215. *Structure of Benzene. Part V. Fluorescence Spectra of Benzene and Hexadeuterobenzene Vapour.*

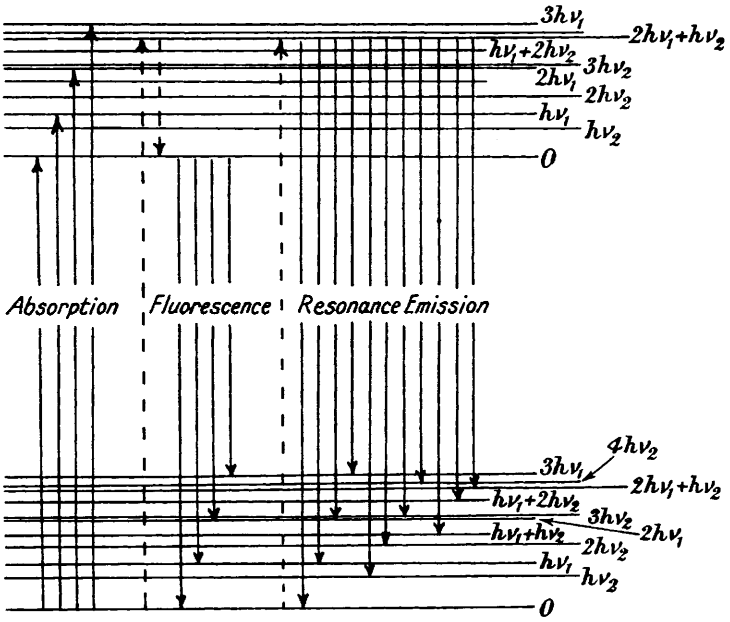
By C. K. Ingold and C. L. Wilson.

(1) *General Principles.*—It is well-known that vibrations can record their frequencies in the infra-red absorption spectrum only if they involve a periodic variation in the dipole moment vector, and in the Raman spectrum only if they give rise to an oscillation of the polarisability tensor. In very symmetrical molecules there are usually several normal vibrations which leave both the dipole moment and the polarisability invariant, and accordingly the frequencies of these vibrations cannot be observed in either of the spectra mentioned. It thus becomes desirable to study other spectra, for which the appearance of vibrational frequencies is determined by different principles. One naturally turns to ultraviolet spectra for this purpose because the modes of nuclear vibration which can gain or lose quanta during an electron transition are determined by the change of shape which the molecule undergoes as a consequence of the electron switch, and by the nature of any vibrations which may already have been present in the initial electronic state. The preceding papers bring our study of benzene and hexadeuterobenzene to the point at which, having done all that seems profitable in connexion with the infra-red and Raman spectra we must attempt to get further information about these molecules from their electronic spectra.

In an ideally simple case we have to consider only one electronically excited state in addition to the ground state. Each of these states possesses a zero-point energy level (0-level) and a series of vibrationally excited levels corresponding to the successive quanta and combinations of quanta of the different normal vibrations. We may assume the temperature to be such that in thermal equilibrium hardly any of the ground-state molecules are vibrationally excited. It then follows that in absorption almost all molecules start from the 0-level of the ground state, and they finish, in proportions determined by the Franck–Condon theory, some on the 0-level of the excited state and some on each of the successive higher levels of each of those vibrational series belonging to the excited state for which the electron switch can set up the vibrations. Which vibrations will thus be excited we need not yet discuss, and it will suffice to remark that the totality of vibrations is broadly divisible into two groups, the "allowed" and the "forbidden," the former being those for which the probability of excitation may be great, and the latter those for which this probability is given by a simplified theory as zero and by a refined theory as small at most. Fig. 1 is drawn for an imaginary molecule with two normal vibrations, one allowed and the other forbidden in transitions from a "vibrationless" state, *i.e.*, from a 0-level. Absorption is illustrated on the left-hand side. The spectrum will consist of a series of bands stretching from the 0–0-band (*i.e.*, that representing transition between the two 0-levels) towards the Schumann region, the spacing of the bands having the frequency of the allowed vibration. This, however, is a nuclear frequency of the electronically excited state, and we are more interested at present in the ground state.

Hence we turn to fluorescence, the three steps in which are illustrated in the centre part of Fig. 1. The molecule is first excited by absorption of light of any wave-length or spectrum of wave-lengths which will bring it to one or to several of the vibration-rotation levels belonging to the electronically excited state. Next, the excited molecules lose vibrational energy by inelastic collisions, the whole excited assembly approaching statistical " equilibrium " in which nearly all molecules occupy the 0-level of the excited state. Then, starting from this level the molecules fluoresce, some reaching the zero-level of the ground state and others the vibrationally excited levels of the " allowed " vibrations of the ground state. The rules controlling the excitation of vibrations are the same as for absorption, and hence the spectrum will have the same general character. However, the fluorescence spectrum will progress from the 0–0-band towards the visible, and the spacing of the bands will be defined by the frequencies of vibrations belonging to the ground state. The preliminary excitation may be accomplished by high-frequency discharge as an alternative to the photochemical method, but this makes no difference to the spectrum, provided other conditions are the same. The essential conditions for observation of a pure fluorescence spectrum are that the excited molecule should live sufficiently long, and that molecular collisions should be sufficiently frequent, to reduce practically all excited molecules to their zero-point level before emission. We can control the frequency of collisions by means of the pressure, and it follows that for fluorescence the pressure must be above a certain limit.

FIG. 1.

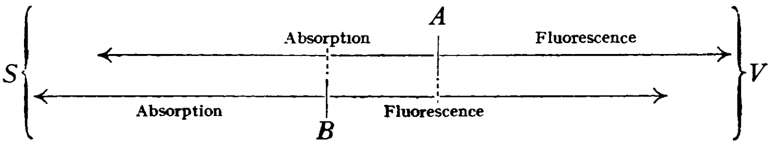


Schematic representation of absorption, fluorescence, and resonance emission.

The classical picture of the excitation of nuclear vibrations in these spectra is that the electron transition suddenly alters the positions at which the nuclei are in equilibrium before the nuclei themselves have had time to move (Franck's principle), so that immediately following the electron change they start vibrating from their old positions towards their new equilibrium positions, past these and back again. In transitions from a " vibrationless " state, therefore, all depends on the relation of the old equilibrium configuration to the new, and hence, if the molecule is highly symmetrical and the transition brings about no profound change of symmetry of the equilibrium configuration, the number of modes of vibration that can be excited is strictly limited. Of course, even a " vibrationless " state has its zero-point energy so that initially the nuclei are not at, but only near, their equilibrium positions : it is still true, however, that the number of modes of vibration that can be *strongly* excited in the circumstances mentioned is subject to severe restriction. This applies both to absorption and to fluorescence. If, however, the molecule is vibrating in the initial state in such a way that the electron switch often " catches " the molecule when the latter is " out of shape," then the vibrations set up as a consequence of the transition will be much more diversified. This is what happens in resonance emission, which is illustrated on the right-hand side of Fig. 1. Ideally, the molecule is first excited by a definitely monochromatic radiation to some one vibrational level of the system belonging to the excited state; and then, by maintaining a very low pressure, it is kept at that level until it emits. If the probability of excitation to the level corresponding to the frequency of the exciting light is small, the resulting emission spectrum will be feeble; but, provided that there are sufficiently few molecular collisions, the molecule can only emit from the level to which it was excited. This level will involve vibrations some of which may have lower symmetry than the molecule itself, and hence, on emission, vibrations of the ground state may be excited which would not have appeared to any marked extent in the ordinary fluorescence spectrum. The resonance spectrum will commence with a band having the frequency of the exciting light and extend with complex overlapping spacings towards the visible.

It will be clear from the foregoing why we have chosen the fluorescence and resonance spectra as those electronic spectra which are calculated most directly to assist our problem of elucidating the vibrations of the normal benzene molecule. In this paper we describe the fluorescence spectra of benzene and hexadeuterobenzene. These spectra are more complicated than has been represented in the ideal case described above, first because of the multiplicity of electronically excited states, and secondly because more than one type of vibration is excited in transitions from these states.

The multiplicity of electron levels gives rise to an effect which can be understood from the following scheme for the fluorescence and absorption spectra of a molecule with just two levels, *A* and *B*. Let *A* be the 0–0-band for transition between excited state *A* and the ground state; the fluorescence spectrum will then extend from *A* towards the visible *V*, and the absorption spectrum from *A* towards the Schumann region, *S*. Similarly the excited state *B* will give a 0–0-band at *B*, a fluorescence spectrum in region *BV*, and an absorption spectrum in region *BS*. In the region *BA*, therefore, the observed fluorescence will consist of as much of the *B*-fluorescence band series as can get out between the *A*-absorption bands; the rest of the *B*-fluorescence in this region will be re-absorbed, vibrationally degraded by inelastic collisions, and then again emitted as a reinforcement of the *A*-fluorescence spectrum. In the region *AV*, on the other hand, we shall observe an overlapping of the *A*- and *B*-fluorescence band systems.



