PART - II

CHAPTER - IV

ROTATIONAL ANALYSES OF PbCl BANDS

SPECTRUM OF LEAD MONOCHLORIDE MOLECULE

This chapter deals with the work done on the spectrum of lead monochloride molecule. Detailed analysis of $A \longrightarrow X_1$ system is presented here. The $A \longrightarrow X_1$ system consists of the bands degraded towards red in the region $\lambda\lambda$ 4200-5700 Å. Vibrational analysis of $A \longrightarrow X_1$ system of PbCl molecule was done by Morgan (1936) and Rochester (1936). Rotational analysis of this band system has been carried out by Rao and Rao (1964). They were able to pick up only single P and R branch lines and hence case (c) (½ - ½) transition has been attributed to this system of PbCl molecule. However, Philip Methew (1979) was able to pick up P, Q and R branches. He calculated rotational constants which did not agree with the constants obtained by Rao and Rao. In order to confirm the nature of transition involved and evaluate accurate constants a reinvestigation of $A \longrightarrow X_1$ system of PbCl molecule has been undertaken.

The detailed rotational analyses of (0,5), (0,4), (0,3) and (2,1) bands lying at 4916.4 Å, 4846.0 Å, 4777.5 Å and 4548.9 Å respectively carried out using high resolution and dispersion are discussed in the present chapter.

EXPERIMENTAL PROCEDURE AND ANALYSIS

The spectrum of PbCl molecule was excited in a conventional type quartz discharge tube using a high frequency oscillator providing 125 Watts of power at 10-15 MHz. Continuous evacuation of the discharge tube was done by a high vacuum pump. The discharge tube was heated externally to maintain the characteristic sky blue colour of the discharge. Under these conditions the spectrum of PbCl was seen to develop with strong intensity without any impurities. Overlapping orders were avoided by using Carl-Zeiss pre-disperser.

Measurements of rotational lines were made on Abbe (Carl-Zeiss) comparator against internal standards of sharp atomic lines of Lead and Chlorine. In order to pick up the branches intensity records of the rotational lines obtained by microdensitometer coupled with Potentiometric recorder were employed. The rotational analysis has been carried out by following the standard methods (Herzberg, 1950). The correctness of J assignments of rotational lines is confirmed by applying the criterion suggested by Youngner and Winans (1960). i.e. When a change of $\pm$ 1 in J assignment was made the straight line graph of $\frac{\Delta_2 F'(J)}{(J + 1/2)}$ against $(J + 1/2)^2$ shows a deviation from straight line into upward or downward curve at low J values. From the graphical plots B and D values for upper and lower states are evaluated. The line frequencies calculated from the constants agree with the observed ones within the limit of experimental errors.

The above method is applied to all the bands of PbCl under the present study.

1. ROTATIONAL ANALYSIS OF (0,5) BAND AT 4916.4 Å

The 4916.4 Å band of PbCl has been recorded on Kodak 103 - 0 and ORWO WU_3 spectroscopic plates in the 5th order of the 2 - meter plane grating spectrograph (Carl-Zeiss) at an inverse dispersion of 0.8775 Å/mm with a slit of 30 microns. Exposures of about 8 hours were found enough to record the structure of the band with good intensity. The accuarcy of measurements of wavenumbers is upto ± 0.05 cm^{-1} for sharp and unblended lines.

The rotational structure of the band as seen on negative has been reproduced in Plate 1 (a) and (b) which reveals the presence of only two branches, identified as R and P branch of which

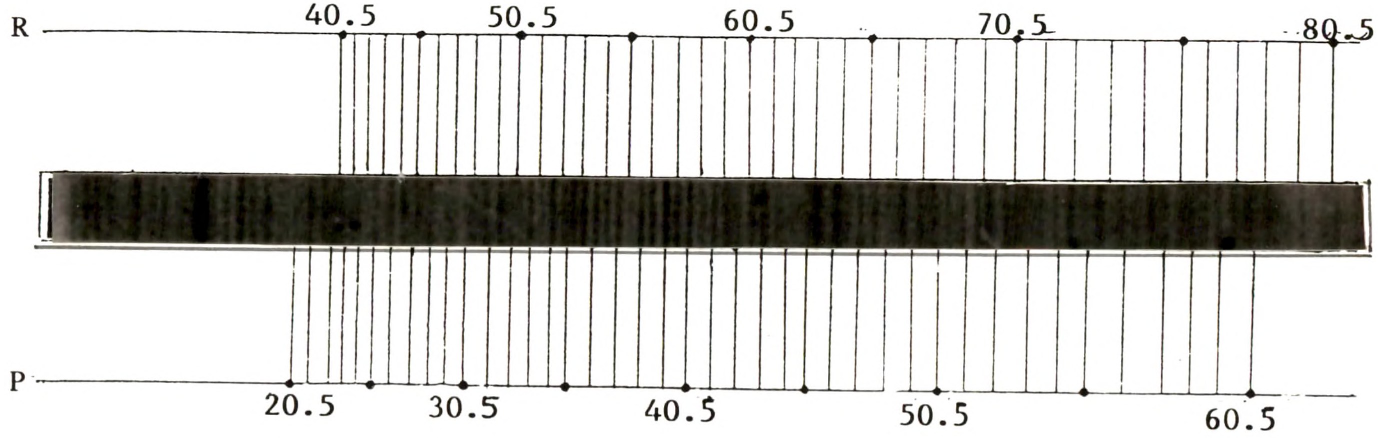

PLATE - 1(a)

ROTATIONAL STRUCTURE OF 4916.4 Å BAND OF PbCl MOLECULE

DISPERSION 0.8775 Å/mm

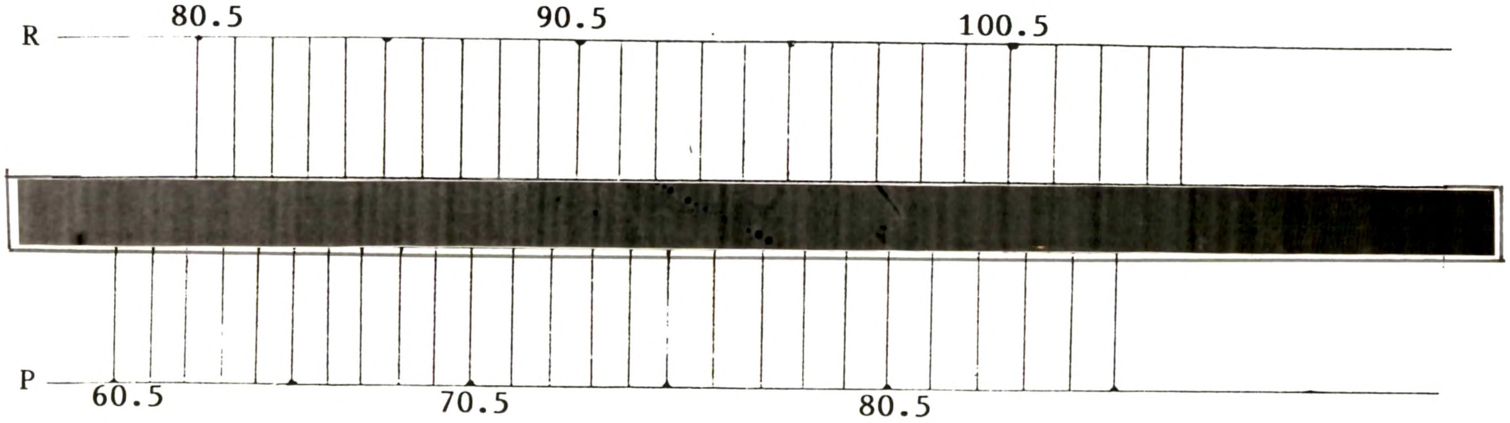

PLATE - 1(b)

ROTATIONAL STRUCTURE OF 4916.4 Å BAND OF PbCl MOLECULE

DISPERSION 0.8775 Å/mm

R is the head forming branch. As an intense Q branch is not found, the electronic transition should be of type for which $\Delta\Lambda = 0$. The rotational analysis has been carried out by following the standard method (Herzberg, 1950) by forming the combination differences,

$$\Delta_2 F'(J) = R(J) - P(J) \text{ and}$$

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

The graphs of $\Delta_2 F(J)$ against J and $\frac{\Delta_2 F(J)}{(J+1/2)}$ against $(J+1/2)^2$ for upper and lower state are shown in figures 8 and 9 respectively. J assignments, vacuum wavenumbers and combination differences are given in Table 5. The position of ν_{origin} is calculated to be 20334.374 cm^{-1}, using the values of ν_{head}, B'_o and B''_o in the equation

$$\nu_{head} - \nu_{origin} = \frac{(B'_o + B''_o)^2}{4(B'_o - B''_o)},$$

which is in good agreement with the observed value of 20334.14 cm^{-1}. The combination differences and constants of lower state of this band are in good

