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Rotational Analysis of the Absorption Bands of ICl

W. E. Curtis and J. Patkowski

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XI. *Rotational Analysis of the Absorption Bands of* ICl.

By W. E. Curtis, *D.Sc., Professor of Physics, Armstrong College, Newcastle-on-Tyne, and* J. Patkowski, *Professor of Physics, University of Wilno, Poland.*

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[Plate 10.]

The main absorption system of ICl in the visible region extends from λ5730 upwards, and its vibration structure has been studied by various workers.* The analysis of this is complete, and the existence of two isotopic molecules, ICl^{35} and ICl^{37}, has rendered it possible to determine the vibrational quantum numbers unambiguously. The vibrational constants of the molecule in the normal and excited states have been evaluated, and approximate values of the rotational constants estimated. Precise values of the latter can only be obtained from a fairly complete analysis of the rotation structure. It was known that this would present difficulties, but since some obvious regularities were discernible on preliminary high-dispersion plates, it seemed to be worth attempting.

The difficulties arise from two main causes, namely, the relatively high moment of inertia of the molecule, leading to a relatively close spacing of the lines of a branch, and the existence of the two isotope molecules, each giving rise to a complete system. In addition, the vibrational structure is relatively close and high rotational states are developed, with the consequence that successive bands of the same progression always overlap. Since also there are usually several progressions occurring in the same region, it will be realized that the complexity is considerable, and it was important, therefore, to select the most favourable point for the initial attack. If only one band can be correctly analysed the extension in either direction should not present serious difficulty. The region chosen, 6500–6800A, was one in which there was comparatively little overlapping of progressions and at the same time a reasonably open vibration structure. Further, three successive bands of one progression occurring in this region contained some easily recognizable series, although, as will be shown later, this appearance is

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* For references see Jevons, " Report on Band Spectra of Diatomic Molecules," 1932.

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due to superposition of branches, and actually hindered rather than facilitated the analysis.

Experimental.

Two sets of plates were taken, one in 1928 using a silica tube 30 cm. long and the other in 1931 with a pyrex tube 240 cm. long. In the former set it was necessary to heat the tube slightly, to about 50° C., in order to secure a suitable intensity of absorption. In the latter set the vapour pressure at atmospheric temperature was sufficient for the purpose. A few plates were taken with the tube at various temperatures up to 200° C. in the hope that the consequent intensity changes of the various progressions might prove helpful in the analysis, but although there were clearly marked selective effects, it was not found necessary to make any systematic use of them.

For the first tube the ICl was prepared by passing chlorine over iodine, whilst the second was filled with commercial ICl obtained from Kahlbaum. In both sets of experiments it was distilled into the tube after several successive preliminary distillations, and care was taken to dry it as thoroughly as possible, as the smallest trace of moisture has been found to favour dissociation.* As a further precaution a little P_2O_5 was distilled into the tube before sealing off. The occurrence of dissociation would have brought up the iodine absorption bands, but although a watch for these was always kept, no trace of them was ever detected, even at 200° C.

The spectrograph employed was a 21-foot concave grating (Eagle mounting), the property of Dr. WILFRED HALL, of Tynemouth, to whom we desire to express our best thanks. The second order was employed, giving a dispersion of about 1·3A. per mm. For the faster regions a 500-watt pointolite lamp served as a suitable source, but in the extreme red a carbon arc was found to be preferable in order to avoid unduly long exposures. Although the temperature of the grating room could be held steady by a thermostatic installation, the liability to occasional mechanical disturbances due to traffic effectively limited the duration of exposures to several hours. Ilford panchromatic plates were used.

The reduction of the measurements to wave numbers presented some difficulty, on account of the marked departure from normal dispersion, together with the wide spacing of the iron arc lines in this region. After investigating the accuracy and convenience of various reduction formulæ a quadratic form was decided upon, viz., $\nu = a + bs + cs.^2$ In the ranges employed, of 200 cm.^{-1} or less, this did not appear to leave any systematic error where additional standards were available. The very large number of lines measured made it impracticable to follow the usual method of reducing several plates independently, but although only one complete set of measurements has been obtained for each band, the agreement of the results in the overlapping portions gives ground for the belief that relatively little accuracy has been sacrificed. It is, at any rate,

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* CURTIS and DARBYSHIRE, 'Trans. Faraday Soc.,' vol. 27, p. 81 (1931).

clear that the very large amount of extra labour which would have been involved in duplicating all the measurements would not have been justified by any substantial gain in accuracy.

So far as possible the wave-number determinations were based on iron-arc standard lines of the same order (the second) as that used for the absorption bands. Where these were too few, namely, above 6600A, third-order standards were employed, but only after a special investigation had shown that no appreciable error was likely to be introduced by this procedure. The standard wave-lengths were taken from the 'Transactions of the International Astronomical Union,' vol. 2, 1922.

Allocation of Lines to Branches and Determination of Rotational Quantum Numbers.

The strongest bands in the region studied are those belonging to the progression $v'' = 1$. The $v'' = 0$ progression is also fairly strong, particularly at the more refrangible end, and the $v'' = 2$ progression is becoming prominent as the less refrangible end is approached. Any given band of the $v'' = 1$ progression may thus be overlaid by at least one band of each of the other two. The "tail" of the next band $(v' + 1)$ of the same progression is also quite strong as far as the $(v' - 1)$ head, and the whole complex is duplicated on account of the isotope effect, although in practice only the stronger portions of the ICl^{37} system come into account owing to the less abundance of that molecule. The first step in the analysis of the spectrum was to trace as completely as possible one band of the $v'' = 1$ progression, and the next to identify the neighbouring bands in the same progression, when the rotational numbering should then be obtainable by making use of combination relationships. These once established, it should be possible to proceed to the identification of bands of any other progressions occurring in the same region, and then to pick up some at least of the weaker isotopic counterparts of all these.

The first measurements were made on the bands $v'' = 1$, $v' = 9$, 10, 11, the structure of which looked comparatively simple. In each band two branches forming fairly close doublets were easily recognized, but their interpretation proved unexpectedly difficult, since neither the intervals nor the intensities of the doublets showed a regular variation with v'. It was at that time natural to suppose that the ICl bands would resemble the I_2 and Cl_2 visible systems, both of which are composed of P and R branches only, of approximately equal intensity, and changing regularly in relative position from band to band. The explanation was not forthcoming until the neighbouring bands ($v' = 8$ and 12) had been analysed; in these a third weak branch was detected which supplied the necessary clue. On plotting the relative positions of the corresponding doublets and triplets in the five successive bands it became evident, as will be seen from fig. 1, that the doublets were spurious, being produced by the fortuitous overlapping of two members of the triplets, and, moreover, by a different two for each.

It is somewhat remarkable that the overlapping persists throughout the whole observed length of the branch, *i.e.*, for 60 lines or more, but this is a consequence of the low J value at which the R head is formed, together with the extremely small value of the coefficient of J^4 in the expression for the rotation term.

The existence of three branches, presumably P, Q, and R, having been established, it was next necessary to determine which was which, and to assign the appropriate rotation quantum numbers. The usual mode of procedure, which is to search for sets of combination differences which shall be identical for all the bands of one progression, did not prove successful in the present case on account of the close similarity of the bands. That is to say, if the M th line (reckoned from the extrapolated head) of a branch A was combined with the $(M + x)$ th line of another branch B, several neighbouring values of x could be found, all giving the set of differences $A(M) - B(M + x)$ sensibly the same for all the five bands under investigation. The difficulty was partly attributable to the rather low accuracy (in relation to the high resolving power) of the individual

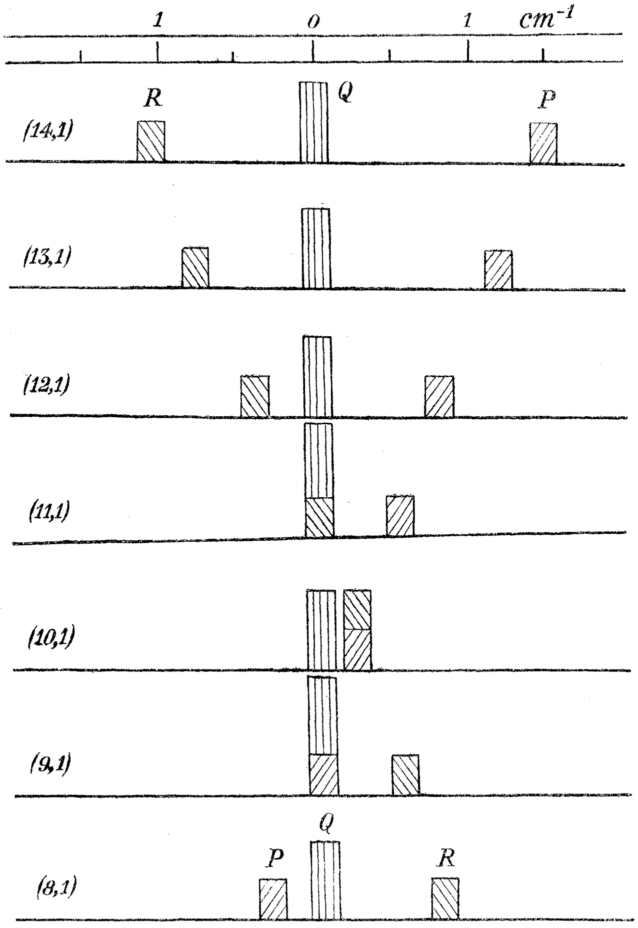

FIG. 1.—Relative positions of branches in $v'' = 1$ bands.

wave numbers, occasioned by the high proportion of "blends," partly to the extensive superposition of branches, as mentioned above, and also to the small change in the rotational constants from one band to the next. In order to arrive at quite definite conclusions it was found necessary to work with the rate of change of the provisional combination differences instead of with the differences themselves. A graphical method was first tried, but failed to give the requisite degree of accuracy. On the other hand, comparison of the calculated second differences, averaged over corresponding portions of each band, gave very definite indications as to the proper manner of combination. Table I shows the significant part of the results so obtained for the bands $v'' = 1$, $v' = 8$, and 12, the intermediate ones being omitted for brevity and also because of the systematic blending in them.

Table I.—Combination Second Differences in cm.$^{-1}$

	A (M) — B (M + x).			B (M) — C (M + x).			A (M) — C (M + x).		
x	2	3	4	2	3	4	5	6	7
$v' =$ 8	0·156	0·228	0·299	0·151	0·222	0·294	0·378	0·449	0·521
$v' =$ 12	0·146	0·228	0·309	0·144	0·225	0·306	0·368	0·451	0·531
Diff.	+0·010	0·000	—0·010	+0·007	—0·003	—0·012	+0·010	—0·002	—0·010

The true combinations are evidently A (M) — B (M + 3), B(M) — C (M + 3), and A(M) — C(M + 6), and since these bands all have a common lower state, namely, $v'' = 1$ of the normal molecule, it follows that in any one band the lines A (M), B (M + 3), and C(M + 6) all have the same upper rotational level. Now it is easily shown for a normal three-branch band that if the R branch forms a head for a low value of J, as must occur here (since $\frac{\omega'' - \omega'}{\omega''}$ is comparatively large) the Q branch lines will lie roughly midway between the corresponding P and R lines, the latter being on the side of higher frequency. We may thus identify A (M), B (M + 3), and C (M + 6) with R (J — 1), Q (J), and P(J + 1), since these have the upper level J in common. The intensities harmonize with this allocation, those of A and C being about the same, and considerably below that of B.

