EMISSION SPECTRUM OF PrO

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Abstract

The bands of PrO at 8488·95 A and 7986·44 A of system I and at 7662·85 A of system III have been photographed on 6·6 meter concave grating spectrograph at a dispersion of 1·2 A/mm and their rotational structure analysed. They are assigned transitions from $v' = 0$ and 1 levels of $A^2\Pi_{3/2}$ and $v' = 0$ level of $B^2\Pi_{3/2}$ to a common $v'' = 0$ level of the ground, $X^2\Pi_{3/2}$ state.

Introduction

A group of red degraded bands, in the region 5000–6000 A was excited in flames and arcs fed with praseodymium salts by Watson (1938) who had attributed them to PrO. Subsequently, Gatterer and Krishnamurty (1952) obtained several more of the red degraded bands extending from the visible to the infrared region, in a "Carbon Flame" using a purified carbon rod impregnated with praseodymium chloride solution. Rosen and Swensson (1957) studied these bands (4400–8800 A) in more detail and classified them into twelve band systems. In their studies they mentioned also that Hautecler carried out the rotational analysis of the strongest bands of system I and assigned them to a $^2\Sigma$ – $^2\Sigma$ type of transition.

The present studies were undertaken in order to carry out a detailed rotational structure analysis of as many of these bands as possible and to establish the electronic transitions involved. The 0–0 band at 8488·95 A and the 1–0 band at 7986·44 A of system I and the 0–0 band at 7662·85 A of system III, were photographed at dispersions of 2·5 A/mm and 1·2 A/mm. The rotational structure of these bands consisted of three branches, *viz.*, the P, Q and R branches which could only arise out of a transition involving $\Delta\Lambda = \pm 1$, contrary to what Hautecler suggested. Detailed analysis of these studies are presented in this paper.

EXPERIMENTAL

All the twelve systems of bands (designated I to XII) could be excited in a DC arc, the carbon electrodes of which were fed with specpure powder of Pr_6O_{11} and metallic praseodymium. The resulting spectra emitted from the arc were photographed on a Jarrell-Ash 3·4 meter grating (30,000 lines per inch) spectrograph in the first order at a dispersion of 2·5 A/mm. The 8488·95 A and 7986·44 A bands of system I and the 7662·85 A band of

TABLE I

Deslandres Scheme for bands of Systems I and II of PrO

v′ \ v″	0		1		2		3	4
0	11776·8							
	934							
	12710·7	831	11879·7					
	741							
	741		740					
	12517·8	831	11686·5					
1	934		934					
	13451·6	832	12620·1	826	11794·1			
	736							
	737				735			
			12422·7	827	11595·7			
2			935		934			
			13357·5	828	12529·3	826	11703·5	
					732			
					731		733	
3					12327·9			
					932			
					13259·8	824	12436·0	
							729	
							12231·7	
							934	
							13165·4	
								1216·9

system III were photographed on 6·6 meter concave grating (30,000 lines per inch) spectrograph in the first order at a dispersion of 1·2 A/mm. Kodak I N plates were used to record the spectra. The plates were measured on an Abbe comparator and the wave numbers of the rotational lines computed using the iron and thorium lines as standards.

RESULTS AND DISCUSSION

Vibrational Structure. The observed bands could be arranged into two doublet transitions, systems I and II belonging to one and III and IV to a second electronic transition. Tables I and II show the vibrational analysis of the bands in two Deslandres schemes. Both the doublet transitions have the lower electronic state in common with $\Delta G''_{1/2}$ 831 cm.$^{-1}$ This state is assumed to be ground state of PrO.

TABLE II

Deslandres Scheme for bands of Systems III and IV of PrO

v' \ v''	0		1		2
0	13046·0	831	12215·3		
	611				
	13657·1				
	753		754		
	744				
1	13798·6	829	12969·7	826	12143·3
	603		597		
	*14401	834	*13567		
			739		
2			*14306		

* Bands are very weak.

