CHAPTER VI

ROTATIONAL ANALYSIS OF THE A - X SYSTEM OF InI MOLECULE.

From the vibrational analyses of the A - X and B - X systems of InI molecule carried out during the present investigation, the common lower state - X with frequency 176.9 cm^{-1} and the A - state with frequency 157.8 cm^{-1} and the B - state with frequency 146.7 cm^{-1} were identified. Since the systems were also observed in absorption by Wehrli (1934) and

Wehrli and E. Mischer (1934), the lower state - X involved in the transition probably could be the ground state of the molecule.

In order to understand the exact nature of the electronic states involved in the transition of A - X and B - X system of InI molecule, three bands 0,0; 0,1 and 1,0 of a A - X system and one band viz 0,0 of B - X system were photographed at high dispersion to study the rotational structure of the bands if they could be resolved.

In this chapter rotational analysis of 0,0; 0,1 and 1,0 bands of A - X system is discussed. Since 0,0 band of B - X system could not be adequatly resolved into separate branches, the rotational constants for the band have been evaluated from observed values of the second differences of wave-numbers of poorly resolved lines by standard methods (Herzberg 1950).

The 0,0; 0,1 and 1,0 bands of A – X system of InI molecule were photographed in the seventh order of a two meter plane grating spectrograph (Carl – Zeiss) at a reciprocal dispersion of 0.35A°/mm and at a resolution of 3×10^5 with a slit width of fifteen microns. The time of exposure was about five hours to record the spectra of satisfactory intensity. The 0,0 band of B – X system was photographed at reciprocal dispersion of 0.43 A°/mm with a slit width of fifteen microns in the seventh order of a plane grating spectrograph giving an exposure of about four hours. Ilford N-40 plates were used to record the spectra. Measurements were made on Abbe comparator using iron arc standards. The eror in the measurements of sharp and well resolved lines does not exceed $\pm$ 0.05 cm^{-1}. For unresolved and overlapping lines, it may be a little more.

6.1 ROTATIONAL ANALYSIS OF THE 0,0; 0,1 and 1,0 BANDS of A - X SYSTEM :

In the spectrogram taken with a slit width of fifteen microns at a reciprocal dispersion of 0.35 A°/mm, the 0,0; 0,1 and 1,0 bands degraded to violet revealed the presence of single P and R branches of which P is the head forming branch.

The 0,0 band at 4098.5 A° has been clearly resolved showing the presence of single P and R branches of which P forms the band head. The spectrogram is reproduced in plate 8 (a,b). The most intense branch near the head was identified as P branch. The returning part of the P branch was faint and less extensive. The R branch lines corresponding to low J values were less intense and their intensity increased towards high J values. The splitting of the branch lines is clearly seen as we shift away from the head. The vacuum wavenumbers and J assignments of rotational lines of 0,0 band are given in Table 14. The

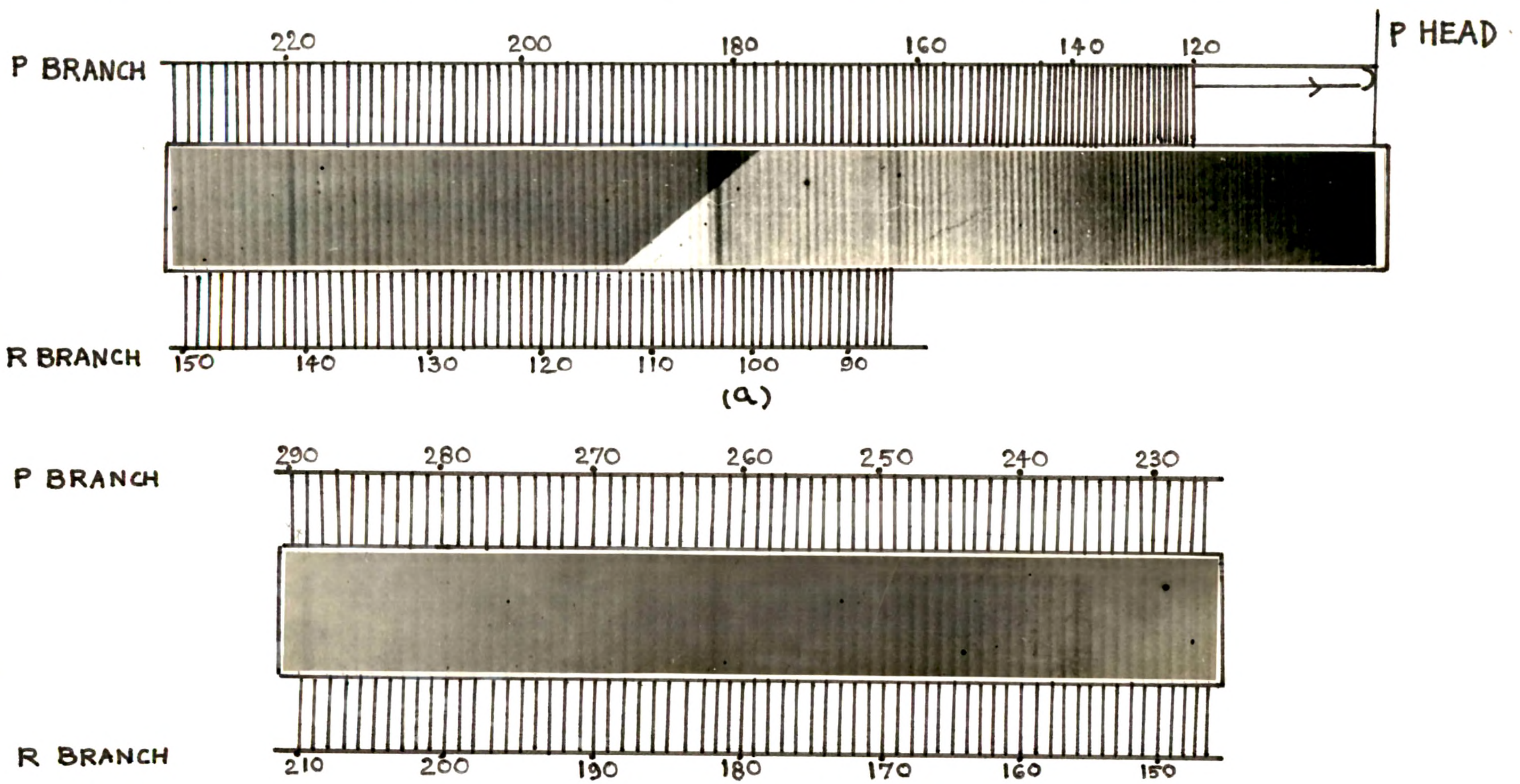


PLATE 8 (a) & (b)

ROTATIONAL STRUCTURE OF 0,0 BAND OF A — X SYSTEM OF InI MOLECULE AT 0.3 Å/mm.

