

## 216. Structure of Benzene. Part VI. Resonance Emission Spectrum of Benzene and Hexadeuterobenzene.

By C. K. INGOLD and C. L. WILSON.

(1) *General Principles*.—As explained in Part V, the fluorescence and resonance spectra differ chiefly in the circumstance that in the former the excited state from which transition takes place is vibrationless (except for zero-point energy), whereas in the latter it is strongly vibrating. In general, the existence of vibrations in the excited state will produce vibrations in the ground state additional to those which can appear strongly in transitions from the vibrationless excited state. The resonance spectra are therefore expected to be very complicated, and accordingly it is desirable at the outset to have some idea of what may be expected from the selection rules governing the excitation of vibrations in transitions from a vibrating state.

This question has been treated by Herzberg and Teller (*Z. physikal. Chem.*, 1933, **21**, 410), who show that the symmetry of the molecule places certain restrictions on the vibrational changes that can accompany such electronic transitions. By considering the structure of the matrix element, the square of which measures the probability of transition, and deducing the conditions under which it would vanish, they obtain the following general selection rule: the total vibrational wave-functions of the initial and final states must have the same symmetry properties.\* In order to clarify the meaning of this theorem in relation to the problems in which we are interested, some general definitions are required.

Normal vibrations may be classified according to their behaviour on the application of those symmetry operations (such as reflexion across a plane, inversion through a centre, or rotation about an axis of symmetry) which, if applied to the equilibrium configuration of the molecule, would convert it into a configuration indistinguishable from the original one. For any such operation one of three things may happen to a normal vibration: either all the displacement vectors remain unchanged (become multiplied by  $+1$ ), or they all become inverted (multiplied by  $-1$ ), or they become compounded with the vectors of other vibrations of the same frequency (transformed into linear combinations). In the first case the normal vibration is said to be "symmetric with respect to the symmetry operation"; in the second it is "antisymmetric to the operation"; in the third it is "degenerate with respect to the operation." If for *all* the symmetry operations permitted by the equilibrium configuration of the molecule the displacement vectors of a normal vibration remain unchanged, then the vibration is said to be "totally symmetrical"; otherwise it is "non-totally symmetrical" and may be "degenerate." It is degenerate if there are two or more independent vibrations such that they and all combinations of them have the same frequency; a familiar example is provided by a linear triatomic molecule such as carbon dioxide, where the bending vibration has two-fold degeneracy, the separate members of identical frequency being independent if taken in two perpendicular planes. For non-degenerate vibrations the effect of symmetry operations is always mere multiplication by  $\pm 1$ . For degenerate vibrations the same result may follow certain operations, but there will be at least one by which linear combinations are formed; such an operation is possible where there is an axis of at least three-fold symmetry.

Vibrational wave-functions distinguish themselves from vibrations with respect to their behaviour towards symmetry operations in the following way. If a vibration is excited with an odd quantum number, the corresponding vibrational wave-function will be an "odd" function of the co-ordinate in which we measure the vibration (normal co-ordinate); that is, it will change sign when the co-ordinate changes sign. It follows that the wave-function will possess the same symmetry properties as the vibration itself, so that on the application of different symmetry operations it will be multiplied by  $+1$  or by  $-1$  or transformed into a linear combination exactly as the vibration would have been. On the other hand, if a vibration is excited to an even quantum number, the corresponding vibrational wave-

\* Strictly, this deduction is subject to the assumption that the probability of electron transition is independent of nuclear position.

function will be an " even " function of the displacement co-ordinate ; it will keep the same sign when the co-ordinate changes sign. In this case, therefore, the wave-function will in general be more symmetrical than the vibration itself, inasmuch as a symmetry operation which would have multiplied the vibration by  $-1$  will multiply the wave-function by  $+1$ . In particular, the wave-function of a non-degenerate vibration excited to an even quantum number will always be multiplied by  $+1$  ; in short, it will be totally symmetrical. All these properties follow from the fact that the wave functions depend on Hermitean polynomials (cf. Pauling and Wilson, " Introduction to Quantum Mechanics," 1935), which are odd or even functions of their arguments according as the quantum number is odd or even.

Since normal vibrations are all mutually independent, the total vibrational wave-function is simply the product of the wave-functions of the separate normal vibrations.

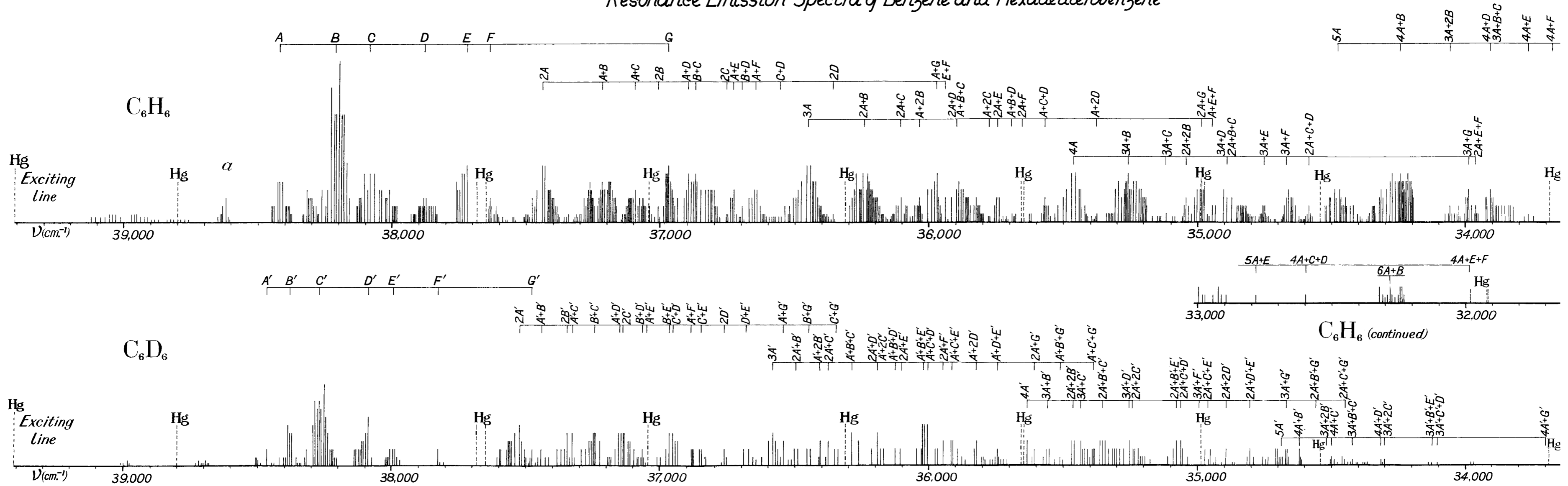
Now Herzberg and Teller's theorem states that only those vibrational changes can accompany an electron transition which do not change the symmetry properties of the total vibrational wave-function. We have to see what this means for the three classes of vibrations, the totally symmetrical, the non-totally symmetrical non-degenerate, and the degenerate vibrations. It should be stated that we are now using a slightly different standard of symmetry : the term totally symmetrical will be taken to refer to the totality of symmetry properties (permitted symmetry operations) which are *common* to the ground and excited states, and the terms non-totally symmetrical and degenerate will carry a similar interpretation. If a vibration is totally symmetrical with respect to the symmetry of either of the separate states, it must obviously be totally symmetrical with respect to the common symmetry. If a vibration is non-totally symmetrical or degenerate to the common symmetry properties, it is evidently non-totally symmetrical or degenerate, as the case may be, in each of the separate states.

A totally symmetrical vibration, no matter with how many quanta it is excited, always has a totally symmetrical wave-function. Therefore a totally symmetrical vibration can undergo any change of quantum number without changing the symmetry properties of its *own* wave-function. It follows that the excitation or suppression, during an electron transition, of a totally symmetrical vibration cannot make any difference to the symmetry properties of the *total* vibrational wave-function, in which the wave-function of the totally symmetrical vibration simply appears as a factor. In short, the excitation of totally symmetrical vibrations is permitted without restriction as to quantum number in transitions from a vibrating state, just as in transitions from a vibrationless state (Part V).