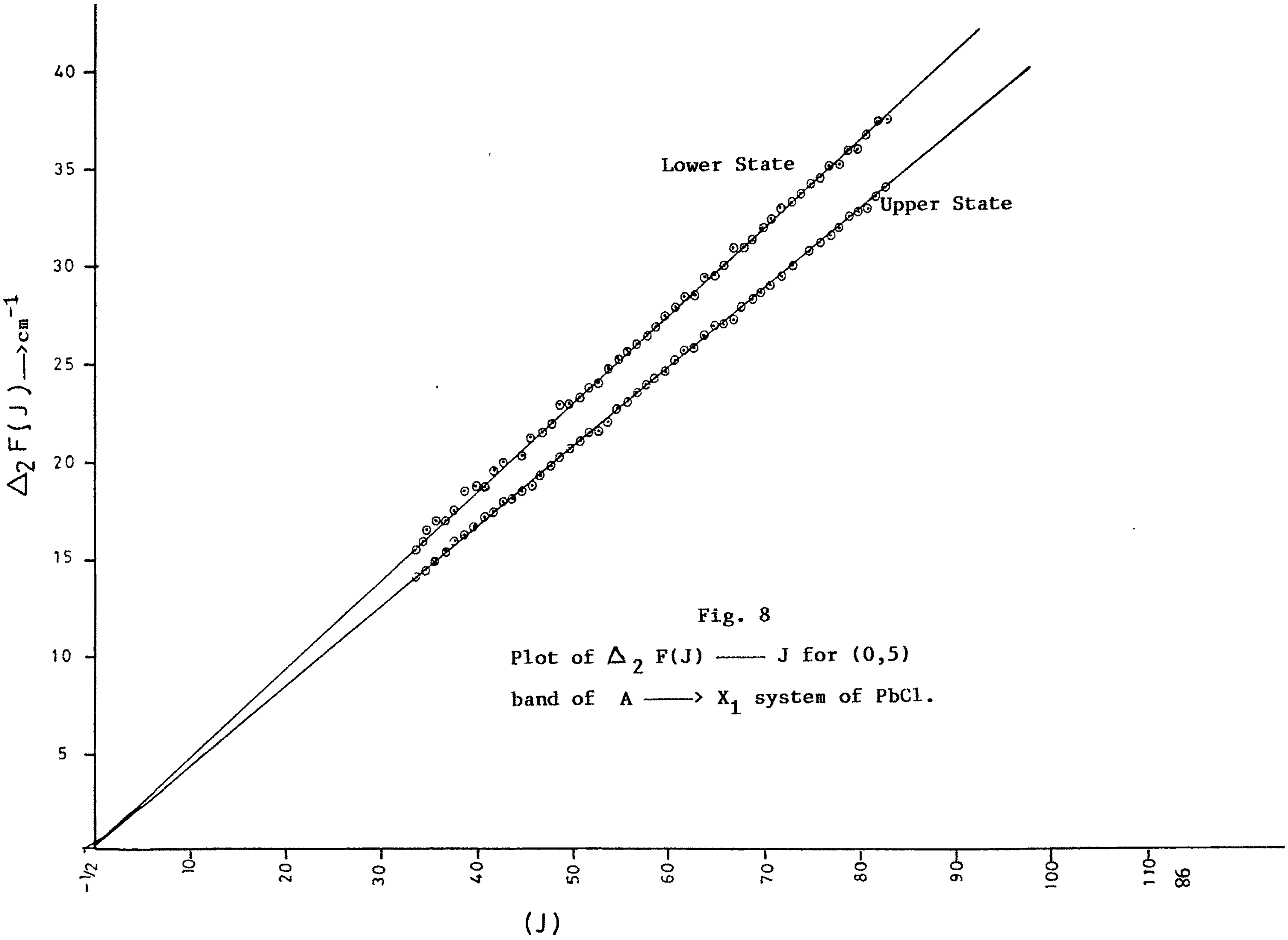

Fig. 8

Plot of Δ_2 F(J) —— J for (0,5) band of A ——> X_1 system of PbCl.

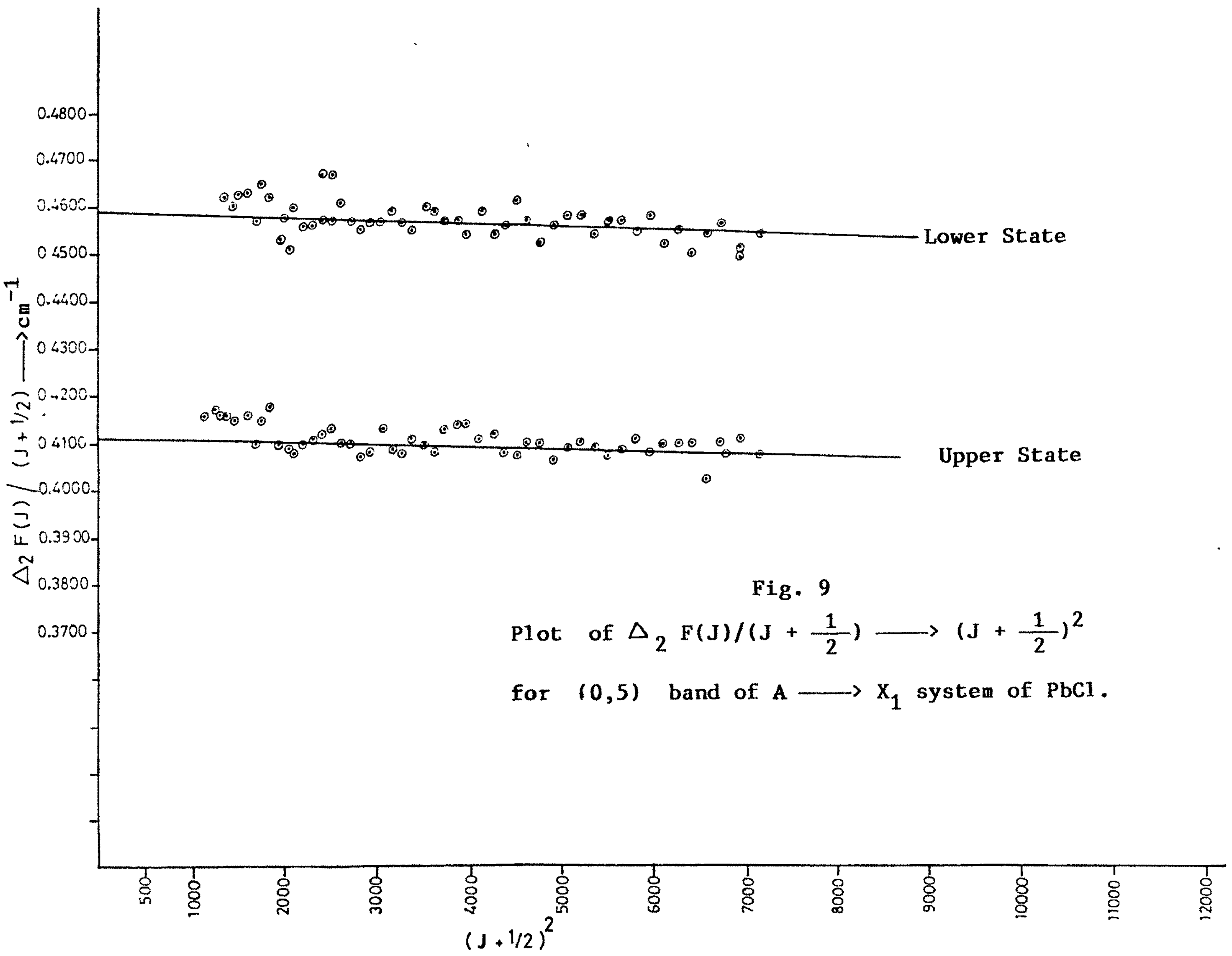

Fig. 9

Plot of $\Delta_2 F(J)/(J + \frac{1}{2}) \longrightarrow (J + \frac{1}{2})^2$

for (0,5) band of A ⟶ X_1 system of PbCl.

TABLE - 5

J ASSIGNMENTS, VACUUM WAVENUMBERS AND COMBINATION DIFFERENCES OF THE (0,5) BAND OF $A(\frac{1}{2}) \longrightarrow X_1(\frac{1}{2})$ SYSTEM OF PbCl MOLECULE.

J	R(J) cm^{-1}	P(J) cm^{-1}	$\Delta_2F''(J)$ $=R(J-1)-P(J+1)$ cm^{-1}	$\Delta_2F'(J)$ $=R(J)-P(J)$ cm^{-1}
1	2	3	4	5
11.5				
12.5				
13.5				
14.5				
15.5				
16.5				
17.5				
18.5				
19.5				
20.5		20324.25		
21.5		20323.55		
22.5		20322.57		
23.5		20321.86		
24.5		20321.31		
25.5		20320.63		
26.5		20319.72		
27.5		20318.64		
28.5		20317.84		
29.5		20317.12		
30.5		20316.11		
31.5		20315.10		
32.5		20313.97		
33.5	20327.35	20313.22		14.13
34.5	20326.71	20312.11	16.42	14.60
35.5	20326.03	20310.93	16.91	15.10

1	2	3	4	5
36.5	20324.83	20308.94	17.45	15.89
37.5	20324.83	20308.94	17.45	15.89
38.5	20324.02	20307.85	18.44	16.17
39.5	20323.04	20306.39	18.82	16.65
40.5	20322.42	20305.20	18.72	17.22
41.5	20321.74	20304.32	19.51	17.42
42.5	20320.88	20302.91	19.85	17.97
43.5	20319.93	20301.89	19.91	18.09
44.5	20319.39	20300.97	20.28	18.42
45.5	20318.42	20299.65	21.13	18.77
46.5	20317.51	20298.26	21.41	19.25
47.5	20316.76	20297.01	21.91	19.75
48.5	20315.80	20295.60	22.88	20.20
49.5	20314.52	20293.88	23.04	20.64
50.5	20313.69	20292.76	23.15	20.93
51.5	20312.68	20291.93	24.12	21.55
52.5	20311.48	20289.93	24.12	21.55
53.5	20310.60	20288.56	24.66	22.04
54.5	20309.53	20286.82	52.16	22.71
55.5	20308.32	20285.44	25.71	22.88
56.5	20307.09	20283.82	26.03	23.27
57.5	20306.11	20282.29	26.37	23.82
58.5	20304.90	20280.72	27.12	24.18
59.5	20304.90	20280.72	27.12	24.18
59.5	20303.48	20278.99	27.52	24.49
60.5	20302.56	20277.38	27.89	25.18
61.5	20301.25	20275.59	28.36	25.66
62.5	20300.30	20274.20	28.59	26.10
63.5	20298.98	20272.66	29.37	26.32
64.5	20297.74	20270.93	29.48	26.81
65.5	20296.41	20269.50	30.08	26.91

1	2	3	4	5
66.5	20294.90	20267.66	30.89	27.24
67.5	20293.41	20265.52	31.09	27.89
68.5	20292.09	20263.81	31.20	28.26
69.5	20290.66	20262.21	31.92	28.45
70.5	20289.21	20260.17	32.49	29.04
71.5	20287.66	20258.17	32.98	29.49
72.5	20286.11	20256.23	33.14	29.88
73.5	20284.59	20254.52	33.79	30.07
74.5	20282.99	20252.32	34.24	30.67
75.5	20281.57	20250.35	34.55	31.22
76.5	20279.88	20248.44	35.26	31.44
77.5	20278.26	20246.31	35.23	31.95
78.5	20277.05	20244.65	35.98	32.40
79.5	20275.04	20242.28	35.97	32.76
80.5	20273.62	20241.08	36.79	32.54
81.5	20271.84	20238.25	37.38	33.59
82.5	20270.36	20236.26	37.30	34.10
83.5	20268.61	-	-	-
84.5	20266.37	-	-	-
85.5	20264.41	-	-	-
86.5	20262.42	-	-	-
87.5	20260.73	-	-	-
88.5	20258.83	-	-	-
89.5	20256.88	-	-	-
90.5	20255.25	-	-	-
91.5	20252.95	-	-	-
92.5	20251.25	-	-	-
93.5	20248.73	-	-	-
94.5	20246.93	-	-	-
95.5	20244.95	-	-	-
96.5	20242.68	-	-	-
97.5	20241.08	-	-	-

1	2	3	4	5
98.5	20239.15	-	-	-
99.5	20236.51	-	-	-
100.5	20233.98	-	-	-
101.5	20231.87	-	-	-
102.5	20230.07	-	-	-
103.5	20227.30	-	-	-
104.5	20225.01	-	-	-

agreement with those reported by Rao and Rao (1964).

