97. *Excited States of Benzene. Part III. Analysis of the First Ultraviolet Band System of the Fluorescence Spectrum of Benzene.*

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The measurements of Ingold and Wilson on the ultraviolet fluorescence spectrum of benzene are analysed according to the requirements outlined in the abstract of Part I. Cases of apparent Fermi resonance are pointed out. The recognised fundamental frequencies of both combining states are assigned to vibrations.

(1) *Data.*—Measurements on the ultraviolet fluorescence spectrum of benzene have been recorded by Ingold and Wilson (*J.*, 1936, 941, 1210). Following the procedure employed in the treatment of the absorption spectrum, a selection was first made from their long list of measured maxima, of those which appear to be the main maxima of individual bands, as judged from the plates and microphotometer records. These frequencies and the assignments we propose for them are recorded in Tables I, II, and III, which are arranged on the same general plan as Tables I, II, and III of Part II.

The symbolism has been made to correspond as far as possible with that used by Sponer and her collaborators: our series A—D, F, M, and N can be correlated directly with hers. Our fluorescence series A—D, F, and H—N correspond to those absorption series to which the same

TABLE I.

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

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
38612·4	m	A^0_0	36973·6	mw	H^0_{-1}	35402·2	m	D^0_{-2}; G^0_{-1}
571·4	w	I^0_0	933·0	w	J^1_{-1}	385·1	ms	Y^1_{-1}
522·4	mw	C^0_0	908·0	m	D^3_0	348·1	ms	B^1_{-2}; F^1_{-1}
452·1	mw	A^1_0	895·4	m	N^2_0	321·5	s	
447·5			875·6	w	U^0_0	241·6	mw	D^1_{-2}; G^1_{-1}
406·5	mw	B^0_1	840·1	m	B^4_0	218·6	m	Y^2_{-1}; N^0_{-2}
365·1	w	C^1_0	831·6	m		184·2	m	B^2_{-2}; F^2_{-}
359·5			824·2	m		157·6	ms	
350·2	w	M^0_0	772·5	w	J^2_{-1}	081·1	w	D^2_{-2}; G^2_{-1}
344·3			740·3	mw	D^4_0	055·3	mw	Y^3_{-1}; N^1_{-2}
338·9			734·7	w	N^3_0	026·3	m	Q^0_0
317·0	w	D^0_1	697·0	w	B^5_0	34996·2	m	B^3_{-2}; F^3_{-1}
290·6	mw	A^2_0	683·8	w		894·1	w	Y^4_{-1}; N^2_{-2}
284·3			669·0	w		862·0	w	Q^1_0
281·4			657·3	mw	W^0_0	781·9	w	P^0_{-1}
245·0	w	B^1_1	640·6	mw		744·3	w	Y_{-1}^{5}
204·7	w	C^2_0	625·0	m	A^0_{-2}	702·5	w	Q^2_0
195·5			559·8	ww	C^0_{-2}; E^0_{-1}	644·8	w	A^0_{-4}
