

## Rotational analysis of 3664 Å band of NiCl

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**Abstract.** Nickel chloride was excited in a high frequency discharge source and the band at 3664 Å was photographed at an inverse dispersion of 0.59 Å/mm on a two metre plane grating spectrograph. The rotational analysis was carried out and the molecular constants of the upper state are reported. The rotational isotopic shifts due to  $^{37}\text{Cl}$  support the rotational analysis. The electronic transition involved is identified to be  $\beta^2\Delta_{5/2} \rightarrow X_1^2\Delta_{5/2}$ .

**Keywords.** Rotational analysis; molecular constants; isotopic shifts; electronic transition.

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### 1. Introduction

The emission spectrum of nickel chloride was first reported by More (1938) and later studied by others (Krishnamurthy 1952; Reddy and Rao 1960; Rao *et al* 1962; Rao and Rao 1969; Darji and Shah 1980; Gopal 1981; Gopal and Joshi 1981, 1982, 1983; Shah *et al* 1983). From these studies several fragmentary systems are reported. But only two band systems have been identified as  $F^2\Delta \rightarrow X^2\Delta$  (6395–6930 Å) and  $G^2\Delta \rightarrow X^2\Delta$  (7270–7750 Å) (Rao and Rao 1969). However from the study of poorly resolved rotational structure of the bands of *F* and *G* systems electronic transitions  $F^2\Delta_{5/2} \rightarrow X^2\Delta_{5/2}$  and  $G^2\Delta_{5/2} \rightarrow X^2\Delta_{5/2}$  have been suggested by them. The electronic transitions are not yet ascribed to the remaining systems of NiCl from the study of rotational structure of the bands. The nature of the ground state of NiCl is also not yet established unambiguously. Further the various band systems of this molecule are designated differently by different workers. The spectrum of NiCl is complex due to the large number of electronic transitions between closely spaced high multiplicity molecular states. This gives rise to many sub-systems overlapping with each other. Thus only a few bands have rotational structure free from overlapping and suitable for rotational analysis. This makes the study of the spectrum of NiCl more difficult. However the complex nature of the spectrum of NiCl involving transitions between high multiplicity energy states demands careful investigation. The present paper reports, for the first time, a rotational analysis of the (0, 0) band of  $\beta \rightarrow X$ , system at 3664 Å reported by Darji and Shah (1980). From the analysis of this band the rotational constants have been evaluated and the nature of electronic transition responsible for the emission of this band system has been discussed.

## 2. Experimental details

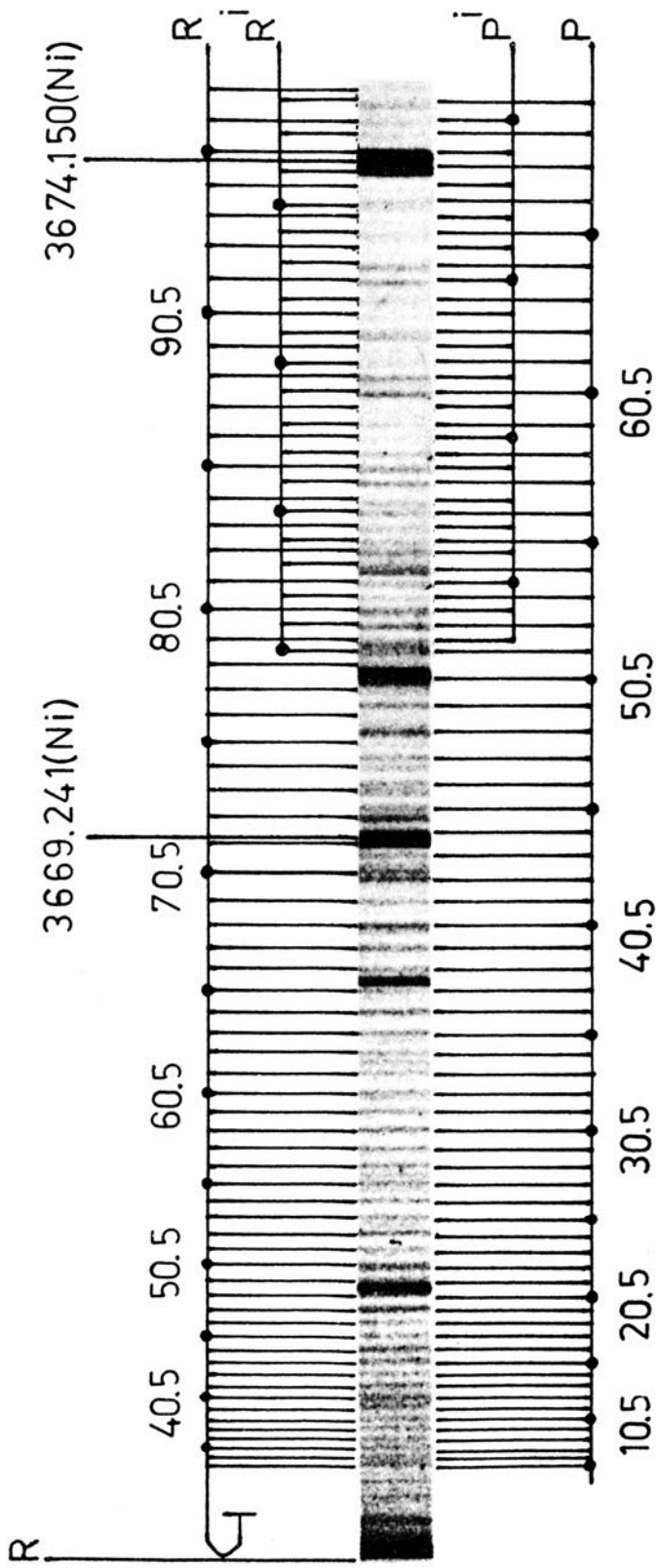
The spectrum of NiCl molecule in the region 3600–3800 Å has been excited in a high frequency discharge source using a pure sample (BDH) of dehydrated nickel chloride. The characteristic light blue colour of the discharge was maintained bright in which the bands developed strong in intensity. The (0,0) band at 3664 Å was recorded on Kodak 103–0 spectroscopic plates in the 7th order of the two metre plane grating spectrograph (Carl–Zeiss) at an inverse dispersion of 0.59 Å/mm with a fine slit of 20 μm. Standard method was used to measure the plates using Abbe comparator. The accuracy of the measurement is up to  $\pm 0.05 \text{ cm}^{-1}$  for sharp and unblended lines. To pick up the branches, intensity records of the rotational lines obtained by microdensitometer coupled with a potentiometric recorder were employed.

