

213. *Structure of Benzene. Part III. Raman Spectra of Liquid Benzene and Liquid Hexadeuterobenzene.*

By W. R. ANGUS, C. K. INGOLD, and A. H. LECKIE.

(1) *Methods.*—The scattering spectrum of benzene has been studied by a large number of investigators from whose results it is possible to fix the frequency separations of the stronger lines with considerable accuracy, though the position is not quite so satisfactory with respect to intensities and polarisations. We have studied the Raman spectra of benzene and hexadeuterobenzene, as well as of several partly deuterated benzenes, the results for which will be reported later; all these spectra have been photographed under somewhat greater dispersion than is commonly employed. We have measured photometrically both the peak intensities and the integrated intensities of the principal lines; the integrated intensities do not seem to have been determined previously. We have correlated the intensities for benzene and hexadeuterobenzene by photographing the scattering spectrum of an artificial mixture containing 50 mols. % of each. Finally, we have measured the polarisations of all the lines for which this measurement was practicable.

Apparatus.—The photographs were taken with a Hilger E 390 glass prism spectrograph, which was housed in an air-thermostat with only the slit projecting. The exciting light was derived from a vertical quartz-mercury lamp, and was filtered for either the 4358 or the 4047 Å. line as required. The tubes, which were of the usual form with a fused-on window at one end

and a horn-shaped light trap at the other, were made of Jena G glass, had 2.5 c.c. effective capacity, and were sealed after introduction of the sample by distillation in a vacuum. They were mounted vertically on a reflecting prism close to the slit of the spectrograph (cf. Wood, *Phil. Mag.*, 1928, 6, 729; Angus, Leckie, and Wilson, *Proc. Roy. Soc.*, 1936, A, 155, 183).

Frequencies.—The frequencies of the Raman lines were evaluated by Hartmann interpolation from copper arc lines. The dispersion being about 20 Å. per mm., the error of measurement is one wave number; the concordance of the frequencies obtained from different plates is, however, sufficient to justify quoting the mean frequencies of the more easily observed lines to tenths of a wave number, although full significance cannot be given to the decimal. Our measurements for benzene are derived from seven and those for hexadeuterobenzene from fourteen plates.

Intensities.—For the purpose of making intensity measurements, tracings of the spectra were taken by means of a Zeiss recording microphotometer. In principle, it is necessary to correlate the microphotometer deflection with the plate blackening, and the blackening with the light intensity for each wave-length. In practice, the quantitative comparison of light intensities at widely differing wave-lengths is a somewhat elaborate experimental problem, but it is easy, nevertheless, empirically to correlate microphotometer deflections with light intensities over a range of wave-length sufficiently large to include the isotopic frequency shifts in which we are interested, and yet sufficiently small to render negligible the error due to the variation of plate sensitivity with wave-length. We have done this by putting on each Raman plate a graded series of intensity standards obtained by photographing through the spectrograph the continuous spectrum of a tungsten filament of constant brightness. The exposures being constant, the amount of light entering the spectrograph was varied in known ratios by changing either the slit width or the distance of the light source from the slit, the former method being found on the whole to be the more convenient. The microphotometer tracings obtained from these standards (with the same settings of the instrument as those used in deriving the tracing of the corresponding Raman spectrum) enabled deflections to be directly correlated with intensities. Of course, the error due to the variation of plate sensitivity with wave-length is not negligible when lines of widely differing frequencies are compared, and hence we record that the plates used were "Ilford Double X-Press," so that, should the sensitivity characteristics of these plates become available, the necessary corrections can be applied.

For the measurement of the peak intensity of a Raman line all that is necessary is to measure the deflection at the top of the microphotometer contour, translate this into an intensity, and then subtract the similarly determined mean intensity of the background on either side of the line. The measurement of integrated intensity involves measuring the deflections at various wave-lengths throughout the whole breadth of the line, replotting the contour on an intensity scale, and evaluating the area included by the new contour above the level representing the continuous background. When the contours of two lines merge so that neither can be measured completely, it has been assumed that each is symmetrical about its maximum.

