

98. *Excited States of Benzene. Part IV. Analysis of the First Ultraviolet Band System of the Absorption Spectrum of Hexadeuterobenzene.*

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The measurements of Sponer on the ultraviolet absorption spectrum of hexadeuterobenzene are analysed as outlined in the abstract of Part I. An attempt is made to assign all the observed bands. A list is given of ten fundamental frequencies of the electronically excited state, and all are assigned to vibrations. Part of the theoretical support for the assignments is given in this paper, and the remainder in Part XI.

(1) *Data.*—The first ultraviolet absorption system of hexadeuterobenzene has been described by Sponer (*J. Chem. Physics*, 1940, **8**, 705). She assigned many bands, and we accept nearly all her assignments. Her list of measured maxima was not so long as those we have already discussed; and, there being no very clear basis for selection, we have copied her complete list and tried to assign all the bands, as shown in Tables I, II, and III.

The notation has been made to agree with hers as far as possible: the band-series A—E, G, and K—N are as named by her. The series A—E, G, H, J, M, N, Q, W, and X correspond to those series in the absorption spectrum of benzene to which we gave the same labels (Part II, Section 1). The other series have less close analogies, or no analogies, with the discussed series in related spectra. Lower-case letters are used to label a few bands, the interpretation of which is more than usually tentative.

(2) *Band Series A—F and F'.*—The band series A—D depend on one-quantum changes in the degenerate carbon-bending vibration $E_g^+(C\ 1)$. As with ordinary benzene (Part II, Section 2), these series form the main framework of the absorption spectrum (cf. Part I, Section 4).

Series E involves a one-quantum excitation in the upper electronic state of the degenerate carbon-stretching vibration $E_g^+(C\ 2)$. It is relatively somewhat stronger than for benzene, and, as in that case, we assume that it obtains most of its intensity by resonance with the nearby bands of series A (cf. Part II, Section 3). A weak series called F appears, the bands of which lie below those of series E by 80 cm.^{-1} . This is the sequence interval, *i.e.*, the difference between the fundamental frequencies of a vibration in the lower and upper electronic states, for the vibration $E_g^+(C\ 1)$ of hexadeuterobenzene: we conclude that, as compared with E bands, the

TABLE I.

Absorption Spectrum of Hexadeuterobenzene. Frequencies and Intensities (Sponer); and Assignments (cf. Tables II and III).

