100. *Excited States of Benzene. Part VI. Description and Analysis of the First Ultraviolet Band System of the Absorption Spectrum of 1 : 3 : 5-Trideuterobenzene.*

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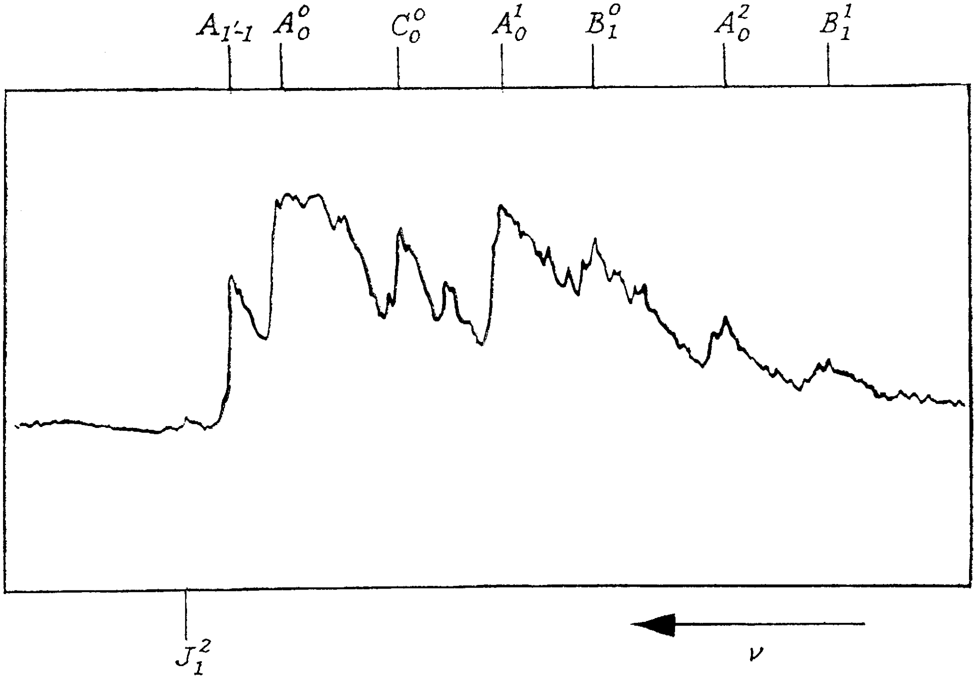
The ultraviolet absorption spectrum of 1 : 3 : 5-trideuterobenzene is described, and measurements of the frequencies of many bands are recorded. A complete vibrational analysis of the spectrum is given. The partial loss of symmetry arising from the isotopic loading of this molecule modifies, and thus confers spectral activity on, vibrations which did not involve themselves with the electronic transitions of benzene and hexadeuterobenzene. Fourteen fundamental frequencies of the upper electronic state, and six of the lower state, are recognised, and all are assigned to their vibrations. Part of the theoretical basis of these assignments is reserved for treatment in Part XI.

(1) *Measurements.*—The 1 : 3 : 5-trideuterobenzene was prepared by deuteration of aniline and subsequent deamination (Best and Wilson, *J.*, 1946, 239). Its purity was established by isotopic analysis, and by the already reported work on its infra-red and Raman spectra (Bailey, Poole, and others, *J.*, 1946, 255). It was transferred to the absorption assembly by sublimation at a low pressure from the cooled solid. The assembly, pumped to 10^{-3} mm. with the trideuterobenzene at liquid-air temperature, consisted of a quartz tube, 50 cm. long and 2·5 cm. diameter, with sealed-in end-windows, and a side-tube giving connexion, through a quartz-to-Pyrex graded seal, with a Pyrex bulb containing the liquid or solid sample. In operation, the controlled temperature of this bulb determined the pressure in the absorption tube. The temperatures employed varied from − 50° to + 20°, the corresponding pressures ranging from less than 1 mm. to about 74 mm.

FIG. 1.



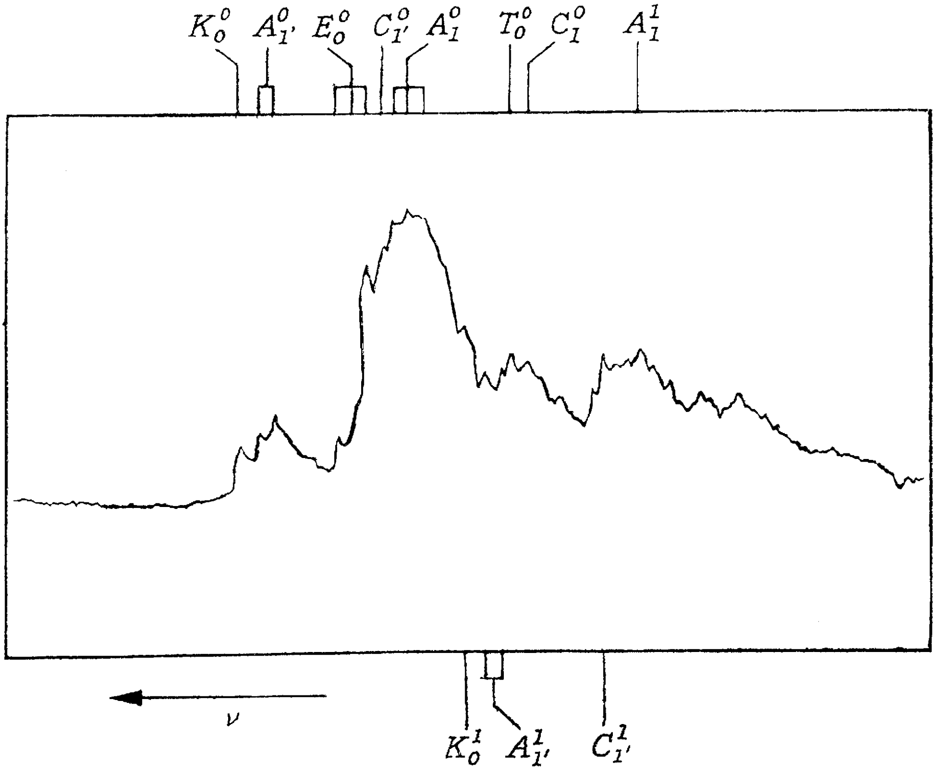
Microphotometer record of part of the first strong period in the absorption system of 1 : 3 : 5-*trideuterobenzene. The spectrum is shown from about* 38800 *cm.*$^{-1}$ *to about* 38300 *cm.*$^{-1}$. *In this record the conditions were chosen for exhibiting medium bands, such as* $A_{1'-1}$. *For this reason the upper part of the band* A_0^0 *has become truncated : this band is really much stronger, relatively to the other bands, than would appear from this photograph.*

