CHAPTER VI

SPECTRA OF MERCURY IODIDE MOLECULE

The experimental results and the vibrational analyses of the band systems in the ultraviolet for mercury iodide molecule are reported in this chapter.

In order to make a preliminary survey of the various band systems of mercury iodide molecule a Hilger medium quartz spectrograph was employed. Using the same experimental techniques employed for the production of the spectra of mercury chloride and mercury bromide, the spectrograms were recorded. The reproduction of the spectrum of mercury iodide in the region 3100-2303 A° is given in Plate 1(c).

The bands of HgI in the region 3100-2650 A° were first reported in emission by Wieland (1929) and from his absorption and fluorescence studies (1932), he classified them into two systems. Rao et al. (1944) reinvestigated the spectrum in emission at higher dispersion and the bands were ascribed to two component systems (C and D) of a $^2\Pi$ — $^2\Sigma$ electronic transition with a doublet interval of 3538 cm^{-1}. However, the bands in the region 2850-2800 A° were not accounted in the suggested vibrational analysis. Hence in the present study the spectrum of the molecule was photographed on a plane grating spectrograph at a dispersion of 1.85 A°/mm. Exposure time of about ninety minutes was found adequate to obtain satisfactory spectrograms. The two groups of bands lying in the region 3075-2804 A° and 2850-2650 A° are reproduced in Plates 6 and 7 respectively. Sixty eight additional bands in the present investigation are assigned for C and D systems and their visually estimated intensities, wavelengths, wave numbers in vacuum and assignments are given in Table XVIII and Table XIX. The assignments of the bands were made using the vibrational constants reported by Rao et al. (1944). The calculated values of the wave numbers are in close agreement with the observed ones. The differences between them are given

