95. *Excited States of Benzene. Part I. Introductory Consideration of Some Spectral Properties of Vibrations accompanying Electronic Transitions of Benzene and Deuterated Benzenes.*

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Previous investigations (" Structure of Benzene ", Parts I—XXI, *J.*, 1936 and 1946) having provided some knowledge of the geometry and dynamics of the electronic ground state of the benzene molecule, attention is now turned to the first electronically excited state. This can be studied with respect to its vibrations, not directly as the ground state can, but only in admixture with the ground state, through the joint effect of the vibrations of both states on the vibrational structure of transitions between the ground and the excited state. In this introductory paper, the principles underlying the work are explained, and some of the more useful relevant results of the application of general spectroscopic theory are given. The experimental material consists in the near-ultraviolet absorption and fluorescence band systems of benzene, hexadeuterobenzene, and certain partly deuterated benzenes with oriented deuterium atoms : a number of such spectra are described for the first time. The evaluation of this material (Parts II—X) involves vibrational analyses extended to cover large numbers of bands which are not amongst the strongest in the spectra. Taking account of existing knowledge of vibrations of the ground state, fundamental frequencies have been assigned to many vibrations of the electronically excited molecules. In the course of the analysis, and for the purpose of obtaining upper-state fundamental frequencies which cannot be directly observed, extensive use is made (Part XI) of the principle that isotopic substitution does not change the internal force-field of a molecule in any given electronic state. The results of this study of upper-state frequencies are employed (Part XII) in order to calculate the dimensions, force-system, and zero-point energies of the excited molecules; and it is the first time in the study of band-spectroscopy that such a set of conclusions has been derived for any excited polyatomic molecule.

(1) *Scope.*—The study of the vibrations and force system of the electronic ground state of benzene is now sufficiently advanced to assist the pursuit of similar problems relating to the excited electronic states of this molecule. In these papers it is proposed to develop such studies. The observational material consists in ultraviolet absorption and emission spectra, dependent on transitions between the electronic ground state and various electronically excited states of benzene in its several isotopically modified forms.

We take up this subject for two reasons. First, benzene was the starting point of, and is the most fully studied example in, the rapidly developing, modern theory of the relation between the colour and structure of organic compounds : it is likely to retain a fundamental position in that theory.

Secondly, with reference to the study of spectroscopy for its own sake, the present position is that the principles underlying the analysis of the electronic spectra of atoms and diatomic molecules are fully known, that the vibration and rotation spectra of diatomic and polyatomic molecules are also in principle fully understood, but that the electronic spectroscopy of polyatomic molecules is still in its exploratory stages; and benzene, with its high symmetry and practical possibilities of isotopic modification, is an almost ideal example with which to develop this branch of spectroscopy.

In the present papers considerable use is made of both the mentioned properties of the benzene molecule. With their help we achieve the first determination of a force system of an electronically excited polyatomic molecule. New observations are provided on the absorption and fluorescence spectra of deuterated benzenes. Brief preliminary accounts of the investigation have already been given (*Nature*, 1946, **157**, 46; **158**, 163).

(2) *Electronic States and Transitions of Benzene.*—Benzene has the symmetry D_{6h}, *i.e.*, a 6-fold axis, a perpendicular 2-fold axis, and a centre, plus such other symmetry as this implies. When thinking of the electronic motion, and therefore of nuclear charges but not of nuclear masses, we shall write this symmetry $\mathbf{D}_{6h}$. This is because the nuclear charges control the electronic motion, the forms of which we shall symbolise by means of heavy type (italics being reserved, as heretofore, for the representation of nuclear motion). Just as with nuclear motion, so also with electronic motion, the possible forms can be classified according to what symmetry they preserve. The 12 classes, 8 non-degenerate (**A**, **B**) and 4 doubly degenerate (**E**), are symbolised $\mathbf{A}_{1g}$, $\mathbf{A}_{1u}$, $\mathbf{A}_{2g}$, $\mathbf{A}_{2u}$, $\mathbf{B}_{1g}$, $\mathbf{B}_{1u}$, $\mathbf{B}_{2g}$, $\mathbf{B}_{2u}$, $\mathbf{E}_g^+$, $\mathbf{E}_u^+$, $\mathbf{E}_g^-$, $\mathbf{E}_u^-$. Here, **A** connotes 6-fold, **B** 3-fold, $+$ 2-fold, and $-$ 1-fold symmetry about the z-axis (normal to the ring), **1** means 2-fold, and **2** 1-fold symmetry about the y-axis (through para-atoms), whilst **g** signifies symmetry and **u** antisymmetry relative to the centre. These symbols refer to the total electronic orbital wave function, just as the corresponding italic symbols relate to the total nuclear vibrational wave function (as well as to the normal co-ordinate in the special case of a fundamental vibration).

Actually, the above 12 symmetry classes do not all contain electronic states, just as the symmetry classes for nuclear motion do not all contain fundamental vibrations (see *J.*, 1946, 227, especially Table VII). It can be shown, by a simple application of symmetry theory, that non-ionised benzene, because of the even number of its electrons, cannot have electronic states which are antisymmetrical with respect to the molecular plane. This reduces the list of symmetry classes which are available for occupation by electronic states to the six following: $\mathbf{A}_{1g}$, $\mathbf{A}_{2g}$, $\mathbf{B}_{1u}$, $\mathbf{B}_{2u}$, $\mathbf{E}_g^+$, $\mathbf{E}_u^-$.

The electronic ground state of benzene is a singlet state, and therefore only singlet states will participate in the stronger transitions involving the ground state. We shall be concerned only with singlet states, and therefore have no need to introduce a symbol for the electronic spin. Nor shall we have to concern ourselves with the electronic spin wave functions.

Benzene has several ultraviolet absorption systems. The first runs out from about 2600 A., and it is with the detailed study of this that our investigation commences. A stronger system starts at about 2000 A., and this is overlapped by a still stronger one at about 1850 A. After that two Rydberg series appear, which run out to a common limit at 1350 A.

