

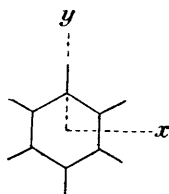
**218.** *Structure of Benzene. Part VIII. Assignment of Vibration Frequencies of Benzene and Hexadeuterobenzene.*

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THE investigation of Part VII into the coincidence argument clears the ground for an unprejudiced attack on the problem of establishing a benzene model from the spectral frequencies of benzene and its isotopic modifications. We are no longer bound to assume that a centre of symmetry is absent, though it will not be overlooked that we have not directly proved that it is present. The most expeditious plan will be to consider the requirements of the plane, regular, hexagonal model, since this is the most symmetrical of all possible models. We shall refer to it as the  $D_{6h}$  model, this being the symbol representing its symmetry classification in the theory of point groups. It is always easy to leave out symmetry, as we shall illustrate in taking account also of the requirements of the Kekulé model (symmetry  $D_{3h}$ ) and of the trigonally puckered model ( $D_{3d}$ ).

(1) *Vibration Forms of Benzene.*—These have been calculated by mathematical methods by E. B. Wilson (*Physical Rev.*, 1934, **45**, 706) and Bosche and Manneback (*Ann. Soc. sci. Bruxelles*, 1934, **54**, 230). Elementary symmetry theory, such as has been given by Placzek (*Leipziger Vorträge*, 1931, p. 71; Marx's "Handbuch der Radiologie," **6**, ii, 209), can however be used to derive in a relatively simple fashion all that is determinate concerning the vibration forms in the absence of assumptions about the force system.

We take Cartesian axes with  $z$  parallel to the six-fold axis of symmetry, and  $x$  and  $y$  disposed as shown in the inset. The model  $D_{6h}$  has many elements of symmetry, but its complete symmetry can be specified by an appropriately chosen set of elements the presence of which implies the presence of all the others. The specifying set of elements may be chosen in various ways depending on the purpose for which it is wanted, and our first selection will consist of the following four elements: (1) the three-fold axis of symmetry in the  $z$ -direction [ $C_3^{(z)}$ ]; (2) the two-fold axis in the  $z$ -direction [ $C_2^{(z)}$ ]; (3) the two-fold axis in the  $y$ -direction [ $C_2^{(y)}$ ]; (4) the centre of symmetry ( $i$ ).



Each of these elements implies a symmetry operation (rotation or inversion), and the reason why all other symmetry elements are included is that their operations can be composed out of two or more of these four operations. Thus the six-fold axis  $C_6^{(z)}$  is covered by  $C_3^{(z)}$  and  $C_2^{(z)}$  since rotation by  $\pi/3$  about  $z$  is equivalent to rotation by  $\pi$  followed by back-rotation by  $2\pi/3$ . The two-fold axis  $C_2^{(z)}$  is given, because rotation by  $\pi$  about  $x$  is the same as successive rotations by  $\pi$  about  $y$  and  $z$ . The four two-fold axes inclined by  $\pm\pi/3$  to  $C_2^{(z)}$  and  $C_2^{(y)}$  are given by associating  $C_3^{(z)}$  with the other specified elements. The plane  $\sigma_h$  perpendicular to  $z$  is covered by the two-fold  $z$ -axis and the centre,  $C_2^{(z)}$  and  $i$ , since rotation by  $\pi$  round an axis, followed by inversion through a centre, is equivalent to reflexion across a plane perpendicular to the axis. The six planes passing through the  $z$ -axis can in the same way be derived by associating two-fold axes with the centre. We may note particularly the operational equations

$$C_2^{(x)} = C_2^{(y)} \cdot C_2^{(z)} \text{ and } \sigma_h = C_2^{(z)} \cdot i$$

The vibrations of the model are either non-degenerate or two-fold degenerate. The non-degenerate vibrations are all symmetric to  $C_3^{(z)}$ , but they may be either symmetric or antisymmetric to  $C_2^{(z)}$ ,  $C_2^{(y)}$ , and  $i$ , and hence they can exhibit  $2^3 = 8$  distinct types of behaviour to the complete set of four symmetry operations. The degenerate vibrations all behave alike to  $C_3^{(z)}$  and  $C_2^{(y)}$ , but they may be either symmetric or antisymmetric to  $C_2^{(z)}$  and  $i$ , and hence they show  $2^2 = 4$  types of behaviour to the operations collectively. Altogether, then, we have twelve symmetry classes. The common result of operation  $C_2^{(y)}$  when applied to a degenerate vibration is most simply represented by so choosing the components of the degenerate pair that one (normal co-ordinate  $\xi$ ) is symmetric and the other (normal co-ordinate  $\eta$ ) is antisymmetric to the operation. The common behaviour of degenerate vibrations to the operation  $C_3^{(z)}$  is best expressed by choosing the components in the complex form representing opposing rotations (normal co-ordinates  $\xi + \sqrt{-1}\eta$  and  $\xi - \sqrt{-1}\eta$ ), which then suffer a simple change of phase (multiplication of the normal co-ordinates by  $e^{\mp 2\pi\sqrt{-1}/3}$ ) on application of the operation.

The specification of the twelve possible symmetry classes is given in cols. 2–5 of Table I; it is easy to see that all possible alternatives are included. The labels in col. 1 have the following significance:

$$\left\{ \begin{array}{l} A = \text{symmetric to } C_6^{(z)} \\ B = \text{,, } C_3^{(z)} \text{ [but not to } C_6^{(z)}] \\ E^+ = \text{degenerate but symmetric to } C_2^{(z)} \\ E^- = \text{,, and not symmetric to } C_2^{(z)} \end{array} \right. \left\{ \begin{array}{l} 1 = \text{symmetric to } C_2^{(y)} \\ 2 = \text{antisymmetric to } C_2^{(y)} \\ g = \text{symmetric to } i \\ u = \text{antisymmetric to } i \end{array} \right.$$

In the succeeding columns symmetry and antisymmetry to the operations listed at the top are denoted by + and – according as the normal co-ordinate is multiplied by +1 or –1. For brevity,  $\varepsilon^{\mp}$  is written for multiplication of the complex co-ordinate by  $e^{\mp 2\pi\sqrt{-1}/3}$ . Behaviour with respect to two additional operations, the two-fold axis  $C_2^{(x)}$  and the plane  $\sigma_h$ , is recorded in cols. 6 and 7; these entries are obtained from those in the earlier columns by multiplication in accordance with the operation equations given previously.

The next step is to obtain the number of vibrations belonging to each symmetry class. First, we place the molecule in a potential hollow of its own symmetry so that those degrees of freedom which would normally appear as translations and rotations become included amongst the vibrations. Next, we divide the molecule into “point-sets,” such that all

TABLE I.

 Symmetry Classification of the Vibrations of the Benzene Model  $D_{6h}$ .

