62. *Structure of Benzene. Part XVIII. The Raman Spectra of* 1 : 4-*Dideuterobenzene and* 1 : 2 : 4 : 5-*Tetradeuterobenzene : Description and Analysis.*

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1 : 4-Dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene have the same symmetry (V_h). The distribution of protium and deuterium atoms in these molecules secures that each of those vibrations which are doubly degenerate in benzene or hexadeuterobenzene (symmetry D_{6h}), or in 1 : 3 : 5-trideuterobenzene (symmetry D_{3h}), becomes replaced by two definite and distinct vibrations, each with its characteristic frequency. The symmetry elements present in the di- and tetra-deuterobenzene molecules include a centre. Each molecule thus has 15 "gerade" and 15 "ungerade" fundamental vibrations, of which the former only are active in the Raman effect. This paper is concerned with the "gerade" vibrations of both molecules; the next paper deals with their "ungerade" vibrations.

The Raman spectra of the two V_h benzenes have been studied, and 30 or more lines have been measured in each spectrum. Accurate frequencies and approximate degrees of polarisation are recorded, as well as rough estimates of integrated intensity. The expected resolutions in these spectra of the degeneracies characteristic of the spectra of the D_{6h} and D_{3h} benzenes have been observed, although the frequency separations were in some cases so slight that a careful study of densitometric contours was necessary.

All the 15 "gerade" fundamental frequencies have been observed and identified in each spectrum. Evidence of identity is based on the observed frequencies, intensities, and polarisations, considered in the light of the selection rules for intensity and polarisation, and our empirical knowledge of the spectral regions in which frequencies corresponding to particular types of vibration should appear. Important confirmation arises from comparisons of the frequencies of the two V_h benzenes with one another, and with the already known and identified fundamental frequencies of the D_{6h} and D_{3h} benzenes. The main arguments involving such comparisons are based upon the product rule (Teller and Redlich); but use is also made of considerations relating to those modifications in the normal co-ordinates of certain vibrations which are expected to arise from particular redistributions of deuterium atoms. A scheme of approximate but orthogonal normal co-ordinates is suggested.

The identification of fundamental frequencies, as worked out in this and the next paper, permits the assignment, in accordance with the selection rules, of all the higher harmonic frequencies found in the Raman spectra of the two benzenes.

1 : 4-Dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene have the same symmetry and therefore the same spectroscopic selection rules. Accordingly, it is convenient to deal with these two molecules together. Each possesses, in particular, a centre of symmetry. Hence no frequency can occur in both the Raman and infra-red spectrum of either substance. Therefore each molecule has one set of fundamental frequencies which can appear only in the Raman spectrum, and another, different, set of fundamental frequencies which are active only in the infra-red spectrum; and each molecule has a set of fundamental frequencies which are inactive in both spectra. It follows that for these molecules the analyses of the Raman and the infra-red spectra are largely independent of each other. In this paper we record and analyse the Raman spectra of 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene. In the next paper the infra-red spectra of the same two molecules are described and analysed, a note being added with reference to the inactive frequencies in order to complete the tale of the fundamental vibrations of these compounds.

The Raman spectrum of 1 : 4-dideuterobenzene was first recorded by Redlich and Stricks (*Monatsh.*, 1936, **67**, 213), who classified the vibrations, and gave an assignment (which was correct as far as it went) of some of the fundamental frequencies. These authors' record of Raman-active frequencies was, however, very incomplete; and, even so, it included some frequencies which we cannot confirm. Langseth and Lord (*Kgl. Danske Vidensk. Selsk.*, 1938, **16**, 6) described the Raman spectra of 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene, and suggested an assignment of all the Raman-active fundamental frequencies. There are, however, a number of divergences between these authors' observations and ours, and consequently some differences in the assignment of frequencies. It would appear that neither Redlich and Stricks nor Langseth and Lord had very pure material at their disposal. Some of the discrepancies between Langseth and Lord's results and ours are clearly traceable to their use of unfiltered mercury radiation for the excitation of the spectra (cf. Part XV, this vol., p. 245).

The present work was carried out with 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene prepared by Wilson and his collaborators (Parts XII and XIII, this vol., pp. 235, 239). The spectra showed the samples to be of a high standard of isotopic purity. The general conditions of the measurements, and the standards of accuracy achieved, were as described for the case of 1 : 3 : 5-trideuterobenzene (Part XVII, this vol., p. 256). Our results for the frequency, intensity, and polarisation of the di- and tetra-deuterobenzene are recorded in the first three columns of Tables I and II. The braces in the first columns indicate groups of overlapping Raman lines. The frequencies in which a decimal is given are believed to be correct to within one wave-number; other frequencies may be in error by several wave-numbers. No special accuracy is claimed for the densitometrically determined relative intensities, given in parenthesis after some of the qualitative indications of intensity in the second columns of the tables, or for the similarly measured depolarisation factors, contained in the third columns.

TABLE I.

Raman Spectrum of 1 : 4-*Dideuterobenzene and Assignment.*

Frequency (cm.$^{-1}$).	Intensity.	Depolarisation factor.	Assignment.	Symmetry class.	Symmetry of components.
596·6	ms (1·5)	0·85	Fundamental	A_g	—
600·9			Fundamental	B_{1g}	—
634·1	m (0·5)	—	Fundamental	B_{3g}	—
736	mw (0·3)	0·8	Fundamental	B_{3g}	—
849·5	m (0·5)	0·83	Fundamental	B_{2g}	—
908·5	ms (0·9)	0·83	Fundamental	B_{1g}	—
967	ms–m	—	Fundamental	B_{3g}	—
978·0	s (10·0)	0·41	Fundamental	A_g	—
991	mw	—	$^{12}C_5{}^{13}CH_4D_2$	—	—
1173·4	ms (2·1)	0·87	Fundamental	A_g	—
1196	w	—	2 × 596·6 = 1193·2	A_g	A_g, A_g
			2 × 597 = 1194	A_g	B_{1u}, B_{1u}
			596·6 + 600·9 = 1197·5	B_{1g}	A_g, B_{1g}
			2 × 600·9 = 1201·8	A_g	B_{1g}, B_{1g}
1267	w	—	2 × 634·1 = 1268·2	A_g	B_{3g}, B_{3g}
1309·0	mw (0·2)	—	Fundamental	B_{1g}	—
1543·4	mw	—	634·1 + 908·5 = 1542·6	B_{2g}	B_{3g}, B_{1g}
1569·3	ms (1·5)	0·8	Fundamental	B_{1g}	—
1587·0	s (3·0)	0·83	Fundamental	A_g	—
2216·6	w	—	2 × 1106 = 2212	A_g	B_{3u}, B_{3u}
			908·5 + 1309·0 = 2217·5	A_g	B_{1g}, B_{1g}
			634·1 + 1587·0 = 2221·1	B_{3g}	B_{3g}, A_g
2280·0	s (4·5)	0·62	Fundamental	A_g	—
2378	w	—	970 + 1413 = 2383	B_{3g}	A_u, B_{3u}
2395·4	mw	—	992 + 1413 = 2405	B_{1g}	B_{2u}, B_{3u}
2582·7	m	—	1106 + 1469 = 2575	B_{1g}	B_{3u}, B_{2u}
2828	ww	—	2 × 1413 = 2826	A_g	B_{3u}, B_{3u}
2870	mw	—	597 + 2275 = 2872	B_{3g}	B_{1u}, B_{2u}
			596·6 + 2280·0 = 2876·6	A_g	A_g, A_g
			1309·0 + 1569·3 = 2878·3	A_g	B_{1g}, B_{1g}
			600·9 + 2280·0 = 2880·9	B_{1g}	B_{1g}, A_g
2895	w	—	1309·0 + 1587·0 = 2896·0	B_{1g}	B_{1g}, A_g
2913	w	—	634·1 + 2280·0 = 2914·1	B_{3g}	B_{3g}, A_g
2935·4	m	—	2 × 1469 = 2938	A_g	B_{2u}, B_{2u}
3042	ms (10)	0·50	Fundamental	B_{1g}	—
3055·0	s		Fundamental	A_g	—
3153·4	m	—	876 + 2275 = 3151	B_{3g}	B_{1u}, B_{2u}
			1569·3 + 1587·0 = 3156·3	B_{1g}	B_{1g}, A_g
3170·7	m	—	2 × 1587·0 = 3174·0	A_g	A_g, A_g

Our results may be compared with those already given in the literature. There are five frequencies, previously recorded as belonging to the Raman spectrum of 1 : 4-dideuterobenzene, which we do not confirm. These are 1008 and 2453 cm.$^{-1}$, given by Redlich and Stricks, and 400, 1166·6 and 2261 cm.$^{-1}$, reported by Langseth and Lord, the last two as having considerable intensity. The non-existence of the frequency 1166·6 cm.$^{-1}$ is important, and is established in detail later. We record in the same spectrum, however, twelve lines, including several of considerable strength, which were not observed by the earlier workers. These have the frequencies 991, 1196, 1309·0, 1543·4, 2378, 2395·4, 2582·7, 2828, 2870, 2895, 2913, and 2935·4 cm.$^{-1}$. Detailed evidence is submitted later with respect to the frequencies to which theoretical importance is attached, namely, 1309·0, 2582·7, and 2935·4 cm.$^{-1}$. Eighteen previously recorded Raman lines are confirmed, although the frequencies found for some of them differ by a few wave-numbers from the older values.

The position with respect to the Raman spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene is similar. Five of the lines which Langseth and Lord report we cannot confirm. These are stated to have the frequencies 605·3, 630·3, 949·9, 2112, and 2219 cm.$^{-1}$. On the other hand, we find fifteen Raman lines, some having considerable intensity, which Langseth and Lord did not observe; they have the frequencies 615·1, 904, 972, 984, 1232·3, 1431, 1533, 1550, 1593·6, 1645, 2344, 3078, 3119, 3143, and 3226 cm.$^{-1}$. Evidence as to the first few frequencies of each of these two lists is given later, since they are involved in the discussion of certain fundamental frequencies. Eighteen of Langseth and Lord's frequencies are confirmed by our measurements to within a few wave-numbers at most. A notable difference between their observations and our own with respect to the intensity of the line at 1140·3 cm.$^{-1}$ (1137·4 cm.$^{-1}$ according to their measurement) is discussed in connexion with the assignment of fundamental frequencies.

TABLE II.