Freq. (cm. ⁻¹).	Inty. (25°).	Assgnt.	Freq. (cm. ⁻¹).	Inty. (-35°).	Assgnt.	Freq. (cm. ⁻¹).	Inty. (-35°).	Assgnt.
36487	vw	B ₋₁ ²	38494·8	w	R ₀ ⁰	40271	ew	A ₂ ²
626·2	m	B ₋₁ ¹	505·1	w	A ₀ ²	280	mw	E ₁ ²
657	vw	L ₋₁ ⁰	514	vw	D ₁ ⁰	303	ew	
686	w	D ₋₁ ⁰	533	vw	K ₀ ¹	325	ew	C ₂ ¹
764·6	s	B ₋₁ ⁰	564	w	C ₀ ¹	351·9	mw	B ₃ ⁰
			574	vw	M ₀ ⁰	375	w	U ₂ ⁰
	Inty. (0°)		580·6	w		406	w	A ₂ ¹
			588·1	w		421·2	m	E ₁ ¹
37278	w	S ₁ ¹	591·9	w	B ₁ ⁰	426	ew	
294	w	B ₀ ³	592·5	w		436·8	mw	E ₁ ¹
340	ew	D ₀ ⁰	647·1	s		441·7	vw	
348	vw			653·7	w	A ₀ ¹	461·8	w
358	ew	N ₀ ⁰	676·1	mw	K ₀ ⁰	480·3	w	F ₁ ⁰
365	vw			705·3	m	C ₀ ⁰	498·4	
371	vw		709·3	m			545·5	vs
419·6	m	S ₀ ⁰	736	vw	A ₁₋₁ ⁰	566·6	s	E ₁ ⁰
432·1	m	B ₀ ²	760·3	w	E ₋₁ ⁰	580·9	m	
460·9	w	L ₀ ¹	787·5	vs	A ₀ ⁰	610·5	w	Q ₀ ⁰
488·4	m	D ₀ ¹	790·2	vs			630·8	vw
504·6	m	N ₀ ⁰	39056	ew	P ₀ ¹	663	ew	q ₀ '
508·8	w			067	ew	G ₀ ¹	852	w
540	vw	V ₀ ⁰	118	ew	j ₁ '''	969	ew	G ₂ ⁰
548·8	w			190	ew	P ₀ ⁰	995	vw
572·2	s	B ₁ ¹	199	vw			41083	vw
599·3	m	L ₀ ⁰	208	vw	C ₀ ⁰	151	w	E ₂ ²
630·5	m	D ₀ ⁰	334	ew	B ₂ ¹	200	w	C ₃ ¹
656·0	w	B ₁₋₁ ⁰	372·8	w	R ₁ ⁰	233	w	B ₄ ²
674·4	w	C ₆ HD ₆ ?	385·4	w	A ₁ ²	295	mw	E ₂ ¹
712·0	vs	B ₀ ⁰	402·9	w	T ₀ ⁰	310·6	mw	
720	vw			455·0	w	M ₁ ⁰	318	mw
730	vw	K ₀₋₁ ⁰	470·4	w	B ₂ ⁰	332	ew	C ₃ ⁰
765·8	w	C ₋₁ ⁰	502·9	w	U ₁ ⁰	357·1	w	F ₂ ⁰
797	vw	O ₀ ²	526·6	s	A ₁ ¹	417·6	mw	A ₃ ⁰
844·6	s	A ₋₁ ⁰	533·8	w			440·7	s
872	vw	J ₀ ²	546·2	w	E ₀ ¹	453·6	m	
939	w	O ₀ ¹	553	w			480·5	mw
986·2	mw	H ₀ ¹	566·4	mw		502·5	vw	q ₁
38001·8	m	J ₀ ²	587·7	m	C ₁ ⁰	530	ew	q ₁ '
010·5	mw			609·3	vw	F ₀ ⁰	555	ew
044·0	w	j ₁ ¹	669·0	vs	A ₁ ⁰	728	vw	X ₂ ⁰
085·9	m	O ₀ ⁰	693·4	s	E ₀ ⁰	773	ew	q ₁ '''
095·1	w	I ₀ ⁰	706·6	m			961	ew
126·7	m	H ₀ ⁰	953	ew	X ₀ ⁰	42198	ew	E ₃ ¹
150·3	s	J ₀ ¹	973	ew			326	m
185·1	m	j ₀ ⁰	40093	ew	G ₁ ⁰	348	m	Q ₂ ⁰
205	m	j ₀ '	120	ew	W ₀ ⁰	373	ew	q ₂
220·0	m	j ₀ ''	146	ew	N ₀ ⁰	390	ew	q ₂ '
242	m	j ₀ '''	181	ew	C ₂ ²	43195	w	E ₄ ⁰
			213	ew	B ₃ ¹	220	vw	Q ₃ ⁰

Notes.—(1) The temperatures in the column of intensities are those of saturated vapour at the pressure in the absorption tube. The intensity indications (ranging from vs = very strong to ew = extremely weak) are to be judged with reference to these temperatures.

(2) The significance of the numerical parts of the symbols in the column of assignments is explained under Table I of Part II (p. 419). The letter symbols in this Table are defined in the following tables.

TABLE II.