The true J numbering was next determined by finding the values which must be assigned to J in order that the quotient $\{R\,(J - 1) - P\,(J + 1)\} \div (J + \frac{1}{2})$ should be constant. This should be equal to $4B''$ if the J^4 term in the rotational energy expression is small, as is shown to be so here. Using the mean differences from all five bands there was no difficulty in deciding upon the correct numeration. For a particular set of J values the above quotient showed no systematic variation from the average value, whilst a change of $\frac{1}{2}$ in the numeration gave rise to a marked systematic effect. The same method applied to the Q-P and R-Q differences did not give satisfactory results, indicating the presence of an appreciable " combination defect."

The numeration of the $v'' = 1$ bands having been settled in this way, that of the other two progressions was readily determined by making use of the combinations relating them to the former. That of the weaker isotopic system was also obtainable, since the combination differences appropriate to this could be calculated from the first set by multiplying by the constant factor μ_1/μ_2 ($= 0 \cdot 9577$), where μ_1 and μ_2 are the reduced masses of the ICl^{35} and ICl^{37} molecules respectively.

The wave numbers, intensities, and quantum allocations for the bands due to the more abundant isotopic molecule are given in Table II. The intensities are visual estimates on the usual 0–10 scale, and are only intended to form a consistent set within one band. They run very irregularly because of the extreme prevalence of blending. It was at first intended to indicate known blends by some distinguishing mark ; as the work progressed it became evident that it would be more economical to indicate those which were not blends ; ultimately it appeared that the latter were much too few to serve for the derivation of constants, and there was thus no particular reason to distinguish them. In order to save space wave-lengths have not been tabulated.

Corresponding small portions of each $v'' = 1$ band are reproduced in Plate 10. The allocation to branches and their numeration are indicated for this progression only, although practically all the stronger lines of the spectrum were accounted for by the analysis.

TABLE II.—ICl^{35} Bands.

(9,0) Band.

P and Q Branches.				R Branch		
J_P.	J_Q.	ν.	Int.	J.	ν.	Int.
17	19	15328·100	4	21	15328·294	4
18	20	26·500	6	22	26·923	1
19	21	25·029	3	23	25·318	3
20	22	23·389	5	24	23·724	2
21	23	21·721	4	25	21·962	4
22	24	19·894	4	26	20·254	1
23	25	18·066	4	27	18·330	5
24	26	16·115	4	28	16·462	3
25	27	14·109	5	29	14·495	1
26	28	12·047	4	30	12·312	4
27	29	09·859	6	31	10·253	1
28	30	07·667	4	32	08·092	3
29	31	05·361	7	33	05·723	3
30	32	03·007	3	34	03·395	2
31	33	00·552	7	35	01·065	7
32	34	15298·032	4	36	15298·448	1
33	35	95·450	4	37	95·863	3
34	36	92·763	3	38	93·182	1
35	37	89·984	4	39	90·443	2
36	38	87·200	6	40	87·593	1
37	39	84·267	5	41	84·640	4
38	40	81·329	5	42	81·733	3
39	41	78·225	6	43	78·765	2
40	42	75·135	6	44	75·581	8
41	43	72·016	10	45	72·382	2
42	44	68·714	4	46	69·145	6
43	45	65·308	4	47	65·706	6
44	46	61·818	7	48	62·386	1
45	47	58·251	10	49	58·811	0
46	48	54·801	9	50	55·318	1
47	49	51·257	10	51	51·660	1
48	50	47·532	5			
49	51	43·686	2			
50	52	39·815	3			
51	53	35·862	2			
52	54	31·818	2			
53	55	27·734	3			
54	56	23·602	3			
55	57	19·343	5			
56	58	14·998	3			
57	59	10·604	2			
58	60	06·064	8			
59	61	01·671	4			
60	62	15196·965	2			
61	63	92·194	7			
62	64	87·323	4			
63	65	82·529	3			

TABLE II (continued).

(10,0) Band.

Q Branch.			P and R Branches.			
J.	ν.	Int.	J_P.	J_R.	ν.	Int.
9	15498·868	2	7	11	15499·296	1
10	98·286	2	8	12	98·571	1
11			9	13	97·849	2
12	96·713	1	10	14	97·050	2
13	95·829	1	11	15	96·031	2
14	94·790	2	12	16	94·958	1
15	93·609	1	13	17	93·833	1
16	92·395	1	14	18	92·671	3
17	91·110	2	15	19	91·329	8
18	89·691	2	16	20	89·972	2
19	88·069	0	17	21	88·424	9
20	86·791	2	18	22	86·993	2
21	85·161	1	19	23	85·378	2
22	83·474	1	20	24	83·732	1
23	81·769	2	21	25	81·948	2
24	79·911	2	22	26	80·140	4
25	78·043	1	23	27	78·253	2
26	75·993	2	24	28	(76·26)	
27	73·950	2	25	29	74·196	4
28	71·846	2	26	30	72·051	4
29	69·588	5	27	31	69·815	4
30	67·307	3	28	32	67·579	5
31	64·950	2	29	33	65·251	6
32	62·525	4	30	34	62·732	5
33	58·986	0	31	35	60·167	5
34	57·416	4	32	36	57·640	4
35	54·751	4	33	37	54·943	4
36	51·954	2	34	38	52·243	2
37	49·149	3	35	39	(49·42)	
38	46·241	3	36	40	46·480	3
39	43·233	2	37	41	43·601	3
40	40·236	2	38	42	40·527	3
41	37·129	2	39	43	37·393	2
42	33·932	4	40	44	34·256	3
43	30·577	2	41	45	(30·95)	
44	27·229	2	42	46	27·513	1
45	23·746	4	43	47	24·033	3
46	20·260	5	44	48	20·496	3
			45	49	16·924	1

Wave numbers in brackets have been calculated using combination differences.

TABLE II (continued).

(11, 0) Band.

P Branch.			Q and R Branches.			
J.	ν.	Int.	J_Q.	J_R.	ν.	Int.
			7	9	15655·323	3
			8	10	54·655	3
			9	11	53·923	1
			10	12	53·241	6
			11	13	52·209	2
			12	14	51·348	3
11	15650·575	1	13	15	50·350	4
12	49·514	2	14	16	49·203	2
13	48·265	7	15	17	48·079	3
14	47·022	1	16	18	46·793	6
15	45·745	1	17	19	45·450	3
16	44·330	2	18	20	44·033	3
17	42·895	1	19	21	42·520	4
18	41·334	1	20	22	40·996	6
19	39·796	1	21	23	39·295	4
20	37·919	4	22	24	37·581	5
21	36·315	1	23	25	35·783	4
22	34·374	2	24	26	33·899	5
23	32·321	1	25	27	31·955	6
24	30·256	2	26	28	29·892	3
25	28·161	1	27	29	27·752	3
26	25·960	3	28	30	25·524	3
27	23·745	3	29	31	23·225	4
28	21·261	4	30	32	20·871	4
29	18·995	6	31	33	18·418	5
30	16·407	4	32	34	15·935	5
31	13·842	1	33	35	13·309	4
32	11·240	5	34	36	10·629	5
33	08·386	4	35	37	07·870	5
34	05·585	5	36	38	05·047	6
35	02·718	1	37	39	02·124	5
36	15599·761	3	38	40	15599·100	6
37	96·689	1	39	41	96·016	7
38	93·657	2	40	42	92·928	6
39	90·348	3	41	43	89·695	4
40	87·052	3	42	44	86·339	3
41	83·640	1	43	45	82·981	4
42	80·105	2	44	46	79·545	7
43	76·637	1	45	47	75·970	2
44	73·065	2	46	48	72·365	3
45	69·437	2	47	49	68·567	5
46	65·768	2	48	50	64·622	1
47	61·649	2	49	51	60·756	2
48	57·934	4	50	52	56·721	4
49	53·818	4	51	53	52·478	4
50	49·625	1	52	54	48·567	1
51	45·506	3	53	55	44·471	1

TABLE II (continued).

(8, 1) Band.

P Branch.			Q Branch.			R Branch.		
J.	ν.	Int.	J.	ν.	Int.	J.	ν.	Int.
	Unresolved from Q Branch.					4	14794·401	7
			3	14793·779	7	5	94·120	0
			4	93·510	1	6	93·779	7
			5	93·156	2	7	93·510	1
			6	92·697	2	8	93·156	2
			7	92·188	7	9	92·697	2
			8	91·721	2	10	92·188	7
			9	91·067	2	11	91·414	1
			10	90·371	2	12	90·733	1
			11	89·587	4	13	89·941	4
			12	88·746	7	14	89·161	2
			13	87·765	6	15	88·149	7
			14	86·803	4	16	87·268	3
			15	85·750	3	17	86·206	2
			16	84·588	5	18	85·113	2
			17	83·396	3	19	83·932	7
			18	82·119	4	20	82·652	2
			19	80·775	4	21	81·282	3
			20	79·351	5	22	80·006	3
			21	77·860	5	23	78·457	6
			22	76·267	7	24	76·889	3
			23	74·658	7	25	75·332	7
			24	72·945	6	26	73·588	3
			25	71·117	8	27	71·835	3
			26	69·347	6	28	70·012	3
			27	67·365	7	29	68·140	4
			28	65·346	5	30	66·116	2
			29	63·396	5	31	64·049	5
			30	61·285	5	32	61·974	6
			31	59·008	5	33	59·846	5
30	14756·661	4	32	56·827	6	34	57·463	6
31	54·262	4	33	54·486	4	35	55·204	4
32	51·838	5	34	52·110	6	36	52·778	5
33	49·361	3	35	49·583	4	37	50·317	3
34	46·803	4	36	46·989	6	38	47·820	6
35	44·137	5	37	44·406	5	39	45·146	3
36	41·395	2	38	41·722	5	40	42·458	4
37	38·581	3	39	38·983	5	41	39·753	5
38	35·692	4	40	36·079	5	42	36·873	3
39	32·895	5	41	33·151	10	43	33·961	2
40	29·866	2	42	30·181	2	44	31·007	2
41	26·811	2	43	27·129	3	45	27·956	6
42	23·689	4	44	24·021	4	46	24·761	4
43	20·468	1	45	20·874	4	47	21·614	2
44	17·213	9	46	17·517	8	48	18·380	4
45	13·840	2	47	14·163	3	49	15·078	4
46	10·377	1	48	10·817	4	50	11·620	4
47	06·844	2	49	07·257	2	51	08·197	3
48	03·314	3	50	03·701	2	52	04·660	2

TABLE II (continued).

(8, 1) Band (continued).

P Branch.			Q Branch.			R Branch.		
J.	ν.	Int.	J.	ν.	Int.	J.	ν.	Int.
49	14699·684	2	51	14700·085	4	53	14701·010	4
50	95·963	2	52	14696·410	5	54	14697·322	2
51	92·205	1	53	92·623	4	55	93·528	2
52	88·250	8	54	88·737	3	56	89·705	2
53	84·402	2	55	84·817	3	57	85·699	8
54	80·408	2	56	80·774	4	58	81·808	3
55	76·351	3	57	76·803	3	59	77·746	1
56	72·204	2	58	72·663	4	60	73·620	3
57	67·998	2	59	68·442	3	61	69·385	1
58	63·665	2	60	64·117	3	62	65·134	2
59	59·374	5	61	59·754	5	63	60·878	2
60	54·926	2	62	55·355	3	64	56·273	3
61	50·423	2	63	50·853	3	65	51·898	1
62	45·834	2	64	46·298	3	66	47·358	3
63	41·176	5	65	41·679	4	67	42·709	3
64	36·423	2	66	36·937	5	68	37·976	2
65	31·626	2	67	32·123	2	69	33·068	4
66	26·778	2	68	27·253	3	70		
			69	22·298	1			

(9,1) Band.