Raman Spectrum of 1 : 2 : 4 : 5-*Tetradeuterobenzene and Assignment.*

Frequency (cm.$^{-1}$).	Intensity.	Depolarisation factor.	Assignment.	Symmetry class.	Symmetry components.
585·8	ms (1·4)	0·84	Fundamental	B_{1g}	—
589·0			Fundamental	A_g	—
615·1	m (0·3)	—	Fundamental	B_{3g}	—
663·6	ms (0·9)	0·82	Fundamental	B_{2g}	—
767·1	m (0·4)	0·83	Fundamental	B_{3g}	—
862·2	ms (1·5)	0·87	Fundamental	A_g	—
929·7	m (0·3)	—	Fundamental	B_{3g}	—
954	m–mw	—	Fundamental	B_{1g}	—
960·9	s (10·0)	0·39	Fundamental	A_g	—
972	m–mw	—	$^{12}C_5{}^{13}CH_2D_4$	—	—
984	mw	—	$^{12}C_5{}^{13}CH_2D_4$	—	—
1057	ww	—	1439 − 383 = 1056 †	B_{2g}	B_{3u}, B_{1u}
1098·1	w	—	2 × 548 = 1096	A_g	B_{1u}, B_{1u}
1140·3 *	ww	—	352 + 793 = 1145	A_g	A_u, A_u
1232·3	ww	—	2 × 615·1 = 1230·2	A_g	B_{3g}, B_{3g}
1255·3	m (0·4)	0·88	Fundamental	B_{1g}	—
1431	ww	—	663·6 + 767·1 = 1430·7	B_{1g}	B_{2g}, B_{3g}
1533	w	—	2 × 767·1 = 1534·2	A_g	B_{3g}, B_{3g}
1543	m	—	615·1 + 929·7 = 1544·8	A_g	B_{3g}, B_{3g}
1550	m		585·8 + 960·9 = 1546·7	B_{1g}	B_{1g}, A_g
			589·0 + 960·9 = 1549·9	A_g	A_g, A_g
1564·0	ms (4)	0·87	Fundamental	B_{1g}	—
1572·1	ms		Fundamental	A_g	—
1593·6	w	—	663·6 + 929·7 = 1593·3	B_{1g}	B_{2g}, B_{3g}
1645	ww	—	2 × 819 = 1638	A_g	B_{2u}, B_{2u}
2161	w	—	585·8 + 1564·0 = 2149·8	A_g	B_{1g}, B_{1g}
			589·0 + 1564·0 = 2153·0	B_{1g}	A_g, B_{1g}
			585·8 + 1572·1 = 2157·9	B_{1g}	B_{1g}, A_g
			589·0 + 1572·1 = 2161·1	A_g	A_g, A_g
			812 + 1353 = 2165	B_{1g}	B_{3u}, B_{2u}
			819 + 1353 = 2172	A_g	B_{2u}, B_{2u}
2253	w	—	812 + 1439 = 2251	A_g	B_{3u}, B_{3u}
			819 + 1439 = 2258	B_{1g}	B_{2u}, B_{3u}
2272	ms (8)	0·53	Fundamental	B_{1g}	—
2285·0	s		Fundamental	A_g	—
2344	w	—	767·1 + 1572·1 = 2339·2	B_{3g}	B_{3g}, A_g
3045·0	s (5)	0·72	Fundamental	A_g	—
3078	ww	—	793 + 2280 = 3073	B_{2g}	A_u, B_{2u}
			793 + 2280 = 3073	B_{3g}	A_u, B_{3u}
3119	w	—	2 × 1564·0 = 3128·0	A_g	B_{1g}, B_{1g}
3143	mw	—	2 × 1572·1 = 3144·2	A_g	A_g, A_g
			862·2 + 2285·0 = 3147·2	A_g	A_g, A_g
3226	w	—	960·9 + 2272 = 3233	B_{1g}	A_g, B_{1g}

* See first footnote, p. 283. † See second footnote, p. 283.

The last three columns of each of Tables I and II contain results of our analyses of the spectra. The entries in the fourth columns of the tables indicate our assignment of the frequencies either to fundamental or to higher harmonic vibrations. All the frequencies receive satisfactory explanations. Some of the higher harmonic frequencies are capable of several interpretations, and where this is so the alternatives are given. All interpretations accord with the selection rules (Part XI, this vol., p. 222). The fifth columns of the two tables contain the symbols which specify the symmetry properties of the fundamental and higher harmonic vibrations (cf. Part XI). Fuller descriptions of the forms of the fundamental vibrations are given later. The sixth column of each table contains the symmetry labels of the fundamental components of the higher harmonic frequencies; they are given in order that the symmetry classes of the components can readily be identified, and the application of selection rules checked. Concerning the identification of the fundamental components it will be appreciated that only the " gerade " fundamental frequencies (with subscript *g* in their symmetry symbols), all of which are Raman-active, are determined in this paper. The " ungerade " fundamental frequencies (having subscript *u* in their symmetry symbols) are either infra-red-active or spectrally inactive.

DISCUSSION OF ASSIGNMENT.

In the following discussion we shall deal mainly with the identification and assignment of fundamental frequencies. Overtones and combination tones will be discussed individually only in so far as their assignment involves special considerations or bears in some direct manner on the identification of fundamental frequencies.

1 : 4-Dideuterobenzene and 1 : 2 : 3 : 4-tetradeuterobenzene illustrate the benzene model of V_h symmetry. They have no three-fold axes and therefore do not give rise to degenerate vibrations. Thus the 30 vibrational degrees of freedom of each of these molecules correspond to 30 distinct vibration frequencies. The existence of a centre of symmetry secures that no vibration can record its frequency in both the Raman and the infra-red spectrum. Of the 30 fundamental vibrations, 15 are " gerade," *i.e.*, symmetric to the centre of symmetry, and 15 " ungerade," *i.e.*, antisymmetric with respect to the centre. The 15 gerade vibrations are active in the Raman spectrum; the 15 ungerade vibrations are all inactive in the Raman spectrum, but 13 of them are active in the infra-red spectrum, whilst two are spectrally inactive. We are concerned in this paper with the 15 gerade, that is, Raman-active, fundamental vibrations. They are divisible into four symmetry classes as follows (Part XI, Table IX, this vol., p. 228) :

Symmetry class	A_g	B_{1g}	B_{2g}	B_{3g}
No. of frequencies	6	5	1	3
Raman polarisation	Pol.	Depol.	Depol.	Depol.

The distinctions of symmetry between these classes may be briefly explained.

The V_h model has three two-fold axes of symmetry, the *z*-axis perpendicular to the plane of the benzene ring, the *y*-axis which runs through the two deuterium atoms in 1 : 4-dideuterobenzene or the two protium atoms in 1 : 2 : 4 : 5-tetradeuterobenzene, and the *x*-axis which is perpendicular to the others. The A_g vibrations preserve all three of these two-fold axes of symmetry. The B_{1g} vibrations preserve only the *z*-axis, the B_{2g} vibrations only the *y*-axis, and the B_{3g} vibrations only the *x*-axis. It follows that the A_g and B_{1g} vibrations lie in the plane of the ring, whilst the B_{2g} and B_{3g} vibrations involve atomic motion perpendicular to the plane.

During the A_g vibrations the polarisability ellipsoid of the molecule oscillates with respect to the lengths of its principal axes, but these axes remain fixed along the *x*, *y*, and *z* directions. In the B_{1g}, B_{2g}, and B_{3g} vibrations the lengths of all the principal axes of the polarisability ellipsoid remain fixed, but only one of the three axes is fixed with respect to direction : and the ellipsoid as a whole undergoes rotatory oscillations about this stationary principal axis. In the B_{1g} vibrations the oscillations occur about the *z*-axis, in the B_{2g} vibration about the *y*-axis, and in the B_{3g} vibrations about the *x*-axis.

The A_g vibrations are totally symmetrical with respect to the V_h model, and therefore, by the well-known rule, the corresponding Raman lines belong to the category of so-called " polarised " lines. This simply means that, so far as symmetry considerations alone determine the matter, their depolarisation factors are *allowed* to fall below the value of 6/7. But they are not bound to do so; for in any particular vibration some detailed consideration relating to its form may determine that its Raman depolarisation factor will in fact not fall appreciably below 6/7. Everything depends on what happens to the polarisability ellipsoid. If the lengths *a*, *b*, and *c* of the three principal axes of the ellipsoid so vary that their mean, $(a + b + c)/3$, remains nearly constant, the Raman depolarisation factor will not differ sensibly from 6/7.

In vibrations of the B_{1g}, B_{2g}, and B_{3g} symmetry classes the magnitudes *a*, *b*, and *c* remain individually constant, and hence their mean cannot vary. All these vibrations, therefore, give rise to so-called " depolarised " Raman lines, that is, lines whose depolarisation factors are completely fixed by symmetry principles, and are equal in every case to 6/7.

Two conclusions can be drawn with respect to the treatment of Raman polarisation data in the assignment of frequencies to vibrations. The first is that a Raman frequency having a measured depolarisation factor which is significantly below 6/7 can be assigned with certainty to a vibration of the A_g class. The second is that if we should have some independent reason to assign to a vibration of the A_g class a Raman frequency the depolarisation factor of which is found to be approximately equal to 6/7, we should be prepared to show special reason why, for that particular vibration, even though the magnitudes *a*, *b*, and *c* must all vary, their mean, $(a + b + c)/3$, will remain approximately constant during the vibration.

The A_g Fundamental Frequencies.—The six Raman lines of 1 : 4-dideuterobenzene, and the six of 1 : 2 : 4 : 5-tetradeuterobenzene, which we assign to the fundamental vibrations of the totally symmetrical A_g class have the following frequencies (in cm.$^{-1}$) and depolarisation factors (in parentheses).

$C_6H_4D_2$	596·6	978·0	1173·4	1587·0	2280·0	3055·0
	(0·85)	(0·41)	(0·87)	(0·83)	(0·62)	(0·50)
$C_6H_2D_4$	589·0	862·2	960·9	1572·1	2285·0	3045·0
	(0·84)	(0·87)	(0·39)	(0·87)	(0·53)	(0·72)

The lines having the frequencies 978·0, 2280·0, and 3055·0 cm.$^{-1}$ in the spectrum of 1 : 4-dideuterobenzene, and those which have the frequencies 960·9, 2285·0, and 3045·0 cm.$^{-1}$ in that of 1 : 2 : 4 : 5-tetradeuterobenzene, at once show themselves to belong to fundamental vibrations of the A_g class by their great intensity and considerable degree of polarisation. They are the strongest lines in their respective spectra, and their depolarisation factors all lie well below the limit of $6/7 = 0{\cdot}86$. The assignment to the same symmetry class of the remaining frequencies listed above, in spite of the circumstances that the corresponding depolarisation factors do not fall appreciably below 6/7, depends on a more detailed consideration of the normal co-ordinates of the A_g vibrations.

The six A_g vibrations of the V_h benzene model may be regarded as composed by orthogonal combinations from vibrations of the forms of those of the A_{1g} and E_g^+ symmetry classes of the D_{6h} benzene model, as exemplified in benzene itself and in hexadeuterobenzene (Part XI, Table V, this vol., p. 227). The A_{1g} class contains the two totally symmetrical vibrations of the D_{6h} model. The E_g^+ class contains four doubly degenerate vibrations, but we are here concerned only with that component (labelled "*a*" in Fig. 1 of Part XI, this vol., p. 231) of each degenerate vibration which retains all three of the two-fold axes of symmetry, z, y, and x, and is therefore totally symmetrical with respect to V_h symmetry. [The remaining component (labelled "*b*" in Fig. 1 of Part XI) of each of the degenerate E_g^+ vibrations retains only one two-fold axis, namely, the z-axis. The four E_g^+ component vibrations having this symmetry represent forms which enter into the composition of the B_{1g} vibrations of the benzenes of V_h symmetry.]

The A_{1g} vibrations of the D_{6h} model of benzene consist of a "carbon vibration," in which each carbon atom carries its hydrogen atom with it, the whole CH-group moving practically as a unit, and a "hydrogen vibration," in which the atoms of each CH-group move in antiparallel fashion about a nearly stationary centre of gravity, most of the motion being in the hydrogen atom because of its relative lightness. The forms of these vibrations are determined by their orthogonality and symmetry. The carbon vibration involves the symmetrical expansion and contraction of the benzene ring, whilst the hydrogen vibration consists essentially of the synchronous stretching and shortening of the six carbon–hydrogen bonds. The $E_g^+(a)$ vibrations consist of two "carbon vibrations," in which the atomic motions in each CH-group are parallel, and two "hydrogen vibrations," in which they are antiparallel. The forms of these four vibrations are not fully fixed by their orthogonality and symmetry, but it was shown in Part VIII (J., 1936, 971) that they are rather accurately differentiated by the internal forces into a carbon bending, a carbon stretching, a hydrogen bending and a hydrogen stretching vibration. Altogether then we have to consider the possible interaction of three carbon and three hydrogen vibrations.

In the carbon vibrations the moving unit is essentially the CH-group, and this undergoes so small a proportionate change of mass on deuterium substitution that the form, frequency, and spectral activity of the vibrations are not much altered. Thus we can identify the three A_g carbon frequencies of the V_h benzenes very easily by comparison with the single A_{1g} and the two E_g^+ carbon frequencies of the D_{6h} benzenes.