TABLE 14

VACUUM WAVENUMBERS AND J ASSIGNMENTS FOR THE ROTATIONAL LINES OF THE 0,0 BAND OF A - X SYSTEM OF InI MOLECULE

J	$R(J)\,cm^{-1}$	$P(J)\,cm^{-1}$	J	$R(J)\,cm^{-1}$	$P(J)\,cm^{-1}$
115	24413.30	24395.92	130	24417.90	24398.35
116	13.58	96.07	131	18.24	98.51
117	13.89	96.22	132	18.55	98.67
118	14.18	96.38	133	18.88	98.84
119	14.50	96.56	134	19.18	99.03
120	14.79	96.69	135	19.53	99.19
121	15.08	96.85	136	19.87	99.36
122	15.40	97.00	137	20.17	99.54
123	15.71	97.16	138	20.54	99.70
124	16.01	97.36	139	20.84	99.89
125	16.33	97.56	140	21.21	24400.10
126	16.65	97.73	141	21.57	00.30
127	16.95	97.90	142	21.88	00.55
128	17.25	98.04	143	22.21	00.74
129	17.58	98.18	144	22.46	00.93

Table 14 (contd..)

J	R(J)cm^{-1}	P(J)cm^{-1}	J	R(J)cm^{-1}	P(J)cm^{-1}
145	24422.78	24401.12	162	24428.84	24404.58
146	23.12	01.32	163	29.30	04.79
147	23.50	01.52	164	29.64	05.03
148	23.83	01.72	165	29.98	05.25
149	24.19	01.91	166	30.34	05.49
150	24.51	02.10	167	30.73	05.63
151	24.88	02.31	168	31.10	05.92
152	25.26	02.51	169	31.48	06.28
153	25.60	02.68	170	31.88	06.53
154	25.96	02.82	171	32.26	06.75
155	26.30	03.00	172	32.63	06.98
156	26.66	03.25	173	33.01	07.24
157	27.07	03.47	174	33.36	07.57
158	27.41	03.66	175	33.77	07.73
159	27.61	03.91	176	34.16	08.01
160	28.13	04.09	177	34.55	08.27
161	28.49	04.34	178	34.96	08.49

Table 14 (contd..)

J	R(J) cm^{-1}	P(J) cm^{-1}	J	R(J) cm^{-1}	P(J) cm^{-1}
179	24435.35	24408.65	196	24442.11	24413.10
180	35.72	08.90	197	42.53	13.44
181	36.13	09.14	198	42.97	13.70
182	36.51	09.36	199	43.35	13.91
183	36.90	09.59	200	43.75	14.11
184	37.29	09.81	201	44.16	14.32
185	37.70	10.01	202	44.57	14.50
186	38.05	10.23	203	44.99	14.72
187	38.47	10.55	204	45.43	14.91
188	38.88	10.86	205	45.83	15.18
189	39.29	11.13	206	46.21	15.51
190	39.68	11.39	207	46.63	15.85
191	40.08	11.68	208	47.07	16.15
192	40.50	11.95	209	47.50	16.44
193	40.89	12.24	210	47.89	16.78
194	41.32	12.50	211	48.29	17.15
195	41.72	12.79	212	48.73	17.39
			213	49.14	17.72
			214	49.55	18.04

rotational analysis of 0,0 band was carried out by the scheme suggested by Herzberg (1950) and Youngner and Winans (1960). The combination differences $\Delta_2 F'(J) = R(J) - P(J)$ and $\Delta_2 F''(J) = R(J - 1) - P(J + 1)$ for the upper and lower states involved in the band were determined and are listed in Tables 15 and 16 respectively. The absolute J numbering was assigned using the plots of $\frac{\Delta_2 F'(J)}{J + \frac{1}{2}}$ against $(J + \frac{1}{2})^2$; fig.6, and $\frac{\Delta_2 F''(J)}{J + \frac{1}{2}}$ against $(J + \frac{1}{2})^2$; fig.7 for the upper and lower states respectively. The graphs were St. lines even for low J values. Rotational constants derived from the intercept and the slope of the graphs (Fig.6-7 ~~and 8~~) are given in Table 19. The criterion suggested by Youngner and Winans (1960) was applied to check the correctness of J assignments i.e., a marked deviation from the st. lines was observed for low J values when the absolute numbering was changed by ± 1.

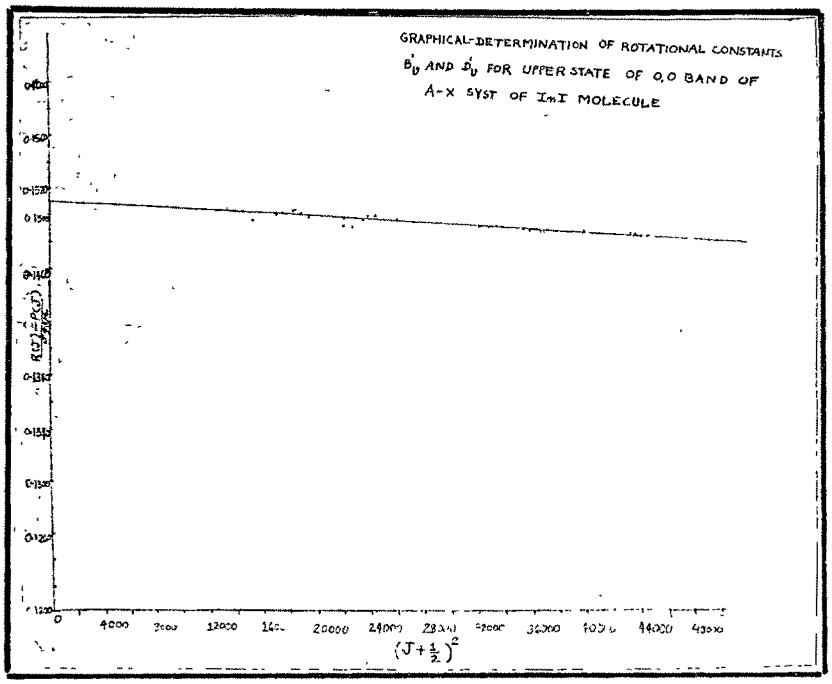

GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS
B'_v AND D'_v FOR UPPER STATE OF 0,0 BAND OF
A-X SYST OF InI MOLECULE
$(J+\frac{1}{2})^2$

