

103. *Excited States of Benzene. Part IX. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of 1 : 2 : 4 : 5-Tetradeuterobenzene.*

By FRANCESCA M. GARFORTH, CHRISTOPHER K. INGOLD, and HARRY G. POOLE.

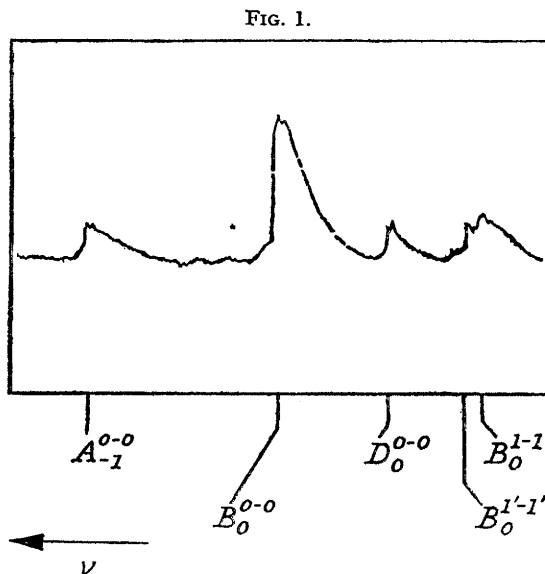
The ultraviolet absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene is described, and measurements of the frequencies of many bands are recorded. A complete vibrational analysis of the spectrum is offered. The spectral effects of resolved degeneracies are generally similar to those observed with 1 : 4-dideuterobenzene. Seventeen fundamental frequencies of the upper electronic state and seven of the lower state are recognised, and all are assigned to their vibrations. The basis of the assignment is partly given, completion being reserved for Part XI.

1) *Measurements.*—The 1 : 2 : 4 : 5-tetradeuterobenzene was prepared by deuteration of 1 : 4-dibromobenzene with heavy sulphuric acid, followed by debromination by means of the Grignard reaction, as described by Best and Wilson (*J.*, 1946, 239). The absorption spectrum of its vapour was photographed and measured, exactly as described for 1 : 3 : 5-trideuterobenzene.

In general, the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene is similar to the absorption spectra of other benzenes : it has four main series, involving positive progressions and negative sequences, obviously having the usual type of interpretation (cf. Part I, Section 4, and Fig. 1, p. 409). The spectrum especially resembles that of 1 : 4-dideuterobenzene, *e.g.*, in its double-headed bands, illustrated in Fig. 1, in the display of certain series in duplicate, in the moderate growth of complexity along the progressions, and in the rapid development of complexity in the sequences. Our interpretation of these features is just the same as for 1 : 4-dideuterobenzene (cf. Part VIII, Section 1). The resemblances mentioned are only general : there are differences of detail, which will be discussed in the following sections. Moreover, in some of its weaker series, the spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene much more closely resembles the spectrum of hexadeuterobenzene than that of 1 : 4-dideuterobenzene; and this is especially true for some series whose analogues in the spectrum of 1 : 4-dideuterobenzene are very closely similar to series found in the absorption spectrum of benzene.

Our detailed observations are recorded in Table I, using the conventions previously employed (cf. Part VI, Section 1). The vapour pressures corresponding to the temperatures mentioned in the column of intensities are estimated to be approximately as follows : at 20°, 74 mm.; at 0°, 27 mm.; at -35°, 3 mm. In the column of assignments, quantum numbers are indicated according to the system used for the spectrum of 1 : 4-dideuterobenzene (cf. Part VIII, Section 1),

whilst the letter-symbols of the present spectrum are defined by the equations of Table II. The vibration frequencies in Table II are assigned to vibrations in Table III. The method of naming



Reproduction of part of a microphotometer record of the absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene, showing the double-headed bands.

The original record has been re-photographed and intensified several times in order to obtain a line thick enough for the preparation of a block. The original record resolves the band-heads much more clearly than does the reproduction. The region shown runs from about 37450 cm^{-1} to 37800 cm^{-1} .

TABLE I.

Absorption Spectrum of 1 : 2 : 4 : 5-Tetradeuterobenzene. Frequencies, Intensities, and Assignments (cf. Tables II and III).

Freq. (cm^{-1}).	Inty. (20°).	Assgnt.	Freq. (cm^{-1}).	Inty. (0°).	Assgnt.	Freq. (cm^{-1}).	Inty. (0°).	Assgnt.
36666	ew	B_{-1}^{0-0}	37671.9	w	C_{-1}^{0-0}	38203.9	w	$C_0^{12'-12'}$
676	ew		688.8	w		211	w	
	Inty. (0°).		761.8	m	A_{-1}^{0-0}		Inty. (-35°).	
			768.5	m				
37184	ew	$B_0^{12'-12'}$	797	ew	$J_0^{3'-3'}$	235	w	$B_1^{11'-11'}$
198	ew		808	ew	$J_0^{21'-12'}$	241.6	w	
209.9	ew	$B_0^{3'-3'}$	846	ew	$j_0^{11'-11'}$	266.0	w	$A_0^{21'-21'}$
256.4	vw		$D_0^{11'-11'}$	880	w	$J_0^{2'-2}$	272.3	
280.5	vw	$N_0^{1-1}, N_0^{1'-1'}$	906	w	$J_0^{2'-11'}$	282.3	mw	$A_0^{12'-12'}$
335	mw		922	w	J_0^{2-2}	294.1	mw	
343.3	mw	B_0^{2-2}	939	vw	$J_0^{2'-2'}$	344.1	vw	$C_0^{11'-11'}$
351.1	mw		$B_0^{2'-2'}$	948	vw	$J_0^{2-11'}$	352.8	
399.3	mw	D_0^{1-1}	962	vw	j_0^{1-1}	360	vw	$C_0^{2'-2'}$
406.7	mw		$D_0^{1'-1'}$	982	vw	j_0^{1-1}	365	
425.7	mw	N_0^{0-0}	999	vw	$j_0^{1'-1'}$	381.8	mw	$B_1^{1'-1'}$
467.8	ms		B_0^{1-1}	38045.5	vw	$J_0^{1'-1}$	388	
481.2	ms	$B_0^{1'-1'}$	073.3	w	J_0^{1-1}	432.7	m	$A_0^{11-11'}$
493.7	ms		081.5	vw	$J_0^{1'-1'}$	437.6	mw	
499	vw	K_0^{0-0}	086.9	vw	H_0^{0-0}	442.5	mw	$A_0^{2'-2'}$
506	vw		094.2	vw		450.4	mw	
546	m	D_0^{0-0}	103	vw	$J_0^{1-1'}$	457.4	vw	K_0^{0-0}
550.6	m		117.6	w	$A_0^{22'-22'}$	468.5	vw	
627.8	s	B_0^{0-0}	124.7	vw	$A_0^{13'-13'}$			
632.8	s		140.0	mw				