From consideration of the electronic configuration for the ground and first excited states of PbCl, the transition of A ——> X_1 system is expected to be $^2\Sigma \longrightarrow {}^2\Pi_{1/2}$ when comparison is done with the similar molecule PbF having the ground state $X_1\ {}^2\Pi_{1/2}$.

However, an examination of rotational structure of this band reveals the presence of only two branches P and R. The branch which forms the head and which becomes extremely weak at high J values is easily identified as the R branch. The fact that no splitting of rotational lines has been observed even at high J values, strongly indicates Hund's case (c) equivalent to the transition (½ - ½). Theoretically if Hund's case (c) applies to the ground and first excited states, the transition of A ——> X_1 system PbCl, is expected to be (½ - ½) which gives rise to two branches P and R, similar to a $^2\Pi_{1/2} \longrightarrow {}^2\Pi_{1/2}$ transition in Hund's case (a). The J numbering of rotational lines of this band is fixed from the comparison of the lower state combination differences for the common lower state of the bands reported by Rao and Rao (1964).

The nature of electronic transition responsible for the emission of A ——> X_1 system of PbCl molecule has been discussed in detail in chapter VI. The rotational constants obtained from the analysis of (0,5) band are given in Table 6.

TABLE - 6

ROTATIONAL CONSTANTS OF (0,5) BAND OF PbCl MOLECULE

State	Constants	Values
A(½)	B'_o	$0.10275\ cm^{-1}$
	D'_o	$0.61 \times 10^{-7}\ cm^{-1}$
	I'_o	$272.711 \times 10^{-40} gcm^2$
	r'_o	2.3419 Å
X(½)	B''_5	$0.11475\ cm^{-1}$
	D''_5	$0.72 \times 10^{-7}\ cm^{-1}$
	I''_5	$244.192 \times 10^{-40} gcm^2$
	r''_5	2.2161 Å
	ν_o	$20334.374\ cm^{-1}$

2. ROTATIONAL ANALYSIS OF (0,4) BAND AT 4846.0 Å

The 4846.0 Å band of PbCl has been recorded on Kodak 103 - 0 and ORWO - WU_3 spectroscopic plates in the 5th order of the 2 - meter plane grating spectrograph (Carl-Zeiss) at an inverse despersion of 0.90166 Å/mm with a slit of 30 microns. Exposures of about 8 hours were found enough to record the structure of the band with good intensity. The accuracy of the measurement is upto ± 0.05 cm^{-1} for sharp and unblended lines. The

The rotational structure of the band reproduced in plate 2 (a) and (b) reveals the presence of P and R branches, of which R is the head forming branch. As the intense Q branch is not found the transition should be of the type for which $\Delta\Lambda = 0$. The rotational analysis has been carried out by the standard method (Herzberg 1950) by taking combination relations.

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

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

The graphs of $\Delta_2F(J)$ against J and

$\Delta_2F(J)/(J + \frac{1}{2})$ against $(J + \frac{1}{2})^2$

are shown in fig. 10 and 11 respectively from which rotational constants are calculated.

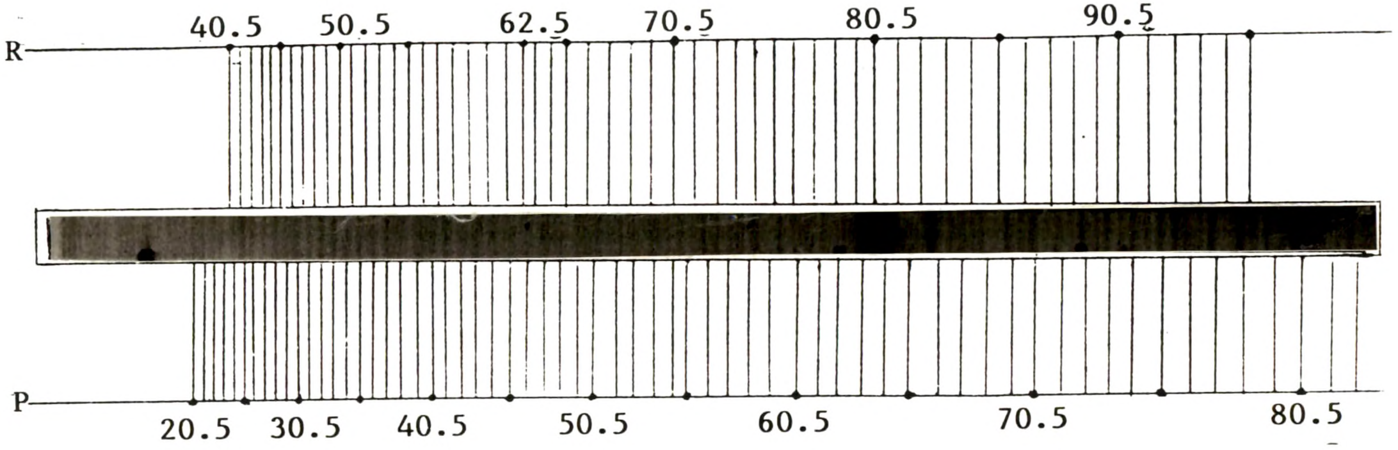

PLATE - 2(a)

ROTATIONAL STRUCTURE OF 4846 Å BAND OF PbCl MOLECULE

DISPERSION 0.90166 Å/mm

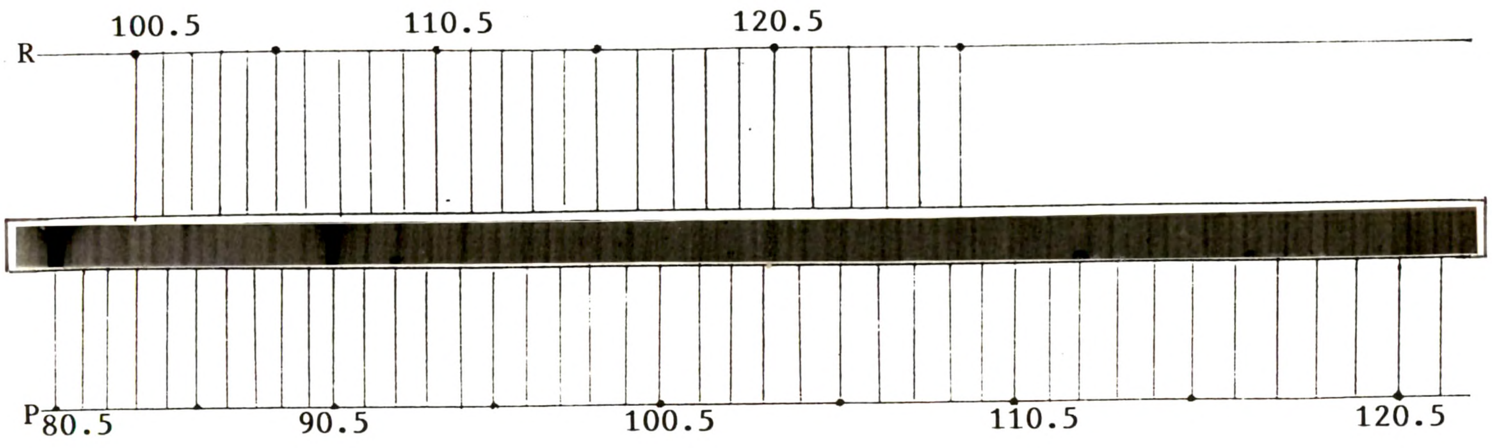

PLATE - 2(b)