Fig. 6

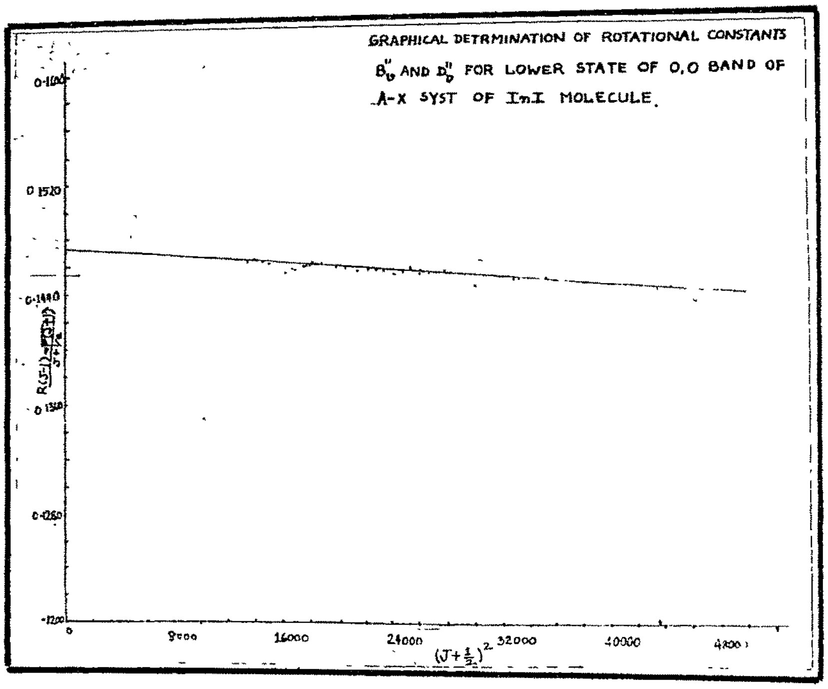

GRAPHICAL DETRMINATION OF ROTATIONAL CONSTANTS
B''_v AND D''_v FOR LOWER STATE OF 0,0 BAND OF
A-X SYST OF InI MOLECULE.
$(J+\frac{1}{2})^2$

Fig. 7

The spectrograms revealing rotational structure of 0,1 and 1,0 bands are reproduced in plates 9 and 10 respectively. The vacuum wavenumbers and J assignments of rotational lines of 0,1 and 1,0 bands are given in Table 17 and 18. Rotational analyses of 0,1 band at 4128.4 A° and 1,0 band at 4072.7 A° were carried out by comparing the combination differences of the lower states of 0,0 and 1,0 bands and those of the upper states of 0,0 and 0,1 bands for the same J value. The upper state combination difference $\Delta_2 F'(J)$ and lower state combination difference $\Delta_2 F''(J)$ for 0,1 and 1,0 bands respectively are listed in Tables 15 and 16. The rotational constants for 0,1 and 1,0 bands are determined from the graphs shown in figures 8,9, 10, 11 ~~and 12~~. The rotational constants obtained are collected in Table 19.

The vibration - rotation interaction constant α_e and vibrational quantum $\Delta G_{\frac{1}{2}}$ for the upper and lower states were determined graphically for A - X system from fig. 12,13 ~~and 14~~. For this purpose the

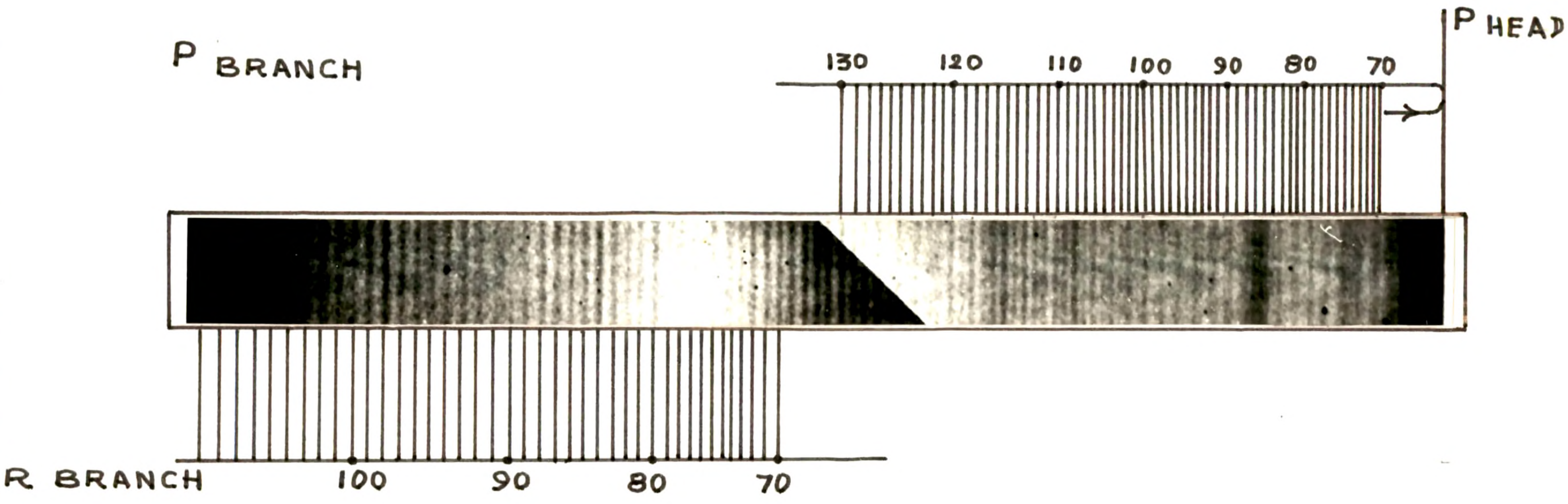


PLATE 9.

ROTATIONAL STRUCTURE OF 0,1 BAND OF A ⟶ X SYSTEM OF InI MOLECULE AT 0.3 Å/mm.

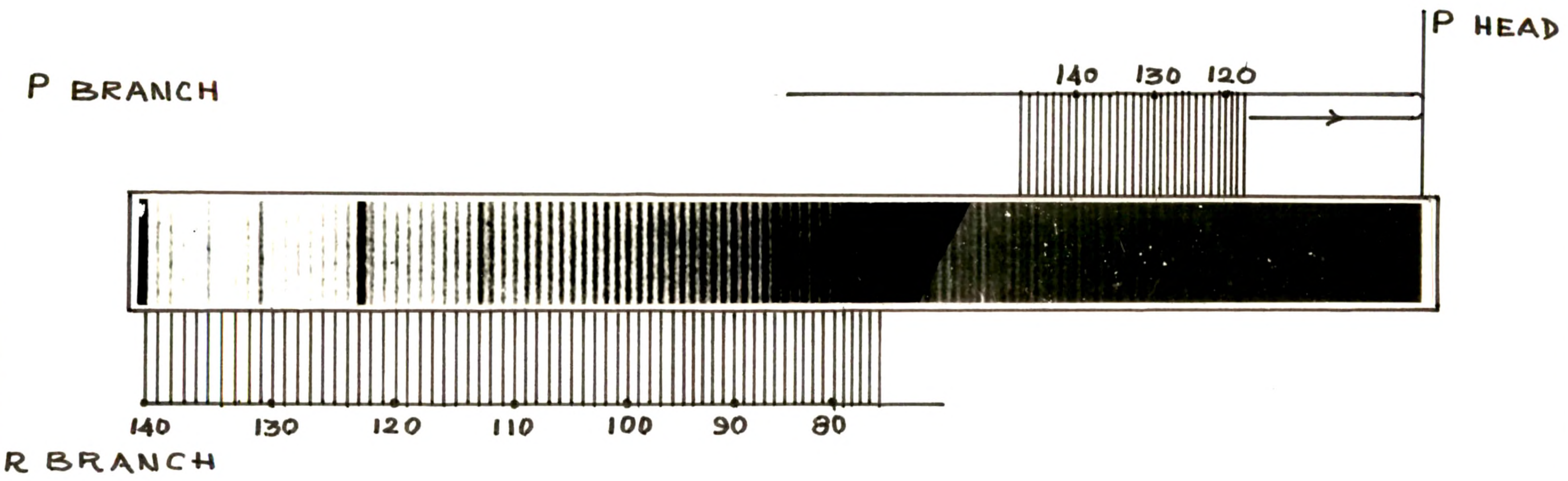


PLATE 10.

