

55. *Structure of Benzene. Part XI. Introductory Consideration of the Spectral Properties of the Vibrations of Some Deuterated Benzenes.*

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The investigation, described in Parts I—X, of the vibrational spectra of benzene and hexadeuterobenzene having established the model of the benzene molecule in equilibrium configuration, as well as the frequencies of all its spectrally active fundamental vibrations, attention is now turned to the problem of the inactive fundamentals, with a view to the eventual determination of the force field. In this paper the method of investigation is explained, and some of the more useful relevant results of the application of general spectroscopic theory are given. The main work consists in the measurement and identification of the spectrally active fundamental frequencies of certain partly deuterated benzenes by study of their Raman and infra-red spectra. Subsidiary parts of the investigation deal with the fluorescence spectra of some of the more symmetrical isotopically isomeric benzenes, and with those higher harmonics which appear in the Raman and infra-red spectra of all the benzenes studied, including benzene itself and hexadeuterobenzene.

(A) *Scope and Method.*

(1) *Spectrally Active Vibrations and Equilibrium Configuration.*—This work was started (Parts I—IX, J., 1936, 912 *et seq.*, 1210) with the object of elucidating, by spectroscopic methods, the equilibrium configuration of the benzene molecule, its vibrational modes and frequencies, and the system of forces within the molecule which maintains the configuration and controls the frequencies.

The method was to study the frequencies, intensities, and any other observable spectral characteristics of as many vibrations as leave their record in the infra-red absorption spectrum, in the Raman spectrum, and in the vibrational structure of bands which compose the electronic band system of the near ultra-violet; and to do this not only for ordinary benzene, but also for a number of the isotopically modified benzenes which are obtainable from ordinary benzene by the replacement of some or all of its hydrogen atoms by deuterium.

There are several reasons for pursuing parallel studies with isotopically isomeric forms: all depend on the circumstance that, in replacing an element by its isotope, we alter no nuclear charges, nor therefore any electronic eigenfunctions, so that the whole internal force system remains unchanged. One result of this is that the sole effect of an isotopic substitution on the vibration frequencies of a molecule arises from known changes in certain atomic masses. There are accordingly calculable relationships between the frequencies of corresponding fundamental vibrations of any pair of isotopically isomeric molecules. Such relationships are independent of the common, initially unknown force system, but they will depend both on the configuration assumed for the molecule in equilibrium and on the particular fundamental modes of vibration to which they apply. Accordingly, the experimental verification of a set of relationships for all the observed frequencies affords a means, not only of establishing the geometry of the equilibrium configuration, or "model," of the molecule, but also of identifying the frequencies observed in the spectra, *i.e.*, of assigning them to the various vibrational modes of which the model is capable.

In Parts I—IX the programme thus far outlined was carried out for the molecules C_6H_6 and C_6D_6 . The chief results were (a) the complete establishment of the plane, regular hexagonal model, and (b) the correct assignment to the appropriate vibrations of the model of the eleven fundamental frequencies which record themselves either in the Raman spectrum or in the infra-red spectrum of benzene.

(2) *Spectrally Inactive Vibrations and Force Field.*—The remaining part of the programme depended on effects of isotopic substitution, not on frequency alone, but also on spectroscopic intensity. The general principles underlying the calculation of effects on intensity were discussed and illustrated by Lord and Teller in Part X (J., 1937, 1728). Quantitatively these effects may be rather complicated; but for a symmetrical molecule there exist also qualitative effects which are easily predicted: the intensity of any vibration in any particular type of spectrum may be in principle zero, or in principle different from zero, depending on whether the quantity (an electric moment or polarisability), whose value, averaged over the whole molecular configuration, controls the intensity, vanishes or not as a result of being averaged over a symmetrical system. "Selection rules" may be formulated which express these symmetry-dependent properties, and tell us whether any particular mode of vibration will be "forbidden" or "allowed" in a given type of spectrum.

Owing to the high symmetry of the benzene molecule a number of its fundamental vibrations leave no direct record of their frequencies in either the Raman or the infra-red spectrum. The same is true, of course, for hexadeuterobenzene, which is identical in symmetry with benzene. The determination for these two molecules of the "forbidden" frequencies, which became a main preoccupation after the "allowed" frequencies had been identified, was obviously desirable in order to complete our knowledge of the vibrations of benzene in these two isotopic forms.

The plan for doing this was as follows. Vibrations, which are forbidden in a spectrum for reasons of symmetry, may become allowed and in principle observable if at least part of the symmetry is removed by dissymmetric substitution; but then the vibrations appear with altered frequencies, which in general bear no simple relation to the original inactive frequencies. If, however, the substitution is an isotopic one, there exist, as has been mentioned, certain relationships between the altered active and original inactive frequencies. In general these relationships are not of themselves sufficient to enable the inactive frequencies to be calculated; but they form the main part of the body of data needed for this purpose. The rest one must hope to secure from either or both of two supplementary investigations. The first of these depends on success in the interpretation of the vibrational structure of the electronic band systems of benzene, hexadeuterobenzene, and perhaps of partly deuterated benzenes. The second consists in a detailed study of the overtones and combination tones of these substances, special attention being paid to the active first overtones and binary combination tones involving inactive fundamentals. This was the scheme, and (except for a slight setback mentioned later) this is very much how the matter has worked out.

There was yet another reason for studying the vibrational spectra of the partly deuterated benzenes, and a further application to be made of the principle that isotopic substitution does not change the force field, for one of the objects of the work is to provide material for the determination of the forces within the benzene molecule. Now it is true of benzene, as of all but very simple molecules, that the number of its fundamental frequencies is smaller than the number of its elastic constants, even of its harmonic elastic constants. Therefore even a complete knowledge of the fundamental frequencies of ordinary benzene does not provide sufficient data for the calculation of the force system. But the same force system occurs in all the deuterated benzenes, and hence their frequencies, when determined, are also available to augment the body of data.

A further remark is necessary concerning our scheme. It was important, of course, not only to observe the frequencies of the partly deuterated benzenes, but also to identify the corresponding vibrations. Owing to the high symmetry of benzene and hexadeuterobenzene, the Raman and infra-red spectra of these molecules each contain relatively few fundamental frequencies: had it been otherwise we might not have been able to interpret the spectra. If we should at once proceed to a deuterated benzene so dissymmetrically substituted that all vibrations are spectroscopically "allowed," very complex spectra would be observed, the interpretation of which would present great difficulties. Therefore the method we have followed is to remove symmetry from the benzene molecule in graded steps by properly oriented substitution, thus allowing previously forbidden vibrations to appear a few at a time. This procedure gives us the best chance of arriving eventually at a completely correct interpretation even of the most complex spectra, because at each stage of complexity the added complication is limited, and a full understanding of the related simpler spectra is available to assist and control interpretation. As in the already published work on benzene and hexadeuterobenzene, considerable use has been made of the frequency shifts produced by isotopic substitution for the purpose of assigning frequencies to their proper vibrations; and therefore when two isotopically isomeric benzenes exist, such as mono- and penta-deuterobenzene, which have identical symmetry and therefore the same active vibrations, both have been examined. These considerations determined the general scheme, which was to work in order through the list, given in Table I, of isotopically isomeric benzenes (cf. Part I, *loc. cit.*; also *Nature*, 1937, 139, 880).

TABLE I.

Benzenes Examined and their Symmetry Classification.

Symmetry.	Formulae.	Some symmetry elements.
D_{6h}	C_6H_6 ; C_6D_6	3-Fold axis; centre
D_{3h}	1 : 3 : 5- $C_6H_3D_3$	3-Fold axis (no centre)
D_{2h} (= V_h)	1 : 4- $C_6H_4D_2$; 1 : 2 : 4 : 5- $C_6H_2D_4$	Centre (no 3-fold axis)
D_{1h} (= C_{2v})	C_6H_5D ; C_6HD_5	(No centre; no 3-fold axis)

Each line in the table represents a symmetry class. In all the molecules the plane of the ring is a plane of symmetry. The numerical subscripts in the symmetry labels (col. 1) mean that the axis perpendicular to the ring-plane is a six-fold, three-fold, two-fold, and one-fold symmetry axis, and also that the ring-plane contains six, three, two, and one two-fold axes, in the four symmetry classes taken in order. Some other symmetry properties of the classes are explicitly given in the table. Clearly the four classes correspond to a progressive reduction of symmetry.