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

	Freq. (cm. ⁻¹).	<i>p</i> '.	<i>p</i> '.	<i>s</i> .
A	= 38290 + 499 + 879 <i>p</i> ' - 943 <i>p</i> '' - 141 <i>s</i>	0-3	0, 1	0-2
B	= " - 579 + 879 <i>p</i> ' - 943 <i>p</i> '' - 141 <i>s</i>	0-4	0, 1	0-3
C	= " + 2 × 499 - 579 + 879 <i>p</i> ' - 943 <i>p</i> '' - 141 <i>s</i>	0-3	0, 1	0-2
D	= " + 499 - 2 × 579 + 879 <i>p</i> ' - 943 <i>p</i> '' - 141 <i>s</i>	0, 1	0, 1	0-2
E	= " + 1403 + 879 <i>p</i> ' - 943 <i>p</i> '' - 141 <i>s</i>	0-4	0, 1	0-2
F	= " + 499 - 579 + 1403 + 879 <i>p</i> '	0-2		
F'	= " + 2 × 1403 + 879 <i>p</i> '	0, 1		
G	= " + 499 + 2 × 208 + 879 <i>p</i> ' - 141 <i>s</i>	0-2		0, 1
H	= " - 579 + 2 × 208 - 141 <i>s</i>			0, 1
I	= " + 499 - 2 × 350			
J	= " - 141 <i>s</i>			1-3
j	= " - 105 - 141 <i>s</i>			0, 1
j'	= " - 85			
j''	= " - 70			
j'''	= " - 48 + 879 <i>p</i> '	0, 1		
K	= " + 499 - 114 - 943 <i>p</i> '' - 141 <i>s</i>		0, 1	0, 1
L	= " - 579 - 114 - 943 <i>p</i> '' - 141 <i>s</i>		0, 1	0, 1
M	= " + 499 - 208 + 879 <i>p</i> '	0, 1		
N	= " - 579 - 208 + 879 <i>p</i> ' - 141 <i>s</i>	0, 3		0, 1
O	= " - 208 - 141 <i>s</i>			0-2
P	= " + 2 × 454 - 141 <i>s</i>			0, 1
Q	= " + 2320 + 879 <i>p</i> '	0-3		
q	= " + 2340 + 879 <i>p</i> '	0-2		
q'	= " + 2372 + 879 <i>p</i> '	0-2		
q''	= " + 3265			
q'''	= " + 3483			
R	= " + 499 - 295 + 879 <i>p</i> '	0, 1		
S	= " - 579 - 295 - 141 <i>s</i>			0, 1
T	= " + 499 + 2 × 306			
U	= " + 499 - 165 + 879 <i>p</i> '	1, 2		
V	= " - 579 - 165			
W	= " + 499 + 2 × 663 + 879 <i>p</i> '	0, 1		
X	= " + 499 + 2 × 590 + 879 <i>p</i> '	0-2		

Note: The frequency 38290 cm.⁻¹ is that of the electronic origin. The other frequencies are vibration frequencies, and they are assigned to vibrations in Table III. Concerning the frequencies 105, 85, 70, 48, 2340, 2372, 3265, and 3483 cm.⁻¹, see text (Sections 4 and 7).

TABLE III.

Absorption Spectrum of Hexadeuterobenzene. 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.
879	943	64	<i>A</i> _{1g} (C)
(382)	—	114	<i>A</i> _{2u} (H)
306	—	295	<i>B</i> _{2g} (C)
663	—	165	<i>B</i> _{2g} (H)
499	579	80	<i>E</i> _g ⁺ (C 1)
1403	—	—	<i>E</i> _g ⁺ (C 2)
2320	—	—	<i>E</i> _g ⁺ (H 1)
(830)	—	—	<i>E</i> _g ⁺ (H 2)
208	350	141	<i>E</i> _u ⁺ (C)
590	—	—	<i>E</i> _u ⁺ (H)
454	—	208	<i>E</i> _g ⁻ (H)

Note: Concerning the frequencies 382 cm.⁻¹ and 830 cm.⁻¹, see text (Sections 5 and 11).

F bands have one additional quantum of this vibration in each of the combining states. Thus series F is related to E, just as D is to B, or as C is to A.

Generally, the series here discussed display progressions in the totally symmetrical vibration, *A*_{1g}(C). They are mainly positive in the interval 879 cm.⁻¹, but the beginnings of negative progressions in 943 cm.⁻¹ can also be seen. The stronger bands of the progressions are the

starting points of negatively-running sequences in the low frequency vibration $E_u^+(C)$, the sequence interval for this vibration of hexadeuterobenzene being 141 cm.^{-1} .