(*The original microphotometer record had to be rephotographed and intensified several times in order to obtain a tracing thick enough for the preparation of a block. The fine line on the original record resolves the closely overlaid bands considerably more completely than does the reproduction.*)

The light-source was a water-cooled, hydrogen-discharge tube. The spectrograph, Hilger's quartz, Littrow-pattern instrument of 170 cm. focal length, was kept in a thermostatted room at 20·0°. Its dispersion, in the region 2700—2200 A., in which it was focused for these experiments, was about 3 A./mm., or about 48 cm.$^{-1}$/mm. at 2500 A. The slit-width was adjusted to 0·02 mm. The spectra were recorded on 25 cm. × 10 cm., Kodak, L15 plates, which were developed for 3·0 mins. at 18°, fixed in a hardening-fixing bath, washed, and dried in dust-free air. The iron-arc was used to provide a comparison spectrum, which was recorded just above and just below the absorption spectrum, without disturbing the plate, with the aid of a suitably perforated Hartmann diaphragm.

Direct measurement of the bands by means of the travelling microscope was, on the whole, not satisfactory, though in favourable cases a setting could be reproduced to 0·01 mm. The usual difficulty, however, was to set the microscope accurately to the intensity maxima of any but sharp and well-isolated bands, the eye being but a poor judge of intensity variation in complex band-groups. For this reason we have preferred to evaluate the spectra in the form of microphotometer records, taken with the aid of a Zeiss recording microphotometer. Each spectrogram was thus reproduced, at a dispersion of about 6 cm.$^{-1}$/mm., in a series of records of total length 120—150 cm. For the evaluation of records, the methods described by Poole (*J.*, 1946, 248) were assisted, in the present experiments, by over-printing, on each microphotometer record of the absorption spectrum, a record of the associated iron-arc spectrum, this being done without disturbance either to the plate or to the record-holder by adjusting, between exposures, the diaphragm which limits the effective length of the microphotometer slit. The width of the microphotometer slit was adjusted to 0·03 mm. : spectral features 1 cm.$^{-1}$ apart could then be resolved, whilst the maxima of the sharper bands could be located to within this limit.

FIG. 2.



Microphotometer record of part of the second strong period in the absorption system of 1 : 3 : 5-*trideuterobenzene. The spectrum is shown from about* 39800 *cm.*$^{-1}$ *to about* 39300 *cm.*$^{-1}$. *The conditions are chosen to show strong bands, with the result that weak ones cannot, or can scarcely, be seen. The band* A_0^0 *of the first strong period becomes replaced in this period by the whole group from* K_0^0 *to* A_1^0. *In later periods the complexity grows until the contour appears almost continuous.*

(*See remark in parenthesis under Fig.* 1.)

Qualitatively, the general structure of the spectrum is the same as that of the absorption spectrum of benzene or of hexadeuterobenzene (cf. Part I, Section 4, and Fig. 1, p. 409), except for one very obvious difference, *viz.*, that, as the progressions run out towards shorter waves, the sequence pattern, instead of being rather closely repeated, becomes rapidly more complicated, until after four or five repetitions the now very numerous overlapped bands become blurred into a continuous contour—in which, at best, the main components only can be very roughly located. Thus we can observe the spectrum over a considerably greater frequency range than that over which we can make measurements of the bands. This stage-wise development of practical continuity, the first step of which is illustrated by a comparison of Figs. 1 and 2, shows clearly how an apparently continuous spectrum can arise from a polyatomic molecule, not necessarily because of any dissociation or pre-dissociation, but simply from the number and variety of the allowed vibrational transitions. We explain the present somewhat rapid development of complexity along the spectrum on the ground that, in this D_{3h} benzene, not one but two totally symmetrical carbon vibrations can undergo quantum changes without symmetry restriction and with comparable probabilities, so that, in the upper electronic state, one totally symmetrical quantum can be excited in two ways, two in three ways, and so on.

Each of the stronger bands of the totally symmetrical progressions is the parent of a sequence due to n—n transitions of the degenerate, low-frequency vibration, and the successive bands of the sequence show increasing complexity. This phenomenon was also apparent in the absorption spectra of benzene and hexadeuterobenzene. We explain it on the ground (Part II, Section 1) that when in either electronic state several degenerate quanta are excited, anharmonicity splits up the higher-order degeneracies which would otherwise characterise the combination. Thus two degenerate quanta give three, not exactly coincident, energy levels, and therefore a triple band if the other combining level is single, and the selection rules allow all three combinations. More complex band groups can arise when several degenerate quanta are involved in either, or, still more, in both, of the combining electronic states.

Two special causes of band complexity are best illustrated in the individual cases in which they arise. One is the exchange of a lower-state quantum for an upper-state quantum of nearly the same frequency. The other is resonance, which causes bands that might have been invisible to appear more or less strongly on the flanks of strong bands. Superposed on all these effects is that of molecular rotation, a quite general cause of discrete band structure. Even the simplest bands exhibit a more or less distinct structure, overlying that general degradation of intensity towards the red which shows that the molecule becomes slightly expanded in the upper electronic state.

We have found band complexity of some value as a guide to assignment. When, for instance, in a smoothed and nearly featureless region of the spectrum, a single sharp band (such as Y_0'—see Section 8) stands out, one can feel sure that it is simply constituted, involving few excited quanta, and probably no more than one degenerate quantum in either electronic state.

Our measurements of the frequencies of the bands are in Table I. Each region of the spectrum was studied with the aid of at least 4, and sometimes 7, independent plates, of which 20 were taken in all. Where a decimal is quoted, the frequencies, corrected to vacuum, are believed to be accurate to within 1 cm.$^{-1}$, whilst in other cases errors of a few wave-numbers are possible. The qualitative indications of intensity (ranging from ew = extremely weak, through m = medium, etc., to vs = very strong) relate to absorption in a 50-cm. column of vapour at the saturation pressure corresponding to the temperature stated: the pressure at 0° is computed to be 27 mm., and, at − 35°, rather less than 3 mm. We do not record the weakest of the measured extremely weak bands, since we believe that some at least of them are only accidental concentrations of intensity in a continuous background, presumably composed of overlapped bands too numerous and too weak for separate observation. The symbol δ, applying to the last four entries of the Table, means " diffuse ": in these cases the uncertainty in the recorded frequency is of the order of 10 cm.$^{-1}$.