Rotational Structure. The rotational structures of the bands at 8488·95 A and 7986·44 A of system I are shown in Fig. 1. A closer examination of the structure of these bands indicates the existence of three series of lines, one of them being more intense than the other two. The intense lines are

TABLE III

Vacuum wave numbers (in $cm.^{-1}$*) and line assignments of the* 0–0 (8488·95 A) *and* 1–0 (7986·44 A) *bands of the* $A^2\Delta_{5/2} - X^2\Pi_{3/2}$ *(system I) of PrO*

J + 0·5	0–0 Band			1–0 Band		
	P	Q	R	P	Q	R
24	11747·16	11760·95	11775·59	12488·33	..	..
25	45·77	60·07	75·29	86·88	12501·24	..
26	44·36	59·15	74·99	85·37	00·20	12516·06
27	42·83	58·19	74·58	83·87	499·25	15·68
28	40·96	57·20	74·13	82·06	98·29	15·27
29	39·50	56·17	73·68	80·54	97·27	14·85
30	37·92	55·11	73·17	79·00	96·20	14·32
31	36·32	54·03	72·68	77·43	95·16	13·78
32	34·69	52·90	72·07	75·54	93·97	13·21
33	32·86	51·74	71·50	73·81	92·83	12·62
34	30·83	50·47	70·81	72·06	91·62	11·98
35	29·02	49·19	70·16	69·89	90·34	11·28
36	27·13	47·90	69·38	68·02	89·04	10·53
37	25·08	46·62	68·66	66·22	87·74	09·80
38	23·16	45·25	67·90	64·28	86·39	09·03
39	21·00	43·84	67·06	62·38	84·98	08·19
40	18·98	42·38	66·11	60·50	83·52	07·30
41	16·98	40·96	65·32		82·07	06·39
42	14·92	39·49	64·28		80·53	05·41
43	12·95	37·92	63·36		79·00	04·44
44	10·60	36·32	62·43		77·43	03·44
45	08·53	34·69	61·32		75·81	02·34
46	06·41	33·04	60·17		74·17	01·23
47	04·15	31·37	59·15		72·48	00·20
48	01·91	29·62	57·89		70·70	498·97
49		27·87	56·75		68·92	97·77
50		26·08	55·58		67·28	96·52
51		24·24	54·35		65·24	95·16
52		22·39	53·07		63·39	93·97
53					61·46	92·58
54					59·51	91·23
55					57·42	89·81

TABLE IV

Vacuum wave numbers (in cm.$^{-1}$) and line assignments of the 0–0 (7662·85 Å) *band of the* $B^2\Sigma_{1/2}$ – $X^2\Pi_{3/2}$ *(system III) of PrO*

J + 0·5	P	Q	R
24		13032·14	
25		31·48	
26		30·82	
27		30·02	
28		28·59	
29		27·69	13045·37
30		26·88	45·13
31		25·98	44·87
32		25·03	44·53
33	13005·03	24·07	44·13
34	03·38	23·08	43·72
35	01·79	22·12	43·31
36	00·01	21·02	..
37	12998·53	20·01	42·29
38	96·86	18·90	41·85
39	94·99	18·00	41·29
40	92·97	16·50	40·63
41	91·24	15·31	40·02
42	89·39	14·04	39·47
43	87·50	12·76	38·70
44	85·49	11·42	38·03
45	83·48	10·06	37·17
46	81·46	08·69	35·94
47	12979·36	13007·32	13035·47
48	77·22	05·83	34·52
49	75·17	04·33	33·84
50		02·82	32·76
51		01·27	31·48
52		12999·62	30·82
53		98·06	29·80
54		96·42	28·59
55		94·65	27·69
56		92·97	26·44
57		91·24	25·28
58		89·39	24·07
59		87·50	22·76
60		85·73	21·56
61		83·79	20·01
62		81·84	18·52
63		79·91	17·31
64		77·96	15·93
65		75·81	14·50
66		73·82	13·02
67		71·71	11·42
68		69·58	10·06
69		67·38	08·69
70		65·14	07·32

taken to be Q branch lines in each band. The successive differences of these (Q branch) lines were then plotted against a running number J. According to relation, $Q(J+1) - Q(J) = 2(B_v' - B_v'') + 2(B_v' - B_v'')J$, the gradient of such a plot gives the intercept $2(B_v' - B_v'')$. The J numbering of

TABLE V

$\Delta_1 F''(J)$ values of the $v'' = 0$ level of the $X^2\Pi_{3/2}$ state of PrO

