THE RAMAN SPECTRA
OF THE DEUTERATED BENZENES

BY

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I. Introductory Remarks.

There exists today rather strong evidence of widely different sorts indicating that the benzene molecule has the symmetry of a plane hexagon (D_{6h} in standard symmetry notation). In particular the recent spectroscopic investigations of benzene and benzene-d_6 by INGOLD and his associates have cleared up several confusing points which had hitherto stood in the way of a whole-hearted acceptance of the D_{6h} structure. The spectra of the partially deuterated benzenes should be expected to confirm this structure. Such a confirmation is highly desirable, however, because of the particular nature of the evidence for the D_{6h} structure furnished by the spectra of benzene and benzene-d_6. One may calculate in a perfectly general way that the D_{6h} model should have a certain number of mutually exclusive Raman and infrared active fundamentals, and when analysis of the data for benzene and benzene-d_6 shows that the proper number, and no more, are observed, one decides in favor of the D_{6h} structure. This argument is somewhat negative in character, and it is reassuring to have constructive evidence for the D_{6h} model from the spectra of a series of deuterium derivatives possessing a wide variety of selection rules. In the following paper this evidence is presented and discussed.

Stepwise substitution of deuterium for hydrogen in

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benzene gives a series of compounds which resemble one another quite closely in physical properties, but which cover a wide range of molecular symmetries. Since the selection rules governing the activity of internal vibrations in the Raman effect, and indeed in all types of molecular spectra, are derived from considerations of molecular symmetry, one should expect to find a great latitude in the selection rules for the eleven partially deuterated benzenes. This variation in selection restrictions has the valuable result that, on the basis of a D_{6h} structure for benzene and insofar as symmetry alone is concerned, all the fundamental frequencies become Raman-active in eight of the eleven compounds. We may therefore expect to obtain from the Raman spectra of the derivatives not only a confirmation of the D_{6h} structure but also much information about the internal frequencies which are spectroscopically latent in benzene. It was chiefly with this latter expectation in mind that the present investigation was undertaken.

II. Brief Survey of Theoretical Background.

The study and interpretation of the spectra of any molecule are greatly facilitated if the molecule possesses a high degree of symmetry, that is, if there are many symmetry operations which one can perform on the stationary molecule. In the first place, considerations of symmetry form the basis for a method of classifying internal vibrations which is of the greatest usefulness in understanding the nature of, and interrelations between, the vibrational degrees of freedom. The application of symmetry arguments to the classification of harmonic vibrations in molecules has been

made by WIGNER[1] and by PLACZEK[2]. Secondly the problem of interpreting Raman and infra-red spectra is quite considerably simplified when the originating molecule is highly symmetrical, inasmuch as the presence of symmetry lays heavy restrictions on the spectroscopic activity of internal vibrations. The nature of these restrictions for the various symmetry classes of harmonic molecular vibrations has been formulated by PLACZEK[2]. Thirdly the simplification of the functional relationships among the several vibrational frequencies which is produced by the presence of molecular symmetry may be of great advantage in interpreting the spectra of various isotopic configurations of the same molecule. This simplification takes a most useful form in the product rule found by E. TELLER[3].

All of these generalizations which are so helpful in the study of molecular spectra have been discussed both in theoretical and practical detail several times. We give in the following paragraphs only such a brief resumé of them as will enable the reader to follow the ensuing applications without having to refer to the original articles.

To describe completely the symmetry of a given point group, there is required only a small number of essential

[1] WIGNER, Gött. Nachrichten, **1930**, 133.

[2] G. PLACZEK, Handbuch der Radiologie, Bd. VI/2, p. 283. The treatments of PLACZEK and of WIGNER are fundamentally equivalent, but since WIGNER uses the formalism of the mathematical theory of groups, one must have a least a superficial knowledge of group theory to apply his results to concrete molecules. On the other hand the method of PLACZEK requires no specialized knowledge. For a lucid and detailed discussion of the application of PLACZEK's procedure to various reasonable structures for benzene, see ANGUS, BAILEY, HALE, INGOLD, LECKIE, THOMPSON, RAISIN, and WILSON, "Structure of Benzene VIII", J. Chem. Soc. (London) **1936**, p. 971.

[3] ANGUS et al. loc. cit. p. 978 state the product rule without proof. The rule was first published, with proof, by O. REDLICH, who found it independently: Z. phys. Chem. B, **28**, 371 (1935).

symmetry elements. The point group may, and frequently does, possess other elements of symmetry, but it is always possible to express the latter as the result of successive application of the essential symmetry operations. When the constituent atoms of a molecule whose symmetry is that of a given point group undergo vibratory motion, the configuration of the motion may or may not maintain the fundamental symmetry elements. Correspondingly we are able to classify the normal vibrations according to the kind of symmetry elements which they preserve. The two extreme classes are the one in which all symmetry elements are preserved — called the totally symmetrical class — and the one in which all are violated. It is obvious that all possible vibrations of the molecular system must be classifiable somewhere within the range of these two extremes. The procedure which we have used for finding the number of vibrations present in the several symmetry classes of each of the symmetry groups to which the various deuterated benzenes belong is that of Placzek[1]. The results are listed in the accompaning Tables I to VI.

In column 1 of the Tables we have listed the symbols[2] for the various symmetry classes. These symbols represent in shorthand fashion the symmetry properties of each class, which are described in full in column 2. The symbols $+$ and $-$ show respectively that a given symmetry class is symmetric or antisymmetric to the indicated symmetry element. In the Tables for D_{6h} and D_{3h}, the violation of the three-fold axis, which is not a simple antisymmetric violation, and which results in the presence of two vibrations of equal frequency, is indicated by $\varepsilon^{\pm 1}$*. Column 3 gives

[1] Placzek loc. cit.
[2] Placzek's notation; cf. Tisza, Zeitschr. f. Phys. 82, 285 (1932).
* Cf. Placzek, loc. cit. p. p. 284—285, and Tables. p. 295.

the number of real frequencies, and in addition, the null-frequencies of translation and rotation in each class. Finally in Column 4 are found the Raman and infra-red selection principles for the vibrations of each class. Here the + sign indicates that the symmetry class is spectroscopically active and a — sign that it is inactive. We have

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Table I.

$D_{6h} : C_6 H_6 , \ C_6 D_6 .$

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Symmetry Class	Essential Elements of Symmetry				Number of Vibrations	Selection Rules	
	C_3^z	C_2^z	C_2^y	i		Raman	Infra-red
A_{1g}	+	+	+	+	2	+	—
A_{1u}	+	+	+	—	0	—	—
A_{2g}	+	+	—	+	1 R_z	—	—
A_{2u}	+	+	—	—	1 T_z	—	+
B_{1g}	+	—	+	+	0	—	—
B_{1u}	+	—	+	—	2	—	—
B_{2g}	+	—	—	+	2	—	—
B_{2u}	+	—	—	—	2	—	—
E_g^+	$\varepsilon^{\pm 1}$	+	±	+	4	+	—
E_u^+	$\varepsilon^{\pm 1}$	+	±	—	2	—	—
E_g^-	$\varepsilon^{\pm 1}$	—	±	+	1 $R_{x,y}$	+	—
E_u^-	$\varepsilon^{\pm 1}$	—	±	—	3 $T_{x,y}$	—	+

not included the rules for the state of polarization of the Raman lines, because these can be summed up very briefly by saying that all Raman lines should have a depolarization factor of $^6/_7$ except those due to frequencies of the first class in each Table. For these latter, the depolarization is not determined by symmetry, and may lie between zero and $^6/_7$.

In Fig. 1 are reproduced schematically the modes of harmonic vibration, insofar as these are determined by

Table II.
D_{3h} : sym-$C_6H_3D_3$.

Symmetry Class	Essential Elements of Symmetry			Number of Vibrations	Selection Rules	
	C_3^z	C_2^y	σ_h		Raman	Infra-red
A_1'	+	+	+	4	+	—
A_1''	+	+	—	0	—	—
A_2'	+	—	+	3 R_z	—	—
A_2''	+	—	—	3 T_z	—	+
E'	$\varepsilon^{\pm 1}$	±	+	7 $T_{x,y}$	+	+
E''	$\varepsilon^{\pm 1}$	±	—	3 $R_{x,y}$	+	—

Table III.
V_h : para-$C_6H_4D_2$, para-$C_6H_2D_4$.

Symmetry Class	Essential Elements of Symmetry			Number of Vibrations	Selection Rules	
	C_2^y	C_2^z	i		Raman	Infra-red
A_{1g} ··········	+	+	+	6	+	—
A_{1u} ··········	+	+	—	2	—	—
B_{1g} ··········	+	—	+	1 R_y	+	—
B_{1u} ··········	+	—	—	5 T_y	—	+
B_{2g} ··········	—	+	+	5 R_z	+	—
B_{2u} ··········	—	+	—	3 T_z	—	+
B_{3g} ··········	—	—	+	3 R_x	+	—
B_{3u} ··········	—	—	—	5 T_x	—	+

Table IV.
C_{2v} : C_6H_5D, m-$C_6H_4D_2$, vic-$C_6H_3D_3$, m-$C_6H_2D_4$, C_6HD_5.

Symmetry Class	Essential Elements of Symmetry		Number of Vibrations	Selection Rules	
	C_2^y	σ_z		Raman	Infra-red
A_1	+	+	11 T_y	+	+
A_2	+	—	3 R_y	+	—
B_1	—	+	10 T_x R_z	+	+
B_2	—	—	6 T_z R_x	+	+

Table V.

C_{2v}^*: ortho-$C_6H_4D_2$, ortho-$C_6H_2D_4$.

Symmetry Class	Essential Elements of Symmetry		Number of Vibrations	Selection Rules	
	C_2^x	σ_z		Raman	Infra-red
A_1	$+$	$+$	11 T_x	$+$	$+$
A_2	$+$	$-$	5 $\quad R_x$	$+$	$-$
B_1	$-$	$+$	10 T_y R_z	$+$	$+$
B_2	$-$	$-$	4 T_z R_y	$+$	$+$

Table VI.

C_s: unsym-$C_6H_3D_3$.

Symmetry Class	Essential Elements of Symmetry	Number of Vibrations	Selection Rules	
	σ_z		Raman	Infra-red
A'.............	$+$	21 $T_x T_y$ R_z	$+$	$+$
A''.............	$-$	9 T_z $R_x R_y$	$+$	$+$

symmetry, for the thirty degrees of internal freedom in benzene. For convenience in discussing the frequencies in the deuterium derivatives, the vibrations have been numbered according to WILSON[1]. In all but one of the partially deuterated benzenes, the doubly-degenerate frequencies split up into their components. Therefore it becomes desirable to assign to the components a notation which distinguishes sharply between them and at the same time indicates their common ancestry. The following convention is adopted: That component of a degenerate benzene vibration which preserves a two-fold axis passing through para carbon atoms is denoted by "a", and the other com-

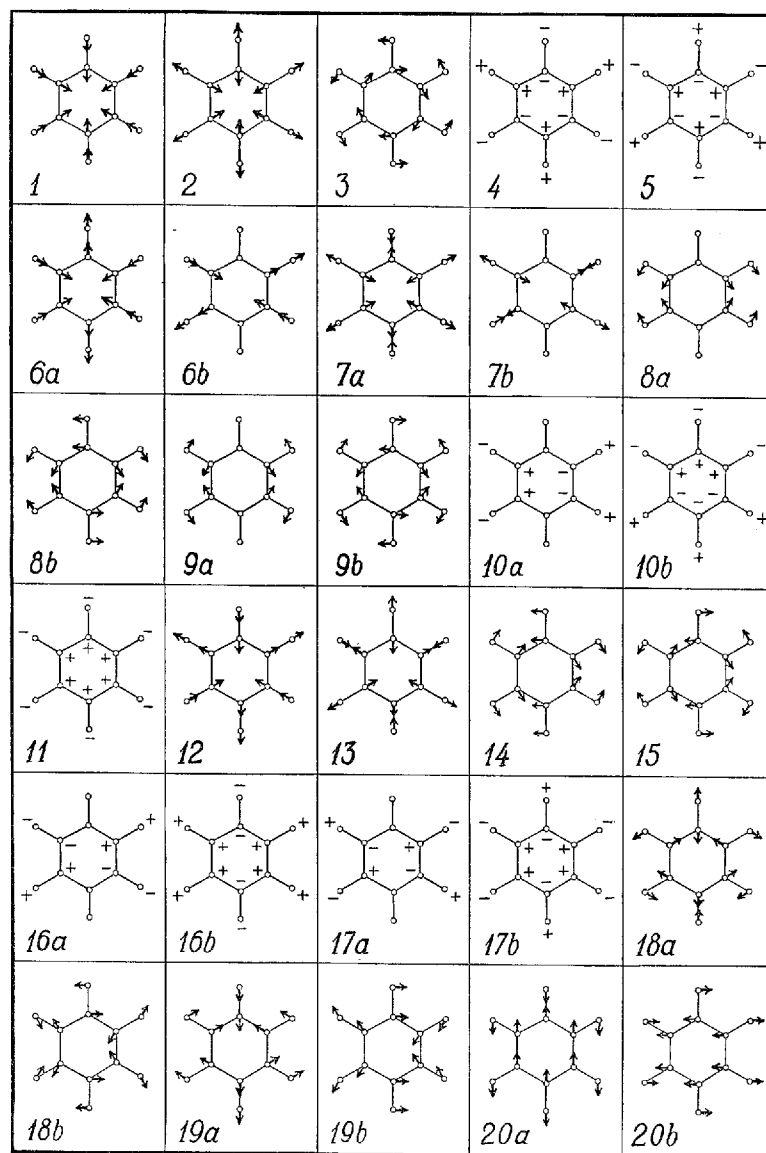[1] WILSON, Phys. Rev. **45**, 706 (1934).

Fig. 1.

ponent by "b". The degenerate vibrations are labelled according to this convention in Fig. 1. One may readily classify each component of the degenerate vibrations in the derivatives with the help of Fig. 1 (cf. Fig. 2, below). Our convention agrees with the notation of WILSON except for the four frequencies of class E_g^+. We have taken the liberty of reversing WILSON's convention for these latter vibrations because his own notation is not entirely consistent and because the other notation is the more natural for the vibrations in substituted benzenes possessing lower symmetry than D_{6h}.

It should be remarked that the modes of vibration shown in Fig. 1 are specifically those for a D_{6h} structure only. From a formal standpoint, as soon the D_{6h} symmetry is destroyed by deuterium substitution, these modes lose their identity and others, determined by the new symmetry and by the appearance of additional constants in the force system, come into being. Of course substitution by deuterium changes the total mass of the molecule only slightly, and therefore vibrations which in D_{6h} may be regarded as essentially carbon vibrations (e.g., ν_1, ν_6, ν_8,) will have modes which are not greatly different in the substituted benzenes[1]. The modes which are essentially hydrogen vibrations, however, (ν_2, ν_3, ν_5 etc.) will be changed greatly due to the large percentage mass difference between hydrogen and deuterium. Consequently the enumeration of frequencies in the intermediate deuterium derivatives on the basis of the D_{6h} frequencies is to a considerable extent arbitrary. The actual modes in the various derivatives are to be ob-

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[1] Changes in the carbon vibrations may be regarded as approximately equivalent to those produced by a small isotopic mass shift. Such changes have been discussed by TELLER, Hand- u. Jahrb. der chem. Phys. Bd. 9, II, p. 141 ff.

tained by combination of the appropriate modes of D_{6h}. The exact nature of the superposition of the D_{6h} vibration forms depends on specific characteristics of the force system, and these characteristics are not determinable from symmetry considerations alone. We shall presently have occasion to discuss in some detail the remarkable effect on certain carbon modes of vibration which deuterium substitution produces because of the special nature of the potential function in benzene.

The modes in Fig. 1 are therefore to be regarded simply as a guide to the general nature of the vibrations in the derivatives. For this reason we have made no attempt to depict the D_{6h} vibrational amplitudes on the proper scale. The only conditions satisfied are those of symmetry.

The results of Tables I—VI are summarized pictorially in Fig. 2. By assembling in this fashion the features of the different symmetry groups, it is possible to get a somewhat clearer and more coherent idea of the interrelations among the frequencies, and of the effect of symmetry on spectroscopic activity, when one passes from one derivative to another.

There is no unique way of arranging the six symmetry groups. The one which we have adopted has been chosen arbitrarily with the idea of presenting most clearly the changes in selection principles and in frequency classification brought about by a step-wise removal of the fundamental elements of D_{6h} symmetry. The elements of the diagram are self-explanatory: each rectangular block represents one symmetry class belonging to the symmetry group whose symbol is listed at the extreme right and left sides of the Figure. Within each block are written the numbers of the real frequencies and the symbols of the rotational and

translational null-frequencies which belong to that class. Above each block is placed the symbol for the symmetry class and an indication of its spectroscopic activity: R if Raman-active, I if infrared-active, a dash if inactive in one and two dashes if inactive in both.

