

**104.** *Excited States of Benzene. Part X. Analysis of the First Ultraviolet Band System of the Absorption Spectrum of Monodeuterobenzene.*

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The measurements of Beck and Sporer on the ultraviolet absorption spectrum of monodeuterobenzene are analysed as outlined in the abstract of Part I. A list of eighteen fundamental frequencies of the upper electronic state is given: all are assigned to their vibrations. Most of the basis of the assignment is given, but completion is reserved for Part XI.

(1) *Data*.—The first ultraviolet absorption system of monodeuterobenzene has been described by Beck and Sponer (*J. Chem. Physics*, 1942, **10**, 575). They assigned many of the bands, and we accept most of their assignments. It would hardly have been possible for them to proceed any further with the analysis of the spectrum on the basis of the knowledge that was then available of the frequencies of the electronic ground state. Having now a much more complete knowledge of these frequencies, as well as some useful experience in the interpretation of the somewhat simpler electronic band systems of more symmetrically substituted benzenes, we have attempted a substantially complete analysis of the spectrum.

The first two columns of Table I contain Beck and Sponer's frequency and intensity data, whilst the third column records our assignments according to a literal notation, the interpretation of which is contained in Tables II and III. The symbols have been made to correspond as closely as possible to those used in connection with the absorption spectra of other benzenes, especially 1 : 4-dideuterobenzene (Part VIII).

One general difference between Beck and Sponer's analysis and ours may be mentioned. They assumed certain of the weak bands to depend on an allowed electronic transition, implying a reduced electronic symmetry as a result of isotopic substitution. On the other hand, we

TABLE I.

*Absorption Spectrum of Monodeuterobenzene. Frequencies, Intensities, and Assignments (cf. Tables II and III).*

Freq. (cm. <sup>-1</sup> ).	Inty.	Assgnt.	Freq. (cm. <sup>-1</sup> ).	Inty.	Assgnt.	Freq. (cm. <sup>-1</sup> ).	Inty.	Assgnt.
37026	w	R <sub>0</sub> <sup>1'-1'</sup>	37788	3	J <sub>0</sub> <sup>11'-2'</sup>	38215	5	N <sub>0</sub> <sup>'0-0</sup>
041	w	B <sub>0</sub> <sup>3'-3'</sup>	796	3	J <sub>0</sub> <sup>2'-11'</sup>	227	5	C <sub>0</sub> <sup>2'-2'</sup>
046	w	B <sub>0</sub> <sup>12'-12'</sup>	801	3	J <sub>0</sub> <sup>2'-2'</sup>	235	5br	C <sub>0</sub> <sup>11'-11'</sup>
119	2	D <sub>0</sub> <sup>11'-11'</sup>	820	3	J <sub>0</sub> <sup>2'-2</sup>	256	5	M <sub>0</sub> <sup>'1'-1'</sup>
134	3	N <sub>0</sub> <sup>'1'-1'</sup>	828	3	J <sub>0</sub> <sup>2'-11'</sup>	275	5	B <sub>1</sub> <sup>'-1'</sup>
185	4	R <sub>0</sub> <sup>0-0</sup>	844	2	J <sub>0</sub> <sup>11'-2</sup>	300.8	7	Q <sub>0</sub> <sup>0-0</sup>
201	4	B <sub>0</sub> <sup>2'-2'</sup>	851	2	J <sub>0</sub> <sup>2'-2</sup>	320.8	7	A <sub>0</sub> <sup>2'-2'</sup>
207	4	B <sub>0</sub> <sup>11'-11'</sup>	860	2	j <sub>0</sub> <sup>1-1'</sup>	326.8	7	A <sub>0</sub> <sup>11'-11'</sup>
226	w	L <sub>0</sub> <sup>'-1'</sup>	884	2	j <sub>0</sub> <sup>1-1</sup>	335	7	A <sub>0</sub> <sup>2-2</sup>
256	4	N <sub>0</sub> <sup>0-0</sup>	896	4	j <sub>0</sub> <sup>1'-1</sup>	343	6L	K <sub>0</sub> <sup>'-1'</sup>
270	3	D <sub>0</sub> <sup>'-1'</sup>	914	2br	h <sub>0</sub> <sup>0-0</sup>	352	5L	D <sub>0</sub> <sup>0-0</sup>
275	4		948	4	J <sub>0</sub> <sup>11'-1'</sup>	374.5	7	M <sub>0</sub> <sup>0-0</sup>
280	4	D <sub>0</sub> <sup>1-1</sup>	961	4	J <sub>0</sub> <sup>'-1'</sup>	395	7br	C <sub>0</sub> <sup>'-1'</sup>
295	4	N <sub>0</sub> <sup>0-0</sup>	969	3	J <sub>0</sub> <sup>11-1</sup>	399	6	C <sub>0</sub> <sup>1-1</sup>
328	4	i <sub>0</sub> <sup>''</sup>	971	4		413.2	7	M <sub>0</sub> <sup>'0-0</sup>
346	4	i <sub>0</sub> <sup>'</sup>	975	2	H <sub>0</sub> <sup>0-0</sup>	421.8	7	k <sub>0</sub> <sup>0-0</sup>
360.7	6	B <sub>0</sub> <sup>'-1'</sup>	982	4	J <sub>0</sub> <sup>'-1</sup>	433.7	6	B <sub>1</sub> <sup>0-0</sup>
367.8	6	B <sub>0</sub> <sup>-1</sup>	997	4	443.0	7		
375	1		38006	4	H <sub>0</sub> <sup>0-0</sup>	480.1	8	A <sub>0</sub> <sup>'-1'</sup>
381	1	L <sub>0</sub> <sup>0-0</sup>	013	3	A <sub>0</sub> <sup>22'-22'</sup>	487.8	8	A <sub>0</sub> <sup>1-1</sup>
387	4		020	2	A <sub>0</sub> <sup>31'-31'</sup>	496	5	K <sub>0</sub> <sup>0-0</sup>
433.5	6	D <sub>0</sub> <sup>0-0</sup>	036	4	j <sub>0</sub> <sup>0-0</sup>	504.1	7	
442	2		059	5br	M <sub>0</sub> <sup>'-1'</sup>	554.7	8	C <sub>0</sub> <sup>0-0</sup>
454	2	B <sub>0</sub> <sup>0-0</sup>	108	3	R <sub>1</sub> <sup>0-0</sup>	583	6	A <sub>0</sub> <sup>2-0</sup> ; I <sub>0</sub>
520	7	B <sub>0</sub> <sup>0-0</sup>	114	5	B <sub>1</sub> <sup>2'-2'</sup>	598	7	I <sub>0</sub> <sup>1</sup>
529	5	w <sub>-1</sub>	118	—		640.8	10	A <sub>0</sub> <sup>0-0</sup>
564	2br	v <sub>0</sub> <sup>'-1</sup>	123	—	B <sub>1</sub> <sup>11'-11'</sup>	688	4	P <sub>0</sub> <sup>0-0</sup>
578	4	C <sub>-1</sub> <sup>0-0</sup>	125	vw		733	4	J <sub>1</sub> <sup>2-2</sup>
604	2	v <sub>0</sub> <sup>'</sup>	130	4	B <sub>2</sub> <sup>2-2</sup>	799	4	G <sub>0</sub> <sup>2'-2'</sup>
630	4	v <sub>0</sub>	142	4	Q <sub>0</sub> <sup>1'-1'</sup>	869	4br	J <sub>1</sub> <sup>1'-1'</sup>
636	3		156	4	Q <sub>0</sub> <sup>1-1</sup>	891	4	J <sub>1</sub> <sup>1-1</sup>
659	6	A <sub>-1</sub> <sup>0-0</sup>	161	w	A <sub>0</sub> <sup>3'-3'</sup>	913	4	H <sub>1</sub> <sup>'0-0</sup>
668	2br	J <sub>0</sub> <sup>3-3</sup>	165	5	A <sub>0</sub> <sup>12'-12'</sup>	938	6	G <sub>0</sub> <sup>1-1</sup>
677	2	J <sub>0</sub> <sup>12'-21'</sup>	174	5	A <sub>0</sub> <sup>21'-21'</sup>	958	6	G <sub>0</sub> <sup>'1'-1'</sup>
700	3	j <sub>0</sub> <sup>11'-2'</sup>	183	5	A <sub>0</sub> <sup>3-3</sup>	963	4	G <sub>0</sub> <sup>1-1</sup>
739	3	j <sub>0</sub> <sup>2'-11'</sup>	196	5	D <sub>1</sub> <sup>1-1</sup>	39022	5	R <sub>0</sub> <sup>0-0</sup>
767	3	J <sub>0</sub> <sup>2-2'</sup>	210	5	M <sub>0</sub> <sup>'-1'</sup>	059	6	Q <sub>1</sub> <sup>'-1'</sup>

