99. *Excited States of Benzene. Part V. Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of Hexadeuterobenzene.*

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The measurements of Ingold and Wilson on the ultraviolet fluorescence spectrum of hexadeuterobenzene are analysed as outlined in the abstract of Part I. A number of fundamental frequencies of both electronic states are recognised, and are assigned to their vibrations.

(1) *Data.*—The ultraviolet fluorescence spectrum of hexadeuterobenzene has been studied experimentally by Ingold and Wilson (*J.*, 1936, 941, 1210). In analysing their data, we have followed the procedure adopted in the case of the fluorescence spectrum of benzene, including the re-examination of original plates and microphotometer records (cf. Part III, Section 1). The results of this analysis are set out in Tables I, II, and III, which are arranged like the corresponding tables in the preceding papers.

The notation applied to the various series has been made to agree as closely as possible with that used for the fluorescence spectrum of benzene, and for the absorption spectrum of hexadeuterobenzene. The following identically named series correspond in the fluorescence spectra of benzene and hexadeuterobenzene in the closest way possible, *viz.*, that the same vibrations enter in the same manner into each, although, of course, the actual frequencies are different : A, B, C, D, H, J, M, N, O, P, Q. The following identically named series correspond in the absorption and fluorescence spectra of hexadeuterobenzene in the closest possible way, *viz.*, that all non-totally symmetrical vibrations enter in the same way, and with the same frequencies, into each, the only difference being that the totally symmetrical progressions run mainly towards the positive direction in absorption and towards the negative in fluorescence : A, B, C, D, H, J, K, L, M, N, O, R, S, U, V. The following identically named series also correspond in the absorption and fluorescence spectra of hexadeuterobenzene, but less closely, the further difference being that a non-totally symmetrical vibration enters into the absorption spectrum through the excitation of one quantum in the upper electronic state and into the fluorescence spectrum through a similar excitation in the electronic ground state : I, Q, T.

TABLE I.

Fluorescence Spectrum of Hexadeuterobenzene. Frequencies and Intensities (*Ingold and Wilson*); *and Assignments* (*cf. Tables II and III*).

