214. *Structure of Benzene. Part IV. Infra-red Absorption Spectra of Benzene and Hexadeuterobenzene both as Vapour and as Liquid.*

By C. R. Bailey, J. B. Hale, C. K. Ingold, and J. W. Thompson.

(1) *Methods.*—Notwithstanding many previous investigations, our knowledge of the absorption spectra of benzene in the region containing the fundamental vibration frequencies is markedly imperfect owing to lack of either accuracy or range in the observations, and to inadequate agreement between them. Many workers have used liquid benzene, though some have employed the substance as vapour; but it has never been made clear whether the spectra given by the liquid and the vapour are the same or different: some comparisons indicate one conclusion, others the opposite. No one has used the same sample both as liquid and as vapour in a general survey of the spectrum, thus eliminating the possibility that any bands observed in one case but not in the other are due to impurities.

We have investigated as precisely as possible the absorption spectrum not only of benzene but also of hexadeuterobenzene over a range larger than is necessary to include all of the active fundamentals, and in each case have made a detailed study of the forms of the principal band heads. In each case also we have used the same specimen of highly purified material both in the form of vapour and as liquid. We shall show that the spectra given by the liquids and by their vapours are markedly different and that the liquid spectra, though they are most instructive when the spectra of the vapours are known, can be very misleading in the absence of that knowledge. In the case of benzene, indeed, the liquid spectrum *has* proved misleading.

Apparatus.—This was essentially the monochromator arrangement described by Bailey and Cassie (*Proc. Roy. Soc.*, 1931, *A*, **132**, 252). It was necessary, however, to supplement the series of optical systems employed by them by a potassium bromide system in order to extend the range of the apparatus in the long-wave region of the spectrum. Another modification, which greatly facilitated the readings, was the introduction of a photo-electric relay into the galvanometer system. We shall refer to this, but need not describe the whole apparatus since this has been done before; however, its main principles may be indicated sufficiently to clarify a discussion of the errors.

Light from a Nernst filament is condensed on the first slit, S_1, of the spectrometer, a Hilger constant-deviation instrument, and after passing through the prism emerges through the second slit, S_2. The prism is mounted on a turntable controlled by a drum by means of which the wave-length of the emerging light can be read. The wave-length is also controlled by the exact orientation of a Wadsworth mirror at which the resolved light undergoes reflexion within the spectrometer, so that, when a prism has been mounted on the table, the proper drum reading can be made to correspond to a standard wave-length by rotating this mirror. The mirror is set by observing the emergence of the mercury green line from S_2 when the Nernst filament is temporarily replaced by a mercury arc, and a convenient check on the setting is obtained by measurement of the 4·26 μ band of carbon dioxide, of which sufficient for this purpose is always present in the atmosphere. For observations on vapours, the light emerging from S_2 is reflected by a movable mirror through either of two identical absorption tubes, one containing the vapour and the other evacuated, and is then received by one of a pair of coupled thermopiles. For observations on liquids the two tubes are replaced by two identical cells, one full and the other empty. The thermopiles are connected to a sensitive Zernicke B galvanometer, which is critically damped for the resistance of the thermopiles. The light from this instrument falls on the dividing line of a split photo-electric cell, and this is coupled with a second, less sensitive galvanometer, the deflections of which are many times greater than those of the primary galvanometer. A micrometer screw attached to the carriage bearing the photo-cell enables the zero of the secondary galvanometer to be adjusted. The lamp of the primary galvanometer is, of course, lit from constant voltage. The primary galvanometer, its lamp, and the photo-cell are mounted together on an anti-vibration support constructed on the same principles as those applied in relation to the simple galvanometer system previously in use. The slit-widths used, and the spectral regions included therein, are those specified by Bailey, Cassie, and Angus (*Proc. Roy. Soc.*, 1930, *A*, **130**, 133).

Errors.—There are four principal sources of error. The first is the error in the drum reading, which is about 3″ of arc in the orientation of the prism table, and is equivalent to 0·003 μ in a single determination of wave-length. The second is the error, about 5′ of arc, in the setting of the prism at minimum deviation : this is equivalent to 1·5″ of arc in the position of the turntable, and thus to 0·0015 μ in terms of wave-length. The third error arises from the fact that the prism, although thermally insulated, is not maintained at a strictly constant temperature. Its temperature, however, is read both during the setting of the Wadsworth mirror and during the absorption measurements, and corrections for the temperature-dependence of the refractive index of the prism are applied. Provided the temperatures are accurate to 0·3°, there should be no sensible error due to temperature in the corrected data. A fourth possibility of error arises in the setting of the Wadsworth mirror since it is necessary to judge when the monochromatic image of the slit S_1 comes into best coincidence with slit S_2 by observing the point at which the intensity of the emergent green light is a maximum. This error is quite small, and on the whole the maximal uncertainty in a single measurement of wave-length may be placed at 0·005 μ. All the band heads are measured several times, so that the error in the mean wave-lengths quoted should be somewhat less than this. However, taking the error as 0·005 μ, we obtain for the maximal uncertainty in the frequencies : 5 cm.$^{-1}$ at 3000 cm.$^{-1}$, and 1 cm.$^{-1}$ at 500 cm.$^{-1}$; these frequencies correspond to the two ends of the spectral range containing the fundamental bands of benzene and hexadeuterobenzene.

