-red absorption spectra of 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene have been mapped over a range of wave-lengths, 3—27$\mu$, large enough to include the bands arising from all the 13 active fundamental vibrations. Bands representing 21 vibration frequencies have been observed in each of the two spectra; and a number of the bands have been resolved with respect to their rotational branches.

The bands belonging to 12 of the allowed fundamental vibrations have been specifically identified in each spectrum. For the thirteenth allowed fundamental vibration there are several possible bands in either spectrum, and a definite assignment is deferred pending comparison with the infra-red spectra of other partly deuterated benzenes. The assignments offered are based on the observed frequencies, intensities, and band contours, considered in the light of the theoretical rules, and our empirical knowledge of the spectral regions in which frequencies corresponding to particular types of vibration should appear. Confirmation arises from comparisons of the frequencies of the two compounds with one another, and with relevant frequencies of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene : such comparisons are made with the help of the product rule of Teller and Redlich. Use is also made of considerations relating to the normal co-ordinates of the vibrations, and a scheme of approximate but orthogonal normal co-ordinates is given.

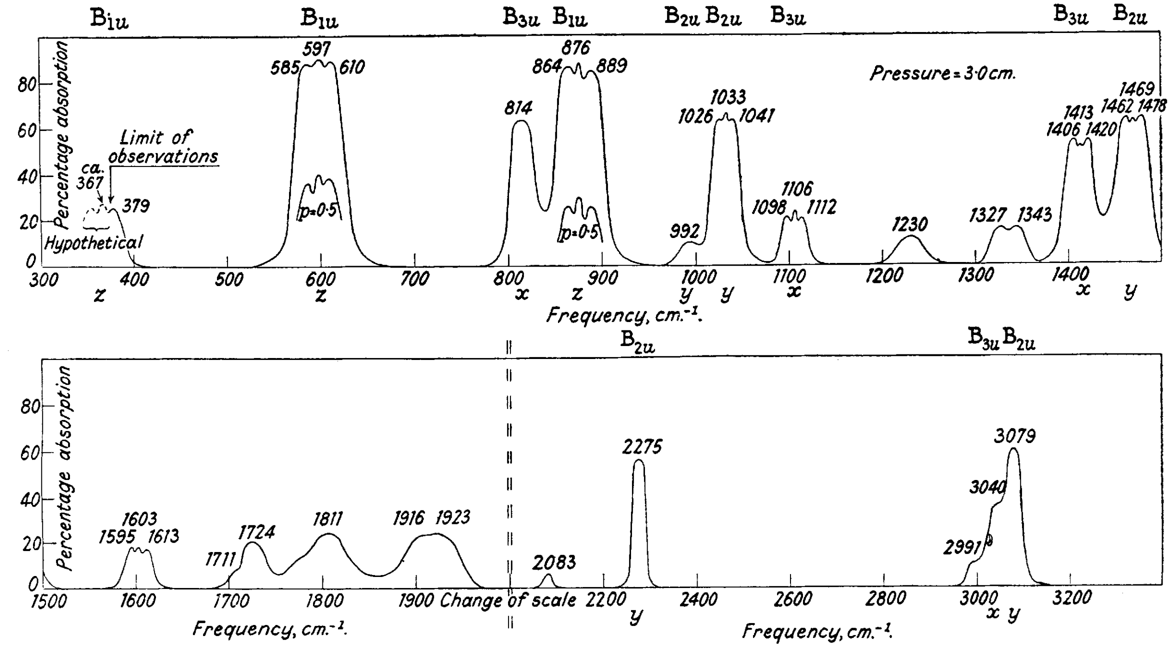
These 13 allowed fundamental vibrations belong to the series of 15 " ungerade " fundamental vibrations which 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene, in accordance with their symmetry, must each possess. The remaining 2 " ungerade " vibrations are forbidden both in the infra-red and in the Raman spectrum. However, their frequencies in 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene are known, on account of an argument which identifies their normal co-ordinates with those of certain vibrations of benzene and hexadeuterobenzene, and makes use of observed higher harmonic frequencies in the infra-red, Raman, and fluorescence spectra of the last two substances.

The fundamental frequencies, identified in this and the preceding paper, permit an assignment, agreeing with the selection rules, of all the higher harmonic frequencies appearing in the infra-red spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene.

No connected account of the infra-red spectra of 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene has yet been given, although a few brief references have been made to observations on individual frequencies (Ingold, *Z. Elektrochem.*, 1938, **44**, 20; *Proc. Roy. Soc.*, 1938, *A*, **169**, 149). We now describe these spectra, studied, as they have been, in absorption by the vapours of the two compounds over a range of wave-lengths, 3—27$\mu$, sufficient to include all the active fundamental frequencies.

The samples of the di- and tetra-deuterobenzene used were those which were prepared by Wilson and his collaborators, as recorded in Parts XII and XIII (this vol., pp. 235, 239). The spectrometric apparatus and methods were as described in Parts IV and XVI (J., 1936, 931; this vol., p. 252).

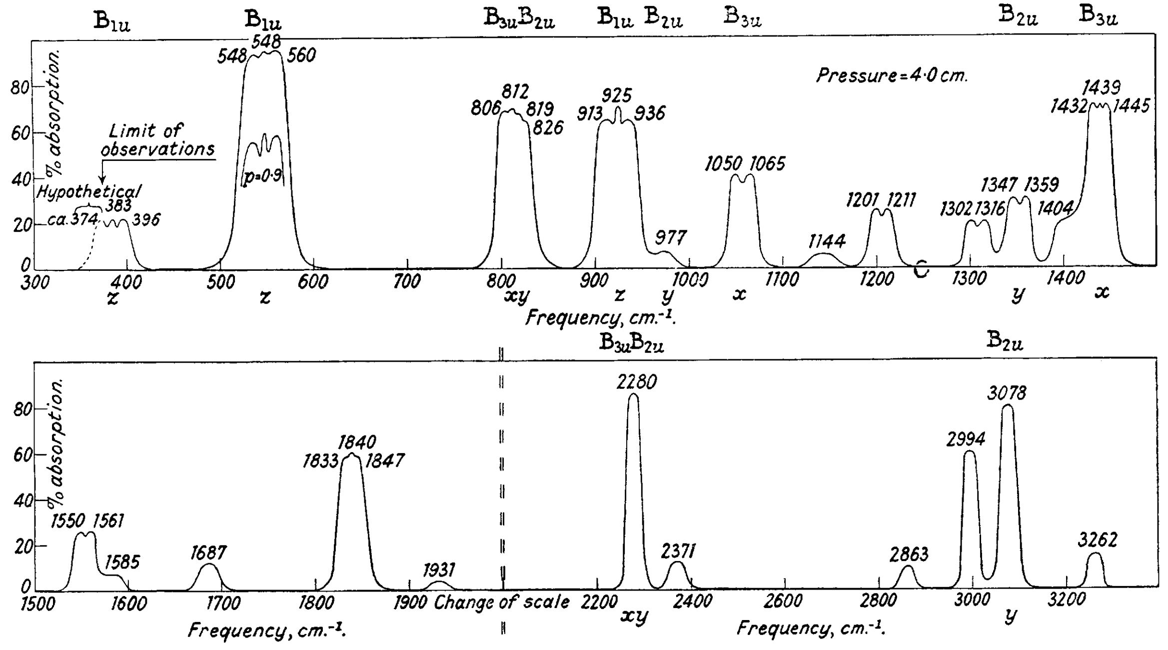
FIG. 1.



*Infra-red spectrum of* 1 : 4-*dideuterobenzene.*

Absorption bands were traced with the vapours at various pressures between 0·5 cm. and 7·0 cm. in an absorption tube 45 cm. long. The main general surveys were carried out with the vapour of 1 : 4-dideuterobenzene at 3 cm., and that of 1 : 2 : 4 : 5-tetradeuterobenzene at 4 cm. pressure. General maps of the spectra on a frequency scale are given in Figs. 1 and 2. In each diagram the continuous curve represents an average

FIG. 2.