ROTATIONAL STRUCTURE OF 1,0 BAND OF A$\longrightarrow$X SYSTEM OF InI MOLECULE AT 0.3 Å/mm.

TABLE 15

COMBINATION DIFFERENCES $\Delta_2 F'(J)$ FOR THE UPPER STATES OF 0,0 AND 0,1 BAND OF A - X SYSTEM OF InI MOLECULE.

J	$\Delta_2F'(J)=R(J)-P(J)\ cm^{-1}$ 0,0 band	0,1 band	J	$\Delta_2F'(J)=R(J)-P(J)\ cm^{-1}$ 0,0 band	0,1 band
70		10.58	84		12.63
71		10.72	85		12.77
72		10.87	86		12.89
73		11.02	87		13.05
74		11.14	88		13.22
75		11.26	89		13.33
76		11.41	90		13.47
77		11.57	91		13.61
78		11.74	92		13.76
79		11.88	93		13.89
80		12.08	94		14.04
81		12.21	95		14.16
82		12.50	96		14.35
83		12.60	97		14.60

Table 15 (contd..)

J	$\Delta_2F'(J)=R(J)-P(J)\ cm^{-1}$ 0,0 band	0,1 band	J	$\Delta_2F'(J)=R(J)-P(J)\ cm^{-1}$ 0,0 band	0,1 band
98		14.81	114		16.96
99		14.90	115	17.38	17.08
100		15.07	116	17.51	17.19
101		15.26	117	17.67	17.26
102		15.40	118	17.80	17.49
103		15.47	119	17.94	17.74
104		15.59	120	18.10	18.06
105		15.75	121	18.23	18.13
106		15.97	122	18.40	18.24
107		16.07	123	18.55	18.43
108		16.21	124	18.65	18.58
109		16.38	125	18.77	18.75
110		16.46	126	18.92	18.93
111		16.59	127	19.05	19.07
112		16.76	128	19.21	19.19
113		16.80	129	19.40	19.36

TABLE 15 (contd.)

J	$\Delta_2F'(J)=R(J)-P(J)\,cm^{-1}$ 0,0 band	0,1 band	J	$\Delta_2F'(J)=R(J)-P(J)\,cm^{-1}$ 0,0 band	0,1 band
130	19.55	19.52	146	21.80	
131	19.73	19.69	147	21.98	
132	19.88	19.88	148	22.11	
133	20.04	20.05	149	22.28	
134	20.15	20.08	150	22.41	
135	20.34	20.35	151	22.57	
136	20.51		152	22.75	
137	20.63		153	22.92	
138	20.84		154	23.14	
139	20.95		155	23.30	
140	21.11		156	23.41	
141	21.27		157	23.60	
142	21.33		158	23.75	
143	21.47		159	23.85	
144	21.53		160	24.04	
145	21.66		161	24.15	

Table 15 (contd..)

J	$\Delta_2F'(J)=R(J)-P(J)\ cm^{-1}$ 0,0 band	0,1 band	J	$\Delta_2F'(J)=R(J)-P(J)\ cm^{-1}$ 0,0 band	0,1 band
162	24.26		178	26.47	
163	24.51		179	26.70	
164	24.61		180	26.82	
165	24.73		181	26.99	
166	24.85		182	27.15	
167	25.10		183	27.31	
168	25.18		184	27.48	
169	25.20		185	27.69	
170	25.35		186	27.82	
171	25.51		187	27.92	
172	25.65		188	28.02	
173	25.77		189	28.16	
174	25.79		190	28.29	
175	26.04		191	28.40	
176	26.15		192	28.55	
177	26.28		193	28.65	

Table 15 (contd..)

J	$\Delta_2 F'(J)=R(J)-P(J)\,cm^{-1}$		J	$\Delta_2 F'(J)=R(J)-P(J)\,cm^{-1}$	
	0,0 band	0,1 band		0,0 band	0,1 band
194	28.82		210	31.11	
195	28.93		211	31.14	
196	29.01		212	31.34	
197	29.09		213	31.42	
198	29.27		214	31.51	
199	29.44				
200	29.64				
201	29.84				
202	30.07				
203	30.27				
204	30.52				
205	30.65				
206	30.70				
207	30.78				
208	30.92				
209	31.06				

TABLE 16

COMBINATION DIFFERENCES $\Delta_2F''(J)$ FOR THE LOWER STATES OF 0,0 AND 1,0 BANDS OF A - X SYSTEM OF InI MOLECULE

J	$\Delta_2F''(J)=R(J-1)-P(J+1)\,cm^{-1}$ 0,0 Band	1,0 Band	J	$\Delta_2F''(J)=R(J-1)-P(J+1)\,cm^{-1}$ 0,0 Band	1,0 Band
115	16.93		127	18.77	18.76
116	17.08		129	18.90	18.96
117	17.20		130	19.07	19.06
118	17.33		131	19.23	19.24
119	17.49		132	19.40	19.38
120	17.65	17.56	133	19.52	19.49
121	17.79	17.73	134	19.69	19.63
122	17.92	17.87	135	19.82	19.72
123	18.04	18.04	136	19.99	19.88
124	18.15	18.14	137	20.17	20.01
125	18.28	18.33	138	20.28	20.13
126	18.43	18.41	139	20.44	20.32
127	18.61	18.64	140	20.54	20.54

Table 16 Contd....

J	$\Delta_2F''(J)=R(J-1)-P(J+1)\,cm^{-1}$ 0,0 Band	1,0 Band	J	$\Delta_2F''(J)=R(J-1)-P(J+1)\,cm^{-1}$ 0,0 Band	1,0 Band
141	20,66	20.71	158	23.16	
142	20.83	20.86	159	23.32	
143	20.95	20.98	160	23.42	
144	21.09	21.08	161	23.55	
145	21.14	21.23	162	23.70	
146	21.26	21.36	163	23.81	
147	21.40	21.46	164	24.05	
148	21.59	21.62	165	24.15	
149	21.73	21.76	166	24.35	
150	21.88	21.97	167	24.42	
151	22.00		168	24.45	
152	22.20		169	24.57	
153	22.44		170	24.73	
154	22.60		171	24.90	
155	22.71		172	25.02	
156	22.83		173	25.06	
157	23.00		174	25.28	

Table 16 Contd.......

J	$\Delta_2 F''(J)=R(J-1)-P(J+1)\,cm^{-1}$ 0,0 Band	1,0 Band	J	$\Delta_2 F''(J)=R(J-1)-P(J+1)\,cm^{-1}$ 0,0 Band	1,0 Band
175	25.35		191	27.73	
176	25.50		192	27.84	
177	25.67		193	28.00	
178	25.90		194	28.10	
179	26.06		195	28.22	
180	26.21		196	28.28	
181	26.36		197	28.41	
182	36.54		198	28.62	
183	26.70		199	28.86	
184	26.89		200	29.03	
185	27.06		201	29.25	
186	27.15		202	29.44	
187	27.19		203	29.66	
188	27.34		204	29.81	
189	27.49		205	29.92	
190	27.61		206	29.98	

Table 16 Contd......

