64. *Structure of Benzene. Part XX. The Raman and Infra-red Spectra of Monodeuterobenzene: Description and Analysis.*

By C. R. Bailey, R. R. Gordon, J. B. Hale, N. Herzfeld, C. K. Ingold, and H. G. Poole.

The Raman spectrum of monodeuterobenzene has been studied, and measurements have been made on 35 lines. Accurate frequencies are recorded, as well as approximate degrees of polarisation and rough measurements of relative integrated intensity. The infra-red spectrum of the compound has also been examined over a spectral range, 3—27 μ, great enough to include all the fundamental vibration frequencies. The frequencies of 55 intensity maxima, corresponding to 27 distinct vibrational origins, have been determined.

The spectra have been completely analysed, and 29 of the 30 fundamental frequencies of the molecule have been assigned to their proper vibrations. The frequency of one vibration remains uncertain. The assignment is based partly on the intensity and polarisation of the Raman lines, and the intensity and rotational contours of the infra-red bands, considered in the light of selection rules; partly also on an empirical knowledge of the spectral regions in which particular vibrations should appear; and partly, or even largely, on comparisons, made in the light of the product theorem, or of considerations respecting the normal co-ordinates of the vibrations, with the already understood spectra of benzene and 1 : 4-di-, 1 : 3 : 5-tri-, 1 : 2 : 4 : 5-tetra- and hexadeuterobenzene. The observed higher harmonic frequencies are fully assigned.

The molecule of monodeuterobenzene does not possess a centre of symmetry, and accordingly many of its fundamental frequencies are allowed by the selection rules to appear in both the Raman and the infra-red spectra. A considerable number do in fact appear in both spectra, which it is therefore necessary to consider together.

The Raman spectrum of monodeuterobenzene has been described before in various degrees of detail, first by Angus, Bailey, Gleave, Ingold, Leckie, Raisin, and Wilson (*Nature*, 1935, **135**, 1033), and next by Redlich and Stricks (*Monatsh.*, 1936, **67**, 213); notes on particular features of the spectrum have been recorded by Ingold (*Z. Elektrochem.*, 1938, **44**, 20; *Proc. Roy. Soc.*, 1938, *A*, **169**, 149); and a fairly full description of it given by Langseth and Lord (*Kgl. Danske Vidensk. Selsk.*, 1938, **16**, 6).

As to interpretation, Angus *et al.* exhibited a correlation between the recorded Raman frequencies of monodeuterobenzene and the seven fundamental frequencies of benzene, which were first correctly assigned to their vibrations in the communication cited. Redlich and Stricks gave the same correlation. Langseth and Lord offered a more extended assignment of the fundamental frequencies of monodeuterobenzene, but they were handicapped by lack of information about the infra-red spectrum. It is true that, according to the selection rules, all frequencies which are allowed to appear in the infra-red spectrum are also allowed in the Raman spectrum. But a number of them cannot be observed in the Raman spectrum, and all that can were not in fact observed by Langseth and Lord : any serious lack of completeness in the observations always renders an assignment problem very difficult.*

The infra-red spectrum of monodeuterobenzene has not been described before, although reference to some particular features of the spectrum has been made by Ingold (*locc. cit.*).

The sample of monodeuterobenzene employed in the present work was prepared by Weldon and Wilson (Part XII, this vol., p. 235). The spectra showed it to be very pure. The general conditions of the spectrometric measurements, and the standards of accuracy achieved, were as described for 1 : 3 : 5-trideuterobenzene in Part XVII (this vol., p. 255).

The numerical results of our study of the Raman spectrum of monodeuterobenzene are recorded in Table I. The first column contains the measured Raman frequencies, whilst the second gives qualitative indications of the intensities of the lines, followed in some cases by figures representing the results of a series of photometric measurements of the relative integrated intensities of the stronger lines. The braces in the first column indicate groups of overlapping lines, and it will be seen that some of the intensity data apply to line groups rather than single lines. Depolarisation factors are recorded in the third column : these figures, like the data for relative intensities, are only approximate. The remaining columns of Table I record our analysis of the spectrum : the observed frequencies are identified either as fundamental or allowed higher harmonic frequencies, and all are assigned to their symmetry classes. Where alternative assignments of higher harmonic frequencies are possible, the alternatives are given.

TABLE I.

Raman Spectrum of Monodeuterobenzene, and Assignment.

Frequency (cm.$^{-1}$).	Intensity.	Depolarisation factor.	Assignment.	Symmetry class.	Symmetry of components.
380	mw	—	Fundamental	B_2	—
601·8	ms (2·5)	0·81	Fundamentals	A_1, B_1	—
757	ww	—	2 × 380 = 760	A_1	B_2, B_2
778·7	m (0·5)	—	Fundamental	B_2	—
849·9	m (1·2)	0·79	Fundamental	A_2	—
857·1	m		Fundamental	B_1	—
922	w	—	Fundamental	B_2	—
ca. 972	w (broad)	—	$^{12}C_5{}^{13}CH_5D$	—	—
980·0	s (10·0)	0·28	Fundamental	A_1	—
990	w	—	Fundamental 380 + 608 = 988	B_2 A_1	— B_2, B_2
1006·8	s (2·5)	0·40	Fundamental	A_1	—
1031·0	m (0·4)	—	Fundamental	A_1	—
1075	m (0·3)	—	Fundamental	B_1	—
1158·2	ms (1·0)	0·8	Fundamental	B_1	—
1175·6	ms (1·8)	0·8	Fundamental	A_1	—
1292	m (0·3)	—	Fundamental	B_1	—
1396	ww	—	2 × 698 = 1396	A_1	B_2, B_2
1449	mw	—	Fundamental	B_1	—
1479	mw	—	Fundamental	A_1	—
1557	ww	—	2 × 778 = 1556	A_1	B_2, B_2
1574·3	ms (1·8)	0·8	Fundamental	B_1	—
1591·1	ms (2·5)	0·8	Fundamental	A_1	—
1605	w	—	601 + 1006·8 = 1608 603 + 1006·8 = 1610	A_1 B_1	A_1, A_1 B_1, A_1
1617	w	—	608 + 1006·8 = 1615 698 + 922 = 1620	B_2 A_1	B_2, A_1 B_2, B_2
2269·0	ms (2·0)	0·61	Fundamental	A_1	—
2310·6	m (0·6)	—	858 + 1450 = 2308 2 × 1158·2 = 2316·4	A_1 A_1	B_1, B_1 B_1, B_1
2589·8	m (0·5)	—	2 × 1292 = 2584 1006·8 + 1591·1 = 2597·9	A_1 A_1	B_1, B_1 A_1, A_1
2615	w	—	1158·2 + 1450 = 2608 1031·0 + 1591·1 = 2622·1	A_1 A_1	B_1, B_1 A_1, A_1
2900	ww	—	2 × 1450 = 2900	A_1	B_1, B_1
2998	m (0·8)	—	1450 + 1574·3 = 3024	A_1	B_1, B_1
3027	mw (18)	0·43	1450 + 1591·1 = 3041·1	B_1	B_1, A_1
3041	ms		Fundamental	B_1	—
3054·8	s		Fundamental	A_1	—
3060	ms		Fundamental	A_1	—
3077	mw		Fundamental 1480 + 1591·1 = 3171·1	B_1 A_1	— A_1, A_1
3164·6	m (0·7)	—	1574·3 + 1591·1 = 3165·4	B_1	A_1, B_1
3182	m (0·3)	—	2 × 1591·1 = 3182·2	A_1	A_1, A_1

Our results for the Raman spectrum agree with those of Langseth and Lord as far as there is overlap :

---

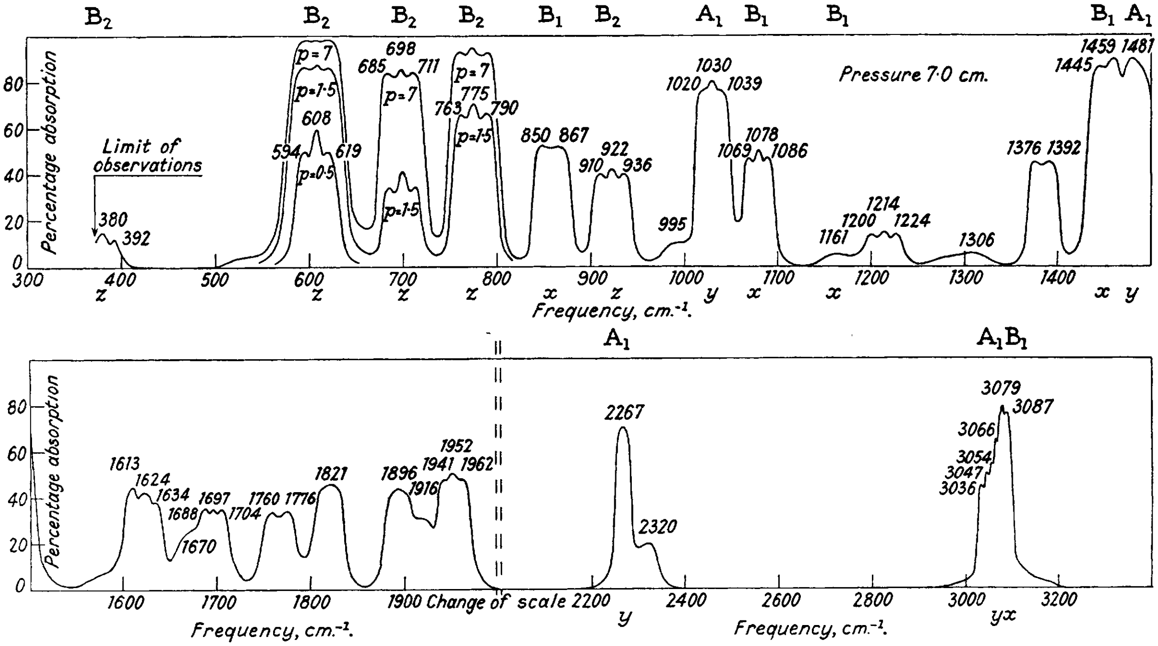
* We are in the same trouble ourselves with respect to pentadeuterobenzene. We have made a very full study of the Raman spectrum of this substance, and could suggest a tentative assignment of all its observed frequencies. But any such assignment would contain uncertainties which cannot be cleared up until the infra-red spectrum has been investigated.

21 of their frequencies agree with ours to within a few wave-numbers. However, we record a further 16 frequencies, some not particularly weak, which are not reported by Langseth and Lord, and these include 4 which we assign as fundamental frequencies. Two of Langseth and Lord's frequencies, given by them as 403 and 1418 cm.$^{-1}$, are not confirmed by this work (cf. p. 313).

The spectrum is too rich in detail to be usefully reproduced in a general form, but microphotometric records of particular regions are given in Figs. 3—6 (pp. 307—315).

