PART II

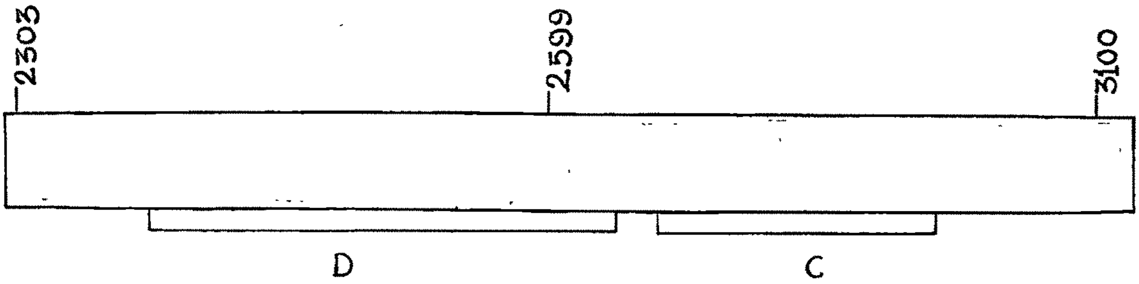
CHAPTER IV

SPECTRA OF MERCURY CHLORIDE MOLECULE

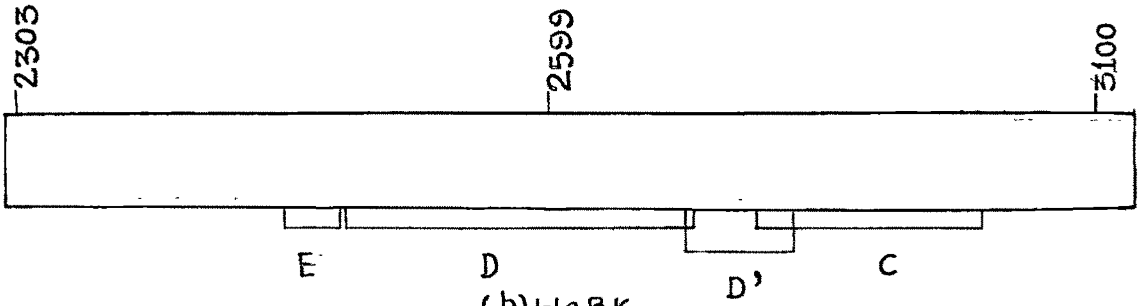
This chapter deals with the experimental observations and the analyses of two band systems of mercury chloride molecule in the ultraviolet region carried out during the present investigation.

A preliminary survey of the ultraviolet spectra of mercury chloride was made on a Hilger medium quartz spectrograph. The spectra were excited in a conventional type of pyrex discharge tube, by means of a high frequency oscillator, with external electrodes. Continuous evacuation of the discharge tube by a high vacuum pump was found necessary. The heat of the discharge was enough to vaporise the substance. However, external heating by a burner was necessary to maintain the characteristic bright green colour of the discharge. Under these conditions of excitation which could be maintained easily, the bands developed better without any impurity such as OH bands. The spectrum of HgCl molecule in the region 3100-2303 A° is reproduced in Plate 1(a). The C and D systems of HgCl molecule related to the $^3P-^1S$ resonance line of mercury atom are obtained. Concentrated attempts were made to obtain the HgCl bands in the region 2380-2100 A° analogous to the bands of HgI molecule in that region. Even heavily exposed plates did not show any evidence of such bands.