The A_{1g} carbon frequencies of benzene and hexadeuterobenzene, and the frequencies which we identify as the A_{1g}-like carbon frequencies of the A_g class of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, form the following monotonic series :

	C_6H_6.	1 : 4-$C_6H_4D_2$.	1 : 2 : 4 : 5-$C_6H_2D_4$.	C_6D_6.
A_{1g} or A_{1g}-like carbon frequencies, cm.$^{-1}$	991·6	978·0	960·0	943·2

These frequencies all belong to the most intense, and most strongly polarised, lines in their respective spectra, and there can be no doubt about their correspondence. It is evident that the interaction between these vibrations and the E_g^+-like vibrations, an interaction which is allowed when the restrictions imposed by D_{6h} symmetry become relaxed under V_h symmetry, is in fact insufficient to shift the frequencies appreciably. The first reason for this is that no E_g^+-like frequencies lie in the near neighbourhood of the A_{1g}-like carbon frequencies. The second reason is that the nearest E_g^+-like frequencies, *viz.*, the hydrogen bending frequencies, 1173·4 cm.$^{-1}$ in 1 : 4-dideuterobenzene and 862·2 cm.$^{-1}$ in 1 : 2 : 4 : 5-tetradeuterobenzene, have normal co-ordinates, which, as we shall see below, are of such a form that there could be no appreciable interaction between these vibrations and the A_{1g}-like carbon vibrations.

The frequencies which we identify as belonging to the E_g^+-like carbon bending vibrations of 1 : 4-dideutero- and 1 : 2 : 4 : 5-tetradeutero-benzene bracket themselves in a quite regular manner between the analogous frequencies of benzene and hexadeuterobenzene :

	C_6H_6.	1 : 4-$C_6H_4D_2$.	1 : 2 : 4 : 5-$C_6H_2D_4$.	C_6D_6.
E_g^+ and E_g^+-like carbon bending frequencies, cm.$^{-1}$	605·6	600·9, 596·6	589·0, 585·8	577·4

The close correspondence as to frequency, and the similarity in intensity and polarisation between these Raman lines leave no doubt as to the correctness of the assignment. Confirmation follows from the observation that, in agreement with the prediction that these frequencies of benzene and hexadeuterobenzene possess a two-fold degeneracy which should become resolved in the di- and tetra-deutero-compounds, the relevant single lines in the Raman spectra of benzene and hexadeuterobenzene become replaced by strongly overlapped doublets in the spectra of the di- and tetra-deuterobenzenes (cf. Part XV, this vol., p. 248).*

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* The strong overlapping must tend to reduce the apparent frequency separation, and, accordingly, our estimated separations may be a little low.

The problem of deciding which member of the split pair of E_g^+-like carbon bending frequencies of 1 : 4-dideuterobenzene belongs to the A_g symmetry class, and which to the B_{1g} class, and likewise which of the corresponding pair of frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene has to be assigned to each of these symmetry classes, is difficult. In principle the degree of polarisation of the Raman lines could provide a distinction, but in practice the difference is too small, and the overlapping of the lines too great, for diagnostic purposes. The following argument may, however, be submitted.

We have given in Fig. 1 of Part XI approximate graphical representations of the normal co-ordinates of components of the degenerate E_g^+ carbon bending vibration of the D_{6h} benzene model (this vol., p. 231). The diagrams are based on the demonstrated separation of the E_g^+ vibrations to produce *inter alia* a nearly pure carbon bending vibration (Part VIII, *loc. cit.*). The normal co-ordinates of these D_{6h} benzene vibrations are so chosen that the " *a* " vector diagram has the same symmetry as the A_g class, and the " *b* " diagram the same symmetry as the B_{1g} class, of vibrations of the V_h benzenes. We then find that those hydrogen atoms of benzene which become deuterium atoms in 1 : 4-dideuterobenzene are depicted as remaining stationary in the " *b* " diagram, but as having more motion than the other hydrogen atoms in the " *a* " diagram. If the molecular behaviour were exactly as described, we should expect that the B_{1g} carbon bending frequency of 1 : 4-dideuterobenzene would be exactly the same as the E_g^+ frequency of benzene, whilst the corresponding A_g frequency would be significantly reduced. The diagrams are, of course, not strictly exact, but they do suggest that we should assign the lower of the split frequencies of 1 : 4-dideuterobenzene to the A_g carbon bending vibration, and the one which more nearly approximates to the benzene frequency to the corresponding B_{1g} vibration. By a similar argument, in which the comparison is between the normal co-ordinates of 1 : 2 : 4 : 5-tetradeuterobenzene and hexadeuterobenzene, we are led to assign the upper of the split pair of frequencies of the tetradeutero-compound to the A_g vibration, and the lower one to the B_{1g} vibration.

The above argument by itself could not be regarded as conclusive because the frequency differences are really too small to be discussed safely on the basis of approximate normal co-ordinates. However, the conclusions are supported by two other indications. One is that they lead to better product ratios than would be obtained if the assignment of the members of either doublet were reversed. The other is that they assign the slightly stronger member of each doublet to a vibration of the totally symmetrical class, and we might expect on general grounds that any observable difference of intensity between the doublet members would be in this direction.

The frequencies assigned to the E_g^+-like carbon stretching vibrations of 1 : 4-dideutero- and 1 : 2 : 4 : 5-tetradeutero-benzene similarly make a smooth sequence with the analogous E_g^+ frequencies of benzene and hexadeuterobenzene :

	C_6H_6.	1 : 4-$C_6H_4D_2$.	1 : 2 : 4 : 5-$C_6H_2D_4$.	C_6D_6.
E_g^+ and E_g^+-like carbon stretching frequencies, cm.$^{-1}$	(1596)	1587·0, 1569·3	1572·1, 1564·0	1551·5

The correspondence between the frequencies, as well as the intensities and polarisations of these Raman lines, and the splitting in the di- and tetra-deutero-compounds of a frequency which is degenerate in benzene and hexadeuterobenzene, make the assignment quite certain. (Here it should be mentioned that the degenerate benzene frequency actually appears as a doublet for the special reason that the unperturbed fundamental frequency, 1596 cm.$^{-1}$, is accidentally degenerate with a combination tone of a type with which it can interact, with mixing of the wave-functions and a splitting of the frequencies.)

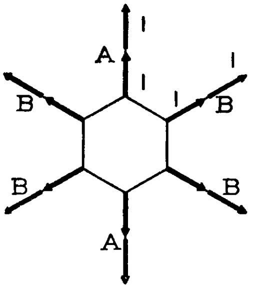
Referring to the forms of the E_g^+ carbon stretching vibrations of the D_{6h} benzene model, as depicted in Fig. 1 of Part XI (this vol., p. 231), we may, as before, compare the " *a* " diagram, considered now as an approximate picture of the E_g^+-like carbon stretching vibration of the A_g class of the V_h benzenes, with the " *b* " diagram, regarded as a similarly approximate representation of the corresponding vibration of the B_{1g} class. Since those CH-groups of benzene which become CD-groups in 1 : 4-dideuterobenzene, and those CD-groups of hexadeuterobenzene which become CH-groups in 1 : 2 : 4 : 5-tetradeuterobenzene, have no motion in the " *a* " diagram, but have more motion than other CH- or CD-groups in the " *b* " diagram, we might expect that the upper member of the split pair of frequencies in 1 : 4-dideuterobenzene, and the lower member of the split pair in 1 : 2 : 4 : 5-tetradeuterobenzene, will belong to the A_g class of vibrations. We recognise, however, that this is not a conclusive argument, applied, as it is here, to only slightly separated frequencies.

As regards 1 : 4-dideuterobenzene the above tentative allocation of the doublet components between the A_g and B_{1g} classes is confirmed by the fact that it gives better product ratios than its alternative. It is also confirmed by the intensities, since the upper frequency, which we assign to the A_g class, appears with substantially greater intensity than its companion. However, there is disagreement with respect to 1 : 2 : 4 : 5-tetradeuterobenzene. Here again the upper frequency of the doublet appears with distinctly greater intensity than its companion; also an assignment which places the upper frequency in the A_g symmetry class yields better product ratios than its alternative. Whilst no completely certain conclusion can be reached, we are inclined to put more faith in these experimental indications than in the argument based on a comparison of approximate normal co-ordinates.

The markedly wider frequency separation of the dideutero- than of the tetradeutero-benzene doublet may be occasioned by a small dynamical interaction between the parent D_{6h} forms of the two carbon stretching frequencies of the A_g class, *viz.*, the E_g^+-like and A_{1g}-like frequencies. This would have the effect of modifying the conclusions that might be drawn from a consideration of approximate normal co-ordinates. The A_{1g}-like frequencies, because of the great intensity with which they appear, might not be appreciably displaced by interaction, but the E_g^+-like carbon stretching frequencies could be significantly raised, thus widening the doublet in 1 : 4-dideuterobenzene, but closing it up, or even causing the components to cross over, in 1 : 2 : 4 : 5-tetradeuterobenzene. An alternative theory assumes a disturbance due to near-degeneracy with combination tones between the A_{1g}-like carbon frequency and the two E_g^+-like carbon bending frequencies. Interaction apart, these two combination frequencies should fall between the members of the fundamental doublet in 1 : 4-dideuterobenzene, but below the lower doublet frequency in 1 : 2 : 4 : 5-tetradeuterobenzene. Each combination tone would be allowed by symmetry to interact with one of the fundamentals of the doublet. Interaction would thus spread out the former doublet, but might compress, or even invert, the latter. The combination tones appear, with appreciably displaced frequencies, as satellites to the doublet in the spectrum of the tetradeutero-compound. The fact that they cannot clearly be distinguished in the dideuterobenzene spectrum is no evidence against the theory, because each combination tone might be so displaced by the interaction as to be obscured under that fundamental with which it does not interact.

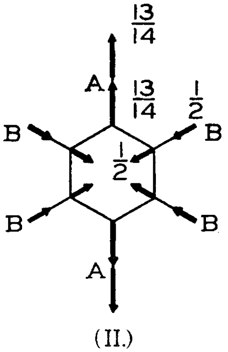
The normal co-ordinates of the three A_g carbon vibrations are illustrated by the vector diagrams (I), (II), and (III), in which either A represents deuterium and B protium, or *vice versa*. The small figures denote approximate amplitudes, which are relative within each diagram. In order to avoid confusion they are given only for 1 : 4-dideuterobenzene : how they should be changed to suit the case of 1 : 2 : 4 : 5-tetradeuterobenzene will be obvious.

The six D_{6h} vibrations from which the A_g vibrations of the V_h model can be regarded as being derived include one hydrogen bending vibration and two hydrogen stretching vibrations. The hydrogen bending vibration belongs to the E_g^+ symmetry class and is degenerate, but its particular normal co-ordinate which we label " *a* " has the appropriate symmetry. On reduction of the symmetry of the model from D_{6h} to V_h, this vibration would in principle undergo modification by interaction with others of the A_g class; but we know that the three carbon vibrations of this class are very little modified, and it is obvious that there can be very little interaction with hydrogen stretching vibrations of much higher frequency. Thus the form of the single hydrogen-bending vibration should be preserved almost unchanged in the A_g class of V_h vibrations. But according to our approximate vector diagram of this D_{6h} vibration (Part XI, Fig. 1, this vol., p. 231) the hydrogen atoms whose masses are changed, when we replace benzene by 1 : 4-dideuterobenzene or hexadeuterobenzene by 1 : 2 : 4 : 5-tetradeuterobenzene, do not move. To this approximation, therefore, the A_g hydrogen bending frequency of 1 : 4-dideuterobenzene should be identical with the E_g^+ hydrogen bending frequency of benzene; and the analogous A_g frequency of 1 : 2 : 4 : 5-tetradeuterobenzene should be the same as the corresponding E_g^+ frequency of hexadeuterobenzene. Prominent Raman lines are found in the expected positions : the correspondence in frequency, intensity, and polarisation is such as to leave no doubt about their identity :



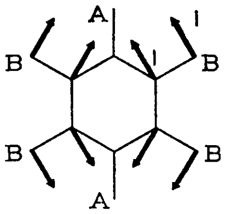
(I.)

