

ROTATIONAL ANALYSIS OF SOME BANDS OF $C^1\Sigma_u^+ - X^1\Sigma_g^+$ SYSTEM OF P_2 MOLECULE INVOLVING LOW v' , v'' VALUES

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ABSTRACT

Ten ultraviolet bands of the $C^1\Sigma_u^+ - X^1\Sigma_g^+$ system of P_2 involving low v' and v'' values have been photographed at dispersion of 0.38 and 0.56 Å/mm. and analysed for their rotational structure. While four of these bands were analysed earlier, six of them, viz., 0-10, 1-12, 2-7, 2-14, 4-8 and 6-9 have been analysed for the first time during the present studies. The rotational constants, B_v 's with low v'' quantum numbers are obtained from which value of B_0'' has been derived. The value of B_0'' is found to be in agreement with the value obtained by Douglas and Rao from their study of $A^1\Pi_g - X^1\Sigma_g^+$ bands of P_2 .

Earlier findings on the perturbation of $v' = 2$ level of the $C^1\Sigma_u^+$ state have been confirmed from the analysis of the 2-7, 2-14 and 2-15 bands. The ν_{00} values of the bands show large deviations from the expected values.

INTRODUCTION

THE spectrum of P_2 molecule consists of an extensive band system in the ultraviolet (1900-3400 Å) which was studied by a number of authors¹⁻⁹ and was shown to involve a $C^1\Sigma_u^+ - X^1\Sigma_g^+$ transition. The band system was first observed by Geuter in emission. Jakowlewa³ obtained the same system in absorption, and proposed a vibrational analysis for the observed bands. Dressler¹ reported two new systems in the vacuum ultraviolet. Douglas and Rao² discovered a $A^1\Pi_g - X^1\Sigma_g^+$ system of P_2 which is analogous to the Lyman-Birge-Hopfield system of N_2 . More recently a number of singlet systems have been observed in absorption by Creutzberg¹² in vacuum ultraviolet.

Herzberg⁴ studied the main system ($C^1\Sigma_u^+ - X^1\Sigma_g^+$) in greater detail, and extended Jakowlewa's analysis. He further showed that vibrational perturbations occurred in $v' = 9$ level. Vibrational levels of $v' = 10$ and 11, were found to be predissociated. These observations were generally corroborated by Ashley,⁵ Milne,⁶ Rao⁷ and Marais⁹ from studies of rotational structure of several of the bands. Marais observed that the perturbation in $v' = 5$ level was rotational in nature and not vibrational, contrary to the observations of Herzberg.⁴ Perturbation in the $v' = 2$ level of the 2-15 band was studied by Herzberg, Herzberg and Milne⁶ who found that the lines with $N' > 46$ followed the usual run while those with N' between 46 and 28 showed increasing deviations. Lines with lower N values were not observed by them. A strong perturbation of the lines with lower N values was found to be responsible for such deviations.

Another feature of the $C^1\Sigma_u^+ - X^1\Sigma_g^+$ system is that the bands involving higher vibrational levels of the ground state were generally obtained in emission with moderately strong intensity. The absorption spectrum was also limited to bands with high v'' levels. Further, there is an overlap of sequences due to widely differing vibrational frequencies of the upper and lower states and this situation limits the number of bands free from overlap to a few that could be analysed for their rotational structure. Bands that were investigated so far involved high v'' values; consequently the rotational constants B_0 , B_e , etc., were derived from large extrapolations.

The aim of the present investigation of P_2 spectrum has therefore been to analyse the rotational structure of as many bands as possible with low v' and v'' values and thereby determine the B_0 values of low vibrational quantum numbers. It has also been proposed to study the reported perturbation in $v' = 2$ level by photographing, at high resolution, additional bands involving $v' = 2$. During the present studies, the 0-6, 0-10, 1-12, 2-7, 2-14, 2-15, 3-16, 4-8, 4-18 and 6-9 bands have been photographed and analysed for their rotational structure. Results of these studies are presented in this paper.

