61. *Structure of Benzene. Part XVII. The Raman and Infra-red Spectra of 1 : 3 : 5-Trideuterobenzene : Description and Analysis.*

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The Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene has been studied and the frequencies of 33 Raman lines determined, 32 of which belong to the molecule $s\text{-}^{12}C_6H_3D_3$, and one to $s\text{-}^{12}C_5{}^{13}CH_3D_3$. The integrated intensities and depolarisation factors of 11 of the stronger lines have been measured. Also the infra-red spectrum of 1 : 3 : 5-trideuterobenzene vapour has been examined, from 3 μ to 27 μ, and the frequencies of 34 intensity maxima determined. These correspond to 23 vibrational frequencies of the molecule $s\text{-}^{12}C_6H_3D_3$, the remaining maxima arising from the resolution into their rotational branches of 5 of the vibration–rotation bands.

These spectra have been completely analysed. The 17 theoretically possible, spectrally active, fundamental frequencies have all been observed and identified. All the appearing higher harmonics have been interpreted. Their study has yielded a good value for one and an approximate value for another of the 3 spectrally inactive fundamental frequencies. Approximate normal co-ordinates are given for the 30 vibrational degrees of freedom represented by the 10 non-degenerate and 10 doubly degenerate vibration frequencies.

A preliminary report of this investigation has already appeared (*Nature*, 1937, **139**, 880); it contains an abridged list of 15 Raman frequencies and 16 infra-red frequencies (less than half the number measured) of 1 : 3 : 5-trideuterobenzene, as well as an assignment of fundamental frequencies. Langseth and Lord have since published an account of their investigation of the Raman spectrum (*Kgl. Danske Vidensk. Selsk.*, 1938, **16**, 6). Their frequencies and assignment of the Raman-active fundamentals agree generally with those of our earlier report, except in the following points. First, their list of frequencies omits two which were given in our original list, and assigned, correctly as we believe, as fundamental frequencies. Secondly, their list includes five frequencies not in our abridged list, three of which were assigned as fundamental frequencies; whereas we shall conclude that one of the three considered to be a fundamental does not exist, and that the other frequencies are all combination tones. There is no existing record, except our own brief one, of the infra-red spectrum of 1 : 3 : 5-trideuterobenzene.

Raman Spectrum.—The sample used was that prepared by Best and Wilson from aniline by deuteration and subsequent deamination (Part XIII, this vol., p. 239). The spectrum showed it to be very pure. The Raman spectrum was measured using quantities of about 6 c.c. of the liquid substance sealed in an ordinary Wood's tube. Before we began using the Crookes glass filter (Part XV, this vol., p. 247), it was noticed that, after many long exposures, just visible traces of a gummy deposit appeared on the tube, though without any significant change in the spectrum, which remained the same when the material was redistilled and the centre fraction put into a new tube.

The frequencies now listed were remeasured with the apparatus of high resolving power described by Poole (Part XV, this vol., p. 245). Some of them differ by a few wave-numbers from those given in our original list, which were obtained with the earlier apparatus described by Angus, Ingold, and Leckie (Part III, J., 1936, 925); but none of the differences of frequency is of any importance. The integrated intensities and depolarisation factors here reported were measured with the old apparatus, and have not been repeated with the newer equipment, since precision in these measurements is entirely limited by the considerable errors

inherent in the photographic comparison of intensities, rather than by the resolving power of the spectrograph employed.

The results are in Table I, the first column of which records the frequencies. They are all mean values derived from a considerable number of plates, and where possible from different excitation frequencies. Where a decimal is quoted the error is believed to be less than 1 cm.$^{-1}$; in other cases errors of a few wave-numbers are possible. The braces indicate groups of overlapping lines. The second column contains a qualitative estimate of intensity on an arbitrary scale (s = strong, ms = moderately strong, m = moderate, mw = moderately weak, w = weak, ww = very weak). We compared the integrated intensities of a number of lines microphotometrically, and the results of the more satisfactory measurements are given in parenthesis in the second column, the value 10 being arbitrarily assigned to the strongest line. These figures are liable to a considerable error which is very difficult to estimate. The third column contains the depolarisation factors of those lines which were sufficiently intense to permit this determination. These values are also rather rough : we think that the smallest depolarisation factors may be in error by 20% of their value, and

TABLE I.

Raman Spectrum of 1 : 3 : 5-*Trideuterobenzene, and Assignment.*

Frequency (cm.$^{-1}$).	Intensity.	Depolarisation factor.	Assignment.	Symmetry class.	Symmetry of components.
372·7	mw	—	Fundamental	E''	—
593·0	ms (1·0)	0·88	Fundamental	E'	—
710·2	ms (0·7)	0·81	Fundamental	E''	—
753	w	—	$2 \times 372·7 = 745·4$	A_1', E'	E'', E''
833·5	ms (0·7)	0·80	Fundamental	E'	—
{ 947	mw—m	—	Fundamental	E''	—
956·2	s (10)	0·15	Fundamental	A_1'	—
969	w	—	$372·7 + 593·0 = 965·7$	E''	E'', E'
{ 993	w	—	$^{12}C_5{}^{13}CH_3D_3$	—	—
1003·6	s (4)	0·15	Fundamental	A_1'	—
1069	w	—	{ $691 + 373 = 1064$	E'	A_2'', E''
			$2 \times 533 = 1066$	A_1'	A_2'', A_2''
{ 1092	w	—	$372·7 + 710·2 = 1082·9$	A_1', E'	E'', E''
1101·8	ms (0·8)	0·86	Fundamental	E'	—
1287	ww	—	$373 + 915 = 1288$	E'	E'', A_2''
1300	w	—	$593·0 + 710·2 = 1303·2$	E''	E', E''
1392	w	—	{ $2 \times 691 = 1382$	A_1'	A_2'', A_2''
			$691 + 710 = 1401$	E'	A_2'', E''
1408	w	—	Fundamental	E'	—
1417	w	—	$2 \times 710·2 = 1420·4$	$A_1'\ E'$	$E''\ E''$
1545	w	—	{ $710·2 + 833·5 = 1543·7$	E''	$E''\ E'$
			$593·0 + 956·2 = 1549·2$	E'	E', A_1'
{ 1573·1	ms (1·5)	0·92	Fundamental	E'	—
1594	w	—	$593·0 + 1003·6 = 1596·6$	E'	E'', A_1'
1607	w	—	$691 + 915 = 1606$	A_1'	A_2'', A_2''
2206	ww	—	$2 \times 1101·8 = 2203·6$	A_1', E'	E', E'
2238·3	m (0·4)	0·77	$833 + 1407 = 2240$	A_1', E'	E', E'
{ 2267·4	w	—	$691 + 1573 = 2264$	E''	A_2'', E'
2281·9	s (5)	0·45	Fundamental	A_1'	—
2292	mw	—	Fundamental	E'	—
2324	ww	—	{ $915 + 1407 = 2322$	E''	A_2'', E'
			$920 * + 1407 = 2327$	E'	A_2', E'
2973·3	m (0·4)	0·69	$1407 + 1573 = 2980$	A_1', E'	E', E'
2999	ww	—	$710 + 2292 = 3002$	E''	E'', E'
{ 3052·7	s (7)	0·45	Fundamental	A_1'	—
3082	mw	—	Fundamental	E'	—
3144·5	m	—	$2 \times 1573·1 = 3146·2$	A_1', E'	E', E'

* Inactive fundamental frequency of the A_2' symmetry class (cf. p. 270).

the largest factors by 10%. The remaining columns of the table record our assignment of the frequencies, either as fundamental frequencies or overtones or combination tones, the symmetry classes to which the fundamentals and higher harmonics belong, and the symmetry classes of the fundamentals from which the higher harmonics are composed. The reasons underlying the assignment, and further details with respect to the forms of the fundamental vibrations, are given later. A general diagram of the spectrum is given in Fig. 2 (p. 258) and a photographic record of one particular region in Fig. 3 (p. 267).

Infra-red Spectrum.—The same sample of 1 : 3 : 5-trideuterobenzene was used for these measurements. It was examined in the form of vapour only. Various pressures between 1 cm. and 7 cm. were employed in an absorption tube 45 cm. long; but the main surveys were carried out at a pressure of 5 cm.

For the region 3 μ to 20 μ the apparatus and general method were those employed by Bailey, Hale, Ingold, and Thompson (Part IV, J., 1936, 931). Later, indeed subsequently to our preliminary note, the exploration of the long-wave portion of the spectrum was extended to 27 μ with the aid of modified apparatus (Bailey, Carson, and Ingold, Part XVI, this vol., p. 252); but only one additional band, a very weak one, evidently a difference tone, was here found. A map of the spectrum on a frequency scale is given in Fig. 1. It shows a mean curve, derived from a number of general surveys as well as many detailed tracings of particular bands.

The wave-lengths and frequencies of the absorption maxima are given in the first two columns of Table II.

Fig. 1.

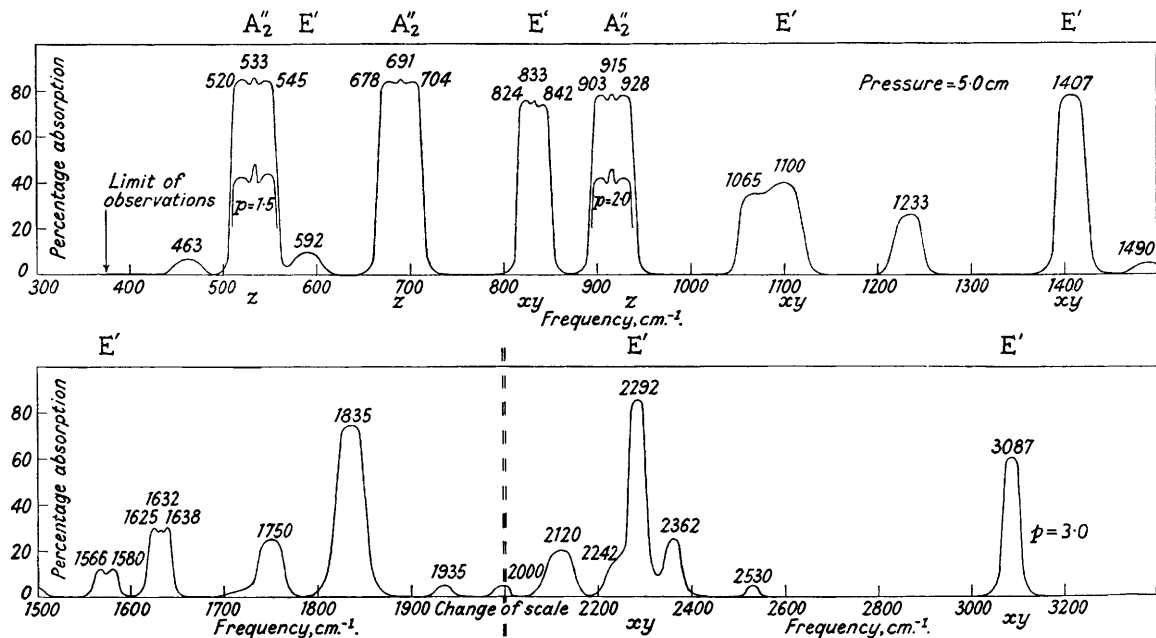*Infra-red spectrum of 1 : 3 : 5-trideuterobenzene.*

Table II.