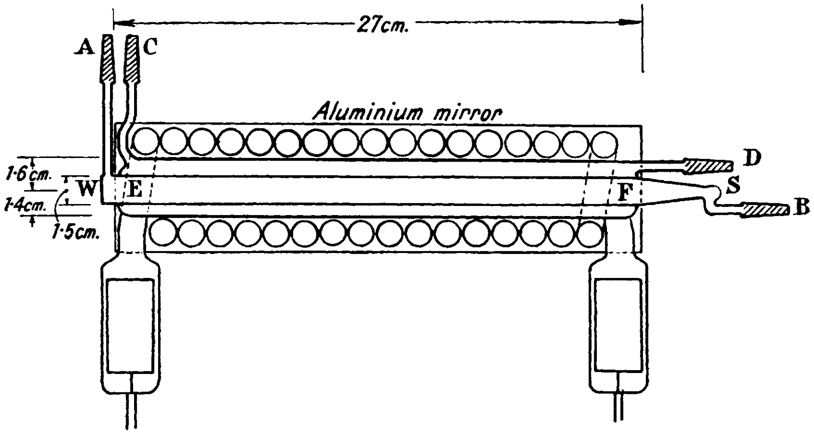
The plurality of " allowed " vibrations merely means that the transitions from the excited state will terminate, not on a single series of equally spaced levels belonging to the ground state, but on a complex array of levels, just as has been described in the foregoing simplified consideration of the resonance spectrum.

It remains to indicate more definitely what modes of vibration are " allowed " in the fluorescence spectrum. Franck's principle tells us that in transitions from a vibrationless state the old equilibrium positions become turning points in the vibrations about the new. Hence, as Herzberg and Teller have pointed out (*Z. physikal. Chem.*, 1933, **21**, 410), only those vibrations can be strongly excited which preserve all symmetry common to the equilibrium configurations of the initial and final states (" totally symmetrical " vibrations). How many quanta may be given to such vibrations will be determined in accordance with Condon's quantum-mechanical extension of Franck's principle. Strictly, any quantum number can appear, but those will have greater probability for which the classical vibration amplitude gives turning points agreeing more closely with the nuclear configuration as it stood before the transition. In practice, one finds a series of bands corresponding to the first few quantum numbers of a given vibration, and one of these bands is shown by its intensity to represent the quantum number of greatest probability; the other band intensities fall off in either direction.

(2) *Experimental Method.*—The apparatus to be described is more elaborate, and in particular the light source is more definitely monochromatic and some hundreds of times more powerful, than would have been necessary merely to photograph the fluorescence spectra of benzene and hexadeuterobenzene under the dispersion desired. We wished, however, to use the same apparatus for the resonance spectra, the light of which is very feeble owing to the necessarily great rarefaction of the vapour. The following account is therefore applicable to both the present investigation and that of the following paper.

The fluorescence cell is shown in Fig. 2. It consists of a tube *AB*, through which the vapour can be passed, and a jacket *CD*, through which a liquid, to act as both a light-filter and cooling agent, can be circulated. The whole is of clear-blown quartz. There is an optically polished sealed-on quartz window at *W*, and a blown-out shoulder at *S*. The section *FS* was made conical to minimise axial reflexion. The seal *E* was put as close to *W* as was practicable, and the length *EF* was so chosen that, when *W* was centred against the slit of the spectrograph and the tube was properly alined, the conical volume from which light is accepted by the spectrograph nearly fills the whole width of the vapour tube at *F*. The shoulder *S* served a double purpose. First, it facilitated alinement, since light from a small source placed inside the spectrograph emerged from the slit and could be seen through *S*, or received on a screen placed behind *S*, when the alinement was true. Secondly, the comparison spectrum could be sent in through *S*, thus obviating the necessity for leaving a space between *W* and the slit to accommodate a reflecting prism. The tubes *B* and *D* are arranged to permit the slipping on of the helical lamp over that end, and the tube *C* is slightly offset in order to allow the lamp to come as near as possible to the window *W*. The seal of the tube *C* is slightly blown-out to facilitate the escape of any gas bubbles formed by photochemical decomposition of the light-filter, and, as a further precaution against the bridging by gas bubbles of the space above the top of the vapour tube, the latter is sealed in slightly below the centre line of the jacket.

FIG. 2.



Fluorescence Cell, Filter and Lamp.

The light-source is a helical mercury lamp (Fig. 2) with an arc-length of about 2·5 m. It was constructed of clear-blown quartz by Messrs. The Thermal Syndicate Ltd., and provided with Swedish-iron electrodes and a neon filling. Nearly the whole of the output of this lamp is concentrated in the 2537 A. mercury line, and, as the lamp remains cool when running, the line is sharp; these are important factors for the work on the resonance spectrum. The lamp is constructed to carry 0·25 amp., but as its life was guaranteed only for 1000 hours at this current, we preferred to use 0·175 amp. at 1000 volts and lengthen the exposures, especially as the lamp had ample power. When in position over the fluorescence tube, the lamp was completely enclosed, except its electrode chambers, by a cylindrical aluminium mirror with plane ends cut out to permit projection of the ends of the vapour tube. No air blast was used, as the temperature of the absorption tube did not rise above 30° even when the cooling coil used to keep the light-filter cold was not being employed.

The joints of the vapour tube, *A* and *B*, were connected through Pyrex tubes of appropriate resistance to gas-flow to two traps, between which, after complete evacuation of the apparatus, the benzene or hexadeuterobenzene could be made to distil through the fluorescence tube at any desired pressure by the maintenance of suitable temperatures in the traps. The trap joined to *B* was connected also to another trap which was cooled in liquid air in order to prevent loss of material into the pump. The ground joints were made tight by external application of de Khotinsky cement.

The joints of the filter jacket, *C* and *D*, were connected to an all-glass circulating system containing a reservoir of pure 2*M*-aqueous acetic acid. The head necessary to maintain circulation was established by means of a glass air-lift working on oil-free compressed air. The reservoir also contained a glass coil through which cooling water could be circulated. The primary object of the acetic acid filter is to cut off photochemically active light of shorter wave-length than the required 2537 A. line.

The whole of the apparatus so far described was mounted, with position-seals where necessary, on a small bench which was placed on the spectrograph table, with the window *W* of the vapour tube as close as possible to the slit. The bench had screw adjustments to facilitate the alinement of the fluorescence tube with respect to the spectrograph. The tube leading from the liquid-air trap was then joined by means of position-seals to independently mounted auxiliary apparatus consisting of a " cut-out," a gauge, and a pump. In order to prevent mechanical disturbances originating in the pump or in the gauge from reaching the apparatus on the spectrograph table, two large glass spiral tubes with mutually perpendicular axes were incorporated in the gas-line. The cut-out was a device by which, should any crack or leak develop during a long exposure, an electrical contact would be made by the increasing pressure, thus permitting the passage of a current which by operating a relay would put out the lamp and prevent the spoiling of the plate. The gauge was of the " reduced " McLeod pattern. The pump was a Gaede Duplex pump which reduced the permanent-gas pressure to 0·00001 mm., and could be run continuously for weeks without attention except for oiling twice daily.

The spectrograph was a Hilger E1 instrument (Littrow pattern) having a dispersion of 3 A. per mm. at 2600 A. In the fluorescence experiments the exposures ranged from a fraction of a minute to a few minutes. In spite of the shortness of these exposures, it was found desirable, in order to obtain the greatest possible degree of resolution, to thermostat the room to the temperature at which the spectrograph was focused (20·0°); and a constant temperature was in any case necessary for the resonance experiments in which the exposures ranged from half a day to a fortnight. The necessary vapour pressures have been fairly well fixed by previous investigations on benzene : 25 mm. is a convenient pressure for the observations of the fluorescence spectra, and 0·01 mm. for the resonance spectra. Intermediate pressures were also used in order to trace the transition from one type of spectrum into the other, and to make sure that the spectra to be measured contained no lines which did not belong to them.

Wave-lengths were measured by reference to iron-arc comparison spectra placed above and below the fluorescence spectrum. Three suitably placed holes, each 1 mm. in diameter, bored in the Hartmann plate enabled the three spectra to be photographed in positions in which all were simultaneously visible in the field of the microscope. Many of the weaker lines are difficult to read in the ordinary microscope and are more accurately measured on microphotometer records by means of a microscope with travel in two perpendicular directions.* These records were taken, usually with considerable enlargement, by means of a Zeiss recording microphotometer, and, needless to say, no weak line was accepted which did not appear on records made from independent primary plates. The absolute frequencies are subject to an error of 1 cm.$^{-1}$ or even more, but the frequency differences of neighbouring lines should be accurate to 0·2—0·1 cm.$^{-1}$ according to the amount of separation.

(3) *Fluorescence Spectrum of Benzene Vapour.*—Investigations of absorption and fluorescence are connected through the circumstance that both should lead to the identification of the same electron levels. We therefore mention first the fact that Henri has described the absorption spectrum of benzene vapour by means of the formula :

$$\nu = \begin{cases} 38612{\cdot}4 + 921{\cdot}7n - 162p + 121q \\ 37483{\cdot}5 + 924n - 164{\cdot}5p + 121q \end{cases}$$

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* This instrument was kindly lent by Professor E. N. da C. Andrade.

where n, p, and q are whole numbers. This means that there are two electron levels, 38612 and 37483 cm.$^{-1}$ above the zero-level of the ground state, that absorption creates vibrations of frequency 922 and 121 cm.$^{-1}$ in the excited molecule, and that vibrations of frequency 163 cm.$^{-1}$ were already present in the normal molecule ("Structure des Molécules," Paris, 1925). The numbers n, p, and q are, of course, the quantum numbers of the vibrations. Krönenberger investigated the absorption spectrum of solid benzene at − 259° and deduced a formula which changes the second of Henri's electron levels, and also makes certain alterations to the vibration frequencies (*Z. Physik*, 1930, **63**, 494).