158·4	ww	D^1_1	538·3	m	Y^0_0	550·0	m	Y^0_{-2}
132·8	w	A^3_0	497·8	s	B^0_{-1}; F^0_0	523·6	m	B^0_{-3}; F_{-2}
125·3			478·1	s		492·3	ms	
121·8			415·6	m	D^0_{-1}; G^0_0	409·6	w	D^0_{-3}; G^0_{-2}
084·0	w	B^2_1	388·2	ms		390·6	mw	Y^1_{-2}
046·5	w	C^3_0	336·3	s	B^1_{-1}; F^1_0	361·3	mw	B^1_{-3}; F^1_{-2}
034·6			317·5	s		328·7	m	
004·7	w	V^0_0	248·8	m	D^1_{-1}; G^1_0	250·7	w	D^1_{-3}; G^1_{-2}
37991·3	ww	D^2_1	226·7	ms		230·5	mw	Y^2_{-2}; N^0_{-3}
966·4	w	$\left\{\begin{matrix}H^0_0\\A^4_0\end{matrix}\right.$	216·2	ms	N^0_{-1}	202·6	w	B^2_{-3}; F^2_{-2}
961·1			175·6	ms	B^2_{-1}; F^2_0	167·3	m	
956·1			156·4	s		090·0	ww	D^2_{-3}; G^2_{-2}
945·7			092·9	mw	D^2_{-1}; G^2_0	069·1	w	Y^3_{-2}; N^1_{-3}
925·8	w	J^1_0	080·3	m		036·5	w	Q^0_{-1}
875·0	ww	C^4_0	064·7	ms		003·7	mw	B^3_{-3}; F^3_{-2}
870·5			055·0	m	N^1_{-1}	33908·4	w	Y^4_{-2}
836·6	ww	V^1_0	014·5	m	B^3_{-1}; F^3_0	875·3	ww	Q^1_{-1}
822·3	ww	O^0_0	35996·8	ms		792·3	ww	P^0_{-2}
794·5	ww	A^5_0	990·4	ms		711·6	ww	Q^2_{-1}
766·1	w	J^2_0	926·8	mw	D^3_{-1}; G^3_0	560·8	w	Y^0_{-3}
616·3	m	A^0_{-1}	899·4	m		536·5	w	B^0_{-4}; F^0_{-3}
580·5	w	I^0_{-1}	892·9	mw	N^2_{-1}	499·0	mw	
544·1	ww	C^0_{-1}; E^0_0	857·0	mw	B^4_{-1}; F^4_0	419·2	ww	D^0_{-4}; G^0_{-3}
528·2	w		832·0	m		394·1	ww	Y^1_{-3}
482·5	ss	B^0_0	823·0	m		371·8	ww	B^1_{-4}; F^1_{-3}
414·7	w	B^0_{1-1}	789·1	w	P^0_0	334·3	w	
392·2	s	D^0_0	753·7	w	D^4_{-1}; G^4_0	256·4	ww	D^1_{-4}; G^1_{-3}
320·6	ss	B^1_0	736·1	w		235·5	w	Y^2_{-3}; N^0_{-4}
230·1	ms	D^1_0	698·6	w	B^5_{-1}; F^5_0	213·9	ww	B^2_{-4}; F^2_{-3}
219·0	s	N^0_0	665·6	w		178·8	w	
161·9	s	B^2_0	648·3	w	W^0_{-1}	045·4	ww	Q^0_{-2}
067·8	ms	D^2_0	634·7	mw	A^0_{-3}	013·5	ww	B^3_{-4}; F^3_{-3}
059·8	ms	N^1_0	546·6	ms	Y^0_{-1}	32550·3	ww	B^0_{-5}; F^0_{-4}
020·3	w	V^0_{-1}	509·4	s	B^0_{-2}; F^0_{-1}	511·5	w	
000·3	ms	B^3_0	483·2	s		347·1	ww	B^1_{-5}; F^1_{-4}
36990·7	ms							

Note : (1) Intensities are represented by a series of qualitative indications ranging from ww = very weak, through m = medium, etc., to ss = very strong.

(2) The numerical part of the notation in which assignments are expressed is explained in the note below Table I of Part II (p. 419). The letter-symbols used in this Table are defined in the following Tables.

TABLE II.

Fluorescence Spectrum of Benzene. Key to Series Assignment (*cf. Table I*).