The numerical results of our study of the infra-red spectrum of monodeuterobenzene are summarised in Table II. The first column contains the wave-lengths, and the second the frequencies, of the 55 measured intensity maxima. Many of these maxima arise from the resolved rotational contours of the bands, some of which exhibit obvious P, Q, and R branches, whilst others appear with only two intensity maxima, which we take to belong to P and R branches;* yet other bands are recorded with an unresolved contour, having only a single intensity maximum. Therefore, in the third column of the table, we have indicated those frequencies which we assume to represent the 27 vibrational origins of the measured bands; they are either the frequencies of Q branch maxima, or the means of the frequencies of P and R maxima, or, in the case of unresolved bands, the frequencies of their single maxima. The next column contains the frequency separations, where known, of the P and R intensity maxima: these data help with the assignment problem, inasmuch as they tell us whether the varying electric moment associated with the vibration lies in the plane of the benzene ring or normal to the plane. The next column contains, as an indication of the intensity of each band, the percentage of radiant energy absorbed, at the wave-length of the absorption maximum, by a 45 cm. column of vapour at 7 cm. pressure. The remaining three columns of the table summarise our conclusions with respect to the assignment of the frequencies: each observed band is assigned to an allowed fundamental or higher harmonic vibration, the symmetry of which is specified. Where alternative assignments of the higher harmonic frequencies are possible, the alternatives are given.

FIG. 1.



Infra-red spectrum of monodeuterobenzene.

A map of the infra-red spectrum of monodeuterobenzene is given in Fig. 1. It is based on a number of general surveys as well as many detailed tracings of particular bands.

It is of interest to compare the observed values of those fundamental frequencies which could be measured in both the Raman and infra-red spectra. The recorded values of all such doubly appearing fundamental frequencies are included in Table III. It will be seen that the differences found by the two methods of observation average about 2 cm.$^{-1}$, the signs of the differences being casually distributed. For convenience we include in the table those values, chosen with due regard to the relative ease and precision of the individual spectral measurements, which we have adopted for the doubly appearing frequencies in calculations of product ratios and the theoretical values of harmonic frequencies.

---

* One band is recorded with only Q and R branches, but that is because the P branch extends outside the long-wave limit of our measurements. The P branch of another band is too strongly overlapped to be separately measurable.

TABLE II.

Infra-red Spectrum of Monodeuterobenzene, and Assignment.

Wave-length (μ).	Frequency (cm.$^{-1}$).	Q or PR–mean.	PR–diff.	% Absorp-tion.	Assignment.	Symmetry class.	Symmetry of com-ponents.
— 26·3 25·5	— 380 392	380	∼24	15	Fundamental	B_2	—
16·83 16·45 16·15	594 608 619	608	25	∼100	Fundamental	B_2	
14·60 14·32 14·07	685 698 711	698	26	85	Fundamental	B_2	—
13·11 12·91 12·66	763 775 790	775	27	95	Fundamental	B_2	—
11·76 11·53	850 867	858·5	17	55	Fundamental	B_1	—
10·98 10·84 10·68	910 922 936	922	26	42	Fundamental	B_2	—
10·03	995	995	—	10	Fundamental	B_2	—
9·800 9·705 9·625	1020 1030 1039	1030	19	80	Fundamental	A_1	—
9·355 9·275 9·205	1069 1078 1086	1078	17	50	Fundamental	B_1	—
8·613	1161	1161	—	5	Fundamental	B_1	
8·332 8·247 8·167	1200 1214 1224	1214	24	15	601 + 608 = 1209	B_2	A_1, B_2
7·659	1306	1306	—	5	608 + 698 = 1306	A_1	B_2, B_2
7·270 7·184	1376 1392	1384	16	45	608 + 778 = 1386	A_1	B_2, B_2
6·919 6·856	1445 1459	1452	14	90	Fundamental	B_1	—
6·752	1481	1481	—	90	Fundamental	A_1	—
6·200 6·157 6·120	1613 1624 1634	1624	21	40	608 + 1006·8 = 1615 698 + 922 = 1620 778 + 849·9 = 1628 601 + 1031·0 = 1632 603 + 1031·0 = 1634	B_2 A_1 B_1 A_1 B_1	B_2, A_1 B_2, B_2 B_2, A_2 A_1, A_1 B_1, A_1
5·988	1670	1670	—	<20	698 + 970 = 1668	B_1	B_2, A_2
5·923 5·891 5·544	1688 1697 1704	1697	16	35	2 × 849·9 = 1700 778 + 922 = 1700	A_1 A_1	A_2, A_2 B_2, B_2
5·688 5·630	1760 1776	1768	16	35	849·9 + 922 = 1772 778 + 995 = 1773	B_1 A_1	A_2, B_2 B_2, B_2
5·492	1821	1821	—	45	849·9 + 970 = 1820	A_1	A_2, A_2
5·273	1896	1896	—	45	858 + 1031·0 = 1889 922 + 970 = 1892 601 + 1292 = 1893 603 + 1292 = 1895 922 + 980·0 = 1902	B_1 B_1 B_1 A_1 B_2	B_1, A_1 B_2, B_2 A_1, B_1 B_1, B_1 B_2, A_1
5·220	1916	1916	—	<30	922 + 995 = 1917 850 + 1076 = 1926	A_1 B_2	B_2, B_2 A_2, B_1
5·152 5·123 5·097	1941 1952 1962	1952	21	50	922 + 1031·0 = 1953 778 + 1175·6 = 1954 970 + 995 = 1965	B_2 B_2 B_1	B_2, A_1 B_2, A_1 A_2, B_2
4·411	2267	2267	—	70	Fundamental	A_1	—
4·310	2320	2320·	—	<20	2 × 1158·2 = 2316 1031·0 + 1292 = 2323	A_1 B_1	B_1, B_1 A_1, B_1
3·294 3·282 3·275	3036 3047 3054	3047	18	50	1450 + 1591·1 = 3041 1480 + 1574·3 = 3054	B_1 B_1	B_1, A_1 A_1, B_1
3·262	3066	3066	—	65	Fundamental	A_1	—
3·247 3·240	3079 3087	3079	∼16	80	1480 + 1591·1 = 3071 Fundamental	A_1 B_1	A_1, A_1 —

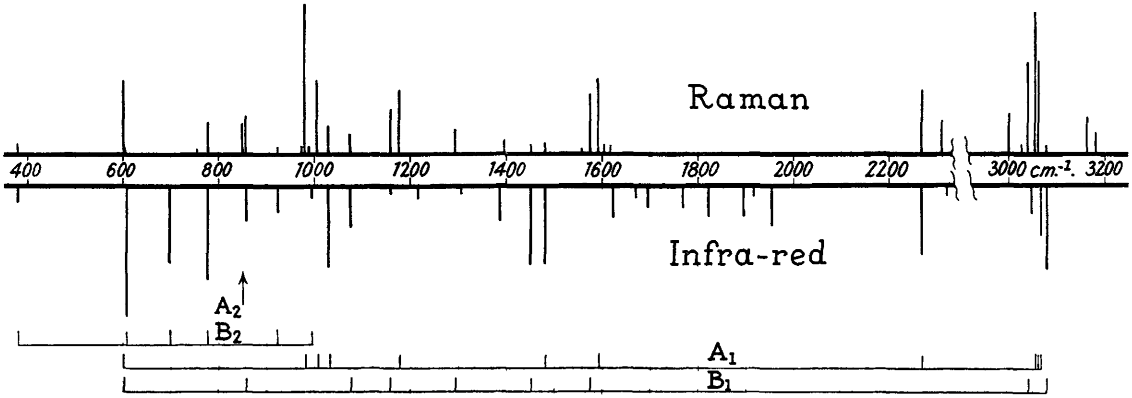
Table III also contains notes concerning those fundamental frequencies which have been measured in only one of the two spectra, even though in many cases they are allowed by the selection rules to appear in both. One of the frequencies (608 cm.$^{-1}$) which could not be measured in the Raman spectrum was nevertheless visible (" vis.") as a disturbance to the normal intensity distribution in the neighbouring strong Raman line (601·8 cm.$^{-1}$). Two other fundamental frequencies, although allowed in the Raman spectrum, could not be observed. One, at 3066 cm.$^{-1}$, lies in a region so much overlapped by neighbouring strong lines that it might well be obscured (" obsc."). The other, at 698 cm.$^{-1}$, is in a region favourable to observation; yet it was invisible (" inv.") on the plates. One strong infra-red frequency, that at 922 cm.$^{-1}$, appears weakly in the Raman spectrum excited by Hg 4046·56 A., but cannot be observed in the spectrum excited by Hg 4358·34 A. because of accidental coincidence with an excitation by Hg 4347·50 A. of the strong Raman frequency 980·0 cm.$^{-1}$. Several frequencies which should appear in the infra-red spectra lie in regions of weak general absorption (" absp."), in which, however, we were unable to observe any definite and reproducible intensity maxima (see Fig. 1). Other expected infra-red frequencies lie so close to observed bands that they may be assumed to be obscured by overlapping (Fig. 1). One Raman frequency, that at 849·9 cm.$^{-1}$, is forbidden (" F ") in the infra-red.

TABLE III.

Comparisons of Fundamental Frequencies in the Raman and the Infra-red Spectra of Monodeuterobenzene.

Raman (cm.$^{-1}$)	380	601·8	vis.	inv.	778·7	849·9	857·1	922	980·0
Infra-red (cm.$^{-1}$)	380	obsc.	608	698	775	F	858·5	922	obsc.
Difference (cm.$^{-1}$)	±0	—	—	—	+3·7	—	−1·4	±0	—
Adopted frequency (cm.$^{-1}$)	380	601, 603	608	698	778	849·9	857·1	922	980·0
Raman (cm.$^{-1}$)	(990)	1006·8	1031·0	1075	1158·2	1175·6	1292	1449	1479
Infra-red (cm.$^{-1}$)	995	absp.	1030	1078	1161	absp.	absp.	1452	1481
Difference (cm.$^{-1}$)	+5	—	+1·0	−3	−2·8	—	—	−3	−2
Adopted frequency (cm.$^{-1}$)	995	1006·8	1031·0	1076	1158·2	1175·6	1292	1450	1480
Raman (cm.$^{-1}$)	1574·3	1591·1	2269·0	3041	3054·8	3060	obsc.	3077	
Infra-red (cm.$^{-1}$)	absp.	absp.	2267	obsc.	obsc.	obsc.	3066	3079	
Difference (cm.$^{-1}$)	—	—	+2·0	—	—	—	—	−2	
Adopted frequency (cm.$^{-1}$)	1574·3	1591·1	2269·0	3041	3054·8	3060	3066	3079	

FIG. 2.



Diagrammatic comparison of the Raman and infra-red spectra of monodeuterobenzene.

There is one case in which we have employed adopted, rather than observed, frequencies, not because we have two observed values of the same fundamental frequency, but because one observed value represents two fundamental frequencies. The Raman line having a single observed intensity maximum at 601·8 cm.$^{-1}$ represents two nearly degenerate fundamental vibrations, and should theoretically be a close doublet. However, we could not resolve it. This is not surprising, because the corresponding doublet line in the Raman spectrum of 1 : 4-dideuterobenzene was resolved, and the two maxima were found to be only 3·8 cm.$^{-1}$ apart. Presumably in the monodeuterobenzene doublet the separation would be about half this, say 2 cm.$^{-1}$; and when two lines, each spreading over more than 20 cm.$^{-1}$, are so nearly coincident, resolution may well become impossible for the reason that the overlapping may build up a greater total intensity between the theoretical maxima than at those maxima. We assume the single observed maximum at 601·8 cm.$^{-1}$ to arise in this way from two nearly coincident lines, whose individual maxima must lie on either side of this frequency—in fact, very close to 601 cm.$^{-1}$ and 603 cm.$^{-1}$, if our estimate of the doublet separation is correct. In view of the difficulty of obtaining direct confirmation, we have adopted these values for the fundamental frequencies concerned.

