

Fine Structure Analysis of 4702 Å Band of the Molecule

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Abstract

The emission spectrum of the cobalt monochloride molecule has been excited in a high frequency discharge tube source and the (0,0) band of H-system at 4702 Å was photo-graphed at an inverse dispersion of 0.973 Å/mm in the 5th order of a two meter plane grating spectrograph (Carl-Zeiss). The fine structure analysis of the band has been carried out and the molecular constants are reported for the first time. Rotational isotopic shift due to ^{37}Cl support the analysis. The electronic transition involved is of the type $0^- \rightarrow 0^-$ of case (c) which is equivalent of $^3\Sigma^+ \rightarrow ^3\Sigma^+$ or $^5\Sigma^+ \rightarrow ^5\Sigma^+$.

1. Introduction

The molecular spectrum of cobalt monochloride molecule has been investigated in emission using heavy current and high frequency discharges by several workers [1-9]. From these studies it is known to be consisting of several fragmentary sub systems designated by various workers as A, B, C, D, E, F, G, H, H_1 , I, I_1 , J, J_1 , K, L, M, M_1 , M_2 , M_3 , M_4 , M_5 , M_6 , M_7 , M_8 , N_1 , N_2 , and 0 in the region 4200-7950 Å. Mesnage [1,2] recorded the bands in the region 4300-4850 Å and in the region 5550-5850 Å, but did not give any analysis. More [3] reported the vibrational analysis of three systems designated as 1, 2 and 3 in the region 4200-4750 Å. The bands of these systems are single headed and degraded to longer wavelengths. Krishnamurthy [4] has identified two more systems designed as 4 and 5 in the same spectral region. Krishnamurthy additionally proposed the vibrational analysis of six groups of line-like bands slightly degraded to red in the region 5350-6000 Å. Rao and Rao [5] disclosed the existence of a number of new band systems of CoCl in the photographic infrared region 6850-7950 Å and in the visible region 4600-5100 Å. Reddy et. al [6,7] reinvestigated the bands in the region 5350-5900 Å and in

the region 4200-5900 Å and reported vibrational constants. Darji et. al [8] reported the rotational analysis of the [0,0] band of the I_1 -system. It is interesting to note that the rotational analysis of only one band of CoCl is reported so far. This may be due to the heaviness of the molecule and the involvement of high multiplicity levels in the ground and excited states of CoCl molecule. Authors report here the fine structure analysis of the (0,0) band of H-system of CoCl molecule at 4702 Å for the first time. From the analysis molecular constants of upper and lower levels have been evaluated and the nature of electronic transition responsible for the emission of this band system has been discussed.