A non-totally symmetrical non-degenerate vibration gives a wave-function with the same symmetry properties as the vibration if the quantum number is odd, and a totally symmetrical wave-function if the quantum number is even. The wave-function of such a vibration will have the same symmetry properties in the initial and final states if, when the quantum number was odd in the initial state, it remains odd in the final state, and, when it was even in the initial state, it remains even in the final state ; in either case the *change* of quantum number is even. Therefore the total vibrational wave-function will maintain its symmetry properties if the change of quantum number of the non-totally symmetrical non-degenerate vibration is even. It follows that such a vibration is allowed to change its quantum number by an even number during an electron transition, and that therefore successive excitations of the vibration will differ by gaps of two quanta.

If several non-totally symmetrical non-degenerate vibrations have exactly the same symmetry properties, there is an additional way of satisfying the rule of constant symmetry in the total vibrational wave-function. Two vibrations of the same symmetry will give wave-functions which for corresponding quantum numbers also have the same symmetry. Hence, if we change the quantum number of one of these vibrations by an odd number, so that a symmetry operation which would formerly have multiplied its wave-function by  $+1$  now multiplies it by  $-1$ , or *vice versa*, we have only to arrange that the other vibration shall also change its quantum number by an odd number in order to obtain a repetition of the effect on the result of the symmetry operation, and therefore no effect at all when this operation is applied to the total vibrational wave-function which contains these two wave-functions as factors : again the total wave-function will maintain its symmetry. There-

*Fig. 1*  
*Resonance Emission Spectra of Benzene and Hexadeuterobenzene*



fore non-totally symmetrical non-degenerate vibrations of exactly similar symmetry can conspire together in pairs each to undergo an odd change of quantum number, the number of quanta involved in the joint change being, of course, even. Herzberg and Teller's theory therefore permits, not only the above-mentioned excitations of individual vibrations each in successive multiples of twice its quantum, but also joint excitations of pairs of vibrations of like symmetry, each in successive multiples of the sum of the quanta of the two associated vibrations.

If degenerate vibrations are present, the condition governing the excitation of non-totally symmetrical non-degenerate vibrations must be expressed in a slightly more general way: it is sufficient if the total change of quantum number for all vibrations antisymmetrical to a given symmetry operation is even for all symmetry operations. It will be clear from the foregoing that the total vibrational wave-function will then have invariant symmetry. The effect of this generalisation is to make it possible in certain circumstances for a degenerate and a non-degenerate vibration to combine as has been described for two non-degenerate vibrations of equal symmetry. These circumstances are that both vibrations should be antisymmetric to the same symmetry operations, and that the degenerate vibration should further satisfy the conditions peculiar to degenerate vibrations.

Degenerate vibrations must fulfil the condition stated in the previous paragraph with respect to all those symmetry operations to which they are antisymmetric, but a still broader statement is necessary to take account also of the restrictions on their behaviour in the symmetry operations to which they are degenerate. The general condition is that, before and after the transition, linear combinations of the degenerate vibrational wave-functions can be formed which have identical symmetry properties. However, unless we know with what quantum numbers degenerate vibrations were present in the excited state, it is impossible to deduce from this what changes of quantum number are permitted to accompany transition to the ground state.

We may summarise the consequence of Herzberg and Teller's theory in relation to resonance spectra as follows. Totally symmetrical vibrations, being unrestricted as to change of quantum number, should be excited with successive quantum numbers, and should give rise to bands progressing with a spacing equal to one quantum, that is, to the fundamental frequency of the vibration. Non-totally symmetrical non-degenerate vibrations should give bands progressing with spacings equal to twice the fundamental vibration frequencies. If several such vibrations have identical symmetry, we may expect progressions with spacings equal to the sum of the fundamental frequencies of pairs of vibrations of like symmetry. If degenerate vibrations are present, there may be a possibility of spacings equal to the sum of the frequencies of a non-totally symmetrical non-degenerate vibration and a degenerate vibration. The appearance of the degenerate vibrations themselves will be subject to restrictions which cannot definitely be predetermined although they will in general include the restrictions applying to non-totally symmetrical vibrations.

(2) *Resonance Spectrum of Benzene excited by the Mercury 2537 Å. Line.*—This was observed by Pringsheim and Reimann (*Z. Physik*, 1924, **29**, 115) and by Reimann (*Ann. Physik*, 1926, **80**, 43). It was investigated in some detail by Kistiakowsky and Nelles (*Physical Rev.*, 1932, **41**, 495), whose conclusions have, however, been considerably modified in a recent paper by Cuthbertson and Kistiakowsky (*J. Chem. Physics*, 1936, **4**, 9). These authors do not publish their actual measurements, so we have not made a detailed check of our results against theirs; they do, however, record conclusions concerning the frequency progressions, and when their paper appeared we had already formed views which agree much better with theirs than with the previously published conclusions, although some notable differences remain.

Our results, obtained by methods described in the preceding paper, are recorded in Table II, and are plotted on a frequency scale in the upper part of Fig. 1 (folder). As before, intensities are qualitative, being obtained from uncalibrated microphotometer records.

One difficulty of interpretation, mentioned also by Cuthbertson and Kistiakowsky, arises from the variety of shapes exhibited by the bands and their tremendous breadth, a

circumstance doubtless connected with the violent rotation which the molecule must undergo on absorption of the exciting frequency; some bands are  $150 \text{ cm.}^{-1}$  broad. In order to provide ourselves with a definite rule of procedure, we have assumed that when a band contains one outstanding maximum this locates the origin; that when it contains two, the mean frequency must be taken; and that when it contains three the centre one is to be accepted. Nevertheless, the real origins may, of course, be separated from these adopted points by perhaps  $20 \text{ cm.}^{-1}$  in the case of the broader bands.

On examining Fig. 1, it will be seen that the whole spectrum can be divided into sections of  $989 \text{ cm.}^{-1}$  starting from the exciting line. The first section is unique, the second is different and also unique, the third, fourth, and fifth are different again but similar to one another, whilst the sixth to the ninth are similar to the third, fourth, and fifth except that now some of the bands are disappearing, until in the eighth and ninth sections only one remains.

The first section contains one definite but rather slight band (*a*) separated by  $790 \text{ cm.}^{-1}$  from the exciting line, and a whole array of faint lines to which it seems unsafe to ascribe a definite origin. We are not even sure that these faint lines really belong to the resonance spectrum as they were indistinct on the plates taken at the lowest pressures.

The second section of the spectrum contains six distinct and well-spaced bands (*A—F*), one of which (*B*) is of outstanding intensity. Their separations from the exciting line are  $989, 1197, 1326, 1531, 1690,$  and  $1776 \text{ cm.}^{-1}$  respectively.

The third section consists of a semi-continuous mass of bands only a few of which bear any close resemblance to bands of the second section. If, however, we take the frequency separations of the second section and add them together in pairs in all the possible ways, including those derived by using the same frequency twice, we find that the frequencies thus obtained correctly locate all the band origins of the third section except that one band is left over. This band we therefore treat as an overlap from the second section; it is labelled (*G*), and its separation from the exciting line is  $2439 \text{ cm.}^{-1}$ .

The remainder of the spectrum can now be explained by supposing that higher combinations of the frequency differences  $A - G$  are subject to the restriction that a band becomes weak, and in general too weak to be observed, if its frequency separation involves more than four *A*-frequencies or more than two other frequencies. (Some exceptions to this occur in combinations involving *A* and the very strong frequency *B*.) We can partly justify the assumed difference of persistence between the *A*-frequencies and the others by identifying *A* with a totally symmetrical vibration and the others with non-totally symmetrical vibrations; it then follows from the theory of Herzberg and Teller that the frequencies *B—G* are already combinations, most of them probably binary combinations, of fundamental frequencies, so that the double occurrence of one which is already twice a fundamental or the sum of two fundamentals is equivalent as to change of quantum number with a four-fold occurrence of *A*.