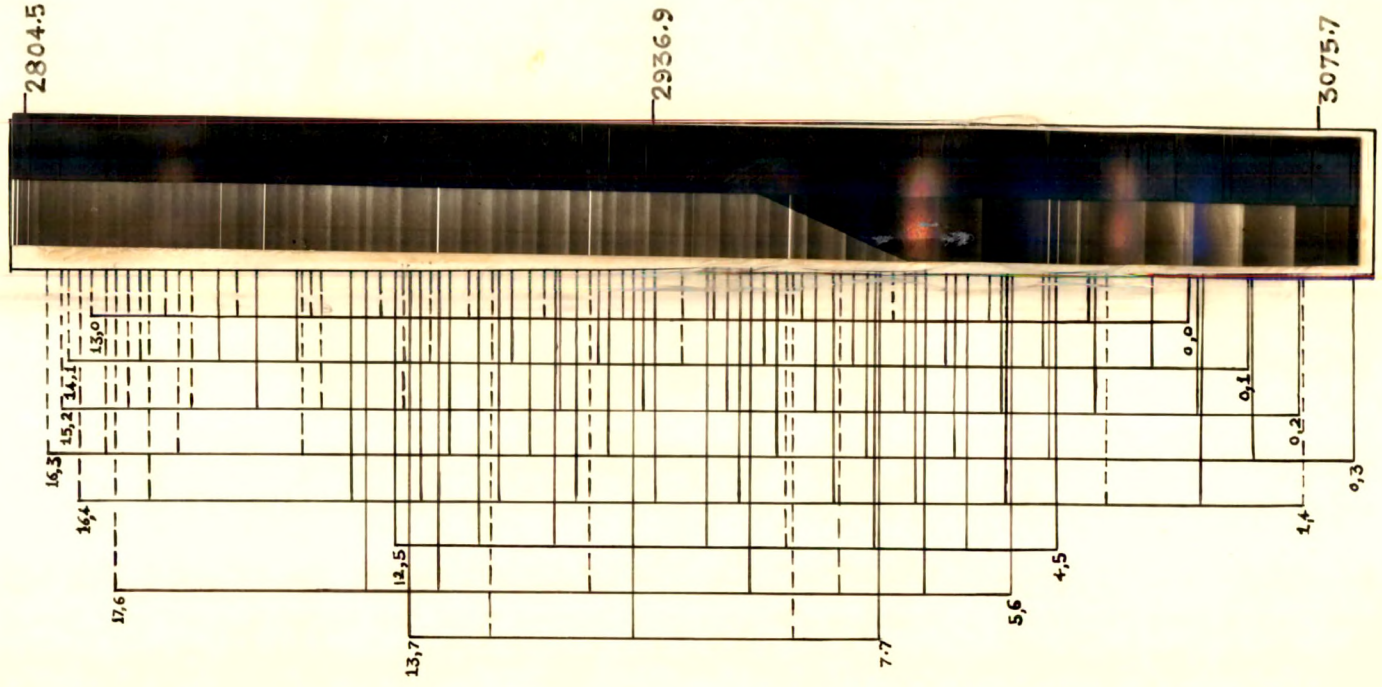

PLATE. 6.

SPECTROGRAM OF HgI TAKEN AT A DISPERSION OF 1.85 A°/M.M.
C-SYSTEM.

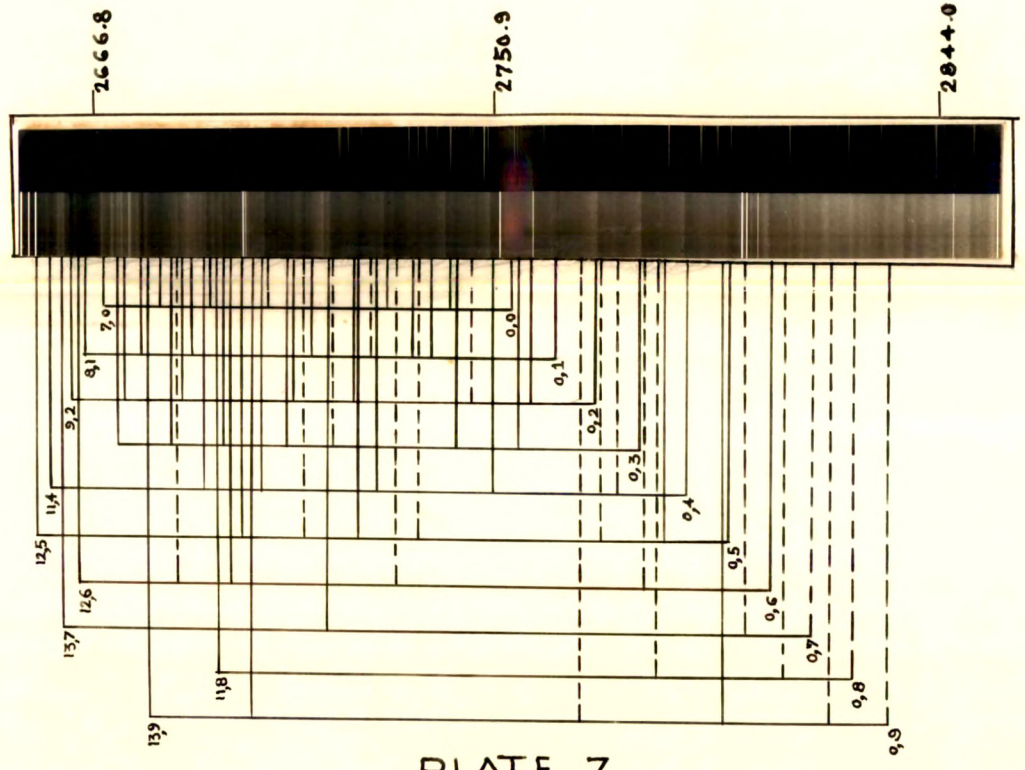

PLATE. 7.

SPECTROGRAM OF Hg I TAKEN AT A DISPERSION OF 1.85 A°/M. M.
D-SYSTEM.