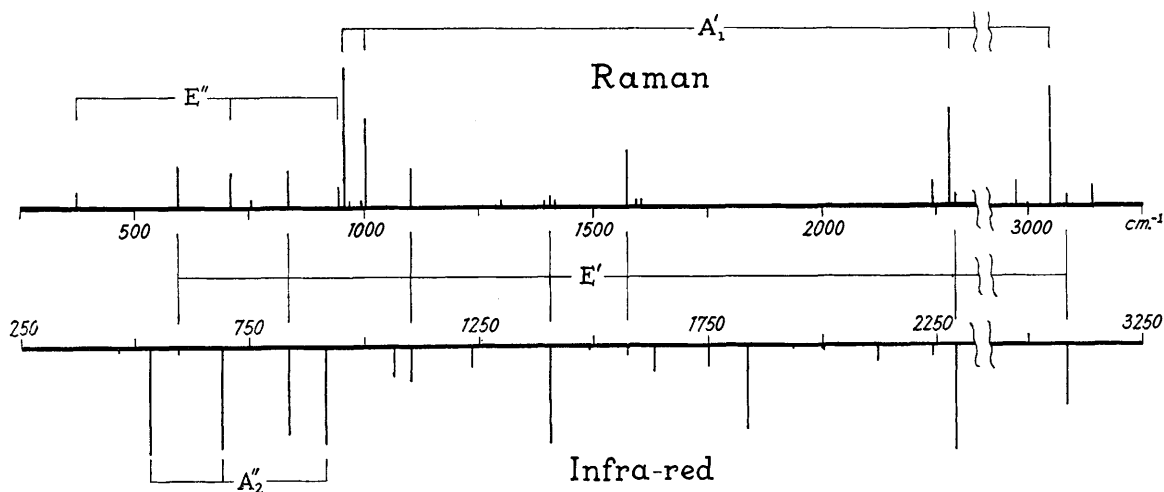*Infra-red Spectrum of 1 : 3 : 5-Trideuterobenzene, and Assignment.*

Wavelength (μ).	Frequency (cm.$^{-1}$).	Q or PR-mean.	PR-diff.	% Absorption.	Assignment.	Symmetry class.	Symmetry of components.
21·60	463	463	—	7	$\begin{cases} 1004 - 533 = 471 \\ 834 - 373 = 461 \end{cases}$	A_2'' A_2''	A_1', A_2'' E', E''
19·23	520⎫						
18·75	533⎬	533	25	86	Fundamental	A_2''	—
18·34	545⎭						
16·90	592	592	—	10	Fundamental	E'	—
14·76	678⎫						
14·47	691⎬	691	26	85	Fundamental	A_2''	—
14·20	704⎭						
12·14	824⎫						
12·01	833⎬	833	18	76	Fundamental	E'	—
11·88	842⎭						
11·07	903⎫						
10·93	915⎬	915	25	78	Fundamental	A_2''	—
10·78	928⎭						
9·393	1065	1065	—	35	$691 + 373 = 1064$	E'	A_2'', E''
9·092	1100	1100	—	40	Fundamental	E'	—
8·110	1233	1233	—	26	$533 + 710 = 1243$	E'	A_2'', E''
7·104	1407	1407	—	78	Fundamental	E'	—
6·712	1490	1490	—	5	$956 + 533 = 1489$	A_2''	A_2', A_2''
6·386	1566⎫	1573	14	12	Fundamental	E'	—
6·328	1580⎭						
6·155	1625⎫				$\begin{cases} 915 + 710 = 1625 \\ 691 + 947 = 1638 \end{cases}$	E' E'	A_2'', E'' A_2'', E''
6·129	1632⎬	1632	13	30			
6·104	1638⎭						
5·713	1750	1750	—	25	$920\ ^* + 833 = 1753$	E'	A_2', E'
5·450	1835	1835	—	74	$100 + 833 = 1837$	E'	A_1', E'
5·167	1935	1935	—	5	$833 + 1102 = 1935$	E'	E', E'
5·001	2000	2000	—	5	$593 + 1407 = 2000$	E'	E', E'
4·717	2120	2120	—	20	$1407 + 710 = 2117$	A_2''	E', E''
4·459	2242	2242	—	14	$833 + 1407 = 2240$	E'	E', E'
4·363	2292	2292	—	85	Fundamental	E'	—
4·234	2362	2362	—	25	$956 + 1407 = 2363$	E'	A_1', E'
3·953	2530	2530	—	5	$956 + 1573 = 2529$	E'	A_1', E'
3·240	3087	3087	—	60	Fundamental	E'	—

* Inactive fundamental frequency of the A_2' symmetry class (cf. p. 270).

The possible error in the frequency measurement is about 1 cm.$^{-1}$ at the lower end of the frequency range and about 5 cm.$^{-1}$ at the upper end. Since some of the intensity maxima are evidently due to the rotational structures of bands, each dependent on a single vibration, the corresponding vibration frequencies are separately noted in the third column. For bands whose structures have been resolved into P, Q, and R branches, the frequency of the absorption maximum of the Q branch is the vibration frequency. For one band we find only P and R branches, the Q branch having apparently been missed, due perhaps to the use of too wide a spectrometer slit; in this case we take the mean of the frequencies of the P and R maxima as the vibration frequency. For unresolved bands the vibration frequency is taken as that of the single intensity maximum. In the fourth column of the table we note, where possible, the frequency separation of the P and R absorption maxima, since this is a useful guide to the classification of the relevant vibration frequencies. The next column contains, as an indication of intensity, the percentage of light absorbed, at the wave-lengths of the absorption maxima, by 45 cm. of vapour at 5 cm. pressure. The remaining three columns contain our assignment of the fundamental frequencies and combination tones, the symmetry classes to which they belong, and the symmetry classes of the fundamentals composing the higher harmonics.

A diagrammatic comparison of this spectrum with the Raman spectrum is given in Fig. 2. Since the selection rules for 1 : 3 : 5-trideuterobenzene allow certain frequencies to appear in both the infra-red and the Raman spectrum, a comparison between the measured frequencies of those vibrations which show such a double appearance provides a useful indication of accuracy. The frequencies of all the seven fundamental

FIG. 2.

Diagrammatic comparison of Raman and infra-red spectra of 1 : 3 : 5-trideuterobenzene.

vibrations which are thus allowed to appear doubly have been measured in both spectra. For six of them the deviations range from 0 to 2 cm.$^{-1}$. The seventh is at the top of the frequency range, and the difference is 5 cm.$^{-1}$, which is about the observational error in this region of the infra-red spectrum. (Also it happens that in this case the Raman frequency is a difficult one to measure accurately.) A comparison of the doubly appearing fundamental frequencies is given in Table III, together with the values which, in calculations, we have adopted for these frequencies—having taken account of the relative accuracies of the individual Raman and infra-red frequency measurements, which naturally depend on various factors, including intensity and the near presence of other active frequencies.

TABLE III.

Doubly appearing Fundamental Frequencies.

Raman (cm.$^{-1}$)	593·0	833·5	1101·8	1408	1573·1	2292	3082
Infra-red (cm.$^{-1}$)	592	833	1100	1407	1573	2292	3087
Adopted value (cm.$^{-1}$)	593·0	833·5	1101·8	1407	1573·1	2292	3084

DISCUSSION OF ASSIGNMENT.

The Raman and infra-red spectra of 1 : 3 : 5-trideuterobenzene are compared diagrammatically in Fig. 2. The leading lines correspond to the assignment of fundamental frequencies already given in Tables I and II. We shall discuss the assignment of all the fundamental frequencies, but overtones and combination tones will be considered individually only in so far as their assignment involves special considerations.

It has been shown (Part XI, Table VIII, this vol., p. 228) that the 30 vibrational degrees of freedom of the 1 : 3 : 5-trideuterobenzene molecule consist of 10 non-degenerate and 10 doubly degenerate fundamental vibrations, and that the 20 distinct vibrational frequencies are divided between 5 symmetry classes, characterised by the spectral activity shown below :

Symmetry class	A_1'	A_2'	A_2''	E'	E''
No. of frequencies	4	3	3	7	3
Raman activity	R (pol.)	—	—	R (depol.)	R (depol.)
Infra-red activity	—	—	I (par.)	I (perp.)	—

Here R means allowed in the Raman spectrum, and I allowed in the infra-red spectrum. The abbreviations in parenthesis indicate whether the Raman fundamental frequencies should appear as " polarised " or " depolarised " lines, and whether the fundamental bands of the infra-red spectrum should be of the " parallel " or of the " perpendicular " type. It is seen that 17 of the fundamental frequencies are allowed either in the Raman or in the infra-red spectrum, 7 being allowed in both. The Raman spectrum should contain 14 fundamental frequencies, and the infra-red spectrum 10. Three fundamental frequencies are forbidden in both spectra.

We consider below first the 17 active fundamental frequencies of the A_1', A_2'', E', and E'' classes, then the active higher harmonics, and finally the 3 inactive fundamental frequencies of the A_2' class.

The A_1' Fundamental Frequencies.—The four fundamental vibrations of the A_1' symmetry class, being totally symmetrical with respect to the D_{3h} model, record themselves in the Raman spectrum only, and are characterised by the high intensity and considerable polarisation of their Raman lines. Actually, the four strongest lines in the Raman spectrum are considerably polarised, and they are the only strongly polarised lines amongst the eleven which were examined with respect to polarisation. Their frequencies (in cm.$^{-1}$) and depolarisation factors (in parenthesis) are as follows :

$$956 \cdot 2 \ (0 \cdot 15) \qquad 1003 \cdot 6 \ (0 \cdot 15) \qquad 2281 \cdot 9 \ (0 \cdot 45) \qquad 3052 \cdot 7 \ (0 \cdot 45)$$

Only two other Raman lines are known to have depolarisation factors which can either possibly or certainly be considered to fall below the value $0 \cdot 86$, characteristic of depolarised Raman frequencies, by amounts exceeding the error of measurement :

$$2238 \cdot 3 \ (0 \cdot 77) \qquad 2973 \cdot 3 \ (0 \cdot 69)$$

These lines are very much weaker and their polarisation is slight—in one case sufficiently slight to be somewhat doubtful. They can readily be understood as combination tones (see below).

The four A_1' fundamental vibrations of the D_{3h} model of 1 : 3 : 5-trideuterobenzene may be considered to be composed by orthogonal linear combination from vibrations of the form of those of the A_{1g} and B_{1u} classes of the D_{6h} model of benzene or hexadeuterobenzene (Part XI, Table V, this vol., p. 227). Each of these D_{6h} symmetry classes contains two vibrations, and in each class one vibration is a so-called " carbon vibration," in which each carbon atom carries its hydrogen atom with it, the whole CH-group moving practically as a unit, whilst the other is a so-called " hydrogen vibration," in which the two atoms of each CH-group move in opposite directions about a nearly stationary centre of gravity, most of the motion being in the hydrogen atom because of its relative lightness. In principle, therefore, we have to consider the combinations of two carbon and two hydrogen vibrations. On account, however, of the relative lightness of the hydrogen atoms, there is very little interaction between the hydrogen and the carbon vibrations. Thus we can consider the interaction of the two carbon, and of the two hydrogen, vibrations separately.

We deal first with the carbon vibrations. Because the moving unit is essentially the CH-group, their frequencies are not expected to be greatly altered by deuterium substitution. The A_{1g} carbon vibration of the D_{6h} benzene model (totally symmetrical contraction and expansion of the ring) is known from the Raman spectra to have the frequency $991 \cdot 6$ cm.$^{-1}$ in benzene and $943 \cdot 2$ cm.$^{-1}$ in hexadeuterobenzene. The B_{1u} carbon vibration of the D_{6h} model is inactive both in the Raman and the infra-red spectra : but Kohlrausch first perceived that its frequency must lie in the neighbourhood of 1000 cm.$^{-1}$, *i.e.*, close to the A_{1g} carbon frequency (*Z. physikal. Chem.*, 1935, **30**, B, 305; *Naturwiss.*, 1935, **23**, 624). His argument was based on the observation that all symmetrical trisubstituted derivatives of benzene have a strong, polarised Raman line in this region. Ingold supplemented this argument by pointing out that, for instance, that mono-, 1 : 3 : 5-tri-, and penta-deuterobenzene have *two* strong, polarised Raman lines in the region 950—1000 cm.$^{-1}$, whilst 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, like benzene and hexadeuterobenzene, exhibit only one, as the selection rules require, assuming Kohlrausch to be correct (*Z. Elektrochem.*, 1938, **44**, 30). In Part XXI, we shall conclude that the inactive B_{1u} carbon vibration in benzene has the frequency 1010 cm.$^{-1}$, and in hexadeuterobenzene the frequency 963 cm.$^{-1}$.