J	$\Delta_2F''(J)=R(J-1)-P(J+1)\,cm^{-1}$ 0,0 Band	1,0 Band
207	30.06	
208	30.19	
209	30.29	
210	30.35	
211	30.50	
212	30.57	
213	30.69	
214	30.82	

TABLE 17

VACUUM WAVENUMBERS AND J ASSIGNMENTS FOR THE ROTATIONAL LINES OF THE 0,1 BAND OF A - X SYSTEM OF InI MOLECULE

J	R(J) cm^{-1}	P(J) cm^{-1}	J	R(J) cm^{-1}	P(J) cm^{-1}
70	24227.82	24217.24	84	24231.23	24218.60
71	28.04	17.32	85	31.47	18.70
72	28.27	17.40	86	31.68	18.79
73	28.50	17.48	87	31.93	18.88
74	28.70	17.56	88	32.19	18.97
75	28.91	17.65	89	32.39	19.06
76	29.14	17.73	90	32.62	19.15
77	29.38	17.81	91	32.84	19.23
78	29.63	17.89	92	33.07	19.31
79	29.86	17.98	93	33.28	19.39
80	30.13	18.05	94	33.53	19.49
81	30.35	18.14	95	33.75	19.59
82	30.73	18.23	96	34.03	19.68
83	30.95	18.35	97	34.38	19.78

Table 17 (contd..)

J	R(J) cm^{-1}	P(J) cm^{-1}	J	R(J) cm^{-1}	P(J) cm^{-1}
98	24234.69	24219.88	115	24239.36	24222.28
99	34.91	20.01	116	39.56	22.37
100	35.22	20.15	117	39.81	22.45
101	35.54	20.28	118	40.03	22.54
102	35.84	20.44	119	40.36	22.62
103	36.10	20.63	120	40.78	22.72
104	36.41	20.82	121	41.05	22.92
105	36.74	20.99	122	41.37	23.13
106	37.13	21.16	123	41.72	23.29
107	37.40	21.33	124	42.06	23.48
108	37.71	21.50	125	42.43	23.68
109	38.06	21.68	126	42.78	23.85
110	38.28	21.82	127	43.13	24.06
111	38.51	21.92	128	43.46	24.27
112	38.78	22.02	129	43.85	24.49
113	38.90	22.10	130	44.18	24.66
114	39.16	22.20	131	44.54	24.85

Table 17 (contd..)

J	$R(J) cm^{-1}$	$P(J) cm^{-1}$
132	24244.96	24225.08
133	45.25	25.20
134	45.59	25.51
135	46.01	25.66

TABLE 18

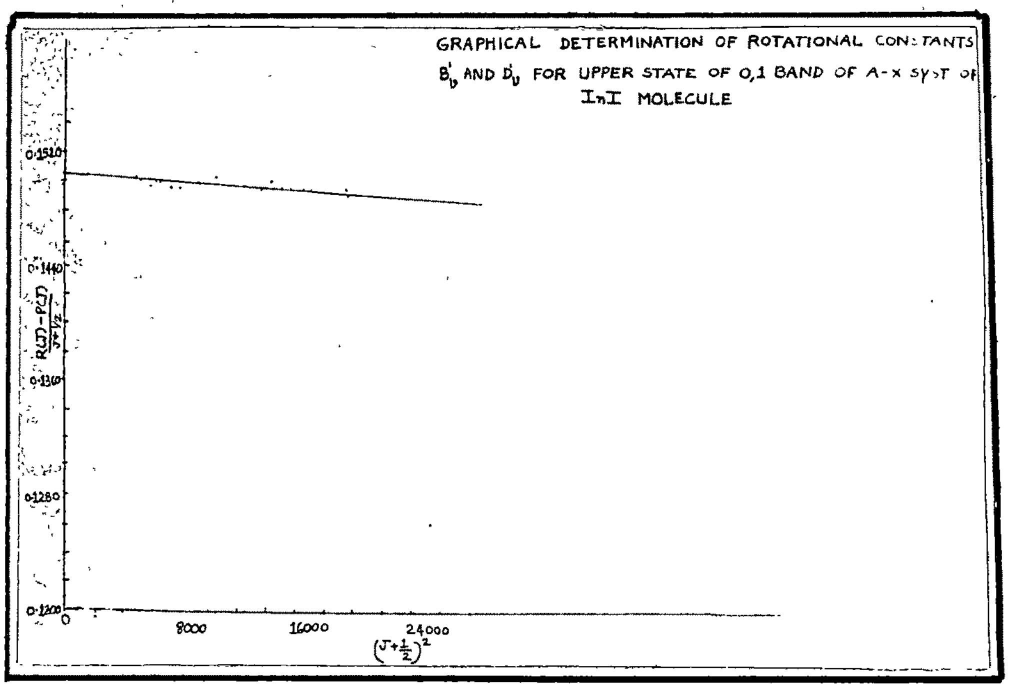
VACUUM WAVENUMBERS AND J ASSIGNMENTS FOR THE ROTATIONAL LINES OF THE 1,0 BAND OF A - X SYSTEM OF InI MOLECULE

J	R(J) cm^{-1}	P(J) cm^{-1}	J	R(J) cm^{-1}	P(J) cm^{-1}
120	24569.54	24551.48	136	24574.15	24553.84
121	69.84	51.71	137	74.44	53.96
122	70.11	51.81	138	74.73	54.14
123	70.38	51.97	139	75.03	54.31
124	70.68	52.07	140	75.33	54.41
125	70.92	52.24	141	75.63	54.49
126	71.24	52.35	142	75.95	54.62
127	71.50	52.51	143	76.24	54.77
128	71.81	52.60	144	76.56	54.97
129	72.10	52.74	145	76.86	55.16
130	72.39	52.85	146	77.15	55.33
131	72.69	53.04	147	77.46	55.50
132	72.99	53.15	148	77.78	55.69
133	73.25	53.31	149	78.10	55.84
134	73.56	53.50	150	78.39	56.02
135	73.84	53.62			

TABLE 19

ROTATIONAL CONSTANTS FOR 1,0; 0,0 and 0,1 BANDS OF A – X SYSTEM OF InI MOLECULE

v', v"	ν_0 cm^{-1}	B' cm^{-1}	B" cm^{-1}	D' cm^{-1}	D" cm^{-1}
1,0	24548.535	$.0374_2$	$.0368_1$	0.12×10^{-7}	0.087×10^{-7}
0,0	24393.853	$.0377_1$	$.0368_2$	0.087×10^{-7}	0.075×10^{-7}
0,1	24216.705	0.0376_1	0.0364_1	0.1×10^{-7}	0.06×10^{-7}


GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS
B'_υ AND D'_υ FOR UPPER STATE OF 0,1 BAND OF A-X SYST OF
InI MOLECULE
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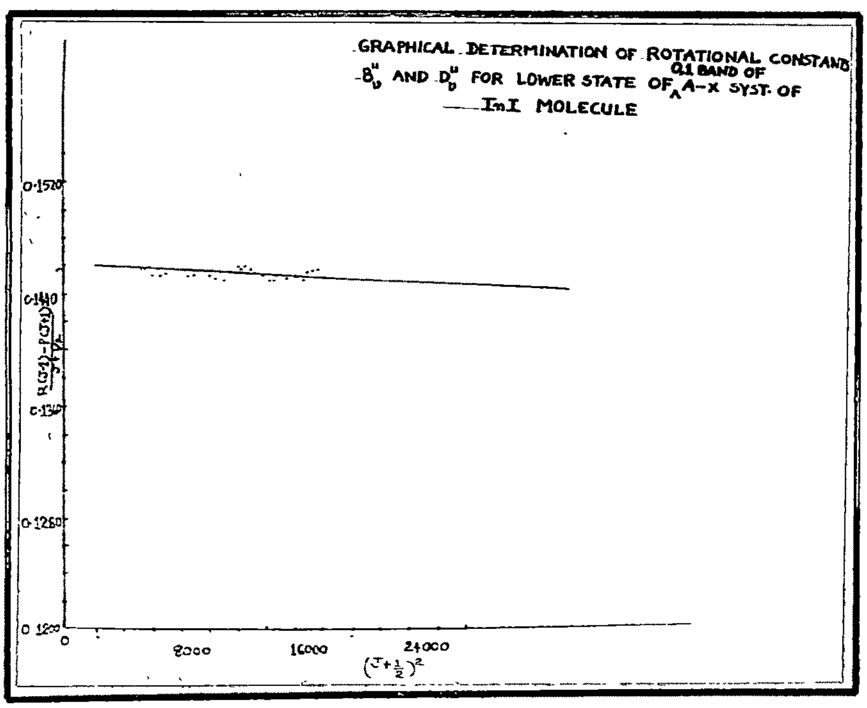
0·1440
0·1360
0·1280
0·1200
0
8000
16000
24000
(J+½)²

Fig. 8


GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS
B''_υ AND D''_υ FOR LOWER STATE OF 0,1 BAND OF A-X SYST. OF
InI MOLECULE
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0·1440
0·1360
0·1280
0·1200
0
8000
16000
24000
(J+½)²

Fig. 9

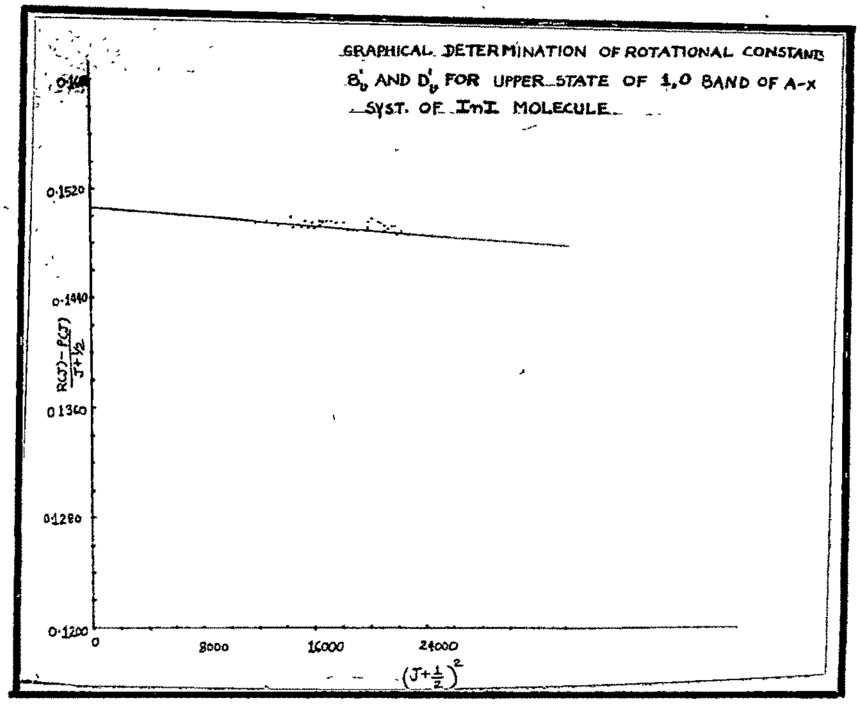
GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS
B'_v AND D'_v FOR UPPER STATE OF 1,0 BAND OF A-X
SYST. OF InI MOLECULE
0·1520
0·1440
0·1360
0·1280
0·1200
$\frac{R(J)-P(J)}{J+1/2}$
0
8000
16000
24000
$(J+\frac{1}{2})^2$

Fig. 10

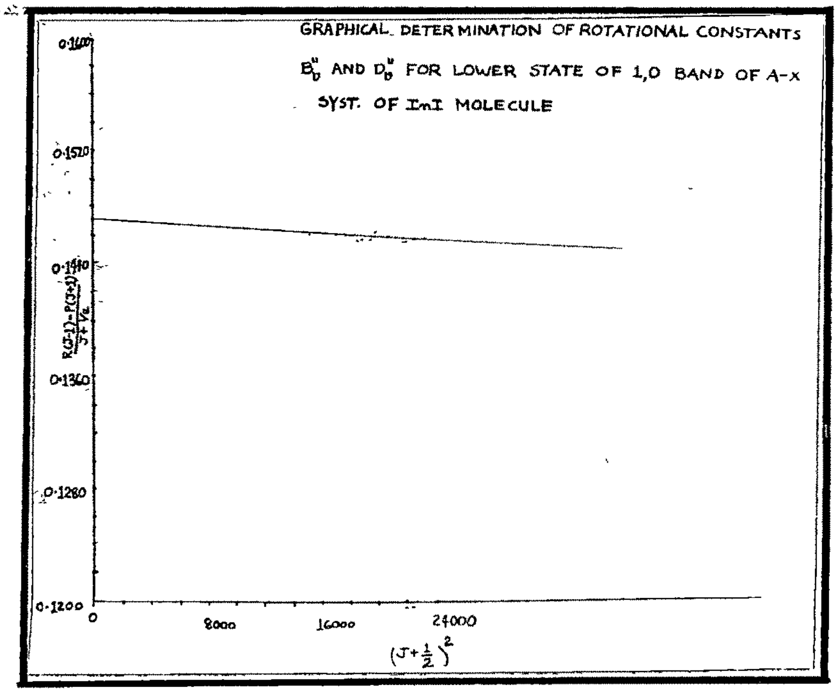
GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS
B''_v AND D''_v FOR LOWER STATE OF 1,0 BAND OF A-X
SYST. OF InI MOLECULE
0·1600
0·1520
0·1440
0·1360
0·1280
0·1200
$\frac{R(J-1)-P(J+1)}{J+1/2}$
0
8000
16000
24000
$(J+\frac{1}{2})^2$