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
38789·1	m	A^0_0	37502·7	m	N^0_0	36207·4	w	B^4_{-1}
737·3	ww	A^0_{1-1}	486·3	m	D^1_0	191·4	w	S^2_{-1}
709·8	mw	C^0_0	459·4	w	L^1_0	064·0	ww	B^5_{-1}
672·7	w	K^0_0	430·4	ms	B^2_0	047·8	ww	S^3_{-1}
653·9	w	A^1_0	418·4	ms	S^0_0	014·3	w	Q^0_0
647·1	m		373·5	w	N^1_0	35957·5	ww	A^0_{-3}
625·3	ww	U^0_0	362·5	w		934·8	w	X^0_0
616·4	ww	P''	352·1	w	D^2_0	928·7	w	
588·5	mw	B^0_1	346·5	w		878·2	ww	Q^1_0
581·2	mw	M^0_0	291·1	m	B^3_0	852·8	ww	W^0_{-1}
569·0	mw	C^1_0	276·3	m	S^1_0	825·2	ms	B^0_{-2}
563·5	w		224·0	ww	N^2_0	778·3	ww	F^0_{-1}
532·7	ww	K^1_0	216·4	ww	D^3_0	763·2	ww	B^0_{1-3}
503·4	mw	A^2_0	211·8	ww		748·2	w	D^0_{-2}
493·0	mw	R^0_0	150·1	w	B^4_0	717·2	ww	L^0_{-2}
474·9	w	G^0_0	133·7	w	S^2_0	684·7	m	B^1_{-2}
446·5	w	B^1_1	016·1	ww	B^5_0	618·8	mw	N^0_{-2}
436·5	w	M^1_0	011·1	ww		604·6	w	D^1_{-2}
427·4	w	C^2_0	004·8	ww	I^0_0	577·1	ww	L^1_-
416·2	ww		36990·5	ww	S^3_0	560·4	ww	Y^0_{-1}
409·3	ww		965·7	ww	P'	554·6	ww	
368·5	w	A^3_0	898·7	w	A^0_{-2}	544·3	mw	B^2_{-2}
352·8	ww	R^1_0	888·1	ww		533·9	w	S^0_-
322·8	ww	T^0_0	877·2	ww		478·5	ww	N^1_{-2}
311·6	ww	B^2_1	845·0	ww	A^0_{1-3}	470·3	ww	D^2_{-2}
300·4	ww	M^2_0	824·2	ww	C^0_{-2}	426·6	ww	Z^0_0
286·6	ww	C^3_0	800·4	ww	W^0_0	402·4	ww	B^3_{-2}
147·1	ww	J^1_0	766·9	ss	B^0_{-1}	391·3	ww	S^1_{-2}
141·6	ww		716·9	w	F^0_0	245·9	ww	S^2_{-2}
124·4	ww	H^0_0	704·8	w	B^0_{1-2}	069·7	mw	Q^0_{-1}
085·5	ww	O^0_0	686·7	m	D^0_{-1}	014·3	ww	A^0_{-4}
078·4	ww		656·1	mw	L^0_{-1}	34990·5	w	X^0_{-1}
007·2	w	J^2_0	626·5	s	B^1_{-1}	930·7	ww	Q^1_{-1}
37999·9	w		560·0	m	N^0_{-1}	906·1	ww	W^0_{-2}
984·8	w	H^1_0	545·1	m	D^1_{-1}	884·5	mw	B^0_{-3}
947·1	ww	O^1_0	511·6	ww	L^1_{-1}	744·5	w	B^1_{-3}
933·9	ww		500·2	ww	Y^0_0	682·8	ww	N^0_{-3}
871·5	ww	J^3_0	486·4	m	B^2_{-1}	602·0	ww	B^2_{-3}
841·4	m	A^0_{-1}	476·1	m	S^0_{-1}	592·7	ww	S^0_{-3}
795·1	ww	E^0_0	421·4	w	N^1_{-1}	482·3	ww	Z^0_{-1}
783·4	ww	A^0_{1-2}	406·3	w	D^2_{-1}	117·3	ww	Q^0_{-2}
764·5	w	C^0_{-1}	388·1	ww	P	33969·4	ww	W^0_{-3}
727·1	ww	K^0_{-1}	362·8	ww	Y^1_0	944·2	w	B^0_{-4}
709·4	ss	B^0_0	346·3	mw	B^3_{-1}	789·1	ww	B^1_{-4}
628·8	m	D^0_0	332·4	mw	S^1_{-1}	737·2	ww	N^0_{-4}
597·1	mw	L^0_0	278·5	ww	N^2_{-1}	644·3	ww	S^0_{-4}
570·1	s	B^1_0	269·0	ww	D^3_{-1}	004·6	ww	B^0_{-5}
548·4	w	V^0_0						

Note: The intensity symbols, and the numerical parts of the assignment symbols are explained in the notes beneath Table I of Part III (p. 428), and the note under Table I of Part II (p. 419). The letter-symbols here used are defined in the following Tables.

TABLE II.