A schematic comparison of the Raman and infra-red spectra of monodeuterobenzene is given in Fig. 2.

DISCUSSION OF ASSIGNMENT.

In the following discussion we shall deal mainly with the assignment of the fundamental frequencies. Reference to individual overtones and combination tones will be made only when special considerations are involved.

Monodeuterobenzene illustrates the benzene model of symmetry C_{2v}; the y-axis, that is, the para-axis passing through the deuterium atom, is a two-fold axis of symmetry, and the molecule has two planes of symmetry, one of which is the plane of the ring. In the absence of any three-fold axis, there are no strictly degenerate vibrations; and thus the 30 vibrational degrees of freedom correspond to 30 distinct fundamental frequencies. As there is no centre of symmetry, many of the fundamental frequencies are allowed, as we have seen, to appear in both the Raman and infra-red spectra. They are divisible into four symmetry classes as follows (Part XI, Table X, this vol., p. 228).

Symmetry class	A_1	B_1	A_2	B_2
No. of frequencies	11	10	3	6
Raman polarisation	Pol.	Depol.	(Depol.)	Depol.
Infra-red band type	$\psi\perp r$	$\psi\perp r$	—	$\psi\parallel$

The eleven A_1 frequencies represent planar vibrations having the full symmetry of the molecular model. They are allowed to appear in both the Raman and the infra-red spectra. The principal components, *a*, *b*, and *c*, of the polarisability preserve their directions but vary as to magnitude during these vibrations. The entry " Pol." means that the Raman lines are allowed by symmetry to have depolarisation factors falling below the limiting value 6/7. However, the depolarisation factors need not in all cases fall appreciably below 6/7; and they will not do so when *a*, *b*, and *c* so vary that their average $(a + b + c)/3$ remains nearly constant. On the other hand, no depolarisation factors under 6/7 are allowed in the other symmetry classes, and hence an observed low depolarisation factor is diagnostic for A_1 symmetry. The electric moment oscillates along the y-axis. Hence the vibrations give rise to what we call pseudo-perpendicular bands (" $\psi\perp r$ ") in the infra-red spectrum. A pseudo-perpendicular band can be recognised from its similarity to the perpendicular bands of the symmetrical-top benzenes: a PR-separation of about 15 cm.$^{-1}$ is expected.

The class called B_1 contains the 10 planar vibrations which do not preserve the two-fold axis of symmetry. In them, the principal components of the polarisability preserve their magnitudes but change their directions. There is a libration of the polarisability ellipsoid about the z-axis (normal to the plane of the ring), and a variable dipole moment parallel to the x-axis. These vibrations give depolarised Raman lines and pseudo-perpendicular infra-red bands.

An interesting situation arises in the A_2 symmetry class. It contains 3 out-of-plane vibrations, which preserve the two-fold y-axis of symmetry. They are allowed by the symmetry of their class to appear in the Raman spectrum, but when we look beyond these class requirements, and consider from the point of view of symmetry the forms of the normal co-ordinates, we find that two of the three vibrations cannot in fact appear in the Raman spectrum, because they can cause no change in any component of the polarisability. The third vibration is really allowed in the Raman effect. It sets up a libration of the polarisability ellipsoid about the y-axis. All three vibrations of this class are forbidden by symmetry in the infra-red spectrum.

The 6 vibrations of the B_2 class preserve neither the plane of the ring nor the two-fold y-axis. The polarisability ellipsoid undergoes libration about the x-axis, and the electric moment varies parallel to the z-axis. These vibrations give depolarised Raman lines, and infra-red bands of the type which we call pseudo-parallel, because of their similarity to the parallel bands of the symmetrical-top benzenes. The bands are broad, the expected PR-separation being about 25 cm.$^{-1}$: such broad bands are peculiar to this symmetry class.

The symmetry C_{2v} of monodeuterobenzene is a sub-group of the symmetry V_h of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene; it is also a sub-group of the symmetry D_{3h} of 1 : 3 : 5-trideuterobenzene; and the symmetries V_h and D_{3h} in their turn are sub-groups of symmetry D_{6h} of benzene and hexadeuterobenzene. We have seen (Part XI, *loc. cit.*) how the symmetry classes of the vibrations of point-groups of high symmetry become mixed together in pairs when a symmetry element, by reference to which they were distinguished, disappears in a sub-group. We have also seen how the mixing of the classes of the parent group causes a sharing, throughout the combination class of the sub-group, of such spectral activity as may have been characteristic of only one of the classes of the original group. Such sharing is naturally limited by the principle that a modification of atomic masses which can only slightly alter a normal co-ordinate cannot have a large effect on intensity. It follows that, if the vibration before the modification of symmetry was forbidden in a particular spectrum, it will not usually appear strongly after the modification, whilst if it was originally strong, it will not normally become very weak. These are general considerations, subject to modification in particular cases; but it remains true that intensity in the spectrum of a less symmetrical benzene is closely connected with the genesis of its vibrations in those of more highly symmetrical benzenes. Much of the evidence on which we base our assignment of the Raman and infra-red fundamental frequencies of monodeuterobenzene is derived from comparisons between these spectra, on the one hand, and the already understood Raman and infra-red spectra of the V_h, D_{3h}, and D_{6h} benzenes, on the other. The relations between the symmetry classes belonging to these different types of molecular symmetry are part of the argument, and are summarised in Table V of Part XI (this vol., p. 227).

The A_1 Fundamental Frequencies.—The eleven fundamental vibrations of the A_1 symmetry class comprise five carbon vibrations and six hydrogen vibrations. They are allowed by the selection rules in both Raman and infra-red spectra.

We shall first consider the carbon vibrations which derive from carbon vibrations of the four related symmetry classes of the D_{6h} benzene model, and, as compared with these vibrations of benzene, are not expected to be much changed in form or frequency by the introduction of a deuterium atom; for in all cases the motion can, as an approximation, be regarded as affecting the CH-groups, and the CD-groups as a whole. There is a similarly close relation between these vibrations of monodeuterobenzene and the corresponding vibration of 1 : 4-dideuterobenzene, and even of 1 : 3 : 5-trideuterobenzene. The following list contains the frequencies (in cm.$^{-1}$) assigned to these five vibrations of monodeuterobenzene together with their Raman depolarisation factors (in parenthesis) where known :

980·0 (0·28) 1006·8 (0·40) 601 (0·8) 1591·1 (0·8) 1480 (—)

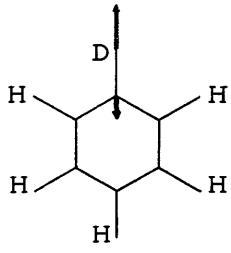
The frequency 980·0 cm.$^{-1}$ corresponds, as is shown by its outstanding strength and high polarisation in the Raman effect, to the carbon ring breathing frequency, 991·6 cm.$^{-1}$, of benzene. The frequency 1006·8 cm.$^{-1}$, which appears fairly strongly and with considerable polarisation in the Raman spectrum, corresponds to the planar, trigonal, carbon bending vibration of benzene, the frequency of which, 1010 cm.$^{-1}$, is only known indirectly, since the vibration is inactive in both Raman and infra-red spectra of benzene. These statements concerning the correspondence of the monodeuterobenzene vibrations with those of benzene represent only a first approximation. For Ingold pointed out the existence of two strong, polarised Raman lines, in the region *ca.* 950—1000 cm.$^{-1}$, of mono-, 1 : 3 : 5-tri- and penta-deuterobenzene, but not of benzene, 1 : 4-di-, 1 : 2 : 4 : 5-tetra- and hexa-deuterobenzene; and these facts imply a mixing of the characters of the breathing and trigonal bending vibrations in the mono-, tri-, and penta-deutero-compounds, as symmetry considerations allow (*Z. Elektrochem.*, 1938, **44**, 20; *Proc. Roy. Soc.*, 1938, *A*, **169**, 149). Langseth and Lord noted that the frequencies of the two vibrations are spread apart in these compounds, as they should be if the allowed interaction actually occurs (*Kgl. Danske Vidensk. Selsk.*, 1938, **16**, 6). Without the interaction, the frequencies in monodeuterobenzene should be about 985 cm.$^{-1}$ and 1000 cm.$^{-1}$, and the upper frequency would be spectrally inactive : we find two frequencies at 980·0 and 1006·8 cm.$^{-1}$, both active (lines A and C in Figs. 3*a* and 3*b*, p. 307). The situation is very similar to that obtaining in 1 : 3 : 5-trideuterobenzene (Part XVII, this vol., p. 255), except that in this compound the mixing is appreciably more drastic, as may be judged either from the greater frequency shifts or the increased relative intensity of the higher frequency. The normal co-ordinate diagrams for monodeuterobenzene will be as for the A_{1g} and B_{1u} carbon vibrations of benzene (Part XI, Fig. 1, this vol., p. 231), but modified to give the CD-group a larger relative amplitude in the lower frequency, and a smaller relative amplitude in the upper.

The frequency 601 cm.$^{-1}$ is an estimated value for the lower component of an unresolved, close doublet (mean frequency 601·8 cm.$^{-1}$) appearing in the Raman spectrum. It corresponds to the Raman frequency 605·6 cm.$^{-1}$ of benzene, and to the lower component, 596·6 cm.$^{-1}$, of the resolved Raman doublet of 1 : 4-dideuterobenzeno. The vibration concerned consists essentially of a stretching and contraction of the carbon ring along the *y*-axis, accommodated almost entirely by the bending of the ring angles rather than by alterations in the bond lengths. The benzene frequency is degenerate, and becomes replaced by a pair of frequencies in mono- and 1 : 4-di-deuterobenzene. The reason why we choose the lower frequency of each of these pairs to represent the totally symmetrical bending vibration has been explained for the case of 1 : 4-dideuterobenzene in Part XVIII (this vol., p. 277). The normal co-ordinate diagram for the monodeuterobenzene vibration must be very similar to that given in Part XVIII for the corresponding vibration of 1 : 4-dideuterobenzene [diagram (II), this vol., p. 278]. The normal co-ordinates are also closely similar to the appropriately chosen normal co-ordinate of the degenerate benzene vibration; and, as we explained in Part XVIII, this is the reason why the Raman depolarisation factors approximate to 6/7, even though in mono- and 1 : 4-dideuterobenzene the vibrations are totally symmetrical.

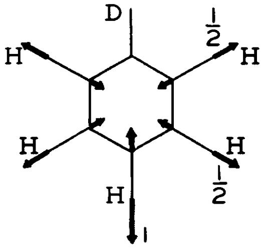
The monodeuterobenzene frequency 1591·1 cm.$^{-1}$ is the upper component of a resolved, Ramand oublet. It corresponds to the Raman benzene frequency 1596 cm.$^{-1}$, and to the upper component, 1587 cm.$^{-1}$, of a similar Raman doublet of 1 : 4-dideuterobenzene. The vibration consists of a lateral dilatation and contraction of the carbon ring produced mainly by stretching and compressing of the bonds. The frequency, which is degenerate in benzene, becomes split into a pair of frequencies in mono- and 1 : 4-di-deuterobenzene; and we select the upper member of each pair for the totally symmetrical stretching vibration of these molecules, for the reasons given, in the case of 1 : 4-dideuterobenzene, in Part XVIII (*loc. cit.*). The normal co-ordinate of the monodeuterobenzene vibration must be very similar to that depicted in Part XVIII [diagram (III), this vol., p. 278] for the vibration of 1 : 4-dideuterobenzene. Both are similar to the appropriate normal co-ordinate of the degenerate benzene vibration, and that is why the Raman depolarisation factors of these totally symmetrical vibrations of mono- and 1 : 4-di-deuterobenzene are close to 6/7.