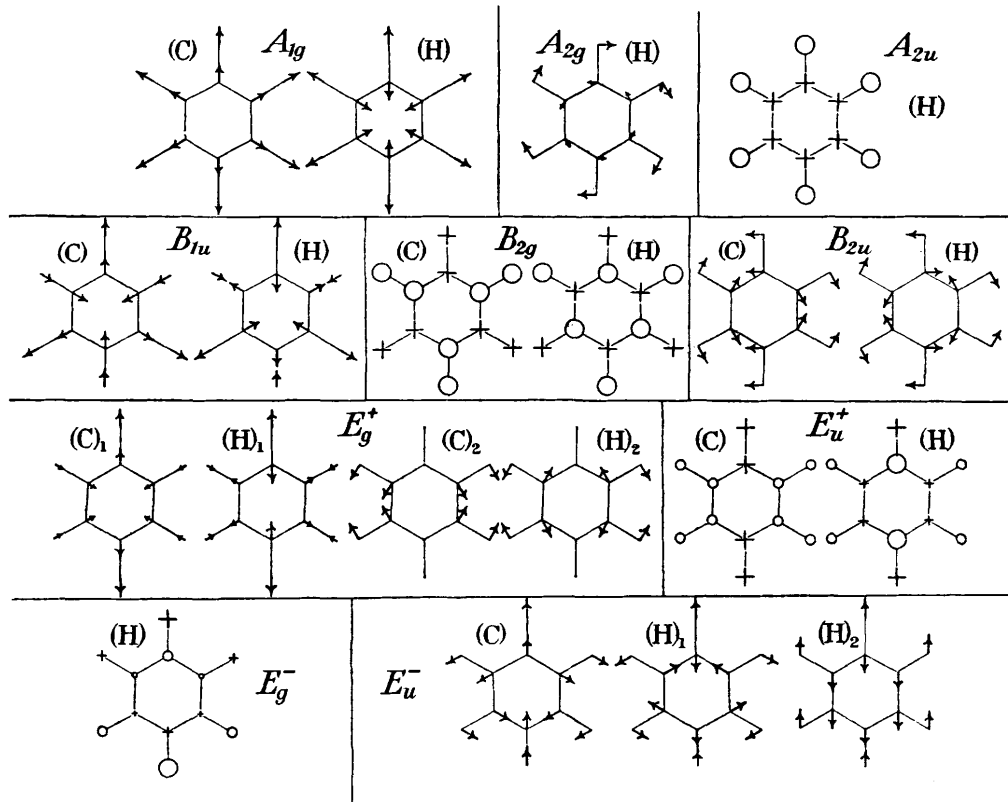
1.	2.	3. 4.				5.		6. 7.		8. 9.		10.	11.	12.	13.
		Specification elements.				Other elements.		Contributions.		T. and R.					
Symmetry class.	$C_3^{(z)}$	$C_2^{(z)}$	$C_2^{(y)}$	$i$	$C_2^{(x)}$	$\sigma_h$	C.	H.	C.	H.	R.	Vibs.	Infra-red.	Raman.	
$A_{1g}$	+	+	+	+	+	+	1	1	—	—	—	2	F	$a_{zz} = a_{yy}, a_{jk} = 0$	
$A_{1u}$	+	+	+	—	—	—	0	0	—	—	—	0	F	F	
$A_{2g}$	+	+	—	+	—	+	1	1	—	—	$R^{(z)}$	1	F	F	
$A_{2u}$	+	+	—	—	—	—	1	1	—	—	$T^{(z)}$	1	$M_x = M_y = 0$	F	
$B_{1g}$	+	—	+	+	—	—	0	0	—	—	—	0	F	F	
$B_{1u}$	+	—	+	—	—	+	1	1	—	—	—	2	F	F	
$B_{2g}$	+	—	—	+	+	—	1	1	—	—	—	2	F	F	
$B_{2u}$	+	—	—	—	+	+	1	1	—	—	—	2	F	F	
$E_g^+$	$\epsilon^{\mp}$	+	$\pm$	+	$\pm$	+	2	2	—	—	—	4	F	$a_{zz} = -a_{yy}, a_{zj} = 0$	
$E_u^+$	$\epsilon^{\mp}$	+	$\pm$	—	$\pm$	—	1	1	—	—	—	2	F	F	
$E_g^-$	$\epsilon^{\mp}$	—	$\pm$	+	$\pm$	—	1	1	—	—	$R^{(xy)}$	1	F	$a_{jj} = a_{xy} = 0$	
$E_u^-$	$\epsilon^{\mp}$	—	$\pm$	—	$\pm$	+	2	2	—	—	$T^{(xy)}$	3	$M_z = 0$	F	
$x \}$	$\epsilon^{\mp}$	{	—	—	—	+	Non-degen. (A, B)		10		(F = forbidden)				
$y \}$		{	—	+	—	—	2-Fold degen. (E)		10						
$z$	+	+	—	—	—	—	Total		20		4 vibs. <span style="margin-left: 100px;">7 vibs.</span>				

 ( $j, k =$  co-ordinate axes  $x, y, z$ .)

the mass-points of a point-set can be generated from one point by the symmetry operations of the model. In benzene the six carbon atoms form one point-set and the six hydrogen atoms the other. It happens that both have the same symmetry; and, since the generating point of each may be taken on the  $y$ -axis and is in the  $xy$ -plane, we may say that in each case the point-set has the proper symmetry  $C_2^{(y)}$  and  $\sigma_h$ . The idea behind this subdivision is that, whilst the displacements of the points of a set are interrelated by symmetry, the connexion between the two sets arises only through the force-system; and, since the number of vibrations must be independent of the forces, that number will be correctly obtained if we suppose the sets to be uncoupled, each contributing its vibrations independently of the other. To each point-set, therefore, we apply the following general rule, the truth of which is most easily seen by considering simple examples: A point-set contributes as many vibrations to a symmetry class as there are independent linear combinations of the spatial co-ordinates ( $x, y, z$ ) which show the behaviour of the class to the operations of the proper symmetry of the set. The symmetry properties of the co-ordinates are given at the bottom of the table; they are obtained by considering how the co-ordinates of a point ( $x, y, z$ ) would be changed by the symmetry operations. We are concerned in particular with behaviour to the operations  $C_2^{(y)}$  and  $\sigma_h$ . As an example we may consider the symmetry class  $A_{1g}$  (table, top line). The carbon point-set will contribute one vibration to this class because there is one co-ordinate, viz.,  $y$ , which transforms in the required way (multiplication by +1 in each case) to  $C_2^{(y)}$  and  $\sigma_h$ . The hydrogen point-set will also contribute one vibration. Restoration of the coupling between the point-sets merely results in the mixing of these vibrations, so that there are still two vibrations of symmetry  $A_{1g}$ , but now both involve the motion of both carbon and hydrogen atoms. Proceeding in this way through the other eleven symmetry classes we obtain the figures in cols. 8 and 9. Allowance being made for the fact that each degenerate vibration has two degrees of freedom, the total number of degrees of freedom comes to 36; but we have now to take away those 6 degrees of freedom which go over into translations and rotations when our imaginary force-field is removed. These degrees of freedom can easily be identified by their symmetry properties. Thus a translation parallel to  $z$  will have the symmetry properties of the  $z$ -co-ordinate and will therefore belong to class  $A_{2u}$ , so that we must deduct it from the two "vibrations" assigned to this class. The identification of the other translations and rotations is indicated in col. 10, where  $T^{(z)}$  and  $T^{(xy)}$  signify translations parallel to  $z$  and in the  $xy$  plane, and  $R^{(z)}$  and  $R^{(xy)}$  denote rotations about the  $z$ -axis and about axes in the  $xy$ -plane. The 20 vibrations proper, corresponding in all to 30 degrees of freedom, are enumerated in col. 11.

The remaining principle which is available to assist the determination of the vibration forms is that they must be "orthogonal," or, in other words, must represent independent degrees of vibrational freedom. The condition for orthogonality is that, for any two vibrations, the sum over all the mass-points in the molecule of the product of the mass of a point and the scalar product of its displacements in the two vibrations must vanish. Since the scalar product contains the cosine of the angle between the displacements, this condition will be satisfied by always taking corresponding displacements at right angles. If we cannot do this, we must at least make the acute angles or parallel displacements (positive cosines) balance the obtuse angles or antiparallel displacements (negative cosines). In

FIG. 1.

Vibration Forms of Benzene ( $D_{6h}$ ) Model.

Notes.—Vectors perpendicular to plane of ring represented +  $\circ$

For each point-set  $\uparrow : \uparrow = + : + = \circ : \circ = 1 : 1/2$ .

particular, when the carbon and hydrogen point-sets each contribute only one vibration to a symmetry class, the two vibrations formed by combination must involve parallel displacements for one point-set and antiparallel for the other, since these are the only types of combination permitted by the orthogonal relation and the symmetry restrictions of the class. In general, the vibration diagrams of all vibrations falling within those symmetry classes which do not contain more than two vibrations are completely fixed by orthogonality and symmetry.

The vibration forms are shown in relation to their symmetry classes in Fig. 1. The hexagonally symmetrical  $A$ -series contains 4 vibrations divided between 3 classes. The first class,  $A_{1g}$ , contains the two totally symmetrical vibrations, which show the normal parallel and antiparallel relation between the displacements of the point-sets. We shall designate these vibrations  $A_{1g}^{(C)}$  and  $A_{1g}^{(H)}$  on the grounds of the following approximate

considerations, which are dependent on the fact that the mass of a hydrogen atom is much smaller than that of a carbon atom. In parallel coupling the carbon atoms will carry the attached hydrogen atoms with them, CH moving practically as a unit; this condition is indicated by the superscript (C). In antiparallel coupling, on the other hand, each CH-group will vibrate internally about a point near its centre of gravity, and consequently most of the motion will be in the hydrogen atoms; this is indicated by the superscript (H). The class  $A_{2g}$  contains one vibration,  $A_{2g}^{(H)}$ , which involves antiparallel coupling of the displacements of the point-sets; parallel coupling gives the complementary member of the class, which is the rotation  $R^{(C)}$ . The class  $A_{2u}$  also contains one vibration,  $A_{2u}^{(H)}$ , with antiparallel coupling, its complement with parallel coupling being the translation  $T^{(C)}$ . The vibrations of the different classes are obviously orthogonal, corresponding vectors being mutually perpendicular.

The trigonally symmetrical  $B$ -series contains 6 vibrations divided in pairs between 3 symmetry classes. There are no translations or rotations belonging to these classes. The vibrations are therefore  $B_{1u}^{(C)}$ ,  $B_{1u}^{(H)}$ ,  $B_{2g}^{(C)}$ ,  $B_{2g}^{(H)}$ ,  $B_{2u}^{(C)}$ ,  $B_{2u}^{(H)}$ , and they are orthogonal within each class on account of the parallel-antiparallel relation, and as between classes because corresponding vectors are always perpendicular. They are orthogonal to the vibrations of the  $A$ -series because either corresponding vibration vectors are perpendicular, or each point-set splits into sub-sets of three mass-points, and the sub-sets contribute equally and oppositely to the sum of scalar products.