TABLE I—*contd.*

Freq. (cm. <sup>-1</sup> ).	Inty.	Assgnt.	Freq. (cm. <sup>-1</sup> ).	Inty.	Assgnt.	Freq. (cm. <sup>-1</sup> ).	Inty.	Assgnt.
39068	5	Q <sub>1</sub> <sup>1-1</sup>	39592	—	K' <sub>0</sub>	40472.5	8}	A <sub>2</sub> <sup>0-0</sup>
077	w	A <sub>1</sub> <sup>3'-3'</sup>	595.7	7}	E' <sub>0</sub> <sup>0-0</sup>	480.7	8}	E <sub>1</sub> <sup>0-0</sup>
090.6	6	G <sub>0</sub> <sup>0-0</sup>	622	7}		489.6	8	E <sub>1</sub> <sup>0-0</sup>
116.7	7	G' <sub>0</sub> <sup>0-0</sup>	650	5br	O <sub>0</sub> <sup>1'-1'</sup>	506.6	7}	E <sub>1</sub> <sup>0-0</sup>
221	6	Q <sub>1</sub> <sup>0-0</sup>	675	5	U <sub>0</sub> <sup>0-0</sup>	520.6	7}	
228	6		744	6	O <sub>0</sub> <sup>0-0</sup>	597	6	U <sub>0</sub> <sup>0-0</sup>
241	6	A <sub>1</sub> <sup>2'-2'</sup>	788	3	J <sub>2</sub> <sup>1-1'</sup>	718	6}	O <sub>1</sub> <sup>0-0</sup>
256	6L}		808.0	7	O <sub>0</sub> <sup>0-0</sup>	729	6}	
263	6L}	A <sub>1</sub> <sup>2-2</sup>	867	5}		836	5	T <sub>1</sub> <sup>1'-1'</sup>
271	6L}		878	4}	G <sub>1</sub> <sup>1'-1'</sup>	918	6	Z <sub>0</sub> <sup>1'-1'</sup>
288	6L}	E <sub>0</sub> <sup>2'-2'</sup>	894	5	G' <sub>1</sub> <sup>1-1</sup>	949	6	X <sub>0</sub> <sup>1'-1'</sup>
(307)	—	C <sub>1</sub> <sup>1'-1</sup>	917	5br	T <sub>0</sub> <sup>1'-1'</sup>	986	6	Y <sub>0</sub> <sup>0-0</sup>
331	L	M <sub>1</sub> <sup>0-0</sup>	964	5	Z <sub>0</sub> <sup>0-0</sup>	998	6	T <sub>0</sub> <sup>0-0</sup>
343	6	k <sub>1</sub> <sup>0-0</sup>	40011	6L	G <sub>1</sub> <sup>0-0</sup>	41040	6br	X <sub>0</sub> <sup>1-1'</sup>
364	7	B <sub>2</sub> <sup>0-0</sup>	019	7	S <sub>0</sub> <sup>0-0</sup>	083	6br	Z <sub>0</sub> <sup>0-0</sup>
392.6	7}		027	5}		111	6br	X <sub>0</sub> <sup>0-0</sup>
401.4	7}	A <sub>1</sub> <sup>1'-1'</sup>	039	6}	G <sub>1</sub> <sup>0-0</sup>	164	6	M <sub>3</sub> <sup>0-0</sup>
419.6	8	E <sub>0</sub> <sup>1'-1'</sup>	077	7	T <sub>0</sub> <sup>0-0</sup>	196	7	X <sub>0</sub> <sup>0-0</sup>
437	5}		252	6L	M <sub>2</sub> <sup>0-0</sup>	205	6	X <sub>0</sub> <sup>0-0</sup>
466	7}	E <sub>0</sub> <sup>1'-1'</sup>	288	6	B <sub>3</sub> <sup>0-0</sup>	393	7br	A <sub>3</sub> <sup>0-0</sup>
473	7	C <sub>1</sub> <sup>0-0</sup>	311	6br}		408	6br	E <sub>2</sub> <sup>0-0</sup>
552.7	9}		322	6}	A <sub>2</sub> <sup>1'-1'</sup>	427	—	E <sub>2</sub> <sup>0-0</sup>
561.1	9}	A <sub>1</sub> <sup>0-0</sup>	340	6	E <sub>1</sub> <sup>1-1</sup>	770	6	Y <sub>0</sub> <sup>0-0</sup>
571	8}		373	6L	E <sub>1</sub> <sup>1-1</sup>	42108	—}	X <sub>1</sub> <sup>0-0</sup>
581.3	8}	E <sub>0</sub> <sup>0-0</sup>	390	br	C <sub>2</sub> <sup>0-0</sup>	116	6}	

