

65. Structure of Benzene. Part XXI. The Inactive Fundamental Frequencies of Benzene, Hexadeuterobenzene, and the Partly Deuterated Benzenes.

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The determination of the 20 fundamental frequencies of benzene, hexadeuterobenzene, and 1 : 3 : 5-trideuterobenzene, and likewise of the 30 fundamental frequencies of mono-, 1 : 4-di-, and 1 : 2 : 4 : 5-tetra-deuterobenzene is here completed. In particular, the frequencies have been found of those fundamental vibrations which are forbidden in both the Raman and the infra-red spectrum, and thus cannot be observed directly. Some assignments, deferred from preceding papers, of active fundamental frequencies have been made. Much of the evidence is derived from comparisons amongst active fundamental frequencies of partly deuterated benzenes, using the Teller-Redlich product theorem. Much more comes from the study of active higher harmonic frequencies: regularities are pointed out relating to the appearance of analogous higher harmonic frequencies in spectra of isotopically different benzenes. Some evidence comes from appearances in Raman and infra-red spectra due to the perturbing effects of cohesive forces, and some from bands representing vibrational changes accompanying the electronic transition responsible for absorption and fluorescence spectra in the ultra-violet. Assignments are suggested for all the higher harmonic frequencies which have been observed in the relevant Raman and infra-red spectra, the analysis of which is thus completed.

(A) Methods.

STARTING from the experimental material presented in the preceding papers, we seek in this paper to complete, as far as is possible at the present time, the identification of the inactive fundamental frequencies of benzene and hexadeuterobenzene, according to the plan announced in Part I (J., 1936, 912; cf. Part XI, this vol., p. 222).

Of the 20 fundamental frequencies, representing 30 vibrational degrees of freedom, of benzene or hexadeuterobenzene, 11 frequencies, corresponding to 19 vibrational degrees of freedom, are active either in the Raman or in the infra-red spectrum. These were all identified in Part VIII (J., 1936, 971). The 9 inactive frequencies, which correspond to 11 vibrational degrees of freedom, are divided amongst five symmetry classes as follows (cf. Fig. 1 of Part XI, this vol., p. 231) :

Class.	Vibration.
A_{2g} (planar, with 6-fold symmetry)	$A_{2g}^{(H)}$ (hydrogen bending).
B_{1u} (planar, with 3-fold symmetry)	$\{ B_{1u}^{(C)}$ (carbon bending).
	$\{ B_{1u}^{(H)}$ (hydrogen stretching).
B_{2g} (out-of-plane, with 3-fold symmetry)	$\{ B_{2g}^{(C)}$ (carbon bending).
	$\{ B_{2g}^{(H)}$ (hydrogen bending).
B_{2u} (planar, with 3-fold symmetry)	$\{ B_{2u}^{(C)}$ (carbon stretching).
	$\{ B_{2u}^{(H)}$ (hydrogen bending).
E_u^+ (out-of-plane, no 3- or 6-fold axis)	$\{ E_u^{+(C)}$ (carbon bending).
	$\{ E_u^{+(H)}$ (hydrogen bending).

Each symmetry class provides a more or less distinct problem, the main clue to which is to be found amongst the Raman and infra-red spectra of partly deuterated benzenes. In principle these spectra determine the product of the frequencies in each inactive symmetry class of benzene or of hexadeuterobenzene; and this they do because they contain active frequencies, which can be assigned with certainty on the internal evidence of the spectra, and can then be related by means of the Teller-Redlich product theorem to the

inactive frequency products of benzene or of hexadeuterobenzene. For the determination of each inactive product there is usually one spectrum of a partly deuterated benzene, or a very small number of such spectra, which provides the essential key, by reason of the certainty of the assignment of its active frequencies, and the simplicity of their relation to the inactive frequency product: other spectra of partly deuterated benzenes must, of course, be shown to be capable of being interpreted consistently. The key spectrum, for the determination of the A_{2g} frequency of benzene or hexadeuterobenzene is the Raman spectrum of 1:4-dideuterobenzene; for the B_{1u} frequency product, it is the Raman spectrum of 1:3:5-trideuterobenzene, for the B_{2g} product it is the infra-red spectrum of the last-named substance. For the E_u^+ product, the Raman spectrum of 1:3:5-trideuterobenzene and the infra-red spectra of 1:4-di- and 1:2:4:5-tetra-deuterobenzene are all of importance. Only in the case of the B_{2u} symmetry class, the clue, which ought to be apparent in the infra-red spectra of 1:4-di- and 1:2:4:5-tetra-deuterobenzene, is not unambiguous, and therefore more complicated, and rather less certain, methods of argument have to be applied.

In the case of the A_{2g} symmetry class the frequency product is a single frequency. Owing to the anharmonicity of molecular vibrations, frequency products, as given by the Teller-Redlich theorem, are liable to an error of the order of 1%, even when all the observed frequencies used in applying the theorem are much more accurately known. However, a first estimate, correct only to about 1%, of the A_{2g} frequency of benzene or hexadeuterobenzene will permit an identification of those observed combination tones which involve a change in the quantum number of this vibration; and then, a study of their frequencies will enable the fundamental A_{2g} frequency to be estimated more accurately. In the case of each of the symmetry classes which contains two vibrations, we require, besides the frequency product, at least one independent datum relating to the frequencies in order to be able to fix each frequency individually. The main source of such additional data consists in the combination tones which have been observed in the Raman and infra-red spectra of benzene and hexadeuterobenzene. To a limited extent the observed combination tones in partly deuterated benzenes assist the problem. Naturally any available data beyond the necessary minimum can be used to improve the accuracy with which the frequencies are estimated. An interpretation of the active combination tones of benzene and hexadeuterobenzene was attempted in Part VIII, but it could not be completed in the absence at that time (1936) of a knowledge of the key spectra amongst the partly deuterated benzenes. On this occasion we try to make our interpretation complete.

There are two other sources of data concerning inactive frequencies, but they are of more limited value. One is concerned with the band structure of electronic spectra. The ultra-violet fluorescence spectra of benzene and hexadeuterobenzene contain in combination bands a number of vibration frequencies of the electronic ground state. Some of these occur in combination with frequencies, which cannot be independently determined, belonging to the electronic excited state; these particular bands do not provide independent evidence concerning ground state frequencies. Other bands lead to recognised ground state frequencies which are already known because they are amongst those found in the Raman or the infra-red spectrum. The most useful contribution which the electronic spectra make on the subject of the inactive ground state frequencies relates to the carbon vibration of the E_u^+ symmetry class. Not only is the frequency itself accurately determined for benzene and for hexadeuterobenzene, but also an argument is provided which conclusively identifies the symmetry class to which these frequencies belong.

The remaining source of information about inactive frequencies depends on the deforming action of molecules on one another in the liquid state, with consequent loss of symmetry, enabling frequencies, which the selection rules for an isolated molecule would forbid in a particular type of spectrum, to appear weakly in the spectrum of the liquid. In Part VII (J., 1936, 966) we showed that certain Raman frequencies of benzene appear weakly in the infra-red spectrum of the liquid, and that likewise some infra-red frequencies feebly appear in the Raman spectrum of liquid benzene—in both cases contrary to the selection rules for the gaseous benzene molecule. In the same way, frequencies which the selection rules for the gaseous molecule would exclude from both Raman and infra-red spectra might appear weakly in one or other spectrum of the liquid. Pitzer and Scott have recently made a hypothetical assignment of some weakly appearing frequencies of liquid benzene to inactive vibrations (*J. Amer. Chem. Soc.*, 1943, 65, 803). A number of their inferences are undoubtedly correct, but, as they recognise, arguments are involved which are not in themselves conclusive. The main use of frequencies which appear through the breaking of selection rules is that they sometimes lend support to already reached conclusions. The difficulty about employing them as an original basis for the determination of theoretically inactive frequencies is that, with no selection rules, not only are all fundamental frequencies allowed, but so also are all the very numerous higher harmonics, some of which may well appear more strongly in the spectra than do some of the fundamental frequencies, just as so often happens when the loss of symmetry accompanying partial deuterium substitution causes a relaxation of selection rules.

(B) *The A_{2g} , E_u^+ , B_{1u} , and B_{2g} Fundamental Frequencies of Benzene and Hexadeuterobenzene.*

In this section we apply the above methods in a discussion of the frequencies of various inactive vibrations of benzene and hexadeuterobenzene. Owing to an already mentioned difficulty, we are not able in this simple way unambiguously to determine the frequencies of one vibration, *viz.*, the carbon stretching vibration of B_{2u} symmetry. Therefore, at first we omit this symmetry class. In Section C we proceed to an assignment of observed higher harmonic frequencies, and a discussion of relationships between them. With some assistance

from this study we turn in Section D to the omitted fundamental frequencies of the B_{2u} symmetry class; and we deal at the same time with the assignment of frequencies to the B_{2u} -like carbon vibrations of partly deuterated benzenes, the one assignment problem which was left incomplete in Parts XVII, XIX, and XX.

(1) *The A_{2g} Fundamental Vibration of Benzene.*—The frequencies of this vibration have been calculated from an assumed potential function on several occasions: rather widely differing values have been suggested. Kohlrausch derived for benzene and hexadeuterobenzene the frequencies 1258 and 1058 cm^{-1} respectively (*Z. physikal. Chem.*, 1935, 30, B, 305), Lord and Andrews the frequencies 1190 and 930 cm^{-1} (*J. Physical Chem.*, 1937, 41, 145), and Penney and Duchesne 1307 and 1017 cm^{-1} respectively (*Bull. Soc. roy. Sci. Liège*, 1939, 11, 514). In Part VIII we gave 1240 and 940 cm^{-1} for these two frequencies. Langseth and Lord derived the frequencies 1195 and 930 cm^{-1} from an application of the product theorem to observed Raman frequencies of 1:4-di- and 1:2:4:5-tetra-deuterobenzene (*Kgl. Danske Vidensk. Selsk.*, 1938, 16, 6); but the assignments they employed are now known to be incorrect (Part XVIII, this vol., p. 272). Pitzer and Scott suggested the value 1298 cm^{-1} for benzene (*loc. cit.*), this being one of the weaker frequencies observed by Bailey, Hale, Ingold, and Thompson in the infra-red spectrum of liquid benzene (Part IV, J., 1936, 931).

The important spectrum for the determination of this frequency is the Raman spectrum of 1:4-dideuterobenzene in which the five B_{1g} frequencies are easily located: none can have any alternative assignment. These frequencies are collectively related to the four E_g^+ frequencies and the A_{2g} frequency of benzene. Employing the product theorem with our usual arbitrary allowance for anharmonicity (Part XI, *loc. cit.*), we set up the equation

$$\frac{\Pi A_{2g} E_g^+(C_6H_6)}{\Pi B_{1g}(1:4-C_6H_4D_2)} = \frac{A_{2g} \times 605.6 \times 1596 \times 3046.8 \times 1178.0}{600.9 \times 1569.3 \times 3042 \times 908.5 \times 1309.0} = 1.353 \text{ (assumed; harmonic value} = 1.367),$$

and thus calculate for the A_{2g} frequency the value 1331 cm^{-1} .

There are two observed combination tones of benzene which cannot be satisfactorily explained otherwise than with the aid of the A_{2g} fundamental frequency. One is the Raman frequency 2925 cm^{-1} , the intensity of which (Part III, J., 1936, 925) shows it to be an allowed combination; the other is the rather prominent infra-red frequency 2356 cm^{-1} observed with liquid benzene (Part IV, *loc. cit.*). Their interpretations indicate the values 1329 and 1319 cm^{-1} for the A_{2g} frequency:

$$\begin{array}{l} C_6H_6, \text{ Raman, } 2925 \text{ cm}^{-1} \dots\dots\dots (A_{2g}) 1329 + (E_g^+) 1596 = 2925 \text{ cm}^{-1}. \\ C_6H_6, \text{ Infra-red, } 2356 \text{ cm}^{-1} \dots\dots\dots (A_{2g}) 1319 + (E_u^-) 1037 = 2356 \text{ cm}^{-1}. \end{array}$$

The only alternative to the first explanation involves an assumed B_{2u} carbon frequency of 1750 cm^{-1} , and the only real alternative to the second requires the same vibration to have the frequency 1435 cm^{-1} . We believe that it has neither frequency (Section D, 2), and, since in any case it cannot have both, an A_{2g} frequency in the neighbourhood 1319—1329 cm^{-1} is independently established. It is true that the frequency 2356 cm^{-1} agrees numerically with that of a first overtone of the E_g^+ fundamental frequency 1178 cm^{-1} ; but all first overtones are forbidden in the infra-red spectrum of benzene, and we have not observed any first overtone in the infra-red spectrum of either liquid benzene or liquid hexadeuterobenzene, or, for that matter, in those infra-red spectra of partly deuterated benzenes for which first overtones are allowed by the selection rules.

The Raman spectrum of liquid benzene contains a weak line of frequency 1326 cm^{-1} , which has no good explanation as a higher harmonic frequency: this may be the A_{2g} fundamental frequency, appearing despite the selection rules. We adopt 1326 cm^{-1} , the average of our various estimates, as the best value of this frequency.