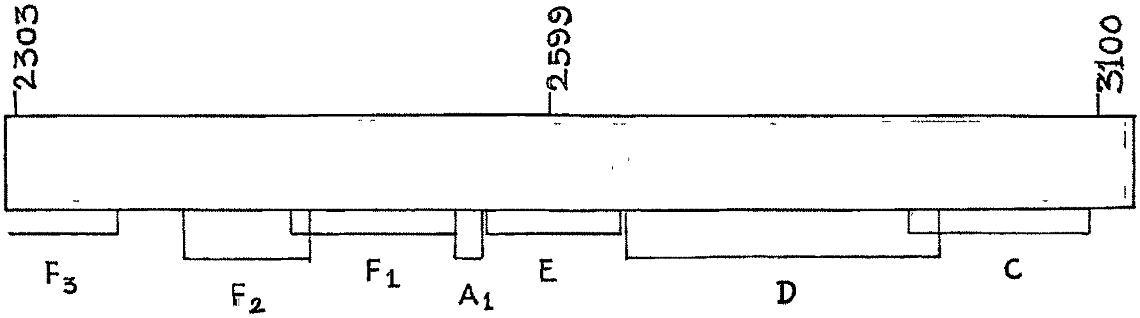
Having established the conditions of excitation the spectra of mercury chloride molecule were photographed on a two-metre plane grating spectrograph at a dispersion of 1.85 A°/mm. Ilford N40 and N50 plates were employed to record the spectra and exposures of about an hour were found adequate to obtain good spectrograms. Measurements of the bands were made against iron arc lines on a comparator. In what follows will now be given the results obtained and the analyses carried out on the grating spectra of HgCl molecule.



(a) HgCl



(b) HgBr



(c) HgI

PLATE. 1

BAND SPECTRA OF HgCl, HgBr AND HgI TAKEN WITH A M. Q. SPECTROGRAPH

(i) HgCl BANDS IN THE REGION 2920-2650 A°:

A group of HgCl bands in the region 2900-2700 A°, attributed earlier to one of the components of a $^2\Pi - ^2\Sigma$ electronic transition, has been obtained and a grating spectrogram of it is reproduced in Plate 2 as seen on the negative. The spectrogram reveals that the bands in the region 2800-2700 A° are very strong and most of them are degraded to violet. Some of the bands in the region 2850-2700 A° show their degradation towards the longer wavelengths. The bands near both the ends of the spectrogram are weak in intensity and are not well developed. The visually estimated intensities, wavelengths, wave numbers in vacuum and the assignments of the violet degraded bands in the region 2920-2659 A° are given in Table IV. The deviations of calculated wave numbers from the observed ones are shown in the fifth column. The wave numbers reported by Krishnamurthy (1958) are included in the last column for comparison.

In the present study it was found that the band at 36392.2 cm^{-1} which was selected by Krishnamurthy (1958) as the (0,0) band of the C system of HgCl molecule is actually degraded to red and hence cannot be included in the group of violet degraded bands. At the outset only