P and Q Branches.				R Branch.		
J_P.	J_Q.	ν.	Int.	J.	ν.	Int.
	2	14960·607	2	4	14960·997	6
1	3	60·336	3	5	60·607	2
2	4	59·987	2	6	60·336	3
3	5	59·566	10	7	59·987	2
4	6	59·26	1	8	59·566	10
5	7	58·770	1	9	59·064	1
6	8	58·111	1	10	58·492	1
7	9	57·562	4	11	57·823	4
8	10	56·871	5	12	57·124	4
9	11	56·094	3	13	56·313	4
10	12	55·206	5	14	55·425	3
11	13	54·286	7	15	54·521	7
12	14	53·156	6	16	53·496	7
13	15	52·111	5	17	52·447	6
14	16	50·961	5	18	51·323	4
15	17	49·733	7	19	50·021	2
16	18	48·419	5	20	48·693	2
17	19	47·042	6	21	47·318	2
18	20	45·569	6	22	45·986	1

TABLE II (continued).

(9, 1) Band (continued).

P and Q Branches.				R Branch.		
J_P.	J_Q.	ν.	Int.	J.	ν.	Int.
19	21	14944·014	5	23	14944·332	6
20	22	42·396	5	24	42·814	5
21	23	40·731	5	25	41·111	3
22	24	38·991	7	26	39·421	4
23	25	37·155	5	27	37·585	4
24	26	35·234	6	28	35·693	3
25	27	33·260	6	29	33·707	5
26	28	31·203	6	30	31·661	3
27	29	29·034	6	31	29·525	3
28	30	26·885	4	32	27·354	3
29	31	24·600	8	33	25·094	4
30	32	22·302	4	34	22·789	4
31	33	19·874	6	35	20·393	5
32	34	17·213	6	36	17·809	2
33	35	14·839	5	37	15·306	5
34	36	12·193	5	38	12·729	2
35	37	09·448	7	39	09·968	4
36	38	06·697	5	40	07·265	6
37	39	03·857	6	41	04·400	3
38	40	00·923	5	42	01·469	4
39	41	14897·909	5	43	14898·476	3
40	42	94·810	6	44	95·394	3
41	43	91·647	6	45	92·235	4
42	44	88·465	5	46	88·903	4
43	45	85·179	8	47	85·815	2
44	46	81·802	7	48	82·490	2
45	47	78·357	4	49	78·828	3
46	48	74·765	5	50	75·362	3
47	49	71·249	9	51	71·843	3
48	50	67·557	5	52	68·215	3
49	51	63·846	5	53	64·392	2
50	52	60·050	10	54	60·628	2
51	53	56·116	5	55	56·729	1
52	54	52·162	5	56	52·802	3
53	55	48·123	5	57	48·748	1
54	56	43·994	7	58	44·639	5
55	57	39·830	7	59	40·474	2
56	58	35·583	5	60	36·146	2
57	59	31·252	5	61	32·097	5
58	60	26·807	6	62	27·427	1
59	61	22·265	7	63	22·960	2
60	62	17·827	6	64	18·778	2
61	63	13·139	5	65	13·768	3
62	64	08·450	9	66	08·941	2
63	65	03·613	5	67	04·110	3
64	66	14798·875	4	68	14799·378	2
65	67	93·890	5	69	94·481	5
66	68	88·836	6	70	89·227	6
67	69	83·632	3	71	84·241	1

TABLE II (continued).

(9, 1) Band (continued).

P and Q Branches.				R Branch.		
J_P.	J_Q.	ν.	Int.	J.	ν.	Int.
68	70	14778·457	6	72	14779·100	1
69	71	73·233	3	73	73·937	1
70	72	67·931	4	74	68·486	4
71	73	62·602	5	75	63·231	5
72	74	57·078	2	76	57·463	6
73	75	51·519	5	77	52·110	6
74	76	45·894	4	78	46·507	1
75	77	40·130	3	79	40·765	3
76	78	34·350	3	80	35·005	2
77	79	78·632	3	81	29·310	2
78	80	22·732	6			
79	81	16·668	2			
80	82	10·377	1			
81	83	04·365	3			
82	84	14698·167	1			
83	85	91·871	1			
84						
85						

(10, 1) Band.

Q Branch.			P and R Branches.			
J.	ν.	Int.	J_P.	J_R.	ν.	Int.
9	15118·068	5				
10	17·305	6	8	12	15117·529	6
11	16·535	7	9	13	16·696	7
12	15·604	3	10	14	15·794	4
13	14·637	8	11	15	14·863	8
14	13·559	7	12	16	13·783	7
15	12·446	7	13	17	12·640	7
16	11·229	7	14	18	11·447	7
17	09·931	4	15	19	10·204	6
18	08·629	7	16	20	08·787	7
19	07·186	8	17	21	07·422	8
20	05·666	6	18	22	05·888	6
21	04·080	7	19	23	04·301	7
22	02·444	5	20	24	02·654	5
23	00·717	7	21	25	00·941	7
24	15098·905	3	22	26	15099·127	5
25	97·008	7	23	27	97·251	7
26	95·026	7	24	28	95·291	7
27	93·022	7	25	29	93·251	7
28	90·893	6	26	30	91·163	6
29	88·749	7	27	31	88·980	7

TABLE II (continued).

(10, 1) Band (continued).

Q Branch.			P and R Branches.			
J.	ν.	Int.	J_P.	J_R.	ν.	Int.
30	15086·475	7	28	32	15086·723	7
31	84·138	6	29	33	84·405	8
32	81·735	7	30	34	81·964	8
33	79·261	4	31	35	79·497	4
34	76·709	10	32	36	76·951	10
35	74·050	4	33	37	74·294	4
36	71·339	7	34	38	71·600	7
37	68·557	6	35	39	68·837	6
38	65·697	6	36	40	65·939	6
39	62·757	8	37	41	63·010	8
40	59·746	4	38	42	59·994	6
41	56·658	6	39	43	56·877	6
42	53·484	7	40	44	53·681	7
43	50·237	8	41	45	50·454	8
44	46·913	7	42	46	47·146	7
45	43·503	7	43	47	43·765	7
46	40·049	7	44	48	40·251	7
47	36·466	8	45	49	36·786	8
48	32·868	5	46	50	33·04	5
49	29·169	4	47	51	29·434	4
50	25·397	6	48	52	25·647	6
51	21·558	6	49	53	21·774	6
52	17·617	6	50	54	17·872	6
53	13·601	7	51	55	13·846	7
54	09·519	7	52	56	09·740	7
55	06·363	5	53	57	05·687	5
56	01·103	6	54	58	01·448	6
57	14996·752	7	55	59	14997·059	7
58	92·456	6	56	60	92·716	6
59	87·912	7	57	61	88·256	2
60	83·37	5	58	62	83·69	5
61	78·780	7	59	63	79·148	7
62	74·445	4	60	64	74·445	4
63	69·31	5	61	65	69·56	5
64	64·28	5	62	66	64·49	5
65	59·539	8	63	67	59·987	3
66	54·521	7	64	68	55·206	5
67	49·733	7	65	69	50·021	2
68	44·332	6	66	70	44·685	1
69	38·991	7	67	71	39·421	4
70	33·707	5	68	72	34·200	3
71	28·278	3	69	73	29·034	6
72	22·789	4	70	74	23·578	2
73	17·213	6	71	75	17·809	2
74	11·585	3	72	76	12·193	5
75	06·175	1	73	77	06·697	5
76	00·573	4	74	78	00·923	5
77	14894·810	6	75	79	14895·394	3
78	88·903	3				

TABLE II (continued).

(11, 1) Band.

P Branch.			Q and R Branches.			
J.	ν.	Int.	J_Q.	J_R.	ν.	Int.
	Unresolved from Q Branch.		4		15275·581	8
			5		75·135	6
			6		74·709	3
				8	74·531	3
			7		74·191	4
				9	73·950	4
			8		73·567	5
				10	73·295	5
			9	11	72·837	7
			10	12	71·985	10
			11	13	71·154	6
			12	14	70·222	5
			13	15	69·107	7
			14	16	68·046	4
			15	17	66·877	7
			16	18	65·706	7
15	15264·484	2	17	19	64·310	5
16	63·153	2	18	20	62·924	7
17	61·818	7	19	21	61·444	7
18	60·177	1	20	22	59·900	6
19	58·811	0	21	23	58·282	10
20	56·857	1	22	24	56·565	6
21	55·082	1	23	25	54·798	9
22	53·306	1	24	26	52·908	6
23	51·269	10	25	27	50·966	10
24	49·336	2	26	28	48·960	6
25	47·226	0	27	29	46·850	10
26	45·052	2	28	30	44·670	4
27	42·836	3	29	31	42·432	3
28	40·507	2	30	32	40·126	6
29	38·160	3	31	33	37·697	3
30	35·625	1	32	34	35·228	5
31	33·082	2	33	35	32·630	3
32	30·461	4	34	36	29·984	4
33	27·734	3	35	37	27·274	4
34	24·960	4	36	38	24·490	5
35	22·072	2	37	39	21·602	7
36	19·138	4	38	40	18·718	7
37	16·098	2	39	41	15·591	5
38	13·006	3	40	42	12·491	4
39	09·842	2	41	43	09·364	7
40	06·581	1	42	44	06·064	8
41	03·230	2	43	45	02·691	6
42	15199·880	4	44	46	15199·288	6
43	86·241	4	45	47	95·769	6
44	92·746	3	46	48	92·194	7
45	89·116	2	47	49	88·559	5

TABLE II (continued).

(11, 1) Band (continued).

P Branch.			Q and R Branches.			
J.	ν.	Int.	J_Q.	J_R.	ν.	Int.
46	15185·404	4	48	50	15184·744	8
47	81·544	3	49	51	80·947	10
48	77·722	10	50	52	77·073	8
49	73·759	2	51	53	73·035	5
50	69·649	3	52	54	69·023	6
51	65·580	5	53	55	64·913	6
52	61·890	3	54	56	60·671	4
53	57·325	5	55	57	56·360	7
54	52·790	6	56	58	52·013	7
55	48·334	5	57	59	47·497	3
56	44·133	11	58		43·003	4
				60	42·725	4
57	39·149	1	59		38·384	3
				61	38·170	5
58	34·497	2	60		33·708	2
				62	33·425	4
59	29·743	3	61		28·936	2
				63	28·636	2
60	24·822	7	62		24·142	5
				64	23·807	1
61	20·099	4	63		19·205	3
				65	18·922	3
62	14·863	8	64		14·143	3
				66	13·783	7
63	09·931	4	65		08·977	0
				67	08·629	7
			66		03·862	3
				68		
			67		15098·587	1
				69	98·223	1
			68		93·251	7
			69		87·823	2
			70		82·367	1
			71		76·951	10
			72		71·339	7

TABLE II (continued).

(12, 1) Band.

