APPENDIX

APPENDIX A_1

In the study of band spectra, it is desirable to take the spectrogram by giving less exposure time to the plate. This requires the use of highly intense sources. The source used in the early work by the present author was H.F. power oscillator (125 W, at 5 to 16 Mc/s). The excitation produced by this source was less intense. In order to increase the intensity, a high power H.F. oscillator was needed. It was therefore decided to fabricate such an oscillator. This oscillator will be much more useful when the study will be undertaken with PGS 2 spectrograph in higher orders. The details of the fabrication etc., are given below.

Fig. No. 1 shows the schematic diagram of the arrangement of high frequency oscillatory system.

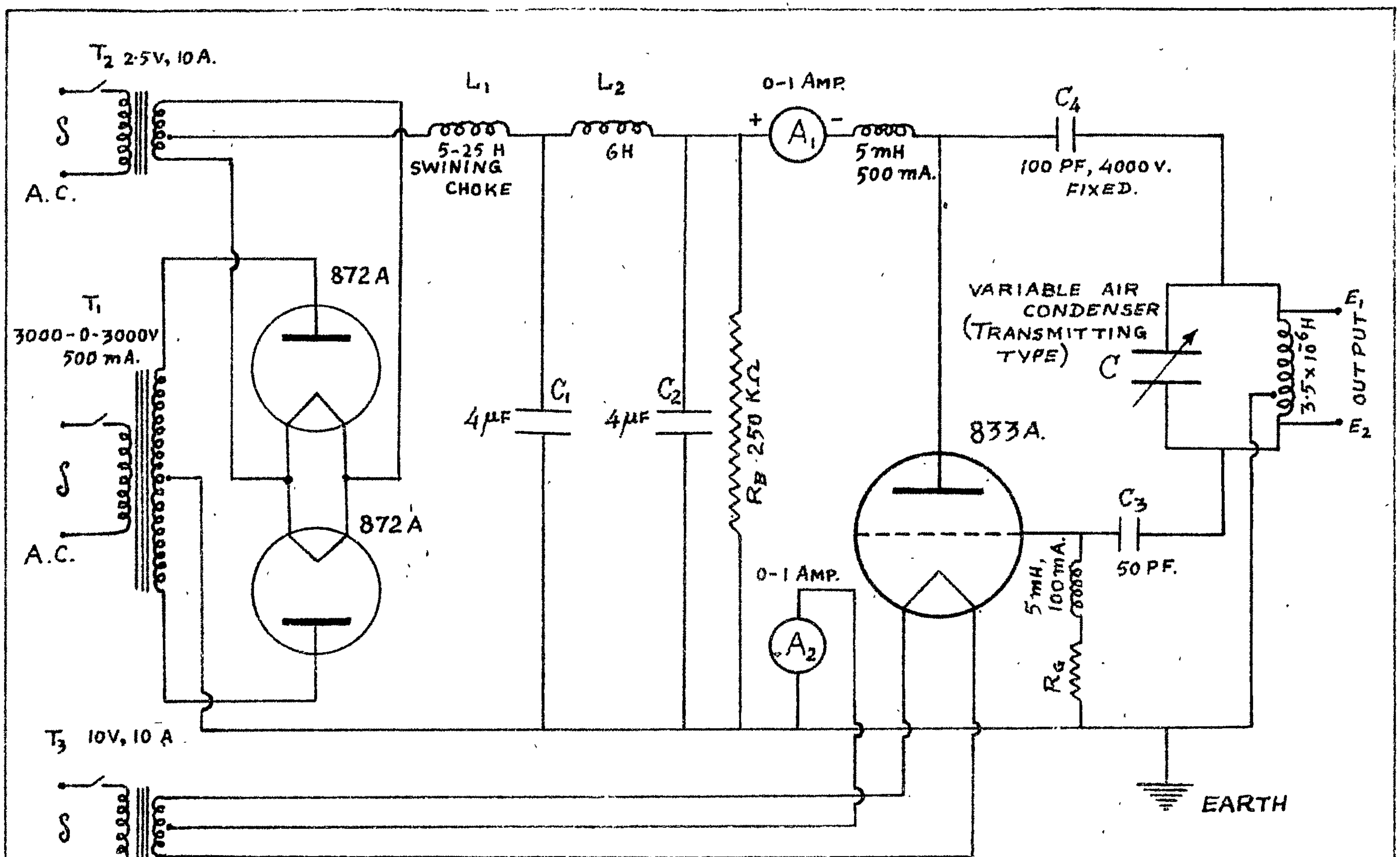
V is the variac to regulate the voltage output of H.T. The variac is capable of delivering voltage of 220-230 at 15 amperes. The H.T. is supplied to the oscillator O. The resulting high frequency voltage is then applied to the evacuated dicharge tube at E_1 and E_2. The component parts of the circuit are described in detail below.