	Freq. (cm.$^{-1}$).	p'.	p''.	s.
A =	$38090 + 521 - 992p'' - 161s$		0—4	0—5
B =	,, $- 608 + 923p' - 992p'' - 161s$	0, 1	0—5	0—5
C =	,, $+ 2 \times 521 - 608 - 992p'' - 161s$		0—2	0—4
D =	,, $+ 521 - 2 \times 608 + 923p' - 992p'' - 161s$	0, 1	0—4	0—4
E =	,, $+ 2 \times 521 - 1600 - 992p''$		0, 1	
F =	,, $- 1600 - 992p'' - 161s$		0—4	0—5
G =	,, $+ 521 - 608 - 1600 - 992p'' - 161s$		0—3	0—4
H =	,, $- 608 + 2 \times 243 - 992p''$		0, 1	
I =	,, $+ 2 \times 243 - 992p''$		0, 1	
J =	,, $- 992p'' - 161s$		0, 1	1, 2
M =	,, $+ 521 - 265$			
N =	,, $- 608 - 265 - 992p'' - 161s$		0—4	0—3
O =	,, $- 265$			
P =	,, $- 608 - 2 \times 849 - 992p''$		0—2	
Q =	,, $- 3060 - 992p'' - 161s$		0—2	0—2
U =	,, $- 2 \times 608$			
V =	,, $+ 521 - 608 - 992p'' - 161s$		0, 1	0, 1
W =	,, $+ 521 - 2 \times 986 - 992p''$		0, 1	
Y =	,, $- 703 - 849 - 992p'' - 161s$		0—3	0—5

TABLE III.

Fluorescence Spectrum of Benzene. Assignment to Vibrations of the Vibration Frequencies (*cm.*$^{-1}$) *contained in Table II.*

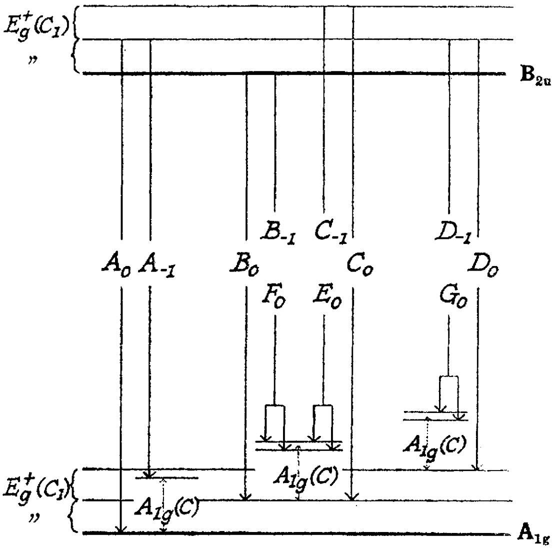
Upper-state fundamental frequencies (+).	Lower-state fundamental frequencies (−).	Diffs. of upper- and lower-state fundamentals (−).	Vibration.
923	992	69	A_{1g}(C)
—	703	—	B_{2g}(C)
—	986	—	B_{2g}(H)
521	608	87	E_g^+(C 1)
—	1600	—	E_g^+(C 2)
—	3060	—	E_g^+(H 1)
—	243	161	E_u^+(C)
—	849	265	E_g^-(H)

letters are given in Part II, except for the difference that in absorption one observes mainly positive progressions in the upper-state frequency of the totally symmetrical carbon vibration, whereas in fluorescence one finds mainly negative progressions in the lower-state frequency of this vibration. Other fluorescence series, *viz.*, P—Y, also correspond to the absorption series labelled by the same letters, except that, in addition to the difference mentioned, there is now the further difference that at least one non-totally symmetrical vibration enters through its upper-state frequency into the absorption series, and through its lower-state frequency into the fluorescence series.

(2) *Band Series* A—G, U, *and* V.—These series involve the same vibrations as those which control the character of the absorption series A—F, *viz.*, two primary perturbing vibrations, E_g^+(C 1) and E_g^+(C 2), each producing what we call " active origins ", the totally symmetrical vibration, A_{1g}(C), which leads to the main progressions, and the low-frequency vibration, E_u^+(C), which gives rise to the sequences (cf. Part II, Sections 2 and 3).