ROTATIONAL STRUCTURE OF 4846 Å BAND OF PbCl MOLECULE

DISPERSION 0.90166 Å/mm

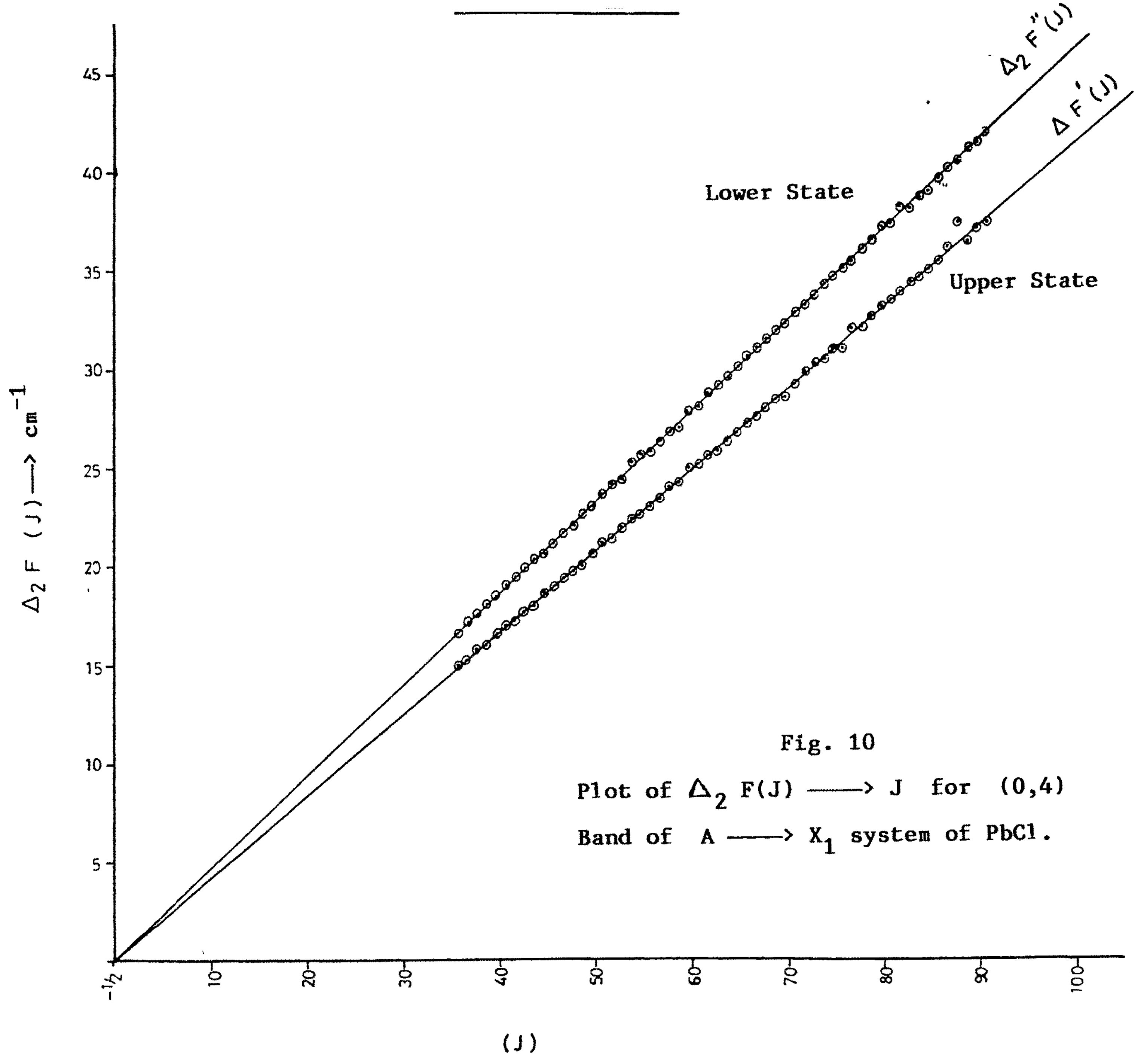

Fig. 10

Plot of Δ_2 F(J) ——> J for (0,4)

Band of A ——> X_1 system of PbCl.

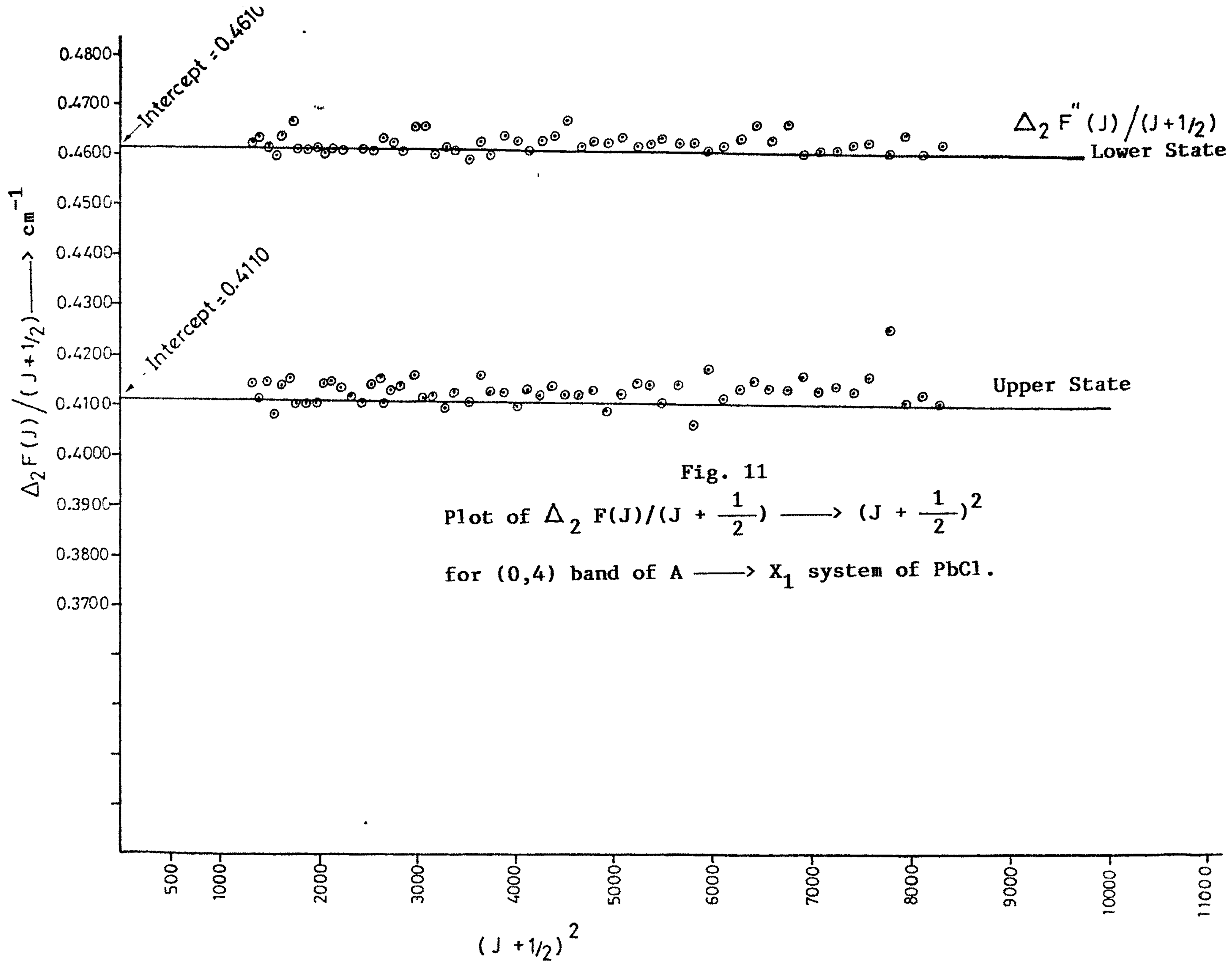

Fig. 11

Plot of $\Delta_2 F(J)/(J + \frac{1}{2}) \longrightarrow (J + \frac{1}{2})^2$

for (0,4) band of A $\longrightarrow$ X_1 system of PbCl.

The J assignments, wavenumbers of P and R branch lines and combination differences for the rotational lines of (0,4) band are given in Table 7. The rotational constans evaluated from the analysis of this band are collected in Table 8.

TABLE - 7

J ASSIGNMENTS, VACUUM WAVENUMBERS AND COMBINATION DIFFERENCES OF THE (0,4) BAND OF PbCl MOLECULE

J 1	R(J) cm^{-1} 2	P(J) cm^{-1} 3	$\Delta_2F''(J)$ cm^{-1} 4	$\Delta_2F'(J)$ cm^{-1} 5
20.5		20619.43		
21.5		20618.78		
22.5		20617.06		
23.5		20617.30		
24.5		20616.47		
25.5		20615.63		
26.5		20614.75		
27.5		20613.95		
28.5		20613.10		
29.5		20612.13		
30.5		20611.31		
31.5		20609.88		
32.5		20608.98		
33.5		20608.01		
34.5	20621.53	20606.85		14.68
35.5	20620.81	20605.91	16.63	14.90
36.5	20620.11	20604.90	17.13	15.21
37.5	20619.43	20603.68	17.53	15.75
38.5	20618.48	20602.58	17.91	15.90
39.5	20618.06	20601.52	18.52	16.54
40.5	20616.99	20599.96	19.10	17.03
41.5	20616.17	20598.96	19.32	17.21
42.5	20615.29	20597.67	19.80	17.62
43.5	20614.38	20596.37	20.30	18.01
44.5	20613.62	20594.99	20.68	18.63
45.5	20612.74	20593.70	21.16	19.04
46.5	20611.86	20592.46	21.62	19.40

1	2	3	4	5
47.5	20610.88	20591.12	22.07	19.76
48.5	20609.88	20589.79	22.57	20.09
49.5	20608.98	20588.31	23.02	20.67
50.5	20608.01	20586.86	23.59	21.15
51.5	20606.85	2585.39	24.01	21.46
52.5	20605.35	20584.00	24.39	21.35
53.5	20604.90	20582.46	24.57	22.44
54.5	20603.38	20580.78	25.57	22.60
55.5	20602.37	20579.33	25.71	23.04
56.5	20600.98	20577.67	26.28	23.31
57.5	20599.91	20576.09	26.72	23.82
58.5	20598.45	20574.26	27.75	24.19
59.5	20597.08	20572.16	27.70	24.92
60.5	20595.89	20570.75	28.00	25.14
61.5	20594.63	20569.08	28.70	25.55
62.5	20592.95	20567.19	29.08	25.76
63.5	20591.96	20565.55	29.50	26.41
64.5	20590.21	20563.45	30.01	26.76
65.5	20589.29	20561.95	30.56	27.34
66.5	20587.22	20559.65	31.04	27.57
67.5	20586.24	20558.25	31.38	27.99
68.5	20584.31	20555.84	31.87	28.47
69.5	20582.95	20554.37	32.31	28.61
70.5	20581.21	20552.00	32.85	29.21
71.5	20579.90	20550.10	33.19	29.80
72.5	20578.20	20548.02	33.71	30.18
73.5	20576.52	20546.19	34.59	30.33
74.5	20574.62	20543.61	34.61	31.01
75.5	20572.88	20541.91	35.08	30.97
76.5	20571.61	20539.54	35.42	32.07
77.5	20569.52	20537.46	35.97	32.06
78.5	20568.24	20535.64	36.54	32.60

