CHAPTER V

VIBRATIONAL ANALYSIS OF INDIUM MONOIODIDE

The spectrum of Indium monoiodide in the region λλ3948-4293 A° was studied at low dispersion by Wehrli (1934) and Wehrli and E. Miescher (1934). It consists of three systems of bands viz A - X, B - X and C - X. The single headed bands in the region λλ3948-4293 A° were studied in absorption and emission and an electronic transition of the type $A^3\Pi_{0^+} \longrightarrow X\ ^1\Sigma^+$ was assigned to them. Double headed bands in the same

region were studied in absorption as well as emission and an electronic transition of the type $B\ ^3\Pi_1 \rightleftarrows X\ ^1\Sigma^+$ was ascribed to them. Some bands belonging to B - X system showed a double degradation. Third system viz C - X was observed in absorption and was assigned to an electronic transition $C\ ^1\Pi \longleftarrow X\ ^1\Sigma^+$. This system was observed on a continuum having intensity maximum at 3180 A°. In an attempt to record the A - X and B - X systems of InI molecule at higher dispersion, a group of bands in the region λλ3490-3603 A° was observed for the first time. These new bands were later photographed and analysed. Moreover the bands belonging to A - X and B - X systems were recorded at a higher dispersion and were remeasured and accurate vibrational constants have been obtained.

5.1 Vibrational analysis of InI molecule in the region λλ3490-3603 A° ($D \longrightarrow B\ ^3\Pi_1$ system)

The spectrum of Indium monoiodide was excited in a high frequency discharge (10-15 MH_z) by keeping

pure Indium metal in the presence of Iodine vapours in a conventional type of a quartz discharge tube. The colour of the discharge was bright blue in which the bands were found to develope better. The spectrum was photographed in the second order of a 2 meter plane grating spectrograph at a reciprocal dispersion of 3.5 A°/mm. Exposure time of about 45 minutes was found necessary to record the spectrum of satisfactory intensity on Ilford N-30 plates. The measurements were made on Abbe comparator against internal standard lines. Spectrogram in the region λλ3490-3603 A° is reproduced in plate 4. The band head data consisting of visually estimated intensities, wave numbers in vacuum, vibrational assignments and the difference between observed and calculated wave numbers are given in Table 12. The observed bands were arranged in a Deslandres Table 13.

The spectrogram in the region λλ 3490-3603 A° reveals Q heads and corresponding very weak P heads

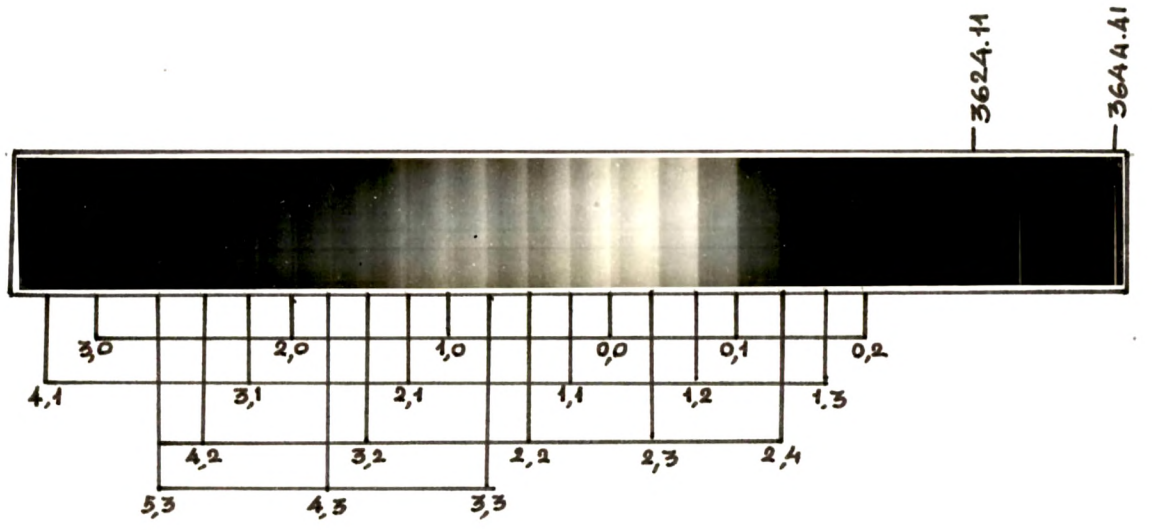

PLATE 4.