*Note:* In this Table quantum numbers are indicated according to the conventions stated in the Note beneath Table I, Part VIII (p. 464), except that the sequence-forming vibration with the higher frequencies, identical with the vibration  $A_u(C)$  of 1:4-dideuterobenzene, is the  $A_2(C)$  vibration of monodeuterobenzene, whilst the sequence-forming vibration having the lower frequencies, approximately corresponding to the  $B_{1u}(C)$  vibration of 1:4-dideuterobenzene, is the  $B_2(C)$  vibration of monodeuterobenzene.

consider all the observed bands to depend on the forbidden electronic transition  $A_{1g}-B_{2u}$ , their spectral activity arising from deformation of the molecule by vibrations.

(2) *Band Series A—D, U, v, v', v'', and w.*—As usual, band series A—D furnish the main spectral pattern. The parent bands  $A_0^{0-0}$ ,  $B_0^{0-0}$ ,  $C_0^{0-0}$ , and  $D_0^{0-0}$  arise from upward 0—1, 1—0, 1—2, and 2—1 transitions, respectively, of the main perturbing vibration, in combination with the electronic transition. These parent bands form the starting points of positive progressions in the ring-swelling vibration, and the bands of these progressions themselves form the starting points of negatively running sequences due to  $n-n$  transitions in certain out-of-plane vibrations of low frequencies. We also find in the spectrum a much weaker series called U, which is analogous to the similarly named series in the absorption spectrum of benzene, and depends upon upward 0—2 transitions of the perturbing vibration.

The fundamental frequencies of the main perturbing vibration, as given by the positions of the four parent bands of series A—D, are 603 cm.<sup>-1</sup> in the ground state and 517 cm.<sup>-1</sup> in the electronically excited state. Actually this vibration of monodeuterobenzene consists of the two planar, carbon-bending vibrations,  $A_1(C)$  and  $B_1(C)$ , of nearly identical frequencies, and thus we might have expected the bands of the series A—D to appear as close doublets. In fact, in the absorption spectra of 1:4-di- and 1:2:4:5-tetra-deuterobenzene, a similar cause does lead to the appearance of close doublets in the corresponding band series. However, in the case of monodeuterobenzene, Beck and Spomer failed to obtain evidence of any such doublet character, and some photographs which we have taken of the same spectrum have yielded a like result. This appears the less remarkable when it is recalled that these two vibrations appear in the Raman spectrum as a single unresolved line at 601.8 cm.<sup>-1</sup> (Bailey *et al.*, *J.*, 1946, 299). Experience in the resolution of the corresponding Raman doublets of 1:4-di- and 1:2:4:5-tetra-deuterobenzene (Poole, *J.*, 1946, 245; cf. *ibid.*, p. 272) suggests that the separation of the monodeuterobenzene frequencies is unlikely to exceed 2 cm.<sup>-1</sup>. From our study of some of the sharper bands of the ultraviolet absorption spectrum of monodeutero-

TABLE II.

Absorption Spectrum of Monodeuterobenzene. Key to Assignments (cf. Table I).