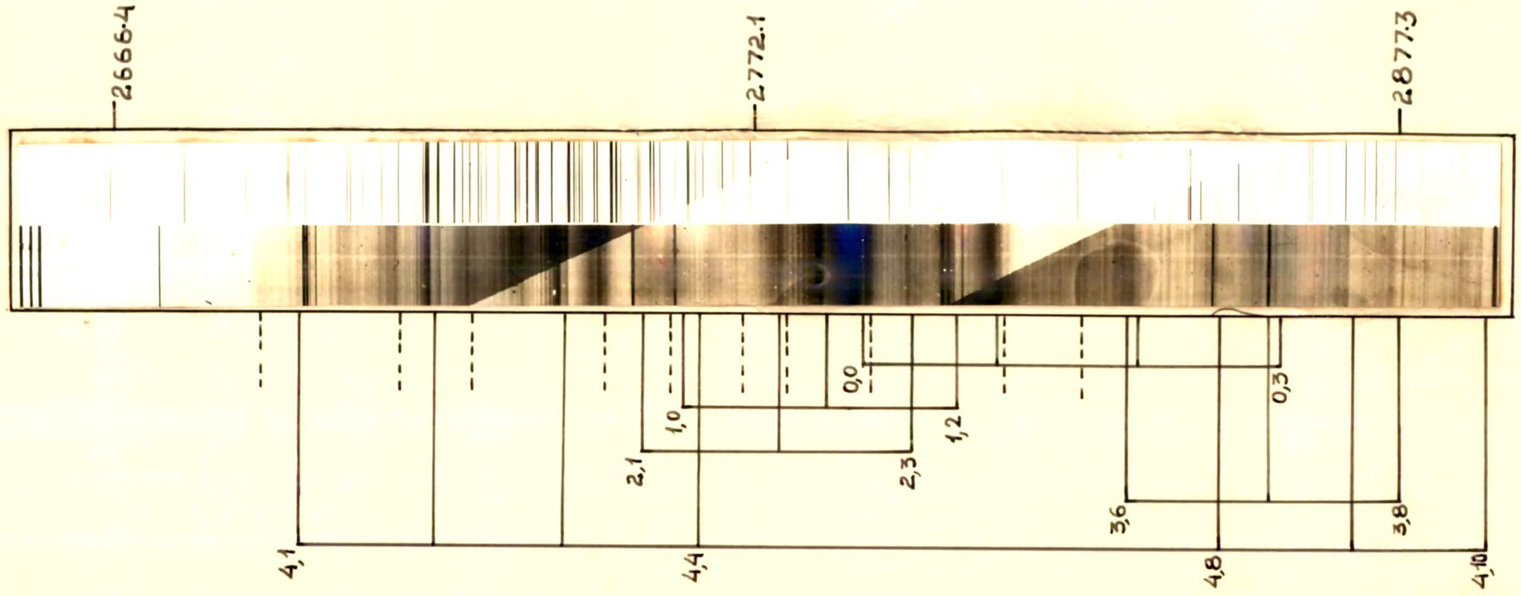


PLATE - 2

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

TABLE IV

BAND HEAD DATA ON HgCl MOLECULE (C-SYSTEM)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Value given by Krishnamurthy
1	2919.37	34244.0	1,7	0.0	
4	2913.59	34311.8	4,11	0.0	34319.8
3	2910.15	34352.6	2,8	0.0	
					34398.0
2	2905.10	34412.2	0,5	0.7	
					34432.3
3	2900.80	34463.2	3,9	1.1	
					34477.4
2	2896.29	34516.8	1,6	0.5	
5	2891.75	34571.0	4,10	-1.5	34574.6
3	2887.33	34623.9	2,7	-1.9	
2	2882.20	34685.5	0,4	-4.0	34684.4 34704.2
5	2878.62	34728.6	3,8	0.0	
2	2873.46	34791.0	1,5	-0.5	
6	2869.90	34834.2	4,9	-1.9	34836.2
2	2864.98	34894.0	2,6	-0.3	
2	2858.52	34972.9	0,3	2.3	34978.4
2	2856.42	34998.7	3,7	0.7	
0	2850.65	35069.5	1,4	0.0	
4	2847.99	35101.9	4,8	0.7	35097.8 35191.0
0	2835.84	35252.6	0,2(P_{12})	—	
1	2835.49	35256.9	0,2	2.4	

contd...

TABLE IV (Contd.)

Inten-sity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Value given by Krishnamurthy
5	2834.54	35268.8	3,6	-2.5	35261.8
1	2827.80	35352.8	1,3	2.2	35354.1
2	2825.94	35376.0	4,7	4.0	
0	2820.48	35444.5	2,4	0.0	35458.1
0	2817.89	35477.1	5,8	2.5	
6	2813.18	35536.5	0,1(P_{12})	—	
8	2812.79	35541.4	0,1	0,1	35540.9 35553.5
6	2805.33	35635.9	1,2	1.4	35635.9
6	2797.92	35730.2	2,3	1.6	35732.8
4	2796.57	35747.6	5,7	3.6	
7	2790.45	35826.0	0,0(P_{12})	—	35823.7
10	2790.00	35831.7	0,0	0.0	35833.0
7	2783.52	35915.1	1,1(P_{12})	—	35915.1
9	2783.10	35920.6	1,1	-0.7	36003.7
5	2776.07	36011.5	2,2	-1.0	
4	2768.99	36103.6	3,3	-1.0	
1	2761.79	36197.7	4,4	0.2	36198.3
1	2760.70	36212.0	1,0	1.0	

contd....