Polarisations.—The general arrangement was a modification of that described by Cabannes and Rousset (*Ann. Physique*, 1933, 19, 229). Filtered light from a vertical mercury arc was focused on the Raman tube by means of a lens, and the angle of convergence, 20°, was measured. The scattered light emerging from the window at the bottom of the tube passed directly into the analysing system, which consisted of a brass tube, 22 cm. long and 1.9 cm. in diameter, containing a reflecting prism, a Wollaston prism, and a half-wave plate, so arranged that the two plane polarised components of the scattered light fall in adjacent positions, one above the other, on the slit. The light, entering downwards, is first reflected in a horizontal direction, and then split into its vertically and horizontally polarised components by the Wollaston prism. The half-wave plate, placed in the path of the vertically polarised component, brings its plane of polarisation into parallelism with that of the horizontally polarised component, thus ensuring the equal transmission of both components by the optical system of the spectrograph. A glass plate placed in the path of the horizontally polarised component compensates for loss of light by reflection. The exit end of the tube containing this system was fitted with a brass plate bevelled to replace the Hartmann diaphragm of the spectrograph. By means of this apparatus (made for us by Messrs. Adam Hilger, Limited) good polarisation photographs were obtained with exposures of 24 hours. Microphotometer records of the two component spectra were then made, and the intensities of the lines in each were measured as described above. For any line, the ratio of the intensity in the spectrum of the horizontally polarised scattered light to the intensity in the spectrum for the vertically polarised component is the depolarisation factor ρ . Correction was made for the lack of parallelism of the incident light in accordance with Anantha-

krishnan's formula $\rho = \rho_{\text{uncorr.}} - (\theta^2/2)$ (*Proc. Indian Acad. Sci.*, 1935, 2A, 133) where θ is measured in radians. This correction is of importance only when the depolarisation factor is small.

The measurement is subject to considerable experimental error, mainly owing to the smallness of the lines from which the microphotometer records have to be made, and the proportionate error of the intensity measurements is naturally greatest for the weak components of the highly polarised lines. For these lines (*e.g.*, $\rho = 0.08$) the error in a single measurement of the depolarisation factor may amount to 25%, but by taking the average of a number of independent determinations the uncertainty in the result has been reduced to 10%. For the depolarised lines, on the other hand, the error is smaller, since the component spectra are of comparable intensity, but here again we have sought to increase our accuracy by averaging a number of independent results. In all polarisation measurements we have used peak intensities, rather than integrated intensities, because it is simpler and can be justified on the following grounds. The lines fall into two fairly distinct classes, "polarised" lines for which ρ is of order 0.1—0.3 and "depolarised" lines for which ρ is close to its theoretical maximum, 0.86. For the polarised lines the value of ρ is greater in the rotational wings than in the *Q*-branch; but then the wings are so weak in comparison with the *Q*-branch that it is permissible to disregard them, especially as the observational error for these lines is considerable in any case. The depolarised lines, on the other hand, have a substantially uniform polarisation throughout their breadth, so that no error at all is introduced by using simply the centre of the *Q*-branch.

(2) *Benzene*.—The Raman frequencies of benzene are presented in Table I as part of the experimental basis on which discussion will be founded. It is convenient to consider these frequencies under four headings corresponding to sections (a)—(d) of the table. Section (a) includes the eight strong or medium lines which have been observed by nearly all investigators. It will be shown that all these are fundamentals. A selection is given of the more accurate of previous frequency measurements, and these are averaged along with our own results. Section (b) contains fourteen weak lines the reality of which can scarcely be doubted, as they have been observed by different authors and for the most part with more than one exciting frequency. Any interpretation of the Raman spectrum of benzene which claims to be complete should be able to account for these lines. Section (c) contains sixteen additional very weak lines observed by Grassmann and Weiler, who have used much longer equivalent exposures than anyone else. Only two of these lines have hitherto been obtained by other authors, but indirect confirmation of some of them follows from the fact that we can assign them in accordance with the theory of selection rules; we believe that most (if not all) of these lines are authentic. Section (d), which is included for completeness, gives the four satellites of the strong line at 992 cm^{-1} , the detailed structure of which has been intensively investigated. We assume that these weak lines do not provide a problem in the assignment of vibration frequencies, but represent essentially the rotational structure of the strong line, the contour of which overlaps the whole region occupied by this group. Gerlach (see below), however, has made the interesting suggestion that the strongest of the satellites, that at 984 cm^{-1} , is really the strong line of the isotopic benzene $^{12}\text{C}_5^{13}\text{C}^1\text{H}_6$, which must be present to the extent of about 6% in ordinary benzene.