The two-fold degenerate  $E$ -series contains 10 vibrations shared between 4 classes. In Fig. 1 we give only a single representation of each degenerate vibration although, of course, each is a mixture, the two independent components of which may be chosen in various ways. In the first class  $E_g^+$  a single point-set contributes two vibrations, and these must be chosen to be orthogonal to each other and to the contributions of the same point-set to all the previous vibrations. One way of doing this is indicated in the diagrams in which the two contributions of each point-set are made into four complete vibrations by parallel and antiparallel coupling. However, these vibration forms are not uniquely determined, and all that can be stated is that the real forms, if not these, must be some orthogonal linear combination of them determined by the force system. In spite of this theoretical indeterminacy, the isotope shifts show that the four vibrations split up, as our diagram illustrates, into two which depend mainly on the movement of CH groups and two depending essentially on the motion of hydrogen atoms, so that we may designate them  $E_g^{+(C)1}$ ,  $E_g^{+(H)1}$ ,  $E_g^{+(C)2}$ ,  $E_g^{+(H)2}$ . The next class  $E_u^+$  contains a pair of vibrations with the normal parallel and antiparallel coupling,  $E_u^{+(C)}$  and  $E_u^{+(H)}$ . The class  $E_g^-$  contains a single vibration,  $E_g^{-(H)}$ , involving antiparallel coupling, its complement with parallel coupling being the "degenerate" rotation,  $R^{(xy)}$ . In the final class  $E_u^-$  each point-set contributes two vibrations, so that four coupled vibrations could be made by parallel and antiparallel combinations, except for the fact that one of the parallel combinations represents the "degenerate" translation,  $T^{(xy)}$ . The remaining three vibrations must be chosen to satisfy the symmetry and orthogonality relations, as has been done in the construction of the diagrams. These forms, however, are not uniquely determined, and the real forms must be combinations of them dependent on the force-system. The vibrations may be designated  $E_u^{-(C)1}$ ,  $E_u^{-(H)1}$ ,  $E_u^{-(H)2}$ , although the isotope shifts show that there is a certain amount of mixing of the characters implied in these symbols.

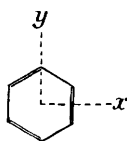
A vibration may appear in the infra-red spectrum if any component of the time-variable part,  $\Delta M$ , of the electric moment does not vanish. This is true for classes  $A_{2u}$  and  $E_u^-$  as is indicated in col. 12 of Table I. Thus four fundamental frequencies are allowed in the infra-red spectrum. For the one of class  $A_{2u}$  the non-vanishing component of the change of moment is  $M_z$ , so that the band is of "parallel" type as is obvious from Fig. 1. For the three vibrations of class  $E_u^-$  the non-vanishing components are  $M_x$  or  $M_y$  or both, so that these bands are of "perpendicular" type, as can also be seen from Fig. 1.

A vibration is allowed in the Raman spectrum when any component of the time-variable part,  $\Delta\alpha$ , of the polarisability does not vanish. This is true for classes  $A_{1g}$ ,  $E_g^+$ , and  $E_g^-$ . Seven fundamental frequencies may thus appear in the Raman spectrum. A Raman line is "depolarised," *i.e.*, its depolarisation factor is 6/7, if the average value, for all directions,

of the change of polarisability vanishes, *i.e.*, if  $\frac{1}{3}(\Delta\alpha_{xx} + \Delta\alpha_{yy} + \Delta\alpha_{zz}) = 0$ ; otherwise the line is "polarised," *i.e.*, its depolarisation factor may lie anywhere between 0 and 6/7. Only totally symmetrical vibrations give "polarised" lines. Thus the two vibrations of class  $A_{1g}$  should give "polarised" lines, whilst the four of class  $E_g^+$  and the one of class  $E_g^-$  should give "depolarised" lines. These statements, and the entries in col. 13 of Table I, are fully justified in Placzek's theory (*loc. cit.*).

We may consider the requirements of the Kekulé model as an example of the effects to be expected from loss of symmetry. The relation of the symmetry of this model to that of the  $D_{6h}$  model is most simply expressed by first choosing the elements of symmetry which specify the latter in a different way from that adopted above. Using operational relations similar to those given earlier, we can replace  $C_2^{(y)}$  by  $C_2^{(z)}$  and  $i$  by  $\sigma_h$  in the specification of  $D_{6h}$ : this new specification is such that, by merely leaving out the element  $C_2^{(z)}$ , we derive a complete specification of the Kekulé symmetry  $D_{3h}$ :

$$\begin{array}{l} D_{6h} \dots\dots\dots C_3^{(z)} \quad C_2^{(z)} \quad C_2^{(x)} \quad \sigma_h \\ D_{3h} \dots\dots\dots C_3^{(z)} \quad - \quad C_2^{(x)} \quad \sigma_h \end{array}$$



Owing to the loss of  $C_2^{(z)}$ , the number of symmetry classes of the vibrations of  $D_{3h}$  will be only half the number obtained for those of  $D_{6h}$ , since a pair of classes which were distinguished from each other only by symmetry or anti-symmetry with respect to  $C_2^{(z)}$  will now become a single class. The highest symmetry axis is  $C_3^{(z)}$ , and hence vibrations are either symmetric to this or are degenerate. The labelling conventions are:

$$\begin{cases} A = \text{symmetric to } C_3^{(z)} \\ E = \text{degenerate} \end{cases} \quad \begin{cases} 1 = \text{symmetric to } C_2^{(x)} \\ 2 = \text{antisymmetric to } C_2^{(x)} \end{cases} \quad \begin{cases} ' = \text{symmetric to } \sigma_h \\ '' = \text{antisymmetric to } \sigma_h \end{cases}$$

On examining Table I it is seen that, with respect to the specifying elements of  $D_{3h}$ , no distinction is to be drawn between the properties of classes  $A_{1g}$  and  $B_{2u}$ ; these were distinguished in relation to  $D_{6h}$  inasmuch as one was symmetric and the other antisymmetric to  $C_2^{(z)}$ ; but now  $C_2^{(z)}$  has disappeared [and with it  $C_2^{(y)}$  and  $i$ ]. Therefore the four vibrations of the two old classes  $A_{1g}$  and  $B_{2u}$  will go into a single new class,  $A_1'$ ; they are, in fact the totally symmetrical vibrations of the model  $D_{3h}$ . Similarly, the other vibration classes belonging to the model  $D_{6h}$  can be grouped into pairs the separate members of which are distinguished only by symmetry or antisymmetry with respect to  $C_2^{(z)}$ , so that when this element of symmetry is removed each of the pairs of classes gives a single class corresponding to the model  $D_{3h}$ . The scheme according to which the old symmetry classes associate themselves to form the new is given in Table II, together with the numbers of vibrations contained in each of the new symmetry classes.

The selection rules governing the appearance of these vibrations in the infra-red and Raman spectra are determined by the following considerations. Any component of the change of dipole moment or of the change of polarisability which vanished in both of two combining symmetry classes must have done so because of symmetry elements other than  $C_2^{(z)}$ ; hence that component will vanish in the combination class. Any component which was non-vanishing in one only of the two combining classes must require symmetry or antisymmetry with respect to  $C_2^{(z)}$  in order to vanish; hence that component will not vanish in the combination class. Any component which was non-vanishing in both the combining classes will obviously be non-vanishing in the combination class. It follows that if the vibrations of both of two combining classes were forbidden in the infra-red or in the Raman spectrum, the vibrations of the combination class will be forbidden in the infra-red or in the Raman spectrum as the case may be; whereas if the vibrations of either of two combining classes were allowed in the infra-red or the Raman spectrum, *all* the vibrations of the combination class will be allowed in the infra-red or in the Raman spectrum as the case may be. It is easy to see which infra-red bands will be "parallel" and which "perpendicular." As before, the totally symmetrical vibrations (class  $A_1'$ ) will give "polarised" Raman lines, whilst all the other Raman-active fundamentals will give "depolarised" lines. These conclusions are summarised in Table II. There should be 8 fundamentals in the infra-red,

and 14 in the Raman spectrum (4 polarised); 7 fundamental frequencies should be common (there is no centre of symmetry now) to the infra-red and Raman spectra.

TABLE II.

Symmetry Classification of the Vibrations of the Benzene Model  $D_{3h}$ .

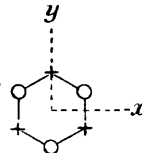
Symmetry class.	Combining classes.	No. of vibrations.	No. allowed.	
			Infra-red.	Raman.
$A_{1'}$	$A_{1g}, B_{2u}$	4	F	4 (P)
$A_{1''}$	$A_{1u}, B_{2g}$	2	F	F
$A_{2'}$	$A_{2g}, B_{1u}$	3	F	F
$A_{2''}$	$A_{2u}, B_{1g}$	1	1 (//)	F
$E'$	$E_g^+, E_u^-$	7	7 ( $\perp^r$ )	7 (D)
$E''$	$E_g^-, E_u^+$	3	F	3 (D)
Total		20	8	14

(F = forbidden; P = polarised; D = depolarised; // and  $\perp^r$  = parallel or perpendicular bands.)