TABLE I—*contd.*

Freq. (cm. ⁻¹).	Inty.	Assgnt.	Freq. (cm. ⁻¹).	Inty.	Assgnt.	Freq. (cm. ⁻¹).	Inty.	Assgnt.
	(-35°).		(-35°).	(-35°).		(-35°).	(-35°).	
38495.5	m	C ₀ ¹⁻¹	39535.5	m	C ₁ ⁰⁻⁰	40573.7	mw	X ₀ ⁰⁻⁰
500.3	m	C ₀ ^{1'-1'}	542.5	m	C ₁ ⁰⁻⁰	630	ew	V ₁ ⁰⁻⁰
508.8	m	C ₀ ¹⁻¹	549.3	vw	L ₀ ⁰⁻⁰	641	ew	V ₁ ⁰⁻⁰
515	m	M ₀ ⁰⁻⁰	560.8	w	K ₀ ⁰⁻⁰	685.3	mw	R ₁ ⁰⁻⁰
524.6	m	B ₁ ⁰⁻⁰	566	w	K ₀ ⁰⁻⁰	700.9	mw	R ₁ ⁰⁻⁰
528	m	B ₁ ⁰⁻⁰	604.2	w	A ₁ ⁰⁻⁰	795	mw	S ₁ ⁰⁻⁰
552	m	A ₀ ¹⁻¹	617.6	vs	A ₁ ⁰⁻⁰	808	mw	S ₁ ⁰⁻⁰
566	ms	A ₀ ¹⁻¹	623.3	vs	A ₁ ⁰⁻⁰	999	mw	G ₂ ⁰⁻⁰
581.2	s	A ₀ ^{1'-1'}	633.4	s	E ₀ ⁰⁻⁰	41009	m	U ₂ ⁰⁻⁰
589.6	ms	A ₀ ^{1'-1'}	645.7	s	E ₀ ⁰⁻⁰	017.5	m	U ₂ ⁰⁻⁰
599.6	w	k ₀ ⁰⁻⁰	714	vw	T ₁ ⁰⁻⁰	178.7	vw	C ₃ ¹⁻¹
642.9	ms	C ₀ ⁰⁻⁰	740.6	w	V ₀ ⁰⁻⁰	190	vw	C ₃ ¹⁻¹
647.9	ms	C ₀ ⁰⁻⁰	747.4	w	V ₀ ⁰⁻⁰	203	vw	C ₃ ^{1'-1'}
724.2	vs	A ₀ ⁰⁻⁰	768.2	ew	G ₁ ^{2'-2'}	207	vw	C ₃ ^{1'-1'}
728.5	vs	A ₀ ⁰⁻⁰	798.5	mw	R ₀ ⁰⁻⁰	260	m	A ₃ ^{1'-1'}
759.9	w	κ	812	ew	G ₁ ^{2'-2'}	280.7	m	A ₃ ^{1'-1'}
813	vw	T ₀ ⁰⁻⁰	830	vw	G ₁ ^{2'-2'}	297	m	E ₂ ^{1'-1'}
860.4	vw	G ₀ ^{2'-2'}	895.4	mw	G ₁ ^{1'-1'}	304	m	E ₂ ^{1'-1'}
872.7	vw	G ₀ ^{2'-2'}	903.9	mw	G ₁ ^{1'-1'}	304.6	w	C ₃ ⁰⁻⁰
974.5	w	C ₀ ¹⁻¹	914.1	mw	S ₀ ⁰⁻⁰	343.6	w	C ₃ ⁰⁻⁰
990.1	w	C ₀ ¹⁻¹	937.0	vw	G ₁ ¹⁻¹	394	ms	A ₃ ⁰⁻⁰
39002.4	mw	G ₀ ^{1'-1'}	937.0	vw	G ₁ ¹⁻¹	415	s	A ₃ ⁰⁻⁰
030.8	mw	C ₀ ¹⁻¹	951.8	vw	G ₁ ^{1'-1'}	427.0	m	E ₂ ⁰⁻⁰
043	w	C ₀ ¹⁻¹	964.3	vw	G ₁ ^{1'-1'}	430.6	m	E ₂ ⁰⁻⁰
060.2	w	G ₀ ^{1'-1'}	975.7	w	U ₁ ^{1'-1'}	438	m	E ₂ ⁰⁻⁰
087.4	vw	U ₀ ^{1'-1'}	993.2	w	U ₁ ^{1'-1'}	450	mw	X ₁ ⁰⁻⁰