Parts I—X dealt with benzene and hexadeuterobenzene. The examinations of the Raman and infra-red spectra of the remaining five of the benzenes listed has since been carried out according to plan, except that the tenth and last spectrum of the series is missing. This is the infra-red spectrum of pentadeuterobenzene, on the study of which we were just about to embark in 1939 when the work was interrupted. It is probably our lack of acquaintance with this spectrum that is responsible for the circumstance that one of the inactive

frequencies of benzene in the list we shall present is still lacking complete confirmation. These papers are therefore in the nature of an interim report, and are published as such (contrary to our original intention) in view of the importance of the inactive frequencies in connexion with the thermodynamic functions of benzene and its derivatives, the study of which is at present being actively pursued in other laboratories.

Concerning the ultra-violet band spectra of benzene and its deuterio-derivatives, we have revised our earlier somewhat tentative analysis of the fluorescence spectra of benzene and hexadeuterobenzene in the light of the important advances in the interpretation of electronic spectra which have been made by Sklar, Sponer, Teller, and others within the last few years. We have also photographed and similarly analysed the fluorescence spectrum of 1 : 3 : 5-trideuterobenzene. These spectra have given useful new information concerning the vibrations of the electronic ground states of these molecules, but not to the extent that was hoped. What was not clear when we commenced this work in 1936 is obvious now, namely, that these spectra are chiefly valuable for increasing our knowledge of the vibrational frequencies, not of the normal state of the molecule, but of the electronically excited state which, along with the normal state, is involved in the electron transition responsible for the band system.

More important than these spectra as a source of supplementary information for the determination of the inactive frequencies has been the study of overtones and combination tones. A large number of these weaker frequencies have been measured in the various spectra. An interpretation of those which occur in the Raman and infra-red spectra of benzene and hexadeuterobenzene was attempted in 1936, but with only partial success. We now advance an interpretation of the spectra of these and the other benzenes which is so complete and consistent that we think it is likely to prove permanent.

Valuable contributions to the subject have been made by other workers since 1936. These will be referred to in their context, but it may be mentioned here that some important evidence concerning the inactive frequencies has emerged as a result of thermodynamic studies by Andrews, Lord, and, very recently, by Pitzer and Scott. The Raman spectra of partly deuterated benzenes have already been studied by Redlich and Stricks, and much more extensively by Langseth and Lord. However, it was necessary to go over the ground again since these workers overlooked some of the fundamental Raman frequencies, and wrongly identified some others—omissions and errors which frustrated an attempt by Andrews to reconcile the frequencies collectively with his own thermodynamic results. There are no previous measurements of the infra-red spectra of partly deuterated benzenes, except that some of our own measurements have been published in preliminary short notes to which references are given later.

(B) *Symmetry and the Fundamental Vibrations.*

An application to the vibrations of the benzene molecule of the methods of symmetry theory as developed for the spectroscopic field by Brester and Placzek was outlined in Part VIII (*loc. cit.*). We here set forth the arguments in a somewhat broader manner, suitable to the intended range of applications. Our previous discussion was designed primarily to provide for an initial uncertainty with respect to the molecular model. This time we assume the plane, regular hexagonal model, but now we wish particularly to consider the effect of modifying its symmetry by substitution.

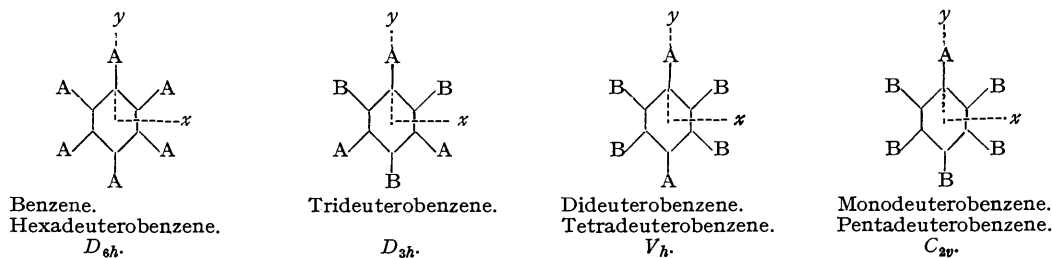
(1) *Symmetry of the Molecular Models.*—It is necessary to recall the method of specifying symmetry. A molecular model, regarded as a system of atomic point-masses situated at the equilibrium positions of the nuclei, possesses certain "elements" of symmetry, that is, operations of rotation round an axis, reflexion across a plane and inversion through a centre which convert the model into itself. A complete "group" of such elements possesses the fundamental group property that each of its elements is a product of two of its elements. These relations between the elements mean that only a limited number of them are independent. A set of elements so selected from the group that none of the set can be derived as products from others of the set, whilst all the remaining elements of the group can be expressed as products of members of the set, may be called a "specifying set."* Unlike a group of symmetry elements, which is a unique expression of the symmetry, a specifying set of elements can generally be chosen in alternative ways, any one of which is sufficient, though not more than sufficient, to define the whole group and therefore the symmetry.

When a parent molecule is so substituted that part of its symmetry is destroyed, the resulting molecule will possess fewer elements, which will form a group. Such a group is called a "sub-group" of the parent group. From the sub-group we can select, usually in more than one way, a specifying set of elements for the substituted molecule. If all the elements of such a specifying set are included amongst the elements of a specifying set for the parent molecule, the former specifying set will be described as a "sub-set" of the latter.

Rectangular co-ordinate axes, x , y , z , fixed in the molecules to be considered, are taken as shown in the diagrams below, in each of which either A represents protium and B deuterium, or *vice versa*. The Schönflies symbols for the different types of symmetry are indicated: D_{6h} denotes the parent group while D_{3h} , V_h , and C_{2v} are its sub-groups. In group D_{6h} the co-ordinate axes are axes of symmetry; and there are four other symmetry axes, which are obtained by rotation of x , y , by $\pm 2\pi/3$ about z ; these will be labelled x_{\pm} , y_{\pm} .

In Table II the symmetry elements of these groups are set out: I represents identity (the "operation"

* A name seems wanted: "sub-group" and "class" already have other established meanings. Elements of a "specifying set" were called "specification elements" in Part VIII. They should not be called "essential elements" (as has since been done), because in general alternative specifying sets exist, with the result that not all, possibly not even any, of the elements of a particular specifying set are "essential" to the definition of the group.



of doing nothing), J inversion through a centre of symmetry, C_p^j rotation by $\pm 2\pi/p$ around axis j , σ_j reflexion across a plane perpendicular to j , and S_p^j rotation by $\pm 2\pi/p$ around j ($= x, y, z$) with accompanying reflexion across the perpendicular plane. Each operational symbol represents one operation, except C_p^j and S_p^j , which, because of the two directions of rotation, comprise two operations, unless $p = 2$, when each denotes only one ($S_2^j = J$).

TABLE II.
Symmetry Elements of Groups D_{6h} , D_{3h} , V_h , and C_{2v} .

D_{6h} (multiplicity 24).				D_{3h} (multiplicity 12).			
Element.	Multy.	Element.	Multy.	Element.	Multy.	Element.	Multy.
$I = C_2^y \cdot C_2^y$	1	J	1	$I = C_2^y \cdot C_2^y$	1	$I = C_2^y \cdot C_2^y$	1
C_3^z	1	$\sigma_z = J \cdot C_2^z$	1	C_3^z	2	C_3^z	2
C_2^x	2	$S_6^z = J \cdot C_3^z$	2	C_2^y	1	C_2^y	1
$C_6^z = C_2^x \cdot C_3^z$	2	$S_3^z = J \cdot C_6^z$	2	$C_2^y \pm = C_3^z \cdot C_2^y$	2	$C_2^y \pm = C_3^z \cdot C_2^y$	2
C_2^y	1	$\sigma_y = J \cdot C_2^y$	1	σ_z	1	σ_z	1
$C_2^x = C_3^z \cdot C_2^y$	1	$\sigma_x = J \cdot C_2^x$	1	$S_3^z = \sigma_z \cdot C_3^z$	2	$S_3^z = \sigma_z \cdot C_3^z$	2
$C_2^y \pm = C_3^z \cdot C_2^y$	2	$\sigma_{y\pm} = J \cdot C_2^y \pm$	2	$\sigma_x = \sigma_z \cdot C_2^y$	1	$\sigma_x = \sigma_z \cdot C_2^y$	1
$C_2^x \pm = C_3^z \cdot C_2^x$	2	$\sigma_{x\pm} = J \cdot C_2^x \pm$	2	$\sigma_{x\pm} = \sigma_z \cdot C_3^z \cdot C_2^y$	2	$\sigma_{x\pm} = \sigma_z \cdot C_3^z \cdot C_2^y$	2
V_h (multiplicity 8).				C_{2v} (multiplicity 4).			
Element.	Multy.	Element.	Multy.	Element.	Multy.	Element.	Multy.
$I = C_2^y \cdot C_2^y$	1	J	1	$I = C_2^y \cdot C_2^y$	1	$I = C_2^y \cdot C_2^y$	1
C_2^z	1	$\sigma_z = J \cdot C_2^z$	1	C_2^y	1	C_2^y	1
C_2^y	1	$\sigma_y = J \cdot C_2^y$	1	σ_z	1	σ_z	1
$C_2^x = C_2^z \cdot C_2^y$	1	$\sigma_x = J \cdot C_2^x$	1	$\sigma_x = \sigma_z \cdot C_2^y$	1	$\sigma_x = \sigma_z \cdot C_2^y$	1