$C_6H_4D_2$, 978·0 cm.$^{-1}$
$C_6H_2D_4$, 960·9 cm.$^{-1}$



(II.)

$C_6H_4D_2$, 596·6 cm.$^{-1}$
$C_6H_2D_4$, 589·0 cm.$^{-1}$



(III.)

$C_6H_4D_2$, 1587·0 cm.$^{-1}$
$C_6H_2D_4$, 1572·1 cm.$^{-1}$

	C_6H_6.	1 : 4-$C_6H_4D_2$.	1 : 2 : 4 : 5-$C_6H_2D_4$.	C_6D_6.
E_g^+ and E_g^+-like hydrogen bending frequencies, cm.$^{-1}$	1178·0	1173·0	862·2	867·2

Langseth and Lord record the 1 : 4-dideuterobenzene line as a doublet; but it is not, as we shall show presently; and there is no reason why it should be, since the " *b* " member of the degenerate E_g^+ hydrogen bending vibration becomes a component of the B_{1g} symmetry class, which contains another hydrogen bending frequency, and therefore provides opportunity for strong interaction and a large frequency displacement.

The remaining D_{6h} vibrations from which we have to compose the A_g vibrations of the V_h benzenes consist of two hydrogen stretching vibrations, the totally symmetrical A_{1g} hydrogen vibration, and the " *a* " component of the degenerate E_g^+ hydrogen stretching vibration. These vibrations must undergo extensive mutual modification in the partly deuterated benzenes, because the coupling of the individual protium and deuterium motions through a structure of intermediate heavier atoms is insufficient to force them into comparable amplitudes at a common frequency : either the protium atoms must vibrate and the deuterium atoms remain nearly stationary, or *vice versa*. Thus initial normal co-ordinates, similar to those of the A_{1g} hydrogen and $E_g^+(a)$

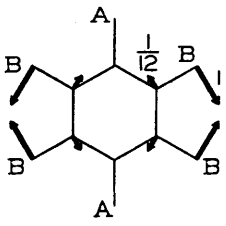
hydrogen stretching vibrations of D_{6h} benzenes, pass under V_h symmetry into combinations of the form $A_{1g} \pm E_g^+$, one of which represents an almost pure protium stretching vibration, and the other an almost pure deuterium stretching vibration. The presence of A_{1g} character in the combination ensures that the Raman lines will be very strong and considerably polarised.

In the Raman spectra these frequencies are found in the expected positions; they appear very strongly, and with marked polarisation :

	1 : 4-$C_6H_4D_2$.	1 : 2 : 4 : 5-$C_6H_2D_4$.
$A_{1g} \pm E_g^+$-like hydrogen stretching frequencies, cm.$^{-1}$	2280·0, 3055·0	2285·0, 3045·0

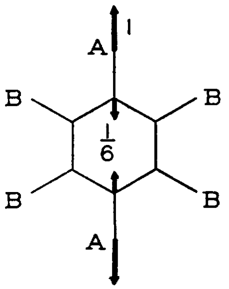
The polarisation identifies these frequencies with certainty, even though the protium frequency in 1 : 4-dideuterobenzene and the deuterium frequency in 1 : 2 : 4 : 5-tetradeuterobenzene are represented by components of doublets. They are the stronger components by a factor of about 3-fold, their weaker companions, at 3042 cm.$^{-1}$ in the dideutero- and at 2272 cm.$^{-1}$ in the tetradeutero-compound, belonging to the B_{1g} class of vibrations.

The approximate normal co-ordinates of these A_g hydrogen vibrations are shown in diagrams (IV), (V), and (VI). As before, amplitude indications are given for the case of 1 : 4-dideuterobenzene : it is easy to see what they should be for 1 : 2 : 4 : 5-tetradeuterobenzene.



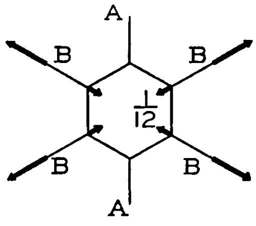
(IV.)

$C_6H_4D_2$, 1173·4 cm.$^{-1}$
$C_6H_2D_4$, 862·2 cm.$^{-1}$



(V.)

$C_6H_4D_2$, 2280·0 cm.$^{-1}$
$C_6H_2D_4$, 3045·0 cm.$^{-1}$



(VI.)

$C_6H_4D_2$, 3055·0 cm.$^{-1}$
$C_6H_2D_4$, 2285·0 cm.$^{-1}$

The reason why three of the vibrations of this symmetry class are represented by Raman lines which are indistinguishable from ordinary depolarised lines, even though the vibrations are totally symmetrical with respect to V_h symmetry, will be clear. The normal co-ordinates of these particular vibrations are closely similar to those of the E_g^+ vibrations of a D_{6h} benzene; there is little or no admixture of A_{1g} character. In these vibrations of the D_{6h} model the principal axes *a*, *b*, and *c* of the polarisability ellipsoid remain fixed in the *x*, *y*, and *z* directions and the changes of magnitude which accompany displacement in the normal co-ordinate are such that the average, $(a + b + c)/3$, remains constant ($\Delta a = -\Delta b$; $\Delta c = 0$). The same will be very nearly true for the E_g^+-like A_g vibrations of the V_h model, and hence the depolarisation factor will be very nearly 6/7.

The above assignments of A_g frequencies may be tested by means of the product rule :

$$\frac{\Pi A_{1g},\, E_g^+(C_6H_6)}{\Pi A_g(C_6H_4D_2)} = \frac{991{\cdot}6 \times 605{\cdot}6 \times 1596 \times 1178{\cdot}0 \times 3061{\cdot}9 \times 3046{\cdot}8}{978{\cdot}0 \times 596{\cdot}6 \times 1587{\cdot}0 \times 1173{\cdot}4 \times 2280{\cdot}0 \times 3055{\cdot}0} = 1{\cdot}392 \text{ (harmonic value, } 1{\cdot}414)$$

$$\frac{\Pi A_g(C_6H_4D_2)}{\Pi A_g(C_6H_2D_4)} = \frac{978{\cdot}0 \times 596{\cdot}6 \times 1587{\cdot}0 \times 1173{\cdot}4 \times 2280{\cdot}0 \times 3055{\cdot}0}{960{\cdot}9 \times 589{\cdot}0 \times 1572{\cdot}1 \times 862{\cdot}2 \times 3045{\cdot}0 \times 2285{\cdot}0} = 1{\cdot}417 \text{ (harmonic value, } 1{\cdot}414)$$

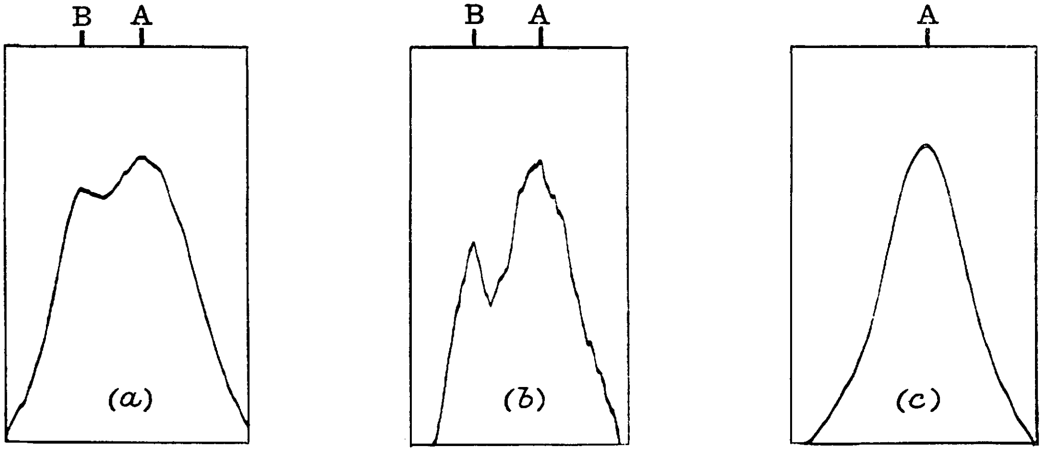
$$\frac{\Pi A_g(C_6H_2D_4)}{\Pi A_{1g},\, E_g^+(C_6D_6)} = \frac{960{\cdot}9 \times 589{\cdot}0 \times 1572{\cdot}1 \times 862{\cdot}2 \times 3045{\cdot}0 \times 2285{\cdot}0}{943{\cdot}2 \times 577{\cdot}4 \times 1551{\cdot}5 \times 867{\cdot}3 \times 2292{\cdot}6 \times 2264{\cdot}9} = 1{\cdot}403 \text{ (harmonic value, } 1{\cdot}414)$$

The B_{1g} Fundamental Frequencies.—Before discussing the assignment of these frequencies it is necessary to refer in more detail to some of the already noted differences between Langseth and Lord's experimental record (*loc. cit.*) and our own.

In the Raman spectrum of 1 : 4-dideuterobenzene these authors record a line at 1166·6 cm.$^{-1}$, which they estimate to be about half as strong as the close-lying line at 1175·4 cm.$^{-1}$. They agree with Redlich and Stricks, and with ourselves, that the latter is an A_g fundamental frequency. However, they assign the frequency 1166·6 cm.$^{-1}$ as a B_{1g} fundamental frequency, whereas we shall conclude that this frequency does not exist.

Microphotometric records of the relevant region of the spectrum are reproduced in Figs. 1*a*, 1*b*, and 1*c*. They are on the same scale of frequency. The A_g frequency which Langseth and Lord measure at 1175·4 cm.$^{-1}$, and which we find at 1173·4 cm.$^{-1}$, is marked " *A* " on the records. It is excited by the near-violet line, Hg 4358·34 A. The line which appears on two of the records, and is marked " *B*," would have the frequency 1168·1 cm.$^{-1}$, if excited by Hg 4358·34 A., or 2935·4 cm.$^{-1}$ if excited by the far-violet, Hg 4046·56 A. The different records were obtained from plates in exposing which different light filters (see under Fig.) were inserted between the mercury lamp and the Raman tube (cf. Part XV, this vol., p. 247). If the Raman lines, *A* and *B*, both originated in the same exciting line, Hg 4358·34 A., the ratio of their intensities should remain the same under the three conditions of excitation. Clearly, it does not. On the other hand, if line *B* should originate in Hg 4046·56 A., then it would follow from the absorption characteristics of the filters employed that, relatively to line *A*, the intensity of line *B* should be diminished by the cobalt filter, and reduced to vanishing by the nitrite filter—exactly as we find. The line *B* therefore has the frequency 2935·4 cm.$^{-1}$ (we assign it as the first overtone of an infra-red fundamental frequency, see Table I); and the symmetry of the microphotometric contour in Fig. 1*c* shows that no frequency of about 1167—1168 cm.$^{-1}$ can be assumed to be obscured under this much higher frequency in plates such as those which yielded Figs. 1*a* and 1*b*. Obviously the Raman line which Langseth and Lord recorded as having frequency 1166·6 cm.$^{-1}$ is really the overtone of frequency 2935·4 cm.$^{-1}$.

FIG. 1.



