256. *Structure of Benzene. Part IX. Direct Observation of the Fluorescence Spectra of Benzene and Hexadeuterobenzene Vapour in the Region of Absorption.*

By Christopher L. Wilson.

The resonance spectrum emitted by benzene vapour at 0·1 mm. when irradiated by the mercury line at 2537 A. is due to transitions from a vibration level in the excited state to one of the various permitted vibration levels of the ground state. Rotation may be disregarded for the present purpose since its only effect is to give the vibration bands a certain fine structure. Although the initial energy level, and consequently the position of the whole spectrum on a frequency scale, depends upon the excitation employed, the vibrational structure is dependent only on the vibrational levels of the ground state.

Upon increasing the pressure of benzene vapour the vibrational energy of the excited molecule is dissipated by molecular collision before emission. Consequently the resonance spectrum is quenched and replaced by the characteristic high-pressure fluorescence. This is due to transitions from the non-vibrating electronically excited molecule to the various possible vibration levels in the ground state.

These matters have been dealt with fully in Parts V and VI of this series (this vol., pp. 941, 955). In the former, the high-pressure fluorescence spectra of benzene and hexadeuterobenzene were satisfactorily analysed by the assumption of three electron levels and two vibrational frequencies of the ground state. Only one of these levels (A_0^0) * was directly observed as the common origin of the two vibrational progressions, each of which has a spacing equal to one of the vibration frequencies.

The other two electron levels (B_0^0 and C_0^0) would be represented by bands on the short-wave side of A_0^0, in a region of strong absorption, and they, along with the first few corresponding vibration bands, were unobserved. However, an estimation of the energies of C_0^0 and B_0^0 could have been made by an analysis of as much of their vibrational progressions as appears on the long-wave side of A_0^0 which is the limit of strong absorption; any such argument, however, could not have been regarded as conclusive.

The levels B_0^0 and C_0^0 for benzene and hexadeuterobenzene have now been directly observed by a method depending on an observation of Cuthbertson and Kistiakowsky (*J. Chem. Physics*, 1936, **4**, 9) which had not been published at the time of our previous work. They showed that if the resonance emission of benzene is quenched, not by an additional pressure of benzene molecules, but by some non-absorbing foreign gas, it is possible to observe the whole of the fluorescence spectrum arising from the three electron levels we are interested in, and in particular that portion of it which overlaps the region of absorption. It is reasonable to expect such a difference in behaviour between benzene at a high pressure and at a low pressure in the presence of a foreign gas, since absorption and emission are different functions of the pressure; the former, following an exponential law, falls off the more rapidly as the partial pressure of benzene is reduced.

In the experiments now described nitrogen at 760 mm. and benzene at 0·1—0·3 mm. gave the best results. This high pressure of foreign gas was necessary because even at 40 mm. the resonance emission was incompletely quenched; the characteristic doublet at 38,212 cm.$^{-1}$ was still prominent.

The Spectra and their Analysis.—Only that portion of the fluorescence on the short-wave side of A_0^0 has been measured, since a full description of the rest is given in Part V. The results for benzene are in Table II (in which I represents the intensity), and the arrangement into vibrational progressions of 162 cm.$^{-1}$ spacings in Table III. The spectrum is shown in the upper half of the fig., in which the lines are plotted on a frequency scale. The intensities are qualitatively estimated from microphotometer tracings.

Cuthbertson and Kistiakowsky's brief description of the spectrum as well as our previous