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

	Freq. (cm.$^{-1}$).	p'.	p''.	s.
A	$= 38290 + 499 + 879p' - 943p'' - 141s$	0, 1	0—4	0—3
B	$=$,, $- 579 + 879p' - 943p'' - 141s$	0, 1	0—5	0—5
C	$=$,, $+ 2 \times 499 - 579 - 943p'' - 141s$		0—3	0—3
D	$=$,, $+ 499 - 2 \times 579 - 943p'' - 141s$		0—2	0—3
E	$=$,, $+ 499 - 2 \times 496$			
F	$=$,, $- 579 - 2 \times 496 - 943p''$		0, 1	
G	$=$,, $- 579 + 2 \times 382$			
H	$=$,, $- 579 + 2 \times 208 - 141s$			0, 1
I	$=$,, $- 579 - 2 \times 350$			
J	$=$,, $- 141s$			1—3
K	$=$,, $+ 499 - 114 - 943p'' - 141s$		0, 1	0, 1
L	$=$,, $- 579 - 114 - 943p'' - 141s$		0—2	0, 1
M	$=$,, $+ 499 - 208 - 141s$			0—2
N	$=$,, $- 579 - 208 - 943p'' - 141s$		0—4	0—2
O	$=$,, $- 208 - 141s$			0, 1
P	$=$,, $- 579 - 2 \times 662$			
P′	$=$,, $- 2 \times 662$			
P″	$=$,, $- 579 + 2 \times 454$			
Q	$=$,, $- 2275 - 943p'' - 141s$		0—2	0, 1
R	$=$,, $+ 499 - 295 - 141s$			0, 1
S	$=$,, $- 579 - 295 - 943p'' - 141s$		0—4	0—3
T	$=$,, $- 579 + 2 \times 306$			
U	$=$,, $+ 499 - 165$			
V	$=$,, $- 579 - 165$			
W	$=$,, $- 662 - 828 - 943p''$		0—3	
X	$=$,, $- 2275 + 499 - 579 - 943p''$		0, 1	
Y	$=$,, $+ 499 - 2286 - 943p'' - 141\mathrm{s}$		0, 1	0, 1
Z	$=$,, $- 579 - 2286 - 943p''$		0, 1	

TABLE III.

Fluorescence 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	A_{1g}(C)
—	2286	—	A_{1g}(H)
382	496	114	A_{2u}(H)
306	—	295	B_{2g}(C)
—	828	165	B_{2g}(H)
499	579	80	E_g^+(C 1)
—	2275	—	E_g^+(H 1)
208	350	141	E_u^+(C)
454	662	208	E_g^-(H)

(2) *Band Series* A—D.—These four series control the general pattern of the spectrum (cf. Part I, Section 4). They confirm the already given frequencies of the electronic origin, and of the fundamental vibrations, E_g^+(C 1) and A_{1g}(C), in both the upper and lower electronic states (Part IV, Section 2).

The fluorescence spectrum of hexadeuterobenzene does not show the striking resonance effects which in the fluorescence spectrum of benzene arise from the almost exact degeneracy of the combination E_g^+(C 1) + A_{1g}(C) with the fundamental frequency E_g^+(C 2) in the electronic ground state of benzene. In the ground state of hexadeuterobenzene, the combination has the frequency 1522 cm.$^{-1}$, whilst the fundamental frequency, as we know from the Raman spectrum, is 1552 cm.$^{-1}$; and in the fluorescence spectrum, as in the Raman spectrum, one finds no obvious transfer of intensity due to resonance between these two energy levels. Indeed, in the fluorescence spectrum, we can see nothing of the band which could arise from a transition between the " vibrationless " upper state and the E_g^+(C 2) fundamental level of the lower electronic state. The position is over-lapped by the tail of the combination band situated 1522 cm.$^{-1}$ below the electronic origin, but a band 1552 cm.$^{-1}$ from the origin, unless it were quite weak, should be visible as a disturbance to the rotational envelope.

(3) *Band Series* H, I, *and* J.—These series depend on changes of two or zero in the quantum number of the low-frequency vibration, E_u^+(C). They contribute, along with similar series in the absorption spectrum of hexadeuterobenzene, to the determination of the lower- and upper-state fundamental frequencies of this vibration, *viz.*, 350 cm.$^{-1}$ and 208 cm.$^{-1}$, as already noted in Part IV, Section 3.

Series H consists of a negatively running sequence in 141 cm.$^{-1}$, which starts with a band H_0^0 situated 415 cm.$^{-1}$ above B_0^0. In this sequence we are observing downward 2—0, 3—1, . . . , transitions of the E_u^+(C) vibration, in combination with those electronic and vibrational transitions which, when alone, produce the active origin B_0^0. These bands provide a value for the upper-state overtone frequency of the vibration E_u^+(C).

The band I_0^0, lying 704 cm.$^{-1}$ below B_0^0, arises from a downward 0—2 transition of the vibration E_u^+(C), combined in the same way with the electronic and vibrational transitions characteristic of B_0^0. This band gives us a value for the lower-state overtone frequency. Because of the degenerate character of the vibration, and its not particularly small Boltzmann factors, the transitions 2—0 and 0—2 might also be expected to appear without an accompanying change in any other vibration (Part I, Section 5). But the bands which could thus arise cannot be verified because of overlapping.