1	2	3	4	5
79.5	20566.12	20532.98	37.19	33.14
80.5	20564.52	20531.05	37.44	33.47
81.5	20562.51	20528.68	38.22	33.83
82.5	20560.76	20526.30	38.11	34.46
83.5	20559.04	20524.40	38.61	34.64
84.5	20557.24	20522.15	39.06	35.09
85.5	20555.40	20519.98	39.67	35.42
86.5	20553.68	20517.57	40.14	36.11
87.5	20552.64	20515.26	40.40	37.38
88.5		20513.28		
89.5		20510.66		
90.5		20508.37		
91.5		20506.53		
92.5		20504.06		
93.5		20501.97		
94.5		20498.92		
95.5		20496.96		
96.5		20494.32		
97.5		20491.40		
98.5		20488.42		
99.5		20486.28		
100.5		20483.29		
101.5		20480.58		
102.5		20478.31		
103.5		20475.41		
104.5		20472.47		
105.5		20469.93		
106.5		20466.92		
107.5		20464.45		
108.5		20461.43		
109.5		20458.63		
110.5		20455.64		

TABLE - 8

ROTATIONAL CONSTANTS OF (0,4) BAND OF PbCl MOLECULE

State	Constants	Values
$A(\frac{1}{2})$	B'_o	$0.10275\ cm^{-1}$
	D'_o	$0.5950 \times 10^{-7}\ cm^{-1}$
	I'_o	$272.711 \times 10^{-40}\ g\,cm^2$
	r'_o	2.3419 Å
$X(\frac{1}{2})$	B''_4	$0.11525\ cm^{-1}$
	D''_4	$0.7350 \times 10^{-7}\ cm^{-1}$
	I''_4	$243.133 \times 10^{-40}\ g\,cm^2$
	r''_4	2.212 Å
	ν_o	$20628.85\ cm^{-1}$

3. ROTATIONAL ANALYSIS OF (0,3) BAND AT 4777.5 Å

The 4777.5 Å band of PbCl has been recorded on Kodak 103 - 0 and ORWO WU-3 spectroscopic plates in the 5th order of 2 - meter plane grating spectrograph (Carl-Zeiss) at an inverse despersion of 0.9205 Å/mm with a slit of 30 microns. Exposures of about 8 hours were found enough to record the structure of the band with good intensity. The accuracy of the measurement is upto ± 0.05 cm^{-1} for sharp and unblended lines. A detailed examination of rotational structure of this band reveals the presence of only two branches P and R. The branch which forms the head and which becomes extremely weak at high J values is easily identified as the R branch.

The rotational structure of the head reproduced in plate No.3 (a) and (b). As the intense Q branch is not found the transition should be of the type for which $\Delta\Lambda = 0$. The rotational analysis has been carried out by the standard method (Herzberg, 1950) by taking combination relations.

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

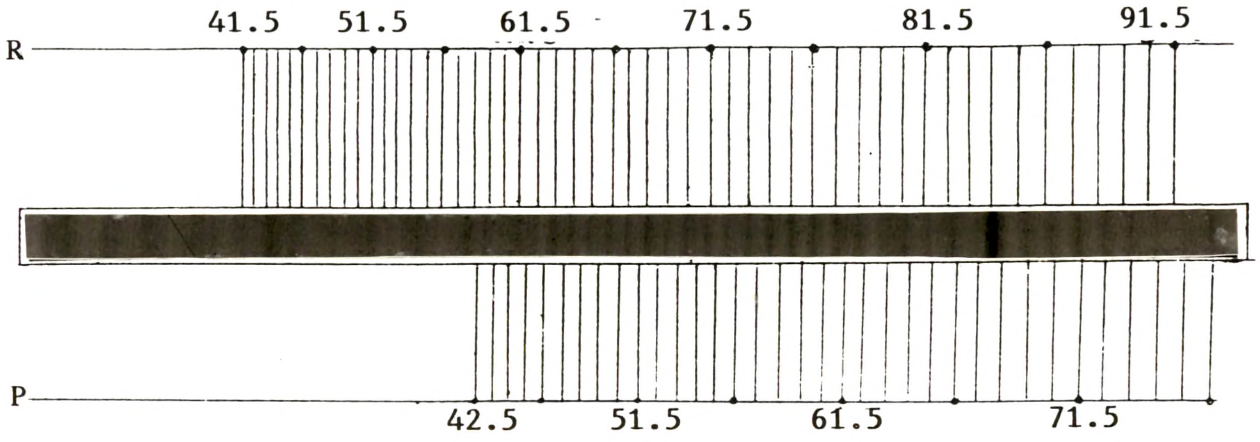

PLATE - 3(a)

ROTATIONAL STRUCTURE OF 4777.5 Å BAND OF MOLECULE

DISPERSION 0.92054 Å/mm

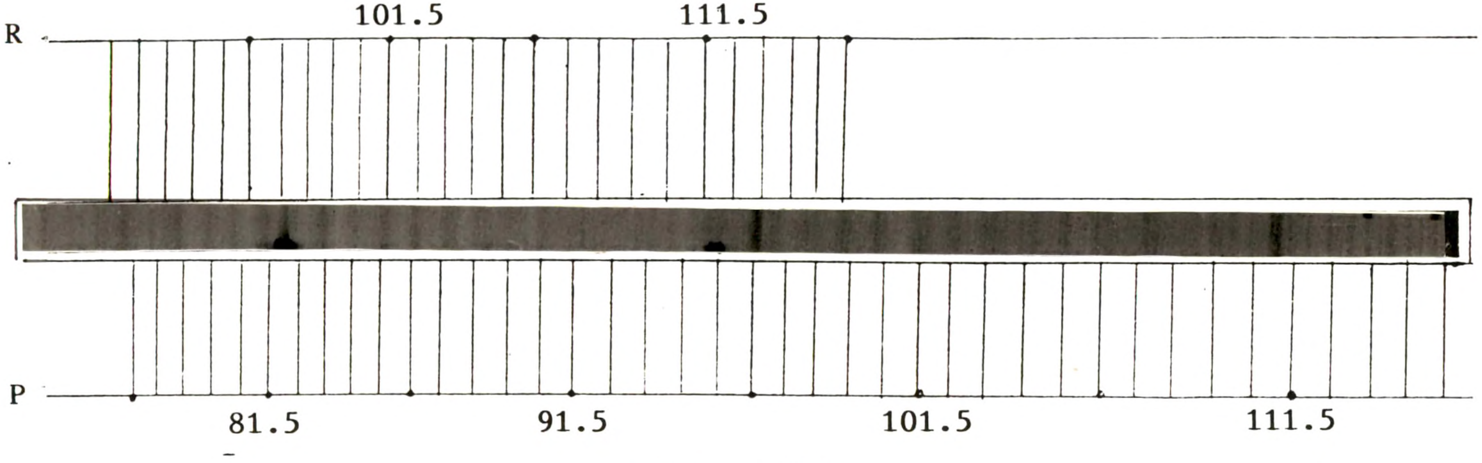

PLATE - 3(b)

ROTATIONAL STRUCTURE OF 4777.5 Å BAND OF PbCl MOLECULE

DISPERSION 0.92054 Å/mm

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

The graphs of $\Delta_2 F(J) \longrightarrow J$ and

$$\frac{\Delta_2 F(J)}{(J + 1/2)} \longrightarrow (J + \tfrac{1}{2})^2$$

are shown in fig. 12 and 13 from which rotational constants are calculated. The J numbering, vacuum wavenumbers of P and R branch lines and values of combination differences for the rotational lines of (0,3) band are given in Table 9. The rotational constants obtained from the analysis are listed in Table 10.