Assignments are expressed by means of a literal notation the key to which is in Tables II and III. The subscripts and superscripts represent the quantum numbers, in either electronic state, of the A_1'(C), A_1'(C′), and E''(C) vibrations, as explained in the Note below Table I. The letter-symbols distinguish those vibrational changes which are peculiar to the different band-series, and are defined by the equations of Table II, which also gives the observed ranges of the above-mentioned quantum numbers. Identification of the vibrations symbolised in Table III will be assisted by reference to Part I, Section 6, especially to Table III in that Section (p. 413) (for diagrams, see *J.*, 1946, pp. 260—271).

The band-series A—E, G, H, J, M, and N correspond as closely as the different symmetries of the molecules allow to the identically named series in the absorption spectra of benzene and hexadeuterobenzene (Parts II and IV).

(2) *Band Series* A—D *and* E, e.—As with the D_{6h} benzenes, so with the D_{3h} benzene, the bands of series A—D constitute the main framework of the absorption spectrum (cf. Part I, Section 4). They are dependent on unit quantum changes in the planar, carbon-bending vibration E'(C 1), which directly produce the four origins, A, B, C, and D. Progressions in the two trigonal ring-swelling vibrations, A_1'(C) and A_1'(C′), are, of course, mainly positive, although several one-quantum members of the corresponding negative progressions can be seen, much weakened by their Boltzmann factors. In all these progressions both the totally symmetrical carbon vibrations are involved, that with the lower frequency in either state giving stronger bands than the other (see Figs 1 and 2). Thus the one-quantum member of the positive A progression is

TABLE I.

Absorption Spectrum of 1 : 3 : 5-*Trideuterobenzene. Frequencies, Intensities, and Assignments* (*cf. Tables II and III*).

Freq. (cm.$^{-1}$).	Inty. (0°).	Assgnt.
36586	ew	B^{0}_{-1}
638	vw	B^{0}_{-1}
37135	vw	B^{3}_{0}
146	vw	
206	vw	D^{2}_{0}
225	vw	N^{1}_{0}
296·1	mw	B^{2}_{0}
347·5	vw	D^{1}_{0}
358·2	w	
368·7	vw	N^{0}_{0}
379·8	w	
386	ew	v^{0}_{0}
391	w	
402·7	vw	s^{1}_{0}
408·0	vw	
445·0	ms	B^{1}_{0}
472·0	w	U^{0}_{0}
510·1	m	D^{0}_{0}
523	w	B^{0}_{1-1}
558·8	m	s^{0}_{0}
590·0	s	B^{0}_{0}
634·9	m	T'
658·4	w	C^{0}_{-1}
692·0	mw	$A^{0}_{-1'}$
732·9	mw	J^{3}_{0}
740·0	m	A^{0}_{-1}
774	vw	$A^{0}_{1'-2}$
805·8	vw	j^{2}_{0}
820·6	vw	Q^{1}_{0}
879	mw	J^{2}_{0}
889	mw	H^{1}_{0}
937	w	I^{0}_{0}
957·4	w	j^{1}_{0}
970	w	Q^{0}_{0}
985	w	l'
38032	m	J^{1}_{0}
039·9	m	H^{0}_{0}
122·6	mw	N^{1}_{1}
	Inty. (−35°)	
169	vw	B^{2}_{1}
177	w	
208	ew	U^{1}_{1}
233·8	vw	A^{3}_{0}
240·9	vw	
255·1	vw	D^{1}_{1}
274·7	vw	N^{0}_{1}
324·9	w	C^{2}_{0}
331·4	w	B^{1}_{1}, M^{1}_{0}
341·9	ew	$D^{1}_{1'}$
361·9	w	U^{0}_{1}
394·5	mw	A^{2}_{0}
403	w	D^{0}_{1}
Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.
38432·0	ew	$B^{1}_{1'}$, L^{1}_{0}
450·8	vw	s^{0}_{1}
456·3	vw	
466	w	C^{1}_{0}
470	w	
481·8	ms	B^{0}_{1}, M^{0}_{0}
490·7	vw	
500·3	w	$D^{0}_{1'}$
515	w	r^{1}_{0}
545·9	s	A^{1}_{0}
551·3	vw	
580·5	mw	$B^{0}_{1'}$
584·9	mw	L^{0}_{0}
615·2	m	C^{0}_{0}
669·5	ms	r^{0}_{0}
685·8	vs	A^{0}_{0}
693·5	vs	
697·0	vs	
729·3	m	$A_{1'-1}$
760·1	w	J^{2}_{1}
772·9	vw	
836·5	vw	G^{2}_{0}
847·7	vw	
860·0	vw	F^{1}_{0}
923	w	$J^{1}_{1'}$
954	vw	S^{0}_{0}
988·3	mw	G^{1}_{0}
996·2	w	
39008·0	w	F^{0}_{0}
019·9	vw	$J^{1}_{1'}$
062	w	B^{2}_{2}
138	vw	G^{0}_{0}
144·0	ms	
149	w	D^{1}_{2}
163	vw	P^{0}_{0}
177	w	
191·9	vw	l_{0}
203	w	C^{2}_{1}
218·7	w	B^{1}_{2}, M^{1}_{1}
243	vw	O^{1}_{0}
272·3	vw	W^{1}_{0}
280·1	w	A^{2}_{1}
295	w	D^{0}_{2}
305·5	w	$C^{2}_{1'}$
350·2	w	C^{1}_{1}
368·1	ms	B^{0}_{2}, M^{0}_{1}
394·0	m	O^{0}_{0}
406	vw	W^{0}_{0}
413·1	w	
431·4	s	A^{1}_{1}
441	s	
449·6	s	
458	s	$C^{1}_{1'}$
Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.
39465	mw	$B_{1+1'}$ E^{1}_{0} L^{0}_{1}
472·8	vw	
485·8	mw	
498·8	vw	C^{0}_{1}
507·7	m	
518·3	m	T^{0}_{0}
523·7	vw	$A^{1}_{1'}$ K^{1}_{0}
535·5	w	
547·8	w	
575·2	vs	A^{0}_{1}
585·4	vs	
595	vs	
601	s	$C^{0}_{1'}$
610·6	s	E^{0}_{0}
618·5	w	
630·5	ms	
670·9	s	$A^{0}_{1'}$ K^{0}_{0}
681·3	s	
694·5	s	
745·3	ew	G^{2}_{1}
808·8	ew	J^{1}_{2}
840·6	ew	$G^{2}_{1'}$
894	vw	G^{1}_{1}
901	w	F^{0}_{1}
911	vw	R^{1}_{0}
982·6	vw	$G^{1}_{1'}$
40020	mw	G^{0}_{1}
037	mw	
048·7	mw	R^{0}_{0}
052·9	mw	
060	mw	
078	ew	l_{1}
116·9	w	$G^{0}_{1'}$
127	w	
250	mw	B^{0}_{3}
280·3	mw	$A^{2}_{1+1'}$
316	mw	W^{0}_{1}
330·1	m	A^{1}_{2}
340·5	m	
348	m	$C^{1}_{1+1'}$
357·9	m	E^{1}_{1}
369·8	m	
403·1	mw	C^{0}_{2}
413	mw	T^{0}_{1}
421·4	mw	$A^{1}_{1+1'}$
431·3	mw	
471	ms	A^{0}_{2}
478	s	
483	ms	
490·2	s	$C^{0}_{1+1'}$
505·8	ms	E^{0}_{1}
520	ms	