106.7	vw	U ₀ ^{1'-1'}	40037.2	mw	G ₁ ⁰⁻⁰	460.3	mw	X ₁ ⁰⁻⁰
122	vw	P ₀ ⁰⁻⁰	048.4	mw	G ₁ ⁰⁻⁰	592.9	w	R ₂ ⁰⁻⁰
138.9	mw	G ₀ ⁰⁻⁰	059.2	mw	I ₀ ⁰⁻⁰	702.3	w	S ₂ ⁰⁻⁰
148.0	mw	G ₀ ⁰⁻⁰	075.7	mw	I ₀ ⁰⁻⁰	773	ew	U ₃ ^{1'-1'}
185.2	mw	G ₀ ⁰⁻⁰	095.1	mw	G ₁ ⁰⁻⁰	861.7	w	Y ₀ ⁰⁻⁰
206.2	mw	G ₀ ⁰⁻⁰	106.3	mw	G ₁ ⁰⁻⁰	911.5	mw	U ₀ ⁰⁻⁰
230.1	w	U ₀ ⁰⁻⁰	123.5	mw	U ₁ ⁰⁻⁰	42070	vw	C ₄ ¹⁻¹
241.1	vw	U ₀ ⁰⁻⁰	135	vw	C ₂ ^{11'-11'}	080.5	ew	C ₄ ¹⁻¹
259.2	vw	C ₁ ^{2'-2'}	162.4	vw	C ₂ ^{2'-2'}	097.1	ew	C ₄ ¹⁻¹
323.2	mw	A ₁ ^{11'-11'}	242	mw	A ₂ ^{2'-2'}	155	w	A ₄ ^{1'-1'}
329.1	mw	A ₁ ^{2'-2'}	252.9	mw	E ₁ ^{2'-2'}	167	mw	A ₄ ^{1'-1'}
342.0	mw	A ₁ ^{2'-2'}	274	mw	C ₂ ¹⁻¹	181.2	mw	E ₃ ^{1'-1'}
350.6	w	E ₀ ^{11'-11'}	291.0	mw	C ₂ ¹⁻¹	190	mw	E ₃ ^{1'-1'}
364	vw	K ₁ ⁰⁻⁰	300.4	mw	C ₂ ^{1'-1'}	204	w	X ₂ ^{1'-1'}
379.5	mw	C ₁ ¹⁻¹	318.4	ew	B ₃ ⁰⁻⁰	214	w	X ₂ ^{1'-1'}
391.4	vw	C ₁ ¹⁻¹	338.4	mw	A ₂ ¹⁻¹	234	ew	C ₃ ⁰⁻⁰
400.5	mw	C ₁ ^{1'-1'}	352.7	m	A ₂ ¹⁻¹	305.3	ms	A ₄ ⁰⁻⁰
412.5	mw	M ₀ ⁰⁻⁰	376.7	ms	A ₂ ^{1'-1'}	316.5	ms	E ₃ ⁰⁻⁰
421.0	vw	B ₂ ⁰⁻⁰	390.8	ms	E ₁ ^{1'-1'}	346	m	X ₂ ⁰⁻⁰
430	vw	Q ₀ ⁰⁻⁰	400.0	m	E ₁ ^{1'-1'}	749	w	Y ₁ ⁰⁻⁰
446	mw	A ₀ ¹⁻¹	430.1	mw	C ₂ ⁰⁻⁰	804	w	U ₄ ⁰⁻⁰
459	m	A ₀ ¹⁻¹	440.8	mw	C ₂ ⁰⁻⁰	820	w	U ₄ ⁰⁻⁰
474.0	ms	A ₁ ^{1'-1'}	446.8	ew	L ₁ ⁰⁻⁰	43080	mw	E ₄ ^{1'-1'}
483.3	ms	A ₁ ^{1'-1'}	457.6	w	K ₁ ⁰⁻⁰	101	mw	X ₃ ^{1'-1'}
490.1	m	E ₀ ^{1'-1'}	501.5	s	A ₂ ⁰⁻⁰	131	ew	C ₃ ⁰⁻⁰
495.3	mw	k ₀ ⁰⁻⁰	517.5	s	A ₂ ⁰⁻⁰	192	m	A ₃ ⁰⁻⁰
500.5	m	E ₀ ^{1'-1'}	525	s	E ₁ ⁰⁻⁰	201	m	A ₃ ⁰⁻⁰
518.3	w	W ₀ ⁰⁻⁰	540.1	ms	E ₁ ⁰⁻⁰			
			552.0	mw	X ₀ ⁰⁻⁰			