*Infra-red spectrum of* 1 : 2 : 4 : 5-*tetradeuterobenzene.*

of data derived from several general surveys, as well as numerous detailed tracings of particular bands. The bands shown represent 21 vibration frequencies in each spectrum. A number of the bands have been resolved into their rotational branches.

Numerical details are given in the first five columns of Tables I and II. In each table the first two columns refer to individual intensity maxima, whilst the third records the frequency of the vibration responsible for each vibration–rotation band. As a guide to band type, there is recorded next the separation in cm.$^{-1}$ of the maxima of the P and R branches of those bands which were sufficiently resolved to permit this measurement. The next entry is the percentage absorption, at the strongest absorption maximum of each band, in 45 cm. length of vapour at the pressure, 3 or 4 cm., of the main spectrometric survey. The last three columns of each table contain our assignment of the fundamental frequencies and combination tones, the symmetry classes to which they belong, and the symmetry classes of the fundamental composing the higher harmonics.

TABLE I.

*Infra-red Spectrum of* 1 : 4-*Dideuterobenzene and Assignment.*

| **Wave-length** ($\mu$). | Frequency (cm.$^{-1}$). | Q or PR–mean. | PR–diff. | % Absorption; $p$ = 3 cm. | Assignment. | Symmetry class. | Symmetry of components. |
|---|---|---|---|---|---|---|---|
| 26·4 | 379 | *ca.* 367 | — | *ca.* 14 | Fundamental | $B_{1u}$ | — |
| 17·10<br>16·75<br>16·39 | 585<br>597<br>610 | 597 | 25 | 90 | Fundamental | $B_{1u}$ | — |
| 12·29 | 814 | 814 | — | 63 | Fundamental | $B_{3u}$ | — |
| 11·57<br>11·42<br>11·24 | 864<br>876<br>889 | 876 | 25 | 86 | Fundamental | $B_{1u}$ | — |
| 10·08 | 992 | 992 | — | 10 | Fundamental | $B_{2u}$ | — |
| 9·752<br>9·667<br>9·608 | 1026<br>1033<br>1041 | 1033 | 15 | 66 | Fundamental | $B_{2u}$ | — |
| 9·106<br>9·043<br>8·990 | 1098<br>1106<br>1112 | 1106 | 14 | 22 | Fundamental | $B_{3u}$ | — |
| 8·131 | 1230 | 1230 | — | 12 | 597 + 634 = 1231 | $B_{2u}$ | $B_{1u}$, $B_{3g}$ |
| 7·535<br>7·445 | 1327<br>1343 | 1335 | 16 | 17 | 597 + 736 = 1333<br>367 + 967 = 1334 | $B_{2u}$<br>$B_{2u}$ | $B_{1u}$, $B_{3g}$<br>$B_{1u}$, $B_{3g}$ |
| 7·108<br>7·073<br>7·041 | 1406<br>1413<br>1420 | 1413 | 14 | 56 | Fundamental | $B_{3u}$ | — |
| 6·838<br>6·807<br>6·764 | 1462<br>1469<br>1478 | 1469 | 16 | 64 | Fundamental | $B_{2u}$ | — |
| 6·269<br>6·240<br>6·201 | 1595<br>1603<br>1613 | 1603 | 18 | 15 | 970 + 634 = 1604<br>876 + 736 = 1612 | $B_{3u}$<br>$B_{2u}$ | $A_u$, $B_{3g}$<br>$B_{1u}$, $B_{3g}$ |
| 5·845 | 1711 | 1711 | — | 5 | 970 + 736 = 1706<br>404 + 1309 = 1713 | $B_{3u}$<br>$B_{1u}$ | $A_u$, $B_{3g}$<br>$A_u$, $B_{1g}$ |
| 5·801 | 1724 | 1724 | — | 21 | 814 + 909 = 1723<br>876 + 849 = 1725<br>992 + 736 = 1728 | $B_{2u}$<br>$B_{3u}$<br>$B_{1u}$ | $B_{3u}$, $B_{1g}$<br>$B_{1u}$, $B_{2g}$<br>$B_{2u}$, $B_{3g}$ |
| 5·522 | 1811 | 1811 | — | 23 | 970 + 849 = 1819 | $B_{2u}$ | $A_u$, $B_{2g}$ |
| 5·217<br>5·200 | 1916<br>1923 | 1916<br>1923 | — | 23 | 992 + 909 = 1901<br>970 + 967 = 1937 | $B_{3u}$<br>$B_{3u}$ | $B_{2u}$, $B_{1g}$<br>$A_u$, $B_{3g}$ |
| 4·800 | 2083 | 2083 | — | 5 | 1106 + 978 = 2084 | $B_{3u}$ | $B_{3u}$, $A_g$ |
| 4·396 | 2275 | 2275 | — | 55 | Fundamental | $B_{2u}$ | — |
| 3·343 | 2991 | 2991 | — | 7 | 1413 + 1569 = 2982<br>1413 + 1587 = 3000 | $B_{2u}$<br>$B_{3u}$ | $B_{3u}$, $B_{1g}$<br>$B_{3u}$, $A_g$ |
| 3·289<br>3·247 | 3040<br>3079 | 3040<br>3079 | —<br>— | 33<br>60 | Fundamental *<br>1469 + 1587 = 3056<br>Fundamental * | $B_{2u}$<br>$B_{2u}$<br>$B_{3u}$ | —<br>$B_{2u}$, $A_g$<br>— |

* See p. 294.

## DISCUSSION OF ASSIGNMENT.

Each of the $V_h$ benzenes, 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene, possesses 30 fundamental vibrations, each associated in principle with a different frequency, 15 of the vibrations being symmetric, and 15 antisymmetric, with respect to the centre of symmetry of the molecule. The former group, the "gerade" vibrations, are all active in the Raman effect, and were dealt with in the preceding paper. We are now concerned with the latter group, the "ungerade" vibrations, which are all inactive in Raman spectra; but 13 of them are active for absorption, and may be sought in infra-red spectra. These, as well as the two inactive vibrations,