We may first discuss series A—G, which largely governs the general structure of the spectrum. This spectrum is considerably affected by the already mentioned resonance in the electronic ground state between the combination, E_g^+(C 1)608 + A_{1g}(C)992 = 1600 cm.$^{-1}$, and the fundamental frequency, E_g^+(C 2) = 1600 cm.$^{-1}$. As we know, the resonance causes these energy levels to fall apart by 20 cm.$^{-1}$. With successively added A_{1g}(C) quanta, the resonance splitting becomes repeated, with increasing separations, which amount to 26, 31, 37, and 39 cm.$^{-1}$, respectively, for 1, 2, 3, and 4 extra quanta of the totally symmetrical vibration. (The last of the measured separations is rendered inaccurate by the weakness of the bands.) Because of these splittings the transition corresponding to every band of the negative progressions B and C, which owe their spectral activity to a one-quantum change in the vibration E_g(C 1), excepting only the parent bands B_0 and C_0, will terminate on *both* of a pair of split levels; and likewise, the transitions of all the bands, without exception, of series E and F, which depend on a one-quantum change in the vibration E_g^+(C 2), will end on the same pairs of split levels. Fig. 1 will make the relationship clear. A similar resonance occurs with one added E_g^+(C 1) quantum, *i.e.*, between the combination 2 × E_g^+(C 1)608 + A_{1g}(C)992 = 2208 cm.$^{-1}$, and the combination E_g^+(C 1)608 + E_g^+(C 2)1600 = 2208 cm.$^{-1}$. In this case the splitting amounts to 27 cm.$^{-1}$: whether it increases further with added A_{1g}(C) quanta cannot be determined from the spectrum. It follows that the transitions of bands of the D series, excepting D$_0$, and, likewise, the transitions of all bands of the G series, must end on pairs of split levels belonging in common to both series. This is also illustrated in Fig. 1.

FIG. 1.



Resonance doublets in fluorescence progressions of benzene.

We can thus understand the general distribution of duplexity amongst the bands. Bands of the A progression are simple, whilst bands of the otherwise analogous progressions B, C, and D each start with a simple band and continue with doublets. Actually a further complication enters, which causes the doublets to develop into triplets higher in the progressions; this, however, is more conveniently discussed later (Section 6). It should be mentioned also that the above discussion applies without modification only to the 0—0 bands of sequences in 161 cm.$^{-1}$; for the higher members of such sequences become split, as has been explained before, by an anharmonicity effect, and these (generally smaller) splittings become superposed on those mentioned above.

A sharp though weak band U$_0^0$ lies 608 cm.$^{-1}$ below B$_0^0$. It clearly arises by a transition from the " vibrationless " excited state to the second quantum level of the E_g^+(C 1) vibration in the ground state. The transition is allowed because the vibration is degenerate (cf. Part I, Section 5). Furthermore, although this second quantum level is triple, the transition is allowed to end only on one of its three components : this helps us to understand a sharpness which is not the most common characteristic of quite weak bands.

Series V starts with a band V$_0^0$ situated 87 cm.$^{-1}$ below the electronic origin, and is associated with a progression in 992 cm.$^{-1}$, and a sequence in 161 cm.$^{-1}$, each of two members. These bands involve 1—1 transitions of the vibration E_g^+(C 1), and are allowed, even though the quantum number does not change, because the vibration is degenerate (cf. Part I, Section 5).

(3) *Band Series* H, I, *and* J.—These series depend on the excitation, in either or both electronic states, of the low-frequency vibration E_u^+(C), whose fundamental frequencies are 404 cm.$^{-1}$ and 243 cm.$^{-1}$ (cf. Part II, Section 4). The series are closely similar to the correspondingly named series of the absorption spectrum; the main differences arise from the fact that, in the downward transitions of fluorescence, different Boltzmann factors modify the intensities.

Series H and I, which commence with bands situated 2 × 243 cm.$^{-1}$ above the active origin B$_0^0$, and above the forbidden electronic origin J$_0^0$, respectively, both involve downward 2—0 transitions of the vibration E_u^+(C). In series H this transition is combined with a 0—1 transition of the activating vibration E_g^+(C 1). Series I, which does not involve the vibration E_g^+(C 1), is nevertheless allowed because the vibration is degenerate (cf. Part I, Section 5). Series J depends on transitions 1—1, 2—2, . . . , of the vibration E_u^+(C), without associated changes in any other non-totally symmetrical vibration. A sequence in 161 cm.$^{-1}$ runs as if from the electronic origin, except that the 0—0 band is missing, and these bands start progressions in 992 cm.$^{-1}$. This series of bands is also allowed because of the degenerate nature of the vibration (*loc. cit.*).