These bands, and analogous bands of the fluorescence spectrum (Part V, Section 2), determine the electronic origin for hexadeuterobenzene,

$$J_0^0 = 38290 \pm 1 \text{ cm.}^{-1},$$

as well as the following vibration frequencies :

$$\begin{array}{ll} A_{1g}(C)_{\text{ground}} = 943 \text{ cm.}^{-1} & A_{1g}(C)_{\text{excited}} = 879 \text{ cm.}^{-1} \\ E_g^+(C 1)_{\text{ground}} = 579 \text{ cm.}^{-1} & E_g^+(C 1)_{\text{excited}} = 499 \text{ cm.}^{-1} \\ E_g^+(C 2)_{\text{excited}} = 1403 \text{ cm.}^{-1} & E_u^+(C)_{\text{ground}} - E_u^+(C)_{\text{excited}} = 141 \text{ cm.}^{-1} \end{array}$$

The fundamental frequencies of the electronic ground state, as thus determined, agree satisfactorily with the values given by the Raman spectrum of liquid hexadeuterobenzene, *viz.*, $A_{1g}(C) = 943.2 \text{ cm.}^{-1}$, and $E_g^+(C 1) = 577.4 \text{ cm.}^{-1}$ (Poole, *J.*, 1946, 245).

A weak progression, called F' , consists of a band lying 2793 cm.^{-1} above the electronic origin, followed by a second band after the usual interval 879 cm.^{-1} . We associate these bands with a transition, which starts from the "vibrationless" ground state, and involves the excitation in the upper electronic state of two quanta of the degenerate carbon-stretching vibration $E_g^+(C 2)$. Such transitions are allowed on account of the degenerate nature of the vibration (Part I, Section 5).

(3) *Band Series G, H, I, and J.*—These series depend especially on the low-frequency vibration, $E_u^+(C)$. Series G and H, which start with bands lying 416 cm.^{-1} above A_0^0 and B_0^0 , involve the excitation in the upper electronic state of two quanta of this vibration, in combination with the electronic and vibrational transitions characteristic of series A and B respectively. The sequences in 141 cm.^{-1} , which are contained in series G and H, therefore involve upward transitions of the type 0—2, 1—3, . . ., in the vibration $E_u^+(C)$.

In the single band I_0^0 , lying 695 cm.^{-1} below A_0^0 , we observe the loss of two ground-state quanta of the vibration $E_u^+(C)$ in an upward 2—0 transition, which takes place in combination with the electronic and vibrational transitions characteristic of A_0^0 . Lower-state overtone frequencies are seldom observed in the absorption spectra of benzenes, but here the very low value of the frequency renders the Boltzmann factor less inhibitory than usual.

On account of the degenerate nature of the vibration $E_u^+(C)$ we are allowed to observe the excitation of two of its upper-state quanta, in combination with the electronic transition, but without associated changes in any other non-totally symmetrical vibration (cf. Part I, Section 5). This is actually observed in the absorption spectrum of ordinary benzene (cf. Part II, Section 4). A corresponding observation with hexadeuterobenzene is, however, precluded, because the bands which would be thus produced would coincide with the strong bands of series C.

The degeneracy of the vibration $E_u^+(C)$ also permits the occurrence, in combination with the electronic transition, of 1—1, 2—2, and, in general, n — n transitions of this vibration (provided that $n \neq 0$), without associated changes in any other non-totally symmetrical vibration. Such transitions give rise to the series, called J, which is found in the absorption and fluorescence spectra of ordinary benzene (Part II, Section 4; Part III, Section 3). A similar series, also called J, is found in the absorption (and in the fluorescence) spectrum of hexadeuterobenzene. It appears as a negatively running sequence in 141 cm.^{-1} , which starts as if from the electronic origin, except that the 0—0 band is missing.

From all these bands, and from analogous bands of the fluorescence spectrum (Part V, Section 3), we deduce the following fundamental frequencies of hexadeuterobenzene :

$$E_u(C)_{\text{ground}} = 350 \text{ cm.}^{-1} \quad E_u(C)_{\text{excited}} = 208 \text{ cm.}^{-1}$$

The ground-state frequency agrees well with other estimates. This fundamental frequency is forbidden in both Raman and infra-red spectra, but Poole has recently observed it in the Raman spectrum of liquid hexadeuterobenzene, its weak appearance there being evidently due to the perturbing effect of cohesive forces. His observed frequency was 350 cm.^{-1} (*loc. cit.*). Herzfeld, Ingold, and Poole estimated this frequency from combination tones in the Raman and infra-red spectra of hexadeuterobenzene. Their value is 352 cm.^{-1} (*J.*, 1946, 316).