TABLE I—*contd.*

Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.	Freq. (cm.$^{-1}$).	Inty. (−35°).	Assgnt.
40573·7	ms	$A^0_{1+1'}$ K^0_1	41028	w	y^0_0	41449·6	m	A^0_{2+1} K^0_2
580·7	ms		086	w	$C^2_{2+1'}$	458·5	m	
587·4	ms		163	mw	$A^2_{2+1'}$	479·9	mw	
603·9	m	$E^0_{1'}$	227·0	mw	A^1_3	510	vw	$E^0_{1+1'}$
617·4	vw		235·0	m	$C^1_{2+1'}$	547·2	vw	e^0_0
651·0	w	$A^0_{2'}$, $K^0_{1'}$	246	w	E^1_2	565	vw	$A^0_{1+2'}$
663·2	m		259	mw		830·4	m	$Y_0{}'$
670·1	w		270	m	$X_0{}'$	875	w	Y^0_1
920	mw	G^0_2	306·5	mw	T^0_2	~42130	w(δ)	A^1_4
933	mw		319·1	mw	$A^1_{2+1'}$	168	w	$X^{-'}$
945	mw	R^0_1	371	ms	A^0_3	~42260	m(δ)	A^0_4 E^0_3
996	mw	Y^0_0	386	ms	$C^0_{2+1'}$	~42290		
41012	w	$G^0_{1+1'}$	396	ms	E^0_2	~42350	mw(δ)	$A^0_{3+1'}$
019·8	w							

Note : In the assignment column, the upper-state quantum numbers, called p' and q' in Table II, are given as subscripts with (stated or implied) positive signs, and the lower-state numbers, p'' and q'' in Table II, as subscripts with negative signs. These mark progressions in the totally symmetrical vibrations A_1'(C) and A_1'(C′), p' and p'' referring to the former, and q' and q'' to the latter. The absence of a dash upon a subscript means that it refers to the totally symmetrical vibration, A_1'(C), of lower frequency, and therefore to p' or p''; whilst a subscript with a dash relates to the totally symmetrical vibration of higher frequency, A_1'(C′), and thus to its quantum number q' or q''. The quantum number s of Table II, which is common to both the upper and lower electronic states, is given in the assignment column as a superscript. It marks sequences in the low-frequency vibration E''(C). With regard to the naming of the vibrations, see Part I, Section 6.

TABLE II.

Absorption Spectrum of 1 : 3 : 5-*Trideuterobenzene. Key to Assignments* (*cf. Table I*).

	Freq. (cm.$^{-1}$).	p', p''.	q', q''.	s.
A	$= 38184 + 513\left\{\begin{matrix} + 893p' + 988q' \\ - 956p'' - 1005q'' \end{matrix}\right\} - 150s$	0—4 0—2	0,1 0, 1	0—3
B	= ,, $- 594\left\{\begin{matrix} + 893p' + 988q' \\ - 956p'' - 1005q'' \end{matrix}\right\} - 150s$	0—3 0, 1	0, 1 0, 1	0—3
C	= ,, $+ 2 \times 513 - 594\left\{\begin{matrix} + 893p' + 988q' \\ - 956p'' \end{matrix}\right\} - 150s$	0—2 0, 1	0—2	0—2
D	= ,, $+ 513 - 2 \times 594 + 893p' + 988q' - 150s$	0—2	0, 1	0—2
E	= ,, $+ 1428 + 893p' + 988q' - 150s$	0—3	0, 1	0, 1
e	= ,, $+ 513 + 2 \times 1428$			
F	= ,, $+ 824 + 893p' - 150s$	0, 1		0, 1
G	= ,, $+ 513 + 2 \times 223 + 893p' + 988q' - 150s$	0—2	0, 1	0—2
H	= ,, $- 594 + 2 \times 223 - 150s$			0, 1
I	= ,, $+ 513 - 2 \times 373$			
J	= ,, $+ 893p' + 988q' - 150s$	0—2	0, 1	1—3
j	= ,, $+ 513 - 594 - 150s$			1, 2
K	= ,, $+ 513 + 2 \times 495 + 893p' - 150s$	0—2		0, 1
L	= ,, $- 594 + 2 \times 495 + 893p' - 150s$	0, 1		0, 1
l	= ,, $+ 513 + 495 + 893p'$	0, 1		
l′	= ,, $+ 513 - 710$			
M	= ,, $+ 513 - 215 + 893p' - 150s$	0, 1		0, 1
N	= ,, $- 594 - 215 + 893p' - 150s$	0, 1		0, 1
O	= ,, $+ 1428 - 215 - 150s$			0, 1
P	= ,, $+ 2 \times 495$			
Q	= ,, $- 215 - 150s$			0, 1
R	= ,, $+ 513 + 2 \times 680 + 893p' - 150s$	0, 1		0, 1
r	= ,, $+ 513 + 680 - 710 - 150s$			0, 1
S	= ,, $- 594 + 2 \times 680$			
s	= ,, $- 594 + 680 - 710 + 893p' - 150s$	0, 1		0, 1
T	= ,, $+ 513 + 2 \times 411 + 893p'$	0—2		
T′	= ,, $+ 513 - 2 \times 531$			
U	= ,, $- 594 - 119 + 893p'$	0, 1		0, 1
v	= ,, $- 594 - 200$			
W	= ,, $+ 513 + 2 \times 360 + 893p' - 150s$	0, 1		0, 1
X′	= ,, $+ 3085 + 893p'$	0, 1		
Y	= ,, $+ 513 + 2300 + 893p'$	0, 1		
Y′	= ,, $+ 513 + 3135$			
y	= ,, $+ 513 + 2330$			

Note : The frequency 38184 cm.$^{-1}$ is that of the forbidden electronic origin. The other frequencies are vibration frequencies. They are assigned in Table III.

TABLE III.