In order to deduce the requirements of the trigonally puckered model,  $D_{3d}$ , we specify its symmetry, and the relation of this to the symmetry of the  $D_{6h}$  model, in the following way :

$$\begin{matrix} D_{6h} & . & . & . & . & . & C_3^{(z)} & C_2^{(z)} & C_2^{(x)} & i \\ D_{3d} & . & . & . & . & . & C_3^{(z)} & - & C_2^{(x)} & i \end{matrix}$$

Examination of Table I shows that we again obtain six symmetry classes, each compounded from two of the  $D_{6h}$  classes as noted in Table III. The labelling conventions are as follows :

$$\begin{cases} A = \text{symmetric to } C_3^{(z)} \\ E = \text{degenerate} \end{cases} \begin{cases} \{_1 = \text{symmetric to } C_2^{(z)} \\ \{_2 = \text{antisymmetric to } C_2^{(x)} \end{cases} \begin{cases} \{_g = \text{symmetric to } i \\ \{_u = \text{antisymmetric to } i \end{cases}$$


As Table III shows, 8 fundamental frequencies should appear in the infra-red spectrum; these include the 4 infra-red fundamentals of the  $D_{6h}$  model, and 4 more which in that model would be inactive in both the infra-red and the Raman spectrum. There should be 9 fundamentals in the Raman spectrum (4 polarised); and these comprise the 7 Raman fundamentals of the  $D_{6h}$  model together with 2 more which in the  $D_{6h}$  model would likewise be inactive in both spectra. The  $D_{3d}$  model has a centre of symmetry, and hence there can be no frequency common to the infra-red and the Raman spectrum.

TABLE III.

Symmetry Classification of the Vibrations of the Benzene Model,  $D_{3d}$ .

Symmetry class.	Combining classes.	No. of vibrations.	No. allowed.	
			Infra-red.	Raman.
$A_{1g}$	$A_{1g}, B_{2u}$	4	F	4 (P)
$A_{1u}$	$A_{1u}, B_{2g}$	2	F	F
$A_{2g}$	$A_{2g}, B_{1u}$	1	F	F
$A_{2u}$	$A_{2u}, B_{1g}$	3	3 (//)	F
$E_g$	$E_g^+, E_g^-$	5	F	5 (D)
$E_u$	$E_u^+, E_u^-$	5	5 ( $\perp^r$ )	F
Total		20	8	9

(For key, see footnote to Table II.)

(2) *Isotopic Frequency Shifts : Teller's Product Theorem.*—As was mentioned in Part I, the problem of proving that any observed fundamental frequency belongs to a particular vibration form of a particular model is greatly facilitated by the fact that it has recently become possible to calculate numerical relations between the frequencies which the normal vibrations of any assumed model should exhibit in molecules which differ only isotopically

with respect to one or more of their atoms. The basis for this calculation is a theorem which was discovered by Dr. E. Teller and communicated by him to us in 1934; it was cited and applied by us in the preliminary notes on which these papers are based (*Nature*, 1935, **135**, 1033; **136**, 680). A less general form of the same theorem was discovered independently by Redlich (*Z. physikal. Chem.*, 1935, **28**, B, 371). It is assumed that the vibrations are harmonic, and that the force-system remains unchanged by isotopic substitution. On the other hand, the theory assumes no knowledge of the force-system, nor indeed of any factor except the geometry of the model and the masses involved.

The theorem relates to the product of the frequencies of vibrations of the same symmetry class, and shows how to calculate the ratio of such products for two isotopically related molecules. The ratio is expressed as a function of the masses of the atoms and moments of inertia of the molecules :

$$\tau = \frac{\frac{\nu_N}{\prod_{\nu'} \nu_{\nu'}}}{\frac{\nu_N}{\prod_{\nu'} \nu_{\nu'}}} = \sqrt{\frac{\prod_{\nu'} \left(\frac{m''}{m'}\right)^{n_N}}{\left(\frac{M''}{M'}\right)^{t_N} \cdot \prod_{j'} \left(\frac{I_j''}{I_j'}\right)^{r_N}}}$$

In this formula the dashes distinguish the isotopically related molecules. On the left-hand side, each product of the frequencies  $\nu$  is taken over all the  $\nu_N$  frequencies of the symmetry class  $N$ , degenerate frequencies being counted only once. On the right-hand side, in the numerator we have the product, taken over the total number,  $p$ , of point-sets which contribute to the vibrations, of the ratio of the masses,  $m$ , of the generating points of each point-set, each ratio being raised to a power  $n_N$ , equal to the number of vibrations contributed by the point-set to the symmetry class. The contributions must be calculated, as has already been explained, in relation to a conception of vibration which is enlarged to include the translations and rotations as "null-vibrations," that is, vibrations whose frequencies vanish in the absence of an external field. A degenerate frequency is counted as a single contribution. The denominator on the right-hand side represents the allowance that must be made for the circumstance that the symmetry class  $N$  may contain null-vibrations. For each translation so included, the formula provides a factor which is the ratio of the molecular masses  $M$ ;  $t_N$  is the number of translations in the symmetry class  $N$ . For each included rotation there is a factor consisting of the ratio of the molecular moments of inertia,  $I_j$ , belonging to the appropriate axis of inertia  $j$ ;  $r_N$  is the number of rotations in the symmetry class  $N$ . "Degenerate" null-vibrations are counted only once in reckoning  $t_N$  and  $r_N$ .

In our case only the hydrogen point-sets suffer a change of mass as between the isotopically related molecules, and hence the numerator  $\prod_{\nu'}^p$  is either 2 or 4 according as  $n_N$  (Table I, col. 9) is 1 or 2. Where there is a translational null-frequency (Table I, col. 10) the denominator under the square root will contain the factor 14/13. Where there is a rotational null-frequency the denominator will have the factor 1.21. This last factor is calculated by assuming the  $D_{6h}$  model and the following dimensions: distance between adjacent carbon nuclei, 1.39 A.; distance between a carbon nucleus and the nearest hydrogen nucleus, 1.08 A. As the model is flat, the ratio  $I_j''/I_j'$  is the same for all axes  $j$ . Thus calculated, the ratios,  $\tau$ , for benzene (') and hexadeuterobenzene (") of the products of the frequencies falling within the different symmetry classes are as shown in Table IV. In order to obtain the ratios for the Kekulé model, it is necessary only to multiply these ratios together in pairs according to the combination scheme of Table II. A similar method can be applied to other models of lower symmetry than  $D_{6h}$ , although in general it will be necessary first to make any changes in the tabulated values which may be required by alterations in the moments of inertia.

TABLE IV.

Product Ratios for the Symmetry Classes of  $D_{6h}$ .

Class.	$A_{1g}$	$A_{2g}$	$A_{2u}$	$B_{1u}$	$B_{2g}$	$B_{2u}$	$E_g^+$	$E_u^+$	$E_g^-$	$E_u^-$
No. of vibns. ....	2	1	1	2	2	2	4	2	1	3
Ratio ( $\tau$ ) .....	1.41	1.29	1.36	1.41	1.41	1.41	2.00	1.41	1.29	1.93



As Dr. Teller pointed out to us originally, the observed ratios are expected to be slightly smaller than the calculated values on account of anharmonicity. This has the effect of reducing the vibration frequency, and the reduction should be greater for the protium than for the deuterium compound, since the vibrations of the former have on the average the greater amplitude.

(3) *Assignment of Fundamental Frequencies.*—Our plan from now onward will be to make the  $D_{6h}$  model our primary working hypothesis, since the evidence about the coincidences did not exclude it, and indeed rather tended in its favour.

The first fundamental frequency of benzene to be correctly identified was the Raman frequency,  $992\text{ cm.}^{-1}$ , which Placzek recognised (*Liepziger Vorträge*, 1931, p. 100) by its intensity to be the totally symmetrical "breathing" frequency of the carbon ring [ $A_{1g}^{(C)}$ ]. This assignment is confirmed by the fact that the line is highly polarised, and it has been clear since 1933 that the only other Raman line which is both strong and polarised, that at  $3062\text{ cm.}^{-1}$ , must represent the totally symmetrical hydrogen vibration [ $A_{1g}^{(H)}$ ]: it is known empirically that vibrations which are dependent essentially on the stretching of carbon-hydrogen bonds always have frequencies in this neighbourhood. These assignments are confirmed below by the isotope shifts. A tentative and partly successful attempt to allocate frequencies to all the eleven vibrations which, if the  $D_{6h}$  model is correct, should be active in either the infra-red or the Raman spectrum was made by E. B. Wilson, whose suggestions were based on the endeavour to fit frequencies to an assumed force system of simple type which had previously been adjusted to suit the two  $A_{1g}$  frequencies (*Physical Rev.*, 1934, **46**, 146). The identification which we shall try to justify agrees with Wilson's in five of the nine extra frequencies he assigned, but differs with respect to the other four. This new assignment, together with its basis in Teller's product theorem, was first advanced by us in the preliminary notes already mentioned; it has since been adopted by Kohlrausch (*Naturwiss.*, 1935, **23**, 624; *Z. physikal. Chem.*, 1935, **30**, B, 305; *Physikal. Z.*, 1936, **37**, 58) and by Redlich and Stricks (*J. Chem. Physics*, 1935, **3**, 834; *Monatsh.*, 1936, **67**, 213).