	Freq. (cm. <sup>-1</sup> ).	<i>p</i> '.	<i>p</i> ''.	<i>s</i> .	<i>t</i> .	<i>u</i> .	<i>v</i> .
A	= 38124 + 517 + 920 <i>p</i> ' - 981 <i>p</i> '' - 150 <i>s</i> - 161 <i>t</i>	0-3	0, 1	0-3	0-3		
B	= " - 603 + 920 <i>p</i> ' - 150 <i>s</i> - 161 <i>t</i>	0-3		0, 1	0-3		
C	= " + 2 × 517 - 603 + 920 <i>p</i> ' - 981 <i>p</i> '' - 150 <i>s</i> - 161 <i>t</i>	0-2	0, 1	0-2	0, 1		
D	= " + 517 - 2 × 603 + 920 <i>p</i> ' - 150 <i>s</i> - 161 <i>t</i>	0, 1		0, 1	0, 1		
E	= " + 1446 + 920 <i>p</i> ' - 150 <i>s</i> - 161 <i>t</i>	0-2		0, 1	0-2		
E'	= " + 1472 + 920 <i>p</i> ' - 150 <i>s</i> - 161 <i>t</i>	0-2		0, 1	0, 1		
G	= " + 517 + 2 × 230 + 920 <i>p</i> ' - 150 <i>s</i>	0, 1		0, 1			
G'	= " + 517 + 2 × 243 + 920 <i>p</i> ' - 150 <i>s</i> - 161 <i>t</i>	0, 1		0, 1	0-2		
H	= " - 603 + 2 × 230						
H'	= " - 603 + 2 × 243 + 920 <i>p</i> '	0, 1					
h'	= " + 517 - 2 × 603 + 2 × 243						
I	= " + 2 × 230						
I'	= " + 230 + 243						
i'	= " - 380 - 404						
i''	= " - 2 × 404						
J	= " + 920 <i>p</i> ' - 150 <i>s</i> - 161 <i>t</i> - 137 <i>u</i> - 174 <i>v</i>	0, 1		0-3	0-2	0-2	0-2
j	= " - 150 <i>s</i> - 161 <i>t</i> - 137 <i>u</i> - 174 <i>v</i>			0, 1	0, 1	0, 1	0, 1
K	= " + 517 - 134 - 161 <i>t</i>				0, 1		
k	= " + 2 × 517 - 603 - 134 + 920 <i>p</i> '	0, 1					
K'	= " + 517 + 2 × 476						
L	= " - 603 - 134 - 161 <i>t</i>				0, 1		
M	= " + 517 - 265 - 150 <i>s</i> - 161 <i>t</i>			0, 1	0, 1		
M'	= " + 517 - 226 + 920 <i>p</i> ' - 161 <i>t</i>	0-3			0, 1		
N	= " - 603 - 265						
N'	= " - 603 - 226 + 920 <i>p</i> ' - 161 <i>t</i>	0, 1			0, 1		
O	= " + 517 + 2 × 585 + 920 <i>p</i> ' - 161 <i>t</i>	0, 1			0, 1		
O'	= " + 517 + 2 × 552						
P	= " - 603 + 2 × 585						
Q	= " + 517 - 338 + 920 <i>p</i> ' - 150 <i>s</i> - 161 <i>t</i>	0, 1		0, 1	0, 1		
R	= " - 603 - 338 + 920 <i>p</i> ' - 161 <i>t</i>	0-2			0, 1		
S	= " + 517 + 2 × 690						
T	= " + 517 + 2 × 720 + 920 <i>p</i> ' - 161 <i>t</i>	0, 1			0, 1		
U	= " + 2 × 517 + 920 <i>p</i> '	0, 1					
v	= " + 517 - 1005						
v'	= " + 517 - 1037						
v''	= " + 517 - 1077						
w	= " - 603 + 990 - 981 <i>p</i> ''		1				
X'	= " + 3072 + 920 <i>p</i> ' - 161 <i>t</i>	0, 1			0, 1		
x'	= " + 517 - 603 + 3072 - 161 <i>t</i>				0, 1		
X''	= " + 3081						
Y	= " + 517 + 2348						
Y'''	= " + 517 + 3129						
z	= " + 517 + 2443 - 161 <i>t</i>				0, 1		
z'	= " - 603 + 2443						

Note: The frequency 38124 cm.<sup>-1</sup> is that of the electronic origin. The other frequencies are assigned to vibrations in Table III and in the Note thereunder.

benzene we derive the impression that the actual separation is appreciably smaller than 2 cm.<sup>-1</sup>. Furthermore, this absorption spectrum yields a similar result in relation to the upper electronic state: here, also, the separation of the corresponding doublet level is probably well within 2 cm.<sup>-1</sup>. The similarity of these results might have been expected by analogy with 1:4-di- and 1:2:4:5-tetra-deuterobenzene, for each of which the measured doublet separations in the two electronic states are closely similar.

According to the selection rules, any of the 21 planar vibrations of monodeuterobenzene could be progression-forming; but we should expect to find the greatest activity of this type shown by that vibration, *A*<sub>1</sub>(C), which is most closely similar to the main progression-forming vibration of benzene. In fact, the positive progressions in the absorption spectrum of monodeuterobenzene are essentially simple, and are dominated by the single vibration *A*<sub>1</sub>(C), which occurs up to several quanta of frequency 920 cm.<sup>-1</sup> in the electronic upper state, and with one quantum of frequency 981 cm.<sup>-1</sup> in the lower state. The tendency to form branching progressions, involving a series of quantum changes of more than one vibration, appears to be very much less developed than in the case of 1:3:5-trideuterobenzene (Part VI). On the other hand, in the single band *w*<sub>-1</sub> we observe, in combination with the electronic and vibrational transitions of B<sub>0</sub><sup>0-0</sup>, the replacement of a single quantum of the vibration *A*<sub>1</sub>(C) in the electronic

TABLE III.

*Absorption Spectrum of Monodeuterobenzene. Assignment to Vibrations of the Vibration Frequencies (cm.<sup>-1</sup>) contained in Table II.*

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (-).	Diffs. of upper- and lower-state fundamentals (-).	Vibration.
920	981	61	A <sub>1</sub> (C)
990	1005	—	A <sub>1</sub> (C')
517	603	86	A <sub>1</sub> (C 1)
1472	—	—	A <sub>1</sub> (C 2)
—	1037	—	A <sub>1</sub> (H')
2348	—	—	A <sub>1</sub> (H 1)
3129	—	—	A <sub>1</sub> (H 2)
3081	—	—	A <sub>1</sub> (H' 2)
517	603	86	B <sub>1</sub> (C 1)
1446	—	—	B <sub>1</sub> (C 2)
—	1077	—	B <sub>2</sub> (H')
3072	—	—	B <sub>1</sub> (H 2)
243	404	161	A <sub>2</sub> (C)
585	—	265	A <sub>2</sub> (H')
230	380	150	B <sub>2</sub> (C)
—	—	338	B <sub>2</sub> (C')
476	—	134	B <sub>2</sub> (H 1)
552	—	226	B <sub>2</sub> (H' 1)
690	—	—	B <sub>2</sub> (H 2)
720	—	—	B <sub>2</sub> (H' 2)

*Note:* By the addition of one quantum of the A<sub>2</sub>(C) vibration to one, and one of the B<sub>2</sub>(C) vibration to the other, of the two combining states, differences of 137 cm.<sup>-1</sup> and 174 cm.<sup>-1</sup> may arise, which appear explicitly in equations j and j' of Table II. Concerning the frequency 2443 cm.<sup>-1</sup>, see text (Section 9). The difference frequency 338 cm.<sup>-1</sup>, together with the ground-state fundamental frequency 698 cm.<sup>-1</sup>, known from the infra-red spectrum, gives the value 360 cm.<sup>-1</sup> for the fundamental frequency of the vibration B<sub>2</sub>(C') in the upper electronic state (Section 7).

ground state by one quantum of the near-trigonal planar bending vibration A<sub>1</sub>(C'), of frequency 990 cm.<sup>-1</sup>, in the upper electronic state; and in the single band ν<sub>0</sub> we see, in combination with the electronic and vibrational transitions of A<sub>0</sub><sup>0-0</sup>, the loss of a single ground-state quantum, of frequency 1005 cm.<sup>-1</sup>, of the same vibration, A<sub>1</sub>(C') in the electronic ground state. These bands can be regarded as vestiges of positive and negative progressions in the vibration A<sub>1</sub>(C'). The single bands ν<sub>0</sub>' and ν<sub>0</sub>'' are similar to ν<sub>0</sub> except that the place of the vibration A<sub>1</sub>(C') is taken by either of two other vibrations. These are the planar protium-bending vibrations A<sub>1</sub>(H') and B<sub>1</sub>(H'), having the frequencies 1037 cm.<sup>-1</sup> and 1077 cm.<sup>-1</sup> in the electronic ground state.