The table includes a series of inter-operational equations so chosen as to exhibit for each group a specifying set of operations. The first half of any group of operations consists of pure rotations, whilst the second half comprises the same rotations applied after an inversion or reflexion. The specifying set thus disclosed for D_{6h} is C_3^z, C_2^x, C_2^y, J . It is possible from this, by the omission of C_3^z , to derive a specifying sub-set for V_h ; but it is impossible by any omission so to derive sub-sets which are specifying for D_{3h} and C_{2v} . However, since $C_2^z \cdot J = \sigma_z$ and $C_2^z \cdot \sigma_z = J$, we can replace J by σ_z in the original set; and likewise, since $C_2^z \cdot C_2^y = C_2^x$ and $C_2^z \cdot C_2^x = C_2^y$ we can replace C_2^y by C_2^x . These changes make it possible to derive specifying sub-sets for any sub-group. Specifying sets for D_{6h}, D_{3h}, V_h , and C_{2v} contain 4, 3, 3, and 2 elements respectively; three series of related sets and sub-sets are shown in Table III.

TABLE III.
Specifying Sets of Elements for the Groups D_{6h}, D_{3h}, V_h , and C_{2v} .

Group.	Set and sub-set I.	Set and sub-sets II.	Set and sub-set III.
D_{6h}	C_3^z, C_2^x, C_2^y, J	$C_3^z, C_2^x, C_2^y, \sigma_z$	$C_3^z, C_2^x, C_2^y, \sigma_z$
D_{3h}	None	$C_3^z, \sigma_z, C_2^y, \sigma_z$	None
V_h	$\sigma_z, C_2^x, C_2^y, J$	$\sigma_z, C_2^x, C_2^y, \sigma_z$	$\sigma_z, C_2^x, C_2^y, \sigma_z$
C_{2v}	None	$\sigma_z, \sigma_x, C_2^y, \sigma_z$	None

(2) *Symmetry of the Vibrations.*—The vibrations of a molecule consist, in harmonic approximation, of fundamental (or "normal") modes, characterised by their frequencies ν_v and their normal co-ordinates, q_v . The latter are independent linear combinations of the spatial co-ordinates of the nuclei, and therefore can be taken to represent internal degrees of freedom. They have the property, both in classical and in quantum mechanics, that the potential energy is the sum of square terms, each depending on only one normal co-ordinate:

$$V = \frac{1}{2} \sum_v k_v q_v^2 \quad (k_v = 4\pi^2 \nu_v^2)$$

It follows, classically and quantumly, that the vibrations are orthogonal, none calling forces into play that affect another. Classically, displacements in normal co-ordinates, q_v , are sine functions of the time, having frequencies ν_v . Quantumly, the same frequency characterises the radiation associated with allowed transitions among vibrational states whose vibrational wave functions are identical but for factors which are functions of

q_v . Displacement in a normal co-ordinate may be represented geometrically by a set of vectors attached to the nuclei ("vibration forms").

Since V arises purely from internal forces, it must have the full symmetry of the molecular model. The invariance of V under all the symmetry operations requires that each operation must convert each q_v either (1) into q_v , or (2) into $-q_v$, or (3) into a different q_v , or linear combination of q_v 's, having the same value of k_v , *i.e.*, the same frequency. According to what happens, the vibration is said to be either (1) symmetric, or (2) anti-symmetric, or (3) degenerate, with respect to the operation. The last possibility arises in the trigonally symmetrical groups D_{6h} and D_{3h} , which have a number of "doubly degenerate" normal vibrations, *i.e.*, pairs of identical frequency. For in these groups any vibration diagram which has *not* trigonal symmetry (C_3^z) can appear in three forms which are geometrically identical except for orientation; and since there is one relation between the three, namely, that the sum of their displacements is zero, they can clearly be made from two independent q_v 's of the same frequency. Vibrations are classified with reference to their behaviour in the whole group of operations belonging to the model, but the classes will, of course, be correctly given if we consider, not the whole group, but a specifying set of operations, because any such set determines the group.

In Part VIII we classified the vibrations of D_{6h} molecules by reference to specifying set I of Table III, because of the spectroscopic importance of the centre of symmetry, J . It is more convenient now to use set II and its sub-sets, which are specifying for all the types of symmetry with which we are now concerned. In later papers we shall require the sub-sets of set III.

In any symmetry group which does not contain the element C_3^z , every vibration must be either symmetric or antisymmetric to each of the symmetry elements. In tables which follow, symmetry and antisymmetry with respect to a symmetry element are respectively denoted by + and by - (meaning multiplication of the normal co-ordinate by +1 and by -1). In any symmetry group which contains C_3^z , the non-degenerate vibrations are symmetric to C_3^z , but may be either symmetric or antisymmetric to each of the other elements of the specifying set. Degenerate vibrations behave in a special manner to C_3^z and C_2^y , but are either symmetric or anti-symmetric towards C_2^z and towards σ_z . Their common behaviour towards C_2^y may be simply expressed by so choosing the independent components of the degenerate pair that one is symmetric and the other antisymmetric to the symmetry operation: this result is denoted by the symbol \pm . The common effect of applying operation C_3^z to degenerate vibrations may be represented by choosing the components of the degenerate pair in the complex form expressing opposing rotations, which then suffer a simple change of phase. This result is designated ϵ^\mp (meaning multiplication of the complex normal co-ordinates by $e^{\mp 2\pi i/3}$).

By setting out all the possible combinations of these different types of behaviour, which vibrations may exhibit under the symmetry operations of a specifying set, we define the "symmetry classes" into which the vibrations may fall. For the groups with which we are concerned, these symmetry classes are labelled with symbols which indicate their symmetry properties according to the set of conventions listed in Table IV.

TABLE IV.

Symmetry Class Symbols of Groups D_{6h} , D_{3h} , V_h , C_{2v} .		
Group.	Class symbol.	Class symbol.
D_{6h}	A = sym. to C_3^z , and to C_2^z	1 = sym. to C_2^y
	B = sym. to C_3^z , not to C_2^z	2 = antisym. to C_2^y
	E^+ = degen., sym. to C_3^z	g = sym. to J
	E^- = degen., antisym. to C_3^z	u = antisym. to J
D_{3h}	A = sym. to C_3^z	1 = sym. to C_2^y
	E = degenerate	2 = antisym. to C_2^y
		$''$ = antisym. to σ_z
V_h	A = sym. to C_2^z , and to C_2^y	g = sym. to J
	B_1 = sym. to C_2^z , not to C_2^y	u = antisym. to J
	B_2 = sym. to C_2^y , not to C_2^z	
C_{2v}	B_3 = antisym. to C_2^z , and to C_2^y	
	A = sym. to C_2^y	1 = sym. to σ_z
	B = antisym. to C_2^y	2 = antisym. to σ_z

The first column of each of the Tables VII—X (pp. 227—228) contains the descriptive labels of the symmetry classes. The next few columns in each table show in detail the symmetry properties of the various classes with respect to the symmetry elements of those specifying sets which have been chosen to represent the symmetry groups.

The vibrations of any pair of symmetry classes of group D_{6h} , which are so chosen that their behaviour with respect to the operations of the specifying set differ only in relation to one or more symmetry elements which disappear in a sub-set, will retain no distinction of symmetry in the corresponding sub-group. Thus each symmetry class of each of the sub-groups D_{3h} , V_h , and C_{2v} may be regarded as compounded by the fusion of two or more classes of the group D_{6h} . The D_{6h} classes which bear this relation to the classes of the groups D_{3h} , V_h , and C_{2v} are shown next after the detailed symmetry properties of the classes in the tables relating to these sub-groups. Inasmuch as group C_{2v} is a sub-group of D_{3h} and also of V_h , there is a similar fusion of the classes of these latter groups to form those of group C_{2v} . The whole pattern of relationships between the symmetry classes of the different groups and sub-groups is shown in Table V.

TABLE V.

Relations between Symmetry Classes of Group D_{6h} and its Sub-groups.