Hückel first discussed the lower electronic states of benzene as molecular states of the six unsaturation electrons; and his work has been brilliantly developed by Sklar. The six atomic orbitals, $2p\pi$, of these electrons combine to produce the following molecular orbitals, in order of increasing energy: $2\mathbf{a}_{2u}$, $2\mathbf{e}_g^-$, $2\mathbf{e}_u^+$, $2\mathbf{b}_{2g}$. The symmetry symbols have the meanings given, except that, by custom, lower-case letters are used for single-electron wave-functions. The prefix 2 refers to the principal quantum number. Pauli's principle allows the $\mathbf{a}_{2u}$ and $\mathbf{b}_{2g}$ shells each to accommodate two, and the degenerate $\mathbf{e}_g^-$ and $\mathbf{e}_u^+$ shells four, electrons. The ground state, formed by filling the $2\mathbf{a}_{2u}$ and $2\mathbf{e}_g^-$ shells, has the symmetry $(\mathbf{a}_{2u})^2(\mathbf{e}_g^-)^4 = \mathbf{A}_{1g}$. The lowest excited states are obtained by promoting a $2\mathbf{e}_g^-$ electron to a $2\mathbf{e}_u^+$ orbital. Two non-degenerate states and one degenerate state thus arise, which have the symmetries $(\mathbf{a}_{2u})^2(\mathbf{e}_g^-)^3(\mathbf{e}_u^+) = \mathbf{B}_{2u}, \mathbf{B}_{1u}, \mathbf{E}_u^-$. These symmetry relations are readily verified by multiplying together the appropriate sets of operators (as given, *e.g.*, in Table VII, *J.*, 1946, 227). According to Sklar's calculations of the energy relationship, the $\mathbf{B}_{2u}$ state lies the lowest of these three (*J. Chem. Physics*, 1937, **5**, 669). Goeppert-Mayer and Sklar's further calculations place the $\mathbf{B}_{1u}$ state higher, and the $\mathbf{E}_u^-$ state higher still on the energy scale (*ibid.*, 1938, **6**, 645). Revised calculations by A. London give the same order (*ibid.*, 1945, **13**, 396). Neither the $\mathbf{B}_{2u}$ nor the $\mathbf{B}_{1u}$ state has the symmetry of a component of the electric moment, and therefore transitions between the ground state and each of these states are forbidden. On the other hand, the $\mathbf{E}_u^-$ state has the symmetry of an x- or y-component of the electric moment, so that transitions between the ground state and this state are allowed.

Sklar first assigned (*loc. cit.*) as a $\mathbf{B}_{2u}$ state the upper state of the transition starting near 2600 A. Though the transition would in this case be forbidden under the equilibrium symmetry of the nuclear system, it would be able to occur, when, in either of the interacting states, the molecular symmetry became suitably reduced by an appropriate nuclear vibration. Goeppert-Mayer and Sklar (*loc. cit.*), and also Nordheim, Sponer, and Teller (*ibid.*, 1940, **8**, 455), assigned the absorption system starting around 2000 A. as a forbidden transition to a $\mathbf{B}_{1u}$ state, and the strong absorption system beyond 1850 A. as an allowed transition to an $\mathbf{E}_u^-$ state,* The last-named

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* Probably this state is the one of chief importance for the polarisability (refractive index) of benzene, not the state involved in the 2600 A. transition, as supposed by Ingold, Raisin, and Wilson (*J.*, 1936, 915).

authors supposed the Rydberg series to arise by excitation of the same loosely held $\mathbf{e}_g^-$ electron to orbitals with principal quantum numbers higher than 2.

(3) *Selection Rules for Vibrations involved with Electronic Transitions of Benzene.*—The general selection rules for the vibrational changes that may accompany an allowed electronic transition were given by Herzberg and Teller (*Z. physikal. Chem.*, 1933, *B*, **21**, 410). In the case in which the equilibrium symmetries of the nuclear system in the upper and lower electronic states are identical, the quantum numbers of the totally symmetrical vibrations should be the principal ones to change. Thus one expects, accompanying the 0—0 band, strong progressions, 0—1, 0—2, 0—3, ... , in these vibrations. Progressions in upper-state vibrations should predominate in absorption, whilst progressions in lower-state vibrations should be the most important in fluorescence. We must also expect that sequences involving transitions 1—1, 2—2, . . . , *n*—*n*, ... , in all the non-totally symmetrical vibrations will be prominent in both absorption and fluorescence, except in so far as these bands are weakened by the Boltzmann factors of their initial vibrational levels. As weak frequencies we might observe such as depend on even changes of quantum number in non-totally symmetrical vibrations, *e.g.*, transitions 0—2, 1—3, etc., and even combinations, such as combined 0—1, 0—1 changes of pairs of non-totally symmetrical vibrations of the same symmetry class.

In a forbidden transition the 0—0 band cannot appear. Associated with the electronic change there must be a vibrational transition of such a type as will produce the perturbation which makes the electronic transition possible. For any particular type of forbidden electronic transition, the symmetry conditions which the vibrational change must fulfil in order to achieve this result are readily calculated. The simplest form of vibrational perturbation would be a one-quantum change, as in a 0—1, 1—2, ... , or 1—0, ... , transition of some non-totally symmetrical vibration of the right symmetry. But generally, transitions may occur when, in either or both of the interacting electronic states, such vibrations are excited with such quantum numbers that the product of all the involved vibrational wave functions has the symmetry needed to produce the perturbation. Finally, upon each vibrational transition fulfilling these conditions, all the vibrational changes which may accompany an allowed electronic transition may be superposed.