The fluorescence spectrum of benzene vapour was first observed by McVicker, Marsh, and Stewart, who used electrical excitation (J., 1923, **123**, 642), and by McVicker and Marsh, who were the first to employ the optical method (*ibid.*, p. 820; cf. Marsh, *ibid.*, p. 3315). Marsh represented the spectrum by means of the formula $\nu = 37494 - 921{\cdot}4n - 159p - 2p^2$, in which the electron term agrees with the second of Henri's; but the comparison with absorption was pushed too far : there is certainly no active frequency of 921 cm.$^{-1}$ belonging to the *ground* state of benzene. The spectrum was also investigated by Pringsheim and Reimann (*Z. Physik*, 1924, **29**, 115), and in more detail by Reimann (*Ann. Physik*, 1926, **80**, 43) who gives the formula

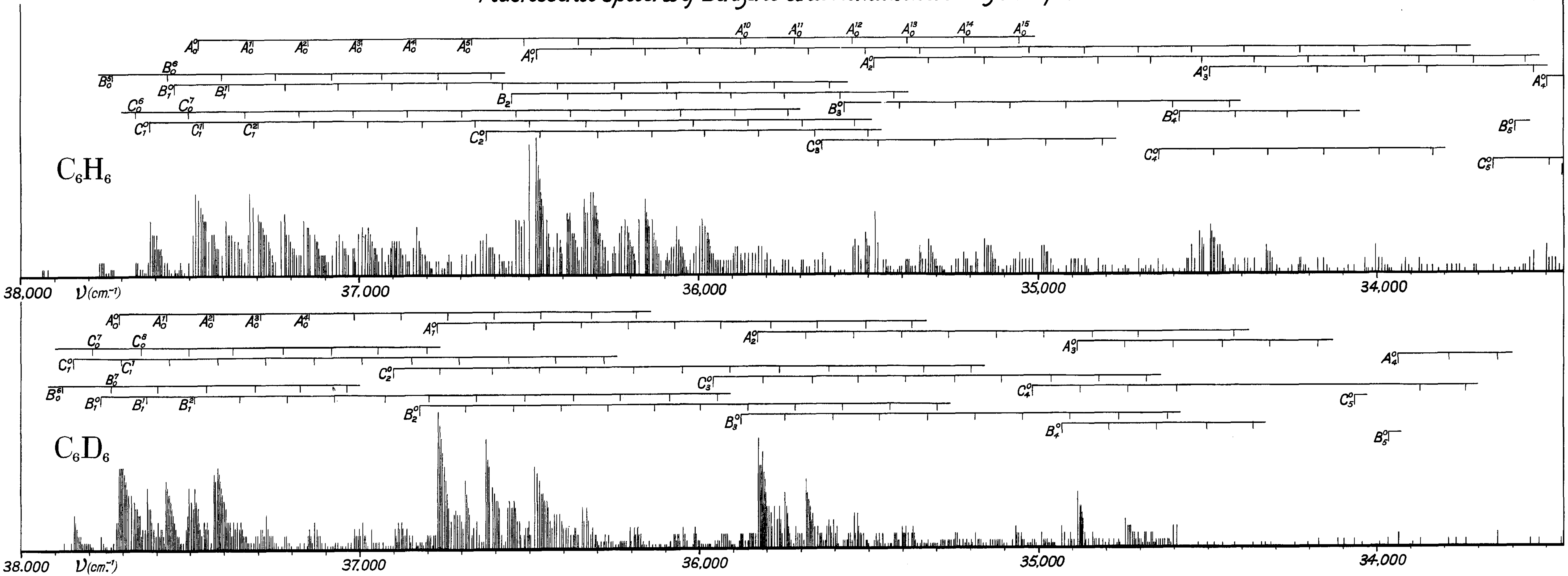
$$\nu = \begin{cases} 39490 - 1000n - 163p \\ 39400 - 1000n - 163p \end{cases}$$

Here, although the electron terms are unacceptable, the vibration frequencies for the ground state are substantially correct though rather roughly estimated. From the fluorescence spectrum of solid benzene at − 259°, Krönenberger deduced a single electron term at 39000 cm.$^{-1}$, and the same vibration frequencies as those given by Reimann, 1000 cm.$^{-1}$ and 163 cm.$^{-1}$ (*loc. cit.*). Austin and Black have suggested five electron terms (*Physical Rev.*, 1930, **35**, 452) and Black three (*Nature*, 1930, **125**, 274), but all the formulæ given by these authors contain a large positive vibrational term, so that either the formulæ do not truly express the structure of the spectrum or the spectrum represented does not originate in transitions from a substantially vibrationless excited molecule. The same remark applies to the interpretation given by Shapiro (*Nature*, 1929, **124**, 372; cf. Almasy and Shapiro, *Physical Rev.*, 1930, **35**, 1422). Very recently Cuthbertson and Kistiakowsky (*J. Chem. Physics*, 1936, **4**, 9) have made a suggestion which amounts to combining Henri's two electron terms with Reimann's two vibration frequencies, and with this we agree as far as it goes. It was, however, made clear by Reimann's work that the spectrum contains some further complication, and this Cuthbertson and Kistiakowsky deal with by supposing, either that each of Henri's electron levels is really double, or that at least one vibration frequency of the order 80 cm.$^{-1}$ is excited. The fullest previous description of the spectrum is that given by Reimann, and from this the presence of a vibration frequency or doublet separation of 80 cm.$^{-1}$ seems possible; but Reimann's measurements are recorded only to the nearest A. (*ca.* 15 cm.$^{-1}$), and our measurements with larger dispersion show that the spectrum has a considerably more complex structure than he supposed. We require, in fact, a third electron level, one not observed by Henri in absorption. It may be added that the problem of interpretation would have been more difficult had we not had both benzene and hexadeuterobenzene to consider; the advantage of this is that accidental approximate coincidences in one spectrum of band maxima belonging to different series become resolved in the other, so that they can be recognised.

The wave-length measurements are recorded in Table II (p. 948), in which I represents intensity, but a better appreciation of the structure of the spectrum will be obtained by reference to the upper part of Fig. 3 (folder), in which it is plotted on a frequency scale. The various bands, although doubtless not fully resolved, show a similar rotational structure. Each individual band is fairly narrow and exhibits a single sharp intensity maximum at or very near its short-wave end. We assume that the intensity maximum locates the origin of the band. The intensities here recorded are obtained by measurement of microphotometer records, and therefore should be qualitatively correct although no calibration factor was introduced in order to take account of the relation between light intensity and photographic blackening.

Fig. 3

Fluorescence Spectra of Benzene and Hexadeuterobenzene Vapour



The spectrum has usually been described as a series of band maxima progressing in intervals of 1000 cm.$^{-1}$ (more exactly 990 cm.$^{-1}$), each interval containing a progression in intervals of 163 cm.$^{-1}$ (more exactly 161 cm.$^{-1}$), and the whole of this doubly periodic band system being repeated with smaller intensity at frequencies shifted about 80 cm.$^{-1}$ towards the visible. This description is roughly true, but a glance at Fig. 3 will indicate the extent to which it must be modified. Many of the principal maxima are double or treble, and the splitting shows no immediately obvious regularity either in occurrence, form, or frequency separation. Moreover, the minor maxima, of which, according to the customary description, there should be only one, bisecting each of the main 161 cm.$^{-1}$ intervals, are really for the most part complicated multiplets, with almost every kind of multiplicity, frequency separation, spacing in the interval, and intensity distribution. Throughout the whole spectrum no two 161 cm.$^{-1}$ intervals are filled in exactly the same way.

As mentioned already, we can account for this spectrum in detail by assuming three electron levels and two vibration frequencies. The numerical formula is

$$\nu = \begin{Bmatrix} 37473 \\ 38535 \\ 38607 \end{Bmatrix} - 990{\cdot}4n - 160{\cdot}8p$$

We may call the electron terms A_0^0, B_0^0, and C_0^0 respectively, and introduce the notation A_n^p, etc., to indicate a band displaced from A_0^0 towards the visible by $(990{\cdot}4n + 160{\cdot}8p)$ cm.$^{-1}$, the integers n and p being, of course, the quantum numbers with which the two vibrations are excited. Some part of the complication referred to above is due to the circumstance that a given 161 cm.$^{-1}$ progression is not confined to the 990 cm.$^{-1}$ interval in which it originates; it may extend through much of the next such interval, and even into the next but one. In addition to this, there is an overlapping of the A-, B-, and C-band systems on the long-wave side of A_0^0, and a filtering out of the fluorescence light by absorption on the short-wave side.

The electron level C_0^0 is easily fixed as the common zero-point of the observed progressions, C_0^p, C_n^0, etc.; evidently it is Henri's upper level. The observed electron level A_0^0 is likewise Henri's lower level. On the basis of the data now reported, the position of the level B_0^0 can be determined only by indirect arguments, which however it is unnecessary to give, since in later work (Part IX) this level has been directly observed. The levels C_0^0 and B_0^0 are thus quite close together and form an example of the electronic doublet separation envisaged by Cuthbertson and Kistiakowsky. However, we find no similar doublet splitting of the level A_0^0 which heads the main part of the spectrum. The filling up by subsidiary maxima of the 161 cm.$^{-1}$ intervals of the A-band system can be fully explained by interpenetration of the A-system by the B- and C-systems. We can thus account for all the maxima (and there are over 100), except two weak ones, the frequencies of which suggest that they may be anti-Stokes combinations due to insufficient quenching of the vibrations of the excited state. The details of this analysis are given in Table III (p. 950).

