96. *Excited States of Benzene. Part II. Analysis of the First Ultra-violet Band System of the Absorption Spectrum of Benzene.*

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The measurements of Radle and Beck on the ultraviolet absorption spectrum of benzene are analysed according to the requirements outlined in the abstract of Part I.   A list is given of eleven fundamental frequencies of the upper electronic state.   They are all assigned to vibrations, but in this paper the assignments are supported only by evidence which is internal to the spectrum under consideration.   An important part of the basis of some of the assignments depends on comparisons between the ultraviolet absorption and fluorescence spectra of different isotopically substituted benzenes.   Such arguments of comparison are reserved for collective treatment in Part XI.

(1) *Data.*—An extensive series of measurements on the first ultraviolet absorption system of benzene has been recorded by Radle and Beck (*J. Chem. Physics*, 1940, **8**, 507), who also made a number of assignments.   For the continued analysis of the spectrum our procedure was first to select from their list of measured intensity maxima all those which stand out prominently from their background of weak, overlapped bands.   It is unlikely that any of these more prominent frequencies represents a branch of some separately listed band; or that any is an accidental intensity maximum caused by overlapping; and, furthermore, all these bands seem strong enough to demand some fairly simple explanation in terms of allowed vibrational changes.

The frequencies and intensities of all the bands which seemed to us worth trying to assign are in Table I.   The Table also contains our assignments.   Most of the older assignments are adopted, though some have had to be changed; many assignments are new.   The result is that none of the frequencies which we originally thought should be explained now remains without a plausible explanation.

The assignments are expressed by means of a literal notation, the key to which is in Tables II and III.   The meanings of the subscripts and superscripts are explained in the Note below Table I : they can also be understood from the examples given in Figs. 1 and 2 of Part I.   The letters by which the equations of Table II are represented have been chosen to correspond as far as possible to those used previously.   Equations A—G (p. 419) agree with those given by Sponer. Nordheim, Sklar, and Teller (*J. Chem. Physics*, 1939, **7**, 207), except for certain dropped or added terms.   The ranges of quantum numbers, given on the right in Table II, relate only to the listed, prominent bands : larger ranges could often be given by taking account of bands, which, though definite, do not stand out strongly against their environment.

TABLE I.

Absorption Spectrum of Benzene.   Frequencies and Intensities (Radle and Beck) ; and Assignments (cf. Tables II and III).

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
36317·2	2	F_0^1, B_{-1}^1	38891·3	25	H_1^0	40202·5	140	C_2^1
334·6	1		919·9	55	G_0^1	248·3	160	B_3^0
478·0	3	F_0^0, B_{-1}^0	929·0	55		252·5	160	
496·2	4		967·0	30	U_0^1	292·8	510	A_2^1
624·7	3	A_{-2}^0	39010·0	25	B_2^2	297·7	350	
990·7	8	B_0^3	038·6	170	Y_0^0	319·8	130	E_1^1
37000·9	8		047·0	25	A_1^3	344·7	160	
156·8	25	B_0^2	056·0	25		366·4	420	C_2^0
160·4	25		063·0	25		372·0	230	
216·7	18	N_0^0	082·0	250	G_0^0	456·0	6500	A_2^0
230·2	21	D_0^1	086·8	250		482·7	335	E_1^0
321·1	140	B_0^1	122·0	25	C_1^2	489·4	325	
392·5	55	D_0^0	124·0	25		543·0	35	O_1^1
452·5	25	A_{-1}^1	134·2	130	U_0^0	558·9	250	K_1^0
457·3	12		168·5	130	B_2^1	686·5	170	O_1^0
481·9	420	B_0^0	204·5	280	A_1^2	704·8	335	
616·8	85	A_{-1}^0	209·3	230		812·2	55	U_2^1
766·8	25	J_0^2	215·6	140		840·1	25	Q_0^2
926·8	35	J_0^1	236·0	150	D_2^0	883·3	30	Y_2^0
956·5	18	H_0^0	255·1	170	M_1^0	894·5	30	R_0^0
962·6	12		265·5	170		903·5	55	
967·8	25		272·1	140		930·4	55	G_2^0
990·8	18	D_1^2	281·4	170	C_1^1	968·5	230	U_2^0
38043·8	30	C_0^3	330·6	350	B_2^0	41002·3	190	Q_0^1
084·1	55	B_1^2	371·2	750	A_1^1	028·5	55	A_3^2
089·4	12		376·1	510		053·9	55	
121·8	25	A_0^3	398·9	130	E_0^1	075·9	120	W_1^0
125·4	18		423·1	160		081·7	120	
133·2	35		445·3	675	C_1^0	099·7	140	M_3^0
141·3	30	N_1^0	487·1	55	I_1^1	165·3	450	Q_0^0
154·0	30	D_1^1	534·2	7000	A_1^0	173·5	55	B_4^0
204·3	55	C_0^2	560·8	335	E_0^0	218·4	350	A_3^1
210·0	55	L_0^0	568·7	250		239·6	75	E_2^1
245·4	160	B_1^1	638·2	335	K_0^0	266·6	140	
281·1	230	A_0^2	765·4	190	O_0^0	285·7	210	C_3^0
285·2	210		783·2	250		377·9	3500	A_3^0
292·3	170		841·5	55	G_1^1	399·2	170	E_2^0
316·6	130	D_1^0	847·3	45		402·3	170	
343·3	190	M_0^0	850·7	70		409·9	190	
350·0	140		894·1	55	U_1^1	478·6	350	K_2^0
359·7	250	C_0^1	962·1	120	Y_1^0	606·6	140	O_2^0
365·2	160		971·9	70	A_2^3	624·3	325	
407·0	550	B_1^0	40004·8	140	G_1^0	700·1	55	T_0^0
448·4	950	A_0^1	010·2	160		741·0	140	S_0^0
452·4	950		023·6	40	X_0^0	760·9	70	Q_1^2
523·0	630	C_0^0	050·2	190	U_1^0	824·1	25	R_1^0
562·4	140	I_0^0	090·8	55	B_3^1	884·5	160	U^0
612·2	7500	A_0^0	109·1	85	A_2^2	923·9	160	Q_1^1
649·0	25	P_0^0	131·5	230		974·1	140	Z_0^0
655·0	25		137·3	55		42018·9	55	M_4^0
766·9	21	G_0^2	159·9	210	W_0^0	088·0	100	Q_1^0
839·7	35	J_1^1	177·7	230	M_2^v	111·8	70	
851·5	35		186·8	140		137·6	85	A_4^1