P Branch.			Q Branch.			R Branch.		
J.	ν.	Int.	J.	ν.	Int.	J.	ν.	Int.
			6	15422·978	2		Unresolved from Q Branch.	
			7	22·388	2			
			8	21·721	3			
			9	21·008	3			
			10	20·181	6			
			11	19·334	3			
			12	18·365	3			
			13	17·348	4			
			14	16·179	3			
			15	15·005	5			
14	15414·158	1	16	13·709	5			
15	12·886	5	17	12·358	5			
16	11·399	2	18	10·912	5			
17	09·786	3	19	09·383	6			
18	08·326	3	20	07·796	5			
19	06·615	1	21	06·146	5			
20	04·849	1	22	04·389	5			
21	03·144	1	23	02·502	5			
22	01·116	1	24	00·583	5			
23	15399·215	4	25	15398·570	5			
24	97·073	1	26	96·491	5			
25	94·959	2	27	94·312	6			
26	92·876	4	28	92·256	5			
27	90·405	2	29	89·709	8			
28	88·051	1	30	87·350	4			
29	85·522	1	31	84·980	7	33	15384·708	4
30	82·988	3	32	82·374	4	34	82·151	3
31	80·418	1	33	79·717	4	35	79·480	2
32	77·701	1	34	77·012	4	36	76·727	4
33	74·928	4	35	74·227	4	37	73·928	2
34	71·948	3	36	71·303	4	38	71·003	5
35	69·004	2	37	68·342	3	39	68·025	1
36	66·042	1	38	65·299	3	40	64·960	1
37	62·928	2	39	62·214	4	41	61·832	2
38	59·884	3	40	58·953	4	42	58·573	2
39	56·480	2	41	55·678	4	43	55·322	2
40	53·198	3	42	52·342	4	44	51·919	2
41	49·722	2	43	48·849	3	45	48·424	3
42	46·211	2	44	45·315	3	46	44·893	2
43	42·598	1	45	41·703	6	47	41·267	5
44	38·976	5	46	38·007	6	48	37·542	3
45	35·283	4	47	34·246	6	49	33·804	3
46	31·295	3	48	30·350	4	50	29·826	4
47	27·410	2	49	26·500	6	51	25·830	2
48	23·389	5	50	22·380	5	52	21·721	4
49	19·305	1	51	18·330	5	53	17·673	3
50	15·063	2	52	14·109	5	54	13·534	1
51	10·901	2	53	09·859	6	55	09·294	1
52	06·662	2	54	05·361	7	56	04·879	1
53	02·106	1	55	01·065	7	57	00·552	7

TABLE II (continued).

(12, 1) Band (continued).

P Branch.			Q Branch.			R Branch.		
J.	ν.	Int.	J.	ν.	Int.	J.	ν.	Int.
54	15297·627	1	56	15296·495	4	58	15295·863	3
55	93·182	1	57	91·940	3	59	91·285	1
56	88·452	1	58	87·200	6	60	86·535	2
57	83·681	1	59	82·535	4	61	81·733	3
58	78·765	2	60	77·630	3	62	76·919	1
59	73·950	3	61	72·792	5	63	72·016	6
60	69·145	7	62	67·661	2	64	67·199	1
61	63·876	1	63	62·576	1	65	61·818	7
62	58·811	0	64	57·372	1	66	56·560	6
63	53·405	0	65	52·027	1	67	51·257	10
64	48·227	1	66	46·850	10	68	45·976	3
65	42·836	3	67	41·363	1	69	40·507	2
66	37·697	3	68	35·862	2	70	35·228	5
67	31·818	2	69	30·461	4			
			70	24·960	4			
			71	19·343	5			

(13, 1) Band.

P Branch.			Q Branch.			R Branch.		
J.	ν.	Int.	J.	ν.	Int.	J.	ν.	Int.
			1	15566·832	3		Unresolved from Q Branch.	
			2					
			3	66·245	3			
			4					
			5	65·432	8			
			6	64·898	5			
5	15564·622	1	7	64·350	3			
6	64·062	0	8	63·684	4			
7	63·301	0	9	62·942	4			
8	62·567	4	10	62·100	3			
9	61·649	2	11	61·168	5			
10	60·704	2	12	60·236	6			
11	59·612	2	13	59·139	4			
12	58·495	1	14	57·934	4			
13	57·220	1	15	56·721	4			
14	55·960	2	16	55·383	6			
15	54·587	1	17	54·038	5			
16	53·079	4	18	52·478	4			
17	51·574	1	19	50·981	4	21	15550·802	1
18	49·939	2	20	49·333	4	22	49·091	1

TABLE II (continued).

(13, 1) Band (continued).

P Branch.			Q Branch.			R Branch.		
J.	ν.	Int.	J.	ν.	Int.	J.	ν.	Int.
19	15548·266	2	21	15547·592	4	23	15547·338	2
20	46·513	2	22	45·742	4	24	45·506	3
21	44·631	4	23	43·902	4	25	43·603	1
22	42·609	1	24	41·944	4	26	41·577	1
23	40·491	3	25	39·824	5	27	39·529	2
24	38·510	2	26	37·693	4	28	37·317	2
25	36·231	3	27	35·469	3	29	35·042	2
26	33·938	2	28	33·204	4	30	32·735	2
27	31·633	3	29	30·747	3	31	30·281	2
28	29·070	4	30	28·289	2	32	27·840	2
29	26·550	1	31	25·715	3	33	25·239	1
30	24·036	2	32	23·057	2	34	22·563	3
31	21·255	1	33	20·311	5	35	19·839	1
32	18·490	2	34	17·507	4	36	16·918	2
33	15·611	1	35	14·646	3	37	14·055	2
34	12·678	3	36	11·645	2	38	11·033	3
35	09·605	2	37	08·593	4	39	07·940	1
36	06·612	2	38	05·442	2	40	04·801	1
37	03·302	2	39	02·207	5	41	01·590	3
38	00·004	1	40	15498·868	2	42	15498·286	2
39	15496·713	1	41	95·494	3	43	94·790	2
40	93·210	2	42	92·008	3	44	91·110	2
41	89·691	2	43	88·424	9	45	87·618	1
42	86·049	1	44	84·819	2	46	84·046	2
43	82·286	2	45	81·062	1	47	80·140	4
44	78·541	1	46	77·246	2	48	76·382	3
45	74·619	1	47	73·321	2	49	72·451	1
46	70·694	1	48	69·345	3	50	68·464	1
47	66·629	2	49	65·251	6	51	64·302	2
48	62·525	4	50	61·093	2	52	60·167	5
49	58·301	1	51	56·881	1	53	55·941	1
50	54·029	0	52	52·558	1	54	51·522	1
51	49·570	3	53	48·117	2	55	47·054	1
52	45·095	1	54	43·601	3	56	42·592	1
53	40·527	3	55	39·052	2	57	37·895	1
54	35·914	0	56	34·256	3	58	33·183	1
55	31·246	0	57	29·598	1	59	28·354	1
56	26·462	0	58	24·778	3	60	23·746	4
57			59	19·787	2	61	18·693	2
58	16·590	4	60	14·810	4	62	13·709	5
59	11·399	2	61	09·786	3			
60	06·146	5	62	04·389	5			
			63	15399·215	4			
			64	93·884	1			
			65	88·519	2			
			66	83·988	3			
			67	77·326	1			

TABLE II (continued).

(14, 1) Band.

P Branch.			Q Branch.			R Branch.		
J.	ν.	Int.	J.	ν.	Int.	J.	ν.	Int.
			4	15701·225	3			
			5	00·778	2			
			6	00·233	3		Unresolved from Q Branch.	
			7	15699·630	3			
			8	98·964	6			
			9	98·163	3			
			10	97·394	1			
			11	96·431	1			
			12	95·419	3			
			13	94·280	1	15	15693·998	8
			14	93·134	4	16	92·863	1
13	15692·423	1	15	91·815	4	17	91·582	2
14	91·105	2	16	90·448	2	18	90·156	1
15	89·643	5	17	88·991	6	19	88·690	1
16	88·189	1	18	87·469	4	20	87·117	3
17	86·527	2	19	85·844	4	21	85·453	1
18	84·898	1	20	84·120	4	22	83·723	4
19	83·169	1	21	82·343	3	23	81·879	4
20	81·366	3	22	80·486	3	24	80·013	3
21	79·393	1	23	78·511	3	25	78·014	1
22	77·359	3	24	76·466	6	26	75·946	4
23	75·280	3	25	74·314	4	27	73·775	4
24	73·065	2	26	72·099	5	28	71·510	7
25	70·805	2	27	69·788	3	29	69·190	2
26	68·485	2	28	67·408	5	30	66·742	6
27	65·930	1	29	64·951	3	31	64·229	2
28	63·587	1	30	62·379	2	32	61·684	2
29	60·939	1	31	59·739	3	33	59·024	2
30	58·195	2	32	57·052	10	34	56·205	4
31	55·323	3	33	54·167	5	35	53·241	6
32	52·472	5	34	51·348	8	36	50·350	4
33	49·514	2	35	48·265	7	37	47·465	1
34	46·466	0	36	45·175	1	38	44·330	2
35	43·254	2	37	41·994	4	39	40·996	6
36	40·104	2	38	38·740	5	40	37·731	5
37	36·829	1	39	35·411	4	41	34·374	2
38	33·433	1	40	31·955	6	42	30·981	0
39	29·892	3	41	28·513	2	43	27·444	1
40	26·385	1	42	24·815	3	44	23·745	3
41	22·730	1	43	21·261	4	45	20·108	2
42	18·995	6	44	17·412	2	46	16·213	4
43	15·120	2	45	13·534	4	47	12·336	1
44	11·240	5	46	09·608	2	48	08·386	4
45	07·204	1	47	05·585	5	49	04·352	1
46	03·182	2	48	01·518	2	50	00·129	1
47	15599·100	6	49	15597·294	2	51	15596·016	7
48	94·714	1	50	92·928	6	52	91·511	3
49	90·348	3	51	88·541	2	53	87·052	3
50	85·960	1	52	84·122	2	54	82·577	1
51	81·451	1	53	79·545	7	55	78·020	1
52	76·902	2	54	74·858	2	56	73·254	2

Table II (continued).

(14, 1) Band (continued).

P Branch.			Q Branch.			R Branch.		
J.	ν.	Int.	J.	ν.	Int.	J.	ν.	Int.
53	15572·161	1	55	15570·133	2	57	15568·567	5
54	67·347	1	56	65·432	8	58	63·684	4
55	62·567	4	57	60·704	2	59	58·671	1
56	57·478	1	58	55·960	2	60		
57	52·478	4	59	50·981	4	61	48·567	1
58	47·338	2	60	45·742	4	62	43·291	4
59	41·944	4	61	40·491	3	63	37·897	2
60	36·816	2	62	35·042	2	64	32·407	2
61	31·317	2	63	29·536	0			
62	25·715	3	64	24·036	2			
63	20·311	5	65	18·490	2			
64	14·646	3	66	12·678	3			
65	08·878	3						
66	02·903	2						

(10, 2) Band.

Q Branch.			P and R Branches.			
J.	ν.	Int.	J.	J.	ν.	Int.
27	14715·078	4				
28	12·977	3	26	30	14713·204	2
29	10·817	4	27	31	11·140	3
30	08·626	5	28	32	(08·91)	
31	06·428	5	29	33	06·696	3
32	03·982	2	30	34	04·365	3
33	01·613	3	31	35	01·944	3
34	14699·089	4	32	36	14699·359	2
35	96·401	5	33	37	96·883	2
36	93·769	2	34	38	94·074	2
37	91·057	3	35	39	91·288	2
38	88·250	8	36	40	88·474	2
39	85·349	7	37	41	85·699	8
40	82·318	5	38	42	82·655	2
41	79·301	5	39	43	79·555	5
42	76·210	3	40	44	76·351	3
43	72·981	4	41	45	73·290	2
44	69·743	5	42	46	70·007	1
45	66·383	1	43	47	66·655	1
46	62·979	3	44	48	63·217	2
47	59·374	5	45	49	59·754	5
48	55·922	3	46	50	56·273	3
49	52·189	4	47	51	52·534	4
50	48·447	4	48	52	48·787	2

Wave numbers in brackets were calculated using combination differences.