(4) *Band Series j, j', j'', j'''.*—Between the 1—1 band of the J sequence and the electronic origin lie four weak bands, separated from the latter by the intervals 105, 85, 70, and 48 cm.^{-1} .

Two of them appear to have companions displaced either by the positive progression interval, 879 cm.⁻¹, or by the negative sequence interval, 141 cm.⁻¹. No definite assignments are suggested for these bands, and all we seek to show is that they are not incapable of being plausibly interpreted.

Three of them have allowed explanations (cf. Part I, Section 5) as combinations, involving not more than two vibrational quanta in either electronic state, of frequencies otherwise determined. They are as follows :

$$\begin{aligned} j &= \begin{cases} J_0^0 - E_g^+(\text{H } 2)867 + B_{2g}(\text{C})306 + E_g^-(\text{H})454 = J_0^0 - 107 \text{ cm.}^{-1} \\ J_0^0 - E_u^-(\text{H } 1)813 + E_g^+(\text{C } 1)499 + E_u^+(\text{C})208 = J_0^0 - 106 \text{ cm.}^{-1} \end{cases} \\ j' &= J_0^0 - E_u^+(\text{H})793 + E_g^+(\text{C } 1)499 + E_u^+(\text{C})208 = J_0^0 - 86 \text{ cm.}^{-1} \\ j'' &= J_0^0 - E_g^-(\text{H})662 + A_{2u}(\text{H})382 + E_u^+(\text{C})208 = J_0^0 - 72 \text{ cm.}^{-1} \end{aligned}$$

The fourth, $j''' = J_0^0 - 48 \text{ cm.}^{-1}$, might have an explanation of the same general form, but involving one of the not accurately known upper-state fundamental frequencies, for instance, one of the four planar deuterium-bending frequencies.

Alternatively, any of the bands might represent a 1—1 transition of some degenerate vibration for which the Boltzmann factor is not prohibitively small. An interpretation of $j' = J_0^0 - 85 \text{ cm.}^{-1}$ as a 1—1 transition of the vibration $E_g^+(\text{C } 1)$, unaccompanied by any other vibrational change, cannot be excluded. And any of the other bands might have a similar explanation involving 1—1 transitions of one of the degenerate deuterium-bending vibrations, $E_g^+(\text{H } 2)$ and $E_u^-(\text{H } 1)$, whose frequencies in the upper electronic state we do not yet know with precision.

(5) *Band Series K and L.*—One of the most striking qualitative differences between the absorption spectra of benzene and of hexadeuterobenzene is the following. In both spectra the recurrent gaps of 161 cm.⁻¹ or 141 cm.⁻¹ between the stronger bands of both series A and B are each cut into two roughly equal parts by the somewhat weaker bands of series C and D respectively. But in the hexadeuterobenzene spectrum every gap of 141 cm.⁻¹ belonging to series A and B is further divided, now about three-quarters down, by a band which is not very much weaker than the half-way band. The three-quarter-way bands associated with series A form series K, and those belonging to series B form series L. Each K or L band lies 114 cm.⁻¹ below an A or B band.

Sponer has already suggested that these K and L bands involve 1—1 transitions of some vibration superposed upon the transitions characteristic of A or B bands. Strong evidence for the correctness of this view is afforded by comparison with the fluorescence spectrum (Part V, Section 4). Here the K and L bands again appear, with approximately the same intensities relative to the now-altered intensities of the associated A and B bands, and with the same negatively directed displacement of 114 cm.⁻¹, even though the main progressions run the opposite way to what they do in absorption.

For reasons given in an accompanying paper (Part XI), we assign these bands to excitations in each electronic state of the hexagonal, out-of-plane vibration $A_{2u}(\text{H})$. The interval 114 cm.⁻¹ then represents the difference between the fundamental frequencies of this vibration in the lower and upper electronic states.