TABLE XVIII

ADDITIONAL BANDS OF C-SYSTEM OF HgI MOLECULE

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Wave number reported by Rao et al.
4	3030.89	32984.0	3,4	0.2	32988
4	2987.19	33466.5	3,0	0.1	33466.5
1	2986.04	33479.4	8,9	2.6	33479.4
2	2975.11	33603.5	7,6	0.2	
1	2966.92	33695.1	8,7	2.3	
2	2965.06	33716.3	7,5	0.0	33711.3
2	2959.46	33780.1	9,8	-1.2	
4	2952.01	33865.4	10,9	-1.7	33862.0
3	2949.83	33890.4	9,7	0.3	
3	2942.42	33975.7	10,8	2.0	
3	2941.80	33982.9	6,1	-1.1	33982.9
2	2935.74	34053.0	11,9	-2.2	
2	2923.62	34194.2	10,6	0.8	
3	2920.01	34240.2	12,9	1.5	
3	2913.44	34313.7	7,0	0.0	
3	2901.61	34453.6	12,7	0.8	34451.3

Contd...

TABLE XVIII (Contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Wave number reported by Rao et al.
3	2896.59	34513.2	8,0	-1.6	34512.1
3	2890.37	34587.5	9,1	-0.2	
3	2884.37	34659.5	10,2	1.0	
3	2879.68	34715.9	9,0	4.4	34716.8
3	2868.72	34848.5	11,2	1.9	
2	2864.64	34898.2	10,0	-5.7	
3	2863.69	34909.7	12,3	-1.2	
2	2848.78	35092.4	11,0	0.4	
2	2843.47	35153.0	12,1	-0.7	
1	2839.91	35202.0	15,5	-1.7	
2	2839.44	35207.9	13,2	-1.9	
1	2834.86	35264.7	14,3	-0.7	
2	2833.74	35278.7	12,0	3.0	
1	2830.47	35320.7	15,4	1.8	
2	2829.57	35330.7	13,1	-0.7	
1	2826.78	35365.6	18,8	7.8	

Contd...

TABLE XVIII (Contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Wave number reported by Rao et al.
1	2826.19	35372.9	16,5	2.7	
2	2825.51	35381.5	14,2	3.4	
0	2822.75	35416.0	17,6	3.3	
1	2821.09	35436.9	15,3	0.7	
2	2819.31	35455.2	13,0	0.0	
0	2818.51	35469.3	18,7	3.1	
1	2817.12	35486.8	16,4	1.7	
2	2815.82	35503.2	14,1	3.3	
0	2813.27	35535.4	17,5	3.1	
2	2811.42	35557.8	15,2	0.1	
1	2807.97	35602.4	16,3	-0.3	
2	2805.69	35627.4	14,0	-2.9	
2	2798.76	35719.5	16,2	-2.7	
2	2792.51	35799.5	15,0	-1.6	
2	2789.28	35841.0	16,1	-2.8	

TABLE XIX

ADDITIONAL BANDS OF D-SYSTEM OF HgI MOLECULE

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Wave number reported by Rao et al.
0	2853.11	35036.2	1,13	1,0	
0	2845.30	35135.4	1,12	1.0	
1	2837.31	35234.3	1,11	0.7	
0	2833.18	35285.7	3,14	-1.2	
1	2831.49	35306.7	2,12	-1.0	
1	2829.18	35335.6	1,10	-1.4	
1	2825.76	35378.3	3,13	-3.5	
2	2823.27	35409.5	2,11	2.5	
2	2820.84	35440.0	1,9	1.2	
3	2817.65	35480.1	0,7	3.1	
2	2812.82	35541.0	1,8	3.7	
2	2803.93	35653.8	1,7	1.0	
1	2800.49	35697.5	6,15	3.6	35698.2
3	2785.47	35890.0	3,8	0.7	
2	2768.08	36115.5	5,9	-3.3	
2	2730.68	36610.1	6,6	2.6	36613.0
3	2722.13	36725.0	6,5	4.9	36727.8
3	2717.48	36787.9	5,3	0.5	36795.8
2	2710.48	36882.9	7,5	0.9	36884.3
2	2692.93	37123.3	12,10	5.8	37126.2
2	2679.76	37305.6	16,14	2.1	

in column 5. The wave numbers of the unanalysed bands reported by Rao et al. (1944) are included in the last column. The bands analysed by them are marked on the plates with full lines and those analysed in the present work are marked with dotted lines.