Absorption Spectrum of 1 : 3 : 5-*Trideuterobenzene. 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.
893	956	67 } (+ 32)	A_1'(C)
988	1005	—	A_1'(C′)
2300	—	—	A_1'(H)
3135	—	—	A_1'(H′)
360	—	—	A_2''(C)
411	531	119	A_2''(H 1)
—	—	200	A_2''(H 2)
513	594	81	E'(C 1)
1428	—	—	E'(C 2)
2330	—	—	E'(H 1)
3085	—	—	E'(H′ 1)
824	—	—	E'(H 2)
223	373	150	E''(C)
495	710	215 } (− 30)	E''(H 1)
680	—	—	E''(H 2)

Note : Concerning the frequency 824 cm.$^{-1}$, see text (Section 3). A value 715 cm.$^{-1}$ for the upper-state fundamental frequency of vibration A_2''(H 2) follows from the known ground-state frequency (Section 7).

double (A^0_1 and $\mathrm{A}^0_{1'}$), the lower frequency being the stronger, whilst the two-quantum member is triple (A^0_2, $\mathrm{A}^0_{1+1'}$, $\mathrm{A}^0_{2'}$), the lowest frequency being the strongest and the uppermost the weakest (cf. Part I, Section 6).

This pattern of progressions is overlapped by that of the E series. The parent band, E^0_0, lies between A^0_1 and $\mathrm{A}^0_{1'}$ (see Fig. 2). The one-quantum member of this progression is again double, the stronger band, E^0_1, fitting in between A^0_2 and $\mathrm{A}^0_{1+1'}$, and the weaker one, E_1, between $\mathrm{A}^0_{1+1'}$ and $\mathrm{A}_{2'}$. As with the D_{6h} benzenes, so also with the D_{3h} compound, the E series is dependent on a one-quantum excitation of the planar carbon-stretching vibration E'(C 2), and is considered to obtain much of its intensity by resonance with the A series (Part II, Section 3).

The whole of this pattern of progressions is overlapped by the corresponding C pattern, whilst the combined A-and-C pattern becomes repeated at lower frequencies in the similar B-and-D pattern. Finally, all the stronger bands of all these branching progressions start negatively-running sequences involving 1—1, 2—2, . . . , transitions of the degenerate, out-of-plane, carbon vibration, E''(C).

The above-mentioned series, together with analogous band-series in the fluorescence spectrum of 1 : 3 : 5-trideuterobenzene (Part VII, Section 2), allow us to fix the position of the electronic origin,

$$\mathrm{J}^0_0 = 38184 \pm 1\ \mathrm{cm.}^{-1}$$

as well as the following fundamental vibration frequencies :

$$E'(\mathrm{C}\ 1)_{\mathrm{ground}} = 594\ \mathrm{cm.}^{-1} \qquad E'(\mathrm{C}\ 1)_{\mathrm{excited}} = 523\ \mathrm{cm.}^{\ 1}$$

$$E'(\mathrm{C}\ 2)_{\mathrm{excited}} = 1428\ \mathrm{cm.}^{-1}$$

$$A_1'(\mathrm{C})_{\mathrm{ground}} = 956\ \mathrm{cm.}^{-1} \qquad A_1'(\mathrm{C})_{\mathrm{excited}} = 893\ \mathrm{cm.}^{-1}$$

$$A_1'(\mathrm{C}')_{\mathrm{ground}} = 1005\ \mathrm{cm.}^{-1} \qquad A_1'(\mathrm{C}')_{\mathrm{excited}} = 988\ \mathrm{cm.}^{-1}$$

and the following frequency difference :

$$E''(\mathrm{C})_{\mathrm{ground}} - E''(\mathrm{C})_{\mathrm{excited}} = 150\ \mathrm{cm.}^{-1}$$

The ground-state frequencies, as found in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene, are quoted for comparison : E'(C 1) = 593·0 cm.$^{-1}$, A_1'(C) = 956·2 cm.$^{-1}$, A_1'(C′) = 1003·6 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *J.*, 1946, 332).

The existence of two totally symmetrical vibrations of not very different frequencies, and of comparable activity for the development of progressions, leads to a phenomenon which is sufficiently uncommon to be notable, *viz.*, the appearance of satellite bands displaced from their principals by a small *positive* interval, in this case 32 cm.$^{-1}$. The bands $\mathrm{A}_{1'-2}$ and $\mathrm{A}_{1'-1}$ are examples of such satellites. The latter appears in Fig. 1 : it lies 32 cm.$^{-1}$ on the high-frequency side of the very strong parent band A^0_0. Such satellites may be explained by an exchange of a ground-state quantum of the totally symmetrical vibration of lower frequency for an upper-state quantum of the totally symmetrical vibration with the higher frequency. In general such positive intervals may arise when both of the following conditions are fulfilled. The first is that two vibrations of the same symmetry class undergo such mutual modifications of normal co-ordinates in the altered electronic system that the presence of either vibration in the initial state tends to excite both in the final state. The totally symmetrical carbon vibrations of 1 : 3 : 5-trideuterobenzene constitute one such case; and the out-of-plane vibrations of partly deuterated benzenes in general provide other cases (cf. *J.*, 1946, 259, *et seq.*). The second condition is that the upper-state frequency of one such pair of vibrations lies above the lower-state frequency of the other. Intervals of this kind have been observed before by Ginsberg and Matsen in the absorption spectra of aniline and phenol (*J. Chem. Physics*, 1945, **13**, 167, 309).

The single band, called e^0_0, lying 2850 cm.$^{-1}$ above A^0_0, is attributed to the excitation, in the upper electronic state, of the first overtone of the stretching vibration E'(C 2), in association with those electronic and vibrational transitions which characterise the principal absorption origin A^0_0. The very appreciable intensity of this overtone band can be understood, since it falls among bands of the A progression, from which it could gain intensity by resonance.

(3) *Band Series* F.—The parent band, F^0_0, of series F is sharp, though somewhat weak. It lies 824 cm.$^{-1}$ above the electronic origin. We incline to the view that it is an individual band, and not an outlying component of the band G^1_0; but we have not been able fully to satisfy ourselves on this point. A similar difficulty arises in connexion with the other bands of the series. If these bands are indeed separate, then we can see no alternative to regarding them as involving the excitation in the upper electronic state of one quantum of the planar deuterium-bending vibration belonging to the E' symmetry class. The band F^0_0 would then arise in a transition from the " vibrationless " ground state to the fundamental level of this vibration in the upper electronic state.