### TABLE II.

*Infra-red Spectrum of* 1 : 2 : 4 : 5-*Tetradeuterobenzene and Assignment.*

| Wave-length ($\mu$). | Frequency (cm.$^{-1}$). | Q or PR–mean. | PR–diff. | % Absorption; $p$ = 4 cm. | Assignment. | Symmetry class. | Symmetry of components. |
|---|---|---|---|---|---|---|---|
| *ca.* 26·7 | *ca.* 374 | | | | | | |
| 26·1 | 383 | 383 | *ca.* 22 | 18 | Fundamental | $B_{1u}$ | — |
| 25·3 | 396 | | | | | | |
| 18·65 | 536 | | | | | | |
| 18·25 | 548 | 548 | 24 | 95 | Fundamental | $B_{1u}$ | — |
| 17·85 | 560 | | | | | | |
| 12·41 | 806 | | | | | | |
| 12·31 | 812 | 812 | *ca.* 13 | 70 | Fundamental | $B_{3u}$ | — |
| 12·21 | 819 | 819 | *ca.* 14 | 68 | Fundamental | $B_{2u}$ | — |
| 12·11 | 826 | | | | | | |
| 10·95 | 913 | | | | | | |
| 10·81 | 925 | 925 | 23 | 70 | Fundamental | $B_{1u}$ | — |
| 10·68 | 936 | | | | | | |
| 10·26 | 977 | 977 | — | 7 | Fundamental | $B_{2u}$ | |
| 9·522<br>9·392 | 1050<br>1065 | 1057 | 15 | 40 | Fundamental | $B_{3u}$ | — |
| 8·738 | 1144 | 1144 | — | 6 | 548 + 589 = 1137<br>383 + 767 = 1150 | $B_{1u}$<br>$B_{2u}$ | $B_{1u}$, $A_g$<br>$B_{1u}$, $B_{3g}$ |
| 8·324<br>8·263 | 1201<br>1211 | 1206 | 10 | 25 | 548 + 664 = 1212 | $B_{3u}$ | $B_{1u}$, $B_{2g}$ |
| 7·680<br>7·599 | 1302<br>1316 | 1309 | 14 | 20 | 383 + 930 = 1313<br>548 + 767 = 1315 | $B_{2u}$<br>$B_{2u}$ | $B_{1u}$, $B_{3g}$<br>$B_{1u}$, $B_{3g}$ |
| 7·425<br>7·361 | 1347<br>1359 | 1353 | 12 | 30 | Fundamental | $B_{2u}$ | — |
| 7·118 | 1404 | 1404 | — | 20 | 812 + 586 = 1398<br>812 + 589 = 1401<br>819 + 586 = 1405<br>819 + 589 = 1408<br>793 + 615 = 1408<br>548 + 862 = 1410 | $B_{2u}$<br>$B_{3u}$<br>$B_{3u}$<br>$B_{2u}$<br>$B_{3u}$<br>$B_{1u}$ | $B_{3u}$, $B_{1g}$<br>$B_{3u}$, $A_g$<br>$B_{2u}$, $B_{1g}$<br>$B_{2u}$, $A_g$<br>$A_u$, $B_{3g}$<br>$B_{1u}$, $A_g$ |
| 6·986 | 1432 | | | | | | |
| 6·948 | 1439 | 1439 | 13 | 70 | Fundamental | $B_{3u}$ | — |
| 6·920 | 1445 | | | | | | |
| 6·451<br>6·405 | 1550<br>1561 | 1556 | 11 | 25 | 793 + 767 = 1560<br>977 + 586 = 1563<br>977 + 589 = 1566 | $B_{3u}$<br>$B_{3u}$<br>$B_{2u}$ | $A_u$, $B_{3g}$<br>$B_{2u}$, $B_{1g}$<br>$B_{2u}$, $A_g$ |
| 6·307 | 1585 | 1585 | — | 7 | 819 + 767 = 1586<br>925 + 664 = 1589 | $B_{1u}$<br>$B_{3u}$ | $B_{2u}$, $B_{3g}$<br>$B_{1u}$, $B_{2g}$ |
| 5·927 | 1687 | 1687 | — | 12 | 819 + 862 = 1681<br>925 + 767 = 1692 | $B_{2u}$<br>$B_{2u}$ | $B_{2u}$, $A_g$<br>$B_{1u}$, $B_{3g}$ |
| 5·455 | 1833 | | | | | | |
| 5·435 | 1840 | 1840 | 14 | 60 | 977 + 862 = 1839 | $B_{2u}$ | $B_{2u}$, $A_g$ |
| 5·414 | 1847 | | | | | | |
| 5·181 | 1931 | 1931 | — | 4 | 977 + 961 = 1938 | $B_{2u}$ | $B_{2u}$, $A_g$ |
| 4·386 | 2280 | 2280 | — | 85 | Fundamentals * | $B_{2u}$<br>$B_{3u}$ | —<br>— |
| 4·217 | 2371 | 2371 | — | 12 | 793 + 1564 = 2357<br>812 + 1564 = 2376<br>812 + 1572 = 2384 | $B_{1u}$<br>$B_{2u}$<br>$B_{3u}$ | $A_u$, $B_{1g}$<br>$B_{3u}$, $B_{1g}$<br>$B_{3u}$, $A_g$ |
| 3·493 | 2863 | 2863 | — | 12 | 2280 + 586 = 2866<br>2280 + 586 = 2866<br>2280 + 589 = 2869<br>2280 + 589 = 2869 | $B_{3u}$<br>$B_{2u}$<br>$B_{2u}$<br>$B_{3u}$ | $B_{2u}$, $B_{1g}$<br>$B_{3u}$, $B_{1g}$<br>$B_{2u}$, $A_g$<br>$B_{3u}$, $A_g$ |
| 3·339 | 2994 | 2994 | — | 60 | 1439 + 1564 = 3003<br>1439 + 1572 = 3011 | $B_{2u}$<br>$B_{3u}$ | $B_{3u}$, $B_{1g}$<br>$B_{3u}$, $A_g$ |
| 3·248 | 3078 | 3078 | — | 80 | Fundamental | $B_{2u}$ | — |
| 3·066 | 3262 | 3262 | — | 15 | 2280 + 972 = 3252<br>977 + 2285 = 3262 | $B_{3u}$<br>$B_{2u}$<br>$B_{2u}$ | $B_{2u}$, $B_{1g}$<br>$B_{3u}$, $B_{1g}$<br>$B_{2u}$, $A_g$ |
| 2·598 | 3849 | 3849 | — | 8 | 2280 + 1564 = 3844<br>2280 + 1564 = 3844<br>3078 + 767 = 3845<br>2280 + 1572 = 3852<br>2280 + 1572 = 3852<br>812 + 3045 = 3857<br>819 + 3045 = 3864 | $B_{3u}$<br>$B_{2u}$<br>$B_{1u}$<br>$B_{2u}$<br>$B_{3u}$<br>$B_{3u}$<br>$B_{2u}$ | $B_{2u}$, $B_{1g}$<br>$B_{3u}$, $B_{1g}$<br>$B_{2u}$, $B_{3g}$<br>$B_{2u}$, $A_g$<br>$B_{3u}$, $A_g$<br>$B_{3u}$, $A_g$<br>$B_{2u}$, $A_g$ |
| 2·475 | 4041 | 4041 | — | 12 | 3078 + 961 = 4039<br>3078 + 972 = 4050 | $B_{2u}$<br>$B_{3u}$ | $B_{2u}$, $A_g$<br>$B_{2u}$, $B_{1g}$ |
| 2·231 | 4482 | 4482 | — | 12 | 1439 + 3045 = 4484 | $B_{3u}$ | $B_{3u}$, $A_g$ |

* See p. 294.

are discussed in this paper. The two inactive vibrations form one symmetry class, and the 13 infra-red-active vibrations divide themselves into three symmetry classes, as shown below (Part XI, Table IX, this vol., p. 228):

| Symmetry class | $A_u$ | $B_{1u}$ | $B_{2u}$ | $B_{3u}$ |
|---|---|---|---|---|
| No. of frequencies | 2 | 3 | 5 | 5 |
| Direction of $M'$ | — | $z$ | $y$ | $x$ |
| Band type | — | $\psi \parallel$ | $\psi \perp r$ | $\psi \perp r$ |

The distinctions of symmetry may be briefly explained. The molecular model has three two-fold axes of symmetry, $z$ normal to the ring, $y$ through the unique para-positions, and $x$ perpendicular to the other two axes. The $A_u$ vibrations are symmetric with respect to all three of these axes, but the other vibrations are symmetric with respect to only one axis, and are antisymmetric with respect to the other two axes. The $B_{1u}$, $B_{2u}$, and $B_{3u}$ vibrations are symmetric with respect to the $z$, $y$, and $x$ axes respectively.

As to spectral activity, the $A_u$ vibrations do not involve an oscillating electric moment, but the $B_{1u}$, $B_{2u}$, and $B_{3u}$ vibrations are associated with oscillating electric moments parallel to the $z$, $y$, and $x$ axes respectively. Thus the $A_u$ vibrations are spectrally inactive. The $B_{1u}$ vibrations give rise to what we call $z$-bands, or pseudo-parallel bands, in the infra-red spectrum. Their contours are very similar to those of the parallel bands of a symmetrical-top ($D_{6h}$ or $D_{3h}$) benzene; in particular, they are characterised by a separation of about 24 cm.$^{-1}$ between the intensity maxima of the P and R rotational branches. The $B_{2u}$ vibrations will produce $y$-bands, and the $B_{3u}$ vibrations $x$-bands, types which may be collectively described as pseudo-perpendicular. They are similar to each other, and to the perpendicular bands of symmetrical-top benzenes; and thus they are characterised by distinctly smaller separations, roughly 15 cm.$^{-1}$, between the intensity maxima of their P and R branches. These characters are a useful guide in the assignment of infra-red bands.