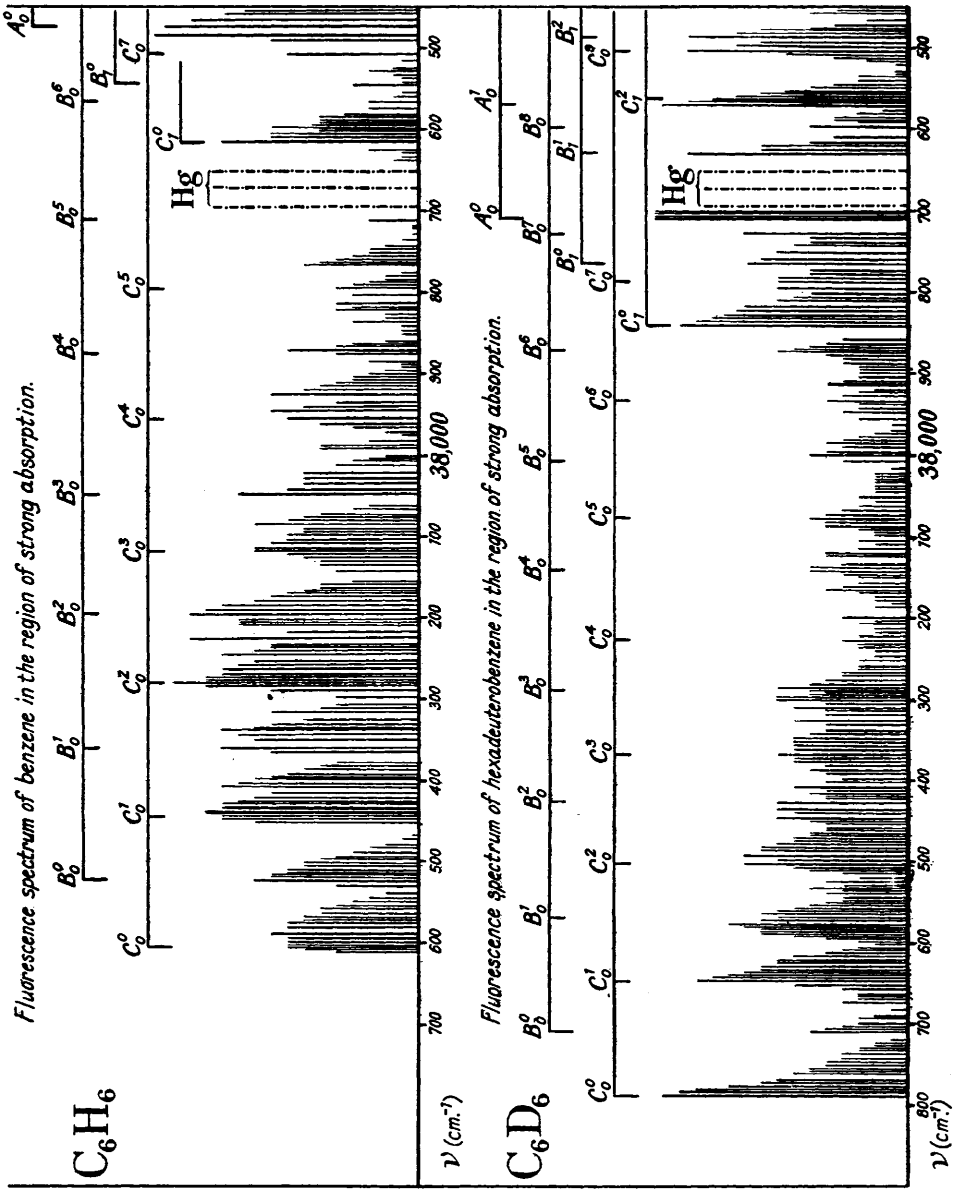
* The general notation $(A, B, \text{ or } C)_n^p$ was used to represent a band, n and p being the quantum numbers of the two vibrations.

deductions are adequately confirmed. The two progressions are separated by 83 cm.$^{-1}$ and revised values of the frequencies of B_0^0 and C_0^0 are given in Table I.

TABLE I.

Electron Terms in Fluorescence of Benzene and Hexadeuterobenzene (*cm.*$^{-1}$).