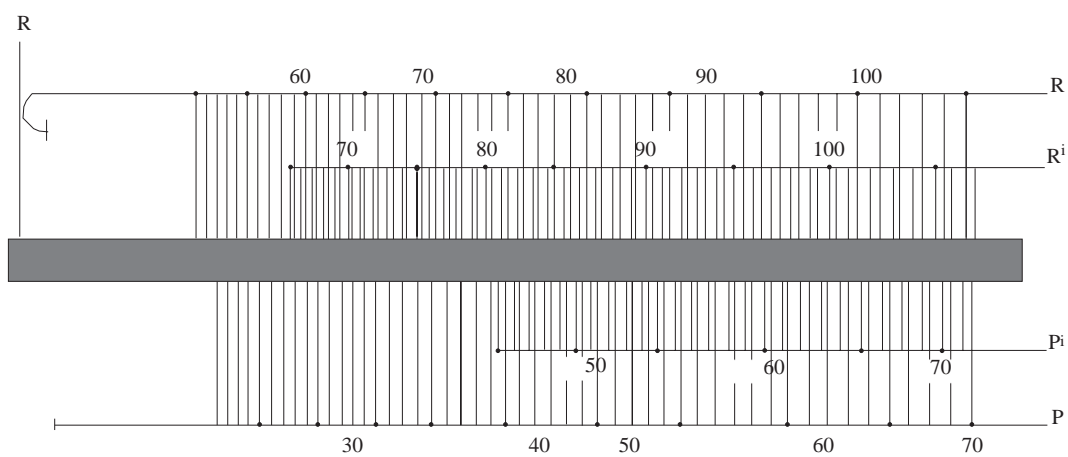
2. Experimental

The fifth order spectrum of 4702 Å band has been recorded with a dispersion of 0.973 Å/mm on a two metre plane grating spectrograph (Carl-Zeiss) using a high frequency discharge tube source. Dehydrated pure sample of cobalt chloride (BDH) has been employed. External heating was necessary to maintain the characteristic light blue colour of the discharge. The fine structure of the band is recorded on Kodak 103-0 Spectroscopic plates with a fine slit of 30 μ m. An exposure of about 8 hours was necessary to record the structure of the band with sufficient intensity. Measurements of fine structure lines on Abbe Comparates (Carl-Zeiss) was accurate up to $\pm 0.05 \text{ cm}^{-1}$ for sharp and unblended lines. Intensity record on a microdensitometer coupled with potentiometric recorder was helpful to pickup the branch lines unambiguously.

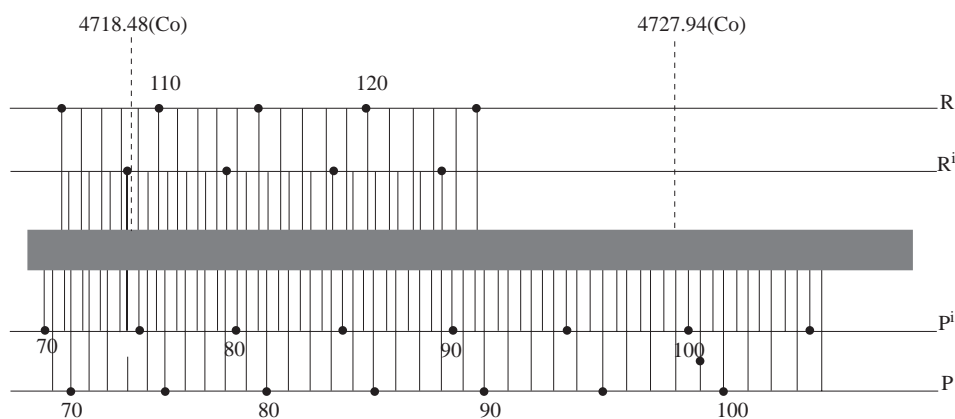
3. Results and Discussion

The high dispersion spectrum as seen on the negative is reproduced in Fig 1 (a and b) and reveals the presence of only two branches identified as R and P of which R form the head. The branch lines are well resolved with sufficient intensity. By following the standard method of Herzberg [9] the fine structure analysis has been carried out. The correctness of J numbering has been checked by the criterion suggested by Youngner and Winans [10]. From the graphical plots molecular constants B'_0 , B''_0 , D'_0 and D''_0 has been evaluated. B'_0 and B''_0 values have also been computed from the combination differences. The method of least square fit has been employed to determine standard deviation. The number in the parenthesis indicate these deviation with a confidence of 95%. The molecular constants obtained from the present analysis together with the constant of lower state of (0,0) band of I-system reported by Darji et al [8] are given in Tabel 1. The line frequencies calculated from the constants agree well with the observed ones. The analysis has been confirmed by the isotopic shift due to chlorine³⁷ in the branch lines. J numbering, vacuum wave numbers of branch lines and its isotopic lines are given in Tabel 2. However no other band of the system have suitable structure for analysis. It is observed that P branch lines ran faster than R-branch lines. From the observed features of the fine structure and the comparison of lower state combination differences and its constants reported by Darji et. al [8], it is clear that the lower state of this band and the lower state of 4834 Å band is same. Hence the lower state of this