Nine very weak lines which we consider to be of doubtful authenticity have been omitted from the table. Of these, two have been reported by Mesnage, one by Weiler, and six by Wood; however, they have not been obtained by anyone else, not even by Grassmann and Weiler with their much longer exposures. The reported frequencies are: 439, 592 (Mesnage), 2569 (Weiler), 2596, 2745, 2765, 2784, 3573, and 3627 cm^{-1} (Wood). Wood's line at 2596 cm^{-1} could be obtained only with helium excitation, and therefore may not have been correctly identified. The frequencies 2745, 2765, and 2784 cm^{-1} were not confirmed by Wood himself in independent investigations, whilst his remaining lines, 3573 and 3627 cm^{-1} , have been re-interpreted by Lord as being in reality the strong 992 cm^{-1} frequency excited by the mercury lines 4916 and 5461 Å.

The peak intensities of the principal Raman lines of benzene have previously been measured by Mesnage and by Carelli and Went. We record their results, along with our data for peak and integrated intensities, in Table II. In every case the intensity scale has been chosen to give the value 10.0 to the line 992 cm^{-1} .

TABLE I.

Frequency Displacements of the Raman Lines of Benzene (cm.⁻¹).

(a) Strong (s) and medium lines.

Ref.	(1).	(2).	(3) (s).	(4).	(5).	(6).	(7).	(8) (s).
A.....	604·6	849·1	991·3	1179·0	1583·6	1604·1	3046·9	3061·3
B.....	603·9	848·7	991·2	1178·1	1583·4	1607·4	3048·5	3062·3
C.....	606·7	850·0	992·2	1178·2	1585·5	1606·9	3047·9	3061·7
D.....	605·9	847·6	992·4	1180·2	1584·8	1608·7	3046·2	3062·2
E.....	606·4	849·7	992·6	1175·6	1585·9	1604·2	3048·3	3061·5
This paper.....	605·9	848·6	990·1	1177·1	1585·3	1607·3	3043·3	3062·3
Mean.....	605·6	848·9	991·6	1178·0	1584·8	1606·4	3046·8	3061·9