TABLE IV (contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v'')	$\nu_{obs} - \nu_{cal}$	Value given by Krishnamurthy
3	2754.39	36295.0	2,1	-4.6	36302.7
					36459.2
5	2740.72	36476.0	4,3(P_{12})	-	
					36476.2
10	2740.41	36480.1	4,3	1.5	
					36558.3
5	2734.06	36564.8	5,4	-4.7	
3	2725.66	36677.5	3,1	2.3	
					36738.5
3	2719.65	36758.5	4,2(P_{12})	-	
					36761.5
8	2719.29	36763.4	4,2	0.9	
					36837.3
2	2713.05	36848.0	5,3	-2.6	
1	2706.36	36939.0	6,4	-0.5	36934.4
1	2699.50	37032.9	7,5	3.4	37033.4
1	2698.40	37048.0	4,1	-1.3	
					37116.1
1	2691.97	37136.5	5,2	2.0	
					37203.3
0	2679.80	37305.1	7,4	-1.6	37303.1
1	2673.60	37391.6	8,5	-3.9	37388.2
1	2665.91	37499.6	7,2	-4.9	37493.3
1	2659.50	37589.9	7,3	1.3	37589.9

the violet degraded bands were considered. Attempts were made to find out the lower state interval of about 290 cm^{-1} among some of the intense bands. It was found possible to arrange almost all the violet degraded bands by selecting the (0,0) band at 35831.7 cm^{-1} and considering the well separated bands as forming the sequences. Unlike those reported by Krishnamurthy (1958) the regularities of intervals obtained in the present study are quite consistent. The irregularity of intervals observed in the Deslandres table reported by him may be due to the poor resolution used to record the spectrum. The bands at 36476.2 and 36459.2 cm^{-1} were considered by him as the Q and P heads of the (1,1) band. In the same way the bands at 36761.5 cm^{-1} and 36738.5 cm^{-1} were considered as the Q and P heads of the (1,0) band. In the present study, the spectrogram reveals that all these bands are accompanied by weaker heads. The separation between the intense band and the accompanying weaker head was found to be of the order of about that observed between the P_2 and Q_2 heads in the case of the D system of HgCl molecule. In the present analysis the bands at 36480.1 and 36463.2 cm^{-1} are analysed as the isotopic Q_{12} heads of the (4,3) band and the bands at 36763.4 and 36740.8 cm^{-1} are assigned as the isotopic Q_{12} heads of the (4,2) band. The weaker heads observed here are interpreted as the corresponding P_{12} heads. The vibrational scheme of the bands of C system of $HgCl^{35}$ molecule is shown in Table V. The relative intensities of the bands are given in parentheses. It is seen from the arrangement of the bands that the lower state frequency is nearly equal to the ground state vibrational frequency of the HgCl molecule. The following vibrational quantum equation representing the observed bands of the C system in a satisfactory manner is derived from the analysis:

$$\nu_{head} = 35786.19 + \left[382.00(v'+\tfrac{1}{2}) - 1.00(v'+\tfrac{1}{2})^2\right] - \left[292.60(v''+\tfrac{1}{2}) - 1.45(v''+\tfrac{1}{2})^2\right]$$

The wave numbers were calculated using the above expression and they were found to be in good agreement with the observed ones.

The vibrational isotope effect due to chlorine was observed for thirty two bands. The isotopic factors $(\rho-1)$ and (ρ^2-1) for the HgCl molecule are -0.023 and-0.0465 respectively. Theoretical isotope shifts were calculated using the formula

$$\nu^i - \nu = (\rho-1)\left[\omega_e'(v'+\tfrac{1}{2}) - \omega_e''(v''+\tfrac{1}{2})\right] - (\rho^2-1)\left[\omega_e'x_e'(v'+\tfrac{1}{2})^2 - \omega_e''x_e''(v''+\tfrac{1}{2})^2\right]$$

The observed and calculated isotope shifts of the bands along with their assignments are given in Table VI and they show a good agreement. This group of violet degraded bands in the region 2920-2659 A° has been designed as the C system of the HgCl molecule and as suggested by Howell (1943) the system is considered as one of the components of a $^2\pi - ^2\Sigma$ transition. With the (0,0) band of this system at 35831.7 cm^{-1}, the $^2\pi$ interval with the farther ultraviolet D system comes out to be 3895 cm^{-1} for the HgCl molecule which is inkeeping with the value observed for HgF (Howell, 1943) and HgI (Rao et al., 1944).