HgI BANDS IN THE REGION 2650-2540 A°:

The bands of HgI molecule in the region 2650-2537 A° recorded on a medium quartz spectrograph are shown in Plate 1(c). Vibrational analysis for the bands in the region 2650-2550 A° was reported by Sastry (1942). However, the lower state frequency suggested by him was not in harmony with the ground state frequency of the mercury iodide molecule. Krishnamurthy (1960) reinvestigated this group of bands. Taking the (0,0) bands of the two subsystems at 39354.4 cm^{-1} and 38494.5 cm^{-1}, all the bands in the region 2650-2540 A° were analysed and were attributed to an electronic transition $^2\Pi \rightarrow {}^2\Sigma$ with a doublet separation of 858.9 cm^{-1}. The analogous groups of bands of ZnI and CdI molecules occurring in the regions 2450-2250 A° and 2550-2350 A° respectively were analysed by Ramsastry (1948) and Ramsastry et al. (1946). They attributed an electronic transition $^2\Sigma \rightarrow {}^2\Sigma$ to the group of bands of CdI molecule. Both the groups were correlated with the $^1P-{}^1S$

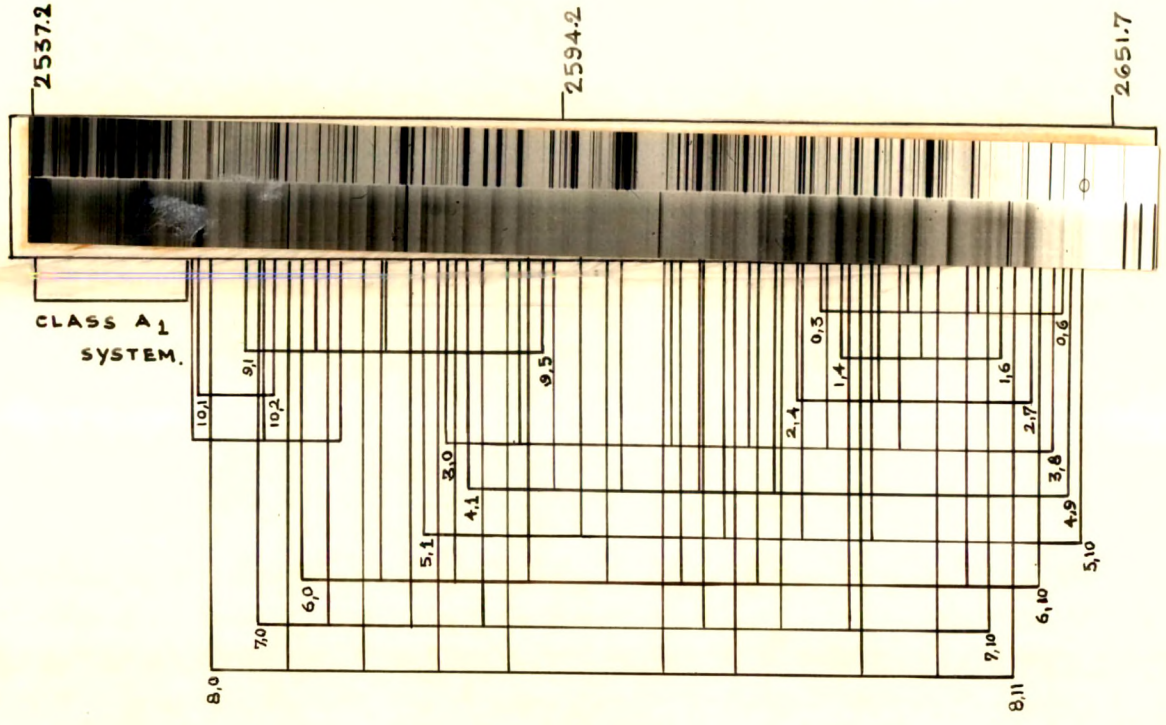

PLATE.8.