The remaining advantage which molecular symmetry lends to spectroscopic interpretation is the ready calculation of various frequency relationships among the isotopic forms of the same molecule by means of the product rule of E. TELLER[1]. The product rule is a theorem which enables us to compute, independently of spectroscopic observation, the ratio (denoted by τ) between the product of a certain set of frequencies in one isotopic form of a molecule, and the product of the same set in another isotopic form. By a "set" we mean a collection of frequencies whose modes of vibration have a common symmetry. If the two isotopic forms under consideration belong to the same symmetry group, the sets to which the product rule is applicable are simply the symmetry classes of that group. For example if we wish to apply the product rule to the calculation of frequency product ratios for benzene and benzene-d_6, we may apply it individually to each of the ten blocks of frequencies shown in Fig. 2. If we wish to compare the frequencies of p-benzene-d_2 and p-benzene-d_4, we may utilize the product rule for the eight classes of V_h. On the other hand, if the isotopic forms belong to two different symmetry groups, the sets are the symmetry classes of a third group, namely the one which has as elements of symmetry the elements common to the two groups. Hence to compare the frequencies in benzene (D_{6h}) and p-benzene-d_2 (V_h), for example, it is necessary to classify them
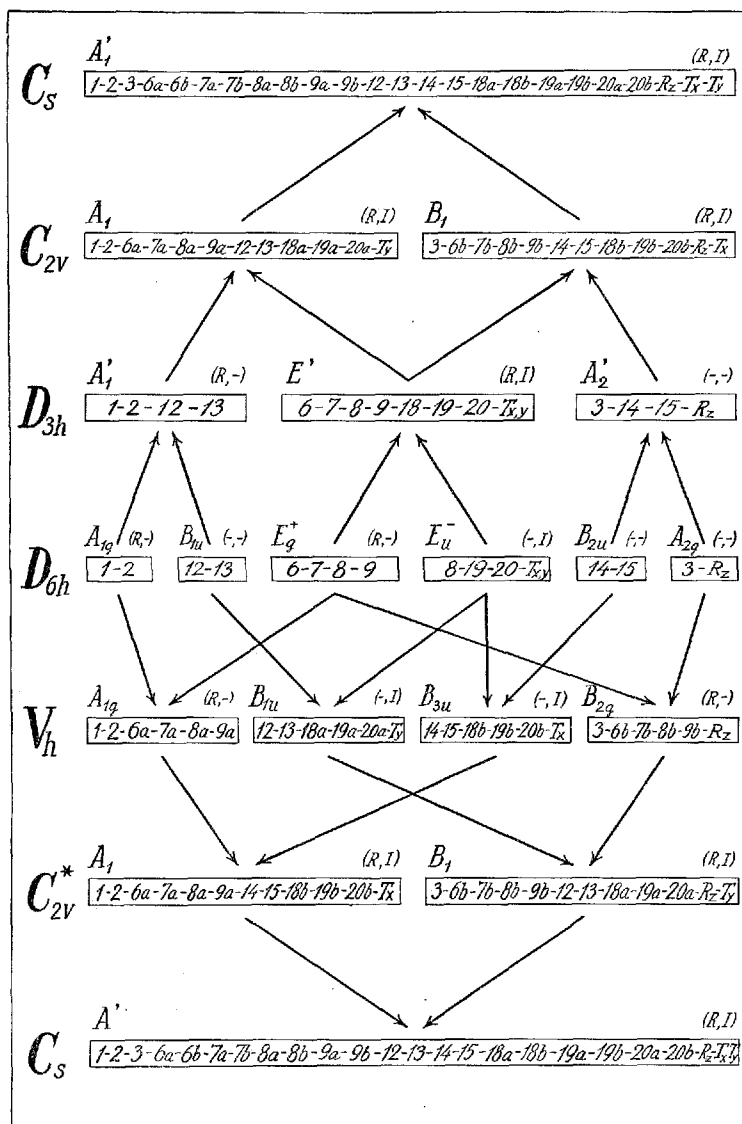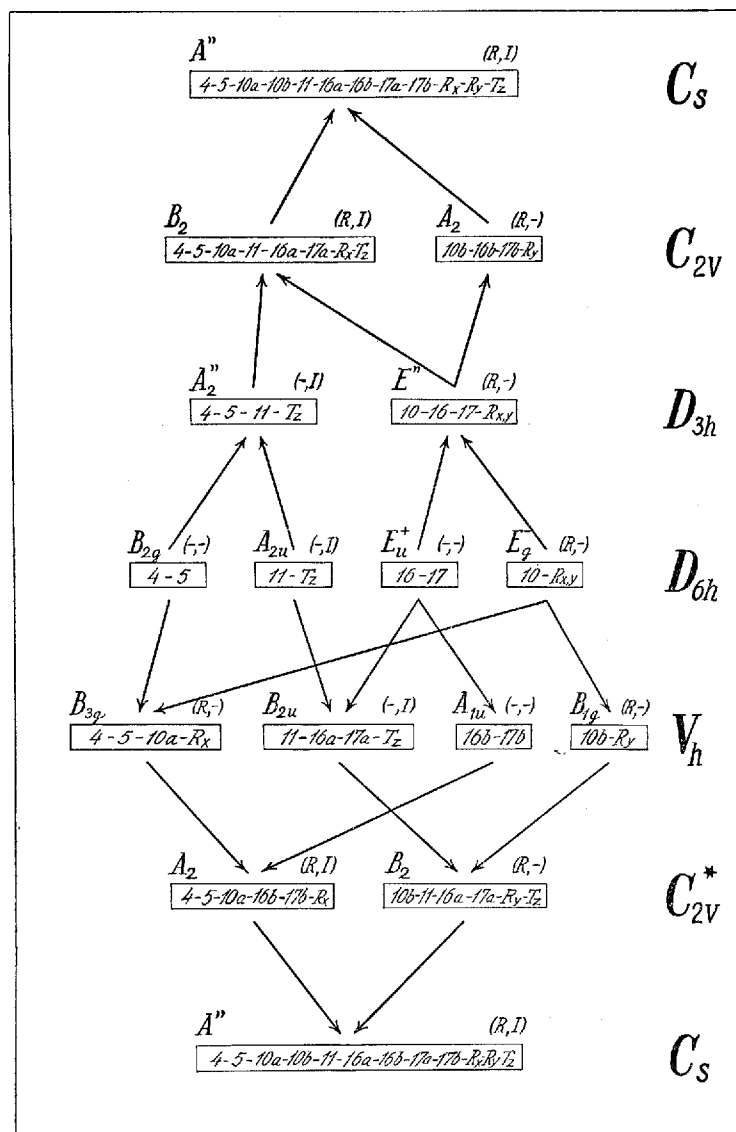
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[1] ANGUS et al; REDLICH, loc. cit.

C_s A'_1 (R,I)
1-2-3-6a-6b-7a-7b-8a-8b-9a-9b-12-13-14-15-18a-18b-19a-19b-20a-20b-R_z-T_x-T_y

C_{2v} A_1 (R,I) B_1 (R,I)
1-2-6a-7a-8a-9a-12-13-18a-19a-20a-T_y 3-6b-7b-8b-9b-14-15-18b-19b-20b-R_z-T_x

D_{3h} A'_1 (R,-) E' (R,I) A'_2 (-,-)
1-2-12-13   6-7-8-9-18-19-20-$T_{x,y}$ 3-14-15-R_z

D_{6h} A_{1g} (R,-) B_{1u} (-,-) E_g^+ (R,-) E_u^- (-,I) B_{2u} (-,-) A_{2g} (-,-)
1-2   12-13   6-7-8-9   8-19-20-$T_{x,y}$ 14-15   3-R_z

V_h A_{1g} (R,-) B_{1u} (-,I) B_{3u} (-,I) B_{2g} (R,-)
1-2-6a-7a-8a-9a   12-13-18a-19a-20a-T_y 14-15-18b-19b-20b-T_x 3-6b-7b-8b-9b-R_z

C_{2v}^* A_1 (R,I) B_1 (R,I)
1-2-6a-7a-8a-9a-14-15-18b-19b-20b-T_x 3-6b-7b-8b-9b-12-13-18a-19a-20a-R_z-T_y

C_s A' (R,I)
1-2-3-6a-6b-7a-7b-8a-8b-9a-9b-12-13-14-15-18a-18b-19a-19b-20a-20b-R_z-$T_{x,y}$

Fig. 2 a.

A'' (R,I)
$4\text{-}5\text{-}10a\text{-}10b\text{-}11\text{-}16a\text{-}16b\text{-}17a\text{-}17b\text{-}R_x\text{-}R_y\text{-}T_z$ C_S

B_2 (R,I) A_2 $(R,\text{-})$
$4\text{-}5\text{-}10a\text{-}11\text{-}16a\text{-}17a\text{-}R_x\text{-}T_z$ $10b\text{-}16b\text{-}17b\text{-}R_y$ C_{2V}

A_2'' $(\text{-},I)$ E'' $(R,\text{-})$
$4\text{-}5\text{-}11\text{-}T_z$ $10\text{-}16\text{-}17\text{-}R_{x,y}$ D_{3h}

B_{2g} $(\text{-},\text{-})$ A_{2u} $(\text{-},I)$ E_u^+ $(\text{-},\text{-})$ E_g $(R,\text{-})$
$4\text{-}5$ $11\text{-}T_z$ $16\text{-}17$ $10\text{-}R_{x,y}$ D_{6h}

B_{3g} $(R,\text{-})$ B_{2u} $(\text{-},I)$ A_{1u} $(\text{-},\text{-})$ B_{1g} $(R,\text{-})$
$4\text{-}5\text{-}10a\text{-}R_x$ $11\text{-}16a\text{-}17a\text{-}T_z$ $16b\text{-}17b$ $10b\text{-}R_y$ V_h

A_2 (R,I) B_2 $(R,\text{-})$
$4\text{-}5\text{-}10a\text{-}16b\text{-}17b\text{-}R_x$ $10b\text{-}11\text{-}16a\text{-}17a\text{-}R_y\text{-}T_z$ C_{2V}^*

A'' (R,I)
$4\text{-}5\text{-}10a\text{-}10b\text{-}11\text{-}16a\text{-}16b\text{-}17a\text{-}17b\text{-}R_x\text{-}R_y\text{-}T_z$ C_S

Fig. 2 b.

according to the eight blocks in V_h, because the common elements of D_{6h} and V_h are simply the elements of V_h.

In Tables VII—IX we reproduce the τ-ratios, calculated by TELLER's rule[1], for various important symmetry group relationships. The Tables are perhaps best explained by two simple examples:

In Table VII, column 2, row 1 we find that the τ-ratio of the product of frequencies in symmetry class A_{1g} in benzene to the product of the same frequencies in benzene-d_6 is 1.414. Reference to Fig. 2 shows that only the frequencies ν_1 and ν_2 are in this class. Hence we know that:

$$\tau = 1.414 = \frac{\nu_1 \cdot \nu_2 \ \ (\text{in } C_6H_6)}{\nu_1 \cdot \nu_2 \ \ (\text{in } C_6D_6)}$$

In Table VIII, column 5, row 2, τ is listed as 1.961. Hence we know from Fig. 2 that:

$$\tau = 1.961 = \frac{\nu_6 \cdot \nu_7 \cdot \nu_8 \cdot \nu_9 \cdot \nu_{18} \cdot \nu_{19} \cdot \nu_{20} \ \ (\text{in sym-}C_6H_3D_3)}{\nu_6 \cdot \nu_7 \cdot \nu_8 \cdot \nu_9 \cdot \nu_{18} \cdot \nu_{19} \cdot \nu_{20} \ \ (\text{in } C_6D_6)}$$

We have not given τ's for relations involving the isotopic derivatives for C_{2v} symmetry or less. For many of these relations we have no particular need, and application of most of the others to the spectra is either impossible, or of no assistance in making an assignment because several alternative assignments of lines satisfy the rule equally well.

The product rule can be used advantageously to calculate unobservable frequencies in benzene and benzene-d_6. For example we find in Fig. 2 that the frequencies ν_3 and

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[1] The necessary moments of inertia have been calculated by taking the C-C distance as 1.40 Å and the C-H distance as 1.08 Å.

ν_{6b} to ν_{9b} are in one Raman-active block in V_h. Since frequencies ν_6 to ν_9 are also observable in D_{6h}, we may calculate the remaining, unobservable ν_3 in both benzene and benzene-d_6 by utilizing τ-values from column 6,

Table VII.

D_{6h}	A_{1g}	A_{2g}	A_{2u}	B_{1u}	B_{2g}	B_{2u}	E_g^+	E_u^+	E_g^-	E_u^-
$C_6H_6:C_6D_6$	1.414	1.286	1.362	1.414	1.414	1.414	2.000	1.414	1.286	1.925

Table VIII.

D_{6h} / D_{3h}	$A_{1g}\ B_{1u}$ / A_1'	$A_{2g}\ B_{2u}$ / A_2'	$A_{2u}\ B_{2g}$ / A_2''	$E_g^+\ E_u^-$ / E'	$E_g^-\ E_u^+$ / E''
$C_6H_6:\text{sym-}C_6H_3D_3$	1.414	1.345	1.387	1.959	1.346
$\text{sym-}C_6H_3D_3:C_6D_6\ldots\ldots$	1.414	1.351	1.388	1.961	1.352

Table IX.

D_{6h} / V_h	$A_{1g}\ E_g^+$ / A_{1g}	E_u^+ / A_{1u}	E_g^- / B_{1g}	$B_{1u}\ E_u^-$ / B_{1u}	$A_{2g}\ E_g^+$ / B_{2g}	$A_{2u}\ E_u^+$ / B_{2u}	$B_{2g}\ E_g^-$ / B_{3g}	$B_{2u}\ E_u^-$ / B_{3u}
$C_6H_6:\text{p-}C_6H_4D_2$	1.414	1.000	1.000	1.396	1.367	1.396	1.324	1.396
$\text{p-}C_6H_4D_2:\text{p-}C_6H_2D_4$	1.414	1.414	1.286	1.396	1.370	0.988	1.030	1.396
$\text{p-}C_6H_2D_4:C_6D_6\ldots\ldots$	1.414	1.000	1.000	1.396	1.373	1.396	1.330	1.396

Table IX. There are other possibilities of calculating unobserved frequencies which will be considered in detail later. It should be remarked here that use of the product rule to compute unobservable frequencies is a perfectly valid procedure within the limits of the assumption of identical harmonic potential functions for isotopic molecules. It is of course necessary that the assignment of

observed frequencies be made correctly, but no special
knowledge of the potential system is assumed or
required.

III. Experimental Procedure and Results.

Previous investigations of the Raman spectra of various
deuterated benzenes have been made by Redlich and
Stricks[1] and by Ingold and associates[2]. Redlich and
Stricks prepared benzene-d_1 and the three benzene-d_2's
by decomposing appropriate Grignard reagents with deu-
terium oxide. They attempted to prepare higher derivatives
by the decarboxylation of calcium salts of benzene-car-
boxylic acids with $Ca(OD)_2$, but obtained only mixtures of
the various derivatives. The Raman spectra of benzene-d_1
and the benzene-d_2's reported in their papers agree in
general with those to be discussed here but are less com-
plete. In addition they show very definite evidence that the
compounds were not pure but contained rather considerable
amounts of lower derivatives including benzene itself.
Redlich and Stricks assign the six totally symmetrical
vibrations as well as ν_{10a} in para-benzene-d_2 and para-
benzene-d_4 to observed frequencies on the basis of cal-
culations made from equations obtained from Wilson's
potential system[3]. Since the assignment which we shall
make later on agrees with theirs, we have no further reason
for discussing their results.

Ingold and his associates have reported the preparation
of benzene-d_1, para-benzene-d_2 and sym-benzene-d_3. They

[1] Redlich and Stricks, Monatshefte f. Chem. **67**, 213; **68**, 47, 374 (1936).

[2] Ingold and associates, Nature **135**, 1033 (1935); **139**, 880 (1937).

[3] Wilson, loc. cit.

have given preliminary data on the Raman spectrum of
benzene-d_1 which are incomplete but which are in agree-
ment with those of REDLICH and STRICKS. They have also
reported briefly on the Raman and infrared absorption
spectra of sym-benzene-d_3. We agree with the frequencies
and assignments of Raman lines which they have given,
and will not discuss their report further. Part of the infrared
frequencies are of value to us in deciding about certain
doubtful assignments, and will be considered in some
detail later on. Unfortunately no indications of relative
intensities of the infrared bands are given in their brief
note and our interpretations using the infrared data are for
this reason somewhat insecure.

The spectrograph used in the present investigation was
the four-prism instrument previously described[1]. Since the
quantities of liquid being studied were not particularly
small (6—10 cc.), no special microtechnique was necessary.
The spectroscopic data obtained are correspondingly more
reliable, particularly with regard to weak lines, than those
obtained by investigators who have used very small amounts
of liquid. The excitation source was unfiltered mercury
radiation from arcs operated so as to give almost no con-
tinous background. The Raman lines obtained were due
to excitation both by Hg-4358 and by Hg-4047. All lines
in the spectra reported here have appeared from both
excitation sources except for one or two isolated instances
in which a strong line from one source coincided with a
weak line from the other. In such cases the weak line has
always been found on at least two plates.

The frequencies of the Raman lines were measured
from photographic enlargements by interpolation between

[1] LANGSETH, Zeitschr. f. Phys. 72, 350 (1931).

Table X. Observed Fr...

C_6H_6		C_6H_5D		$C_6H_4D_2$							
				ortho		meta		para		unsym.	
$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I
606.4	4	381	0 d	384	0 d	374	0 d	400	0 d	395	0
849.7	1	403	0 d	581.6	0	598.4	4	593.6	4	562	0
992.5	10	598.5	5	598.3	5	710.5	2	598.8	4	593.5	6
1177.9	5	602.0	5	658	0 d	818	1/2 d	634.0	2	635.0	2
1585.9	3	780	1	692	0 d	838.1	1	738.0	1	707	2
1604.2	2	851.7	2	773.8	0	855	0 d	850	1 d	772.2	1
3048.3	5	859.5	2	782.1	1	970.5	10	911.1	4	785	0
3061.5	8	980.9	10	825	0	1006.1	5	966	1 d	822.7	0
		1008.6	5	841.6	1	1030	0	978.5	10	841.1	3
		1032.4	1	856	0 d	1051	0	1166.6	2	915	1
		1077	1 d	976.0	10	1081.5	1/2 d	1175.4	4	927	1
		1158.2	2	992.8	3	1107.7	1	1273.4	0 d	966.4	10
		1176.5	4	1035	0 d	1143.9	0	1568.3	3	987.4	2
		1418	0 d	1055.4	1	1168.4	2	1589.2	5	996.0	2
		1575.7	3	1077	0 d	1177.2	1	2223	0 d	1054.7	0
		1593.8	5	1130.7	2	1397.2	1	2261	1 d	1070.2	0
		1610	0	1160.0	2	1418.8	0	2279.4	8	1128.3	1
		2269.8	3	1177.5	2	1563.0	1	3042.3	3	1139.1	3
		2313.0	1	1248	0 d	1583.1	3	3054.6	8	1270	1
		3040	3 d	1384.8	0	2249.2	1	3155.3	0	1366	0
		3055.5	8	1402.8	1	2264.9	1	3174.5	0	1390	1
		3064.2	6	1573	2 d	2272.1	2			1461	0
		3167.9	1	1588.0	4	2284.4	4			1556	2
				2257.9	1	2308.4	1/2			1578	5
				2273.3	3	2337	0 d			2207.2	0
				2280.8	5	2991.8	1			2234.2	0
				2298	0	3047	4 d			2270	4
				2313.5	1	3058.8	8			2283.6	8
				2993	0	3153	0			2297.3	1
				3001	0					3023.4	0
				3035.3	3					3045.1	6
				3053	8 d					3055.7	8
				3064	8 d					3087	0

C_6D_6

$\tilde{\nu}$	I
579.3	1
663.5	3
869.1	4
945.2	10
1553.2	3
2265.7	6
2293.2	8

uencies and Intensities.