D_{6h}	A_{1g}, B_{1u}	E_g^+, E_u^-	A_{1u}, B_{1g}	E_u^+, E_g^-	A_{2g}, B_{2u}	E_g^+, E_u^-	A_{2u}, B_{2g}	E_u^+, E_g^-
D_{3h}	A_1'		A_1''		A_2'		A_2''	
C_{2v}	A_1		A_2		B_1		B_2	
V_h	A_g	B_{2u}	A_u	B_{2u}	B_{1g}	B_{3u}	B_{1u}	B_{3g}
D_{6h}	A_{1g}, E_g^+	B_{1u}, E_u^-	A_{1u}, E_u^+	B_{1g}, E_g^-	A_{2g}, E_g^+	B_{2u}, E_u^-	A_{2u}, E_u^+	B_{2g}, E_g^-

(3) *Distribution of Vibrations with Respect to Symmetry.*—The number of vibrations which a molecule possesses in any symmetry class depends, not only on symmetry, but also on the numbers and types of the atoms involved. Placzek's method of calculating the number commences by placing the molecular model in a potential hollow of its own symmetry, so that the translational and rotational degrees of freedom become included amongst the vibrations. The model is then divided into "point-sets," a point-set consisting of those mass-points which can be generated from one mass-point by the symmetry operations of the model. Thus 1 : 3 : 5-trideuterobenzene has four point-sets, the 1 : 3 : 5-carbon atoms, the 2 : 4 : 6-carbon atoms, the protium

TABLE VI.

Proper Symmetries of Point-sets of Benzenes of Symmetries D_{6h} , D_{3h} , V_h , and C_{2v} .

(In the formulæ either A = H and B = D or A = D and B = H.)

Molecule.	Point-set.	Prop. sym.	Molecule.	Point-set.	Prop. sym.
C_6A_6 (D_{6h})	{ 1 : 2 : 3 : 4 : 5 : 6-C 1 : 2 : 3 : 4 : 5 : 6-A	C_{2v} "			
$C_6A_3B_3$ (D_{3h})	{ 1 : 3 : 5-C 1 : 3 : 5-A 2 : 4 : 6-C 2 : 4 : 6-B	" " " "	C_6AB_5 (C_{2v})	{ 1-C 1-A 4-C 4-B 2 : 6-C 2 : 6-B 3 : 5-C 3 : 5-B	C_{2v} " " " C_s " " "
$C_6A_2B_4$ (V_h)	{ 1 : 4-C 1 : 4-A 2 : 3 : 5 : 6-C 2 : 3 : 5 : 6-B	" " C_s "			

Proper sym. C_{2v} :—Group : $I, C_2^y, \sigma_z, \sigma_x$. Specifying set : C_2^y, σ_z .
Proper sym. C_s :—Group : I, σ_z . Specifying set : σ_z .

atoms and the deuterium atoms. Any point-set has a "proper symmetry," which consists of all those operations of the model which can be performed on a point of the set without generating any other point of the set. The operations of a proper symmetry form a group, and this, if not the group of the symmetry of the model itself, is always a sub-group of that group. Accordingly, a proper symmetry can be defined by a selection of symmetry elements constituting a specifying set, which, if not specifying for the model itself, can always be chosen as a sub-set of a set which is specifying for the model. Table VI shows the point-sets into which our benzene molecules may be divided, together with their proper symmetries, the groups of elements composing these symmetries, and convenient specifying sets.

The general rule giving the number of vibrations contributed by a point-set to a symmetry class is that it is equal to the number of independent linear combinations of the spatial co-ordinates which show the behaviour

TABLE VII.

Normal Vibrations of Benzene Model D_{6h} .

(Examples : C_6H_6, C_6D_6 .)

Symmetry class.	Specifying set of elements.				Vibs. per point-set C_{2v} .	Trans. and rot.	Vibs.	Non-vanishing components of	
	C_3^z .	C_2^z .	C_2^y .	σ_z .				M (Infra-red activity).	α (Raman activity).
A_{1g}	+	+	+	+	1	—	2	F	$\alpha_{xx} = \alpha_{yy}; \alpha_{zz}$
A_{1u}	+	+	+	—	0	—	0	F	F
A_{2g}	+	+	—	+	1	R_z	1	F	F
A_{2u}	+	+	—	—	1	T_z	1	M_z	F
B_{1g}	+	—	+	—	0	—	0	F	F
B_{1u}	+	—	+	+	1	—	2	F	F
B_{2g}	+	—	—	+	1	—	2	F	F
B_{2u}	+	—	—	—	1	—	2	F	F
E_g^+	ϵ^{\mp}	+	\pm	+	2	—	4	F	$\alpha_{xx} = -\alpha_{yy}; \alpha_{xy}$
E_u^+	ϵ^{\mp}	+	\pm	—	1	—	2	F	F
E_g^-	ϵ^{\mp}	—	\pm	—	1	$R_{x,y}$	1	F	α_{zz}, α_{yz}
E_u^-	ϵ^{\mp}	—	\pm	+	2	$T_{x,y}$	3	$M_{x,y}$	F
x	ϵ^{\mp}	{ —	—	+	Non-degenerate		10	Parallel 1 Pol. 2	
y			+	+	2-Fold degenerate		10	Perpr. 3 Depol. 5	
z	+	+	—	—	Degrees of freedom		30	In common : 0	

Frequencies : 20. Active : 11. Inactive : 9.

of the class towards the elements of the proper symmetry of the point-set. Statements of the symmetry properties of the co-ordinates, x, y, z , are included in Tables VII—X. The total number of vibrations in any symmetry class will be the sum of the numbers contributed by the point-sets; for these are not coupled to one another by symmetry, but only through the force field, which cannot affect the *number* of degrees of freedom having any given symmetry.

TABLE VIII.
Normal Vibrations of Benzene Model D_{3h} .
(Example: 1 : 3 : 5- $C_6H_6D_3$.)

Symmetry class.	Specifying set of elements.			Component D_{6h} classes.	Trans. and rot.	Vibs.	Non-vanishing components of		
	C_3^z .	C_2^y .	σ_h .				M (Infra-red activity).	α (Raman activity).	
A_1'	+	+	+	A_{1g}, B_{1u}	—	4	F	$\alpha_{xx} = \alpha_{yy}; \alpha_{zz}$	
A_1''	+	+	—	A_{1u}, B_{1g}	—	0	F	F	
A_2'	+	—	+	A_{2g}, B_{2u}	R_z	3	F	F	
A_2''	+	—	—	A_{2u}, B_{2g}	T_z	3	M_z	F	
E_1'	e^{\mp}	\pm	+	E_{g^+}, E_{u^+}	T_x, y	7	$M_{x,y}$	$\alpha_{xx} = -\alpha_{yy}; \alpha_{xy}$	
E_1''	e^{\mp}	\pm	—	E_{u^+}, E_{g^-}	$R_{x,y}$	3	F	α_{xz}, α_{yz}	
x	e^{\mp}	{	-	Non-degenerate		10	Parallel 3		
y				+	2-Fold degenerate		10	Perpr. 7	
z					-	Degrees of freedom 30			Pol. 4 Depol. 10
Frequencies: 20.						Active: 17.	Inactive: 3.	In common: 7	

TABLE IX.
Normal Vibrations of Benzene Model V_h .
(Examples: 1 : 4- $C_6H_4D_2$; 1 : 2 : 4 : 5- $C_6H_2D_4$.)

Symmetry class.	Specifying set of elements.			Component D_{6h} classes.	Trans. and rot.	Vibs.	Non-vanishing components of	
	C_3^z .	C_2^y .	σ_h .				M (Infra-red activity).	α (Raman activity).
A_g	+	+	+	A_{1g}, E_{g^+}	—	6	F	$\alpha_{xx}; \alpha_{yy}; \alpha_{zz}$
A_u	+	+	—	A_{1u}, E_{u^+}	—	2	F	F
B_{1g}	+	—	+	A_{2g}, E_{g^+}	R_z	5	F	α_{xy}
B_{1u}	+	—	—	A_{2u}, E_{u^+}	T_z	3	M_z	F
B_{2g}	—	+	—	B_{1g}, E_{g^-}	R_y	1	F	α_{xz}
B_{2u}	—	+	+	B_{1u}, E_{u^-}	T_y	5	M_y	F
B_{3g}	—	—	—	B_{2g}, E_{g^-}	R_x	3	F	α_{yz}
B_{3u}	—	—	+	B_{2u}, E_{u^-}	T_x	5	M_x	F
x	—	—	+	Non-degenerate		30	ψ -Parallel 3	
y	—	+	+	Degenerate		0	ψ -Perpr. 10	
z	+	—	—	Degrees of freedom 30			Pol. 6 Depol. 9	
Frequencies: 30.						Active: 28.	Inactive: 2.	In common: 0

TABLE X.
Normal Vibrations of Benzene Model C_{2v} .
(Examples: C_6H_5D, C_6HD_5 .)