(4) *Band Series* M, N, O, *and* P.—These four series involve the excitation, in one or both electronic states, of a vibration, which, for reasons given in Part XI, we identify as the out-of-plane, hydrogen vibration, E_g^-(H). Its fundamental frequencies in the two states are 849 cm.$^{-1}$ and 585 cm.$^{-1}$ (cf. Part II, Section 6).

Series M and N correspond closely to the identically named series of the absorption spectrum (*loc. cit.*). The band M_0^0 lies 265 cm.$^{-1}$ below A_0^0. We explain it by assuming a 1—1 transition of the vibration E_g^-(H) superposed on the electronic and vibrational transition of A_0^0. The band N_0^0 is similarly related to B_0^0. A weak band O_0^0 appears 265 cm.$^{-1}$ below the forbidden electronic origin : the same band is found in the absorption spectrum (*loc. cit.*). It is explained as arising from a 1—1 transition of the vibration E_g^-(H), without a concomitant change in any other vibration, this type of transition being allowed (cf. Part I, Section 5) on account of the degenerate nature of the vibration E_g^-(H).

The progression P starts with a band P_0^0 displaced 1695 cm.$^{-1}$ below B_0^0, the main active origin for fluorescence. We interpret P_0^0 by assuming a downward 0—2 transition of the vibration E_g^-(H), in combination with the electronic and vibrational transition characteristic of B_0^0. The frequency in the lower electronic state of the first overtone of the vibration E_g^-(H) is thus 1695 cm.$^{-1}$. It can also be directly measured in the Raman spectrum of liquid benzene, and is there 1693 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *J.*, 1946, 324). Progression P of the absorption spectrum (Part II, Tables I and II) is similar, except that the involved first overtone is that of the upper electronic state.

(5) *Band Series* Q.—An excitation of the degenerate hydrogen-stretching vibration E_g^+(H 1) is responsible for the appearance of this series, which corresponds to the absorption series Q, with the difference that in absorption the activating vibrational excitation takes place in the upper electronic state, while in fluorescence it occurs in the lower state. The origin Q_0^0 of the Q series of the fluorescence spectrum lies 3060 cm.$^{-1}$ below the electronic origin. It is interpreted as arising in a downward 0—1 transition of the vibration E_g^+(H 1). Mention should be made of the fact that the band Q_0^0 coincides with the position in which we might expect to find one of the members of a weak doublet which in our notation would be labelled B^3_{-2}, F^3_{-1}; but a study of the intensities shows that the observed band is not thus explicable, and must represent a new active origin.

The value we obtain, 3060 cm.$^{-1}$, for the fundamental frequency of the vibration E_g^+(H 1) in the electronic ground state differs by 0·4% from the value, 3047 cm.$^{-1}$, given by the Raman spectrum of liquid benzene. The discrepancy is rather larger than usual, but a special reason can be given why the use of liquid benzene for observation of the Raman spectrum might create a relatively large disturbance in the case of this particular vibration. For the frequency lies close to the very strong Raman frequency, 3062 cm.$^{-1}$, belonging to the totally symmetrical vibration, A_{1g}(H). Now, although in the gaseous molecule any interaction between the two vibrations would be completely excluded by their orthogonality, in the liquid substance the intermolecular forces will produce deformations of equilibrium configuration which must entail some loss of orthogonality of the original normal co-ordinates. Accordingly, in the liquid, some dynamical interaction between the vibrations might arise, which could result in a perceptible downward displacement of the weaker frequency. One can well believe that such effects of deformation are more likely to attain considerable magnitudes with hydrogen vibrations than with carbon vibrations, because of the exterior situation of the hydrogen atoms.