Two out-of-plane vibrations, A<sub>2</sub>(C) and B<sub>2</sub>(C), are concerned in the formation of the sequences, which are associated with the main bands of progressions A—D. The elementary frequency intervals, representing the differences between the fundamental frequencies of these vibrations in the lower and the upper electronic states, are 161 cm.<sup>-1</sup> and 150 cm.<sup>-1</sup>. It is significant that the larger difference is identical with the larger of the two corresponding differences of 1 : 4-dideuterobenzene, and with the single sequence interval of benzene. The vibration A<sub>2</sub>(C) of monodeuterobenzene is identical with the vibration A<sub>u</sub>(C) of 1 : 4-dideuterobenzene, and with one form of the degenerate vibration E<sub>u</sub><sup>+</sup>(C) of benzene; for in these vibrations the atoms on the para-axis, which in the deuterated compounds contains the deuterium atoms, do not move. It follows that the interval 161 cm.<sup>-1</sup> belongs to the A<sub>2</sub>(C) vibration, and that the interval 150 cm.<sup>-1</sup> belongs to the B<sub>2</sub>(C) vibration. The sequences mentioned, like the corresponding sequences of 1 : 4-dideuterobenzene, are of the "simply branching" type (Part VIII, Section 2): in all the recorded bands, each of the two sequence-forming vibrations is excited with the same number of quanta in the two electronic states.

From these bands we may learn the frequency of the electronic origin,

$$J_0^{0-0} = 38124 \pm 1 \text{ cm.}^{-1}$$

and the following fundamental vibration frequencies :

A <sub>1</sub> (C 1) <sub>ground</sub> = 603 cm. <sup>-1</sup>	A <sub>1</sub> (C 1) <sub>excited</sub> = 517 cm. <sup>-1</sup>
B <sub>1</sub> (C 1) <sub>ground</sub> = 603 cm. <sup>-1</sup>	B <sub>1</sub> (C 1) <sub>excited</sub> = 517 cm. <sup>-1</sup>
A <sub>1</sub> (C) <sub>ground</sub> = 981 cm. <sup>-1</sup>	A <sub>1</sub> (C) <sub>excited</sub> = 920 cm. <sup>-1</sup>
A <sub>1</sub> (C') <sub>ground</sub> = 1005 cm. <sup>-1</sup>	A <sub>1</sub> (C') <sub>excited</sub> = 990 cm. <sup>-1</sup>
A <sub>1</sub> (H') <sub>ground</sub> = 1037 cm. <sup>-1</sup>	B <sub>1</sub> (H') <sub>ground</sub> = 1077 cm. <sup>-1</sup>

Independent values for all of these ground-state frequencies have been obtained from the Raman spectrum of liquid monodeuterobenzene:  $A_1(\text{C } 1) = B_1(\text{C } 1) = 601.8 \text{ cm.}^{-1}$ ,  $A_1(\text{C}) = 980.0 \text{ cm.}^{-1}$ ,  $A_1(\text{C}') = 1006.8 \text{ cm.}^{-1}$ ,  $A_1(\text{H}') = 1031 \text{ cm.}^{-1}$ ,  $B_1(\text{H}') = 1075 \text{ cm.}^{-1}$  (Bailey *et al.*, *loc. cit.*)

(3) *Band Series E and E'*.—These bands are very similar to the corresponding bands of 1 : 4-dideuterobenzene (Part VIII, Section 3). They are double bands, two of which, one belonging to the E and the other to the E' series, lie just above each of the main bands of progression A, starting at the second member. We assume these bands to be formed in 0—1 transitions of the two carbon-stretching vibrations of similar frequencies,  $A_1(\text{C } 2)$  and  $B_1(\text{C } 2)$ , in combination, in some cases, with the usual progression- and sequence-forming vibrations. Probably these bands gain much of their intensity by resonance with the neighbouring A bands, and they may also suffer upward displacements of frequency. For this reason we take, as heretofore, the lower of the frequencies of the two intensity maxima of each band as the better approximation to the unperturbed position of its vibrational origin.

The two parent bands,  $E_0^{0-0}$  and  $E_0'^{0-0}$ , lie  $1446 \text{ cm.}^{-1}$  and  $1472 \text{ cm.}^{-1}$ , respectively, above the electronic origin. We connect these bands with the vibrations  $B_1(\text{C } 2)$  and  $A_1(\text{C } 2)$ , respectively. The assignment is based on a consideration of normal co-ordinates closely similar to that employed in assigning the corresponding bands of 1 : 4-dideuterobenzene (Part VIII, Section 3). We thus derive the following fundamental frequencies :

$$A_1(\text{C } 2)_{\text{excited}} = 1472 \text{ cm.}^{-1} \qquad B_1(\text{C } 2)_{\text{excited}} = 1446 \text{ cm.}^{-1}$$

The corresponding ground-state frequencies, as given by the Raman spectrum of liquid monodeuterobenzene, are as follows:  $A_1(\text{C } 2) = 1591.1 \text{ cm.}^{-1}$  and  $B_1(\text{C } 2) = 1574 \text{ cm.}^{-1}$ . One observes that the frequency separation between the two vibrations is slightly greater in the upper electronic state than in the ground state, just as with 1 : 4-dideuterobenzene.