J + 0·5	R (J) − Q (J + 1)			Q (J) − P (J + 1)		
	System I		System III	System I		System III
	0–0	1–0	0–0	0–0	1–0	0–0
26	16·80	16·81	..	16·32	16·33	..
27	17·38	17·39	..	17·23	17·19	..
28	17·96	18·00	..	17·70	17·75	..
29	18·57	18·65	18·49	18·25	18·27	..
30	19·14	19·16	19·15	18·79	18·77	..
31	19·78	19·81	19·84	19·34	19·62	19·69
32	20·33	20·38	20·46	20·04	20·16	20·00
33	21·03	21·00	21·05	20·91	20·76	20·69
34	21·62	21·64	21·60	21·45	21·73	21·29
35	22·26	22·21	22·29	22·06	22·32	22·11
36	22·76	22·79	22·82	22·82	22·85	22·49
37	23·41	23·41	23·39	23·46	23·46	23·15
38	24·06	24·05	24·16	24·25	24·01	23·91
39	24·68	24·67	24·79	24·86	24·48	24·72
40	25·15	25·23	25·32	25·40		25·26
41	25·83	25·86	25·98	26·04		25·92
42	26·56	26·41	26·71	26·54		26·54
43	27·04	27·01	27·28	27·32		27·28
44	27·74	27·63	27·97	27·79		27·93
45	28·28	28·17	28·48	28·28		28·60
46	28·80	28·75	28·93	28·89		29·33
47	29·53	29·50	29·64	29·64		30·10
48	30·02	30·05	30·19			
49	30·67	30·49	30·64			
50	31·34	31·28	31·49			
51	31·96	31·77	31·86			
52		32·51	32·76			
53		33·07	33·38			

the Q branch can be determined from the graph since the gradient equals the intercept at $J = 0$. From a comparison of the combination relations, $R(J) - Q(J+1)$ and $Q(J) - P(J+1)$ and the knowledge of J numbering for the Q branch lines, the numbering of P and R branch lines is assigned. The vacuum wave numbers and line assignments of the bands at 8488·65 Å and 7986·44 Å of system I and the band at 7663·85 Å of system III are given in Tables III and IV respectively. Equivalent sets of corresponding combination relations obtained in the 0–0 and 1–0 bands of system I and 0–0 band of system III are shown in Table V. The close agreement of the combination differences provides the confirmatory evidence that the bands have a common vibrational level, *viz.*, $v'' = 0$ in the final state assumed as $X^2{}_{3/2}\Pi$.

TABLE VI

Vibrational and rotational constants (in cm.$^{-1}$) of $X^2\Pi$, $A^2\Delta$, $B^2\Delta$, states of PrO

(*a*) $X^2\Pi_{3/2}$		
	$B_{0\,\mathrm{eff.}}$	$0{\cdot}304_7$
	$D_{0\,\mathrm{eff.}}$	$0{\cdot}17 \times 10^{-8}$
	ω_e	835
	$\omega_e x_e$	2
(*b*) $A^2\Delta_{5/2}$		
	$B_{0\,\mathrm{eff.}}$	$0{\cdot}287_0$
	$B_{1\,\mathrm{eff.}}$	$0{\cdot}286_0$
	ω_e	746
	$\omega_e x_e$	2·5
(*c*) $B^2\Delta_{5/2}$		
	$B_{0\,\mathrm{eff.}}$	$0{\cdot}289_0$
	$\Delta G_{1/2}$	754

(*d*) Band origins

$A^2\Delta_{5/2}$ ..	$X^2\Pi_{3/2}$ ..	ν_{0-0} ..	11772·2
$A^2\Delta_{5/2}$ ..	$X^2\Pi_{3/2}$ ..	ν_{1-0} ..	12513·44
$B^2\Delta_{5/2}$ ..	$X^2\Pi_{3/2}$ ..	ν_{0-0} ..	13041·36

The $\Delta_2F''(J)$ as well as $\Delta_2F'(J)$ values when plotted against J, gives half-integral values for J. This observation enabled us to conclude that the electronic states involved are states of even multiplicity. The rotational constants were evaluated in the usual way (*see* for example, Herzberg, 1950) from the combination differences $\Delta_2F(J)$.

The rotational and vibrational constants derived from the above analysis are given in Table VI.

NATURE OF ELECTRONIC TRANSITION

The rotational terms of the initial and final states could be represented by a simple formula, $F(J) = B_v J(J+1)$, J being half integral. The lines of the P, Q and R branches are evaluated from the term values in all the bands. Identification of only three branches, P, Q and R, without any satellite branches indicates that the transitions involved a change of $\Delta\Lambda = \pm 1$ between the initial and final states. The doublet nature of the electronic transitions, with large spin splittings of 934 cm.$^{-1}$ and 611 cm.$^{-1}$ respectively, in each transition, indicates that the initial and final states assumed as $^2\Delta$ and $^2\Pi$ states, belong to Hund's coupling case (*a*). The splittings observed are indeed the sums or differences of the upper and lower state splittings depending on the nature of states being inverted or regular. It is, however, assumed that the $^2\Delta$ and $^2\Pi$ states are regular.