(2) *The A_{2g} Fundamental Vibration of Hexadeuterobenzene.*—The Raman spectrum of 1:2:4:5-tetra-deuterobenzene is not a safe guide to the A_{2g} frequency of hexadeuterobenzene, because of the overlapping of a relevant line by a much stronger Raman line, and the difficulty of distinguishing the former from heavy-carbon satellites of the latter. On the other hand, we can use the determined value of the A_{2g} frequency in benzene to calculate directly the frequency of the same vibration in hexadeuterobenzene. From the equation

$$\Pi A_{2g}(C_6H_6)/\Pi A_{2g}(C_6D_6) = 1326/\Pi A_{2g}(C_6D_6) = 1.283 \text{ (assumed; harmonic value} = 1.286),$$

we calculate 1034 cm^{-1} for the hexadeuterobenzene frequency.

There are two observed combination tones of hexadeuterobenzene which necessarily involve the A_{2g} fundamental frequency. One appears in the Raman spectrum at 2575 cm^{-1} according to Wood (*J. Chem. Physics*, 1935, 3, 444), 2571 cm^{-1} according to Angus, Ingold, and Leckie (Part III, *loc. cit.*), and 2567 cm^{-1} according to Poole (Part XV, Table I, this vol., p. 252). The other is an infra-red frequency, measured by Bailey, Hale, Ingold, and Thompson (Part IV, *loc. cit.*) as 1860 cm^{-1} using hexadeuterobenzene vapour, and as 1866 cm^{-1} using liquid hexadeuterobenzene. Both these combination tones have the characteristics of allowed higher harmonics, and may be explained as follows:

$$\begin{array}{l} C_6D_6, \text{ Raman, } 2571 \text{ cm}^{-1} \dots\dots\dots (A_{2g}) 1020 + (E_g^+) 1551.5 = 2571 \text{ cm}^{-1}. \\ C_6D_6, \text{ Infra-red, } 1863 \text{ cm}^{-1} \dots\dots\dots (A_{2g}) 1050 + (E_u^-) 813 = 1863 \text{ cm}^{-1}. \end{array}$$

The only alternative to the first interpretation necessitates that the B_{2u} carbon vibration should have the frequency 1750 cm^{-1} , and the only alternative to the second requires the same vibration to have the frequency 1290 cm^{-1} . We believe that neither condition is satisfied (Section D, 3), and, since both cannot be fulfilled,

the existence of an A_{2g} frequency in the region 1020—1050 cm^{-1} is independently established. We shall point out later (Section C, 3) that similarly constituted combination tones show a marked tendency to recur in the spectra of different benzenes, and it is therefore a favourable feature of the explanations given that the A_{2g} vibration is required to combine with just the same fundamental vibrations in hexadeuterobenzene as in benzene, *viz.*, the E_g^+ carbon stretching vibration and the E_u^- hydrogen bending vibration.

An A_{2g} frequency in the neighbourhood of the calculated value would interpret the frequencies of both harmonics to within the deviations which might arise from anharmonicity. Choosing a weighted mean to equalise the percentage deviations, we adopt 1037 cm^{-1} as the best value for the A_{2g} frequency of hexadeuterobenzene.

This value together with known frequencies may be compared with the B_{2g} frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene. The product ratio is as follows :

$$\frac{\Pi B_{1g}(1 : 2 : 4 : 5\text{-C}_6\text{H}_2\text{D}_4)}{\Pi A_{2g}, E_g^+(\text{C}_6\text{D}_6)} = \frac{585.8 \times 1564.0 \times 2272 \times 1255.3 \times 954}{1037 \times 577.4 \times 1551.5 \times 2264.9 \times 867.3} = 1.366 \text{ (harmonic value} = 1.372)$$

For the A_{2g} class itself, we have

$$\Pi A_{2g}(\text{C}_6\text{H}_6)/\Pi A_{2g}(\text{C}_6\text{D}_6) = 1326/1037 = 1.279 \text{ (harmonic value} = 1.286).$$

(3) *The E_u^+ Fundamental Vibrations of Benzene.*—The presence in the Raman spectrum of liquid benzene of a weak, diffuse line of frequency $405 \pm 5 \text{ cm}^{-1}$ has been reported by several investigators (Weiler gives 406 cm^{-1} , Mesnage 409.7 cm^{-1} , Krishnamurti 407 cm^{-1} , Wood and Collins 400 cm^{-1} , and Grassmann and Weiler 404 cm^{-1} —for references see Part III). This line does not represent any of the allowed fundamental frequencies, and it cannot be explained as an allowed combination tone. Lord and Andrews assigned it to the E_u^+ carbon vibration, which they assumed to be appearing, contrary to the selection rules, on account of intramolecular forces (*J. Physical Chem.*, 1937, 41, 149). They regarded this assignment as somewhat arbitrary, mainly because it would also have been plausible to assign the frequency to the B_{2g} carbon vibration. However, the correctness of Lord and Andrews's choice was proved when it was shown that the corresponding vibration of 1 : 3 : 5-trideuterobenzene, which is allowed in the Raman effect, has the frequency 375 cm^{-1} (Ingold *et al.*, *Nature*, 1937, 139, 880); and that, indeed, for all the partly deuterated benzenes yet examined, this vibration has frequencies in the range 350—400 cm^{-1} (Ingold, *Z. Elektrochem.*, 1938, 44, 20; *Proc. Roy. Soc.*, 1938, 169, 149; and these papers).

Another estimate of the frequency, as well as an independent proof of the nature of the vibration, emerges from an analysis of the near-ultra-violet electronic bands of benzene. Using the absorption spectrum, Sponer, Nordheim, Sklar, and Teller obtained the value 400 cm^{-1} for this frequency (*J. Chem. Physics*, 1939, 7, 207); from the fluorescence spectrum we obtain 404 cm^{-1} , a value believed to be good to $\pm 2 \text{ cm}^{-1}$ (details will be published later). The positions in the absorption and fluorescence band-systems of those bands which involve this frequency prove the vibration to be degenerate; and, since all the degenerate vibrations of benzene, except those of the E_u^+ class, are active in the Raman or infra-red spectrum, and are therefore known, the vibration in question must be an E_u^+ vibration.

A very weak line, of frequency 802 cm^{-1} , in the Raman spectrum of benzene has been reported by Grassmann and Weiler. This line, if real, can hardly be explained otherwise than as a first overtone of the E_u^+ carbon vibration.

Concerning the E_u^+ hydrogen vibration of benzene, calculations based on an assumed potential system have given values ranging from 890 to 1160 cm^{-1} (Part VIII; Lord and Andrews; Penney and Duchesne). Langseth and Lord deduced 845 cm^{-1} from the product rule, but used an incorrect assignment of frequencies in the Raman spectrum of 1 : 3 : 5-trideuterobenzene. More recently, Ziegler and Andrews (*J. Amer. Chem. Soc.*, 1942, 64, 2482) found difficulty in accounting for their thermodynamic data on the basis of Langseth and Lord's proposed frequencies, and acutely inferred that this one might be too low; and, shortly after, Pitzer and Scott (*loc. cit.*) suggested that it should be taken as 985 cm^{-1} , the approximate frequency of a shoulder observed by Bailey, Hale, Ingold, and Thompson (Part IV) on the side of a strong infra-red band of liquid benzene; but they admitted that the shoulder might alternatively represent the (also forbidden) A_{1g} frequency, 991.6 cm^{-1} , as we had originally supposed (Part VIII). Actually there is a third way of accounting for that shoulder, as we shall point out in Section B, 7.

In the infra-red spectrum either of benzene vapour or of liquid benzene we find a band of considerable intensity, which cannot be explained except as a combination tone involving the E_u^+ hydrogen vibration :

$$\text{C}_6\text{H}_6, \text{ Infra-red, } 1808, 1810 \text{ cm}^{-1} \dots\dots\dots (E_u^+) 961 + (E_g^-) 848.9 = 1810 \text{ cm}^{-1}.$$

The second of the participating fundamental vibrations is known from the Raman spectrum. Each of the interacting vibrations has the characteristic that, in one of the normal co-ordinates by which it can be represented, the atoms on the y -axis do not move. These normal vibrations must therefore recur, with the same frequencies, in monodeuterobenzene and 1 : 4-dideuterobenzene. We have measured the E_g^- vibration in the Raman spectrum of monodeuterobenzene at 850 cm^{-1} , and in the Raman spectrum of 1 : 4-dideuterobenzene at 849.5 cm^{-1} . The E_u^+ vibration is, of course, inactive in mono- and 1 : 4-di-deuterobenzene. However, the combination of the two fundamental frequencies should be active in the infra-red spectra of these molecules, and should appear with about the frequency and intensity with which it occurs in the infra-red

spectrum of benzene. Bands of about the same intensity, and with but slightly changed frequencies, do in fact appear in the infra-red spectra of mono- and 1 : 4-di-deuterobenzene vapour. In each case there is no alternative explanation to that now offered :

$$\begin{array}{ll} \text{C}_6\text{H}_6\text{D}, \text{ Infra-red, } 1821 \text{ cm.}^{-1} & \dots\dots\dots (E_u^+) 971 + (E_g^-) 850 = 1821 \text{ cm.}^{-1}. \\ 1 : 4\text{-C}_6\text{H}_4\text{D}_2, \text{ Infra-red, } 1811 \text{ cm.}^{-1} & \dots\dots\dots (E_u^+) 962 + (E_g^-) 849.5 = 1811 \text{ cm.}^{-1}. \end{array}$$

This evidence would indicate a mean value of 965 cm.^{-1} for the E_u^+ hydrogen frequency of benzene.

Confirming these indications, we have two independent values for the E_u^+ frequency product. One derives from the infra-red spectrum of 1 : 4-dideuterobenzene, the three B_{1u} frequencies in which are collectively related to the infra-red A_{2u} frequency and the E_u^+ frequencies of benzene. From the equation

$$\frac{\Pi A_{2u}, E_u^+(\text{C}_6\text{H}_6)}{\Pi B_{1u}(1 : 4\text{-C}_6\text{H}_4\text{D}_2)} = \frac{671 \times \Pi E_u^+}{367 \times 597 \times 876} = 1.382 \text{ (assumed; harmonic value} = 1.396),$$

we find $\Pi E_u^+(\text{C}_6\text{H}_6) = 395.3 \times 10^3 \text{ cm.}^{-2}$. The second estimate is based on the Raman spectrum of 1 : 3 : 5-trideuterobenzene, the three E'' frequencies in which are collectively related to the E_g^- Raman frequency and the E_u^+ frequencies of benzene. The equation used is

$$\frac{\Pi E_g^-, E_u^+(\text{C}_6\text{H}_6)}{\Pi E''(1 : 3 : 5\text{-C}_6\text{H}_3\text{D}_3)} = \frac{848.9 \times \Pi E_u^+}{372.7 \times 710.2 \times 947} = 1.337 \text{ (assumed; harmonic value} = 1.345),$$

and from it we find $\Pi E_u^+(\text{C}_6\text{H}_6) = 394.8 \times 10^3 \text{ cm.}^{-2}$.

Taking all the data together, we choose 405 cm.^{-1} and 970 cm.^{-1} as the best values of the two E_u^+ vibrations of benzene. All the measurements are then within their probable limits of error. The frequency product becomes $393 \times 10^3 \text{ cm.}^{-2}$.

(4) *The E_u^+ Fundamental Vibrations of Hexadeuterobenzene.*—Starting from the E_u^+ carbon frequency 405 cm.^{-1} of benzene, the corresponding frequency of hexadeuterobenzene has been calculated as 314 cm.^{-1} and as 305 cm.^{-1} with the aid of an assumed potential system (Lord and Andrews; Penney and Duchesne). After the corresponding frequency of 1 : 3 : 5-trideuterobenzene had been located at 375 cm.^{-1} (1937), it seemed more probable that the hexadeuterobenzene frequency lay in the region of 350 cm.^{-1} , as Langseth and Lord, and Pitzer and Scott subsequently assumed.

A careful search has now been made for a low weak frequency in the Raman spectrum of liquid hexadeuterobenzene, corresponding to the weak frequency 405 cm.^{-1} in the Raman spectrum of liquid benzene. It has been found at 350 cm.^{-1} (Part XV, Table I, this vol., p. 252). The line is very weak and difficult to measure with precision, but undoubtedly real.

This frequency has also been found by analysis of the fluorescence spectrum of hexadeuterobenzene. The measured value is 349 cm.^{-1} (details will be published later). The positions in the band system of the bands involving this frequency show that the vibration is degenerate, and is therefore an E_u^+ vibration, all other degenerate vibrations being already known.