(4) *Band Series G, G', H, H', h', I, I', i', i'', J, and j*.—These bands are concerned in various ways with the already mentioned out-of-plane vibrations  $A_2(\text{C})$  and  $B_2(\text{C})$ . Series G and G' resemble the correspondingly named series in the absorption spectrum of 1 : 4-dideuterobenzene (Part VIII, Section 4). Characteristically, their band-series involve a gain of two quanta of the vibrations  $B_2(\text{C})$  and  $A_2(\text{C})$ , respectively, in combination in either case with the electronic and vibrational transitions of series A. Similarly, the bands of series H and H' involve gains of two quanta of the vibrations  $B_2(\text{C})$  and  $A_2(\text{C})$ , respectively, in association with the electronic and vibrational transitions of series B. Series h', which is represented in the spectrum by a single band only, corresponds to series H', except for the additional presence in each of the combining states of one quantum of either vibration  $A_1(\text{C } 1)$  or vibration  $B_1(\text{C } 1)$ . Bands corresponding to  $I_0$  and  $I_0'$  were not found in the spectrum of 1 : 4-dideuterobenzene, but these bands have an identified analogue in the band  $I_0^0$  of the absorption spectrum of benzene: band  $I_0$  is considered to involve the gain of two quanta of the vibration  $B_2(\text{C})$ , whilst band  $I_0'$  is regarded as arising from the gain of one quantum of each of the vibrations  $B_2(\text{C})$  and  $A_2(\text{C})$  in a transition from the "vibrationless" ground state. Band  $i_0'$  is associated with a loss of two such quanta in a transition from the binary combination level of the  $B_2(\text{C})$  and  $A_2(\text{C})$  vibrations of the electronic ground state to the "vibrationless" level of the electronically excited state. Finally, band  $i_0''$  is connected with a similar loss of two quanta of the vibration  $A_2(\text{C})$  in a transition from the first overtone level of this vibration in the ground state to the "vibrationless" level of the excited state.

Series J is concerned with transitions characterised by the excitation of either or both of the vibrations  $A_2(\text{C})$  and  $B_2(\text{C})$  under the condition that the total number of their quanta in the lower state is the same as the total number in the upper state. In this series the spectral activity is entirely due to these sequence-forming vibrations, and we connect with this the circumstance that the strong preference, shown in the sequences of most other series for totally symmetrical combinations of these vibrations, does not here arise (cf. Part VIII, Section 4). Accordingly, the main sequence of the J series, like those of the J series of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, exhibits what we call "complex branching": it includes many bands in which each individual vibration is present with different quantum numbers in the two combining states. The main sequence therefore appears here, just as in the absorption spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene, as an array of numerous weak bands, which, except for a few gaps, fill the spectrum for a region extending over several hundred wave-numbers on the long-wave side of the electronic origin. Part of the sequence is repeated in the present spectrum with a positive displacement by the usual progression interval. Series j is similar to series J except that each of the combining states now possesses additionally

one quantum of either the vibration  $A_1(C\ 1)$  or the vibration  $B_1(C\ 1)$ . This series is less fully developed than the other, but it also shows "complex branching", like the similar series of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene (Part VIII, Section 4, and Part IX, Section 4).

The series discussed in this Section, together with the already considered sequences of series A—D, furnish the following fundamental vibration frequencies :

$$\begin{array}{ll} A_2(C)_{\text{ground}} = 404 \text{ cm.}^{-1} & A_2(C)_{\text{excited}} = 243 \text{ cm.}^{-1} \\ B_2(C)_{\text{ground}} = 380 \text{ cm.}^{-1} & B_2(C)_{\text{excited}} = 230 \text{ cm.}^{-1} \end{array}$$

The two  $A_2(C)$  frequencies agree with the  $E_u^+(C)$  frequencies of benzene and with the  $A_u(C)$  frequencies of 1 : 4-dideuterobenzene : as we have remarked before, these vibrations are identical in the three benzenes. The two ground-state frequencies agree with previous values : Herzfeld, Ingold, and Poole gave the value 405  $\text{cm.}^{-1}$ , largely on the evidence provided by Raman and infra-red combination tones (*J.*, 1946, 316); whilst Bailey *et al.* measured the infra-red fundamental band  $B_2(C)$  and gave 380  $\text{cm.}^{-1}$  as the frequency of the Q branch (*loc. cit.*).

(5) *Band Series K, k, K', and L.*—We concur with Beck and Spomer in the view that the bands of the series here called K and L, which are found negatively displaced by 134  $\text{cm.}^{-1}$  from the bands of series A and B, respectively, are to be correlated, as nearly as the different symmetries of the molecules allow, with the bands of the series, also called K and L, which appear prominently in the absorption and fluorescence spectra of hexadeuterobenzene (Part IV, Section 5, and Part V, Section 4). These series were connected with 1—1 transitions of the hexagonal, out-of-plane vibration  $A_{2u}(H)$ . The K and L bands in the present spectrum are thus regarded as arising in 1—1 transitions of the vibration  $B_2(H\ 1)$ , in combination with the electronic and vibrational transitions of series A or B. The bands of series k are similarly related to series C, and a corresponding explanation is applied to them. The vibration  $B_2(H\ 1)$  is that which in the ground state furnishes the very strong band of lowest frequency in the infra-red spectrum; and from the known frequency of this band, and the difference-frequency, 134  $\text{cm.}^{-1}$ , we can compute the fundamental frequency in the upper electronic state. Consistently, we find a band,  $K_0'$ , 951  $\text{cm.}^{-1}$  above  $A_0^0$ , which evidently represents the excitation in the upper state of the first overtone of this vibration, in combination with the transitions of the main active origin. From the position of this band, and from the difference frequency, we derive the following fundamental frequencies :

$$B_2(H\ 1)_{\text{ground}} = 610 \text{ cm.}^{-1} \qquad B_2(H\ 1)_{\text{excited}} = 476 \text{ cm.}^{-1}$$

The ground-state frequency as evaluated in the infra-red spectrum, is 608  $\text{cm.}^{-1}$  (Bailey *et al.*, *loc. cit.*).