*The $B_{1u}$ Fundamental Frequencies.*—The identification in each spectrum of the bands which corresponds to the three vibrations of this symmetry class is based mainly on the band contours. We give below the Q-branch frequencies (in cm.$^{-1}$) of the bands assigned to these vibrations, and (in parenthesis) the frequency separations of the intensity maxima of the P and R branches:

| | | | |
|---|---|---|---|
| 1 : 4-$C_6H_4D_2$ | *ca.* 367 (—) | 597 (25) | 876 (25) |
| 1 : 2 : 4 : 5-$C_6H_2D_4$ | 383 (*ca.* 22) | 548 (24) | 925 (23) |

Five of these bands certainly have, and the sixth probably has, a pseudo-parallel structure. All the other bands which have been resolved with respect to their rotational branches are of the pseudo-perpendicular type.

All six frequencies lie too low to be explained as summation tones; and the strength with which the frequencies 597 and 876 cm.$^{-1}$ of 1 : 4-dideuterobenzene, and the frequencies 548 and 925 cm.$^{-1}$ of 1 : 2 : 4 : 5-tetradeuterobenzene, appear in their respective spectra are such as to preclude any attempt to interpret these four bands as difference tones. Therefore they must be fundamental bands, and, from their contours, $B_{1u}$ fundamental bands.

The bands at 367 cm.$^{-1}$ in the spectrum of 1 : 4-dideuterobenzene, and at 383 cm.$^{-1}$ in that of 1 : 2 : 4 : 5-tetradeuterobenzene, were difficult to observe with precision, because their long-wave sides spread beyond the limit within which satisfactory measurements of absorption could be made with the apparatus available. However, the two bands clearly correspond, and for one of them it was possible directly to establish a pseudo-parallel structure. Obviously they cannot be summation tones. Their intensity is not so great that we can immediately dismiss the idea explaining them as difference tones; but there are no difference tones of known fundamental frequencies which could give pseudo-parallel bands of the required frequencies. This argument of exclusion is not quite complete because, for each of the benzenes, there is one fundamental frequency which has not been definitely determined. However, we expect a fundamental $B_{1u}$ band, in each spectrum, in just the frequency region in which the observed bands appear: these expected fundamental frequencies should lie between 405 and 352 cm.$^{-1}$, the frequencies of the spectrally inactive $E_u^+$ carbon vibrations of benzene and hexadeuterobenzene, and close to 373 cm.$^{-1}$, the corresponding frequency of 1 : 3 : 5-trideuterobenzene, which is observed in the Raman effect. The low-frequency infra-red bands of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene fulfil these requirements and there are no other observed bands which do so. The relatively low intensity of the bands is not a difficulty, because the corresponding vibration in benzene is spectrally inactive, and, being a carbon vibration, is not changed sufficiently by deuterium substitution to give bands of great intensity. Similarly, the corresponding frequencies of mono-, 1 : 3 : 5-tri-, and penta-deuterobenzene, which are active in the Raman effect, appear only weakly in the Raman spectra of these substances. As a final argument we can apply the product theorem of Teller and Redlich:

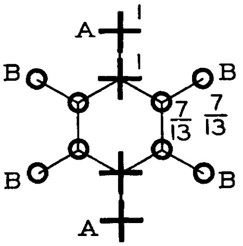
$$\frac{\Pi B_{1u}(1:4\text{-}C_6H_4D_2)}{\Pi B_{1u}(1:2:4:5\text{-}C_6H_2D_4)} = \frac{367 \times 597 \times 876}{383 \times 548 \times 925} = 0{\cdot}989 \text{ (harmonic value} = 0{\cdot}988)$$

The $B_{1u}$ vibrations of the $V_h$ benzenes may be regarded as arising from vibrations of the forms of the two $E_u^+$ vibrations and the single $A_{2u}$ vibration of a $D_{6h}$ benzene. The $E_u^+$ vibrations are non-trigonal; they involve out-of-plane motions of the atoms; they are degenerate, but we are concerned only with that normal co-ordinate of each vibration which has the symmetry of the $V_h$ vibrations that are to be formed, *viz.*, symmetry with respect to the two-fold $z$-axis and antisymmetry with respect to the two-fold $x$- and $y$-axes; finally, they consist of one " carbon " vibration, in which the atoms of each CH-group move on parallel lines in phase, and one " hydrogen " vibration, in which the atoms of each CH-group move along the same lines but in opposite phase. The single $A_{2u}$ vibration is hexagonally symmetrical, involves out-of-plane motions of the atoms, and is a " hydrogen " vibration.

With the arrangement of unequal hydrogen masses which is characteristic of benzenes of $V_h$ symmetry, these vibrations undergo some mutual modifications. But the resulting frequencies suggest that the mutual disturbance is not very profound, a circumstance which may be connected with the fact that all the original frequencies are proportionately well separated (*e.g.*, 405, 671, 970 cm.$^{-1}$ in benzene). The following comparison shows that, whilst corresponding $B_{1u}$ frequencies of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene are always within 50 cm.$^{-1}$ of each other, they are always bracketed between the analogous benzene and hexadeuterobenzene frequencies, and always themselves bracket the mean of the latter frequencies :

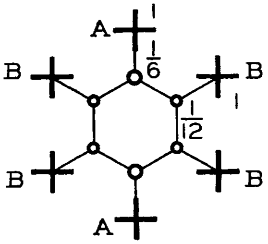
| | $C_6H_6$. | $C_6D_6$. | Mean. | | 1 : 4-$C_6H_4D_2$. | 1 : 2 : 4 : 5-$C_6H_2D_4$. |
|---|---|---|---|---|---|---|
| $E_u^+$ carbon ......... | 405 | 352 | 378 | $B_{1u}$ .............. | 367 | 383 |
| $A_{2u}$ .................. | 671 | 497 | 584 | | 597 | 548 |
| $E_u^+$ hydrogen ...... | 970 | 793 | 882 | | 876 | 925 |

It therefore seems clear that the original $D_{6h}$ normal co-ordinates, of course after some modification of the atomic amplitudes, will provide a better approximation to the actual normal co-ordinates of the vibrations of the $V_h$ benzenes than that which would start with the extreme assumption, such as we have several times made in the two preceding papers, that the hydrogen vibrations decompose into pure protium and deuterium vibrations, possibly with a correlated change in the carbon vibrations of the same symmetry class. This type of decomposition operates most generally and most exactly with hydrogen stretching vibrations, less thoroughly in planar bending vibrations, and with least generality and precision in bending vibrations normal to the ring.



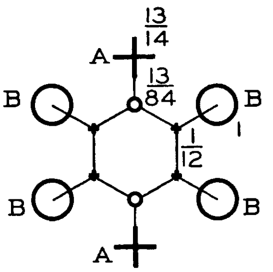
(I.)

$C_6H_4D_2$, 367 cm.$^{-1}$.
$C_6H_2D_4$, 383 cm.$^{-1}$.



(II.)

$C_6H_4D_2$, 597 cm $^{-1}$.
$C_6H_2D_4$, 548 cm.$^{-1}$.



(III.)

$C_6H_4D_2$, 876 cm.$^{-1}$.
$C_6H_2D_4$, 925 cm.$^{-1}$.

If we were to assume such a decomposition in the present case, and were then to try to assign the observed frequencies to the resulting normal co-ordinates, we should reach the unacceptable result that ratios of frequencies of supposedly isomorphous protium and deuterium vibrations considerably exceed $\sqrt{2}$. Therefore, we set up, as representing the best type of approximation we can make without a knowledge of the force field, the vector diagrams (I), (II), and (III) : except with regard to the atomic amplitudes, they are similar to the relevant diagrams applying to $D_{6h}$ benzenes.