C₆H₃D₃ vic. $\tilde{\nu}$	I	sym. $\tilde{\nu}$	I	C₆H₂D₄ ortho $\tilde{\nu}$	I	meta $\tilde{\nu}$	I	para $\tilde{\nu}$	I	C₆HD₅ $\tilde{\nu}$	I
374	1 d	373	1	369	0 d	375	0 d	585.0	6	371	0 d
592	5	593.7	3	589.3	6	589.0	6	605.3	$\frac{1}{2}$	584.8	6
657	0 d	711.7	2	625.4	1 d	632.3	2	630.3	0	614	0
712.0	2	815	0 d	688.3	3	705.1	5	662.3	4	632	0
744	0 d	834.3	2	710	1	711.1	5	765.3	2	664.2	4
779.3	1	956.6	10	738.7	2	832.5	2	859.7	5	691.3	2
825	0 d	1003.9	6	778	0 d	847.0	3	927	1 d	711.6	5
838.7	4	1072	0 d	813.1	1	953.8	10	949.9	1	812.0	1
863.4	0	1101.7	2	842.2	5	986.4	4	959.6	10	836.4	4
920	0 d	1396.2	0	932.3	3	994.3	5	1051	$\frac{1}{2}$ d	847.9	2
965.3	10	1415.1	0	960.4	10	1057	0 d	1098	0 d	857.9	5
992.3	5	1575.9	3	974.0	2	1095.7	3	1137.4	1	950.9	10
031	0	2241	1 d	1004.1	0	1175.9	1	1253	1 d	977.1	4
055.6	1	2272	1 d	1057	0	1197.7	1	1541.5	1	1034.2	1
095.5	3	2283.8	3	1069	0	1209	1 d	1563.0	3	1098.9	1
131.0	1	2974.6	2	1099.4	1	1374	0 d	1571.7	5	1140.1	1
150.4	2	3055.1	4	1136.5	4	1409	0 d	2113	0 d	1173.5	2
363.2	0	3148	0 d	1170.0	2	1541	0 d	2158	0 d	1225	0 d
385.6	1			1252	0 d	1564.6	5	2219	0 d	1323	0 d
554.5	0			1289	1 d	1571.3	5	2245	0 d	1360	1 d
575.3	4			1348.5	0	2198.5	0	2265.0	6	1412	0 d
582.2	3			1372.3	2	2223.2	0	2283.0	8	1532	0 d
240.2	1			1478	1 d	2271.8	5	3042.9	8	1557.9	6
259.8	2			1547.7	1	2287.2	8			1570.4	6
280.8	4			1571.8	5	3051.4	8			2221	0
288.1	8			1578.1	2					2246	0
312	1 d			2160	0 d					2256	0
982	1 d			2187.0	0					2268.3	7
050.6	5			2208.9	0					2288.8	9
058.7	8			2251	1 d					3050.6	8
				2270.0	6						
				2289.9	8						
				2984	0 d						
				3046.2	3						
				3058.3	6						

standard lines of the iron arc. The frequencies of the very strong lines have been determined from at least two plates, and on each plate from three sources of excitation: Hg-4047, 4078 and 4358 Å. Since the lines excited by these three sources on any one plate vary greatly in intensity and breadth, measurements of one Raman frequency from the three different sources serve as valuable checks on one another. The positions of the strong highly polarized lines are the most easily measured, and may be considered accurate to $\pm$ 0.2 cm.$^{-1}$. The frequencies of the other lines may usually be trusted to $\pm$ 0.5 cm.$^{-1}$. Exceptions to this statement must be made for the very faint lines and for lines marked "d" in Table X, whose frequencies may be in error by 1—2 cm.$^{-1}$, or, in one or two instances, by somewhat more.

The deuterated benzenes were prepared by the modified Grignard process described by LANGSETH and KLIT[1]. The method is quite satisfactory except for the great difficulty of removing the very last traces of water from the ether in which the Grignard reaction takes place. A trace of water leads to the presence in each deuterated benzene of small amounts of certain lower deuterated benzenes, but n e v e r of i s o m e r s of the particular compound under consideration. This is made abundantly clear by the method which has been used in analyzing the spectroscopic data.

Our procedure was as follows: First all lines in the spectrum of each derivative were measured, assigned to source of excitation and listed according to frequency and intensity. This was done for each derivative independently and without regard to the spectra of other derivatives. The sets of frequencies of the derivatives were next considered

[1] LANGSETH and KLIT, Kgl. Danske Vidsk. Selsk. math.-fys. Medd. **XV**, No. 13 (1938).

in the order of their deuterium content. The spectrum of benzene-d_1 was compared with that of benzene, and since the spectrum of benzene is accurately known, it was possible to decide which, if any, of the weak lines found in the benzene-d_1 spectrum might be attributed to strong lines in benzene. Having thus established the spectrum of benzene-d_1, the frequencies of the benzene-d_2 derivatives could be examined in the same way, comparing weak lines with the strong lines of benzene-d_1. The same procedure was repeated for all the derivatives. The criteria which were always satisfied before an observed line was rejected as belonging to a derivative of lower deuterium content were: 1) the frequency must coincide within $\pm$ 0.3 cm.$^{-1}$ with that of a strong line of a lower derivative; 2) the intensity of the line must have a reasonable ratio ($<1:20$) to that of the strong line in a lower derivative; 3) the lower derivative must be a proper isomer. By a "proper isomer" is meant an isomer which can be formed from the higher deuterium derivative by replacing one of the latter's deuterium atoms with hydrogen. Thus of the benzene-d_2's only meta-benzene-d_2 is to be expected as an impurity in sym-benzene-d_3, since the replacement of any one of the latter's three deuterium atoms by hydrogen gives only the meta derivative. Similarly unsym-benzene-d_3 will be the only benzene-d_3 derivative present in para-benzene-d_4, and so on.

In practice only the strong totally symmetrical lines in the regions about 990, 2290 and 3050 cm.$^{-1}$ are of sufficient intensity to appear as improper lines, and since those in the neighborhood of 990 cm.$^{-1}$ are extremely sharp, their identification by frequency measurement is quite secure. Except for these lines, only three other cases in all of spurious lines have been found.

The observed frequencies for each derivative are given

in Table X. The intensities listed have been estimated
visually on an arbitrary scale of 10. Particularly diffuse
lines are marked "d" and particularly weak ones "0".

IV. Discussion of Observed Spectra.

The order of discussion of an interlacing series of
spectra is necessarily arbitrary. In principle it must lie
somewhere within the extremes of considering all the fre-
quencies of each derivative separately, and of tracing
the course of each individual frequency through the
several derivatives in the series. The extreme procedures
are neither possible nor desirable—the first because it rules
out the very advantages which accrue from a knowledge
of series variations; the second because the changes in
symmetry properties of one frequency in the different
members of the series cause it to lose, to a greater or lesser
extent, the characteristics by which it may be singled out
as a specific vibration. We therefore adopt the middle
course of considering first those vibrations whose nature
makes it likely that they will maintain their characteristic
features throughout the series. When these frequencies have
been properly catalogued, they will be eliminated from the
spectra, and we will then take up the simplified spectra,
singly or in appropriate groups, and will identify as many
of the observed frequencies as possible.

1. The Totally Symmetrical Vibration ν_1.

It is clear that those vibrations which we have referred
to as "essentially carbon vibrations" will vary least in
frequency in the several deuterated benzenes. In particular,
the one vibration which should preserve its identity through-

out the series is the totally symmetrical carbon frequency ν_1. ν_1 has been identified unequivocally in benzene and benzene-d_6, in which it occurs respectively at 992.5 and 945.2 cm.$^{-1}$. Let us therefore consider this frequency in the intermediate derivatives[1].

a. Interpretation of Irregular Frequency Shifts.

If we assume that the substitution of each deuterium atom produces the same downward shift in ν_1, this shift should be one-sixth of the benzene—benzene-d_6 shift, namely 7.9 cm.$^{-1}$ per D-atom[2]. The value of ν_1 should therefore change in regular fashion, and should be a constant for the various isomers of a given isotopic species. These changes are shown by the lower dotted line in Fig. 3. When the spectra are examined, one finds that for four compounds (the ortho- and the para-substituted derivatives) the predicted shift is closely confirmed by the presence of a line whose great intensity leaves little room to doubt that it is ν_1.

In the other derivatives, ν_1 is found near enough to the predicted point to confirm its identity, but far enough away to show that something is disturbing the validity of the assumption on which the shifts were calculated. The nature of the disturbance is indicated by the existence in the spectra of these derivatives of a companion line close to, and on

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[1] Cf. the preliminary discussion by KLIT and LANGSETH, J. Chem. Phys. **5**, 925 (1937).

[2] We know that the shift in ν_1 from benzene to benzene-d_6 (47 cm.$^{-1}$) is not much larger than that which would be produced by the substitution of six C^{13}-isotopes in the ring (38 cm.$^{-1}$). Hence the effect on ν_1 of substituting one D-atom should be about that of replacing one C^{12} by a C^{13} isotope. On the basis of the discussion by TELLER, loc. cit., of frequency changes produced by small percentage mass increments, our assumption may be justified.

the high frequency side of, ν_1. To understand the presence of this line, which is of quite variable intensity and which appears to exert a pronounced influence on ν_1, we must recall that a frequency of very nearly 1000 cm.$^{-1}$ has been assigned to the trigonal vibration form ν_{12} in benzene (see Fig. 1) by Kohlrausch[1].

The frequency ν_1 would be entirely unconcerned about the presence of a nearby fundamental such as ν_{12} if there were no dynamical relation between the two vibrations. The criterion[2] for dynamical connection between two harmonic vibrations is simply that the two frequencies occupy the same symmetry block. Therefore if the vibration form ν_{12} does indeed have a frequency of about 1000 cm.$^{-1}$, it can only interact with ν_1 in derivatives belonging to symmetry groups D_{3h}, C_{2v}, and C_s, as a glance at Fig. 2 quickly reveals. It is, however, just in the derivatives of these symmetry types that we find the striking disagreement between estimated and observed values of ν_1 and the presence of the unexpectedly strong companion line.

To obtain an understanding of the nature and extent of the interaction between ν_1 and ν_{12}, it is helpful to estimate the frequency changes of the latter in the various derivatives on the assumption that no interaction takes place. Interaction is forbidden by symmetry in the groups D_{6h}, V_h and C_{2v}^*, and accordingly ν_{12} should have its undisturbed position in compounds of these groups. The frequency is Raman-active only in C_{2v}^*, and in the spectra of ortho-benzene-d_2 and ortho-benzene-d_4 the separation, Δ, of ν_{12} from ν_1 is 16.8 cm.$^{-1}$ and 13.6 cm.$^{-1}$ respectively. We know from the

[1] Kohlrausch, Zeitschr. phys. Chem. B, 30, 305 (1935). The arguments for his assignment have been reviewed by Lord and Andrews, Journ. Phys. Chem. 41, 153 (1937).

[2] Cf. for example Placzek, loc. cit., p. 283 ff.
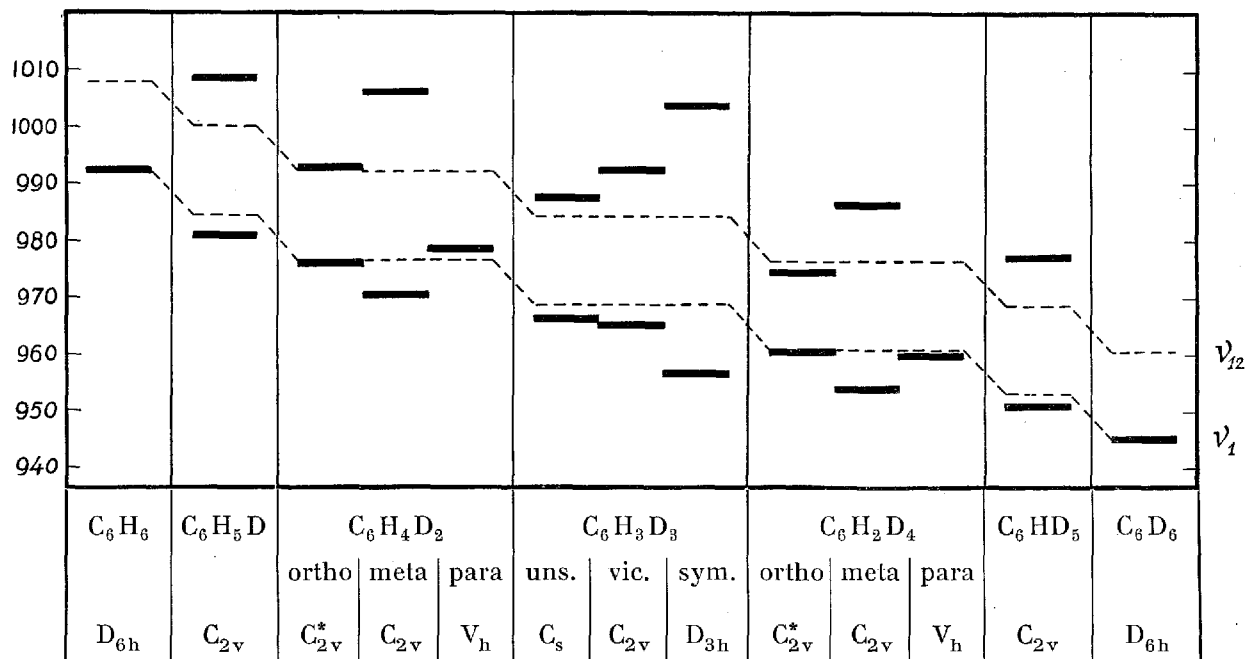
Fig. 3.

In all the deuterated benzenes with C_{2v} symmetry except the two ortho compounds, ν_{12} is symmetric to the two-fold axis, which passes through two para carbon atoms. In the ortho compounds the two-fold axis passes between the two ortho carbon atoms and thus ν_{12} violates the axis (see Fig. 1). To emphasize this distinction we have marked the compounds C_{2v}^{*}.

product rule that the shift in ν_{12} on passing from benzene to benzene-d_6 must be almost precisely the same as that for ν_1. This means that Δ should be about the same in all derivatives, and that any noticeably altered separation is to be ascribed to interaction between the two. In Fig. 3 the upper dotted line shows the calculated value of ν_{12} found by adding 15.5 cm.$^{-1}$, the mean of the observed Δ's, to the frequency of the lower dotted line[1]. The observed values of ν_1 and ν_{12} are shown by the solid lines in Fig. 3.

The formal mathematical procedure for computing precisely the positions and relative intensities of ν_1 and ν_{12} in the various derivatives offers no difficulties in principle. There is no way of evaluating all the necessary harmonic constants, however, and therefore in practice there exists no rigorously correct method of computing Δ and $\dfrac{I_{12}}{I_1}$, the intensity ratio of ν_{12} to ν_1, One must resort to some approximation procedure. For example, one may make simplifying assumptions about the molecular potential system so that the number of harmonic constants is reduced

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[1] We should remark that our use of the product rule in concluding that Δ is approximately the same for the two D_{6h} molecules requires the two quite reasonable assumptions that 1) the hydrogen stretching frequencies ν_2 and ν_{13} undergo the same percentage shift from benzene to benzene-d_6; 2) The anharmonicities of the carbon vibrations ν_1 and ν_{12} are about equal. On the basis of these assumptions Δ should differ in the two compounds by about 5 $^0/_0$, i. e. by less than 1 cm^{-1}. This is probably somewhat smaller than our error in estimating Δ.

In the preliminary note of KLIT and LANGSETH, the upper dotted line was calculated by assuming that the change in ν_{12} from ortho-benzene-d_2 to ortho-benzene-d_4 might be used to extrapolate ν_{12} in both directions. This procedure is quite heavily dependent on the accuracy which ν_{12} is observed in the ortho compounds, since small errors in either value of ν_{12} may lead to rather large differences between Δ in benzene and in benzene-d_6. The figure in their communication shows that the differences in these two Δ's are rather too large, i. e., that either ν_{12} is too far from ν_1 in benzene or too close in benzene-d_6.

sufficiently to evaluate all of them from available data. Such a potential system has been suggested by WILSON[1], who described the potential energy of the planar vibrations in terms of four constants only, namely those for the stretching and bending of the C-C and C-H bonds.

Even so simplified a potential system as this gives complicated secular determinants for the totally symmetrical frequencies in all the deuterated benzenes except sym-benzene-d_3. The determinant for the A_1' class in this compound, however, may be easily set up and solved. Only the three constants K (for C-C stretching), k (C-C-C bending) and q (C-H stretching) are involved, and the frequency equations are:

$$\sum_{i}^{4} \lambda_i = \frac{m_H + m_D}{m_H m_D} q + \frac{1}{M} (K + 12k + 2q)$$

$$\sum_{i}^{6} \lambda_i \lambda_j = \frac{M(m_H + m_D) + m_H m_D}{M^2 m_H m_D} \cdot (K + 12k + q)q + \frac{12}{M^2} \cdot Kk + \frac{1}{m_H m_D} \cdot q^2$$

$$\sum_{i}^{4} \lambda_i \lambda_j \lambda_k = \frac{2M + m_H + m_D}{2M^2 m_H m_D} \cdot (K + 12k)q^2 + \frac{m_H + m_D}{M^2 m_H m_D} \cdot 12 Kkq$$

$$\prod_{i}^{4} \lambda_i = \frac{12}{M^2 m_H m_D} \cdot Kkq^2$$

$$(1)$$

where $\lambda_i = 4\pi^2 \nu_i^2$.

The force constants may be evaluated from the observed benzene spectrum. The mean values[2] from benzene and benzene-d_6 are: K = 7.595; k = 0.656; q = 5.079, all in units of 10^5 dynes per cm. With the aid of this single set

[1] WILSON, loc. cit.
[2] Cf. LORD and ANDREWS, loc. cit.

of constants we may calculate the accompanying frequency table:

Table XI.

Compound		Frequency in cm.$^{-1}$			
		ν_1	ν_{12}	ν_2	ν_{13}
C_6H_6	obs.	992.5	—	3061.5	—
	calc.	993.8	1011.8	3070.3	3071.0
sym-$C_6H_3D_3$	obs.	956.6	1003.9	3055.1	2283.8
	calc.	951.2	1004.5	3070.7	2285.8
C_6D_6	obs.	945.2	—	2293.2	—
	calc.	944.6	961.2	2284.8	2286.7

It will be seen that the agreement with observation is good; in particular the wide separation of ν_1 and ν_{12} in sym-benzene-d_3 is rather well calculated. The fact that we are able to compute so closely the positions of the components of the doublet supports the assignment of the upper component to ν_{12}. The discrepancies between observation and calculation of ν_2 and ν_{13} may be ascribed chiefly to anharmonicity, the mean value of the constant q being too large for benzene and too small for benzene-d_6.

The agreement is close enough to warrant a computation of the amplitudes for the four A_1' frequencies. The amplitudes implicit in Equations (1) for vibrational quantum number $\frac{3}{2}$ are listed in Table XII, Column 2. It will be seen immediately from the numerical values of the amplitudes that the four A_1' vibrations may be regarded as essentially the totally symmetrical vibrations of two superposed but independent triangular molecules. In ν_1 and ν_{13} the amplitudes of the hydrogen atoms and of their parent carbon atoms are small compared with those of the deuteriums

and of the other carbons. In ν_{12} and ν_2, on the other hand, the motion is essentially that of the triangle $(C\text{-}H)_3$, the deuterium atoms and the other carbon atoms remaining practically at rest. The positions of ν_1 and ν_{12} — which

Table XII.