(i) The High-Tension Source

The power supply and the oscillator are shown in Fig. 2. The continuous duty power transformer T_1 is capable of giving 3000-0-3000 volts at 700 ma. in its secondary and is insulated for 10 Kv. The voltage in the secondary is controlled by a variac kept in the primary (220-230 volts A.C. 50 c/s supply). The voltage across the secondary is then applied to two high voltage mercury vapour rectifier tubes 872 A. The filament supply of 2.5 volts at 10 Amps. for these rectifier tubes is given by a separate transformer T_2. The rectified voltage is then filtered through a choke input filter system consisting of a swinging choke CL_1, a fixed choke L_2 and two condeners C_1 and C_2. (L_1 = 5-25 H, 800 mA and 10 Kv insulation; L_2 = 6H, 800 mA and 10 Kv insulation; C_1, C_2 = 4 μF, oil filled with 10 Kv insulation and working volts 6000.) Across the H.T. output a bleeder resistance R_B (250 KΩ) is connected. The whole power supply is provided with a fuse in the H.T. lead.

(ii) The Oscillator

The oscillator is a series fed Hartley circuit the valve T is a transmitting triode 833 A. The filament current of 10 amperes at 10 volts is given by a separate transformer T_3. The oscillations are generated in a tuned circuit consisting of a variable transmitting type air condenser and a coil L. The coil L is made by winding a spiral of 3" diameter using a 18 S.W.G. copper wire. By using 8 turns it is possible to get an inductance of about 3.5×10^{-6} H. The H.T. is fed to the anode through a choke. The variable air condenser is taken on the panel for convenient tuning. The exact tuning of the oscillator is indicated by the sharp dip in the ammeter A_1. The oscillator is built on a wooden board with porcelain insulators and stiff wiring. The inductance of the tuned circuit is adjusted to give frequency in the range 55 to 65 Mc./sec.



T2 2·5V, 10A.
S
A.C.
T1
3000-0-3000V
500 mA.
S
A.C.
T3 10V, 10 A
S
A.C.
872 A
872 A
L1
5-25 H
SWINING
CHOKE
L2
6H
4μF
C1
4μF
C2
RB 250 KΩ
0-1 AMP.
+
A1
-
5mH
500 mA.
0-1 AMP.
A2
833A.
C4
100 PF, 4000 V.
FIXED.
VARIABLE AIR
CONDENSER
(TRANSMITTING
TYPE)
C
C3
50 PF.
5mH,
100mA.
RG
3·5 x 10⁻⁶H
E1
OUTPUT
E2
EARTH

FIG. A.

The oscillator is coupled to the discharge tube at E_1 and E_2 by leads taken from the ends of the tank coil L. These leads are brought on the top of the oscillator using good insulator blocks. Next to ascertain the order of the voltage applied, it is necessary to measure the voltage by a suitable voltmeter at the input supply.

This oscillator operates satisfactorily. It excites the molecules selected in the present investigation to the desired degree of intensity so that the time of exposure can be considerably reduced.

APPENDIX A_2

In the present investigation it was planned to get a two meter plane grating spectrograph (PGS2) from M/s Carl Zeiss Jena but due to some unavoidable circumstances its arrival was considerably delayed and hence the present work was undertaken with the available instruments. (viz. three spectrographs, the details of which have been described in chapter 3.) When the thesis was under preparation the instrument was received. It was therefore thought desirable to obtain some high dispersion spectrograms to check at least a few of the conclusions drawn from low dispersion spectrograms. The molecule CdI was selected as it was the heaviest of all and the bands obtained with low dispersion spectrographs could not provide more definite information. The bands in the ultra-violet and the visible region were photographed with this PGS 2 spectrograph with a dispersion of about 7 A°/mm. in the first order. Some of the results obtained will now be described under the following headings.

(i) C and D systems in the ultra-violet

(ii) B - system of CdI

(iii) Bands of CdI in the red-region

(i) C and D systems in the ultra-violet region. (Plate 13).

In the work reported by earlier workers on these systems maximum dispersion of 10 A°/mm was used and wavelengths of only three bands of C - system were known. As reproduced in plate (A_1) a fairly large number of additional bands of D system and a good number of sequence members of (0,1) and (0,2) bands have been observed. The measurements of the bands of C - system have been given in table (30) and the analysis in the table (31). The following quantum equation represents all the observed bands.