(2) *Benzene.*—Apart from certain observations on the detailed structure of particular bands, the infra-red spectrum of benzene vapour has been investigated on four previous occasions. First, Lambert and Lecomte (1932) described a spectrum, which (as will appear later) is closely similar to that given by liquid benzene, and in particular is characterised by three strong bands at about 8·6, 11·8, and 12·9 μ. Secondly, Kettering and Sleator recorded a markedly different spectrum, from which, notably, the three bands mentioned are completely absent. Thirdly, Titeica obtained a spectrum having intermediate character : the band at 8·6 μ was prominent, whilst those at 11·8 and 12·9 μ although present were less pronounced; nevertheless, Titeica remarked on the differences between his results and the data which had been recorded for the liquid. Fourthly, Barnes and Brattain recorded a spectrum generally similar to that of Kettering and Sleator but with two additional well-marked bands, one indeed prominent, at 12·4 and 13·35 μ. These data together with our principal results for benzene vapour are given in Table I. Our spectrum confirms that of Kettering and Sleator in all main features and does not reveal any of the additional prominent bands referred to above; neither does it show the continuous deep back-ground of absorption obtained by Lambert and Lecomte and by Titeica, nor the semi-continuous back-ground of overlapping bands recorded by Barnes and Brattain. Our spectrum is, however, considerably more accurately measured than that of Kettering and Sleator and contains several very small bands not observed by them. We agree closely with them with regard to the intensities of the principal bands; for instance, we find the 3·247μ band to be considerably stronger than the 5·553 μ band, and comparable in intensity with the other outstanding bands at 6·773, 9·644, and 14·90 μ. In order to keep sight of the salient features of this spectrum, the entries in Table I are restricted to the wave-lengths of the central absorption maxima of the more important bands lying within the spectral range of the fundamental frequencies. These bands have furthermore been divided into three categories of intensity, the most intense being shown in Clarendon type, those of intermediate intensity in italics, and those of least intensity in ordinary type.

TABLE I.

Wave-lengths (in μ) of the Principal Absorption Maxima in Benzene Vapour.

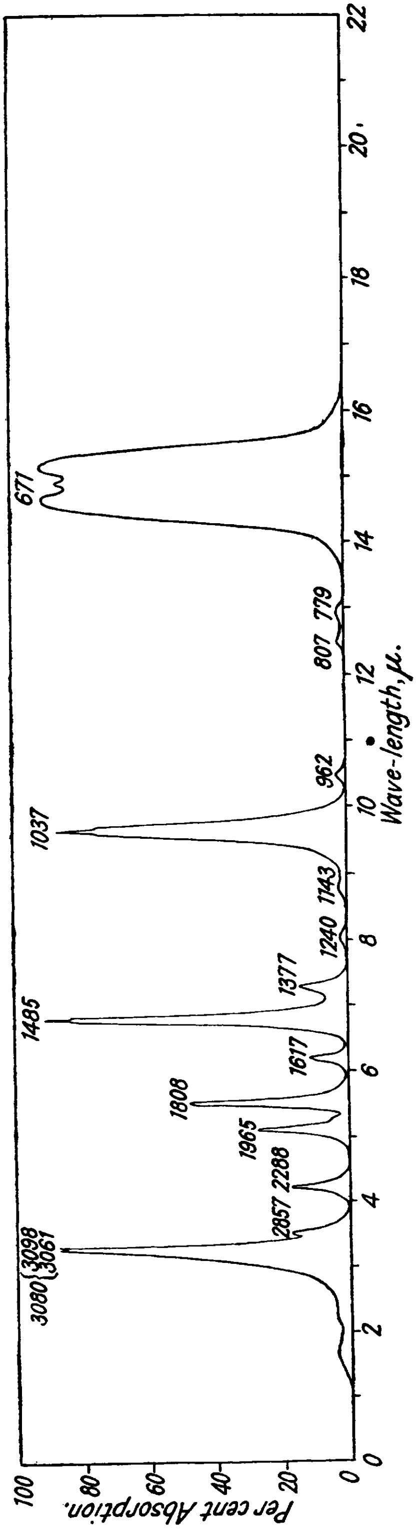
L.L.		[Beyond range of observation]				*6·8*	—	—	*8·6*
K.S.	**3·45**	—	*5·2*	*5·6*	6·1	**6·8**	7·25	—	—
T.	*3·25*	4·50	5·00	*5·66*	—	**6·67**	—	7·97	*8·55*
B.B.	*3·25*	*4·45*	*5·15*	**5·60**	6·18	**6·77**	7·32	—	—
This paper	**3·247**	4·370	*5·089*	*5·533*	6·185	**6·733**	7·261	—	—