We may first consider the Raman frequencies. Our provisional model requires seven fundamental Raman lines, two polarised and five depolarised. In Raman spectra fundamental frequencies are generally so much stronger than overtones and combination tones that they can at once be recognised. In the Raman spectrum of hexadeuterobenzene there are seven lines of outstanding intensity; all others are very weak by comparison; also two of the seven lines are polarised and the remainder depolarised. In benzene the position is more complicated in that one of the seven frequencies is double ( $1585, 1606\text{ cm.}^{-1}$ ), making altogether eight prominent lines. However, E. B. Wilson suggested (*loc. cit.*) that this doubling is due to "resonance splitting." Fermi first showed in the example of carbon dioxide that an accidental agreement of frequency between a fundamental and a combination tone (not between two fundamentals, which by definition are in independent degrees of freedom) could lead to a mutual disturbance of the vibrations with the result that they are replaced by others, one of greater and one of less frequency than the original coincident frequency. This type of interaction is subject to certain restrictions of symmetry. Wilson's suggestion was that the observed doubling of the benzene line is due to resonance between a fundamental of frequency close to the mean value  $1596\text{ cm.}^{-1}$  and a combination tone (calculated frequency  $1598\text{ cm.}^{-1}$ ) from the fundamentals  $992\text{ cm.}^{-1}$  and  $606\text{ cm.}^{-1}$ . This is an interaction which on our assignment would be permitted by symmetry, and the effect of it would be that, instead of a weak line nearly coinciding with a strong line, there would be two lines of intermediate intensity, one having a greater and the other a smaller frequency than the original common frequency. The idea receives confirmation in the circumstance that the corresponding frequency in hexadeuterobenzene,  $1559\text{ cm.}^{-1}$ , is single; this is as it should be, since now there is no coincidence with the combination tone from the corresponding fundamental frequencies,  $945$  and  $577\text{ cm.}^{-1}$  (calculated frequency  $1522\text{ cm.}^{-1}$ ; the combination tone itself is too weak to be observed). This point accepted, the application of the product rule to the isotope shifts indicates the assignment unequivocally. There is no difficulty about correlating the lines of the two spectra: for the two polarised lines the correlation is clear from the polarisation and intensity, and for all the

others it is fixed by the fact that the isotope shifts must be in the right direction and cannot exceed the factor  $\sqrt{2}$ .

The model requires four infra-red fundamentals. Benzene vapour gives four outstanding infra-red bands at 671, 1037, 1485, and 3080  $\text{cm}^{-1}$  respectively, together with a band of intermediate intensity at 1808  $\text{cm}^{-1}$  and a somewhat weaker band at 1965  $\text{cm}^{-1}$  which we have also considered as possible fundamentals. The frequency 3080  $\text{cm}^{-1}$  really represents two bands, but we shall explain this later. Hexadeuterobenzene vapour gives three outstanding bands at 503, 813, and 2294  $\text{cm}^{-1}$ , two bands of intermediate intensity at 1333 and 1450  $\text{cm}^{-1}$ , and two weaker bands at 1616 and 1154  $\text{cm}^{-1}$ , all of which we have taken into account in the selection of fundamentals. It is immediately obvious that for both compounds the extreme frequencies correspond and are fundamentals: in each case the high frequency is shown by its magnitude to be the C—H stretching fundamental which must be present (Part VII), whilst the low frequency must be a fundamental since it is too low for a summation tone and too intense for a difference tone.\* These frequencies can be assigned, and the other fundamentals chosen and assigned in a unique manner, by an application of the product theorem to the isotope shifts, together with two supplementary considerations. The first of these is that the collective intensity in a symmetry class should agree for the isotopically related molecules after allowance has been made for the greater amplitude of the vibrations of the lighter molecule. The second is that the high frequency, a C—H stretching vibration, cannot be the single frequency of class  $A_{2u}$ , which is a C—H bending vibration, in spite of the fact that the former happens to have the right frequency shift: it is known empirically that C—H bending frequencies are much smaller. These considerations resolve the ambiguities of an unsupported application of the product rule, and it is satisfactory that the one legitimate choice of fundamentals selects the strongest bands. We attribute the duplexity of the benzene band at 3080  $\text{cm}^{-1}$  to resonance between a fundamental in this neighbourhood and the allowed combination tone from the Raman fundamental frequency 1596  $\text{cm}^{-1}$  and the infra-red fundamental 1485  $\text{cm}^{-1}$  (calculated frequency 3081  $\text{cm}^{-1}$ ); this is an interaction which according to our assignment would be permitted by symmetry. The corresponding hexadeuterobenzene band, at 2294  $\text{cm}^{-1}$ , is single, as this explanation would require, since the calculated frequency of the corresponding combination tone is 2892  $\text{cm}^{-1}$ .

The assignment of the eleven fundamental frequencies which are active in either the infra-red or the Raman spectrum, together with the values of the Teller product-ratios are given in Table V. It will be noted that the observed product-ratios are always a little less than the corresponding calculated values, in agreement with the effect to be expected from the anharmonicity of the vibrations.

TABLE V.  
*Assignment of Raman and Infra-red Fundamental Frequencies.*

Activity.	Symmetry class.	Frequencies ( $\text{cm}^{-1}$ ).		Product-ratios.	
		$\text{C}_6\text{H}_6$ .	$\text{C}_6\text{D}_6$ .	Found.	Calc.
Raman	$A_{1g}$ { (C) (H)	992 3062	945 2292	1.40	1.41
	$E_g^+$ { (C) (H)	606, 1596 1178, 3047	577, 1559 867, 2264		
	$E_g^-$ (H)	849	661	1.28	1.29
Infra-red	$A_{2u}$ (H)	671	503	1.34	1.36
	$E_u^-$ { (C) (H)	1485 1037, 3080	1333 813, 2294	1.91	1.93

The two  $A_{1g}$  vibrations, each of which represents a combination of symmetrical contractions and expansions of the carbon and hydrogen rings, split up remarkably completely into

\* A difference tone of frequency  $\nu_A - \nu_B$  implies the presence before absorption of thermally excited vibrations of frequency  $\nu_B$ . The proportion of molecules with these vibrations depends on the Boltzmann factor  $\exp. (-h\nu_B/kT)$ , which is small for the usual values of  $T$  and  $\nu_B$ .

one vibration involving the pulsation of undeformed CH groups and one vibration in which nearly all the motion is in the hydrogen atoms, each atom-pair, CH, vibrating about its centre of gravity. If this were an absolutely accurate description of the motions, the proportional frequency shift,  $(\nu_{C_6H_6}/\nu_{C_6D_6}) - 1$ , would be 4% for the carbon vibration and 36% for the hydrogen vibration, whereas the actual shifts are 5% and 34% respectively. These are the frequencies which give the very strong and highly polarised Raman lines, and reference to the tables in Part III will show that the intensities and polarisations of corresponding lines for benzene and hexadeuterobenzene agree to within the accuracy of measurement.