The scheme of amplitudes, given for 1 : 4-dideuterobenzene by the small figures associated with the diagrams, satisfies the orthogonality relationship, as well as the condition that no vibration shall contain any translatory motion of the molecule as a whole; but the scheme is still arbitrary. First, it assumes that, in the carbon vibration (I), the amplitudes within each CH and CD group are equal. This is certainly incorrect in the direction of under-estimating the content of hydrogen motion (Part XVII, this vol., p. 261); but we have no simple way of making a more exact assessment of the relative amplitudes : an altered assumption would naturally entail changes in the amplitudes of the two hydrogen vibrations, (II) and (III). In the latter, the relations between the CH- and CD-amplitudes are for another reason not fully determined : the orthogonality principle would still be satisfied if we should multiply the stated amplitudes of the four atoms of the two CD-groups of (II) by a single constant factor, provided we also multiply the amplitudes of the eight atoms of the four CH-groups of (III) by the same factor. A corresponding scheme for 1 : 2 : 4 : 5-tetradeuterobenzene would involve the following relative amplitudes : For (I) : CH, 1, 1; CD, 13/28, 13/28. For (II) : CH, 1/12, 1; CD, 1/6, 1. For (III) : CH, 1/12, 1; CD, 13/336, 13/56. It would readily be possible in fixing these amplitudes to choose these disposable quantities in such a way as to render qualitatively intelligible the relationships between the various frequencies; but it is not possible precisely to calculate the amplitudes without a knowledge of the force field.

*The $B_{2u}$ Fundamental Frequencies.*—It is helpful to give some preliminary consideration to the nature of the vibrations. There are five : and they are symmetric to the two-fold $y$-axis, but antisymmetric to the two-fold axes $x$ and $z$. Their motion lies in the plane of the ring, and they create a variable dipole moment in the $y$-direction. The five are collectively related to the two non-degenerate $B_{1u}$, and the three degenerate $E_u^-$, vibrations of the $D_{6h}$ benzene model, with the understanding that the only normal co-ordinate of each degenerate vibration which is relevant in this connexion is that which has the symmetry above specified. The trigonally symmetrical $B_{1u}$ vibrations consist of one carbon bending vibration and one hydrogen stretching vibration. These are inactive in the infra-red spectra of the $D_{6h}$ benzenes. The non-trigonal $E_u^-$ vibrations comprise another hydrogen stretching vibration, a hydrogen bending vibration, and what we have called elsewhere a ring " deformation " vibration, which involves both stretching and bending of the bonds. These vibrations are active in the infra-red spectra of $D_{6h}$ benzenes.

When the five $D_{6h}$ vibrations interact under the less symmetrical distribution of atomic masses characteristic of the $V_h$ benzene model, the $B_{1u}$ carbon vibration, in which the moving unit is essentially the whole CH-group, will be only slightly changed, though it is the change which gives the vibration a finite intensity in the infra-red spectrum. The $B_{1u}$ and $E_u^-$ hydrogen stretching vibrations will as usual interact practically completely (cf. Part XVII, this vol., p. 260) to form a pure protium, and a pure deuterium, stretching vibration. Reference to the $D_{6h}$ normal co-ordinates shows that the $E_u^-$ hydrogen bending vibration will appear practically unchanged as a vibration of the $V_h$ model. It follows that the $E_u^-$ deformation vibration can only be slightly changed, since there is no other frequency of the symmetry class with which it can interact extensively.

The frequencies (cm.$^{-1}$) of those infra-red bands of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene which we assign as fundamentals of $B_{2u}$ symmetry with respect to the $V_h$ model, are here listed for convenience. Where the resolution of a band into its component branches has been effected, the frequency separation of the P and R intensity maxima is noted (in parenthesis), as partial confirmation of the conclusion that these are bands of the pseudo-perpendicular type :

| | | | | | |
|---|---|---|---|---|---|
| 1 : 4-$C_6H_4D_2$ ......................... | 992 (—) | 1033 (15) | 1469 (16) | 2275 (—) | 3060 (– ) |
| 1 : 2 : 4 : 5-$C_6H_2D_4$ .................... | 819 (14) | 977 (—) | 1353 (12) | 2280 (—) | 3078 (—) |

We may now consider the assignment in more detail, dealing first with the carbon bending vibration. Klit and Langseth have already noted (*J. Chem. Physics*, **1937**, **5**, 925) that those carbon frequencies of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene which are related to the $B_{1u}$ carbon frequencies of benzene and hexadeuterobenzene should be uniformly spaced between the latter. These spectrally inactive carbon frequencies of the $D_{6h}$ benzenes are determined in Part XXI (this vol., p. 316) : they are 1010 cm.$^{-1}$ for benzene, and 963 cm.$^{-1}$ for hexadeuterobenzene. The predicted positions of the $B_{2u}$ carbon frequencies of the $V_h$ benzenes are thus 994 cm.$^{-1}$ for 1 : 4-dideuterobenzene, and 979 cm.$^{-1}$ for 1 : 2 : 4 : 5-tetra-deuterobenzene. Bands in these positions appear in the spectra. They are weak, and of nearly equal intensity, as they should be. There are no other bands that could be assigned to this vibration. Both these frequencies are required as fundamental frequencies for the interpretation of observed combination tones.

The hydrogen stretching frequencies are easily identified. In the spectrum of 1 : 4-dideuterobenzene the only allowed deuterium stretching frequency is that of the $B_{2u}$ symmetry class; and a single, strong band appears, of peak frequency 2275 cm.$^{-1}$, which cannot represent anything else than this deuterium stretching vibration. Two protium stretching frequencies are allowed, one of the present symmetry class, and one of the $B_{3u}$ class; and two strong bands appear in the relevant region, at frequencies 3040 and 3079 cm.$^{-1}$. The question of which of these belongs to the $B_{2u}$ class is discussed below. In the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene two deuterium stretching frequencies, one belonging to the $B_{2n}$, and one to the $B_{3u}$ symmetry class, are allowed by the selection rules; but only one strong, unresolved band, of peak frequency 2280 cm.$^{-1}$, appears in the relevant part of the spectrum. We conclude that the two active frequencies are too nearly coincident to render possible with our apparatus a resolution of the overlapped bands. A single protium stretching frequency, that belonging to the $B_{2u}$ class, is allowed in this spectrum; and a single, strong band appears in the appropriate position at 3078 cm.$^{-1}$.

Concerning the allocation of the frequencies 3040 and 3079 cm.$^{-1}$ of 1 : 4-dideuterobenzene, an application of the product theorem makes it rather improbable that the lower of these belongs to the $B_{2u}$ symmetry class, but indicates that the upper frequency might very possibly belong to this class. However, the acceptance of this indication involves assigning the lower frequency to the $B_{3u}$ class, and the difficulty then arises that the intensities of the two bands are the wrong way round. The $B_{2u}$ protium stretching vibration produces a variable dipole moment in the $y$-direction, whilst the corresponding $B_{3u}$ protium vibration produces one in the $x$-direction. Therefore the $B_{3u}$ band should be the stronger since the protium bonds, which extend and contract during the vibration, are inclined at angles of 30° to the $x$-direction, but at 60° to the $y$-direction. Actually it is the higher frequency, 3079 cm.$^{-1}$, which appears considerably the more strongly, and it is this frequency which in consequence we must assign to the $B_{3u}$ vibration. The difficulty of the unsatisfactory product ratio, arising from the apparent necessity of assigning the frequency 3040 cm.$^{-1}$ to the $B_{2u}$ vibration, is overcome by noting that a combination tone exists, $(A_g)1587 + (B_{2u})1469 = (B_{2u})3056$, which could enter into resonance with the $B_{2u}$ fundamental frequency with the production of a doublet. Such a phenomenon is observed in the infra-red spectrum of benzene itself (Part IV, J., 1936, 931) : the hydrogen stretching fundamental frequency, 3080 cm.$^{-1}$, appears as a double band, with maxima at 3061 and 3098 cm.$^{-1}$, and it is the corresponding combination tone, $(E_g^+)$ 1596 + $(E_u^-)$ 1485 = $(E_u^-)$ 3081, which is responsible for the doubling.* We therefore

---

* This may be an over-simplification: the band appears to have a third, weaker maximum (Leberknight, *Physical Rev.*, 1933, **43**, 971). It could be explained by the known circumstance that one of the fundamental components of the resonating combination tone is itself doubled by resonance with a combination frequency.

assume a similar doubling in the spectrum of 1 : 4-dideuterobenzene : one component of the split frequency is recognised in the band at 3040 cm.$^{-1}$, whilst the other, we assume, is contained in, and contributes a minor part of the intensity of, the much stronger band at 3079 cm.$^{-1}$. As usual, we take the mean of the split frequencies, 3060 cm.$^{-1}$, as the unperturbed fundamental frequency. The adoption of this as the $B_{2u}$ protium stretching frequency gives an acceptable product ratio, as we shall show later.