Note: The notation by which quantum numbers are expressed in the assignment column of this Table is the same as that used in Table I of Part VIII, and is explained in the Note beneath that Table (p. 464).

TABLE II.

Absorption Spectrum of 1 : 2 : 4 : 5-Tetradeuterobenzene. Key to Assignments (cf. Table I).

	Freq. (cm. ⁻¹).	<i>p</i> '.	<i>p</i> ''.	<i>s</i> .	<i>t</i> .	<i>u</i> .	<i>v</i> .
A	= 38219 + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 895p' - 961p'' - 150s - 141t$	0-5	0, 1	0-2	0-3		
B	= " - $\left\{ \begin{smallmatrix} 591 \\ 586 \end{smallmatrix} \right\} + 895p' - 961p'' - 150s - 141t$	0-3	0, 1	0-2	0-3		
C	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + \left\{ \begin{smallmatrix} 509.5 - 591 \\ 505 - 586 \end{smallmatrix} \right\} + 895p' - 961p'' - 150s - 141t$	0-5		0, 1	0, 1	0-2	
D	= " + $\left\{ \begin{smallmatrix} 509.5 - 591 \\ 505 - 586 \end{smallmatrix} \right\} - \left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} - 150s - 141t$			0, 1	0, 1		
E	= " + 1414 + 895 <i>p</i> ' - 150 <i>s</i> - 141 <i>t</i>	0-4		0, 1	0-2		
G	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 2 \times 233 + 895p' - 150s - 141t$	0-2		0, 1	0-2		
G'	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 2 \times 208 + 895p' - 150s - 141t$	0, 1		0, 1	0-2		
H	= " - $\left\{ \begin{smallmatrix} 591 \\ 586 \end{smallmatrix} \right\} + 2 \times 233$						
J	= " - 150 <i>s</i> - 141 <i>t</i> - 175 <i>u</i> - 116 <i>v</i>			0-2	0-3	0-2	0, 1
j	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} - \left\{ \begin{smallmatrix} 591 \\ 586 \end{smallmatrix} \right\} - 150s - 141t - 175u$			0, 1	0, 1	0, 1	
K	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 2 \times 419 + 895p'$	0, 1					
K'	= " - $\left\{ \begin{smallmatrix} 591 \\ 586 \end{smallmatrix} \right\} + 2 \times 419 + 895p'$	0, 1					
k	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} - 128 + 895p'$	0, 1					
k'	= " - $\left\{ \begin{smallmatrix} 591 \\ 586 \end{smallmatrix} \right\} - 128$						
κ	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 419 - 383$						
L	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 2 \times 665$						
L'	= " + 2 × 665 × 895 <i>p</i> '	0, 1					
M	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} - 210 + 895p'$	0, 1					
N	= " - $\left\{ \begin{smallmatrix} 591 \\ 586 \end{smallmatrix} \right\} - 210 - 150s - 141t$			0, 1	0, 1		
P	= " + 2 × 452						
Q	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 2 \times 351$						
R	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 2 \times 535 + 895p'$	0-2					
S	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 2 \times 591 + 895p'$	0-2					
T	= " - $\left\{ \begin{smallmatrix} 591 \\ 586 \end{smallmatrix} \right\} + 2 \times 591 + 895p'$	0, 1					
U	= " - $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + \left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 895p' - 141t$	0-4			0, 1		
V	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 2 \times 509.5 + 895p'$	0, 1					
W	= " + 2 × 649						
X	= " + 2355 + 895 <i>p</i> '	0, 1					
X'	= " + 2333 + 895 <i>p</i> ' - 141 <i>t</i>	0-3			0, 1		
Y''	= " + $\left\{ \begin{smallmatrix} 509.5 \\ 505 \end{smallmatrix} \right\} + 3133 + 895p'$	0, 1					

Note : The frequency 38219 cm.⁻¹ is that of the electronic origin. The other frequencies are vibration frequencies, which are assigned to vibrations in Table III. The frequencies in braces are to be read alternatively. The symbols for quantum numbers are those used in Table II of Part VIII, and are defined in the Note beneath Table I of Part VIII (p. 464).

the vibrations will be made clear by reference to Part I, Section 7, and especially to Table V of that section (p. 415) (for diagrams of the vibrations, see *J.*, 1946, pp. 278-299).

The naming of the band series has been made to agree as far as possible with that used for the absorption spectrum of 1 : 4-dideuterobenzene : series A-E, G, G', H, H', J, j, K, L, M, N, P, Q, R, U, W, X, X', and Y'' correspond in the two spectra. Series A-E, G, H, J, M, and N correspond to the identically named series of all the absorption spectra of all the benzenes studied.

TABLE III.

Absorption Spectrum of 1 : 2 : 4 : 5-Tetradeuterobenzene. Assignment to Vibrations of the Vibration Frequencies (cm.⁻¹) contained in Table II.

Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (-).	Diffs. of upper- and lower-state fundamentals (-).	Vibration.
895	961	—	$A_g(C)$
509.5	591	81	$A_g(C\ 1)$
1414	—	—	$A_g(C\ 2)$
3133	—	—	$A_g(H\ 1)$
2355	—	—	$A_g(H\ 2)$
208	—	141	$A_u(C)$
591	—	—	$A_u(H)$
505	586	81	$B_{1g}(C\ 1)$
1414	—	—	$B_{1g}(C\ 2)$
2333	—	—	$B_{1g}(H\ 2)$
233	383	150	$B_{1u}(C)$
419	—	128	$B_{1u}(H\ 1)$
665	—	—	$B_{1u}(H\ 2)$
452	—	210	$B_{2g}(H)$
351	—	—	$B_{3g}(C)$
649	—	—	$B_{3g}(H\ 1)$
535	—	—	$B_{3g}(H\ 2)$

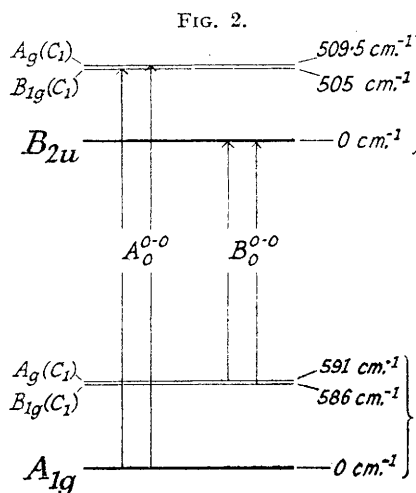
Note: By the addition of one quantum of the $A_u(C)$ vibration to one state, and one of the $B_{1u}(C)$ vibration to the other, difference frequencies of 175 cm.⁻¹ and 116 cm.⁻¹ arise, which appear explicitly in equations J and j of Table II.

(2) *Band Series A—D, U, and V.*—Series A—D, as usual, provide the main framework of the spectrum (cf. Part I, Section 4). As with 1 : 4-dideuterobenzene, they arise from one-quantum changes in *both* of the similar vibrations $A_g(C\ 1)$ and $B_{1g}(C\ 1)$, with the result that the bands of all four series are close doublets. The scheme of transitions for the two simplest active origins, A_0^{0-0} and B_0^{0-0} , is illustrated in Fig. 2. The reason why the origins C_0^{0-0} and D_0^{0-0} also appear as doublets, and not as higher multiplets, corresponding to the increase in the number of split levels with advancing quantum number, is doubtless the same as for 1 : 4-dideuterobenzene (Part VIII, Section 2).