It is probable that the first overtone of this vibration in the upper electronic state is involved in a progression, which is not separately assigned in Table I, because of the difficulty of being sure that the bands concerned are really separate from some neighbouring broad bands of the E series. If we should assign this progression separately, the first band would lie 763 cm.⁻¹ above the main origin A_0^0 , the interval, 763 cm.⁻¹, corresponding to the upper-state overtone frequency. From these assignments, the following fundamental frequencies may be derived :

$$A_{2u}(\text{H})_{\text{ground}} = 496 \text{ cm.}^{-1} \quad A_{2u}(\text{H})_{\text{excited}} = 382 \text{ cm.}^{-1}$$

The fundamental frequency for the electronic ground state agrees with the value, 496.5 cm.⁻¹, observed by Bailey, Carson, and Ingold as the frequency of the long-wave fundamental band in the infra-red spectrum of hexadeuterobenzene vapour (*J.*, 1946, 252). Both the frequencies are well confirmed by the fluorescence spectrum (cf. Part V, Section 4).

It has to be explained why bands corresponding to the K and L bands of hexadeuterobenzene are not observed in either the absorption or the fluorescence spectrum of benzene. Of course, a rather smaller Boltzmann factor will apply to benzene. But the main reason, we believe, is that the sequence interval of the $A_{2u}(\text{H})$ vibration of benzene is so close to 161 cm.⁻¹, that the

expected bands are obscured under the 1—1 bands of the E_u^+ (C) sequences. On the other hand, the benzene progression corresponding to the difficultly verifiable overtone progression of hexadeuterobenzene is readily observed in the absorption spectrum of benzene, its position there being favourable for observation.

(6) *Band Series M, N, O, and P.*—Series M and N consist of a number of bands of considerable intensity each situated 208 cm^{-1} below one of the stronger bands of series A and B. Spomer has suggested (*loc. cit.*) that these bands involve 1—1 transitions of some vibration, in combination with the electronic and vibrational transitions characteristic of A or B bands. As before, comparison with the fluorescence spectrum (Part V, Section 5) well supports this view.

Partly on the internal evidence of the spectrum, and partly from comparisons between different spectra (Part XI) we assign the interval 208 cm^{-1} as the difference between the fundamental frequencies of the vibration $E_g^-(\text{H})$ in the two electronic states. This vibration being degenerate, its 1—1 transitions need not be accompanied by other vibrational changes (Part I, Section 5). Consistently, we find the interval 208 cm^{-1} appearing in series O as a negative displacement from the electronic origin. Series O is present also in the fluorescence spectrum (Part V, Section 5).

The degeneracy of the vibration would also permit the excitation of its first overtone without accompanying vibrational changes (*loc. cit.*). Consistently, we find in the absorption spectrum a series called P, which starts with a band 909 cm^{-1} above the electronic origin, the interval 909 cm^{-1} being evidently the upper-state overtone frequency.

These assignments enable us to deduce the following fundamental frequencies :

$$E_g^-(\text{H})_{\text{ground}} = 662 \text{ cm}^{-1} \qquad E_g^-(\text{H})_{\text{excited}} = 454 \text{ cm}^{-1}$$

The fundamental frequency in the electronic ground state, as given by the Raman spectrum of liquid hexadeuterobenzene, is 661.7 cm^{-1} (Poole, *loc. cit.*). Both the frequencies are well confirmed by the fluorescence spectrum (Part V, Section 5).

It is not impossible that some part of the intensity of the bands of series M, N, and O, in either absorption or fluorescence or both, may be due to 1—1 transitions of the vibration $E_u^-(\text{H})$, since the difference between the fundamental frequencies of this vibration in the lower and upper electronic states happens to be quite close to 208 cm^{-1} . The Boltzmann factors would be smaller for this vibration (*cf.* Section 10).