The same frequency enters into several Raman and infra-red combination tones :

$$\begin{array}{ll} \text{C}_6\text{D}_6, \text{ Raman, } 844.5 \text{ cm.}^{-1} & \dots\dots\dots (E_u^+) 348 + (A_{2u}) 496.5 = 844.5 \text{ cm.}^{-1}. \\ & \dots\dots\dots (E_u^+) 348 + (E_u^-) 813 = 1161 \text{ cm.}^{-1}. \\ \text{C}_6\text{D}_6, \text{ Infra-red, } 926, 925 \text{ cm.}^{-1} & \dots\dots\dots (E_u^+) 349 + (E_g^-) 577.4 = 926 \text{ cm.}^{-1}. \\ \text{,, ,, } 1009, 1012 \text{ cm.}^{-1} & \dots\dots\dots (E_u^+) 350 + (E_g^-) 661.7 = 1012 \text{ cm.}^{-1}. \\ \text{,, ,, } 1212, 1218 \text{ ,, } & \dots\dots\dots (E_u^+) 351 + (E_g^-) 867.3 = 1218 \text{ cm.}^{-1}. \end{array}$$

The first of each pair of observed infra-red frequencies relates to the vapour and the second to the liquid, whilst the Raman frequencies relate as usual to the liquid. These combination tones also suggest an E_u^+ frequency of about $349\text{--}350 \text{ cm.}^{-1}$, but four of the five combination frequencies are too weak to be accurately measured, and the only one of the five which is known to within $\pm 1 \text{ cm.}^{-1}$ is the Raman frequency of 844.5 cm.^{-1} . This line, however, probably derives some of its considerable strength by resonance with the fundamental line at 867.3 cm.^{-1} , and its frequency is therefore expected to have been displaced in a downward direction : hence the only conclusion to be drawn from the measurement is that 348 cm.^{-1} is likely to be slightly too low an estimate of the E_u^+ carbon frequency.

Prior estimates of the frequency of the E_u^+ hydrogen vibration range widely, though two of the suggested values are close to the mark. In Part VIII we calculated 780 cm.^{-1} by a method so crude that one would not have expected it to give an accurate answer; and Pitzer and Scott (*loc. cit.*) assigned to the vibration a reported Raman frequency 790 cm.^{-1} , which, however, it has not been possible to confirm (Part XV, *loc. cit.*). Ziegler and Andrews helped to locate the true value by pointing out that Langseth and Lord's estimate of 690 cm.^{-1} was almost certainly too low (*loc. cit.*). Values as high as 1007 cm.^{-1} and 1070 cm.^{-1} have been calculated by Penney and Duchesne and by Lord and Andrews respectively (*loc. cit.*).

In the infra-red spectrum of hexadeuterobenzene, either as vapour or as liquid, a band of considerable strength appears which cannot be interpreted except as a combination involving the E_u^+ hydrogen frequency :

$$\text{C}_6\text{D}_6, \text{ Infra-red, } 1450, 1454 \text{ cm.}^{-1} \dots\dots\dots (E_u^+) 792 + (E_g^-) 661.7 = 1454 \text{ cm.}^{-1}.$$

This is obviously the combination band which corresponds to the $1808\text{--}1810 \text{ cm.}^{-1}$ band of benzene; and

just as the latter band reappears in the infra-red spectrum of mono- and 1 : 4-di-deuterobenzene, so the hexadeuterobenzene band at 1450—1454 cm^{-1} ought to reproduce itself in the infra-red spectra of penta- and 1 : 2 : 4 : 5-tetra-deuterobenzene. The infra-red spectrum of pentadeuterobenzene has not yet been observed; and unfortunately the expected combination band of 1 : 2 : 4 : 5-tetradeuterobenzene would be obscured by the strong fundamental band centred at 1439 cm^{-1} .

The Raman spectrum of hexadeuterobenzene contains a moderately weak line at 1578 cm^{-1} , which would be difficult to explain except as a first overtone. Anticipating conclusions reached later to the effect that the B_{2g} and B_{2u} hydrogen fundamental frequencies lie too high to be used in explanation, we regard the line as an overtone of the E_u^+ hydrogen vibration :

$$\text{C}_6\text{D}_6, \text{ Raman, } 1578 \text{ cm}^{-1} \dots\dots\dots 2 \times (E_u^+) 789 = 1578 \text{ cm}^{-1}.$$

It should be remarked that this is not an entirely independent piece of evidence, since the location of the B_{2g} hydrogen frequency, and its consequent exclusion from any part in the interpretation of the Raman line, depends on the correct choice of the E_u^+ hydrogen frequency, and therefore on the rest of the evidence considered in this Section.

Two independent estimates of the E_u^+ frequency product are available, one based on the infra-red spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene, and the other on the Raman spectrum of 1 : 3 : 5-trideuterobenzene. From the equations (cf. Part XVI, Table I, this vol., p. 255)

$$\frac{\Pi B_{1u}(1 : 2 : 4 : 5\text{-C}_6\text{H}_4\text{D}_2)}{\Pi A_{2u}, E_u^+(\text{C}_6\text{D}_6)} = \frac{383 \times 548 \times 925}{496.5 \times \Pi E_u^+} = 1.382 \text{ (assumed; harmonic value } = 1.396)$$

we find $\Pi E_u^+(\text{C}_6\text{D}_6) = 282.9 \times 10^3 \text{ cm}^{-2}$; whilst the equation

$$\frac{\Pi E''(1 : 3 : 5\text{-C}_6\text{H}_3\text{D}_3)}{\Pi E_g^-, E_u^+(\text{C}_6\text{D}_6)} = \frac{372.7 \times 710.2 \times 947}{661.7 \times \Pi E_u^+} = 1.343 \text{ (assumed; harmonic value } = 1.351)$$

gives the result $\Pi E_u^+(\text{C}_6\text{D}_6) = 282.1 \times 10^3 \text{ cm}^{-2}$.

In consideration of all the data, we select 352 cm^{-1} and 793 cm^{-1} as the best values of the two E_u^+ vibrations of hexadeuterobenzene. All the measured frequencies then fall within their probable limits of error. The frequency product is $279 \times 10^3 \text{ cm}^{-2}$. The product ratio

$$\Pi E_u^+(\text{C}_6\text{H}_6)/\Pi E_u^+(\text{C}_6\text{D}_6) = 405 \times 970/352 \times 793 = 1.408 \text{ (harmonic value } = 1.414)$$

is satisfactory.

(5) *The B_{1u} Fundamental Vibrations of Benzene.*—The frequencies of these two vibrations of benzene have several times been calculated from an assumed potential system. Kohlrausch first correctly located the B_{1u} carbon bending frequency of benzene in the neighbourhood of 1000 cm^{-1} ; Lord and Andrews calculated the value 1008 cm^{-1} , and Penney and Duchesne 1007 cm^{-1} (*loc. cit.*). The calculation of the B_{1u} hydrogen stretching frequency is, of course, not critical: it is bound to lie close to the totally symmetrical hydrogen stretching frequency 3062 cm^{-1} .

The B_{1u} frequency product for benzene is immediately obtainable from the Raman spectrum of 1 : 3 : 5-trideuterobenzene, as was first pointed out in our preliminary account of this work (*Nature*, 1937, 139, 880); for the four A_1' frequencies of this substance are collectively related to the A_{1g} and B_{1u} frequencies of benzene, and the A_{1g} frequencies are known. From the equation

$$\frac{\Pi A_{1g}, B_{1u}(\text{C}_6\text{H}_6)}{\Pi A_1'(1 : 3 : 5\text{-C}_6\text{H}_3\text{D}_3)} = \frac{991.6 \times 3061.9 \times \Pi B_{1u}(\text{C}_6\text{H}_6)}{956.2 \times 1003.6 \times 2281.9 \times 3052.7} = 1.400 \text{ (assumed; harmonic value } = 1.414)$$

we find $\Pi B_{1u}(\text{C}_6\text{H}_6) = 3082 \times 10^3 \text{ cm}^{-2}$.

As stated above, the hydrogen frequency is bound to be close to 3062 cm^{-1} , and this is confirmed because it enters of necessity into the following combination tones :

$$\begin{array}{ll} \text{C}_6\text{H}_6, \text{ Raman, } 3467 \text{ cm}^{-1} \dots\dots\dots & (B_{1u}) 3062 + (E_u^+) 405 = 3467 \text{ cm}^{-1}. \\ \text{C}_6\text{H}_6, \text{ Infra-red, } 3655 \text{ cm}^{-1} \dots\dots\dots & (B_{1u}) 3049 + (E_g^+) 605.6 = 3655 \text{ cm}^{-1}. \end{array}$$

Since this former measurement is probably somewhat more accurate, we take a weighted mean, 3060 cm^{-1} as the value of the B_{1u} hydrogen frequency.

Combining this value with the frequency product, we obtain 1008 cm^{-1} for the B_{1u} carbon frequency. The latter is necessarily involved in the interpretation of the following combination tone :

$$\text{C}_6\text{H}_6, \text{ Infra-red, } 1617, 1616 \text{ cm}^{-1} \dots\dots\dots (B_{1u}) 1011 + (E_g^+) 605.6 = 1617 \text{ cm}^{-1}.$$

The two values are for vapour and liquid. In consideration of this evidence, we adopt 1010 cm^{-1} as the best value of the B_{1u} carbon frequency. The B_{1u} product for benzene then becomes $3091 \times 10^3 \text{ cm}^{-2}$.

(6) *The B_{1u} Fundamental Vibrations of Hexadeuterobenzene.*—Kohlrausch, Lord and Andrews, and Penney and Duchesne have calculated the values 948, 960, and 956 cm^{-1} respectively for the B_{1u} carbon frequency.

The B_{1u} frequency product is obtainable from the Raman frequencies of 1 : 3 : 5-trideuterobenzene: the equation

$$\frac{\Pi A_1'(1 : 3 : 5\text{-C}_6\text{H}_3\text{D}_3)}{\Pi A_{1g}, B_{1u}(\text{C}_6\text{D}_6)} = \frac{956.2 \times 1003.6 \times 2281.9 \times 3052.7}{943.2 \times 2292.6 \times \Pi B_{1u}(\text{C}_6\text{D}_6)} = 1.400 \text{ (assumed; harmonic value } = 1.414)$$

leads to $\Pi B_{1u}(\text{C}_6\text{D}_6) = 2208 \times 10^3 \text{ cm}^{-2}$.

There are no known combination tones which can be used to fix the value of the B_{1u} hydrogen frequency with the assurance that alternative interpretations are impossible. However, the frequency must lie close to the totally symmetrical hydrogen stretching frequency 2293 cm.^{-1} , and, as with benzene, we adopt a slightly lower value, *viz.*, 2290 cm.^{-1} . This provides good explanations of two infra-red combination tones (although in each case a possible, but less satisfactory, alternative explanation exists) :

$$\begin{array}{ll} C_6D_6, \text{ Infra-red, } 2903 \text{ cm.}^{-1} & \dots\dots\dots (B_{1u}) 2290 + (E_g^+) 605.6 = 2896 \text{ cm.}^{-1}. \\ C_6D_6, \text{ Infra-red, } 4545 \text{ cm.}^{-1} & \dots\dots\dots (B_{1u}) 2290 + (E_g^+) 2264.9 = 4555 \text{ cm.}^{-1}. \end{array}$$

From this value, and the frequency product, we obtain 964 cm.^{-1} as the B_{1u} carbon frequency of hexadeuterobenzene. Furthermore, from the equation

$$\Pi B_{1u}(C_6H_6) / \Pi A_{1g}(C_6H_6) = \Pi B_{1u}(C_6D_6) / \Pi A_{1g}(C_6D_6),$$

which follows from the equality of the A_{1g} and B_{1u} theoretical product ratios, we can, as a close approximation, cancel all the hydrogen frequencies. Inserting the A_{1g} carbon frequencies in this simplified equation, along with the already determined B_{1u} carbon frequency for benzene, we find 961 cm.^{-1} for the B_{1u} carbon frequency of hexadeuterobenzene. On the available evidence we adopt 963 cm.^{-1} as the most probable value. The B_{1u} frequency product then becomes $2205 \times 10^3 \text{ cm.}^{-2}$. The product ratio with benzene is satisfactory :

$$\Pi B_{1u}(C_6H_6) / \Pi B_{1u}(C_6D_6) = 1010 \times 3060 / 963 \times 2290 = 1.401 \text{ (harmonic value} = 1.414).$$

(7) *The B_{2g} Fundamental Vibrations of Benzene.*—The B_{2g} carbon frequency of benzene has been estimated as 538 cm.^{-1} in Lord and Andrews's calculations, and as 547 cm.^{-1} in those of Penney and Duchesne, whilst for the B_{2g} hydrogen frequency the values obtained by these investigators were 1520 cm.^{-1} and 1516 cm.^{-1} respectively (*loc. cit.*). In Part VIII we calculated 1000 cm.^{-1} as the probable region of the B_{2g} hydrogen frequency. By assuming that observed B_{2g} -like carbon frequencies of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene could be linearly extrapolated to give the allied frequencies of benzene and hexadeuterobenzene, Langseth and Lord deduced 648 cm.^{-1} for the B_{2g} carbon frequency of benzene, and thence, by the product rule, 1048 cm.^{-1} for the B_{2g} hydrogen frequency; however, the assumed linear relation is not supported by our work, and one of the observed frequencies could not be confirmed. Pitzer and Scott came nearer the mark by supposing the B_{2g} carbon frequency to be given by a very weak, but perhaps doubtful, Raman frequency 685 cm.^{-1} ; the product formula then gave 1016 cm.^{-1} for the B_{2g} hydrogen frequency (*loc. cit.*).