Symmetry class.	Specifying elements.		Component D_{6h} classes.	Trans. and rot.	Vibs.	Non-vanishing components of		
	C_2^y .	σ^z .				M (Infra-red activity).	α (Raman activity).	
A_1	+	+	$A_{1g}, B_{1u}, E_{g^+}, E_{u^-}$	T_y	11	M_y	$\alpha_{xx}; \alpha_{yy}; \alpha_{zz}$	
A_2	+	—	$A_{1u}, B_{1g}, E_{u^+}, E_{g^-}$	R_y	3	F	α_{zz}	
B_1	—	+	$A_{2g}, B_{2u}, E_{g^+}, E_{u^-}$	T_x, R_z	10	M_x	α_{xy}	
B_2	—	—	$A_{2u}, B_{2g}, E_{u^+}, E_{g^-}$	T_z, R_x	6	M_z	α_{yz}	
x	—	+	Non-degenerate		30	ψ -Parallel 6		
y	+	+	Degenerate		0	ψ -Perpr. 21		
z	—	—	Degrees of freedom 30			Pol. 11 Depol. 19		
Frequencies: 30.						Active: * 30.	Inactive: * 0.	In common: 27

The numbers of vibrations calculated in this way include the so-called "null vibrations," *i.e.*, those which become ordinary translations and rotations when the imposed external force-field is removed. From the symmetry properties of translations and rotations, the symmetry classes to which these degrees of freedom belong may easily be identified. They are indicated in Tables VII—X by the following notation: T_j represents a translation parallel to j , and R_j a rotation about an axis parallel to j ; T_{jk} denotes a translation, having two degrees of freedom, in the jk -plane, while R_{jk} similarly signifies a rotation with two degrees of freedom about axes in the jk -plane ($j, k = x, y, z$). The null vibrations being thus accounted for, the numbers of true vibrations in the symmetry classes follow by difference as shown in the tables.

* Note.—Two of the three A_2 frequencies, which are allowed to be Raman active (α_{zz} need not vanish) by their symmetry classification, can be shown to be inactive (α_{zz} vanishes) by more detailed considerations (cf. Part XX). The remaining one is active (α_{zz} does not vanish).

(4) *Spectral Activity of the Vibrations.*—It is well known that intensity in the infra-red absorption spectrum is dependent on integrals (matrix elements) which measure the amplitude of the x -, y -, and z -components of the oscillating electric moment associated with the vibrational transition. The integrals are of the form

$$M_j = \int \psi M_j^\mp \psi' dq \quad (j = x, y, z)$$

where ψ and ψ' are the total vibrational wave-functions (wholly real) of the combining states, and M_j^\mp is the difference between the j -component of the electric moment of the molecule for a given nuclear configuration and the j -component of its electric moment in equilibrium configuration. For a non-linear n -atomic molecule, ψ is the product of $3n - 6$ wave functions, ψ_v , of the form of the wave-function of the linear harmonic oscillator, each a function of only one argument, *viz.*, the normal co-ordinate q_v ; and correspondingly dq represents the product of the $3n - 6$ differentials dq_v . The conditions for the appearance in the infra-red spectrum of the fundamental frequency of vibration v is that at least one of the integrals M_x , M_y , M_z shall not vanish when ψ and ψ' differ only with respect to the single factors ψ_v and ψ'_v , which are functions of the same q_v , and differ in quantum number by unity. It follows from the forms of the harmonic oscillator wave functions (Hermite polynomials multiplied into exponential functions) that $\psi_v \psi'_v$ is an odd function of q_v , and that therefore the integrals will *not* vanish as a result of the integration by dq_v *only* if M_j^\mp changes sign with q_v , that is, if M_j^\mp has the same symmetry properties as q_v . The symmetry properties of M_x^\mp , M_y^\mp , and M_z^\mp are those of the co-ordinates x , y , and z ; and these may be read in Tables VII—X, and directly compared with the properties of the normal co-ordinates of the various symmetry classes. The components of the transition moment, M , which do not vanish are indicated in the penultimate columns of the tables: the entry F means that all three components vanish, and that the vibrations of the symmetry class are forbidden in the infra-red.

For the symmetrical-top benzene molecules of the D_{6h} and D_{3h} groups, a useful distinction exists between the fundamental infra-red bands of vibrations for which the transition moment is parallel to z and those for which it has the x - or y -direction. The former, called "parallel bands," have a relatively broad rotational structure, because the two principal moments of inertia perpendicular to the transition moment are the two smaller ones. The latter, the "perpendicular bands," have a distinctly narrower structure, essentially because one of the two moments of inertia perpendicular to the transition moment is the large one. For instance, the separations of the intensity maxima of the P- and R-branches of the parallel bands of C_6H_6 , $C_6H_3D_3$, and C_6D_6 are about 25 cm.^{-1} , whilst the corresponding separations for the better resolved perpendicular bands are closer to 16 cm.^{-1} . Even in the asymmetrical-top molecules of the V_h and C_{2v} symmetry groups a similar qualitative distinction applies, because, although all three principal moments of inertia are now different, the one about the z -axis must still be equal to the sum of the other two, which, because of the small masses of protium and deuterium compared to carbon, will not differ greatly from each other. Thus we can still distinguish relatively broad "pseudo-parallel" bands (as we call them), whose transition moments are parallel to z , from the narrower "pseudo-perpendicular" bands, the transition moments of which have the x - and y -directions. These distinctions, which provide a check upon the assignment frequencies, are noted in the tables.

Intensity in the Raman spectrum is dependent, according to Placzek's theory, on matrix elements of the components of the oscillating polarisability which is associated with a vibrational transition:

$$\alpha_{jk} = \int \psi \alpha_{jk}^\mp \psi' dq \quad (j, k = x, y, z)$$

Here α_{jk}^\mp represents the difference between the jk -component of the polarisability of the molecule in a given nuclear configuration and the same component of its polarisability in equilibrium configuration; ψ , ψ' , and dq have the significance already mentioned. A transition in which one normal vibration changes its quantum number by unity may record its frequency in the Raman spectrum provided that at least one of the integrals α_{xx} , α_{yy} , α_{zz} , α_{xy} , α_{yz} , α_{zx} , does not vanish; and, as discussed above in connexion with the dipole moment integrals, any polarisability integral α_{jk} will *not* vanish *only* if α_{jk}^\mp has the symmetry properties of the normal co-ordinate of the vibration. A polarisability component α_{jk}^\mp will suffer symmetry transformations which, since they are products of those undergone by the co-ordinates j and k , can be deduced by multiplying together the operators, listed in Tables VII—X, which express the behaviour of the two co-ordinates*; the resulting symmetry properties can then be directly compared with those of the vibrations in the various symmetry classes. Those components of the transition polarisability which do not vanish are indicated in the last columns of Tables VII—X, where, as before, the entry F means that all components vanish, and that the vibrations of the symmetry class are forbidden.

The main experimental distinction between Raman frequencies relates to their state of polarisation. Placzek has shown that only vibrations which are symmetric with respect to all the elements of symmetry of the molecular model, the so-called "totally-symmetrical" vibrations, can give rise to Raman lines whose depolarisation factors may fall below the value of $6/7$; such lines are described as "allowed to be polarised," or, more simply, as "polarised," although their depolarisation factors may lie anywhere between zero and the upper limit. All other vibrations which are active for the Raman spectrum produce so-called "depolarised" lines, for which

* In carrying out this multiplication of operators it should be noted that the product $(\epsilon^\mp)(\epsilon^\mp)$ has the two values $+$ and ϵ^\mp , since two rotations by $\pm 2\pi/3$ may produce rotation by 0 or $\pm 2\pi/3$. Similarly the product $(\pm)(\pm)$ has the three values $+$, $-$, and \pm .

the depolarisation factor is equal to 6/7. These distinctions, which are of importance for the assignment of frequencies, are noted in the tables.

(C) *Geometrical Forms of Normal Co-ordinates.*

(1) *Benzenes of D_{6h} Symmetry.*—As we pointed out in Part VIII, the vibration forms of benzenes of the D_{6h} symmetry group can be largely determined by simple geometrical reasoning based on the symmetry and orthogonality of the normal co-ordinates, without any prior knowledge of the frequencies or the force system.

Orthogonality means that the work done by displacement in any one normal co-ordinate against the forces called into play by displacement in any other normal co-ordinate is zero; or, in terms suitable to direct geometrical application, that 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 displacement vectors in two vibrations must vanish for every pair of vibrations.