The fourth section of the spectrum is like the third, including like the latter a frequency involving *G*, but it includes also two further bands. These can be interpreted as belonging generically to the third section, since they correspond to the only other binary combinations of the frequencies *A—G* which should be observable in this fourth section of the spectrum.

The fifth section is similar to the fourth. The sixth section resembles the fifth except that several bands have disappeared. In the seventh section several more bands have disappeared, and indeed, the only frequency which still leaves a moderately strong record is the one involving *B* and a multiple of *A*. In the eighth and ninth sections this frequency is the sole survivor.

The details of this analysis of the spectrum are given in Table III. The component frequency differences arrived at in this way are :

<i>a.</i>	<i>A.</i>	<i>B.</i>	<i>C.</i>	<i>D.</i>	<i>E.</i>	<i>F.</i>	<i>G.</i>
790	989	1197	1326	1531	1690	1776	2439 $\text{cm.}^{-1}$

but we reserve for the moment discussion of what fundamental vibration frequencies are concerned in the make-up of these differences. We are uncertain whether or not to treat *F* as  $a + A$ , for although the frequencies would agree, comparison of the fine structures of

the bands does not give further support to this idea, and the frequency relation does not repeat itself in hexadeuterobenzene.

We may compare the above frequencies with Cuthbertson and Kistiakowsky's, which are here labelled to correspond as far as possible to ours :

$$432, (a) 791, (A) 990, (D) 1542, (? G) 2557, 3174 \text{ cm.}^{-1}.$$

These authors assumed that combination frequency separations could involve frequency *A* any number of times but the other frequencies only once, and also that the latter frequencies do not combine with each other. We know of no selection rule of this character, and on the empirical side we could not possibly represent the frequencies of all our bands on this basis. Nor could we represent our results without the frequencies *B*, *C*, and *E*—quite apart from the fact that they appear strongly, and in an uncombined form, in the second section of the spectrum. Cuthbertson and Kistiakowsky's frequency  $432 \text{ cm.}^{-1}$  lies in a region where our spectrum is so diffuse that we hesitate to assign a vibration frequency; furthermore, we do not want this frequency for the interpretation of the combination bands—indeed, it would be a positive embarrassment. We could not ourselves conclude in favour of the presence of a frequency  $3174 \text{ cm.}^{-1}$ , since if it were present it would coincide with a strong combination band (from *A* and *B*), which is an intermediate member of a long series of similar bands progressing in regular intervals of  $989 \text{ cm.}^{-1}$ . Finally, the difference between Cuthbertson and Kistiakowsky's  $2557 \text{ cm.}^{-1}$  and our  $2439 \text{ cm.}^{-1}$  (*G*) may perhaps be explained as an arithmetical error, since Cuthbertson and Kistiakowsky's statements about their frequency are mutually inconsistent by  $110 \text{ cm.}^{-1}$ , almost the difference between their frequency and ours.

(3) *Resonance Spectrum of Hexadeuterobenzene Excited by the Mercury 2537 A. Line.*—This was also examined by Cuthbertson and Kistiakowsky but not in much detail. They claim the frequencies  $944$  and  $2460 \text{ cm.}^{-1}$ , but again do not give details of the measurements.

Our results are given in Table IV, and a plot of the spectrum is reproduced in the lower part of Fig. 1. The previous remarks concerning intensities, and the selection of band origins, apply. The chief general difference between the spectrum of benzene and that of hexadeuterobenzene is that the latter is not nearly so strong—for instance, we were able to measure over 600 lines in the benzene spectrum, but not quite 300 in the hexadeuterobenzene spectrum, in spite of the fact that for the latter the exposures had been approximately doubled. We may attribute this difference to the varying disposition of the absorption bands of the two compounds, and in particular to weaker absorption by hexadeuterobenzene at the frequency of the exciting line.

Once again the spectrum can be split up into sections, but this time the length of each is  $944 \text{ cm.}^{-1}$ . The first section contains only a sprinkling of weak lines similar to those to which we refused to assign definite origins in the first section of the benzene spectrum; there is no properly developed band. The second section contains six well-spaced bands (*A'*—*F'*), of which the third (*C'*) is particularly strong, and the sixth (*F'*) is quite weak.

TABLE I.

*Fundamental Frequencies in the Resonance Emission Spectra of Benzene and Hexadeuterobenzene (cm.<sup>-1</sup>).*

	Frequency displacement.		Fundamental frequencies.		Fundamentals in other spectra.		
	C <sub>6</sub> H <sub>6</sub> .	C <sub>6</sub> D <sub>6</sub> .	C <sub>6</sub> H <sub>6</sub> .	C <sub>6</sub> D <sub>6</sub> .	C <sub>6</sub> H <sub>6</sub> .	C <sub>6</sub> D <sub>6</sub> .	Spectrum.
(i) <i>Totally symmetrical.</i>							
(A)	989	(A')	989	944	{ 990	943	Fluorescence Raman
					{ 992	945	
(ii) <i>Non-totally symmetrical.</i>							
(a)	790	—	(395)	—	—	—	—
(B)	1197	(C')	598	569	606	577	Raman
(C)	1326	(B')	663	514	671	503	Infra-red
(D)	1531	(E')	(765)	(707)	—	—	—
(E)	1690	(D')	845	661	849	666	Raman
(F)	1776	(F')	(888)	(791)	—	—	—
(G)	2439	(G')	(1219)	(961)	—	—	—

TABLE II.