TABLE I—*contd.*

Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.	Freq. (cm.$^{-1}$).	Inty.	Assgnt.
42204·1	55	C_4^0	42845·0	130	Q_2^1	43929·1	160⎫	Q_3^0
286·6	250⎫	A_4^0	892·1	40	Z_1^0	952·9	40⎭	
297·7	950⎭		43009·3	325⎫	Q_2^0	44133·0	35	A_6^0
318·3	160⎫	E_3^0	032·0	85⎭		488·8	30	S_3^0
328·2	40⎭		215·8	300	A_5^0	847·9	35⎫	Q_4^0
396·9	55	K_3^0	573·7	170	S_2^0	869·8	25⎭	
544·2	110	O_3^0	716·6	35	U_5^0	45050·4	18	A_7^0
621·1	55	T_1^0	765·6	25	Q_3^1	402·9	13	S_4^0
658·2	140	S_1^0	808·9	25	Z_2^0	766·1	12⎫	Q_5^0
800·9	130	U_4^0				786·5	9⎭	

Note : In the assignment columns the upper-state quantum number, denoted by p' in Table II, is given as a simple subscript, and the lower-state quantum number, p'', as a subscript with a negative sign; these mark progressions in A_{1g}(C). The quantum number s of Table II, which is common to both states, is given in the assignment columns as a superscript; it marks sequences in E_u^+ (C).

As is apparent from Table I a close group of intensity maxima is often regarded as a single band. Which maxima should be so grouped is a matter for judgment, the main guide being the appearance of the spectrum. Presumably owing to the rotational structure, many bands are double headed; and some bands contain one or more additional maxima. Apart altogether from rotation, certain vibrational effects are expected to lead to complexity of band structure. One possible cause of this kind is the near-superposition of bands which involve 0—0 and 1—1 transitions with respect to some vibration whose frequency is nearly the same in the upper and lower electronic states : benzene has at least one such frequency. Another cause is the splitting, due to the anharmonicity of the vibrations, of those higher-order degeneracies which would otherwise characterise overtones and combinations of degenerate fundamental vibrations. Thus the second quantum level of an E_u^+ vibration consists of three close-lying levels, the symmetries of the components being $(E_u^+)^2 = A_{1g}, A_{2g}, E_g^+$ (cf. Table XII, *J.*, 1946, 234). We explain in this way the fact, which may not be particularly conspicuous in tables, but is very obvious in original plates or in microphotometer records made from them, that, as we pass, *e.g.*, along any sequence, 0—0, 1—1, 2—2 . . . , with respect to the vibration E_u^+(C), the complexity of the bands increases notably.

TABLE II.

Absorption Spectrum of Benzene. Key to Series Assignments in Table I.

	Freq. (cm.$^{-1}$).	p'.	p''.	s.
A =	$38090 + 521 + 923p' - 992p'' - 161s$	0—7	0—2	0—3
B =	,, $- 608 + 923p' - 992p'' - 161s$	0—4	0, 1	0—3
C =	,, $+ 2 \times 521 - 608 + 923p' - 161s$	0—4		0—3
D =	,, $+ 521 - 2 \times 608 + 923p' - 161s$	0—2		0, 1
E =	,, $+ 1470 + 923p' - 161s$	0—3		0, 1
F =	,, $- 1600 - 161s$			0, 1
G =	,, $+ 521 + 2 \times 243 + 923p' - 161s$	0—2		0—2
H =	,, $- 608 + 2 \times 243 + 923p'$	0, 1		
I =	,, $+ 2 \times 243 + 923p'$	0, 1		
J =	,, $+ 923p' - 161s$	0, 1		1, 2
K =	,, $+ 521 + 2 \times 513 + 923p'$	0—3		
L =	,, $- 608 + 2 \times 365$			
M =	,, $+ 521 - 265 + 923p'$	0—4		
N =	,, $- 608 - 265 + 923p'$	0, 1		
O =	,, $+ 521 + 2 \times 585 + 923p' - 161s$	0—3		0, 1
P =	,, $- 608 + 2 \times 585 + 923p'$			
Q =	,, $+ 3080 + 923p' - 161s$	0—5		0—2
R =	,, $+ 3080 - 265 + 923p'$	0, 1		
S =	,, $+ 521 + 3130 + 923p'$	0—4		
T =	,, $\left\{ \begin{array}{l} + 521 + 3080 + 923p' \\ + 2 \times 243 + 3130 + 923p' \end{array} \right\}$	0, 1		
U =	,, $+ 2 \times 521 + 923p' - 161s$	0—5		0, 1
W =	,, $+ 521 + 2 \times 775 + 923p'$	0, 1		
X =	,, $+ 521 + 2 \times 706$			
Y =	,, $\left\{ \begin{array}{l} + 365 + 585 + 923p' \\ + 243 + 706 + 923p' \end{array} \right\}$	0—2		
Z =	,, $+ 3885 + 923p'$	0—2		

Note : The frequency 38090 cm.$^{-1}$ is that of the electronic origin. The other frequencies are vibration frequencies : they are assigned to vibrations in Table III. Concerning the frequency 3885 cm.$^{-1}$, see text (Section 8).

TABLE III.

Absorption 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	$A_{1g}(C)$
3130	—	—	$A_{1g}(H)$
513	—	—	$A_{2u}(H)$
365	—	—	$B_{2g}(C)$
775	—	—	$B_{2g}(H)$
521	608	87	$E_g^+(C\ 1)$
1470	1600	—	$E_g^+(C\ 2)$
3080	—	—	$E_g^+(H\ 1)$
243	—	161	$E_u^+(C)$
706	—	—	$E_u^+(H)$
585	—	265	$E_g^-(H)$

(2) *Band Series* A, B, C *and* D.—As explained in Part I, Section 4, these bands determine he general pattern of the spectrum.   Three vibrations are involved, *viz.*, $E_g^+(C\ 1)$, unit quantum changes in which create the four spectrally active origins, $A_{1g}(C)$, multiple quantum changes in which give the progressions, and $E_u^+(C)$, which by null quantum changes produces the sequences.