A NEW BAND SYSTEM ($D \rightarrow B\,^3\Pi_1$) OF InI MOLECULE IN THE REGION $\lambda\lambda$ 3603 — 3490 Å AT 3.5 Å/mm.

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TABLE 12

Band head data of the $D \longrightarrow B\ ^3\Pi_1$ system for Q heads of InI molecule.

Visually estimated Intensity	Wave Length A°	Wave number in Vacuum (cm^{-1}) ν	Assignment $v' - v''$	Difference $\nu_{obs} - \nu_{cal}$ cm^{-1}
3	3603.30	27744.3	0, 2	-3.1
5	3596.40	27797.7	1, 3	-0.4
7	3589.80	27848.8	2, 4	-0.6
9	3584.76	27887.6	0, 1	-1.7
8	3578.60	27935.8	1, 2	-1.7
7	3572.22	27985.9	2, 3	-0.3
10	3566.14	28033.8	0, 0	0.0
9	3560.47	28078.0	1, 1	-1.4
8	3554.64	28124.2	2, 2	-1.2
6	3548.59	28172.2	3, 3	+0.5
5	3542.24	28223.0	1, 0	-0.9
4	3536.83	28266.0	2, 1	-1.3
3	3530.98	28312.5	3, 2	+1.6
3	3525.30	28358.1	4, 3	+2.9

Table 12 (Cont)

Visually estimated Intensity	Wave Length A°	Wave number in Vacuum (ν cm^{-1})	Assignment $v' - v''$	Difference $\nu_{obs} - \nu_{cal}$ cm^{-1}
3	3518.70	28411.4	2, 0	-0.6
2	3513.71	28451.9	3, 1	-1.0
2	3508.11	28497.3	4, 2	+2.7
2	3495.89	28596.8	3, 0	+0.7
1	3490.80	28638.2	4, 1	+1.7

TABLE 13

DESLANDRES TABLE FOR Q HEADS OF D $\longrightarrow$ B $^3\pi_1$ SYSTEM OF InI MOLECULE

v' \ v''	0	1	2	3	4
0	$28033.8^{146.2}$	$27887.6^{143.3}$	27744.3		
	189.2	190.4	191.5		
1	$28223.0^{145.0}$	$28078.0^{142.2}$	$27935.8^{138.1}$	27797.7	
	188.4	188.0	188.4	188.2	
2	$28411.4^{145.4}$	$28266.0^{141.8}$	$28124.2^{138.3}$	$27985.9^{137.1}$	27848
	185.4	185.9	188.3	186.3	
3	$28596.8^{144.9}$	$28451.9^{139.4}$	$28312.5^{140.3}$	28172.2	
		186.3	184.8	185.9	
4		$28638.2^{140.9}$	$28497.3^{139.2}$	28358.1	

of the violet degraded bands. The most intense band at 28033.8 cm^{-1} has been taken as 0,0 band and the vibrational analysis has been carried out in the usual way. The Q heads of the observed bands were fitted in the following vibrational quantum equation :

$$\nu_Q = 28011.73 + 191.9\,(v' + \tfrac{1}{2}) - 0.8\,(v' + \tfrac{1}{2})^2 - 148.0\,(v'' + \tfrac{1}{2}) + 1.3\,(v'' + \tfrac{1}{2})^2 \quad (35)$$

The analysis reveals the lower state frequency of 148.0 cm^{-1} which is in close agreement with the vibrational frequency of the B - state of InI molecule (viz 146.7 cm^{-1}) obtained by M. Wehrli and E.Miescher (1934) from the vibrational analysis of B $^3\Pi_1$ - $X^1\Sigma^+$ system. This suggests that the lower state involved in the new band system is not the ground state of InI molecule having the vibrational frequency of 177.1 cm^{-1}. Further the upper state (D) frequency 191.9 cm^{-1} obtained from present analysis does not agree with any of the experimentally known frequencies for InI molecule.

Therefore the system may be ascribed to an electronic transition between two excited states, the lower state of which may be $B\,^3\pi_1$. The system $D \longrightarrow B\,^3\pi_1$ being not observed in absorption so far also indicates that ground state is not involved in the above electronic transition. The ν_e value for the new system indicates that the upper state (D) must lie at 53062.23 cm^{-1}. However the nature of the upper state can be confirmed by rotational analysis only.