With regard to the hydrogen bending vibrations, we base our considerations on the conclusion of Part VIII (J., 1936, 971) that the $E_u^-$ vibrations of $D_{6h}$ benzenes contain a very nearly pure hydrogen bending vibration. The already given normal co-ordinate diagrams of this degenerate vibration (Fig. 1 of Part XI, this vol., p. 231) are constructed on this basis. They show that in the particular normal co-ordinate with which we are now concerned, namely, that which has two-fold symmetry with respect to the $y$-axis, the four atoms which lie on the $y$-axis do not move [cf. diagram (VII), p. 296]. It follows that the form of the vibration will be preserved in 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene. It also follows that its frequency in 1 : 4-dideuterobenzene will be the same as it is in benzene, whilst its frequency in 1 : 2 : 4 : 5-tetradeuterobenzene will be the same as in hexadeuterobenzene. All this, of course, is true to the extent to which the normal co-ordinate diagram is exact. In benzene and hexadeuterobenzene the vibration is active in the infra-red spectrum : its frequencies are 1037 cm.$^{-1}$ in benzene, and 813 cm.$^{-1}$ in hexadeuterobenzene. In the infra-red spectrum of 1 : 4-dideuterobenzene we find a strong, pseudo-perpendicular band of frequency 1033 cm.$^{-1}$. This is evidently the $B_{2u}$ fundamental band : it is susceptible of no other explanation. In the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene there are two strongly overlapped bands, having the frequencies 812 and 819 cm.$^{-1}$, either of which might be the $B_{2u}$ band. Whilst the product rule does not exclude the choice of the lower of these frequencies, it favours the assignment of the frequency 819 cm.$^{-1}$ to the $B_{2u}$ class of fundamental frequencies (see below).

As we have shown, the ring deformation vibration will not be largely changed in form in passing over from $D_{6h}$ benzenes to $V_h$ benzenes; and hence its frequencies in 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene may be expected to lie within the range of the related frequencies, 1485 and 1333 cm.$^{-1}$, of benzene and hexadeuterobenzene. In the spectrum of the $V_h$ benzenes several bands are observed in this frequency range. In 1 : 4-dideuterobenzene there are active frequencies at 1335, 1413, and 1469 cm.$^{-1}$; and in 1 : 2 : 4 : 5-tetradeuterobenzene at 1353, 1404, and 1439 cm.$^{-1}$. The product theorem shows quite clearly (see below) that we must select the frequency 1469 cm.$^{-1}$ of 1 : 4-dideuterobenzene, and the frequency 1353 cm.$^{-1}$ of 1 : 2 : 4 : 5-tetradeuterobenzene, for assignment to the $B_{2u}$ symmetry class. The other frequencies mentioned are then quite readily assigned, either as $B_{3u}$ fundamental frequencies, or as combination tones.

We must now give details of the above-mentioned inferences derived from the product theorem. They are obtained by comparing the $B_{2u}$ infra-red frequencies of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene with each other, with the $A_1'$ Raman frequencies of 1 : 3 : 5-trideuterobenzene, and with $A_{1g}$ Raman and $E_u^-$ infra-red frequencies of benzene and hexadeuterobenzene.

Applying the product formula to known Raman frequencies of benzene, 1 : 3 : 5-trideuterobenzene and hexadeuterobenzene, and making our usual allowance for the effect of anharmonicity (Part XI, this vol., pp. 232, 233), we have

$$\frac{\Pi A_{1g}, B_{1u}(C_6H_6)}{\Pi A_1'(C_6H_3D_3)} = \frac{991{\cdot}6 \times 3061{\cdot}9 \times \Pi B_{1u}(C_6H_6)}{956{\cdot}2 \times 1003{\cdot}6 \times 2281{\cdot}9 \times 3052{\cdot}7} = 1{\cdot}400 \text{ (assumed, the harmonic value being } 1{\cdot}414)$$

and likewise

$$\frac{\Pi A_1'(C_6H_3D_3)}{\Pi A_{1g}, B_{1u}(C_6D_6)} = \frac{956{\cdot}2 \times 1003{\cdot}6 \times 2281{\cdot}9 \times 3052{\cdot}7}{943{\cdot}2 \times 2292{\cdot}6 \times \Pi B_{1u}(C_6D_6)} = 1{\cdot}400 \text{ (assumed, the harmonic value being } 1{\cdot}414)$$

The derived products, $\Pi B_{1u}(C_6H_6) = 3082 \times 10^3$ cm.$^{-2}$, and $\Pi B_{1u}(C_6D_6) = 2208 \times 10^3$ cm.$^{-2}$, have the ratio 1·396 (harmonic value, 1·414).

Applying the product rule now to the former of these products, known infra-red frequencies of benzene, and the assigned $B_{2u}$ fundamental frequencies of 1 : 4-dideuterobenzene, we obtain

$$\frac{\Pi B_{1u}, E_u^-(C_6H_6)}{\Pi B_{2u}(C_6H_4D_2)} = \frac{3082 \times 10^3 \times 1037 \times 1485 \times 3080}{992 \times 1033 \times 2275 \times 3060 \times 1469} = 1{\cdot}395 \text{ (harmonic value} = 1{\cdot}396)$$

This result shows that the deformation frequency 1469 cm.$^{-1}$ of 1 : 4-dideuterobenzene has been correctly chosen from amongst the possibilities mentioned earlier. It also shows that we could not replace the frequency 3060 cm.$^{-1}$ of the protium stretching vibration by the lower frequency 3040 cm.$^{-1}$ without raising the product ratio to 0·7% above the harmonic value : such a high value cannot be ruled out as impossible, but it would be unusual.

A further application of the product rule to corresponding data for hexadeuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene yields the result

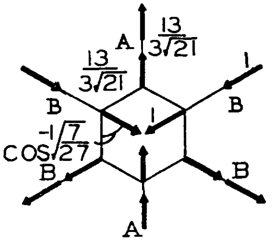
$$\frac{\Pi B_{2u}(C_6H_2D_4)}{\Pi B_{1u}, E_u^-(C_6D_6)} = \frac{977 \times 819 \times 2280 \times 3078 \times 1353}{2208 \times 10^3 \times 813 \times 1333 \times 2294} = 1{\cdot}384 \text{ (harmonic value} = 1{\cdot}396)$$

This shows that the deformation frequency of 1 : 2 : 4 : 5-tetradeuterobenzene, 1353 cm.$^{-1}$, has been correctly selected from amongst the possibilities mentioned. It is also clear that the replacement of the deuterium bending frequency, 819 cm.$^{-1}$, by its alternative, 812 cm.$^{-1}$, would lead to a product ratio lying about 2% below the harmonic value, that is, lower than is usual for product ratios of this magnitude.

Finally we may apply the product rule in a direct comparison of the assigned $B_{2u}$ fundamental frequencies of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene. The result is satisfactory :

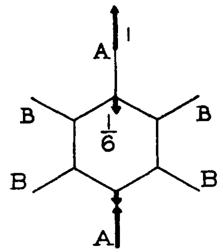
$$\frac{\Pi B_{2u}(C_6H_4D_2)}{\Pi B_{2u}(C_6H_2D_4)} = \frac{992 \times 1033 \times 2275 \times 3060 \times 1469}{977 \times 819 \times 2280 \times 3078 \times 1353} = 1{\cdot}379 \text{ (harmonic value} = 1{\cdot}396)$$

Vector diagrams of these vibrations (IV—VIII) are given below, together with a scheme of amplitudes, applying to 1 : 4-dideuterobenzene, which preserves the orthogonality of the vibrations and their freedom from molecular translation. Arbitrarily we make the amplitudes within each CH- or CD-group equal in diagrams (IV) and (VIII). It is necessary in these diagrams slightly to change the directions of the vectors which lie off the $y$-axis from those directions which would apply to a $D_{6h}$ benzene; and arbitrarily we have made all the directional changes equal (they amount only to about 0·6°). The amplitudes of a corresponding scheme for 1 : 2 : 4 : 5-tetradeuterobenzene are obvious, except in the cases of diagrams (IV) and (VIII); for these the amplitudes are unity for the CH-groups and $3\sqrt{78}/28$ for the CD-groups; and angles between the $y$-axis and those atomic vectors which do not lie along that axis have the value $\cos^{-1}\sqrt{13/54}$.