(6) *Band Series M, M', N, N', O, O', and P.*—Series M, N, O, and P correspond exactly to the similarly named series in the absorption spectrum of benzene (Part II, Section 6), and likewise to those which appear in the spectrum of 1 : 4-dideuterobenzene (Part VIII, Section 6). In all these spectra, series M and N consist of bands negatively displaced by 265  $\text{cm.}^{-1}$  below the bands of series A and B, respectively; whilst series O and P consist of bands positively displaced by 1170  $\text{cm.}^{-1}$  above the bands of series A and B. The vibration concerned is identical in the three benzenes, because the atoms on that para-axis, which in the deuterated compounds contains the deuterium atoms, do not move. It is the  $E_g^-(H)$  vibration of benzene, the  $B_{2g}(H)$  vibration of 1 : 4-dideuterobenzene, and the  $A_2(H')$  vibration of monodeuterobenzene; and, in each case, it consists of counter-rotatory motions of the carbon and hydrogen hexagons about the common para-axis. Series M and N arise from 1—1 transitions of this vibration, in combination with the transitions of series A and B, respectively, whilst series O and P are produced by upward 0—2 transitions of the same vibration in a similar state of combination with A or B transitions.

Series M', N', and O' are in our assignments constituted similarly to series M, N, and O, respectively, except that the characteristic vibration now corresponds, as nearly as the different symmetries of the molecules allow, to the second component of the degenerate vibration,  $E_g^-(H)$ , of benzene. This vibration of monodeuterobenzene is called  $B_2(H'\ 1)$ , and its form and frequency have become considerably modified by the presence of the deuterium atom. The difference between its fundamental frequencies in the lower and the upper states is now reduced to 226  $\text{cm.}^{-1}$ , and it is by this interval that the bands of series M' and N' are displaced below the bands of series A and B. Similarly the positive displacement in series O' is reduced to 1103  $\text{cm.}^{-1}$ .

These data allow us to compute the following fundamental frequencies :

$$\begin{array}{ll} A_2(H')_{\text{ground}} = 850 \text{ cm.}^{-1} & A_2(H')_{\text{excited}} = 585 \text{ cm.}^{-1} \\ B_2(H'\ 1)_{\text{ground}} = 778 \text{ cm.}^{-1} & B_2(H'\ 1)_{\text{excited}} = 552 \text{ cm.}^{-1} \end{array}$$

The ground-state values, as given in the Raman spectrum of liquid monodeuterobenzene, are  $A_2(\text{H}^1) = 849.9 \text{ cm.}^{-1}$ , and  $B_2(\text{H}^1 1) = 778.7 \text{ cm.}^{-1}$  (Bailey *et al.*, *loc. cit.*).

(7) *Band Series Q, R, S, and T.*—We deal in this section with the band series which arise from excitations of the three remaining vibrations of  $B_2$  symmetry class. Series Q and R consist of bands negatively displaced by  $338 \text{ cm.}^{-1}$  below the bands of series A and B, respectively. In explanation of these bands, we assume 1—1 transitions of the relevant vibration in combination with the electronic and vibrational transitions of series A and B. The interval  $338 \text{ cm.}^{-1}$  thus represents the difference between the fundamental frequencies of the vibration in the two electronic states, and the magnitude of the difference suggests that the vibration concerned is that which is most nearly analogous to the trigonal out-of-plane vibration,  $B_{2g}(\text{C})$ , of benzene (cf. Parts II and IV). This vibration of monodeuterobenzene is labelled  $B_2(\text{C}')$ . Its fundamental frequency in the lower electronic state is known from infra-red measurements to be  $698 \text{ cm.}^{-1}$  (Bailey *et al.*, *loc. cit.*), and we have to use this value for the computation of the upper-state fundamental frequency, since we have been unable to identify its overtone in the recorded ultraviolet spectrum. On the other hand, we recognise two other upper-state overtones in the constitution of band series S and T, which are assigned as involving upward 0—2 transitions of the vibrations  $B_2(\text{H} 2)$  and  $B_2(\text{H}^1 2)$ , respectively, in combination with the electronic and vibrational transitions of series A. These assignments, which are well borne out by comparisons among the different isotopic benzenes (Part XI), provide the following fundamental frequencies:

$$\begin{array}{ll} B_2(\text{C}')_{\text{excited}} = 360 \text{ cm.}^{-1} & B_2(\text{H} 2)_{\text{excited}} = 690 \text{ cm.}^{-1} \\ & B_2(\text{H}^1 2)_{\text{excited}} = 720 \text{ cm.}^{-1} \end{array}$$

The corresponding fundamental frequencies of the electronic ground state, as given in the infra-red spectrum, are  $B_2(\text{C}') = 698 \text{ cm.}^{-1}$ ,  $B_2(\text{H} 2) = 922 \text{ cm.}^{-1}$ , and  $B_2(\text{H}^1 2) = 995 \text{ cm.}^{-1}$ .

(8) *Band Series X', x', X'', Y, and Y'''.*—These series are characterised by excitations in the upper electronic state of one or another of the various hydrogen-stretching vibrations. We can distinguish band series connected with the single deuterium-stretching vibration and with three of the five protium-stretching vibrations. The band  $Y_0^{0-0}$ , which lies  $2348 \text{ cm.}^{-1}$  above  $A_0^{0-0}$ , is attributed to the excitation of one quantum of the deuterium-stretching vibration, in combination with the electronic and vibrational transitions of  $A_0^{0-0}$ . The band has no other probable explanation, and the frequency separation is the same, to within a few wave numbers, as that of the corresponding band in the absorption spectrum of 1 : 4-dideuterobenzene (Part VIII, Section 8). We should expect to find a band of appreciable intensity  $2348 \text{ cm.}^{-1}$  above the electronic origin, but the presence of such a band cannot be verified, because this position coincides with that of the strong band  $A_3^{0-0}$ .

The series  $X'$  starts with a band of moderate intensity,  $3072 \text{ cm.}^{-1}$  above the electronic origin. We here assume a transition from the "vibrationless" ground state to the fundamental level of one of the protium-stretching vibrations in the upper electronic state. The band starts a progression of two members and also a sequence of two members. The bands of the weak series  $x'$  are displaced below those of series  $X'$  by  $86 \text{ cm.}^{-1}$ , so that series  $x'$  is related to series  $X'$  just as C is to A or as D is to B. For series  $x'$  we assume the additional presence, in each of the combining states, of one quantum of one of the main perturbing vibrations,  $A_1(\text{C} 1)$  or  $B_1(\text{C} 1)$ . We tentatively ascribe the band  $X''_0^{0-0}$ , situated  $3081 \text{ cm.}^{-1}$  above the electronic origin, to a transition from the "vibrationless" ground state to the one-quantum level in the upper electronic state of another of the protium-stretching vibrations. Finally, we interpret the band  $Y'''_0^{0-0}$ , lying  $3129 \text{ cm.}^{-1}$  above  $A_0^{0-0}$ , as arising in a transition which combines an excitation in the upper electronic state of one quantum of a third of the protium-stretching vibrations with the electronic and vibrational changes associated with  $A_0^{0-0}$ .