The fact that the two frequencies $956 \cdot 2$ cm.$^{-1}$ and $1003 \cdot 6$ cm.$^{-1}$ of 1 : 3 : 5-trideuterobenzene appear in the Raman spectrum with intensities of the same order of magnitude, whilst the parent A_{1g} and B_{1u} carbon vibrations of the benzenes of D_{6h} symmetry are respectively very strong and completely inactive, shows at once that the mutual interaction, which is forbidden under D_{6h} symmetry but permitted by D_{3h} symmetry, has in the trideuterobenzene profoundly modified the parent vibration forms. The frequencies confirm this, since, instead of being separated by only 18—20 cm.$^{-1}$, as are the A_{1g} and B_{1u} carbon frequencies of benzene, and likewise those of hexadeuterobenzene, they are 47·4 cm.$^{-1}$ apart : such a widening of that frequency difference which would be expected in the absence of dynamical interaction is a characteristic result of mechanical resonance. A " molecule " C_6X_6 of D_{6h} symmetry, in which X is a " hydrogen isotope " of atomic weight 3/2, would have the two frequencies close to 967 and 986 cm.$^{-1}$, instead of $956 \cdot 2$ and $1003 \cdot 6$ cm.$^{-1}$, as we find in $C_6H_3D_3$. The frequency ratio is 1·05, which is sufficiently close to $\sqrt{14/13} = 1 \cdot 04$ to show that interaction has resulted

in a large degree of separation of the normal vibrations into a trigonal " breathing " vibration of the CD-groups only, the CH-groups remaining nearly stationary, and a similar " breathing " vibration of the CH-groups only with the CD-groups nearly stationary. Thus as an approximation we may represent these normal co-ordinates by the simple vector diagrams (I) and (II) below. They are combinations of the type $A_{1g} \pm B_{1u}$ of the relevant D_{6h} vibration forms.

These conclusions agree with those which Langseth and Lord have derived (*loc. cit.*) from an approximate calculation based on Wilson's simplified potential system. They deduce for the ratio of the intensity of the higher to that of the lower frequency the value 0·67, and for the depolarisation factors of the lower and higher frequencies 0·10 and 0·09 respectively : we find experimentally 0·4 for the intensity ratio and 0·15 for both depolarisation factors. A microphotometer record showing the two Raman lines is reproduced in Fig. 3 (p. 267).

Frequencies essentially dependent on the stretching of benzenoid C–D and C–H bonds are always in the region of 2280 cm.$^{-1}$ and 3050 cm.$^{-1}$ respectively, and, since these values are more or less independent of the nature of the remainder of the molecule, they may be regarded as characteristic of the stretching of uncoupled C–D and C–H units. The two higher, intense and strongly polarised, Raman frequencies of 1 : 3 : 5-tri-deuterobenzene, 2281·9 cm.$^{-1}$ and 3052·7 cm.$^{-1}$, obviously represent a practically pure deuterium stretching vibration with stationary protium atoms, and an equally pure protium stretching vibration with stationary deuterium atoms. Since each must be totally symmetrical with respect to D_{3h} symmetry, they must have the vibration forms represented by (III) and (IV) below. There will, of course, be small opposing motions in the carbon atoms to which the moving deuterium or protium atoms are attached. The small figures associated with representative vectors in diagrams (I)—(IV) denote the relative amplitudes within each vibra-tion, as they emerge in the approximation to which we are working. They correspond to a theoretical frequency ratio of $\sqrt{13/7} = 1·36$, whilst the observed ratio is 3052·7/2281·9 = 1·34. The deviation is hardly greater than such as might be ascribed to anharmonicity effects. Diagrams (III) and (IV), like (I) and (II), represent orthogonal combinations, $A_{1g} \pm B_{1u}$, of the relevant D_{6h} vibration forms.

(I; 956·2 cm.$^{-1}$.) (II; 1003·6 cm.$^{-1}$.) (III; 2281·9 cm.$^{-1}$.) (IV; 3052·7 cm.$^{-1}$.)
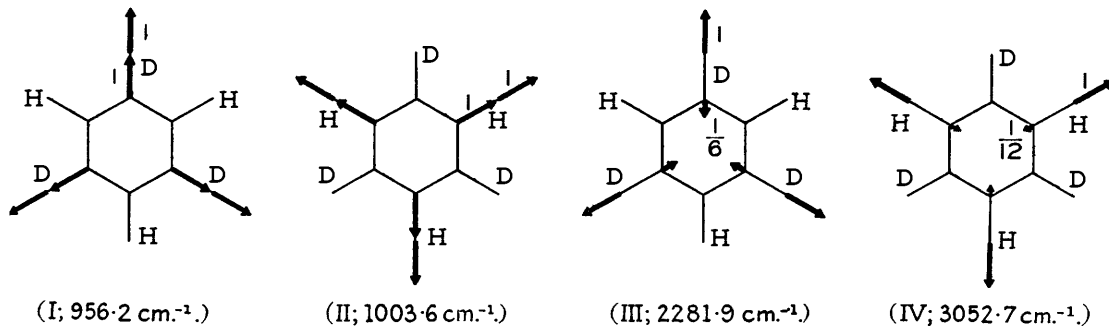
We should expect the dynamical interaction allowed under D_{3h} symmetry to transform the parent A_{1g} and B_{1u} hydrogen vibrations of the D_{6h} benzene model in this manner. The uncoupled stretching frequencies of C–D and C–H groups are widely different from each other; and thus the available coupling mechanism through intermediate heavier atoms is too weak to set up normal modes in which the two kinds of hydrogen atoms, in stretching motions of comparable amplitude, are forced into a common frequency. Therefore the main result of the coupling is only to maintain the proper phase relation between the moving deuterium atoms in one normal mode, and between the moving protium atoms in the other.

Langseth and Lord calculate the intensity ratio of the lines at 2281·9 and 3052·7 cm.$^{-1}$ as about unity. If we make the (possibly somewhat drastic) simplification of neglecting the effect on intensity of the small carbon motions, then the intensities of these two lines should be proportional to their frequencies. The frequency ratio is 1·34, whereas we make the measured intensity ratio about 1·4. Langseth and Lord's simplified force-field calculation leads to computed depolarisation factors of 0·34 and 0·40 for the frequencies 2281·9 and 3052·7 cm.$^{-1}$ respectively. Our determinations give for both frequencies the depolarisation factor 0·45.

It will be obvious why neither of the other two polarised, or possibly polarised, Raman frequencies, 2238·0 and 2973·3 cm.$^{-1}$, can be accepted as a deuterium or protium stretching frequency of the A_1' symmetry class. For, first, these frequencies are outside the narrow spectral regions in which deuterium and protium stretching frequencies always appear; and secondly, if either should be accepted as a fundamental frequency, it would involve the rejection from the list of fundamental frequencies of one of the much stronger and more highly polarised frequencies 2281·9 and 3052·7 cm.$^{-1}$, and the rejected frequency would then be impossible to explain.

The A_2'' Fundamental Frequencies.—The three fundamental vibrations of this class retain the trigonal symmetry of the model, but involve motions of the atoms perpendicular to the plane of the ring. The corre-sponding frequencies can be recorded in the infra-red spectrum only, where they must produce bands of the " parallel " type. Judging from the known out-of-plane frequencies of benzene and hexadeuterobenzene, the A_2'' frequencies of trideuterobenzene should lie in the spectral region 350—1000 cm.$^{-1}$.

In the infra-red spectrum of 1 : 3 : 5-trideuterobenzene there are three bands having the contours charac-

teristic of parallel bands. Their Q-branch frequencies (in cm.$^{-1}$), and the separations (in cm.$^{-1}$) of the intensity maxima of their P- and R-branches, are as follows : (The theoretical PR-separation for a parallel band is about 25 cm.$^{-1}$.)

$$533 \text{ (P–R 25)} \qquad 691 \text{ (P–R 26)} \qquad 915 \text{ (P–R 25)}$$

They are strong—far too strong to be difference tones—and they cannot be explained as summation tones : they must therefore be fundamental frequencies. And since no fundamental frequencies, except those of the A_2'' class, can give parallel bands, their assignment to this class is unequivocal. Consistently, the same frequencies do not appear in the Raman spectrum, and they are in the correct spectral region. None of the other bands in the infra-red spectrum, which have been resolved with respect to their rotational branches, has a parallel structure.

The three fundamental vibrations of the A_2'' class of the D_{3h} model of 1 : 3 : 5-trideuterobenzene may be regarded as compounded from vibrations of the forms of those of the A_{2u} and B_{2g} symmetry classes of the D_{6h} benzene model (Part XI, Table V, this vol., p. 227). The A_{2u} class contains only one vibration, which is a " hydrogen vibration " of six-fold symmetry, active in the infra-red spectrum. All the hydrogen atoms move in phase along lines parallel to the six-fold axis, the carbon atoms undergoing only a small antiparallel motion of such amplitude as to maintain a stationary centre of gravity. The B_{2g} class contains a " carbon vibration " and a " hydrogen vibration," each of trigonal symmetry. They are spectrally inactive. In both, all the atoms move on lines parallel to the six-fold axis, but adjacent carbon atoms, and likewise adjacent hydrogen atoms, remain always in opposite phase. The carbon vibration is defined as that in which the atoms of each CH-group move in phase; in the hydrogen vibration they move in opposite phase.

Before considering the nature of that dynamical interaction between these three vibrations which becomes permitted when the symmetry of the model is reduced to that of 1 : 3 : 5-trideuterobenzene, it is advantageous to note the special geometrical and dynamical conditions which obtain within the B_{2g} class of benzene itself. Owing to the geometry and valency structure of the molecule, the " carbon " and " hydrogen " vibrations of this symmetry class have not all the characteristics which the names might indicate, and which are indeed found in the carbon and hydrogen vibrations of most other symmetry classes. We may instance the already discussed A_{1g} and B_{1u} classes of benzene. In each of these classes the ratio of the carbon and hydrogen ampli-tudes in the carbon vibration is approximately 1 : 1 (it is the same for hexadeuterobenzene); whilst in the hydrogen vibration it is approximately 1/12 : 1 (1/6 : 1 for hexadeuterobenzene). Relatively to this situ-ation, there are in the B_{2g} class considerable transfers of hydrogen motion to the carbon vibration, and of carbon motion to the hydrogen vibration. To take a simplified illustration, let us suppose that the carbon vibration involves deformation only of the C·C·C valency angles, and not at all of the C·C·H valency angles—in other words, that every group C·(CH)·C preserves a plane for every value of the normal co-ordinate. Then the ratio of the carbon and hydrogen amplitudes would be, not about 1 : 1, but about 1/4 : 1 (and the same for hexadeuterobenzene). This follows by considering what would happen if we should bend equally, but altern-ately up and down, those six parts of a horizontal model of the molecule which lie outside the hexagon formed by joining the mid-points of the C–C bonds : the movement of each carbon atom would then force upon the corresponding hydrogen atom a movement of greater amplitude in the ratio $\{(CC) + 4(CH)\}/(CC) = 4\cdot11$, where (CC) and (CH) represent the lengths of the C–C and C–H bonds. Actually the C·C·H valency angles will be deformed to some extent, but the valency structure will certainly produce an approach towards the situation described, in which a high proportion of the kinetic energy of motion in what we have called a " carbon vibration " is contributed by the hydrogen atoms. Naturally, the redistribution of kinetic energy between the two vibrations must be reciprocal, and consequently the so-called " hydrogen vibration " will contain a similarly high proportion of carbon motion. In fact the orthogonality condition requires that, if the ratio of the carbon and hydrogen amplitudes in the " carbon vibrations " were as stated above, the corre-sponding ratio for the " hydrogen vibration " would be, not about 1/12 : 1 (or 1/6 : 1 in hexadeuterobenzene), but about 1/3 : 1 (or 2/3 : 1 in hexadeuterobenzene). We find these conclusions well confirmed by the frequencies, which are determined in Part XXI : from the frequency shifts between benzene and hexadeutero-benzene it is clear that the carbon and hydrogen atoms contribute not far from equally to the kinetic energy in each of the vibrations. The fundamental distinction remains, of course, that in the carbon vibration the atoms of each CH-group move in parallel, whereas in the hydrogen vibration their movement is antiparallel.