The monodeuterobenzene frequency 1480 cm.$^{-1}$ is the upper component of yet another doublet arising from the resolution of degeneracy in a benzene vibration. The benzene frequency, 1485 cm.$^{-1}$, is active in the infra-red spectrum only. It becomes replaced in 1 : 4-dideuterobenzene by a doublet, also active only in the infra-red, the upper frequency having the value 1469 cm.$^{-1}$. The doublet of monodeuterobenzene is allowed to appear in both the infra-red and the Raman spectra, and in fact appears strongly in the former and weakly in the latter. The vibration, which we call a ring deformation, since it involves both stretching and bending of the carbon bonds, is totally symmetrical for monodeuterobenzene, but not for 1 : 4-dideuterobenzene, or any benzene of higher symmetry. However, the monodeuterobenzene vibration must be very similar to the 1 : 4-dideuterobenzene infra-red vibration of identical symmetry, which is described and depicted in Part XIX [diagram (VIII), this vol., p. 296]. Both must be closely similar to the appropriate component of the degenerate deformation vibration of benzene itself. The reasons for choosing the upper frequency of the monodeuterobenzene doublet to represent the totally symmetrical deformation vibration are similar to the reasons, given in Part XIX, for assigning the upper member of the 1 : 4-dideuterobenzene doublet to the vibration of related symmetry.

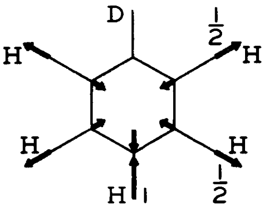
Hydrogen stretching vibrations of the A_1 class.



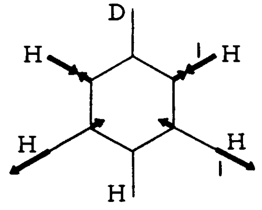
(I; 2269·0 cm.$^{-1}$)



(II; 3054·0 cm.$^{-1}$)

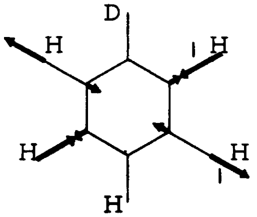


(III; 3060. cm.$^{-1}$)

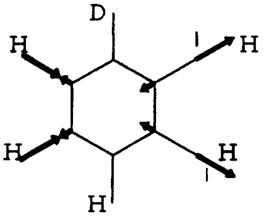


(IV; 3066 cm.$^{-1}$)

Hydrogen stretching vibrations of the B_1 class.



(V; 3041 cm.$^{-1}$)



(VI; 3079 cm.$^{-1}$)

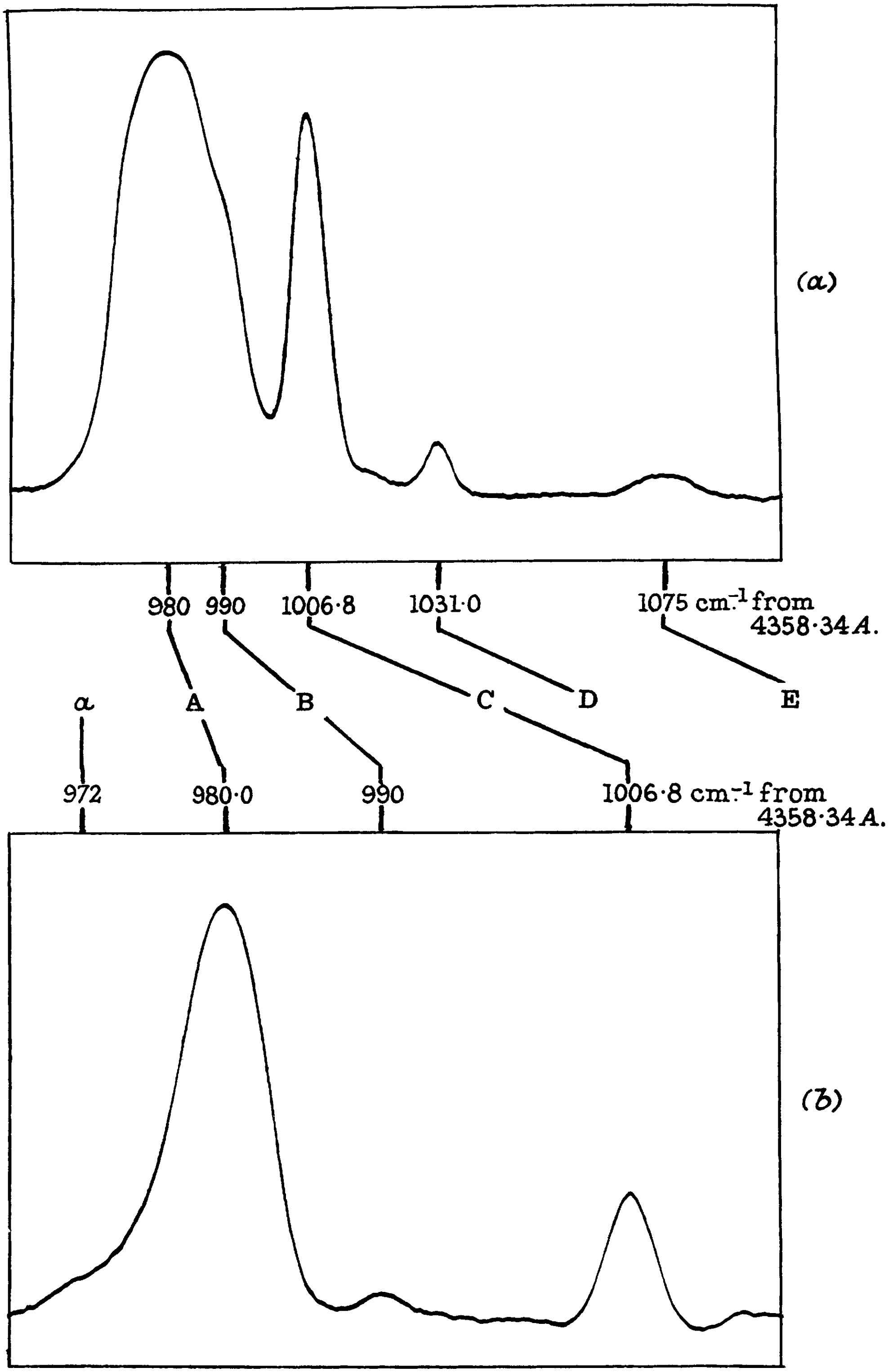
The A_1 symmetry class of vibrations of monodeuterobenzene contains two hydrogen bending frequencies and four hydrogen stretching frequencies. The following is a list of the assigned frequencies (in cm.$^{-1}$); Raman depolarisation factors (in parenthesis), and infra-red PR-frequency separations {in braces}, are added where known :

1175·6 (0·8) 1031·0 {19} 2269·0 (0·61) 3054·8 (0·43) 3060 {(—)} 3066 {(—)}

The first two of these frequencies belong to the protium bending vibrations. The third is obviously a deuterium stretching vibration, and the last three protium stretching vibrations.

Benzene has two planar hydrogen bending vibrations which have counterparts in the totally symmetrical class of vibrations of monodeuterobenzene. Both the benzene vibrations are degenerate, but in each case one normal co-ordinate possesses (at least) the total symmetry of monodeuterobenzene. One benzene frequency appears strongly in the Raman spectrum of that substance, at 1178·0 cm.$^{-1}$. Its counterpart in monodeuterobenzene is now identified as the upper member (line G, Fig. 4*b*, p. 311), 1175·6 cm.$^{-1}$, of a Raman doublet (lines F and G, Fig. 4*b*). It corresponds, again, to the upper member, 1173·4 cm.$^{-1}$, of the strong doublet appearing in the Raman spectrum of 1 : 4-dideuterobenzene. The monodeuterobenzene frequency, unlike the others, is allowed to appear in the infra-red spectrum : we found weak absorption in this region, but the band was too feeble to be distinguished against the background. The reason for taking the upper member of the monodeuterobenzene doublet to represent the totally symmetrical vibration is the same as the reason, given in Part XVIII, for assigning the upper member of the 1 : 4-dideuterobenzene doublet to the vibration of total symmetry. The approximate normal co-ordinate is graphically shown [diagram (VII), p. 310]. In it, the atoms on the y-axis do not move. The normal co-ordinate and frequency will thus remain the same in 1 : 4-dideuterobenzene, monodeuterobenzene, and benzene. In fact we find the frequencies very little altered, and this confirms the assumption underlying the normal co-ordinate diagram, *viz.*, that the vibration is a pure hydrogen bending vibration. Since the vibration in benzene, being degenerate, must have a Raman depolarisation factor of 6/7, the corresponding Raman lines of mono- and 1 : 4-di-deuterobenzene must have the same depolarisation factor, even though, in these substances, general considerations of symmetry would not so restrict the value.

Fig. 3.



(a) *Microphotometer record of part of the Raman spectrum of monodeuterobenzene excited by* Hg 4358·34 A. (*line* A *is over-exposed*). (b) *Record on a more open scale of part of the same region* (*from a less strongly exposed plate*).

The other relevant hydrogen bending frequency of benzene is found in the infra-red spectrum of that substance at 1037 cm.$^{-1}$; it is forbidden in the Raman spectrum. This vibration is also degenerate. The frequency of the correlated totally symmetrical vibration of monodeuterobenzene appears strongly in the infra-red spectrum at 1030 cm.$^{-1}$, and the band has a companion of higher frequency (Fig. 1). The corresponding band in the infra-red spectrum of 1 : 4-dideuterobenzene appears at 1033 cm.$^{-1}$; it also has a companion of higher frequency. The 1 : 4-dideuterobenzene frequencies are forbidden in the Raman effect, but the monodeuterobenzene frequencies are allowed by the selection rules to appear in the Raman spectrum. Both in fact appear, though not very strongly, the lower at 1031·0 cm.$^{-1}$ (lines *D* and *E*, Fig. 3*a*). The reasons underlying the choice of the lower monodeuterobenzene frequency 1030—1031 cm.$^{-1}$, to represent the totally symmetrical vibration correlated with the frequency 1037 cm.$^{-1}$ of benzene, are identical with the reasons given in Part XIX, for the assignment of the 1 : 4-dideuterobenzene frequency, 1033 cm.$^{-1}$, to a corresponding vibration. In the approximation in which these vibrations are regarded as pure hydrogen bending vibrations, the deuterium atoms of mono- and 1 : 4-di-deuterobenzene do not move; and thus the normal co-ordinates of the vibration for benzene and mono- and 1 : 4-di-deuterobenzene should be identical [diagram (VIII), p. 310]. In this approximation, therefore, the frequencies should be identical, and the monodeuterobenzene frequency should have zero intensity in the Raman effect, even though it is not forbidden by the symmetry of the vibration. The deviations from identity amongst the frequencies, and the finite intensity with which the monodeuterobenzene frequency appears in the Raman spectrum, show that the assumed normal co-ordinate is not quite exact, as indeed, we concluded in Part VIII in relation to the vibration of benzene itself (J., 1936, 983).