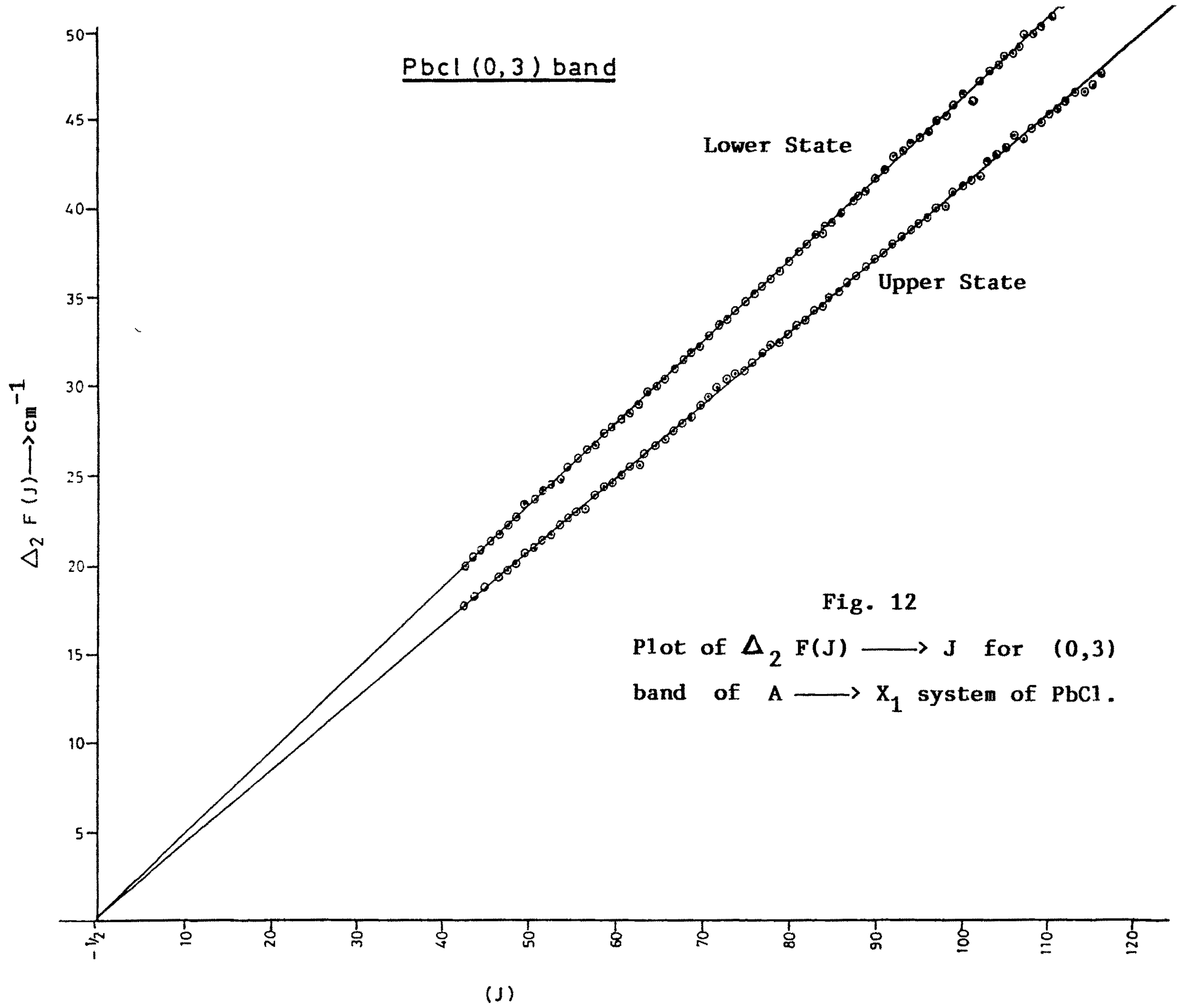

Fig. 12

Plot of Δ_2 F(J) ——> J for (0,3) band of A ——> X_1 system of PbCl.

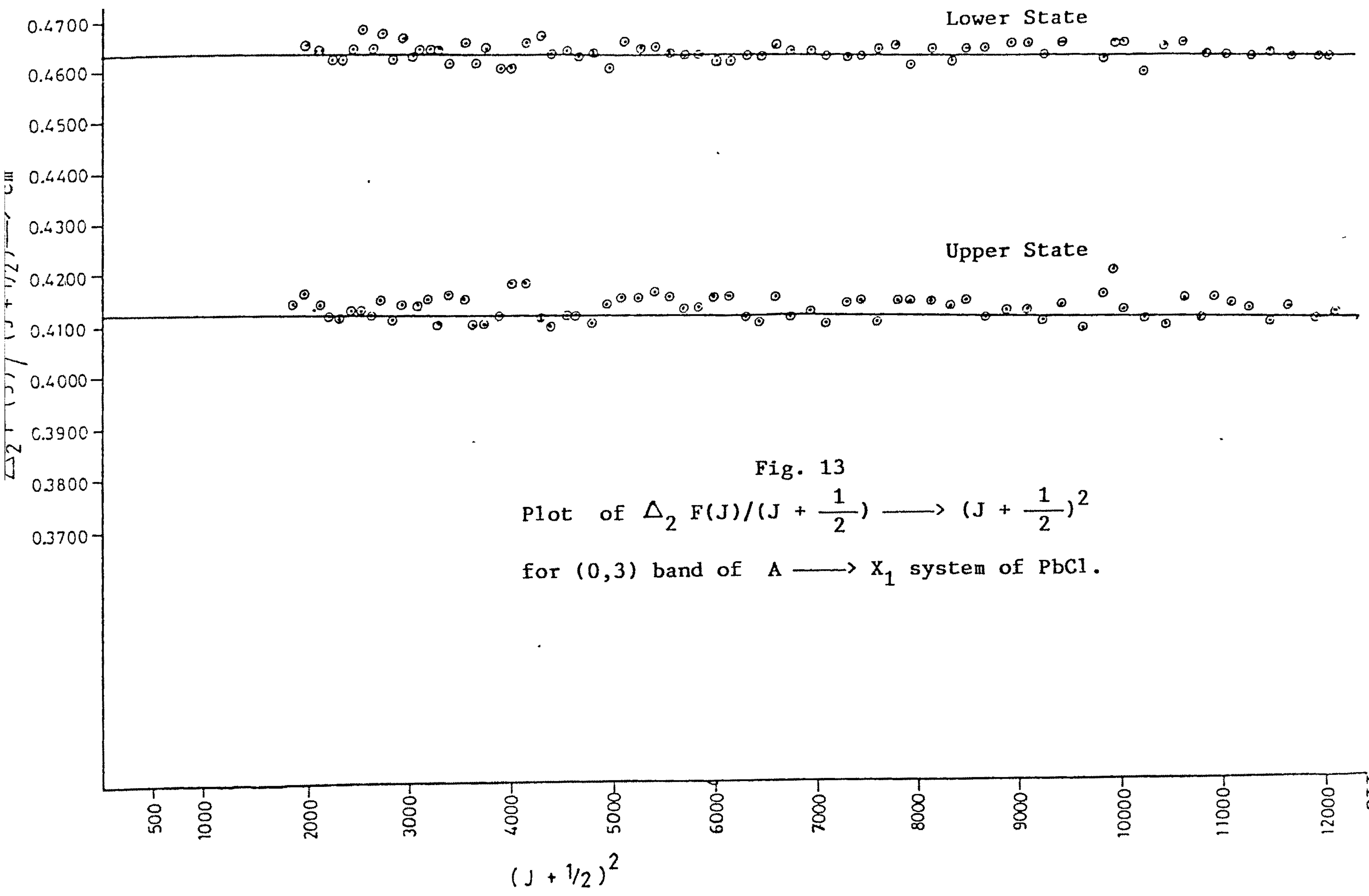

Fig. 13

Plot of $\Delta_2 F(J)/(J + \frac{1}{2}) \longrightarrow (J + \frac{1}{2})^2$

for (0,3) band of $A \longrightarrow X_1$ system of PbCl.

TABLE - 9

J ASSIGNMENTS, VACUUM WAVENUMBERS AND COMBINATION DIFFERENCES OF THE (0,3) BAND OF PbCl MOLECULE

J	R(J) cm^{-1}	P(J) cm^{-1}	Δ_2 F"(J) cm^{-1}	Δ_2 F'(J) cm^{-1}
1	2	3	4	5
20.5		20914.92		
21.5		20914.92		
22.5		20913.20		
23.5		20912.54		
24.5		20911.50		
25.5		20910.24		
26.5		20909.47		
27.5		20909.10		
28.5		20908.44		
29.5		20907.54		
30.5		20906.55		
31.5		20905.38		
32.5		20904.65		
33.5		20903.43		
34.5		20902.21		
35.5		20900.45		
36.5		20899.76		
37.5		20898.33		
38.5		20897.82		
39.5		20896.10		
40.5		20895.25		
41.5		20893.56		
42.5	20909.98	20892.18	19.92	17.80
43.5	20908.91	20890.92	20.46	18.29
44.5	20908.10	20889.52	20.88	18.52
45.5	20907.08	20888.03	21.36	19.05
46.5	20906.11	20886.74	21.73	19.37
47.5	20905.08	20885.35	22.16	19.73

1	2	3	4	5
48.5	20904.17	20883.95	22.72	20.22
49.5	20903.02	20882.36	23.40	20.66
50.5	20901.79	20880.77	23.68	21.02
51.5	20900.91	20879.34	24.27	21.57
52.5	20899.28	20877.52	24.47	21.76
53.5	20898.82	20876.44	24.64	22.38
54.5	20897.90	20874.64	25.51	22.76
55.5	20896.55	20873.31	25.99	23.24
56.5	20894.80	20871.41	26.45	23.39
57.5	20894.24	20870.10	26.71	24.14
58.5	20892.59	20868.09	27.43	24.50
59.5	20891.42	20866.81	27.66	24.61
60.5	20889.95	20864.93	28.30	25.02
61.5	20888.67	20863.12	28.44	25.55
62.5	20887.08	20861.51	28.95	25.57
63.5	20885.61	20859.72	29.75	25.89
64.5	20884.06	20857.33	29.91	26.73
65.5	20882.78	2855.70	30.53	27.08
66.5	20881.10	20853.53	31.04	27.57
67.5	20879.72	20851.74	31.42	27.98
68.5	20877.93	20849.68	31.97	28.25
69.5	20876.75	20847.75	32.20	29.00
70.5	20875.20	20845.73	33.03	29.47
71.5	20873.62	20843.72	33.44	29.90
72.5	20872.09	20841.76	33.85	30.33
73.5	20870.46	20839.77	34.29	30.69
74.6	20868.81	20837.80	34.67	31.01
75.5	20867.21	20835.79	35.13	31.42
76.5	20865.63	20833.68	35.50	31.95
77.5	20864.07	20831.71	35.98	32.36
78.5	20862.14	20829.65	36.49	32.49
79.5	20861.12	20828.39	36.94	32.73
80.5	20858.79	20825.20	37.81	33.59

1	2	3	4	5
81.5	20857.04	20823.31	37.95	33.73
82.5	20855.06	20820.84	38.45	34.22
83.5	20853.05	20818.59	38.81	34.46
84.5	20851.07	20815.92	39.17	35.15
85.5	20848.95	20813.39	39.61	35.56
86.5	20847.36	20811.46	40.31	35.68
87.5	20844.98	20808.64	40.80	36.34
88.5	20843.37	20806.56	40.97	36.81
89.5	20841.25	20804.01	41.68	37.24
90.5	20839.26	20801.69	41.93	37.57
91.5	20836.66	20798.62	42.74	38.04
92.5	20834.78	20796.52	43.02	38.26
93.5	20832.35	20793.64	43.80	38.71
94.5	20830.08	20790.98	44.10	39.10
95.5	20827.58	20788.25	44.32	39.33
96.5	20825.77	20785.76	44.96	40.01
97.5	20822.64	20782.62	45.19	40.02
98.5	20821.65	20780.58	45.65	41.07
99.5	20818.21	20776.99	46.41	41.22
100.5	20816.62	20775.24	46.08	41.38
101.5	20813.88	20772.13	47.26	41.75
102.5	20812.01	20769.36	47.80	42.65
103.5	20809.12	20766.08	48.02	43.04
104.5	20807.34	20763.99	48.56	43.35
105.5	20804.82	20760.69	48.86	44.13
106.5	20802.29	20758.48	49.83	43.81
107.5	20799.43	20754.99	49.78	44.44
108.5	20797.25	20752.51	50.24	44.74
109.5	20794.38	20749.19	50.70	45.19
110.5	20791.98	20746.55	51.43	45.43
111.5	20788.96	20742.95	51.68	46.01
112.5	20786.74	20740.30	52.01	46.44
113.5	20783.36	20736.95	52.33	46.41
114.5	20781.10	20734.41	51.99	46.69
115.5	20778.79	20731.37		47.42