Amplitudes in 10^{-10} cm.				Transformation coefficients		Change of polarisability in 10^{-25} c.c.		Intensity	Depolarization
C_H	C_D	H	D	ξ	η	A	γ	I	ϱ
0.830	4.805	0.927	6.083	0.799	0.0407	4.97	1.53	1.00	0.10
5.015	—0.148	5.681	—0.193	0.683	0.0014	4.10	1.18	0.67	0.09
0.939	—0.003	—9.869	0.002	0.001	0.7043	—2.97	—2.34	0.75	0.40
0.007	—1.612	0.018	7.573	—0.113	—0.6064	—3.24	—2.22	0.76	0.34

(row labels: ν_1 ...., ν_{12} ..., ν_2 ...., ν_{13} ...)

appear anomalous from the point of view illustrated by Fig. 3 — are thus simply to be understood as the result of the special mechanical situation existing in sym-benzene-d_3. When a straightforward quantitative calculation of the frequencies is carried out, experiment and calculation agree.

b. Approximate Calculation of Intensities in Sym-Benzene-d_3.

If one regards the A_1' vibrations as approximately those of two independent equilateral triangles, one can explain in a simple and pictorial fashion several features of the Raman spectra of benzene and its symmetrical tri derivatives. For example it is possible to estimate in the following way the intensity relationships of the A_1' frequencies from the intensities of the A_{1g} vibrations in benzene and benzene-d_6. It is known[1] that the polarizability changes, $\Delta \alpha$ and $\Delta \alpha'$,

[1] LORD and TELLER, J. Chem. Soc., London, 1937, p. 1728.

for ν_1 in benzene and benzene-d_6 are nearly equal, the decreased amplitude of the carbon atoms in the latter being more or less counterbalanced by an increased amplitude of the deuterium atoms. Provided that this same sort of compensation holds for the vibrations of the triangles[1], the intensity of ν_1, the deuterium triangular vibration, should be about equal to that of ν_{12}, the hydrogen triangular vibration. The sum of the two should be rather close to that of ν_1 in A_{1g}, since the amplitudes in ν_1 and ν_{12} in A_1' are respectively larger than those of ν_1 in benzene-d_6 and in benzene by about $\sqrt{2}$. This compensates for the fact that only one triangle contributes to the individual intensities in A_1' rather than two superposed and cooperating triangles as in A_{1g}. Small deviations from the approximation of equality can be estimated by noting in Table XII, Column 2, that the "hydrogen triangle" does contribute a little to the polarizability change due to ν_1, and that the other triangle l o w e r s the change in ν_{12} a trifle. The addition to $\Delta a'$ in ν_1 is about 17 $^0/_0$, and the decrement in ν_{12} about 3 $^0/_0$. Hence the intensity ratio of ν_{12} to ν_1 in A_1' should be

$$\frac{I_{12}}{I_1} = \left(\frac{\Delta a\ (1-0.03)}{\Delta a'\ (1+0.17)}\right)^2 = \frac{0.94}{1.37} = 0.69.$$

The intensity of the two lines together should be about equal to that of ν_1 in benzene or in benzene-d_6.

Since the anisotropy of ν_1 is about equal in benzene and benzene-d_6, we should expect ν_1 and ν_{12} in A_1' to exhibit the same depolarization factor, namely $\varrho = 0.09$.

The above reasoning, combined with the observed

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[1] It should hold, because the amplitude ratios $C_H : H$ and $C_D : D$ both in ν_1 and in ν_{12} are very nearly equal to their respective values in ν_1 in benzene and benzene-d_6.

equality of intensity of ν_2 in benzene and in benzene-d_6, leads also to the conclusion that the intensities of ν_2 and ν_{13} in A_1' should be very nearly equal (no correction is necessary here) and should be approximately half of the intensity of ν_2 in benzene. ϱ for ν_2 in A_1' should be 0.4 and for ν_{13}, 0.35[1].

In addition it is possible on the basis of the "triangle picture" of the A_1' vibrations to understand the striking constancy of the 1000 cm.$^{-1}$ frequency found in symmetrical tri-derivatives of benzene[2]. If the mass of the deuterium atoms be greatly increased, it is found from Equations (1) that the amplitudes D and C_D in ν_{12} and ν_2 practically become zero, and that amplitudes H and C_H change very little from the tabulated values. Thus we can see that as long as the force system of the "hydrogen triangle" $(CH)_3$ is essentially unaltered, the totally symmetrical vibrations of the triangle, ν_{12} and ν_2, will be independent of the nature and mass of the symmetrically substituted groups. Not only will the frequency remain constant in these derivatives, but also the intensity and polarization of the Raman line. We can therefore explain the high intensity—it should be half as intense as the 992 cm.$^{-1}$ line in benzene—and strong polarization — $\varrho = 0.09$ in principle — of this line which led observers[3] to attribute it to the same mode of vibration as ν_1 in benzene, and to conclude therefrom that benzene had D_{3h} symmetry.

[1] Cf. LORD and TELLER, loc. cit., p. 1736.

[2] KOHLRAUSCH, Physik. Zeitschr. **37**, 58 (1936).

[3] KOHLRAUSCH, Zeitschr. phys. Chem. B, **30**, 308 (1935) and references there cited. KOHLRAUSCH has recently shown (Naturwiss. **39**, 635 (1937)) on general dynamical grounds that ν_{12} in symmetrical tri-derivatives should lie in the approximate range 990—1010 cm.$^{-1}$. His method of proof gives no insight into the nature of the vibration, however, and cannot be directly applied to yield information concerning intensities and depolarization factors.

The same point of view leads to the prediction that all symmetrical tri derivatives of benzene-d_6 (except sym-$C_6H_3D_3$) should possess a strong line of very nearly half the intensity of ν_1 in benzene-d_6, and with a depolarization factor 0.09, quite close to 950 cm.$^{-1}$.

c. Precise Calculation of Intensities in Sym-benzene-d_3.

From the amplitudes of the A'_1 frequencies in sym-benzene-d_3 as listed in Table XII it is possible to make a precise calculation of intensities and polarizations of the Raman lines of the A'_1 class by the method of Lord and Teller[1]. By their method the first step is to relate the various amplitudes in the A'_1 vibrations to the amplitudes in those vibrations whose intensities serve as a standard of comparison. In our instance the latter are the vibrations of classes A_{1g} and B_{1u} in benzene. The relations have the form:

$$\left.\begin{aligned}
\chi_{CH} &= \xi\chi_{C_1} + \zeta\chi_{C_{12}} + \eta\chi_{C_2} + \vartheta\chi_{C_{13}} \\
\chi_{CD} &= \xi\chi_{C_1}^* + \zeta\chi_{C_{12}}^* + \eta\chi_{C_2}^* + \vartheta\chi_{C_{13}}^* \\
\chi_{H} &= \xi\chi_{H_1} + \zeta\chi_{H_{12}} + \eta\chi_{H_2} + \vartheta\chi_{H_{13}} \\
\chi_{D} &= \xi\chi_{H_1}^* + \zeta\chi_{H_{12}}^* + \eta\chi_{H_2}^* + \vartheta\chi_{H_{13}}^*
\end{aligned}\right\} \quad (2)$$

In these equations the χ's are amplitudes, the nature of each being specified by its subscript. The four on the left are those listed for any one frequency of class A'_1 in Table XII. The χ's on the right hand side of each equation represent amplitudes in benzene. χ_{C_1} means, for example, the amplitude of the carbon atoms in ν_1. The *'s denote the amplitudes of carbon and of hydrogen atoms 1, 3, and 5 (cyclic enumeration) as distinguished from carbon and

---

[1] Lord and Teller, loc. cit.

hydrogen atoms in the 2nd, 4th and 6th positions. ξ, ζ, η and ϑ are purely numerical coefficients having one set of values for each of the four frequencies in class A_1'. The utility of the coefficients lies in the fact that by means of them the polarizability changes due to each of the four frequencies in A_1' may be reckoned from the polarizability changes in the four frequencies of symmetry A_{1g} and B_{1u} in benzene. For example, the relationships for ν_1 in A_1' are:

and
$$A_{1'} = \xi_1 A_1 + \zeta_1 A_{12} + \eta_1 A_2 + \vartheta_1 A_{13}$$
$$\gamma_{1'} = \xi_1 \gamma_1 + \zeta_1 \gamma_{12} + \eta_1 \gamma_2 + \vartheta_1 \gamma_{13}$$

in which $A_{1'}$ and $\gamma_{1'}$ are the respective symbols[1] for the isotropic and anisotropic parts of the polarizability change due to ν_1 in sym-benzene-d_3. The A's and γ's on the right are the corresponding quantities for the benzene frequencies whose numbers they carry as subscripts. Similar equations obtain for A and γ in the other three A_1' frequencies.

The well-known expression:

$$I_{rel} = \text{const. } (5 A^2 + 13 \gamma^2)$$

gives the relation between the quantities A and γ and the intensity, I_{rel}, of the Raman line, say ν_1 in A_1', referred to some standard intensity (e.g., that of ν_1 in benzene). The value of the proportionality constant depends of course on the standard chosen. The depolarization factor, ϱ, is:

$$\varrho = \frac{6\gamma^2}{5 A^2 + 7\gamma^2}.$$

[1] Note that $A_{1'}$ is a symbol for a physical quantity, and is not to be confused with A_1', which has an entirely different, purely descriptive significance as the symbol for a symmetry class.

To calculate I_{rel} and ϱ we take the values of A_1, A_2, γ_1 and γ_2 from the paper of Lord and Teller. The fact that A_{12}, A_{13}, γ_{12} and γ_{13} are zero because of symmetry frees us from the necessity of determining the coefficients ζ and ϑ. The coefficients ξ and η for the four A_1' frequencies are found without the necessity of computing B_{1u} amplitudes by using the relationships $\chi_{C_{12}} = -\chi_{C_{12}}^*$; $\chi_{C_{13}} = -\chi_{C_{13}}^*$ and $\chi_{H_{12}} = -\chi_{H_{12}}^*$; $\chi_{H_{13}} = -\chi_{H_{13}}^*$ which are required by the B_{1u} symmetry.

The results of calculations made in this way are listed in the last four columns of Table XII. The intensities are referred to the intensity of ν_1 in A_1' as unity. If it is desired to convert them to the scale used by Lord and Teller (ν_1 in benzene $= 10$) it is only necessary to multiply each by a factor of seven.

We should point out here that our calculation of intensities has been made from amplitudes corresponding to an assumed potential system. In their calculations Lord and Teller had sufficient data to utilize a perfectly general potential system, and their amplitudes are exact within the limits of the assumption of a harmonic force field. The amplitudes given in Table XII are probable pretty close to the correct values, however, because we have found that the Wilson potential system gives almost exactly the values listed by Lord and Teller for ν_1 and ν_2 in benzene and benzene-d_6, and because the equations (1) come very close to giving the observed A_1' frequency values.

d. Perturbation Calculation of $\dfrac{I_{12}}{I_1}$.

If we were able to carry out calculations similar to the preceding for the other "anomalous" separations and intensities of ν_1 and ν_{12}, the same sort of agreement with ex-

periment would doubtless be found. It is simpler and more fruitful, however, to consider the frequency relationships of ν_1 and ν_{12} from a somewhat different standpoint. Let us suppose that instead of replacing the hydrogen atoms stepwise by deuterium in preparing the deuterated benzenes, we had simply increased the mass of all the H-atoms by one-sixth atomic unit at each step. We would then obtain five molecules, all of D_{6h} symmetry, intermediate between benzene and benzene-d_6. The values of ν_1 and ν_{12} for these five should certainly be given by the dotted lines in Fig. 3, since ν_1 and ν_{12} can never interact in molecules of D_{6h} symmetry. If we perturb slightly the vibrations ν_1 and ν_{12} in the D_{6h} molecules by a redistribution of the total hydrogen mass[1] we may investigate the resulting interaction of ν_1 and ν_{12}, if any, by applying perturbation theory in the manner of FERMI[2].

The energy of the D_{6h} vibrations ν_1 and ν_{12} in terms of their normal coordinates q_1 and q_{12} is:

$$2H = \dot{q}_1^2 + \dot{q}_{12}^2 + 4\pi^2\nu_1^2 q_1^2 + 4\pi^2\nu_{12}^2 q_{12}^2 .$$

By making the substitution $\nu_{12} + \nu_1 = S$, $\nu_{12} - \nu_1 = \Delta$ we rearrange to

$$2H = \dot{q}_1^2 + \dot{q}_{12}^2 + \pi^2 S^2 (q_1^2 + q_{12}^2) + 2\pi^2 \Delta S (q_{12}^2 - q_1^2) + \\ + \pi^2 \Delta^2 (q_1^2 + q_{12}^2) .$$

If the distribution of mass among the hydrogen atoms now be changed, the symmetry of the molecule will alter and changes must therefore be made in the energy expression.

---

[1] E. g. by changing from the hypothetical molecule $C_6H_6^{1.5}$ to one of the isomers of $C_6H_3D_3$, or by going from $C_6H_6^{1.67}$ to a $C_6H_2D_4$ isomer.

[2] FERMI, Zeitschr. f. Phys., 71, 250 (1931); cf. also PLACZEK, Handb. d. Radiolog. Bd. VI/2, p. 316 ff.

By far the most important of these changes should be the introduction of a quadratic term involving the crossproduct $q_1 q_{12}$. The coefficient, β, of the crossterm is zero in the D_{6h} molecules because of symmetry. Other changes include the addition of small corrective terms involving the $\dot{q}$'s, but these ought to be quite small because the total mass of the hydrogen atoms remains constant. The energy expression then takes the form:

$$
\begin{aligned}
2H = \ & \dot{q}_1^2 + \dot{q}_{12}^2 + \pi^2 S^2 (q_1^2 + q_{12}^2) && \text{(a)} \\
& + 2\pi^2 \varDelta S (q_{12}^2 - q_1^2) + 2\beta q_1 q_{12} && \text{(b)} \\
& + \pi^2 \varDelta^2 (q_1^2 + q_{12}^2) + f(\dot{q}_1, \dot{q}_{12}) && \text{(c)}
\end{aligned} \quad \right\} \quad (3)
$$

Since in the D_{6h} molecules $\varDelta \simeq 0.01 \, S$, we shall feel justified in regarding the terms in (a) as our unperturbed energy expression, the terms in (b) as a small perturbation, and those in (c) as negligible.

The energy levels and wave functions corresponding to (a) are simply those of a doubly-degenerate harmonic oscillator. The levels are given by:

$$
W_n^0 = (n+1) \frac{hS}{2}
$$

in which n is the total vibrational quantum number. Associated with the nth level are $n + 1$ wave functions. Since the Raman frequencies ν_1 and ν_{12} are chiefly due to transitions from the level $n = 0$ to the level $n = 1$, we shall write down the form of the wave functions for the first two levels. For $n = 0$,

$$
\psi_0^0 = N_0 \, e^{-\frac{\pi^2 S}{h} (q_{12}^2 + q_1^2)}
$$

in which N_0 is a numerical factor. For $n = 1$ there are two wave functions:

$$\psi^0_{1_{10}} = N_1 e^{-\frac{\pi^2 S}{h}(q^2_{12} + q^2_1)} q_{12}$$

$$\psi^0_{1_{01}} = N_1 e^{-\frac{\pi^2 S}{h}(q^2_{12} + q^2_1)} q_1$$

N_1 is a numerical factor. It will be noticed that the algebraic symmetry properties of $\psi^0_{1_{10}}$ are those of the normal co-ordinate q_{12}, and of $\psi^0_{1_{01}}$, those of q_1.

These energy levels and wave functions are to be corrected for the perturbation terms (b) by means of the perturbation theory of degenerate levels[1]. The correction to W^0_0 and to ψ^0_0 is zero. To W^0_1 we must add the corrective term W'_1 obtained by solving the secular determinant:

$$\begin{vmatrix} \dfrac{h\varDelta}{2} - W'_1 & \dfrac{h\beta}{4\pi^2 S} \\[2ex] \dfrac{h\beta}{4\pi^2 S} & \dfrac{-h\varDelta}{2} - W'_1 \end{vmatrix} = 0 .$$

Thus we find:

$$\begin{aligned} W_1 &= W^0_1 + W'_1 \\ &= W^0_1 \pm \sqrt{\left(\frac{h\varDelta}{2}\right)^2 + \left(\frac{h\beta}{4\pi^2 S}\right)^2}. \end{aligned} \qquad (4)$$

The double level W^0_1 therefore splits symmetrically into two under the action of the perturbation. The wave functions of the two split levels have the form:

$$\left.\begin{aligned} \psi_{1_{10}} &= A(B\psi^0_{1_{10}} - C\psi^0_{1_{01}}) \\ \psi_{1_{01}} &= A(C\psi^0_{1_{10}} - B\psi^0_{1_{01}}) \end{aligned}\right\} (5)$$

[1] See, for example, PAULING and WILSON, Quantum Mechanics, (McGraw-Hill, New York. 1935). Page 165.

where the coefficients of the ψ^0's are:

$$A = \left[\left(\frac{h\beta}{4\pi^2 S}\right)^2 + \left(\frac{h\Delta}{2} + \sqrt{\left(\frac{h\Delta}{2}\right)^2 + \left(\frac{h\beta}{4\pi^2 S}\right)^2}\right)^2\right]^{-\frac{1}{2}}$$

$$B = \left[\frac{h\Delta}{2} + \sqrt{\left(\frac{h\Delta}{2}\right)^2 + \left(\frac{h\beta}{4\pi^2 S}\right)^2}\right]$$

$$C = \frac{h\beta}{4\pi^2 S}.$$

The formulation of each ψ_1 by combination of the ψ_1^0's shows that the characteristics of the perturbed levels will be a mixture of the properties of the unperturbed ones. The numerical coefficients AB and AC are analogous to the ξ's and η's by which the amplitudes of the A_1' frequencies in sym-benzene-d_3 were expressed in terms of the A_{1g} and B_{1u} frequencies in benzene. AB and AC depend essentially on Δ and β alone. It is therefore helpful to consider the following limiting cases:

(1) If we allow $\beta \to 0$, Δ being kept constant and finite,

$$\psi_{1_{10}} \to \psi_{1_{10}}^0 ; \quad \psi_{1_{01}} \to \psi_{1_{01}}^0 ;$$

and

$$W_1 \to W_1^0 \pm \frac{h\Delta}{2} \ (\text{i. e., } \frac{3}{2}h\nu_1 \text{ and } \frac{3}{2}h\nu_{12}).$$

That is, removal of the interaction between ν_1 and ν_{12} leads, as we should expect, to the original wave functions and energy levels of the D_{6h} molecule.