The six hydrogen stretching vibrations of monodeuterobenzene are expected to separate sharply into one deuterium stretching and five protium stretching vibrations. The deuterium, and three of the protium, stretching vibrations fall within the A_1 symmetry class; the other two protium stretching vibrations belong to the B_1 class. It is convenient to deal with them all together. Approximate normal co-ordinates of all six vibrations are given in diagrams (I)—(VI). Here, as elsewhere in this paper, the small carbon amplitudes in hydrogen vibrations are left unspecified because the formulæ by which we might have represented them are complicated even though only approximate.

The deuterium stretching vibration (I) appears as a single strong frequency in both Raman and infra-red spectra. There is no difficulty in identifying the frequency as 2269·0 cm.$^{-1}$.

Three strong lines appear in the Raman spectrum in the region of protium stretching frequencies. They occur at 3041, 3054·8, and 3060 cm.$^{-1}$ (lines *X*, *Y*, and *Z* in Fig. 4*a*, which is further discussed on p. 312). The centre line is considerably more intense than either of the others. Moreover it is considerably polarised. It will certainly be correct to assign this strongest Raman frequency, 3054·8 cm.$^{-1}$, to the vibration (II), in which all the five protium bonds are stretched in phase.

The normal co-ordinate of one vibration (V) is an unmodified reproduction of a normal co-ordinate assigned (Part XI, Fig. 1, this vol., p. 231) to the degenerate, E_g^+, hydrogen stretching vibration of benzene. This appears in the Raman spectrum of benzene with a frequency of 3046·8 cm.$^{-1}$. In so far as the normal co-ordinate represents a pure hydrogen stretching vibration, the atoms on the *y*-axis do not move; and hence the same vibration should appear with the same frequency in the Raman spectrum of 1 : 4-dideuterobenzene. It is there found with the very slightly displaced frequency 3042 cm.$^{-1}$ (Part XVIII, this vol., p. 272). The same vibration should occur in monodeuterobenzene, and should appear, with an identical frequency, in the Raman spectrum only, even though the selection rules would not forbid its appearance in the infra-red spectrum. To this vibration we must obviously assign the frequency 3041 cm.$^{-1}$, which has been found only in the Raman effect.

The only other hydrogen stretching vibration which could appear at all strongly in the Raman spectrum of monodeuterobenzene is that represented in diagram (III). We assign to this vibration the remaining member of the Raman group of hydrogen stretching lines, namely, that with the frequency 3060 cm.$^{-1}$.

The normal co-ordinate of diagram (VI) is identical with one of the normal co-ordinates assigned (Part XI, Fig. 1, *loc. cit.*) to the degenerate, E_u^-, hydrogen stretching vibration of benzene, which appears in the infra-red spectrum at 3080 cm.$^{-1}$. In so far as the vibration is a pure hydrogen stretching motion, the atoms on the *y*-axis remain stationary in this normal co-ordinate. Hence the same vibration should appear, with the same frequency, in the infra-red spectrum of 1 : 4-dideuterobenzene; where in fact it is observed at 3079 cm.$^{-1}$ (Part XIX, this vol., p. 288). We may also expect the vibration to occur, with an identical frequency, in the infra-red spectrum of monodeuterobenzene, and not at all, or at most only weakly, in the Raman spectrum of that substance; even though it is not forbidden in the Raman effect by the selection rules. The strongest band in the protium-stretching region of the infra-red spectrum is indeed found at 3079 cm.$^{-1}$. The vibration appears weakly at most in the Raman spectrum, the feeble line at 3077 cm.$^{-1}$ having an alternative possible explanation as an allowed combination tone. Accordingly we assign the frequency 3079 cm.$^{-1}$ to the vibration illustrated in diagram (VI).

The normal co-ordinate of diagram (IV) is identical with that of the B_{2u} protium stretching vibration of 1 : 4-dideuterobenzene [diagram (VI), Part XIX, this vol., p. 296]. This is active in the infra-red spectrum of that compound, and it was assigned the frequency 3060 cm.$^{-1}$ (Part XIX, this vol., p. 294). The infra-red spectrum of monodeuterobenzene exhibits a complex group of band maxima in the protium-stretching neighbourhood, and it is difficult to select with certainty the independent vibration frequencies from the overlapped rotational band-structures. However, besides the strongest frequency, 3079 cm.$^{-1}$, which has already been assigned, there are at least two others, one probably given by the maximum at 3066 cm.$^{-1}$ of intermediate intensity, and one by the maximum at 3047 cm.$^{-1}$, the weakest of the three. We assign the frequency 3066 cm.$^{-1}$ to the fundamental vibration represented by diagram (IV). Its frequency agrees satisfactorily with the frequency of the corresponding vibration of 1 : 4-dideuterobenzene; and the intensity of the band is smaller than that of the band at 3079 cm.$^{-1}$, as should be the case according to an argument presented in Part XIX (*loc. cit.*) in connexion with the similarly related frequencies of 1 : 4-dideuterobenzene. The lowest and weakest frequency, 3047 cm.$^{-1}$, we explain as a combination tone, or possibly an overlapped pair of combination tones, deriving added intensity by resonance with one of the neighbouring fundamental frequencies (Table I, p. 300).

The A_1 series of assignments may be checked by reference to the product rule. The necessary product ratios are in Part XI, Table XI (this vol., p. 232). For the product of the inactive B_{1u} frequencies of benzene we take the value calculated in Part XIX (this vol., p. 295). The following ratios are typical:

$$\frac{\Pi A_{1g},\, B_{1u},\, E_g^+,\, E_u^-(\mathrm{C_6H_6})}{\Pi_2 A_1(\mathrm{C_6H_5D})} = \frac{991{\cdot}6 \times 3061{\cdot}9 \times 3082 \times 10^3 \times 605{\cdot}6 \times 1596 \times 1178{\cdot}0 \times 3046{\cdot}8 \times 1485 \times 1037 \times 3080}{980{\cdot}0 \times 3054{\cdot}8 \times 1006{\cdot}8 \times 3060 \times 601 \times 1591{\cdot}1 \times 1175{\cdot}6 \times 2269{\cdot}0 \times 1480 \times 1031{\cdot}0 \times 3066}$$
$$= 1{\cdot}399 \text{ (harmonic value } = 1{\cdot}405)$$

$$\frac{\Pi A/(\mathrm{C_6H_5D})}{\Pi A_g,\, B_{2u}(1:4\text{-}\mathrm{C_6H_4D_2})} = \frac{980{\cdot}0 \times 3054{\cdot}8 \times 601 \times 1591{\cdot}1 \times 1175{\cdot}6 \times 2269{\cdot}0 \times 1006{\cdot}8 \times 3060 \times 1480 \times 1031{\cdot}0 \times 3066}{978{\cdot}0 \times 3055{\cdot}0 \times 596{\cdot}6 \times 1587{\cdot}0 \times 1173{\cdot}4 \times 2280{\cdot}0 \times 992 \times 3060 \times 1469 \times 1033 \times 2275}$$
$$= 1{\cdot}388 \text{ (harmonic value } = 1{\cdot}405)$$

$$\frac{\Pi A_1(\mathrm{C_6H_5D})}{\Pi A_1',\, E'(1:3:5\text{-}\mathrm{C_6H_3D_3})} = \frac{980{\cdot}0 \times 1006{\cdot}8 \times 3054{\cdot}8 \times 3060 \times 601 \times 1591{\cdot}1 \times 1480 \times 1031{\cdot}0 \times 1175{\cdot}6 \times 2269 \times 3066}{956{\cdot}2 \times 1003{\cdot}6 \times 2281{\cdot}9 \times 3052{\cdot}7 \times 593{\cdot}0 \times 1573{\cdot}1 \times 1407 \times 833{\cdot}5 \times 1101{\cdot}8 \times 2292 \times 3084}$$
$$= 1{\cdot}936 \text{ (harmonic value } = 1{\cdot}973)$$

The differences between the theoretically calculated and experimentally derived product ratios are of about the expected magnitude, and can be attributed to effects of anharmonicity.

The B_1 Fundamental Frequencies.—It seems natural to deal next with the remaining planar vibrations: there are ten, all belonging to the B_1 symmetry class. They comprise four carbon and six hydrogen vibrations. According to the selection rules, they are allowed in both Raman and infra-red spectra.

The four carbon vibrations are closely similar to certain vibrations of benzene itself. The frequency of one of the four, that corresponding to the B_{2u} carbon vibration of benzene, is left undetermined. The same point arose in Part XIX in connexion with 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, in which the cognate vibration is allowed in the infra-red spectrum. The normal co-ordinate diagram is given in that paper [diagram (IX), this vol., p. 298]. However, we postpone making assignments to this vibration until the evidence can be considered collectively (next paper).

The frequencies of the other three carbon vibrations have already been identified by implication as the non-totally symmetrical members of the doublets formed by the splitting in monodeuterobenzene of those planar carbon frequencies which are degenerate in benzene. The assigned frequencies (in cm.$^{-1}$) are as follows: Raman depolarisation factors (in parenthesis), and infra-red frequency separations {in braces} of the P and R rotational branches, are added in so far as they are known:

603 (0·8)   1574·3 (0·8)   1450 {14}

One of the doublets which contain these frequencies is the strong, unresolved, Raman doublet, centred at 601·8 cm.$^{-1}$, representing planar bending of the carbon ring. In the approximation in which this is regarded as a pure carbon bending vibration, the atoms on the y-axis remain stationary, and therefore the normal co-ordinate, which is shown diagrammatically in Part XVIII [diagram (VII), this vol., p. 284], should be the same in benzene, monodeuterobenzene, and 1 : 4-dideuterobenzene. Thus the frequency should be nearly the same in the three compounds. In fact, it is 605·6 cm.$^{-1}$ in benzene, and 600·9 cm.$^{-1}$ in 1 : 4-dideuterobenzene: our estimate of its value in monodeuterobenzene is 603 cm.$^{-1}$.

Next there is the Raman doublet corresponding to the planar stretching of the carbon ring: the lower frequency of this doublet, 1574·3 cm.$^{-1}$, must be assigned to the vibration of the B_1 symmetry class. An approximate normal co-ordinate diagram for the corresponding vibration of 1 : 4-dideuterobenzene is shown in Part XVIII [diagram (VIII), this vol., p. 284], and a similar diagram, with slightly changed relative amplitudes, would apply to monodeuterobenzene.

The remaining B_1 vibration, corresponding to deformation of the ring, is represented by the lower frequency, 1450 cm.$^{-1}$, of the strong infra-red doublet, which also appears, although weakly, in the Raman effect. The approximate vector diagram of the analogous vibration of 1 : 4-dideuterobenzene, given in Part XIX [diagram (XIII), this vol., p. 298], will apply, with slightly altered directions and amplitudes, to monodeuterobenzene.

The frequencies which have been assigned to the six hydrogen vibrations of the B_1 class are given below (in cm.$^{-1}$); Raman depolarisation factors (in parenthesis), and infra-red PR-frequency separations {in braces}, are added when known:

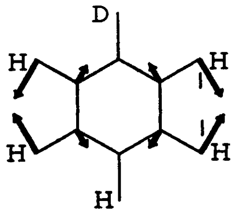
858(0·8){17}   1076{17}   1158·2(0·8)   1292{(—)}   3041{(—)}   3079{~16}

The last two of these frequencies represent protium stretching vibrations, and these have already been discussed. One is recorded as the moderately strong Raman line at 3041 cm.$^{-1}$, diagram (V), and the other as the strong infra-red band at 3079 cm.$^{-1}$, diagram (VI).