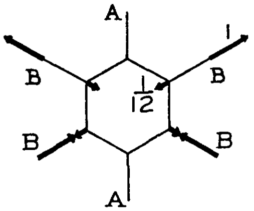
(IV.)

$C_6H_4D_2$, 992 cm.$^{-1}$.
$C_6H_2D_4$, 977 cm.$^{-1}$.



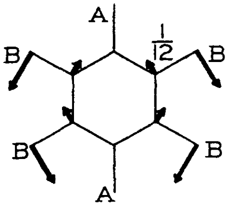
(V.)

$C_6H_4D_2$, 2275 cm.$^{-1}$.
$C_6H_2D_4$, 3078 cm.$^{-1}$.



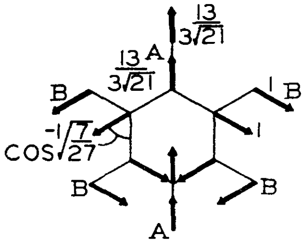
(VI.)

$C_6H_4D_2$, 3060 cm.$^{-1}$.
$C_6H_2D_4$, 2280 cm.$^{-1}$.



(VII.)

$C_6H_4D_2$, 1033 cm.$^{-1}$.
$C_6H_2D_4$, 819 cm.$^{-1}$.



(VIII.)

$C_6H_4D_2$, 1469 cm.$^{-1}$.
$C_6H_2D_4$, 1353 cm.$^{-1}$.

*The $B_{3u}$ Fundamental Frequencies.*—The members of this class of $V_h$ vibrations have their motion in the plane of the ring, and produce an electric moment oscillating along the $x$-direction. They can be regarded as derived from the two $B_{2u}$ vibrations, and the three $E_u^-$ vibrations, of the $D_{6h}$ benzene model. The $B_{2u}$ vibrations of this model consist of one carbon stretching, and one hydrogen bending, vibration, both trigonally symmetrical. The $E_u^-$ vibrations comprise, according to the conclusions of Part VIII (J., 1936, 971), a hydrogen stretching, a hydrogen bending, and a ring deformation vibration; but we are concerned now only with that normal co-ordinate of each of these degenerate vibrations which is symmetric with respect to the two-fold $x$-axis and antisymmetric with respect to the two-fold $y$- and $z$-axes. With the less symmetrical distribution of atomic masses in the $V_h$ benzenes, these vibrations must to some extent mix together, and thus modify one another. The two hydrogen bending vibrations may be expected to interact radically with the production of two new vibrations, one of which will be essentially a protium bending, and the other a deuterium bending, vibration. The carbon stretching vibration, however, cannot undergo any profound change, because the moving masses are effectively whole CH- and CD-groups. And the hydrogen stretching vibration will not change appreciably, because, in so far as it is a pure stretching vibration, the atoms on the $y$-axis do not move, even under $D_{6h}$ symmetry, so that the vibration is already of such a form as to affect only one kind of hydrogen in a $V_h$ benzene. It follows that the remaining member of the class, the ring deformation vibration, cannot be profoundly altered.

We do not in this paper completely solve the problem of identifying the frequencies of the $B_{3u}$ family of vibrations. As to four of them there is no special difficulty : frequencies from the spectra can be assigned with a high probability of correctness. The fifth is the carbon stretching vibration : it is possible to point, in each spectrum, to several active frequencies, any of which (subject to necessary correlations between the spectra) might represent the fundamental frequency in question; but it is not possible, on the evidence now given, to make a definite assignment of frequencies to this vibration, and the matter is therefore left for further consideration in Part XXI (this vol., p. 316). The determination of the $B_{2u}$ carbon frequency in benzene and in hexadeuterobenzene, and the assignment of the related, but spectrally active, frequencies of the partly deuterated benzenes, really constitute a single problem, best treated comprehensively.

For convenience we set out the frequencies (in cm.$^{-1}$), which have been definitely assigned to the $B_{3u}$ class of vibrations. The PR-separations, given in parenthesis where known, show that as far as could be ascertained, the bands are, as they should be, of the pseudo-perpendicular type :

| | | | | |
|---|---|---|---|---|
| 1 : 4-$C_6H_4D_2$ | 814 (—) | 1106 (14) | 1413 (14) | 3079 (—) |
| 1 : 2 : 4 : 5-$C_6H_2D_4$ | 812 (13) | 1057 (15) | 1439 (13) | 2280 (—) |

The ring deformation frequencies are easily identified, even though there are two unassigned bands to choose from in the relevant region, 1333—1485 cm.$^{-1}$, of each spectrum. The band at 1413 cm.$^{-1}$ in the spectrum of 1 : 4-dideuterobenzene could scarcely be a combination tone on account of its intensity, and its frequency is definitely wanted as a fundamental frequency for the explanation, as higher harmonics, of three of the Raman frequencies of the substance. The frequency and intensity of the band at 1439 cm.$^{-1}$ in the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene show that this is not a combination tone; and its frequency is required as a fundamental frequency for the interpretation of certain Raman and infra-red combination tones, notably the infra-red frequency at 4482 cm.$^{-1}$. Those bands within the region considered, one in each spectrum, which remain unassigned as fundamental bands, are quite weak, and can readily be understood as allowed combination tones.

The deuterium bending frequencies are equally obvious. They are represented by the bands at 814 cm.$^{-1}$ in the spectrum of 1 : 4-dideuterobenzene, and 812 cm.$^{-1}$ in the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene : those are the only unassigned bands within the appropriate region, about 800—1000 cm.$^{-1}$, of either spectrum. Their frequencies and intensities clearly show them to be fundamental bands.

The protium bending frequencies present a slightly more difficult problem, but there is little doubt that we are correct in choosing the strongest unassigned band in the relevant region, about 1000—1300 cm.$^{-1}$, of either spectrum. For 1 : 4-dideuterobenzene this is the band at 1106 cm.$^{-1}$, the frequency of which is, moreover, required as a fundamental frequency for the explanation of certain Raman and infra-red combination tones, notably that appearing at 2083 cm.$^{-1}$ in the infra-red spectrum. The rejected, weaker band at 1230 cm.$^{-1}$ is readily interpreted as a combination tone. The chosen band in the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene has the frequency 1057 cm.$^{-1}$; there is no good explanation of this frequency as a combination tone, although it does not itself appear to enter as a component into the constitution of any observed combination tone. The rejected, weaker frequencies at 1144, 1206, and 1309 cm.$^{-1}$ all have satisfactory explanations as combination tones.

In a pure hydrogen stretching vibration of this symmetry class, the atoms on the $y$-axis do not move. Since the vibration in question must be a very nearly pure hydrogen stretching vibration, its frequency should be almost exactly the same for 1 : 4-dideuterobenzene as for benzene. In the spectrum of 1 : 4-dideuterobenzene a strong band appears at 3079 cm.$^{-1}$, in close agreement with the corresponding benzene frequency of 3080 cm.$^{-1}$. Similarly, the corresponding frequency in 1 : 2 : 4 : 5-tetradeuterobenzene should be very nearly the same as in hexadeuterobenzene. In the spectrum of the former compound it is represented, together with the $B_{2u}$ deuterium stretching frequency, by the single unresolved band of peak frequency 2280 cm.$^{-1}$, which may not, of course, be exactly the vibration frequency of either component of this composite band. In the circumstances the agreement with the hexadeuterobenzene frequency of 2294 cm.$^{-1}$ may be considered satisfactory.