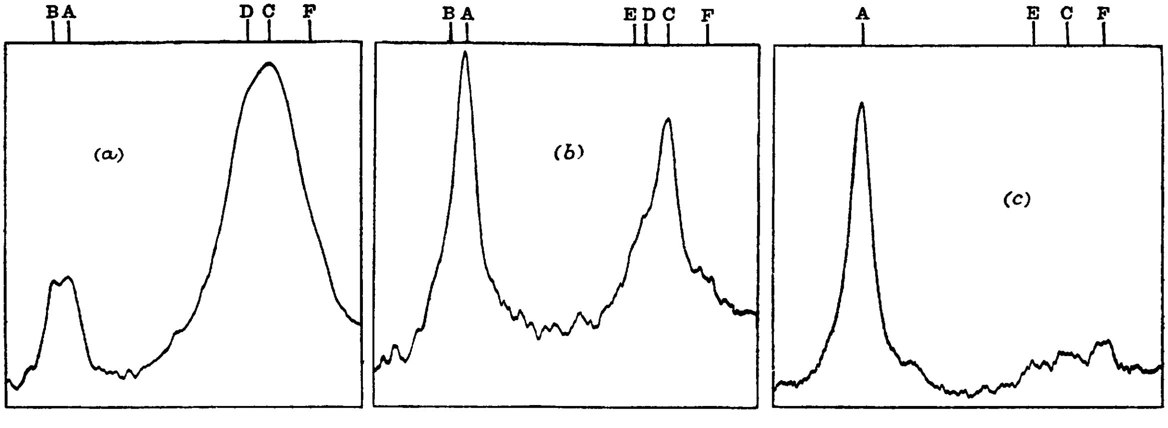
Microphotometric records of the region ca. 1160—1185 *cm.*$^{-1}$ *from* Hg 4358·34 A. *of the Raman spectrum of* 1 : 4-*dideuterobenzene,* (a) *with praseodymium filter,* (b) *with cobalt filter,* (c) *with nitrite filter* (2 *cm. of saturated aqueous sodium nitrite*).

A = 1173·4 *cm.*$^{-1}$ *from* Hg 4358·34 A.
B(= 1168·1 ,, ,, ,,) = 2935·4 *cm.*$^{-1}$ *from* Hg 4046·56 A.

Next we give the evidence for the existence of a line which Langseth and Lord do not report, but which appears in our records with a frequency of 1309·0 cm.$^{-1}$. The importance of this frequency is that, if it can be established, it cannot be anything other than a fundamental frequency of the B_{1g} class.

Microphotometric traces of the relevant part of the spectrum are reproduced in Figs. 2*a*, 2*b*, and 2*c*. They

FIG. 2.

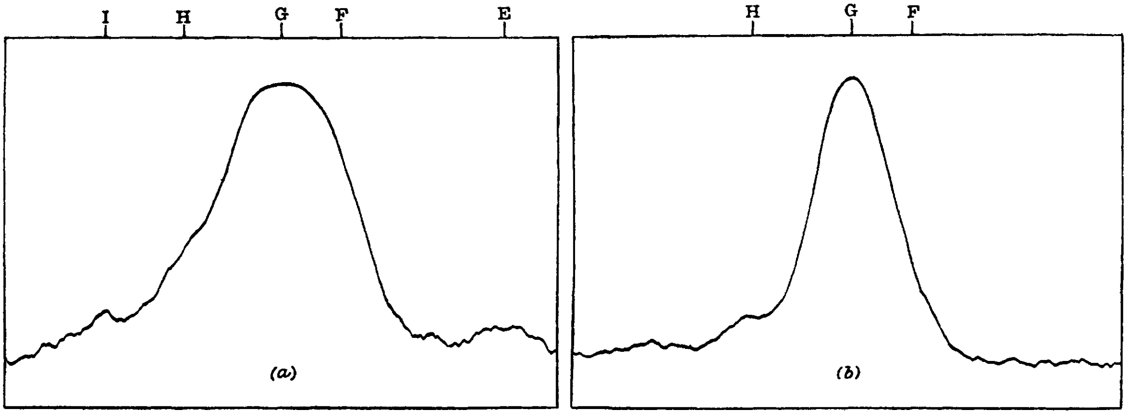


Microphotometer records of the region ca. 1220—1340 *cm.*$^{-1}$ *from* Hg 4358·34 A. *of the Raman spectrum of* 1 : 4-*dideuterobenzene,* (a) *with praseodymium filter,* (b) *with* 1 *cm. nitrite filter,* (c) *with* 2 *cm. nitrite filter.*

A = 1173·4 *cm.*$^{-1}$ *from* Hg 4358·34 A.
E = 1267 *cm.*$^{-1}$,, ,,
F = 1309·0 *cm.*$^{-1}$,, ,,
B(= 1168·1 *cm.*$^{-1}$,, ,,) = 2935·4 *cm.*$^{-1}$ *from* Hg 4046·56 A.
C(= 1287·7 *cm.*$^{-1}$,, ,,) = 3055·0 *cm.*$^{-1}$,, ,,
D(= 1275 *cm.*$^{-1}$,, ,,) = 3042 *cm.*$^{-1}$,, ,,

are on the same scale of frequency. The plate which yielded the record of Fig. 2*a* was taken with the praseodymium filter. Line *A* is the line of frequency 1173·4 cm.$^{-1}$ excited by Hg 4358·34 A. The lines labelled *B*, *C*, and *D* are all excited by Hg 4046·56 A. Line *B* is the overtone, 2935·4 cm.$^{-1}$, already mentioned. Line *C* represents the very strong, totally symmetrical, protium stretching vibration of frequency 3055·0 cm.$^{-1}$. It has been over-exposed with the result that its companion *D*, corresponding to the non-totally symmetrical vibration of frequency 3042 cm.$^{-1}$, appears only as a change of slope in the microphotometric contour. In the plate which gave the record of Fig 2*b* the whole Raman spectrum excited by the line Hg 4046·56 A. has been greatly weakened by the use of a 1-cm. layer of saturated sodium nitrite solution as filter. Line *B* has almost disappeared; line *C* is now weaker than line *A*, and line *D*, now almost resolved from *C*, is weaker still. An additional fairly prominent line now appears at *F*, partly overlapped by *C*, and another weaker and unresolved line at *E*. In exposing the plate which gave the record of Fig. 2*c* the nitrite filter was doubled in thickness. The line *C* has still just registered, but it must be inferred from its weakness that line *D*, and indeed, all other Raman frequencies excited by the line Hg 4046·56 A., have vanished. There remain the lines *E* and *F*, the frequencies of which (means of several measurements) are 1267 cm.$^{-1}$ and 1309·0 cm.$^{-1}$ respectively. Line *E* is assigned as a first overtone (see Table I, p. 273). Line *F* is assigned as a fundamental. Its presence is clearly established in the records of Figs. 2*c* and 2*b*; and in Fig. 2*a* a slight change of slope in the trace can be seen, which is undoubtedly due to this line.

FIG. 3.



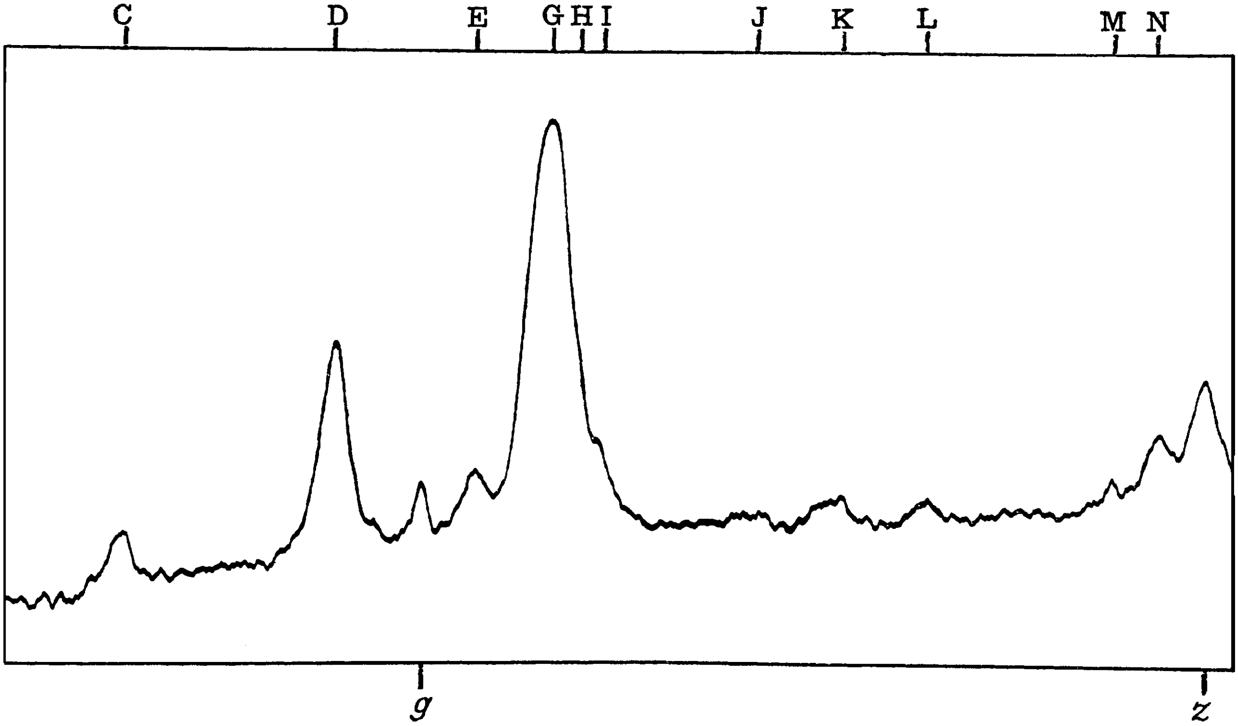
Microphotometer records of the region ca. 920—1000 *cm.*$^{-1}$ *from* Hg 4358·34 A. *of the Raman spectrum of* 1 : 2 : 4 : 5-*tetradeuterobenzene :* (a) *from somewhat strongly exposed plate,* (b) *from more weakly exposed plate, both with strong nitrite filter.*

E = 929·7 *cm.*$^{-1}$ *from* Hg 4358·34 A.
F = 954 *cm.*$^{-1}$,, ,,
G = 960·9 *cm.*$^{-1}$,, ,,
H = 972 *cm.*$^{-1}$,, ,,
I = 984 *cm.*$^{-1}$,, ,,

The remaining experimental points of difference which affect the assignment of B_{1g} frequencies relate to the Raman spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene. Reference is necessary in particular to the region around the carbon-ring " breathing frequency," 960·9 cm.$^{-1}$. On the low-frequency side of this line, Langseth and Lord report a line at 949·9 cm.$^{-1}$, which we do not find, whilst, as to the high-frequency side, they say nothing about two satellites, at 972 and 984 cm.$^{-1}$, which, though overlapped, are very obvious on our photographs. We do suspect the existence of a satellite on the low-frequency side of the main line, but at a smaller separation than Langseth and Lord's reported line would have. Unfortunately, the presence of such a satellite cannot be decided unambiguously on purely experimental grounds, and an attempted decision is inevitably influenced by the theoretical expectation of a B_{1g} fundamental frequency within a very few wave-numbers of the breathing frequency. The matter being at present one for judgment, we reproduce a sample of the evidence in the form of microphotometer records of the relevant region of two spectrograms taken with different lengths of exposure (Fig. 3, *a* and *b*). The strong-intensity maximum, marked *G*, belongs to the breathing frequency, 960·9 cm.$^{-1}$, whilst the much weaker maximum, *E*, represents an out-of-plane fundamental frequency, 929·7 cm.$^{-1}$, which will be considered later. On the high-frequency side of the strong line one sees (*H* and *I*) the two satellites, 972 and 984 cm.$^{-1}$, in Fig. 3*a*. The former is clearly the stronger, and it is the only one of the two which is visible (*H*) on the lightly exposed plate from which the record of Fig. 3*b* was obtained; and it is here better resolved, because of the narrower contour of the main line. Its frequency separation from the main line is 11 cm.$^{-1}$, just the same as that of Langseth and Lord's reported line on the low-frequency side. There is, however, clearly no line, of intensity equal to or greater than that of the line at 972 cm.$^{-1}$, at an equal separation on the other side of the main line, *i.e.*, at about 949·9 cm.$^{-1}$. On the other hand, there may be a rather weak line at 954 cm.$^{-1}$, only 7 cm.$^{-1}$ from the centre of the main line, and so far buried beneath it as to be on the limits of observability. There seems always to be slight disturbance in this region to the densitometric contour of the main line. In Fig. 3*a* it can be discerned (*F*) as an incipient shoulder reaching well up the side of the heavily exposed main line, and, in Fig. 3*b*, as an incipient shoulder (*F*) affecting the observed slope only in the lower part of this narrower contour.