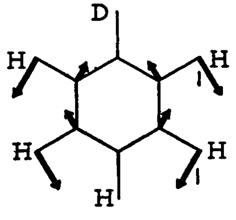
The remaining four vibrations of the B_1 class are hydrogen bending vibrations. Approximate normal co-ordinates of these, as well as of the two hydrogen bending vibrations of the A_1 class, which have already been discussed, are given in diagrams (VII)—(XII). We proceed with the consideration of the vibrations of the B_1 class [diagrams (IX)—(XII)].

The deuterium bending vibration [diagram (IX)] is easily recognised in the spectra. There is no alternative but to assign to this vibration the strong frequency 858 cm.$^{-1}$, which appears as a pseudo-perpendicular band in the infra-red spectrum, and as a depolarised line in the Raman spectrum (line *Q*, Fig. 5, p. 313). There is no observed frequency other than this one which could be assigned to the vibration of diagram (IX) : certainly the neighbouring Raman frequency 848·9 cm.$^{-1}$ (line *P*, Fig. 5) cannot be so assigned since it is required for another purpose, mentioned later.

Planar hydrogen bending vibrations of the A_1 class.

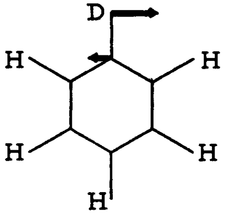


(VII; 1175·6 cm.$^{-1}$)

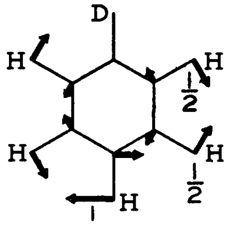


(VIII; 1031·0 cm.$^{-1}$)

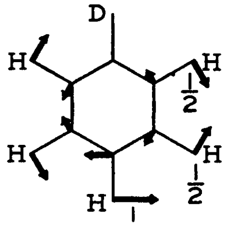
Planar hydrogen bending vibrations of the B_1 class.



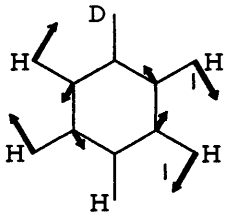
(IX; 858 cm.$^{-1}$)



(X; 1158·2 cm.$^{-1}$)



(XI; 1076 cm.$^{-1}$)



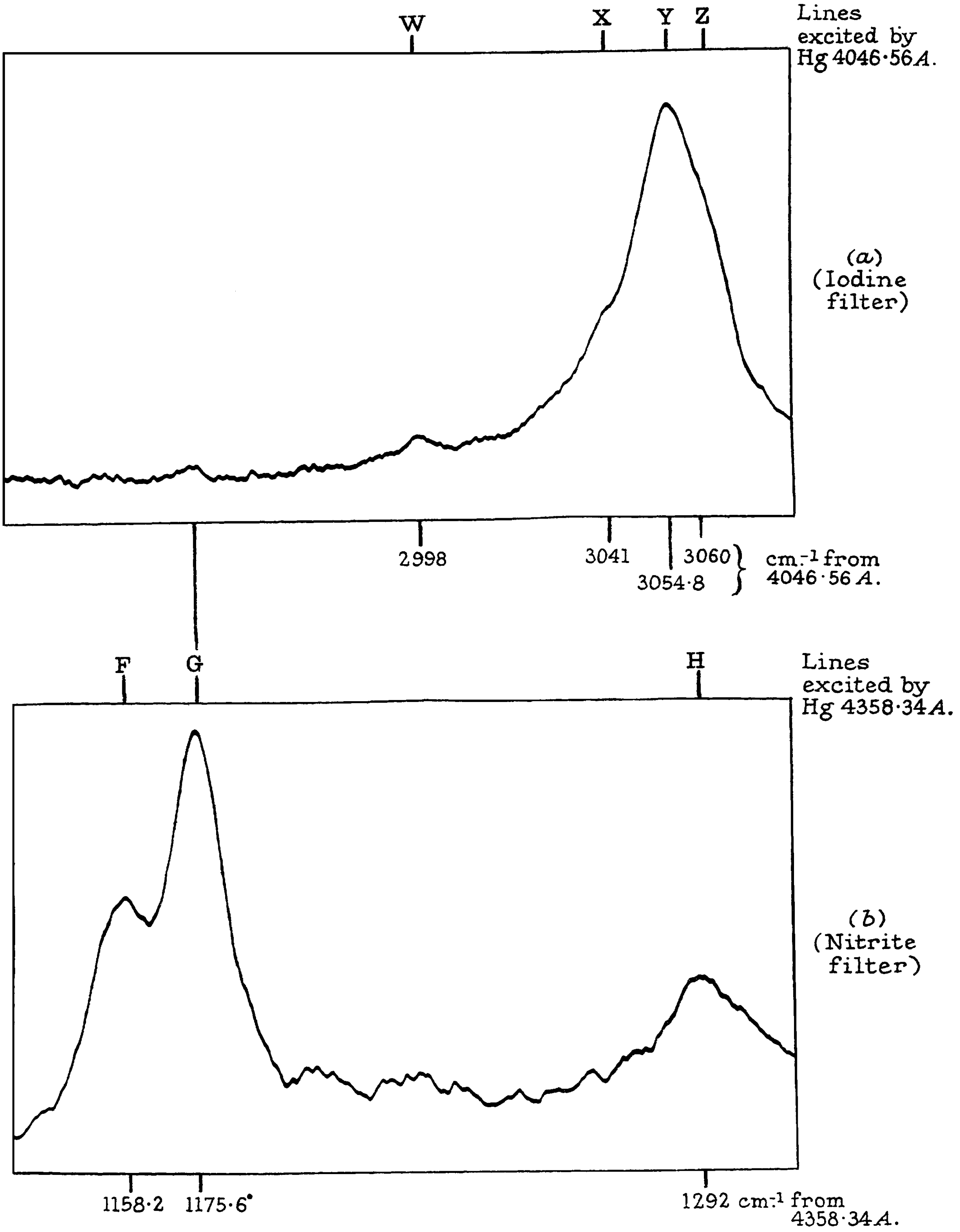
(XII; 1292 cm.$^{-1}$)

The protium bending vibration represented in diagram (X) should be moderately strong in the Raman effect, and weak in the infra-red spectrum. In these respects it resembles the vibration of diagram (VII). In fact, the vibrations (VII) and (X) may be regarded as having a common origin in the degenerate Raman vibration of benzene of frequency 1178·0 cm.$^{-1}$, even though practically the whole of the modification produced by the loss of symmetry becomes concentrated in vibration (X), vibration (VII) remaining almost unchanged. The two relevant frequencies, 1158·2 and 1175·6 cm.$^{-1}$, of monodeuterobenzene, are represented by the Raman lines *F* and *G* of Fig. 4*b* (p. 311). The higher frequency has already been assigned (p. 306) in the A_1 symmetry class to the nearly unmodified vibration (VII), and we must now assign its companion, 1158·2 cm.$^{-1}$ (line *F*, Fig. 4*b*) to the more altered B_1 vibration, approximately represented by diagram (X). The frequency appears weakly, but measurably (1161 cm.$^{-1}$), in the infra-red spectrum.

The protium bending vibration illustrated by diagram (XI), like that shown in diagram (VIII), should appear moderately strongly in the infra-red spectrum, and weakly in the Raman spectrum. These vibrations may be supposed to be derived by the breaking down of the degeneracy of the benzene infra-red vibration of frequency 1037 cm.$^{-1}$, even though most of the change induced by the loss of symmetry appears in vibration (XI), vibration (VIII) remaining little altered. The corresponding frequencies of monodeuterobenzene, 1031·0 and 1076 cm.$^{-1}$, appear strongly in the infra-red spectrum (Fig. 1), and somewhat weakly in the Raman spectrum (lines *D* and *E*, Fig. 3*a*). The former frequency having been assigned in the A_1 symmetry class to vibration (VIII), we must assign the latter, 1076 cm.$^{-1}$ (line *E*, Fig. 3*a*), to the B_1 vibration, approximately represented in diagram (XI).

The vibration represented by diagram (XII) is identical in the approximation to which our vector diagrams are valid with the vibration of 1 : 4-dideuterobenzene to which the frequency 1309·0 cm.$^{-1}$ was assigned in Part XVIII (this vol., p. 272). A monodeuterobenzene frequency in this neighbourhood would therefore be expected. The 1 : 4-dideuterobenzene frequency appeared with no more than a moderate intensity in the Raman spectrum; it is forbidden, and did not appear, in the infra-red spectrum. The corresponding monodeuterobenzene frequency would therefore be expected to appear with moderate intensity in the Raman spectrum, whilst it should at best be weak in the infra-red spectrum. Actually, in the whole range, 1000—1350 cm.$^{-1}$, in which planar bending frequencies of protium can be sought, there is only one unassigned Raman frequency. It is represented by a line of moderate intensity at 1292 cm.$^{-1}$, labelled *H* in the microphotometer

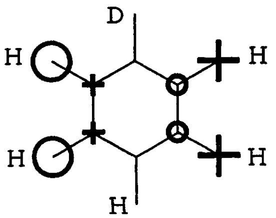
FIG. 4.



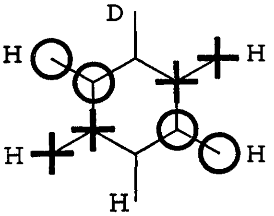
Microphotometric records of a region (1130—1316 *cm.*$^{-1}$ *from* Hg 4358·34 A. ≡ 2897—3083 *cm.*$^{-1}$ *from* Hg 4046·56 A.) *of the Raman spectrum of monodeuterobenzene, excited by mercury radiation :* (a) *with an iodine filter, and* (b) *with a nitrite filter.*

reproduction of Fig. 4*b*. There can be no reasonable doubt that this is the required frequency. In the infra-red spectrum there is weak absorption in this region, but the band cannot be clearly distinguished from the background of overlapping combination tones. (In the Raman spectrum there are overlapped combination tones on the high-frequency side of the line at 1292 cm.$^{-1}$, but here it is only the combination tones which cannot be separately distinguished.)