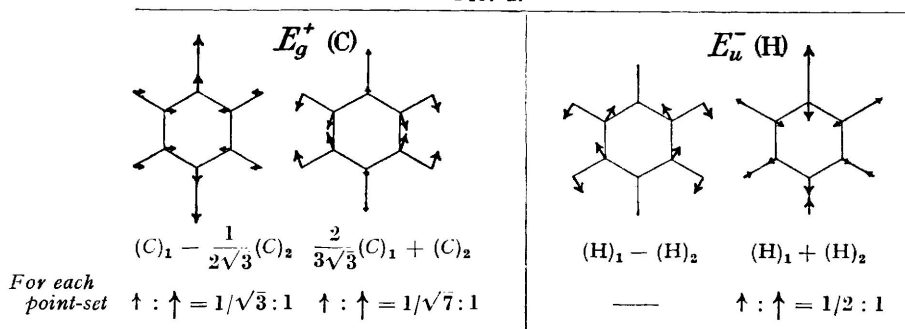
The four  $E_g^+$  vibrations likewise split up rather accurately, as is evident from the isotope shifts, into two which depend on the relative motion of undeformed CH groups ("carbon vibrations"), and two which depend on the motion of hydrogen atoms relatively to the carbon atoms to which they are attached ("hydrogen vibrations"). Furthermore, the carbon vibrations divide themselves fairly well into one which involves the stretching of C—C bonds ("carbon-stretching vibration") and one which involves the bending of  $\widehat{C\cdot C\cdot C}$  valency angles ("carbon-bending vibration"). This follows because if one assumes as an approximation that the restoring force in the  $A_{1g}^{(C)}$  vibration arises solely from the alteration of length of the bonds between adjacent carbon atoms, derives the force-constant, and then calculates the frequency of a vibration of symmetry  $E_g^+$  under the assumption that this carbon-stretching force-constant is the only one involved, the value obtained is close to one of the two which are observed. With the simplifying assumption indicated, the carbon-stretching  $E_g^+$  vibration should have a frequency  $\sqrt{5/2}$  times that of the totally symmetrical carbon vibration, *e.g.*, 1582  $\text{cm.}^{-1}$  for benzene (found: 1596  $\text{cm.}^{-1}$ ). Evidently the higher carbon frequency is a nearly pure stretching frequency, so that the lower, which has to be orthogonal, must be mainly a bending frequency. Again, the two hydrogen vibrations can be characterised one as depending on the stretching of C—H bonds (hydrogen-stretching vibration), and one as depending on the bending of  $\widehat{C\cdot C\cdot H}$  valency angles (hydrogen-bending vibration). This is evident from the fact that the higher of these frequencies is very close to the  $A_{1g}^{(H)}$  frequency which cannot involve hydrogen bending for reasons of symmetry. The higher hydrogen frequency is therefore essentially a stretching frequency, and the lower must be mainly a bending vibration. Now the  $E_g^+$  vibration forms given in Fig. 1 have to be made into combinations, but the foregoing approximate considerations based on the observed frequencies show that the real vibration forms cannot be very different from those given, *i.e.*, there cannot be a great deal of mixing. The two hydrogen vibrations are separated in the Fig. into a stretching and a bending vibration, and the two carbon vibrations into one which is mainly of the stretching type and one mainly of the bending type. These last vibrations can, indeed, be combined in an orthogonal manner to make, *e.g.*, a perfectly pure bending vibration and a purer stretching vibration:  $(C)_1 - (1/2\sqrt{3})(C)_2$  (bending) and  $(2/3\sqrt{3})(C)_1 + (C)_2$  (stretching); the result of this, however, is only a slight modification of the smaller vibration vectors (Fig. 2), and we do not know that it represents reality any more accurately than did the original vibration forms. As an approximation, therefore, we may identify the frequencies with the vibration forms of Fig. 1 in the following way:

	$E_g^{+(C)1}$ (C-bending).	$E_g^{+(H)1}$ (H-stretching).	$E_g^{+(C)2}$ (C-stretching).	$E_g^{+(H)2}$ (H-bending).
$\nu$ ( $C_6H_6$ ) .....	606	3047	1596	1178
$\nu$ ( $C_6D_6$ ) .....	577	2264	1559	867

The vibration  $E_g^{-(H)}$  presents an unsolved problem in the matter of intensities. As there is only one vibration in the symmetry class, the intensities in the isotopically related spectra should correspond; *i.e.*, the benzene intensity should be slightly greater. Actually, the integrated intensities are: benzene 0.9, hexadeuterobenzene 1.4; and, in spite of the fact that no correction has been applied for the variation of plate-sensitivity with wave-length, the difference is probably beyond the experimental error. A possible way of escape suggests itself as a consequence of the consideration that in the Raman measurements we have

experimented with liquids. Theoretically it is necessary only that the collective intensities within a symmetry class should bear a simple relation as between the isotopic molecules. Now, the second member of the symmetry class  $E_g^-$  is theoretically a rotation, but in the liquid state this would go over into a rotatory vibration which would not normally be observed but might yet put right the collective intensities. The clearing up of this point is at present our strongest motive for investigating the Raman spectra of gaseous benzene and hexadeuterobenzene.

FIG. 2.

Alternative  $E_g^+$  and  $E_u^-$  Vibration Forms.

The vibration  $A_{2u}^{(H)}$ , which gives rise to the unique "parallel" bands in the infra-red spectra, is also worth further investigation. As there is only a single vibration in the symmetry class, we should expect the bands to have the same form except for the difference of breadth depending on the different moments of inertia; and as far as we can judge this is so. On the other hand, we should have expected a narrower and stronger  $Q$ -branch than is found, and can only assume that our slit-breadth has caused a certain averaging of those intensities which vary strongly within a small range of wave-length. The  $A_{2u}$  band should be the simplest of all the infra-red bands, and it would be desirable to investigate it with a much larger resolving power.

The relation between the  $E_g^-$  and  $A_{2u}$  frequencies illustrates the inadequacy of the "valence-force" approximation in its application to benzene. The simplest valence-force system is that which was used by Wilson for his assignment. Six force constants are assumed, three for the carbon bonds and three for the hydrogen bonds; in each case one constant is for stretching, one for bending in the plane of the ring, and one for bending in a direction normal to the ring. Each of the vibrations mentioned is the only one in its symmetry class. In the vibration  $E_g^-$ , the plane of the hydrogen ring rocks with respect to the carbon ring about a common diameter, whilst in the vibration  $A_{2u}$  the hydrogen ring moves co-axially with respect to the carbon ring. Each vibration therefore involves one and the same force-constant, *viz.*, that applying to the bending of hydrogen bonds perpendicularly to the carbon ring, and hence the two frequencies should differ simply on account of the different reduced masses. The reciprocal of the reduced mass appropriate to the  $E_g^-$  vibration is  $1/m_H + (r_H^2/r_C^2)(1/m_C)$ , where the  $m$ 's are the masses and the  $r$ 's the ring-radii of the two kinds of atoms. The corresponding factor for the  $A_{2u}$  vibration is  $1/m_H + 1/m_C$ . The frequencies should be in the ratio of the square roots of these factors, and for benzene the ratio should be 1.081; the observed ratio is  $849/661 = 1.266$ . The discrepancy amounts to more than 100  $\text{cm}^{-1}$  when we try to calculate one frequency from the other by using the theoretical ratio. Much greater discrepancies can be found in the other symmetry classes for which simultaneous equations have to be solved in calculation from the force-system, and therefore considerable circumspection is necessary in relation to the published calculations of Kohlrausch and others based on this force system. The only force "constants" which seem to behave in a reasonably constant manner are the two stretching constants.

We have still to refer to the three vibrations of class  $E_u^-$  which give "perpendicular"

bands in the infra-red spectrum. Two of the bands show an increased intensity and one a rather strongly decreased intensity in hexadeuterobenzene as compared with benzene. The high frequency,  $E_u^{-(\text{H})}$ , represents an almost pure hydrogen stretching vibration, as is evident from the proximity of the figures to those of the totally symmetrical frequency,  $A_{1g}^{(\text{H})}$ . The other two frequencies divide themselves roughly into a carbon vibration,  $E_u^{-(\text{C})}$ , and a hydrogen bending vibration,  $E_u^{-(\text{H})}$ , but, as is obvious from the isotope shifts, there is some mixing of these characters. The vibration forms of Fig. 1 have to be made into linear combinations, and we can give a definitely improved representation by combining  $E_u^{-(\text{H})}$  with  $E_u^{-(\text{C})}$  as orthogonal sum and difference. One of the vibrations thus obtained represents pure bending and the other pure stretching of the hydrogen bonds (Fig. 2); the bending vibration, however, has still to undergo a certain amount of admixture with the carbon vibration  $E_u^{-(\text{C})}$ .

In order to complete this consideration of the eleven "active" fundamental frequencies we refer to Part VI, where three vibrations,  $A_{2u}^{(\text{H})}$ ,  $E_g^{-(\text{H})}$ , and  $E_g^{+(\text{C})}$ , are identified as 2-quantum progressions in the resonance spectrum, and to Part VII, where it is shown that owing to molecular deformation in the liquid state the Raman fundamentals appear in the infra-red spectrum whilst the infra-red fundamentals appear (weakly) in the Raman spectrum.

We cannot go far with the identification of the nine inactive frequencies in advance of observations on the partly deuterated benzenes, but a few tentative assignments can be made. One source of inactive frequencies consists in the "forbidden" bands of the liquid infra-red spectra. There are two such bands that can be correlated in the benzene and hexadeuterobenzene spectra, but are not any of the known Raman fundamentals. One at least of these is most unlikely to be a combination tone because of its large intensity and low frequency (773  $\text{cm}^{-1}$  in benzene and 754  $\text{cm}^{-1}$  in hexadeuterobenzene); as regards the other (1298  $\text{cm}^{-1}$  in benzene and 979  $\text{cm}^{-1}$  in hexadeuterobenzene) it is impossible to be certain on this point. However, both frequencies occur (weakly) in the Raman spectra of both benzene and hexadeuterobenzene. The electronic spectra constitute a second possible source of inactive frequencies. We may first note the low vibration frequency of the fluorescence spectra (161  $\text{cm}^{-1}$  in benzene, 141  $\text{cm}^{-1}$  in hexadeuterobenzene). Its strength suggests a vibration having the common symmetry of the upper and lower states, but if this is true we cannot understand why no signs of the frequency can be found in the resonance emission spectra. The frequency is really much lower than any fundamentals are expected to be, and altogether it does not seem clear that it should be regarded as a fundamental. In the resonance spectra there are three unassigned possible fundamentals for which the isotope shift is known, and one which could be found only in the benzene spectrum. The complete list of candidates for the status of fundamentals which are forbidden in both the Raman and the infra-red spectrum is given in Table VI.