Symbol.	C_6H_6.	C_6D_6.	$\Delta\nu$.
A_0^0	37,473	37,709	236
B_0^0	38,522	38,710	188
C_0^0	38,605	38,789	184



There is one minor difficulty. Each band in the C-series from C_0^1 onwards has been assumed to possess at least two maxima about 30 cm.$^{-1}$ apart, and although the results might have indicated a fourth electron level there is no support for this alternative either in the rest of the fluorescence spectrum (Part V) or in the spectrum of hexadeuterobenzene (below). Rotational fine structure gives the bands considerable width (C_0^0 is 75 cm.$^{-1}$ broad) and perhaps a variation of the normal intensity relations within a band can be caused by the superposition of the bands of an absorption system which originates at A_0^0 and progresses towards the ultra-violet. The satellites associated with C_0^4 and C_0^5 are particularly strong and were recorded in our previous measurements (Part V).

Hexadeuterobenzene gives an analogous spectrum (see fig., lower half); B_0^0 and C_0^0 are located at positions indicated in Table I, and, compared with benzene, they are shifted towards the ultra-violet by reason of the smaller zero-point energy of the heavier molecule. The separation between the two progressions, now of 142 cm.$^{-1}$ spacing (see Table V), is 79 cm.$^{-1}$.

In the figure both spectra have been continued as far as the A_0^0 band head to indicate their complementary nature to Fig. 3 of Part V.

Experimental.

The apparatus has been described previously (Part V, *loc. cit.*). and was adapted to the present requirements.

TABLE II.

Fluorescence Spectrum of Benzene Vapour.

(Short-wave section.)

λ (air), A.	ν (vac.), cm.$^{-1}$.	*I.*	λ (air), A.	ν (vac.), cm.$^{-1}$.	*I.*	λ (air), A.	ν (vac.), cm.$^{-1}$.	*I.*	λ (air), A.	ν (vac.), cm.$^{-1}$.	*I.*
2589·07	38612·4	5	2603·88	38392·8	8	2621·03	38141·6	5	2637·77	37899·5	3
9·36	08·0	7	4·31	86·4	7	1·63	32·8	6	8·10	94·8	2
9·55	05·2	8	4·65	81·4	6	1·77	30·8	6	8·30	91·9	1
9·67	03·4	8	4·85	78·5	5	2·15	25·3	7	8·57	88·0	1
2590·04	38597·9	8	5·76	65·1	9	2·39	21·8	8	8·76	85·3	3
0·38	92·8	8	6·14	59·5	12	2·71	18·1	10	9·48	75·0	5
0·71	87·9	9	6·77	50·2	10	2·97	14·3	10	9·79	70·5	8
1·20	80·6	8	7·17	44·3	11	3·42	06·8	9	2640·05	66·8	5
1·64	74·1	8	7·54	38·9	12	3·64	03·6	8	0·30	63·2	4
1·82	71·4	7	7·72	36·2	10	4·03	38098·0	8	0·52	60·1	2
2·10	67·2	7	8·11	30·5	9	4·37	93·0	7	1·06	52·3	1*b*
2·42	62·5	6	8·49	24·9	7	4·49	91·3	7	1·45	46·7	1
2·77	57·3	6	9·03	17·0	9	4·99	84·0	10	1·79	41·8	1
3·00	53·8	5	9·43	11·1	6	5·36	78·7	8	2·16	36·6	4
3·40	47·9	4	9·70	07·2	5	5·62	74·9	7	2·49	31·8	2*b*
3·68	43·7	3	2610·36	38297·5	5	5·85	71·6	6	2·82	27·1	2
4·07	38·0	2	0·83	90·6	9	6·24	65·9	4*b*	3·16	22·3	5
4·62	29·8	5	1·26	84·3	13	6·54	61·6	3	3·32	20·0	4
5·12	22·4	10	1·46	81·4	15	7·58	46·5	11	3·75	13·8	5
5·33	19·2	9	1·78	76·6	13	7·90	41·9	8	4·52	02·8	4*b*
5·53	16·3	9	1·97	73·9	13	8·40	34·6	7	5·10	37794·5	5
5·70	13·7	8	2·24	69·9	12	8·84	28·2	7*b*	5·40	90·2	4
5·96	09·9	8	2·70	63·2	12	9·35	20·9	7	5·56	87·9	3
6·31	04·7	7	3·05	58·0	11	9·97	11·9	5*b*	5·86	83·7	2
6·53	01·4	7	3·42	52·6	10	2630·38	06·0	4	6·10	80·2	2
6·94	38495·4	6	3·94	45·0	12	0·53	03·8	3	6·43	75·5	1
7·06	93·6	5	4·26	40·3	10	0·73	00·9	2	7·09	66·1	7
7·45	87·8	4	4·48	37·1	9	1·40	37991·3	6	7·29	63·2	6*b*
7·88	81·4	3	4·66	34·5	9	1·54	89·2	6	7·54	59·7	5
8·09	78·3	2	5·26	25·7	14	2·07	81·6	3	7·77	56·4	4
8·50	72·3	1	5·80	17·8	8	2·55	74·7	1	8·09	51·8	3
8·80	67·8	0	6·39	09·2	11	2·78	71·3	2	8·41	47·3	3
9·86	52·1	10	6·55	06·9	11	3·12	66·4	4	8·77	42·1	2
2600·17	47·5	12	6·70	04·7	11	3·49	61·1	6	9·17	36·4	1*b*
0·41	44·0	12	7·33	38195·5	14	3·84	56·1	8	9·80	27·5	0
0·79	38·4	13	7·71	89·9	13	4·56	45·7	9	2650·18	22·1	0
1·10	33·8	12	8·13	83·8	12	4·91	40·7	7	0·32	20·1	0
1·40	29·4	12	8·49	78·6	10	5·23	36·1	5	0·42	18·7	0
1·66	25·5	11	8·86	73·2	9	5·94	25·8	9	0·89	12·0	3
1·99	20·6	10	9·13	69·2	8	6·34	20·1	7	7·63	37616·3	18
2·29	16·2	9	9·32	66·5	7	6·68	15·2	6	2662·78	37543·6	4
2·95	06·5	12	9·57	62·8	6	6·96	11·2	5	5·22	09·2	8
3·14	03·7	11	9·87	58·4	6	7·22	07·4	4	6·50	37491·2	5
3·43	38399·4	10	2620·09	55·2	4	7·45	04·1	4	7·12	82·5	20
3·58	97·2	9									