SPECTROGRAM OF HgI TAKEN AT
A DISPERSION OF 1.85 Å/M.M.
E-SYSTEM

resonance lines of the corresponding metal (Zn and Cd) atoms. In view of this the group of bands in the region 2650-2550 A° was photographed on a plane grating spectrograph at a dispersion of 1.85 A°/mm. Exposures of about two hours were found adequate to produce good spectrograms. The bands of HgI molecule extending from 2650-2537 A° are reproduced in Plate 8 as seen on negative. The bands are weak in intensity and are degraded to red. They show two intensity maxima with a fall of intensity around 2600 A°. The relative intensities, wavelengths, wave numbers in vacuum and the assignments of the bands are given in Table XX. The differences ($\nu_{obs.} - \nu_{cal.}$) are given in column 5 and the wave numbers reported by Krishnamurthy (1960) are shown in the last column.

The vibrational analysis for this group of bands is revised in the present work. The observed bands were considered to form a single main system. And the analysis showed that the lower state frequency for this group of bands was nearly equal to the ground state vibrational frequency of the HgI molecule. The vibrational quantum equation derived from the present analysis accounts all the observed bands and is given below:

TABLE XX

BAND HEAD DATA ON HgI MOLECULE (E-SYSTEM)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Wave number reported by Krishnamurthy
2	2651.40	37704.7	3,9	3.7	37708.2
2	2649.72	37728.6	2,8	6.6	37728.9
3	2648.50	37746.0	5,10	5.0	37746.0
4	2647.28	37764.1	4,9	-3.1	37766.0
5	2645.85	37783.9	0,6	-1.9	
2	2645.45	37789.5	3,8	-7.5	37791.7
2	2644.03	37809.8	6,10	-0.2	37810.2
3	2643.14	37822.5	2,7	-8.5	37823.1
7	2641.53	37845.6	8,11	-4.4	37844.6
3	2640.67	37858.0	1,6	-6.0	37858.9
3	2638.64	37887.0	7,10	3.0	37887.6
5	2637.90	37897.7	0,5	-3.3	
4	2637.40	37904.8	3,7	-4.2	37903.4
3	2636.54	37917.2	6,9	0.8	37922.1
3	2634.80	37942.2	2,6	-1.8	
8	2633.41	37962.3	8,10	7.3	37963.9
4	2631.97	37983.0	1,5	3.0	
4	2629.67	38016.2	0,4	-1.2	38015,0
5	2629.26	38022.2	3,6	1.2	

Contd....

TABLE XX (Contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Wave number reported by Krishnamurthy
4	2627.21	38052.0	2,5	-6.0	
3	2626.95	38055.6	5,7	-4.4	
4	2626.62	38060.4	8,9	-1.6	38062.1
6	2623.81	38101.2	7,8	3.2	38082.4 38101.3
3	2621.68	38132.0	3,5	-3.0	38131.1
8	2620.98	38142.3	0,3	-2.7	
8	2619.08	38170.0	5,6	2.0	
6	2618.60	38177.0	2,4	3.0	38177.0
8	2616.87	38202.2	7,7	-3.2	38203.2
8	2616.12	38213.0	4,5	2.0	
6	2614.29	38241.4	6,6	-4.6	38228.1
7	2613.39	38253.0	3,4	2.0	38252.9
3	2611.93	38274.5	8,7	-4.5	38274.9
5	2610.78	38291.3	5,5	5.3	38291.0
4	2609.57	38309.0	10,8	-4.0	38309.3
5	2608.45	38326.0	4,4	-1.0	38326.2
2	2607.10	38345.0	1,2	1.0	38345.4
3	2606.54	38353.6	6,5	6.0	
2	2605.42	38370.0	3,3	1.0	38371.8

Contd...