The active origins determine the forbidden electronic origin,

$$\mathrm{J}_0^0 = 38090 \pm 2 \text{ cm.}^{-1}$$

whilst the bands collectively give the following fundamental frequencies,

$$E_g^+(C\ 1)_{\text{ground}} = 608 \text{ cm.}^{-1} \qquad E_g^+(C\ 1)_{\text{excited}} = 521 \text{ cm.}^{-1}$$
$$A_{1g}(C)_{\text{ground}} = 992 \text{ cm.}^{-1} \qquad A_{1g}(C)_{\text{excited}} = 923 \text{ cm.}^{-1}$$

as well as the frequency difference,

$$E_u^+(C)_{\text{ground}} - E_u^+(C)_{\text{excited}} = 161 \text{ cm.}^{-1}$$

The long progressions of series A, B and C show the effect of anharmonicity in the ring-breathing vibration of the upper electronic state.   The frequency drops from an average initial value of 923·5 cm.$^{-1}$ for the first full quantum to 917 cm.$^{-1}$ for the seventh.   Apart from a casual scatter of ± 1 cm.$^{-1}$ the fall is linear.   It seems to make only a very small difference whether, in the upper electronic state, the stack of $A_{1g}(C)$ levels rises from the zero-point level (as for series B), or is superposed on one quantum of the $E_g^+(C\ 1)$ vibration (series A), or on two such quanta (series C).   The linear frequency fall indicates an energy formula of the usual anharmonic type,

$$E/h = \nu(p' + 1/2) - x\nu(p' + 1/2)^2,$$

with $\nu = 924$ cm.$^{-1}$ and $x\nu = 0\cdot5$ cm.$^{-1}$.

(3) *Band Series* E *and* F.—A unit quantum change in any of the four E_g^+ vibrations, superposed on the $\mathbf{A_{1g}}$—$\mathbf{B_{2u}}$ electronic change, can in principle produce a non-vanishing transition moment; and the origin E_0^0 of the positive E progression in 923 cm.$^{-1}$, and of the related negative sequences in 161 cm.$^{-1}$, has been assumed by Sponer, Nordheim, Sklar, and Teller (*loc. cit.*) to arise in consequence of an upward 0—1 transition of the carbon-stretching vibration, $E_g^+(C\ 2)$.

In the electronic ground state, this vibration is well known from the Raman spectrum of liquid benzene : unperturbed, its frequency as given in this spectrum would be about 1596 cm.$^{-1}$; but it becomes mixed with the combination $E_g^+(C\ 1)606 + A_{1g}(C)\ 992 = 1598$ cm.$^{-1}$, and the frequencies resulting from the resonance are found at 1585 and 1606 cm.$^{-1}$.   The frequency of the vibration in the electronically excited state, as given by the position of the E_0^0 band in the absorption spectrum of benzene vapour, would be approximately 1470 cm.$^{-1}$.   Sponer has, however, drawn attention to the difficulty that the corresponding band of hexadeuterobenzene is somewhat displaced from the position in which we should expect it, if the plausible assumption be made that the ratio of the $E_g^+(C\ 2)$ frequencies in the upper and lower electronic states should be nearly the same in benzene and hexadeuterobenzene.   In consequence, she considered, but

did not actually recommend, alternative assignments for the E bands (*J. Chem. Physics*, 1940, **8**, 705). Having examined the absorption spectra of a number of deuterated benzenes, we confirm Sponer's observation as part of a general phenomenon : all the absorption spectra possess prominent " E " series of bands, but the positions of the E_0^0 origins are appreciably irregular.

Our study of the fluorescence spectra of various deuterated benzenes has disclosed another apparent anomaly. Corresponding to the E bands of the absorption spectrum, we should expect, in fluorescence, a prominent progression of bands having an origin, F_0^0, related to B_0^0, the main active origin for fluorescence, just as E_0^0 is related to A_0^0, the main active origin for absorption. The origin F_0^0 would lie below the electronic origin, J_0^0, by a frequency interval equal to the ground-state frequency of the E_g^+(C 2), or E_g^+(C 2)-like, fundamental vibration—a frequency which for benzene and all deuterated benzenes is known from Raman spectra. However, in our experience, an F progression is never prominent in fluorescence, save in such a case as that of benzene itself, in which there is a special reason for a strong appearance. This reason is that the B and F progressions become of necessity mixed together by the already-mentioned resonance arising in the ground state of benzene from the near-degeneracy of the E_g^+(C 2) fundamental frequency with the E_g^+(C 1) + A_{1g}(C) combination tone. This resonance allows the E_g^+(C 2) fundamental vibration to " borrow " spectral activity from the highly active combination E_g^+(C 1) + A_{1g}(C), just as, conversely, in the Raman effect, the intrinsically weak combination " borrows " activity from the strong fundamental—the transfer of intensity being in each case associated with displacements of frequency.

In spite of these two difficulties, we believe that the original assignment of Sponer, Nordheim, Sklar, and Teller is correct. We assume a resonance quite analogous to that just mentioned, but in the electronically excited state. In particular, we assume that the E bands, although allowed by symmetry under this assignment, would not in fact be strong enough for observation (at least under our conditions) in the absorption spectrum of any benzene, were they not able to " borrow " most of their intensity from the closely neighbouring A bands. The associated frequency shifts, mostly borne by the E bands because of their relative weakness, account, according to our picture, for the somewhat displaced positions in which we find certain of the E_0^0 origins. Typically, the assumed resonance is between the strongly active combination tone, E_g^+(C 1) + A_{1g}(C), and the weakly active fundamental frequency, E_g^+(C 2), both of the upper electronic state. In all the benzenes we have studied, these frequencies, as determined by the position of the A and E bands, that is, after any separation caused by resonance, lie 1—3% apart, the fundamental giving the E bands having always a higher frequency than the combination which produces the A bands. Now Herzfeld, Ingold, and Poole (*J.*, 1946, 327) surveyed all the known cases of resonance, due to accidental degeneracy between fundamentals and combination tones of identical symmetry, in the electronic ground states of benzenes : their data were in the Raman and infra-red spectra of ordinary benzene and several of its deuterated derivatives. They found marked intensification of the weaker of the interacting frequencies to be usual when, after any displacement resulting from resonance, the frequencies lay 2—4% apart. They also found that frequencies which, apart from their resonance, would have lain within 1% of each other, usually underwent a further separation of the order of 1%. Thus our postulated resonance effects of the electronically excited state seem plausible, and indeed, typical. We may assume that in benzene, for example, the relevant frequencies would, apart from their resonance, fall rather more closely together than in, say, hexadeuterobenzene, with the result that the frequency controlling the position of the E_0^0 origin will be raised by resonance somewhat more in the former case than in the latter.