TABLE II (continued).

(11, 2) Band.

Q and R Branches.				P Branch.		
J.	J.	ν.	Int.	J.	ν.	Int.
22	24	14878·357	4			
23	25	76·749	6			
24	26	74·904	1			
25	27	73·118	3		Unresolved from Q Branch.	
26	28	71·249	9			
27	29	69·069	1			
28	30	66·912	4			
29	31	64·716	3			
30	32	62·440	4			
31	33	60·050	10	29	14860·628	2
32	34	57·640	6	30	(57·9)	
33	35	55·050	6	31	(55·4)	
34	36	52·451	4	32	52·802	3
35	37	49·750	4	33	50·171	1
36	38	47·029	5	34	47·337	1
37	39	44·109	7	35	44·639	5
38	40	41·266	4	36	41·670	1
39	41	38·264	4	37	38·645	1
40	42	35·199	4	38	35·583	5
41	43	32·097	5	39	32·415	2
42	44	—		40	(29·13)	
43	45	25·515	3	41	25·954	1
44	46	22·265	7			
45	47	18·778	2			

Wave numbers in brackets were calculated using combination differences.

Rotational Term Differences and Constants.

Since the bands are of the $^3\Pi_1 \leftarrow {}^1\Sigma$ type* one would expect to find combination relationships between the P and R lines of the form

$$R\,(J-1) - P\,(J+1) = F''\,(J+1) - F''\,(J-1)$$
$$\text{and } R\,(J) - P\,(J) = F'\,(J+1) - F'\,(J-1)$$

The former should give identical values for the same J and v'', whatever the value of v', and the latter identical values for the same J and v'. Supposing, as is undoubtedly so here, that F′ refers to the Π state, it will be subject to Λ type doubling, and one component only will be concerned in the R, P differences. It can therefore be determined directly from them, whereas for the other component, which gives rise to the Q branches, no similar differences can be formed, and it can therefore only be evaluated indirectly. In the present band the separation of the two components is very small, and it has been thought sufficient to determine the former alone accurately, although some discussion will be given later of the manner in which the doublet separation varies with J.

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* BROWN and GIBSON, 'Phys. Rev.,' vol. 40, p. 529 (1932); SCHLAPP, *ibid.*, vol. 39, p. 806 (1932).

TABLE III.—Rotational Term Differences for $v'' = 0$.

$$R(J-1) - P(J+1) = F''(J+1) - F''(J-1).$$

J. \ v'	9	10	11
10			4·748
11			5·141
12		5·463	5·658
13		5·900	6·219
14		6·520	6·464
15		7·073	7·018
16		7·607	7·455
17		7·965	7·869
18		8·455	8·283
19		8·939	8·874
20		9·381	9·135
21		9·832	9·659
22	10·238	10·171	10·199
23	10·808	10·733	10·740
24	11·209	11·182	11·134
25	11·677	11·681	11·621
26	12·103	12·133	12·038
27	12·587	12·561	12·638
28	12·969	13·002	12·960
29	13·455	13·528	13·485
30	13·943	14·029	13·910
31	14·280	14·411	14·284
32	14·803	14·872	14·839
33	15·329	15·336	15·286
34	15·739	15·831	15·700
35	16·195	16·252	16·174
36	16·798	16·566	16·620
37	17·119	17·113	16·972
38	17·638	17·550	17·522
39	18·047	17·987	17·995
40	18·427	18·470	18·474
41	18·879	18·967	18·995
42	19·332	19·578	19·379
43	19·915	20·031	19·863
44	20·514	20·469	20·258
45	20·780		20·571
46	21·125		21·332
47	21·613		21·611
48	22·020		22·152
49	22·571		22·740
50	22·949		23·061
51	23·500		
52	23·926		

TABLE III (continued).—Rotational Term Differences for $v'' = 1$.

$R(J-1) - P(J+1) = F''(J+1) - F''(J-1)$.

v' / J.	8	9	10	11	12	13	14
4						2·210	
5	2·680	2·886					
6	3·053	3·045				2·944	
7	3·408	3·465					
8	3·923	3·893				3·783	
9	4·410	4·360		4·309		4·194	
10	4·932	4·778		4·843		4·738	
11	5·385	5·336		5·249		5·189	
12	5·664	5·712		5·960		5·722	
13	6·145	6·163	6·082	6·279	6·023	6·140	
14	6·545	6·580	6·492	6·670	6·448	6·581	
15	7·042	7·006	7·007	7·069	6·966	7·157	
16	7·374	7·479	7·441	7·289	7·562	7·565	7·471
17	7·917	7·927	7·895	7·869	7·853	7·995	7·965
18	8·346	8·433	8·339	8·066	8·390	8·455	8·413
19	8·846	8·927	8·793	8·849	8·860	8·870	8·790
20	9·274	9·290	9·263	9·228	9·214	9·407	9·297
21	9·707	9·702	9·660	9·618	9·796	9·869	9·758
22	10·165	10·163	10·171	10·175	10·168	10·311	10·173
23	10·659	10·752	10·597	10·563	10·723	10·581	10·658
24	11·092	11·072	11·050	11·056	11·187	11·107	11·074
25	11·543	11·611	11·491	11·513	11·513	11·568	11·528
26	11·936	12·077	11·961	11·962	12·097	11·970	12·084
27	12·450	12·536	12·404	12·401	12·532	12·507	12·459
28	12·827	12·985	12·846	12·806	13·048	12·979	12·836
29	13·351	13·391	13·327	13·335	13·503	13·281	13·315
30	13·878	13·833	13·754	13·768	13·894	13·787	13·867
31	14·278	14·448	14·212	14·209	14·296	14·245	14·270
32	14·688	14·686	14·686	14·698	14·781	14·670	14·715
33	15·171	15·161	15·123	15·166	15·402	15·162	15·218
34	15·709	15·646	15·568	15·625	15·704	15·634	15·770
35	16·068	16·092	16·025	16·090	16·109	15·951	16·101
36	16·623	16·536	16·487	16·532	16·552	16·537	16·412
37	17·086	16·886	16·957	16·978	16·843	16·914	16·917
38	17·422	17·397	17·417	17·432	17·448	17·342	17·573
39	17·954	17·919	17·919	17·909	17·805	17·823	17·945
40	18·335	18·321	18·383	18·372	18·303	18·249	18·266
41	18·769	18·800	18·793	18·838	18·749	18·752	18·736
42	19·285	19·221	19·245	19·350	19·240	19·304	19·254
43	19·660	19·667	19·743	19·745	19·597	19·745	19·741
44	20·121	20·119	20·091	20·248	20·039	20·171	20·240
45	20·630	20·629	20·64	20·660	20·624	20·416	20·563
46	21·112	20·986	21·020	21·147	21·014	20·989	21·008
47	21·447	21·346	21·499	21·566	21·504	21·521	21·499
48	21·930	21·969	21·991	22·010	21·962	21·839	21·988
49	22·417	22·440	22·379	22·545	22·479	22·233	22·426
50	22·873	22·812	22·940	22·979	22·903	22·881	22·901
51	23·370	23·200	23·30	22·854	23·164	23·369	23·227
52	23·795	23·720	23·747	23·622	23·724	23·775	23·855
53	24·252	24·221	24·199	24·283	24·094	24·253	24·164
54	24·659	24·562	24·715	24·701	24·491	24·695	24·485
55	25·118	25·045	25·156	24·890	25·082	25·060	25·099

TABLE III (continued).—Rotational Term Differences for $v'' = 1$.

$R\ (J - 1) - P\ (J + 1) = F''\ (J + 1) - F''\ (J - 1)$—continued.

v' J.	8	9	10	11	12	13	14
56	25·530	25·477	25·590	25·764	25·613		25·542
57	26·040	25·995	26·05	26·174	26·114	26·002	25·916
58	26·325	26·483	26·539	26·617	26·602	26·496	26·623
59	26·882	26·812	27·003	27·191	26·718	27·037	26·868
60	27·323	27·335	27·50	27·398	27·409		27·354
61	27·786	27·696	28·23	27·862	27·724		
62	28·209	28·484	28·269	28·239	28·328		28·256
63	28·711	28·552	28·48		28·692		28·645
64	29·252	29·070	29·127		29·180		29·019
65	29·495	29·942	29·760		29·502		29·504
66		30·136	30·14		30·000		
67		30·484	30·29				
68		30·877	30·953				
69		31·447	31·628				
70		31·879	32·212				
71		32·149	32·492				
72		32·722	32·724				
73		33·206	33·277				
74		33·807	33·640				
75		34·136					
76		34·599					
77		34·731					
78		35·442					
79		36·130					
80		36·400					
81		36·838					
82		37·439					
83							
84							
85							

TABLE III (continued).—Rotational Term Differences for $v'' = 2$.

$$R(J-1) - P(J+1) = F''(J+1) - F''(J-1).$$

v' / J.	10	11
28		12·490
29		13·349
30		13·669
31	13·845	14·110
32	14·257	14·545
33	14·836	15·103
34	15·408	15·411
35	15·891	15·970
36	16·245	16·405
37	16·704	16·868
38	17·328	17·335
39	17·723	17·899
40	17·998	18·155
41	18·467	
42	19·044	
43	19·438	
44	19·801	
45	20·078	
46	20·756	
47	21·220	

The lower state differences for $v'' = 0, 1$, and 2 are collected in Table III. There are three sets of values for $v'' = 0$ ($v' = 9$–11) seven for $v'' = 1$ ($v' = 8$–14) and two for $v'' = 2$ ($v' = 10, 11$). The order of agreement between the respective sets gives some indication of the accuracy of the original wave numbers. As has already been pointed out, this is rather low on account of the prevalence of blending, deviations from the mean of about 0·1 cm^{-1} being quite frequent, but by using suitable methods it has nevertheless been possible to derive accurate values of the rotation constants. The upper state differences, R (J) — P (J), have not been tabulated.

The usual expression for the rotation terms is of the form $F(J) = BJ(J+1) + DJ^2(J+1)^2$, with higher terms in J if required. In this case they are not, and, in fact, D is so small that it was found impossible to determine it satisfactorily from the differences themselves. They are given by

$$F(J+1) - F(J-1) = (4J+2)\{B + 2D(J^2+J+1)\}$$

A preliminary value of B was first obtained by dividing each difference by (4J + 2). Since D is very small, these quotients tend to a constant value (*i.e.*, B) as J decreases. D was then calculated for each vibration state in the following manner. The value, D_e, appropriate to the equilibrium state of the molecule was first obtained from the expression $D_e = -\frac{4B_e^3}{\omega_e^2}$. D_v was then calculated from the formulæ

$$D_v = D_e + \beta(v + \tfrac{1}{2})$$

and

$$\beta = \frac{\alpha^2}{6\omega_e} + \frac{20\,B_e^{\,2}\,\alpha - 32\,B_e^{\,3}\,x_e}{\omega_e^{\,2}},$$

where the symbols have their usual meanings in band spectrum notation.*

Some difficulty was occasioned by the fact that in this case neither B_v nor ω_v are accurately linear functions of v, as assumed in the definitions of α and x_e, with the consequence that neither of these quantities is strictly constant. The correction to B which is in question is so small, however, that it appeared to be quite satisfactory to use mean values for α and x_e.