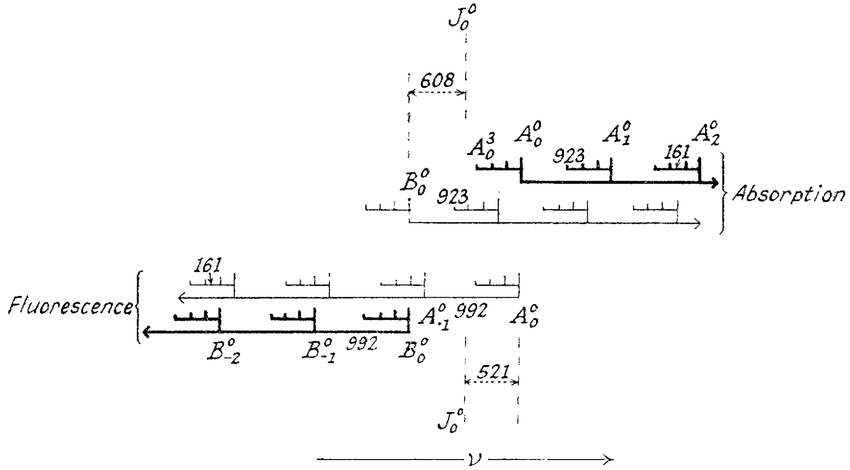
In benzene, the $\mathbf{A}_{1g}$—$\mathbf{B}_{2u}$ transition is forbidden because the product $\mathbf{A}_{1g} \,.\, \mathbf{B}_{2u}$ has not the symmetry of an electric moment, wherefore the transition moment (which is an electric moment averaged over the product of the wave functions) must vanish. Sklar pointed out (*loc. cit.*) that a vibration of E_g^+ symmetry provides a suitable perturbation, since it so operates on the product as to cause it to take on the symmetry of an electric moment in the plane of the aromatic ring : $E_g^+(\mathbf{A}_{1g} \,.\, \mathbf{B}_{2u}) \equiv \mathbf{E}_u^- \equiv x, y$ (as can be verified, *e.g.*, from Table XII, *J.*, 1946, 234). Amongst fundamental vibrations, an E_g^+ vibration is the only kind that can so act. Sklar assumed that, in the observed electronic transition near 2600 A., one of the four E_g^+ fundamentals provides the necessary perturbation. Sponer, Nordheim, Sklar, and Teller then showed in some detail (*J. Chem. Physics*, 1939, **7**, 207) that this theory can account very well for the salient features of the structure of the absorption and fluorescence spectra arising from this transition. The main perturbing vibration is the planar, carbon-bending, degenerate fundamental, E_g^+(C 1) (cf. Fig. 1, *J.*, 1946, 231). Its frequency, as given in the Raman spectrum of liquid benzene, is 606 cm.$^{-1}$; this, of course, applies to the electronic ground state. The absorption and fluorescence spectra themselves give the frequencies 608 cm.$^{-1}$ in the ground state and 521 cm.$^{-1}$ in the excited state.

Symmetry considerations would allow the other three E_g^+ fundamental vibrations to act in a similar way, and also any vibrational higher harmonics of E_g^+ symmetry. Furthermore, although there are no fundamental vibrations of B_{1g} symmetry, a vibrational combination tone of this symmetry could give rise to spectral activity by producing a transition moment perpendicular to the plane of the ring : $B_{1g}(\mathbf{A}_{1g} \,.\, \mathbf{B}_{2u}) \equiv \mathbf{A}_{2u} \equiv z$.

(4) *Main Structure of the First Ultraviolet Absorption and Fluorescence Systems of Benzene.*—The general pattern of the two related spectra is shown in a simplified form in Fig. 1. In absorption, two active origins, A_0^0 and B_0^0, 1129 cm.$^{-1}$ apart, are the starting points of progressions in the interval 923 cm.$^{-1}$, which run to higher frequencies (we call them positive), the progression starting from the higher frequency being much the stronger. In fluorescence, the same two origins are the starting points of progressions in the interval 992 cm.$^{-1}$, which run to lower frequencies (and are called negative), the progression starting from the lower frequency being much the stronger. From each band in these progressions, sequences start out : in both absorption and fluorescence they are negative; and the interval, 161 cm.$^{-1}$, is common to them all. Then (though this is omitted from Fig. 1 for simplicity), the whole of the described pattern

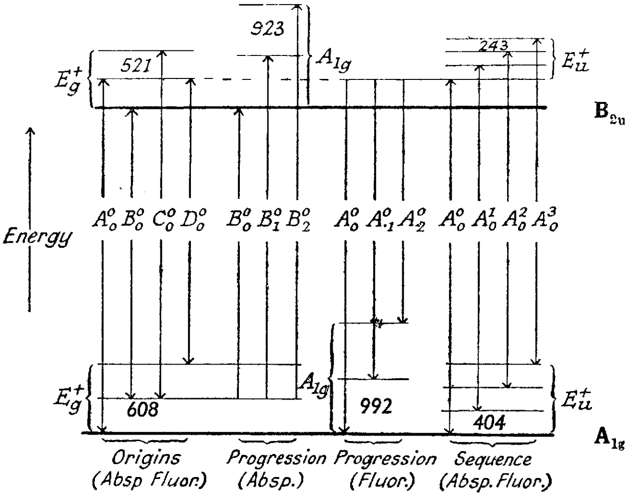
is repeated much more weakly with a shift of 87 cm.$^{-1}$ towards lower frequencies; that is, there is a third origin C_0^0 at this separation from A_0^0, and a fourth D_0^0 the same distance below B_0^0, each carrying the same set of progressions and sequences. We shall be concerned with many bands which do not conform to this description, which nevertheless represents the main framework of the two spectra.

FIG. 1.



General pattern of the stronger bands in the first ultraviolet absorption and fluorescence systems of benzene vapour.

FIG. 2.



Interpretation of the general pattern.

The interpretation will be clear from Fig. 2. In absorption, the origins A_0^0 and B_0^0 involve upward transitions, 0—1 and 1—0 respectively, of the perturbing E_g^+(C 1) vibration.* The second is weakened by the Boltzmann factor (0·055 at room temperature) of its initial vibrational level. Their separation is 608 + 521 = 1129 cm.$^{-1}$. The origins C_0^0 and D_0^0 involve upward transitions, 1—2 and 2—1 respectively, of the same vibration. They are both weakened, the latter very much so, by their Boltzmann factors. They lie 608 — 521 = 87 cm.$^{-1}$ below A_0^0 and B_0^0, respectively. In fluorescence, A_0^0 and B_0^0 involve downward transitions, 1—0 and 0—1

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* It is therefore unnecessary to assume close-lying electronic levels as did Ingold and Wilson (*J.*, 1936, 941).

respectively, of the E_g^+(C 1) vibration. Since we are concerned with fluorescence at pressures permitting a thermal distribution of vibrational energy in the excited state, the former of these transitions will be weakened by the Boltzmann factor of its initial state. The origins C_0^0 and D_0^0 correspond, in fluorescence, to downward transitions, 2—1 and 1—2 respectively, and therefore the former will be weakened more than the latter. The positions of the four active origins evidently determine that of the forbidden electronic origin, J_0^0, as well as the values of the two frequencies of the perturbing E_g^+(C 1) vibration.