As to the assignment of the three protium-stretching frequencies of the upper state,  $3072$ ,  $3081$ , and  $3129 \text{ cm.}^{-1}$ , among the five relevant normal modes of vibration, we can immediately identify the frequency  $3072 \text{ cm.}^{-1}$  as belonging to the vibration  $B_1(\text{H} 2)$ , on account of the intensity with which it appears with a direct displacement from the electronic origin. This strongly suggests that the vibration is a close analogue of the  $E_g^+(\text{H} 1)$  vibration of benzene, and of the  $B_{1g}(\text{H} 2)$  vibration of 1 : 4-dideuterobenzene. The frequencies are consistent with this assignment. The normal co-ordinate of the vibration  $B_1(\text{H} 2)$  of monodeuterobenzene (cf. *J.*, 1946, 306, diagram V) is very nearly identical with that of the  $B_{1g}(\text{H} 2)$  vibration of 1 : 4-dideuterobenzene, and with one of the normal co-ordinates of the degenerate vibration,  $E_g^+(\text{H} 1)$ , of benzene. The equivalence is not exact because of the coupling of the protium motions, but this is always very weak. We therefore expect the frequencies to be the same to



within a few wave numbers. The value given for the upper-state frequency for the benzene vibration was 3080  $\text{cm}^{-1}$  (cf. Part II), and for the 1 : 4-dideuterobenzene vibration was 3075  $\text{cm}^{-1}$  (cf. Part VIII), so that our present value, 3072  $\text{cm}^{-1}$ , for the monodeuterobenzene frequency is about what we should expect.

Another of the protium-stretching frequencies which we can identify with fair certainty is 3129  $\text{cm}^{-1}$ . This is recorded in the spectrum as a displacement from the main active origin  $A_0^0$ , and not from the electronic origin. It therefore presumably belongs to that vibration which most closely approximates to the totally symmetrical protium-stretching vibration,  $A_{1g}(\text{H})$ , of benzene, or to the totally symmetrical protium-stretching vibration,  $A_g(\text{H } 2)$  of 1 : 4-dideuterobenzene. In monodeuterobenzene this vibration will be the one in which all five protium bonds stretch and contract in phase (cf. *J.*, 1946, 306, diagram II). The benzene frequency was 3130  $\text{cm}^{-1}$ , and the 1 : 4-dideuterobenzene frequency was 3132  $\text{cm}^{-1}$  (Parts II and VIII), and therefore the value, 3129  $\text{cm}^{-1}$ , found for the most nearly analogous vibration,  $A_1(\text{H } 2)$ , of monodeuterobenzene seems reasonable.

The third upper-state protium-stretching frequency, 3081  $\text{cm}^{-1}$ , is assigned to the vibration  $A_1(\text{H}' 2)$ , on the negative ground that the remaining two protium-stretching vibrations would hardly be expected to appear in the spectrum. This follows from a consideration of their normal co-ordinates. Approximate diagrams of these have been given by Bailey *et al.* (*J.*, 1946, 306, diagrams IV and VI), and, to this approximation, both vibrations are antisymmetric with respect to the centre of symmetry of the electronic system. The selection rules show that the fundamental frequency of an exactly *ungerade* vibration could not be excited in a transition, like the present one, from a *gerade* to an *ungerade* electronic state (Part I, Section 4, *et seq.*). It is no doubt for a similar reason that the same vibrations in the ground state, although theoretically allowed in the Raman spectrum inasmuch as they are not exactly *ungerade*, cannot in fact be observed in that spectrum. The actual vibration to which we assign the upper-state frequency 3081  $\text{cm}^{-1}$  is not even approximately *ungerade* (cf. *loc. cit.*, diagram III). Its upper-state fundamental frequency should therefore be excited with appreciable intensity in the ultraviolet absorption spectrum, just as its lower-state fundamental frequency should appear in the Raman spectrum, where in fact it has been recognised.

The following upper-state fundamental frequencies result from these assignments :

$$\begin{array}{ll} A_1(\text{H } 1)_{\text{excited}} = 2348 \text{ cm}^{-1} & A_1(\text{H } 2)_{\text{excited}} = 3129 \text{ cm}^{-1} \\ A_1(\text{H}' 2)_{\text{excited}} = 3081 \text{ cm}^{-1} & B_1(\text{H } 2)_{\text{excited}} = 3072 \text{ cm}^{-1} \end{array}$$

Corresponding fundamental frequencies of the lower electronic state, as obtained from the Raman spectrum of liquid monodeuterobenzene, are as follows:  $A_1(\text{H } 1) = 2269.0 \text{ cm}^{-1}$ ,  $A_1(\text{H } 2) = 3054.0 \text{ cm}^{-1}$ ,  $A_1(\text{H}' 2) = 3060 \text{ cm}^{-1}$ ,  $B_1(\text{H } 2) = 3041 \text{ cm}^{-1}$  (Bailey *et al.*, *loc. cit.*). As usual, the hydrogen-stretching frequencies of the upper electronic state are all somewhat larger than the corresponding frequencies of the electronic ground state.

(9) *Band Series z and z'*.—These series start with bands displaced by 2443  $\text{cm}^{-1}$  above the active origins  $A_0^0$  and  $B_0^0$ , respectively. The common displacement is presumably the frequency of an overtone or combination tone derived from vibrations whose fundamental frequencies in the upper electronic state are not exactly known. It would be plausible to suppose, for instance, that the frequency 2443  $\text{cm}^{-1}$  represents the upper-state first overtone of one of the five planar protium-bending vibrations, whose frequencies in the electronic ground state range from 1031  $\text{cm}^{-1}$  to 1292  $\text{cm}^{-1}$ . In the absence of additional evidence, we are not able to make a more definite suggestion.

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