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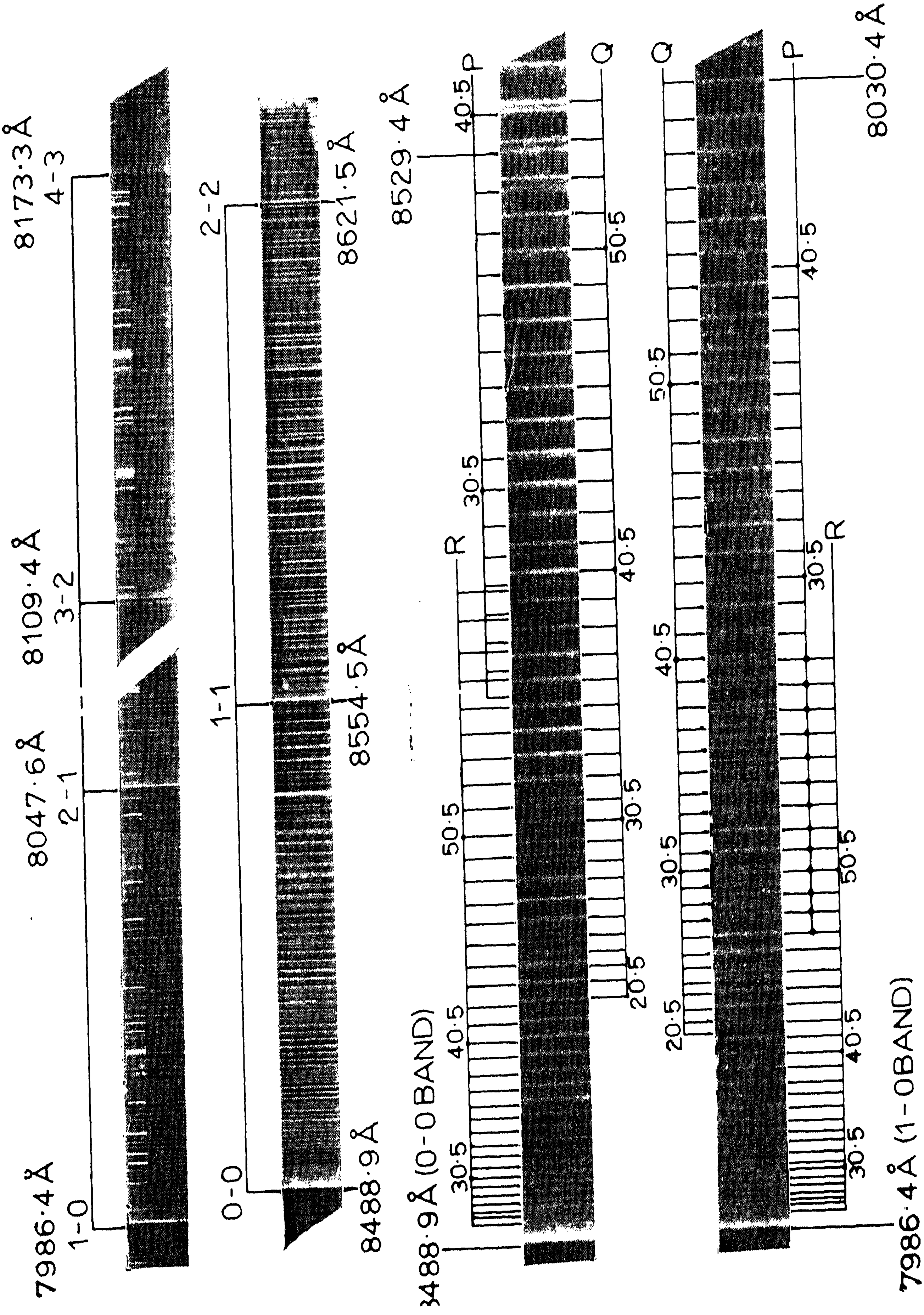

NEAR INFRARED BANDS OF PrO