TABLE III.

Series Assignment of Band Maxima in the Fluorescence Spectrum of Benzene Vapour.

n-Spacing ($\Delta\nu$).	Band No.	Frequency (ν, cm.$^{-1}$).	p-Spacing ($\delta\nu$).	n-Spacing ($\Delta\nu$).	Band No.	Frequency (ν, cm.$^{-1}$).	p-Spacing ($\delta\nu$).
	B_0^0	38522·4	162·9		C_0^0	38605·2	161·2
	B_0^1	38359·5	164·0		C_0^1	38444·0	162·6
	B_0^2	38195·5	149·0		C_0^2	38281·4	163·3
978·8	B_0^3	38046·5	176·0	988·9	C_0^3	38118·1	162·0
	B_0^4	37870·5	158·5		C_0^4	37956·1	161·6
	B_0^5	37712·0			C_0^5	37794·5	
			Mean 162·1				Mean 162·1
	B_1^0	37543·6			C_1^0	37616·3	

TABLE IV.

Fluorescence Spectrum of Hexadeuterobenzene Vapour.

(Short-wave section.)

λ (air), A.	ν (vac.), cm.$^{-1}$.	*I.*	λ (air), A.	ν (vac.), cm.$^{-1}$.	*I.*	λ (air), A.	ν (vac.), cm.$^{-1}$.	*I.*	λ (air), A.	ν (vac.), cm.$^{-1}$.	*I.*
2577·27	38789·1	15	2593·23	38550·4	5	2610·73	38292·0	5	2630·30	38007·2	4
7·63	83·7	14	3·32	49·1	4	0·89	89·7	6	0·80	37999·9	6
7·83	80·7	13	3·60	44·9	4	1·10	86·6	8	1·11	95·5	5
8·10	76·7	11	4·03	38·5	5	1·38	82·5	6	1·52	89·5	4
8·33	73·2	9	4·23	35·6	4	1·69	78·0	5	1·85	84·8	5
8·52	70·3	8	4·42	32·7	6	2·07	72·4	4	2·10	81·2	4
9·16	60·7	7	4·62	29·8	4	2·40	67·6	4	2·46	76·0	3
9·34	58·0	6	4·94	25·0	5	2·73	62·7	3	2·58	74·2	2
9·56	54·7	6	5·19	21·3	3	2·91	60·1	3	2·81	70·9	1
9·79	51·3	5	5·62	14·9	4	3·30	54·4	3	3·32	63·6	1
2580·00	48·1	5	5·90	10·8	6	3·75	47·8	2	3·84	56·1	3
0·26	44·2	4	6·17	06·8	7	4·22	40·9	2	4·46	47·1	4
0·72	37·3	4	6·49	03·4	10	4·51	36·7	3	4·75	43·0	3
0·94	34·0	3	6·70	38498·9	8	4·78	32·7	3	5·21	36·4	3
1·22	29·8	3	7·10	93·0	10	5·06	28·6	4	5·38	33·9	5
1·42	26·8	2	7·55	86·3	9	5·37	24·1	3	5·84	27·3	4
1·57	24·5	2	7·82	82·3	9	5·75	18·6	2	6·05	24·3	3
1·85	20·3	1	8·11	78·0	8	6·07	13·9	2	6·31	20·5	2
2·55	09·8	6	8·32	74·9	7	6·52	07·4	3	6·74	14·3	5
2·76	06·7	5	8·64	70·2	7	6·70	04·7	2	6·97	11·0	5
2·97	03·6	4	8·76	68·4	6	6·96	00·9	4	7·13	08·7	4