EXPERIMENTAL

For obtaining the P_2 bands, sealed-in quartz discharge tubes containing traces of phosphorus were prepared in the manner described by Tomkins and Fred.¹⁰ Yellow phosphorus was distilled into a small bulb attached to the discharge tube. Helium at a pressure of 2-3 mm. admitted into the discharge tube served as carrier gas for exciting the spectrum. A microwave oscillator of frequency 2450 mc./sec. was used to excite the spectra. It was

found that the P_2 bands were most intense when the colour of the discharge was greenish-yellow. During the period of exposure it was found necessary to keep the window of the discharge tube hot in order to prevent any deposition of phosphorus. This was managed by heating the window with a low flame.

The resulting spectrum was photographed on 6.6 metre concave grating spectrograph keeping the discharge tube in an end-on position. Bands in the region of $2300 \text{ \AA} - 2600 \text{ \AA}$ were photographed in the third order at a dispersion of 0.38 \AA/mm . A chlorine filter of 8 cm. length (at one atmospheric pressure) was used to cut off the overlapping orders. Figure 1 shows

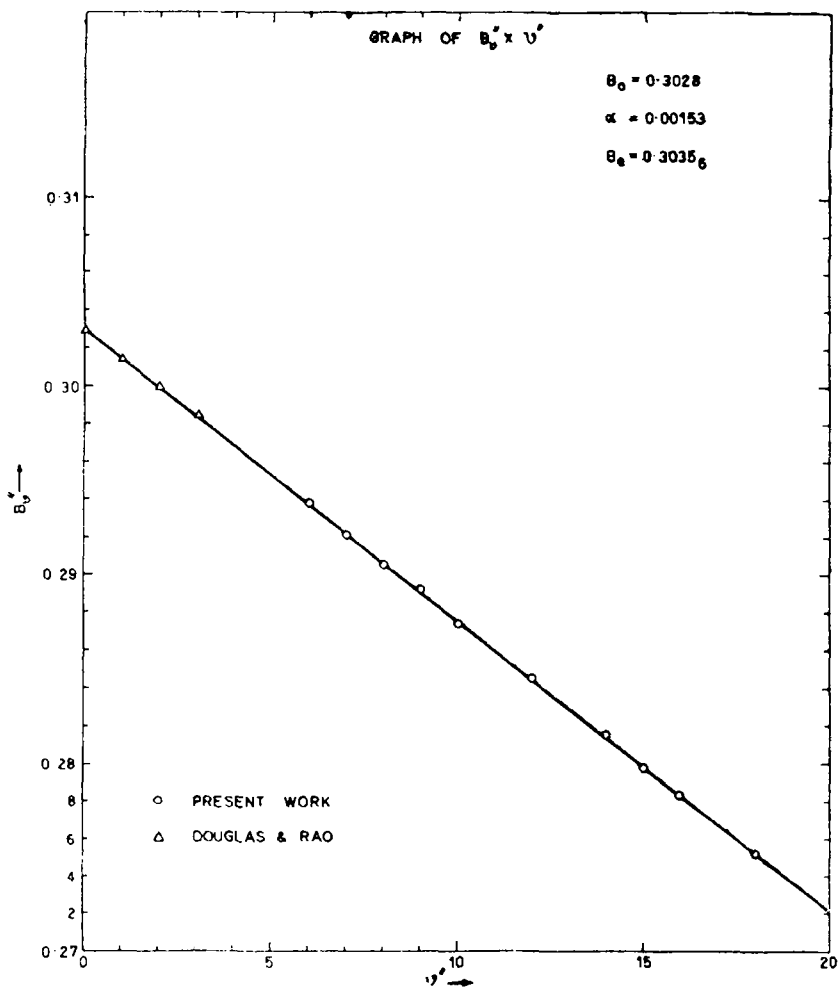


FIG. 2. Plot of B_v'' of $X^1\Sigma_g^+$ state against v'' .

four of the bands at 2543.8 Å (0-10), 2607.1 Å (1-12), 2356.4 Å (2-7) and 2672.2 Å (2-14), that have been analysed for their rotational structure. Bands lying in other regions were photographed in the second order at a dispersion of 0.56 Å/mm. Kodak 103-a0 plates were used for photographing the spectra.

ANALYSIS AND DISCUSSION

The bands 0-6, 0-10, 1-12, 2-7, 2-14, 4-8 and 6-9, have been analysed for the first time in the present studies. The 4-18, 3-16 and 2-15 bands were analysed earlier; however, they have been photographed in the present studies at a higher dispersion and resolution and reanalysed. The bands 1-12 and 3-16 do not have a state in common with any other band analysed. The extrapolated values of combination differences have been used as a guide in the analysis.