It is further observed (Plate 2) that some of the bands degraded to red are mixed up with the above discussed group of bands. These are seen to occur in the close neighbourhood of the strong violet degraded bands. They may be responsible for making the appearance of the bands diffuse and broad when observed under low dispersion. The relative intensities, wavelengths and wave numbers of these bands are given in Table VII. As the number of bands is less it is not possible to present a detailed vibrational analysis for them. However, two v"-progressions as shown below were picked out and an interval having the same order of magnitude of lower state frequency ($\omega_e" = 292.5$ cm^{-1})

TABLE VI

VIBRATIONAL ISOTOPE SHIFT IN HgCl BANDS

Assignment (v',v")	$\Delta\nu = \nu^{35} - \nu^{37}$	
	Observed shift cm^{-1}	Calculated shift cm^{-1}
1,7	-33.8	-33.6
4,11	-30.8	-29.2
0,5	-29.9	-30.6
3,9	-26.7	-27.8
2,7	-26.8	-25.0
4,10	-24.1	-24.6
0,4	-27.3	-24.6
3,8	-17.9	-22.3
1,5	-21.3	-22.0
4,9	-19.2	-19.3
2,6	-19.5	-19.2
0,3	-17.1	-18.3
3,7	-15.3	-16.5
1,3	- 7.1	- 9.7
4,7	-10.0	- 8.1
2,4	-10.9	- 7.2
5,8	- 6.5	- 5.2
0,1	- 4.7	- 5.7

Contd....

TABLE VI (Contd.)

Assignment (v', v'')	$\Delta\nu = \nu^{35} - \nu^{37}$	
	observed shift cm^{-1}	Calculated shift cm^{-1}
2,3	- 2.6	- 1.6
1,1	3.6	3.1
2,2	6.3	5.1
3,3	8.6	7.2
4,4	9.0	8.8
3,2	12.7	13.5
4,3 (P_{12})	18.0	-
4,3	16.9	16.0
5,4	17.9	18.0
3,1	21.4	20.1
4,2 (P_{12})	23.2	-
4,2	22.8	22.0
5,3	22.0	24.2
5,2	29.9	30.6

TABLE VII

RED DEGRADED BANDS OF HgCl MOLECULE IN THE REGION 2825-2693 A°

Intensity	Wavelength λ A°	Wave number in vacuum ν cm^{-1}	Wave number reported by Krishnamurthy
4	2825.69	35379.5	
5	2813.58	35531.5	
7	2791.66	35816.0	
8	2790.62	35823.3	
4	2769.28	36099.8	36099.0
3	2768.64	36108.2	36114.3
5	2759.10	36233.0	
6	2747.36	36374.6	36378.0
7	2747.12	36392.2	36392.2
1	2727.25	36656.5	36658.2
3	2726.22	36670.0	
2	2713.38	36843.5	
2	2712.60	36854.1	
3	2693.06	37121.5	36116.1

was observed amongst them. The (0,0) band of this group of bands may be taken at 35823.8 cm^{-1}.

	292.3	
35823.8		35531.5
284.4		284.5
	292.2	
36108.2		35816.0
284.0		283.8
	292.4	
36392.2		36099.5
277.8		274.8
	295.4	
36670.0		36374.6
		281.9
		36656.5

(ii) HgCl BANDS IN THE REGION 2650-2380 A°:

The spectrum of HgCl molecule occurring in the region 2650-2380 A° was recorded at a dispersion of 1.85 A°/mm. The spectrogram revealed well developed bands which were resolved into Q_2 and P_2 heads. Isotope effect due to chlorine was nicely observed. A detailed vibrational analysis of this group of bands was carried out by Wieland (1929) and Cornell (1938). However, it was felt necessary to record the fine structure of some of the bands and to give their rotational analysis. The visually estimated intensities, wavelengths, wave numbers in vacuum and the assignments of the additional bands observed in the present investigation are displayed in Table VIII. The vibrational assignments of the bands were based on the constants suggested by Wieland (1929). The differences between the observed and calculated wave numbers are given in column 5.