band is ${}^3\Sigma^+$ or ${}^5\Sigma^+$. Since the band structure clearly shows only two branches the transition must obey the selection rule $\Delta\Lambda = 0$. Hence the upper state is also ${}^3\Sigma^+$ or ${}^5\Sigma^+$. Thus the transition responsible for the emission of this band system is suggested to be ${}^3\Sigma^+ \rightarrow {}^3\Sigma^+$ or ${}^5\Sigma^+ \rightarrow {}^5\Sigma^+$. Further the rotational lines do not show any sign of splitting even at high J values, we may conclude that the transition is $0^- \rightarrow 0^-$ of Hund's case (c) which is equivalent of ${}^3\Sigma^+ \rightarrow {}^3\Sigma^+$ or ${}^5\Sigma^+ \rightarrow {}^5\Sigma^+$.



(a)



(b)

Figure 1. Fine Structure of 4702 Å band of CoCl at 0.973 Å/mm

Table 1. Molecular Constants of 4702 Å band of CoCl

State	Constants	Values	Values reported by Darji et.al
Upper	B'_0	0.1536(±10)cm ⁻¹	-
	D'_0	1.67 x 10 ⁻⁷ cm ⁻¹	-
	r'_0	2.236(±7)x 10 ^{-8^{0A}}	-
	I'_0	182.24(±11)x10 ⁻⁴⁰ g cm ²	-
Lower	B''_0	0.1624(±10)cm ⁻¹	0.16272(±11) cm ⁻¹
	D''_0	1.79 x 10 ⁻⁷ cm ⁻¹	1.51 x 10 ⁻⁷ cm ⁻¹
	r''_0	2.175(±7)x 10 ^{-8^{0A}}	2.1721(±8) Å
	I''_0	172.43(±51)x10 ⁻⁴⁰ g cm ²	171.96(±12)x10 ⁻⁴⁰ g cm ⁻¹
	ν_0	21258.125 cm ⁻¹	

Table 2. Data on the 4702 Å band of CoCl (cm⁻¹)

J	R(J)	P(J)	$R^i(J)$	$P^i(J)$
21	-	21246.86	-	-
22	-	46.06	-	-
23	-	45.33	-	-
24	-	44.64	-	-
25	-	44.00	-	-
26	-	43.18	-	-
27	-	42.36	-	-
28	-	41.69	-	-
29	-	41.05	-	-
30	-	39.98	-	-
31	-	39.04	-	-
32	-	38.31	-	-
33	-	37.27	-	-
34	-	36.35	-	-
35	-	35.67	-	-
36	-	34.51	-	-
37	-	33.62	-	-
38	-	32.78	-	-
39	-	31.86	-	-
40	-	30.74	-	21231.56
41	-	29.64	-	30.51
42	-	28.57	-	29.47
43	-	27.64	-	28.59
44	-	26.61	-	27.64
45	-	25.58	-	26.61

Table 2. Cont.

J	R(J)	P(J)	$R^i(J)$	$P^i(J)$
46	-	24.26	-	25.39
47	-	23.07	-	24.26
48	-	22.26	-	23.58
49	-	20.83	-	22.16
50	-	19.68	-	20.98
51	-	18.20	-	19.68
52	-	17.38	-	18.61
53	-	16.20	-	17.73
54	-	14.75	-	16.20
55	21248.25	13.74	21248.54	15.48
56	47.58	12.43	47.91	13.98
57	46.96	11.26	47.27	12.85
58	46.16	09.95	46.50	11.57
59	45.51	08.27	45.88	09.85
60	44.85	07.27	45.13	08.08
61	44.24	05.98	44.64	07.92
62	43.21	04.46	43.73	06.17
63	42.53	03.17	42.98	05.06
64	41.73	01.71	42.26	03.72
65	41.01	200.35	41.49	02.33
66	40.13	198.92	40.78	201.01
67	39.20	97.45	39.98	199.36
68	38.52	95.98	39.20	98.10
69	37.61	94.47	38.31	96.69
70	36.68	92.99	37.61	95.10
71	35.67	91.46	36.35	93.70
72	34.51	89.87	35.38	92.11
73	33.62	88.37	34.51	90.11
74	32.78	86.71	33.62	89.11
75	31.86	85.20	32.78	87.62
76	30.50	83.45	31.37	85.74
77	29.47	81.91	30.50	84.26
78	28.40	80.05	29.47	82.57
79	27.36	78.33	28.40	81.09
80	26.31	76.57	27.36	79.35
81	25.40	75.29	26.51	78.03
82	24.26	73.43	25.29	76.25
83	23.07	71.75	24.26	74.73
84	21.92	69.98	23.07	72.95