(4) *Fluorescence Spectrum of Hexadeuterobenzene Vapour.*—This spectrum is briefly referred to in the paper by Cuthbertson and Kistiakowsky already mentioned which appeared after our experiments had been completed. These authors observed the two vibrational spacings and one electron level and deduced the presence of a second—all results with which our own work is in substantial agreement. As with benzene, we find three electron levels and two active vibrations.

TABLE I.

Electron Terms and Vibration Frequencies in the Fluorescence Spectra of Benzene and Hexadeuterobenzene (cm.$^{-1}$).

Electron terms.				Vibration frequencies.		
Symbol.	C_6H_6.	C_6D_6.	$\Delta\nu$.	Quantum No.	C_6H_6.	C_6D_6.
A_0^0	37473	37709	236			
B_0^0	38535	38707	172	n	990·4	942·8
C_0^0	38607	38785	178	p	160·8	141·2

TABLE II.

Fluorescence Spectrum of Benzene Vapour.

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.*
2635·38	37933·9	½	2680·40	37296·8	4½	2712·26	36858·7	1	2752·68	36317·5	6
5·59	30·9	½	0·80	91·2	4	2·61	54·0	1	3·25	10·0	6
6·39	19·4	½	0·99	88·6	4	3·64	40·1	2	3·67	04·5	5
2647·19	37764·7	1	1·44	82·3	3½	4·06	34·3	2	3·96	00·6	5
7·53	59·8	1	1·84	76·8	3	4·26	31·6	3½	4·18	36297·7	4½
7·70	57·4	1	2·22	71·5	3	4·80	24·2	2½	4·37	95·2	4
7·98	53·4	1	2·66	65·4	2½	5·19	18·9	2	4·53	93·1	3
8·55	45·3	0	3·00	60·7	2	5·67	12·4	1½*b*	4·79	89·7	3
9·12	37·1	0	3·46	54·3	1½	6·22	05·0	1½	5·33	82·6	2½
9·62	30·0	½	3·77	49·9	1	6·62	36799·5	1	5·69	77·8	2
9·85	26·8	½	4·13	45·0	1	7·04	93·9	1	5·94	74·6	2
2650·09	23·3	½	5·20	30·1	4	7·44	88·5	½	6·50	67·2	1
4·66	37658·4	1	6·09	19·0	4½	7·73	84·5	½	7·61	52·6	1½
4·97	54·0	1	6·33	14·5	3	8·62	72·5	1	7·90	48·8	2
5·62	44·8	½	6·83	07·5	3	9·17	65·1	1	8·18	45·1	1½
6·02	39·1	½	7·10	03·8	2½	2720·10	52·5	½	9·09	33·1	3
6·44	33·2	0	7·62	37196·6	2	0·44	47·0	½	9·58	26·7	3½
6·82	27·8	0	8·05	90·6	2	1·00	40·3	1	2760·39	16·2	4
7·06	24·4	1	8·43	85·4	1½	1·42	34·7	1½	0·85	10·1	3½
7·62	16·5	4	9·06	76·7	1½	1·89	28·3	1	1·19	05·6	3
8·10	09·7	3	9·25	74·0	1½	4·21	36697·0	1½	1·56	00·7	2½
8·35	06·2	3	2690·00	63·7	4*b*	5·19	83·8	1½	1·83	36197·2	2
8·78	00·1	2	0·71	53·9	3½	6·29	69·0	1	2·12	93·4	2
9·00	37597·0	3	1·01	49·8	3	7·16	57·3	1½	2·38	90·0	1½
9·23	93·7	2	1·33	45·3	3	8·41	40·6	2½	2·66	86·3	1
9·44	90·7	2	2·37	31·0	3	8·83	34·9	2½	3·48	75·6	4
9·66	87·6	2	2·63	27·4	2½	9·57	25·0	3	4·95	56·4	5½
9·91	84·1	2	2·88	23·9	2½	2730·17	16·9	2	5·20	53·1	4½
2660·16	80·5	1½	3·14	20·4	2	0·54	12·0	2	5·41	50·3	4
0·64	73·8	1	3·48	15·7	1½	0·91	07·0	2	5·75	45·9	3½
1·30	64·5	1	3·80	11·3	1½	1·42	00·2	1½	6·39	37·5	4
1·65	59·5	½	4·01	08·4	1½	2·40	36587·1	1½*b*	6·90	30·9	3
2·07	53·6	0	4·33	04·0	1½	2·98	79·3	1	7·27	26·0	2½
2·74	44·1	½	4·60	00·3	1½	3·46	72·8	1	7·51	22·9	2
2·94	41·3	0	4·89	37096·3	1	3·88	67·2	½	7·85	18·5	1
3·23	37·2	0	5·18	92·3	1	4·44	59·8	1	8·34	12·1	1
3·57	32·4	½	6·07	80·0	1½	5·19	49·7	1	8·79	06·2	0
3·87	28·2	1	6·96	67·8	2½	6·05	38·3	4	9·49	36097·1	1
4·19	23·7	½	7·54	59·8	3	6·72	29·3	4	9·81	92·9	1½
4·72	16·2	0	8·23	50·4	2½	7·32	21·3	3½	2770·34	86·0	1
5·80	01·1	1	8·60	45·3	2	7·91	13·7	4	0·78	80·3	2
6·59	37489·9	3	8·99	39·7	2	9·08	36497·8	9½	1·25	74·2	2
7·22	81·1	6	9·48	33·2	1½	2740·56	78·1	10	1·98	64·7	3½
7·82	72·5	5½*b*	2700·53	18·8	2	0·97	72·7	8	2·39	59·3	2½
8·37	64·9	5	0·73	16·1	2	1·23	69·2	7	2·88	53·0	2
8·80	58·9	4½	1·06	11·5	1	1·46	66·1	6	3·20	48·8	2
9·10	54·7	4	1·88	00·3	3	1·80	61·6	5½	3·48	45·2	1½
9·41	50·6	4	2·58	36990·7	3½	2·16	56·8	5	3·77	41·4	1
9·98	42·3	2½	3·30	80·8	3	2·82	48·1	4	4·08	37·4	½
2670·65	32·9	3	3·83	73·6	3½*b*	3·14	43·8	3	4·39	33·3	0
1·03	27·6	3	4·31	67·1	3	3·42	40·1	2	5·05	24·8	1
1·23	24·8	2½	4·69	61·9	2½	4·23	29·3	2	5·84	14·5	1½
1·51	20·9	2	5·13	55·9	2	5·26	15·6	3	6·35	07·9	2*b*
1·71	18·1	2	5·46	51·4	2	5·81	08·4	2½	7·21	35996·8	3½
1·95	14·7	2	5·81	46·6	1½	5·95	06·5	2	7·70	90·4	4
2·72	04·0	1½	6·18	41·5	1	6·19	03·3	1½	8·42	81·1	3½
3·56	37392·2	4	6·95	31·0	2*b*	7·33	36388·2	4½	8·89	75·0	3
4·03	85·6	3	7·68	21·1	1	7·74	82·8	4	9·04	73·1	3
4·30	81·9	3	8·22	13·7	1½	8·05	78·7	4½	9·25	70·3	2½
4·76	75·4	3	8·64	08·0	2	8·46	73·3	3	9·52	66·8	2
5·38	66·8	2½	9·12	01·4	2½	8·87	67·9	3	9·86	62·4	1½
6·08	57·0	2½	9·56	36895·4	2½	9·16	64·0	2½	2780·17	58·4	1½
6·43	52·1	2	9·85	91·5	2½	9·52	59·3	2	0·56	53·4	1
6·79	47·1	2	2710·12	87·8	2½	9·90	54·2	1	1·14	45·9	1
7·52	36·9	1	0·53	82·2	2½*b*	2750·64	44·5	2	1·45	41·9	1
8·18	27·7	3	0·82	78·3	2	1·26	36·3	5½	1·85	36·7	1
8·69	20·6	6	1·38	70·7	1½	1·56	32·3	4½	2·41	29·5	½
9·37	11·1	5*b*	1·98	62·5	1½	2·02	26·2	4½	2·62	26·8	1

TABLE II.—(*contd.*).