The bands, as expected, show two series of P and R branches. The rotational lines with odd N values are stronger in intensity. In the case of weak bands and those that are badly overlapped, only the strong lines are measured.

Vacuum wave numbers of the P and R lines are given in Table I. Though the 3-16 band has been measured and analysed it is not included in Table I as it does not give any additional information.

The upper state combination differences, namely $\Delta_2 F'(N) = R(N) - P(N)$ of the bands with $v' = 0, 2$ and 4 are given in Table II. The lower state combination differences $\Delta_2 F''(N) = R(N-1) - P(N+1)$ of $v'' = 7$ state are given in Table III. The data of the 0-7 band are from Herzberg, Herzberg and Milne⁶ and are included here for purpose of comparison. The upper state combination differences of 0-7 band agree with those of 0-6 and 0-10 bands in Table II. The data from the same 0-7 band provide comparison with the lower state combination differences of 2-7 band analysed in the present studies. The 2-7 band is also the one showing a perturbation in the $v' = 2$ level.

(a) *Determination of B_v and D_v .*—The rotational constants B_v and D_v are determined by employing the equation:

$$\Delta_2 F(N) = 4B_v(N + \frac{1}{2}) - 8D_v(N + \frac{1}{2})^3.$$

TABLE I

Vacuum wave numbers (in cm^{-1}) of the lines of $C^1\Sigma_u^+ - X^1\Sigma_g^+$ bands of P_2

N	0-6		0-10		1-12	
	R (N)	P (N)	R (N)	P (N)	R (N)	P (N)
9	42223.68	38333.84
11	22.42	42211.33	39297.35	..	38342.22	30.98
13	20.74	07.76	95.90	39282.93	40.81	27.89
15	18.46	03.65	94.06	79.26	39.20	24.25
17	16.00	199.21	92.04	75.15	37.11	20.36
19	13.18	94.30	89.48	70.62	34.90	16.10
21	09.78	88.90	86.48	65.99	31.99	11.38
23	05.87	83.22	83.36	60.79	28.82	06.42
25	01.67	77.08	79.75	55.09	25.40	00.92
27	196.93	70.43	75.78	49.23	21.61	295.32
29	91.06	63.40	71.33	42.92	17.26	89.13
31	86.34	56.08	66.65	36.31	12.66	82.60
33	80.43	48.17	61.49	29.24	07.76	75.68
35	74.02	39.86	55.95	21.83	02.83	68.34
37	67.21	31.14	50.00	14.03	38296.58	61.12
39	59.96	21.96	43.73	05.78	90.46	52.92
41	52.30	12.42	36.99	197.30	83.91	44.42
43	44.16	02.36	29.87	88.49	77.02	35.68
45	35.56	091.92	22.50	78.96	69.50	26.44
47	26.63	80.95	14.61	69.09	..	16.73
49	17.17	69.82	06.44	58.85	..	06.42

TABLE I (Contd.)

N	2-7		2-14		2-15	
	R (N)	P (N)	R (N)	P (N)	R (N)	P (N)
51	07·29	57·98	197·99	48·12
53	42096·87	45·90	..	37·22
55	86·06	25·95
57	74·79	14·32
9	42425·40	42416·56*
10
11	23·83	13·23*	37409·29	37398·41*
12	96·88*
13	21·96	09·41*	07·80	95·11*	36715·45	..
14	06·92	93·34*
15	19·49	05·09*	06·03	91·43*	13·76	..
16	04·86	89·45*
17	16·56	00·30*	03·85	87·25**	11·64	..
18	02·61
19	13·23*	395·01	01·28	82·95	09·15	36690·98
20	399·86	80·47*
21	09·41*	89·39	98·41*	78·07	06·21	86·12
22	96·88	75·64
23	05·09*	83·10	95·11*	72·97	03·06	81·11
24	93·34*	70·17
25	00·30*	76·49	91·43*	67·39	699·57	75·66
26	89·45*	64·51

TABLE I (Contd.)