(7) *Band Series Q, q, q', q'', and q'''.*—Progression Q, the parent band of which lies 2320 cm^{-1} above the electronic origin, is the most prominent of the progressions occupying the high-frequency end of the absorption spectrum of hexadeuterobenzene. Obviously this series is to be correlated with the series, also called Q, in the absorption spectrum of benzene. We therefore assign the hexadeuterobenzene series in the same way as the benzene series, assuming the parent band Q_0^0 to involve transitions from the "vibrationless" level of the electronic ground state to the one-quantum level of the E_g^+ hydrogen-stretching vibration in the electronically excited state. This assignment gives the following fundamental frequency of the upper state :

$$E_g^+(\text{H } 1)_{\text{excited}} = 2320 \text{ cm}^{-1}$$

The bands of the Q series in the hexadeuterobenzene spectrum are accompanied by a fairly regular pattern of weak satellites. Those which lie 20 cm^{-1} above the Q bands constitute series q, and the very weak ones 52 cm^{-1} above the Q bands form series q'; a single very weak band 75 cm^{-1} above one of the Q bands is called q''. We think that these bands represent combination frequencies which have gained intensity by resonance with the neighbouring Q bands, and, except for this, would probably have been unobservably weak. For each satellite series, several possible explanations exist, each requiring the assumption of some plausible value of an upper-state frequency which is not exactly known—a fundamental of one of the symmetry classes, A_{2g} , B_{2u} , and E_u^- . The alternative interpretations are too hypothetical to list, but we give as example, the following explanation, in which the first of the involved fundamental frequencies is independently determined (Part XI), whilst the second is chosen to fit :

$$q'' = J_0^0 + 940(B_{1u}) + 2325(E_u^-)$$

All that can really be said of the second component frequency is that, since it is the fundamental frequency of a deuterium-stretching vibration, it must be close to the known E_g^+ frequency, 2320 cm^{-1} .

A further weak high-frequency band called q''' lies 1163 cm^{-1} above Q_0^0 . No well-supported

assignment can be given, but it may be noted that the band might be attributed to the excitation, in combination with the electronic and vibrational transition of Q_0^0 , of the first overtone of the vibration $E_u^+(\text{H})$, the fundamental frequency of which, as otherwise determined, is 590 cm.^{-1} .

(8) *Band Series R, S, and T.*—Series R and S commence with bands, R_0^0 and S_0^0 , lying 295 cm.^{-1} below the active origins A_0^0 and B_0^0 respectively. As with some of the series considered in Sections 5 and 6, we suppose series R and S to involve 1—1 vibrational transitions, superposed on the electronic and vibrational transitions characteristic of series A and B respectively. The interval 295 cm.^{-1} is, then, the difference between the fundamental frequencies of some vibration in the lower and upper electronic states. Comparison with the fluorescence spectrum (Part V, Section 7), in which the same displacements are found in association with oppositely running progressions, gives strong support to this interpretation.

We identify the vibration concerned as the trigonal, out-of-plane vibration, $B_{2g}(\text{C})$ (cf. Part XI). To it we also relate the series T, represented in Table I by the single band T_0^0 , although in fact this may start a progression, the upper members of which we do not assign, because of the difficulty of being sure that they are distinct from some neighbouring, complex bands of series E. The band T_0^0 lies 613 cm.^{-1} above the main active origin A_0^0 , and we interpret the interval as the first overtone in the upper electronic state of the vibration $B_{2g}(\text{C})$.

These assignments, supported by others relating to the fluorescence spectrum, lead to the following fundamental frequencies :

$$B_{2g}(\text{C})_{\text{ground}} = 601\text{ cm.}^{-1} \quad B_{2g}(\text{C})_{\text{excited}} = 306\text{ cm.}^{-1}$$

This fundamental vibration is forbidden in the infra-red and Raman spectra, but a study of these spectra of certain partly deuterated benzenes, and of higher harmonic frequencies in the spectra of hexadeuterobenzene, led Herzfeld, Ingold, and Poole (*loc. cit.*) to assign the value 601 cm.^{-1} as the fundamental $B_{2g}(\text{C})$ frequency of the ground state of hexadeuterobenzene.