Following up these considerations, it is possible, even without a knowledge of the potential field, to develop an approximate picture of the vibration forms which supervene when, in 1 : 3 : 5-trideuterobenzene, these initially assumed B_{2g} vibration forms are further changed by interaction with an initial third form corre-sponding to the A_{2u} vibration of the D_{6h} model. In the last-named vibration form nearly all the motion is in the hydrogen atoms. Realising that, in vibrations which preserve the trigonal symmetry of 1 : 3 : 5-tri-deuterobenzene, the somewhat weak coupling, through intermediate heavier atoms, of the individual hydrogen atomic motions will tend to decompose the total hydrogen vibrations of the symmetry class into trigonally symmetrical vibrations of the separate protium and deuterium point-sets, and realising, furthermore, that this decomposition can be simply effected by sum-and-difference combination between the A_{2u} vibration form and a B_{2g}-derived vibration *which is equally rich in hydrogen motion*, it is evident that we may envisage, as the first step in the process of interaction, the passing over of hydrogen kinetic energy mainly into one of the two B_{2g} vibration forms, between which at the outset it was approximately equally divided. The first step

will produce a vibration, rich in carbon motion, which will survive as one of the final A_2'' forms given by this approximation. It will also give a vibration, rich in hydrogen motion, which will not survive but, after combination with the A_{2u} form, will yield the two remaining A_2'' vibrations.

There are two ways in which the first step might be accomplished; for the hydrogen motion might be concentrated in the B_{2g} carbon vibration, defined as having parallel motions within each CH-group, or it might be concentrated in the B_{2g} hydrogen vibration, characterised by antiparallel motions in each CH-group. The ambiguity cannot be settled theoretically except by calculations based on an assumed force-field; but the observed frequencies make it clear that the hydrogen motion concentrates in the B_{2g} carbon vibration. We compare below the observed E'' frequencies of 1 : 3 : 5-trideuterobenzene with the mean values of the B_{2g} and A_{2u} frequencies of benzene and hexadeuterobenzene—with frequencies, that is to say, which must be very close to those of an imaginary molecule of C_6X_6 of D_{6h} symmetry, in which X represents a " hydrogen isotope " of mass 3/2 (frequencies are in cm.$^{-1}$) :

	C_6H_6.	C_6D_6.	" C_6X_6."	A_2'' of $C_6H_3D_3$.
B_{2g} carbon	703	601	652	691
B_{2g} hydrogen	985	827	906	915
A_{2u}	671	497	584	533

The experimental basis for the values of the inactive B_{2g} frequencies of benzene and hexadeuterobenzene is given in Part XXI. They are the result of such dynamical interaction as is imposed by the force field, and permitted in the B_{2g} symmetry class, in a molecule of D_{6h} symmetry. But when, in the D_{3h} molecule, interaction with the A_{2u} vibration form becomes allowed, we observe the normal results of mechanical resonance. Considering the described two stages of the transformation of the vibrations when the " molecule " C_6X_6 is converted, by a redistribution of the hydrogen masses, into 1 : 3 : 5-$C_6H_3D_3$ with reduction of symmetry, we observe that a first effect of the kinetic energy exchange between the two B_{2g} vibration forms is to raise the upper frequency, 906 cm.$^{-1}$, to the observed 915 cm.$^{-1}$, a frequency preserved as one of the final A_2'' frequencies. Hence we expect the lower frequency, 652 cm.$^{-1}$, to be reduced, as a result of this first step of interaction, by a roughly similar amount, i.e., to 643 cm.$^{-1}$. This will be the vibration form in which the ratio of the carbon and hydrogen amplitudes is the same as in the A_{2u} form; and, in the interaction between these two, which produces the isomorphous vibrations of the protium and deuterium point-sets, we find the upper frequency, estimated as about 643 cm.$^{-1}$, raised by 48 cm.$^{-1}$ to the observed 691 cm.$^{-1}$, whilst the lower frequency, 584 cm.$^{-1}$, is reduced, as it should be, by a roughly similar amount, viz., by 51 cm.$^{-1}$, to the observed 533 cm.$^{-1}$.

We may symbolise the result of the interaction $A_{2u} \pm B_{2g}(C^x)$ (for 533 and 691 cm.$^{-1}$) and $B_{2g}(H^x)$ (for 915 cm.$^{-1}$), where the cross indicates the exchange of hydrogen and carbon kinetic energy in the first stage of interaction. Graphically the result is expressed by the vector diagrams (V), (VI), and (VII), in which the

(V; 533 cm.$^{-1}$.)   (VI; 691 cm.$^{-1}$.)   (VII; 915 cm.$^{-1}$.)
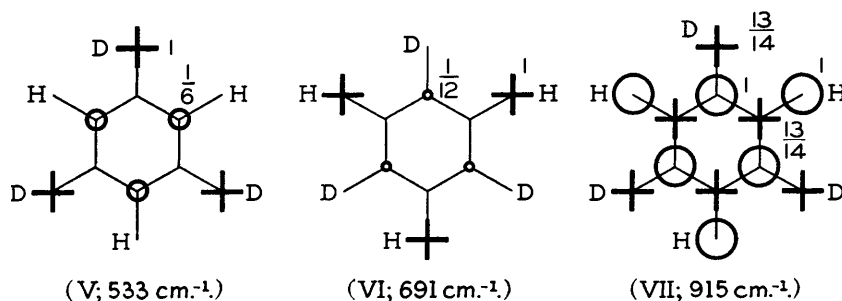
symbols $+$ and $\bigcirc$ signify vectors perpendicular to the plane of the paper, and the small figures associated with representative atoms denote amplitudes, relative within each diagram, to the degree of approximation to which we are working. They are determined by the orthogonality principle, and the necessity to preserve the vibrations from including any translatory motion of the molecule as a whole.

It is clear from the diagrams that the lower two frequencies depend primarily on isomorphous motions of the separate deuterium and protium point sets; and it is satisfactory that the ratio of these frequencies, 691/533 $=$ 1·30, is as close as it is to the theoretical value $\sqrt{13/7} = 1\cdot36$. Some part of the difference, perhaps as much as a third of it, might be ascribed to the effect of anharmonicity. The remainder means that in reality there must be somewhat more carbon motion in these vibrations than our diagrams (V) and (VI) represent, whilst the carbon amplitudes in the remaining vibration must be slightly smaller than those shown in diagram (VII).

If we should assume the preliminary concentration of hydrogen motion to be directed into the B_{2g} hydrogen vibration form of the D_{6h} benzene model, and of the carbon motion into the B_{2g} carbon vibration form, the finally resulting A_2'' vibration forms of the D_{3h} molecule, which may be symbolised $A_{2u} \pm B_{2g}(H^{\leftrightarrow})$, and $B_{2g}(C^{\leftrightarrow})$, would become modified. The vector diagrams of the first two would not be very different from those of diagrams (V) and (VI) : the essential difference would be that the small carbon motions would be

found in the three carbon atoms which diagrams (V) and (VI) represent as stationary. However, the remaining vibration form would differ radically from that of diagram (VII), inasmuch as the motions within each CH-group would be parallel, not anti-parallel. On trying to fit this alternative scheme to the observed A_2'' frequencies, we meet with the following difficulty. The frequency of the vibration $B_{2g}(C^{\leftrightarrow})$ ought not to lie far from 652 cm.$^{-1}$—not lower than 601 cm.$^{-1}$, nor higher than 703 cm.$^{-1}$. The obvious frequency to allocate to this vibration is the observed 691 cm.$^{-1}$. We are then left with frequencies 533 cm.$^{-1}$ and 915 cm.$^{-1}$ for assignment to the isomorphous deuterium and protium vibrations $A_{2u} \pm B_{2g}(H^{\leftrightarrow})$. But the ratio of these numbers, 915/533, is greater than $\sqrt{2}$, and the whole assignment is therefore unacceptable.

The E' Fundamental Frequencies.—The seven frequencies of this class belong to doubly degenerate vibrations involving atomic motions which lie in the plane of the ring but do not possess its trigonal symmetry. They are active in the Raman spectrum, where they must give depolarised lines; and they are also active in the infra-red spectrum, where they must yield bands of the perpendicular type. These frequencies can be picked out practically at once as frequency coincidences in the two spectra (see Fig. 2), and in some cases they can be checked as to Raman polarisation and infra-red band-type. They are listed below in cm.$^{-1}$. The first of the figures in the parentheses under each frequency is the measured Raman depolarisation factor (theoretical value for a depolarised line, 0·86), whilst the second figure is the infra-red PR-separation in cm.$^{-1}$ (theoretical approximate value for a perpendicular band, 16 cm.$^{-1}$); a dash means that no measurement could be made :

593·0	833·5	1101·8	1407	1573·1	2292	3084
(0·88, —)	(0·80, 18)	(0·86, —)	(—, —)	(0·92, 14)	(—, —)	(—, —)

Actually there are two other coinciding frequencies, but they can be interpreted as combination tones, and it will shorten description to defer explaining why neither can be accepted as a fundamental, in place of any of those just listed, until after the latter have been discussed.

The vibrations of the E' class of the D_{3h} model of trideuterobenzene are to be regarded as formed by combination of those of the $E_g{}^+$ and $E_u{}^-$ classes of the D_{6h} benzene model (Part XI, Table V, this vol., p. 227). The $E_g{}^+$ class contains four doubly degenerate vibrations, active in the Raman spectrum only. Their normal co-ordinates cannot be precisely determined by symmetry considerations only, but it was shown in Part VIII (J., 1936, 971) that they separate rather accurately into a carbon bending, a carbon stretching, a hydrogen bending and a hydrogen stretching, vibration (cf. Part XI, Fig. 1, this vol., p. 231). The $E_u{}^+$ class contains three doubly degenerate vibrations, active in the infra-red spectrum only. Their vibration forms are not fully determined by symmetry, but it was shown in Part VIII (*loc. cit.*) that they split up fairly well into a carbon " deformation " vibration (as we shall call it, since it involves both bending and stretching of the CC-valencies), a hydrogen bending vibration, and a hydrogen stretching vibration (cf. Part XI, Fig. 1, *loc. cit.*). There is a small, but appreciable, exchange of character between the carbon deformation and hydrogen bending vibrations.

The three carbon frequencies are easily dealt with, for in their vibrations the moving unit is essentially the CH- or CD-group; wherefore the frequencies are not much shifted by deuterium substitution. For the same reason the spectral activity of the vibrations, and their vibration forms, are but little altered. Thus the carbon bending frequency, which is found in the Raman spectrum only of benzene at 605·6 cm.$^{-1}$, and in the Raman spectrum only of hexadeuterobenzene at 577·4 cm.$^{-1}$, appears at 593·0 cm.$^{-1}$ (practically the mean of the other two frequencies), strongly in the Raman spectrum and feebly in the infra-red spectrum of 1 : 3 : 5-trideuterobenzene. Similarly the carbon stretching frequency, which appears in the Raman spectrum only of benzene at 1596 cm.$^{-1}$ (although split into a doublet by resonance with a combination tone), and in the Raman spectrum only of hexadeuterobenzene at 1551·5 cm.$^{-1}$, is found at 1573·1 cm.$^{-1}$ in trideuterobenzene; and it is represented by a strong line in the Raman spectrum and a weak band in the infra-red spectrum of the compound. The carbon deformation frequency is active only in the infra-red spectrum of benzene, where it is found at 1485 cm.$^{-1}$, and only in the infra-red spectrum of hexadeuterobenzene, where it is found at 1333 cm.$^{-1}$; and, consistently, it appears strongly in the infra-red spectrum of trideuterobenzene, and weakly in the Raman spectrum, at 1407 cm.$^{-1}$, again almost exactly the mean of the other two frequencies. The normal co-ordinates of these three doubly degenerate vibrations are shown in diagrams (VIII), (IX), and (X). The indicated amplitudes are determined by the preservation of orthogonality and the necessity to avoid including any translatory motion of the whole molecule in any of the vibrations.