L.L.	**9·7**	—	—	*11·8*	—	*13·0*	—	**14·8**
K.S.	**9·65**	—	—	—	—	—	—	**14·95**
T.	**9·65**	10·58	11·30	11·90	—	12·92	—	**14·75**
B.B.	**9·76**	—	—	—	*12·41*	—	13·35	[Beyond range]
This paper	**9·644**	—	—	—	—	—	—	**14·90**

References.—L.L., Lambert and Lecomte, *Ann. Physique*, 1932, **118**, 329. K.S., Kettering and Sleator, *Physica*, 1933, **4**, 39. T., Titeica, *Bul. Soc. Române Fizica*, 1933, **35**, 89. B.B., Barnes and Brattain, *J. Chem. Physics*, 1935, **3**, 446. Further observations on bands below 3 μ by Dreisch (*Z. Physik*, 1924, **30**, 200). Observations on particular bands by Meyer, Bronk, and Levin (*J. Opt. Soc. Amer.*, 1927, **15**, 257), Silverman (*Physical Rev.*, 1932, **41**, 486), and Leberknight (*ibid.*, 1933, **43**, 971).

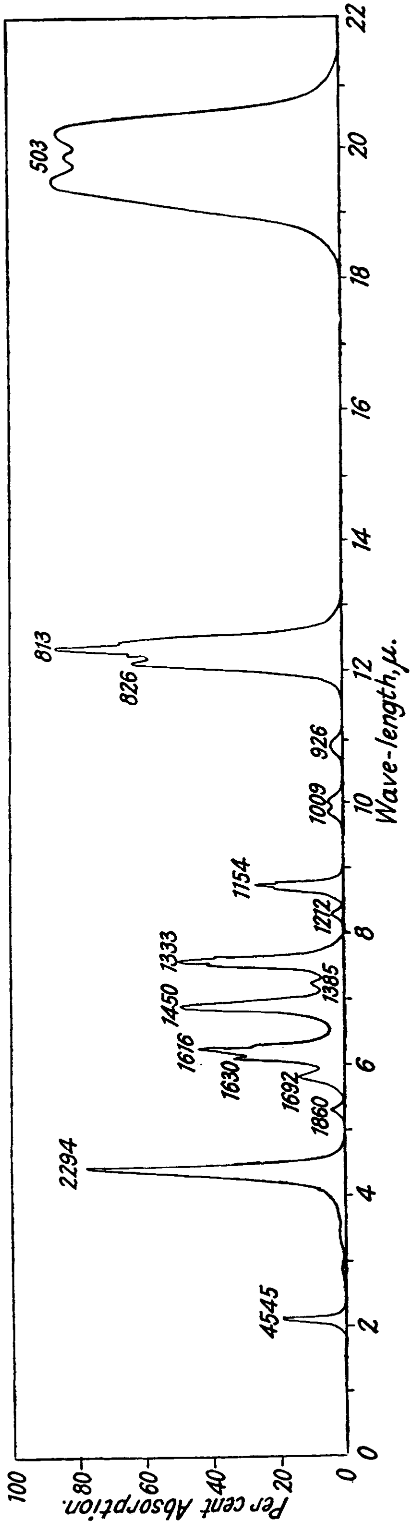
Our detailed results for the wave-lengths of the absorption maxima together with the corresponding frequencies and intensities are assembled in Table II (where λ = wave-length, and ν = frequency). As a measure of intensity we record the percentage absorption at 4·0 cm. vapour pressure in an absorption tube 45 cm. long. A general map of the vapour spectrum is shown in Fig. 1 (p. 934). Concerning the different widths of the bands appearing on this graph, it will be appreciated that since $d\nu/d\lambda = -(1/\lambda^2)$ the scale of wave-lengths is much more open with respect to frequencies at the long-wave than at the short-wave end; *e.g.*, 25 times more open at 15 μ than at 3 μ.

Fig. 1.



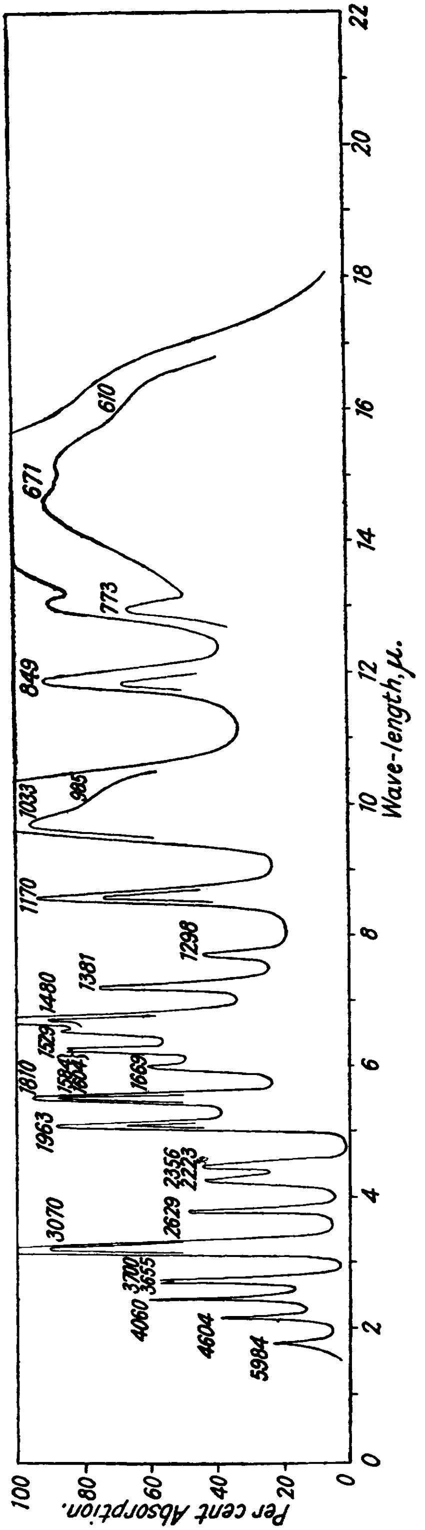
Infra-red absorption of benzene (vapour).
(Length 45 cm. Pressure 4·0 cm.)