The resulting vibration frequency,

$$E'(\mathrm{H}\ 2)_{\text{excited}} = 824 \text{ cm.}^{-1}$$

is only a very little smaller than the corresponding ground-state frequency, 833·5 cm^{-1}., as given in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene (Herzfeld, Ingold, and Poole, *loc. cit.*). If we should look for a band depending analogously on an E' protium-bending frequency of the upper-state, assuming this frequency to lie somewhat near the corresponding lower state frequency (1101·8 cm.$^{-1}$, as given in the Raman spectrum) then we find several possible bands, all of which, however, are capable of alternative assignments. One naturally looks in the fluorescence spectrum for bands displaced by 833·5 and 1101·8 cm.$^{-1}$ below the electronic origin. Bands are indeed found in these positions, but, unfortunately, an alternative explanation is possible for each of them. In all the circumstances we regard our suggested assignment of the F series as provisional.

(4) *Band Series* G, H, I, J, *and* j.—All these series depend in special ways on the degenerate, low-frequency vibration, E''(C). Series G and H, which commence with bands, G^0_0 and H^0_0, lying 446 cm.$^{-1}$ above A^0_0 and B^0_0 respectively, involve the excitation, in the upper state, of two quanta of this vibration, in association with those electronic and vibrational transitions which characterise series A and B respectively. The sequences, in 150 cm.$^{-1}$, of series G and H therefore involve upward transitions of the type 0—2, 1—3, ... , in the vibration E''(C).

The single weak band, I^0_0, situated 760 cm.$^{-1}$ below A^0_0, can be explained by assuming the loss of two ground-state quanta of the same vibration, in association with the transitions of A^0_0. The same band appears in the fluorescence spectrum, where it is the parent of a series (Part VII, Section 3). The resulting overtone-frequency is appreciably greater than twice the fundamental frequency, but this may be a real effect of anharmonicity, since we find a similar relationship in the Raman spectrum.

The degeneracy of the vibration, E''(C), would permit (Part I, Section 6) the excitation, in combination with the electronic transition, of its first overtone, without the need for accompanying excitations of other vibrations. In fact, an extremely weak band, situated 446 cm.$^{-1}$ above the electronic origin, has been observed, though we do not record it, since some equally faint intensity maxima have been rejected in case they should be spurious frequencies due to the overlapping of bands. The same symmetry conditions (*ibid.*) allow 1—1, 2—2, ... , transitions of the vibration E''(C) to accompany the electronic transition, without simultaneous changes in other non-totally symmetrical vibrations. Such transitions produce series J, a rather prominent series, closely similar to the identically named series of the D_{6h} benzenes. In the absorption spectrum of 1 : 3 : 5-trideuterobenzene, we find a negatively-running sequence in 150 cm.$^{-1}$, which starts as if from the electronic origin, except that the 0—0 band is absent. The same sequence is found in the fluorescence spectrum (Part VII, Section 3). In absorption the main bands of the sequence are also the starting points of positive progressions in the two totally symmetrical vibrations, A_1'(C) and A_1'(C').

Displaced below the bands of the J sequence by about 80 cm.$^{-1}$ lie the bands of a weak companion series, which we call j. It can be explained by assuming 1—1, 2—2, . . . , transitions of the vibration E''(C), superposed on 1—1 transitions of the vibration E'(C 1). These bands, too, are found in the fluorescence spectrum (*ibid.*). They are labelled j_0^1, j_0^2, . . . , and have two causes of spectral activity, *viz.*, the excitation of the vibrations E'(C 1) and E''(C), the latter being probably the more important. The series has a theoretical parent, j_0^0, in which the second vibration would be unexcited, the band arising from a pure 1—1 transition of the vibration E'(C 1). We might expect this band to be much weaker. In the absorption spectrum, the band can be seen, but is too weak to be included in our record. In the fluorescence spectrum the same band, though still very weak, can be measured satisfactorily: its frequency is 38105 cm.$^{-1}$ (Part VII, Table I).

These series furnish the following values for fundamental frequencies :

$$E''(\mathrm{C})_{\text{ground}} = 373 \text{ cm.}^{-1} \qquad\qquad E''(\mathrm{C})_{\text{excited}} = 223 \text{ cm.}^{-1}$$

The ground-state frequency, as measured in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene is 372·7 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *loc. cit.*).

(5) *Band Series* K, L, l, l', M, N, O, P, *and* Q —In Section 3 we did not quite fully describe the appearance of the branching progressions in the frequencies, 893 and 988 cm.$^{-1}$, of the two totally symmetrical vibrations, A_1'(C) and A_1'(C'). It has to be added that whenever an A_1'(C') quantum is present (as indicated by a dashed subscript in the band symbol), the corresponding band, if strong, is accompanied on its high-frequency side by a close companion of considerable strength. The companion bands to series A constitute series K (cf. Fig. 2), and those to series B form series L. Since the bands of series K and L are clearly gaining a great deal of their intensity by resonance with the neighbouring bands of series A and B, the upper-state vibration which is characteristic of series K and L must have total symmetry. There being no fundamental of an appropriate frequency, we take the vibration frequency to be that of a first overtone. The frequency is 996 cm.$^{-1}$, but this is probably raised a few wave-numbers by the resonance.

A single weak band P_0^0 lies 993 cm.$^{-1}$ above the electronic origin. We assign this band to the excitation in the upper electronic state of the same first overtone. The implication is that the corresponding fundamental vibration is degenerate, the overtone being here excited in its degenerate (E') form, not in its totally symmetrical (A_1') form (Part I, Sections 5 and 6).

With this same vibration we connect two series, M and N, which are prominent alike in the absorption and in the fluorescence spectrum (Part VII, Section 4). The bands of series M lie uniformly 215 cm.$^{-1}$ below bands of series A, whilst those of series N are displaced by the same amount below those of series B. The two series clearly correspond to the identically named series of the absorption and fluorescence spectra of benzene and of hexadeuterobenzene, though the common interval is 265 cm.$^{-1}$ for benzene, and 208 cm.$^{-1}$ for hexadeuterobenzene. We interpret the present series M and N in the same way as the others, *viz.*, as involving 1—1 transitions in some special vibration, in combination with those electronic and vibrational transitions which characterise series A and B, respectively. A weak series, called O, also occurs, the bands of which are displaced by 215 cm.$^{-1}$ below bands of series E. We assume the same 1—1 vibrational transition, now in combination with the electronic and vibrational transitions of series E.

A weak series called Q is present, which starts with a band, Q_0^0, situated 214 cm.$^{-1}$ below the electronic origin. A band in the same position is present in the fluorescence spectrum (Part VII, Section 4). In the production of these bands the 1—1 transition is unaccompanied by other vibrational changes, and this shows the vibration to be degenerate (Part I, Sections 5 and 6). Corresponding bands are found 265 cm.$^{-1}$ below the electronic origin in the absorption and fluorescence spectra of benzene, and 208 cm.$^{-1}$ below the origin in the corresponding spectra of hexadeuterobenzene.