References.—A, Söderqvist, *Z. Physik*, 1930, **59**, 446. B, Dabodghao, *Indian J. Physics*, 1930, **5**, 207. C, Nisi, *Jap. J. Physics*, 1930, **6**, 1. D, Mesnage, *J. Phys. Radium*, 1931, **2**, 406. E, Klit and Langseth, *Nature*, 1935, **135**, 956. Other measurements by : Raman and Krishnan, *Indian J. Physics*, 1928, **2**, 399; *Proc. Roy. Soc.*, 1929, *A*, **122**, 23; Cabannes and Daure, *Compt. rend.*, 1928, **186**, 1533; Daure, *ibid.*, 1928, **186**, 1833; *Ann. Physique*, 1929, **12**, 375; Pringsheim and Rosen, *Z. Physik*, 1928, **50**, 741; Wood, *Phil. Mag.*, 1928, **6**, 729; *Physical Rev.*, 1930, **36**, 1431; Dadiou and Kohlrausch, *Physikal. Z.*, 1929, **30**, 384; *Sitzungsber. Akad. Wiss. Wien*, 1929, II, *A*, **138**, 41, 607; Fujioka, *Sci. Papers Inst. Phys. Chem. Res.*, Tokyo, 1929, **11**, 205; Bhagavantam, *Indian J. Physics*, 1930, **5**, 603; Langer and Meggers, *Bur. Stand. J. Res.*, 1930, **4**, 711; Cleeton and Dufford, *Physical Rev.*, 1931, **37**, 362; Weiler, *Z. Physik*, 1931, **69**, 586; Cabannes, *J. Phys. Radium*, 1931, **2**, 381; Hanle, *Ann. Physik*, 1931, **11**, 885; 1932, **15**, 345; Placzek and van Wijk, *Z. Physik*, 1931, **67**, 582; Krishnamurti, *Indian J. Physics*, 1931, **6**, 543; Werth, *Physical Rev.*, 1932, **39**, 299; Wood and Collins, *ibid.*, 1932, **42**, 386; Simons, *Soc. Sci. Fennica Comm. Phys.-Math.*, 1932, **6**, 5; Grassmann and Weiler, *Z. Physik*, 1933, **86**, 321; Brodsky, Sack, and Besugli, *Physikal. Z. Sovietunion*, 1934, **5**, 146; Epstein and Steiner, *Z. physikal. Chem.*, 1934, *B*, **28**, 131. Cf. also Lord, *J. Chem. Physics*, 1936, **4**, 83.

(b) Weak lines.

Ref.	(9).	(10).	(11).	(12).	(13).	(14).	(15).	(16).	(17).	(18).	(19).	(20).	(21).	(22).
F.....	407	687	1029	1407	1477	—	—	2455	2543	—	2928	2948	3164	3187
G.....	400	677	1028	1402	1477	1690	2291	2451	2542	2618	2920	2948	3163*	3186*
H.....	404	692	1034	1403	1480	1697	2296	2455	2545	2618	2927	2949	3166	3187
Mean...	404	685	1030	1404	1478	1693	2293	2454	2543	2618	2925	2948	3164	3187

* Weiler's values.

References.—F, Krishnamurti; G, Wood and Collins; H, Grassmann and Weiler, *loc. cit.* Other measurements by : Pringsheim and Rosen, Wood, Dadiou and Kohlrausch, Langer and Meggers, Weiler, Hanle, Dabodghao, Nisi, Söderqvist, Werth, Mesnage, Brodsky, Sack and Besugli, *loc. cit.*; Cabannes and Rousset, *Ann. Physique*, 1933, **19**, 229; Cujumjelis, *Praktika*, 1932, **7**, 242.

(c) Very weak lines.

(23).	(24).	(25).	(26).	(27).	(28).	(29).	(30).
781	802	824	1285	1326	1449	1827	1936
(31).	(32).	(33).	(34).	(35).	(36).	(37).	(38).
1988	2030	2128	2358	2688	3467	3680	3916

References.—Grassmann and Weiler, *loc. cit.*; line 24 also found by Krishnamurti, *loc. cit.*, and lines 23 and 24 by Nisi, *loc. cit.*

(d) Satellites of the strong line (992 cm.⁻¹).

(39).	(40).	(41).	(42).
979	984	[992]	999
			1005

References.—Grassmann and Weiler, *loc. cit.*; Howlett, *Nature*, 1931, **128**, 796; *Canadian J. Res.*, 1931, **5**, 572; Epstein and Steiner, *loc. cit.*; Bloch and Bloch, *Compt. rend.*, 1933, **196**, 1787; Specchia and Scandura, *Nuovo Cimento*, 1935, **12**, 129. Line 39 was also found by Krishnamurti, and line 40 by Mesnage, Weiler, *loc. cit.*, Gerlach, *Sitz. Math.-Naturwiss. Bayer Akad. München*, 1932, 39, and Bhagavantam, *Proc. Indian Acad. Sci.*, 1935, **2**, 86.