The strength of the resonance effects arising from an accidental near-degeneracy of a fundamental frequency with a combination tone of the same symmetry class depends, not only on the frequency separation, but also on the force system. In the force system characterising the electronic ground state of benzene, marked resonance effects in general arise, as we have seen, when the nearly degenerate, unperturbed frequencies lie up to 4% apart. We also know, however, that, in the ground state of benzene, the particular resonance in which we are now interested, *viz.*, that between the E_g^+(C 2) fundamental and the E_g^+(C 1) + A_{1g}(C) combination, is not quite typical in this respect. In fact, this case of resonance is more restricted than many, since, for a given separation of the unperturbed frequencies, smaller effects are observed than appear in analogous cases. For evidence we again turn to Raman spectra. It is true that with benzenes in which the unperturbed frequencies E_g^+(C 2) and E_g^+(C 1) + A_{1g}(C) of the ground state are practically coincident, large resonance effects are found in the Raman spectrum. But with hexadeuterobenzene, and also with 1 : 3 : 5-trideuterobenzene, in each of which the relevant frequencies lie 2% apart, no marked resonance effects involving these frequencies are

observed. We restrict illustration to these cases, because, in other benzenes, each of the E_g^+-like fundamental frequencies itself splits into two, and this introduces a complication. Now, corresponding to our hypothesis concerning absorption, *viz.*, that the perturbation produced by an E_g^+(C 2) fundamental vibration of the upper electronic state would not generate E bands strong enough for our observation, unless they could " borrow " intensity from neighbouring A bands, we assume that, in fluorescence, an E_g^+(C 2) fundamental of the ground state would not give prominent F bands, unless they could analogously " borrow " intensity from neighbouring B bands. Whether they can thus borrow intensity depends on that amount of mixing of the wave functions, which, when symmetry permits, and the frequencies are close enough to present no great obstacle, is in fact engendered by the force system. But the amount of mixing is already indicated by the " borrowings " observed in Raman spectra : they arise from the same " mixings ", even though the intensity transferences are in the opposite direction. Thus we can partly understand, by reference to the Raman spectra, how in fluorescence an F series of bands is observed with benzene, but not with 1 : 3 : 5-trideuterobenzene or hexadeuterobenzene.

Two F bands are observed in the absorption spectrum of benzene, but they are naturally very weak. They involve upward 1—0 transitions, and, because of the high frequency of the E_g^+(C 2) vibration in the electronic ground state, they are greatly weakened by the small Boltzmann factor of the initial vibrational level.

The E bands have a double-band structure, the maximum at the lower frequency being the stronger. We accept this frequency as being the best available approximation to the vibrational origin. The resonance splitting involving the F bands is nearly symmetrical. Therefore we take the mean of the split maxima as giving the fundamental frequency of the unperturbed vibration. The result of this assumption is in qualitative accord with the intensities of the split bands.

The fuller study of the F series which is possible with the aid of the fluorescence spectrum is described in Part III, Section 2. Taking account of both the absorption and fluorescence spectra, we derive the following fundamental frequencies :

$$E_g^+(C\ 2)_{ground} = 1600\ cm.^{-1} \quad E_g^+(C\ 2)_{excited} = 1470\ cm.^{-1}$$

The value for the ground state, as given by the Raman spectrum of liquid benzene, is 1596 cm.$^{-1}$.

(4) *Band Series* G, H, I, *and* J.—The three positive progressions in 923 cm.$^{-1}$, labelled G, H, and I, start at a common distance of approximately 480 cm.$^{-1}$ above the active origins A_0^0 and B_0^0, and the forbidden electronic origin J_0^0, respectively. The common separation can be shown to represent the first overtone of the out-of-plane vibration E_u^+(C) of the excited state (see below). As noted in Section 1, the two-quantum level of this degenerate vibration is triple, with the associated symmetries A_{1g}, A_{2g} and E_g^+. The symmetry principles outlined in Part I, Section 5, show that transitions from the " vibrationless " level of the electronic ground state can end only on an E_g^+ level. Therefore only the E_g^+ form of the overtone can be involved in the transition giving the first band I_0^0 of the progression which starts about 480 cm.$^{-1}$ above the electronic origin J_0^0. The same symmetry principles (*loc. cit.*) show that transitions which start from the first E_g^+(C 1) vibrational level of the ground electronic state may terminate on any of the three overtone levels, but are expected to end predominantly on the A_{1g} level. Therefore this level chiefly, and the others to a smaller extent, may be involved in the transition giving the first band H_0^0 of the progression which starts about 480 cm.$^{-1}$ above B_0^0. Transitions from the vibrationless ground state can also end on any of the complex group of higher levels which are obtained by combining each of the three forms of the E_u^+(C) overtone of the upper electronic state with the E_g^+(C 1) fundamental frequency of the upper state. Such transitions can combine to produce the initial band G_0^0 of the progression which starts about 480 cm.$^{-1}$ above A_0^0.