3·23	38699·7	3	9·00	64·9	6	7·87	38187·6	2	7·37	05·3	3
3·70	92·6	3	9·22	61·6	5	8·15	83·5	1	7·78	37899·4	3
3·89	89·8	2	9·42	58·6	5	8·48	78·7	2	8·07	95·2	3
4·38	82·4	1	9·78	53·3	5	8·76	74·6	2	8·33	91·5	3
5·03	72·7	4	2600·00	50·1	6	9·14	69·1	3	8·65	86·9	4
5·25	69·4	3	0·24	46·5	8	9·30	66·8	5	9·03	81·4	4
5·48	66·0	3	0·71	39·6	7	9·66	61·5	4	9·24	78·4	5
5·65	63·4	3	0·92	36·5	8	9·88	58·3	3	9·72	71·5	8
6·00	58·2	4	1·53	27·4	8	2620·43	50·3	3	9·82	70·1	7
6·29	53·9	7	1·90	22·0	5	0·65	47·1	4	2640·04	66·9	6
6·74	47·1	13	2·07	19·5	5	1·03	41·6	6	0·35	62·5	5
7·00	43·3	12	2·30	16·1	6	1·25	38·4	6	0·74	56·9	4
7·20	40·3	11	2·59	11·8	5	1·51	34·6	4	1·82	41·4	16
7·39	37·4	10	2·76	09·3	7	2·21	24·4	5	2·20	36·0	15
7·56	34·9	9	3·25	02·1	5	2·62	18·9	5	2·53	31·3	14
7·88	30·1	9	3·52	38398·1	4	2·93	14·9	3	2·80	27·4	13
8·20	25·3	8	4·01	90·8	5	3·20	10·0	2	3·13	22·7	12
8·33	23·4	8	4·20	88·1	6	3·46	06·2	3	3·43	18·4	10
8·80	16·4	7	4·64	81·6	5	3·98	38098·7	2	4·02	09·9	8*b*
9·11	11·8	5	4·99	76·4	7	4·22	95·2	2	4·20	07·4	7
9·28	09·2	4	5·14	74·2	7	4·37	93·0	3	4·49	03·2	6
9·51	05·8	3	5·53	68·5	8	4·89	85·5	5	5·06	37795·1	8
9·75	02·2	2	6·00	61·5	7	5·15	81·7	5	5·60	87·4	8
2590·06	38597·6	3	6·32	56·8	7	5·38	78·4	6	5·88	83·4	8
0·27	94·5	5	6·59	52·8	7	5·71	73·6	5	6·19	78·9	6
0·42	92·2	7	7·00	46·8	7	6·11	67·8	4	6·52	74·2	6
0·67	88·5	9	7·29	42·5	6	6·45	62·9	3	7·20	64·5	10
0·81	86·4	9	7·52	39·2	5	6·82	57·5	2	7·61	59·0	9
0·96	84·2	9	8·00	32·1	5	7·25	51·3	3	8·14	51·1	8
1·16	81·2	10	8·43	25·8	7	7·64	45·6	2	8·77	42·1	7
1·38	78·0	11	8·86	19·5	5	7·86	42·4	2	8·99	39·0	6
1·70	73·2	9	9·22	14·2	5	8·09	39·1	2	9·35	33·9	6
1·98	69·0	8	9·40	11·6	7	8·45	33·9	2	9·83	27·1	10
2·35	63·5	9	9·83	05·2	5	8·74	29·7	2	2651·10	09·0	30
2·53	60·8	8	2610·16	00·4	8	8·98	26·2	2	1·30	06·1	28
2·74	57·7	7	0·34	38297·7	8	9·15	23·8	2	6·79	37628·2	23
3·03	53·4	6	0·50	95·4	6	9·72	15·5	1	9·03	37596·5	21