The polarisations of the principal Raman lines of benzene have been studied in a more or less qualitative manner by several authors. As an example we quote in Table III the most recent results of Cabannes and Rousset : *P* means that the line is "polarised," *i.e.*, its depolarisation factor is small, whilst *D* signifies that it is "depolarised," *i.e.*, the factor ρ is of the order of its theoretical maximum, 6/7. Placzek and van Wijk have used an

TABLE II.

Peak and Integrated Intensities of Principal Raman Lines of Benzene.

Line, cm. ⁻¹ .	Peak intensities.			Integrated intensities.		Line, cm. ⁻¹ .	Peak intensities.			Integrated intensities.
	M.	C.W.	This paper.	This paper.	This paper.		M.	C.W.	This paper.	This paper.
(1) 605·6	1·5	1·2	1·8	2·1	2·1	(5) 1584·8	1	—	1·7	1·9
(2) 848·9	0·7	0·85	0·9	0·9	0·9	(6) 1606·4	1	1·6	1·4	1·6
(3) 991·6	10	10·0	10·0	10·0	10·0	(7) 3046·8	3·6	—	4·4	4·8
(4) 1178·0	—	2·2	2·0	2·2	2·2	(8) 3061·9	6	6·0	7·8	10·6

References.—M, Mesnage, *loc. cit.*; C.W., Carelli and Went, *Z. Physik*, 1932, **76**, 236.

accurate comparative method, which, although it does not give the absolute values of the depolarisation factor, shows up clearly small differences in the degree of depolarisation; the method is especially important in its application to the so-called depolarised lines, and we quote the values obtained. Probably the most valuable of the previous absolute measurements of ρ are those of Simons, which are also given in the table along with our own results. The line at 3047 cm.⁻¹ is insufficiently separated from the stronger line at 3062 cm.⁻¹ to permit a satisfactory measurement of the former, and for the same reason the value given for the latter is not up to the standard of accuracy of the other results. It is satisfactory, however, to observe that our absolute depolarisation factors for the first five depolarised lines vary amongst themselves in just the way that would be expected from Placzek and van Wijk's comparative data.

TABLE III.

Depolarisation Factors of the Principal Raman Lines of Benzene.

Line, cm. ⁻¹ .	ρ' . P.W.	Absolute ρ .			Line, cm. ⁻¹ .	ρ' . P.W.	Absolute ρ .		
		C.R.	S.	This paper.			C.R.	S.	This paper.
(1) 605·6	0·99	<i>D</i>	0·86	0·81	(5) 1584·8	0·99	<i>D</i>	0·89	0·81
(2) 848·9	0·90	<i>D</i>	—	0·77	(6) 1606·4				0·81
(3) 991·6	0·35	0·07	0·07	0·09	(7) 3046·8	0·49	<i>D</i>	—	<i>D</i>
(4) 1178·0	0·78	<i>D</i>	0·89	0·70	(8) 3061·9			0·4	—
(21) 3187	—	<i>P</i>	—	—					

References.—P.W., Placzek and van Wijk, *Z. Physik*, 1931, **67**, 582; C.R., Cabannes and Rousset, *Ann. Physique*, 1933, **19**, 229; S, Simons, *Soc. Sci. Fennica Comm. Phys.-Math.*, 1932, **6**, 5. Other measurements by Carelli, Pringsheim, and Rosen, *Z. Physik*, 1928, **51**, 511; Cabannes, *Compt. rend.*, 1928, **187**, 654; *Trans. Faraday Soc.*, 1929, **25**, 813; *J. Phys. Radium*, 1931, **2**, 381 (linear and circular); Daure, *Ann. Physique*, 1929, **12**, 375; Bhagavantam, *Indian J. Physics*, 1930, **5**, 603; 1932, **7**, 79; Bär, *Naturwiss.*, 1931, **19**, 463; *Helv. Phys. Acta*, 1931, **4**, 130; Hanle, *Ann. Physik*, 1931, **11**, 885; 1932, **15**, 345 (circular); Bhagavantam and Venkateswaran, *Nature*, 1932, **129**, 580; Venkateswaran, *Phil. Mag.*, 1933, **15**, 263.