## 3. Results and discussion

The O–O band of  $\beta \rightarrow X$  system at 3664 Å photographed at high resolution and reproduced as seen on the negative (figures 1 a and b) reveals the presence of only two branches identified as R and P which are blended at low  $J$  values. As an intense Q branch is not seen the electronic transition should be of the type  $\Delta\Lambda = 0$ . The rotational analysis was carried out following the standard method (Herzberg 1950) of forming combination differences. The  $\Delta_2 F''(J)$  values of this band when compared with those of the lower state of  $F$  and  $G$  systems, reported by Rao and Rao (1969), and also with the  $L_1$  system reported by Darji and Sureshkumar (in press) were found to agree well i.e. the systems  $F$ ,  $G$ ,  $L_1$  and  $\beta$  have a common lower state and is designated as  $X_1^2\Delta_{5/2}$  as suggested by Rao and Rao (1969). Since a Q branch is not seen the transition should be  $\beta^2\Delta_{5/2} \rightarrow X_1^2\Delta_{5/2}$ .  $J$  assignments and vacuum wave numbers of the rotational lines are given in table 1, and the rotational constants obtained by the least squares fitting of the lines are given in table 2, together with the ground state constants reported by Rao and Rao (1969). The rotational lines of the isotopic molecule Ni<sup>37</sup>Cl have also been observed (see figure 1 and table 1) and the isotopic shifts support the analysis.

**Table 1.** Rotational constants of 3664 Å band of NiCl.

State	Constants	New values	Values reported by previous workers (Rao and Rao 1969)
$\beta^2\Delta_{5/2}$	$B'_0$	$0.15575 (\pm 21) \text{ cm}^{-1}$	—
	$D'_0$	$1.638 \times 10^{-7} \text{ cm}^{-1}$	—
	$r'_0$	$2.2293 (\pm 15) \text{ Å}$	—
	$I'_0$	$179.65 (\pm 24) \times 10^{-40} \text{ gcm}^2$	—
	$B''_0$	$0.16712 (\pm 23) \text{ cm}^{-1}$	$0.167 \text{ cm}^{-1}$
	$D''_0$	$1.607 \times 10^{-7} \text{ cm}^{-1}$	$2.0 \times 10^{-7} \text{ cm}^{-1}$
$X_1^2\Delta_{5/2}$	$r''_0$	$2.1521 (\pm 15) \text{ Å}$	$2.137 \text{ Å}$
	$I''_0$	$167.43 (\pm 23) \times 10^{-40} \text{ gcm}^2$	$167.56 \times 10^{-40} \text{ gcm}^2$
	$\nu_0$	$= 27282.81 \text{ cm}^{-1}$	



(a)

(b)