## Resonance Emission Spectrum of Benzene.

$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I</i> *	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I</i> .	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I</i> .	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I</i> .
2555.25	39123.4	$\frac{1}{2}$	2623.64	38103.6	6	2672.95	37400.7	3	2703.40	36979.5	6
6.73	00.7	$\frac{1}{2}$	4.47	38091.6	4	3.13	37398.2	3	3.58	77.1	6
7.55	39088.2	$\frac{1}{2}$	5.06	83.0	6	3.60	91.6	2	3.76	74.6	6
8.62	71.8	$\frac{1}{2}$	6.19	66.6	6	4.05	85.3	2	4.11	70.1	7
9.67	55.8	1	7.33	50.1	4	4.36	81.0	1	4.67	62.1	5
2560.45	43.9	1	8.44	39.8	4	4.70	76.2	$\frac{1}{2}$	5.14	55.7	4
1.22	32.2	1	9.04	25.3	3	5.92	59.2	$\frac{1}{2}$	5.44	51.6	3
2.32	15.4	$\frac{1}{2}$	9.34	21.0	3	6.55	50.4	$\frac{1}{2}$	5.79	46.8	2
5.05	38973.9	1	2630.03	11.0	4	7.06	43.3	1	6.58	36.1	3
5.82	62.2	1	0.90	37998.5	2	8.39	24.8	0	8.40	11.2	3
6.51	51.8	1	1.04	96.4	2	8.88	18.0	$\frac{1}{2}$	9.08	01.9	4
7.32	39.4	$\frac{1}{2}$	1.35	92.0	2	9.24	12.9	1	9.69	36894.6	6
8.36	23.7	$\frac{1}{2}$	1.61	88.2	2	9.54	08.7	$\frac{1}{2}$	2710.30	85.4	5
9.00	14.0	$\frac{1}{2}$	1.96	83.1	2	2680.06	01.5	1	1.02	75.6	5
9.98	38899.1	0	5.70	29.3	1	0.40	37296.8	1	1.52	68.6	6
2570.84	86.3	0	6.35	19.9	1	1.26	84.8	3	1.96	62.8	5
1.77	72.1	0	6.51	17.6	1	1.77	77.7	2	3.01	48.5	4
3.88	40.2	0	6.89	12.1	1	2.22	71.5	3	4.19	32.5	4
4.86	25.4	0	7.64	01.2	2	2.40	69.0	4	4.87	23.3	4
5.57	14.7	0	7.86	37898.2	2	2.97	61.2	5	5.49	14.9	3
7.27	38789.1	0	8.10	94.8	2	3.11	59.1	4	5.73	11.6	3
8.31	73.5	0	8.55	88.3	2	3.31	56.4	4	5.91	09.2	3
9.21	60.0	0	8.75	85.4	2	3.47	54.1	3	6.41	02.4	3
2586.53	38650.2	$\frac{1}{2}$	8.95	82.6	3	3.63	51.9	3	6.59	00.0	3
7.14	41.1	1	9.17	79.4	2	3.77	49.9	3	6.95	36795.1	2
7.47	36.2	1	9.61	73.1	3	4.00	46.8	2	7.22	89.0	2
7.70	32.8	2	2640.10	66.1	2	4.91	34.1	2	8.07	79.9	$\frac{1}{2}$
8.60	19.4	3	0.58	59.2	2	5.31	28.4	3	9.77	56.9	$\frac{1}{2}$
9.19	10.5	$\frac{1}{2}$	1.10	51.7	2	5.71	22.9	4	2720.00	53.8	1
9.57	04.9	0	1.35	48.1	2	6.13	17.3	5	0.22	50.8	1
2600.16	38447.6	2	1.95	39.6	2	6.30	14.9	4	1.17	38.8	3
0.34	45.0	2	2.22	35.7	1	6.83	07.5	4	1.53	33.2	3
0.62	40.9	2	2.44	32.5	1	7.55	37197.6	4	2.00	26.8	4
1.60	26.4	5	7.46	37760.8	5	7.91	92.6	5	2.75	17.7	1
2.00	20.4	5	7.90	54.5	4	8.14	89.5	5	3.52	06.4	$\frac{1}{2}$
2.77	09.1	5	8.35	48.2	4	8.35	86.5	5	3.70	03.9	2
3.65	38396.2	2	8.97	39.3	6	8.89	79.1	4	4.26	36696.3	2
3.90	92.5	2	9.54	31.2	6	9.35	72.7	3	4.71	88.8	0
4.20	88.0	2	2650.36	19.5	7	9.74	67.2	3	6.20	70.3	3
4.49	83.8	2	6.27	37635.6	2	2690.14	61.7	2	7.00	59.5	3
4.78	79.6	1	6.46	32.9	3	1.32	45.5	0	7.71	49.9	4
5.01	74.8	1	6.65	30.2	2	1.64	41.1	1	8.41	40.6	4
7.96	32.7	1	7.39	19.7	1	2.16	33.9	1	9.27	29.0	2
8.15	29.9	1	8.01	11.0	2	2.38	30.8	1	9.79	22.0	1
8.96	18.0	4	8.30	06.8	1	2.68	26.7	2	2730.17	16.9	1
9.30	13.0	3	8.69	01.4	$\frac{1}{2}$	2.97	22.7	2	0.65	10.5	1
9.68	07.5	3	9.71	37586.9	$\frac{1}{2}$	3.17	19.9	3	0.89	07.3	$\frac{1}{2}$
2610.18	00.0	3	2660.53	75.3	0	3.52	15.1	3	1.67	36596.8	$\frac{1}{2}$
0.65	38293.2	2	0.93	69.7	0	3.56	14.6	3	2.49	85.8	$\frac{1}{2}$
1.28	84.0	2	2.40	48.9	$\frac{1}{2}$	3.73	12.2	3	3.08	77.9	$\frac{1}{2}$
1.67	78.3	1	2.62	45.8	$\frac{1}{2}$	3.94	09.3	3	3.48	72.5	$\frac{1}{2}$
1.93	74.5	1	2.98	40.9	0	4.54	01.1	3	4.42	60.0	$\frac{1}{2}$
2.84	62.5	4	5.30	08.1	$\frac{1}{2}$	5.06	37093.9	4	5.09	51.1	$\frac{1}{2}$
3.74	48.0	2	5.54	04.7	$\frac{1}{2}$	5.76	84.3	2	6.15	37.9	2
4.19	41.3	4	5.71	02.3	1	6.39	75.6	3	7.14	23.7	1
5.18	26.9	25	6.10	37496.8	1	6.80	70.0	2	7.33	21.2	2
6.03	14.5	20	6.38	92.9	1	7.03	66.8	3	7.49	19.0	1
6.41	08.9	20	6.71	88.3	$\frac{1}{2}$	7.20	64.5	3	8.43	06.5	3
7.24	38196.8	30	7.45	77.8	3	7.34	62.6	3	9.08	36497.8	3
7.86	87.7	20	8.13	68.3	2	7.53	60.0	2	9.65	90.2	4
8.33	80.9	20	8.71	60.2	4	7.90	54.9	2	2740.81	74.8	5
9.00	71.1	12	2670.09	40.8	7	9.01	39.6	2	2.19	56.4	7
9.70	60.9	3	0.77	31.3	7	9.58	31.8	1	3.22	42.7	7
2621.57	33.7	2	1.65	18.9	4	2700.43	20.2	$\frac{1}{2}$	3.97	32.8	5
1.83	30.0	2	1.87	15.8	4	1.34	07.7	2	4.17	31.0	5
2.25	23.8	3	2.04	13.5	4	1.80	01.4	$\frac{1}{2}$	4.60	24.4	5
2.46	20.7	3	2.31	09.7	4	2.79	36987.8	2	5.25	15.8	3
2.66	18.3	3	2.78	03.1	3	3.28	81.0	6	5.70	09.8	2

\* *I* = Intensity.

TABLE II.—(contd.).