(2) If $\Delta \to 0$, β remaining constant and finite,

$$\psi_{1_{10}} \to \frac{1}{\sqrt{2}}(\psi_{1_{10}}^0 - \psi_{1_{10}}^0) ; \quad \text{i. e., } \psi_{1_{10}} \to \text{const.} \cdot e^{-\frac{\pi^2 S}{h}(q_{12}^2 + q_1^2)} \cdot (q_{12} - q_1)$$

$$\psi_{1_{01}} \to \frac{1}{\sqrt{2}}(\psi_{1_{10}}^0 + \psi_{1_{01}}^0) ; \quad \text{i. e., } \psi_{1_{01}} \to \text{const.} \cdot e^{-\frac{\pi^2 S}{h}(q_{12}^2 + q_1^2)} \cdot (q_{12} + q_1)$$

and
$$W_1 \to W_1' \pm \frac{h\beta}{4\pi^2 S}$$

The physical significance of the ψ's in limiting case (2) may be grasped by considering the factors $(q_{12} - q_1)$ and $(q_{12} + q_1)$. Here the normal coordinates q_1 and q_{12} differ only in that the amplitudes of atoms in the 2, 4 and 6-positions in the molecule have opposite signs in the two coordinates[1], i. e., have all positive signs in q_1 and all negative in q_{12}. Hence the amplitudes of all six atoms in the 2, 4 and 6-positions must be zero when ψ contains $(q_{12} + q_1)$ as a factor, and those of the 1, 3 and 5 atoms must vanish if ψ contains $(q_{12} - q_1)$. Symmetry requires the amplitudes of all carbon atoms as well as of all hydrogen atoms to be equal in q_1. Therefore if the accidental degeneracy of ν_1 and ν_{12} is exact, the two vibrations are independent "triangular" vibrations of the sort discussed on page 30. Thus in the limit (2) the result we have found to hold approximately for ν_1 and ν_{12} in the A_1' vibrations of sym-benzene-d_3 holds precisely in any perturbed D_{6h} derivative.

To discover how closely ν_1 and ν_{12} in the various deuterated benzenes approach one or another of the above extremes, it is necessary to consider the relative magnitudes of Δ and β. We have seen that in all the hypothetical D_{6h} molecules between C_6H_6 and C_6D_6 Δ has a value of about 16 cm.$^{-1}$. This is small compared with S, but by no means zero. We should therefore expect to find the limit (2) approached only if β were to become quite large. We can state at once, however, that we know from considerations

---

[1] This difference follows from the symmetry of the A_{1g} and B_{1u} vibrations, from the assumption (experimentally reasonable) that $\nu_2 = \nu_{13}$ both in benzene and in benzene-d_6 and from the assumption (which is not correct experimentally, but which limiting case (2) implies) that $\nu_1 = \nu_{12}$ both in benzene and in benzene-d_6.

of symmetry that β is identically zero for perturbations of C_{2v}^* and V_h symmetry, i. e. in the four ortho and para deuterium derivatives. Hence in these compounds limiting case (1) obtains, and we expect to find no perturbation interaction of ν_1 and ν_{12}. We have no independent way of finding the values of β in the other compounds, but we can estimate them in a relative way as follows: Let us adopt as a standard the value, β_1, of β in benzene-d_1. If the intro- duction of one deuterium atom into benzene gives rise to the term $\beta_1 q_1 q_{12}$ in the potential energy expression, the introduction of a second should be expected to give rise to a like term. When the second atom is introduced ortho or para to the first, however, the sign of the term is reversed and we find, as we have just stated, that the value of β for ortho and para derivatives is zero. On the other hand we should find in meta-benzene-d_2 that the terms are of like sign and therefore expect that β in this compound should have twice the value of β_1. The same reasoning leads to $3\beta_1$ for β in sym-benzene-d_3, and to β_1 for the other derivatives except those of symmetry C_{2v}^* and V_h. We can now evaluate β_1 empirically from the separation of ν_1 and ν_{12} in benzene-d_1 (for example), and determine the energy levels in the remaining compounds by Equa- tion (4). The separations of the levels calculated in this way are listed in Table XIII. The whole number n listed in column 3 is the numerical factor by which β_1 must be multiplied to obtain the value of β for the compound under consideration. The actual frequencies of ν_1 and ν_{12} can be found by adding and by subtracting half the splitting to, and from, $\dfrac{S}{2}$. The calculated and observed splittings are in agreement except for the two meta- and the symmetrical tri compounds. The separations for these compounds have

been overestimated, but at least we can explain in a semi-quantitative fashion the irregularities in the positions of ν_1 and ν_{12} in all the deuterated benzenes.

The wave functions (5) may be used in straightforward fashion (following PLACZEK, loc. cit. p. 321) to determine

Table XIII.

Separation and Relative Intensities of ν_1 and ν_{12}.

Compound	S (calc.)	n	Splitting		$\frac{I_{12}}{I_1}$	
			(calc.)	(obs.)	(calc.)	(obs.)
C_6H_6	2000	0	15.5	—	(0)	—
C_6H_5D	1994	1	(27.7)	27.7	0.28	0.37
$C_6H_4D_2$ o	1968	0	15.5	16.8	(0)	0.15
m	1968	2	48.8	35.6	0.39	0.47
p	1968	0	15.5	—	(0)	—
$C_6H_3D_3$ s	1953	3	71.6	47.3	0.51	0.63*
v	1953	1	28.0	27.0	0.27	0,35
u	1953	1	28.0	21.0	0.15	0.24
$C_6H_2D_4$ o	1937	0	15.5	13.6	(0)	0.18
m	1937	2	49.6	32.6	0.36	0.35
p	1937	0	15.5	—	(0)	—
C_6HD_5	1921	1	28.3	26.2	0.26	0.30
C_6D_6	1906	0	15.5	—	(0)	—

the intensity ratio of ν_{12} to ν_1. The derivation of the expression for this ratio is much simplified when we make use of the fact that the polarizability change due to ν_{12} in a D_{6h} molecule is zero by symmetry. We therefore obtain (cf. PLACZEK, Eq. (12) p. 321)

$$\frac{I_{12}}{I_1} = \frac{2W_1' - \Delta}{2W_1' + \Delta} \tag{6}$$

where $2W_1'$ is the observed splitting of the levels, and Δ is their unperturbed separation. The intensity ratios given

* Cf. also the calculated values on p. 32 and in Table XII.

by this expression are shown in Column 6 of Table XIII. These may be compared with the micro-photometrically measured values in Column 7. The agreement is as satisfactory as can be expected. The finite intensity observed for ν_{12} in the two ortho compounds is not in real contradiction to the calculated value zero. Although no intensity should accrue to ν_{12} because of interaction with ν_1 in these compounds, the small intensity actually observed arises from an allowed but very weak interaction with frequencies other than ν_1 (cf. Fig. 2).

The perturbation procedure leads also to the conclusion that ν_1 and ν_{12} should have, except in the ortho derivatives, the same depolarization factor. We cannot say a priori what this factor will be in the several derivatives, but it may be inferred from the equality of ϱ for ν_1 in benzene and benzene-d_6 that ν_1 in the intermediate hypothetical D_{6h} compounds should exhibit this same value of ϱ. This fact, coupled with the procedure by which Equation (6) was derived, leads to the conclusion that ν_1 and ν_{12} should possess the same depolarization factor, 0.09, in all the deuterated benzenes except the ortho and para di and tetra derivatives. ϱ for ν_{12} in the ortho compounds should be $\frac{6}{7}$ by symmetry.

The pertubation procedure we have used in computing the various separations and intensities of ν_1 and ν_{12} perhaps appears crude, and the results obtained with it may seem disappointingly approximate in character. Certainly no one would resort to such approximation methods if it were possible to use more rigorous procedures. The example of our calculations for ν_1 and ν_{12} in sym-benzene-d_3 illustrates the point. Here one can make more precise calculations of frequencies and intensities[1]. A comparison of these cal-

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[1] On the basis of an assumed potential function, however.

culations with those made on the assumption of resonance interaction shows that at least the latter give a quite correct qualitative picture, and approach rather closely to a correct quantitative one.

The chief value of the perturbation calculations, however, is the corroboration which they lend to the D_{6h} structure. If a D_{6h} structure be assumed for benzene, the explanation we have given of the positions and relative intensities of ν_1 and its companion follows readily and quite completely. On the assumption of any other symmetry, and in particular of such symmetries as D_{3h} (KEKULÉ structure) and D_{3d} (bent structure), the irregularities of frequency and intensity may be explained only in complex and ad hoc fashion. The structures other than D_{6h} cannot be excluded by a strictly logical process, but when we may choose between a simple (D_{6h}) and a complicated structural basis for explaining observed spectra, our choice is clear. It is in this sense that the variations in ν_1 and ν_{12} in the deuterated benzenes may be said to offer "strong support" to the D_{6h} structure.

e. Fine Structure of ν_1.

The discussion just given of the interaction between ν_1 and ν_{12}, and of the intensity changes resulting therefrom, is of assistance in explaining the complicated structure of ν_1 in benzene. Under high dispersion this frequency appears not as a single line but as a strong central line with four weak satellites, a pair on each side. The fine structure has been studied by a number of investigators since its original discovery by HOWLETT[1]. The results of four of these investigations are summarized in Table XIV. While there are one

[1] HOWLETT, Nature **128**, 796 (1931).

or two minor differences in the results, it will be seen that the four studies are essentially in very good agreement as to the relative spacings of the components. Other investigations[1] have generally been carried out with spectrographs

Table XIV.

Compo-nent	Frequency in cm.$^{-1}$ and Separation from Component III				
	a	b	c	d	Average
I	980.3 −11.9	979.0 −13.5	979.4 −13.6	— —	979.6 −13.0
II	983.9 −8.3	984.0 −8.5	983.3 −8.9	984.5 −8.2	983.9 −8.5
III	992.2	992.5	992.2	992.7	992.4
IV	998.8 6.6	999.0 6.5	999.1 6.9	— —	999.0 6.7
V	1005.3 13.1	1005.0 12.5	1004.8 12.6	— —	1005.0 12.7

Reference a: HOWLETT, Can. Journ. Res. **5**, 572 (1931).
          b: GRASSMANN and WEILER, Zeitschr. f. Phys. **86**, 321 (1933).
          c: EPSTEIN and STEINER, Zeitschr. phys. Chem. **B 26**, 131 (1934).
          d: CHENG, HSUEH and WU, Journ. Chem. Phys. **6**, 8 (1938).

of lower dispersion than those used in the four researches listed in the Table.

An examination of the fine structure was made by one of us (A. L.) in 1931, although the results of the study had not been published previous to our earlier communication on this subject[2]. The frequencies and relative spacings obtained in 1931 agree well with the averages listed in Table XIV.

[1] Cf. the summary of ANGUS, INGOLD and LECKIE, J. Chem. Soc. (London) **1936**, p. 928.
[2] LANGSETH and LORD, Journ. Chem. Phys. **6**, 203 (1938).

At the same time visual estimates of the relative inten-
sities were made which agree roughly with estimates by
other investigators (refs. a, b, d in Table XIV). All the
visual estimates are in accord that satellite V is by far the
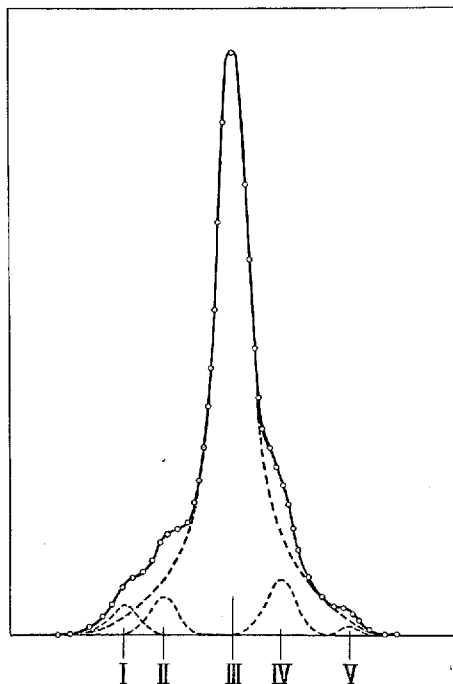
Fig. 4.

weakest, that II and IV are of about equal intensity, and
that I is approximately half as strong as II. Because visual
estimates are of little more than qualitative significance,
and because our interpretation of the fine structure enables
a quantitative intensity calculation for the components, we
have made a microphotometric determination of the
intensities.

An intensity curve for the complex line is shown in Fig. 4.
It was obtained from a microphotometer tracing with the

help of the blackening-intensity calibration curve charac-
teristic of the type of plate used in photographing the
spectrum (Ilford Zenith). Experience has shown the blacken-
ing-intensity curve for this kind of plate varies little from
one plate to another. Therefore it has been possible to
translate blackening into intensity even though no graduated
intensities had been recorded on the plate itself. No cor-
rection for the variation of plate sensitivity with wavelength
has been necessary since the range of wavelength is very
narrow.

The curve has been resolved into its components by
assuming the shape shown in Fig. 4 for component III
and then subtracting the intensity of that component from
the total. The relative intensities have been determined by
integration of the curves of each component. Since the
assumption of the shape of III is to a certain extent arbi-
trary, the intensities of the satellites may be somewhat in
error even if the outline intensity is accurately plotted. It
is not likely that the positions of the maxima in cm.$^{-1}$ are
much in error, however, because they are less sensitive
than the areas to the choice of the shape of component III.
For this reason we shall adopt the frequency values given
by Figure 4 as the "best" values for the components rather
than try to average our values with those of other observers.
As one can see from Table XV, this decision is not an
important one, since the values found from Fig. 4 agree
well with the averages given in Table XIV. The various
results yielded by Fig. 4 are listed in the rows marked "c"
in Table XV.

Since the calculation of the ratio of intensities of com-
ponents I and IV depends on the experimental intensity
ratio of the components of the doublet at 1600 cm.$^{-1}$ in

benzene, we have made a determination of the latter ratio. Fig. 5 gives the intensity curves for the doublet obtained in just the same way as the curves in Fig. 4. The integrated intensities of the doublet components have a ratio of 0.60 ± 0.05, the lower frequency being the more intense.

Table XV.

Component		I	II	III	IV	V
Frequency in cm.$^{-1}$	a	979.6	983.9	992.4	999.0	1005.0
	b	979.6	983.8	992.5	997.9	1005.5
	c	978.9	983.8	992.5	998.2	1006.4
	d	979.5	[986.3]	(992.5)	997.8	[ca. 1003]
Separation from Component III	a	— 13.0	— 8.5	—	6.7	12.7
	b	— 12.9	— 8.7	—	5.4	13.0
	c	— 13.6	— 8.7	—	5.7	13.9
	d	— 13.0	— 6.2	—	5.3	—
Intensity Relative to Component III	b	5	10	100	10	1
	c	3.5	4.2	100	5.3	0.6
	d	4.1	5.3	100	6.9	0.7
	e	4.5	(5.3)	(100)	6.8	0.8

a: Average values from Table XIV.
b: Visual measurements (1931).
c: Microphotometric measurements (1938).
d: Theoretical values.
e: Microphotometric intensities corrected.

Satellite II was first attributed to ν_1 in the molecule $C_5^{12}C^{13}H_6$ by GERLACH[1]. If one calculates the position of ν_1 in this molecule[2], one expects a decrease of 6.2 cm.$^{-1}$ from the position of ν_1 in benzene. The observed decrease, 8.7 cm.$^{-1}$, is 2.5 cm.$^{-1}$, or about 40 $\%$, larger (Table XV). This anomalously large decrease is similar to that found

[1] GERLACH, Sitz. Math.-Nat. Bayr. Akad. **1932**, 39.
[2] By computing ν_1 in the hypothetical molecule $C_6^{12.167}H_6$; cf. TELLER, loc. cit. p. 142 ff.

for ν_1 in benzene-d_1, and may be attributed to the same cause, namely, interaction between ν_1 and ν_{12}. If interaction were not present ν_{12} should shift from 1010 cm.$^{-1}$ in benzene to about 1003 cm.$^{-1}$ in $C_5^{12}C^{13}H_6$. Interaction decreases the size of the actual shift, however, and also leads to a transfer of intensity to ν_{12} from ν_1 such as we have found in the deuterated benzenes. It is therefore quite in accordance
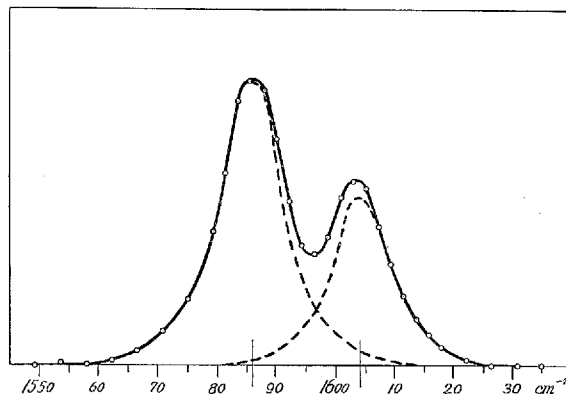
Fig. 5.

with our expectations that satellite II is accompanied by a weaker satellite (V) at 1005 cm.$^{-1}$. The intensity ratio of V to II may be computed by Equation (6), p. 43. For $2 W_1'$ we may use the frequency difference between V and II, i.e. 22.6 cm.$^{-1}$ (see Table XV), and for $2 W_1'—\varDelta$, twice the observed displacement of ν_1, 2×2.5 or 5.0 cm.$^{-1}$. We thus find $\varDelta = 17.6$ cm.$^{-1}$ (in fair agreement with the value used in Table XIII and in Fig. 3) and $2 W_1' + \varDelta = 40.2$ cm^{-1}. The intensity ratio is thus 0.124; hence satellite II ought to be eight times as strong as V. This agrees very well with the value of seven which may be calculated from data in Table XV, row c.

The total intensity of ν_1 and ν_{12} in $C_5^{12}C^{13}H_6$ ought to

be that of the unperturbed ν_1, and since this is approximately equal to the intensity of ν_1 in benzene, the total intensity of satellites II and V should be just that of III except for the rarity of $C_5^{12}C^{13}H_6$ molecules. If we assume the concentration of these to be six in one hundred molecules of benzene, we calculate that the individual intensities of II and V should be respectively 5.3 and 0.66, the intensity of the central line being set at 100. The calculated frequencies and intensities for II and V are shown in Table XV. The calculated frequencies are enclosed in square brackets to emphasize that these are not to be compared with experiment, since they are computed without taking account of resonance between ν_1 and ν_{12}.