N	2-7		2-14		2-15	
	R(N)	P(N)	R(N)	P(N)	R(N)	P(N)
27	395.01*	69.38	87.25*	61.47	95.65	69.74
28	58.12
29	90.75	61.76	..	55.04	93.01	63.65
30	80.47*	52.40
31	84.36	55.21	78.87	..	87.73	58.90
32	76.51	45.94
33	77.74	46.34	73.71	42.24	82.84	..
34	71.12	38.72
35	70.84	37.45	68.23	34.92	77.26	44.24
36	65.58	31.13
37	63.56	28.22	62.57	27.37	71.99	36.76
38	59.52	23.26
39	55.87	18.63	56.61	19.36	66.32	29.04
40	53.54	15.20
41	47.76	08.59	50.10	11.06	60.42	21.02
42	37346.70	37306.72
43	42339.23	42298.14	43.51	02.47	36653.74	36612.87
44	39.89	298.18
45	30.25	87.31	36.44	93.52	47.05	04.02
46	32.81	88.82
47	20.87	76.00	29.11	84.18	39.86	595.02
48	25.25	79.44

TABLE I (Contd.)

N	4-8		4-18		6-9	
	R(N)	P(N)	R(N)	P(N)	R(N)	P(N)
49	11·01	64·26	21·31	74·55	32·33	85·60
50	17·32	69·63
51	00·78	52·12	13·17	64·49	24·75	76·02
52	09·08	59·56
53	290·10	39·53	04·89	54·24	16·66	65·96
54	00·46	49·03
55	78·98	26·55	296·04	43·60	08·00	55·80
56	91·55	38·26
57	67·38	..	86·81	32·51	599·30	45·00
58	82·09	26·89
59	55·29	..	77·38	21·15	90·27	34·02
60	72·32	15·61
61	42·85	..	67·48	09·44	80·73	22·61
62	62·46	03·42
63	29·89	..	57·28	197·29	70·99	11·02
64	52·07	90·91
65	46·71	84·84	60·81	498·93
66	41·06
67	35·75	..	50·26	..
68	30·22
69	24·46	..	39·38	..
70	18·53
71	12·86	..	28·24	..

TABLE I (Contd.)

N	2-7		2-14		2-15	
	R (N)	P (N)	R (N)	P (N)	R (N)	P (N)
72
73	00.75	..	16.71	..
74
75	188.31	..	509.75	..
76
77	492.51	..
5	42768.43	..
7	..	42591.00	..	35577.56	67.84	..
9	42598.24	88.59	..	74.99	66.74	..
11	96.74	86.00	35582.99	72.28	65.15	42754.34*
13	94.89	82.19	81.95	69.36	63.21	50.58*
15	92.49	77.98	80.46	65.94	60.78	46.28*
17	89.70	73.34	78.72	62.33	57.82	41.31*
19	86.40	68.21	76.58	58.30	54.34*	36.20*
21	82.70	62.64	74.20	54.02	50.58*	30.42*
23	78.53	56.61	71.36	49.42	46.28*	24.29*
25	73.87	50.13	68.29	44.46	41.31*	17.63*
27	68.81	43.16	64.90	39.14	36.20*	10.75
29	63.33	35.59	61.12	33.49	30.42*	03.12
31	57.32	27.88	56.97	27.54	24.29*	695.09
33	50.84	19.58	52.52	21.22	17.63*	86.55
35	43.92	10.78	47.78	14.53	10.11	77.58

TABLE I (Contd.)

N	2-7		2-14		2-15	
	R (N)	P (N)	R (N)	P (N)	R (N)	P (N)
37	36.53	01.60	42.65	07.63	02.57	68.15
39	28.68	491.84	37.20	00.33	694.48	58.12
41	20.38	81.68	31.39	492.71	85.93	47.69
43	11.61	70.99	25.21	84.77	76.82	36.85
45	02.30	59.92	18.74	76.38	67.25	25.47
47	492.55	48.40	11.84	67.69	57.30	13.59
49	82.35	36.24	04.66	58.63	46.72	01.24
51	71.61	23.68	497.10	449.34	635.83	..
53	60.35	10.69	89.03	39.50	24.36	..
55	80.68	29.40	12.41	..
57	71.97	18.90
59	63.16	07.72
61	54.00	396.29
63	44.37	84.02
65	34.45	70.74
67	24.22
69	13.38
71	02.04
73	390.25

* Blended lines.