$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I.</i>	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I.</i>	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I.</i>	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I.</i>
2745·97	36406·2	2	2786·76	35873·4	4	2837·91	35226·9	5	2888·20	34613·5	0
6·30	01·9	2	7·47	64·3	3	8·79	15·9	4	8·75	06·9	0
6·62	36397·6	1	7·76	60·5	3	9·36	08·9	4	9·07	03·1	0
6·83	94·8	1	8·02	57·2	3	9·83	03·1	3	9·36	34599·6	$\frac{1}{2}$
7·05	91·9	1	8·20	54·9	3	2840·27	35197·6	3	9·92	93·0	1
7·40	87·3	$\frac{1}{2}$	8·87	46·1	2	0·77	91·4	3	2890·49	86·1	2
7·88	80·9	1	9·96	32·2	2	1·04	88·1	2	1·00	80·0	1
8·28	75·6	$\frac{1}{2}$	2790·59	24·2	3	2·70	67·5	$\frac{1}{2}$	1·60	72·8	$\frac{1}{2}$
8·99	66·3	0	1·05	18·2	2	4·32	47·5	$\frac{1}{2}$	5·55	25·7	2
9·60	58·2	1	1·21	16·2	2	4·93	39·9	$\frac{1}{2}$	5·96	20·8	2
9·94	53·7	0	1·42	13·5	2	5·26	35·9	$\frac{1}{2}$	6·93	09·2	3
2754·23	36297·0	2	1·67	10·3	2	6·84	16·4	1	7·21	05·9	3
4·93	87·9	3	1·93	07·0	1	8·55	35095·3	$\frac{1}{2}$	8·60	34489·4	4
5·54	79·9	4	2·19	03·6	1	9·11	87·3	$\frac{1}{2}$	8·97	84·9	3
6·15	71·8	6	2·45	00·3	1	2851·48	59·2	2	2900·10	71·4	4
7·08	59·6	4	2·67	35797·5	1	2·09	51·7	2	0·05	66·7	3
7·34	56·1	4	4·19	78·0	$\frac{1}{2}$	2·60	45·5	3	0·77	63·5	2
7·55	53·4	4	4·53	73·7	$\frac{1}{2}$	3·35	36·3	2	1·50	54·9	2
8·06	46·7	6	6·00	54·9	2	4·27	25·0	1	1·99	48·8	3
8·58	39·9	6	6·43	49·4	3	5·22	13·2	3	2·32	45·1	2
9·17	33·8	4	7·14	40·4	3	5·96	04·2	4	3·53	30·8	2
9·58	26·7	6	7·91	30·5	0	6·84	34993·2	4	4·29	21·8	2
9·82	23·6	5	8·23	26·4	$\frac{1}{2}$	7·41	86·7	5	5·68	05·3	1
9·92	22·2	5	8·95	17·2	0	7·76	82·2	4	6·53	34395·2	$\frac{1}{2}$
2760·00	21·2	4	9·31	12·6	$\frac{1}{2}$	8·22	76·6	5	7·03	89·3	0
0·39	16·1	4	9·64	08·4	0	9·16	65·1	1	8·66	70·0	0
0·68	12·3	4	2800·90	35692·3	1	9·67	58·8	$\frac{1}{2}$	9·14	64·4	$\frac{1}{2}$
1·00	08·1	3	1·23	88·1	$\frac{1}{2}$	2860·57	47·8	2	9·48	60·4	1
1·46	02·0	3	1·56	83·9	$\frac{1}{2}$	1·50	36·5	2	2910·32	50·4	2
1·67	36199·3	3	1·96	78·8	1	4·08	05·0	4	0·77	45·1	2
2·11	93·5	3	6·02	27·2	1	5·18	34891·6	3	1·15	40·6	2
2·61	87·0	2	6·49	21·2	1	6·58	74·6	3	1·38	37·9	1
2·92	82·9	2	9·57	35582·2	1	8·24	54·4	2	2·73	22·0	3
3·39	76·8	1	2810·20	74·2	2	8·68	49·0	2	3·28	15·5	4
3·64	73·5	1	0·58	69·4	3	9·32	41·3	2	3·62	11·5	3
3·83	71·0	1	0·93	65·0	2	9·69	36·8	2	4·95	34295·9	4
4·58	61·2	$\frac{1}{2}$	1·65	55·9	2	2870·11	31·9	2	6·06	82·8	5
4·95	56·4	0	2·23	48·5	$\frac{1}{2}$	0·33	29·0	2	6·56	76·9	6
5·80	45·2	0	3·53	32·1	1	0·79	23·4	2	7·60	64·7	5
6·08	41·6	$\frac{1}{2}$	4·38	21·4	2	1·08	19·9	2	8·64	52·5	5
6·44	36·9	1	5·51	07·1	3	1·47	15·2	1	9·01	48·2	5
6·71	33·4	1	6·89	35489·7	4	1·84	10·7	1	9·40	43·6	6
6·98	29·8	1	8·42	70·4	6	2·21	06·2	1	9·86	38·2	5
7·43	24·0	2	9·57	56·0	6	2·70	00·3	$\frac{1}{2}$	2920·15	34·8	5
8·15	14·6	2	2820·58	43·3	4	3·13	34795·1	$\frac{1}{2}$	0·40	31·9	5
8·93	04·4	3	1·20	35·5	4	3·81	86·8	$\frac{1}{2}$	0·81	27·1	4
9·91	36091·6	1	2·34	21·2	2	4·96	72·9	$\frac{1}{2}$	1·06	24·2	5
2770·28	86·8	2	2·54	18·7	1	5·40	67·6	1	1·29	21·5	5
0·73	80·7	2	2·84	15·0	1	5·73	63·6	1	1·74	16·2	6
1·57	70·0	$\frac{1}{2}$	3·15	11·0	$\frac{1}{2}$	6·24	57·4	2	2·47	07·6	5
2·21	61·7	$\frac{1}{2}$	4·23	35397·5	$\frac{1}{2}$	6·60	53·1	2	2·74	04·5	5
2·83	53·6	2	4·79	90·5	0	6·83	50·2	2	3·06	00·7	4
3·61	43·5	2	5·20	85·3	0	7·10	47·1	1	3·43	34196·4	3
3·89	39·8	2	5·62	80·1	$\frac{1}{2}$	7·32	44·4	$\frac{1}{2}$	2933·48	34079·3	1
4·19	35·4	3	5·96	75·8	1	8·00	36·2	$\frac{1}{2}$	4·57	66·6	1
4·43	32·8	2	8·82	40·1	1	8·55	29·5	0	5·22	59·1	2
4·99	25·6	1	9·39	32·9	1	9·69	15·8	0	5·87	51·5	1
6·92	00·5	4	9·79	27·9	1	2880·19	09·8	0	6·42	45·1	1
7·75	35989·7	4	2830·25	22·2	1	1·94	34688·7	0	7·46	33·1	1
8·48	80·3	5	0·77	15·7	1	2·30	84·4	$\frac{1}{2}$	8·45	25·1	2
9·28	69·9	6	1·54	06·1	4	2·56	81·2	1	9·28	12·0	$\frac{1}{2}$
9·70	64·5	3	2·50	35294·1	5	2·84	77·9	2	9·90	04·8	1
2780·11	59·2	2	3·30	84·1	3	3·54	69·4	3	2940·44	33998·6	3
0·38	55·7	1	4·25	72·3	4	4·05	63·3	4	0·73	95·2	3
1·64	39·4	3	4·70	66·8	5	4·92	52·9	3	1·23	89·5	4
2·14	30·4	0	5·00	63·0	5	5·12	50·5	3	2·14	78·9	2
3·40	16·7	3	5·45	57·1	6	5·14	47·0	3	3·30	65·6	1
4·79	35898·8	4	6·00	50·6	4	6·14	38·0	2	3·52	63·0	2
5·45	90·3	5	6·33	46·5	4	7·39	23·2	$\frac{1}{2}$	3·79	59·9	1
6·20	80·6	4	7·00	38·2	5	7·74	19·0	0	5·00	45·3	1



TABLE II.—(contd.).

$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	I.	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	I.	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	I.	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	I.
2946.84	33924.8	3	2985.86	33481.4	2	3004.44	33274.4	2	3036.45	32923.6	2
7.15	21.2	3	7.95	58.0	1	5.13	66.8	2	7.46	12.7	1
8.11	10.2	4	8.69	49.8	$\frac{1}{2}$	5.62	61.3	3	9.00	32896.0	1
8.76	02.7	3	9.23	43.7	$\frac{1}{2}$	6.00	57.1	4	9.45	32783.3	1b
9.11	33898.7	3	2990.24	32.4	$\frac{1}{2}$	6.70	49.4	2	6.81	32597.7	1b
9.87	89.9	2	1.61	17.1	$\frac{1}{2}$	7.39	41.8	2	3092.89	32322.9	2
2950.30	85.0	2	5.03	33378.9	$\frac{1}{2}$	7.74	37.9	2	4.12	10.0	1
0.81	79.1	2	5.42	74.6	$\frac{1}{2}$	8.08	34.1	2	4.97	01.1	$\frac{1}{2}$
2.06	64.8	2	6.17	66.2	1	8.90	25.1	4	5.89	32291.5	1
3.10	52.9	2	6.58	61.7	1	9.54	18.0	3	6.93	80.7	2
4.29	39.2	2	7.47	51.8	1	9.98	13.2	3	7.54	74.3	1
4.76	33.8	2	8.48	40.5	2	3010.28	09.9	4	8.58	63.5	$\frac{1}{2}$
5.61	24.1	2	9.60	28.1	2	1.09	00.9	2	9.65	52.4	1
9.40	33780.8	$\frac{1}{2}$	3000.08	22.7	2	2.97	33180.2	$\frac{1}{2}$	3100.37	44.9	2
2960.70	66.0	1	0.43	18.9	2	3.88	70.2	0	1.06	37.7	2
2.45	46.0	$\frac{1}{2}$	2.64	33294.4	4	3029.59	32998.2	2	1.80	30.0	1
2974.94	33604.4	1	2.99	90.5	3	3030.97	83.2	1	3190.86	31330.5	$\frac{1}{2}b$
7.50	33575.5	1b	3.38	86.1	2	1.86	73.5	1	4.58	31294.0	$\frac{1}{2}b$
2981.32	32.4	2b	3.87	80.7	2	4.59	43.8	1	9.23	48.5	$\frac{1}{2}b$
3.77	04.9	2									

If we combine the five strong frequencies ( $A'—E'$ ) as pairs or doubles in the 15 possible ways, 14 frequencies are obtained which fall within the spectral range of the third section; the fifteenth coincides with the first band of the fourth section. The 14 frequencies of the third section all coincide with band maxima, and leave only two maxima to be accounted for. One of these would appear to involve the weak frequency  $F'$ , since its frequency separation agrees with the sum  $A' + F'$ . The other,  $G'$ , we assume to be generically connected with the second section. The only binary combination frequency which might have appeared in the third section but cannot be seen is one which involves the weak frequency  $F'$ ; it is  $B' + F'$ . The fourth section is like the third, except for the appearance of three additional band maxima; these may be regarded as overlaps from the band system of the third section, since they correspond in position to the only three binary combinations of frequency separations  $A' - G'$  that would be expected to appear in this section. The fifth section resembles the fourth, except that bands corresponding to some which were previously weak have disappeared. In the sixth section a good many more have disappeared. A few lines beyond the sixth section were just visible on the plates but were too diffuse for satisfactory measurement.