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.*
2783·21	35919·2	1*b*	2830·77	35315·7	2	2883·27	34672·7	0	2946·56	33928·0	½*b*
3·71	12·7	1*b*	1·20	10·3	1½	3·65	68·1	½	7·55	16·6	1*b*
4·27	05·5	1	1·76	03·4	1	4·38	59·4	0	8·26	08·4	½
4·74	35899·4	1½	2·02	00·1	1	5·59	44·8	1	9·24	33897·1	0
5·25	92·9	2	2·25	35297·3	½	6·77	30·7	½	2951·14	75·3	1
5·89	84·6	2	2·90	89·2	½	7·62	20·5	0	1·77	68·1	½
6·64	74·9	1½	3·31	84·1	½	9·27	00·7	0	3·28	50·8	½
6·99	71·6	1	3·56	80·9	0	2890·66	34584·1	0	4·65	35·1	½
7·63	62·2	1½	3·90	76·7	0	2·04	67·5	0	6·12	18·3	0
8·42	52·0	1½	5·64	55·1	½	2·50	62·1	1	8·48	33791·3	½
9·25	41·4	1½	6·72	41·6	1	2·95	56·7	1	9·68	77·6	½
9·98	32·0	1½*b*	7·22	35·4	1	3·75	47·1	2	2960·98	62·8	½
2790·67	23·1	2	8·58	18·6	1½	4·42	39·1	1	1·73	54·2	½
1·40	13·8	2	8·93	14·2	1	5·72	23·6	3	2·98	40·0	0
2·18	03·8	1	9·41	08·3	1	6·30	16·7	2½	5·47	11·6	½
2·58	35798·7	1½	2840·13	35199·3	½	6·76	11·3	2	6·00	05·6	½
3·32	89·1	1	0·42	95·7	½	8·35	34492·3	3½	2970·44	33655·2	½
4·19	78·0	½	1·35	84·2	1½	8·65	88·7	3	2·37	33·4	0
4·77	70·5	0	1·78	78·9	1	9·03	84·2	2½	4·47	09·6	0
6·09	53·7	1	3·50	57·6	2½	9·40	79·8	2½	6·13	33590·9	0
6·69	46·0	1	4·09	50·3	2	2900·16	70·8	2	7·17	79·2	0
7·47	36·1	1	4·43	46·1	2	0·66	64·8	2	8·17	67·9	½
8·40	24·2	½	4·99	39·2	2	1·21	58·3	1½	8·80	60·8	½
8·92	17·5	0	5·34	34·9	1½	1·46	55·3	1	9·92	48·2	1
2800·41	35698·6	1	5·68	30·7	1	1·88	50·3	½	2980·96	36·5	1½
0·92	92·1	1	6·01	26·6	1	3·09	36·0	0	4·29	33499·0	2
1·70	82·1	½	6·77	17·2	½	3·91	26·3	½	4·96	91·5	1
2·33	74·1	½	7·59	07·1	0	4·41	20·3	1	5·85	81·6	1
3·71	56·5	1	8·05	01·5	0	5·32	09·6	½	6·65	72·6	1
4·36	48·3	1	8·76	35092·7	½	6·92	34390·6	1	7·69	60·9	½
5·43	34·7	1½	9·70	81·1	½	7·66	81·9	1	2991·42	19·2	½
5·98	27·7	1	2850·51	71·2	1	8·41	73·0	0	3·07	00·7	0
7·24	11·7	½	0·87	66·7	1	9·40	61·3	1	3·67	33394·1	0
9·03	35589·0	0	1·80	55·3	1½	2911·09	41·3	0	5·67	71·8	½
9·56	82·3	0	2·48	46·9	1	2·16	28·7	2	9·04	34·3	1
2810·55	69·8	0	3·18	38·3	1	2·55	24·1	1½	3000·07	22·9	1
2·38	46·6	2	4·16	26·3	1	3·15	17·1	1½	1·97	01·8	½
2·92	39·8	2½	4·93	16·9	1*b*	3·63	11·4	1	6·07	33256·4	0
3·72	29·7	2	7·11	34990·2	2	4·79	34297·8	½	7·96	35·5	0
4·34	21·9	1	7·61	84·0	2	5·56	88·7	0	9·91	13·9	0
5·33	09·4	3	8·14	77·5	1½	7·73	63·2	0	3013·10	33178·8	1
5·78	03·7	2½	8·55	72·5	1½	8·80	50·7	½	3·94	69·5	1
6·06	00·2	2	9·33	63·0	1	2920·08	35·6	½	4·87	59·3	1
6·32	35496·9	2	9·88	56·6	½	0·52	30·5	1	5·62	51·0	½
7·41	83·2	4½	2861·21	40·0	0	0·83	26·8	1	3034·86	32940·9	0
7·64	80·3	4½	3·05	17·6	½	1·59	17·9	½	6·18	26·6	0
8·30	72·0	2	4·24	03·0	1	2·19	10·9	½	7·04	17·2	½
9·47	57·2	1	4·97	34894·1	1	2·90	02·6	0	3040·72	32877·4	0
2820·21	47·9	1	5·22	91·1	1	5·23	34175·4	1	5·03	30·9	0
0·45	44·9	½	5·96	82·1	1	6·62	59·1	1	8·08	32798·0	0
0·70	41·8	½	6·76	72·4	½	7·49	49·0	½	3050·11	76·2	0
1·26	34·7	½	7·61	62·0	1	8·28	39·8	0	1·75	58·6	½
2·06	24·7	0	7·85	59·1	½	2930·33	15·9	0	5·65	16·8	0*b*
2·88	14·4	0	8·29	53·8	0	1·95	34097·0	0	3061·46	32654·7	0
3·38	08·1	½	2870·94	21·6	1	2·97	85·2	½	4·28	24·7	0*b*
3·85	02·2	½	1·90	10·0	½	4·35	69·1	½	3071·28	32550·3	0*b*
4·93	35388·7	1	2·63	01·1	½	7·17	36·5	1	3·48	27·0	0
5·22	85·1	1	4·22	34781·9	½	7·67	30·7	0	4·94	11·5	0
5·59	80·4	1	5·67	64·3	0*b*	8·00	26·8	0	7·42	32485·3	0
6·01	75·2	½	6·87	49·8	0	9·06	14·6	0	3082·80	28·7	0*b*
6·46	69·6	½	7·33	44·3	½	2940·00	03·7	2	6·15	32393·5	0*b*
7·08	61·8	½	7·86	37·9	0	0·69	33995·7	1	3090·57	47·1	0
8·18	48·1	2	8·34	32·1	0	1·33	88·3	1	3100·54	32243·1	0*b*
8·44	44·8	1½	2880·79	02·5	1	2·12	79·2	½	6·85	32177·6	0
8·74	41·1	1	1·43	34694·8	0	2·90	70·2	½	3110·43	40·6	0
9·46	32·1	1	1·87	89·5	0	3·35	65·0	0	1·33	31·1	0
2830·31	21·5	2½	2·48	82·2	½	3·84	59·3	0	3120·20	32040·0	0

TABLE III.

Series Assignment of Band Maxima in Fluorescence Spectrum of Benzene.

n-Spacing (Δν).	Band No.	ν (cm.⁻¹).	*p*-Spacing (δν).
	A_0^0	37472·5	
	A_0^1	37311·1	161·4
	A_0^2	37149·8	161·3
	A_0^3	36990·7	159·1
	A_0^4	36831·6	159·1
	A_0^5	36669·0	162·6
	A_0^6	36513·7	155·3
994·7	A_0^7	36354·2	159·5
	A_0^8	36190·0	164·2
	A_0^9	36033·3	156·7
	A_0^{10}	35874·9	158·4
	A_0^{11}	35717·5	157·4
	A_0^{12}	35546·6	170·9
	A_0^{13}	35385·1	161·5
	A_0^{14}	35218·6	166·7
	A_0^{15}	35055·3	163·3
		Mean	161·1
	A_1^0	36478·1	
	A_1^1	36317·5	160·6
	A_1^2	36156·4	161·1
	A_1^3	35996·8	159·6
	A_1^4	35832·0	164·8
	A_1^5	35674·1	157·9
	A_1^6	35509·4	164·7
	A_1^7	35348·1	161·3
995·9	A_1^8	35184·2	163·9
	A_1^9	35026·3	157·9
	A_1^{10}	34862·0	164·3
	A_1^{11}	34702·5	159·6
	A_1^{12}	34547·1	155·4
	A_1^{13}	34390·6	156·5
	A_1^{14}	34226·8	163·8
	A_1^{15}	34069·1	157·7
	A_1^{16}	33916·6	152·5
	A_1^{17}	33762·8	153·8
		Mean	159·7
	A_2^0	35483·2	
	A_2^1	35321·5	161·7
	A_2^2	35157·6	163·9
	A_2^3	34990·2	167·4
	A_2^4	34821·6	168·6
	A_2^5	34668·1	153·5
990·9	A_2^6	34516·7	151·4
	A_2^7	34361·3	155·4
	A_2^8	34202·6	158·7
	A_2^9	34036·5	166·1
	A_2^{10}	33875·3	161·2
	A_2^{11}	33711·6	163·7
	A_2^{12}	33560·8	150·8
		Mean	160·2
	A_3^0	34492·3	
	A_3^1	34328·7	163·6
	A_3^2	34175·4	153·3
993·3	A_3^3	34003·7	171·7
	A_3^4	33850·8	152·9
	A_3^6	33536·5	314·3
	A_3^7	33371·8	164·7
	A_3^8	33213·9	157·9
		Mean	159·8
	A_4^0	33499·0	
987·5	A_4^1	33334·3	164·7
	A_4^2	33178·8	155·5
		Mean	160·1
	A_5^0	32511·5	

n-Spacing (Δν).	Band No.	ν (cm.⁻¹).	*p*-Spacing (δν).
	B_0^5	37726·8	
	B_0^6	37564·5	162·3
	B_0^7	37404·0	160·5
	B_0^8	37245·0	159·0
	B_0^9	37080·0	165·0
	B_0^{10}	36931·0	149·0
	B_0^{11}	36765·1	165·9
	B_0^{12}	36612·0	153·1
		Mean	159·3
	B_1^0	37544·1	
	B_1^1	37381·9	162·2
	B_1^2	37219·0	162·9
	B_1^3	37059·8	159·2
	B_1^4	36901·4	158·4
	B_1^5	36740·3	161·1
993·7	B_1^6	36579·3	161·0
	B_1^7	36415·6	163·7
	B_1^8	36248·8	166·8
	B_1^9	36092·9	155·9
	B_1^{10}	35936·7	156·2
	B_1^{11}	35778·0	158·7
	B_1^{12}	35611·7	166·3
		Mean	161·2
	B_2^0	36549·7	
	B_2^1	36388·2	161·5
	B_2^2	36226·7	161·5
979·9	B_2^3	36064·7	162·0
	B_2^4	35905·6	159·2
	B_2^5	35746·0	159·5
	B_2^6	35582·3	163·7
	B_2^7	35424·7	157·6
		Mean	160·7
	B_3^0	35569·8	
	B_3^1	35408·1	161·7
	B_3^2	35241·6	166·5
985·7	B_3^3	35081·1	160·5
	B_3^4	34917·6	163·5
	B_3^5	34764·3	153·3
	B_3^6	34600·7	163·6
	B_3^7	34436·0	164·7
		Mean	162·0
	B_4^0	34584·1	
993·2	B_4^1	34420·3	163·8
	B_4^2	34263·2	157·1
	B_4^3	34097·0	166·2
		Mean	162·7
	B_5^0	33590·9	