The B_{2g} frequency product can be determined by reference either to the infra-red spectrum of 1 : 3 : 5-trideuterobenzene or to the Raman spectrum of 1 : 4-dideuterobenzene. The former source is the more self-contained since the three A_2'' fundamental bands of 1 : 3 : 5-trideuterobenzene, whose frequencies are employed, are immediately recognised by their parallel structure, and this knowledge is used in order to settle the assignment of the three B_{2g} Raman lines of 1 : 4-dideuterobenzene, the frequencies of which are used in the alternative method.

The A_2'' frequencies of 1 : 3 : 5-trideuterobenzene are related to the infra-red A_{2u} frequency of benzene, and to the B_{2g} frequency product of benzene. From the equation

$$\frac{\Pi A_{2u}, B_{2g}(C_6H_6)}{\Pi A_2''(1 : 3 : 5-C_6H_3D_3)} = \frac{671 \times \Pi B_{2g}}{533 \times 691 \times 915} = 1.373 \text{ (assumed; harmonic value} = 1.387),$$

we derive $\Pi B_{2g}(C_6H_6) = 689.6 \times 10^3 \text{ cm.}^{-2}$. The B_{2g} frequencies of 1 : 4-dideuterobenzene are connected with the Raman E_g^- frequency of benzene, and with the B_{2g} product. The equation

$$\frac{\Pi E_g^-, B_{2g}(C_6H_6)}{\Pi B_{2g}(1 : 4-C_6H_4D_2)} = \frac{848.9 \times \Pi B_{2g}}{634.1 \times 736 \times 967} = 1.316 \text{ (assumed; harmonic value} = 1.324),$$

leads to $\Pi B_{2g}(C_6H_6) = 699.6 \times 10^3 \text{ cm.}^{-2}$. We adopt the mean value $694.6 \times 10^3 \text{ cm.}^{-2}$ for this product.

The B_{2g} hydrogen frequency is easily located by means of an infra-red band, of rather less than moderate intensity, which has been observed with both gaseous and liquid benzene, and can have no satisfactory explanation other than the following :

$$C_6H_6, \text{ Infra-red, } 1377, 1381 \text{ cm.}^{-1} \dots\dots\dots (B_{2g})976 + (E_u^+) 405 = 1381 \text{ cm.}^{-1}.$$

Confirmation follows from consideration of a more prominent combination band, the strongest but one in the spectrum, which we explain as follows :

$$C_6H_6, \text{ Infra-red, } 1965, 1963 \text{ cm.}^{-1} \dots\dots\dots (B_{2g}) 995 + (E_u^+) 970 = 1965 \text{ cm.}^{-1}.$$

For this band there is a possible alternative explanation requiring a lower value of the B_{2g} frequency, *viz.*, $(B_{2g}) 955 + (B_{1u}) 1010 = 1965 \text{ cm.}^{-1}$; but we think the interpretation first given to be much the more probable, because only if it is adopted do certain infra-red combination bands of mono-, 1 : 4-di-, 1 : 2 : 4 : 5-tetra- and hexa-deuterobenzene—combination bands which are also amongst the strongest in their respective spectra—receive a corresponding explanation. The correspondences will be considered in Section C, 3, where they will be shown to exemplify the rule that prominent combination frequencies (discounting such as derive their intensity by Fermi resonance) in a spectrum of a more symmetrical benzene almost always have counterparts in spectra of less symmetrical benzenes.

The mean B_{2g} hydrogen frequency derived from these combination tones, 984 cm.^{-1} , is almost exactly the frequency of the shoulder at 985 cm.^{-1} in the infra-red spectrum of liquid benzene. It is certain that this shoulder represents a forbidden fundamental frequency, and it is obviously more satisfactory to identify it with the B_{2g} hydrogen frequency, than to assign it, as we did in Part VIII, as the A_{1g} carbon frequency, which lies 7 cm.^{-1} higher, or, as Pitzer and Scott have more recently done (*loc. cit.*), as the E_u^+ hydrogen frequency, which we have found to lie 15 cm.^{-1} lower. In consideration of all this evidence we adopt the directly observed value 985 cm.^{-1} as that of the B_{2g} hydrogen fundamental frequency.

From this value and the B_{2g} frequency product deduced above, it can be calculated that the B_{2g} carbon frequency is 705 cm.^{-1} . This is likely to be correct to within a few wave-numbers.

Confirmation follows from the well-established existence of a weak, but not very weak, Raman line which, if we accept a conclusion reached later, can only have the following explanation :

$$\text{C}_6\text{H}_6, \text{ Raman, } 2294 \text{ cm.}^{-1} \dots\dots\dots (B_{2g}) 698 + (E_g^+) 1596 = 2294 \text{ cm.}^{-1}.$$

The line is not regarded as a first overtone of the B_{2u} hydrogen fundamental frequency, because in Section D, 1 we ascribe too high a value to this frequency.*

Further confirmation arises from the consideration of a stronger Raman line, which we explain as follows :

$$\text{C}_6\text{H}_6, \text{ Raman, } 1404 \text{ cm.}^{-1} \dots\dots\dots 2 \times (B_{2g}) 702 = 1404 \text{ cm.}^{-1}.$$

There exists a possible alternative explanation on the following lines : $(B_{1u})1010 + (E_u^+)405 = 1415 \text{ cm.}^{-1}$; but the overtone explanation is in our opinion to be preferred, because analogous overtones appear, with the same order of intensity, in the Raman spectra of all the partly deuterated benzenes we have examined; and overtones tend to appear in sets (Section C, 3). No correlation with observed higher harmonic frequencies of partly deuterated benzenes would be possible if we should seek to explain the benzene line as a $B_{1u} + E_u^+$ combination.

We adopt a weighted mean of our three values for the B_{2g} carbon frequency, *viz.*, 703 cm.^{-1} . The B_{2g} frequency product then becomes $692.5 \times 10^3 \text{ cm.}^{-2}$.

(8) *The B_{2g} Fundamental Frequencies of Hexadeuterobenzene.*—Lord and Andrews calculated 395 cm.^{-1} , and Penney and Duchesne 403 cm.^{-1} , for the B_{2g} carbon frequency; as a result of extrapolating from observed 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene frequencies, Langseth and Lord suggested 575 cm.^{-1} . For the B_{2g} hydrogen frequencies, Lord and Andrews, and Penney and Duchesne obtained 1480 cm.^{-1} and 1460 cm.^{-1} respectively, whilst in Part VIII we estimated 920 cm.^{-1} ; Langseth and Lord's estimate was 856 cm.^{-1} .

The B_{2g} frequency product may be obtained either from the infra-red spectrum of 1 : 3 : 5-trideuterobenzene or the Raman spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene. From the equation (cf. Part XVI, Table I, this vol., p. 255)

$$\frac{\Pi A_2''(1:3:5\text{-C}_6\text{H}_3\text{D}_3)}{\Pi A_{2u}, B_{2g}(\text{C}_6\text{D}_6)} = \frac{533 \times 691 \times 915}{496.5 \times \Pi B_{2g}} = 1.374 \text{ (assumed; harmonic value} = 1.388)$$

we find $\Pi B_{2g}(\text{C}_6\text{D}_6) = 494.0 \times 10^3 \text{ cm.}^{-2}$, whilst the equation

$$\frac{\Pi B_{2g}(1:2:4:5\text{-C}_6\text{H}_2\text{D}_4)}{\Pi E_g^-, B_{2g}(\text{C}_6\text{D}_6)} = \frac{615.1 \times 767.1 \times 929.7}{661.7 \times \Pi B_{2g}} = 1.321 \text{ (assumed; harmonic value} = 1.329)$$

gives $\Pi B_{2g}(\text{C}_6\text{D}_6) = 501.9 \times 10^3 \text{ cm.}^{-2}$. We adopt the mean, $497.9 \times 10^3 \text{ cm.}^{-2}$.

The B_{2g} hydrogen frequency is given by a prominent infra-red combination band, which is observed both with gaseous and liquid hexadeuterobenzene, and has only one reasonable explanation :

$$\text{C}_6\text{D}_6, \text{ Infra-red, } 1616, 1619 \text{ cm.}^{-1} \dots\dots\dots (B_{2g}) 826 + (E_u^+) 793 = 1619 \text{ cm.}^{-1}.$$

This band clearly corresponds to the benzene band at $1965\text{--}1963 \text{ cm.}^{-1}$, and, like the latter, is the strongest combination band but one in its spectrum.

These results suffice to determine the B_{2g} carbon frequency, but an independent clue to its value is probably to be found in another infra-red combination band. This is also observed with both gaseous and liquid hexadeuterobenzene, and its preferred interpretation is as follows :

$$\text{C}_6\text{D}_6, \text{ Infra-red, } 1385, 1393 \text{ cm.}^{-1} \dots\dots\dots (B_{2g}) 600 + (E_u^+) 793 = 1393 \text{ cm.}^{-1}.$$

There is a possible alternative explanation, namely, $(B_{2u})825 + (E_g^+)577.4 = 1402 \text{ cm.}^{-1}$, but we favour the interpretation first given, because bands which could, and in at least one case must, receive an analogous interpretation can then be traced in the infra-red spectra of all the other benzenes we have examined; and this is not true for the alternative explanation.

Having regard to this evidence, we take 601 cm.^{-1} and 827 cm.^{-1} as the most probable values of the B_{2g} carbon and B_{2g} hydrogen frequencies of hexadeuterobenzene. The product becomes $497.0 \times 10^3 \text{ cm.}^{-2}$. The product ratio with benzene is satisfactory :

$$\frac{\Pi B_{2g}(\text{C}_6\text{H}_6)}{\Pi B_{2g}(\text{C}_6\text{D}_6)} = 703 \times 985/601 \times 827 = 1.393 \text{ (harmonic value} = 1.414).$$

* The Raman line appears to be much too strong to be attributed to the minute deuterium content of ordinary benzene.

(C) *The Active Higher Harmonic Frequencies of Benzene and Hexadeuterobenzene.*

Having at this stage determined 18 fundamental vibration frequencies of benzene and of hexadeuterobenzene, we are able to make a nearly complete assignment of the active higher harmonic frequencies of these compounds; and this we now do, because the results provide evidence, concerning the activity of higher harmonics in general, which is relevant to our discussion of the last two fundamental frequencies. Several of the higher harmonics involve these fundamental frequencies: logically they should be omitted from the tables of this Section, and separately considered at the end of the paper. But actually we include them in the tables in order to shorten discussion, anticipating for the purpose the results of our consideration of the outstanding fundamental frequencies.

TABLE I.
Raman Frequencies of Benzene.

Frequency (cm. ⁻¹).	Intensity.	Assignment.	Symmetry.	Symmetry of components.
405	w	Forbidden fundamental (405)	E_u^+	—
605·6	ms	Fundamental	E_g^+	—
677—692	w	Forbidden fundamentals (671, 703)	A_{2u}, B_{2g}	—
781 *	ww	Forbidden 1178·0 - 405 = 773	A_{1u}, A_{2u}, E_u^+	E_u^+, E_u^+
804	ww	$2 \times 405 = 810$	A_{1g}, E_g^+	E_u^+, E_u^+
824	ww	$1485 - 671 = 814$	E_g^-	E_u^+, A_{2u}
848·9	m	Fundamental	E_g^-	—
979	w	$1584·8 - 605·6 = 979·2$	A_{1g}, E_g^+	E_g^+, E_g^+
984	w	$^{12}C_6^{13}CH_6$	A_{1g} -like	—
991·6	s	Fundamental	A_{1g}	—
999	w	$1606·4 - 605·6 = 1000·8$	A_{1g}, E_g^+	E_g^+, E_g^+
1005	w	$^{12}C_6^{13}CH_6$	B_{1u} -like	—
1030	w	Forbidden fundamental (1037)	E_u^-	—
1178·0	ms	Fundamental	E_g^+	—
1285 *	ww	Forbidden $605·6 + 671 = 1277$	E_u^+	E_g^+, A_{2u}
1326	ww	Forbidden fundamental (1326)	A_{2g}	—
1404	mw	$2 \times 703 = 1406$	A_{1g}	B_{2g}, B_{2g}
		$\{ 405 + 1010 = 1415 \}$	E_g^-	E_u^+, B_{1u}
1449 *	ww	$\{ 405 + 1037 = 1442$	E_g^-	E_u^+, E_u^-
		$\{ 605·6 + 848·9 = 1454·5$	E_g^-	E_g^+, E_g^-
1478	ww	Forbidden fundamental (1485)	E_u^-	—
1584·8	ms	Fundamental in resonance with		
1606·4	ms	$\{ 605·6 + 991·6 = 1597·2 \}$	E_g^+	E_g^+, A_{1g}
1693	ww	$2 \times 848·9 = 1697·8$	A_{1g}, E_g^+	E_g^-, E_g^-
1827	ww	$\{ 848·9 + 985 = 1833·9$	E_g^-	E_g^-, B_{2g}
		$\{ 848·9 + 991·6 = 1840·5$	E_g^-	A_{1g}, E_g^-
1936	w	$\{ 605·6 + 1326 = 1931·6$	E_g^+	E_g^+, A_{2g}
		$\{ 2 \times 970 = 1940$	A_{1g}, E_g^+	E_u^+, E_u^+
1988	ww	$\{ 970 + 1010 = 1980$	E_g^-	E_u^+, B_{1u}
		$\{ 2 \times 991·6 = 1983·2$	A_{1g}	A_{1g}, A_{1g}
		$\{ 2 \times 1010 = 2020$	A_{1g}	B_{1u}, B_{1u}
2030	ww	$\{ 848·9 + 1178·0 = 2026·9$	E_g^-	E_g^-, E_g^+
		$\{ 1010 + 1037 = 2047$	E_g^+	B_{1u}, E_u^-
2128	ww	$1037 + 1110 = 2147$	E_g^-	E_u^-, B_{2u}
2294	w	$703 + 1596 = 2299$	E_g^-	B_{2g}, E_g^+
2358	w	$2 \times 1178·0 = 2356·0$	A_{1g}, E_g^+	E_g^-, E_g^+
2454	w	$\{ 848·9 + 1596 = 2444·9$	E_g^-	E_g^-, E_g^+
		$\{ 970 + 1485 = 2455$	E_g^-	E_u^+, E_u^-
2543	w	$1037 + 1485 = 2522$	A_{1g}, E_g^+	E_u^-, E_u^-
2618	m	$970 + 1648 = 2618$	E_g^-	E_u^+, B_{2u}
2688	ww	$\{ 1037 + 1648 = 2685$	E_g^+	E_u^-, B_{2u}
		$\{ 3080 - 405 = 2675 \}$	E_g^-	E_u^-, E_u^+
2925	w	$1326 + 1596 = 2922$	E_g^+	E_u^-, E_g^+
2948	m	$2 \times 1485 = 2970$	A_{1g}, E_g^+	E_u^+, E_u^-
3046·8	ms	Fundamental	E_g^+	—
3061·9	s	Fundamental	A_{1g}	—
3164	m		A_{1g}, E_g^+	—
3186	m	$\{ 1596 + \{ 1584·8 = 3180·8$	A_{1g}, E_g^+	—
		$\{ 1606·4 = 3202·4$	A_{1g}, E_g^+	—
3467 *	ww	$405 + 3060 = 3465$	E_g^-	E_u^+, B_{1u}
3680 *	ww	$605·6 + 3061·9 = 3667·5$	E_g^+	E_g^+, A_{1g}