(9) *Band Series U, V, and W.*—Series U and V comprise a number of weak bands negatively displaced by a common interval, 165 cm.^{-1} , from the stronger bands of series A and B respectively. The U and V bands are always overlapped by the relatively strong bands displaced by the ubiquitous interval, 141 cm.^{-1} , from the same A and B bands. Doubtless for this reason, the first band, U_0^0 , of the U progression, overlapped as it is by the strong band A_0^1 , has not been measured in the absorption spectrum. However, it has been measured ($38625\cdot3\text{ cm.}^{-1}$) in the fluorescence spectrum (Part V, Table I). We explain series U and V by assuming a 1—1 vibrational transition, in combination with the electronic and vibrational transitions characteristic of series A and B respectively. Comparison with the fluorescence spectrum, where we find the same interval in association with oppositely running progressions, gives strong support to this interpretation (Part V, Section 8). The interval 165 cm.^{-1} is, then, the difference between the fundamental frequencies of some vibration in the two electronic states.

For reasons given later, we identify the vibration involved as the trigonal, out-of-plane vibration $B_{2g}(\text{H})$ (cf. Part XI). To the same vibration we relate the series W, the parent band of which, W_0^0 , lies 1326 cm.^{-1} above the main active origin A_0^0 . This interval we regard as the first overtone of the vibration $B_{2g}(\text{H})$ in the upper electronic state.

From these assignments, and others related to the fluorescence spectrum, we may deduce the following fundamental frequencies :

$$B_{2g}(\text{H})_{\text{ground}} = 828\text{ cm.}^{-1} \quad B_{2g}(\text{H})_{\text{excited}} = 663\text{ cm.}^{-1}$$

The ground-state value agrees with the value, 827 cm.^{-1} , derived by Herzfeld, Ingold, and Poole (*loc. cit.*) by the methods mentioned above in connexion with the $B_{2g}(\text{C})$ vibration (preceding Section).

(10) *Band Series X.*—The three observed bands of this progression lie positively displaced by 1180 cm.^{-1} from the three strongest bands of series A. The common interval is evidently an upper-state frequency of total symmetry, excited in combination with the electronic and vibrational transitions characteristic of series A. For reasons given later (Part XI) we assign the interval as the first overtone of out-of-plane degenerate vibration $E_u^+(\text{H})$. The fundamental frequency which results from this assignment is as follows :

$$E_u^+(\text{H})_{\text{excited}} = 590\text{ cm.}^{-1}$$

We were not able to find, in either the absorption or the fluorescence spectrum of hexadeuterobenzene, any distinct bands displaced from A or B bands by the sequence interval of this

vibration. This may be due in part to the proximity of the sequence interval to that of the vibration $E_g^-(H)$, *viz.*, 208 cm^{-1} . Possibly 1—1 transitions of the vibration $E_u^+(H)$ contribute to the intensity of those bands which arise mainly from 1—1 transitions of the vibration $E_g^-(H)$ (cf. Section 6). The fundamental frequency $E_u^+(H)$ of the electronic ground state has been determined by Herzfeld, Ingold, and Poole (*loc. cit.*), largely from combination tones in the Raman and infra-red spectra of hexadeuterobenzene. Their value is 793 cm^{-1} .

(11) *The Bands at 39118 and 39953 cm^{-1} .*—Sponer (*loc. cit.*) has very reasonably suggested that the band at 39118 cm^{-1} might be assigned to a transition from the "vibrationless" ground state to the one-quantum level of the planar deuterium-bending vibration, $E_g^+(H\ 2)$, in the upper electronic state. This transition is allowed by the selection rules. It must also be remarked that the band at 39953 cm^{-1} , instead of being part of a doublet structure attributed to the band X_0^0 in Table I, might arise from a transition from the "vibrationless" ground state to the two-quantum level of the vibration, $E_g^+(H\ 2)$, in the upper electronic state. This transition would also be allowed by the selection rules. These assignments, necessarily tentative, lead to the following upper-state fundamental frequency :

$$E_g^+(H\ 2)_{\text{excited}} = 830\ \text{cm}^{-1}$$

The corresponding ground-state frequency, as given in the Raman spectrum of liquid hexadeuterobenzene, is 867.3 cm^{-1} (Poole, *loc. cit.*). Indications of a closely similar planar deuterium-bending frequency of the upper electronic state are found in the absorption spectrum of 1 : 3 : 5-trideuterobenzene (Part VI, Section 4).

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