n-Spacing (Δν).	Band No.	ν (cm.⁻¹).	*p*-Spacing (δν).
	C_0^6	37658·4	
	C_0^7	37501·1	157·3
	C_0^8	37336·9	164·2
	C_0^9	37176·7	160·2
	C_0^{10}	37018·8	157·9
	C_0^{11}	36858·7	160·1
	C_0^{12}	36697·0	161·7
	C_0^{13}	36538·3	158·7
	C_0^{14}	36378·7	159·6
	C_0^{15}	36216·2	162·5
	C_0^{16}	36053·0	163·2
	C_0^{17}	35892·9	160·1
	C_0^{18}	35736·1	156·8
		Mean	160·3
	C_1^0	37616·5	
	C_1^1	37458·9	157·6
	C_1^2	37296·8	162·1
	C_1^3	37131·0	165·8
	C_1^4	36973·6	157·4
	C_1^5	36812·4	161·2
991·5	C_1^6	36657·3	155·1
	C_1^7	36497·8	159·5
	C_1^8	36336·3	161·5
	C_1^9	36175·6	160·7
	C_1^{10}	36014·5	161·1
	C_1^{11}	35852·0	162·5
	C_1^{12}	35692·1	159·9
	C_1^{13}	35539·8	152·3
		Mean	159·8
	C_2^0	36625·0	
	C_2^1	36466·1	158·9
	C_2^2	36304·5	161·6
990·3	C_2^3	36137·5	167·0
	C_2^4	35981·1	156·4
	C_2^5	35823·1	158·0
	C_2^6	35656·5	166·6
	C_2^7	35500·2	156·3
		Mean	160·7
	C_3^0	35634·7	
	C_3^1	35472·0	162·7
	C_3^2	35303·4	168·6
989·9	C_3^3	35146·1	157·3
	C_3^4	34977·5	168·6
	C_3^5	34810·0	167·5
		Mean	165·9
	C_4^0	34644·8	
	C_4^1	34484·2	160·6
	C_4^2	34324·1	160·1
989·6	C_4^3	34159·1	165·0
	C_4^4	33995·7	163·4
	C_4^5	33835·1	160·6
		Mean	161·9
	C_5^0	33655·2	
	C_5^1	33491·5	163·7
	C_5^2	33322·9	168·6
	C_5^3	33169·5	153·4
		Mean	161·9

TABLE IV.

Fluorescence Spectrum of Hexadeuterobenzene Vapour.

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.*
2589·66	38603·6	1	2663·04	37539·9	1	2686·71	37209·2	½	2716·05	36807·3	½
2590·43	38592·1	½	3·44	34·3	1	7·26	01·6	0*b*	6·56	00·4	1
0·96	84·2	½	3·60	32·0	½	8·29	37187·3	0	6·72	36798·2	1
1·34	78·5	½	3·84	28·6	½	8·61	82·9	0	6·94	95·2	1
1·78	72·0	0	4·38	21·0	½	9·23	74·3	½*b*	7·12	92·8	1
2·05	68·0	0	4·81	15·0	1	9·95	64·4	½*b*	7·60	86·3	0
2639·66	37872·4	½	4·98	12·6	1½	2690·65	54·7	0	7·96	81·4	1
2641·15	51·0	½	5·32	07·8	2½	0·83	52·2	1	8·23	77·8	1
1·67	43·6	2½	5·68	02·7	4½	0·98	50·1	1½	9·03	66·9	10
1·91	40·1	2	6·19	37495·6	3½	1·39	44·5	1	9·39	62·1	9
2·23	35·6	1½	6·39	92·8	3	1·60	41·6	½	9·65	58·6	8
2·48	32·0	1	6·85	86·3	4½	2·17	33·7	2	9·92	54·9	7
2·63	29·8	1	7·20	81·4	3½	2·65	27·1	1½	2720·31	49·6	6
2·87	26·4	1	7·48	77·4	3	2·86	24·2	1	0·62	45·5	5
3·06	23·7	½	7·62	75·5	2	3·25	18·9	1	0·87	42·1	4
3·20	21·7	½	7·85	72·2	1½	3·65	13·4	½	1·17	38·0	3
3·81	13·0	½	8·29	66·1	1	4·22	05·5	½	1·65	31·6	2
4·06	09·4	½	8·76	59·4	2	4·88	37096·4	0*b*	2·26	23·3	2½*b*
4·54	02·5	½	9·15	54·0	1½	5·47	88·3	0	2·75	16·7	3
4·81	37798·7	½	9·46	49·6	2	5·98	81·3	0	3·20	10·6	2½*b*
5·11	94·4	0	9·68	46·5	1½	6·25	77·6	0	3·66	04·8	2½
5·52	88·5	0	2670·20	39·3	½	6·61	72·6	½	4·03	36699·5	2
7·20	64·5	1	0·83	30·4	5½	7·10	65·9	½	4·29	96·0	1½
7·65	58·1	½	1·12	26·4	5	7·72	57·4	0	4·98	86·7	5
8·02	52·8	0	1·69	18·4	6	8·09	52·3	0	5·28	82·6	4
8·33	48·4	0	1·97	14·4	5½	8·95	40·5	0	5·42	80·7	3
9·35	33·9	0	2·22	11·0	5	9·19	37·2	½	5·67	77·4	2½
9·73	28·5	½	2·43	08·0	4½	9·84	28·3	½*b*	6·20	70·3	1
2650·39	19·1	2	2·63	05·2	4	2700·73	16·1	1½	6·57	65·3	1½
0·53	17·1	2	2·91	01·3	3½	1·09	11·1	1	7·25	56·1	2
1·07	09·4	6	3·22	37397·0	3	1·55	04·8	1	7·77	49·1	1
1·33	05·7	6	3·51	92·9	2	1·76	02·0	1½	8·32	41·8	½*b*
1·62	01·6	6	3·82	88·6	2	1·91	36999·9	1	8·75	36·0	½*b*
1·86	37698·2	6	4·18	83·5	2	2·60	90·5	2	9·46	26·5	8
2·04	95·6	5½	4·45	79·8	1	2·79	87·9	1	9·79	22·0	6½
2·40	90·5	5	4·90	73·5	2	2·93	85·9	1	2730·03	18·8	6
2·59	87·8	4½	5·19	69·4	1½	3·24	81·6	½	0·80	08·5	4½
2·93	83·0	4	5·69	62·5	2	3·45	78·8	0	1·27	02·2	4
3·47	75·3	4	6·19	55·5	1½	4·41	65·7	1½	1·75	36595·8	3½
4·12	66·1	3½	6·43	52·1	2	4·76	60·9	½	2·01	92·3	3½
4·40	62·1	3	6·83	46·5	1½	5·03	57·2	½	2·26	88·9	3
4·67	58·3	3	7·04	43·6	1	5·47	51·2	½	2·74	82·5	1*b*
5·10	52·2	2½	7·35	39·3	1	5·94	44·8	½	3·19	76·5	0
5·23	50·3	2½	7·48	37·5	1	6·72	34·1	½	3·50	72·3	½
5·46	47·1	1	7·85	32·3	½	7·41	24·7	0	4·10	64·3	3
5·77	42·7	1½	8·10	28·8	½	8·06	15·9	0	4·42	60·0	3½
6·31	35·0	1½	8·64	21·3	½	8·49	10·0	0*b*	4·85	54·3	3
6·75	28·8	4½	9·20	13·5	½*b*	9·03	02·7	0	5·08	51·2	3
7·09	24·0	3	9·58	08·2	1	9·32	36898·7	1½	5·54	45·1	3½
7·37	20·0	3	9·94	03·2	1*b*	9·64	94·3	1	5·71	42·8	3
7·68	15·6	2	2680·48	37295·7	½	9·80	92·2	½	6·14	37·0	2
8·08	10·0	1½	0·81	91·1	1½	2710·10	88·1	2	6·62	30·6	2
8·34	06·3	1	1·08	87·3	1½	0·43	83·6	1½	6·85	27·6	1
8·99	37597·1	2	1·18	85·9	1	0·90	77·2	2	7·66	16·8	1
9·42	91·0	1	1·38	83·2	1	1·09	74·6	1½	8·05	11·6	1½
9·61	88·3	1½	1·87	76·3	2½	1·35	71·1	1	8·41	06·8	1½
9·80	85·6	1½	2·32	70·1	1½	1·68	66·6	1	8·59	04·4	2
2660·17	80·4	1	2·63	65·8	1	2·00	62·2	1½	8·90	00·2	1
0·34	78·0	½	2·98	60·9	1	2·55	54·8	1*b*	9·15	36496·9	1
0·90	70·1	5	3·14	58·7	1	2·81	51·2	½	9·94	86·4	6
1·19	66·0	4½	3·58	52·6	½	3·27	45·0	1	2740·71	76·1	5½
1·35	63·8	4	3·88	48·4	½	3·93	36·0	½	1·17	70·0	5
1·46	62·2	4	4·27	43·0	0	4·12	33·4	0	1·58	64·6	4
1·65	59·5	3½	5·11	31·4	0	4·36	30·2	0	1·95	59·6	4
1·87	56·4	3	5·35	28·0	0	4·80	24·2	½	2·20	56·3	3½
2·10	53·2	2½	5·64	24·0	1	5·02	21·2	½	2·70	49·7	3½
2·44	48·4	2	6·19	16·4	1*b*	5·16	19·3	½	2·89	47·1	3
2·78	43·6	1½	6·52	11·8	½	5·48	15·0	0	3·36	40·9	2

TABLE IV.—(*contd.*).