Originally we assigned the line at 972 cm.$^{-1}$ as the expected B_{1g} fundamental frequency, but the alternative frequency, 954 cm.$^{-1}$, if real, gives much better product ratios, and, as the evidence for this frequency strengthened, we have tended to favour its assignment to the B_{1g} fundamental vibration. Unfortunately, neither assignment can be conclusively established at the present time, if only because all these satellites of the carbon breathing frequency have alternative explanations as fundamental frequencies of heavy carbon molecules. There could be four such frequencies, two for vibrations similar to the A_{1g} carbon vibration of benzene, and two representing vibrations corresponding to the B_{1u} carbon vibration of benzene. One of each pair would belong to a molecule with the heavy carbon atom on the two-fold symmetry axis, and the other to a molecule with the ^{13}C atom off this axis. The satellites 972 and 984 cm.$^{-1}$ are very likely to be B_{1u}-like frequencies of heavy carbon molecules, whilst 954 cm.$^{-1}$ would be a possible value for an A_{1g}-like frequency of one of these molecules. Probably the best way to achieve a decision would be to get some benzene free from heavy carbon, a task not beyond the range of modern separative technique.

FIG. 4.



Record of part of the Raman spectrum of 1 : 2 : 4 : 5-*tetradeuterobenzene. Plate taken with* 1 *cm. nitrite filter. Lines marked with capital letters are excited by* Hg 4358·34 A. *The lines labelled with lower-case letters arise from the other excitations noted below.*

From Hg 4358·34 A.:

C = 767·1 *cm.*$^{-1}$.
D = 862·2 *cm.*$^{-1}$.
E = 929·7 *cm.*$^{-1}$.
G = 960·9 *cm.*$^{-1}$.
H = 972 *cm.*$^{-1}$.
I = 984 *cm.*$^{-1}$.
J = 1057 *cm.*$^{-1}$.
K = 1098·1 *cm.*$^{-1}$.
L = 1140·3 *cm.*$^{-1}$.
M = 1232·3 *cm.*$^{-1}$.
N = 1255·3 *cm.*$^{-1}$.

From Hg 4347·50 A. : *g* = 960·9 *cm.*$^{-1}$.
From Hg 4046·56 A. : *z* = 3045·0 *cm.*$^{-1}$.

We have still to refer to Langseth and Lord's observations, and to ours, on the intensity of the line at 1255·3 cm.$^{-1}$ in relation to the intensities of other fundamentals and combination tones, and in particular to the intensity of the line at 1140·3 cm.$^{-1}$. The point of the comparison is that we take the line at 1255·3 cm.$^{-1}$ to represent a fundamental frequency, even though it has a possible explanation as a combination tone (589·0 + 663·6 = 1252·6 cm.$^{-1}$), whereas Langseth and Lord accept instead the line at 1140·3 cm.$^{-1}$, describing it as having an intensity comparable to that of the line of frequency 1255·3 cm.$^{-1}$. A general view of a considerable section of the Raman spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene is shown in the microphotometric record, Fig. 4. The lines marked with capital letters, *C*—*N*, all arise by excitation with Hg 4358·34 A. The frequency 1255·3 cm.$^{-1}$ is labelled *N*; and it is obviously comparable in intensity with the lines labelled *C* and *E*, which both Langseth and Lord, and we, assign as fundamental frequencies. Line *N* is, moreover, considerably stronger than lines *J*, *K*, *L*, and *M*, which we assign as higher harmonics. Langseth and Lord remark on the strength of the line *N* (1253 cm.$^{-1}$ according to their measurements), and discuss the possibility of assigning it as a fundamental; but they do not actually so assign it, because they cannot thus secure agreement with the product rule. We now know that this is because they failed to observe certain other frequencies, both of 1 : 4-di- and of 1 : 2 : 4 : 5-tetra-deuterobenzene, which enter into the relevant product ratio. These frequencies having been observed, the product rule points directly to 1255·3 cm.$^{-1}$ as a fundamental frequency. Langseth and Lord take instead the line at 1140·3 cm.$^{-1}$ (1137·4 cm.$^{-1}$, according to their measurements) as a fundamental frequency, presumably because they could not see how to explain this line as a combination tone; and also because, by correlating its frequency with certain supposed frequencies of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, which we have shown not to exist, they could secure agreement with the product rule. We shall show that the frequency 1140·3 cm.$^{-1}$ (if real) can be satisfactorily explained as a summation tone of the two inactive fundamental frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene, the values of which are determined in Part XXI (cf. also the next paper, and Table II of this paper). And we do not see how the assignment of 1140·3 cm.$^{-1}$ as a fundamental frequency could now be reconciled with the product rule. Furthermore, we differ from Langseth and Lord with respect to the intensity of this line, which we have labelled *L* in Fig. 4. They describe it as " moderately strong," and list it as being of about the same intensity as *N*. As Fig. 4 shows, we find line *L* to be considerably weaker than *N*, and at best comparable in strength with the neighbouring harmonics, *J*, *K*, and *M*.* Langseth and Lord, whose results suggest that they were dealing with a mixture of isotopic forms, do not record line *M*, and though they do record *J* and *K*, both as being weaker than *L*, they list *J* as having greater intensity than *K*, whereas we find *J* to be the weaker line, in agreement with the assignments we have suggested for these higher harmonic frequencies (p. 274).† Our work on 1 : 2 : 4 : 5-tetradeuterobenzene was first carried out, with these results, before the appearance of Langseth and Lord's paper; and it was repeated several years later with a different specimen, with different apparatus, and by different experimenters, but again with the results described.

As stated, we differ from Langseth and Lord in regarding the frequency 1255·3 cm.$^{-1}$ as a fundamental, even though it has a possible explanation as a combination tone. It is, of course, not excluded of general principle that some special combination tone may be exceptionally strong; but this is most unlikely to be true of the particular combination which could yield the frequency under consideration, 589·0 + 663·6 = 1252·6 cm.$^{-1}$. The fundamental vibration of frequency 663·6 cm.$^{-1}$ is completely identical in 1 : 2 : 4 : 5-tetra-, penta-, and hexa-deuterobenzene (p. 285). The vibration having the frequency 589·0 cm.$^{-1}$ in 1 : 2 : 4 : 5-tetradeuterobenzene is not exactly the same, either in form or in frequency, as the corresponding vibrations of penta- and hexa-deuterobenzene; but, as we have already seen, the modification which this vibration undergoes as between one benzene and another is very small. Hence we should expect that if the two frequencies, 663·6 and 589·0 cm.$^{-1}$, unite to form an especially strongly appearing combination tone in the Raman spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene, the corresponding frequencies of penta- and hexa-deuterobenzene should give rise to combinations which are at least visible in the spectra of these substances. In fact, the analogous combination tones cannot be seen at all in our most strongly exposed photographs of these spectra. Thus it appears improbable, on grounds of intensity alone, that the observed line of frequency 1255·3 cm.$^{-1}$ could be a combination tone.

These findings being accepted, we may proceed to the problem of identifying the Raman lines representing the five fundamental vibrations of the B_{1g} symmetry class. For convenience, the frequencies of the selected lines are here given (in cm.$^{-1}$), together with their depolarisation factors (in parentheses) :

$C_6H_4D_2$	600·9 (0·85)	908·5 (0·83)	1309·0 (—)	1569·3 (0·8)	3042 (—)
$C_6H_2D_4$	585·8 (0·84)	954 (—)	1255·3 (0·88)	1564·0 (0·87)	2272 (—)

These vibrations may be regarded as being formed by interaction between vibrations of the forms of those of the A_{2g} and E_g^+ symmetry classes of the D_{6h} benzene model. The A_{2g} class contains a single hydrogen bending vibration, involving in-plane counter-rotatory motion of the carbon and hydrogen hexagons. The E_g^+ class contains, as we have seen, a carbon bending, a carbon stretching, a hydrogen bending and a hydrogen stretching vibration. We are, of course, concerned here only with those normal co-ordinates of the degenerate E_g^+ vibrations which have the symmetry properties required by the B_{1g} vibrations that are to be formed, that is, symmetry with respect to a 2-fold *z*-axis, and antisymmetry with respect to 2-fold *x*- and *y*-axes. The vector diagrams corresponding to these normal co-ordinates are labelled " *b* " in Fig. 1 of Part XI (this vol., p. 231).

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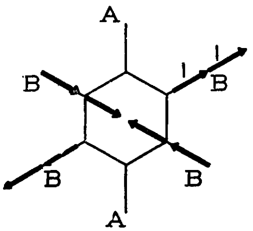
* We have suspected (though we could not reach a conclusion on the point) that the line (*L*) at 1140·3 cm.$^{-1}$ does not belong to 1 : 2 : 4 : 5-tetradeuterobenzene at all, but arises from an isotopic impurity such as 1 : 2 : 4-trideuterobenzene; for the relative strength of the line seemed to vary with the sample. Its strongest appearance in any of our photographs is that reproduced in Fig. 4, and we have reason to believe that the sample used to obtain it was not the best of the different samples we have examined.

† We have assigned *J* as a difference tone (Boltzmann factor 0·16); but it might be a forbidden fundamental (the infra-red-active 1057 cm.$^{-1}$), contravening the selection rules on account of cohesive forces; in either case it should be very weak.

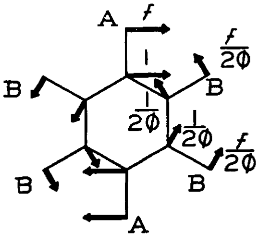
We have already dealt by implication with the carbon bending, the carbon stretching and the hydrogen stretching vibrations. Their frequencies in 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene have been identified each as a member of a close doublet, the other component of which belongs to the A_g symmetry class. A scheme of approximate normal co-ordinates is graphically represented in diagrams (VII), (VIII), and (IX), the indications of relative amplitude referring, as elsewhere, to 1 : 4-dideuterobenzene. The symbols f and ϕ denote factors which are introduced in this scheme to preserve orthogonality and freedom from angular momentum : f is the distance of a hydrogen atom from the centre of the ring, divided by the distance of a carbon atom from the centre of the ring $[(CC) + (CH)]/(CC) = 1{\cdot}78$, and ϕ has the value $(12 + f^2)/(12 + 2f^2) = 0{\cdot}83$.

The ratio of the frequencies, 600·9 and 585·8 cm.$^{-1}$, of the carbon bending vibrations, (VII), of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene is 1·03, in fair agreement with the simplified picture of this vibration which would require the ratio $\sqrt{14/13} = 1{\cdot}04$. In the carbon stretching vibration (VIII), one observes hardly any reduction of frequency in passing from the di- to the tetra-deuterobenzene, and this is clearly because, for either molecule, there is more motion per atom in that isotopic type of hydrogen of which the number of atoms is smaller. The frequencies entered under the vector diagram (IX) fall within the normal range of protium and deuterium stretching frequencies. The protium stretching frequency, as found in this vibration of 1 : 4-dideuterobenzene, agrees to within a few wave-numbers with that E_g^+ frequency, 3046·8 cm.$^{-1}$, of benzene itself. This should be so, because both vibrations are represented by the same approximate vector diagram, in which the deuterium atoms of dideuterobenzene do not move. Similarly, the deuterium stretching frequency, as found in the corresponding vibration of the tetradeuterobenzene, is very nearly the same as for the relevant E_g^+ vibration of hexadeuterobenzene, 2264·9 cm.$^{-1}$.



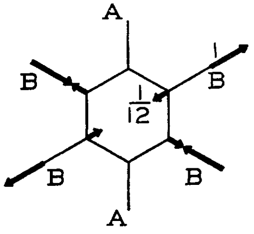
(VII.)

$C_6H_4D_2$, 600·9 cm.$^{-1}$
$C_6H_2D_4$, 585·8 cm.$^{-1}$



(VIII.)

$C_6H_4D_2$, 1569·3 cm.$^{-1}$
$C_6H_2D_4$, 1564·0 cm.$^{-1}$



(IX.)