Actually, the first band of the I progression appears to be simple in structure : its separation from J_0^0 is 473 cm.$^{-1}$. This we take to be the frequency of the E_g^+ form of the E_u^+(C) overtone. The first band of the H progression is triple : the separations of the components from B_0^0 are 486, 481 and 474 cm.$^{-1}$. Since the first of these components is the strongest, one is tempted to associate it with the A_{1g} form of the overtone ; the second and third components might then be related to the A_{2g} and E_g^+ forms, respectively. The first band of the G progression has two main components, as well as several minor components grouped about them ; and the separations of the major components from A_0^0 are 475 and 470 cm.$^{-1}$. This is a complicated case, and all that can be suggested is that the generally smaller separations may be connected with the greater effects of anharmonicity in the higher vibrational combinations of the excited state which are concerned in these transitions. Associated with the stronger bands of the G progression one finds sequences in the interval 161 cm.$^{-1}$. These evidently represent 0—2, 1—3, 2—4 . . .

transitions of the $E_u^+(C)$ vibrations—transitions which are allowed by the selection rules to appear with low intensity (cf. Part I, Section 5).

In addition to the many negative sequences in 161 cm.$^{-1}$, already mentioned or to be later discussed, there is one special one, which starts as if from the electronic origin, except that the band in this position is missing. The first actual band, 161 cm.$^{-1}$ lower, is also the starting point of a positive progression in 923 cm.$^{-1}$. Collectively these bands form series J. Sponer, Nordheim, Sklar, and Teller have already explained them. The explanation is closely analogous to that given above to the I bands, which start with a first overtone of the E_u^+ vibration superposed on the electronic origin, and appear because one of the states containing two quanta of the vibration $E_u^+(C)$ has the symmetry E_g^+. The presence of one quantum of an $E_u^+(C)$ vibration in both the lower and upper electronic states will fulfil the same symmetry conditions as if both quanta were present in the upper state, or both in the lower state (cf. Part I, Section 5).

We take the largest value, 486 cm.$^{-1}$, of the upper-state overtone frequency as likely to be the least disturbed by anharmonicity. This figure, and the well-established sequence interval 161 cm.$^{-1}$, representing the difference between the fundamental frequencies in the lower and upper electronic states, leads to the following fundamental frequencies

$$E_u^+(C)_{\text{ground}} = 404 \text{ cm.}^{-1} \quad E_u^+(C)_{\text{excited}} = 243 \text{ cm.}^{-1}$$

An argument leading to the adopted assignment can be based on the existence of series I and J : their direct association with the forbidden electronic origin shows the vibration to be degenerate (cf. Part I, Section 5). Therefore it has to belong to the symmetry class E_u^+, since all other degenerate vibrations are allowed either in the infra-red or the Raman spectrum, and are therefore very well known. There is a carbon and a hydrogen vibration of the E_u^+ class, and the low values of the frequencies show that they can only belong to the carbon vibration $E_u^+(C)$. Confirmation follows from the actual value of the ground-state frequency. The vibration, though forbidden in the Raman effect, actually appears very weakly in the Raman spectrum of liquid benzene owing to the perturbing effect of liquid forces; and partly on this evidence, and partly from a study of Raman and infra-red combination tones, Herzfeld, Ingold, and Poole gave the ground-state frequency of the vibration as 405 cm.$^{-1}$ (*loc. cit.*), in close agreement with the value now determined. Further confirmation comes from the fluorescence spectrum (Part III, Section 3). All the evidence confirms the conclusions of Kistiakowsky and Solomon, already summarised in Part I, Section 4.

(5) *Band Series* K *and* L.—We deal here with some bands believed to depend on two other vibrations having a connexion with the sequence interval 161 cm.$^{-1}$. A band K_0^0 of moderate strength, the starting point of a progression K, lies at 1026 cm.$^{-1}$ above A_0^0. The intensity of the band suggests that the excitation of some quite simply constituted harmonic of the upper electronic state is superposed on the electronic and vibrational transition characteristic of the main active origin A_0^0. It would be natural to try to confirm this assumption by looking for a considerably weaker band 1026 cm.$^{-1}$ above B_0^0 : such a band would, however, be obscured by the strong band C_0^0. We may also look for a band, again much weaker than K_0^0, 1026 cm.$^{-1}$ above C_0^0 : here we find a band of about the right intensity (at 39522·2 cm.$^{-1}$; intensity 55) : it is omitted from Table I only because, lying amongst rather strong bands, it was not originally selected as prominent enough to demand a simple explanation. A corresponding band 1026 cm.$^{-1}$ above D_0^0 would be too weak for observation.

We assign the frequency 1026 cm.$^{-1}$, which by the selection rules must correspond to total symmetry (cf. Part I, Section 5), as the first-overtone frequency in the upper electronic state of the out-of-plane, hexagonal, hydrogen vibration, $A_{2u}(H)$. The reasons for the assignment will be given in Part XI : they depend largely on comparisons among different isotopically modified benzenes. The difference between the fundamental frequencies of the $A_{2u}(H)$ vibration in the upper and lower electronic states is practically the same as the corresponding difference, 161 cm.$^{-1}$, for the $E_u^+(C)$ vibration. It is therefore probable that the 1—1 transitions of the $A_{2u}(H)$ vibration contribute part of the intensity of the 1—1 bands of all those sequences in 161 cm.$^{-1}$ which start from bands of the A and B progressions : the $A_{2u}(H)$ transitions should not contribute to series J, which depends fundamentally on the degenerate nature of the $E_u^+(C)$ vibration (cf. Part I, Section 5). In the absorption spectrum of hexadeuterobenzene (Part IV), for which molecule the $E_u^+(C)$ and $A_{2u}^+(H)$ sequence intervals no longer coincide, we see the 1—1 bands of the $A_{2u}(H)$ vibration separately in the sequences belonging to the A and B progressions.

A well-marked band L_0^0 of rather low intensity lies 120 cm.$^{-1}$ above the electronic origin. It is difficult to explain on the basis of a loss of lower-state quanta in transitions terminating as do those of A_0^0 or C_0^0. We therefore interpret it as representing a gain of upper-state quanta

superposed on the electronic and vibrational transitions of B_0^0 : a similar relationship with D_0^0 is improbable on grounds of intensity. On this basis the upper-state vibration frequency is 730 cm.$^{-1}$, and must correspond to a harmonic of total symmetry (Part I, Section 5). We assign it in what seems to be the only possible way, *viz.*, as the first overtone of the smallest fundamental frequency but one, that of the trigonal, out-of-plane, vibration, $B_{2g}(C)$. The same fundamental frequency appears (Section 8) in the interpretations of another progression (Y). The assignment of the frequency to the $B_{2g}(C)$ vibration is supported by comparisons with other spectra, and by calculations based on a simplified potential system (Part XI).