The situation respecting the hydrogen bending vibration is determined essentially by the relatively weak coupling of the individual motions of the hydrogen atoms. Considering first the two benzenes of D_{6h} symmetry, we note that in benzene itself the $E_g{}^+$ hydrogen bending frequency occurs in the Raman spectrum only at 1178·0 cm.$^{-1}$, and the $E_u{}^-$ hydrogen bending frequency in the infra-red spectrum only at 1037 cm.$^{-1}$. In hexadeuterobenzene the corresponding frequencies occur in corresponding spectra at 867·3 cm.$^{-1}$ and at 813 cm.$^{-1}$ respectively. The weak coupling determines that these two doubly degenerate vibrations interact in the E' class of vibrations of the D_{3h} molecule of trideuterobenzene, with double decomposition into a nearly pure, doubly degenerate, deuterium bending vibration, the frequency of which is found in about the expected place at 833·5 cm.$^{-1}$, and a nearly pure, doubly degenerate, protium bending vibration, having a frequency which we also find in about the expected position at 1101·8 cm.$^{-1}$. Both the frequencies are moderately

intense in both spectra. These combinations are of the simple type $E_g{}^+ \pm E_u{}^-$. The normal co-ordinates, which result from this approximation, are shown in the vector diagrams (XI) and (XII).

The frequencies may be compared with those to be expected in a D_{6h} " molecule " C_6X_6, in which X is a " hydrogen isotope " of mass 3/2. These C_6X_6 frequencies we estimate as usual by taking the means of the corresponding frequencies of benzene and hexadeuterobenzene (frequencies in cm.$^{-1}$) :

	C_6H_6.	C_6D_6.	" C_6X_6."	E' of $C_6H_3D_3$.
$E_g{}^+$ hydrogen (bending)	1178·0	867·3	1023	1101·8
$E_u{}^-$ hydrogen (bending)	1037	813	925	833·5

(VIII; 593·0 cm.$^{-1}$.) (IX; 1407 cm.$^{-1}$.)

(X; 1573·1 cm.$^{-1}$.)
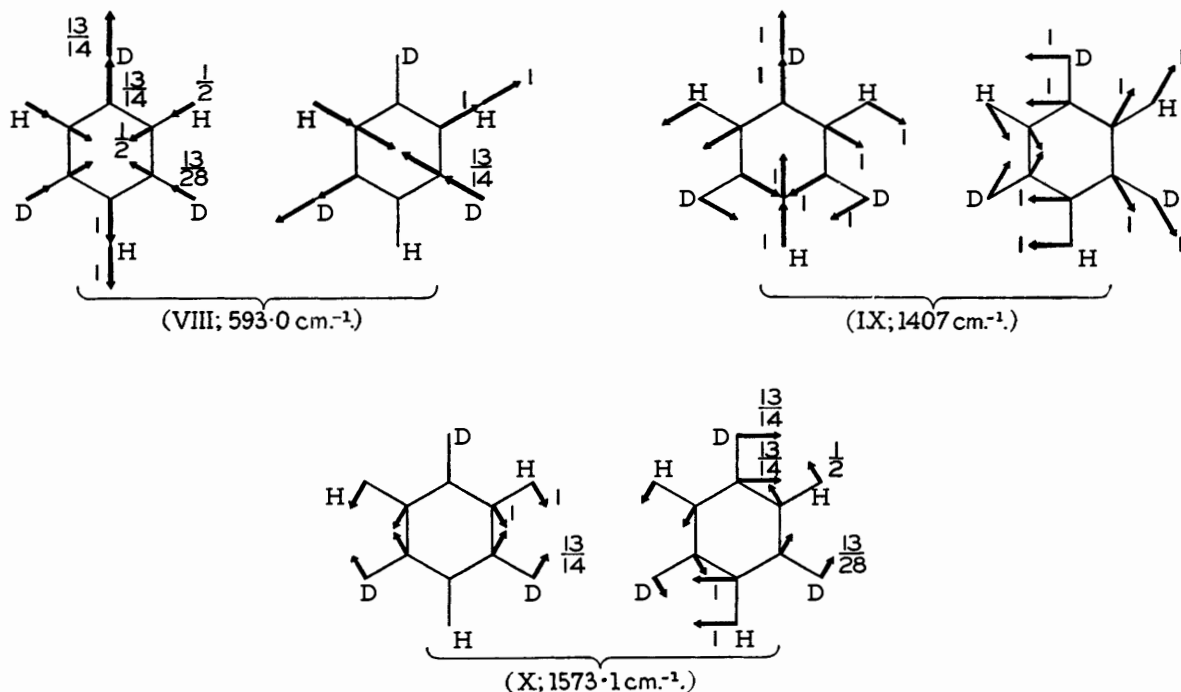
The resonance which becomes allowed when C_6X_6 is converted into $C_6H_3D_3$ by a redistribution of the hydrogen atomic masses has the normal effect of reducing the lower frequency and raising the higher one by nearly equal amounts, in this case by about 80—90 cm.$^{-1}$.

The ratio of the observed E' hydrogen bending frequencies is $1101·8/833·5 = 1·32$. The theoretical ratio for the normal co-ordinates given is $\sqrt{13/7} = 1·36$. A third or less of the difference could be ascribed to

(XI; 833·5 cm.$^{-1}$) (XII; 1101·8 cm.$^{-1}$)
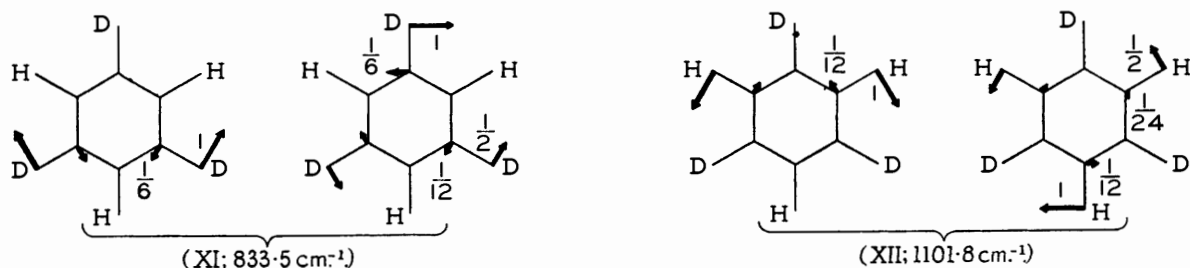
the effect of anharmonicity, but the remainder must mean that there is slightly more carbon motion in the vibrations than our simplified scheme shows. Correspondingly there must be slightly less carbon motion than we have indicated in one or another of the three carbon vibrations (VIII, IX, and X).

A similar situation arises amongst the hydrogen stretching vibrations. In benzene itself the $E_g{}^+$ hydrogen stretching frequency appears in the Raman spectrum only at 3046·8 cm.$^{-1}$; and the $E_u{}^-$ hydrogen stretching frequency in the infra-red spectrum only at 3080 cm.$^{-1}$. In hexadeuterobenzene the corresponding frequencies occur in corresponding spectra at 2264·9 cm.$^{-1}$ and 2294 cm.$^{-1}$. In trideuterobenzene these two doubly degenerate vibrations interact with double decomposition into a nearly pure, doubly degenerate, stretching vibration of the deuterium atoms only, and a practically isomorphous, doubly degenerate vibration of the protium atoms only. Their frequencies are in the expected regions, being found at 2292 cm.$^{-1}$ and 3084 cm.$^{-1}$. They both occur strongly in the infra-red spectrum, and both seem rather weak in the Raman spectrum, though

in this spectrum both are overshadowed by the neighbouring very strong hydrogen stretching frequences of the A_1' symmetry class. The approximate vibration forms of these doubly degenerate vibrations are shown in diagrams (XIII) and (XIV). They require a frequency ratio of $\sqrt{13/7} = 1.36$. The observed frequency ratio, $3084/2292 = 1.35$, differs from this only by an amount which is small enough to be attributed to anharmonicity.

The E_g^+ and E_u^- frequencies of benzene and hexadeuterobenzene being all known, we can check these assignments by means of the product rule. We find

$$\frac{\Pi E_g^+ E_u^-(C_6H_6)}{\Pi E'(C_6H_3D_3)} = \frac{605\cdot6 \times 1485 \times 1596 \times 1037 \times 1178\cdot0 \times 3046\cdot8 \times 3080}{593\cdot0 \times 1407 \times 1573\cdot1 \times 833\cdot5 \times 1101\cdot8 \times 2292 \times 3084} = 1\cdot931 \text{ (Harmonic value, } 1\cdot960\text{)}$$

$$\frac{\Pi E'(C_6H_3D_3)}{\Pi E_g^+ E_u^-(C_6D_6)} = \frac{593\cdot0 \times 1407 \times 1573\cdot1 \times 833\cdot5 \times 1101\cdot8 \times 2292 \times 3084}{577\cdot4 \times 1333 \times 1551\cdot5 \times 813 \times 867\cdot3 \times 2264\cdot9 \times 2294} = 1\cdot947 \text{ (Harmonic value, } 1\cdot962\text{)}$$

The two remaining frequencies which we might have taken into consideration initially, since they are common to the Raman and infra-red spectra, are 1067 ± 2 cm.$^{-1}$ and 2240 ± 2 cm.$^{-1}$. The acceptance of the former as a fundamental frequency in place of $1101\cdot8$ cm.$^{-1}$ can be excluded by the product rule, as well as on grounds of intensity, particularly in the Raman spectrum, and because the strong Raman frequency

XIII; 2292 cm.$^{-1}$.   XIV; 3084 cm.$^{-1}$.
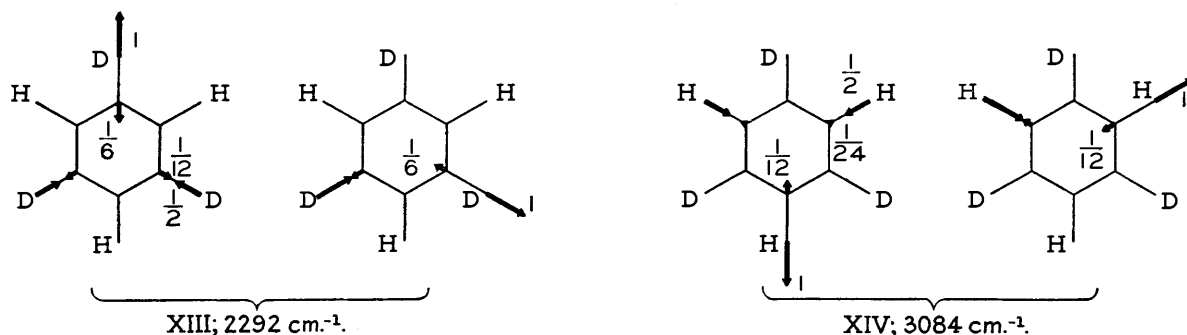
$1101\cdot8$ cm.$^{-1}$ would then be impossible to explain. The acceptance of 2240 cm.$^{-1}$ as a fundamental frequency, in place of 2292 cm.$^{-1}$, is excluded by the product rule, and on grounds of intensity in the infra-red spectrum. Other arguments in the same direction are that 2240 cm.$^{-1}$ is too low to be taken as a deuterium stretching frequency (and it is wrong altogether for any other kind of fundamental frequency), and that it is probably polarised in the Raman spectrum (measured depolarisation factor, $0\cdot77$).

The E'' Fundamental Frequencies.—This symmetry class contains three doubly degenerate vibrations, involving out-of-plane movements which do not preserve the trigonal symmetry of the $1:3:5$-trideutero-benzene molecule. The vibration forms may be regarded as derived from those of the E_u^+ and E_g^- symmetry classes of the D_{6h} benzene model. The E_u^+ class contains one carbon vibration and one hydrogen vibration, whilst the E_g^- class contains a single hydrogen vibration. Since the highest out-of-plane frequency of benzene is an inactive one of 985 cm.$^{-1}$ (see Part XXI), we may expect the three E'' frequencies to lie below, say, 1000 cm.$^{-1}$. They should appear, as depolarised lines, in the Raman spectrum only.

In the Raman spectrum of trideuterobenzene we find three prominent frequencies, other than those already assigned as fundamentals, which, as we show in more detail below, can scarcely be regarded otherwise than as fundamental frequencies (see Fig. 2). They are :

$$372\cdot7 \text{ cm.}^{-1} \qquad 710\cdot2 \text{ cm.}^{-1} \text{ (}\rho, 0\cdot81\text{)} \qquad 947 \text{ cm.}^{-1}$$

The second of these is depolarised, the measured depolarisation factor being $0\cdot81$. The first appears to be depolarised, as far as can be judged from its breadth as revealed by the microphotometric contour; but it was not quite strong enough, and not sufficiently clear of the halation area around the Rayleigh line, to allow of a satisfactory measurement of polarisation. The third is too much overlapped by the neighbouring very strong frequency at $956\cdot2$ cm.$^{-1}$ to permit either measurement or unequivocal judgment with respect to its polarisation. None of the three frequencies appears in the infra-red spectrum. It follows from these reasons, and also by exclusion, that, if the frequencies are indeed fundamental frequencies, they must belong to the E'' symmetry class.