Fig. 2.



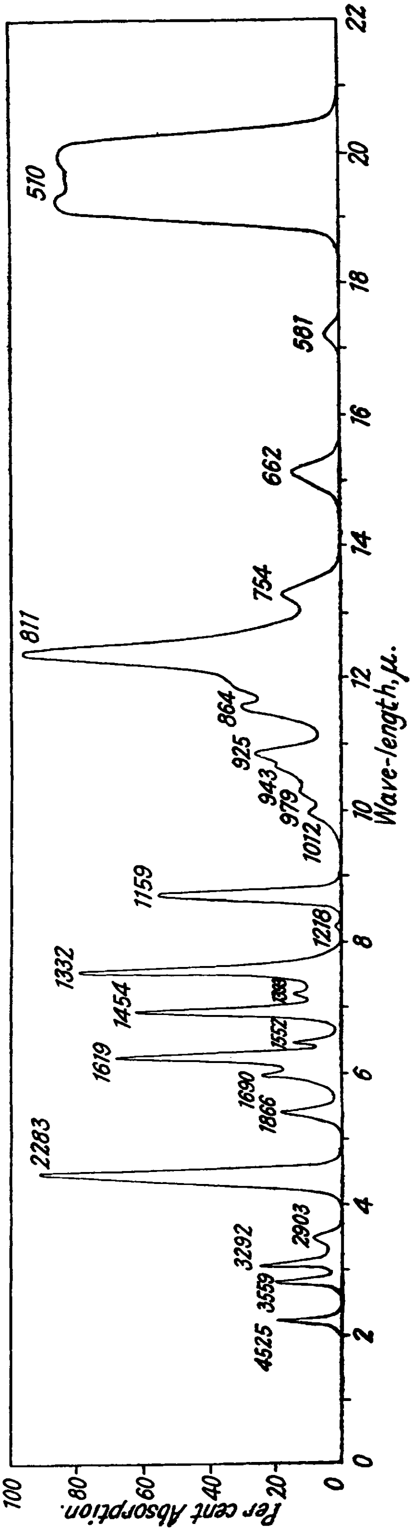
Infra-red absorption of hexadeuterobenzene (vapour).
(Length 45 cm. Pressure 4·0 cm.)

FIG. 3.



Infra-red absorption of benzene (liquid).
(*Two cells : see text.*)

FIG. 4.



Infra-red absorption of hexadeuterobenzene (liquid).
(*Cell : see text.*)

The forms of the principal bands are shown on more expanded scales in Figs. 5—10. In order more effectively to bring out the contrasts, these curves are plotted for vapour pressures chosen in each case to give between 30% and 70% of absorption at the chief intensity maximum. These vapour pressures are noted under the graphs.

FIG. 5.

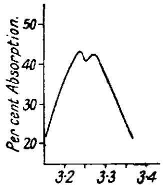


FIG. 6.

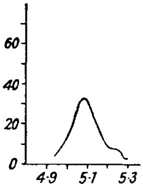


FIG. 7.

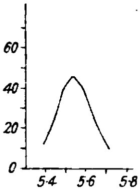


FIG. 8.

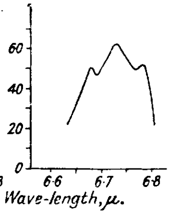


FIG. 9.

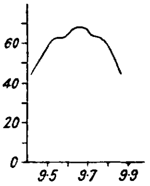


FIG. 10.

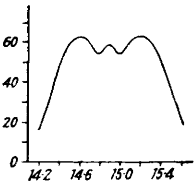


FIG. 5.—C_6H_6, 3080 cm.$^{-1}$ (p = 1·0 cm.).
FIG. 6.—C_6H_6, 1965 cm.$^{-1}$ (p = 4·0 cm.).
FIG. 7.—C_6H_6, 1808 cm.$^{-1}$ (p = 4·0 cm.).
FIG. 8.—C_6H_6, 1485 cm.$^{-1}$ (p = 1·2 cm.).
FIG. 9.—C_6H_6, 1037 cm.$^{-1}$ (p = 1·9 cm.).
FIG. 10.—C_6H_6, 671 cm.$^{-1}$ (p = 0·8 cm.).