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.*
2743·64	36437·2	1½	2776·67	36003·8	½	2805·01	35640·0	1	2835·30	35259·3	½
4·37	27·5	2½	6·94	00·3	½	5·41	34·9	½	6·08	49·6	½
4·83	21·4	2½	7·34	35995·1	0	5·86	29·2	½	6·38	45·9	1
5·47	12·9	2½	7·77	89·5	0*b*	6·22	24·6	1½	6·88	39·6	1
5·97	06·3	2	8·20	83·9	0	6·68	18·8	2	7·38	33·4	½
6·39	00·7	1½	8·65	78·1	0	7·07	13·9	1½	8·24	22·8	½
7·00	36392·6	1½	9·06	72·8	0	7·29	11·1	1	8·74	16·6	0
7·34	88·1	1½	9·37	68·8	0	7·80	04·6	2	9·13	11·7	½
7·96	79·9	1*b*	2780·24	57·5	½	8·24	35599·0	1	9·50	07·1	0
8·53	72·4	1	0·65	52·2	0	8·52	95·5	1½	2840·14	35199·2	½
8·74	69·6	1½	1·01	47·6	½	8·88	90·9	0	0·48	95·0	0
8·92	67·2	1½	1·39	42·7	½	9·97	77·1	½	1·23	85·7	1
9·25	62·8	1	2·00	34·8	1	2810·49	70·5	½	1·78	78·9	½
9·56	58·7	1	2·47	28·7	1	1·05	63·4	½	2·11	74·8	½
2750·50	46·3	3	2·84	24·0	1	1·29	60·4	1	2·65	68·1	½
0·84	41·8	2	3·22	19·0	1	1·75	54·6	1	3·09	62·7	0
1·55	32·4	3	3·61	14·0	½	2·10	50·2	½	3·71	55·0	0
1·84	28·6	2	4·01	08·8	½	2·56	44·3	2½	4·77	41·9	½
2·42	20·9	1	4·20	06·4	0	2·91	39·9	1	5·26	35·9	½
2·80	15·9	1½	4·42	03·5	0	3·39	33·9	2½	5·78	29·4	½
3·33	08·9	1	4·84	35898·1	0	3·58	31·5	1½	6·22	24·0	½
3·49	06·8	1	6·15	81·3	½	4·00	26·2	1	6·62	19·1	½
3·74	03·5	½	6·39	78·2	1	4·26	22·9	1	6·92	15·4	½
4·10	36298·8	0*b*	6·61	75·3	1	4·83	15·7	1	7·42	09·2	½
4·73	90·5	½	6·97	70·7	1	5·34	09·3	½	7·85	03·9	0
5·40	81·7	½	7·39	65·3	½	5·61	05·9	½	8·61	35094·6	0
5·64	78·5	1	8·09	56·3	½	5·97	01·3	0	9·92	79·4	½
5·90	75·1	½	8·36	52·8	1	7·25	35485·2	½	2850·67	69·2	1½
6·36	69·0	1	8·56	50·3	1	7·78	78·5	1	0·99	65·3	1
6·95	61·3	½	9·00	44·6	1	8·21	73·1	½	1·44	59·7	1
7·30	56·7	½	9·30	40·7	1	8·43	70·3	1	2·06	52·1	1
7·97	47·9	0	9·85	33·7	1	8·96	63·6	0	2·35	48·5	½
8·59	39·7	0	2790·51	25·2	8	9·29	59·5	½	2·62	45·2	½
9·11	32·9	½	0·89	20·3	6	9·84	52·6	0	3·52	34·2	0
9·33	30·0	½	1·18	16·6	6	2820·45	44·9	0	3·84	30·2	0
9·70	25·1	½	1·54	12·0	7	0·98	38·3	0	4·25	25·2	0
9·91	22·4	½	1·78	08·9	5½	1·26	34·7	0	4·70	19·7	½
2760·39	16·1	½	2·00	06·1	5	1·91	26·6	1	5·14	14·3	½
1·05	07·4	1½	2·23	03·1	4	2·16	23·4	1	5·60	08·7	0
1·43	02·4	½	2·43	00·6	3	2·44	19·9	1	7·08	34990·5	1
2·27	36191·4	1½	2·89	35794·7	3	2·80	15·4	½	7·38	86·9	½
2·55	87·8	1	3·34	88·9	2½	3·05	12·3	½	7·67	83·3	½
2·99	82·0	1½	3·58	85·8	1½	3·84	02·4	1½	7·91	80·4	½
3·23	78·9	1	4·17	78·3	3	4·13	35398·7	1	8·27	75·9	½
3·61	73·9	1	4·85	69·6	2	4·43	95·0	1	8·55	72·5	0
3·91	70·0	0	5·35	63·2	3	4·73	91·2	1½	8·92	68·0	0
4·22	65·9	½	5·60	60·0	2	5·20	85·3	1	9·32	63·1	½
4·54	61·7	0*b*	5·91	56·0	1	6·07	74·4	1	9·57	60·0	0
4·99	57·0	0	6·52	48·2	4	6·32	71·3	1½	9·82	57·0	0
5·49	49·3	½	6·84	44·1	3	6·76	65·8	1	2860·09	53·7	0
6·27	39·1	0	7·08	41·1	2½	7·02	62·6	½	1·97	30·7	1½
6·98	29·8	0	7·34	37·7	1½	7·40	57·8	0	2·48	24·5	1
7·74	19·9	0	7·57	34·8	1	8·13	48·7	0	3·33	14·1	½
8·01	16·4	0	7·86	31·1	½	8·32	46·3	½	3·99	06·1	1
8·81	06·0	0	8·54	22·4	0	9·01	37·7	0	4·34	01·8	½
9·35	36098·9	0	8·95	17·2	1½	9·33	33·7	0	4·79	34896·4	½
2770·37	85·6	½	9·51	10·0	1	9·64	29·8	0	5·76	84·5	4
1·17	75·2	1	9·90	05·1	1	9·98	25·6	½	6·29	78·1	3
1·47	71·3	1	2800·37	35699·1	1*b*	2830·51	19·0	0	6·51	75·4	3
1·67	68·7	½	1·03	90·7	½	0·90	14·1	0	6·73	72·7	2½
2·03	64·0	1	1·50	84·7	5	1·30	09·1	0	6·96	69·9	2
2·26	61·0	1	1·82	80·6	4	1·62	05·1	0	7·44	64·1	1
2·47	58·3	½	2·11	76·9	3½	1·88	01·9	0	7·81	59·6	½
3·28	47·8	1½	2·43	72·8	3	2·18	35298·1	0	8·41	52·3	½
3·63	43·2	1	2·65	70·0	2	2·90	89·2	½	9·40	40·3	1
4·09	37·2	½	3·01	65·5	2½	3·28	84·4	½	9·76	35·9	½
5·47	19·3	0	3·48	59·5	1½	3·67	79·6	½	2870·28	29·6	½
5·69	16·5	1	4·09	51·7	1½	4·00	75·5	½	0·92	21·8	½
5·86	14·3	1½	4·73	43·6	1	4·75	66·1	½	1·85	10·6	½
6·17	10·2	1	4·78	42·9	1	5·00	63·0	½	2·47	03·0	0

TABLE IV.—(*contd.*).

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.*
2873·30	34793·0	½	2883·77	34666·7	1	2911·13	34340·9	0*b*	2982·22	33522·3	½
4·42	79·2	½	4·03	63·6	1	1·96	31·1	0*b*	8·32	33453·9	½
5·33	68·4	0	4·23	61·1	0	3·35	14·7	0	2991·80	15·0	1
5·75	63·4	½	4·67	55·9	0	9·47	34242·8	0	6·80	33359·2	½
6·07	59·5	0	4·95	52·5	½	2922·68	05·2	0	3001·81	03·6	0*b*
7·31	44·5	2	5·57	45·1	½	5·59	34171·2	½	4·28	33276·2	0*b*
8·04	35·7	1½	6·01	39·8	½	2930·19	17·3	½	3010·71	05·1	0*b*
8·41	31·2	1½	6·48	34·1	½	1·98	34096·7	½	3·07	33179·1	½*b*
8·66	28·2	1½	6·90	29·1	½	4·51	67·3	½	6·70	39·2	0*b*
9·14	22·4	1	7·71	19·4	½	6·54	43·7	0	3020·25	00·2	½*b*
9·65	16·3	1	8·00	15·9	½	2940·94	33992·8	0	9·00	33004·6	½*b*
9·86	13·8	½	8·51	09·8	0	2·97	69·4	½*b*	3032·74	32963·9	½
2880·52	05·8	1	9·16	02·0	1½	5·72	37·7	1	5·68	32·0	1
0·86	01·7	½	9·94	34592·7	1½	9·47	33894·5	0*b*	9·03	32895·7	1
1·17	34698·0	½	2895·18	30·1	0	2951·54	70·7	½	3046·11	19·2	½
1·51	93·9	0	7·50	02·4	0	8·67	33789·1	½	3062·92	32639·1	½
2·18	85·9	1	9·19	34482·3	0*b*	2960·80	64·8	½	8·29	32582·0	0
2·43	82·8	1	2901·17	58·8	0	3·22	37·2	½	3074·40	17·2	½
2·80	78·4	0	4·33	21·3	0	2971·41	33644·3	1*b*	3117·97	32062·9	0*b*
3·33	72·0	0	8·87	34367·6	0	9·85	33549·0	½			

The wave-lengths are in Table IV, and the spectrum is plotted in the lower part of Fig. 3 on a frequency scale, intensities being qualitative as before. The general appearance of this spectrum is very similar to that of benzene, but the overlapping bands of different series fall differently in the two spectra, so that apparently corresponding band groups exhibit quite dissimilar forms.