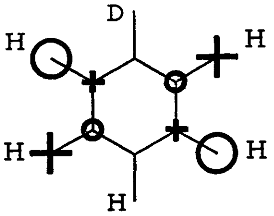
Since our recognition of the frequency 1292 cm.$^{-1}$ depends entirely on observation in the Raman spectrum, and since it was not recorded as a Raman frequency by Langseth and Lord (*loc. cit.*), we here establish its existence with the aid of Figs. 4*a* and 4*b*. These are photographic reproductions on the same scale of microphotometric records of the same spectral region, approximately 1130—1316 cm.$^{-1}$ on the Stokes side of Hg 4358·34 A., or about 2897—3083 cm.$^{-1}$ on the Stokes side of Hg 4046·56 A. The Raman plate which gave the record of Fig. 4*a* was taken with the incident mercury radiation passing through an iodine filter, which strongly reduces the intensity of Hg 4358·34 A. relatively to that of Hg 4046·56 A. The group, *XYZ*, of strong Raman frequencies, 3041, 3054·8, and 3060 cm.$^{-1}$, as well as the weak Raman line, *W*, of frequency 2998 cm.$^{-1}$ (a combination tone), all arise from excitation by Hg 4046·56 A. The plate which produced the record of Fig. 4*b* was taken with incident mercury radiation filtered by 3 cm. of saturated sodium nitrite : this filter practically eliminates the Raman spectrum excited by Hg 4046·56 A. The rather strong doublet *FG* representing the vibration frequencies 1158·2 and 1175·6 cm.$^{-1}$, and the line of moderate intensity *H* having the Raman frequency 1292 cm.$^{-1}$, are therefore excited by Hg 4358·34 A. Now when unfiltered mercury radiation is used for excitation, line *H*, 1292 cm.$^{-1}$ from Hg 4358·34 A., coincides exactly with line *Z*, 3060 cm.$^{-1}$ from Hg 4046·56 A. ; and it is clear that Langseth and Lord, who used unfiltered light, must have assumed the resultant photographic effect to be due to Raman excitation by Hg 4046·56 A. only. However, a comparison of the two photographs here reproduced shows that both Raman lines exist. The fact that the strong line *G* of Fig. 4*b* is only just visible in Fig. 4*a* is sufficient proof that the considerably weaker line *H* cannot have registered in Fig. 4*a* : the existence of line *Z*, having the Raman frequency 3060 cm.$^{-1}$, is thus confirmed. Likewise the fact that the very strong line *Y* of Fig. 4*a* is invisible in Fig. 4*b* demonstrates that line *Z* cannot contribute appreciably to the recorded intensity of the line labelled *H* in Fig. 4*b*. The existence of a line of moderate strength having the Raman frequency 1292 cm.$^{-1}$ is thus established.



(XIII; 849·9 cm.$^{-1}$. Raman)



(XIV; 405 cm.$^{-1}$. inactive)



(XV; 970 cm.$^{-1}$. inactive)

The A_2 Fundamental Frequencies.—Of the nine out-of-plane fundamental vibrations, three belong to the A_2 symmetry class. They preserve only one of the symmetry elements of the molecular model, namely, the two-fold *y*-axis. This fact forbids their appearance in the infra-red spectrum, but it does not of itself forbid them in the Raman effect. However, when we set up the normal co-ordinates, in accordance with the orthogonality principle, as is done graphically in diagrams (XIII)—(XV), we find that the atoms on the *y*-axis do not move. We can therefore, without affecting the vibrations in any way, replace the deuterium atom by protium, or the *p*-protium atom by deuterium, thus introducing new symmetry which, although not possessed by the original molecular model, is relevant to the consideration of the spectral activity of these particular vibrations. One new symmetry element which either substitution would introduce is a centre of symmetry; and, in relation to an added centre, the class of vibrations becomes divided into two sub-classes. One sub-class consists of the vibration represented in diagram (XIII), which is symmetric to the newly introduced centre of symmetry. The other consists of the vibrations of diagrams (XIV) and (XV), which are antisymmetric to the centre. These are forbidden in the Raman effect, and since it makes no difference to the form of the vibration if we drop back again to the original symmetry, the vibrations must be forbidden in the Raman effect even when, as in monodeuterobenzene, the hydrogen atoms on the *y*-axis are isotopically dissimilar, and there is no centre of symmetry. Thus only the vibration of diagram (XIII) can be spectrally active : it is forbidden in the infra-red, but allowed in the Raman spectrum.

The frequency of this vibration is known, as it has been observed as 848·9 cm.$^{-1}$ in the Raman spectrum of benzene and 849·5 cm.$^{-1}$ in the Raman spectrum of 1 : 4-dideuterobenzene. We find it in the Raman spectrum of monodeuterobenzene as a line of frequency 849·9 cm.$^{-1}$; and the measured value is here likely to be slightly too high on account of overlapping with the deuterium planar bending line of measured frequency 857·1 cm.$^{-1}$ (a value likely, for similar reasons, to be a little too low). A microphotometric trace showing these overlapped lines is reproduced in Fig. 5. Of these two vibrations, only the deuterium planar bending vibration should be active in the infra-red spectrum; and, consistently, the infra-red band in this region has the width and symmetry of a single pseudo-perpendicular band, centred about 858·5 cm.$^{-1}$ (Fig. 1).

The intensity of the Raman line at 849·9 cm.$^{-1}$ (line *P*, Fig. 5) should be the same as that of its counterpart belonging to 1 : 4-dideuterobenzene (measured intensity 0·5), and one-half of that of the corresponding line of benzene (measured value 0·9); for in benzene the vibration is doubly degenerate. In the monodeuterobenzene spectrum, the overlapping with the line at 857·1 cm.$^{-1}$ (line *Q*, Fig. 5) is too great to permit of a separate measurement of the integrated intensity of either line. But the intensity of the two lines together was found to be 1·2, and, as is obvious from Fig. 5, the line at 849·9 cm.$^{-1}$ contributes appreciably less than one-half of this intensity.

FIG. 5.

Microphotometric record of a region (830—880 *cm.*$^{-1}$ *from* Hg 4358·34 A.) *of the Raman spectrum of monodeuterobenzene, excited by mercury radiation filtered through nitrite.*

The frequencies of the two inactive vibrations corresponding to diagrams (XIV) and (XV) are derived from the evidence given in Part XXI (this vol., p. 316). A direct observation of the low frequency, as a very faint Raman line, has been recorded by Ingold (398 cm.$^{-1}$; *Z. Elektrochem.*, 1938, **44**, 20; *Proc. Roy. Soc.*, 1938, *A*, **169**, 149) and by Langseth and Lord (403 cm.$^{-1}$; *loc. cit.*). It might appear very weakly, as it undoubtedly does in benzene, on account of a slight abrogation of selection rules, caused by intermolecular forces. We have seen possible traces of this line, but could not presume to record it on the slight evidence afforded by our more recent plates.

The B_2 Fundamental Frequencies.—The six out-of-plane vibrations which do not preserve the two-fold symmetry axis are allowed in both the Raman and the infra-red spectra. The bands in the infra-red spectrum are easily recognised if they are at all strong, for they must be of the pseudo-parallel type, and should be the only bands with the broad rotational envelope characteristic of this type. There is no distinguishing common characteristic of the Raman lines, which are of generally low intensity, although one, the line of lowest frequency, immediately identifies itself by its position in the spectrum.

The frequencies (cm.$^{-1}$) which we have assigned to the vibrations of the B_2 class are as follows; the figures in parenthesis are the measured separation in cm.$^{-1}$ of the P and R intensity maxima of the infra-red bands :

380 (~24)	608 (25)	698 (26)
778 (27)	922 (26)	995 (—)

Four of these frequencies immediately identify themselves in the infra-red spectrum : the very strong band at 608 cm.$^{-1}$, the fairly strong bands at 698 and 778 cm.$^{-1}$, and the band of moderate intensity at 922 cm.$^{-1}$, all are of the pseudo-parallel type. In the Raman spectrum the frequency 778 cm.$^{-1}$ appears with moderate intensity, and the frequencies 608 and 922 cm.$^{-1}$ show weakly, whilst the frequency 698 cm.$^{-1}$ cannot be seen at all in our photographs.

The frequency 380 cm.$^{-1}$ is also easily recognised as one of this class. We know that the B_2 class of vibrations, which are derived from the A_{2u}, B_{2g}, E_u^+, and E_g^- vibrations of benzene, must include a vibration of characteristically low frequency, corresponding to the E_u^+ carbon vibration of benzene. This vibration is forbidden in the Raman spectra of benzene and of 1 : 4-di-, 1 : 2 : 4 : 5-tetra-, and hexa-deuterobenzene; but it is allowed in the Raman spectra of mono-, 1 : 3 : 5-tri- and penta-deuterobenzene; and in the spectra of the last three compounds it plainly appears, as a line of somewhat less than moderate intensity, at 380, 372·7, and 364 cm.$^{-1}$, respectively, the sole feature in these cases of what otherwise is a featureless spectral region for these, indeed for all, benzenes. The vibration is allowed to appear in the infra-red spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene; and, although the frequencies are almost at the long-wave limit of observation with our spectrometer, we have recorded in these spectra somewhat weak bands, at 367 and 383 cm.$^{-1}$ respectively, which again dominate an otherwise featureless spectral region. There can be no doubt that all these frequencies have a common origin in a vibration of the type of the E_u^+ carbon vibration of benzene. The monodeuterobenzene vibration is allowed to record its frequency in the infra-red, as well as in the Raman spectrum. We find it in the infra-red at 380 cm.$^{-1}$; and what can be seen of the rotational envelope is in agreement with the theoretical requirement that the band is of the pseudo-parallel type.

Five of the B_2 frequencies having thus been recognised, the sixth can be approximately located by an application of the product rule. The necessary comparison frequencies are known, *e.g.*, in 1 : 4-di- and 1 : 3 : 5-tri-deuterobenzene. Using either of these sets of frequencies, it can be shown that the sixth B_2 frequency of monodeuterobenzene must be close to 1000 cm.$^{-1}$. It must therefore be near the upper limit for out-of-plane frequencies, none of which, in any benzene, has been found to lie above 1000 cm.$^{-1}$, though several are close to this limit.

In the infra-red spectrum of monodeuterobenzene there is only one band, in the whole range relevant to out-of-plane fundamental frequencies, which has not already been assigned as a fundamental band. This is a rather weak band of frequency 995 cm.$^{-1}$. The band is certainly in the correct position, but since the form of the rotational contour could not be determined, it is necessary to consider what alternative assignments might be possible. First, the strong Raman frequencies, 980·0 and 1006·8 cm.$^{-1}$, might theoretically appear weakly in the infra-red spectrum. Actually there is a general background of weak absorption covering all this region, but the agreement between the Raman frequencies and the frequency of the selective absorption centred at 995 cm.$^{-1}$ seems too poor to justify assigning the latter to either of the vibrations responsible for the Raman frequencies. Next, a combination tone $380 + 608 = 988$ cm.$^{-1}$ is possible. However, here again the agreement of the frequencies is not very good; and the deviation is not in the usual direction. The remaining possibility is that the band represents a vibration, similar to that which has the frequency 1006·8 cm.$^{-1}$, but in a monodeuterobenzene molecule containing a ^{13}C atom: if the latter is in the ortho- or para-position with respect to the deuterium atom, the frequency of this planar, carbon bending vibration should be close to 995 cm.$^{-1}$. However, considering the weakness with which this vibration appears in the infra-red spectrum of 1 : 4-dideuterobenzene, or of other deuterated benzenes in which it is active, we must conclude that only a weak band would be observed even with a pure ^{13}C isomeride (^{12}CD and ^{13}CH must behave very similarly in a carbon vibration). Taking account of the fact that only 1% of the carbon atoms in monodeuterobenzene have mass 13, it appears highly improbable that bands due to the planar carbon bending vibration of heavy-carbon forms of monodeuterobenzene would be detectable at all in the infra-red spectrum as measured by us. On the whole then it appears difficult to avoid assigning the 995 cm.$^{-1}$ frequency to the B_2 fundamental vibration of ordinary monodeuterobenzene, especially as there is no other frequency in the spectrum which can be so assigned.