TABLE XX (Contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Wave number reported by Krishnamurthy
3	2604.22	38384.8	8,6	-6.8	38386.6
2	2603.76	38394.5	5,4	-6.5	
2	2600.25	38446.0	4,3	1.0	38446.4
3	2598.91	38472.0	6,4	-4.0	38470.8
2	2597.48	38487.3	3,2	-2.3	
3	2597.00	38495.0	8,5		38494.5
2	2595.06	38523.2	5,3	2.2	38522.7
3	2592.76	38557.4	4,2	-7.6	38561.3
3	2591.30	38579.1	9,5	1.1	38580.6
4	2590.18	38596.0	6,3	1.0	38598.5
3	2589.01	38613.3	3,1	2.3	38613.4
7	2587.92	38629.5	8,4	7.5	38629.8
9	2585.24	38669.5	7,3	0.5	38668.7
4	2583.77	38691.6	4,1	4.6	
7	2582.21	38714.9	6,2	-0.1	38713.6
3	2581.35	38727.8	3,0	-8.2	38726.3
8	2580.29	38743.6	8,3	2.6	38743.6
5	2579.14	38761.0	5,1	-7.0	38761.9
8	2577.80	38782.0	7,2	-7.0	38781.9
8	2575.07	38822.0	9,3	8.0	38822.6
3	2574.31	38833.7	6,1	-2.7	

Contd....

TABLE XX (Contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Wave number reported by Krishnamurthy
9	2572.56	38860.1	8,2	-0.9	38859.5
					38867.1
5	2570.20	38897.0	12,4	-8.0	38895.8
					38912.5
4	2567.62	38935.0	9,2	2.0	38935.2
7	2566.03	38959.0	6,0	-3.0	38959.5
5	2564.70	38979.0	8,1	-4.0	38979.2
5	2563.08	39003.9	10,2	-0.1	39006.6
3	2562.06	39019.4	12,3	-4.6	39018.8
2	2561.10	39034.0	7,0	-2.0	39034.0
4	2560.08	39050.0	9,1	-5.0	
					39064.5
3	2558.60	39072.2	11,2	-1.8	39073.7
3	2556.40	39105.8	8,0	-2.2	39105.0
3	2555.33	39122.2	10,1	-3.8	
2	2554.09	39141.1	12,2	-3.0	39139.5
4	2551.13	39187.0	11,1	-5.0	39188.6
2	2548.60	39225.5	13,2	3.3	39228.5
2	2545.71	39270.0	12,1	6.0	39270.1
1	2540.60	39349.0	13,1	5.0	39354.4
0	2537.40	39398.6	12,0	-2.0	39398.6
1	2533.21	39463.8	13,0	-5.0	39457.7

$$\nu_{head} = 38533.95 + \left[79.96(v'+\tfrac{1}{2}) - 0.45(v'+\tfrac{1}{2})^2\right] - \left[126.16(v''+\tfrac{1}{2}) - 1.01(v''+\tfrac{1}{2})^2\right]$$

The wave numbers calculated from the above equation are in keeping with the observed ones. The arrangement of the bands in Deslandres table is shown in Table XXI. The relative intensities of the bands are given in parentheses. The distribution of intensity among the bands shows that the Condon parabola is very wide and its apex is formed by the bands having higher v',v" values. This group of bands due to HgI may be attributed to an electronic transition $^2\Sigma \longrightarrow {}^2\Sigma$ and the system may be designated as the E system. This system can be correlated with the E systems of ZnI and CdI. The shift of the system origin towards the red for the analogous systems of the related molecules is well known and such a trend has been observed here also.