TABLE - 10

ROTATIONAL CONSTANTS OF (0,3) BAND OF PbCl MOLECULE

State	Constants	Values
A (½)	B'_o	0.1030 cm^{-1}
	D'_o	0.595 x 10^{-7} cm^{-1}
	I'_o	272.050 x 10^{-40} $g.cm^2$
	r'_o	2.33906 Å
X(½)	B''_3	0.1157 cm^{-1}
	D''_3	0.7350 x 10^{-7} cm^{-1}
	I''_3	242.188 x 10^{-40} $g.cm^2$
	r''_3	2.2069 Å
	ν_o	20924.748 cm^{-1}

4. ROTATIONAL ANALYSIS OF (2,1) BAND AT 4548.9 Å

In order to study the fine structure of $A \longrightarrow X_1$ system of PbCl molecule, spectrum has been photographed in the 5th order of two meter plane grating spectrograph at a reciprocal dispersion of 1.03300 Å/mm. An exposure time of about 8 hours is sufficient to record the spectrum on Kodak 103-0 and ORWO - WU-3 plates. (2,1) band is found suitable for detailed rotational analysis. The accuracy of the measurement is upto ± 0.05 cm^{-1} for sharp and unblended lines.

The rotational structure of the band reproduced in plate No.4(a) and (b). A detailed examination of rotational structure of this band reveals the presence of only two branches P and R. The branch which forms the head and becomes very weak at high J values is easily identified as the R branch. Satellite branches are weak in intensity. Vacuum wavenumbers and J assignments for the lines of (2,1) band of $A \longrightarrow X_1$ system of PbCl molecule are given in Table 11. The rotational analysis has been carried out by the standard method (Herzberg, 1950) by taking combination relations,

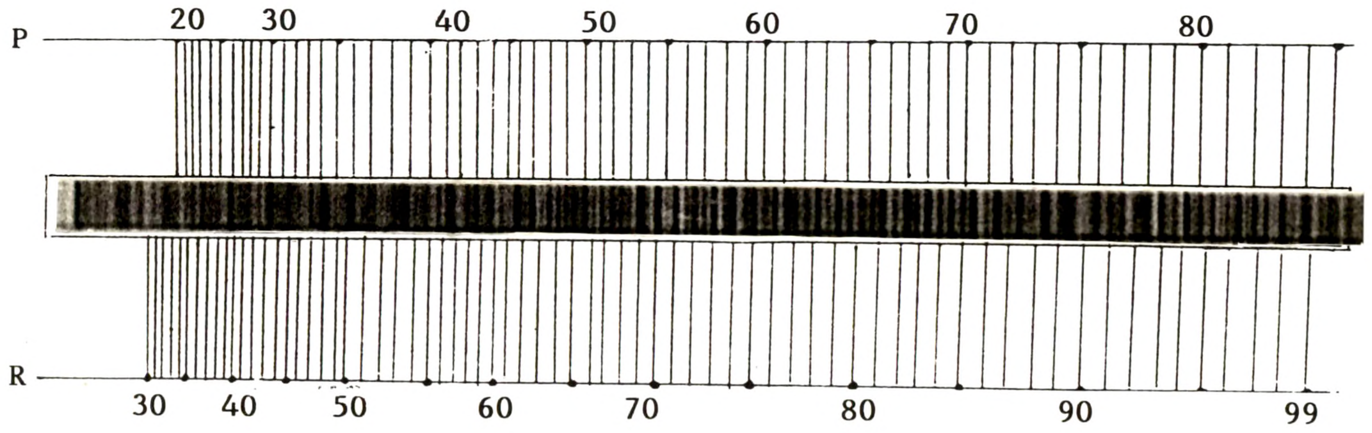

PLATE - 4(a)

ROTATIONAL STRUCTURE OF 4549 Å BAND OF PbCl MOLECULE

DISPERSION 1.03300 Å/mm

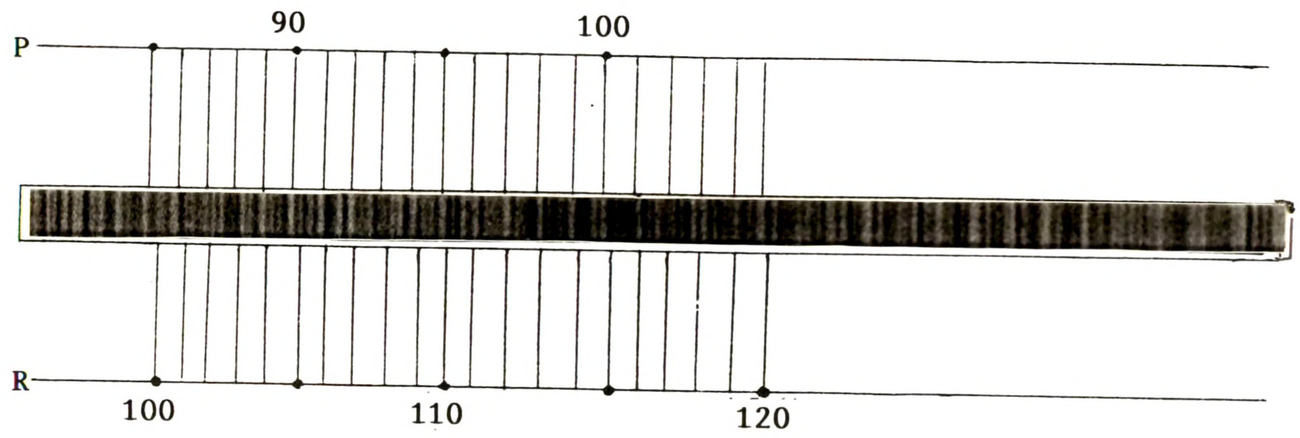

PLATE - 4(b)

ROTATIONAL STRUCTURE OF 4549 Å BAND OF PbCl MOLECULE

DISPERSION 1.03300 Å/mm

TABLE - 11

J ASSIGNMENTS, VACUUM WAVENUMBERS AND COMBINATION DIFFERENCES OF THE (2,1) BAND OF PbCl MOLECULE

J	R(J) cm^{-1}	P(J) cm^{-1}	$\Delta_2F''(J)$ cm^{-1}	$\Delta_2F'(J)$ cm^{-1}
1	2	3	4	5
20.5		21965.81		
21.5		21965.17		
22.5		21964.75		
23.5		21963.64		
24.5		21962.26		
25.5		21961.66		
26.5		21961.01		
27.5		21959.84		
28.5		21959.39		
29.5		21958.25		
30.5		21957.32		
31.5		21956.08		
32.5		21955.04		
33.5		21953.83		
34.5		21952.61		
35.5		21951.36		
36.5		21950.14		
37.5		21948.81		
38.5		21947.64		
39.5		21946.54		
40.4		21945.41		
41.5		21944.62		
42.5		21942.84		
43.5		21941.86		

1	2	3	4	5
44.5		21939.28		
45.5		21938.78		
46.5		21937.21		
47.5		21936.69		
48.5	21953.18	21934.00		
49.5	21951.89	21830.89	23.34	21.00
50.5	21950.29	21929.84	23.64	20.45
51.5	21949.19	21928.25	23.56	20.94
52.5	21948.16	21926.73	24.34	21.43
53.5	21946.93	21924.85	25.19	22.08
54.5	21944.81	21922.97	25.74	21.84
55.5	21944.19	21921.19	26.27	23.00
56.5	21942.38	21918.54	26.53	23.84
57.5	21941.29	21917.66	26.64	23.63
58.5	21939.86	21915.74	27.43	24.12
59.5	21938.19	21913.86	27.67	24.33
60.5	21936.69	21912.19	27.81	24.50
61.5	21935.56	21910.38	28.48	25.18
62.5	21933.32	21908.21	29.10	25.11
63.5	21932.48	21906.46	29.21	26.02
64.5	21930.37	21904.11	30.29	26.26
65.5	21929.01	21902.19	30.31	26.82
66.5	21927.49	21900.06	31.13	27.43
67.5	21925.60	21897.88	31.71	27.72
68.5	21924.14	21895.78	31.90	28.36
69.5	21922.11	21893.70	32.70	28.41
70.5	21920.35	21891.44	32.90	28.91
71.5	21918.54	21889.21	32.89	29.33
72.5	21916.72	21887.46	33.99	29.26
73.5	21914.88	21884.55	33.97	30.33
74.5	21912.88	21882.75	34.53	30.13
75.5	21911.40	21880.35	34.82	31.05

1	2	3	4	5
76.5	21909.50	21878.06	35.80	31.44
77.5	21907.35	21875.60	36.45	31.75
78.5	21905.45	21873.05	36.71	32.40
79.5	21903.39	21870.64	37.53	32.75
80.5	21901.18	21867.92	37.73	33.26
81.5	21899.20	21865.66	37.50	33.54
82.5	21896.93	21863.68	38.94	33.25
83.5	21894.33	21860.26	38.66	34.07
84.5	21892.57	21858.27	38.68	34.30
85.5	21890.64	21855.65	39.54	34.99
86.5	21888.36	21853.03	40.28	35.33
87.5	21886.16	21850.36	40.75	35.80
88.5	21883.83	21847.61	41.30	36.22
89.5	21881.39	21844.86	41.80	36.53
90.5	21879.17	21842.03	41.54	37.14
91.5	21876.56	21839.85	42.18	36.71
92.5	21874.89	21836.99	42.40	37.90
93.5	21872.36	21834.16	43.63	38.20
94.5	21867.41	21828.24	44.67	39.17
96.5	21864.06	21825.30	45.36	38.76
97.5	21862.04	21822.05	44.93	39.99
98.5	21859.62	21819.13	45.14	40.49
99.5	21857.56	21816.90	45.77	40.66
100.5	21855.02	21813.85	46.18	41.17
101.5	21852.27	21811.38	47.38	40.89
102.5	21849.55	21807.64	47.69	41.91
103.5	21846.79	21804.58	47.69	42.21
104.5	21844.02	21801.86	47.77	42.16
105.5	21841.34	21799.02	47.49	42.32

1	2	3	4	5
106.5	21839.10	21796.53	48.90	42.57
107.5	21835.28	21792.44	49.31	42.84
108.5	21832.41	21789.79	-	42.62
109.5	21831.79			
110.5	21830.46			
111.5	21829.37			
112.5	21826.64			
113.5	21823.34			
114.5	21820.68			
115.5	21817.35			
116.5	21814.75			
117.5	21812.15			
118.5	21808.77			

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

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

J assignments of branch lines were fixed by making the plot of $\Delta_2 F(J)/(J + \frac{1}{2})$ against $(J + \frac{1}{2})^2$. From the graphical plots as shown in fig. 14 and 15 rotational constants are calculated. These constants are listed in Table 12.