The transitions 1—1, 2—2, . . . , of the vibration E_u^+(C) occur as the sequences in 141 cm.$^{-1}$ which are found in most of the stronger series of the fluorescence, as of the absorption, spectrum of hexadeuterobenzene. But the degenerate nature of the vibration also permits transitions 1—1, 2—2, . . . , without accompanying changes in other vibrations (*loc. cit.*). Such transitions form the bands of series J, which are prominent in the fluorescence, as well as in the absorption, spectrum of hexadeuterobenzene (cf. Part IV, Section 3). The series consists essentially of a negative sequence in 141 cm.$^{-1}$, which runs as if from the forbidden electronic origin, except that the 0—0 band is missing.

(4) *Band Series* E, F, G, K, *and* L.—For reasons given in Part XI we assign the vibration frequencies peculiar to these bands to the hexagonal, out-of-plane vibration A_{2u}(H). Certain series related to this vibration were also found in the absorption spectrum of hexadeuterobenzene (Part IV, Section 5). However, the fluorescence spectrum of hexadeuterobenzene supplies more complete evidence concerning the fundamental frequencies of this vibration than can be obtained from the absorption spectrum. In different series of the fluorescence spectrum we find the upper-state overtone frequency, the lower-state overtone frequency, and the difference between the fundamental frequencies in the two electronic states, all agreeing with the deduced fundamental frequencies of the vibration, 496 cm.$^{-1}$ and 382 cm.$^{-1}$, in the lower and upper states, respectively.

The series E and F start with bands E_0^0 and F_0^0, situated 993 cm.$^{-1}$ below A_0^0 and B_0^0, respectively. Evidently they involve the excitation of two quanta of this vibration in the lower electronic state, in combination with those electronic and vibrational changes which by themselves produce the bands of series A and B respectively. These bands provide a value, 993 cm.$^{-1}$, for the lower-state overtone frequency. They are rather stronger than overtone bands usually are. In the Raman spectrum of hexadeuterobenzene the overtone of the A_{2u}(H) vibration appears more strongly than is usual for first overtones, and much more strongly than does the corresponding overtone in the Raman spectrum of benzene. We explain this by assuming for hexadeuterobenzene a certain amount of intensification of the overtone frequency, 2 × 496 cm.$^{-1}$, by resonance with the very strong A_{1g}(C) frequency at 943 cm.$^{-1}$, even though the separation of the two amounts to 50 cm.$^{-1}$. Similarly we suppose that the E and F bands of the fluorescence spectrum owe their relative prominence to resonance with those bands of the A_{1g}(C) progressions of series A and B, which lie 50 cm.$^{-1}$ below them.

The weak band G_0^0, situated 765 cm.$^{-1}$ above B_0^0, is assumed to involve a transition from the second quantum level of the A_{2u}(H) vibration in the upper electronic state, the loss of both quanta being superposed on those electronic and vibrational changes which characterise the strong origin B_0^0. This band furnishes a value, 765 cm.$^{-1}$, for the upper-state overtone frequency.

The series K and L, like the identically named series of the absorption spectrum (cf. Part IV, Section 5), consist of a number of bands of moderate intensity, negatively displaced by 114 cm.$^{-1}$ from the more prominent bands of series A and B respectively. They arise from 1—1 transitions of the A_{2u}(H) vibration, in combination with those electronic and vibrational transitions which produce the related A and B bands. The sequence interval, 114 cm.$^{-1}$, corresponds to the difference between the fundamental frequencies of the vibration A_{2u}(H) in the lower and upper electronic states.

(5) *Band Series* M, N, O, P, P′, *and* P″.—If we accept the assignments given in Part XI, all these bands are connected in one way or another with the degenerate, out-of-plane vibration, E_g^-(H). Again the fluorescence spectrum of hexadeuterobenzene provides more complete evidence concerning the fundamental frequencies of this vibration than can be obtained from the absorption spectrum (Part IV, Section 6), since in fluorescence we find the upper- and lower-state overtone frequencies, as well as the difference between the fundamental frequencies in the two states, all agreeing with the deduced fundamental frequencies, 662 cm.$^{-1}$ and 454 cm.$^{-1}$, for the lower and upper states, respectively.