The existence in ordinary benzene of an inactive fundamental frequency of about 400 cm.$^{-1}$ was first suggested by Lord and Andrews, who found that some such assumption seemed needed to give a correct value to the statistically calculated entropy of benzene (*J. Physical Chem.*, 1937, **41**, 149). They regarded the frequency as doubly degenerate, and therefore as belonging to the E_u^+ symmetry class, the frequencies of all other degenerate symmetry classes being known from our earlier work. We confirmed these suggestions by implication when we assigned the frequency $372\cdot7$ cm.$^{-1}$ of $1:3:5$-trideuterobenzene as an E'' fundamental

frequency (*Nature*, 1937, **139**, 880), and one of us subsequently gave the argument in greater detail (*Z. Elektrochem.*, 1938, **44**, 20). So low a frequency as that to which Lord and Andrews drew attention could only belong to a carbon vibration. The frequency of a carbon vibration is not expected to be greatly shifted by deuterium substitution, provided that, if it were not shifted, it would be not so close to some other fundamental frequency of the same symmetry class that substantial resonance would ensue; and the frequencies contemplated are so low that this condition is fulfilled for all the deuterated benzenes. Therefore, even after making allowance for the tendency of the geometry and valency structure relatively to increase the hydrogen amplitudes (see below), and thus somewhat enlarge the frequency shifts, we should expect the corresponding out-of-plane carbon vibrations of all the deuterated benzenes to lie in the region of, say, 350—400 cm.$^{-1}$. This granted, there follows from symmetry considerations a definitely diagnostic series of rules for the spectral activity of such frequencies in the partly deuterated benzenes. Thus they should be active in the Raman spectra of mono-, 1 : 3 : 5-tri-, and penta-deuterobenzene, but not in the Raman spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene; and they should be active in the infra-red spectra of all of these benzenes except the trideutero-compound. Apart from the fact that the infra-red spectrum of pentadeuterobenzene has not yet been examined (Part XI, this vol., p. 223), all these consequences have been verified, and a sufficient proportion of them had been verified in 1937 to make it certain that the basic assumption of Lord and Andrews was sound. Unequivocal confirmation arises in the analysis of the electronic spectra of benzene and hexadeuterobenzene (cf. Part XXI, this vol., p. 316). It may be added that the frequency 372·7 cm.$^{-1}$ of 1 : 3 : 5-trideuterobenzene can have no satisfactory explanation as a difference tone, and, since it obviously cannot be a summation tone, it must be a fundamental frequency, and therefore, as already noted, one belonging to the E'' class, in fact, the frequency of the degenerate carbon vibration of that class.

The frequency 710·2 cm.$^{-1}$ of trideuterobenzene appears too strongly in the Raman spectrum to be a difference tone, and it is too low a frequency to be interpreted as a summation tone. Therefore it is a fundamental frequency, evidently that of one of the two degenerate hydrogen vibrations of the E'' class.

The remaining frequency, 947 cm.$^{-1}$, was the one fundamental frequency which was not included in the list of assigned fundamentals given in 1937, because there was then some dubiety about its assignment. Langseth and Lord (1938, *loc. cit.*) found a weak frequency at 815 cm.$^{-1}$ in the Raman spectrum of trideuterobenzene, and attempted to complete our assignment of Raman-active fundamental frequencies by taking this as the third frequency of the E'' class. We have made a careful search for their frequency 815 cm.$^{-1}$, using exposures which bring into the photographs considerably weaker combination tones than any which they record. We cannot find a frequency of 815 cm.$^{-1}$, and think it must have arisen in Langseth and Lord's plates from an impurity in the sample of trideuterobenzene employed (possibly 1 : 3-dideuterobenzene).

The Raman line at 947 cm.$^{-1}$ is not weak : although its intensity is difficult to judge because of the overlapping, it is probably stronger than the lowest fundamental line at 372·7 cm.$^{-1}$, of the E'' symmetry class, although not so strong as the remaining line at 710·2 cm.$^{-1}$, belonging to the same class. The line at 947 cm.$^{-1}$ appears, for instance, in the lightly exposed plate from which the microphotometric record of Fig. 3a was made. This photograph depicts the region 940—1015 cm.$^{-1}$ of the (Stokes) Raman spectrum excited by Hg 4046·56 A. The region is, of course, dominated by the two very strong lines of frequencies 956·2 and 1003·6 cm.$^{-1}$, which are marked A and B respectively; the line at 947 cm.$^{-1}$ is labelled C, and it will be seen that at least half its breadth is overlapped by the very strong line at 956·2 cm.$^{-1}$. There exist also in the region of this microphotographic record two lines which we classify as " weak " (not " very weak "), but they are quite invisible at the exposure employed. In more heavily exposed plates, such as that which yielded the microphotometric record of Fig. 3b, they are visible, and in the photograph they are marked D and E. Line D, of frequency 969 cm.$^{-1}$, is a combination tone of no special interest, but the other line E of frequency 993 cm.$^{-1}$ has relevance to the present discussion.

The frequency 947 cm.$^{-1}$ (C) cannot be interpreted as a combination tone. For a time there was a doubt as to whether it was not the frequency of a totally symmetrical vibration of a molecule containing the carbon isotope of mass 13, *viz.*, $^{12}C_5{}^{13}CH_3D_3$. However, we are of the opinion that it lies too low as to frequency, and is too great in intensity, to permit of this explanation. Actually there should be four ^{13}C lines, all of comparable intensity, which, apart from obscuration by the lines of the $^{12}C_6$ isomeride, should be capable of observation under our conditions. Their frequencies can be approximately estimated in various ways. Two should be nearly coincident with, and therefore wholly obscured under, the strong frequency 956·2 cm.$^{-1}$; one should be almost coincident with, and wholly obscured under, the strong frequency 1003·6 cm^{-1}; and one should appear in an otherwise clear part of the spectrum at about 990 cm.$^{-1}$. This we observe, with about the expected intensity, at 993 cm.$^{-1}$. There can be no doubt as to the identification : the frequency 993 cm.$^{-1}$ cannot be explained as a combination tone of the main isomeride, and, as we shall show shortly, it cannot itself be accepted in place of 947 cm.$^{-1}$, as the remaining fundamental frequency of the E'' symmetry class.

Confirmation of the choice of the 947 cm.$^{-1}$ frequency comes from an application of the product rule of Teller and Redlich. As shown in Part XXI (this vol., p. 320), it follows by analysis of the infra-red spectra of 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene (Part XIX, this vol., p. 288), that the products of the two $E_u{}^+$ frequencies of benzene and hexadeuterobenzene are as follows :

$$\Pi E_u{}^+(C_6H_6) = 395,300 \text{ cm.}^{-2} \qquad \Pi E_u{}^+(C_6D_6) = 282,900 \text{ cm.}^{-2}$$

Referring to Table XI of Part XI (this vol., p. 232) for the appropriate product ratios, and to the scale of

FIG. 3.
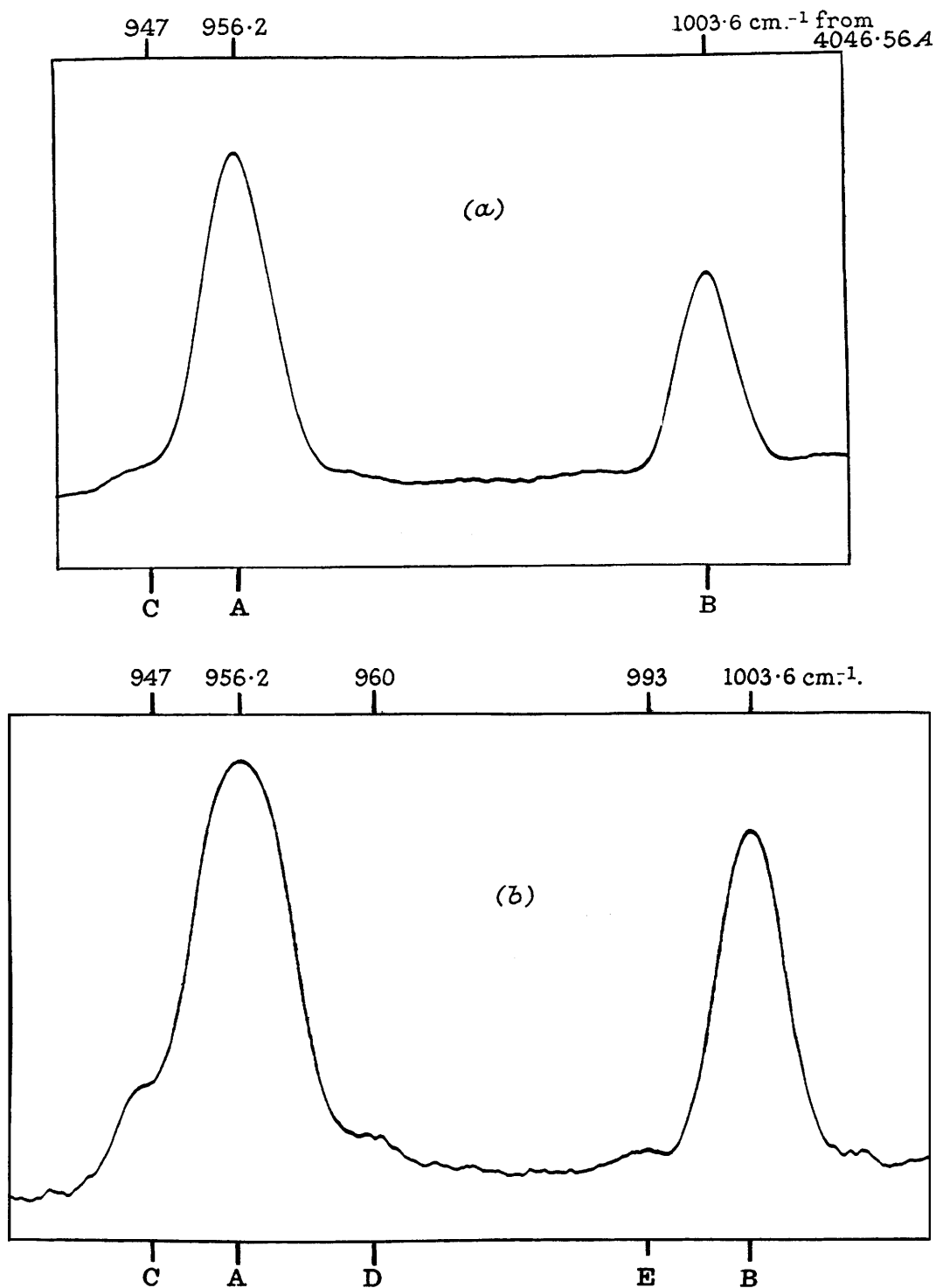
Microphotometer records of part of Raman spectrum of 1 : 3 : 5-*trideuterobenzene excited by mercury radiation :*
(a) *Weak exposure*, (b) *Strong exposure.*

anharmonicity corrections given in the same paper (p. 233), we can set up the following relations, in which ν, the third fundamental frequency of the E'' class of 1 : 3 : 5-trideuterobenzene, is treated as unknown :

$$\frac{\Pi E_u^+ E_g^-(C_6H_6)}{\Pi E''(C_6H_3D_3)} = \frac{395{,}300 \times 848\cdot9}{372\cdot7 \times 710\cdot2 \times \nu} = 1\cdot337 \qquad \frac{\Pi E''(C_6H_3D_3)}{\Pi E_u^+ E_g^-(C_6D_6)} = \frac{372\cdot7 \times 710\cdot2 \times \nu}{282{,}900 \times 661\cdot7} = 1\cdot343$$

The first equation gives $\nu = 948$, the second $\nu = 950$ cm.$^{-1}$. Alternatively we can turn to the evidence provided by fluorescence spectra of benzene and hexadeuterobenzene, and by the Raman and infra-red combination tones of these compounds (Part XXI, this vol., pp. 319, 320), and employ the derived individual values, 405 and 970 cm.$^{-1}$, of the E_u^+ frequencies of benzene, and the corresponding frequencies, 352 and 793 cm.$^{-1}$, of hexadeuterobenzene. Using these values instead of the above products, we obtain, from the benzene frequencies $\nu = 942$, and from the hexadeuterobenzene frequencies $\nu = 938$ cm.$^{-1}$. Thus there can be no doubt that the trideuterobenzene Raman frequency at 947 cm.$^{-1}$ has been correctly chosen as the third E'' fundamental frequency.