D_v having been determined, it becomes possible to calculate the term involving it, subtract this from the observed combination difference and thence derive an improved value of B. If such a value is found from each difference, its probable error will be inversely as $(4J + 2)$, since all the differences are of the same order of accuracy and each is divided by $(4J + 2)$. It is therefore preferable to form the sum of the differences and divide by $\Sigma\,(4J + 2)$. This gives equal weight to all the observations and also necessitates considerably less labour. It has the further advantage of greatly simplifying the application of the D correction. We have, for example,

$$R(J-1) - P(J+1) = B''(4J+2) + D''(J+1)^2(J+2)^2 - D''(J-1)^2J^2,$$

and it is evident that if a summation is carried out over a series of consecutive J values the second and third terms on the right-hand side will cancel out, except for two involving the lowest J's and two involving the highest J's. If the former J's are sufficiently low (say, below 20), the D″ term is negligible, since D″ is of the order of 4×10^{-8}, so that we have

$$\Sigma_J\{R(J-1) - P(J+1)\} = B''\Sigma_J(4J+2) + D''J^2(J+1)^2 + D''(J+1)^2(J+2)^2$$

and therefore

$$B'' = \frac{\Sigma_J\{R(J-1) - P(J+1)\} - 2D''(J+1)^2(J^2+2J+2)}{2\Sigma_J(2J+1)}.$$

A corresponding expression may readily be obtained for B′, making use of the R(J) — P(J) differences. In order that the resulting values should approximate to the same order of accuracy, each series was terminated immediately before the head of the next band in the same progression, since the congestion of strong lines in these regions was always apt to render identification uncertain. On account of the gradually decreasing separation of the heads as v' increases this limiting value of J falls from 65 for $v' = 8$ to 53 for $v' = 14$. The initial value of J depends on how near to the origin the branches can be traced, and varies from $4(v' = 8)$ to $15(v' = 14)$. The methods outlined above were applied in the first instance to the bands $v'' = 1$, $v' = 8 - 14$, but considering the quantity of data the results were somewhat disappointing; the seven values of B″,

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* See Jevons, "Report," pp. 26–29.

for example, varied from the mean by as much as 0·05%, whereas one might reasonably have hoped for an agreement of the order of 0·01%. Such an expectation is, however, based on the assumption that the errors due to blending are fortuitous. This, no doubt, is sometimes legitimate, but it is certainly not so for $v' = 9 - 11$, in each of which two branches are unresolved throughout, with the consequent probability of serious systematic error. This will be greatest when it is the P and R branches which are superposed, since the errors of the two are bound to be opposite in sign and therefore additive when the combination differences are taken. The band $v' = 10$, in which the P and R branches are unresolved, does, in fact, show the largest discrepancy. The values of B′ showed, as usually, an approximately linear variation with v', but again there were pronounced irregularities. In order to examine the nature of these more closely, the two sets of differences between successive values of B were plotted. There appeared to be a certain correspondence between them, and this suggested a method of using the B″ values to correct those of B′. The basis of this is the fact that since the same lines are used in both, except for several at the ends of the series, the error in B resulting from errors, systematic or otherwise, in the original wave numbers, should be the same in both. But we know that the B″ values should all be identical; although they differ appreciably the mean of the seven cannot be much in error, and the deviations from the mean can therefore be applied, with due regard to sign, as corrections to the B′ values. When this was done, a very great improvement in the regularity of the B′ differences was apparent; in fact, they lay extremely well on a straight line, except for the two involving B'_{10}. The end lines involved were therefore carefully examined to see whether any of them appeared to be abnormally inaccurate, as judged by their position relatively to the neighbouring lines of the branch. If we denote by J_f and J_l the first and last J values in question, so that the first and last differences are $F(J_f + 1) - F(J_f - 1)$ and $F(J_l + 1) - F(J_l - 1)$, respectively, the following lines enter into the determinations :—

B″, R branch from $J_f - 1$ to $J_l - 1$
P ,, ,, $J_f + 1$ to $J_l + 1$
B′, R ,, ,, J_f to J_l
P ,, ,, J_f to J_l

The lines which are not common are therefore $R(J_f - 1)$, $R(J_l)$, $P(J_f)$ and $P(J_l + 1)$, and for $v' = 10$ $J_f = 12$ and $J_l = 61$. It was found that P (62) was about 0·4 cm.$^{-1}$ below and P(12) about 0·2 above their respective interpolated wave numbers. The consequent corrections were $-0·000054$ to B″ and $+0·000027$ to B′, and when these were applied the new value of B′ appeared quite satisfactory.

The results of the above procedure are shown graphically in fig. 2, in which the successive differences $B'_v - B'_{v+1}$ are plotted against v, the corresponding values of the B″ differences being also shown. The final corrected B′ differences lie very well on a straight line, indicating that a term in v'^2 is required for the representation of B'_v, in addition to the usual constant and term in v'.

Having obtained an accurate set of B' values, we can now similarly make use of them to correct the B'' values derived from the other two progressions, $v''=0$ and $v''=2$. For the former we have three bands available, viz., $v'=9-11$, and these yield the following preliminary B_0'' values :—

v'	9	10	11
B_0''	0·114213	0·114305	0·113739
B'	0·077304	0·076294	0·074553

If we now assume the correctness of the B' values derived from the $v''=1$ progression, viz.,

	0·076987	0·075874	0·074699,	we get the
corrections	— 0·000318	— 0·000420	+ 0·000146,	and thence
the B_0'' values	0·113895	0·113885	0·113885,	in very much

better agreement (0·01% instead of 0·5%) than before.

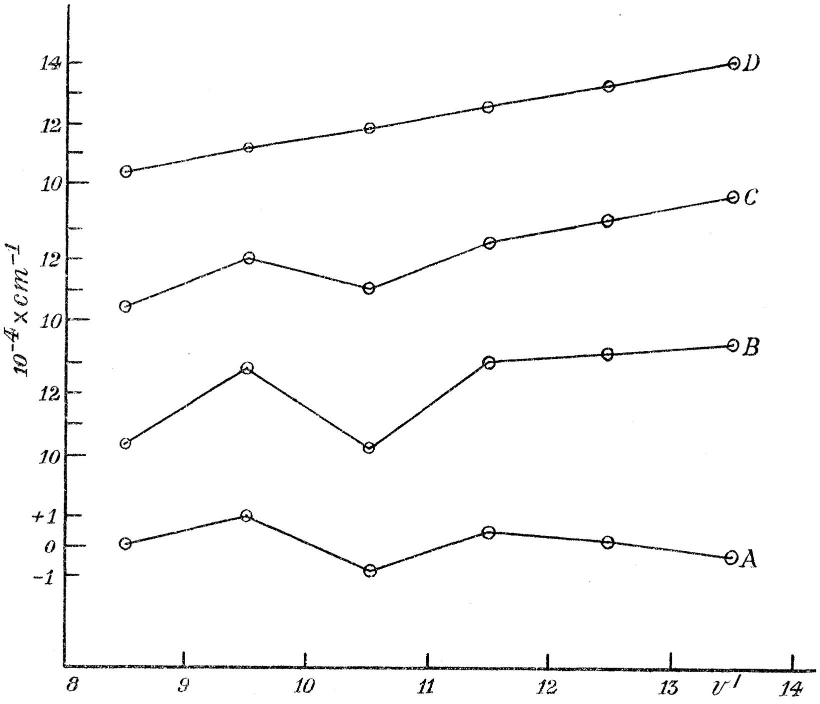

FIG. 2.—Correction of B' values by means of B''. $A = \Delta B''$; $B = \Delta B'$ from original data ; $C = \Delta B'$ after applying corrections from B'' values ; D = final $\Delta B'$ after adjusting two wave numbers in (10, 1).

For B_2'', we have only two bands available, $v'=10$ and 11, and for each a very small range of J values, so that the results are considerably less accurate. The original B'' values were 0·11152 and 0·11256 respectively, which after correction as above become 0·11274 and 0·11290.

The final results are collected in Table IV.

TABLE IV.—Values of B.

v''	0		1		2	
B''	0·11389		0·113366		0·11282	cm.$^{-1}$
$\Delta_1 B''$		+0·00052		+0·00055		

v'	8		9		10		11		12		13		14
B'	0·078019		0·076987		0·075874		0·074699		0·073445		0·072124		0·070723
$\Delta_1 B'$		+0·001032		0·001113		0·001175		0·001254		0·001321		0·001401	
$\Delta_2 B'$			−0·000081		0·000062		0·000079		0·000067		0·000080		

Extrapolation of the B'' values gives $B''_e = 0 \cdot 11414$, whence $r''_e = 2 \cdot 3150$A.

In order to determine B'_e it is necessary to extrapolate from $v' = 8$ to $v' = -\frac{1}{2}$, and a least squares formula was therefore calculated from the seven B' values above. The result was as follows :—

$$B'_v = 0 \cdot 083890 - 3 \cdot 828 \times 10^{-4} (v' + \tfrac{1}{2}) - 3 \cdot 622 \times 10^{-5} (v' + \tfrac{1}{2})^2$$

This gave an exceedingly good fit, the O − Cs being -1, $+3$, -3, $+1$, -1, $+3$ and -1×10^{-7}. That is to say, the maximum discrepancy between observed and calculated values was of the order of 0·004%.

The value of B'_e is thus 0·083890 cm.$^{-1}$, corresponding to $r'_e = 2 \cdot 7001$A. Also $B'_0 = 0 \cdot 083689$, $r'_0 = 2 \cdot 7033$.

In spite of the good fit of the formula it must be admitted that the long extrapolation renders these values somewhat uncertain, especially as discontinuities in the B, v curve are liable to occur.* DARBYSHIRE's conclusion,† that a break in the ω', v' curve occurs in the neighbourhood of $v' = 10$, should be mentioned here, since it would in all probability be associated with a similar break in the B', v' curve. There is no sign of this in the observed values, but they do not extend far enough below $v' = 10$ to rule it out.

Determination of Band Origins.

The rotational constants being known, it is now possible to calculate the rotation term values, and hence the band origins (ν_0), merely by taking the difference between the two rotation terms concerned and subtracting this from the wave number of the line in question.‡ A separate value of ν_0 is thus obtainable from every line, but these differ a good deal in weight. Those derived from lines of low J would naturally be the more reliable as involving a shorter extrapolation, but this is usually offset by a

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* *E.g.*, in Cl_2. See ELLIOTT, 'Proc. Roy. Soc.,' A, vol. 127, p. 627 (1930).

† 'Phys. Rev.,' vol. 40, p. 366 (1932).

‡ See MULLIKEN, 'Phys. Rev.,' vol. 36, p. 703 (1930).

greater probable error in the wave numbers, owing to the congestion of lines near the origin. The procedure adopted was to calculate separate values of ν_0 from every P and R line up to J = 35, plot them and estimate from the graph the most probable value of ν_0. In this way it was possible to eliminate bad observations and to attach suitable relative weights to the P and R results if one of them was affected by systematic blending. The results are given in Table V.

Table V.—Origins of Bands.

v'' v'	0		1		2	Δ G′
8			14794·24			
			166·55			*166·55*
9	15342·01	*381·22*	14960·79			
	160·73		*160·65*			*160·69*
10	15502·74	*381·30*	15121·44	*378·34*	14743·10	
	154·64		*154·71*		*154·75*	*154·70*
11	15657·38	*381·23*	15276·15	*378·30*	14897·85	
			148·45			*148·45*
12			15424·60			
			142·07			*142·07*
13			15566·67			
			135·40			*135·40*
14			15702·07			
ΔG″		*381·25*		*378·32*		

The individual differences are in no case more than 0·05 cm.$^{-1}$ from the mean, a considerable improvement on the previous values, which were derived from measurements of band heads. It may be noted that the latter are consistently a few tenths of a wave number to the red side of the origins, whereas the calculated displacements are from 0·2 to 0·3 cm.$^{-1}$ in the opposite direction. This is probably because of the low intensity of the early R lines composing the head. The settings made on unresolved heads no doubt refer to the Q branches, which are much stronger. The new data are so much more accurate than the old that it should be possible to use them in testing Darbyshire's conclusion, based on vibrational data alone, that a discontinuity in the law of force occurs in the neighbourhood of $v' = 10$. The second differences, which run as follows, 5·90, 5·94, 6·26, 6·38, 6·67, appear to give some support, although the irregularity is not certainly outside the range of experimental error.