Table 2. Cont.

J	R(J)	P(J)	$R^i(J)$	$P^i(J)$
85	20.83	68.25	21.92	71.37
86	19.68	66.53	20.83	69.59
87	18.41	64.56	19.68	67.78
88	17.38	63.02	18.61	66.18
89	15.93	61.11	17.38	64.27
90	14.75	59.31	16.20	62.70
91	13.16	57.11	14.75	60.77
92	12.22	55.60	13.74	58.91
93	10.74	53.35	12.43	56.91
94	09.41	51.69	11.26	55.12
95	08.26	49.75	09.95	53.35
96	06.95	47.82	08.57	51.69
97	05.47	45.81	07.27	49.75
98	04.20	43.94	05.95	47.82
99	02.81	41.95	04.72	45.81
100	01.34	40.04	03.17	43.94
101	199.73	37.86	01.71	41.95
102	98.44	35.90	00.35	40.04
103	96.69	33.50	198.92	37.86
104	95.32	31.65	97.45	35.99
105	93.70	-	95.98	-
106	92.11	-	94.47	-
107	90.37	-	92.48	-
108	88.79	-	90.99	-
109	87.33	-	89.87	-
110	85.74	-	88.37	-
111	84.22	-	86.71	-
112	82.57	-	85.20	-
113	81.00	-	83.69	-
114	79.35	-	81.91	-
115	77.45	-	80.36	-
116	75.92	-	78.88	-
117	74.01	-	76.77	-
118	72.18	-	75.29	-
119	70.51	-	73.43	-
120	68.61	-	71.75	-
121	66.91	-	69.98	-
122	65.02	-	68.25	-

Table 2. Cont.

J	R(J)	P(J)	$R^i(J)$	$P^i(J)$
123	63.42	-	66.52	-
124	61.56	-	64.76	-
125	59.76	-	63.02	-

References

- [1] P. Mesnage, C. R. Acad Sci, **120** (1935) 389.
- [2] P. Mesnage, *Ann Phys*, **12**, (1939) 5.
- [3] K. R. More, *Phys Rev.*, **54** (1938) 122.
- [4] V. g. Krishnamurty, *Indian J. Phys.*, **26** (1952) 177.
- [5] S. V. K. Rao & T. Rao, *Indian J. Phys.*, **35** (1961) 556.
- [6] C. V. Reddy, A. L. Narayana & P. T. Rao, *Indian J. Pure & Appl Phys.*, **22** (1984) 550.
- [7] C. V. Reddy, A. L. Narayana & P. T. Rao, *Optica Pura Y. APplicada (Spain)*., **17** (1984) 289.
- [8] A. B. Darji, M. B. Sureshkumar, N. R. Shah and P. M. Shah *Indian J. Pure & Appl Phys.*, **26** (1988) 26.
- [9] G. Herzberg, *Molecular Spectra and Molecular Structure Vol 1* (Van Nostrand, New York 1950).
- [10] P. Yougner & J. G. Winans, *J. mol Spectrosc (USA)*, **4** (1960) 23.