* Listed only by Grassmann and Weiler and placed in their lowest intensity class (index 0).

(1) *Assignment of the Raman and Infra-red Frequencies of Benzene.*—In Table I we record all the Raman frequencies of benzene which have been claimed as authentic (for references see Part III). The list is a long one, mainly on account of the elaborate investigation which Grassmann and Weiler have made of the weaker frequencies. There are some 14 of these which have not yet been observed by anyone else, and in the Table we grade all these as very weak (ww). Grassmann and Weiler subdivide them amongst their three lowest classes of intensity (with indices 1, 1/2, 0), and therefore we specifically indicate the unconfirmed frequencies of their lowest intensity class, since it is impossible not to regard these with some slight reserve. Our judg-

ment, nevertheless, is that very few, if any, unreal frequencies have found their way into Grassmann and Weiler's list.

The frequency given as 677—692 cm^{-1} was observed as 677 cm^{-1} by Wood and Collins, 687 cm^{-1} by Krishnamurti, and 692 cm^{-1} by Grassmann and Weiler. The spread of these numbers is greater than is usual, and it is difficult to decide whether two weak frequencies lie in this region, or only one.

The table contains our assignments. All except a few of the recorded frequencies are explicable either as fundamentals, or allowed first overtones, or allowed binary summation tones, or forbidden fundamental frequencies; the remainder, which are amongst the very weakest, can be interpreted as allowed difference tones or forbidden combinations.

The term "forbidden," as used here, requires some explanation. As a matter of convenience it is made to cover not only those vibrations which are perturbed and rendered active by intermolecular forces, but also those allowed vibrations of $^{12}\text{C}_5^{13}\text{CH}_6$ which are similar to theoretically forbidden vibrations of C_6H_6 . The nomenclature reflects the fact that it is often difficult to distinguish the perturbing effect of a ^{13}C atom from the effect due to cohesion. On this basis, we might have assigned the line of frequency 1005 cm^{-1} simply as the "forbidden" B_{1u} fundamental (accepted frequency 1010 cm^{-1}). In this case, however, there is no

TABLE II.

Infra-red Frequencies of Benzene.

Frequency (cm^{-1}).		Intensity.	Assignment.	Symmetry.	Symmetry of components.
Vapour.	Liquid.				
—	610	ww	Forbidden fundamental (605.6)	E_g^+	—
671	671	s	Fundamental	A_{2u}	—
779	773	ww	1178.0 — 405 = 773	A_{2u}	E_g^+, E_u^+
—	849	mw	Forbidden fundamental (848.9)	E_g^-	—
962	—	ww	$^{13}\text{C}_5^{13}\text{CH}_6$	E_u^+ -like	—
—	985	w	Forbidden fundamental (985)	E_{2g}	—
1037	1033	s	Fundamental	E_u^-	—
1143	—	ww	Error?	—	—
—	1170	mw	Forbidden fundamental (1178.0)	E_g^+	—
1240	—	ww	405 + 848.9 = 1254	E_u^-	E_u^+, E_g^-
—	1298	ww	Forbidden 605.6 + 703 = 1309	E_g^-	E_g^+, E_{2g}
1377	1381	w	405 + 985 = 1390	E_u^-	E_u^+, B_{2g}
1485	1480	s	Fundamental	E_u^-	—
—	1529	ww	671 + 848.9 = 1520	E_u^-	A_{2u}, E_g^-
—	1584	w}	{ Forbidden fundamental doublet }	E_g^+	—
—	1604	w}			
1617	—	w			
—	—	—	605.6 + 1010 = 1616	E_u^-	E_g^+, B_{1u}
—	1669	w	{ 671 + 991.6 = 1663	A_{2u}	A_{2u}, A_{1g}
—	—	—	{ 703 + 970 = 1673	B_{2g}	E_u^+, E_u^-
1808	1810	m	848.9 + 970 = 1819	E_u^-	E_g^+, E_u^+
1965	1963	mw	970 + 985 = 1955	E_u^-	E_u^-, E_{2g}
—	2223	w	1037 + 1178.0 = 2215	E_u^-	E_u^-, E_g^+
2288	—	w	1110 + 1178 = 2288	E_u^-	B_{2u}, E_g^+
—	2356	w	1037 + 1326 = 2363	E_u^-	E_u^+, E_g^+
—	2629	w	1037 + 1596 = 2633	E_u^-	E_u^-, E_{2g}^+
2857	—	ww	Error?	—	—
3061	—	s}	{ Fundamental in resonance }	E_u^-	E_u^-, E_g^+
3098	—	s}			
—	3655	w	605.6 + 3060 = 3666	E_u^-	E_u^+, B_{1u}
—	3700	w	605.6 + 3080 = 3686	E_u^-	E_g^+, E_u^-
—	—	—	{ 1010 + 3046.8 = 4057	E_u^-	B_{1u}, E_g^+
—	4060	w	{ 991.6 + 3080 = 4072	E_u^-	A_{1g}, E_u^-

doubt as to the cause of the appearance: Langseth and Lord have made it clear that it is the ^{13}C atom (*J. Chem. Physics.*, 1938, 6, 203). In the assignment column of the table we give, in parenthesis, the accepted values of the "forbidden" fundamental frequencies to which certain of the weak lines are assigned. These frequencies are either active in the infra-red spectrum (A_{2u}, E_u^-), and are derived from Part IV (*loc. cit.*), or they are inactive (E_u^+, B_{2g}, A_{2g}), and are deduced in this paper.

The frequencies 979 and 999 cm^{-1} , which, though weak, are not extremely weak, are not difference tones, despite the appearance of the entries in the assignment column. Langseth and Lord explained this situation also (*loc. cit.*): the two lines jointly represent the A_{1g} carbon fundamental frequency of the 5% of molecules which at room temperature are already thermally excited with one quantum of the vibration of frequency 605.6 cm^{-1} ; the subsequent photo-excitation produces lines which are separate from the main A_{1g} carbon line at 991.6 cm^{-1} , because of the resonance splitting of the upper vibrational level.

The infra-red frequencies which were recorded in Part IV (*loc. cit.*) are assembled in Table II, which also contains our assignment. Measurements made with benzene vapour can theoretically reveal, as weak bands, certain frequencies of the heavy-carbon molecule $^{12}\text{C}_5^{13}\text{CH}_6$, which would not have been active but for the presence of the ^{13}C atom. We actually assign one weak band of the vapour spectrum in this way. Such bands might also appear in the spectrum of the liquid; but here cohesive forces constitute a more fruitful

TABLE III.
Raman Frequencies of Hexadeuterobenzene.

Frequency (cm. ⁻¹).	Intensity.	Assignment.	Symmetry.	Symmetry of components.
350	ww	Forbidden fundamental (352)	E_u^+	—
577.4	ms	Fundamental	E_g^+	—
661.7	ms	Fundamental	E_g^-	—
844.5	m	$352 + 496.5 = 848.5$	E_g^+	E_u^+, A_{2u}
867.3	ms	Fundamental	E_g^+	—
943.2	s	Fundamental	E_g^+	—
999	mw	$2 \times 496.5 = 993$	A_{1g}	A_{2u}, A_{2u}
1161	ww	$352 + 813 = 1165$	E_g^-	E_u^+, E_u^-
1329	mw	$\left\{ \begin{array}{l} 2 \times 661.7 = 1323.4 \\ \text{Forbidden fundamental (1333)} \end{array} \right.$	A_{1g}, E_g^+	E_g^-, E_g^-
1522	mw	$\left\{ \begin{array}{l} 577.4 + 943.2 = 1520.6 \\ 661.7 + 867.3 = 1529.0 \end{array} \right.$	E_g^+	E_g^+, A_{1g}
1551.5	ms	Fundamental	E_g^+	E_g^+, E_g^+
1578	mw	$2 \times 793 = 1586$	A_{1g}, E_g^+	E_u^+, E_u^+
1923	w	$\left\{ \begin{array}{l} 352 + 1571 = 1923 \\ (2 \times 963 = 1926) \end{array} \right.$	E_g^-	E_u^+, B_{2u}
2129	mw	$577.4 + 1551.5 = 2129.0$	A_{1g}	B_{1u}, B_{1u}
2139	mw	$813 + 1333 = 2146$	A_{1g}, E_g^+	E_g^+, E_g^+
2264.9	ms	Fundamental	E_g^+	E_u^-, E_u^-
2292.6	s	Fundamental	A_{1g}	—
2571	w	$1037 + 1551 = 2588$	E_g^+	A_{2g}, E_g^+
3104	ww	$2 \times 1551.5 = 3003$	A_{1g}, E_g^+	E_g^+, E_g^+

source of observable frequencies which would be forbidden by the selection rules for ordinary gaseous benzene. It was shown in Part VII (*loc. cit.*) that a number of bands of this nature can immediately be recognised in the spectrum of liquid benzene.

As noted in Table II, we doubt the existence, or the accuracy, of some of the weakest of the recorded frequencies. The others can all be plausibly explained either as allowed fundamental frequencies, or allowed binary combinations, or as forbidden fundamentals, or forbidden combinations. Apart from the heavy-carbon frequency, all forbidden frequencies are found only in the spectrum of the liquid. The accepted values of forbidden fundamental frequencies, as obtained from the Raman spectrum (Part III, *loc. cit.*), or indirect deduction (this paper), are noted in parenthesis.

TABLE IV.
Infra-red Frequencies of Hexadeuterobenzene.

Frequency (cm. ⁻¹).		Intensity.	Assignment.	Symmetry.	Symmetry of components.
Vapour.	Liquid.				
496.5	—	s	Fundamental	A_{2u}	—
—	581	ww	Forbidden fundamental (577.4)	E_g^+	—
—	662	w	Forbidden fundamental (661.7)	E_g^-	—
—	754	ww	$1333 - 577.4 = 756$	E_u^-	E_u^-, E_g^+
813	811	s	Fundamental	E_u^-	—
826 *	—	ww	$^{12}C_5^{13}CD_6?$	—	—
—	864	ww	Forbidden fundamental (867.3)	E_g^+	—
926	925	w	$352 + 577.4 = 929$	A_{2u}	E_u^+, E_g^+
—	943 *	ww	Forbidden fundamental (943.2)	A_{1g}	—
—	979 *	ww	$^{12}C_5^{13}CD_6?$	—	—
1009	1012	ww	$352 + 661.7 = 1014$	E_u^-	E_u^+, E_g^-
1154	1159	mw	$496.5 + 661.7 = 1158.2$	E_u^-	A_{2u}, E_g^-
1212	1218	ww	$352 + 867.3 = 1219$	A_{2u}	E_u^+, E_g^+
1333	1332	m	Fundamental	E_u^-	—
1385	1393	ww	$\left\{ \begin{array}{l} 601 + 793 = 1394 \\ (577.4 + 825 = 1402) \end{array} \right.$	E_u^-	B_{2g}, E_u^+
1450	1454	m	$661.7 + 793 = 1455$	E_u^-	E_g^-, E_u^+
—	1552	w	Forbidden fundamental (1551.5)	E_g^+	—
1616	1619	m	$793 + 827 = 1620$	E_u^-	E_u^+, B_{2g}
1630 *	—	ww	$2294 - 661.7 = 1632$	A_{2u}	E_u^-, E_g^-
1692	1690	w	$\left\{ \begin{array}{l} 825 + 867.3 = 1692 \\ (813 + 867.3 = 1683) \end{array} \right.$	E_u^-	B_{2u}, E_g^+
1860	1866	w	$813 + 1037 = 1850$	E_u^-	E_u^-, E_g^+
2294	2283	s	Fundamental	E_u^-	—
—	2903	ww	$\left\{ \begin{array}{l} 1333 + 1551.5 = 2884 \\ 601 + 2290 = 2891 \end{array} \right.$	E_u^-	E_u^-, E_g^+
—	3292	w	Forbidden $1037 + 2264.9 = 3302$	A_{2u}	B_{2g}, B_{1u}
—	3559	w	$1333 + 2264.9 = 3598$	E_g^+	A_{2g}, E_g^+
4545	4525	w	$\left\{ \begin{array}{l} 2264.9 + 2290 = 4555 \\ 2264.9 + 2294 = 4559 \end{array} \right.$	E_u^-	E_u^-, E_g^+
				E_u^-	E_g^+, B_{1u}
				E_g^+	E_g^+, E_u^-

* The authenticity or accuracy of these values as C_6D_6 frequencies is regarded as questionable (see text).