We shall require for reference a more complete diagram of the vibration forms of the D_{6h} benzene model than was given in the earlier publication, in which only one component of each degenerate pair of normal modes was depicted. In the figure we show vibration forms corresponding to the 30 internal degrees of freedom of benzene. They are exhibited in relation to the symmetry classes of the D_{6h} model. The *A* vibrations, which have a 6-fold *z*-axis, are in the first row, and the *B* vibrations, with only a 3-fold *z*-axis, are in the second row. The next two rows contain the degenerate E^+ vibrations, which have a 2-fold *z*-axis, and the last two the degenerate E^- vibrations, for which the *z*-axis is only one-fold. The vertical dividing lines distinguish symmetry from antisymmetry with respect to the 2-fold *y*-axis, and also with respect to the centre, or alternatively the *xy*-plane, of symmetry. The totally symmetrical vibrations, A_{1g} , are in the first rectangle. The members of each pair of degenerate vibrations are connected by a brace. As is well known, the components of any degenerate pair of vibrations can be chosen in an infinite number of ways. We have in all cases chosen them so that one, labelled *a*, is symmetric with respect to the 2-fold *y*-axis; the other, labelled *b*, then becomes fully determined by the orthogonality principle.

When the carbon and hydrogen point-sets of the D_{6h} model each contribute only one vibration, or one degenerate pair of vibrations, to a symmetry class, one of the two vibrations or degenerate pairs that can be formed by combining the contributions must involve parallel displacements, and the other antiparallel displacements, of corresponding carbon and hydrogen atoms: these are the only types of combination that are permitted by the orthogonality relationship and the symmetry restrictions of the class. In some symmetry classes the combination vibrations are true vibrations; in others one vibration or one degenerate pair is of the "null" type, and this leaves only one true vibration or degenerate pair in the symmetry class.* Thus in all classes which contain either one or two vibrations, or one or two degenerate pairs, the principles of orthogonality and symmetry completely determine the vibration forms. It is otherwise with the symmetry classes E_g^+ and E_u^- , which respectively contain four and three degenerate pairs. For these, the diagrams given in the figure satisfy the orthogonality and symmetry conditions, but so also would any set of four degenerate pairs made by combining orthogonally the four E_g^+ pairs, or any set of three formed similarly from the E_u^- pairs. In order accurately to determine which are the right orthogonal sets we should require to know the force field; but, as was shown in Part VIII, the vibration frequencies themselves provide some approximate guidance, and accordingly, that investigation has been utilised in trying to make the diagrams now given moderately true to reality.

The descriptive labelling of the symmetry classes follows the conventions summarised in Table IV. Within the classes we distinguish by the additional label (C), meaning "carbon-vibration," those vibrations in which, on account of the parallel coupling of the contributions of the carbon and hydrogen point-sets, each carbon atom carries its hydrogen atom with it, the CH-group moving practically as a unit; and likewise, by an additional label (H), signifying "hydrogen-vibration," those vibrations in which, on account of antiparallel coupling, the atoms of each CH-group vibrate with an approximately fixed centre of gravity, most of the motion being in the hydrogen atoms on account of their relative lightness.† Only in the E_g^+ and E_u^- classes have we to introduce additionally a numerical label, 1 or 2, in order to provide completely specific symbols for the vibrations.

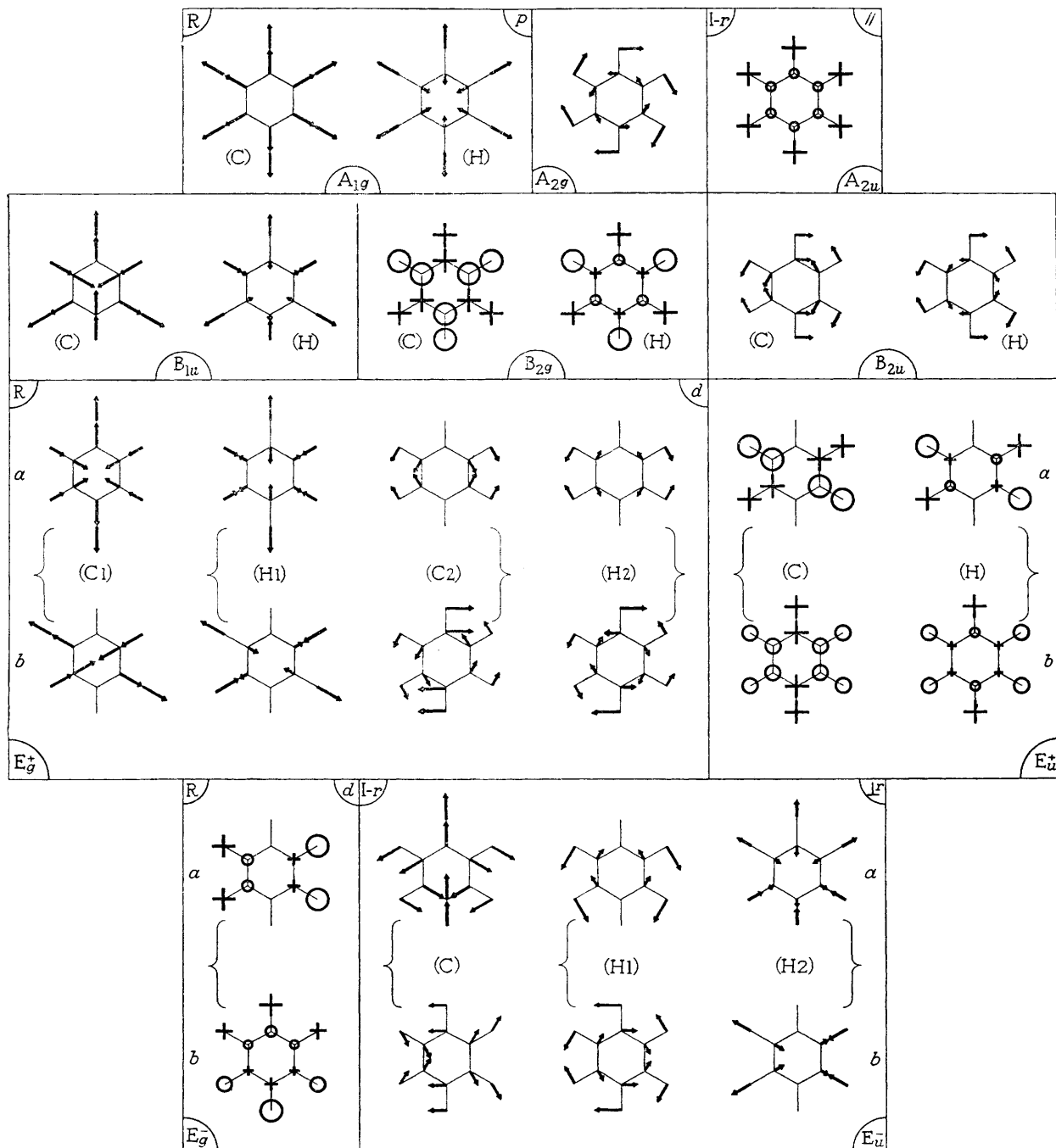
(2) *Benzenes of Lower Symmetry.*—When some of the hydrogen atoms of ordinary benzene are replaced by deuterium with partial loss of molecular symmetry, the classes of the D_{6h} group coalesce in pairs or larger sets, as we have seen, to form smaller numbers of new symmetry classes. All of these contain more than two vibrations, or more than two degenerate pairs of vibrations; and hence, except in a very few special cases, the vibration forms of the partly deuterated benzenes cannot be uniquely determined on the basis of symmetry considerations and the orthogonality principle only. Therefore, in our consideration of the vibrations of these benzenes, the vector diagrams of the figure will be treated only as a starting point: from particular sets of these diagrams, new sets, more closely approximating to the true normal modes, will have to be made by orthogonal linear combination; and this process will have to be guided by all the information which the spectroscopic observations provide—just as with the E_g^+ and E_u^- vibrations of ordinary benzene. This matter involves a good deal of detail, and is best discussed in association with the relevant experimental data.

* Orthogonality to null vibrations merely means that, in a true vibration, the molecule as a whole must possess neither linear nor angular momentum.

† The statement that the carbon and hydrogen amplitudes in a CH-group are about equal in a C-vibration (parallel coupling), and that the hydrogen amplitude is much the greater in a H-vibration (antiparallel coupling) is generally true, but requires some modification in certain cases. The matter is discussed in detail in Part XVII.

FIG. 1.

Vibration forms of the D_{6h} benzene model.



- Notes.—(1) Vectors perpendicular to the plane of the ring represented + O.
 (2) For each point-set \uparrow : \uparrow = + : + = O : O = $\hat{2}$: 1.
 (3) R = Allowed in the Raman spectrum (p = polarised lines; d = depolarised lines).
 I-r = Allowed in the infra-red spectrum (\parallel = parallel bands; \perp r = perpendicular bands).