The very strong band at 3·247 μ shows two distinct maxima, and we believe it to represent a real doublet (due, as will be suggested in Part VIII, to resonance splitting). The separation of the maxima, 38 cm.$^{-1}$, seems too great to be considered as a rotational $P - R$ frequency difference; moreover, the corresponding band in hexadeuterobenzene has only a single maximum. The bands at 5·089 μ and 5·533 μ are both single. The contour of the former, however, shows the presence of a very small band at 5·245 μ, which is too largely overshadowed by its tall neighbour to be observed as a clearly resolved intensity maximum. The contour of the 5·573 μ band exhibits shoulders which suggest that a greater resolution would reveal a symmetrical P–Q–R-form. The very strong band at 6·733 μ has a well-developed P–Q–R-form with the right kind of frequency separation. The third very strong band at 9·645 μ has a somewhat less well-marked P–Q–R-form, again with a similar frequency separation. The fourth very strong band at 14·90 μ again has P–Q–R-form, but the P- and R-branches are stronger than the Q-branch. We expected the reverse because Kettering and Sleator, who resolved the three branches of this band, record the Q-branch as the strongest. However, it happens that atmospheric carbon dioxide has an absorption band in exactly the position of the Q-branch, so that it is impossible to measure its intensity accurately without some substitution device such as we have used. In Part VIII we shall identify this band as being of the " parallel " type, and for such bands in

TABLE II.

Wave-lengths, Frequencies, and Intensities of the Infra-red Absorption Maxima of Benzene Vapour.

No.	λ (μ).	ν (cm.$^{-1}$).	Absorption (%).	Frequency of Q-branch.*	P–R- or Doublet separation.
(a) *Strong* (s) *and medium bands.*					
1 (*s*)	3·227	3098	87	3080	37
	3·267	3061	80		
2	5·089	1965	32	1965	—
3	5·533	1808	51	1808	—
4 (*s*)	6·678	1497	87	1485	23
	6·733	1485	92		
	6·784	1474	87		
5 (*s*)	9·542	1048	84	1037	22
	9·644	1037	87		
	9·749	1026	84		
6 (*s*)	14·62	684	91	671	26
	14·90	671	87		
	15·20	658	91		
(b) *Weak bands.*					
7	4·370	2288	18	2288	—
8	6·185	1617	13	1617	—
9	7·261	1377	15	1377	—
(c) *Very weak bands.*					
10	3·500	2857	*ca.* 6	2857	—
11	5·245	1906	*ca.* 3	1906	—
12	8·065	1240	4	1240	—
13	8·749	1143	4	1143	—
14	10·40	962	4	962	—
15	12·39	807	3	(793)	28
	12·84	779	3		

* Or mean frequency of doublet.

the spectrum of a " symmetrical top " molecule (*i.e.*, a molecule with two of its principal moments of inertia identical) it is possible approximately to calculate the *P*–*R*-separation from the appropriate molecular moment of inertia (Gerhard and Dennison, *Physical Rev.*, 1933, **43**, 197). Calculation gives 26 cm.$^{-1}$, which is the separation observed.

(3) *Benzene* (*Liquid*).—The first comprehensive investigation of the infra-red spectrum of liquid benzene is that of Coblentz (1905) whose measurements cover nearly the whole range of the active fundamentals. It has since been investigated over considerable although smaller ranges by Bell (1925) and Daugherty (1929). The results of these authors together with our data are given in Table III, where once again the entries are restricted to the principal absorption maxima in order not to submerge the salient features of the spectrum in the detail; furthermore, the figures are confined to the spectral range containing the active fundamental frequencies. Bell did not record his frequencies, and the figures ascribed to him are obtained by measurement from his published curve. It will be seen that the different observers are in substantial agreement : all the omissions from the lists of the previous workers are simply due to poor resolution, for the presence of the bands in approximately the positions in which we find them can be observed from the shoulders and inflexions contained in the curves given by these authors.

TABLE III.

Wave-lengths (in μ) of the Principal Absorption Maxima of Liquid Benzene.

C.	3·25	—	5·5	—	—	*6·75*	—	*8·67*	**9·78**	*11·8*	*12·95*	[End of range]
B.	**3·3**	*5·1*	**5·5**	—	6·2	**6·7**	*7·2*	**8·5**	**9·7**	*11·8*	[End of range]	
D.	**3·32**	*5·06*	**5·56**	—	6·20	**6·74**	*7·16*	[Beyond range of measurements]				
This paper	**3·257**	*5·094*	**5·525**	5·991	*6·272*	**6·757**	7·241	*8·547*	**9·680**	*11·78*	*12·94*	**14·90**
Vapour results	**3·247**	*5·089*	*5·533*	—	—	**6·733**	7·261	—	**9·644**	—	—	**14·90**
		4·370			6·185							