Series M and N, like the identically named series of the absorption spectrum (Part IV, Section 6), consist of a number of bands of moderate intensity negatively displaced by 208 cm.$^{-1}$ from bands of series A and B, respectively. They arise from 1—1 transitions of the vibration E_g^-(H), superposed on those electronic and vibrational changes which produce the related A or B bands. The interval 208 cm.$^{-1}$ corresponds to the difference between the fundamental frequencies of the vibration in the two electronic states.

The degeneracy of the vibration permits a 1—1 transition in combination with the electronic transition only, and without other vibrational changes (Part I, Section 5). Thus arises the band O_0^0, which appears 208 cm.$^{-1}$ below the forbidden electronic origin. It is the parent band of the series O, which consists of a negatively-running sequence in the interval, 141 cm.$^{-1}$, *n*—*n* transitions in the vibration E_u^+(C) being here combined with 1—1 transitions of the vibration E_g^+(H). The same series, containing identically the same bands, is observed in the absorption spectrum (Part IV, Section 6).

The bands P and P′ lie 1332 cm.$^{-1}$ below the active origin B_0^0, and the electronic origin J_0^0, respectively. In explanation of them, we assume an excitation of the first overtone of the vibration E_g^-(H) in the lower electronic state, the interval, 1332 cm.$^{-1}$, representing the overtone frequency. Band P involves a combination of the overtone excitation with the electronic and vibrational transition characteristic of the strong fluorescence origin B_0^0. Band P′ involves no vibrational change other than the overtone excitation, this transition being made possible by the degenerate nature of the vibration E_g^-(H) (Part I, Section 5).

A very weak band P″ is situated 907 cm.$^{-1}$ above the main fluorescence origin B_0^0. We assume a prior excitation of the E_g^-(H) vibration by two quanta in the electronically excited state, the transition involving the loss of these quanta in combination with those electronic and vibrational changes which alone would produce the origin B_0^0. This band furnishes a value, 907 cm.$^{-1}$, for the upper-state overtone frequency of the vibration E_g^-(H).

(6) *Band Series* Q, X, Y, *and* Z.—These series all involve the excitation in the lower electronic state of one of the hydrogen-stretching frequencies—either E_g^+(H 1) or A_{1g}(H).

The progression and sequences which constitute series Q start with a band Q_0^0 lying 2275 cm.$^{-1}$ below the electronic origin. In explanation we assume a transition from the "vibrationless" level of the electronically excited state to the fundamental level of the degenerate vibration E_g^+(H 1) in the electronic ground state. As with the corresponding series in the fluorescence spectrum of benzene (cf. Part III, Section 5), the E_g^+(H 1) vibration here appears with a fundamental frequency, 2275 cm.$^{-1}$, which is 0·4% greater than the frequency, 2264·9 cm.$^{-1}$, observed in the Raman spectrum of liquid hexadeuterobenzene (Poole, *J.*, 1946, 252). We suggest a similar explanation, *viz.*, that, in the Raman spectrum of the liquid, the frequency is reduced by an interaction, which becomes permitted in the presence of cohesive forces, with the slightly higher, but close-lying and intense, fundamental frequency A_{1g}(H).

The two strongest bands of series Q have weak companions, negatively displaced by 80 cm.$^{-1}$: they constitute series X. The displacement corresponds to the difference between the fundamental frequencies of the vibration E_g^+(C 1) in the lower and upper electronic states, and we therefore assume the bands of series X to involve 1—1 transitions of this vibration, superposed on those transitions which produce the associated bands of series Q. Thus series X is related to series Q, exactly as series C is to series A, or as series D is to series B.