Some of the spectrograms taken with an optimum slit width revealed for the first time the resolution of rotational structure of the bands of $\Delta v = -1$ and $\Delta v = -2$ sequences of the D system of the HgCl molecule. The (0,1), (0,2) and (1,3) bands, showing their rotational structure are reproduced in Plate 3. As the system has been ascribed to an electronic transition $^2\pi_{3/2} \longrightarrow {}^2\Sigma$ having a $^2\pi$ interval sufficiently large, the coupling constant A/B_v will be very large (as the value of rotational constant B_v will be comparatively smaller for such a heavy molecule). Hence it is reasonable to consider the upper $^2\pi$ state to be belonging to purely Hund's case (a). The head forming branches in a violet degraded band of a $^2\pi_{3/2}(a) \longrightarrow {}^2\Sigma$ transition are the P_2 and $(P_{21} + Q_2)$ as described by Herzberg (1950). The spectrogram reveals the presence of Q_2 and P_2 heads and the separation between them is of the order of 2 to 3 cm^{-1}. The Q_2 branches of the (0,1), (0,2) and (1,3) bands are resolved while the corresponding P_2 branch lines are not resolved. The measurements of the rotational lines

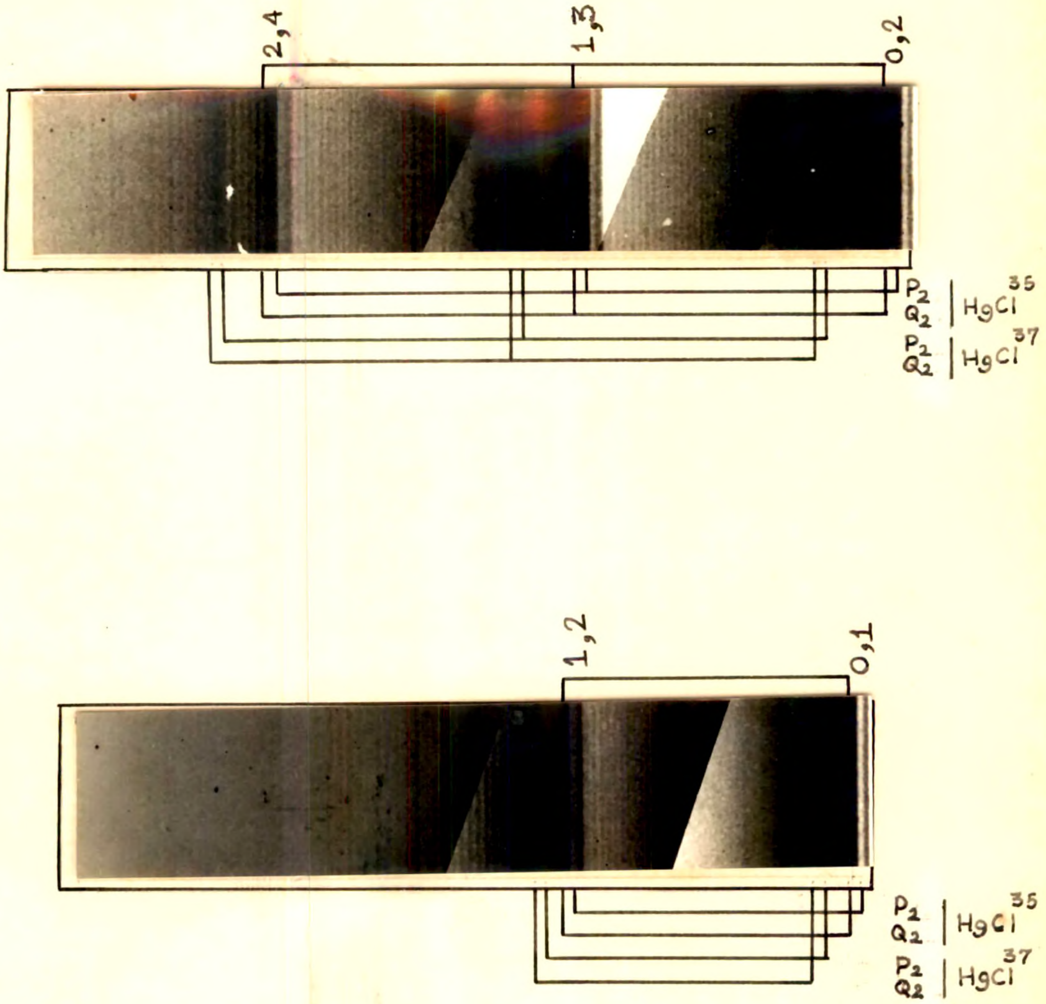


PLATE. 3

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

TABLE VIII

ADDITIONAL BANDS OF D SYSTEM OF HgCl MOLECULE

Intensity	Wavelength λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v', v'')	$\nu_{obs} - \nu_{cal}$
0	2636.90	37912.0	$5,13^{35}$	2.9
1	2620.36	38151.3	$1,7^{37}$	-0.9
2	2617.90	38187.2	$2,8^{35}$	0.5
2	2608.19	38329.3	$7,14^{37}$	-0.3
0	2606.47	38354.0	$4,10^{37}$	-2.7
0	2602.66	38410.7	$1,6^{37}$	-1.7
0	2592.16	38566.3	$7,13^{37}$	1.1
0	2587.31	38638.6	$8,14^{37}$	3.3
1	2569.47	38906.8	$5,9^{35}$	-1.8
5	2553.60	39148.7	$0,2^{35}(P_2)$	-
2	2539.06	39372.8	$4,6^{35}$	-3.2
5	2535.10	39434.3	$0,1^{35}(P_2)$	-
6	2531.23	39494.7	$1,2^{37}(P_2)$	-
4	2513.31	39776.2	$1,1^{35}$	0.3
1	2490.25	40144.5	$3,2^{37}$	-1.3

Contd....

TABLE VIII (contd.)