References.—C., Coblentz, " Investigations of Infra-red Spectra. Part I," Carnegie Institute of Washington Publications, 1905, No. 35, pp. 136, 144, 231. B., Bell, *J. Amer. Chem. Soc.*, 1925, **47**, 2814. D., Daugherty, *Physical Rev.*, 1929, **34**, 1549. Observations in the short-wave region by Puccianti (*Physikal. Z.*, 1899—1900, **1**, 496), Ellis (*Physical Rev.*, 1924, **23**, 48), Dreisch (*Z. Physik*, 1924, **30**, 200), Márton (*Z. physikal. Chem.*, 1925, **117**, 97), Pettit (*Astrophys. J.*, 1927, **66**, 48), Barnes and Fulweiler (*J. Amer. Chem. Soc.*, 1927, **49**, 2034; 1928, **50**, 1033; *Physical Rev.*, 1928, **32**, 618) and Buss (*Z. Physik*, 1933, **82**, 452). Observations on particular bands by Barnes (*Physical Rev.*, 1930, **35**, 1524; **36**, 296) and Silverman (*ibid.*, 1932, **41**, 486).

A comparison of the wave-lengths for the liquid with those of the vapour, which have been copied from Table I into the last two lines of Table III, shows that all the main bands of the vapour spectrum appear in the liquid spectrum. The two vapour bands at 4·370 and 6·185 μ are not real exceptions. The former, which is single in the vapour, is replaced in the liquid by two bands which, being of rather low peak intensity, are omitted from Table III. The latter, if present with the same wave-length in the liquid, would not be observed as a separate maximum owing to the proximity of the new strong band at 6·272 μ. The chief characteristics of the liquid spectrum consist in the appearance of a number of new bands, the three strongest of which (apart from the one just mentioned which so nearly coincides with a vapour band) have just those frequencies which have been found by at least two other workers, but not by us, in the spectrum of the vapour. We therefore consider that the observation of these bands in the vapour spectrum is to be ascribed to the use of too high vapour pressures and to the consequent condensation of liquid films on the end-plates of the absorption tube. We can offer no suggestion, except the obvious one that impurities were present, to account for the remaining vapour bands observed either by Titeica only or by Barnes and Brattain only, but not by ourselves.

Our general map of the liquid spectrum is reproduced in Fig. 3 (p. 935). In all, it shows eight new bands (one double) measurable as distinct maxima in the spectral region of the fundamentals, two new bands observable as inflexions only, and the replacement of one of the old bands by two. Furthermore, the bands of the short-wave region (below 3 μ), which in the vapour were too weak for accurate measurement, show up as five sharp easily measurable maxima. The identities of all these bands will be considered in Part VIII.

The wave-lengths, frequencies, and intensities of the absorption maxima given by the liquid benzene are recorded in Table IV, in which the bands are numbered as far as possible to correspond to the bands of the vapour; numbers above 15 denote bands which do not appear in the spectrum of the vapour and these are further distinguished by asterisks. As a measure of intensity we give the percentage absorption in one or both of the two cells used. In the thicker of these the optical plates were separated by an annular metal washer of 0·76 mm. thickness; the other cell was similar except that the thickness of the washer was only 0·03 mm. In either case the effective thickness of the liquid film enclosed in the cell would be somewhat greater than the thickness of the washer.

TABLE IV.

Wave-lengths, Frequencies, and Intensities of the Infra-red Absorption Maxima of Liquid Benzene.

				Absorption, %.	
No.	λ (μ).	ν (cm.$^{-1}$).		Thick film.	Thin film.
(a) *Strong* (s) *and medium bands* (3—22 μ).					
1 (*s*)	3·257	3070		100	91
2 (*s*)	5·094	1963		90	83
3 (*s*)	5·525	1810		97	90
4 (*s*)	6·757	1480		99	91
5 (*s*)	9·680	1033		100	96
6 (*s*)	14·60	685	671	100	90
	15·20	658		100	87
9	7·241	1381		77	—
*16	5·991	1669		52	—
*17 (*s*)	6·235	1604	1594	85	—
	6·313	1584		85	—
*18 (*s*)	8·547	1170		95	75
*19 (*s*)	11·78	849		92	68
*20 (*s*)	12·94	773		90	66
(b) *Weak bands* (3—22 μ).					
7—8	—	—		(obscured)	
10—15	—	—		(obscured)	
*21	4·244	2356	2290	45	—
*22	4·499	2223		45	—
*23	3·804	2629		50	—
*24	6·540	1529		(overlapped)	
*25	7·703	1298		45	—
*26	*ca.* 10·15	*ca.* 985		(inflexion only)	
*27	*ca.* 16·40	*ca.* 610		(inflexion only)	
(c) *Medium* (m) *and weak bands* (*below* 3 μ).					
*28	1·671	5984		25	—
*29	2·172	4604		40	—
*30 (*m*)	2·463	4060		52	—
*31 (*m*)	2·703	3700		48	—
*32 (*m*)	2·736	3655		47	—

* See above.