The main progressions depend on quantum changes in the totally symmetrical ring-breathing vibration A_{1g}(C). Its frequency, as given in the Raman spectrum, is 992 cm.$^{-1}$. Its frequencies, as given by the progressions in the ultraviolet spectra, are 992 cm.$^{-1}$ in the ground state and 923 cm.$^{-1}$ in the electronically excited state. In absorption, positive progressions (Fig. 2) in the excited state frequency, 923 cm.$^{-1}$, involving upward transitions, 0—1, 0—2, 0—3, . . . , start from each of the active origins. The beginnings of negative progressions in the ground state frequency, 992 cm.$^{-1}$, can also be discerned on the plates, but the bands, which arise from upward transitions, 1—0, . . . , are greatly weakened by their Boltzmann factors. In fluorescence, negative progressions (Fig. 2) in 992 cm.$^{-1}$, involving downward transitions, 0—1, 0—2, . . . , predominate. The beginning of positive progressions in 923 cm.$^{-1}$ can also be seen on the plates, but these bands, which depend on downward transitions, 1—0, . . . , are likewise greatly weakened by their Boltzmann factors.

Kistiakowsky and Solomon first established (*J. Chem. Physics*, **1937**, **5**, 609), by measurements on the temperature-dependence of band intensity, that the sequences in 161 cm.$^{-1}$ arise from 1—1, 2—2, 3—3, . . . , transitions of the degenerate, out-of-plane vibration E_u^+(C). The frequencies of this fundamental vibration are much lower than those of any other. The ground-state frequency, as given by the Raman spectrum of liquid benzene, is 405 cm.$^{-1}$. As will appear in Part II, the absorption and fluorescence spectra of benzene vapour give 404 cm.$^{-1}$ for the frequency of this vibration in the electronic ground state, and 243 cm.$^{-1}$ for its frequency in the excited state. The difference $404 - 243 = 161$ cm.$^{-1}$ forms the sequence interval common to the absorption and fluorescence spectra, in both of which the sequence must obviously run in the negative direction (Fig. 2). In principle, all vibrations can produce such sequences. But the outstanding persistence of the sequences of this vibration is clearly due largely to the fact that its frequencies are so low, and that therefore its Boltzmann factors—at room temperature, $(0{\cdot}14)^n$ for n quanta in the electronic ground state, and $(0{\cdot}31)^n$ for n quanta in the excited state—are not too serious an obstacle to its appearance in n—n transitions up to several quanta.

(5) *More Detailed Statement of Selection Rules for the* $\mathbf{A_{1g}} - \mathbf{B_{2u}}$ *Transition of* D_{6h} *Benzenes.*—The D_{6h} benzenes with which we shall be concerned are ordinary benzene and hexadeuterobenzene. Each has ten non-degenerate vibrations (A, B), including two which are totally symmetrical (A_{1g}), and a further ten doubly degenerate vibrations (E). The whole twenty are distributed among ten symmetry classes, six non-degenerate and four degenerate, as shown in Table I. A complete set of fundamental frequencies for the electronic ground state of each of these molecules has been given by Herzfeld, Ingold, and Poole (*J.*, 1946, 316). These frequencies are reproduced in Table I.

TABLE I.

Vibrations of D_{6h} Benzenes and Fundamental Frequencies in the Electronic Ground State (cm.$^{-1}$).

Symmetry :			A_{1g}.	A_{2g}.	A_{2u}.	B_{1u}.	B_{2g}.	B_{2u}.	E_g^+.	E_u^+.	E_g^-.	E_u^-.
C_6H_6	(C)	(1)	992			1010	703	1648	606	405		1485
		(2)							1596			
	(H)	(1)	3062	1326	671	3060	985	1110	3047	970	849	1037
		(2)							1178			3080
C_6D_6	(C)	(1)	943			963	601	1571	577	352		1333
		(2)							1551			
	(H)	(1)	2293	1037	496	2290	827	825	2265	793	662	813
		(2)							867			2294

The general selection rule for vibrations accompanying the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ electronic transition of a D_{6h} benzene is that, in either or both of the combining states, such vibrations may be excited with such quantum numbers that the product of all the involved vibrational wave functions has either the symmetry E_g^+, or the symmetry B_{1g} (cf. Section 3). Some consequences of this rule are contained in Table II (which can be deduced from Table XII, *J.*, 1946, 234).

TABLE II.

Vibrations allowed in Combination with the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of a* D_{6h} *Benzene.*

$\psi'_{\text{vib.}} \cdot \psi''_{\text{vib.}}$	E_g^+ (perp. bands).		B_{1g} (par. bands).
One quantum (either state)	** E_g^+		—
Two quanta (same or different states)	** E_g^+, A_{1g}		
	E_g^+, A_{2g}	† E_g^+, E_g^+	A_{2g}, B_{2g}
	E_u^+, A_{2u}	† E_g^-, E_g^-	A_{2u}, B_{2u}
	E_u^-, B_{1u}	† E_u^+, E_u^+	E_g^+, E_g^-
	E_g^-, B_{2g}	† E_u^-, E_u^-	E_u^+, E_u^-
	E_u^-, B_{2u}		
One E_g^+ and two other quanta (same state or distributed)	** E_g^+, A_{1g}, A_{1g}		
	* ,, , A_{2g}, A_{2g}	E_g^+, A_{2g}, A_{1g}	E_g^+, E_g^-, A_{1g}
	* ,, , A_{2u}, A_{2u}	,, , B_{2u}, B_{1u}	,, , E_g^-, A_{2g}
	* ,, , B_{1u}, B_{1u}	,, , E_g^+, A_{1g}	,, , E_u^-, A_{2u}
	* ,, , B_{2g}, B_{2g}	,, , E_g^+, A_{2g}	,, , E_u^+, B_{1u}
	* ,, , B_{2u}, B_{2u}	,, , E_u^+, A_{2u}	,, , E_g^+, B_{2g}
	* ,, , E_g^+, E_g^+	,, , E_u^-, B_{1u}	,, , E_u^+, B_{2u}
	* ,, , E_u^+, E_u^+	,, , E_g^-, B_{2g}	,, , E_g^+, E_g^-
	* ,, , E_g^-, E_g^-	,, , E_u^-, B_{2u}	,, , E_u^+, E_u^-
	* ,, , E_u^-, E_u^-		

This table gives the allowed excitations of one, two, and certain sets of three, vibrational quanta : they may be distributed in any manner between the two combining states. The entries marked **, which involve a single E_g^+ quantum, and, apart from this, only totally symmetrical quanta, represent bands which may appear strongly, although, in particular cases, a low transition probability, or a small Boltzmann factor applying to the vibrational energy level of the initial state, may reduce the spectral intensity. The development of strong bands is illustrated by the production of the active origins A_0^0 and B_0^0, and of the totally symmetrical A_{1g}(C) progressions of the upper or lower electronic state, which in absorption or fluorescence proceed from these origins. Table II has been carried far enough to cover only the first three members of each such progression, but the principles on which it could be extended are clear.