The details of this analysis are in Table V. The component frequency differences are :

$A'$ .	$B'$ .	$C'$ .	$D'$ .	$E'$ .	$F'$ .	$G'$ .
944	1029	1139	1322	1415	1582	1932 cm. <sup>-1</sup>

We confirm Cuthbertson and Kistiakowsky's frequency 944 cm.<sup>-1</sup> (our  $A'$ ), but can say nothing about their other frequency 2460 cm.<sup>-1</sup> except that if it occurred it would coincide with a band which we can account for without assuming this frequency.

(4) *Fundamental Vibration Frequencies.*—When one attempts to correlate the benzene bands  $A—G$  with the hexadeuterobenzene band  $A'—G'$  by associating bands of like fine structure, one finds that they fall fairly satisfactorily into the pairs  $AA'$ ,  $BC'$ ,  $CB'$ ,  $DE'$ ,  $ED'$ ,  $FF'$ , and  $GG'$ . Each pair satisfies the requirement that the benzene frequency is greater than the hexadeuterobenzene frequency, but not by a factor in excess of  $\sqrt{2}$ .

The frequencies  $AA'$  are unique with regard to their persistence in the progressions. This circumstance, and the fact that the same frequencies are prominent in the ordinary fluorescence spectra, shows that they represent a totally symmetrical vibration. For such a vibration, as we have seen, the fundamental frequency is equal to the spacing of the bands.

The remaining frequencies show smaller multiple occurrences in progressions, and they do not appear in the ordinary fluorescence spectrum. We assume that they represent non-totally symmetrical vibrations. We know that any of these frequencies may depend only on one such vibration, in which case it will normally be equal to twice

TABLE III.

## Series Assignment of Band Maxima in Resonance Spectrum of Benzene.

(Note.—Exciting line has frequency 39409 cm.<sup>-1</sup>. When a band contains two outstanding lines, the frequency of each is quoted, but these frequencies are averaged in calculating the frequency displacement of the band from this exciting line.)

1st-Order bands.									
	Band.	a.	A.	B.	C.	D.	E.	F.	G.
Frequency, $\nu$ (cm. <sup>-1</sup> )	38619	38420	{ 38227 38197 }	38083	{ 37883 37873 }	37719	37633	36970	
Frequency displacement	790	989	1197	1326	1531	1690	1776	2439	
Peak intensity (P.I.)	3	4	30	6	3	7	3	7	
2nd-Order bands.									
Band.	$\nu$ (calc.).	$\nu$ (obs.).	Diff.	P.I.*	Band.	$\nu$ (calc.).	$\nu$ (obs.).	Diff.	P.I.
2A	37431	{ 37441 37431 }	+ 5	7	3A	36442	{ 36456 36443 }	+ 8	7
A + B	37223	37217	- 6	5	2A + B	36234	36240	+ 6	6
A + C	37094	37094	$\pm 0$	4	2A + C	36105	36104	- 1	3
2B	37015	37008	- 7	7	A + 2B	36026	36035	+ 9	3
A + D	36889	{ 36894 36869 }	{ - 7 - 4 }	6	2A + D	35900	35890	{ - 10 - 7 }	5 5
B + C	36886	{ 36754 36751 }	- 4	1	A + 2C	35768	{ 35778 35774 }	+ 8	$\frac{1}{2}$
2C	36757	36727	- 3	4	2A + E	35741	{ 35749 35740 }	+ 4	3
A + E	36730	36696	+ 15	2	A + B + D	35692	35692	$\pm 0$	1
B + D	36681	{ 36650 36641 }	+ 1	4	2A + F	35655	Obscured by Hg	—	—
A + F	36644	(Obscured in 3A)	—	—	A + C + D	35563	35569	+ 6	3
C + D	36552	36358	+ 9	1	A + 2D	35358	35376	+ 18	1
2D	36347	35970	- 11	6	2A + G	34992	{ 34987 34977 }	- 10	5
A + G	35981	35939	- 4	3	A + E + F	34954	{ 34948 34936 }	- 12	2
E + F	35943								
4th-Order bands.									
4A	35453	{ 35470 35456 }	+ 10	6	5A	34464	{ 34489 34471 }	+ 16	4
3A + B	35245	35257	+ 12	6	4A + B	34256	34244	- 12	6
3A + C	35116	35116	$\pm 0$	1	4A + C	34127	No appearance	—	—
2A + 2B	35037	35045	+ 8	3	3A + 2B	34048	34059	+ 11	2
3A + D	34911	34892	{ - 19 - 16 }	4 4	4A + D	33922	33910	{ - 12 - 9 }	4 4
2A + B + C	34908	No appearance	—	—	3A + B + C	33919	No appearance	—	—
2A + 2C	34779	34753	+ 1	2	3A + 2C	33790	33766	+ 3	1
3A + E	34752	No appearance	—	—	4A + E	33763	No appearance	—	—
2A + B + D	34703	34669	+ 3	4	3A + B + D	33714	No appearance	—	—
3A + F	34666	34586	+ 12	2	4A + F	33677	Obscured by Hg	—	—
2A + C + D	34574	33989	- 14	4	3A + C + D	33585	33604	+ 19	1
2A + 2D	34371	33963	- 2	2	3A + 2D	33382	No appearance	—	—
3A + G	34003				4A + G	33014	32998	- 16	2
2A + E + F	33965				3A + E + F	32976	{ 32983 32973 }	+ 2	1
6th-Order bands.									
6A	33475	{ 33505 33481 }	+ 18	2	7A	32486	No appearance	—	—
5A + B	33267	33252	- 15	4	6A + B	32278	32281	+ 3	2
5A + C	33138	No appearance	—	—	Others	—	No appearance	—	—
4A + 2B	33059	Obscured by Hg	—	—					
5A + D	32933	32924	{ - 9 - 6 }	2 2					
4A + B + C	32930	No appearance	—	—					
4A + 2C	32801	32783	+ 9	1b	8A	31497	No appearance	—	—
5A + E	32774	No appearance	—	—	7A + B	31289	31294	+ 5	$\frac{1}{2}b$
4A + B + D	32725	No appearance	—	—	Others	—	No appearance	—	—
5A + F	32688	No appearance	—	—					
4A + C + D	32596	32598	+ 2	1b					
4A + 2D	32393	No appearance	—	—					
5A + G	32025	No appearance	—	—					
4A + E + F	31987	Obscured by Hg	—	—					

\* P.I. = Peak intensity.

TABLE IV.