(4) *Hexadeuterobenzene* (*Vapour*).—We have already briefly described the spectrum of this substance in a preliminary note, and independently, a description of it has been given by Barnes and Brattain. Neither of these reports, however, covered the whole range of the active fundamentals. We have since extended the range of our measurements to do this, and at the same time have increased their accuracy and made the whole survey more thorough, so that we can now amplify and correct the former record. Our spectrum, whilst agreeing, as far as the ranges coincide, with that of Barnes and Brattain as regards the five strongest bands, is on the whole much simpler, and contains a number of transparent regions which in Barnes and Brattain's diagram are filled with complicated band-groups, many of them not particularly weak. A possible explanation of this difference is suggested by the circumstance that it is most marked in the region of 3·2 μ, where Barnes and Brattain find rather strong absorption whereas we have complete transparency. This is a region in which all hydrocarbons containing light hydrogen possess active frequencies and pentadeuterobenzene is expected to have four active fundamentals in this neighbourhood. It seems clear that this impurity was affecting Barnes and Brattain's results, not only from the internal evidence, but also because the specimen used by them was obtained from Bowman, Benedict, and Taylor whose recorded density indicates the presence of about 14% of pentadeuterobenzene (see Part II). On account of the purity question, we limit the comparison in Table V to the five strong bands already mentioned and to one other which is only just under the limit of intensity below which the divergence of the two sets of results becomes considerable. Table V is an abridged table and is intended for comparison with Table I; the same conventions are employed for the indication of intensity.

TABLE V.

Wave-lengths (in μ) of Principal Absorption Maxima of Hexadeuterobenzene Vapour.

B.B.	**4·36**	*6·22*	*6·95*	*7·57*	8·72	**12·55**	[End of range]
This paper *	**4·359**	*6·189*	*6·897*	*7·503*	8·666	**12·30**	**19·90**

References.—B.B., Barnes and Brattain, *J. Chem. Physics*, 1935, **3**, 446.
* Cf. *Nature*, 1935, **136**, 680.

A general map of this spectrum is reproduced in Fig. 2 (p. 934), and enlargements of most of the principal bands are given in Figs. 11—16. The intensities shown in Fig. 2 are directly comparable with those in Fig. 1: the vapour pressures were the same and the same absorption tube was used for benzene and hexadeuterobenzene. The vapour pressures (p) at which the contours of the separate bands were plotted are indicated under the corresponding diagrams.

FIG. 11.

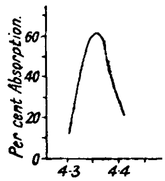


FIG. 12.

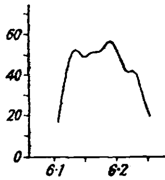


FIG. 13.

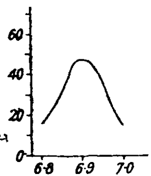


FIG. 14.

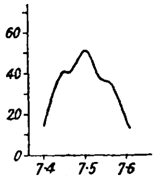


FIG. 15.

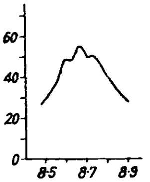


FIG. 16.

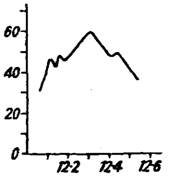


FIG. 11.—C_6D_6, 2294 cm.$^{-1}$ (p = 0·8 cm.).
FIG. 12.—C_6D_6, 1616 cm.$^{-1}$ (p = 5·0 cm.).
FIG. 13.—C_6D_6, 1450 cm.$^{-1}$ (p = 4·0 cm.).
FIG. 14.—C_6D_6, 1333 cm.$^{-1}$ (p = 4·0 cm.).
FIG. 15.—C_6D_6, 1154 cm.$^{-1}$ (p = 8·0 cm.).
FIG. 16.—C_6D_6, 813 cm.$^{-1}$ (p = 1·0 cm.).

The very strong band at 4·359 μ, which corresponds to the double band in benzene at 3·247 μ, shows only a single maximum; although a greater resolving power might reveal a sinuous contour due to *P–Q–R*-separation at the top of the band, there are certainly no signs of the strong doublet splitting visible in the benzene band. The contour of the moderately strong band at 6·189 μ suggests the presence of a distinct band at 6·135 μ, which overlaps the main band and thus gives a dissymmetric appearance to what would otherwise have been a normal *P–Q–R*-formation. The strong band at 6·897 μ shows a single maximum. That at 7·503 μ, which we believe to correspond to the benzene band at 6·733 μ, shows the same kind of *P–Q–R*-structure although the resolution is not quite so complete in the hexadeuterobenzene band; the latter has the smaller *P–R*-separation as would be expected from the greater moment of inertia of the hexadeuterobenzene molecule. The band at 8·66 μ exhibits the normal *P–Q–R*-form. The very strong band at 12·30 μ, which corresponds to the benzene band at 9·644 μ, shows, like the latter, a *P–Q–R*-structure; but the hexadeuterobenzene band contains a small extra maximum at 12·11 μ, which we provisionally account for by assuming the presence of a distinct band at this wave-length. As can be seen from Fig. 2, the form of the very strong "parallel" band at 19·90 μ is generally similar to that of the corresponding band at 14·90 μ in benzene, but we do not give an enlargement of the former as we were troubled when mapping it with stray radiation which rendered the intensities rather inaccurate and probably gave to the contour the unsymmetrical form shown, which we believe to be fictitious.