The existence of satellites I and IV depends on the fact that the frequency of one of the non-totally symmetrical fundamentals in benzene, ν_8 at about 1600 cm.$^{-1}$, accidentally coincides with the sum of ν_1 and a lower frequency, ν_6 (vide infra, p. 56). This fortuitous resonance causes the same sort of splitting as that illustrated in Fig. 3, and results in a mixing of the wave functions of ν_8 and of $\nu_1 + \nu_6$ similar to that depicted by Equation (5). As a consequence of the mixing, a vibrational transition starting from the first exited level of ν_6 and ending on either of the first pair of resonance levels gives rise to Raman scattering very nearly equivalent, save for a numerical factor, to the scattering arising from a transition from the zero to the first excited level of ν_1. The frequencies of the two transitions starting from ν_6 are given simply by the difference between ν_6 (606.4 cm.$^{-1}$) and the frequencies of the doublet (1585.9 and 1604.2 cm.$^{-1}$; see Table X). These differences agree closely with the frequencies of satellites I and IV[1].

[1] The same interpretation of satellite I is given without further com-

A precise calculation[1] of intensities for the two transitions shows that the sum of the two should be very close to the intensity of ν_1 ($0 \to 1$ transition). Therefore to find the total intensity of satellites I and IV we need only to multiply the standard intensity of III (100) by the factor which determines the relative number of molecules occupying the first excited level of ν_6, namely: $2 \times \exp\left(\dfrac{-hc\tilde{\nu}_6}{kT}\right)$. Furthermore with the help of the mixed wave functions one finds that the intensity ratio of I to IV is the same as the ratio of the intensity of the upper component of the resonance doublet to that of the lower, provided that one neglects polarizability changes due to second-order transitions (i. e., the transition from the first excited level of ν_6 to the unperturbed first excited level of ν_8). Experimentally this ratio is 0.60 (see Fig. 5 above), and therefore the intensities of I and IV should be 4.1 and 6.9 at room temperatures.

The calculated frequencies and intensities for the various components are given in the rows marked "d" in Table XV. Comparison of the calculated frequencies with the average of the observed values shows excellent agreement for satellites I and IV, and a discrepancy for II which is well understandable in light of the existence of V. The closeness of the agreement strengthens our confidence in the validity of the interpretation.

The agreement of experimental and calculated intensities (rows "c" and "d", foot of Table XV) is not quite so good.

ment in Table 2 of the article of Grassmann and Weiler (ref. b, Table XIV). It is curious that they apparently overlooked the parallel interpretation of IV.

[1] The details of a similar calculation for the fine structure of the totally symmetrical frequency in carbon tetrachloride are given by Horiuti, Zeitschr. f. Phys. 84, 380 (1933).

The assumptions on which the calculations are based are doubtless more reliable than the intensity measurements, so that we may ascribe the discrepancies to experimental trouble. It is possible that the errors are the result of estimating incorrectly the shape of the lower part of component III in Fig. 4. More probably the error lies in the difficulty of measuring simultaneously and with accuracy the intensities of very strong and very weak lines. This difficulty is accentuated in the present instance because we have not determined directly the blackening curve for the spectrographic plate. To correct for this source of error we may multiply the intensities of all components except III by a factor 1.3, which is the factor required to raise the observed intensity of component II, 4.2, to the theoretical value 5.3. When this correction has been made, all the intensities agree very well with theory, as may be seen by comparing the last two rows of Table XV. We may say, therefore, that the observed intensities of components I, II, IV and V relative to one another are in good accord with theory, and that while their intensities with respect to III are uniformly too low by one-fourth, the discrepancy is not surprising in view of the difficulty of measuring accurately intensities differing by a factor of twenty.

The fine structure expected for ν_1 in benzene-d_6 is simpler than that in benzene. ν_8 appears in benzene-d_6 as a single line only, and therefore a satellite due to $\nu_8 - \nu_6$ should be lacking, since the product of the Boltzmann factor (0.1) and the intensity expected of second-order tones (< 0.01) is overwhelmingly small. The component $(\nu_1 + \nu_6) - \nu_6$ should coincide with ν_1.

The calculated shift of ν_1 in $C_5^{12}C^{13}D_6$ is 5.0 cm.$^{-1}$, and the observed one 5.7 cm.$^{-1}$. Here the difference is more

readily ascribable to experimental error than in benzene, but if we attribute all of it to interaction with ν_{12}, we may compute the intensity ratio of ν_{12} to ν_1 in $C_5^{12}C^{13}D_6$ as 0.03, i.e. ν_{12} should have only about $1/4$ the relative intensity of satellite V in benzene. ν_{12} should be higher than ν_1 by very nearly the same amount as in benzene, and therefore should lie in the neighborhood of 960 cm.$^{-1}$. Actually there is an extremely faint line at 962 cm.$^{-1}$, but its assignment is not entirely conclusive, because both ortho- and para-benzene-d_4 have their strongest lines at this point (at 960.0 ± 0.4 cm.$^{-1}$) and it is conceivable that the extended exposures which revealed the line may have been able to record the benzene-d_4 frequencies even though the total concentration of these lower deuterated benzenes was probably less than 0.02 $^0/_0$. That the line may actually be ν_{12} is given some support by the failure to observe the strongest frequency of meta-benzene-d_4 at 954 cm.$^{-1}$. This frequency should appear with not less than half the intensity of the 962 line if the latter is really due to the other benzene-d_4's.

Table XVI.

Fine Structure of ν_1 in Benzene-d_6.

No.	Frequency of Components in cm.$^{-1}$		Intensity of Components	
	Observed	Calculated	Observed	Calculated
I	939.5	940.2	10	5.8
II	945.2	(945.2)	(100)	(100)
III	962.1	960	0.1	0.2

The fine-structure data on benzene-d_6 are summarized in Table XVI. Not included in the Table are two very faint lines observed at 950.7 and 977.3 cm.$^{-1}$, which belong to benzene-d_5, and which are not to be expected in hydrogen-

free benzene-d_6. The latter of these lines has also been reported by ANGUS, INGOLD and LECKIE[1]. The difference tone $\nu_8 - \nu_6$ should lie in this neighborhood (ca. 975 cm.$^{-1}$), but, for reasons just given, should not be expected to make its appearance.

It should be added that the arguments mentioned on page 44 may be used to show that the four companions of ν_1 in benzene and the two in benzene-d_6 should have the same depolarization factor as the parent line. This agrees qualitatively with the observations of GRASSMANN and WEILER[2] and of CHENG, HSUEH and WU[3], who report that component II is highly polarized in benzene. The latter authors set an upper limit of 0.4 to ϱ.

A carbon isotope effect in ν_1 indicates that the effect may be present in other frequencies. In order for the effect to be observed, however, special conditions must prevail. ν_1 is an intense and a highly polarized (ergo very sharp) line, so that the C^{13} displacement of 8 cm.$^{-1}$ may be resolved by a powerful spectrograph. The remaining lines due to carbon frequencies in benzene are fuzzy because they are depolarized; furthermore they are much weaker than ν_1. Therefore a correspondingly weaker C^{13}-satellite as close as 8 cm.$^{-1}$ may be expected to fuse undetectably into the parent line. For this reason we need not pay further heed to the influence of C^{13} on the Raman lines of benzene.

The effect of the C^{13} isotope in the deuterium derivatives is complicated by the fact that the isotope may occupy several essentially different places in the carbon ring. For example in sym-benzene-d_3, there are two non-equivalent

[1] ANGUS, INGOLD and LECKIE, loc. cit. p. 930.
[2] Table XIV, ref. b.
[3] Table XIV, ref. d.

places for the isotope. As a result, the isotope in one place should produce a companion to ν_1 and in the other a companion to ν_{12} (cf. the discussion of the A'_1 frequencies, page 30). Low frequency satellites have in fact been observed accompanying both ν_1 and ν_{12} in sym-benzene-d_3, with respective separations of 6.3 and 8.2 cm.$^{-1}$. In the other derivatives, the effect is more complicated in principle because the number of non-equivalent positions is larger (except in the para compounds). Practically, however, the effect is similar to that observed in sym-benzene-d_3. It is not of great interest and we will not consider it further.

2. The Remaining Planar Carbon Vibrations.

Except for ν_1, the degenerate vibrations ν_6 and ν_8 are the only Raman-active carbon frequencies in benzene. ν_6 is essentially a bending vibration which lies at 606 cm.$^{-1}$. There are no planar frequencies in its immediate neighborhood, and its undisturbed course through the various deuterium derivatives can easily be traced. The total decrease in ν_6 from benzene to benzene-d_6 is 27 cm.$^{-1}$, and the expected stepwise decrement of 4.5 cm.$^{-1}$ per deuterium atom is usually observed rather closely. The degeneracy of the frequency is released in all intermediate derivatives except sym-benzene-d_3 and therefore the line should appear double in their spectra. Actually the separation of the doublet is so small (ca. 5 cm.$^{-1}$) and the lines are so fuzzy that it has been possible to secure definite resolution of the components only in two instances.

The stretching frequency ν_8 lies at 1600 cm.$^{-1}$ in benzene and at 1553 cm.$^{-1}$ in benzene-d_6. It appears as a doublet in the former because ν_8 is fortuitously close to the sum
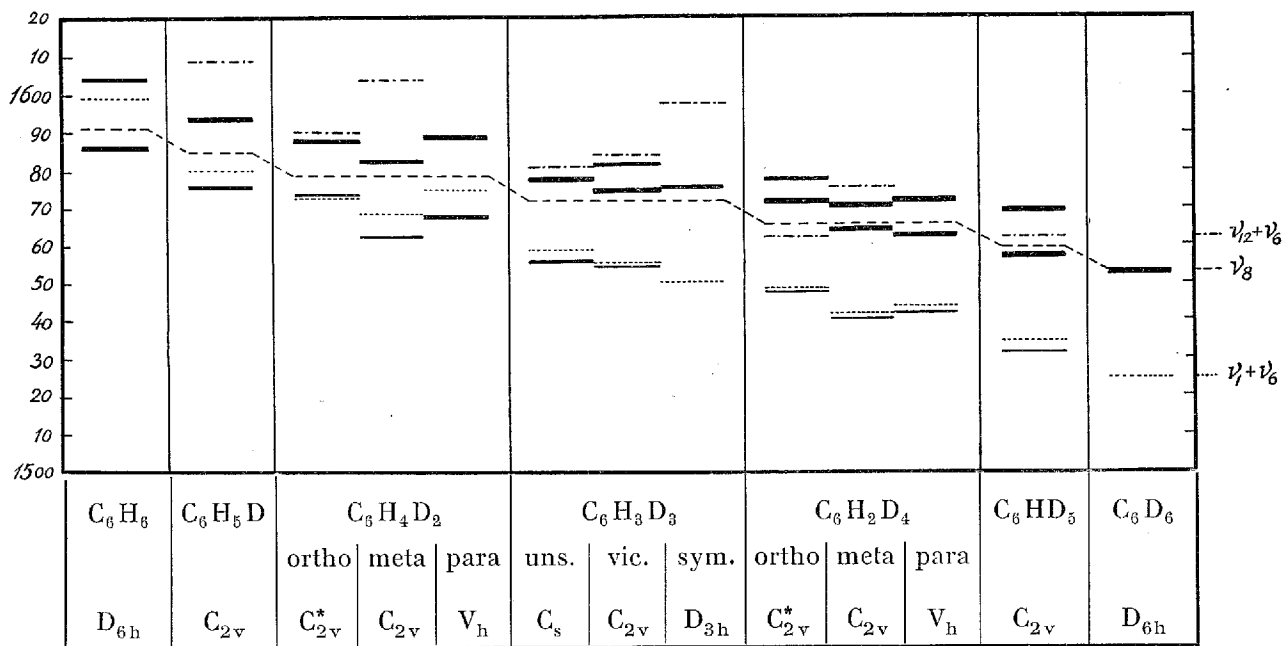
Fig. 6.

The solid lines indicate observed frequencies and the various broken lines the calculated values. In the text the overtone $\nu_1 + \nu_6$ is denoted I and $\nu_{12} + \nu_6$ II for the sake of brevity.

of ν_1 and ν_6, and the consequent interaction of the funda-
mental with the overtone leads to splitting. The accidental
coincidence no longer obtains in benzene-d_6, and if there
is interaction, it is imperceptible. The proximity of ν_8 to
the overtone complicates the problem of interpreting ν_8 in
the deuterated compounds. Further complication ensues
because ν_{12} lies close to ν_1 and therefore the combination
$\nu_6 + \nu_{12}$ can also interact with ν_8. This interaction is for-
bidden by symmetry in benzene, but in all the derivatives
except para-benzene-d_2 and para-benzene-d_4, and of course
benzene-d_6, some combination of ν_{12} and one of the com-
ponents of ν_6 (i.e., ν_{6a} or ν_{6b}) is permitted to interact with
one or the other of the components of ν_8. It is possible to
compute rather closely the unperturbed positions of all
these overtones and to obtain therefrom some idea of the
structure to be expected of the line due to ν_8 in the various
derivatives. Unfortunately it is an extremely difficult ex-
perimental problem to resolve this structure. ν_8 is doubly
degenerate and therefore usually splits into two close com-
ponents of which at least one is completely depolarized
and is correspondingly difficult to separate from its com-
panion (cf. the discussion of ν_6). In Fig. 6 the observed
components of ν_8 are plotted together with the predicted
stepwise shift in ν_8* and with the overtone $\nu_1 + \nu_6$ (I) and
$\nu_{12} + \nu_6$ (II). No attempt has been made to estimate theo-
retically the splitting of ν_8 when the degeneracy is released.
The overtones, which are in principle doublets, are also
plotted as single lines since it seems unlikely, from ex-
perience with ν_6, that they will be resoluble.

* Calculated as for ν_1 in Fig. 3. The unperturbed position of ν_8 in
benzene is estimated to be just as far below the midpoint of the reson-
ance doublet as the calculated position of $\nu_1 + \nu_6$ is above it.

The observed structure of the line generally agrees with that expected from the positions of the overtones. In benzene-d_1 and the benzene-d_2's ν_8 appears as a doublet of about the same separation as that in benzene, in accord with the fact that unperturbed ν_8 and overtone I lie close together. Overtone II appears as a weak line at the predicted point in benzene-d_1. In ortho-benzene-d_2 II lies so near one of the doublet lines that resolution is hardly to be expected, while in the para compound it is forbidden. It has not been found at the predicted place in meta-benzene-d_2. ν_8 lies halfway between I and II in sym-benzene-d_3, and since the separation of the overtones is almost 50 cm.$^{-1}$, it is not surprising that there seems to be no interaction. The line remains single and the overtones are not observed. The position of II is much closer to ν_8 in the other benzene-d_3's but its perturbing effect seems to be slight. It is possible to resolve ν_8 in the vicinal compound into two components of unequal intensity and about 7 cm.$^{-1}$ apart. This doublet is probably the result of the released degeneracy of ν_8, although it is of course conceivable that it arises from interaction of ν_8 with II. In unsym-benzene-d_3 ν_8 is a single line. Apparently neither release of degeneracy nor interaction with II is effective enough to make the components spectroscopically separable. The overtone I is found at the proper place in both compounds — just below its predicted position.

The structure of ν_8 in the remaining compounds (excluding benzene-d_6) is very similar to that in vic-benzene-d_3. The principal line is double and is accompanied by a weak satellite some 25 cm.$^{-1}$ below it. The doublet may be ascribed to the two components of ν_8, or, excepting the case of p-benzene-d_4, where interaction is forbidden by

symmetry, to interaction with II. The satellite is due to overtone I — its observed position is always a wave number or two lower than predicted, which is to expected from interaction with ν_8.

The foregoing discussion shows that there is no feature of the complex group of lines due to ν_8 which cannot be understood on the basis of what we know about this frequency in benzene and benzene-d_6. The purpose of our rather detailed study was to make as certain as possible that the observed structure of ν_8 could be quite completely understood without the necessity of postulating the influence of a nearly fundamental. If a fundamental of the proper symmetry existed in the 1600 cm.$^{-1}$ region, it might exert on ν_8 a perturbing effect like that of ν_{12} on ν_1. There is reason to suspect the existence of such a fundamental. The frequency calculated by Wilson's equations for the trigonal stretching vibration ν_{14} would place it about 1800 cm.$^{-1}$, but it might well lie 200 cm.$^{-1}$ lower. There is no evidence from the structure of ν_8, however, which can be interpreted unequivocally as an indication of the presence of ν_{14} in the immediate neighborhood. Indeed we are inclined to say, on the basis of the evidence just considered, that ν_{14} lies outside the range 1560—1640 cm.$^{-1}$ in benzene and 1520—1600 cm.$^{-1}$ in benzene-d_6.

The region between 1600 and 2000 cm.$^{-1}$ in the Raman spectrum of benzene is entirely free from lines having an intensity greater than about 1 $^0/_0$ of that of ν_1. Indeed it is only by very prolonged exposures that any lines at all have been found here, and these may be explained satisfactorily as allowed overtones[1]. Somewhat surprisingly the same freedom from lines in this region prevails in all the deut-

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[1] Angus, Ingold and Leckie, loc. cit.

erated benzenes. We might have expected that ν_{14}, which from a formal standpoint is Raman-active in eight of the compounds, should appear somewhere within a 200 cm.$^{-1}$ range of its calculated position at 1800 cm.$^{-1}$. Its failure to appear in this region may of course mean only that the polarizability change due to ν_{14} is nearly equal to zero because amplitude changes produced by deuterium substitution are slight. An equally plausible interpretation, however, is that ν_{14} has been miscalculated, and actually lies below the 1560 cm.$^{-1}$ boundary set for benzene. There are numerous weak lines in the region 1200—1500 cm.$^{-1}$ in the spectra of the deuterated benzenes. While it may be that most of these are hydrogen deformation frequencies, it is quite possible that a line due to ν_{14} is lurking among them. Until they have been definitely classified as belonging to other forms of vibration, the possibility remains that ν_{14} has been observed but not identified.

The only planar carbon frequency which remains to be discussed is the infrared-active ν_{19}. The benzene—benzene-d_6 shift of this frequency, from 1480 to 1330 cm.$^{-1}$, is so large that it cannot be considered a purely carbon frequency. Therefore we may except it to vary somewhat irregularly in the deuterated benzenes, although it should never step outside the limits 1300 and 1500 cm.$^{-1}$. The expected irregularity in frequency and the fact that there are several weak lines in this region of the spectra of the derivatives necessitate an identification procedure which is somewhat different from that we have been using. We shall consider ν_{19} together with the planar hydrogen frequencies.

3. The Planar Hydrogen Vibrations.

Each derivative has a total of six hydrogen "stretching" frequencies, namely ν_2, ν_{13} and the two components of ν_7 and of ν_{20}. A part of the six (equal to the number of deuterium atoms in the molecule of the derivative) lie within 15 cm.$^{-1}$ of 2280 cm.$^{-1}$, and the remainder at 3055 $\pm$ 10 cm^{-1} There is no difficulty in identifying the spectroscopically active fundamentals in this region, although sometimes fewer strong lines are observed than are permitted. This means only that the lines are so close that it is not possible to resolve them. The neighborhood of each high frequency fundamental is rich in weak lines which may rather safely be attributed to combination tones. The latter have more intensity than usual, probably because of interaction between the overtones and the fundamentals.