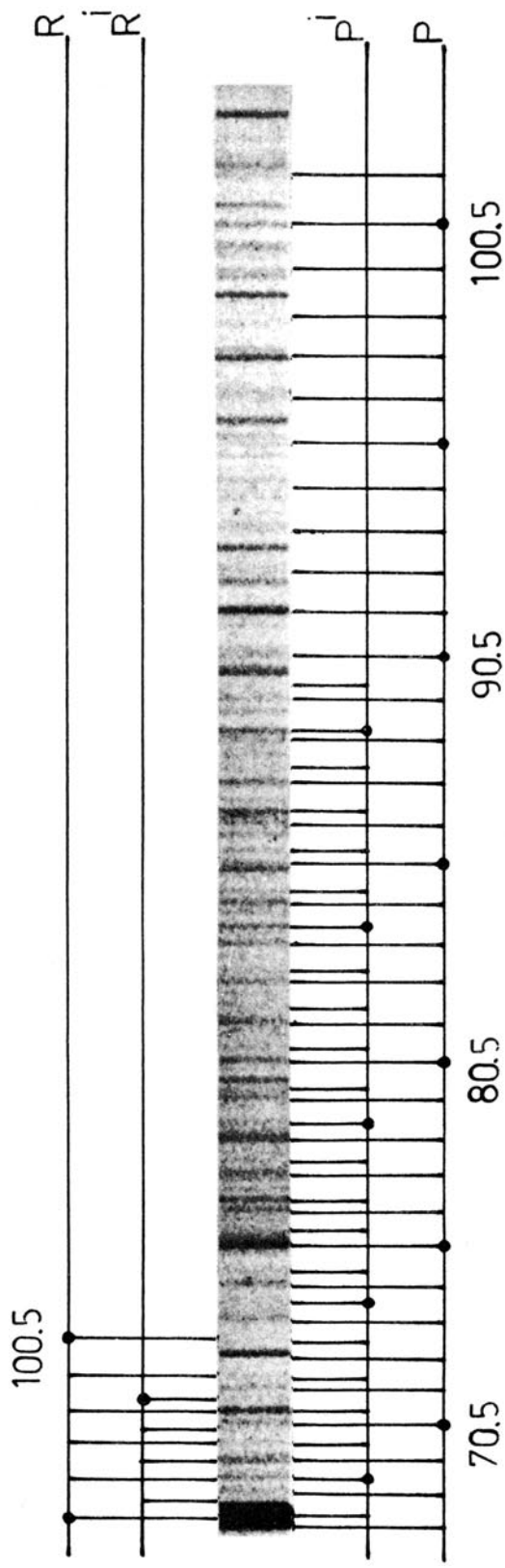


Figure 1a and b. Rotational structure of 3664 Å band of NiCl at 0.59 Å/mm.

**Table 2.** Data on the 3664 Å band of NiCl ( $\text{cm}^{-1}$ ).

$J - \frac{1}{2}$	$R(J)$	$P(J)$	$R(J)^i$	$P(J)^i$
1	2	3	4	5
10		27277.80		
11		77.12		
12		76.59		
13		75.94		
14		75.32		
15		74.56		
16		74.03		
17		73.24		
18		72.52		
19		71.79		
20		70.99		
21		70.15		
22		69.45		
23		68.54		
24		67.67		
25		66.67		
26		65.86		
27		64.88		
28		63.93		
29		62.95		
30		61.99		
31		60.94		
32		59.88		
33	27280.29	58.87		
34	79.83	57.74		
35	79.34	56.72		
36	78.80	55.53		
37	78.36	54.41		
38	77.75	53.23		
39	77.12	52.06		
40	76.59	50.84		
41	75.94	49.57		
42	75.32	48.34		
43	74.63	46.99		
44	74.03	—*		
45	73.24	44.36		
46	72.52	43.13		
47	71.79	41.65		
48	70.99	40.28		
49	70.15	38.85		
50	69.45	—*		
51	68.54	35.91		
52	67.67	34.57		
53	66.77	33.02		27234.85
54	65.86	31.56		33.95
55	64.88	29.89		32.19
56	63.93	28.37		30.73
57	62.95	26.74		29.25
58	61.99	25.16		27.55
59	60.94	23.53		25.98
60	59.88	21.88		24.32

(continued)

Table 2. (continued)

$J - \frac{1}{2}$	$R(J)$	$P(J)$	$R(J)^i$	$P(J)^i$
1	2	3	4	5
61	58.87	20.17		22.38
62	57.74	18.54		20.62
63	56.72	16.89		18.85
64	55.53	14.96		17.23
65	54.41	13.31		15.42
66	53.23	11.42		13.75
67	52.06	—*		12.02
68	50.84	07.96		10.32
69	49.57	06.02		—*
70	48.23	04.06		06.72
71	—*	02.11		04.77
72	45.59	200.16		02.95
73	43.96	197.92		200.91
74	42.83	96.22		199.07
75	41.16	93.90		96.85
76	39.98	92.16		95.40
77	38.31	89.86		93.07
78	—*	88.00		91.38
79	35.40	85.67		89.14
80	33.70	83.55	27235.91	87.08
81	32.19	81.39	34.08	85.21
82	30.73	79.15	33.05	82.88
83	29.12	79.97	31.23	80.47
84	27.47	74.72	29.75	78.40
85	25.82	72.56	27.96	76.49
86	24.12	70.27	26.74	74.09
87	22.46	67.96	24.82	72.08
88	20.70	65.59	23.25	69.62
89	18.95	63.26	21.88	67.36
90	17.32	61.01	20.17	65.23
91	15.42	58.49	18.34	
92	13.85	56.36	18.34	
93	12.02	53.80	14.96	
94	10.45	51.67	13.48	
95	08.50	49.18	11.72	
96	06.72	46.80	09.60	
97	04.77	44.74	07.96	
98	02.95	41.83	05.68	
99	100.91	39.18	04.26	
100	99.07	36.80	02.31	

\*Superposed by atomic line.

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