The newly observed system $D - B\,^3\pi_1$ of InI molecule is an addition to similar systems observed in case of monohalides of the same group reported by previous workers. In case of TlI molecule $E - A\,^3\pi_0$ system was observed with intensity maximum at 3475 A° reported by A. Terenin (1932) with the position of E - state at ν_e = 54000 cm^{-1}. Analogous system $D - A\,^3\pi_0$ was reported for TlBr molecule by H. G. Howell (1941) with upper state D at ν_e = 54500 cm^{-1}. For TlCl molecule systems $D_{1,2}$—— A in the region λλ4180-4283 A° and

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λλ3890-4124 A° were reported by P. T. Rao (1949) and E. Miescher (1941).

5.2 Vibrational analysis of InI molecule in the region λλ3948-4293 A° (A - X and B - X systems)

The spectrum of $^{115}_{49}$InI in the region λλ 3948-4293 A° was studied at low dispersion by Wehrli (1934) and Wehrli and E. Miescher (1934) in absorption and emission. The single headed bands in this region were belonging to A - X system and double headed bands in the same region were classified as belonging to B - X system some of the bands of A - X and B - X system show a changing degradation. Spectrum of A - X and B - X system in the region λλ 4220-3970 A° is reproduced in plate 5.

In the present work the A - X system and B - X system were photographed at higher dispersions viz 1.55 A°/mm and 3.5 A°/mm respectively with the help of plane grating spectrograph. The part of spectrograms of A - X and B - X systems are reproduced in plates 6 and 7 respectively. The work was undertaken

PLATE 5.

A—X AND B—X SYSTEMS OF InI MOLECULE IN THE REGION λλ 4220—3970 Å AT 7.5 Å/mm.

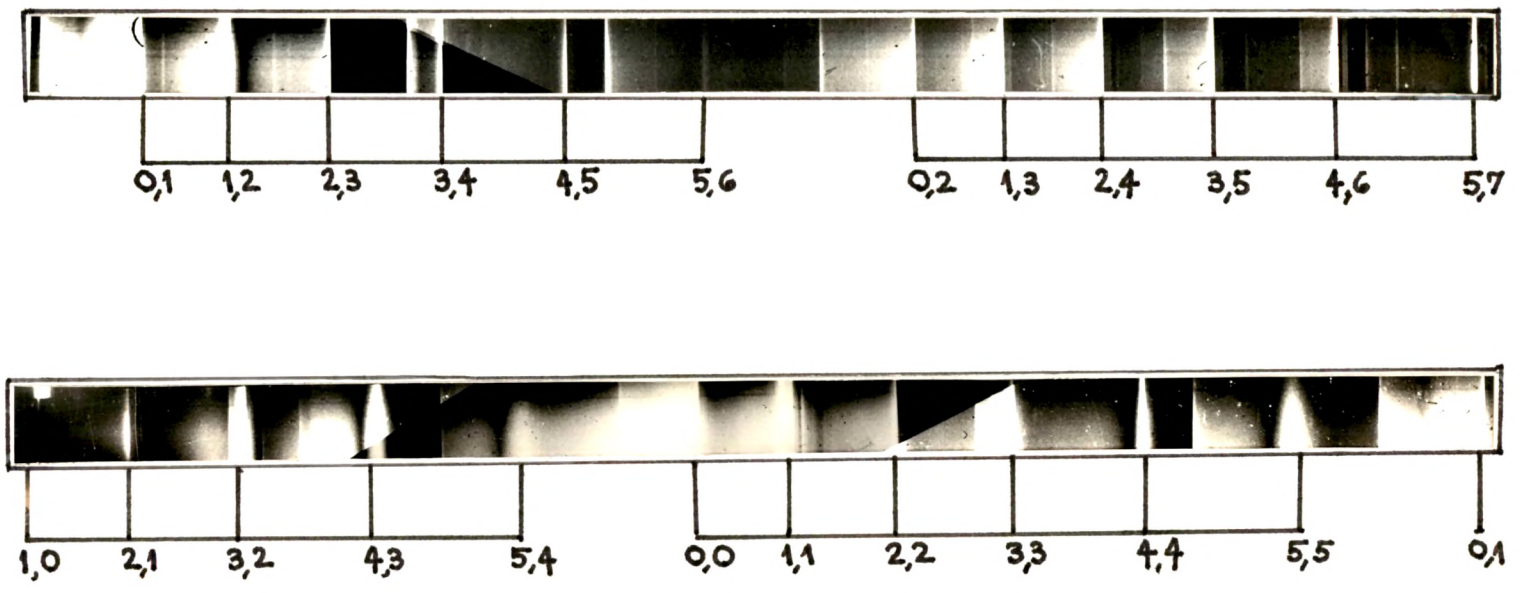

PLATE 6.