The doublet separations of the fundamental vibrational levels, as given by the frequencies of the band maxima, are 4.5 cm.⁻¹ in the excited state and 5.0 cm.⁻¹ in the ground state—a little less, therefore, than for 1 : 4-dideuterobenzene, for which it is 5.5 cm.⁻¹ in either state. With reference to the ground state, Poole also obtained a somewhat smaller separation with 1 : 2 : 4 : 5-tetradeuterobenzene than with 1 : 4-dideuterobenzene, 3.2 cm.⁻¹ as against 4.3 cm.⁻¹, by resolution of the Raman doublets, although (as he appreciated) his individual separations were rendered low by the overlapping of rounded Raman bands (*J.*, 1946, 245, 276).

As regards the ground state, Herzfeld, Ingold, and Poole assigned the uppermost of the split fundamental levels to the $A_g(C\ 1)$ vibration (*J.*, 1946, 272). Part of their argument applies equally to the excited state, and suggests that here also the upper level belongs to the vibration $A_g(C\ 1)$, and the lower to the vibration $B_{1g}(C\ 1)$. Confirmation can, perhaps, be seen in the circumstance that the upper frequency appears to have a greater tendency than has the other to repeat itself in such a progression (characteristic of totally symmetrical vibrations) as that constituted by the three bands A_0^{0-0} , U_0^{0-0} , and V_0^{0-0} , or by other corresponding bands of these three series.

Series U involves the excitation of two upper-state quanta of the vibrations with which we are dealing, and series V the excitation of three such quanta, in transitions which in either case start from ground levels containing no such quanta. The persistence of series U is notable : a



Term scheme illustrating doublet structure of A and B bands. (Not to scale.)

series U is present in the absorption spectrum of 1 : 4-dideuterobenzene, but it is much less extensively developed. On the other hand, a closely corresponding series U is strongly developed in the absorption spectrum of benzene.

In all the series under discussion, progressions in the breathing frequency, $A_g(C)$, 895 cm.⁻¹ in the upper electronic state and 961 cm.⁻¹ in the lower state, follow the usual lines, except for maintaining the doublet structures of the four active origins.

As in the spectrum of 1 : 4-dideuterobenzene, so also in the present spectrum, series A—D involve two sequence intervals, which combine to give "simply branching" sequences (Part VIII, Section 1). The intervals are 141 cm.⁻¹ and 150 cm.⁻¹, but the latter value increases somewhat in the second quantum group, indicating some unelucidated disturbance to an overtone level.

The lower sequence interval is the same as the sequence interval of hexadeuterobenzene, and this identifies the 1 : 2 : 4 : 5-tetradeuterobenzene vibration as $A_u^+(C)$, the normal co-ordinate of which is identical with one normal co-ordinate of the sequence-forming vibration, $E_u^+(C)$, of hexadeuterobenzene (Bailey, Carson, Gordon, and Ingold, *J.*, 1946, 298; cf. their diagram XIV, p. 299). The higher sequence interval must, therefore, belong to the vibration $B_{1u}(C)$.

The series discussed determine the position of the electronic origin,

$$J_0^{0-0} = 38219 \pm 1 \text{ cm.}^{-1}$$

and the following fundamental frequencies :

$$\begin{array}{ll} A_g(C\ 1)_{\text{ground}} = 591 \text{ cm.}^{-1} & A_g(C\ 1)_{\text{excited}} = 509.5 \text{ cm.}^{-1} \\ B_{1g}(C\ 1)_{\text{ground}} = 586 \text{ cm.}^{-1} & B_{1g}(C\ 1)_{\text{excited}} = 505 \text{ cm.}^{-1} \\ A_g(C)_{\text{ground}} = 961 \text{ cm.}^{-1} & A_g(C)_{\text{excited}} = 895 \text{ cm.}^{-1} \end{array}$$

The ground-state frequencies as found in the Raman spectrum of liquid 1 : 2 : 4 : 5-tetradeuterobenzene are as follows : $A_g(C\ 1) = 589.0$ cm.⁻¹, $B_{1g}(C\ 1) = 585.8$ cm.⁻¹, $A_g(C) = 960.9$ cm.⁻¹ (Herzfeld, Hobden, Ingold, and Poole, *J.*, 1946, 272).

(3) *Band Series E.*—The main point for discussion concerning this series is whether the spectrum contains one such series or two. On theoretical grounds we expect two, because two distinct carbon-stretching vibrations, $A_g(C\ 2)$ and $B_{1g}(C\ 2)$, take the place of the degenerate carbon-stretching vibration $E_g^+(C\ 2)$, which is responsible for series E in the absorption spectrum of benzene or hexadeuterobenzene. Now the E bands of the present spectrum are at least double, and it would obviously be possible to assign one member of each pair of maxima to the vibration $A_g(C\ 2)$ and the other to the vibration $B_{1g}(C\ 2)$. However, we think that this might not be a correct interpretation. For all the E bands we have seen in the absorption spectra of isotopic benzenes, even those of benzene, 1 : 3 : 5-trideuterobenzene, and hexadeuterobenzene, have a characteristic double-band form; and when the E series clearly occurs in duplicate, as in the absorption spectrum of 1 : 4-dideuterobenzene, groups of four intensity maxima appear.