(6) *Band Series* W *and* Y.—The series here to be discussed are associated with vibrations of the B_{2g} symmetry class. The parent band, W_0^0, of the progression W lies 1972 cm.$^{-1}$ below the active origin A_0^0, and therefore only 15 cm.$^{-1}$ above the third member of the main A progression, *i.e.*, the band A^0_{-2}. We connect the bands W with the trigonal, out-of-plane, hydrogen vibration, B_{2g}(H). From studies of the infra-red and Raman spectra of benzene and its deuterated derivatives, Herzfeld, Ingold, and Poole concluded (*loc. cit.*) that the fundamental frequency of this vibration (which, actually, is forbidden in the Raman and infra-red spectra of ordinary benzene) is 985 cm.$^{-1}$—quite close, therefore, to the frequency, 992 cm.$^{-1}$, of the carbon

ring-breathing vibration, A_{1g}(C). In fluorescence, the B_{2g}(H) vibration, being non-totally symmetrical and non-degenerate, is not allowed to change by only one quantum; but it can be excited in the lower electronic state by two quanta; and, furthermore, the band which might thus arise would be allowed by the selection rules to intensify itself by resonance at the expense of any close-lying band of the A progression (Part I, Section 5). We suppose that this is what happens; and thus we explain why the first band of the A progression to appear with a prominent companion of the W series is the third member, A^0_{-2}. The value to which we are thus led for the fundamental frequency of the vibration B_{2g}(H), *viz.*, 1972/2 = 986 cm.$^{-1}$, agrees well with the value given by Herzfeld, Ingold, and Poole (985 cm.$^{-1}$).

The presence of a similar progression of companion bands associated with series B cannot be verified because of the resonance splitting which arises in that series (Section 2) : the positions in which the companion bands would be expected are always overlaid by the lower components of the strong B, F doublets. These doublets have, however, a set of companions of still lower frequency with which we must now deal. They are not simply related to the bands just discussed, as can be seen from the fact that they start, not beside the third, but beside the second band of the B progression, B^0_{-1}, that is, beside the first B, F doublet, B^0_{-1}, F^0_0. We call this series Y. It exhibits the peculiar intensity relationship, discussed below, which led to the remark in Section 2 that the higher B, F doublets tend to develop into triplets.

We may first consider the frequencies of the Y bands, the parent of which, Y^0_0, lies 1552 cm.$^{-1}$ below the electronic origin. We interpret this position as indicating a transition from a "vibrationless" excited state to a certain combination level of E_g^+ symmetry (cf. Part I, Section 5) in the ground state, *viz.*, the combination B_{2g}(C)703 + E_g^-(H)849 = 1552 cm.$^{-1}$. The fundamental frequency which we are here required to assume for the B_{2g}(C) vibration agrees exactly with the value, 703 cm.$^{-1}$, which Herzfeld, Ingold, and Poole deduced from their studies (*loc. cit.*). The fundamental frequency of the vibration E_g^-(H) is well established (Part II, Section 6). The explanation given makes the Y series of the fluorescence spectrum analogous to series, also called Y, in the absorption spectrum, if our preferred interpretation of the latter be adopted. The absorption series starts with a band 950 cm.$^{-1}$ above the electronic origin, and this we have assumed to arise in a transition from the "vibrationless" ground state to an E_g^+ combination of the excited state, *viz.*, the combination B_{2g}(C)365 + E_g^-(H)585 = 950 cm.$^{-1}$. Both involved fundamental frequencies of the upper state have been independently evaluated. It should be mentioned that, since the parent band, Y^0_0, of the fluorescence series lies 2074 cm.$^{-1}$ below A^0_0, it is in the position of a band which could arise from an allowed excitation in the ground state of the first overtone of the vibration E_u^-(H), in combination with the electronic and vibrational transition characteristic of A^0_0; for the fundamental frequency of the vibration E_u^-(H) is 1037 cm.$^{-1}$. However, we exclude this explanation, first, because it could not account for the intensity effects described below, and secondly, because it would lead us to expect a stronger band series, starting with a band equally displaced below B^0_0, whereas in fact no such series appears. The second member of the fluorescence progression, the band Y^0_{-1}, also requires the consideration of another possible explanation. For it happens to lie 3066 cm.$^{-1}$ below A^0_0, that is, in the position of a band which might arise from the allowed excitation, in the ground state, of the fundamental frequency of the hydrogen-stretching vibration A_{1g}(H) (Raman frequency 3062 cm.$^{-1}$), in combination with the electronic and vibrational transition of A^0_0. However, we exclude this interpretation also, for just the same two reasons.