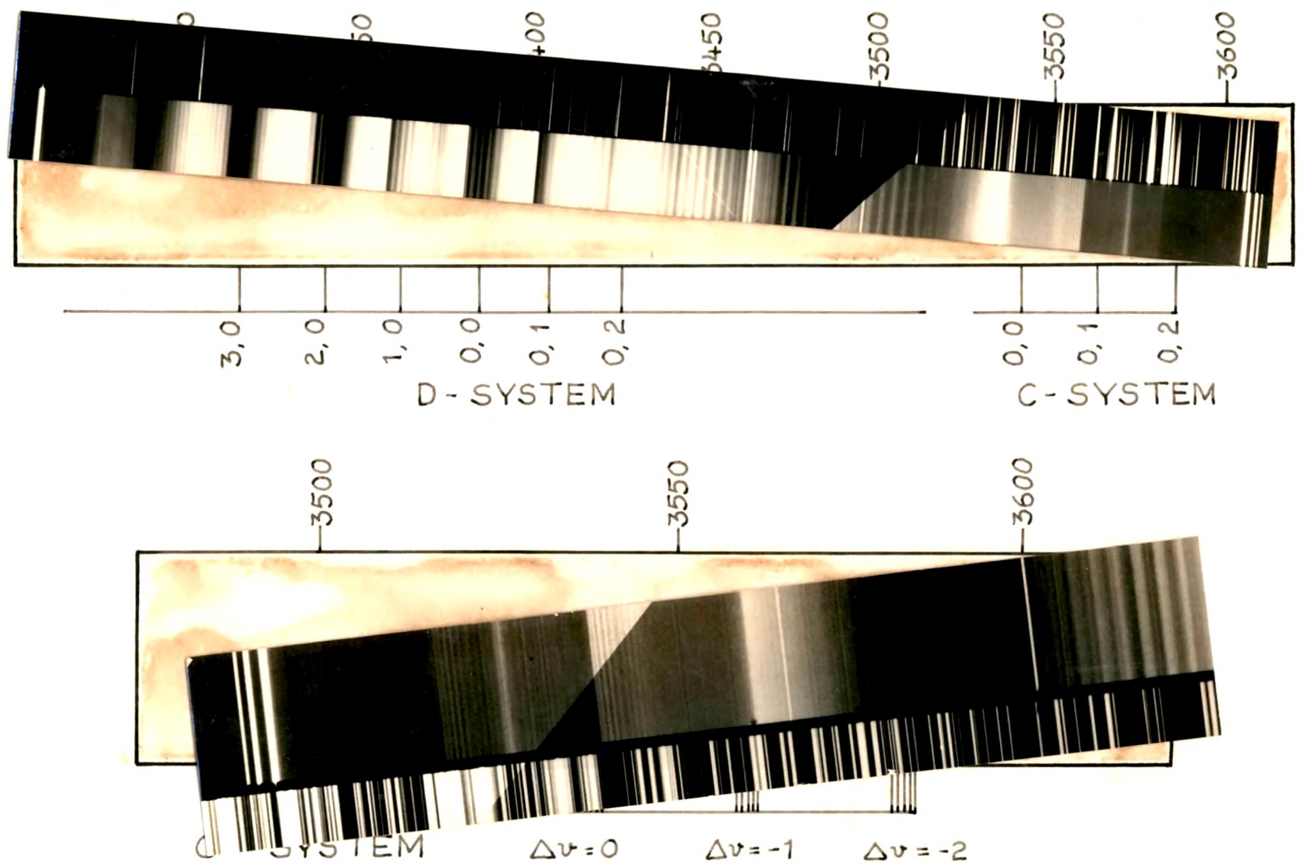


PLATE A1

BAND SPECTRUM OF CdI PHOTOGRAPHED ON PLANE GRATING SPECTROGRAPH IN THE FIRST ORDER.

$$\nu_{head} = 28230.29 + \left[181.60\,(v'+\tfrac{1}{2}) - 0.55\,(v'+\tfrac{1}{2})^2\right] - \left[178.20\,(v''+\tfrac{1}{2}) - 0.60\,(v''+\tfrac{1}{2})^2\right].$$

The nearness of the vibrational constants of the ground state and the excited state accounts for the compact nature of the vibrational structure which gives rise to an appearance similar to rotational structure. The exact $^2\Pi$ interval as observed in the present work is $\nu_e^D - \nu_e^C$ = 29530-28230=1300 cm^{-1} which supports Howell's argument, but his second remark that this interval is slightly higher than the expected one viz. 1140 cm^{-1} requires further investigation of the D system also.