Fig. 11

ε 12
ε 13

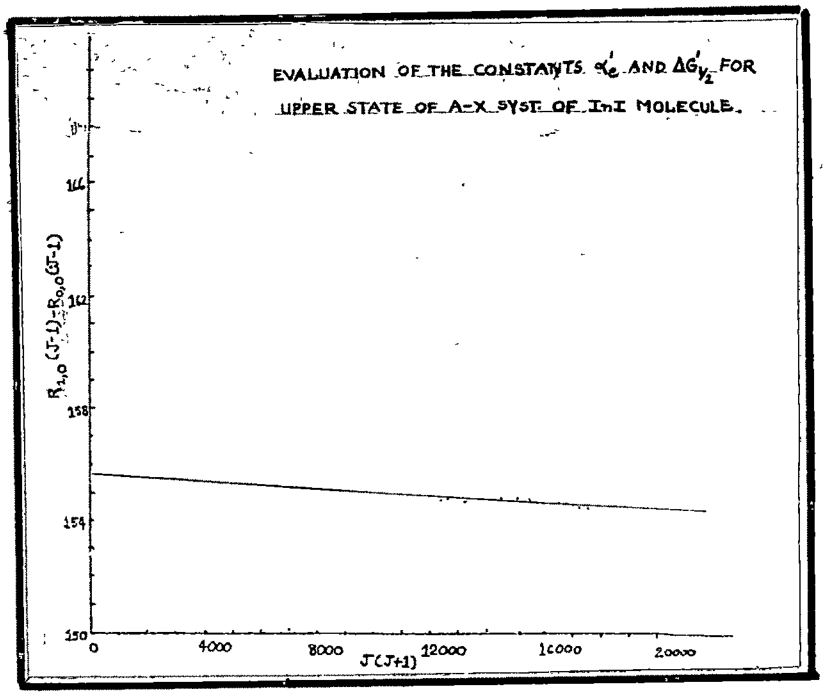

Fig. 12

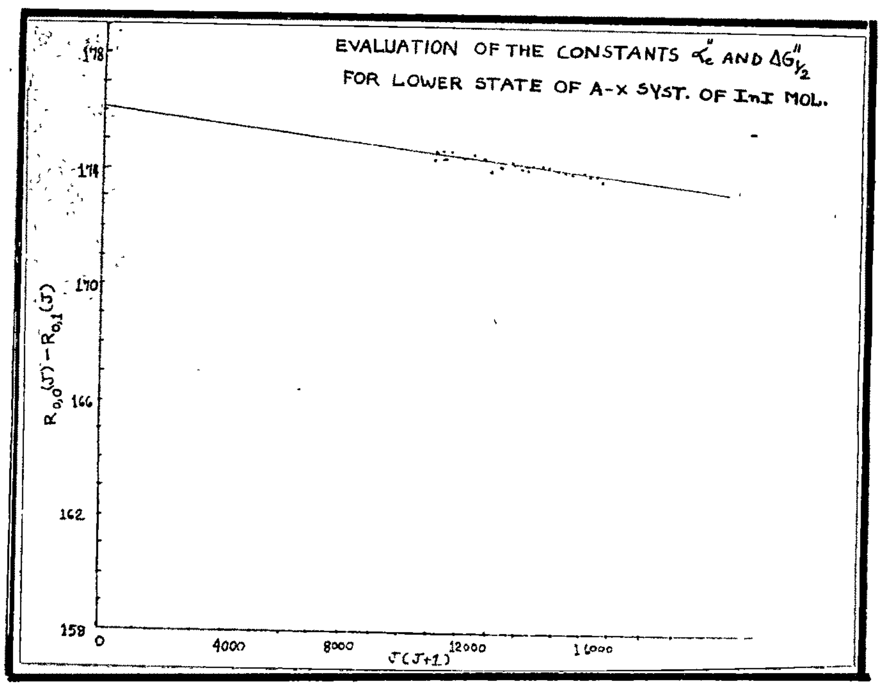

Fig. 13

observed values of the difference in wavenumbers of R branch for 0,0 band and 0,1 band viz $R_{0,0}(J)-R_{0,1}(J)$ were plotted against $J(J+1)$. The values are listed in Table 20. The st. line graph fig. 13 satisfy the following relation

$$R_{0,0}(J) - R_{0,1}(J) = \Delta G''_{\frac{1}{2}} - \alpha''_e (J)(J+1) \qquad (36)$$

The slope and intercept of the st. line gives the values of the constants α''_e and $\Delta G''_{\frac{1}{2}}$ for the lower state - X of A - X system. Similar relationship viz

$$R_{1,0}(J-1) - R_{0,0}(J-1) = \Delta G'_{\frac{1}{2}} - \alpha'_e (J)(J+1) \qquad (37)$$

holds for the upper state - A taking the difference of wavenumbers of R branch of 1,0 and 0,0 bands. The values are listed in Table 21.

The molecular constants for A - X system obtained from the present analysis are given in Table 22 along with the microwave data of Barrett and Mandel (1958).

TABLE 20

GRAPHICAL DETERMINATION OF α_e'' AND $\Delta G_{1/2}''$ VALUES FOR LOWER STATE FROM $R_{0,0}(J)-R_{0,1}(J)$ Vs. J(J+1) OF A-X SYSTEM OF InI MOLECULE

J	$R_{0,0}(J)$ cm^{-1}	$R_{0,1}(J)$ cm^{-1}	$R_{0,0}(J)-R_{0,1}(J)$ cm^{-1}
115	24413.30	24239.36	173.94
116	13.58	39.56	174.02
117	13.89	39.81	174.08
118	14.18	40.03	174.15
119	14.50	40.36	174.14
120	14.79	40.78	174.01
121	15.08	41.05	174.03
122	15.40	41.37	174.03
123	15.71	41.72	173.99
124	16.01	42.06	173.95
125	16.33	42.43	173.90
126	16.65	32.78	173.87
127	16.95	43.13	173.82
128	17.25	43.46	173.79
129	17.58	43.85	173.73
130	17.90	44.18	173.72
131	18.24	44.54	173.70
132	18.55	44.96	173.59
133	18.88	45.25	173.63
134	19.18	45.59	173.59
135	19.53	46.01	173.52

TABLE 21

GRAPHICAL DETERMINATION OF α_e' AND $\Delta G_{\frac{1}{2}}'$ VALUES FOR UPPER STATE FROM $R_{1,0}(J-1)-R_{0,0}(J-1)$ Vs. J(J+1) OF A - X SYSTEM OF InI MOLECULE.

J	$R_{1,0}(J-1)\,cm^{-1}$	$R_{0,0}(J-1)\,cm^{-1}$	$R_{1,0}(J-1)-R_{0,0}(J-1)\,cm^{-1}$
115	24567.92	24413.00	154.92
116	68.17	13.30	154.87
117	68.44	13.58	154.86
118	68.72	13.89	154.83
119	68.98	14.18	154.80
120	69.27	14.50	154.77
121	69.54	14.79	154.75
122	69.84	15.08	154.76
123	70.11	15.40	154.71
124	70.38	15.71	154.67
125	70.68	16.01	154.67
126	70.92	16.33	154.59
127	71.24	16.65	154.59
128	71.50	16.95	154.55
129	71.81	17.25	154.56
130	72.10	17.58	154.52
131	72.39	17.90	154.49
132	72.68	18.24	154.44
133	72.99	18.55	154.44
134	73.25	18.88	154.37
135	73.56	19.18	154.38

TABLE 22

MOLECULAR CONSTANTS OF InI OBTAINED IN THE PRESENT WORK ALONG WITH THE MICROWAVE DATA* (BARRETT AND MANDEL 1958).