$C_6H_4D_2$, 3042 cm.$^{-1}$
$C_6H_2D_4$, 2272 cm.$^{-1}$

The two component hydrogen bending vibrations, considered as belonging one to the A_{2g} class and one to the $E_g^+(b)$ class of vibrations of the D_{6h} model, are expected to mix together to produce two hydrogen bending vibrations of different character, in one of which most of the motion is in the protium atoms, whilst in the other most is in the deuterium atoms.

The selection of these frequencies for 1 : 4-dideutero- and 1 : 2 : 4 : 5-tetradeutero-benzene may be made as follows. In the Raman spectrum of 1 : 4-dideuterobenzene there are six unassigned lines, all of such strength that they must be considered as possible fundamentals. They have the following frequencies (cm.$^{-1}$) :

634·1 736 849·5 908·5 967 1309·0

The first two of these might be out-of-plane bending frequencies, but are too low to be B_{1g} frequencies. The third is shown (p. 285) by a symmetry argument, involving comparison with the Raman spectrum of benzene, to be an out-of-plane bending frequency. The fifth is shown (p. 286) by an argument which is based on the product rule, and involves comparison with the infra-red spectrum of 1 : 3 : 5-trideuterobenzene, likewise to belong to the out-of-plane group of frequencies. The frequencies 908·5 and 1309·0 cm.$^{-1}$ are thus indicated by exclusion to belong to the B_{1g} group of fundamental frequencies, and their selection can be shown to be consistent with the product rule.

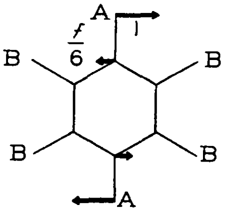
The frequencies which similarly come up for consideration in the Raman spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene are as follows (in cm.$^{-1}$) :

615·1 663·6 767·1 929·7 954 1255·3

The first three of these might be out-of-plane frequencies, but are too low to be B_{1g} fundamentals. The fourth is shown (p. 286), by an argument which is based on the product rule, and involves comparison with the infra-red spectrum of 1 : 3 : 5-trideuterobenzene, to belong to an out-of-plane bending vibration. By exclusion, the frequencies 954 cm.$^{-1}$ and 1255·3 cm.$^{-1}$ remain for assignment as fundamental frequencies of the B_{1g} class. The above assignment leads to the following product ratio :

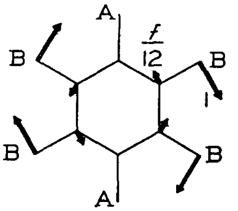
$$\frac{\Pi B_{1g}(C_6H_4D_2)}{\Pi B_{1g}(C_6H_2D_4)} = \frac{600{\cdot}9 \times 1569{\cdot}3 \times 3042 \times 908{\cdot}5 \times 1309{\cdot}0}{585{\cdot}8 \times 1564{\cdot}0 \times 2272 \times 1255{\cdot}3 \times 954} = 1{\cdot}368 \text{ (harmonic value} = 1{\cdot}370)$$

The normal co-ordinate diagrams (X) and (XI), in which the indicated relative amplitudes apply, as usual, to 1 : 4-dideuterobenzene, are only approximate. In particular the small counter-rotatory carbon motions, represented as being concentrated in two, or four, carbon atoms, are expected to be in fact distributed over all the atoms shown as stationary. This is indicated by the frequencies themselves. The ratio of the frequencies entered under diagram (X) is 1·38, and the ratio of those given under diagram (XI) is 1·34. If the atoms which are represented as stationary were in fact completely uncoupled dynamically from the parts of the molecules shown as being in motion, as they would have to be in order to make diagrams (X) and (XI) exactly true, each ratio should be about 1·29. On the other hand, if the hydrogen atoms represented as in motion were attached to a framework of residual atoms, which could be rotated as a rigid whole, but not deformed, each ratio should be about 1·37. This situation is clearly nearer the truth, but it is a difficult one to illustrate by means of amplitude formulæ which are at once simple and satisfy the orthogonality relationship. What we have done in order to secure the simple and orthogonal vector diagrams given is to transfer enough hydrogen motion from the E_g^+ hydrogen bending vibration to the E_g^+ carbon stretching vibration to leave in the former the same ratio of hydrogen to carbon motion as exists in the A_{2g} vibration : combination of the hydrogen vibrations according to the scheme $A_{2g} \pm E_g^+$ then secures a splitting into a pure deuterium bending, and a pure protium bending, vibration—which is certainly a first approximation to the truth, even though, by leaving certain atoms completely stationary, it over-simplifies the actual situation. [There will, of course, be corresponding errors in the representation given in diagram (VIII) of the carbon stretching vibration : the atoms of each CH-group must have more nearly equal amplitudes than is represented.]



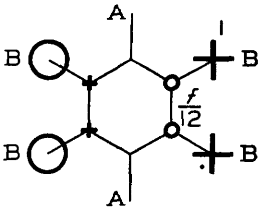
(X.)

$C_6H_4D_2$, 908·5 cm.$^{-1}$
$C_6H_2D_4$, 1255·3 cm.$^{-1}$



(XI.)

$C_6H_4D_2$, 1309·0 cm.$^{-1}$
$C_6H_2D_4$, 954 cm.$^{-1}$



(XII.)

$C_6H_4D_2$, 849·5 cm.$^{-1}$
$C_6H_2D_4$, 663·6 cm.$^{-1}$

The B_{2g} Fundamental Frequencies.—The B_{2g} vibrations of the V_h benzenes involve out-of-plane motion of the atoms, and are characterised by symmetry with respect to the two-fold y-axis, and antisymmetry with respect to the two-fold x- and z-axes. The two D_{6h} classes of vibrations from which the V_h class, B_{2g}, should be compounded are those labelled B_{1g} and E_g^-, with the restriction that we are here concerned only with that normal co-ordinate of each degenerate E_g^- vibration which has symmetry with respect to the two-fold y-axis. Actually the D_{6h} model *of benzene* has no vibrations in the B_{1g} class, and only one (degenerate) vibration in the E_g^- class. Thus the B_{2g} symmetry class of the V_h benzene model contains only one vibration, which must be identical in form with the appropriate component of the one degenerate E_g^- vibration of the D_{6h} benzene model. It involves counter-rotatory motions of the carbon and hydrogen hexagons about a common y-axis.

The normal co-ordinate of the B_{2g} vibration can thus be taken directly from Fig. 1 of Part XI (this vol., p. 231). It is represented in diagram (XII), in which the amplitude indications refer to 1 : 4-dideuterobenzene. From the diagram it is clear that, in this vibration, those hydrogen atoms of ordinary benzene, which become deuterium atoms in 1 : 4-dideuterobenzene, do not move. Therefore the frequency of the B_{2g} vibration of 1 : 4-dideuterobenzene must be identical with the frequency of the E_g^- vibration of ordinary benzene. This has been given as 848·9 cm.$^{-1}$ (Part VIII, J., 1936, 925). By a similar argument, the frequency of the B_{2g} vibration of 1 : 2 : 4 : 5-tetradeuterobenzene must be equal to that of the E_g^- vibration of hexadeuterobenzene, the value of which is 661·7 cm.$^{-1}$ (Table I of Part XV, this vol., p. 252). We have encountered similar frequency relationships before, for instance, in the vibrations represented in diagram (IX), but hitherto only as an approximation, inexactitude being in principle allowed, because of the neglect of interaction with other vibrations of the symmetry class. But this time there are no other vibrations in the symmetry class, and hence the relationship should be exact—except for such slight disturbances as might arise from intermolecular forces, and apart from the unlikely chance of appreciable interaction with a combination tone.

These considerations enable the Raman lines corresponding to the B_{2g} vibrations to be picked out at once in the spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene. The spectrum of the former compound has a prominent line at 849·5 cm.$^{-1}$, and that of the latter a strong line at 663·6 cm.$^{-1}$. Since B_{2g} lines of these frequencies are required by theory to appear prominently (see below), there can be no doubt that the observed lines have the interpretation indicated.*

It was shown in Part III (J., 1936, 925) that the intensity of the hexadeuterobenzene line at 661·7 cm.$^{-1}$ is greater than that of the benzene line at 848·9 cm.$^{-1}$, though each is alone in its symmetry class. The reason

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* Similarly the deuterium atom in monodeuterobenzene, and the protium atom in pentadeuterobenzene, do not move in this vibration. Consistently, the Raman spectrum of the former benzene contains the frequency 850 cm.$^{-1}$, and that of the latter the frequency 662·8 cm.$^{-1}$

was given by Lord and Teller in Part X (J., 1937, 1728) : the reduction in the amplitude of oscillations of the hydrogen hexagon in hexadeuterobenzene as compared with benzene, is more than compensated by the increase of amplitude of the carbon hexagon, with respect to the effect of each of these oscillations on the amplitude of oscillation of the molecular polarisability ellipsoid—which determines intensity. The same reason requires that the 1 : 2 : 4 : 5-tetradeuterobenzene line at 663·6 cm.$^{-1}$ be stronger than the 1 : 4-dideuterobenzene line at 849·5 cm.$^{-1}$; and the difference certainly is in this direction. The measured intensities are as follows, the standard for each benzene being the line of the totally symmetrical carbon vibration, which is given the intensity value 10 : it is plausible to assume that this line will undergo little proportional variation of absolute intensity as between one of these benzenes and another, since it, a carbon vibration, is outstandingly strong, and, in these particular benzenes, has no closely neighbouring frequency in the same symmetry class :

Benzene.	ν (cm.$^{-1}$).	*I.*	Benzene.	ν (cm.$^{-1}$).	*I.*
C_6H_6	848·9	0·9	1 : 4-$C_6H_4D_2$	849·5	0·5
C_6D_6	661·7	1·4	1 : 2 : 4 : 5-$C_6H_2D_4$	663·6	0·9

Theoretically, the intensity ratios, C_6H_6/C_6D_6 and $C_6H_4D_2/C_6H_2D_4$, should be equal : the deviation from equality is not greater than can be attributed to errors in the intensity measurements. Also, the intensity ratios $C_6H_4D_2/C_6H_6$ and $C_6H_2D_4/C_6D_6$ should each be one-half (the vibrations are doubly degenerate in C_6H_6 and C_6D_6) : the observed ratios do not differ from this value by more than the experimental error.

The assignment of B_{2g} frequencies may, then, be accepted. The measured frequencies lead to the following product ratios :

$$\frac{\Pi E_g^-(C_6H_6)}{\Pi B_{2g}(C_6H_4D_2)} = \frac{848 \cdot 9}{849 \cdot 5} = 0 \cdot 999 \qquad \frac{\Pi B_{2g}(C_6H_2D_4)}{\Pi E_g^-(C_6D_6)} = \frac{663 \cdot 6}{661 \cdot 7} = 1 \cdot 003 \qquad \frac{\Pi B_{2g}(C_6H_4D_2)}{\Pi B_{2g}(C_6H_2D_4)} = \frac{849 \cdot 5}{663 \cdot 6} = 1 \cdot 280$$

(harmonic value = 1·000) (harmonic value = 1·000) (harmonic value = 1·285)

The B_{3g} Fundamental Frequencies.—The three vibrations of this symmetry class involve out-of-plane motions of the atoms : and they are symmetric with respect to the 2-fold x-axis of the molecule, but anti-symmetric with respect to the 2-fold y- and z-axes. The cognate symmetry classes of the D_{6h} benzenes are the B_{2g} and E_g^- classes, with the reservation that we are concerned only with that normal co-ordinate of E_g^- vibrations which has 2-fold symmetry about the x-axis. There are two B_{2g} vibrations, a carbon and a hydrogen vibration; they are trigonally symmetrical, and of the out-of-plane type. The single E_g^- vibration involves counter-rotations of the carbon and hydrogen hexagons about a common x-axis. By the interaction permitted under V_h symmetry, these three vibrations modify each other to produce the three B_{3g} vibrations. The frequencies which we assign to these vibrations are the following :

1 : 4-Dideuterobenzene	634·1 cm.$^{-1}$	736 cm.$^{-1}$	967 cm.$^{-1}$
1 : 2 : 4 : 5-Tetradeuterobenzene	615·1 cm.$^{-1}$	767·1 cm.$^{-1}$	929·7 cm.$^{-1}$

Reference is here necessary to an observational point. The moderately intense line 615·1 cm.$^{-1}$ in the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene is not recorded by Langseth and Lord (*loc. cit.*). Instead they report two weak lines at 605·3 and 630·3 cm.$^{-1}$ which we have not been able to find. Our line is quite prominent; and no weak lines are visible in the trough of intensity on either side of it. We obtained this result originally, and again, after an interval of some years, with different material and apparatus.