(ii) B - system of CdI (Plate 14)

The spectrum in the region λλ3900-4800 A.U. have been reproduced in plate (A_2). One of the assumptions made in the analysis of these bands, namely, that the bands appearing in triplets do not form sequences and have different values of Δv , is properly justified. (Refer plate (A_2a) between λλ4500-4800 A.U.). The diffuse nature of the bands (Plate A_2b) appears to be due to isotopic constituents of Cd atom.

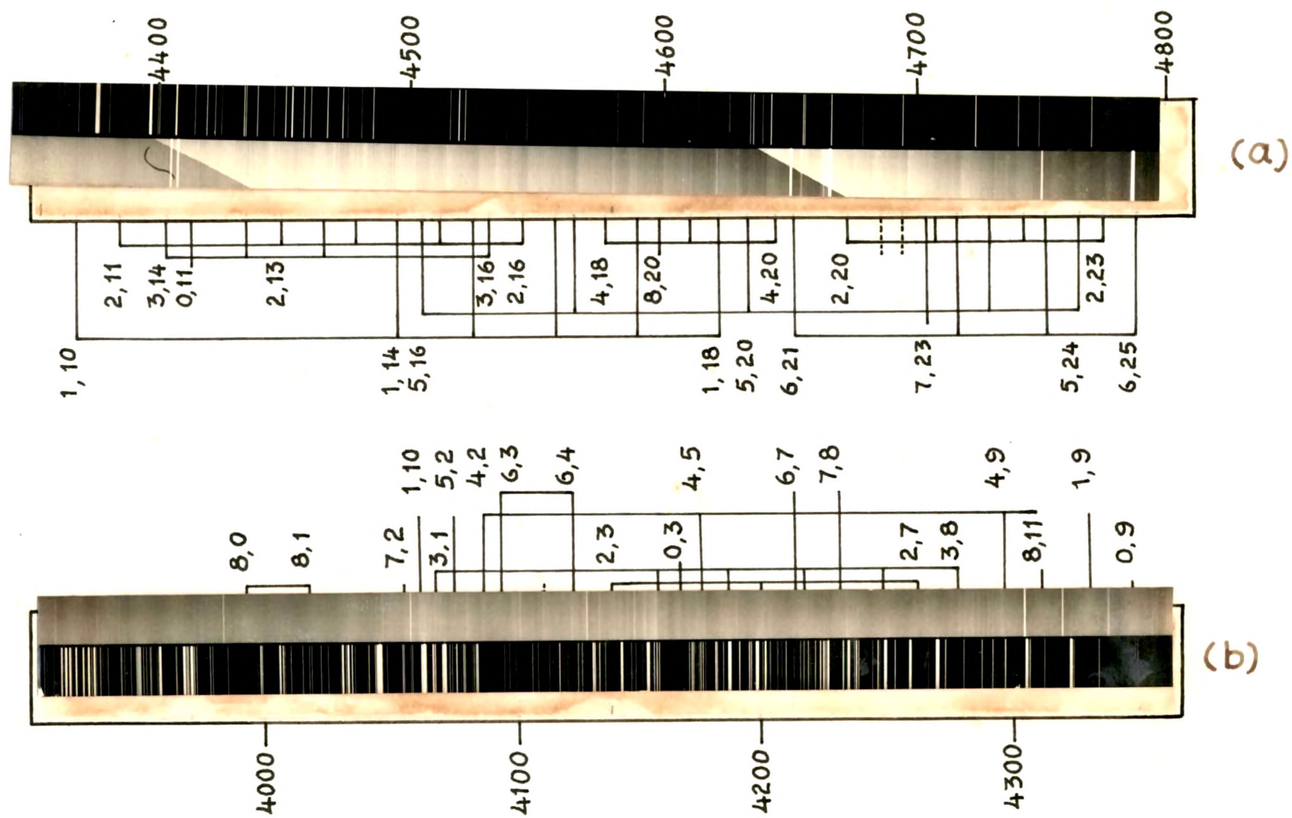
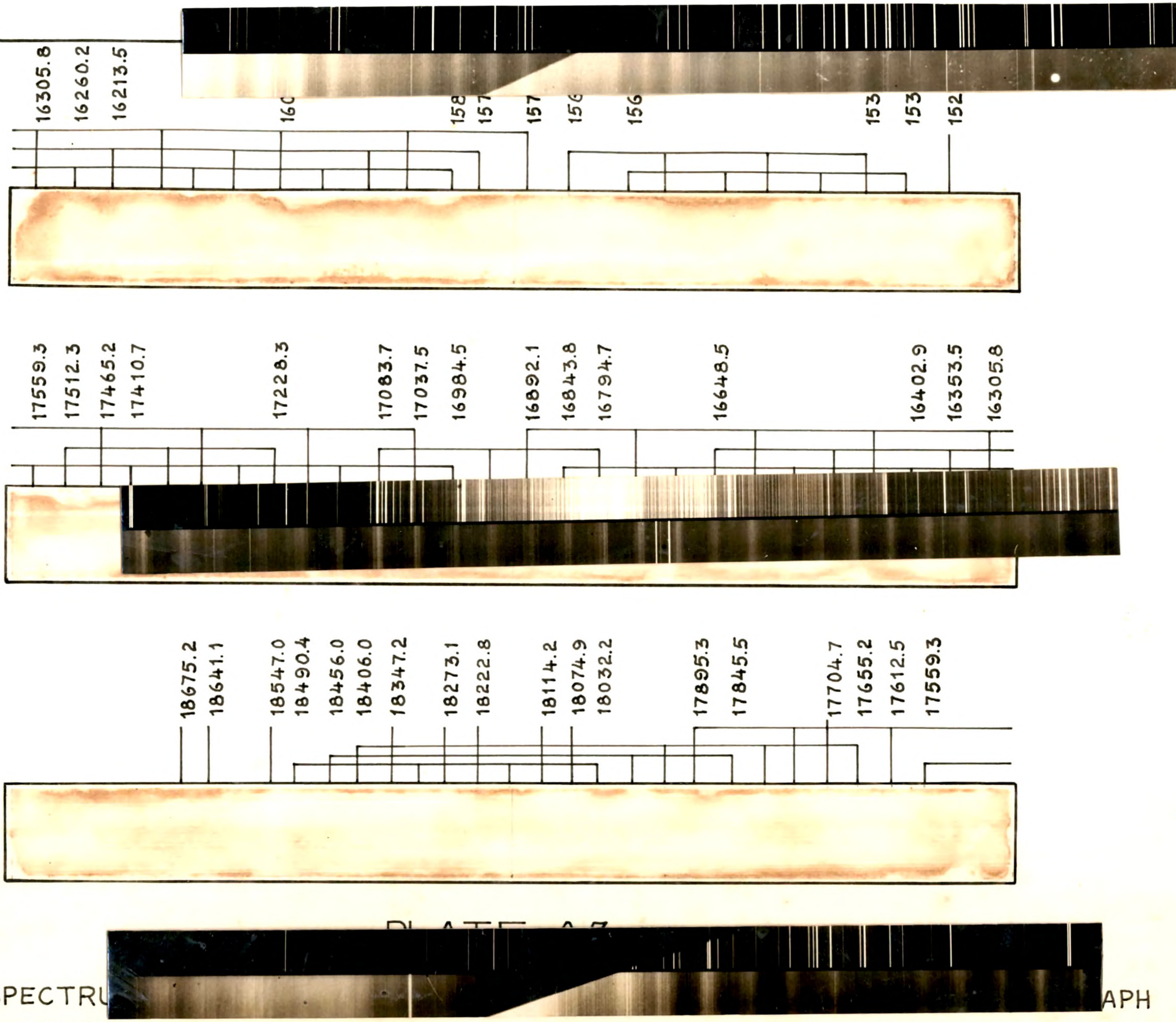