Intensity	Wavelength λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$
1	2487.27	40192.4	4,3^{37}	2.5
1	2486.70	40201.8	4,3^{35}	1.1
2	2465.57	40546.9	6,4^{37}	-0.5
2	2463.16	40586.0	7,5^{37}	-1.1
2	2461.70	40610.0	7,5^{35}	3.3
1	2460.54	40629.2	8,6^{37}	1.9
1	2459.41	40647.8	8,6^{35}	0.1
0	2438.10	41003.1	11,8^{37}	1.6
1	2404.58	41574.6	13,8^{37}	-3.9
1	2402.70	41607.2	14,9^{37}	0.8
2	2401.13	41634.4	15.10^{37}	0.5
0	2391.44	41803.0	20,15^{35}	-3.4
0	2389.69	41833.6	13,7^{37}	-3.3
1	2388.05	41861.1	14,8^{37}	0.4
0	2377.62	42046.0	20,14^{35}	3.7

of these bands were carried out. The dispersion at which the spectrogram was recorded, was not enough to resolve adequately the rotational structure of the bands of such a heavy molecule. However, it was found possible to identify the heads and the branches and to carry out a preliminary rotational analysis.

From the observed spacings of the rotational lines of Q_2 branches the following expressions representing the rotational lines of the three bands were derived:

for (0,1) band,

$$\nu = 39439.6 + 0.0086\ m^2$$

for (0,2) band,

$$\nu = 39151.9 + 0.010\ m^2$$

and for (1,3) band,

$$\nu = 35207.3 + 0.0075\ m^2$$

where m is an arbitrary number. The observed and calculated wave numbers along with the arbitrary numbering of rotational lines are given in Table IX for the three bands. With the help of the observed second differences of the wave numbers of the Q_2 branch lines, the rotational constants were determined by means of the following formula:

TABLE IX

ROTATIONAL LINES OF THE (0,1),(0,2) AND (1,3) BANDS OF D SYSTEM OF HgCl MOLECULE

Arbitrary numbering	Wave number in vacuum ν_{obs} cm^{-1}	Wave number calculated ν_{cal} cm^{-1}
	(0,1) BAND	
(P_2)head	39436.7	
(Q_2)head	39439.6	
69	39480.1	39480.5
70	39481.2	39481.7
71	39482.3	39482.9
72	39483.5	39484.1
73	39484.8	39485.4
74	39486.2	39486.6
75	39487.7	39487.9
76	-	39489.2
77	-	39490.5
78	-	39491.9
79	39493.0	39493.2
80	39494.1	39494.6
81	39495.7	39496.0
82	-	39497.4
83	39498.8	39498.8

contd...