The $\Delta_2 F$ for the upper and lower states are given by:

$$\Delta_2 F''(N) = R(N) - P(N)$$

$$\Delta_2 F''(N) = R(N-1) - P(N+1).$$

TABLE II

Upper state combination differences of the bands with $v' = 0, 2$ and 4 of the $C^1\Sigma_u^+ - X^1\Sigma_g^+$ system of P_2
 $[\Delta_2 F^1(N) = R(N) - P(N)]$

N	0-7	0-6	0-10	2-7	2-14	2-15	4-8	4-18
9		8.84	9.65	..
11	10.97	10.60	10.88	..	10.74	10.71
13	12.97	12.98	12.97	12.55	12.69	..	12.70	12.59
15	14.94	14.81	14.80	14.40	14.60	..	14.51	14.52
17	16.52	16.79	16.89	16.26	16.60	..	16.36	16.39
19	18.96	18.88	18.86	18.22	18.33	18.17	18.19	18.28
21	20.50	20.88	20.49	20.02	20.34	20.09	20.06	20.18
23	22.53	22.65	22.57	21.99	22.14	21.95	21.92	21.94
25	24.56	24.59	24.66	23.81	24.04	23.91	24.52	23.83
27	26.52	26.50	26.55	25.63	25.78	25.91	25.65	25.76
29	28.35	28.58	28.41	28.99	..	29.36	27.74	27.63
31	30.47	30.26	30.34	29.15	..	28.83	29.44	29.43
33	32.27	32.26	32.25	31.40	31.47	..	31.26	31.30
35	34.13	34.16	34.12	33.39	33.31	33.02	33.14	33.15
37	36.25	36.07	35.97	35.34	35.20	35.23	34.93	35.02
39	37.78	38.00	37.95	37.24	37.25	37.28	36.84	36.87
41	39.57	39.88	39.69	39.17	39.03	39.40	38.70	38.68
43	..	41.80	41.83	41.09	41.04	40.87	40.62	40.44
45	43.48	43.64	43.54	42.94	42.92	43.03	42.38	42.36
47	..	45.68	45.52	44.87	44.93	44.84	44.15	44.15
49	47.54	47.35	47.59	46.75	46.76	46.73	46.11	46.03

TABLE II (Contd.)

N	0-7	0-6	0-10	2-7	2-14	2-15	4-8	4-18
51	49.17	49.31	49.77	48.66	48.68	48.73	47.83	47.76
53	51.25	50.97	..	50.57	50.65	50.70	49.66	49.53
55	52.43	52.44	52.20	..	51.28
57	54.30	54.30	..	53.07
59	56.23	56.23	..	55.44
61	58.04	58.12	..	57.71
63	59.99	59.97	..	60.35
65	61.87	61.88	..	63.71

The rotational constants B_v and D_v are tabulated along with the ones determined by earlier investigations in Table IV.

The B_0' , B_2' , B_3' , B_4' and B_6' values agree well with those obtained by Herzberg⁴ and Marais.⁹ In addition B_1' has been obtained for the first time and fits in well with other B_v' values. In the lower state, B_v'' values were determined for $v'' = 5, 6$ and 7 and for those with $v'' \geq 15$. Values for v'' lying between 7 and 15 were extrapolated. The present studies, however, provide experimentally determined B_v values for $v'' = 7, 8, 9, 10, 12$ and 14 . It is, therefore, believed that with the present set of B_v'' values extrapolation to lower v'' values is better justified.

From a graph of the observed B_v'' values against v'' shown in Fig. 2, the values of B_0'' , B_1'' , B_2'' and B_3'' are determined. A comparison of these values with corresponding B_v'' values obtained experimentally from an analysis of the 0-0, 0-1, 0-2 and 0-3 bands of $A^1\Pi_g - X^1\Sigma_g^+$ system of P_2 by Douglas and Rao² shows good agreement between them (Fig. 2).