We suspect that two E series of 1 : 2 : 4 : 5-tetradeuterobenzene exist, but are accidentally coincident to such a degree that a clear resolution of such broad bands has not been possible. In the electronic ground state, as we know from Raman spectra, the separations, in mono-, 1 : 4-di-, 1 : 2 : 4 : 5-tetra-, and penta-deuterobenzene, of the split frequencies derived from the $E_g^+(C\ 2)$ vibration of benzene are 17, 18, 8, and 5 cm.⁻¹ respectively. In the last case the corresponding Raman line can just, but only just, be resolved (unpublished observation by H. G. Poole). The corresponding frequency separations in the upper electronic state should be represented by the separations of duplicate E series. Now we find duplicate E series in the absorption spectra of mono- and 1 : 4-di-deuterobenzene (Parts X and VIII), with separations of 24 and 20 cm.⁻¹—of the same order as the already mentioned separations in the ground state. If, for the $E_g^+(C\ 2)$ -derived vibrations of all these compounds, the frequency separations in the excited state should roughly follow the pattern of those in the ground state, the separations of duplicate E series in 1 : 2 : 4 : 5-tetra- and in penta-deuterobenzene would not improbably prove too small for observation by definite resolutions of the bands. Actually we are able to record a bare resolution of one of the E bands in the absorption spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene, but we could not repeat it for all the bands. The apparent separation of the resolved band, 3.5 cm.⁻¹, is, of course, likely to be rendered too low by the built-up intensity between the theoretical maxima. We have not yet seen the absorption spectrum of pentadeuterobenzene, but expect a similar difficulty in distinguishing duplicate E series there.

Taking, as for other E series, the lower-frequency maxima of the double bands as the better approximation to their vibrational origins, we assume the following as the best available values for the involved fundamental frequencies :

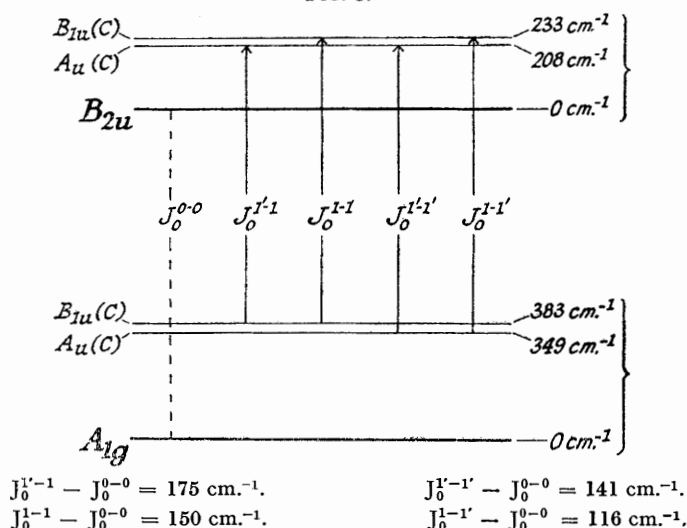
$$A_g(C\ 2)_{\text{excited}} = 1414 \text{ cm.}^{-1} \quad B_{1g}(C\ 2)_{\text{excited}} = 1414 \text{ cm.}^{-1}$$

The ground-state frequencies, as given in the Raman spectrum of liquid 1 : 2 : 4 : 5-tetradeuterobenzene, are $A_g(C\ 2) = 1572.1\text{ cm.}^{-1}$ and $B_{1g}(C\ 2) = 1564\text{ cm.}^{-1}$ (*idem, ibid.*).

(4) *Band Series G, G', H, J, and j.*—These series resemble the similarly named series of the absorption spectrum of 1 : 4-dideuterobenzene. Series G and G' are duplicate series, the former depending on upward 0—2, 1—3, . . . , transitions of the vibration $B_{1u}(C)$, and the latter on similar transitions of the vibration $A_u(C)$, in combination, in each case, with the electronic and vibrational transitions of series A. Of the two possible series H and H', analogously dependent on transitions of the vibrations $B_{1u}(C)$ and $A_u(C)$ respectively, but in combination with the transitions of series B rather than of series A, we can discern clearly only the parent band of series H, the rest of the series and the whole of the duplicate series H' being presumably obscured under the nearly continuous array of bands which in this spectrum, as in the absorption spectrum of 1 : 4-dideuterobenzene, constitute series J.

Just as in the spectrum of 1 : 4-dideuterobenzene, so also in the present spectrum, series J involves transitions between vibrating ground and electronically excited states containing the same *total* numbers of quanta of the vibrations $B_{1u}(C)$ and $A_u(C)$, but no other non-totally symmetrical quanta. Thus the series presents a "complex branching" sequence of many

FIG. 3.



Term scheme illustrating the development of series J. (Not to scale.)

weak bands. The one-quantum transitions are illustrated in Fig. 3; the 0—0 transition is, of course, forbidden. Again as in the spectrum of 1 : 4-dideuterobenzene, series j presents a less fully developed "complex branching" sequence, the transitions of which correspond to those of series J, but have additionally in each of the combining states one quantum of either the vibration $A_g(C\ 1)$ or the vibration $B_{1g}(C\ 1)$. Here the 0—0 transition, though theoretically allowed on account of the presence of the last-named vibrations, is too weak to produce an observed band.