The $B_{2g}(C)$ vibration is one that could produce *n—n* sequences, of which at least the 1—1 bands might possess an appreciable intensity. However, the 1—1 bands would be over-lapped by the 2—2 bands of the strong $E_u^+(C)$ sequences, and, as has been explained (Section 1), these bands are broad and multiple. Although we are not able to identify the 1—1 bands of the $B_{2g}(C)$ vibration in the complex contours of the 2—2 bands of $E_u^+(C)$ sequences, the $B_{2g}(C)$ vibration may contribute appreciably to the total intensity of such bands. For in the absorption spectrum of hexadeuterobenzene (Part IV), each 2—2 band of the $E_u^+(C)$ sequences contains a maximum well removed from the head, and so distinctive in appearance that we assign it as the 1—1 band of the $B_{2g}(C)$ vibration.

Two fundamental frequencies of the upper electronic state of benzene follow from our assignment of the bands discussed :

$$A_{2u}(H)_{\text{excited}} = 513 \text{ cm.}^{-1} \quad B_{2g}(C)_{\text{excited}} = 364 \text{ cm.}^{-1}$$

(6) *Band Series* M, N, O, *and* P.—Sponer has already drawn attention (*loc. cit.*) to bands in the absorption spectrum of benzene which lie 265 cm.$^{-1}$ below the active origins A_0^0 and B_0^0, and below the electronic origin J_0^0. A weak band in the last-named position certainly exists (37822·8 cm.$^{-1}$; intensity 9), though we did not think it prominent enough to include in Table I. However, the bands M_0^0 and N_0^0, 265 cm.$^{-1}$ below A_0^0 and B_0^0 respectively, are prominent, and both start positive progressions in 923 cm.$^{-1}$. Band M_0^0 is the stronger, the intensity ratio of M_0^0 to N_0^0 being roughly the same as that of A_0^0 to B_0^0. The same two bands M_0^0 and N_0^0 are prominent in the fluorescence spectrum of benzene (Part III, Section 4), although here N_0^0 is the stronger, just as B_0^0 is stronger than A_0^0; and the progressions which they start are now negative in 992 cm.$^{-1}$. In fluorescence we again find a band 265 cm.$^{-1}$ below the electronic origin J_0^0.

These relationships prove that (as Sponer has already suggested) the bands arise from 1—1 transitions in some vibration superposed on the transitions characteristic of A_0^0, B_0^0, or J_0^0, the interval 265 cm.$^{-1}$ being the difference between the frequencies of the vibration in the lower and upper electronic states. The presence of bands associated with J_0^0 shows that the vibration is degenerate (Part I, Section 5). Partly on the internal evidence of these spectra, and partly by comparisons with the spectra of other benzenes, we identify the vibration as the out-of-plane, hydrogen vibration $E_g^-(H)$ (cf. Part XI). It is not excluded that a minor proportion of the intensities of the M and N bands derives from another out-of-plane, hydrogen vibration, $E_u^+(H)$, which happens to have almost the same sequence interval.

The bands O_0^0 and P_0^0 in the absorption spectrum of benzene lie 1170 cm.$^{-1}$ above A_0^0 and B_0^0 respectively. Their intensities are roughly in proportion to those of A_0^0 and B_0^0. They start positive progressions in 923 cm.$^{-1}$, though all but the first member of the weaker P progression fall among stronger bands and were therefore not included in Tables I and II. Some members of the stronger O progression can be seen to be the starting points of sequences in 161 cm.$^{-1}$. The bands of both series are double, but those of the O series are broader and exhibit subsidiary maxima.

These bands clearly involve the excitation in the upper electronic state of some higher harmonic of total symmetry (Part I, Section 5), in combination with the electronic and vibrational transitions characteristic of A_0^0 or B_0^0. For reasons given in Part XI, we identify the higher harmonic frequency, 1170 cm.$^{-1}$, as the first overtone of the vibration $E_g^-(H)$. The greater complexity of the O bands than of the P bands is consistent with an assignment to a degenerate vibration; for the upper states of the O transitions will then contain three degenerate quanta, and will split up into a more complex set of levels than will the upper state of the P transitions, which will contain only two.

From the upper-state overtone frequency, 1170 cm.$^{-1}$, and the sequence interval,* 265 cm.$^{-1}$,

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* We consider the main part of the intensity of series M and N to be due to 1—1 transitions of the vibration $E_g^-(H)$ rather than of the vibration $E_u^+(H)$, partly because the Boltzmann factor of the former vibration is larger, and partly because in all these spectra one notices a general correlation of transition probabilities between overtone series and sequences, and the overtone series, O and P, of the vibration $E^-(H)$ are much stronger than is the overtone series X of the vibration $E_u^+(H)$.

supplemented by the observation of a lower-state overtone frequency, 1695 cm.$^{-1}$, in the fluorescence spectrum of benzene (Part III, Section 4), we deduce the following fundamental frequencies of the vibration concerned :

$$E_g^-(\text{H})_{\text{ground}} = 849 \text{ cm.}^{-1} \qquad E_g^-(\text{H})_{\text{excited}} = 585 \text{ cm.}^{-1}$$

The ground-state frequency, as observed in the Raman spectrum of liquid benzene, is 848·9 cm.$^{-1}$.

(7) *Band Series* Q, R, S, *and* T.—We turn to some band series dependent on high vibrational frequencies, due, as we think, to hydrogen-stretching vibrations of the electronically excited molecule. Sponer, Nordheim, Sklar, and Teller sought to determine the values of these hydrogen-stretching frequencies (*loc. cit.*). They directed attention to two bands, one about 2560 cm.$^{-1}$ above B_0^0, and the other about the same distance above A_0^0, each the starting point of a positive progression in 923 cm.$^{-1}$. They suggested that the interval 2560 cm.$^{-1}$ might correspond to the totally symmetrical hydrogen-stretching frequency, $A_{1g}(\text{H})$, in the upper electronic state. The frequency of this vibration in the electronic ground state of benzene, as observed in the Raman spectrum of liquid benzene, is 3062 cm.$^{-1}$.