The entries marked *, which involve, besides a single E_g^+ quantum, two non-totally symmetrical quanta of identical symmetry, represent bands which, with the same limitations as before, may appear strongly in a special case, though not in the general case. The special case is that in which identically the same vibration is excited with one quantum in each of the combining states. Illustrations are provided by the 1—1 bands of the already mentioned sequences, due to *n*—*n* transitions of the vibration E_u^+(C), which start from each of the stronger bands of the A and B progressions. Table II is carried far enough to cover only the 0—0 and 1—1 bands of such sequences, but, again, the principles on which it could be extended are obvious.

Included under the same set of entries are the transitions in which two quanta of the same non-totally symmetrical vibration are present in one of the combining states. Such transitions belong in principle to the category of weak transitions; but since two like quanta jointly possess total symmetry, we may expect that the bands will often be comparatively prominent among the weaker bands of the absorption and fluorescence spectra. Many such bands will be pointed out in the following papers. They appear in positions displaced from A_0^0 or B_0^0, or from other strong bands of the A and B progressions, by the frequency of the first overtone of the vibration concerned, the displacement being towards long waves if the overtone frequency belongs to the electronic ground state, and towards short waves if the frequency belongs to the upper electronic state.

The entries marked † have the following special feature. It is a property of degenerate vibrations that two quanta of the same symmetry class can in combination always produce the symmetry E_g^+ : no non-degenerate vibrations behave in this way (cf. Table XII, *J.*, 1946, 234). It follows that the presence, either in the same state or in different states of a possible transition, of two degenerate quanta of the same symmetry class, in particular, two quanta of the same degenerate vibration, is sufficient to permit the transition. An important case is that in which the same degenerate vibration is present with one quantum in each electronic state. Thus the 1—1 transition of any degenerate vibration is allowed, there being no need for the excitation of an additional E_g^+ quantum, or for any other equivalent combination of vibrations, in order to confer spectral activity. The same is true if two quanta of the same degenerate vibration are present in each state. Thus the 2—2 transition of any degenerate vibration is also allowed, and need not be accompanied by any other vibrational change. The result may be generalised. It follows that sequences due to *n*—*n* transitions of degenerate vibrations may run, not only from A_0^0 and B_0^0 and from the other bands of the A and B progressions, but also from the forbidden electronic origin, except, of course, that in this last case the 0—0 band of the sequence will be missing. For example, an E_u^+ (C) sequence with a missing 0—0 band is always found in association with the electronic origin. Conversely, the recognition of a sequence in this position, or even of the 1—1 band of such a sequence, will immediately show that the responsible vibration is degenerate.

A similar rule applies if two degenerate quanta of the same symmetry class, in particular, two quanta of the same degenerate vibration, are present in one of the combining states. In this case the transition is only weakly allowed; but it is still true that no additional E_g^+ vibration, or combination of vibrations, need be present in order to confer spectral activity. Thus, in the case of degenerate vibrations, we may expect weak bands displaced, not only from A_0^0 and B_0^0 and from the main bands of the A and B progressions, but also from the forbidden electronic origin, by the frequency of the first overtone of the vibration concerned : such bands will be displaced towards long waves if the vibration is in the lower electronic state and towards short waves if it is in the upper state. A number of examples of overtone bands, which, by appearing in positions displaced by the overtone frequency from the forbidden origin, as well as from strong bands, confess themselves to belong to a degenerate vibration, will be found in the accompanying papers.

The unmarked entries in Table II represent transitions which are in principle weak; but, in the case of weakly allowed perpendicular bands only (cf. the centre column of the Table), the following cause may lead to a somewhat strong appearance of certain bands. It is well established that when any two non-orthogonal vibrational states, such as a fundamental and either an overtone of another vibration or a combination tone of two other vibrations, have identical symmetry and nearly the same frequency, a mutual perturbation, or resonance, may arise, which results in a certain amount of mixing of the wave functions, accompanied by limited displacements of the frequencies. It follows that, if the frequency of a vibrational level of a state which, in transitions with a second state, produces a weakly allowed perpendicular band happens to lie close to the frequency of a vibrational level of the first state which, in transitions with identically the same second state, produces a strong perpendicular band, then these two transitions may become mixed together, with the result that the weakly allowed band may in fact appear somewhat strongly, having acquired intensity at the expense of the neighbouring strong band. As the accompanying papers show, examples of band intensification through resonance are common in the electronic spectra of benzenes—quite as common as in the Raman and infra-red spectra, in which the resonance phenomenon has been mainly illustrated hitherto.

Parallel bands cannot be intensified in a similar manner, simply because the symmetry condition for resonance must be fulfilled, and there are no strong parallel bands from which any weak ones could gain intensity.

(6) *Vibrational Selection Rules for the* $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of* D_{3h} *Benzenes.*—The only benzene of this type with which we shall be concerned is 1 : 3 : 5-trideuterobenzene. Its symmetry is $\mathbf{D_{6h}}$ with respect to nuclear charges, but only D_{3h} with respect to nuclear masses.*

In such benzenes the electronic transition is, of course, still forbidden for itself, though it becomes allowed in the presence of a deforming vibration having the right symmetry properties. The vibration must have the symmetry properties of one of the classes E_g^+ and B_{1g} of the group D_{6h} in respect of all those symmetry elements of the group D_{6h} which are preserved in its sub-group D_{3h} (cf. *J.*, 1946, 224). Our discussion of the D_{6h} benzenes (Section 3) shows that this condition is necessary : in order to see that it is sufficient one has only to reflect that a vibration

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* This is not strictly true, because of the finite mass of the electrons; but it is a very close approximation.

cannot have the " wrong " symmetry properties, *i.e.*, those which would cause a cancellation of the transition moment, with respect to elements of symmetry that do not exist in the D_{3h} group. The symmetry classes of the D_{3h} group which have the required symmetry properties are E', and A_1''. Vibrations of the former type can give perpendicular bands, *i.e.*, bands whose transition moments lie in the plane of the molecule. Vibrations of the latter type could produce parallel bands, *i.e.*, those whose transition moments are normal to the plane of the ring. 1 : 3 : 5-Trideuterobenzene has seven fundamental vibrations of the symmetry class E', and in principle a single quantum of any one of these, in either of the combining states, would be sufficient to permit transition. It has no fundamental vibration belonging to the symmetry class A_1'', although vibrational combinations exist which collectively possess this symmetry.