(2) *Assignment of the Raman and Infra-red Frequencies of Hexadeuterobenzene.*—Those Raman frequencies of hexadeuterobenzene which are confirmed by Poole's re-examination of the spectrum (Part XV, Table I, this vol., p. 252) are collected in Table III. Neglecting previous values, we accept Poole's data for all the stronger frequencies as they are definitely more accurate than earlier figures. However, in measuring weak frequencies, a high resolving power is not an unmixed advantage, and therefore, where it seemed desirable, we have accorded weight to previous work, particularly that of Wood, in arriving at mean values (for references see Part XV).

Our assignments, which are also given in the table, are in terms of allowed fundamentals, first overtones, allowed binary summation tones and forbidden fundamental frequencies. One clear case of a forbidden fundamental arises in the low-frequency line at 350 cm^{-1} .

Table IV contains all the observed infra-red frequencies of hexadeuterobenzene, accepting the recent revision (Part XVI, this vol., p. 255) of the long-wave region of the spectrum. A few of the weakest frequencies must be regarded with reserve, especially as it follows from the most recent determinations of physico-chemical constants that the sample of hexadeuterobenzene employed in the investigations quoted may have contained somewhat more pentadeuterobenzene than was formerly supposed (Part XII, this vol., p. 235): we do not yet know the infra-red spectrum of pentadeuterobenzene. Attention is directed in the table to the frequencies of two small "nicks" in the contours of the vapour bands, and to two secondary maxima in a composite band-group of the liquid, as being at present suspect, even though assignments can be suggested. The remaining frequencies can all be plausibly assigned either as allowed fundamental frequencies, or binary combination tones, or, in the case of bands appearing only in the spectrum of the liquid, as forbidden fundamentals or combination tones.

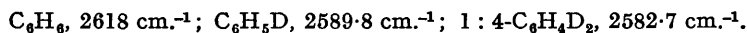
(3) *Comparisons of the Stronger Higher Harmonic Frequencies of Various Benzenes.*—The strongest higher harmonic frequencies which are found in our Raman spectra come into the intensity class which we call "moderate" (m). Table V contains a list of such frequencies, taken from tables in Parts XV, XVII, XVIII, and XX, and this paper:

TABLE V.
Outstanding Higher Harmonic Raman Frequencies.

C_6H_6 .	$\text{C}_6\text{H}_5\text{D}$.	$\text{C}_6\text{H}_4\text{D}_2$.	$\text{C}_6\text{H}_3\text{D}_3$.	$\text{C}_6\text{H}_2\text{D}_4$.	C_6D_6 .
2618	*2310.6	2582.7	*2238.3	*1543	*844.5
*2948	2589.8	*2935.4	*2973.3	*1550	—
*3164	*2998	*3153.4	*3144.5	—	—
*3186	*3164.6	*3170.7	—	—	—
—	*3182	—	—	—	—

All the frequencies marked with an asterisk lie within 4% of a Raman-active fundamental frequency, and in every such case the symmetry class of the combination tone is the same as that of the neighbouring fundamental. The high proportion of such lines amongst the relatively strong higher-harmonic lines shows the common cause of their considerable intensity to be resonance of the type first recognised by Fermi. It is noteworthy also that all but 2 of the 16 frequencies marked with an asterisk lie 2% or further away from the fundamental frequency from which they gain their spectral intensity. This is clearly due to another well-known effect of the resonance, *viz.*, that, when the combination tone would theoretically lie too close to the fundamental frequency, the resonance separates the two, mainly by displacing the weaker frequency. For instance, the theoretical position of a monodeuterobenzene combination tone is 3024 cm^{-1} , which is only 1% away from the fundamental frequency 3054.8 cm^{-1} ; and the combination tone is accordingly observed at 2998 cm^{-1} , which is 2% away from the fundamental frequency.

The only Raman frequencies of the list in Table V whose relatively great intensity cannot be explained in this way are these:

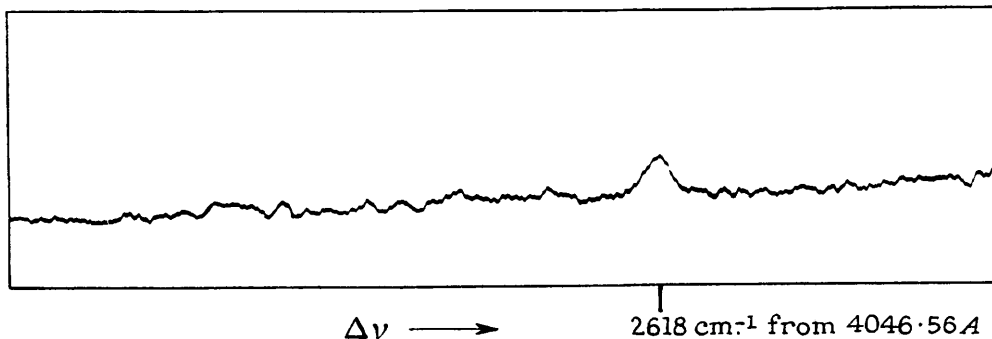


They are evidently in a very special position amongst Raman combination tones. A microphotometer record of the first is reproduced in Fig 1. Microphotometer records of the second and third are shown in Parts XX and XVIII respectively (this vol., pp. 315, 287). Their singularity would suggest the possibility of a common explanation, even if no other circumstances pointed in this direction, and we shall later base conclusions on this idea. Supporting arguments can, however, be given. It seems unlikely to be by chance that all three lie in the same spectral region, with frequencies which diminish with successively introduced deuterium atoms. It seems significant that the only possible common explanation involves the E_u^+ hydrogen frequency, 970 cm^{-1} , which is common to, and restricted to, the three benzenes involved. A common explanation would seem natural in view of the general rule that the strongest combination tones of the various infra-red spectra can be correlated in sets, each with a common form of explanation—provided, of course, we discount effects on intensity due to Fermi resonance, and allow for the appearance of extra combinations when there is a loss of molecular symmetry.

This general rule we propose now to illustrate. The frequencies (cm^{-1}) of the strongest infra-red combination tones are collected together in Table VI. The only omitted combination frequencies which are

more intense than the weakest of those included (disregarding the figures in brackets) are frequencies which are obviously deriving much of their intensity by resonance with fundamentals, and one frequency, 1384 cm^{-1} , belonging to the least symmetrical molecule, monodeuterobenzene. The correlations are indicated by tie-lines and braces. In order to make the scheme more complete, two predicted, unobserved frequencies are included in square brackets: each occurs in such a position in its spectrum that it would be overlapped by a strong fundamental frequency. For the same reason we have included in parenthesis some expected combinations, which are actually observed, but come into a somewhat lower intensity class than that of most of the frequencies in the table.

FIG. 1.



Microphotometer record of part of the Raman spectrum of benzene. The region depicted runs from 2380 cm^{-1} to 2740 cm^{-1} on the Stokes side of Hg 4046.56 Å. In order to avoid inconvenient overlapping, the Raman spectrum excited by Hg 4358.34 Å. has been eliminated by means of an iodine filter. The single line showing is the prominent combination tone 2618 cm^{-1} . The exposure was comparatively short, as is proved by the fact that the combination frequencies 2454 and 2543 cm^{-1} (as well as the weaker 2688 cm^{-1}) have completely failed to register.

The strongest combination band in the infra-red spectrum of benzene is that at 1808 cm^{-1} , and it is constituted exactly as is the strongest hexadeuterobenzene combination band at 1450 cm^{-1} , one of the strongest combination bands of 1:4-dideuterobenzene and one of the strongest of monodeuterobenzene. The common explanation for the bands of benzene and mono- and 1:4-di-deuterobenzene is that represented by the summation $849 + 970 = 1819 \text{ cm}^{-1}$, both fundamental frequencies being the same for the three compounds; the common figures for 1:2:4:5-tetra-, penta-, and hexa-deuterobenzene would be $662 + 793 = 1455 \text{ cm}^{-1}$. In 1:3:5-trideuterobenzene both the fundamental vibrations become mixed and radically altered.

TABLE VI.

Outstanding Higher Harmonic Infra-red Frequencies, excluding those in Resonance with Active Fundamental Frequencies.

Parent D_{6h} Forms.	C_6H_6 .	$\text{C}_6\text{H}_5\text{D}$.	$\text{C}_6\text{H}_4\text{D}_2$.	$\text{C}_6\text{H}_3\text{D}_3$.	$\text{C}_6\text{H}_2\text{D}_4$.	C_6D_6 .
A_{2u}, E_g^-	[1520]			1233		1154
		{ 1697	1603		{ (1687)	
		1768	1724		1206	
$E_u^+(\text{H}), E_g^-$	1808	1821	1811		[1450]	1450
$E_u^+(\text{H}), B_{2g}(\text{C})$	(1669)	(1670)	1603	1632	1404	(1385)
$E_u^+(\text{H}), B_{2g}(\text{H})$	1965	1896, 1952	1923		1556	1616
$B_{1u}(\text{C}), E_g^+(\text{H})$			1916	1835	1840	
$B_{2u}(\text{H}), E_g^+(\text{H})$	2288			1750		1692

The degenerate benzene frequency (E_u^+) 970 cm^{-1} , has one component which becomes altered to 922 and 876 cm^{-1} in mono- and 1:4-di-deuterobenzene respectively, essentially because the vibration becomes mixed with the benzene A_{2u} vibration. These modified E_u^+ frequencies combine, just as the unmodified frequency does, with the E_g^- frequency, 849 cm^{-1} , to give the comparably strong bands at 1768 and 1724 cm^{-1} in the spectra of mono- and 1:4-di-deuterobenzene. We might alternatively describe these bands as derived from the hypothetical benzene combination 1520 cm^{-1} , from (A_{2u}) 671 and (E_g^-) 849 cm^{-1} , by supposing the A_{2u} vibration to be modified through admixture with the E_u^+ vibration. In hexadeuterobenzene the $A_{2u}-E_g^-$ combination, the theoretical frequency of which is $496 + 662 = 1158 \text{ cm}^{-1}$, is not overlapped as in benzene, but appears at 1154 cm^{-1} as the strongest combination band but two in the infra-red spectrum. This band can be regarded as parent of the strong combination band at 1233 cm^{-1} in the infra-red spectrum of 1:3:5-trideuterobenzene, and also as parent, jointly with the band at 1450 cm^{-1} , of the strong combination band at 1206 cm^{-1} in the spectrum of 1:2:4:5-tetra-deuterobenzene.

Analogously to the E_u^+ fundamental frequency, the degenerate E_g^- frequency of benzene, 849 cm^{-1} , has a component which in the partly deuterated benzenes becomes modified (to 778, 736, and 767 cm^{-1} in mono-, 1:4-di- and 1:2:4:5-tetra-deuterobenzene respectively), due in this case to the mixing of a certain pro-

portion of B_{2g} -character into the vibrations. By combination of the modified E_u^+ and E_g^- fundamental frequencies, the infra-red combination bands at 1697, 1603, and 1687 cm^{-1} in mono-, 1:4-di-, and 1:2:4:5-tetra-deuterobenzene respectively may be derived.