The parent bands, Y_0^0 and Z_0^0, of the somewhat weak series Y and Z are found 2286 cm.$^{-1}$ below the active orgins A_0^0 and B_0^0, respectively. We assume these series to arise in an excitation, in the electronic ground state, of one quantum of the totally symmetrical, hydrogen-stretching vibration, A_1 (H), this excitation being superposed on those electronic and vibrational changes which produce the bands of series A and B respectively. The fundamental frequency of the vibration A_{1g}(H), as given by the displacement of Y_0^0 from A_0^0, or of Z_0^0 from B_0^0, is 2286 cm.$^{-1}$. The value given by the Raman spectrum of liquid hexadeuterobenzene is 2292·6 cm.$^{-1}$ (Poole, *loc. cit.*). The difference may not be significant, but if it is, it can be explained on the lines suggested above.

(7) *Band Series* R, S, *and* T.—According to our assignment, which we seek to justify in Part XI, the special vibrational changes which characterise these bands are related to the trigonal, out-of-plane vibration, B_{2g}(C). Closely related series are found in the absorption spectrum of hexadeuterobenzene. Together, these series provide values for the fundamental frequencies, 602 cm.$^{-1}$ and 307 cm.$^{-1}$, of the vibration B_{2g}(C) in the two electronic states (cf. Part IV, Section 8).

Series R and S, like the identically named series of the absorption spectrum, consist of bands of moderate intensity negatively displaced by 295 cm.$^{-1}$ from the stronger bands of series A and B, respectively. We interpret the interval 295 cm.$^{-1}$ as the difference between the two fundamental frequencies of the vibration B_{2g}(C). The bands arise when 1—1 transitions of this vibration become combined with those electronic or vibrational changes which, if alone, would produce the associated bands of series A and B.

The band T_0^0 is situated 613 cm.$^{-1}$ above the main fluorescence origin B_0^0. It is assumed to involve the prior excitation of the first overtone frequency of the vibration B_{2g}(C) in the upper electronic state : the transition involves the loss of these two quanta, in association with those electronic and vibrational changes which characterise B_0^0. A band, also called T_0^0, lying 613 cm.$^{-1}$ above the main absorption origin A_0^0, is found in the absorption spectrum of hexadeuterobenzene (cf. Part IV, Section 8) ; and it is given a similar explanation. The common interval, 613 cm.$^{-1}$, is taken as the upper-state overtone frequency.

(8) *Band Series* U, V, *and* W.—In Part XI we give reasons for connecting these bands with excitations, in either or both of the interacting states, of the trigonal, out-of-plane vibration, B_{2g}(H). Some related series are found in the absorption spectrum of hexadeuterobenzene. Together, the absorption and fluorescence series furnish values for the two fundamental frequencies, 828 cm.$^{-1}$ and 663 cm.$^{-1}$, of the B_{2g}(H) vibration (cf. Part IV, Section 9).

The weak series U and V correspond closely to the similarly named series of the absorption spectrum. In fluorescence, each is represented by a single listed band, though several further V bands can be seen on the plates. In absorption and fluorescence, the common characteristic of U and V bands is that each is negatively displaced by 165 cm.$^{-1}$ from an A or B band. The interval is interpreted as the difference between the fundamental frequencies of the vibration B_{2g}(H) in the lower and upper electronic states. In the formation of U and V bands, a 1—1 transition of this vibration accompanies those electronic or vibrational changes which, when alone, produce the associated A or B bands.

The progression W starts with a band 1490 cm.$^{-1}$ above the electronic origin. We assign this interval as the frequency of a combination between two vibrations in the electronic ground state : $E_g^-(\mathrm{H})662 + B_{2g}(\mathrm{H})828 = 1490$ cm.$^{-1}$. The combination has the symmetry E_g^+, and therefore could constitute the terminal vibrational level of a transition from the " vibrationless " excited state (Part I, Section 5). On the other hand, this particular combination frequency has not been observed in the Raman spectrum, and therefore one naturally looks for some special explanation of the relative strength and persistence of the W progression in the fluorescence spectrum. Our explanation assumes an intensification by resonance with bands of the B progression. Each W band lies only about 30 cm.$^{-1}$ away from a strong B band, and each of these close pairs of bands fulfils the conditions for resonance.

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