The first band, Y^0_0, of the Y series has only moderate intensity : we judge it to be less than one-tenth as intense as either component of the adjacent B, F doublet, the first band of which lies 40 cm.$^{-1}$ higher, and the second 20 cm.$^{-1}$ higher still. The second Y band, Y^0_{-1}, is considerably stronger than the first, and its relationship to the neighbouring B, F doublet is notably altered. It is about half as strong as the first member of the doublet, which has now become appreciably weaker than the second component. Furthermore, the spacing is altered, the first gap having been reduced to 37 cm.$^{-1}$, and the second gap increased to 26 cm.$^{-1}$. The third band, Y^0_{-2}, is nearly as strong as the first component of the adjacent B, F doublet, the collective intensity of the two bands being roughly the same as the intensity of the second component of the doublet. Again the spacing is altered, so that the first gap is reduced to 26 cm.$^{-1}$, and the second increased to 31 cm.$^{-1}$, the middle band having, so to speak, changed partners. These relationships are approximately repeated, with weaker overall intensities, in the next trio of bands, involving Y^0_{-3}, the first gap being here 24 cm.$^{-1}$, and the second 37 cm.$^{-1}$.

We interpret these facts as indicating a resonance in the lower electronic state between the combination tone, B_{2g}(C) + E_g^-(H), associated with the Y bands, and the already known resonance system, composed from the combination tone, E_g^+(C 1) + A_{1g}(C), and the fundamental frequency, E_g^+(C 2)—the resonance system responsible for the B, F doublets. The selection rules would allow the postulated additional resonance (Part I, Section 5); for, in every case, those transitions which would produce close-lying bands start from identical levels of the upper state and end on neighbouring levels of the same symmetry in the lower state. Actually, in the case of the first band, Y_0^0, we would assume very little intensification through the allowed resonance with the B_{-1}^0, F_0^0 doublet. The fluorescence band Y_0^0 is of the same order of intensity, relatively to the spectrum as a whole, as is the absorption band, also called Y_0^0, relatively to its spectrum; and in the latter case no question of intensification by resonance can arise. Furthermore, the allowed resonance in the electronic ground state is not strong enough to produce an observed occurrence of the combination tone B_{2g}(C) + E_g^-(H) in the Raman spectrum of benzene, although the resonance doublet frequencies from E_g^+(C 1) + A_{1g}(C) and E_g^+(C 2) appear quite strongly in that spectrum. With successively added A_{1g}(C) quanta, however, a progressively altering situation arises. We have already seen (Section 2) that resonance beomes more effective in separating the energy levels, collectively belonging to E_g^+(C 1) + $(n + 1)A_{1g}$(C) and E_g^+(C 2) + nA_{1g}(C), as n takes on the successive values 0, 1, 2, 3. It follows that, in the progression of doublet levels, one component will approach, more and more closely as n increases, to the theoretical position of the neighbouring combination level B_{2g}(C) + E_g^-(C) + nA_{1g}(C). This is a factor which will open the way to an effective resonance with the last-named combination level; so that transitions from the same initial state which end upon it, and upon that component of the original doublet level which in the main interacts with it, will tend to share intensity. This is how we explain the intensity effects found in the B, F doublets—or in the Y, B, F triplets, if we choose so to call them. The observed intensities suggest that the assumed sharing becomes substantial when $n = 1$, and is already nearly symmetrical when $n = 2$.

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[*Received, April* 30*th*, 1947.]