(b) *Determination of band origins.*—The band origins have been determined by using equation

$$R(N) + P(N) = 2\nu_0 + (2B_v' - 4D_v') + 2(B_v' - B_v'' - 6D_v') \\ \times N(N+1) - 2(D_v' - D_v'') N^2(N+1)^2.$$

TABLE III

The lower state combination differences of 0-7 and 2-7 bands of $C\ ^1\Sigma_u^+ - X\ ^1\Sigma_g^+$ system of P_2

$$[\Delta_2 F''(N) = R(N-1) - P(N+1)]$$

N	0-7	2-7
12	14.45	..
14	16.99	16.87
16	19.20	19.19
18	21.48	21.55
20	24.06	23.85
22	26.27	26.31
24	28.57	28.60
26	30.83	30.92
28	33.37	33.25
30	35.68	35.54
32	38.06	38.02
34	40.25	40.29
36	42.71	42.62
38	45.10	44.93
40	47.05	47.28
42	..	49.62
44	51.76	51.92
46	..	54.25
48	56.59	56.61
50	58.93	58.89
52	61.24	61.25
54	63.54	63.55

TABLE IV

Rotational constants of C¹Σ_u⁺ and X¹Σ_g⁺ states

<i>v</i> '	B' _v values in cm. ⁻¹			
	Present	Herzberg	Marais	Creutzberg
<i>(a) For the upper state C¹Σ_u⁺</i>				
0	0.2408	0.2408	..	0.2412
1	0.2392	0.2396
2	0.2370	0.2374	..	0.2362
3	0.2358	0.2360	0.2360	0.2358
4	0.2342	..	0.2341	0.2344
6	0.2309	..	0.2309	0.2309
B' _v	0.2416	0.2415	0.2417	0.2421
α _v '	0.00164	0.00153	0.00165	0.00175

$R(N) + P(N) - 2(\overline{B_{v'}} - \overline{B_{v''}}) N(N+1)$ is plotted against $N(N+1)$ and ν_0 is determined from the intercept.

The ν_0 s so obtained are tabulated in Table V, along with the calculated values from the expression:

$$\nu_0 = 46787.282 + (472.62 v' - 2.600 v'^2 + 0.0233 v'^3) \\ - (777.62 v'' - 2.8118 v''^2 - 0.00533 v''^3)$$

computed by Marais and Verleger¹¹ taking ν_0 of a large number of bands.

The value of ν_0 obtained from this expression agree well (within experimental errors) with the band origins derived from rotational data of several bands. Only in the case of bands with $v = 1, 2$ and 3 , they show a considerable deviation, *i.e.* a large (obs.—cal.) values in Table V. The deviations are maximum for bands with $v' = 2$ (about 6 cm.⁻¹). For bands with $v' = 1$

v''	B_v'' values in cm.^{-1}			Douglas and Rao
	Present	Herzberg	Marais	
<i>(b) For the lower state $X^1\Sigma_g^+$</i>				
0	0.3028*	0.30285
1	0.3013*	0.30138
2	0.2998*	0.29988
3	0.2982*	0.29837
6	0.2938	0.2939
7	0.2921	0.2923
8	0.2905
9	0.2892
10	0.2874
12	0.2845
14	0.2815
15	0.2798	0.2800
16	0.2783	0.2787	0.2783	..
18	0.2752	..	0.2753	..
B_v''	0.30356	0.3031	0.3033	0.30359
α_v''	0.00153	0.00138	0.00142	0.00148

* Values obtained from a plot of B_v against v as given in Fig. 2.

and 3, *i.e.*, for 1-12 and 3-16, the expected origins show a deviation of about 2 cm.^{-1} . These observations indicate that except for $v' = 2, 1$ and 3 levels the rest of the vibrational levels behave normally.

Recent work of Creutzberg¹² show similar effects of perturbation. The deviations observed by Creutzberg have been included in Table V for purposes of comparison.

TABLE V

Origins of the P_2 bands arising from $v' = 0, 1, 2, 3, 4$ and 6 as calculated from the expression (given by Marais and Verleger)

$$v_0 = 46787.282 + (472.62 v' - 2.600 v'^2 + 0.0235 v'^3) \\ - (777.62 v'' - 2.8118 v''^2 - 0.00533 v''^3)$$

Band	Band origins in cm.^{-1}		Obs.-Cal.	
	Observed	Calculated	Present	Creutzberg* ¹²
0-6	42223.71	42223.94	-0.23	..
0-10	39297.76	39297.59	+0.17	..
1-12	38342.41	38340.00	+2.41	+2.78
2-7	42425.27	42418.58	+6.69	+7.87
2-14	37407.26	37401.37	+5.89	..
2-15	36714.67	36708.65	+6.02	..
3-16	36484.42	36482.11	+2.31	+2.59
4-8	42598.77	42599.39	-0.62	..
4-18	35583.02	35582.61	+0.41	+0.49
6-9	42767.37	42767.54	-0.17	..