## Resonance Emission Spectrum of Hexadeuterobenzene.

$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I.</i>	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I.</i>	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I.</i>	$\lambda$ (air), A.	$\nu$ (vac.), cm. <sup>-1</sup> .	<i>I.</i>
2562.65	39010.4	0	2662.05	37553.8	3	2734.17	36563.3	2	2827.66	35354.6	3
3.35	38999.8	0	3.03	40.0	4	4.90	53.6	1	8.46	44.6	3
4.32	85.0	$\frac{1}{2}$	4.23	23.1	5	5.74	42.4	3	9.39	32.9	2
4.85	77.0	0	4.79	15.3	3	7.12	23.9	2	2830.36	17.4	2
2581.35	38727.9	0	5.56	04.4	2	7.96	12.8	$\frac{1}{2}$	1.19	10.4	2
2.04	17.5	$\frac{1}{2}$	5.96	37498.8	1	8.69	03.0	2	2.02	00.1	2
2.67	08.1	0	6.71	88.3	0	9.72	36489.3	2	2.82	35290.2	2
3.19	00.2	0	7.12	82.5	1	2742.27	55.3	2	4.04	75.0	2
3.70	38692.6	$\frac{1}{2}$	7.50	77.1	2	3.18	43.2	2	5.80	53.1	3
4.15	85.9	0	8.42	64.2	0	5.71	09.7	1	6.83	40.2	2
4.50	80.6	0	9.15	53.9	1	5.93	06.7	3	7.45	32.6	2
2596.15	38507.1	1	2670.04	41.5	2	7.50	36386.0	1	8.40	20.8	2
6.45	02.7	1	1.06	27.2	1	8.23	76.0	3	9.05	12.7	1
6.70	38498.9	$\frac{1}{2}$	2.00	14.0	1	2750.07	51.9	2	9.62	05.7	1
7.45	87.8	0	4.23	37382.8	2	0.95	40.3	2	2840.41	35196.0	1
8.97	65.5	2	5.26	68.4	2	4.86	36288.8	4	1.95	76.8	$\frac{1}{2}$
2600.24	46.5	0	6.23	55.0	2	6.92	61.6	3	7.25	11.3	1
0.80	38.2	0	6.96	44.6	4	9.80	23.8	2	8.92	35090.7	2
2.08	19.3	1	7.51	37.1	1	2760.55	14.0	2	9.86	80.1	3
3.11	04.1	1	8.29	26.2	4	2.26	36191.6	4	2851.10	63.9	3
3.76	38394.5	1	8.97	16.8	1	3.20	79.2	2	1.58	58.0	2
4.29	86.1	5	2680.73	37292.2	2	4.05	68.1	2	3.24	37.6	1
4.76	79.6	4	1.84	76.8	2	7.35	25.0	2	8.61	34971.8	2
5.26	72.4	4	2.78	63.7	3	9.22	00.6	2	9.64	59.1	$\frac{1}{2}$
6.36	56.2	1	3.35	55.7	3	2773.50	36044.9	2	2860.16	52.8	2
6.80	49.8	0	3.99	46.9	4	4.78	28.2	2	1.20	40.1	0
7.35	41.7	0	4.24	43.4	4	4.96	25.9	5	2.06	32.7	1
7.70	36.5	0	4.49	40.0	4	5.70	16.3	5	3.56	11.3	0
8.54	24.1	1	5.13	31.1	2	6.61	04.5	5	4.88	34895.3	2
8.96	18.0	2	5.73	22.8	3	8.70	35977.4	2	6.99	69.6	0
2610.69	38292.6	5	7.84	37193.6	1	9.46	67.5	2	7.73	60.6	0
1.08	86.9	8	8.25	87.8	1	2780.92	48.4	3	2871.30	17.2	1
1.75	77.1	7	8.76	80.9	1	1.55	40.6	1	2.23	05.9	2
2.24	70.3	8	9.86	65.6	2	3.32	17.7	3	3.43	34791.4	1
2.63	64.2	7	2690.71	53.9	4	3.91	10.1	3	6.17	58.3	1
3.56	50.6	10	1.40	44.4	4	5.24	35893.0	2	7.09	47.1	$\frac{1}{2}$
3.98	44.5	6	2.07	35.0	4	6.42	77.7	1	7.88	37.8	1
4.41	38.2	4	2.28	32.2	4	7.45	64.5	$\frac{1}{2}$	2880.29	08.5	2
5.06	28.6	2	3.29	18.2	3	2790.10	30.5	2	0.75	03.0	2
5.45	23.0	2	3.86	10.4	3	0.70	22.8	3	1.36	34695.7	1
5.75	18.5	2	4.88	37096.4	2	2.15	04.1	1	1.92	88.9	1
6.20	12.0	1	5.38	82.6	1	2.60	35798.4	1	2.30	84.3	1
6.66	05.3	1	6.18	78.5	1	3.20	90.7	$\frac{1}{2}$	3.30	72.3	2
2621.24	38138.5	2	6.81	68.6	1	4.55	73.3	$\frac{1}{2}$	3.82	66.1	2
1.59	33.4	2	7.26	63.7	2	5.40	62.5	$\frac{1}{2}$	4.04	63.4	1
2.21	24.4	2	7.60	59.0	1	6.14	53.0	1	7.54	21.4	2
2.78	17.0	2	8.11	52.0	0	6.73	45.4	2	7.98	16.1	1
3.06	12.0	3	2701.22	09.3	1	7.20	39.5	1	8.40	11.1	$\frac{1}{2}$
3.48	06.0	3	2.13	36996.9	1	7.76	32.3	$\frac{1}{2}$	2897.26	34505.2	$\frac{1}{2}$
4.04	38097.8	4	3.69	75.6	2	8.47	23.2	2	7.68	00.3	1
4.76	87.4	6	4.44	65.3	4	9.48	10.4	$\frac{1}{2}$	8.50	34490.5	$\frac{1}{2}$
6.84	73.8	1	5.43	51.7	4	2805.52	35633.6	3	9.49	78.7	0
9.19	23.2	$\frac{1}{2}$	6.16	41.8	3b	6.93	15.6	1	2900.95	61.4	1
9.39	20.3	1	6.85	32.4	3b	7.49	08.4	2	1.66	53.0	$\frac{1}{2}$
9.74	15.2	1	2710.46	36883.2	2	2810.14	35575.0	1	2.72	40.4	0
9.94	12.3	1	0.84	78.1	2	1.05	63.4	2	3.62	29.7	0
2630.44	05.3	2	1.05	75.1	2	1.92	52.4	2	4.28	21.9	$\frac{1}{2}$
1.19	37994.3	2	2.75	52.0	2	4.32	32.1	$\frac{1}{2}$	5.38	08.8	0
1.70	86.9	2	3.30	44.6	2	5.08	12.5	1	6.11	00.2	0
2.24	79.1	1	4.22	32.0	1	5.86	02.7	$\frac{1}{2}$	7.43	34384.6	0
2.93	69.2	$\frac{1}{2}$	8.61	36772.6	0	8.42	35470.4	3	8.06	77.1	0
2642.80	37827.4	2	9.31	63.1	2	9.23	60.2	3	8.81	68.3	0
3.33	19.8	0	9.93	54.7	1	2821.17	35.8	3	2913.14	17.2	$\frac{1}{2}$
4.29	06.0	0	2724.65	36690.0	2	1.72	29.0	2	3.68	11.0	0
2658.51	37603.9	1	6.07	72.0	2	2.31	21.6	2	4.46	01.6	$\frac{1}{2}$
9.02	37596.6	2	7.19	56.9	1	3.07	12.0	2	2928.28	34139.8	0
9.32	92.4	2	8.19	43.5	$\frac{1}{2}$	3.79	03.0	1	9.35	27.3	0
2660.85	70.8	2	9.64	24.0	1	4.43	35394.9	2	2931.17	06.1	0
1.27	64.8	3	2731.45	36599.0	3	4.88	89.3	2	2942.05	33980.0	0
1.44	62.4	3	2.79	81.8	4	5.21	85.2	2	2.98	69.3	0
1.72	58.5	3	3.56	71.5	3	6.82	65.0	3			

TABLE V.

Series Assignment of Band Maxima in Resonance Spectrum of Hexadeuterobenzene.

(Note.—See note at top of Table III.)