Our general equation for the band maxima is

$$\nu = \left\{\begin{matrix} 37709 \\ 38707 \\ 38785 \end{matrix}\right\} - 942{\cdot}8n - 141{\cdot}2p$$

and we shall call the three electron levels A_0^0, B_0^0, and C_0^0 respectively, implying a correspondence with the levels of the benzene spectrum to which the same symbols were assigned. The level A_0^0 is directly observed, and its position agrees with that given by Cuthbertson and Kistiakowsky. The levels B_0^0 and C_0^0 are obscured by absorption, but have been directly observed by the method to be described in Part IX.

The two vibration frequencies correspond, of course, to those in the benzene formula whose quantum numbers are also called n and p. The complicated character of the vibrational structure of the spectrum arises, as before, partly from the circumstance that many of the low-frequency progressions extend well beyond the high-frequency interval in which they originate, and partly from the overlapping of the B- and C-band-series with the A-band-series. The band maxima, of which again there are upwards of 100, can be explained completely in the manner indicated. Details of the analysis are in Table V.

(5) *Summary of Electronic and Vibrational Frequencies.*—A conspectus of the electron terms and vibrational frequencies concerned in the fluorescence of benzene and hexadeuterobenzene is given in Table I.

Since the only vibrations "allowed" in fluorescence are those which are totally symmetrical with respect to the common symmetry of the initial and final states, the circumstance that transitions from all three electronically excited states to the ground state excite the same vibration frequencies shows that the three excited states share with the ground state exactly the same common symmetry properties. It is very probable therefore that the three excited states have the same symmetry amongst themselves. The frequency of quantum number n is identified by its presence and polarisation in the Raman spectrum (Part III) with a totally symmetrical vibration of the ground state (Part VIII). This frequency can therefore tell us nothing about the shape of the excited molecule, because a vibration which has all the symmetry of the ground state must have all the symmetry common to the ground state and excited state independently of the shape of the latter. The frequency of quantum number p has not yet been definitely assigned to a normal vibration (see Part VIII); but when it is assigned then any symmetry which the vibration lacks may be declared to be lacking in each of the excited states of the molecule.

TABLE V.

Series Assignment of Band Maxima in Fluorescence Spectrum of Hexadeuterobenzene.

n-Spacing ($\Delta\nu$).	Band No.	ν (cm.$^{-1}$).	*p*-Spacing ($\delta\nu$).
	A_0^0	37709·4	139·3
	A_0^1	37570·1	139·7
	A_0^2	37430·4	139·3
	A_0^3	37291·1	141·0
	A_0^4	37150·1	134·0
943·5	A_0^5	37016·1	138·9
	A_0^6	36877·2	139·2
	A_0^7	36738·0	135·8
	A_0^8	36602·2	137·6
	A_0^9	36464·6	148·7
	A_0^{10}	36315·9	133·9
	A_0^{11}	36182·0	
		Mean	138·9
	A_1^0	36766·9	140·4
	A_1^1	36626·5	140·1
	A_1^2	36486·4	140·1
	A_1^3	36346·3	138·9
	A_1^4	36207·4	136·1
941·7	A_1^5	36071·3	136·5
	A_1^6	35934·8	145·9
	A_1^7	35788·9	137·2
	A_1^8	35651·7	142·4
	A_1^9	35509·3	138·0
	A_1^{10}	35371·3	
		Mean	139·6
	A_2^0	35825·2	140·5
	A_2^1	35684·7	140·4
	A_2^2	35544·3	141·9
	A_2^3	35402·4	139·4
	A_2^4	35263·0	139·0
940·7	A_2^5	35124·0	140·7
	A_2^6	34983·3	143·0
	A_2^7	34840·3	134·5
	A_2^8	34705·8	284·5
	A_2^{10}	34421·3	
		Mean	140·4
	A_3^0	34884·5	140·0
	A_3^1	34744·5	142·5
	A_3^2	34602·0	143·2
946·8	A_3^3	34458·8	144·1
	A_3^4	34314·7	143·5
	A_3^5	34171·2	
		Mean	142·6
	A_4^0	33937·7	148·6
	A_4^1	33789·1	144·8
	A_4^2	33644·3	285·1
933·1	A_4^4	33359·2	154·1
	A_4^5	33205·1	273·1
	A_4^7	32932·0	
		Mean	143·6
	A_5^0	33004·6	422·6
941·7	A_5^3	32582·0	
		Mean	140·9
	A_6^0	32062·9	
	B_0^6	37872·4	138·5
	B_0^7	37733·9	136·8
	B_0^8	37597·1	147·5
	B_0^9	37449·6	141·4
	B_0^{10}	37308·2	133·9
	B_0^{11}	37174·3	137·1
	B_0^{12}	37037·2	
		Mean	139·2
	B_1^0	37764·5	135·7
	B_1^1	37628·8	142·5
	B_1^2	37486·3	134·2
	B_1^3	37352·1	140·3
	B_1^4	37211·8	139·2
	B_1^5	37072·6	138·5
	B_1^6	36934·1	138·9
943·3	B_1^7	36795·2	139·1
	B_1^8	36656·1	144·5
	B_1^9	36511·6	142·0
	B_1^{10}	36369·6	136·7
	B_1^{11}	36232·9	147·3
	B_1^{12}	36085·6	138·0
	B_1^{13}	35947·6	
		Mean	139·8
	B_2^0	36821·2	134·5
	B_2^1	36686·7	141·6
	B_2^2	36545·1	138·8
	B_2^3	36406·3	137·3
	B_2^4	36269·0	139·2
	B_2^5	36129·8	134·7
945·9	B_2^6	35995·1	138·8
	B_2^7	35856·3	139·1
	B_2^8	35717·2	140·1
	B_2^9	35577·1	138·8
	B_2^{10}	35438·3	140·2
	B_2^{11}	35298·1	
		Mean	139·0
	B_3^0	35875·3	127·1
	B_3^1	35748·2	143·6
	B_3^2	35604·6	134·3
	B_3^3	35470·3	144·7
	B_3^4	35325·6	139·9
944·6	B_3^5	35185·7	137·2
	B_3^6	35408·5	142·4
	B_3^7	34906·1	142·7
	B_3^8	34763·4	144·0
	B_3^9	34619·4	
		Mean	139·7
	B_4^0	34930·7	137·7
	B_4^1	34793·0	140·5
	B_4^2	34652·5	150·1
	B_4^3	34502·4	134·8
	B_4^4	34367·6	
		Mean	140·3
	C_0^7	37788·5	145·8
	C_0^8	37642·7	140·0
	C_0^9	37502·7	140·2
	C_0^{10}	37362·5	138·5
	C_0^{11}	37224·0	142·7
	C_0^{12}	37081·3	136·5
	C_0^{13}	36944·8	144·4
	C_0^{14}	36800·4	
		Mean	140·4
	C_1^0	37843·6	142·0
	C_1^1	37701·6	139·4
	C_1^2	37562·2	143·8
	C_1^3	37418·4	142·1
	C_1^4	37276·3	142·6
	C_1^5	37133·7	143·2
944·9	C_1^6	36990·5	145·5
	C_1^7	36845·0	140·2
	C_1^8	36704·8	144·8
	C_1^9	36560·0	138·6
	C_1^{10}	36421·4	142·9
	C_1^{11}	36278·5	
		Mean	142·5
	C_2^0	36898·7	136·6
	C_2^1	36762·1	153·6
	C_2^2	36608·5	138·5
	C_2^3	36470·0	137·6
	C_2^4	36332·4	141·0
	C_2^5	36191·4	143·6
941·2	C_2^6	36047·8	139·0
	C_2^7	35908·8	145·6
	C_2^8	37563·2	144·4
	C_2^9	35618·8	140·3
	C_2^{10}	35478·5	140·8
	C_2^{11}	35337·7	138·5
	C_2^{12}	35199·2	
		Mean	141·6
	C_3^0	35957·5	145·5
	C_3^1	35812·0	146·5
	C_3^2	35665·3	131·6
	C_3^3	35533·9	142·7
	C_3^4	35391·2	145·3
937·8	C_3^5	35245·9	136·7
	C_3^6	35109·2	146·1
	C_3^7	34963·1	141·3
	C_3^8	34821·8	139·0
	C_3^9	34682·8	
		Mean	141·6
	C_4^0	35019·7	141·6
	C_4^1	34878·1	142·4
	C_4^2	34755·7	143·0
952·4	C_4^3	34592·7	722·0
	C_4^8	33870·7	133·5
	C_4^9	33737·2	
		Mean	142·5
928·1	C_5^0	34067·3	
	C_6^0	33139·2	

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