We propose certain modifications of these assignments for the following reasons. The band 2560 cm.$^{-1}$ above B_0^0 appears to be too strong to be related in the suggested way to the band at about the same distance from A_0^0; and besides, an alternative reading of the spectrum is possible which would make the band 2560 cm.$^{-1}$ above B_0^0 the second, not the first, member of the progression in 923 cm.$^{-1}$ to which it belongs. If we should change the assignment of this band, but try to retain that of the band 2560 cm.$^{-1}$ above A_0^0, then we should have to expect a similar band 1925 cm.$^{-1}$ above the A_0^0 band of the absorption spectrum of hexadeuterobenzene, this position being fixed rather exactly by an application of the product theorem of Teller and Redlich to the A_{1g} vibrations of the upper electronic states of these two benzenes. But Sponer, who examined the absorption spectrum of hexadeuterobenzene, did not find a band near this position. The nearest bands she could observe lay 1821, 1841, and 1873 cm.$^{-1}$ above A_0^0; and of these, the last two were very weak, only the first having an intensity comparable to that of the benzene band. Actually all three bands, on the score of their frequencies, are unacceptable for correlation on the suggested basis with the benzene band. And if we should suppose that, because of some experimental limitation, the expected band, 1925 cm.$^{-1}$ above A_0^0 in the spectrum of hexadeuterobenzene, evaded observation, then there is still a difficulty. For it can be shown that, if the frequency of the $A_{1g}(\text{H})$ vibration of benzene, and therefore the frequencies of each of the six hydrogen-stretching vibrational degrees of freedom of that molecule, should drop, as is suggested, by about 500 cm.$^{-1}$ when the electronic system passes from the ground state into the excited state, then the electronic origin J_0^0, the exact position of which depends on the difference between the vibrational zero-point energies of the ground and excited states, should suffer a much greater shift than is observed when benzene is deuterated to give hexadeuterobenzene. The zero-point energy differences of the hydrogen-stretching frequencies alone would contribute an upward shift of 390 cm.$^{-1}$, whereas the observed upward shift, containing the total effect of all the 30 vibrational degrees of freedom, is only 200 cm.$^{-1}$. Certainly negative (*i.e.*, downward) contributions to the shift are possible, but it is hardly to be believed that the remaining 24 degrees of freedom, many of whose frequencies we know, can collectively contribute a negative shift as large as 190 cm.$^{-1}$.

The strongest of all the high-frequency bands in the absorption spectrum of benzene is the one lying 2560 cm.$^{-1}$ above A_0^0: we call it Q_0^0. It is the parent of a long progression in 923 cm.$^{-1}$ the bands of which start sequences in 161 cm.$^{-1}$. We assume these bands to involve the excitation of a hydrogen-stretching vibration of the upper electronic state, but we take this vibration to be, not $A_{1g}(\text{H})$, but $E_g^+(\text{H } 1)$. Thus, Q_0^0 is ascribed to a transition from the " vibrationless " ground state to the first quantum level of this vibration in the excited state. The band Q_0^0 is regarded as an active origin, comparable to A_0^0 or E_0^0. The vibration responsible for its appearance, $E_g^+(\text{H } 1)$, would be expected to produce an appreciable spectral activity, because it deforms the carbon ring, and therefore the potential field of the unsaturation electrons, qualitatively in the same way as, though quantitatively to a smaller extent than, the $E_g^+(\text{C } 1)$ vibration, which produces the very strong origin A_0^0 (cf. Fig. 1, *J.*, 1946, 231).

The frequency of the $E_g^+(\text{H } 1)$ vibration in the excited state, as given by the separation of Q_0^0 from the electronic origin J_0^0, is 3080 cm.$^{-1}$. The frequency of the same vibration in the ground state, as given in the Raman spectrum, is 3047 cm.$^{-1}$. Thus our assignment leads to the assumption of a small increase in this hydrogen-stretching frequency—and presumably in all hydrogen-stretching frequencies—when the molecule passes from the ground to the excited state. We confirm this below in relation to the totally symmetrical hydrogen-stretching

frequency. The position predicted on the new basis for the band corresponding to Q_0^0 in the absorption spectrum of hexadeuterobenzene agrees well with that of the band which Sponer found 1821 cm.$^{-1}$ above A_0^0, that is, 2320 cm.$^{-1}$ above J_0^0, and would have liked to correlate with the benzene band.

It is convenient to deal next with the two bands of progression R. They are weak bands lying 265 cm.$^{-1}$ below the first two bands of progression Q. Since in our interpretation Q_0^0 is an active origin, analogous to A_0^0, it would be natural to find associated with it the stronger of those sequences, due to *n—n* transitions, which appear in connexion with A_0^0. The strongest of such sequences, the E_u^+(C) sequence in 161 cm.$^{-1}$, certainly appears, as we have seen. The other two, of which only the 1—1 bands can be observed in connexion with the A series, are the E_g^+(C 1) sequence in 87 cm.$^{-1}$, and the E_g^-(H) sequence in 265 cm.$^{-1}$. The presence, in association with bands of the Q series, of 1—1 bands of sequences in 87 cm.$^{-1}$ cannot be verified because of overlapping. However, along with the two strongest Q bands, 1—1 bands in the other sequence, that in 265 cm.$^{-1}$, clearly appear with about the expected intensity.

We refer next to the progression labelled S, the first member of which, S_0^0, lies 3130 cm.$^{-1}$ above A_0^0. In explanation we assume that an excitation of one quantum of the totally symmetrical hydrogen-stretching vibration, A_{1g}(H), is superposed on the electronic and vibrational changes that produce the active origin A_0^0. The upper-state fundamental frequency which results from this assignment, 3130 cm.$^{-1}$, is a little greater than the known lower-state frequency of the vibration A_{1g}(H), *viz.*, 3062 cm.$^{-1}$. We should expect to find a band 3130 cm.$^{-1}$ above B_0^0. Such a band is present (40616·8 cm.$^{-1}$; intensity 25); but, lying as it does among stronger bands, it was not included in our original list, reproduced in Table I. Since the vibration is totally symmetrical, a band 2 × 3130 cm.$^{-1}$ above A_0^0 might well be visible. Such a band does appear (44869·8 cm.$^{-1}$, intensity 25), but it has an alternative possible explanation.