TABLE IX (Contd.)

Arbitrary numbering	Wave number in vacuum ν_{obs} cm^{-1}	Wave number calculated ν_{cal} cm^{-1}
84	39500.1	39500.2
85	39501.3	39501.7
86	39503.2	39503.2
87	39504.6	39504.6
88	39506.0	39506.1
89	39507.6	39507.7
90	39509.1	39509.2
91	39510.7	39510.8
92	39512.4	39512.3
93	39513.8	39513.9
94	39515.4	39515.5
95	39517.1	39517.2
96	39518.7	39518.8
97	39520.2	39520.5
98	39522.5	39522.1
99	39524.1	39523.8
100	39526.0	39525.6

Contd...

TABLE IX (Contd.)

Arbitrary numbering	Wave number in vacuum ν_{obs} cm^{-1}	Wave number calculated ν_{cal} cm^{-1}
101	39527.6	39527.4
102	39529.3	39529.0
103	39531.0	39530.8
104	39532.8	39532.6
105	39534.3	39534.4
106	39536.0	39536.2
107	39538.2	39538.0
108	39539.9	39539.9
109	39542.1	39541.7
	(0,2) BAND	
P_2 head	39148.7	
Q_2 head	39151.0	
56	39183.0	39183.2
57	39183.9	39184.3
58	39184.9	39185.5
59	39186.1	39186.7
60	39187.2	39187.9

Contd...

TABLE IX (Contd.)

Arbitrary numbering	Wave number in vacuum ν_{obs} cm^{-1}	Wave number calculated ν_{cal} cm^{-1}
61	39189.5	39189.1
62	39190.6	39190.3
63	39191.9	39191.5
64	39193.0	39192.8
65	39194.5	39194.1
66	39195.8	39195.4
67	39197.0	39196.7
68	39198.2	39198.1
69	39199.5	39199.5
70	39201.0	39200.9
71	39202.3	39202.3
72	39203.6	39203.7
73	39205.0	39205.1
	(1,3) BAND	
P_2 head	39204.8	
Q_2 head	39207.3	
67	39240.4	39240.9

Contd...

TABLE IX (Contd.)

Arbitrary numbering	Wave number in vacuum ν_{obs} cm^{-1}	Wave number calculated ν_{cal} cm^{-1}
68	39241.3	39241.9
69	39242.6	39243.0
70	39244.1	39244.0
71	39245.0	39245.1
72	39246.2	39246.1
73	39247.4	39247.2
74	39248.6	39248.3
75	39249.0	39249.4
76	39249.6	39250.6
77	39251.6	39251.7
78	39252.7	39252.9
79	39254.1	39254.1
80	39255.7	39255.3
81	39256.6	39256.5
82	39257.9	39257.7
83	39259.5	39259.2
84	-	39260.2

Contd...

TABLE IX (Contd.)

Arbitrary numbering	Wave number in vacuum ν_{obs} cm^{-1}	Wave number calculated ν_{cal} cm^{-1}
85	39261.6	39261.5
86	-	39262.8
87	-	39264.2
88	39265.2	39265.3
89	39266.9	39266.7
90	39268.2	39268.0
91	39269.9	39269.4
92	39271.2	39270.7
93	39272.3	39272.1
94	39273.4	39273.5
95	39274.6	39274.9
96	39276.3	39276.4
97	39278.1	39277.8
98	39279.5	39279.3
99	39280.8	39280.8
100	39282.6	39282.3
101	39284.3	39283.8

$$P_h - Q_h = \frac{2B'B''}{B'-B''}$$

where it was assumed that the observed Q_2 heads are very near to their band origins. The rotational constants for the vibrational levels v' = 0 and 1 and v" = 1, 2 and 3 of the D system of HgCl molecule were determined and are collected in Chapter VII.

It was intended to photograph the (0,1), (0,2) and (1,3) bands of D system of HgCl molecule at a higher dispersion in order to carry out the detailed rotational analysis. To sort out the spectra of different orders, filters were employed and in the region under consideration this was not found feasible. To overcome this difficulty pre-disperser has been procured recently and attempts are being done in this direction to carry out a detailed rotational analysis of the D system.