(3) *Hexadeuterobenzene*.—The Raman spectrum of hexadeuterobenzene was first photographed (1934) by Murray, Squire, and Andrews, who, using a very small quantity of material, succeeded in observing a single strong line. Contemporaneously with our preliminary communication (1935) giving the frequencies (and an assignment) of the complete series of Raman fundamentals, publications by Klit and Langseth and by Wood appeared which also recorded the frequencies of the principal lines of this spectrum. Since that time we have increased the number and accuracy of our frequency measurements, and in Table IV we quote the more precise figures along with the data recorded by others.

The upper part of the table contains the measurements for the seven lines of moderate to great intensity, which, as will appear later, are all fundamentals. Our frequency measurements for these should be correct to within one wave number.

The lower part of the table contains the frequencies of nineteen weak lines. We have confidence in the reality of almost all of these, but would like to see independent confirmation of the line at 337 cm.⁻¹ which is very weak and inconveniently near to the exciting line. The error in our frequency measurements is greater for these weak lines, but varies

considerably from one line to another. Thus the lines at 1000, 1326, 1530, 1931 cm^{-1} , and several others, are relatively easy to measure, and the mean frequencies quoted are probably not in error by more than 2 cm^{-1} at most. On the other hand, very weak or diffuse lines like those at 337, 710, and 790 cm^{-1} are difficult to measure precisely, and hence the error may amount to 5 cm^{-1} or even more.

Several published results are omitted from the table as being either demonstrably incorrect or at best highly doubtful. The first relates to the double intensity maximum recorded by us for the rather broad line at 1558.6 cm^{-1} : the use of larger dispersion and microphotometric control has shown that this maximum is single. The second is a line of Klit and Langseth's having a frequency separation of 845 cm^{-1} ; this line appears on our plates when the mercury line at 4358 Å. is used for excitation, but not when the 4047 Å. line is employed, and we may therefore conclude that it is really the strong Raman frequency 945 cm^{-1} excited by the mercury line 4339 Å. The third is another of Klit and Langseth's lines, having a frequency displacement 1569 cm^{-1} : Dr. Langseth has privately communicated that this line was due to pentadeuterobenzene present as an isotopic impurity in his sample. From the second section of the table we omit several weak lines recorded by Wood. Two of them, of frequencies 2617 and 2663 cm^{-1} , were regarded as doubtful by Wood himself and we cannot confirm them. A third, frequency 2031 cm^{-1} , was recorded as definite, but it does not appear on our plates in spite of longer equivalent exposures. The fourth is one of two lines of frequencies 3052 and 3108 cm^{-1} which Lord has suggested to be due to pentadeuterobenzene. As regards the former of these we agree with Lord: 3052 cm^{-1} is a frequency at which pentadeuterobenzene should have a strong line, and we know that the material used by Wood, which was that prepared by Bowman, Benedict, and Taylor, must have contained about 14% of pentadeuterobenzene (p. 915). As to the frequency 3108 cm^{-1} , however, we differ from Lord on the interpretation of the evidence before him: the highest strong frequency of pentadeuterobenzene should lie some 50 cm^{-1} lower, and furthermore, the frequency 3108 cm^{-1} is expected to appear in the spectrum of hexadeuterobenzene and can be assigned in accordance with the proper selection rules. Apart from these arguments, we have confirmed the presence of this line.

Owing to the presence of pentadeuterobenzene in the specimens used by other workers, we have not averaged their results with ours: it is always possible for an isotopic impurity to give lines which, although not clearly separated from the lines of the principal compound, overlap them on one side, thus shifting the intensity maximum slightly and creating an error in the frequency.

TABLE IV.