As with the D_{6h} benzenes, so also with the D_{3h} benzene, the observed band systems of the absorption and fluorescence spectra depend overwhelmingly on the perturbing effect of one vibration. This is the degenerate, carbon-bending vibration, which we shall call E'(C 1), since it is very closely similar to the D_{6h} vibration E_g^+(C 1), to which the stronger bands of the spectra of benzene and hexadeuterobenzene are due. Changes by one quantum in this E'(C 1) vibration of 1 : 3 : 5-trideuterobenzene produce the four active orgins, A, B, C, and D, of the absorption and fluorescence spectra, just as described in Section 4, the general spectral pattern being closely similar to that already illustrated in the case of the D_{6h} molecules.

As before, the main progressions, positive in absorption and negative in fluorescence, must depend on quantum changes, unrestricted by symmetry, in totally symmetrical vibrations. We saw that, in the absorption and fluorescence spectra of the D_{6h} benzenes, all the stronger progressions depended on changes in the quantum number of the totally symmetrical carbon vibration, A_{1g}(C). In the D_{3h} benzene there are two totally symmetrical carbon vibrations, which are closely similar. That which has the lower frequency, and which appears more strongly in the Raman effect, we shall call A_1'(C) : in it, most of the synchronous radial motion is in the CD-groups. The other, which has a slightly higher frequency, and appears with somewhat less intensity in the Raman spectrum, we call A_1'(C′) : here most of the swelling motion is in the CH-groups. The general difference between the progressions of the D_{6h} benzenes and those of the D_{3h} benzene will therefore consist in this, *viz.*, that, in place of any given A_{1g}(C) progression of a D_{6h} benzene, we may expect to find overlapping progressions in A_1'(C) and A_1'(C′), as well as mixtures of the two. Guided by the Raman intensities, which largely reflect the ring-swelling character of these vibrations, we may expect the progression of higher frequency to be rather weaker than the other.

In the spectra of D_{6h} benzenes, each of the stronger bands of the main progressions was found to be the starting point of a negatively-running sequence, due to the superposition of 1—1, 2—2, ... , transitions of the low-frequency vibration, E_u^+(C), on the other vibrational changes. Similarly, in the spectra of the D_{3h} compound, the stronger bands of the main progressions start sequences involving *n*—*n* transitions of a closely similar vibration, which we shall call E''(C). The repeating frequency interval in such sequences corresponds to the difference between the fundamental frequencies of the vibration in the lower and upper electronic states.

For the purpose of discussing the weaker frequencies which appear in the absorption and fluorescence spectra of 1 : 3 : 5-trideuterobenzene, we shall require a more expanded statement of the selection rules. Of the twenty vibrations which might be concerned, ten are non-degenerate (A), including four which are totally symmetrical (A_1'), whilst ten are degenerate (E). They fall into five symmetry classes, as shown in Table III, which contains their fundamental frequencies in the electronic ground state, as recorded by Herzfeld, Ingold, and Poole (*loc. cit.*).

TABLE III.

Vibration Classes of D_{3h} *Benzenes. Fundamental Frequencies of* 1 : 3 : 5-*Trideuterobenzene in the Electronic Ground State* (*cm.*$^{-1}$).

Symmetry :	A_1'.		A_2'.	A_2''.	E'.		E''.
(C) (1)	956	1004	1600	691	593	1407	373
(C) (2)					1573		
(H) (1)	2282	3053	920	533	2292	3084	710
(H) (2)			1230	915	834	1102	947

For vibrations accompanying the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ electronic transition of a D_{3h} benzene, such as 1 : 3 : 5-trideuterobenzene, the general selection rule is that, in either or both of the combining states, such vibrations may be excited with such quantum numbers that the product of all the involved vibrational wave-functions has either the symmetry E' or the symmetry A_1''. Some consequences of this rule are given in Table IV (which can be derived from Table XIII, *J.*, **1946**, 234).

TABLE IV.

Vibrations allowed in Combination with the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of a* D_{3h} *Benzene.*

$\psi'_{\text{vib.}} \cdot \psi''_{\text{vib.}}$	E' (perp. bands).		A_1'' (par. bands).
One quantum (either state)	** E'		—
Two quanta (same or different states)	** E', A_1' E', A_2' E'', A_2''	† E', E' † E'', E''	A'_2, A_2'' E', E''
One E' and two other quanta (same state or distributed)	** E', A_1', A_1' * ,, , A_2', A_2' * ,, , A_2'', A_2'' * ,, , E', E' * ,, , E'', E''	E', A_2', A_1' ,, , E', A_1' ,, , E', A_2' ,, , E'', A_2''	E', E'', A_1' ,, , E'', A_2' ,, , E', A_2'' ,, , E', E''

The indications **, * and † have the significance described in Section 5, except that, naturally, E' must be read for E_g^+ in the explanation there given, and the symmetry symbols of the illustrations have to be changed. The conditions for band intensification by resonance are exactly as stated in Section 5.

(7) *Vibrational Selection Rules for the* $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ *Transition of* V_h *Benzenes.*—The two investigated benzenes of this symmetry are 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene. The most notable thing about their vibrations, as compared with those of the benzenes already discussed, is the absence of degeneracy : each degenerate vibration of a D_{6h} benzene becomes replaced in either of these compounds by two distinct vibrations, which may not be very different, or may be widely different, but which in either case go into different symmetry classes.

In the V_h benzenes the electronic transition is again forbidden, although, if the system of nuclear charges belonged to the symmetry group $\mathbf{V_h}$, it would be allowed; but for practical purposes the system of charges still possesses the full symmetry $\mathbf{D_{6h}}$. Those vibrations confer spectral activity which have the symmetry of the E_g^+ or B_{1g} class of the group D_{6h} in respect of those symmetry elements which survive in the sub-group V_h. The required symmetry properties are possessed by the V_h symmetry classes A_g, B_{1g}, and B_{2g}. Vibrations of the two former classes may produce pseudo-perpendicular bands : A_g vibrations can give a transition moment parallel to x, and B_{1g} vibrations a moment parallel to y. Vibrations of the B_{2g} class could give pseudo-parallel bands, with a transition moment parallel to z.