TABLE VI.

	Forbidden infra-red frequencies.						Electronic spectra.				
	1			2			3	4 5 6 7			
	I.-red.	Raman.	Mean.	I.-red.	Raman.	Mean.		Resonance emission.			
$\text{C}_6\text{H}_6$	773	781	777	1298	1285	1291	141	395	765	888	1219
$\text{C}_6\text{D}_6$	754	750	752	979	976	978	161	—	707	791	961
Assignment	$B_{1u}^{(\text{C})}$			—			—	—	—	—	$A_{2g}^{(\text{H})}$

The nine inactive vibrations are  $A_{2g}^{(\text{H})}$ ,  $B_{1u}^{(\text{C})}$ ,  $B_{1u}^{(\text{H})}$ ,  $B_{2g}^{(\text{C})}$ ,  $B_{2g}^{(\text{H})}$ ,  $B_{2u}^{(\text{C})}$ ,  $B_{2u}^{(\text{H})}$ ,  $E_u^{+(\text{C})}$ ,  $E_u^{+(\text{H})}$ . It is necessary to ascertain as far as possible the order of magnitude of their frequencies. If we assume as an approximation that the restoring force in the unknown vibration  $A_{2g}^{(\text{H})}$ , and likewise in the known Raman vibration  $E_g^{+(\text{H})}$  (1178  $\text{cm}^{-1}$  in benzene), arises solely from the bending of the hydrogen bonds, the unknown and known frequencies should differ only on account of the reduced masses; in fact, the frequencies should stand in

the ratio of the square roots of the reciprocals of the reduced masses. In the same approximate way we can connect the unknown vibration  $B_{1u}^{(C)}$  with the Raman vibration  $E_g^{+(C)}$  (606  $\text{cm}^{-1}$  in benzene) on the assumption that in each case the restoring force arises solely from the bending of the carbon-carbon bonds. The vibration  $B_{1u}^{(H)}$  is a hydrogen-stretching vibration, which we can similarly link with the known Raman vibration  $A_{1g}^{(H)}$ . The vibrations  $B_{2g}^{(C)}$  and  $E_u^{+(C)}$  are expected to be low, but cannot be estimated from any known frequency. The frequencies  $B_{2g}^{(H)}$  and  $E_u^{+(H)}$  can be treated as hydrogen-bending frequencies and can be linked, *e.g.*, with the infra-red frequency  $A_{2u}^{(H)}$ . The vibration  $B_{2u}^{(C)}$  is a carbon-stretching vibration which can be calculated on similar principles from the Raman vibration  $A_{1g}^{(C)}$ . Finally, the vibration  $B_{2u}^{(H)}$  is a hydrogen-bending vibration and may be obtained from the Raman vibration  $E_g^{+(H)}$ . The ratios of the reduced masses are as follows, and the conversion factors required to pass from the known to the unknown frequencies will be the square roots of these quantities :

$$\begin{array}{ll} E_g^{+(H)}/A_{2g}^{(H)} & \dots [(1/m_H) + (r_H^2/r_C^2)/m_C]/[(1/m_H) + \{5(r_H^2/r_C^2) - 6(r_H/r_C) + 9\}/8m_C] \\ E_g^{+(C)}/B_{1u}^{(C)} & \dots 8/5 \\ A_{1g}^{(H)}/B_{1u}^{(H)} & \dots 1 \\ A_{2u}^{(H)}/B_{2g}^{(H)} & \dots [(1/m_H) + \{3 - 4(r_H/r_C)\}^2/m_C]/[(1/m_H) + (1/m_C)] \\ A_{1g}^{(C)}/B_{2u}^{(C)} & \dots 3 \\ E_g^{+(H)}/B_{2u}^{(H)} & \dots [(1/m_H) + (1/m_C)]/[(1/m_H) + \{5(r_H^2/r_C^2) - 6(r_H/r_C) + 9\}/8m_C] \\ A_{2u}^{(H)}/E_u^{+(H)} & \dots [1/m_H + \{3(r_H/r_C) - 2\}^2/m_C]/[(1/m_H) + (1/m_C)] \end{array}$$

It must be remembered that the results (Table VII) of any of these calculations, except that concerning the hydrogen-stretching frequency (the third), could be in error by 100  $\text{cm}^{-1}$  or even twice that amount in some cases.

TABLE VII.

*Approximate Frequencies of Inactive Fundamentals.*

	$A_{2g}^{(H)}$	$B_{1u}^{(C)}$	$B_{1u}^{(H)}$	$B_{2g}^{(C)}$	$B_{2g}^{(H)}$	$B_{2u}^{(C)}$	$B_{2u}^{(H)}$	$E_u^{+(C)}$	$E_u^{+(H)}$
$C_6H_6$ .....	1240	766	3062	low	1000	1720	1145	low	890
$C_6D_6$ .....	940	730	2292	low	920	1636	820	low	780

The forbidden infra-red frequency No. 1 (Table VI) agrees with  $B_{1u}^{(C)}$ , and one may also say that it must approximately satisfy the product theorem, because, although the  $B_{1u}^{(H)}$  frequencies have not been observed, they are certain to be close to the predicted values. The resonance frequency No. 7 agrees with  $A_{2g}^{(H)}$ , and the isotope frequency ratio, *i.e.*, the Teller ratio for a symmetry class of one vibration, corresponds so closely to the expected value (Found :  $\tau = 1.27$ . Calc. :  $\tau = 1.29$ ) that this assignment is indicated. Owing to the large uncertainties attaching to the calculated frequencies, the other possible fundamentals can be distributed in several ways amongst the available vibrations, but there would be little value in any attempt to make a definite allocation at the present time.

(4) *Assignment of Overtones and Combination Tones.*—As more than half of the fundamental frequencies have now been identified, it seems profitable to see how far they enable us to explain as overtones or combination tones the weaker Raman lines and infra-red bands. The selection rules place restrictions on the appearance of the various combinations in these spectra, and hence a certain check on the assignment of the fundamentals is obtained by observing whether the combinations appear in the right spectra. We shall, of course, remember that strong combination tones may conceivably appear in the wrong spectra when we experiment with the liquid.

We shall restrict our considerations to first overtones and binary summation tones. The number of combinations allowed in the spectra is then comparatively small, and the possibility of obtaining agreement with observation by accident is correspondingly restricted. Some of the lowest Raman frequencies may be difference tones, which we do not take into account, but it is hardly likely that combinations of more than two fundamental frequencies would be observed in the Raman spectrum. In the infra-red spectrum combination tones are relatively stronger, and it is possible that some of the weakest bands may

represent ternary combinations; and also some of those of lowest frequencies may be difference tones.

The selection rules can be derived from Table I. A combination will be allowed to appear in a particular spectrum when its wave-function has the symmetry properties of one of the allowed symmetry classes, *i.e.*,  $A_{2u}$  or  $E_u^-$  for the infra-red spectrum and  $A_{1g}$ ,  $E_g^+$ , or  $E_g^-$  for the Raman spectrum. The wave-function of an overtone or combination tone has the symmetry properties of the product of the wave-functions of the constituent fundamentals. This follows for combination tones because their wave-functions are actually the products of those of the constituent fundamental vibrations. It follows for overtones from the fact that their wave-functions, being essentially Hermitean functions, are odd or even functions of the normal co-ordinate according as the quantum number is odd or even, and hence transform under symmetry operations exactly as would the appropriate powers of the wave-function of the fundamental. As an example of the method of deriving the selection rules we may consider the wave-function of a binary combination between a  $B_{1u}$  frequency and a  $B_{2g}$  frequency. This must have the symmetry properties denoted by  $++--$  towards the four "specification elements" of Table I; for the symbols  $+$  and  $-$  are abbreviations for the factors,  $+1$  and  $-1$ , by which the symmetry operations multiply the normal co-ordinate or wave-function, so that we have merely to multiply together the factors belonging to the constituents of the combination. The symmetry specified by  $++--$  is, however, that of the class  $A_{2u}$ , and hence the combination considered will be allowed in the infra-red spectrum; moreover, its band will be of the "parallel" type. The activity of other combinations can be deduced in the same way. When degenerate vibrations are involved, different symmetry properties can result according to the way in which the orthogonal pairs are chosen; thus two multipliers  $\epsilon^\mp$  can yield  $+$  or  $\epsilon^\pm$  (depending on how the signs of the exponents are combined), whilst two  $\pm$  factors may give  $+$  or  $-$  or  $\pm$ . The allowed combinations are in Table VIII.

TABLE VIII.