We can obtain a rough, but probably adequate, check on these assignments by means of the product theorem, without making any assumptions concerning the unspecified frequencies of the carbon stretching vibration, excepting that, as a carbon vibration, its frequencies in the two $V_h$ benzenes are unlikely to differ by more than 2 or 3 units per cent. By reference to Table XI of Part XI (this vol., p. 232), we find

$$\Pi B_{3u}(1:4\text{-}C_6H_4D_2)/\Pi B_{3u}(1:2:4:5\text{-}C_6H_2D_4) = 1{\cdot}396 \text{ (harmonic value)}$$

For the ratio of the products of the two sets of four assigned frequencies, we have :

$$814 \times 1106 \times 1413 \times 3079/812 \times 1057 \times 1439 \times 2280 = 1{\cdot}391$$

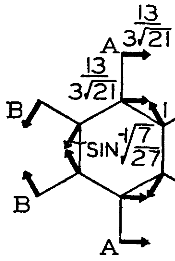
These values are fully consistent with the conclusion that the frequencies of the carbon stretching vibration in the two compounds differ only slightly.

An approximate scheme of normal co-ordinates is graphically presented in diagrams (IX)—(XIII). The amplitude indications apply as before to 1 : 4-dideuterobenzene. In deriving them, assumptions were made, with respect to the vectors of diagrams (IX) and (XIII), which are similar to those applied, as explained earlier, to the vectors in diagrams (IV) and (VIII). The results naturally correspond in their application both to 1 : 4-dideuterobenzene and to 1 : 2 : 4 : 5-tetradeuterobenzene.

*The Infra-red Combination Tones.*—As is shown in Part XI, Table XIV (this vol., p. 234), those binary combinations are allowed in the infra-red spectra of $V_h$ benzenes for which the combining fundamental vibrations have unlike symmetry properties with respect to the centre of symmetry, and have not identical symmetry properties with respect to all three of the two-fold axes.

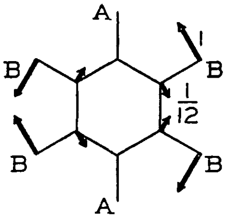
The combination tones appearing in the infra-red spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene are assigned in Tables I and II in accordance with this rule. Where alternative interpretations of an observed combination tone are possible, the alternatives are given. Only a few special points require comment.

In the spectrum of 1 : 4-dideuterobenzene, the agreement between the observed frequencies 1916 and 1923 cm.$^{-1}$ and the frequencies of the combinations by which they are explained (1901 and 1937 cm.$^{-1}$) is poor; but this might be explained as due to the overlapping of two bands of comparable strength. Such an overlap would build up a relatively considerable intensity between the vibrational origins of the separate bands, and thus the observed maxima, especially with poor resolution, would be found closer together than if each band could be observed in the absence of the other. The two neighbouring prominent bands, at 1724 and 1811 cm.$^{-1}$, possibly correspond in constitution to the degenerate combination tone of outstanding strength at 1808 cm.$^{-1}$ in the infra-red spectrum of benzene. We have already discussed the resonance mechanism by which the probable combination tone at 3040 cm.$^{-1}$ might derive its intensity.



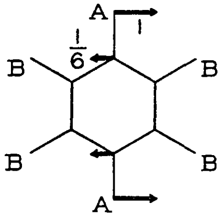
(IX.)

Frequencies uncertain.



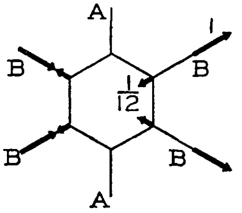
(X.)

$C_6H_4D_2$, 1106 cm.$^{-1}$.
$C_6H_2D_4$, 812 cm.$^{-1}$.



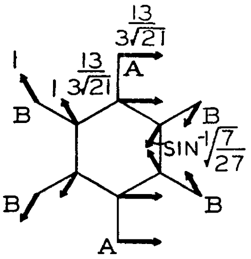
(XI.)

$C_6H_4D_2$, 814 cm.$^{-1}$.
$C_6H_2D_4$, 1057 cm.$^{-1}$.



(XII.)

$C_6H_4D_2$, 3079 cm.$^{-1}$.
$C_6H_2D_4$, 2280 cm.$^{-1}$.



(XIII.)

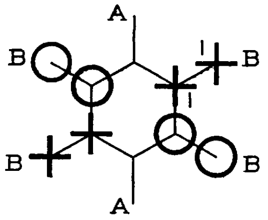
$C_6H_4D_2$, 1413 cm.$^{-1}$.
$C_6H_2D_4$, 1439 cm.$^{-1}$.

The spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene contains two bands which, as combination tones, appear to be of unusually large intensity, *viz.*, those at 1840 and 2994 cm.$^{-1}$. The latter, which is certainly a combination tone, probably derives some of its strength by resonance with the fundamental frequency at 3078 cm.$^{-1}$.

## ADDENDUM: *The Inactive ($A_u$) Fundamental Frequencies.*

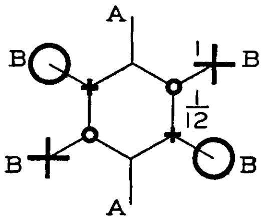
The only fundamental frequencies of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene which are forbidden by the selection rules in both the Raman and the infra-red spectra are the two which belong to the $A_u$ symmetry class. Though they are not directly observed, they are known on account of the following considerations.

The $A_u$ vibrations of the $V_h$ benzene model, whilst antisymmetric with respect to the centre of symmetry, are symmetric with respect to all three two-fold axes. This symmetry and the orthogonality condition suffice to determine that the normal co-ordinates will consist in parallel and anti-parallel combinations of out-of-plane, carbon and hydrogen motions, such as those shown in diagrams (XIV) and (XV), in which the four atoms on the $y$-axis do not move. These $V_h$ vibrations are derived from $D_{6h}$ vibrations belonging to the degenerate $E_u^+$ class, but with the restriction that we select that normal co-ordinate of each degenerate vibration which is symmetric with respect to each of the two-fold axes, $x$, $y$, and $z$. It follows, taking account once more of the orthogonality relation, that the selected normal co-ordinates of these $D_{6h}$ vibrations will also be as shown in diagrams (XIV) and (XV), and that in them the four atoms on the $y$-axis will not move. Since the only atomic masses which are different in benzene and 1 : 4-dideuterobenzene, and which are different in 1 : 2 : 4 : 5-tetra-deuterobenzene and hexadeuterobenzene, lie on the $y$-axis, it follows that the $A_u$ frequencies of 1 : 4-dideuterobenzene are individually the same as the $E_u^+$ frequencies of benzene, and that the $A_u$ frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene are individually the same as the $E_u^+$ frequencies of hexadeuterobenzene. Except for anharmonicity, and such accidents as Fermi resonance, this is an exact relationship. The benzene and hexadeuterobenzene frequencies are also forbidden as fundamental frequencies in both Raman and infra-red spectra; but they are known, first, from fluorescence spectra, and secondly, from combination tones appearing in Raman and infra-red spectra (Part XXI, this vol., pp. 319, 320). These values apply, as explained, to the two partly deuterated benzenes also. They are entered under the vector diagrams below. Their product ratio is satisfactory :



(XIV.)

$C_6H_4D_2$, 405 cm.$^{-1}$.
$C_6H_2D_4$, 352 cm.$^{-1}$.



(XV.)

$C_6H_4D_2$, 970 cm.$^{-1}$.
$C_6H_2D_4$, 793 cm.$^{-1}$.

$$\frac{\Pi A_u(1:4\text{-}C_6H_4D_2)}{\Pi A_u(1:2:4:5\text{-}C_6H_2D_4)} = \frac{405 \times 970}{352 \times 793} = 1{\cdot}408 \text{ (harmonic value} = 1{\cdot}414)$$

The amplitude indications, given in illustration for 1 : 4-dideuterobenzene, err in the direction of attributing too little hydrogen motion to the carbon vibration (XIV), and too much to the hydrogen vibration (XV) (cf. Part XVII, this vol., p. 261); however, we cannot calculate them exactly without making assumptions about the force field.

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