Electronic state	B_e cm^{-1}	r_e A°	$\Delta G_{1/2}$ cm^{-1}	α_e cm^{-1}
$A\ ^3\Pi_0$	0.0376_2	2.710_2	155.7_2	0.6×10^{-4}
$X\ ^1\Sigma^+$	0.0362_2	2.770_1	176.1_2	1.3×10^{-4}
	*0.0368	*2.754		$^*1.04 \times 10^{-4}$

6.2 ELECTRONIC TRANSITION OF A - X SYSTEM

Ground state configuration of InI molecule can be written as $z\sigma^2 y\sigma^2 w\pi^4 x\sigma^2$ analogous to those of the halides of the same group (InCl, InBr and InF) giving rise to $^1\Sigma^+$ ground state. The excited electron configuration is $z\sigma^2 y\sigma^2 w\pi^4 x\sigma v\pi$, which gives rise to $^1\Pi$ or $^3\Pi$ state. $^1\Pi - {}^1\Sigma^+$ transition is attributed to C - X system which is analogous to those of similar molecules. However $^1\Pi$ state is repulsive in the case of InI molecule which gives a continuum at 3180 A°. The $^3\Pi$ state belongs to Hund's case (a) due to its large coupling constant (648.9 cm^{-1}). Hence $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$ states are analogous to $^1\Sigma$, $^1\Pi$ and $^1\Delta$ states respectively. $^3\Pi_2$—— X $^1\Sigma^+$ is a forbidden one whereas $^3\Pi_1$—— X $^1\Sigma^+$ has been ascribed to the B - X system. Therefore $^3\Pi_0$—— X $^1\Sigma^+$ transition may be attributed to the A - X system of InI molecule. The appearance of single P and R branches in case of 0,0; 0,1 and 1,0 bands of A - X system confirms this assignments

6.3 O,O BAND OF B – X SYSTEM OF InI MOLECULE

The rotational analysis of O,O band at 3993.7 A° of B – X system could not be carried out since the structure of the band was not properly resolved into branch lines (P, Q and R branches) even at the highest dispersion which the grating spectrograph could offer (0.43 A°/mm). The spectrogram showing the various heads and rotational lines of the O,O band is reproduced in plate 11.

An attempt was made in the present work to evaluate the rotational constants of the upper state-B from observed values of the second differences of the wavenumbers ($\Delta^2\nu$) of poorly resolved lines following the method suggested by Herzberg (1950). The spectrogram clearly indicates front P head and inner Q head of the band. Assuming the band origin to lie very close to Q head, the P – head to origin wavenumber difference k is given by the relation

$$k = \nu_H - \nu_o = - \frac{d^2}{4e} = - \frac{(B' + B'')^2}{4(B' - B'')} \qquad (38)$$

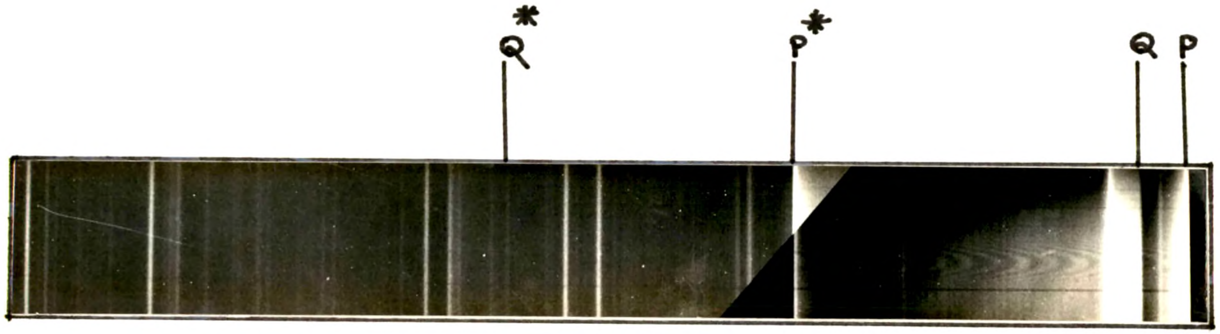

PLATE 11.

VARIOUS HEADS OF 0,0 BAND OF B — X SYSTEM OF InI MOLECULE AT 0.4 Å/mm.

The average value of the second difference of the wavenumbers ($\Delta^2 \nu$) of poorly resolved lines gives 2e value. Here e = B' - B". Observed $\Delta^2 \nu$ values for 0,0 band are listed in Table 23. Microwave data of Barret and Mandel (1958) provides the value for the lower state rotational constant B". Using this, rotational constants for 0,0 band of B - X system obtained in the present work are given below :

B'_0 cm^{-1}	B''_0 cm^{-1}	r'_0 A°	r''_0 A°
0.0388	0.0368	2.683	2.754

TABLE 23

VACUUM WAVENUMBERS AND THEIR SECOND DIFFERENCE ($\Delta^2\nu$) OF SOME POORLY RESOLVED LINES OF (0,0) BAND OF B - X SYSTEM OF InI MOLECULE

Vacuum wavenumber ν cm^{-1}	First difference $\Delta\nu$ cm^{-1}	Second difference $\Delta^2\nu$ cm^{-1}
25043.595	-	-
43.681	0.086	-
43.769	0.088	0.002
43.859	0.090	0.002
43.920	0.061	-0.029
44.015	0.095	0.034
44.109	0.094	-0.001
44.205	0.096	0.002
44.303	0.098	0.002
44.396	0.093	-0.005
44.498	0.102	0.009
44.612	0.114	0.012
44.732	0.120	0.006
44.860	0.128	0.008
44.992	0.132	0.004
45.127	0.135	0.003
45.266	0.139	0.004
45.408	0.142	0.003
45.554	0.146	0.004

Table 23 (contd..)

Vacuum wavenumber ν cm^{-1}	First difference $\Delta\nu$ cm^{-1}	Second difference $\Delta^2\nu$ cm^{-1}
25045.706	0.152	0.006
45.828	0.122	-0.030
45.973	0.145	0.023
46.123	0.150	0.005
46.317	0.194	0.044
46.455	0.138	-0.056
46.599	0.144	0.006
46.751	0.152	0.008
46.904	0.153	0.001
47.064	0.160	0.007
47.329	0.165	0.005
47.496	0.167	0.002
47.666	0.170	0.003
47.849	0.183	0.013
48.019	0.170	-0.013
48.187	0.168	-0.002
48.370	0.183	0.015
48.540	0.170	-0.013
48.713	0.173	0.003
48.890	0.177	0.004

Average value of approximately near second differences $\Delta^2\nu = 0.004$ cm^{-1}.