In the Raman spectrum there are three lines in the range of out-of-plane fundamental frequencies, which have not already been assigned as fundamentals. One is the extremely weak line at 757 cm.$^{-1}$, which we assign with some confidence as a first overtone of the low-frequency fundamental, 380 cm.$^{-1}$. The second is a rather weak, broad line, of frequency *ca.* 972 cm.$^{-1}$, labelled "*a*" in the microphotometer record reproduced in Fig. 3*b* (p. 307). This almost certainly represents the carbon ring "breathing" vibration of monodeuterobenzene molecules containing a ^{13}C atom, *i.e.*, it is the heavy-carbon counterpart of the very strong Raman line (labelled "*A*" in Fig. 3) of frequency 980·0 cm.$^{-1}$. The strength of the line at 972 cm.$^{-1}$ seems too great to admit of its interpretation as a difference tone, such as $1574{\cdot}3 - 601 = 973{\cdot}3$ cm.$^{-1}$.* The third of the unassigned lines is the somewhat weak but sharper line of frequency 990 cm.$^{-1}$, labelled "*B*" in Fig. 3*b* (p. 307). This is probably not a heavy-carbon line: frequencies between about 992 and 1005 cm.$^{-1}$, according to the position of the heavy carbon atom, are expected for that planar, carbon bending vibration which, in ordinary monodeuterobenzene, produces the Raman frequency 1006·8 cm.$^{-1}$; but those frequencies of the heavy carbon group which lie lowest should appear more weakly than others which will have been raised and intensified by resonance with the heavy carbon "breathing" frequencies; and hence we ought not to be observing a ^{13}C frequency at 990 cm.$^{-1}$ when none is visible at, or just above, 1000 cm.$^{-1}$. We must conclude therefore that all these heavy carbon bending frequencies are too weak for observation under our conditions. The line at 990 cm.$^{-1}$ likewise seems too strong for interpretation as a difference tone, $1591{\cdot}1 - 601 = 990{\cdot}1$ or $1591{\cdot}1 - 603 = 988{\cdot}1$ cm.$^{-1}$.* The remaining possibilities are (*a*) that it represents the allowed summation tone $380 + 608 = 988$ cm.$^{-1}$, (*b*) that it is to be identified with the infra-red frequency 995 cm.$^{-1}$ as the B_2 fundamental frequency. We are not able to decide between these possibilities, and as there seems to be little doubt about the origin of the infra-red band at 995 cm.$^{-1}$, we take this as giving the required B_2 fundamental frequency.

Testing these assignments by means of the product rule (cf. Table XI of Part XI, this vol., p. 232), we find the following ratios:

$$\frac{\Pi B_2(\mathrm{C_6H_5D})}{\Pi B_{1u},\,B_{2g}(1:4\text{-}\mathrm{C_6H_4D_2})} = \frac{380 \times 608 \times 698 \times 778 \times 922 \times 995}{367 \times 597 \times 876 \times 634{\cdot}1 \times 736 \times 967} = 1{\cdot}329 \text{ (harmonic value} = 1{\cdot}361)$$

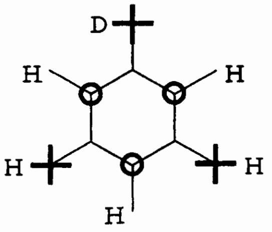
$$\frac{\Pi B_2(\mathrm{C_6H_5D})}{\Pi A_2'',\,E''(1:3:5\text{-}\mathrm{C_6H_3D_3})} = \frac{380 \times 608 \times 698 \times 778 \times 922 \times 995}{533 \times 691 \times 915 \times 372{\cdot}7 \times 710{\cdot}2 \times 947} = 1{\cdot}363 \text{ (harmonic value} = 1{\cdot}374)$$

The first of the experimental ratios is lower than one would expect, but then it involves the 1 : 4-dideuterobenzene infra-red frequency 367 cm.$^{-1}$, which is not accurately known, since a considerable part of the band was outside the range of our measurements. The corresponding frequency, 372·7 cm.$^{-1}$, of 1 : 3 : 5-trideuterobenzene is accurately known from the Raman spectrum.

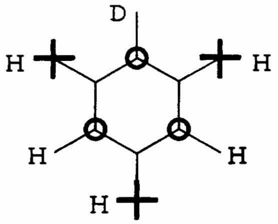
---

* It is true that Langseth and Lord recognised (*J. Chem. Physics*, 1938, **6**, 203) two of the weak frequencies which appear near the ring "breathing" frequency in the Raman spectrum of benzene itself to be constituted as differences of fundamental frequencies, $1606{\cdot}4 - 605{\cdot}6 = 1000{\cdot}8$ and $1584{\cdot}8 - 605{\cdot}6 = 979{\cdot}2$ cm.$^{-1}$, more or less corresponding, therefore, to the frequency differences referred to in the text. But, as the authors pointed out, the Fermi resonance which creates the 1606·4—1584·8 cm.$^{-1}$ doublet in benzene, gives to the difference frequencies the character of fundamentals of thermally excited molecules, rather than ordinary difference tones: compared to ordinary fundamentals, they are reduced in intensity by a Boltzmann factor, but they are not further reduced, as a difference-tone would be, by the intensity factor of second-order harmonics. It is the combination of the two effects which as a rule makes difference tones unobservably weak in the Raman effect.

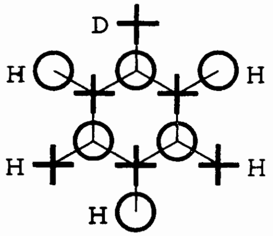
Owing to the complicated nature of the coupling between out-of-plane bending vibrations (cf. Part XVII, this vol., pp. 261, 268), any assignment of normal co-ordinates to the individual frequencies of an out-of-plane symmetry class containing as many as six fundamental vibrations must be more than usually arbitrary. The attempt represented in diagrams (XVI)—(XXI) should be interpreted accordingly. Diagrams (XVI)—(XVIII) approximately correspond to the A_2'' normal co-ordinates of a D_{3h} benzene, as given in Part XVII (*loc. cit.*). The assigned frequencies and their spectral activities appear qualitatively intelligible by comparison with the relevant active frequencies of 1 : 3 : 5-trideuterobenzene (533, 691, and 915 cm.$^{-1}$, all infra-red active). The second frequency should agree exactly, and the third approximately, in the two compounds, if our representations were correct. For the remaining three frequencies, the E_u^+ and E_g^- normal co-ordinates of a D_{6h} benzene, as shown in diagrams (XIX)—(XXI), seem to provide a better approximation than the E'' co-ordinates of a D_{3h} benzene, as represented in Part XVII (*loc. cit.*). The frequencies can be reasonably assigned on either basis (the benzene frequencies are 405, 848·9, and 970 cm.$^{-1}$, the second of them Raman-active), but the scheme illustrated appears to accord somewhat better with the Raman intensities. However, the infra-red activity of the frequency 778 cm.$^{-1}$ is not well represented, and this shows that the division of the six vibrations into two non-combining sets of three is a considerable over-simplification.



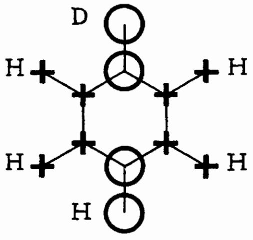
(XVI; 608 cm.$^{-1}$.)



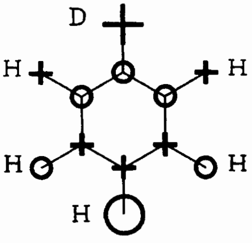
(XVII; 698 cm.$^{-1}$.)



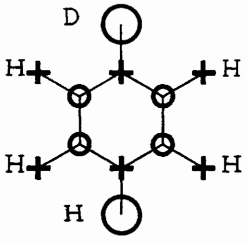
(XVIII; 922 cm.$^{-1}$.)



(XIX; 380 cm.$^{-1}$.)



(XX; 778 cm.$^{-1}$.)

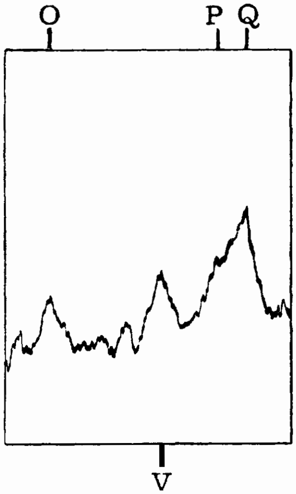


(XXI; 995 cm.$^{-1}$.)

The Raman-active Overtones and Combination Tones.—There is nothing in the symmetry classification of first overtones or binary combination tones to forbid the appearance of any of them in the Raman spectrum. However, it is obvious from the methods of deriving selection rules for combination tones (see Part XI, this vol., p. 233) that binary combinations between any totally symmetrical frequency of the A_1 class and either of the two inactive frequencies of the A_2 class will be inactive in the Raman effect. Combination tones are assigned consistently with these principles in Table I.

The Raman spectrum contains a number of peculiarly prominent higher harmonics, *e.g.*, 2310·6, 2998, 3164·6 and 3182 cm.$^{-1}$, clustered, as is so usual, about one or another of the very strong fundamental lines, *e.g.*, the line at 2269·0 cm.$^{-1}$ and the line group at 3041, 3054·8, and 3060 cm.$^{-1}$. We may assume that the higher harmonics derive their considerable intensity by resonance, of the type first described by Fermi, with neighbouring fundamental frequencies: it is significant that the symmetry category of these higher harmonics is always of a kind which would allow this to occur. In accordance with the general result of perturbation theory that effects of small perturbations on energy are quadratic, we find the frequency shifts arising from Fermi resonance less striking on the whole than the intensity changes. However, one of the above-mentioned combination lines, that at 2998 cm.$^{-1}$, appears to have sustained a notable frequency shift, the theoretical frequency of the combination being 1450 + 1574·3 = 3024 cm.$^{-1}$. This figure lies only 1% away from the very strong

FIG. 6.



Lines excited by Hg 4358·34 A.: O, 778·7 *cm.*$^{-1}$; P, 849·9 *cm.*$^{-1}$; Q, 857·1 *cm.*$^{-1}$.
Line excited by Hg 4046·56 A. V, 2589·8 *cm.*$^{-1}$.

Microphotometer record of part of the Raman spectrum of monodeuterobenzene, excited by unfiltered mercury radiation.

fundamental frequency, 3054·8 cm.$^{-1}$, of the same symmetry class; and this no doubt is responsible for both the frequency shift and the intensity increase apparent in the combination tone.

There is one remarkable Raman combination tone, having the frequency 2589·8 cm.$^{-1}$, which is of the same order of strength as those just mentioned, but it is far removed from any active fundamental frequency. Langseth and Lord do not record this Raman line, and since in Part XXI we make use of it in a theoretical discussion, we here establish its reality with the help of the microphotometer record of Fig. 6. This is the densitometric trace of part of a Raman plate, taken with unfiltered mercury light in order to enable the intensity of the combination tone (marked *V* in Fig. 6), as excited by Hg 4046·56 A., to be visually compared with the intensities of several fundamentals, which, as excited by Hg 4358·34 A., appear close beside it on the plate (the exciting mercury lines are of the same order of intensity). As will be seen, the intensity of the combination tone is comparable with that of any of the active fundamental frequencies 778·7, 849·9, 857·1 cm.$^{-1}$ (marked *O*, *P*, *Q* in Fig. 6).

The Infra-red-active Overtones and Combination Tones.—All first overtones and binary combination tones are allowed in the infra-red spectrum, except that frequencies of the A_1 class do not combine with those of the A_2 class, and that frequencies of the B_1 class do not combine with those of the B_2 class. The higher harmonic frequencies observed in the infra-red spectrum are assigned in accordance with these rules in Table II. Their relation to the higher harmonics of the infra-red spectra of benzene and 1 : 4-dideuterobenzene is considered in the next paper.

SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[*Received, May 7th*, 1945.