PLATE A2.

BAND SPECTRUM OF CdI PHOTOGRAPHED ON PLANE GRATING SPECTROGRAPH IN THE FIRST ORDER.

B - SYSTEM.



BAND SPECTRU APH
IN THE FIRST ORDER. A - SYSTEM.

The measurements taken with grating spectrograms agree with those reported in chapter (4), and are given in table (32). Following the same analysis the bands head equation given below was dervied.

$$\nu_{head} = 24592.4 + \left[77.70\,(v'+\tfrac{1}{2}) - 1.45\,(v'+\tfrac{1}{2})^2\right] - \left[178.00\,(v''+\tfrac{1}{2}) - 0.60\,(v''+\tfrac{1}{2})^2\right].$$

The values of $\nu_{obs}-\nu_{cal}$ show less deviations in comparision to those reported in chapter (4).

(iii) Bands of CdI in the red region (Plate A_3)

The bands in this region have been reproduced in the plate (A_3), and their grouping as reported in chapter (4) have been retained. The following conclusions could be very easily arrived at.

(a) From the observed intervals amongst the bands it is certain that the emitter is a CdI molecule.

(b) From the double nature of some of the heads, one can infer that a low lying $^2\Pi$ state is involved in the emission of these bands.

(c) The diffuse nature of band heads on either side of the spectrum (Plate A_3) might be due to isotopic nature of Cd atom.

It is proposed to study in much more detail the molecular spectra of CdCl, CdBr and CdI by using the PGS2 spectrugraph in higher orders.

TABLE 30

BAND HEADS OF C - SYSTEM OF CdI IN THE REGION $\lambda\lambda$ 3534 - 3586 A.U.

Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}	Wave Number observed by Ramasastry.	Assignment. v',v"
2	3585.78	27880	27880.2	0,2
2	3585.14	27885		1,3
2	3584.37	27891		2,4
2	3583.47	27898		3,5
2	3582.44	27906		4,6
1	3581.03	27917		5,7
1	3580.13	27924		6,8
1	3579.11	27932		7,9
1	3578.21	27939		8,10
1	3577.31	27946		9,11
4	3563.41	28055	28054.5	0,1
4	3562.78	28060		1,2
4	3562.14	28065		2,3
4	3561.25	28072		3,4
4	3560.37	28079		4,5
3	3559.10	28089		5,6
3	3558.21	28096		6,7
3	3557.33	28103		7,8

TABLE 30. (Contd.)

Intensity.	Wavelength in A.U.	Wave Number in vacuum cm^{-1}.	Wave Number observed by Ramasastry.	Assignment. v',v"
2	2556.44	28110		8,9
2	3555.93	28114		9,10
2	3555.05	28121		10,11
10	3541.07	28232	28232.9	0,0
10	3540.57	28236		1,1
10	3539.82	28241		2,2
9	3539.19	28247		3,3
9	3538.44	28253		4,4
8	3537.19	28263		5,5
7	3535.31	28278		8,8
7	3534.44	28285		9,9

TABLE 31

VIBRATIONAL SCHEME FOR C - SYSTEM OF CdI

v" / v'	0	1	2	3	4	5	6
		(177)	(175)				
0	28232(10)	28055(4)	28880(2)	-	-	-	-
		(181)	(180)				
			(176)	(175)			
1	-	28236(10)	28060(4)	27885(2)	-	-	-
			(181)	(180)			
				(176)	(174)		
2	-	-	28241(10)	28065(4)	27891(2)	-	-
				(182)	(181)		
					(175)	(174)	
3	-	-	-	28247(9)	28072(4)	27898(2)	-
					(181)	(181)	
						(174)	(173)
4	-	-	-	-	28253(9)	28079(4)	27906(2)

A2-12

TABLE 31 (Contd.)

v' \ v"	5	6	7	8	9	10	11
	(174)	(172)					
5	28263(8)	28089(3)	27917(1)	-	-	-	-
			(179)				
			(172)				
6	-	-	28096(3)	27924(1)	-	-	-
				(179)			
				(171)			
7	-	-	-	28103(3)	27932(1)	-	-
				(168)	(171)		
8	-	-	-	28278(7)	28110(2)	27939(1)	-
					(175)	(175)	
					(171)	(168)	
9	-	-	-	-	28285(7)	28114(2)	27946(1)

TABLE 32.

BAND HEADS OF B - SYSTEM OF CdI IN THE REGION
λλ 3900-4800 A.U.*

Intensity.	Wave-length in A.U.	Observed Wave Number in vacuum cm^{-1}	v',v"	$\nu_{obs.} - \nu_{cal.}$
2	4786.81	20884.9	6,25	-2.4
2	4776.90	20928.2	2,23	2.3
2	4765.91	20976.5	5,24	0.5
3	4752.50	21035.7	6,24	0.4
3	4746.61	21061.8	4,23	0.8
3	4744.11	21072.9	2,22	-3.4
4	4732.29	21125.5	5,23	-1.3
3	4718.20	21188.6	6,23	4.1
5	4709.69	21226.9	2,21	-1.0
2	4705.70	21244.9	7,23	3.0
4	4701.32	21264.7	-	-
0	4695.80	21289.7	-	-
3	4688.01	21325.6	-	-
2	4674.94	21384.7	2,20	4.0
4	4652.59	21487.4	6,21	0.9
3	4645.82	21518.7	4,20	2.9

* Measurements made on the plates taken on PGS2 spectrograph.

TABLE 32. (Contd.)