				1st-Order bands.							
	Band.	A'.	B'.	C'.	D'.	E'.	F'.	G'.			
Frequency, $\nu$ (cm. <sup>-1</sup> )	.....	38465	38380	38270	38087	37994	37827	37477			
Frequency displacement	.....	944	1029	1139	1322	1415	1582	1932			
Peak intensity (P.I.)	.....	2	5	15	6	2	2	2			
				2nd-Order bands.				3rd-Order bands.			
	Band.	$\nu$ (calc.).	$\nu$ (obs.).	Diff.	P.I.	Band.	$\nu$ (calc.).	$\nu$ (obs.).	Diff.	P.I.	
2A'	.....	37521	37523	+ 2	5	3A'	.....	36577	36582	+ 5	4
A' + B'	.....	37436	37441	+ 5	2	2A' + B'	.....	36492	{ 36503 36489 }	+ 4	2
2B'	.....	37351	37345	- 6	4	A' + 2B'	.....	36407	36407	$\pm$ 0	3
A' + C'	.....	37326	37326	$\pm$ 0	4	2A' + C'	.....	36382	36376	- 6	3
B' + C'	.....	37241	37243	+ 2	4	A' + B' + C'	.....	36297	36289	- 8	4
A' + D'	.....	37143	{ 37154 37144 }	+ 6	4	2A' + D'	.....	36199	36199	$\pm$ 0	4
2C'	.....	37131	{ 37135 37132 }	+ 2	4	A' + 2C'	.....	36187	36912	{ - 7 + 5 }	4
B' + D'	.....	37058	37064	+ 6	2	A' + B' + D'	.....	36114	36125	+11	2
A' + E'	.....	37050	Obscured by Hg	—	—	2A' + E'	.....	36106	36101	- 5	2
B' + E'	.....	36965	36965	$\pm$ 0	4	A' + B' + E'	.....	36021	{ 36026 36016 }	$\pm$ 0	5
C' + D'	.....	36948	36952	+ 4	4	A' + C' + D'	.....	36004	36004	$\pm$ 0	5
A' + F'	.....	36883	36885	+ 2	2	2A' + F'	.....	35939	35948	+ 9	3
C' + E'	.....	36855	{ 36852 36845 }	- 6	2	A' + C' + E'	.....	35911	{ 35918 35910 }	+ 3	3
B' + F'	.....	36798	No appearance	—	—	A' + B' + F'	.....	35854	No appearance	—	—
2D'	.....	36765	36763	- 2	2	A' + 2D'	.....	35821	35823	+ 2	3
D' + E'	.....	36672	{ 36690 36672 }	+ 9	2	A' + D' + E'	.....	35728	35745	+17	2
A' + G'	.....	36533	36542	+ 9	3	2A' + G'	.....	35589	35608	+19	2
B' + G'	.....	36448	{ 36455 36443 }	+ 1	2	A' + B' + G'	.....	35504	35512	+ 8	1
C' + G'	.....	36338	{ 36352 36340 }	+ 8	2	A' + C' + G'	.....	35394	35389	- 5	2
				4th-Order bands.				5th-Order bands.			
4A'	.....	35633	35634	+ 1	3	5A'	.....	34689	{ 34706 34670 }	- 1	2
3A' + B'	.....	35548	{ 35563 35552 }	+ 9	2	4A' + B'	.....	34604	34621	+17	2
2A' + 2B'	.....	35463	{ 35470 35460 }	+ 2	3	3A' + 2B'	.....	34519	Obscured by Hg	—	—
3A' + C'	.....	35438	35436	- 2	3	4A' + C'	.....	34494	34500	+ 6	1
2A' + B' + C'	.....	35353	35355	+ 2	3	3A' + B' + C'	.....	34409	34422	+13	$\frac{1}{2}$
3A' + D'	.....	35255	35253	- 2	3	4A' + D'	.....	34311	34317	+ 6	$\frac{1}{2}$
2A' + 2C'	.....	35243	{ 35253 35243 }	+10	3	3A' + 2C'	.....	34299	34302	+ 3	$\frac{1}{2}$
2A' + B' + D'	.....	35170	No appearance	—	—	3A' + B' + D'	.....	34226	No appearance	—	—
3A' + E'	.....	35162	No appearance	—	—	4A' + E'	.....	34218	No appearance	—	—
2A' + B' + E'	.....	35077	35080	+ 3	3	3A' + B' + E'	.....	34133	{ 34140 34127 }	$\pm$ 0	0
2A' + C' + D'	.....	35060	35064	+ 4	3	3A' + C' + D'	.....	34116	34106	-10	0
3A' + F'	.....	34995	Obscured by Hg	—	—	4A' + F'	.....	34051	No appearance	—	—
2A' + C' + E'	.....	34967	{ 34972 34953 }	- 4	2	3A' + C' + E'	.....	34023	No appearance	—	—
2A' + B' + F'	.....	34910	No appearance	—	—	3A' + B' + F'	.....	33966	No appearance	—	—
2A' + 2D'	.....	34877	34895	+18	2	3A' + 2D'	.....	33933	No appearance	—	—
2A' + D' + E'	.....	34784	34806	+22	2	3A' + D' + E'	.....	33840	No appearance	—	—
3A' + G'	.....	34645	{ 34672 34666 }	+25	2	4A' + G'	.....	33701	Obscured by Hg	—	—
2A' + B' + G'	.....	34560	Obscured by Hg	—	—	3A' + B' + G'	.....	33616	No appearance	—	—
2A' + C' + G'	.....	34450	No appearance	—	—	3A' + C' + G'	.....	33506	No appearance	—	—

the fundamental frequency; alternatively, it may depend on two vibrations, in which event it will be sum of their fundamental frequencies. We first try the assumption that each frequency depends on only one vibration. Provisional fundamental frequencies will then be obtained by halving the frequency displacements; they are shown in Table I. Three of the pairs of frequencies thus obtained agree with fundamental frequencies which are observed either in infra-red spectra or Raman spectra, and since the agreement extends

over both benzene and hexadeuterobenzene, we may regard these three pairs of frequencies as having been definitely identified. These are  $BC'$ ,  $CB'$ , and  $ED'$ .

The other fundamental frequencies must for the present retain their "provisional" character. Of two pairs of these ( $DE'$  and  $FF'$ ) it can be said that they are of the order of magnitude to be expected for certain fundamental frequencies which might be inactive both in the infra-red and in the Raman spectrum; for one can very roughly calculate some of the inactive frequencies by first using the known frequencies to set up a simplified model of the molecular force system and then deducing the unknown frequencies from this. On the other hand, the observed frequency spacings might in either of these cases be the sum of two different fundamentals, a possibility which cannot be controlled until more knowledge of the inactive frequencies has been accumulated. We can find slightly more support for the remaining pair of provisional fundamentals ( $GG'$ ). These are also of the order of magnitude to be expected for a vibration which could be inactive in the infra-red and Raman spectra. However, this vibration is one for which we can calculate the proportionate frequency shift due to isotopic substitution without an exact knowledge, or even any knowledge, of the frequencies themselves, and without reference to the shifts which are undergone simultaneously by other vibrations; and the observed and the calculated frequency shifts agree. Concerning the low benzene frequency ( $a$ ), all that can be stated is that benzene should possess two fundamental frequencies which could be inactive in the infra-red and Raman spectra and are expected to lie below  $500\text{ cm.}^{-1}$ : the provisional frequency ( $a$ ) may be one of them. The observed band spacing cannot be the sum of these two low frequencies because they differ profoundly with respect to symmetry, and there is no other frequency which would be allowed by symmetry to combine with either and is also small enough thus to give the required spacing. Furthermore, the provisional fundamental ( $a$ ) agrees in frequency with a weak line ( $404\text{ cm.}^{-1}$ ) found in the Raman spectrum, although it is not at present established that this line does in fact represent a fundamental frequency. However, in spite of these arguments we prefer to treat the suggested fundamentals ( $a$ ) and ( $GG'$ ) as provisional like ( $DE'$ ) and ( $FF'$ ): the evidence concerning them constitutes only a small part of the experimental material which will have to be collected before the inactive frequencies can be fully elucidated.

We append tables giving the measurements and their analysis into series.

UNIVERSITY COLLEGE, LONDON.

[Received, May 23rd, 1936.]

---