* From the data on the vacuum ultra-violet bands which have for their final state $X^1\Sigma_g^+$ ground state which also have the same $C^1\Sigma_g^+$ level.

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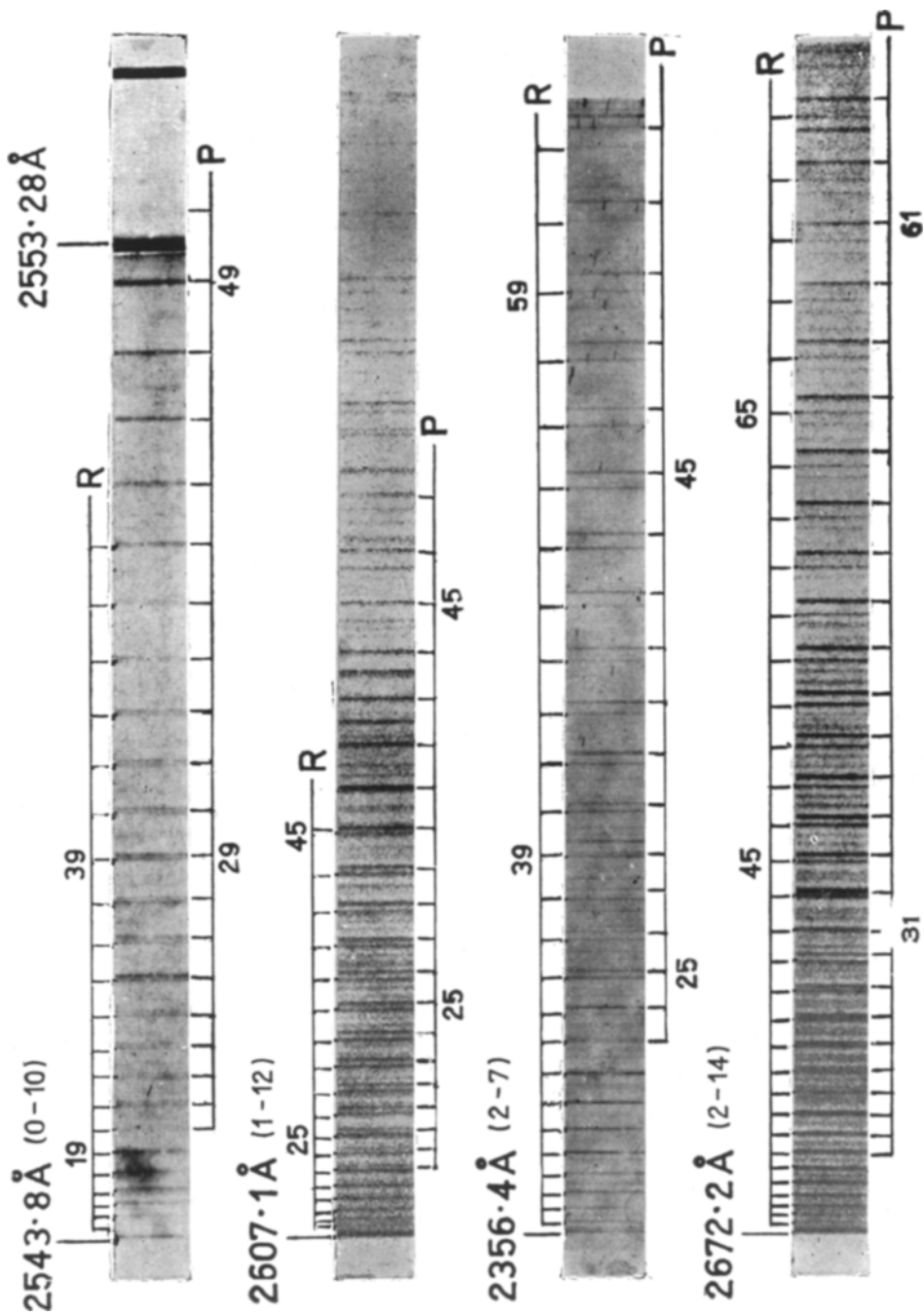


FIG. 1. Ultra-violet bands of $C^1\Sigma_u^+ - X^1\Sigma_u^+$ system of P_2 molecule.