We have now localized twelve of the twenty one planar frequencies. To find the remaining ones — Nos. 3, 14 and 15 (non-degenerate) and Nos. 9, 18 and 19 (double) — we consider first the spectrum of sym-benzene-d_3. The symmetry of this molecule forbids the presence of the three non-degenerate frequencies in the Raman effect. The double frequencies are allowed, but they must appear as single lines since the presence of the three-fold axis preserves their degeneracy. They have been found in benzene and benzene-d_6 to lie within the range 800—1500 cm.$^{-1}$, and therefore may reasonably be expected to occur within these extremes in sym-benzene-d_3. In addition to the two totally symmetrical lines, which have already been identified, there are two fairly strong and four weak lines in this region. Of the weak lines, the one at 1072 cm.$^{-1}$ may be eliminated from consideration because it cannot be included in any

combination which satisfies the product rule for the E' frequencies (Table VIII). Another of the faint lines, at 815 cm.$^{-1}$, is so near to the much stronger line at 834 cm.$^{-1}$, that it satisfies the product rule almost as well as the strong line, provided that the latter be omitted from consideration. Because of its intensity, the stronger line must be included, and on this ground the 815 cm.$^{-1}$ is ruled out as an E' fundamental. The two remaining weak lines lie very close together at 1400 cm.$^{-1}$, and it is not possible (nor important) to decide between them by applying the product rule. The lower component, at 1396 cm.$^{-1}$, is somewhat the stronger, and therefore is assigned to a fundamental, viz. ν_{19}, which should lie between 1330 and 1440 cm.$^{-1}$. As we shall show later, the upper component may be satisfactorily interpreted as an overtone. The two strong lines, 834 and 1102 cm.$^{-1}$, are assigned to ν_{18} and ν_9 respectively.

The identification of frequencies 9, 18 and 19 in sym-benzene-d$_3$ serves as a basis for classifying observed frequencies in many of the other derivatives. When the degeneracy of the E' frequencies is released by removal of the three-fold axis, components 9a, 18a and 19a[1] preserve a two-fold axis passing through two para carbon atoms (cf. page 9). In order for the axis to be preserved during these vibrations, the four atoms lying on it must not move off the axis. The only possible motion for the para hydrogen atoms therefore is one which stretches the C—H bond. Since vibrations 9a, 18a and 19a are hydrogen bending frequencies, it is probable that the para hydrogen atoms do not participate significantly in the motion, and therefore should not influence the values of these frequencies appreciably. The frequencies should accordingly have the

[1] — Except in the two ortho derivatives (C_{2v}^*).

same values in all derivatives having the same distribution of deuterium atoms among the four non-para hydrogen atoms. The arrangement is the same for meta-benzene-d_2, vic- and sym-benzene-d_3, and meta-benzene-d_4. The frequencies which we have assigned to 9a, 18a and 19a in these four compounds are listed for comparison in Table XVII.

Table XVII.

Frequency No.	Observed Frequency in cm.$^{-1}$ in			
	meta-d_2	vic-d_3	sym-d_3	meta-d_4
9a	1108	1096	1102	1096
18a	838	839	834	833
19a	1397	1386	1396	$\begin{cases} 1374 \\ 1409 \end{cases}$

The same reasoning leads us to expect these three frequencies to have nearly equal values in benzene, benzene-d_1 and para-benzene-d_2, and in para-benzene-d_4, benzene-d_5 and benzene-d_6. Insofar as selection rules permit, our expectations are fulfilled save that ν_{19a} is not observed in benzene-d_1. Vibrations 18a and 19a are not Raman-active in the para-derivatives, but ν_{9a} is found in both compounds close to its predicted place.

We have now considered all the planar frequencies except ν_3 and ν_{15}. The former is Raman-active in the para-derivatives, and since we have identified all the other active planar frequencies except 9b in these compounds, it is not difficult to complete the identification. In para-benzene-d_2 there are five lines, all of moderate intensity or greater, in the range where ν_3 and ν_{9b} should appear, namely 860—1180 cm.$^{-1}$. Two of these have been assigned (ν_1 at 978.5 and ν_{9a} at 1176 cm.$^{-1}$). Of the three remaining, the

one lying close to ν_1 at 966 cm.$^{-1}$ is eliminated because it is somewhat less intense than the other two, and because it fits another assignment to be discussed later. We therefore assign the lines at 911 and 1167 cm.$^{-1}$ to ν_{9b} and ν_3 respectively.

The same region in para-benzene-d_4 exhibits two faint lines in addition to the five of higher intensity. The assignment of the moderately strong lines at 950 and 1137 to ν_3 and ν_{9b} is supported by an application of the product rule for class B_{2g} of V_h (Table IX). The only other combination which leads to reasonably close agreement with the τ given by the product rule is 927 and 1137 cm.$^{-1}$. The value of τ calculated from these two frequencies is too large, whereas it should be too small by about 1 $^0/_0$ because of anharmonicity.

It will be noticed that in both the para compounds, one of the lines considered lies close to ν_1 on the low-frequency side, and therefore might be interpreted as due to the C^{13} isotope. The characteristics of the lines are in opposition to this view: in both cases it is too diffuse and too far removed from ν_1. In addition the intensities of both lines are too great to be attributed to the presence of C^{13}.

Identification of ν_3 in the para derivatives enables us to calculate its value in benzene and benzene-d_6 by applying the product rule (Table IX). We find from its location in para-benzene-d_2 that $\nu_3 = 1202$ cm.$^{-1}$ in benzene, and from para-benzene-d_4 that $\nu_3 = 924$ cm.$^{-1}$ in benzene-d_6. Because of anharmonicity, it is to be expected that the value for benzene has been calculated a little too high, and that for benzene-d_6 too low. The ratio of the two actual frequencies should be a trifle lower than that given by the product rule, viz. 1.29, whereas the ratio of the calculated

frequencies is 1.30, or about 1 $^0/_0$ too high. To correct the calculated values, we deduct 0.5 $^0/_0$ from the benzene frequency and add 0.5 $^0/_0$ to that of benzene-d_6. The corrected frequencies are 1195 and 930 cm.$^{-1}$.

The remaining planar frequency, ν_{15}, is a hydrogen bending vibration which is Raman-active only in the C_{2v}, C_{2v}^* and C_s derivatives. Even if one could identify it with certainty in the spectra of these compounds, it would not be possible to apply the product rule to a calculation of its value in benzene because the position of ν_{14} is unknown. ν_{15} may be estimated to lie in the neighbourhood of 1150 cm.$^{-1}$ in benzene and 850 cm.$^{-1}$ in benzene-d_6. In the intermediate derivatives there are six hydrogen in-plane bending frequencies (3, 9 ab, 15 and 18 ab), all of which will lie in the range 800—1180 cm.$^{-1}$. Since this region may also include out-of-plane hydrogen frequencies, it is necessary to consider the out-of-plane vibrations before attempting to assign observed frequencies in the derivatives of low symmetry.

4. The Non-Planar Vibrations.

There are six out-of-plane frequencies in benzene. Two are carbon vibrations involving considerable distortion of the carbon ring, two are hydrogen vibrations in which the carbon ring is distorted slightly, and two are hydrogen vibrations in which the ring is not distorted at all. One of each pair is doubly degenerate. Only the last pair is spectroscopically active, one frequency in the Raman effect (the doubly degenerate ν_{10}) and the other in infrared absorption (ν_{11}).

The positions of the two carbon frequencies depend on

the resistance of the ring to distortion. Since there is no a priori way in which this resistance may be determined, the location of the frequencies has remained in doubt, and the possibility of observing them in the deuterated benzenes was one of the reasons for undertaking the present work. On the basis of evidence furnished by heat capacity measurements, it has been suggested[1] that one of the frequencies (16 ab) lies at 400 cm.$^{-1}$ and the other (4) somewhat higher. This suggestion is supported by the temperature-dependence of the intensities of certain bands in the ultra-violet absorption spectrum of benzene, which has recently been the object of special study by KISTIAKOWSKY and SOLOMON[2].

The most promising spectrum for finding ν_{16} should be that of sym-benzene-d_3, because it is the simplest in which ν_{16} is active (class E″ of D_{3h}). A line is indeed observed in this spectrum at 373 cm.$^{-1}$. While it is of low intensity, it is rather too strong for a combination tone. Its proximity to 400 cm.$^{-1}$ lends support to its interpretation as ν_{16}.

In all the other derivatives except para-benzene-d_4 there are definite indications of one, and sometimes two, frequencies in the region between 350 and 400 cm^{-1}*. The lines vary considerably in intensity, but their persistent occurrence in a narrow region around 373 cm.$^{-1}$ indicates that they arise from the same source as the line at that

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[1] LORD and ANDREWS, loc. cit.

[2] KISTIAKOWSKY and SOLOMON, Journ. Chem. Phys. 5, 609 (1937).

* The one found at 400 cm^{-1} in para-benzene-d_2, provided that it is actually due to ν_{16} in that molecule, appears in contravention of selection rules, and probably arises from the same source as the 400 cm^{-1} line in benzene, i. e., from $C_5^{12}C^{13}H_4D_2$ or from violation of selection rules because of liquid forces. The fact that no corresponding line has been found in para-d_4 may be due to the obscuring effect of a diffuse overtone at 2158 cm^{-1}, which, when excited by Hg-4047 Å, covers the region of the plate where lines of 390 cm^{-1} excited by Hg-4358 Å lie.

frequency in sym-benzene-d_3. They may therefore be assigned to ν_{16} (a or b).

Before considering the other carbon frequency, it is helpful to complete the assignment of observed fundamentals in sym-benzene-d_3. We have already accounted for nine of the twelve lines lying below 2000 cm.$^{-1}$. The other three are a strong line at 712 and two faint ones at 815 and 1072 cm.$^{-1}$. The intensity of the strong line indicates that it is to be ascribed to ν_{10}, a frequency which is Raman-active in benzene. This assignment is borne out by the fact that a strong line is observed at 711 ($\pm$ 1) cm.$^{-1}$ in the three compounds—meta-d_2, vic-d_3 and meta-d_4—in which ν_{10a} should have precisely the same frequency as ν_{10} in sym-benzene-d_3. We have seen above (page 64) that certain of the planar frequencies have approximately equal values in these four compounds. Similar considerations of symmetry require that each of the frequencies ν_{10a}, ν_{16a} and ν_{17a} have exactly the same value in all four derivatives. These frequencies preserve the two-fold axis present in derivatives, and since atoms participating in out-of-plane vibrations move only perpendicular to the plane, the atoms lying on the two-fold axis do not take part in the motion. Therefore the masses of the atoms on the axis are not a factor in the frequency values, and changing the masses has no effect on the frequencies. For the same reason we may expect the values of the same three frequencies to be identical in benzene, benzene-d_1 and para-benzene-d_2, and in para-d_4, benzene-d_5 and benzene-d_6. The assignment of frequencies is considerably facilitated by this circumstance.

It is not easy to decide which of the weak lines at 815 and 1072 cm.$^{-1}$ should be attributed to ν_{17}. Both are faint,

although the latter is perhaps a little stronger. Both appear
in the proper C_{2v} derivatives, but with varying intensity
and wavelength which may be attributed to the difficulty
of measuring weak and diffuse lines, particularly when
they happen to lie, as both 815 and 1072 do, near stronger
lines. The basis for our choice between the two is the rather
negative one that it is easy to explain the line at 1072 as
an overtone if the other is chosen as ν_{17}, while there is no
satisfactory explanation for 815 cm.$^{-1}$ except as a funda-
mental.

   If we assign 815 cm.$^{-1}$ to ν_{17}, 1072 cm.$^{-1}$ may be inter-
preted as a combination tone with the help of the infrared
data of INGOLD et al.[1]. As we shall see presently, there is
an infra-red active frequency of 691 cm.$^{-1}$ which may
belong to a fundamental of class A_2''. The combination of
this frequency with the E'' vibration at 375 cm.$^{-1}$ would
give a frequency of symmetry E' at 1066 cm.$^{-1}$. It should
be both Raman- and infrared-active, and there is indeed
an infrared band observed at 1065 cm.$^{-1}$. The appearance
of the combination tone in the Raman effect may be due in
part to interaction with the nearby fundamental at 1102 cm.$^{-1}$.
That such interaction is an important factor in the spectro-
scopic activity of combination tones is shown by their pre-
valence in the neighborhood of the strong lines around
2280 and 3060 cm.$^{-1}$, which we have previously noticed
(p. 62). The same explanation holds for the doublet struc-
ture of the E' line at 1400 cm.$^{-1}$ (cf. p. 63), since the first
overtone of the E'' fundamental at 711 cm,$^{-1}$ should lie
quite near the fundamental.

   The assignment of the 815 line to ν_{17} enables us to cal-

[1] BAILEY, BEST, GORDON, HALE, INGOLD, LECKIE, WELDON and WILSON,
Nature 139, 880 (1937).

culate the product of ν_{16} and ν_{17} in benzene. We find from the product rule that $\nu_{16} \times \nu_{17}$ is 342,700 cm.$^{-2}$. The τ for the E_u^+ frequencies in D_{6h} is 1.414 (Table VII) and therefore $\nu_{16} \times \nu_{17}$ in benzene-d_6 is 242,200 cm.$^{-2}$. If the very weak line at 406 in the Raman spectrum of benzene be attributed to ν_{16}, the product rule then gives $\nu_{17} = 845$ cm.$^{-1}$. The evidence for ν_{16} in benzene-d_6 is not so definite. ANGUS, INGOLD and LECKIE[1] report an extremely faint line at 337 cm.$^{-1}$. We have found traces of this line, although at slightly higher frequencies than 337 cm.$^{-1}$. In any case the measured frequency is uncertain. If we somewhat arbitrarily set the value of the frequency at 350 cm.$^{-1}$, we may calculate that ν_{17} is about 690 cm.$^{-1}$ in benzene-d_6.

To identify ν_4 we consider first the uninterpreted lines of the spectra of the para derivatives, in which ν_4 is active. Omitting from consideration the extremely faint line at 400 cm.$^{-1}$, we have yet to assign vibrations to frequencies at 634, 738, 850, 966 and 1273 cm.$^{-1}$ in para-benzene-d_2. ν_4 should be the lowest of these, and we therefore assign it to 634 cm.$^{-1}$. This frequency is more than 200 cm.$^{-1}$ above ν_{16}, but calculation[2] indicates that ν_4 should be considerably the higher. ν_{10a} must lie at 850 cm.$^{-1}$, the position of ν_{10} in benzene, and since ν_{10b} should be somewhat lower, in the range 660—850 cm.$^{-1}$, we assign to it the line at 738 cm.$^{-1}$.

Thus there remains a choice between 966 and 1273 cm.$^{-1}$ for ν_5. Before attempting a decision, we must consider the spectrum of para-benzene-d_4. Here the unassigned lines are 662, 765, 927 and 1253 cm.$^{-1}$, which have moderate intensity or greater, and 605, 630, 842, 1051 and 1098 cm.$^{-1}$, which are faint. We can assign immediately the lines at

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[1] ANGUS, INGOLD and LECKIE, loc. cit.

[2] Cf. LORD and ANDREWS, loc. cit., p. 155.

662 and 765 cm.$^{-1}$ to 10a and 10b respectively. The faint line 605 is presumed to be ν_4 (it is somewhat more intense than the nearby line at 630 cm.$^{-1}$, which is extremely weak), and the other faint lines are deemed to belong to other sources than fundamental frequencies. The moderately strong lines at 927 and 1253 cm.$^{-1}$ are therefore eligible for assignment to ν_5.

The product rule for class B_{3g} of V_h (Table IX) gives a value of τ, 1.030, which is satisfied either by the combination

$$\frac{(634 \times 738 \times 966)}{(605 \times 765 \times 927)}$$

or by the alternative one in which 966 and 927 are replaced respectively by 1273 and 1253. The latter combination gives better agreement (1.027) with the theoretical τ, but the former (1.053) does not exceed the limits of error in applying the product rule, particularly in view of the difficulty of measuring both the 966 cm.$^{-1}$ frequency in para-benzene-d_2 and the faint line 605 in para-benzene-d_4. Hence the product rule does not permit here a clear cut decision between the two assignments.

The infrared absorption data for sym-benzene-d_3 may furnish evidence for the position of ν_5 in the para derivatives in the following way. By means of the product rule for class B_{3g} (Table IX) and the observed value of ν_{10} in benzene, the product of ν_4 and ν_5 in benzene may be calculated from the three B_{3g} frequencies in para-benzene-d_2. In turn the product of the three A_2'' frequencies of sym-benzene-d_3 may be computed with the help of the observed value of ν_{11} in benzene and the product rule. In the preliminary report of the infrared absorption spectrum of sym-benzene-d_3 given

by Ingold et al.[1], they report the numerical positions of the
bands without intensity data. From the "parallel" structure
of two bands at 533 and 914 cm.$^{-1}$, they assign the bands
to A_2'' vibrations. If this indication of two of the A_2'' bands
is correct, the third should lie either at 699 or at 921 cm.$^{-1}$,
according to whether ν_5 in para-benzene-d_2 be assigned to
the line at 966 or at 1273 cm.$^{-1}$. There is in fact a band
observed at 691 cm.$^{-1}$, which would fit the former alter-
native. It is not reported as having parallel structure, but
may be weaker than the two other parallel bands and cor-
respondingly difficult to resolve. From the positions of ν_{11}
in benzene and benzene-d_6, and of ν_4 in the para compounds,
both these frequencies should be expected to appear in
the neighbourhood of 600 cm.$^{-1}$ in sym-benzene-d_3. There-
fore the assignment of ν_{11} to the 533 cm.$^{-1}$ band and ν_4 to
691 cm.$^{-1}$ is quite compatible with expectation. The A_2''
band at 914 cm.$^{-1}$ is on this interpretation assigned to ν_5.

On the other hand the alternative which would place
the third A_2'' frequency at 921 cm.$^{-1}$ seems highly unlikely.
There is no band reported within 80 cm.$^{-1}$ of the 914 band.
In addition our prejudices with regard to the location of
ν_4 and ν_{11} make it appear most improbable that either of
these could have a frequency so high as 900 cm.$^{-1}$ in
sym-benzene-d_3. If the assignment of the parallel bands is
accepted, the allocation of ν_5 to the 966 frequency in para-d_2,
to 914 in sym-d_3 and to 927 in para-d_4 is supported both
in the Raman effect and in infrared absorption.