(D) Relations between Fundamental Frequencies.

(1) *The Product Theorem.*—As has been mentioned, the problem of assigning observed frequencies to their proper vibrations is much assisted by the relationships between the frequencies of isotopically isomeric molecules, which are summarised in the product theorem of Teller and Redlich (Part VIII, *loc. cit.*). Their formula is dependent on the assumption of a harmonic potential, but requires no further knowledge of the potential system. It refers to the product Π of the frequencies ν of vibrations of the same symmetry class, c , and shows how to calculate the ratio τ of such products for two isotopically isomeric molecules, which are distinguished in the formula by dashes :

$$\tau = \frac{\Pi(\nu')}{\Pi(\nu'')} = \left\{ \frac{\prod (m'')^n}{\prod (m')^n} \left/ \left(\frac{M''}{M'} \right)^t \cdot \prod \left(\frac{I''}{I'} \right) \right\}^{\frac{1}{2}}$$

(2) *Application to Molecules of Like Symmetry.*—We suppose first that the two molecules under comparison have the same symmetry. In this case p enumerates the point-sets as defined above, m denotes the mass of an atom of a particular point-set, and n the number of its contributions to the vibrations of class c as already defined. In forming the frequency products it is convenient to introduce the common frequency of a degenerate pair of vibrations only once : consistently, in reckoning n a degenerate pair must be counted as a single contribution. Null vibrations must be included with true vibrations in calculating n , but for each of the t translations so included, the formula provides a factor consisting of the ratio of the molecular masses M , and, for each of the included r rotations, a factor which is the ratio of the relevant moments of inertia I . Degenerate null vibrations are counted only once in reckoning t and r .

TABLE XI.

Theoretical (Harmonic) Values of the Frequency Product Ratio, τ , for Some Pairs of the Molecules C_6H_6 , C_6H_5D , 1 : 4- $C_6H_4D_2$, 1 : 3 : 5- $C_6H_3D_3$, 1 : 2 : 4 : 5- $C_6H_2D_4$, C_6HD_5 , C_6D_6 .

(a) Greatest common symmetry D_{6h} .									
Symmetry class.		$\frac{C_6H_6}{C_6D_6}$	Symmetry class.		$\frac{C_6H_6}{C_6D_6}$	Symmetry class.		$\frac{C_6H_6}{C_6D_6}$	$\frac{C_6H_6}{C_6D_6}$
A_{1g}		1.414	B_{1u}		1.414	E_g^+		1.998	
A_{2g}		1.286	B_{2u}		1.414	E_u^+		1.414	
A_{2u}		1.362			1.414	E_g^-		1.286	
						E_u^-		1.925	
(b) Greatest common symmetry D_{3h} .									
D_{6h} classes.		$\frac{C_6H_6}{C_6H_3D_3}$	D_{6h} classes.		$\frac{C_6H_6}{C_6H_3D_3}$	D_{3h} class.		$\frac{C_6H_6}{C_6H_3D_3}$	$\frac{C_6H_3D_3}{C_6D_6}$
A_{1g}, B_{1u}	A_1'	1.414	E_g^+, E_u^-		1.414	E'		1.960	1.962
A_{2g}, B_{2u}	A_2'	1.345	E_u^+, E_g^-		1.351	E''		1.345	1.351
A_{2u}, B_{2g}	A_2''	1.387			1.388				
(c) Greatest common symmetry V_h .									
D_{6h} classes.		$\frac{C_6H_6}{C_6H_4D_2}$	$\frac{C_6H_4D_2}{C_6H_2D_4}$	$\frac{C_6H_2D_4}{C_6D_6}$	D_{6h} classes.		$\frac{C_6H_6}{C_6H_4D_2}$	$\frac{C_6H_4D_2}{C_6H_2D_4}$	$\frac{C_6H_2D_4}{C_6D_6}$
A_{1g}, E_g^+	A_g	1.414	1.414	1.414	B_{1g}, E_g^-		1.000	1.285	1.000
A_{1u}, E_u^+	A_u	1.000	1.414	1.000	B_{1u}, E_u^-		1.396	1.396	1.396
A_{2g}, E_g^+	B_{1g}	1.367	1.370	1.372	B_{2g}, E_g^-		1.324	1.032	1.329
A_{2u}, E_u^+	B_{1u}	1.396	0.988	1.396	B_{2u}, E_u^-		1.396	1.396	1.396
(d) Greatest common symmetry C_{2v} .									
D_{6h} classes.		$\frac{C_6H_6}{C_6H_5D}$	$\frac{C_6H_5D}{C_6H_4D_2}$	$\frac{C_6H_4D_2}{C_6H_3D_3}$	$\frac{C_6H_3D_3}{C_6HD_5}$	$\frac{C_6HD_5}{C_6H_2D_4}$	$\frac{C_6H_2D_4}{C_6HD_5}$	$\frac{C_6HD_5}{C_6D_6}$	$\frac{C_6H_2D_4}{C_6D_6}$
$A_{1g}, B_{1u}, E_g^+, E_u^-$	A_1	1.405	1.405	1.973	1.975	1.405	1.405	1.405	1.405
$A_{2g}, B_{2u}, E_g^+, E_u^-$	B_1	1.381	1.382	1.909	1.914	1.383	1.383	1.385	1.385
$A_{1u}, B_{1g}, E_u^+, E_g^-$	A_2	1.000	1.000	1.345	1.351	1.000	1.000	1.000	1.000
$A_{2u}, B_{2g}, E_u^+, E_g^-$	B_2	1.358	1.361	1.374	1.376	1.361	1.361	1.363	1.363

(3) *Application to Molecules of Unlike Symmetry.*—When the molecules under comparison have different symmetries it is necessary to alter, for one or both of them, the previously defined concepts of point-sets, symmetry classes, and the degrees of freedom contributed by the former to the latter. A special case arises in which the symmetry of one molecule is a sub-group of that of the other, as with 1 : 3 : 5- $C_6H_3D_3$ and C_6H_6 . All that is then necessary is a preliminary degradation of the symmetry of the more symmetrical molecule to that of the less symmetrical molecule, by the placing on certain mass-points of imaginary distinguishing marks, which are supposed not to alter the masses or any other dynamical characteristics. For instance, we might thus mark similarly the 1-, 3-, and 5-hydrogen atoms of benzene : then, instead of getting two point-sets and twelve symmetry classes (two without vibrations), we should have four point-sets and six symmetry classes (one without vibrations), just as with the trideutero-compound. The contributions n of the new point-sets p to the new symmetry classes c must be calculated on this basis. The way is then clear for an application of the formula, which will provide a product-ratio τ for each symmetry class of the less symmetrical molecule,

that is, for each of the sets of classes of the more symmetrical molecule that coalesce to form a single class in the less symmetrical.

In the more general case, in which the symmetry of one molecule is not a sub-group of that of the other, it is necessary to find the sub-group which comprises all the symmetry elements that are common to the two molecules. Then the symmetry of each molecule must be reduced to that of this most symmetrical common sub-group by the imaginary labelling process described above. The numbers of point-sets will thus be increased and the numbers of symmetry classes reduced; but these are the point-sets and symmetry classes for which the contributed degrees of freedom must be calculated before applying the product formula; and it is over these classes that the products of frequencies must be taken. A comparison of the molecules 1 : 3 : 5- $C_6H_3D_3$ and 1 : 4- $C_6H_4D_2$ would provide a case for this procedure. Their symmetries are D_{3h} and V_h respectively, of which the most symmetrical common sub-group is C_{2v} . The last has four symmetry classes, and it is for each of these, or in other words, for those sets of classes of the D_{3h} and V_h symmetry groups which coalesce to form each of them, that the formula provides a product ratio.

(4) *The Product Ratios.*—Table XI gives the theoretical (harmonic) ratios of frequency products for a number of pairs of the isotopically isomeric benzene molecules with which we shall be concerned. The only numerical data used are the isotopic weights, $H = 1.008$, $D = 2.014$, $C = 12.00$, and the inter-nuclear distances, $C-C = 1.39$ A., $C-H = 1.08$ A. The list is not exhaustive, but it includes the more useful ratios.

(5) *Anharmonicity.*—The general effect of anharmonicity is to reduce frequency, and to do so more strongly the greater the vibrational amplitude; amplitudes will on the whole be greater in the lighter of two isotopically isomeric molecules. Since in forming each product ratio we have chosen to put the frequencies of the lighter molecule in the numerator, the ratios are for the most part greater than unity. Thus the general effect of anharmonicity should be to reduce the ratios, as was originally pointed out by Teller. This prediction is borne out by our experience.