Intensity.	Wave-length in A.U.	Observed Wave Number in vacuum cm^{-1}.	v',v"	$\nu_{obs} - \nu_{cal.}$
4	4632.99	21578.3	5,20	-0.7
2	4623.70	21621.7	1,18	3.7
4	4613.17	21671.0	4,19	1.2
4	4611.47	21679.0	-	-
5	4595.81	21752.9	8,20	1.7
4	4590.91	21776.1	1,17	1.7
6	4579.57	21830.0	4,18	5.0
5	4566.42	21892.9	5,18	4.7
5	4558.40	21931.4	1,16	-0.6
3	4550.49	21969.5	-	-
5	4543.90	22001.4	2,16	-2.5
4	4537.19	22033.9	-	-
2	4530.41	22066.9	3,16	-6.0
5	4525.40	22091.3	1,15	0.5
3	4516.88	22133.0	-	-
6	4511.19	22160.9	2,15	-1.8
4	4508.02	22176.5	0,14	0.5
5	4503.71	22198.7	5,16	-3.5

TABLE 32. (Contd.)

Intensity.	Wave-length in A.U.	Observed Wave Number in vacuum cm^{-1}	v',v"	$\nu_{obs.} - \nu_{cal.}$
4	4493.40	22248.6	1,14	-2.2
4	4490.80	22261.5	6,16	-1.0
6	4484.86	22291.0	-	-
6	4478.59	22322.2	2,14	-0.5
6	4467.80	22376.1	8,16	1.7
5	4464.25	22393.9	3,14	2.2
4	4460.59	22412.3	1,13	0.3
4	4446.30	22484.3	2,13	0.4
5	4442.71	22502.5	0,12	2.9
7	4432.50	22554.3	3,13	1.4
5	4428.69	22573.7	1,12	-0.7
6	4410.99	22664.3	0,11	1.1
6	4401.01	22715.7	3,12	0.4
6	4395.59	22743.7	6,13	1.2
6	4382.20	22813.2	2,11	3.3
2	4375.80	22846.6	5,12	2.0
5	4364.69	22904.7	1,10	1.9
5	4347.71	22994.2	0,9	0.2

TABLE 32. (Contd.)

Intensity.	Wave-length in A.U.	Observed Wave Number in vacuum cm^{-1}.	v',v"	$\nu_{obs.} - \nu_{cal.}$
2	4345.91	23003.7	5,11	-4.5
5	4334.64	23063.5	1,9	-5.3
0	4328.86	23094.3	-	-
4	4316.20	23162.0	0,8	0.8
4	4312.24	23183.2	8,11	2.8
4	4295.88	23271.6	4,9	-4.2
4	4276.40	23377.6	3,8	0.7
3	4258.60	23475.3	2,7	-1.0
3	4246.14	23544.2	3,7	-1.1
3	4231.20	23627.3	7,8	3.4
3	4215.11	23717.5	3,6	2.6
2	4212.41	23732.7	6,7	-2.2
3	4198.21	23813.0	2,5	-3.7
3	4185.20	23887.0	3,5	1.3
1	4183.91	23894.4	-	-
3	4173.70	23952.8	4,5	1.0
3	4163.90	24009.2	0,3	-6.0
4	4154.61	24062.9	3,4	5.2

TABLE 32. (Contd.)

Intensity.	Wave-length in A.U.	Observed Wave Number in vacuum cm^{-1}	v',v"	$\nu_{obs.} - \nu_{cal.}$
3	4145.75	24114.3	-	-
3	4142.08	24135.6	-	-
2	4138.13	24158.7	2,3	-3.2
2	4122.81	24248.5	6,4	1.2
3	4111.60	24314.6	-	-
3	4099.69	24385.2	-	-
2	4094.44	24416.5	6,3	-4.0
3	4086.20	24465.7	4,2	-5.7
3	4080.55	24499.6	-	-
2	4074.30	24537.2	5,2	2.6
2	4067.50	24578.2	3,1	-2.7
3	4061.31	24615.7	1,0	-1.1
2	4055.29	24652.2	7,2	-0.1
2	4043.11	24726.5	-	-
1	4017.80	24882.2	8,1	-0.2
1	4001.40	24984.2	-	-
1	3997.59	25008.0	7,0	3.3
1	3989.60	25058.1	8,0	-1.1
0	3987.20	25073.2	-	-
0	3973.36	25160.5	-	-
0	3960.07	25245.0	-	-
0	3948.90	25316.4	-	-
0	3933.42	25416.0	-	-

TABLE 33.