It is possible nevertheless to fit the Raman line at
1273 cm.$^{-1}$ in para-benzene-d_2 into an interpretative scheme
as ν_5 if it be assumed that the bands at 533 and 691 cm.$^{-1}$
are A_2'' bands but that the 914 cm.$^{-1}$ band is not. In this

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[1] Ingold et al., loc. cit.

case the product rule would place ν_5 at 1218 cm.$^{-1}$ in sym-benzene-d_3 and indeed there is a band observed at 1226 cm.$^{-1}$. The band is not reported as having parallel structure, but on the basis of such an interpretation ν_5 would have the thoroughly compatible values of 1273, 1226 and 1253 cm.$^{-1}$ in para-d_2, sym-d_3 and para-d_4 respectively. The 914 band might then be assigned to the overtone $\nu_{11} + \nu_{16}$, which has the symmetry E' (both Raman and infrared-active) and a frequency of approximately 910 cm.$^{-1}$, but which should have a perpendicular rather than parallel structure in the infrared. This interpretation is therefore in direct contradiction to the parallel structure ascribed to the 914 cm.$^{-1}$ band.

We are faced with the necessity of deciding between the two interpretations. The first is quite satisfactory, but it leaves unexplained the two lines at 1253 and 1273 cm.$^{-1}$, of which the former has rather higher intensity than is ordinarily found in overtones. If they may be understood as overtones, there is no further objection. The second interpretation conflicts with the parallel structure observed for the 914 cm^{-1} infrared band in sym-d_3, and leaves lines at 966 and 927 cm.$^{-1}$ in para-d_2 and para-d_4 unexplained. The latter lines might also be ascribed to overtones. There is, however, no way of getting round the conflict with the observed parallel structure of the 914 band short of denying its existence. Therefore it seems to us that the first interpretation is the better. The question of overtones may best be evaded until a knowledge of the infrared absorption spectra of the para derivatives is available.

The product of ν_4 and ν_5 in benzene calculated from the product rule (Table IX) and the assignment of ν_5 to 966 cm.$^{-1}$ in para-benzene-d_2 is 704,000 cm.$^{-2}$. The same

product in benzene-d_6, as calculated from para-benzene-d_4, is 486,200 cm.$^{-2}$. The ratio of these two numbers is 1.448, which is 2.4 $^0/_0$ above the product rule τ of 1.414 for B_{2g} frequencies (Table VII). If we attribute the discrepancy to anharmonicity we may correct the ratio by subtracting 1.2 $^0/_0$ from the product in benzene and adding 1.2 $^0/_0$ to that for benzene-d_6. The corrected products are 695,700 and 492,000 cm.$^{-2}$. Now let us assume that the shift in ν_4 in passing from benzene to para-benzene-d_2 is the same as that from para-d_2 to para-d_4, namely 30 cm.$^{-1}$. Therefore ν_4 in benzene is 664 cm.$^{-1}$, and from the product of ν_4 and ν_5, $\nu_5 = 1048$ cm.$^{-1}$. Similarly the values of ν_4 and ν_5 in benzene-d_6 are found to be 575 and 856 cm.$^{-1}$.

V. Summary of Frequency Assignments.

In the accompanying tables the assignments we have already made are summarized, and further assignments are made for the derivatives of low symmetry, whose observed frequencies have not been considered in detail. The frequencies are catalogued both as to number and symmetry class. It must be remembered, however, that the distribution of numbers among frequencies belonging to the same symmetry class is often arbitrary. It has little significance, for example, to differentiate by number between the various hydrogen planar bending frequencies in a compound of C_s symmetry. The assignment to classes, on the other hand, has been made on a more logical basis. In classifying the observed frequencies of compounds of low symmetry, the same auxilaries have been used as for the more symmetrical derivatives: product rule ratios, con-

siderations of intensity, anticipated frequency shifts, etc. On the whole, the classification in Tables XX and XXI is reliable. When an assignment is considered doubtful, it is marked by an interrogation point.

Throughout the Tables, an observed frequency which is

Table XVIII.

Frequency Assignment for Compounds of D_{6h} and D_{3h} Symmetry.

Symmetry Class		Freq. No.	Frequency in cm.$^{-1}$		
D_{6h}	D_{3h}		Benzene	Sym-benzene-d_3	Benzene-d_6
A_{1g}	A_1'	1	992.5	956.6	945.2
		2	3061.5	3055.1	2293.2
B_{1u}		12	[1010]	1003.9	[962]
		13	[3060]	2283.8	[2290]
A_{2g}	A_2'	3	[1195]	—	[930]
B_{2u}		14	—	—	—
		15	—	—	—
E_g^+	E'	6	606.4	593.7	579.3
		7	3048.3	2272	2265.7
		8	1595	1575.9	1553.2
		9	1177.9	1101.7	869.1
E_u^-		18	1035*	834.3	813*
		19	1485*	1396.2	1333*
		20	3080*	(3055.1)	2294*
B_{2g}	A_2''	4	[664]	691*	[575]
		5	[1048]	914*	[856]
A_{2u}		11	671*	533*	503*
E_g^-	E''	10	849.7	711.7	663.5
E_u^+		16	406	373	350?
		17	[845]	815	[690]?

[ ] = calculated with help of the product rule.
( ) = one observed but unresolved frequency due to two or more vibrations.
* = observed in infrared only.

expected to be double and is found single is assigned to both of the expected vibrations. To denote the duplication, the second assignment is enclosed in parentheses. In Table XVIII certain frequencies which have not been observed have been calculated from the product rule. These are enclosed in square brackets. Frequencies observed in the infrared

Table XIX.

Frequency Assignment for Derivatives of V_h Symmetry.

Symmetry Class	Freq. No.	Frequency in cm.$^{-1}$	
		para-benzene-d_2	para-benzene-d_4
A_{1g}	1	978.5	959.6
	2	3054.6	2283.0
	6 a	593.6	585.0
	7 a	2279.4	3042.9
	8 a	1589.2	1563.0
	9 a	1175.4	859.7
B_{2g}	3	1166.6	949.9
	6 b	598.8	(585.0)
	7 b	3042.3	2265.0
	8 b	1568.3	1571.7
	9 b	911.1	1137.4
B_{3g}	4	634	605
	5	966	927
	10 b	738	765.3
B_{1g}	10 a	850	662.3

( ) = one observed but unresolved frequency due to two or more vibrations.

but not in the Raman spectrum are marked with an asterisk.

It is also desirable to summarize in tabular form comparisons of the theoretical product rule ratios with τ's

Table XX.

Frequency Assignment for Derivatives of
C_{2v} Symmetry.

Sym-metry Class	Freq. No.	Observed Frequency in cm.$^{-1}$				
		benzene-d_1	meta-d_2	vic-d_3	meta-d_4	benzene-d_5
A_1	1	980.9	970.5	965.3	953.8	950.9
	2	3064.2	3058.8	3058.7	3051.4	3050.6
	6 a	598.5	598.4	592	589	584.8
	7 a	2269.8	2284.4	2288.1	2271.8	2268.3
	8 a	1593.8	1583.1	1575.3	1564.6	1557.9
	9 a	1176.5	1107.7	1095.5	1095.7	857.9
	12	1008.6	1006.1	992.3	986.4	977.1
	13	3055.5	3047	2280.8	2287.2	2288.8
	18 a	1032.4	838.1	838.7	832.5	836.4
	19 a	[1473]	1397.2	1385.6	1374	1323
	20 a	(3064.2)	(3058.8)	3050.6	(2287.2)	(2288.8)
B_1	3	1158.2	1168.4	1131.0	847.0	847.9
	6 b	602.0	(598.4)	(592)	(589)	(584.6)
	7 b	3040	2272.1	(2280.8)	(2271.8)	(2268.3)
	8 b	1575.7	1563.0	1582.2	1571.3	1570.4
	9 b	859.5	855	920?	(847)	(857.9)
	14	—	—	—	—	—
	15	(1176.5)	1177.2	1150.4	1175.9	1173.5
	18 b	(1032.4)	1030	863.4	(832.5)	812
	19 b	1418??	(1397.2)	1363.2?	—	1360
	20 b	(3064.2)	(3047)	(3050.6)	(3051.4)	(2268.3)
A_2	10 a	851.7	710.5	712.0	711.1	664.2
	16 a	403	374	374	375	(371)
	17 a	—	818	825	—	691.3
B_2	4	—	—	657?	632	614
	5	1077?	1051?	1031?	—	—
	10 b	780	818?	779.3	705	711.6
	11	—	—	—	—	—
	16 b	381	(374)	(374?)	(375)	371
	17 b	—	—	744	—	—

( ) = one observed but unresolved frequency due to two or more vibrations.

Table XXI.

Frequency Assignment for Derivatives of C_{2v}^* and C_s Symmetry.

Symmetry Class		Freq. No.	Observed Frequency in cm.$^{-1}$		
C_{2v}^*	C_s		ortho-d_2	unsym-d_3	ortho-d_4
A$_1$	A′	1	976.0	966.4	960.4
		2	3064	3055.7	3058.3
		6 a	598.3	593.5	589.3
		7 a	2280.8	2283.6	2289.9
		8 a	1573	1578	1578.1
		9 a	1177.5	1139.1	1170
		14	—	—	—
		15	1160	1128.3	932.3
		18 b	1055.4	1054.7	842.2
		19 b	1402.8	1390	1348.5
		20 b	3035.3	3045.1	2270.0
B$_1$		3	1130.7	841	(932.3)
		6 b	(598.3)	(593.5)	(589.3)
		7 b	2273.3	2270	(2270.0)
		8 b	1588	1556	1571.8
		9 b	(1177.5)	915	1136.5
		12	992.8	987.4	974.0
		13	3053	(3055.7)	3046.2
		18 a	856	(841)	813.1
		19 a	(1402.8)	(1390)	1372.3
		20 a	(3064)	(2270)	(2289.9)
A$_2$	A″	4	—	635	625.4
		5	—	927	—
		10 b	841.6	707	688.3
		16 a	384	395?	369
		17 a	—	822.7	778
B$_2$		10 a	782.1	772.2	738.7
		11	581.6	562	—
		16 b	(384)	(395?)	(369)
		17 b	825?	785	(778)

( ) = one observed but unresolved frequency due to two or more vibrations.

computed from the frequency assignments. In the course
of our analysis such liberal use has been made of the
product rule in computing unobserved frequencies that

Table XXII.
τ's in V_h Derivatives.

D_{6h}	$A_{1g}\ E_g^+$	E_g^-	$A_{2g}\ E_g^+$	$B_{2g}\ E_g^-$
V_h	A_{1g}	B_{1g}	B_{2g}	B_{3g}
C_6H_6: obs....... p-$C_6H_4D_2$ calc.	1.397 1.414	1.000 1.000	— 1.367	— 1.324
p-$C_6H_4D_2$: obs....... p-$C_6H_2D_4$ calc.	1.442 1.414	1.283 1.286	1.350 1.370	1.053 1.030

Table XXIII.
τ's in C_{2v} and C_{2v}^* Derivatives.

C_6H_6:	τ for Class A_1 in C_{2v}		τ for Class B_1 in C_{2v}^*	
	observed	calculated	observed	calculated
C_6H_5D	*	1.405	—	—
ortho- meta- } $C_6H_4D_2$	— 1.972	— 1.975	1.881 —	1.909 —
vic-$C_6H_3D_3$	2.790	2.776	—	—
ortho- meta- } $C_6H_2D_4$	— 3.901	— 3.901	3.572 —	3.655 —
C_6HD_5	5.291	5.484	—	—

* ν_{19a} not observed.

all but one of the classes in Table XVIII contain frequencies
determined in this way. Clearly it serves no useful purpose
to compare τ's for these classes with their theoretical values.

The one class in Table XVIII for which all frequencies have been actually observed is E′. The observed τ (C_6D_6 : sym-$C_6H_3D_3$) is 1.97 whereas theory (Table VIII) is 1.959. The agreement is satisfactory.

Table XXIV.

Vibrations to which No Frequencies Have Been Assigned.

C_6H_6	C_6H_5D	$C_6H_4D_2$			$C_6H_3D_3$			$C_6H_2D_4$			C_6HD_5	C_6D_6
		ortho	meta	para	sym	vic	unsym	ortho	meta	para		
					3							
	4	4	4									
	5											
	11		11	11		11		5	5	11	5	
				12				11	11	12	11	
				13						13		
14	14	14	14	14	14	14	14	14	14	14	14	14
15				15	15					15		15
				16 a b						16 a b		
	17 a b	17 a	17 b	17 a b					17 a b	17 a b	17 b	
				18 a b						18 a b		
				19 a b					19 b	19 a b		
				20 a b						20 a b		

In Table XXII are listed the τ's calculated from observed frequencies and from theory for the Raman-active symmetry classes of V_h. Only the ratios benzene/para-benzene-d_2, and para-benzene-d_2/para-benzene-d_4 are given. The para-benzene-d_4/benzene-d_6 ratios must be correct if the others are, because the benzene/benzene-d_6 ratios are correct.

We have also calculated the theoretical τ-ratios for the totally symmetrical frequencies (A_1) of the C_{2v} derivatives and for the B_1 frequencies of C_{2v}^*. The observed and cal-

culated τ's for six compounds are given in Table XXIII. For a seventh, benzene-d_1, only the theoretical value is given, because one of the totally symmetrical vibrations, ν_{19a}, has not been observed. It has been possible to calculate the value of the unobserved frequency from the product rule, since it is the only one missing. This value is listed in square brackets in Table XX.

The agreement between observed and theoretical τ's in Table XXIII is quite satisfactory in view of the fact that some eleven frequencies are involved in each product. The close agreement found for meta-benzene-d_2 and meta-benzene-d_4 is entirely fictitious, since the observed values should be circa 2 $^0/_0$ too low because of anharmonicity. Hence these two observed τ's, together with that for vic-benzene-d_3, which is too high, are the least satisfactory in the Table.

To complete the tabulation we have assembled in Table XXIV a list of the vibrations in the various derivatives to which no frequencies have been assigned. The large number of unassigned V_h frequencies is of course due to the fact that the V_h molecules have a centre of symmetry and hence a large number of Raman-inactive frequencies. Their determination must be made with the help of a study of their infrared absorption spectra.

Table XXV summarizes all of the unassigned observed frequencies and suggests assignments for some of them. There are about a hundred frequencies, of which roughly half lie above 2000 cm.$^{-1}$. It seems quite clear that these latter are combination tones. The others may be combination tones or unassigned fundamentals. The selection principles for combination tones are considerably more lax in the deuterium derivatives than in benzene itself, and the num-

Table XXV. Unassigned Observed Fre

Benzene-d$_1$		Benzene-d$_2$						Benzene-d			
		ortho		meta		para		sym.		vic.	
Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A
1610	$\nu_1+\nu_{12}$	658	ν_4?	1082	$\nu_{10a}+\nu_{16}$	1273	$2\nu_4$?	1072	$\nu_4+\nu_{16}$	1056	$2\nu_{11}$?
2313	$2\nu_3$	692	—	1144	—	2223	$\nu_4+\nu_{8a}$	1415	$2\nu_{10}$	1555	$\nu_1+\nu_{\epsilon}$
3168	$2\nu_8$	774	$2\nu_{16}$	1419	$2\nu_{10a}$	2261	—	2241	$\nu_{18}+\nu_{19}$	2240	—
		1035	—	2249	$\nu_{10b}+\nu_{19}$	3155	$2\nu_{8b}$?	2975	$2\nu_{14}$?	2260	$2\nu_3$
		1077	—	2265	$\nu_{10a}+\nu_{8b}$	3175	$2\nu_{8a}$	3148	$2\nu_8$	2312	$2\nu_{15}$
		1248	—	2308	$\nu_{10a}+\nu_{8a}$					2982	$2\nu_{14}$?
		1385	$\nu_6+\nu_{10a}$	2337	$2\nu_3$						
		2258	$2\nu_3$	2992	$2\nu_{14}$?						
		2298	$\nu_3+\nu_{9a}$	3153	$2\nu_{8ab}$						
		2314	$2\nu_{15}$								
		2993	$2\nu_{14}$?								
		3001	—								

ber of distinct active fundamental frequencies is considerably larger. It is therefore nearly always possible to find some combination of lower frequencies satisfying selection principles which will add up to a given frequency value within the limits of experimental error and of anharmonic departure from strict additivity. The validity of most of the assignments in Table XXV will remain in doubt until the infrared spectra of the derivatives are known. The assign-

uencies and Suggested Assignments.

| Benzene-d$_4$ | | | | | | | | Benzene-d$_5$ | |
| unsym. | | ortho | | meta | | para | | | |
Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A	Freq. cm.$^{-1}$	A
996	—	710	$2\,\nu_{16}$?	994	—	630	—	632	—
1070	—	1004	—	1057	—	1051	—	1034	—
1270	$2\,\nu_4$	1057	$\nu_{10b} + \nu_{16}$	1198	$\nu_{16} + \nu_{18a}$	1098	—	1099	—
1366	$\nu_6 + \nu_{10a}$	1069	—	1209	»	1253	$\nu_6 + \nu_{10a}$	1140	—
1461	$\nu_{14} + \nu_{17a}$	1099	$\nu_{10a} + \nu_{16}$	1409	$2\,\nu_{10}$	1542	$\nu_1 + \nu_6$	1225	$2\,\nu_4$
2270	$\nu_4 + \nu_{8a}$	1252	$2\,\nu_4$	1541	$\nu_1 + \nu_6$	2113	—	1412	$2\,\nu_{10b}$
2234	$\nu_3 + \nu_{19}$	1289	$\nu_3 + \nu_{16}$	2199	$\nu_4 + \nu_8$	2158	$\nu_6 + \nu_{8b}$	1532	$\nu_1 + \nu_6$
2297	—	1478	$2\,\nu_{10a}$	2223	$\nu_3 + \nu_{19}$	2219	—	2221	$\nu_{8a} + \nu_{10a}$
3023	$2\,\nu_{8b}$	1548	$\nu_1 + \nu_6$			2245	—	2246	$\nu_{8a} + \nu_{17a}$
3087	$2\,\nu_{8a}$	2160	$\nu_6 + \nu_{8b}$					2256	$\nu_{8b} + \nu_{17}$
		2187	$\nu_4 + \nu_{8b}$						
		2209	$\nu_4 + \nu_{8a}$						
		2251	$\nu_{8b} + \nu_{10b}$						
		2984	$2\,\nu_{14}$?						

ments which for one reason or another appear particularly doubtful are marked with interrogation points.

VI. Summary.

The Raman spectra of the eleven deuterium derivatives intermediate between benzene and benzene-d_6 have been obtained, and with the help of the selection principles and Teller's product rule, have been analyzed. The results of the analysis are:

1. Convincing evidence in support of the D_{6h} structure for benzene has been obtained.

2. The locations of seven of the nine spectroscopically inactive frequencies in benzene have been determined from the positions of analogous active frequencies in the derivatives.

3. The frequencies of the two ring distortion vibrations have been established, and are found to agree satisfactorily with those previously suggested on the basis of thermal evidence.

4. The fine structure of the Raman line due to the totally symmetrical carbon frequency in benzene has been given a quantitative explanation. The frequency, intensity and state of polarization of the line's components have been calculated, and agree well with the experimental data.

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