The deviations are not quite regular, but the percentage deviation shows a marked tendency to increase as the product ratios themselves increase. When using product ratios for the purpose of calculating unknown frequencies from known frequencies we have found it useful to adopt the definite scale, given below, of corrections for anharmonicity. Although in any individual case some uncertainty as to the exactly appropriate correction must remain, the adopted corrections are derived from a consideration of all the deviations which are definitely established by known frequencies.

Harmonic τ	~ 1.00	~ 1.28	~ 1.33	~ 1.39	~ 1.9
Negative percentage corr.	0.0	0.25	0.6	1.0	2.0

(E) Spectral Activity of Overtones and Combination Tones.

The study of overtones and combination tones forms an important part of the work to be described; and, since molecules of several different symmetries are now under consideration, we shall require, as basis, a more general consideration of the optical behaviour of these subsidiary frequencies than that which was given in Part VIII.

On account of the steep general decrease in the intensity of active harmonics of successive orders, it will suffice here to confine attention to first overtones and binary summation and difference tones. In the infra-red spectrum, and also in the Raman spectrum (since we observe only Stokes Raman lines), overtones and summation tones arise mainly from molecules which are originally in the vibrational ground state. Difference tones, on the other hand, originate in the relatively few molecules which, before interaction with the light, were thermally excited with respect to that vibration whose frequency occurs with negative sign in the combination frequency. Difference tones are therefore subject to a further factor tending to diminish their intensity, namely, the Boltzmann factor, $\exp(-h\nu_v/kT)$, of the initial, vibrationally excited state.

By an argument similar to that given on p. 229, it follows that the spectral activity of first overtones will be dependent on the symmetry properties of a product $\psi_v\psi'_v$, in which the quantum numbers of ψ_v and ψ'_v differ by two. Since the ψ 's are harmonic oscillator functions of q_v , their product will have the symmetry properties of q_v^2 . Similarly, the optical behaviour of a summation or difference tone will depend on the symmetry properties of a product $\psi_v\psi'_v\psi_v\psi'_v$, in which the quantum numbers of ψ_v and ψ'_v , and of ψ_v and ψ'_v , each differ by one. This product has the symmetry properties of $q_vq_{v'}$. Thus an overtone or combination tone may appear in the infra-red spectrum if at least one M_j , and in the Raman spectrum if at least one α_{jk} , has the symmetry properties of q_v^2 or of $q_vq_{v'}$, as the case may be. The symmetry properties of the squares and products of the q_v 's can be deduced by multiplying together the operators, given in Tables VII—X, which express the behaviour of the q_v 's towards the symmetry elements which are specifying for the model. The result of each such set of multiplications will be a set of operators characteristic of one * of the symmetry classes of the model: this is evidently the symmetry class to which the overtone or combination tone can be considered to belong. The same tables show which, if any, of the M_j , or of the α_{jk} , have corresponding symmetry properties; they show, therefore, the types of spectroscopic activity which are allowed for the overtone or combination tone.

Although all the results we shall require concerning the spectroscopic activity of overtones and combination

* For the reasons given in the footnote to p. 229, the multiplication of sets of operators belonging to two classes which are both degenerate leads to three sets of products, two corresponding to non-degenerate symmetry classes and the third to a degenerate symmetry class. In every other case we obtain only one set of product operators, as stated in the text.

TABLE XII.

Symmetry and Activity of Overtones and Combination Tones of Benzene Model D_{6h} (C_6H_6 , C_6D_6).
Raman-active []. Infra-red active { }.

A_{1g}	A_{2g}	A_{2u}	B_{1u}	B_{2g}	B_{2u}	E_{g^+}	E_{u^+}	E_{g^-}	E_{u^-}	
$[A_{1g}]$	A_{2g}	$\{A_{2u}\}$	B_{1u}	B_{2g}	B_{2u}	$[E_{g^+}]$	E_{u^+}	$[E_{g^-}]$	$\{E_{u^-}\}$	A_{1g}
	$[A_{1g}]$	A_{1u}	B_{2u}	B_{1g}	B_{1u}	$[E_{g^+}]$	E_{u^+}	$[E_{g^-}]$	$\{E_{u^-}\}$	A_{2g}
		$[A_{1g}]$	B_{2g}	B_{1u}	B_{1g}	E_{u^+}	$[E_{g^+}]$	$\{E_{u^-}\}$	$[E_{g^-}]$	A_{2u}
			$[A_{1g}]$	$\{A_{2u}\}$	A_{2g}	$\{E_{u^-}\}$	$[E_{g^-}]$	E_{u^+}	$[E_{g^+}]$	B_{1u}
				$[A_{1g}]$	A_{1u}	$[E_{g^-}]$	$\{E_{u^-}\}$	$[E_{g^+}]$	E_{u^+}	B_{2g}
					$[A_{1g}]$	$\{E_{u^-}\}$	$[E_{g^-}]$	E_{u^+}	$[E_{g^+}]$	B_{2u}
A_1'	$[A_1]$					$[A_{1g}]$	A_{1u}	B_{1g}	B_{1u}	E_{g^+}
A_2'	A_2'	$[A_1']$				A_{2g}	$\{A_{2u}\}$	B_{2g}	B_{2u}	
A_2''	$\{A_2''\}$	A_1''	$[A_1']$			$[E_{g^+}]$	E_{u^+}	$[E_{g^-}]$	$\{E_{u^-}\}$	E_{u^+}
E'	$\{[E']\}$	$\{[E']\}$	$[E'']$	$[A_1']$	A_2'		$[A_{1g}]$	B_{1u}	B_{1g}	
				$\{[E']\}$			A_{2g}	B_{2u}	B_{2g}	
E''	$[E'']$	$[E'']$	$\{[E']\}$	A_1''	$[A_1']$		$[E_{g^+}]$	$\{E_{u^-}\}$	$[E_{g^-}]$	E_{g^-}
				$\{A_2''\}$	A_2'			$[A_{1g}]$	A_{1u}	
			$[E'']$	$\{[E']\}$				A_{2g}	$\{A_{2u}\}$	E_{u^-}
								$[E_{g^+}]$	E_{u^+}	
									$[A_{1g}]$	
									A_{2g}	
									$[E_{g^+}]$	

TABLE XIII.

Overtones and Combination Tones of Model D_{3h}
(1:3:5- $C_6H_3D_3$). Raman []. Infra-red { }.

TABLE XIV.

Symmetry and Activity of Overtones and Combination Tones of Benzene Model V_h (1:4- $C_6H_4D_2$,
1:2:4:5- $C_6H_2D_4$). Raman []. Infra-red { }.

A_g	A_u	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}	
$[A_g]$	A_u	$[B_{1g}]$	$\{B_{1u}\}$	$[B_{2g}]$	$\{B_{2u}\}$	$[B_{3g}]$	$\{B_{3u}\}$	A_g
	$[A_g]$	$\{B_{1u}\}$	$[B_{1g}]$	$\{B_{2u}\}$	$[B_{2g}]$	$\{B_{3u}\}$	$[B_{3g}]$	A_u
		$[A_g]$	A_u	$[B_{3g}]$	B_{3u}	$[B_{2g}]$	$\{B_{2u}\}$	B_{1g}
			$[A_g]$	$\{B_{3u}\}$	$[B_{3g}]$	$\{B_{2u}\}$	$[B_{2g}]$	B_{1u}
				$[A_g]$	A_u	$[B_{1g}]$	$\{B_{1u}\}$	B_{2g}
A_1	$\{[A_1]\}$				$[A_g]$	$\{B_{1u}\}$	$[B_{1g}]$	B_{2u}
A_2	$[A_2]$	$\{[A_1]\}$				$[A_g]$	A_u	B_{3g}
B_1	$\{[B_1]\}$	$\{[B_2]\}$	$\{[A_1]\}$					B_{3u}
B_2	$\{[B_2]\}$	$\{[B_1]\}$	$[A_2]$	$\{[A_1]\}$			$[A_g]$	
	A_1	A_2	B_1	B_2				

TABLE XV.

Overtones and Combination Tones of Model C_{2v}
(C_6H_5D , C_6HD_5). Raman []. Infra-red { }.

tones can be thus very easily deduced from Tables VII—X, it is in practice a necessity to have the results in a more immediately available form; and on this account Tables XII—XV are given, which contain within the frames the symmetry classes of the overtones and combination tones whose frequencies in harmonic approximation are the sums or differences of those of fundamental vibrations of the symmetry classes shown around the sides of the frames. Raman activity and infra-red activity are indicated for the combination classes by brackets and braces respectively. No special indication is given concerning polarisation in the Raman spectrum, or band structure in the infra-red, since, owing to the generally low intensity of overtones and combination tones these spectroscopic characters cannot often be investigated.

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