The strongest but one of the non-resonating combination frequencies of benzene, 1965 cm^{-1} , has been identified as the summation tone of the E_u^+ frequency, 970 cm^{-1} , with the B_{2g} hydrogen frequency; and the strongest combination tone but one in the hexadeuterobenzene spectrum, 1616 cm^{-1} , has an exactly similar explanation. The E_u^+ frequency of benzene, 970 cm^{-1} , remains unaltered in mono- and 1:4-di-deuterobenzene, but the benzene B_{2g} hydrogen frequency, 985 cm^{-1} , becomes changed by admixture to the two frequencies 922 and 985 cm^{-1} of monodeuterobenzene, and to the frequency 967 cm^{-1} of 1:4-dideuterobenzene. Combination between the E_u^+ frequency 970 cm^{-1} and the altered frequencies explains the bands at 1896 and 1952 cm^{-1} in the monodeuterobenzene infra-red spectrum, and the band at 1923 cm^{-1} in the corresponding spectrum of 1:4-dideuterobenzene. Similarly the E_u^+ frequency, 793 cm^{-1} , of hexadeuterobenzene remains preserved in 1:2:4:5-tetradeterobenzene, while the B_{2g} frequency, 827 cm^{-1} , becomes altered to 767 cm^{-1} , thus producing the combination band at 1556 cm^{-1} in the infra-red spectrum of 1:2:4:5-tetradeterobenzene.

A further series of bands, some of them rather weak, arises by combination between the E_u^+ frequencies, 970 cm^{-1} in benzene and mono- and 1:4-di-deuterobenzene, 947 cm^{-1} in 1:3:5-trideuterobenzene, and 793 cm^{-1} in 1:2:4:5-tetra- and hexa-deuterobenzene, and the B_{2g} carbon frequencies or their nearest relations

TABLE VII.

Related First Overtones in Raman Spectra.

	C_6H_6 .	$\text{C}_6\text{H}_5\text{D}$.	$\text{C}_6\text{H}_4\text{D}_2$.	$\text{C}_6\text{H}_3\text{D}_3$.	$\text{C}_6\text{H}_2\text{D}_4$.	C_6HD_5 .	C_6D_6 .
{ Fundamental (I.-R.)	671	608	597	533	548	— *	497
{ Overtone	—	—	1196	1069	1098	— *	999
{ Fundamental	703 †	698	634	691	615	612 §	601 †
{ Overtone	1404	1396	1267	1392	1232	1225 §	—
{ Fundamental (Ram.)	849	778	736	710	767	709 §	662
{ Overtone	1693	— ‡	—	1417	1533	1415 §	1329

* Infra-red not yet investigated.

† Inactive.

‡ Would be overlapped.

§ A general account of the Raman spectrum of this substance will be published later.

|| In this case the intensity could be due to Fermi resonance.

amongst the fundamentals of the partly deuterated benzenes. The strongest of these bands appears at 1632 cm^{-1} in the spectrum of 1:3:5-trideuterobenzene: generally speaking, they diminish in intensity towards the ends of the series. Other relationships can be traced. The strong frequencies 1916, 1835, and 1840 cm^{-1} of 1:4-di-, 1:3:5-tri-, and 1:2:4:5-tetra-deuterobenzene can each be represented as a combination between a B_{1u} -like planar carbon bending vibration, and a planar deuterium bending vibration more or less closely related to that in the E_g^+ class of hexadeuterobenzene vibrations. The moderately prominent bands at 2238 cm^{-1} in the infra-red spectrum of benzene, and at 1692 cm^{-1} in the spectrum of hexadeuterobenzene, are combinations of planar hydrogen bending vibrations: they almost certainly correspond to each other, and, as closely as the difference of molecular symmetry permits, to the prominent band at 1750 cm^{-1} in the spectrum of 1:3:5-trideuterobenzene.

The correlation of higher harmonic frequencies amongst the spectra of the different benzenes may be illustrated also with respect to overtones. For all benzenes all first overtones are allowed in the Raman effect. Considering what a small proportion of the allowed overtones are actually visible in our Raman spectra, the extent to which those which are visible fall into sets is quite remarkable. Leaving out of account overtones between about 2950 and 3150 cm^{-1} and a few others, which doubtless gain intensity by resonance with Raman fundamental frequencies, the three sets of Table VII comprise very nearly all the observed overtones. The fundamental frequencies corresponding to the first set of overtones are A_{2u} -like, and for all benzenes are given by the lowest very strong infra-red frequency; the fundamentals of the second set are B_{2g} -like carbon vibration frequencies, and they are either Raman-active or infra-red-active in the partly deuterated benzenes; the fundamentals of the third set are all E_g^- -like, and for all benzenes are active in the Raman spectrum.

(D) *Tentative Completion of the Assignment of the Fundamental Frequencies of Benzene, Hexadeuterobenzene, and the Partly Deuterated Benzenes: Some B_{2u} and B_{2u} -like Frequencies.*

(1) *Preliminary Consideration of Possible Active B_{2u} -like Carbon Frequencies.*—The B_{2u} carbon stretching frequencies of benzene and hexadeuterobenzene should not differ by more than a few units per cent., and the most nearly allied frequencies of the partly deuterated benzenes are likely to have more or less regularly arranged intermediate values, with the possible exception of any which would in that case fall close to another fundamental frequency of the same symmetry class. For the B_{2u} carbon frequency of benzene, normal co-ordinate calculations have yielded values ranging from 1489 cm^{-1} to 1854 cm^{-1} . Active frequencies allied to the B_{2u} carbon frequencies of D_{6h} benzenes might be expected in the infra-red spectrum of mono-, 1:4-di-, 1:2:4:5-tetra- and penta-deuterobenzene, and also in the Raman spectrum of mono- and penta-deutero-

benzene. According to preconceptions derived from the calculations mentioned, they might reasonably be sought anywhere in the region 1400—1900 cm^{-1} .

The two B_{2u} and three E_u^- vibrations of D_{6h} benzenes combine to form a single symmetry class, labelled B_{3u} , in the V_h benzenes. For 1 : 4-dideuterobenzene, and likewise for 1 : 2 : 4 : 5-tetra-deuterobenzene, four of the five frequencies of this symmetry class have been identified by reference to infra-red spectra. In each case the missing frequency was that of the vibration similar to the B_{2u} carbon stretching vibration of benzene : no further band could, however, be found in the relevant frequency region of the infra-red spectrum of either 1 : 4-di- or 1 : 2 : 4 : 5-tetra-deuterobenzene, which could not be explained as an allowed combination tone ; but unfortunately the possibilities of accidental coincidence with an allowed combination tone are rather numerous in the frequency region which is of importance in this connexion.

The harmonic value of the product ratio $\Pi B_{3u}(1 : 4\text{-C}_6\text{H}_4\text{D}_2)/\Pi B_{3u}(1 : 2 : 4 : 5\text{-C}_6\text{H}_2\text{D}_4)$ is 1.396. The ratio of the products of the four known B_{3u} frequencies of each compound is 1.392. It follows that the missing carbon stretching frequencies cannot lie far apart, and, indeed, are unlikely to differ by much more than 1%.

In mono- and penta-deuterobenzene the missing frequency is one of the ten belonging to the B_1 class. The corresponding symmetry classes of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene are B_{3u} and B_{1g} . The harmonic value of the product ratio $\Pi B_1(\text{C}_6\text{H}_5\text{D})/\Pi B_{3u}B_{1g}(1 : 4\text{-C}_6\text{H}_4\text{D}_2)$ is 1.382. The ratio of the product of the nine known frequencies which belong to the numerator, to the product of the nine which belong to the denominator, of this fraction is 1.333. This figure, which depends on eighteen measured frequencies, may not be very accurate, but it would seem that the B_{2u} -like carbon stretching frequency of monodeuterobenzene may lie from 1% to 4% above that of 1 : 4-dideuterobenzene, the smaller order of difference being more probable on general grounds.

Although we have studied three infra-red spectra in which this frequency is allowed to appear, it may have escaped observation in any or all of them. If it has been observed in all three spectra, the following possible sets of frequencies (cm^{-1}) are available for assignment (Table VIII).

TABLE VIII.
Possible Assignments of B_{2u} -like Carbon Frequencies.

	(1).	(2).	(3).	(4).
$\text{C}_6\text{H}_6\text{D}$	1384	1624	1768	1952
1 : 4- $\text{C}_6\text{H}_4\text{D}_2$	1335	1603	1711	1923
1 : 2 : 4 : 5- $\text{C}_6\text{H}_2\text{D}_4$	1309	1585	1687	1931

No further possibilities present themselves if we assume that the required frequency has been observed in only two of the three spectra. Furthermore, we have found no frequencies in the Raman spectra of mono- or penta-deuterobenzene which suggest themselves for inclusion in the survey, unless it be that the weak frequency 1617 cm^{-1} in the Raman spectrum of monodeuterobenzene is to be identified with the infra-red frequency 1624 cm^{-1} : this is not impossible because the Raman line is heavily overlapped, and the infra-red band has an unsymmetrical appearance as though it were composite.

Assignments (1) and (4) involve frequencies which are rather outside the anticipated range. The frequencies of assignments (2) and (3) fall well within it, and of these alternatives (2) is slightly to be preferred as giving the better product ratio, $\Pi B_{3u}(1 : 4\text{-C}_6\text{H}_4\text{D}_2)/\Pi B_{3u}(1 : 2 : 4 : 5\text{-C}_6\text{H}_2\text{D}_4) = 1.407$ (the harmonic value is 1.396). A further (and considerably stronger) indication in favour of assignment (2) is mentioned in the next section.

(2) *The B_{2u} Fundamental Vibrations of Benzene.*—For the frequency of the carbon vibration, Kohlrausch, and Lord and Andrews, calculated 1854 cm^{-1} , and Penney and Duchesne 1489 cm^{-1} , whilst in Part VIII we gave 1720 cm^{-1} . Pitzer and Scott suggested identifying the frequency with that of the weak Raman line at 1693 cm^{-1} , which they suppose to appear in violation of the selection rules, whereas we think, for reasons given in Section C, 3, that this line is much more likely to represent the first overtone of the Raman-active fundamental frequency, 849 cm^{-1} . For the hydrogen frequency Kohlrausch calculated 1094 cm^{-1} , Lord and Andrews 1145 cm^{-1} , and Penney and Duchesne 1111 cm^{-1} . Pitzer and Scott proposed 1170 cm^{-1} , the frequency of an infra-red band of liquid benzene, which, however, as we suggested (Part VII), and as they agree, might reasonably be associated with the known E_g^+ frequency in that neighbourhood.

The strongest higher harmonic line in the Raman spectrum of benzene (if we exclude those few which can, and doubtless do, borrow intensity from neighbouring fundamental lines) has the frequency 2618 cm^{-1} ; it cannot be explained except as a combination tone involving a B_{2u} fundamental frequency. There are two possible explanations : one assumes a B_{2u} carbon frequency of 1648 cm^{-1} , and the other a B_{2u} hydrogen frequency of 1133 cm^{-1} .

We have already pointed out (Section C, 3) that the outstanding combination frequency 2618 cm^{-1} of benzene is very probably related to the combination frequency 2589.8 cm^{-1} of monodeuterobenzene, and the frequency 2582.7 cm^{-1} of 1 : 4-dideuterobenzene, which are similarly outstanding in their Raman spectra. We prefer the explanation of the benzene line which involves the B_{2u} carbon frequency, essentially because it alone can be extended to cover the similar lines of mono- and 1 : 4-di-deuterobenzene :

C_6H_6 , Raman, 2618 cm^{-1}	(B_{2u}) 1648 + (E_u^+) 970 = 2618 cm^{-1}
$\text{C}_6\text{H}_5\text{D}$, Raman, 2589.8 cm^{-1}	(B_1) 1620 + (A_1) 970 = 2590 cm^{-1}
1 : 4- $\text{C}_6\text{H}_4\text{D}_2$, Raman, 2582.7 cm^{-1}	(B_{3u}) 1613 + (A_u) 970 = 2583 cm^{-1}

There are two notable points about this suggested correlation. One is that it agrees with that assignment of active B_{2u} -like carbon frequencies of mono- and 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene which had seemed most self-consistent amongst the possibilities presented by the infra-red spectra of the partly deuterated benzenes (assignment No. 2, Table VIII). The other is that by requiring the B_{2u} -like frequency to combine in each case with the E_u^+ frequency, 970 cm^{-1} , which remains exactly the same in benzene and in mono- and 1 : 4-di-deuterobenzene, but becomes changed in all other benzenes, it helps us to understand why the correlation does not extend beyond the three compounds in which we find it. The choice of 1648 cm^{-1} as the B_{2u} carbon frequency of benzene also provides a good explanation of a weak Raman frequency, 2688 cm^{-1} , which otherwise can only be interpreted as a difference tone (Table I, p. 324).

The alternative explanation of the benzene frequency 2618 cm^{-1} , namely, $(B_{2u})1133 + (E_u^-)1485 = 2618 \text{ cm}^{-1}$, cannot be extended to cover the similar frequency of monodeuterobenzene (for $1076 + 1480 = 2556 \text{ cm}^{-1}$ is obviously unacceptable), although it could be applied to the corresponding 1 : 4-dideuterobenzene frequency ($1106 + 1469 = 2575 \text{ cm}^{-1}$).