The series discussed in this Section, together with the sequence belonging to the series considered in Section 2, enable us to fix the fundamental frequencies of the vibrations $A_u(C)$ and $B_{1u}(C)$ in both the lower and the upper electronic states :

$$\begin{array}{ll}
 A_u(C)_{\text{ground}} = 349\text{ cm.}^{-1} & A_u(C)_{\text{excited}} = 208\text{ cm.}^{-1} \\
 B_{1u}(C)_{\text{ground}} = 383\text{ cm.}^{-1} & B_{1u}(C)_{\text{excited}} = 233\text{ cm.}^{-1}
 \end{array}$$

The assignment of the lower frequency in each state to the $A_u(C)$ vibration is determined by the identity of the frequencies with those found for the $E_u^+(C)$ vibration of hexadeuterobenzene (Part IV, Section 3); for these vibrations must of principle have identical frequencies in each state (cf. Section 2). Considerations based on the forms of the normal co-ordinates would also lead us to assign the lower frequency in each state to the $A_u(C)$ vibration, in which the hydrogen motion is wholly concentrated in the deuterium atoms (Bailey, Carson, Gordon and Ingold, *loc. cit.*). The ground-state frequencies are subject to an independent check. For the $A_u(C)$ frequency has been indirectly estimated from higher harmonics of Raman and infra-red spectra

as 352 cm.⁻¹ (Herzfeld, Ingold, and Poole, *J.*, 1946, 316); and it has been directly observed as 350 cm.⁻¹ in the form of the E_u^+ fundamental in the Raman spectrum of liquid hexadeuterobenzene (Poole, *J.*, 1946, 245); whilst the $B_{1u}(C)$ fundamental band has been found, at 383 cm.⁻¹, in the infra-red spectrum of 1 : 2 : 4 : 5-tetradeuterobenzene vapour (Bailey, Carson, Gordon, and Ingold, *loc. cit.*).

(5) *Band Series K, K', k, k', κ, L, L', S, and T.*—According to our assignments, all these series are connected in various ways with one or other of the three hydrogen vibrations of the B_{1u} and A_u classes. Progressions K and K' commence with bands situated 837 cm.⁻¹ above A_0^{0-0} and B_0^{0-0} , respectively. Partly from reasons based on comparisons with absorption spectra of other benzenes (Part XI), and partly on the internal evidence of this spectrum, we assign the interval 837 cm.⁻¹ as the first overtone, in the upper electronic state, of the vibration $B_{1u}(H\ 1)$, the nearest analogue this molecule can produce of the hexagonal out-of-plane, hydrogen-bending vibration, $A_{2u}(H)$, of benzene or hexadeuterobenzene. Support is found in the series k and k', which consist of bands displaced by 128 cm.⁻¹ below the stronger bands of series A and B, respectively. We regard them as arising from 1—1 transitions of the vibration $B_{1u}(H\ 1)$, in combination with the transitions of the related A or B bands. Similar bands, for which the displacement is 114 cm.⁻¹, in the absorption spectrum of hexadeuterobenzene were attributed (Part IV, Section 5) to analogously combined 1—1 transitions of the allied vibration, $A_{2u}(H)$, of that molecule. The overtone frequency for 1 : 2 : 4 : 5-tetradeuterobenzene, 837 cm.⁻¹, corresponds to an upper-state fundamental frequency, 419 cm.⁻¹, which, in combination with the fundamental frequency, 383 cm.⁻¹, of one of the other vibrations, $B_{1u}(C)$, of the symmetry class B_{1u} accounts for the single band, κ , which is positively displaced from the main origin, A_0^{0-0} , by the interval 34 cm.⁻¹. Furthermore, our value for the upper-state fundamental frequency of the vibration $B_{1u}(H\ 1)$, when combined with the difference, 128 cm.⁻¹, between the lower- and upper-state fundamentals, provides a correct value for the already known fundamental frequency of this vibration in the electronic ground state.

The bands of series L and L' involve a positive displacement of 1330 cm.⁻¹ from A_0^{0-0} and J_0^{0-0} , respectively. Comparisons with other absorption spectra (Part XI) lead us to assign the common interval as the upper-state first overtone of the vibration $B_{1u}(H\ 2)$.

Progressions S and T commence with bands lying 1183 cm.⁻¹ above A_0^{0-0} and B_0^{0-0} respectively. We interpret the common interval as the first overtone, in the upper electronic state, of the vibration $A_u(H)$. The identification follows from the circumstance that the frequency of the vibration $A_u(H)$ must be identical with that of the vibration $E_u^+(H)$ of hexadeuterobenzene. This follows from a consideration of the normal co-ordinates of the two vibrations (Bailey, Carson, Gordon, and Ingold, *loc. cit.*). The frequency of the hexadeuterobenzene vibration has already been determined as 590 cm.⁻¹ (cf. Part IV, Section 10).

The above assignments lead to the following fundamental frequencies :

$$\begin{array}{ll} B_{1u}(H\ 1)_{\text{ground}} = 547\text{ cm.}^{-1} & B_{1u}(H\ 1)_{\text{excited}} = 419\text{ cm.}^{-1} \\ B_{1u}(H\ 2)_{\text{excited}} = 665\text{ cm.}^{-1} & A_u(H)_{\text{excited}} = 591\text{ cm.}^{-1} \end{array}$$

The ground-state fundamental frequencies of two of these vibrations have been observed in the infra-red spectrum (*idem, ibid.*) : $B_{1u}(H\ 1) = 548\text{ cm.}^{-1}$, $B_{1u}(H\ 2) = 925\text{ cm.}^{-1}$. The remaining ground-state frequency has been indirectly estimated, largely from Raman and infra-red combinations tones : $A_u(H) = 793\text{ cm.}^{-1}$ (Herzfeld, Ingold, and Poole, *loc. cit.*).