It remains to consider the normal co-ordinates of the three degenerate E'' vibrations, which are to be built up from vibration forms similar to the two E_u^+ vibrations, and the single E_g^- vibration, of the D_{6h} benzene model (Part XI, Table V, this vol., p. 227).

Just as with the B_{2g} vibrations of benzene, so also with its E_u^+ vibrations, the geometry and valency structure of the molecule secures the inclusion of more than the normal proportion of hydrogen motion in the carbon vibration and more than the normal proportion of carbon motion in the hydrogen vibration (cf. p. 261). For instance, if in the E_u^+ carbon vibration all the bending were in the CC-bonds, and none of it in the CH-bonds, in other words, if each group C·(CH)·C always preserved a plane, the hydrogen amplitudes would be greater than the carbon amplitudes in the ratio {(CC) + 3(CH)}/(CC) = 3·26, where (CC) and (CH) are the lengths of the C–C and C–H bonds. This we may see, for instance, by bending equally but in alternate directions, those parts of a model of the molecule which lie outside the quadrilateral formed by joining para-carbon atoms to the mid-points of the bonds between the remaining carbon atoms. The hypothesis is, of course, too extreme, but the valency structure will still be expected to act in this direction, and therefore to bring an abnormally large proportion of hydrogen motion into the E_u^+ carbon vibration, and reciprocally, as the orthogonality principle requires, an unusually large proportion of carbon motion into the E_u^+ hydrogen vibration. The existence of this reciprocal transfer is clear from the frequencies, as determined in Part XXI (*loc. cit.*) : the shifts between benzene and hexadeuterobenzene are such as to show that carbon and hydrogen motion contribute not very far from equally to the kinetic energy, alike of the E_u^+ carbon, and the E_u^+ hydrogen, vibration.

The principle that the motions of light atoms can be only very weakly coupled by linking through heavier intermediate atoms leads us to expect that the two hydrogen vibrations of the E'' class of trideuterobenzene will consist essentially of isomorphous vibrations of the protium and deuterium point-sets. One of the D_{6h} vibration forms from which they have to be constructed is the E_g^- form, in which the carbon and hydrogen hexagons rock in opposition about a common diametral axis. In this vibration, the condition that the molecule as a whole shall not possess angular momentum necessitates that, for benzene, the ratio of carbon amplitudes to corresponding hydrogen amplitudes shall be $f/12 : 1$ ($f/6 : 1$ for hexadeuterobenzene), where $f = \{(CC) + (CH)\}/(CC) = 1\cdot78$. Combination with an E_u^+ vibration form, in which the amplitudes have the same ratio, will produce the required decomposition into isomorphous vibrations of the protium and deuterium point-sets. We are prepared to envisage a preliminary redistribution of kinetic energy between the two E_u^+ vibration forms in order to secure an E_u^+ vibration with the necessary amplitude ratio. The frequencies show, however, that all that is required is a quite small additional accumulation of hydrogen kinetic energy in the E_u^+ hydrogen vibration.

The assumption of a modified E_u^+ hydrogen vibration with the amplitude ratios stated above leaves us with an E_u^+ carbon vibration in which the hydrogen amplitudes are greater than the corresponding carbon amplitudes in the ratio $f = 1\cdot78$; it is also to be noted that, in order to preserve this vibration from including any rotation of the molecule as a whole, the amplitudes in a CD-group must be smaller than corresponding amplitudes in a corresponding CH-group, e.g., by the uniform factor $\phi = (12 + f^2)/(12 + 2f^2) = 0\cdot83$. This vibration will survive, in our approximation, as the carbon vibration of the final E'' class of 1 : 3 : 5-trideuterobenzene. The fact that the observed frequency, 372·7 cm.$^{-1}$, is not far from the mean, 377 cm.$^{-1}$, of the E_u^+ carbon frequencies of benzene and hexadeuterobenzene shows that the amplitude ratio in the E_u^+ carbon vibration of benzene itself cannot be very different from $f = 1\cdot78$, and must be much less, therefore, than the limit, 3·26, which would obtain under the assumption of CH-bonds acting as if they were infinitely stiff in this vibration. The normal co-ordinates of the degenerate E'' carbon vibration of 1 : 3 : 5-trideuterobenzene are shown in diagram (XV).

We have assumed that the E_u^+ hydrogen vibration, as it appears in benzene or hexadeuterobenzene, will require a small additional accumulation of hydrogen kinetic energy in order that it shall produce isomorphous protium and deuterium vibrations when combined with the E_g^- vibration according to the formula $E_u^+ \pm E_g^-$. This is indicated by the rather smaller percentage frequency shift, from benzene to hexadeuterobenzene, which is experienced by the E_u^+ hydrogen vibration, as compared with that undergone by the E_g^- vibration. Combination of the modified E_u^+ vibration form with the E_g^- vibration produces, in our approximation, the

normal co-ordinates for the remaining two E'' vibrations of $1:3:5$-trideuterobenzene. They are represented in diagrams (XVI) and (XVII).

Comparing the observed E'' frequencies with those of a hypothetical D_{6h} " molecule " C_6X_6, in which X is a " hydrogen isotope " of mass $3/2$, we obtain the following correlations, in which the normal effects of resonance are observed :

	C_6H_6.	C_6D_6.	" C_6X_6."	E'' of $C_6H_3D_3$.
E_u^+ carbon	405	352	379	372·7
E_u^+ hydrogen	970	793	882	947
E_g^-	848·9	661·7	755	710·2

The very wide separation of the two E_u^+ frequencies of " C_6X_6 " ensures that the small preliminary interaction, which we have assumed the corresponding vibrations to undergo, shall not much alter the frequencies : the lower one, 379 cm.$^{-1}$, is reduced a few wave-numbers to 372·7 cm.$^{-1}$, which survives as an E'' frequency of $C_6H_3D_3$; whilst the upper one, 882 cm.$^{-1}$, is presumably raised slightly, possibly to 890—895 cm.$^{-1}$. The main resonance effect is between this modified frequency and the E_g^- frequency, 755 cm.$^{-1}$, of " C_6X_6 "; and, consistently, we find that the upper frequency is raised, and that the lower one is reduced, in $C_6H_3D_3$ by roughly equal differences of about 50 cm.$^{-1}$.

Our approximate analysis represents the upper two E'' frequencies as belonging to isomorphous protium and deuterium vibrations, with only sufficient carbon motion to cancel any rotation of the molecule as a whole. The ratio of these frequencies is $947/710 = 1·33$. The ratio should be 1·29. The difference shows that in reality there is rather less carbon motion in these vibrations, and consequently slightly more carbon motion in the E'' carbon vibration, than is represented in our simplified diagrams.

(XV; 372·7 cm.$^{-1}$.)   (XVI; 710·2 cm.$^{-1}$.)

(XVII; 947 cm.$^{-1}$.)
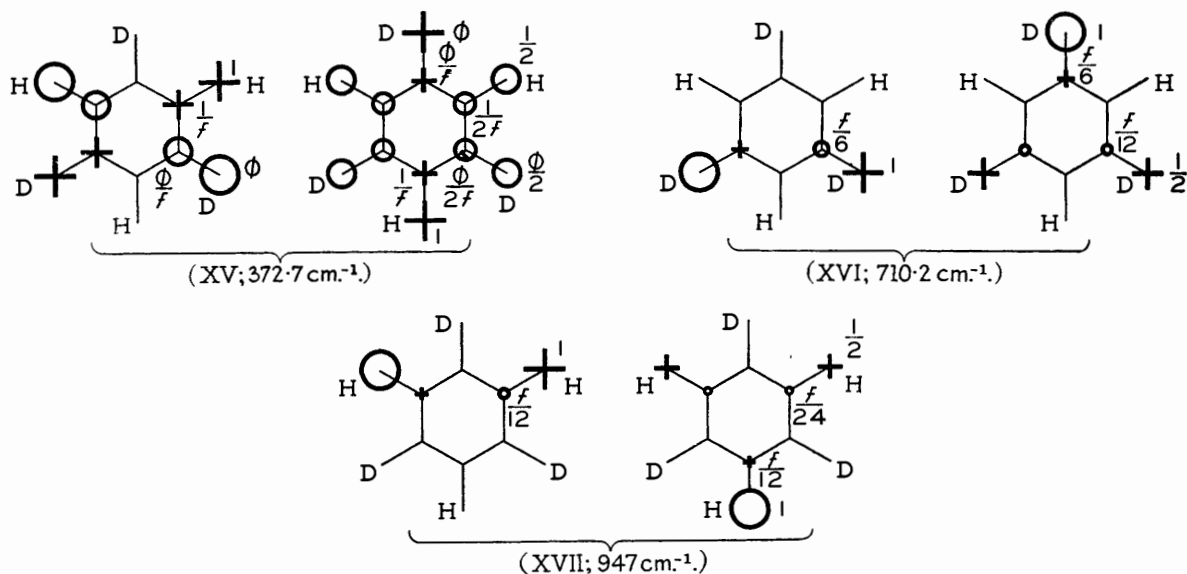
If we should have tried to combine the E_u^+ carbon vibration form with the E_g^- vibration, the E_u^+ hydrogen vibration form would have been left as one of the final E'' vibrations of $1:3:5$-trideuterobenzene. Its normal co-ordinates can be obtained from diagram (XV) by reversing all the carbon vectors. To this vibration we should have had to assign the frequency 947 cm.$^{-1}$. The remaining frequencies, 372·7 and 710·2 cm.$^{-1}$, would then have had to be assigned to the other two E'' vibrations, the normal co-ordinates of which are similar to those of diagrams (XVI) and (XVII), except that the small carbon motions are in different carbon atoms. Thus they are, once again, substantially isomorphous vibrations of the protium and deuterium point-sets, and the ratio of their frequencies could not be what we find, namely, $710·2/372·7$, which exceeds $\sqrt{2}$.

The Raman-active Overtones and Combination Tones.—From Table XIII of Part XI (this vol., p. 234) it will be seen that the following categories of overtones and combination tones are allowed in the Raman spectrum :

(1) All first overtones and binary combination tones between fundamental frequencies of the same symmetry class. (These harmonics all belong to the A_1' symmetry class, and may therefore produce polarised Raman lines. If the fundamentals are degenerate, the harmonics belong equally to the E' symmetry class, and this confers on them infra-red activity also.)

(2) All binary combination tones between fundamental frequencies of different symmetry classes, provided that at least one fundamental frequency is degenerate. (These harmonics belong either to the E' class or the E'' class, and therefore must give depolarised Raman lines. The E' class of harmonics are also active

in the infra-red. When both the fundamentals are degenerate, the derived harmonics belong equally to the E'' class and to the A_2'' class, and hence these harmonics also are active in the infra-red.)

Guided by these rules, we have assigned the observed higher harmonics of the Raman spectrum as shown in Table I (p. 256). In some cases alternative interpretations are possible, and when this is so they are given in the table.* There are no observed harmonics which cannot be interpreted, according to the selection rules, on the basis of the spectrally active fundamental frequencies, and the assignment of these already given. One alternative assignment is given which involves an inactive fundamental frequency (see below).