## Allowed Binary Combination Tones.

Infra-red.		Raman.	
$M //.$	$M \perp.$	$\rho \leq 6/7.$	$\rho = 6/7.$
$A_{1g} + A_{2u}$	$B_{1u} + E_g^+$	$A_{1g} + A_{1g}, A_{2g} + A_{2g}$	$A_{1g} + E_g^+, A_{2g} + E_g^+$
$B_{1u} + B_{2g}$	$B_{2u} + E_g^-$	$A_{2u} + A_{2u}, B_{1u} + B_{1u}$	$A_{2u} + E_u^+, A_{1g} + E_g^-$
$E_g^+ + E_u^+$	$B_{2g} + E_u^+$	$B_{2g} + B_{2g}, B_{2u} + B_{2u}$	$A_{2g} + E_g^-, A_{2u} + E_u^-$
$E_g^- + E_u^-$	$A_{2u} + E_g^-$	$E_u^+ + E_u^+$	$B_{1u} + E_u^+, B_{1u} + E_u^-$
	$A_{1g} + E_u^-$	$E_u^- + E_u^-$	$B_{2g} + E_g^+, B_{2g} + E_g^-$
	$A_{2g} + E_u^-$	$E_g^- + E_g^-$	$B_{2u} + E_u^+, B_{2u} + E_u^-$
	$E_u^+ + E_g^-, E_g^+ + E_u^-$	$E_u^- + E_u^-$	$E_g^+ + E_g^-, E_u^+ + E_u^-$

In Table IX we give a list of all the observed Raman lines of benzene and of hexadeutero-benzene which have not been assigned to fundamental vibrations and therefore might conceivably be first overtones or binary summation tones (all first overtones are allowed in the Raman spectrum). We are able to suggest assignments for many of them, and it is satisfactory that in a considerable number of cases the same assignment suits the frequencies of both spectra. The one line for which the polarisation has been examined is the benzene line at  $3185 \text{ cm.}^{-1}$ ; Cabannes and Rousset found this to be polarised, and it is allowed by the selection rules to be polarised according to the assignment given.

Table X contains all the observed infra-red frequencies of benzene and hexadeutero-benzene, both as gas and as liquid, that have not been identified with fundamental vibrations, and hence might possibly be binary combination tones (first overtones are forbidden in the infra-red spectrum). A number of these frequencies are assigned as binary summation tones, and again in many instances the same assignment fits both compounds. The appearance of the inactive frequency  $B_{1u}^{(c)}$  in several of the combinations lends support to the provisional identification of this frequency as a fundamental.

TABLE IX.

Assignment of First Overtones and Binary Summation Tones in Raman Spectra of Benzene and Hexadeuterobenzene.

Benzene.			Hexadeuterobenzene.		
$\nu$ (obs.).	$\nu$ (calc.).	Combination.	$\nu$ (calc.).	$\nu$ (obs.).	
404, 685, 802	—	—	—	337, 710	
824, 1285	—	—	—	790, 976	
1326	671 + 671 = 1342	$2A_{2u}^{(H)}$	503 + 503 = 1006	1000	
1404	—	—	—	—	
1449	606 + 849 = 1455	$E_g^{+(C)_1} + E_g^{-(H)}$	—	—	
1693	{ 671 + 1037 = 1708 849 + 849 = 1698	$A_{2u}^{(H)} + E_g^{-(H)}$ $2E_g^{-(H)}$	{ 503 + 813 = 1316 } 661 + 661 = 1322 }*	1327	
1827	{ 777 + 1037 = 1814 1219 + 606 = 1825 992 + 849 = 1841	$B_{1u}^{(C)} + E_u^{-(H)_{1-2}}$ $A_{2g}^{(H)} + E_g^{+(C)_1}$ $A_{1g}^{(C)} + E_g^{-(H)}$	{ 752 + 813 = 1565 } — 945 + 661 = 1606 }	1586	
1936	—	—	—	—	
2030	1178 + 849 = 2027	$E_g^{+(H)_2} + E_g^{-(H)}$	867 + 661 = 1528	1530	
1988	992 + 992 = 1984	$2A_{1g}^{(C)}$	945 + 945 = 1890	1884	
2128, 2293	—	—	—	—	
2358	1178 + 1178 = 2356	$2E_g^{+(H)_2}$	—	—	
2454	{ 1596 + 849 = 2445 1219 + 1219 = 2438	$E_g^{+(C)_2} + E_g^{-(H)}$ $2A_{2g}^{(H)}$	961 + 961 = 1922	1931	
—	—	$E_g^{+(C)_1} + E_g^{+(C)_2}$	577 + 1559 = 2136	2128	
2543	1037 + 1485 = 2522	$E_u^{-(H)_{1-2}} + E_u^{-(C)}$	813 + 1333 = 2146	2145	
2618, 2688, 2925	—	—	—	2461, 2571, 2739	
—	—	$A_{1g}^{(C)} + E_g^{+(C)_2}$	945 + 1559 = 2504 }	2510	
—	—	$A_{2g}^{(H)} + E_g^{+(C)_2}$	961 + 1559 = 2520 }	—	
2948	1485 + 1485 = 2970	$2E_u^{-(C)}$	—	—	
3164	—	—	—	—	
3187	1596 + 1596 = 3192	$2E_g^{+(C)_2}$	1559 + 1559 = 3118 }	3110	
—	—	$E_u^{-(H)_{1-2}} + E_u^{-(H)_{1+2}}$	813 + 2294 = 3107 }	—	
3467	—	—	—	—	
3680	3062 + 606 = 3668	$A_{1g}^{(H)} + E_g^{+(C)_1}$	—	—	
3916	3062 + 849 = 3911	$A_{1g}^{(H)} + E_g^{-(H)}$	—	—	
—	—	$A_{1g}^{(C)} + A_{2u}^{(H)}$	945 + 503 = 1448 †	1457	

\* Forbidden fundamental at 1333 cm.<sup>-1</sup>. † Forbidden combination (strong in infra-red).

TABLE X.

Assignment of Binary Combination Tones in Infra-red Spectra of Benzene and Hexadeuterobenzene.

Benzene.			Hexadeuterobenzene.			
$\nu$ (obs.).		$\nu$ (calc.).	Combination.	$\nu$ (calc.).	$\nu$ (obs.).	
Gas.	Liq.				Gas.	Liq.
793, 962	—	—	—	—	826, 926	840, 925
1143, 1240	1298	—	—	—	1009	979, 1012
1377	1381	606 + 777 = 1383	$E_g^{+(C)_1} + B_{1u}^{(C)}$	—	—	—
—	1529	849 + 671 = 1520	$E_g^{-(H)} + A_{2u}^{(H)}$	661 + 503 = 1164	1154	1159
—	—	—	—	—	1212	1218
1617	—	(606 + 1037 = 1643)	$E_g^{+(C)_1} + E_u^{-(H)_{1-2}}$	577 + 813 = 1390	1385	1393
—	1669	922 + 671 = 1663	$A_{1g}^{(C)} + A_{2u}^{(H)}$	945 + 503 = 1448	1450	1454
1808, 1906	1810	—	—	—	1630	—
1965	1963	1178 + 777 = 1955	$E_g^{+(H)_2} + B_{1u}^{(C)}$	867 + 752 = 1619	1616	1619
—	2223	1178 + 1037 = 2215	$E_g^{+(H)_2} + E_u^{-(H)_{1-2}}$	867 + 813 = 1680	1692	1690
2288	—	—	—	—	1860	1866
—	2356	1178 + 1178 = 2358 *	$2E_g^{+(H)_2}$	—	—	—
—	2629	1596 + 1037 = 2633	$E_g^{+(C)_2} + E_u^{-(H)_{1-2}}$	—	—	—
2857	3655	—	—	—	—	—
—	3700	606 + 3080 = 3686	$E_g^{+(C)_1} + E_u^{-(H)_{1+2}}$	(577 + 2294 = 2871)	—	2903
—	4060	992 + 3080 = 4072	$A_{1g}^{(C)} + E_u^{-(H)_{1+2}}$	(945 + 2294 = 3239)	—	3292
—	4604, 5984	—	—	—	—	3559
—	—	—	$E_g^{+(H)_2} + E_u^{-(H)_{1+2}}$	2264 + 2294 = 4558	4545	4525

\* Forbidden combination; present in Raman spectrum.



(5) *Conclusions*.—Our investigation, as far as it has yet progressed, supports the  $D_{6h}$  model; this is indicated by the success with which it is able to explain the salient features of the spectra, and especially the isotope shifts (5 numerical relations).

On the other hand, the  $D_{3h}$  (Kekulé) model uniformly fails to exhibit any of the distinctive spectroscopic features by which it might have revealed itself; most notable is the non-appearance of  $E_g^+$  frequencies in the infra-red spectra of benzene and hexadeuterobenzene vapour.

We have found nothing especially indicative of the  $D_{3d}$  (puckered) model, the reality of which must, however, remain an open question pending the identification of certain further fundamental frequencies ( $E_u^+$  and  $B_{2g}$ ).

We are proceeding with the study of the partly deuterated benzenes according to the plan outlined elsewhere (*Nature*, 1935, **135**, 1033; this series, Part I).

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