The close analogy of series M, N, and Q with series of the D_{6h} benzenes requires us to assume that the interval 215 cm.$^{-1}$, representing a difference of fundamental frequencies in the two electronic states, belongs to a vibration of the E'' class. Connecting it with the degenerate vibration whose overtone is concerned in series K, L, and P, we obtain agreement with the known ground-state frequency of a vibration of that class. We also observe, as is allowed by the selection rules (Part I, Section 6), the weak bands of series l and l′, in which the upper- and lower-state fundamental frequencies are found in combination, as 0—1 and 1—0 transitions, with the electronic and vibrational transitions of the main absorption origin A_0^0.

The following fundamental frequencies result from the evidence here presented:

$$E''(\mathrm{H}\ 1)_{\text{ground}} = 710\ \text{cm.}^{-1} \qquad E''(\mathrm{H}\ 1)_{\text{excited}} = 495\ \text{cm.}^{-1}$$

This vibration is moderately strong in the Raman effect; and in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene it appears with the frequency 710·2 cm.$^{-1}$ (Herzfeld, Ingold, and Poole, *loc. cit.*).

(6) *Band Series* R, r, S, *and* s.—Series R contains a number of characteristic bands, of which the parent R_0^0, lies 1360 cm.$^{-1}$ above A_0^0. A single, much weaker band, S_0^0, is found the same distance above B_0^0. We assume the interval 1360 cm.$^{-1}$ to represent the first overtone of a vibration in the upper electronic state. From comparisons with the spectra of other benzenes (Part XI), we identify the vibration as the third member of the E'' symmetry class. Its fundamental frequency is

$$E''(\mathrm{H}\ 2)_{\text{excited}} = 680\ \text{cm.}^{-1}$$

A number of bands of series A and B have weak companions displaced to lower frequencies by 30 cm.$^{-1}$. These constitute the series r and s, respectively. The interval must represent the reduction of frequency which arises from the exchange of a lower-state vibrational quantum for an upper-state quantum of the same symmetry class—possibly of the same vibration. An appropriate combination between the two vibrations, $E''(\mathrm{H}\ 1)_{\text{ground}} = 710$ cm.$^{-1}$ and $E''(\mathrm{H}\ 2)_{\text{excited}} = 680$ cm.$^{-1}$, could therefore explain these bands. The Boltzman factor for such a transition would not be prohibitively small. Since the motions of the point-sets are mixed together in rather a complicated way in the out-of-plane vibration classes of 1 : 3 : 5-trideuterobenzene (Bailey *et al.*, *J.*, 1940, 225), and therefore probably in different ways in the two electronic states, one can understand, on the basis of Herzberg and Teller's extension of the Franck–Condon principle, how the replacement of one such vibration by another of the same symmetry class can sometimes occur with considerable intensity. However, the alternative possibility cannot be excluded that the drop of 30 cm.$^{-1}$ may represent the difference between the lower- and upper-state frequencies of one of those vibrations whose upper-state frequencies are not certainly (or not accurately) known. Taking account of the effect of Boltzmann factors on intensity, the only vibrations which one could consider in this connexion would be the two planar deuterium-bending vibrations, $A_2'(\mathrm{H}\ 1)$ and $E'(\mathrm{H}\ 2)$, and of these the second becomes excluded if our suggestions of Section 3 be accepted.

(7) *Band Series* T, T′, U, v, *and* W.—The progression T, of rather less than moderate intensity, starts with a band, T_0^0, situated 821 cm.$^{-1}$ above the main active origin A_0^0. A very weak band is visible about the same distance above B_0^0, but it is not sufficiently well measured to be included in the record. The interval 821 cm.$^{-1}$ we take to be an overtone frequency belonging to the excited electronic state. For reasons based partly on the internal evidence of the spectrum, and partly on comparisons with the absorption spectra of other benzenes (Part XI), we identify the vibration concerned as one of the A_2'' class—the nearest analogue in this D_{3h} benzene, to the A_{2u}(H) vibration, which consistently gives overtone progressions in the absorption and fluorescence spectra of the D_{6h} compounds, benzene and hexadeuterobenzene. Band T_0^0 arises from an upward 0—2 transition of the vibration $A_2''(\mathrm{H}\ 1)$, in combination with those electronic and vibrational transitions which produce the active origin A_0^0.

The fundamental frequency of this vibration in the electronic ground state being independently known, one may easily recognise the prior excitation of the corresponding ground-state overtone in the production of the weak, but sharp, band T′, situated 1062 cm.$^{-1}$ below the orgin A_0^0. An extremely weak band is visible about the same distance below B_0^0, although we do not include it amongst our record of measured bands. Band T′, then, arises from an upward 2—0 transition of the vibration $A_2''(\mathrm{H}\ 1)$, in combination with those electronic and vibrational transitions which characterise the origin A_0^0.

The U series consists of a number of weak bands negatively displaced from the stronger B bands by 119 cm.$^{-1}$. The presence of bands correspondingly related to A bands cannot be verified, since any such bands would be overlapped by B bands and by L bands. The U bands are attributed to 1—1 transitions of the vibration A_2''(H 1), in combination with the electronic and vibrational transitions of the associated B bands. The interval 119 cm.$^{-1}$ is thus interpreted as the difference between the fundamental frequencies of the vibration A_2''(H 1) in the lower and upper electronic states.

The frequencies involved in these three series are consistent with one another, and determine the following fundamental frequencies :

$$A_2''(\text{H }1)_{\text{ground}} = 531 \text{ cm.}^{-1} \qquad A_2''(\text{H }1)_{\text{excited}} = 411 \text{ cm.}^{-1}$$

The ground-state frequency agrees, to within the limits of experimental error, with the value, 533 cm.$^{-1}$, given by the infra-red spectrum of 1 : 3 : 5-trideuterobenzene vapour (Bailey *et al.*, *loc. cit.*).

A band, v_0^0, lying 200 cm.$^{-1}$ below B_0^0, is found in both the absorption and the fluorescence spectra of 1 : 3 : 5-trideuterobenzene (cf. Part VII, Section 5). In the latter spectrum it is the parent of a series of weak bands. The presence of bands similarly connected with A_0^0 cannot be verified because the positions in which they would appear are occupied by bands of the D series. As seems necessary, we interpret the v bands by means of the assumption that a 1—1 transition of some characteristic vibration is superposed on the electronic and vibrational transitions of B_0^0, the observed frequency displacement representing the difference between the fundamental frequencies of the vibration in the lower and upper electronic states. A displacement as large as 200 cm.$^{-1}$ is likely to be connected with an out-of-plane vibration ; and the only out-of-plane vibration which is not excluded by our existing information about their frequencies is the second of the A_2'' hydrogen vibrations, A_2''(H 2). Accordingly, we assume a 1—1 transition of this vibration. A more positive reason for the assignment will be given later, inasmuch as we shall show that it produces agreement with the product rule when comparisons are made with other benzenes (Part XI).