The prominent low frequencies, 634·1 cm.$^{-1}$ in dideuterobenzene and 615·1 cm.$^{-1}$ in tetradeuterobenzene, cannot be anything except out-of-plane fundamental frequencies of the B_{3g} class. The middle frequencies, 736 cm.$^{-1}$ and 767·1 cm.$^{-1}$, are indicated, by their values and the intensities with which they appear, as probable members of the class, and the upper frequencies, 967 cm.$^{-1}$ and 929·7 cm.$^{-1}$, as possible members. These selections are unequivocally indicated by comparison with the frequencies of the infra-red parallel bands of 1 : 3 : 5-trideuterobenzene (preceding paper). The three vibrations, A_2'', whose frequencies are known from these bands, are derived from the A_{2u} and B_{2g} vibrations of the D_{6h} benzene model. The single A_{2u} frequency of benzene, or of hexadeuterobenzene, being known from its appearance in the infra-red spectrum, we can use the product rule to calculate the product of the two B_{2g} frequencies (which are inactive in benzenes of the D_{6h} model). Then, knowing this product for benzene or hexadeuterobenzene, and knowing the E_g^- frequency from its occurrence in the Raman spectrum, we can use the product rule to calculate the product of the three B_{3g} frequencies of 1 : 4-di- or 1 : 2 : 4 : 5-tetra-deuterobenzene. Thus we have

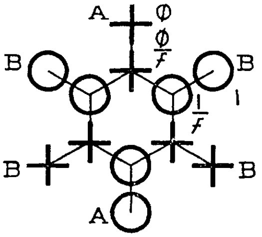
$$\frac{\Pi A_{2u}, B_{2g}(C_6H_6)}{\Pi A_2''(C_6H_3D_3)} = \frac{671 \times \Pi B_{2g}(C_6H_6)}{533 \times 691 \times 915} = 1 \cdot 373 \text{ (assumed, the harmonic value being 1·387).}$$

Hence $\Pi B_{2g}(C_6H_6) = 689{,}600$ cm.$^{-2}$. This leads to

$$\frac{\Pi E_g^- B_{2g}(C_6H_6)}{\Pi B_{3g}(C_6H_4D_2)} = \frac{848 \cdot 9 \times 689{,}600}{\Pi B_{3g}(C_6H_4D_2)} = 1 \cdot 316 \text{ (assumed, the harmonic value being 1·324).}$$

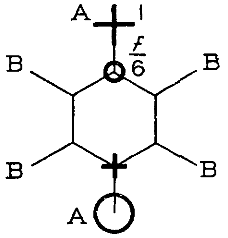
It follows that $\Pi B_{2g}(C_6H_4D_2) = 44 \cdot 5 \times 10^6$ cm.$^{-3}$. The product of the selected dideuterobenzene frequencies is $634 \cdot 1 \times 736 \times 967 = 45 \cdot 1 \times 10^6$ cm.$^{-3}$. The agreement is good, and no other selection from the frequencies of 1 : 4-dideuterobenzene listed on p. 284 would give even a rough agreement. Similarly, from the observed A_{2u} and E_g^- frequencies of hexadeuterobenzene, we can calculate $\Pi B_{2g}(C_6D_6) = 494{,}000$ cm.$^{-2}$, and from this,

$\Pi B_{3g}(C_6H_2D_4) = 43{\cdot}2 \times 10^6$. The product of the selected frequencies of 1 : 2 : 4 : 5-tetradeuterobenzene is $615{\cdot}1 \times 767{\cdot}1 \times 929{\cdot}7 = 43{\cdot}9 \times 10^6$ cm.$^{-3}$. Again, the agreement is excellent, and no other selection from the tetradeuterobenzene frequencies on p. 284 would give any kind of agreement.



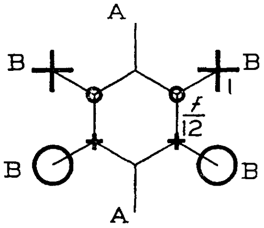
(XIII.)

$C_6H_4D_2$, 634·1 cm.$^{-1}$
$C_6H_2D_4$, 615·1 cm.$^{-1}$



(XIV.)

$C_6H_4D_2$, 736 cm.$^{-1}$
$C_6H_2D_4$, 929·7 cm.$^{-1}$



(XV.)

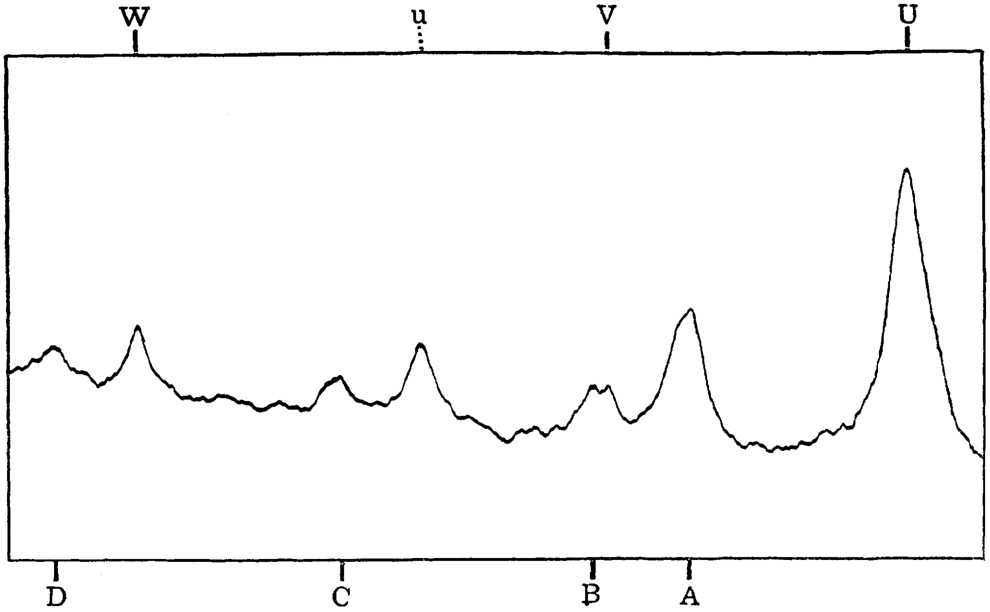
$C_6H_4D_2$, 967 cm.$^{-1}$
$C_6H_2D_4$, 767·1 cm.$^{-1}$

A direct application of the product rule to the assigned B_{3g} frequencies leads to the following confirmatory result :

$$\frac{\Pi B_{3g}(C_6H_4D_2)}{\Pi B_{3g}(C_6H_2D_4)} = \frac{634{\cdot}1 \times 736 \times 967}{615{\cdot}1 \times 767{\cdot}1 \times 929{\cdot}7} = 1{\cdot}029 \text{ (harmonic value} = 1{\cdot}032).$$

The normal co-ordinates of the three vibrations can be approximately determined by the method illustrated already several times in this and the preceding papers. Remembering that the valency structure of benzene will secure that the B_{2g} carbon vibration of the D_{6h} model will contain a larger proportion of hydrogen motion than is normal for carbon vibrations, and that, as the orthogonality principle then determines, the B_{2g} hydrogen vibration will contain a correspondingly smaller proportion of hydrogen motion, we so adjust the carbon and hydrogen amplitudes in these vibrations that the latter, by sum-and-difference combinations with the E_g vibration, will produce forms representing pure protium or pure deuterium vibrations when applied to 1 : 4-dideutero- or 1 : 2 : 4 : 5-tetradeutero-benzene. The resultant vector diagrams are shown in (XIII), (XIV), and (XV). As usual, the amplitude indications are given for the case of the 1 : 4-dideutero-benzene only (f and ϕ have the meanings specified on p. 284).

FIG. 5.



Microphotometer record of part of Raman spectrum of 1 : 4-*dideuterobenzene, taken with unfiltered mercury light. Lines labelled at the bottom of the photograph are excited by* Hg 4358·34 A., *those labelled at the top by* Hg 4046·56 A. (*in one case by* Hg 4077·8 A.).

From Hg 4358·34 A. :
A = 596·6—600·9 *cm.*$^{-1}$.
B = 634·1 *cm.*$^{-1}$.
C = 736 *cm.*$^{-1}$.
D = 849·5 *cm.*$^{-1}$.

From Hg 4046·56 A. :
U = 2280·0 *cm.*$^{-1}$.
V = 2395·4 *cm.*$^{-1}$.
W = 2582·7 *cm.*$^{-1}$.

From Hg 4077·8 A. :
u = 2280·0 *cm.*$^{-1}$.

There can be no doubt as to which observed frequencies correspond to each of these diagrams. We would naturally have tried to assign the lowest frequency in each group of three to the B_{3g} carbon vibration, (XIII), since all calculations based on assumed force fields yield low values for out-of-plane carbon frequencies. Actually this assignment is forced upon us, because only by adopting it can we obtain acceptable ratios for the frequencies of the remaining, approximately isomorphous, protium and deuterium vibrations. Further, the frequency ratio $634{\cdot}1/615{\cdot}1 = 1{\cdot}03$ agrees satisfactorily with expected ratio of about 1·05. Diagram (XIV) will correspond to the lower of the remaining two frequencies of 1 : 4-dideuterobenzene (deuterium motion), and the upper of the two of 1 : 2 : 4 : 5-tetradeuterobenzene (protium motion). The ratio $929{\cdot}7/736 = 1{\cdot}26$ is in satisfactory agreement with the calculated ratio 1·29. To diagram (XV) will belong the remaining frequencies, and their ratio, $967/767{\cdot}1 = 1{\cdot}26$, is also in satisfactory accord with the calculated ratio, 1·29, for isomorphous protium and deuterium vibrations of this type.

Raman-active Overtones and Combination Tones.—The selection rules for higher harmonics in the Raman spectrum of V_h benzenes are simple : all first overtones are allowed, and so also are all combination tones formed from two " gerade," or two " ungerade," fundamental frequencies. Combinations between a " gerade " and an " ungerade " fundamental frequency are forbidden in the Raman effect.

The higher harmonics observed in the Raman spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene are assigned in accordance with these rules in Tables I and II (pp. 273, 274). A number of first overtones appear, and it is notable that they include several which correspond in the two spectra.

We must refer specially to a combination tone, which appears at 2582·7 cm.$^{-1}$ in the Raman spectrum of 1 : 4-dideuterobenzene. It is remarkable for its intensity, and the fact that the line is far removed from any fundamental line, from which it could have derived intensity by resonance if it had lain close enough in frequency. We intend to make use (in another paper) of this combination tone for the purpose of developing an argument relating to one of the inactive fundamental frequencies of benzene. Since neither Redlich and Stricks nor Langseth and Lord (*locc. cit.*) report this Raman line, we here establish its existence with the aid of the microphotometric record of Fig. 5. This record is made from a plate in exposing which unfiltered mercury light was used, so that the line 2582·7 cm.$^{-1}$ (marked *W* in Fig. 5), as excited by Hg 4046·56 A., could be visually compared as to intensity with some fundamental lines (*e.g.*, those marked *C* and *D* in Fig. 5), which, as excited by Hg 4358·34 A., appear in the same part of the spectrogram (the two exciting mercury lines are of the same order of intensity).

The same microphotometer trace shows that there is no line of moderate intensity at 2261 cm.$^{-1}$, as stated by Langseth and Lord.

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