The strongest combination band but two in the infra-red spectrum of benzene vapour has the frequency 2288 cm^{-1} , and cannot be explained otherwise than as a combination band involving a B_{2u} fundamental frequency. It requires either a B_{2u} hydrogen frequency of 1110 cm^{-1} , or a B_{2u} carbon frequency of 1682 cm^{-1} . Our choice, on the evidence already presented, of the B_{2u} carbon frequency of benzene, and of the B_{2u} -like carbon frequencies of the partly deuterated benzenes, entails the adoption of the first of these alternatives :

$$\text{C}_6\text{H}_6, \text{ infra-red, } 2288 \text{ cm}^{-1} \dots\dots\dots (B_{2u}) 1110 + (E_g^+) 1178 = 2288$$

A B_{2u} hydrogen frequency of 1110 cm^{-1} provides an interpretation of a very weak and diffuse Raman line, of reported frequency 2128 cm^{-1} , which would otherwise be difficult to explain (Table I, p. 324).

The product rule may be employed to check these values :

$$\frac{\Pi B_{2u} E_u^-(\text{C}_6\text{H}_6)}{\Pi B_{2u}(1 : 4\text{-C}_6\text{H}_4\text{D}_2)} = \frac{1648 \times 1110 \times 1037 \times 1485 \times 3080}{1603 \times 1106 \times 814 \times 1413 \times 3079} = 1.382 \text{ (harmonic value} = 1.396).$$

(3) *The B_{2u} Fundamental Vibrations of Hexadeuterobenzene.*—Calculations based on an assumed force system have given values for the B_{2u} carbon frequency ranging from 1427 cm^{-1} (Penney and Duchesne) to 1844 cm^{-1} (Kohlrausch; Lord and Andrews); we gave 1636 cm^{-1} in Part VIII. On the other hand very consistent values have been obtained by calculation for the B_{2u} hydrogen frequency: Kohlrausch found 838 cm^{-1} , Lord and Andrews 816 cm^{-1} , and Penney and Duchesne 821 cm^{-1} , whilst we obtained 820 cm^{-1} .

In the Raman spectrum of hexadeuterobenzene a higher harmonic of medium intensity occurs at 1923 cm^{-1} . This could be the first overtone of the B_{1u} carbon frequency 963 cm^{-1} . But, as pointed out in Section C, 3, observed first overtones generally correspond in different Raman spectra; and, although for all the benzenes which we have examined the B_{1u} carbon fundamental frequency is accurately known, we have never observed an undoubted appearance of its first overtone. The overtone hypothesis thus appears somewhat improbable, and the only other explanation of the frequency is that which requires a B_{2u} carbon fundamental frequency of 1571 cm^{-1} :

$$\text{C}_6\text{D}_6, \text{ Raman, } 1923 \dots\dots\dots (B_{2u}) 1571 + (E_u^+) 352 = 1923 \text{ cm}^{-1}$$

The infra-red spectrum of hexadeuterobenzene vapour contains a moderately prominent combination band at 1692 cm^{-1} . It could, perhaps, be interpreted as a summation of E_u^- and E_g^+ hydrogen bending frequencies: $813 + 867 = 1680 \text{ cm}^{-1}$. But we think that this is probably not the correct explanation, because no such combination band, to be explained by the summation $1037 + 1178 = 2215 \text{ cm}^{-1}$, appears in the infra-red spectrum of benzene vapour, or in the corresponding spectra of mono- or 1 : 4-di-deuterobenzene, in which the component fundamental frequencies are almost the same as in benzene. In none of these spectra should there be any difficulty about observing the frequency if it were present. Comparisons with other spectra are vitiated by ambiguous interpretations. The alternative view of the hexadeuterobenzene band at 1692 cm^{-1} is that it is a combination of B_{2u} and E_g^+ hydrogen bending frequencies. It would then correspond exactly to the already discussed benzene band at 2288 cm^{-1} , which is of comparable intensity; and both would correspond, as nearly as the symmetry change allows, to the prominent combination band at 1750 cm^{-1} in the infra-red spectrum of 1 : 3 : 5-trideuterobenzene. In mono- and 1 : 4-di-deuterobenzene the analogous bands would be obscured by strong fundamental bands; in 1 : 2 : 4 : 5-tetra-deuterobenzene a band appears in the expected position, but can be interpreted in more than one way. However, the evidence that the hexadeuterobenzene combination band, measured at 1692 cm^{-1} in the vapour spectrum and at 1690 cm^{-1} in the spectrum of the liquid substance, involves a B_{2u} hydrogen fundamental frequency seems to us quite strong :

$$\text{C}_6\text{D}_6, \text{ Infra-red, } 1692, 1690 \text{ cm}^{-1} \dots\dots\dots (B_{2u}) 825 + (E_g^+) 867 = 1692 \text{ cm}^{-1}$$

The inferred B_{2u} frequency, 825 cm^{-1} , is in good agreement with calculated values.

These assignments may be checked by reference to the product theorem :

$$\frac{\Pi B_{2u}(1 : 2 : 4 : 5\text{-C}_6\text{H}_4\text{D}_2)}{\Pi B_{2u} E_u^-(\text{C}_6\text{H}_6)} = \frac{1585 \times 1057 \times 812 \times 1439 \times 2280}{1571 \times 825 \times 813 \times 1333 \times 2294} = 1.385 \text{ (harmonic value} = 1.396).$$

Finally the B_{2u} assignments for benzene and hexadeuterobenzene may be checked against each other :

$$\Pi B_{2u}(C_6H_6)/\Pi B_{2u}(C_6D_6) = 1648 \times 1110/1571 \times 825 = 1.412 \text{ (harmonic value} = 1.414).$$

(4) *The A_2' Fundamental Vibrations of 1 : 3 : 5-Trideuterobenzene.*—This symmetry class contains the only inactive frequencies of any partly deuterated benzene which are not individually identical with the determined E_u^+ frequencies of benzene or hexadeuterobenzene. The class contains three frequencies, two of which, 920 and 1230 cm.^{-1} , were determined in Part XVII (this vol., p. 255), whilst one was left undetermined. The three vibrations are collectively related to the single A_{2g} vibration, and the pair of B_{2u} vibrations, of either benzene or hexadeuterobenzene; and the A_2' vibration to which no frequency has as yet been assigned is related in particular to the B_{2u} carbon vibration of benzene and hexadeuterobenzene. If our suggestions are correct concerning the frequencies of these carbon vibrations, and of the active B_{2u} -like carbon vibrations of the partly deuterated benzenes, the A_2' carbon frequency of 1 : 3 : 5-trideuterobenzene must obviously lie close to 1600 cm.^{-1} . This conclusion may be made more definite by reference to the product rule, using the

TABLE IX.

Fundamental Frequencies of Benzene, 1 : 3 : 5-Trideuterobenzene and Hexadeuterobenzene.

Symmetry.		Further description.	C_6H_6 . (D_{6h} .)		1 : 3 : 5- $C_6H_3D_3$. (D_{3h} .)		C_6D_6 . (D_{6h} .)	
D_{6h} .	D_{6h} .							
A_1'	A_{1g}	{ C-stretching	991.6	R	956.2	R	943.2	R
		{ H-stretching	3061.9	R	3052.7	R	2292.6	R
A_2'	B_{1u}	{ C-bending	1010	Forbidden	1003.6	R	963	Forbidden
		{ H-stretching	3060	Forbidden	2281.9	R	2290	Forbidden
A_2''	A_{2g}	{ H-bending	1326	Forbidden	1230	Forbidden	1037	Forbidden
		{ C-stretching	1648	Forbidden	1600	Forbidden	1571	Forbidden
A_2''	B_{2u}	{ H-bending	1110	Forbidden	920	Forbidden	825	Forbidden
		{ Out-of-plane	671	I-r	533	I-r	496.5	I-r
E'	A_{2u}	{ Out-of-plane	703	Forbidden	691	I-r	601	Forbidden
		{ Out-of-plane	985	Forbidden	915	I-r	827	Forbidden
E'	E_g^+	{ C-bending	605.6	R	593.0	R, I-r	577.4	R
		{ H-stretching	3046.8	R	2292	R, I-r	2264.9	R
E''	E_u^-	{ C-stretching	1596 *	R	1573.1	R, I-r	1551.5	R
		{ H-bending	1178.0	R	1101.8	R, I-r	867.3	R
E''	E_g^-	{ C-deformation	1485	I-r	1407	R, I-r	1333	I-r
		{ H-bending	1037	I-r	833.5	R, I-r	813	I-r
E''	E_u^+	{ H-stretching	3080 †	I-r	3084	R, I-r	2294	I-r
		{ Out-of-plane	848.9	R	710.2	R	661.7	R
E''	E_u^+	{ Out-of-plane	405	Forbidden	372.7	R	352	Forbidden
		{ Out-of-plane	970	Forbidden	947	R	793	Forbidden

* Split by resonance : observed frequencies 1584.8 and 1606.4 cm.^{-1} .

† Split by resonance : observed frequencies 3061 and 3098 cm.^{-1} .

A_2' hydrogen frequencies of 1 : 3 : 5-trideuterobenzene, as determined in Part XVII, and the B_{2u} and A_{2g} frequencies of benzene or hexadeuterobenzene, as given in this paper : we have

$$\frac{\Pi B_{2u} A_{2g}(C_6H_6)}{\Pi A_2'(1 : 3 : 5-C_6H_3D_3)} = \frac{1648 \times 1110 \times 1326}{1600 \times 920 \times 1230} = 1.340 \text{ (harmonic value} = 1.345)$$

and

$$\frac{\Pi A_2'(1 : 3 : 5-C_6H_3D_3)}{\Pi B_{2u} A_{2g}(C_6D_6)} = \frac{1600 \times 920 \times 1230}{1571 \times 825 \times 1037} = 1.347 \text{ (harmonic value} = 1.351)$$

Any appreciable departure from the value 1600 cm.^{-1} assigned to the A_2' carbon frequency would obviously spoil one or both of these ratios.

(5) *The A_u Fundamental Vibrations of 1 : 4-Di- and 1 : 2 : 4 : 5-Tetra-deuterobenzene, and the Inactive A_2 Vibrations of Mono- and Penta-deuterobenzene.*—For reasons already given (Parts XIX and XX, this vol., pp. 288, 299) the normal co-ordinates and frequencies of the two A_u vibrations of 1 : 4-dideuterobenzene, and also of two of the A_2 vibrations of monodeuterobenzene, are equal, each to each, to those of the E_u^+ vibrations of benzene. Also the normal co-ordinates and frequencies of the two A_u vibrations of 1 : 2 : 4 : 5-tetradeuterobenzene, and of two of the A_2 vibrations of pentadeuterobenzene, are equal, each to each, to those of the E_u^+ vibration of hexadeuterobenzene. The frequencies of all these vibrations of partly deuterated benzenes are therefore determined by the argument given in Sections B, 3 and B, 4 :

$$\begin{array}{l} A_2(C_6H_5D) \text{ and } A_u(1 : 4-C_6H_4D_2) \dots\dots\dots 405, 970 \text{ cm.}^{-1} \\ A_u(1 : 2 : 4 : 5-C_6H_3D_4) \text{ and } A_2(C_6HD_5) \dots\dots\dots 352, 793 \text{ cm.}^{-1} \end{array}$$

(6) *Summary of Fundamental Frequencies.*—The inactive frequencies determined in this paper are used in order to complete a list (Table IX) of the fundamental frequencies (cm.^{-1}) of the three benzenes which have degenerate vibrations and therefore only 20 distinct fundamental frequencies. It must be emphasised that we still regard the B_{2u} and B_{2u} -like carbon frequencies as lacking desirable confirmation. Comparisons of

fundamental frequencies amongst the benzenes which have no degenerate vibrations, and therefore have 30 different fundamental frequencies, will be made when our work on pentadeuterobenzene is complete. We defer until then, or until we have studied in addition 1:2-di- and 1:2:3:4-tetra-deuterobenzene (if that seems necessary), our discussion of the internal force system of benzene.

Table X records the product ratios to which these frequencies lead. The majority of the values lie below those calculated on the basis of a harmonic force field, the deviations ranging from 1.6% low to 0.4% high.

TABLE X.
Product Ratios of Benzene, 1:3:5-Trideuterobenzene and Hexadeuterobenzene.

D_{6h} class.	C_6H_6/C_6D_6 .		D_{3h} class.	$C_6H_6/C_6H_3D_3$.		$C_6H_3D_3/C_6D_6$.	
	Found.	Calc.		Found.	Calc.	Found.	Calc.
A_{1g}	1.404	1.414	A_1'	1.404	1.414	1.402	1.414
B_{1u}	1.401	1.414					
A_{2g}	1.279	1.286	A_2'	1.340	1.345	1.347	1.351
B_{2u}	1.411	1.414					
A_{2u}	1.351	1.362	A_2''	1.379	1.387	1.365	1.388
B_{2g}	1.393	1.414					
E_g^-	1.970	1.998	E'	1.930	1.960	1.948	1.962
E_u^-	1.908	1.925					
E_g^+	1.283	1.286	E''	1.330	1.345	1.357	1.351
E_u^+	1.407	1.414					

All who have participated in producing this group of papers desire to acknowledge important aid. Stipends have been paid to several of our number by the Department of Scientific and Industrial Research, the Ramsay Memorial Trust, and the Carnegie Trust for the Universities of Scotland. The University of London and the Royal Society have both made considerable contributions to the cost of optical apparatus; and all the heavy water used was purchased for us by Imperial Chemical Industries, Ltd.

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[Received, May 7th, 1945.]