There are six fundamental A_g vibrations, five such B_{1g} vibrations, and one such B_{2g} vibration. Thus a large number of vibrations are in principle capable of producing spectral activity. In fact, the near-ultraviolet spectra are mainly dependent on just those two vibrations into which the doubly degenerate E_g^+(C 1) vibration of a D_{6h} benzene splits when the symmetry is reduced to V_h. They are planar, carbon-bending vibrations, both very similar in form and frequency to the vibration E_g^+(C 1) of a D_{6h} benzene. They fall into the A_g and B_{1g} classes, and we call them A_g(C 1) and B_{1g}(C 1). It follows that, in either electronic state, one quantum of the perturbing vibration can be provided in two ways, whilst two quanta may be furnished in three ways. Thus each of the two active origins, A and B, will now be a close doublet, and the bands of the progressions which proceed from these origins will inherit the doublet character. It follows also that the origins C and D, and their progressions, may contain more complicated band groups.

Progressions can in principle be formed by changes of quantum number, unrestricted by symmetry, in any of the totally symmetrical, A_g, vibrations. However, all the more important progressions which in fact appear in the absorption and fluorescence spectra of the V_h benzenes are dependent on symmetry-unrestricted changes in the particular A_g vibration which resembles the ring-swelling, A_{1g}(C), vibration of a D_{6h} benzene. There is only one such vibration, and we call it A_g(C). Thus, apart from the doubling mentioned above, the A and B progressions are on the whole simpler in the spectra of 1 : 4-di- and 1 : 2 : 4 : 5-tetra-deuterobenzene than they are in the spectra of 1 : 3 : 5-trideuterobenzene.

We shall expect negatively-running sequences, due to *n*—*n* transitions of vibrations of low frequency, to start from all the stronger bands of the progressions. However, these sequences, while preserving generally the character described for other benzenes, will involve the complication that the responsible vibration, E_u^+(C) of a D_{6h} benzene is degenerate, and becomes split in a V_h benzene into two low-frequency vibrations which we call A_u(C) and B_{1u}(C). The first is identical with one form of the E_u^+(C) vibration, whilst the second is distinct though similar. However, since the two differ quite appreciably in frequency, we must expect that, in place of any one E_u^+(C) sequence of a D_{6h} benzene, sequences in A_u(C) and B_{1u}(C) will both appear, as well, possibly, as mixtures of the two.

The numbers of vibrations contained in each of the eight V_h symmetry classes, and the frequencies which, according to Herzfeld, Ingold, and Poole, they possess in the electronic ground state of 1 : 4-dideuterobenzene and 1 : 2 : 4 : 5-tetradeuterobenzene, are shown in Table V (cf. *J.*, 1946, 272, 288).

TABLE V.

Vibrations of V_h Benzenes and Fundamental Frequencies in the Electronic Ground State (cm.$^{-1}$).

	Symmetry :	A_g.	A_u.	B_{1g}.	B_{1u}.	B_{2g}.	B_{2u}.	B_{3g}.	B_{3u}.
$C_6H_4D_2$	(C)	978	405		367		992	634	1603
	(C 1)	597		601					
	(C 2)	1587		1569			1469		1413
	(H)	1173	970	1309		849	1033		1106
	(H 1)	2280		909	597		2275	736	814
	(H 2)	3055		3042	876		3060	967	3079
$C_6H_2D_4$	(C)	961	352		383		977	615	1585
	(C 1)	589		586					
	(C 2)	1572		1564			1353		1439
	(H)	862	793	954		664	819		812
	(H 1)	3045		1255	548		3078	930	1057
	(H 2)	2285		2272	925		2280	767	2280

The selection rule for vibrations accompanying the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ electronic transition of a V_h benzene is that in either or both of the combining states such vibrations may be excited with such quantum numbers that the product of all the involved vibrational wave-functions has the symmetry A_g, B_{1g}, or B_{2g}. The way in which this rule works out is illustrated in Table VI (cf. Table XIV, *J.*, 1946, 234). The indications ** and * have meanings analogous to those given to the same symbols in the preceding tables. The conditions for band intensification by resonance are as stated in Section 5.

TABLE VI.

Vibrations allowed in Combination with the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ Transition of a V_h Benzene.

$\psi'_{\text{vib.}} \cdot \psi''_{\text{vib.}}$.	A_g (*x*-bands).	B_{1g} (*y*-bands).	B_{2g} (*z*-bands).
One quantum (either state)	** A_g	** B_{1g}	—
Two quanta (same or different states)	** A_g, A_g * B_{2g}, B_{2g} * A_u, A_u * B_{2u}, B_{2u} * B_{1g}, B_{1g} * B_{3g}, B_{3g} * B_{1u}, B_{1u} * B_{3u}, B_{3u}	** A_g, B_{1g} A_u, B_{1u} B_{2g}, B_{3g} B_{2u}, B_{3u}	A_g, B_{2g} A_u, B_{2u} B_{1g}, B_{3g} B_{1u}, B_{3u}
One A_g, two other quanta (together or dis-tributed)	** A_g, A_g, A_g * A_g, B_{2g}, B_{2g} * ,, , A_u, A_u * ,, , B_{2u}, B_{2u} ** ,, , B_{1g}, B_{1g} * ,, , B_{3g}, B_{3g} * ,, , B_{1u}, B_{1u} * ,, , B_{3u}, B_{3u}	** A_g, A_g, B_{1g} ,, , A_u, B_{1u} ,, , B_{2g}, B_{3g} ,, , B_{2u}, B_{3u}	A_g, A_g, B_{2g} ,, , A_u, B_{2u} ,, , B_{1g}, B_{3g} ,, , B_{1u}, B_{3u}
One B_{1g}, two other quanta (together or distributed)	** B_{1g}, A_g, B_{1g} ,, , A_u, B_{1u} ,, , B_{2g}, B_{3g} ,, , B_{2u}, B_{3u}	** B_{1g}, A_g, A_g * B_{1g}, B_{2g}, B_{2g} * ,, , A_u, A_u * ,, , B_{2u}, B_{2u} ** ,, , B_{1g}, B_{1g} * ,, , B_{3g}, B_{3g} * ,, , B_{1u}, B_{1u} * ,, , B_{3u}, B_{3u}	B_{1g}, A_g, B_{3g} ,, , A_u, B_{3u} ,, , B_{1g}, B_{2g} ,, , B_{1u}, B_{2u}

It is to be noted that although a B_{2g} vibration is allowed by its symmetry classification to produce a z-band, the one available fundamental vibration of that symmetry class, the vibration B_{2g}(H), can be shown by more detailed considerations to be of no use for that purpose. For the normal co-ordinate of this vibration of a V_h benzene is exactly the same as one normal co-ordinate of an E_g^- vibration of a D_{6h} benzene (Herzfeld, Hobden, Ingold, and Poole, *J.*, 1946, 285; cf. their diagram XII). Therefore the B_{2g}(H) vibration of a V_h benzene has the symmetry $\mathbf{E}_g^-$ with respect to the symmetry $\mathbf{D}_{6h}$ of the system of nuclear charges; and a perturbation of this symmetry does not produce bands. That is why the top right-hand compartment of Table VI contains a blank, whereas symmetry considerations, without a normal co-ordinate treatment, would have allowed us to insert B_{2g}.