In order to investigate the question more closely a least squares cubic was calculated for the progression $v'' = 1$, with the following result :—

$$\nu = 13172{\cdot}659 + 209{\cdot}7519\ (v' + \tfrac{1}{2}) - 1{\cdot}94741\ (v' + \tfrac{1}{2})^2 - 0{\cdot}033661\ (v' + \tfrac{1}{2})^3$$

The observations definitely could not be represented satisfactorily without the cubic term. The O — C values are

$v' =$	8	9	10	11	12	13	14
O — C =	— 0·016	+ 0·024	— 0·023	+ 0·005	— 0·009	+ 0·016	— 0·007

It may be significant that the largest discrepancies occur for $v' = 9$ and 10, but they are too small to be acceptable as evidence. More definite indications were obtained by plotting the differences between the observed wave numbers of heads* and the wave numbers of origins calculated from the above formula. The former should be from 0·2 to 0·3 cm.$^{-1}$ higher, as already explained, but an additional systematic discrepancy is to be expected below $v' = 8$ due to extrapolation error. The deviations given above between the calculated origins and those directly determined in this work are too small to show on the scale used. It will be seen from fig. 3 that there is a strong suggestion of a break at about $v' = 9$, as found by DARBYSHIRE, which can hardly be due to extrapolation error.

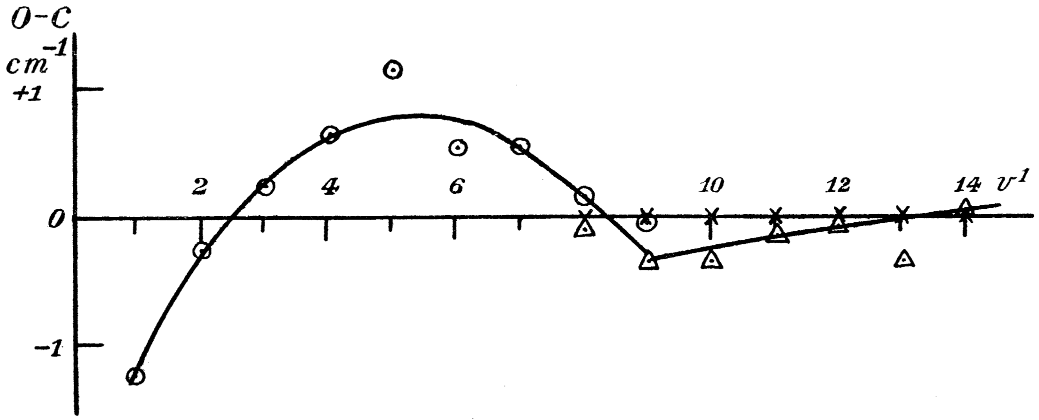

FIG. 3.—Differences of observed and calculated wave numbers, using the formula $\nu = 13172{\cdot}659 + 209{\cdot}7519\ (v' + \frac{1}{2}) - 1{\cdot}94741\ (v' + \frac{1}{2})^2 - 0{\cdot}033661\ (v' + \frac{1}{2})^3$. △ Band heads observed by CURTIS and PATKOWSKI ; ⊙ band heads observed by DARBYSHIRE ; × band origins determined by CURTIS and PATKOWSKI.

The values of ν_e and ω_e obtained by extrapolation of the above formula, namely, 13,744 and 209·7, are probably less reliable than those of DARBYSHIRE, namely, 13,742 and 212·3, since his observations were made on bands relatively close to the origin. On the other hand, the values for $\omega''_{1/2}$, 381·25, and $\omega''_{3/2}$, 378·32, should be better, as also the value 384·18 for ω''_e derived from them (cf. DARBYSHIRE'S 384·6).

The Λ *type doubling.*

As has been mentioned above, the upper rotation states are all double, one component of each doublet giving rise to the P and R branches and the other to the Q branch. All

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* DARBYSHIRE, *loc. cit.* CURTIS and PATKOWSKI, 'Trans. Faraday Soc.,' vol. 25, p. 731 (1929).

the constants hitherto determined relate to the former component, and we may now consider the problem of determining those associated with the latter. Let the rotation terms already considered be distinguished by the suffix *d*, the others by *c*. Then we have

$$R(J-1) - Q(J-1) = F'_d(J) - F'_c(J-1)$$

and

$$Q(J+1) - P(J+1) = F'_c(J+1) - F'_d(J)$$

Whence

$$\begin{aligned} \Delta_2 F'_c(J) &\equiv F'_c(J+1) - F'_c(J-1) \\ &= R(J-1) - P(J+1) + Q(J+1) - Q(J-1) \\ &= \Delta_2 F''(J) + \Delta_2 Q(J) \text{ say.} \end{aligned}$$

Further, in the process of determining B'_c by methods similar to those already employed for B'_d, which involve summation of successive differences, all the terms concerned in $\Delta_2 Q(J)$ will cancel, except the first two and the last two. Thus we have

$$_f\Sigma_l\{\Delta_2 F'_c(J)\} = {_f\Sigma_l}\{\Delta_2 F''(J)\} - Q(J_f - 1) - Q(J_f) + Q(J_l) + Q(J_l + 1)$$

The final derivation of the B'_c values follows exactly the same lines as before, and the same D' values are applicable. The results are given below.

v'	8	9	10	11	12	13	14
B'_c	0·078018	0·076986	0·075763	0·074598	0·073421	0·072501	0·070725
$B'_c - B'_d$	0·000050	—0·000048	+0·000015	—0·000135	—0·000009	0·000077	—0·000008

The rather irregular behaviour of the differences $B'_c - B'_d$ indicates that the B'_c values are of a distinctly lower order of accuracy than the B'_d's already determined. This is probably attributable to errors in the Q wave numbers, for the elimination of which no method such as was used in determining B'_d is available. The average difference $B'_d - B'_c$ is about 4×10^{-5} or 0·05% ; there is no indication as to how it depends on v', if at all.

Its dependence on J was next investigated, by forming the differences

$$\begin{aligned} &\{Q(J+1) - P(J+1)\} - \{R(J) - Q(J)\} \\ &= \{F'_c(J+1) + F'_c(J)\} - \{F'_d(J+1) + F'_d(J)\} \\ &= 2\{F'_c(J+\tfrac{1}{2}) - F'_d(J+\tfrac{1}{2})\} \text{ approximately.} \end{aligned}$$

These ran very irregularly with J, even when means of every successive five were plotted instead of individual values, but by averaging such means over all seven bands, *i.e.*, by using the whole of their constituent lines, a reasonably smooth curve was obtained, as shown in fig. 4.

It is clear from the change of sign near J = 30 that the energy difference between the two components cannot be wholly due to a difference in the B values as assumed above, or even to a difference in the D's. A constant is apparently involved as well.

Miscellaneous.

In this section it is proposed to refer to several matters which do not call for exhaustive discussion. The first of these is the isotope effect. This may be resolved into two components, one vibrational and the other rotational. The former has already been studied by several workers, and has provided the basis for the allocation of vibrational quantum numbers, but the present work affords the first opportunity of examining the rotational effect. The bands of the less abundant isotope, although showing fairly well-marked heads under low dispersion, are somewhat difficult to trace on the grating plates. It was only possible to identify the Q branches of the $v'' = 1$ progression with any degree of completeness; and even these could seldom be followed close up to the origin. It was verified that the isotope displacements followed the usual laws*; in fact, their calculated values were employed as a rule to assist in the identification. Beyond this it did not appear possible to derive any useful results from these data; in particular, it was not possible to determine the mass ratio† $Cl^{37} : Cl^{35}$ any more accurately than it is known already.

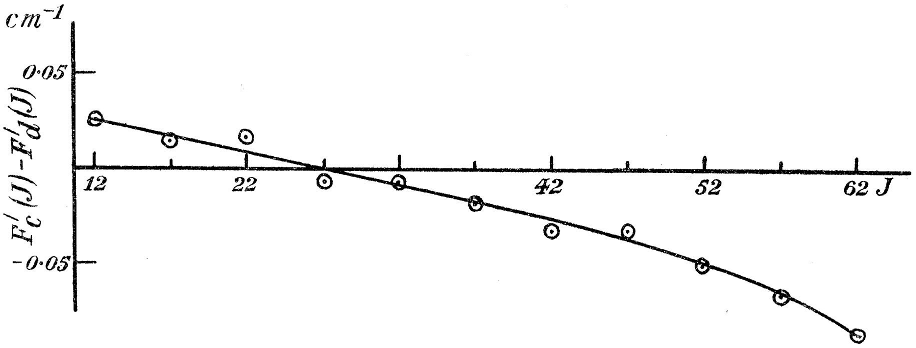

FIG. 4.—Variation of Λ type doubling with J.

In view of the accuracy with which the constants had been evaluated it seemed to be opportune to test various relationships between them which have been proposed from time to time. These are enumerated in JEVONS' "Report," pp. 27–29.

The first three are as follows :—

$$x_e = 3B_e/\omega_e, \quad \alpha = 6B_e^2/\omega_e, \quad D_e = -4B_e^3/\omega_e^2$$

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* See JEVONS' "Report," chapter X.

† The accepted atomic weights are 39·976 and 34·980.

Since we have made use of the last of these for the purpose of evaluating D_e, our results provide no test of its accuracy, but it has been verified in a number of other cases, and is usually regarded as valid. The first and second relationships, however, are not even approximately satisfied by our values. Thus, for example, we have $\omega''_e x''_e = 1{\cdot}465$ and $3B''_e = 0{\cdot}342$, also $\omega'_e x'_e = 1{\cdot}947$ and $3B'_e = 0{\cdot}252$.

The second suggested relationship is also unsatisfactory, since α' and $\alpha'' = 5{\cdot}02$ and $3{\cdot}83 \times 10^{-4}$ respectively, whereas $6B_e^2/\omega_e = 2{\cdot}03$ and $2{\cdot}01 \times 10^{-4}$. Next we have the Birge-Mecke rule that B_e/ω_e is approximately constant for the different electronic states of one molecule. From the close agreement of $6B_e^2/\omega_e$ for the two states it is evident that this cannot hold. The actual values are $2{\cdot}97 \times 10^{-4}$ for the normal state and $4{\cdot}0 \times 10^{-4}$ for the excited state. Morse's variant $\omega_e r^3_e =$ constant is equivalent to $\omega_e^2/B_e^3 =$ constant, which is a special case of RYDBERG's relationship* $(\Delta G_v)^2/B^3_{v+1} =$ constant, where ΔG_v is the difference of vibrational energy between the v and $(v+1)$ states. Since $D_e = -4B^3_e/\omega_e^2$ it is also equivalent to stating that $D'_e = D''_e$, whereas the actual values are $4{\cdot}06$ and $5{\cdot}19 \times 10^{-8}$. For one electronic state, however, $(\Delta G_v)^2/B^3_{v+1}$ is approximately constant, although not exactly, as RYDBERG suggests may be so. For the excited state, for example, it ranges from $6{\cdot}08$ to $5{\cdot}18$.