BAND HEADS OF A - SYSTEM OF CdI IN THE REGION 5290-6550 A.U.

Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}.	Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}.
9	6548.20	15267.4	9	6400.82	15618.7
9	6543.38	15278.4	9	6386.67	15653.3
9	6535.51	15296.8	8	6373.03	15686.8
9	6530.52	15308.5	8	6355.28	15730.6
10	6512.82	15350.1	8	6352.98	15736.3
10	6509.09	15358.9	8	6333.06	15785.8
10	6487.99	15408.8	8	6330.81	15791.4
10	6485.48	15414.8	9	6319.50	15819.7
10	6477.20	15434.5	9	6317.17	15825.5
10	6475.19	15439.3	9	6302.80	15861.6
9	6460.59	15474.2	9	6299.81	15869.1
9	6456.80	15483.3	8	6281.21	15916.1
9	6455.20	15487.1	8	6278.30	15923.5
9	6445.59	15510.2	8	6261.11	15967.2
9	6443.02	15516.4	8	6258.10	15974.9
9	6417.21	15578.8	7	6243.20	16013.0
9	6409.52	15597.5	7	6240.98	16018.7

TABLE 33. (Contd.)

Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}	Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}
5	6228.62	16050.5	8	6057.10	16505.0
6	6220.09	16072.5	5	6040.88	16549.3
6	6214.52	16086.9	8	6039.90	16552.0
7	6204.50	16112.9	8	6036.90	16560.2
7	6202.49	16118.1	9	6023.23	16597.8
8	6187.29	16157.7	9	6020.11	16606.4
8	6181.60	16172.6	8	6004.89	16648.5
8	6169.42	16204.5	8	6002.40	16655.4
8	6165.99	16213.5	7	5988.70	16693.5
9	6150.71	16253.8	7	5987.80	16698.8
9	6148.29	16260.2	7	5971.60	16741.3
9	6134.90	16295.7	7	5969.00	16748.6
9	6131.10	16305.8	7	5954.21	16790.2
8	6113.21	16353.5	7	5952.61	16794.7
8	6109.51	16363.4	7	5937.48	16837.5
7	6094.80	16402.9	7	5935.26	16843.8
7	6077.90	16448.5	8	5921.30	16883.5
7	6075.09	16456.1	8	5918.29	16892.1
8	6060.51	16495.7	8	5903.79	16933.6

TABLE 33. (Contd.)

Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}	Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}.
8	5901.70	16939.6	6	5708.69	17512.3
8	5887.69	16979.9	6	5693.41	17559.3
8	5886.10	16984.5	6	5690.88	17567.1
7	5867.78	17037.5	6	5676.21	17612.5
8	5851.92	17083.7	6	5673.70	17620.3
8	5849.69	17090.2	6	5662.49	17655.2
7	5838.01	17124.4	5	5646.65	17704.7
7	5834.19	17135.6	5	5643.37	17715.0
7	5819.01	17180.3	4	5631.29	17753.0
8	5804.52	17223.2	6	5615.10	17804.2
8	5802.80	17228.3	6	5602.10	17845.5
8	5786.91	17275.6	6	5600.31	17851.2
6	5771.51	17321.7	5	5598.40	17857.3
8	5769.40	17328.0	6	5588.89	17887.7
7	5755.39	17370.2	6	5586.51	17895.3
7	5752.51	17378.9	5	5574.40	17934.2
6	5742.00	17410.7	5	5572.31	17940.9
6	5724.09	17465.2	5	5557.41	17989.0
6	5710.48	17506.8	4	5544.10	18032.2

TABLE 33. (Contd.)

Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}	Intensity.	Wave-length in A.U.	Wave Number in vacuum cm^{-1}
4	5531.00	18074.9	2	5365.10	18633.8
4	5519.01	18114.2	2	5363.00	18641.1
4	5510.12	18183.4	1	5353.21	18675.2
4	5486.29	18222.8	1	5346.00	18700.4
4	5473.70	18264.1	0	5339.28	18723.9
4	5471.01	18273.1	0	5332.71	18747.0
3	5460.61	18307.9	0	5325.29	18773.1
3	5459.30	18312.3	0	5313.01	18816.5
3	5448.91	18347.2	0	5307.40	18836.4
3	5446.00	18357.0	0	5300.70	18860.2
3	5431.50	18406.0	0	5291.69	18892.3
3	5419.70	18446.1			
3	5416.79	18456.0			
1	5406.71	18490.4			
2	5390.20	18547.0			
2	5386.50	18559.8			
2	5375.91	18599.8			