(6) *Band Series M, N, and P.*—Series M and N consist of bands negatively displaced from the stronger bands of series A and B, respectively, by the common interval 210 cm.⁻¹. They are interpreted as involving, in combination with the transitions of series A or B, 1—1 transitions of the vibration, $B_{2g}(H)$. This vibration is identical with one form of the degenerate vibration, $E_g^-(H)$, of hexadeuterobenzene, and is therefore identical in frequency with that vibration (Herzfeld, Hobden, Ingold, and Poole, *J.*, 1946, 285; cf. their diagram XII). In the absorption and in the fluorescence spectra of hexadeuterobenzene we find series, also called M and N, consisting of bands displaced from A or B bands by the identical interval, and these have been interpreted as involving 1—1 transitions of the vibration $E_g^-(H)$. Our assignment of the 1 : 2 : 4 : 5-tetradeuterobenzene series follows from this comparison. We recognise in the appearance of the single band P_0^{0-0} the excitation, in the upper electronic state, of the first overtone of the vibration $B_{2g}(H)$. These assignments lead to the following fundamental frequencies :

$$B_{2g}(H)_{\text{ground}} = 662\text{ cm.}^{-1} \qquad B_{2g}(H)_{\text{excited}} = 452\text{ cm.}^{-1}$$

The ground-state value, derived from the Raman spectrum of liquid 1 : 2 : 4 : 5-tetradeuterobenzene, is 663.6 cm.⁻¹ (*idem, J.*, 1946, 272).

(7) *Band Series Q, R, and W.*—These series are connected with the three vibrations of the symmetry class B_{3g} . They are assigned essentially on the basis of comparisons of the frequencies with those of other benzenes (Part XI). The single band Q_0^{0-0} , situated 702 cm.^{-1} above A_0^{0-0} , is explained as an excitation of the first overtone of the vibration $B_{3g}(C)$ in the upper electronic state, in combination with the electronic and vibrational transitions of A_0^{0-0} . The prominent band, R_0^{0-0} , the parent of progression R, lies 1070 cm.^{-1} above A_0^{0-0} , and is interpreted as an analogously combined excitation of the first overtone of the vibration $B_{3g}(H\ 2)$. Band W_0^{0-0} lies 1299 cm.^{-1} above the electronic origin, and is explained by the assumption of a transition from the "vibrationless" ground state to the two-quantum level of the vibration $B_{3g}(H\ 1)$ in the excited state. These assignments lead to the following fundamental frequencies:

$$\begin{aligned} B_{3g}(C)_{\text{excited}} &= 351\text{ cm.}^{-1} & B_{3g}(H\ 1)_{\text{excited}} &= 649\text{ cm.}^{-1} \\ B_{3g}(H\ 2)_{\text{excited}} &= 535\text{ cm.}^{-1} \end{aligned}$$

The corresponding ground-state frequencies, as found in the Raman spectrum of liquid 1 : 2 : 4 : 5-tetradeuterobenzene are as follows: $B_{3g}(C) = 615.1\text{ cm.}^{-1}$, $B_{3g}(H\ 1) = 929.7\text{ cm.}^{-1}$, $B_{3g}(H\ 2) = 767.1\text{ cm.}^{-1}$ (*idem*, *J.*, 1946, 272).

(8) *Band Series X, X', and Y''.*—Just above the strong band-group $A_0^{0-0} - E_1^{0-0}$ lie two sharp and conspicuous bands, displaced by 2333 cm.^{-1} and 2355 cm.^{-1} from the electronic origin. They are the parent bands of series X' and X, respectively. They probably gain some of their intensity by resonance with the neighbouring A and E bands; and especially is this likely to be true of the nearer band X_0^{0-0} , which starts a more extensive progression than its neighbour X_0^{0-0} . These series are obviously connected with the two deuterium-stretching vibrations—those of the A_g and B_{1g} classes—one-quantum excitations of which are allowed in the spectrum. The parent bands are explained by transitions from the "vibrationless" level of the electronic ground state to the fundamental levels of the vibrations in the excited state. The two vibrations thus have the upper-state fundamental frequencies 2333 cm.^{-1} and 2355 cm.^{-1} . We may reach a decision as to which belongs to the A_g and which to the B_{1g} vibration by an argument quite similar to that employed in connexion with the two analogous protium-stretching vibrations of 1 : 4-dideuterobenzene (Part VIII, Section 8). From a consideration of the normal co-ordinates, we expect the frequency of the $B_{1g}(H\ 2)$ vibration of 1 : 2 : 4 : 5-tetradeuterobenzene to lie very close to that of the $E_g^+(H\ 1)$ vibration of hexadeuterobenzene. The latter has the frequency 2320 cm.^{-1} (*cf.* Part IV); and therefore we assign to the $B_{1g}(H\ 2)$ vibration of 1 : 2 : 4 : 5-tetradeuterobenzene the lower of the two observed frequencies, 2333 cm.^{-1} , recognising that it may have been raised a few wave-numbers above its unperturbed value by the resonance already mentioned.

Progression Y'' starts with a band, $Y_0''^{0-0}$, which is strikingly sharp for the part of the spectrum in which it appears. It lies 3133 cm.^{-1} above A_0^{0-0} , and this interval we take to represent the fundamental frequency of the single protium-stretching vibration, $A_g(H\ 1)$, one-quantum excitations of which are allowed in the spectrum.

Thus we identify the following hydrogen-stretching fundamental frequencies of the excited state of 1 : 2 : 4 : 5-tetradeuterobenzene:

$$\begin{aligned} A_g(H\ 1)_{\text{excited}} &= 3133\text{ cm.}^{-1} & A_g(H\ 2)_{\text{excited}} &= 2355\text{ cm.}^{-1} \\ B_{1g}(H\ 2)_{\text{excited}} &= 2333\text{ cm.}^{-1} \end{aligned}$$

The corresponding ground-state frequencies, as determined by Herzfeld, Hobden, Ingold, and Poole (*loc. cit.*) from the Raman spectrum of the liquid, are as follows: $A_g(H\ 1) = 3045.0\text{ cm.}^{-1}$, $A_g(H\ 2) = 2285.0\text{ cm.}^{-1}$, $B_{1g}(H\ 2) = 2272\text{ cm.}^{-1}$. As usual, the frequencies of the hydrogen-stretching vibrations are higher in the excited state than in the ground state.

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

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