The complete list of wave-lengths, frequencies and intensities of the absorption maxima of hexadeuterobenzene vapour are given in Table VI. As before, we record as the measure of intensity the percentage of absorption in a tube 45 cm. long by vapour at 4·0 cm. pressure.

(5) *Hexadeuterobenzene (Liquid).*—This spectrum has not been previously studied. As with benzene, the spectrum of liquid hexadeuterobenzene differs mainly from that of the same substance as vapour in that the former contains a number of extra bands. This will be seen from the general map of the liquid spectrum reproduced in Fig. 4 (p. 935),

TABLE VI.

Wave-lengths, Frequencies, and Intensities of the Infra-red Absorption Maxima of Hexadeuterobenzene Vapour.

No.	λ (μ).	ν (cm.$^{-1}$).	Absorption (%).	Frequency of Q-branch.*	P–R- or Doublet separation.
(a) *Strong* (s) *and medium bands.*					
1 (*s*)	4·359	2294	90	2294	—
2	6·158	1624	30	1616	16
	6·189	1616	46		
	6·221	1608	30		
3	6·897	1450	52	1450	—
4	7·452	1342	41	1333	18
	7·503	1333	52		
	7·554	1324	37		
5 (*s*)	12·17	822	70	813	18
	12·30	813	90		
	12·44	804	70		
6 (*s*)	19·49	513	87	503	20
	19·90	503	81		
	20·28	493	84		
(b) *Weak bands* (4—22 μ).					
7	5·910	1692	14	1692	—
8	8·606	1162	23	1154	16
	8·666	1154	27		
	8·727	1146	24		
(c) *Very weak bands* (4—22 μ).					
9	5·376	1860	4	1860	—
10	6·135	1630	(overlapped)	1630	—
11	7·219	1385	*ca.* 5	1385	—
12	8·251	1212	4	1212	—
13	9·820	1018	4	1009	18
	10·00	1000	4		
14	10·80	926	4	926	—
15	12·11	826	(overlapped)	826	—
(d) *Weak band* (*below* 4 μ).					
16	2·200	4545	19	4545	—

* Or mean frequency of doublet.

or from the wave-lengths and frequencies given in Table VII. All the main bands of the vapour spectrum, and most of the weak bands also, appear in the spectrum of the liquid; the only exceptions are two weak bands, which in the vapour spectrum are only just clear of large bands, and in the liquid spectrum disappear with the broadening of the latter. There are in the liquid spectrum eleven new bands, ten appearing as distinct maxima, mostly of moderate intensity, and the eleventh showing only as an inflexion. Eight of the eleven new bands lie in the spectral region of the fundamentals, and three on the short-wave side of this.

TABLE VII.

Wave-lengths, Frequencies, and Intensities of the Infra-red Absorption Maxima of Liquid Hexadeuterobenzene.

No.	λ (μ).	ν (cm.$^{-1}$).	Absorption, %.
(a) *Strong* (s) *and medium bands* (4—22 μ).			
1 (*s*)	4·380	2283	92
2 (*s*)	6·178	1619	69
3 (*s*)	6·878	1454	63
4 (*s*)	7·508	1332	80
5 (*s*)	12·33	811	92
6 (*s*)	19·25 20·00	520 500 } 510	89
7	5·917	1690	25
8	8·627	1159	56
9	5·358	1866	18
14	10·81	925	27
*17	6·444	1552	*ca.* 15
*18	10·21	979	13
*19	10·60	943	20
*20	11·57	864	30
*21	13·26	754	17
*22	15·11	662	15
(b) *Weak bands* (4—22 μ).			
10	—	—	(obscured)
11	7·178	1393	*ca.* 10
12	8·213	1218	3
13	9·883	1012	10
15	—	—	(obscured)
*23	*ca.* 11·9	*ca.* 840	(inflexion only)
*24	17·21	581	4
(c) *Medium* (m) *and weak bands* (*below* 4 μ).			
16	2·210	4525	20
*25 (*m*)	2·810	3559	20
*26 (*m*)	3·038	3292	25
*27	3·445	2903	9

In Table VII, Nos. 1—16 are numbered to correspond with the 16 bands of the vapour spectrum; the eleven bands, Nos. 17—27, are distinguished with an asterisk. Two bands, Nos. 9 and 14, which appeared only very weakly in the spectrum of the vapour, have moderate intensity in the liquid spectrum, and hence are found in section (*a*) of this table though they come into section (*c*) of Table VI. The measure of intensity is the percentage of absorption in the cell used, which was made by cementing the potassium bromide plates to the sides of an annular metal washer 0·07 mm. thick, the effective thickness of the liquid film being naturally somewhat greater than this. For the reason mentioned earlier, the intensity of the low-frequency band, No. 6, could not be measured accurately.

The assignment of all these bands and their correlation with those of the benzene spectrum will be considered in Part VIII.

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