Three higher harmonics are of outstanding intensity, namely, those at 2238·3, 2973·3, and 3144·5 cm.$^{-1}$. The second of these is certainly polarised, and the others may be. It seems significant that all belong to the A_1' symmetry class, and that all are within 100 cm.$^{-1}$ of one of the intense fundamental frequencies of this class—the totally symmetrical deuterium and protium stretching frequencies at 2281·9 and 3052·7 cm.$^{-1}$. Probably the higher harmonics " borrow " some of their intensity, as their symmetry permits, from their very strong neighbours by resonance in the well-known way. The same effect should in principle shift the frequencies. Shifts of a few wave-numbers may have occurred; but we should not expect any striking frequency displacements, since the higher harmonics, even in their calculated unperturbed positions, are not very close to the fundamentals; and observation shows that, even if the higher harmonics have undergone a considerable relative increase of intensity, they have not absorbed any large fraction of the intensity of the fundamental frequencies.

The Infra-red Combination Tones.—Table XIII of Part XI (*loc. cit.*) shows that the following higher harmonics may appear in the infra-red spectrum.

(1) Binary combination tones between totally symmetrical (A_1') fundamental frequencies, on the one hand, and infra-red-active (A_2'' and E') fundamental frequencies, on the other. (These combinations should give parallel or perpendicular bands according as the contributing infra-red fundamental band is parallel or perpendicular. The higher harmonics which give perpendicular bands are also allowed to appear in the Raman spectrum.)

(2) Binary combination tones between certain non-degenerate and degenerate fundamental frequencies, *viz.*, combinations of the A_2' class with the E' class, and of the A_2'' with the E'' class. (These should all give perpendicular bands; they are allowed also in the Raman spectrum.)

(3) First overtones of any degenerate fundamental frequency, and binary combination tones of any two degenerate fundamental frequencies. (These should give perpendicular bands, except that combinations of fundamental frequencies of two different degenerate symmetry classes should produce parallel bands. Those which give perpendicular bands are allowed in the Raman spectrum.)

The observed higher harmonics in the infra-red spectrum are assigned in conformity with these rules in Table II (p. 257), alternative interpretations being given where alternatives are possible.† There is one difference tone, namely, that at 463 cm.$^{-1}$, and it is very weak as would be expected. The other combination tones are of the binary summation type, and are for the most part of moderate intensity or less, although one, namely, that at 1835 cm.$^{-1}$, is stronger than is usual for combination tones.

The one combination band which we were able to resolve with respect to its rotational branches, namely, that which has a Q-branch frequency of 1632 cm.$^{-1}$, is clearly of the perpendicular type. There are two possible assignments for this harmonic, and they both require the band should be of the perpendicular type.

Two of the combination frequencies, 1065 cm.$^{-1}$ and 2242 cm.$^{-1}$, appear also in the Raman spectrum (at 1069 cm.$^{-1}$ and 2238·3 cm.$^{-1}$), and this is allowed by the selection rules. However, the double appearance of the frequency 1065—1069 cm.$^{-1}$ may arise from the accidental agreement between the frequency of the combination tone (691 + 373 = 1064 cm.$^{-1}$) and that of a first overtone (2 × 533 = 1066 cm.$^{-1}$), which is allowed in the Raman spectrum only.

Not quite all the higher harmonics of the infra-red spectrum can be interpreted in conformity with the selection rules on the basis of the 17 directly observed fundamental frequencies, and the assignment which has been worked out for them : there is one band of moderate intensity, namely, that at 1750 cm.$^{-1}$, which cannot be so explained. It seems altogether too strong to be a difference tone, or a ternary combination of any kind, and there is no fundamental frequency which could appear in this region of the spectrum. The frequency can only be interpreted, therefore, as a binary summation tone involving one of the inactive fundamental frequencies.

The Inactive Fundamental Frequencies of the A_2' Class.—This is the one symmetry class the vibrations of which are forbidden both in the Raman and in the infra-red spectrum. We are able at present only partially to solve the problem of identifying the frequencies of these vibrations.
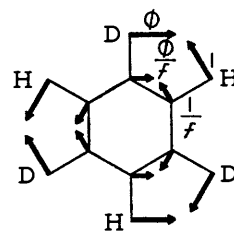
There are three vibrations, and they may be regarded as composed by orthogonal combination of initial vibration forms similar to those of the single A_{2g} vibration and the two B_{2u} vibrations of the D_{6h} benzene model (Part XI, Table V, this vol., p. 227). The A_{2g} vibration is a hydrogen vibration, which involves counter-rotatory movements of the carbon and hydrogen hexagons in the plane of the ring. The B_{2u} vibrations consist of a carbon and a hydrogen vibration, distinguished as usual by the circumstance that the motions in each CH-group are parallel in the former and antiparallel in the latter each of these vibrations involves

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* A few further alternative interpretations become possible when we assume values for the two higher inactive fundamental frequencies of the A_2' class, which are not accurately known. These are not included in Table I.

† The remark in the above footnote applies to Table II also.

a trigonally symmetrical system of atomic movements, in the plane of the ring, and at right angles to the hydrogen valencies. When, under the D_{3h} symmetry of $1:3:5$-trideuterobenzene, interaction between these three vibration forms is permitted, we expect to obtain, in the resulting A_2' class, one carbon and two hydrogen vibrations.

We set up the normal co-ordinates by our usual approximate method, which assumes a decomposition of the initial D_{6h} hydrogen vibrations into isomorphous D_{3h} vibrations of the deuterium and protium point-sets. In one of the original hydrogen vibrations, A_{2g}, the ratios of the carbon and hydrogen amplitudes are fixed by the condition that the whole molecule must not possess angular momentum. Therefore we assume such preliminary interaction between the two initial B_{2u} vibrations as will produce a B_{2u} hydrogen vibration form having carbon and hydrogen amplitudes in corresponding ratios. Interaction of the type $A_{2g} \pm B_{2u}$ between the A_{2g} vibration and the modified B_{2u} hydrogen vibration form then gives the two A_2' hydrogen vibrations of the D_{3h} molecule, namely, the vibrations whose normal co-ordinates are shown in diagrams (XVIII) and (XIX). The residual modified B_{2u} carbon vibration form survives as the A_2' carbon vibration. Its normal co-ordinate is represented in diagram (XX). The symbol f contained in some of the amplitude indications signifies $\{(CC) + (CH)\}/(CC) = 1\cdot78$, whilst ϕ is an abbreviation for $(12 + f^2)/(12 + 2f^2) = 0\cdot83$.
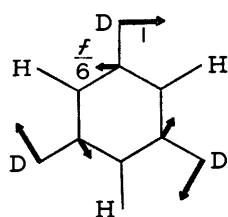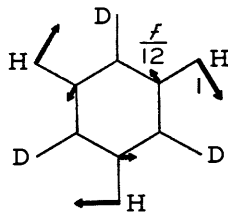
(XVIII; 920 cm.$^{-1}$.)   (XIX; ~1230 cm.$^{-1}$.)   (XX; frequency uncertain.)

The spectral range within which we should expect to find the frequency of the deuterium bending vibration, (XVIII), may be placed at 850—1000 cm.$^{-1}$. The corresponding spectral range which should include the frequency of the protium bending vibration, (XIX), would be about 1100—1300 cm.$^{-1}$. These ranges are simply judged from other known hydrogen bending frequencies. The frequency of the carbon vibration, (XX), depends essentially on the stretching of C–C bonds, and should lie higher. Attempts to calculate the frequency of the corresponding (B_{2u} carbon) vibration of benzene itself have indicated 1500—1800 cm.$^{-1}$ as the likely region. Since the frequency of a carbon vibration of this type is unlikely to be changed by more than a few units per cent. on the introduction of deuterium atoms into the molecule, the same spectral range should include the frequency of the A_2' carbon vibration, (XX), of trideuterobenzene.

The most precise indication we have with respect to any of these frequencies arises from the already mentioned infra-red combination tone at 1750 cm.$^{-1}$. This binary summation tone must involve, as one of the contributing fundamental frequencies, one of the unknown A_2' frequencies. The selection rules require that the other contributing fundamental frequency can only be one of those belonging to the E' symmetry class. Under this restriction, and having regard to the ranges within which the A_2' frequencies are likely to fall, there are only two ways, each involving an assumed A_2' frequency, of composing the summation frequency. The first, $(A_2')\ 1157\cdot0 + (E')\ 593\cdot0 = 1750$, assumes an A_2' frequency, in round figures 1160 cm.$^{-1}$, which might belong to the protium bending vibration, (XIX). The second, $(A_2')\ 916\cdot5 + (E')\ 833\cdot5 = 1750$, involves the assumption of an A_2' frequency, in rounded form 920 cm.$^{-1}$, which might be assigned to the deuterium bending vibration, (XVIII).

We can now make an application of the product theorem, which, although crude, suffices for a decision between these alternative interpretations. In Part XXI we determine the A_{2g} frequency, and also the B_{2u} hydrogen frequency, of benzene. Let us suppose, first, that we know that the A_2' protium frequency of $1:3:5$-trideuterobenzene is 1160 cm.$^{-1}$, and wish to calculate the A_2' deuterium frequency, ν, of this substance. Normally we should require to know, in addition, the B_{2u} carbon frequency of benzene and the A_2' carbon frequency of trideuterobenzene; but we can avoid the use of the necessarily somewhat dubious values, which we might have inserted for these frequencies into the product formula, by introducing instead their assumed ratio, $1\cdot025$, a figure which is probably good to about 1%, even though it has no better basis than that the percentage difference between the frequencies is taken as half the percentage difference between the frequencies of the totally symmetrical carbon stretching vibrations of benzene and hexadeuterobenzene. Taking the product ratio from Table XI of Part XI (this vol., p. 232), and making the usual allowance for anharmonicity (*loc. cit.*), we can set up the following equation :

$$\frac{\Pi A_{2g} B_{2u}(C_6H_6)}{\Pi A_2'(C_6H_3D_3)} = \frac{1326 \times 1110}{1160 \times \nu} \times 1\cdot025 = 1\cdot335$$

The derived value of ν is 973 cm.$^{-1}$. The ratio of the two A_2' hydrogen frequencies of $1:3:5$-trideuterobenzene then becomes $1160/973 = 1\cdot19$. This is an unacceptably low value for the ratio of the frequencies of approximately isomorphous protium and deuterium vibrations. Turning now to the other possibility,

namely, that the A_2' deuterium frequency is 920 cm.$^{-1}$, and inserting this, in place of 1160 cm.$^{-1}$, in the same equation in order to determine ν, now regarded as the A_2' protium frequency, we find for ν the value 1230 cm.$^{-1}$. The ratio of these A_2' hydrogen frequencies is $1230/920 = 1\cdot34$. The theoretical value, if diagrams (XVIII) and (XIX) were strictly accurate, would be $1\cdot29$. The deviation of the found ratio is not greater than that which should be expected to arise from the approximations made in our simplified determination of the normal co-ordinates. Obviously we have placed somewhat too much carbon motion in the hydrogen vibrations and not quite enough in the carbon vibration.

Another indication in favour of our interpretation is that the frequencies 920 and 1230 cm.$^{-1}$ appear reasonable when set beside the A_{2g} and B_{2u} hydrogen frequencies of a " molecule " C_6X_6, in which X is a " hydrogen isotope " of mass 3/2—the C_6X_6 frequencies being estimated, as usual, as means of the corresponding frequencies of C_6H_6 and C_6D_6. The comparison is as follows (frequencies in cm.$^{-1}$) :

	C_6H_6.	C_6D_6.	" C_6X_6."	A_2' of $C_6H_3D_3$.
A_{2g}	1326	1037	1182	~1230
B_{2u} hydrogen	1110	825	968	920

Neglecting, as we probably may, the chance of any drastic displacement of the hydrogen frequencies of $C_6H_3D_3$, due to interaction with the A_2' carbon frequency, we expect the hydrogen frequencies of C_6X_6 to be spread apart, approximately symmetrically, when interaction is permitted on redistribution of the hydrogen masses to form $C_6H_3D_3$. Consistently, we find the upper one raised, and the lower one reduced, each by about 50 cm.$^{-1}$. This normal effect of resonance would not be observed if we should replace the adopted trideutero-benzene frequencies by their alternatives, 1160 and 973 cm.$^{-1}$. It will be understood that, whilst the frequency 920 cm.$^{-1}$ is probably rather exactly determined, the figure 1230 cm.$^{-1}$ might be in error by as much as 2%.

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