*Frequency Displacements of the Raman Lines of Hexadeuterobenzene (cm^{-1}).**(a) Strong (s) and medium lines.*

Ref.	(1).	(2).	(3).	(4) (s).	(5).	(6).	(7) (s).
M.S.A.	—	—	—	943	—	—	—
K.L.	531.6	—	869.8	946.6	1555.4	2266.8	2292.0
W.	581	662	873	945	1548	2266	2293
This paper * †.....	576.7	661.2	867.2	944.7	1558.6	2263.9	2292.3

(b) Weak lines.

Ref.	(8).	(9).	(10).	(11).	(12).	(13).	(14).	(15).	(16).	(17).
W.	—	—	—	—	—	1000	—	—	—	—
This paper	337	710	750	790	976	1000	1327	1457	1530	1586
Ref.	(18).	(19).	(20).	(21).	(22).	(23).	(24).	(25).	(26).	—
W.	—	—	—	—	—	—	2575	—	3108	—
This paper	1884	1931	2128	2145	2461	2510	2571	2739	3110	—

References.—M.S.A., Murray, Squire, and Andrews, *J. Chem. Physics*, 1934, **2**, 714; K.L., Klit and Langseth, *Nature*, 1935, **135**, 956; W, Wood, *J. Chem. Physics*, 1935, **3**, 444.

* Cf. *Nature*, 1935, **135**, 1033.

† Dr. Langseth has privately communicated his agreement with the presence of the line at 661 cm^{-1} ; it was on his plates, but was at first believed to belong to pentadeuterobenzene.

The intensities and polarisations of the Raman lines of hexadeuterobenzene have not previously been measured. Table V contains our results for the peak intensities, integrated

intensities, and depolarisation factors of this compound. The scales of the peak and of the integrated intensities have each been chosen to give the value 10.0 to the strong line 945 cm^{-1} . With regard to the depolarisation factors, it may be noted that, because the two high-frequency fundamentals of hexadeuterobenzene are more widely separated than are those of benzene, the weaker, corresponding to the line in benzene which could only be qualitatively examined for depolarisation, can be measured, although not very exactly; whilst the stronger, corresponding to the benzene line which could be measured only approximately, can in hexadeuterobenzene be measured with some precision. Apart from this difference the previous remarks concerning errors remain applicable.

TABLE V.

Peak and Integrated Intensities and Depolarisation Factors of the Principal Raman Lines of Hexadeuterobenzene.

Line, cm^{-1} .	Intensity.		Depolarisation factors (ρ).	Line, cm^{-1} .	Intensity.		Depolarisation factors (ρ).
	Peak.	Integrated.			Peak.	Integrated.	
(1) 576.7	1.1	1.2	0.76	(5) 1558.6	1.5	2.0	0.82
(2) 661.2	1.3	1.4	0.87	(6) 2263.9	3.2	6.1	0.7
(3) 867.2	1.7	2.3	0.81	(7) 2292.3	6.0	10.6	0.35
(4) 944.7	10.0	10.0	0.08				

Finally, it was necessary to correlate the arbitrary units of intensity adopted for benzene with those used for hexadeuterobenzene. By measuring the peak and integrated intensities of the lines given by an artificial mixture containing 50 mols. % of each compound we found that our units of integrated intensity were substantially identical, as they should be. On the other hand, our unit of peak intensity for hexadeuterobenzene was some 8–10% greater than the corresponding unit for benzene. Comparing the lines which for each spectrum had been used as the intensity standard, and making now the benzene line the fundamental standard we have :

	C_6H_6 (992 cm^{-1}).	C_6D_6 (945 cm^{-1}).
Peak intensity.....	10.0	10.8
Integrated intensity	10.0	9.8

The difference between the scales of peak intensity is obviously due to the greater rotational spreading of the lines of benzene than of hexadeuterobenzene. All the lines of the latter are perceptibly narrower on the microphotometer records than the corresponding lines of benzene, as would be expected from the difference between the moments of inertia of these molecules. Indeed, the square roots of their moments of inertia differ by 10%, and this is practically the difference of the peak intensity scales as it ought to be.

The assignment of the frequencies will be considered in Part VIII.