Progression T consists of two weak bands, the first of which T_0^0, lies 3610 cm.$^{-1}$ above the electronic origin. Two explanations suggest themselves :

$$E_g^+(\text{C 1})521 + E_g^+(\text{H})3080 = 3601 \text{ cm.}^{-1}; \quad 2 \times E_u^+(\text{C})243 + A_{1g}(\text{H})3130 = 3616 \text{ cm.}^{-1}$$

Either would allow the T bands to gain intensity by resonance with the nearby S bands (Part I, Section 5), and it is possible that the T bands owe their appearance to this effect.

Our study of the series discussed in this Section leads to the following fundamental frequencies of the excited state of benzene :

$$A_{1g}(\text{H})_{\text{excited}} = 3130 \text{ cm.}^{-1} \quad E_g(\text{H 1})_{\text{excited}} = 3080 \text{ cm.}^{-1}$$

(8) *Band Series* U, W, X, Y, *and* Z.—Several series remain to be discussed which involve the excitation of higher harmonics in the upper electronic state. The series U, which consists of a progression in 923 cm.$^{-1}$, and two short sequences in 161 cm.$^{-1}$, commences with a band, U_0^0, situated 1044 cm.$^{-1}$ above the electronic origin. Our adopted value for the fundamental frequency of the vibration E_g^+(C 1) in the upper electronic state being 521 cm.$^{-1}$, the band U_0^0 can be attributed to a transition between the " vibrationless " level of the electronic ground state and the first overtone level of the E_g^+(C 1) vibration in the electronically excited state.* Such a transition is allowed because of the degenerate character of the vibration (cf. Part I, Section 5).

The weak progression W commences with a band, W_0^0, lying 2070 cm.$^{-1}$ above the electronic origin. From the absence of bands which would otherwise be expected, we infer that the vibrational excitation peculiar to W_0^0 is superposed either on the pure electronic transition, or on the electronic and vibrational transition of the active origin A_0^0. Provisionally adopting the latter view, we find an upper-state frequency 1550 cm.$^{-1}$. It must correspond to total symmetry (Part I, Section 5). Normal co-ordinate calculations having led us to expect (Part XI) that the fundamental frequency of the vibration B_{2g}(H) in the upper electronic state is close to 775 cm.$^{-1}$, we suggest that the upper-state frequency, 1550 cm.$^{-1}$, which appears to characterise series W, may be the first overtone of this vibration. The conclusion is not definite, because, if the vibrational excitation peculiar to W_0^0 were combined only with the electronic transition, then the upper state frequency would be 2070 cm.$^{-1}$, and it would have the symmetry E_g^+ ; and one could not in that case exclude interpretations involving frequencies of the excited state which are not yet accurately known.

* We have no compelling reason for excluding our former interpretation of the frequency 1044 cm.$^{-1}$ as the fundamental frequency of the planar hydrogen-bending vibration E_g^+(H 2) (cf. *Nature*, 1946, **158**, 163) ; but we now think that the available evidence in favour of this interpretation is not strong enough to justify its adoption in preference to the explanation given in the text.

The single band X_0^0 lies 1934 cm.$^{-1}$ above the electronic origin. As in the last case, we can infer that a special vibrational excitation of the upper electronic state is involved, which accompanies either the pure electronic transition, or the electronic and vibrational transition characteristic of A_0^0. We provisionally adopt the latter view, having shown by calculation (Part XI) that the fundamental frequency of the vibration $E_u^+(H)$ in the upper electronic state is in the neighbourhood of 706 cm.$^{-1}$; for the upper-state frequency, 1411 cm.$^{-1}$, which then follows from the position of X_0^0, can be simply interpreted (cf. Part I, Section 5) as the first overtone of this vibration. As before, it is not certain that this explanation is unique; for if the vibrational excitation should be directly superposed on the pure electronic transition, the upper-state vibration frequency would be 1934 cm.$^{-1}$; and our present uncertainty with regard to the exact values of certain of the fundamental frequencies of excited benzene would then leave open several possibilities.

The parent band, Y_0^0, of progression Y lies 950 cm.$^{-1}$ above the electronic origin. This position excludes the assumption that the special vibrational excitation which characterises the series is superposed either on the electronic and vibrational transition characteristic of A_0^0, or on that of C_0^0. The strength of the progression makes very improbable any analogous relationship with either B_0^0 or D_0^0. We therefore assume a simple relationship with the electronic origin J_0^0: the transition producing Y_0^0 would start from the " vibrationless " level of the ground state and end on a combination level 950 cm.$^{-1}$ above the " vibrationless " level of the excited state. There are two ways in which, consistently with the selection rules (cf. Part I, Section 5), this frequency could arise. They are as follows :

$$B_{2g}(C)365 + E_g^-(H)585 = 950 \text{ cm.}^{-1}; \quad E_u^+(C)243 + E_u^+(H)706 = 949 \text{ cm.}^{-1}$$

We incline to the former of these interpretations, largely because of the existence, in the fluorescence spectrum of benzene, of a prominent progression having an analogous explanation in terms of lower-state frequencies (cf. Part III, Section 6).

Finally, mention must be made of a somewhat weak progression labelled Z, which starts with a band, Z_0^0, situated 3885 cm.$^{-1}$ above the electronic origin. The frequencies of the three bands of the Z series are such that they might well belong to the A series. But their intensities, especially that of Z_0^0, seem to suggest separate assignment, although it must be recognised that in the spectral region in which this band appears, it is possible for an illusory band-intensity to be built up by the superposition of a band on an accidental concentration of the overlapped very weak bands which constitute the general background. If a separate assignment is indeed required, then it probably involves a higher harmonic frequency of 3885 cm.$^{-1}$ in the upper electronic state. Possibilities exist for such a harmonic, involving one of the fundamental frequencies which are not yet accurately known; but we make no definite suggestion, in view of the uncertainty as to whether the Z bands should have a separate assignment.

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