(8) *Vibrational Selection Rules for the* $\mathbf{A}_{1g}$—$\mathbf{B}_{2u}$ *Transition of a* C_{2v} *Benzene.*—Monodeuterobenzene has the symmetry C_{2v}. Its ultraviolet spectra, while generally resembling those of D_{6h} benzenes, may exhibit the additional features of the spectra of the D_{3h} benzene, as well as those of the spectra of the V_h benzenes; for C_{2v} is a sub-group of both D_{3h} and V_h, as well as of D_{6h}.

The electronic transition is still forbidden. There are no degenerate vibrations. Those vibrations confer spectral activity which have the symmetry properties of the E_g^+ or B_{1g} class of the group D_{6h} in respect of those symmetry elements which survive in the sub-group C_{2v}. Such vibrations belong to the C_{2v} symmetry classes A_1, B_1, and A_2; and they are allowed to produce x-bands, y-bands, and z-bands, respectively.

In spite of the large number of allowed vibrations, the ultraviolet band system is again overwhelmingly dependent on perturbations by just those two vibrations into which the doubly degenerate E_g^+(C 1) vibration of D_{6h} benzene splits when the symmetry is degraded to C_{2v}. These two planar, carbon-bending vibrations are closely similar in form and frequency to the E_g^+(C 1) vibration of a D_{6h} benzene. They fall into the symmetry classes A_1 and B_1, and we shall call them A_1(C 1) and B_1(C 1). Thus in the spectra, the active origins A and B should become double, whilst C and D could become multiple, just as described for the V_h benzenes (Section 7).

The selection rules would allow progressions to arise by unrestricted quantum changes in any of the totally symmetrical A_1 vibrations. But in fact, the most important progressions depend on quantum changes in that totally symmetrical vibration, called A_1(C), which most closely resembles the ring-swelling, A_{1g}(C), vibration of a D_{6h} benzene.

We expect negatively-running sequences, due to n—n transitions of low-frequency vibrations, to start from the stronger bands of the main progressions. Corresponding to the degenerate, E_u^+(C), vibration, which, in a D_{6h} benzene, is responsible for such sequences, and to the two responsible vibrations, A_u(C) and B_{1u}(C), of a V_h benzene, there are two, which we call A_2(C) and B_2(C), in a C_{2v} benzene. The first is identical with one form of the E_u^+(C) vibration of a D_{6h} benzene, and with the A_u(C) vibration of a V_h benzene; the second is different from any other vibration. Thus, in place of any particular sequence in a spectrum of a D_{6h} benzene, we may expect overlapping sequences in the vibrations A_2(C) and B_2(C), and also mixed sequences involving both vibrations.

The numbers of vibrations in each of the four C_{2v} symmetry classes, and the frequencies which they possess in the electronic ground state of monodeuterobenzene, according to the determinations of Bailey, Gordon, Hale, Herzfeld, Ingold, and Poole (*J.*, 1946, 299), are shown in Table VII.

TABLE VII.

Vibrations of C_{2v} *Benzenes. Fundamental Frequencies of Monodeuterobenzene in the Electronic Ground State* (*cm.*$^{-1}$).

Symmetry:	A_1.			B_1.		A_2.		B_2.	
(C)	980		1007	1624		405		380	698
(C 1)	601			603					
(C 2)	1591		1480	1574	1450				
(H)	1176		1031	1292	1076	970	850		
(H 1)	2269			1158	858			608	778
(H 2)	3054	3060	3065	3041	3079			992	995

The general selection rule for vibrations accompanying the $\mathbf{A}_{1g}$—$\mathbf{B}_{2u}$ transition of a C_{2v} benzene is that in either or both of the combining states such vibrations may be excited with such quantum numbers that the product of all the involved vibrational wave-functions has the symmetry A_1, B_1, or A_2. The one exception to this is that a single quantum of an A_2 vibration cannot produce spectral activity, because it happens that each of the three fundamental vibrations of the A_2 class satisfies the further condition of having either $\mathbf{E}_g^-$ or $\mathbf{E}_u^+$ symmetry with respect to the $\mathbf{D}_{6h}$ system of nuclear changes, and either of these conditions is sufficient to cancel the transition moment. These rules are illustrated in Table VIII. The significance of the intensity indications ** and *, and the rules governing intensification by resonance, are as explained for the more symmetrical benzenes.

TABLE VIII.

Vibrations Allowed in Combination with the $\mathbf{A}_{1g}$—$\mathbf{B}_{2u}$ *Transition of a* C_{2v} *Benzene.*

$\psi'_{\text{vib.}} \cdot \psi''_{\text{vib.}}$	A_1 (x-bands).	B_1 (y-bands).	A_2 (z-bands).
One quantum	** A_1	** B_1	—
Two quanta	** A_1, A_1 * A_2, A_2 * B_1, B_1 * B_2, B_2	** A_1, B_1 A_2, B_2	A_1, A_2 B_1, B_2
One A_1, two other quanta	** A_1, A_1, A_1 * A_1, A_2, A_2 * ,, , B_1, B_1 * ,, , B_2, B_2	** A_1, A_1, B_1 ,, , A_2, B_2	A_1, A_1, A_2 ,, , B_1, B_2
One B_1, two other quanta	** B_1, A_1, B_1 ,, , A_2, B_2	** B_1, A_1, A_1 * B_1, A_2, A_2 * ,, , B_1, B_1 * ,, , B_2, B_2	B_1, A_1, B_2 ,, , A_2, B_1

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