In the fluorescence spectrum of 1 : 3 : 5-trideuterobenzene, we find the A_2''(H 2) vibration also involved through its first overtone, in the lower electronic state : this overtone, of frequency 1831 cm.$^{-1}$, becomes excited in producing the bands of series V (Part VII, Section 5). The absorption and fluorescence spectra together therefore determine the following fundamental frequencies :

$$A_2''(\text{H }2)_{\text{ground}} = 915 \text{ cm.}^{-1} \qquad A_2''(\text{H }2)_{\text{excited}} = 715 \text{ cm.}^{-1}$$

Previous studies of the infra-red spectrum of 1 : 3 : 5-trideuterobenzene have also yielded the value 915 cm.$^{-1}$ for the ground-state frequency (Bailey *et al.*, *loc. cit.*).

Series W of the fluorescence spectrum consists of a number of weak bands displaced upwards from the stronger bands of the A series by 720 cm.$^{-1}$. We regard this interval as an upper-state overtone frequency. From its low value, and from comparisons with similar series in the absorption spectra of other benzenes (Part XI), we identify the vibration concerned as the trigonal, out-of-plane, carbon-vibration, A_2''(C), the third vibration of the A_2'' symmetry class, and the nearest analogue for this D_{3h} benzene of the vibration B_{2g}(C), whose overtone we find in the absorption spectra of both the D_{6h} benzenes. Thus the parent band, W_0^0, is interpreted by the assumption of an upward 0—2 transition of this vibration, in association with the electronic and vibrational transitions of A_0^0. We infer from this the following fundamental frequency :

$$A_2''(\text{C})_{\text{excited}} = 360 \text{ cm.}^{-1}$$

(8) *Band Series* X′, Y, Y′, *and* y.—We deal in this section with a number of high-frequency bands believed to depend on the excitation of the deuterium- and protium-stretching vibrations of the symmetry classes E' and A_1'. In the first place, the selection rules allow bands due to transitions from the " vibrationless " level of the electronic ground state to the one-quantum levels, in the electronically excited state, of the deuterium- and protium-stretching vibrations of the E' class. Actually, the presence of a band due to a 0—1 transition of the deuterium-stretching vibration, E'(H 1), cannot be verified : the vibration frequency, which can be determined in another way (below), is such that this band, lying 2330 cm.$^{-1}$ above the electronic origin, would coincide with the broad and strong band, E_1^0. On the other hand, the band due to a similar excitation of the protium-stretching vibration, E'(H 1′), is easily recognised in the rather prominent band X_0', the parent of series X′. This band lies 3085 cm.$^{-1}$ above the forbidden electronic origin : formally, it is an " active origin ", similar to A_0^0 and E_0^0, and possibly F_0^0.

The other two parent bands of high frequency which we might expect to appear with considerable intensity are those which would result from the superposition of an upward 0—1 transition of either of the totally symmetrical hydrogen-stretching vibrations upon the electronic and vibrational transitions of A_0^0. In fact, these bands can readily be identified. The excitation in the upper electronic state of the totally symmetrical deuterium-stretching vibration, $A_1'(H)$, is represented by a very sharp band, of rather less than moderate intensity, called Y_0^0, the parent of series Y. It lies 2300 cm.$^{-1}$ above A_0^0. An analogous excitation of the totally symmetrical protium-stretching vibration, $A_1'(H')$, is unmistakably shown by a very sharp band, of medium intensity, called Y_0', which is particularly prominent by reason of its occurrence in a spectral region in which almost all other bands are much broadened and overlapped. Band Y_0' lies 3135 cm.$^{-1}$ above A_0^0.

One other high-frequency band remains to be considered, *viz.*, the weak, but sharp, band, y_0^0, lying 30 cm.$^{-1}$ above Y_0^0, and therefore 2330 cm.$^{-1}$ above A_0^0. It might be thought a possible choice for the assigment we have actually applied to Y_0^0; but for this we naturally selected the stronger of the two bands (Part I, Section 6). Its considerably weaker companion, y_0^0, we now explain by the assumption of a 0—1 transition of the deuterium-stretching vibration of the E' class, $E'(H\ 1)$, in combination with the electronic and vibrational transitions of A_0^0. The selection rules allow the transition to occur with low intensity (Part I, Section 6). We consider that we can observe band y_0^0 at all only because of its proximity to the stronger band Y_0^0, from which it can derive intensity by resonance (Part I, Section 5). The appearance in the absorption spectrum of benzene of similar high-frequency companion bands was interpreted on the same lines (Part II, Section 7, Series S and T).

In the fluorescence spectrum of 1 : 3 : 5-trideuterobenzene we find bands, called X and X′, which are considered to involve transitions from the " vibrationless " excited state to the fundamental levels, in the lower electronic state, of the deuterium- and protium-stretching vibrations of the E' class, *viz.*, $E'(H\ 1)$ and $E'(H\ 1')$. These fluorescence bands lie 2290 and 3080 cm.$^{-1}$, respectively, below the electronic origin (Part VII, Section 6). From them, and from the absorption bands above discussed, we can deduce the following E' fundamental frequencies :

$$E'(H\ 1)_{\text{ground}} = 2290\ \text{cm.}^{-1} \qquad E'(H\ 1)_{\text{excited}} = 2330\ \text{cm.}^{-1}$$
$$E'(H\ 1')_{\text{ground}} = 3080\ \text{,,} \qquad E'(H\ 1')_{\text{excited}} = 3085\ \text{,,}$$

We also obtain the following A_1' fundamental frequencies of the excited state, which are compared below with the corresponding frequencies of the ground state [in brackets] as determined in the Raman spectrum of liquid 1 : 3 : 5-trideuterobenzene (Herzfeld, Ingold, and Poole, *loc. cit.*) :

$$[A_1'(H)_{\text{ground}} = 2282\ \text{cm.}^{-1}] \qquad A_1'(H)_{\text{excited}} = 2300\ \text{cm.}^{-1}$$
$$[A_1'(H')_{\text{ground}} = 3053\ \text{,,}\ ] \qquad A_1'(H')_{\text{excited}} = 3135\ \text{,,}$$

On the whole, the upper-state frequencies of both symmetry classes are higher than the corresponding ground-state frequencies. Differences in the same direction were found for the hydrogen-stretching frequencies of benzene and hexadeuterobenzene (Part II, Section 7 and Part IV, Section 7).

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