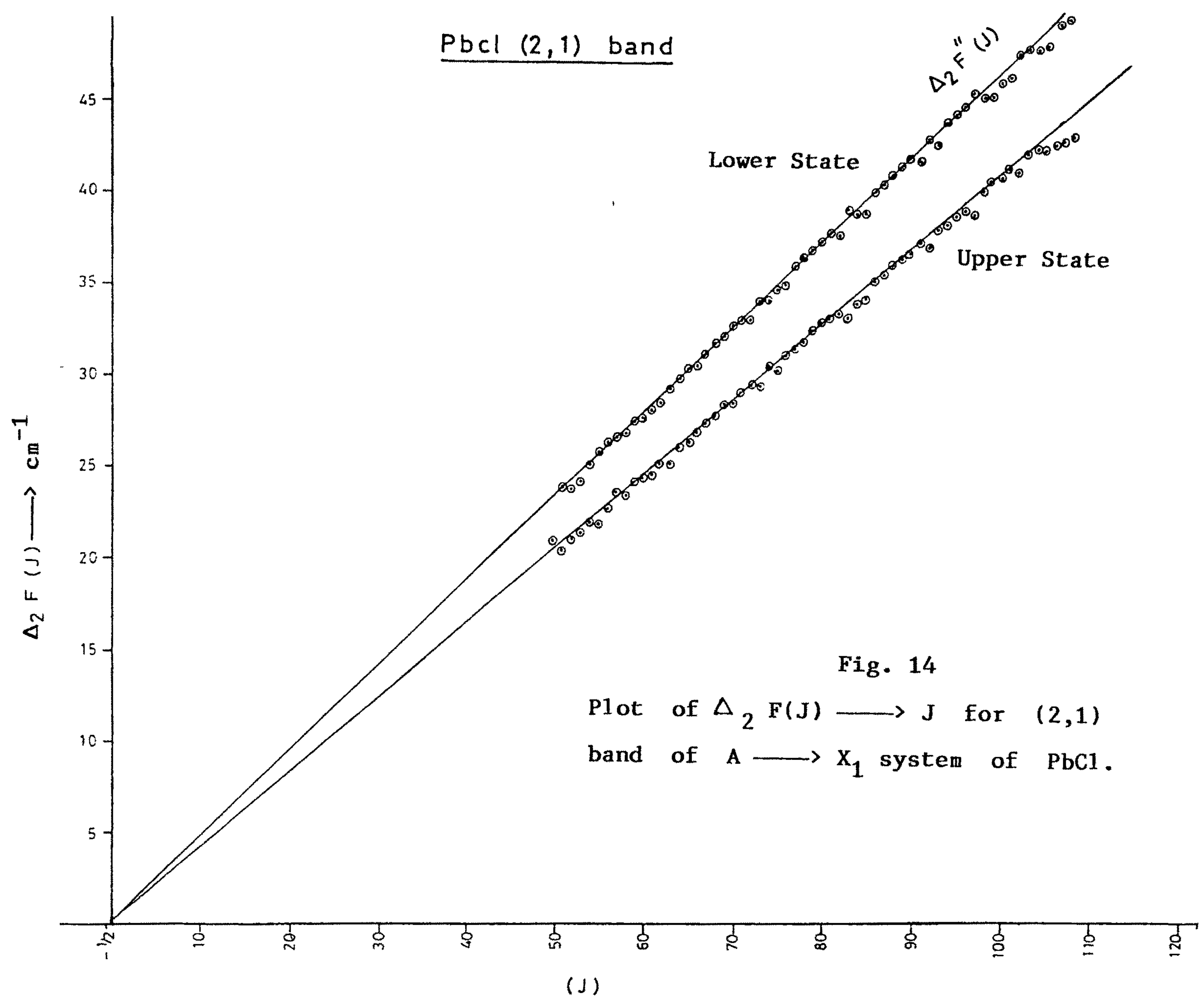

Fig. 14

Plot of Δ_2 F(J) ——> J for (2,1) band of A ——> X_1 system of PbCl.

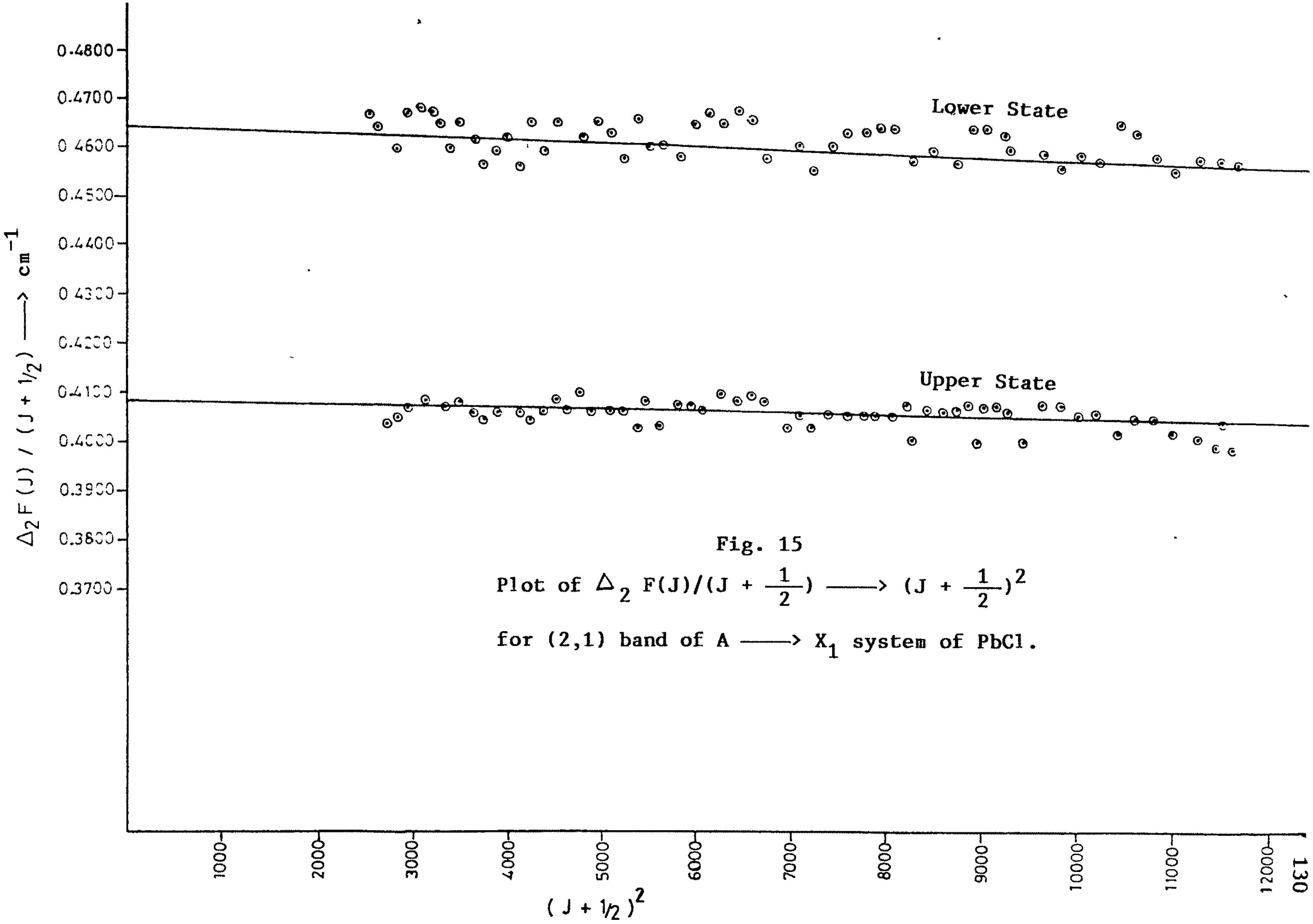

Fig. 15

Plot of $\Delta_2 F(J)/(J + \frac{1}{2}) \longrightarrow (J + \frac{1}{2})^2$

for (2,1) band of A $\longrightarrow$ X_1 system of PbCl.

TABLE - 12

ROTATIONAL CONSTANTS OF (2,1) BAND OF PbCl MOLECULE

State	Constants	Values
$A(\frac{1}{2})$	B'_2	$0.1022\ \mathrm{cm}^{-1}$
	D'_2	$0.6026 \times 10^{-7}\ \mathrm{cm}^{-1}$
	I'_2	$241.5611 \times 10^{-40}\mathrm{g.cm}^2$
	r'_2	2.34819 Å
$X(\frac{1}{2})$	B''_1	$0.1160\ \mathrm{cm}^{-1}$
	D''_1	$0.729 \times 10^{-7}\ \mathrm{cm}^{-1}$
	I''_1	$274.1789 \times 10^{-40}\mathrm{g.cm}^2$
	r''_1	2.20409 Å
	ν_0	$21976.347\ \mathrm{cm}^{-1}$