RYDBERG has also suggested that there is a linear relationship between $(\Delta G_v)^2$ and v, and this is much more nearly exact ; a least squares formula gives strongly systematic residuals, however, amounting to about $0{\cdot}1\%$.

Finally, BIRGE has found that $x_e B_e/\alpha = 0{\cdot}7 \pm 0{\cdot}1$ for many molecules, but in the present case the values for the normal and excited states are $2{\cdot}03$ and $0{\cdot}87$ respectively.

We desire to express our gratitude to the Department of Scientific and Industrial Research and to the Armstrong College Research Committee, who made grants enabling us to obtain assistance with the very laborious work of measuring and reducing the spectrograms, and also to Mr. B. RODERICK, B.Sc., who carried out this work with admirable industry and accuracy.

Summary.

Twelve bands belonging to three progressions ($v'' = 0, 1, 2$) and each consisting of P, Q, and R branches have been completely analysed. The rotation constant B has been determined to a high order of accuracy for each of the states involved with the help of a special method of eliminating errors due to blending. It is found that B′ requires a quadratic term in v' for its representation, the formula being

$$B'_v = 0{\cdot}083890 - 3{\cdot}828 \times 10^{-4}\,(v' + \tfrac{1}{2}) - 3{\cdot}622 \times 10^{-5}\,(v' + \tfrac{1}{2})^2.$$

This fits seven observed values to within $0{\cdot}004\%$.

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* ' Z. Physik,' vol. 73, p. 376 (1931).

The origins of the bands have been determined and a least squares formula calculated for the $v'' = 1$ progression, as follows :—

$$\nu = 13172{\cdot}659 + 209{\cdot}7519\,(v' + \tfrac{1}{2}) - 1{\cdot}94741\,(v' + \tfrac{1}{2})^2 - 0{\cdot}033661\,(v + \tfrac{1}{2})^3.$$

Evidence is presented which supports DARBYSHIRE'S conclusion that there is a discontinuity in the law of force at about $v' = 9$ or 10.

The existence of an extremely small Λ type doubling is established and its variation with J is examined.

Various proposed relationships between certain of the rotational and vibrational constants are tested, using the new data. The following are the values of the chief constants which have been determined :—

	Normal State.	Excited States.	
	$^1\Sigma$	$^3\Pi_1$	$^3\Pi_0$
ω_e	384·18	209·7	~ 203 cm.$^{-1}$
$x_e\omega_e$	1·465	1·947	13 ,,
$y_e\omega_e$	—	0·03366	—
B_e	0·11414	0·08389	0·090 cm.$^{-1}$
α	$5{\cdot}02 \times 10^{-4}$	$3{\cdot}828 \times 10^{-4}$	~ 29×10^{-4} cm.$^{-1}$
γ	$1{\cdot}1 \times 10^{-5}$	$3{\cdot}662 \times 10^{-5}$	—
r_e	2·3150	2·7001	2·61 A

The figures for the $^3\Pi_0$ state are taken from BROWN and GIBSON'S paper* for comparison. The close similarity of the ω_e and B_e values is of interest as supporting the current view that the two states are components of the same triplet level.

$y_e\omega_e$ is the coefficient of $(v + \frac{1}{2})^3$ in the expression for G_v, the vibrational term. γ is the coefficient of $(v + \frac{1}{2})^2$ in the expression for B_v.

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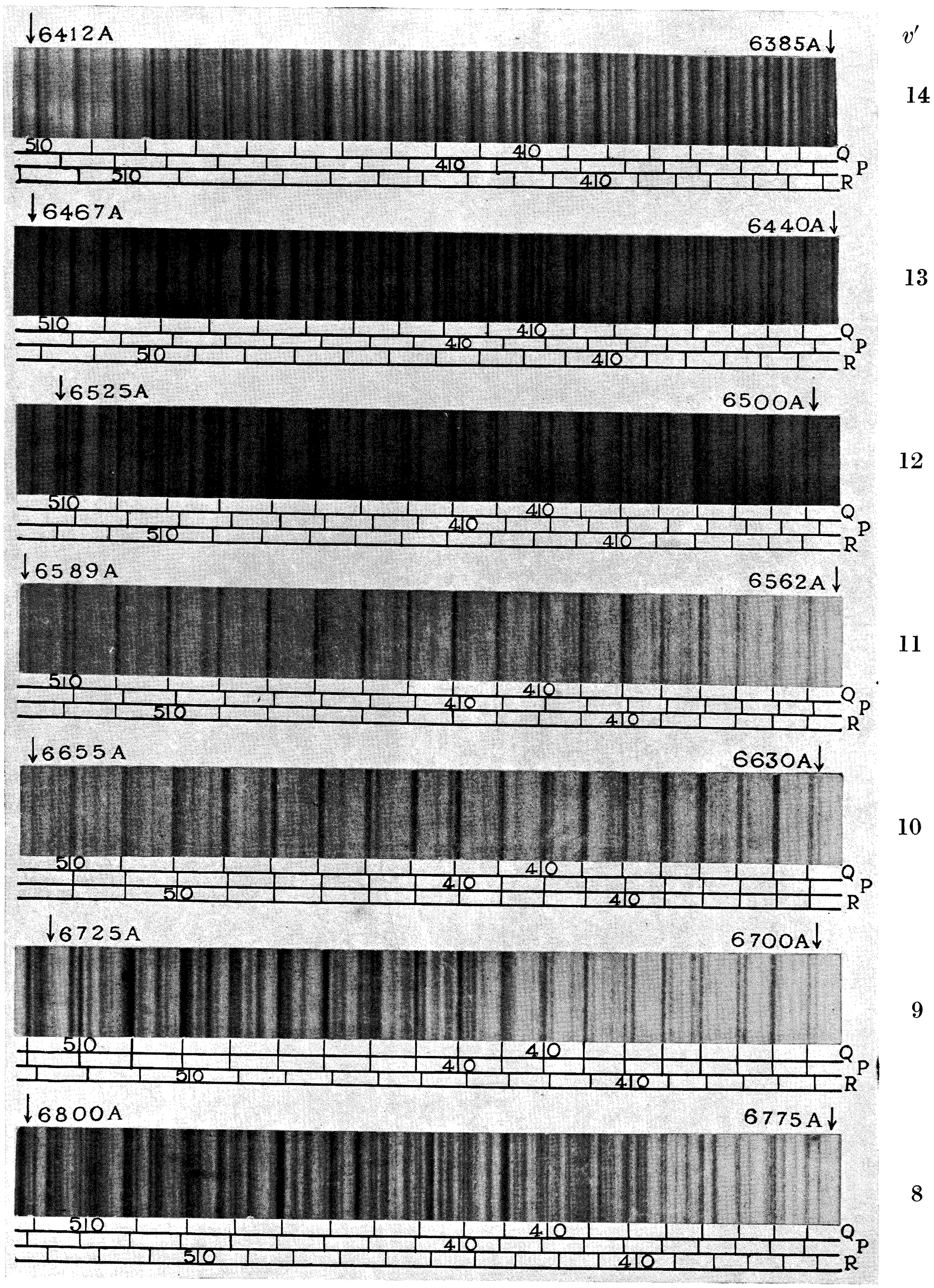
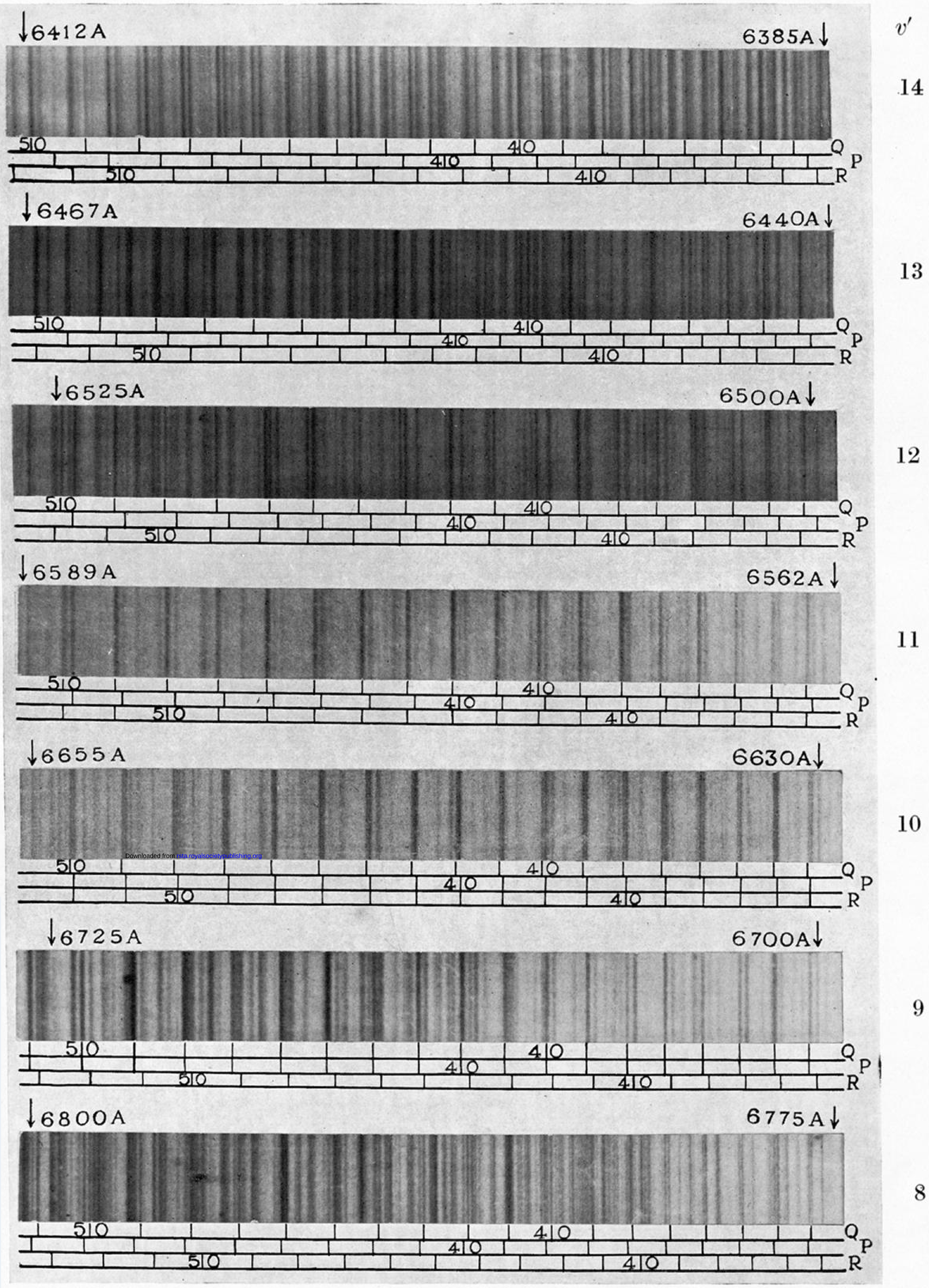
* 'Phys. Rev.,' vol. 40, p. 529 (1932).



Rotational analysis of $v'' = 1$ bands of ICl.

Corresponding portions of seven successive bands are shown. Only the P, Q, and R branches of these are marked, although most of the stronger remaining lines have also been allocated. The spurious doublet structure, due to blending, in $v' = 9$, 10, 11 will be noticed. The absorption is due to a column of ICl 30 cm. long at a pressure of about 100 mm. of mercury and a temperature of 50° C. The spectrograms were taken in the second order of a 21 foot concave grating and have been enlarged sixfold.



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