TABLE V.

Series Assignment of Band Maxima in the Fluorescence Spectrum of Hexadeuterobenzene Vapour.

n-Spacing ($\Delta\nu$).	Band No.	Frequency (ν, cm.$^{-1}$).	p-Spacing ($\delta\nu$).	n-Spacing ($\Delta\nu$).	Band No.	Frequency (ν, cm.$^{-1}$).	p-Spacing ($\delta\nu$).
	B_0^0	38709·8			C_0^0	38789·1	
			140·8				142·0
	B_0^1	38569·0			C_0^1	38647·1	
			141·6				143·7
	B_0^2	38427·4			C_0^2	38503·4	
			137·7				134·9
	B_0^3	38289·7			C_0^3	38368·5	
			148·1				139·9
945·3	B_0^4	38141·6		947·7	C_0^4	38228·6	
			134·4				150·2
	B_0^5	38007·2			C_0^5	38078·4	
			135·7				144·5
	B_0^6	37871·5			C_0^6	37933·9	
			144·4				146·5
	B_0^7	37727·1			C_0^7	37787·4	
			Mean 140·4				Mean 143·1
	B_1^0	37764·5			C_1^0	37841·4	

Pure oxygen-free nitrogen, dried over phosphoric oxide, was allowed to enter the apparatus through a miniature needle valve. After passing over solid benzene maintained at a constant temperature by a bath of liquid ammonia undergoing evaporation at various rates (depending on the partial pressure of benzene required), the gas entered the fluorescence cell. This was followed by a calibrated capillary (approx., 1·5 cm. by 0·3 mm. diameter bore), a liquid-air trap, and a pump. The pressure in the cell was determined by the setting of the needle valve, and was measured by a small mercury manometer which could be isolated whilst an exposure was being made. At 20 mm. of nitrogen (benzene 0·2 mm.) the rate of flow was such that the vapour in the fluorescence cell was renewed every 30 seconds.

The pump was unnecessary in the experiments involving nitrogen at atmospheric pressure. Exposures varied from 10 to 40 hours. The rest of the technique has been described before.

The author thanks Professor C. K. Ingold, F.R.S., for his interest.

UNIVERSITY COLLEGE, LONDON. [*Received, June* 26*th*, 1936.]