GRATING SPECTROGRAM OF InI MOLECULE (A—X SYSTEM) IN THE REGION

$\lambda\lambda$ 4180 - 4072 Å AT 1.55 Å/mm.

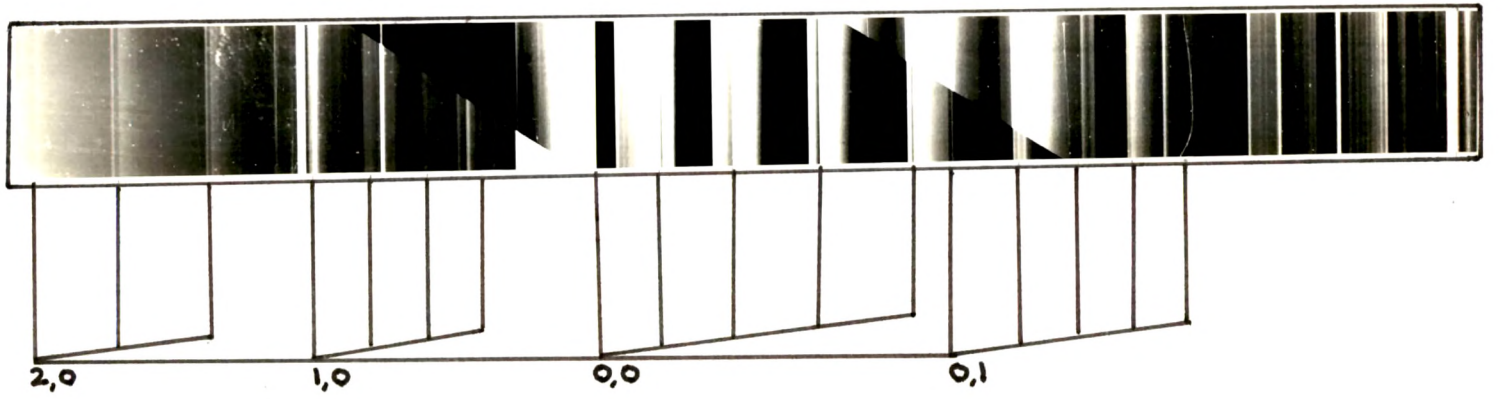

PLATE 7.

GRATING SPECTROGRAM OF InI MOLECULE (B—X SYSTEM) IN THE REGION $\lambda\lambda$ 4061 – 3945 Å AT 3·5 Å/mm.

to confirm the band head data and vibrational analysis reported by Wehrli and E. Miescher (1934), while aiming at the rotational analysis of some of the bands of A - X and B - X systems in the region λλ3948-4293 A°, if they could be resolved for the purpose. Under the higher dispersion used here, bands of B - X system are distinctly seen to be accompanied by an ancillary head which from their intensities and separations from main Q heads should be considered as P heads. The bands of A - X system show a single headed structure. All the bands are measured against iron arc standards and as the measurements are found to be in close agreement with the measurements of M. Wehrli and E. Miescher (1934), they are not given here. However the vibrational constants derived from the present analysis are given below :

A - X system		B - X system	
ω_e'	= 157.8 cm^{-1}	ω_e'	= 146.7 cm^{-1}
$\omega_e'x_e'$	= 1.71 cm^{-1}	$\omega_e'x_e'$	= 2.1 cm^{-1}
ω_e''	= 176.9 cm^{-1}	ω_e''	= 176.9 cm^{-1}
$\omega_e''x_e''$	= 0.4 cm^{-1}	$\omega_e''x_e''$	= 0.4 cm^{-1}
ν_e	= 24401.57 cm^{-1}	ν_e	= 25050.8 cm^{-1}