CHAPTER V

SPECTRA OF MERCURY BROMIDE MOLECULE

In this chapter observations and vibrational analyses of the ultraviolet band systems of mercury bromide molecule obtained during the present investigation are reported.

As in the previous case a medium quartz spectrograph was employed to make a preliminary survey on the band systems of mercury bromide molecule in the ultraviolet region. The spectra were excited in a conventional type of pyrex discharge tube. A high frequency oscillator delivering a power of 125 watts at a frequency of 15 Mc/sec. served for the excitation by using external electrodes.

The discharge tube was continuously evacuated by a high vacuum pump till the steady conditions of the discharge were attained. As in the case of mercury chloride molecule, the heat of the discharge was found sufficient to vaporise the substance. However, intermittent heating by a burner was necessary to maintain enough vapour pressure inside the discharge tube. The characteristic intense blue colour of the discharge was maintained easily for any length of time and the bands developed better under these conditions without any impurity such as the OH bands. The spectrogram of mercury bromide molecule in the region 3100-2303 A° is reproduced in Plate 1(b). The C and D systems of this molecule analogous to the C and D systems of the mercury chloride molecule were obtained. As suggested by Howell (1943) these bands are believed to be related to the $^3P - {}^1S$ resonance line of mercury at 2536.5 A°. In addition to them another group of bands designated as the E system occurring in the region 2470-2440 A° was also obtained for the molecule. The existence of groups of bands due to electronic states having more energy than the E state has been known for the spectra of mercury iodide molecule and hence concentrated attempts were made to obtain the spectrum of mercury bromide in the region 2440-2100 A°. But, even the over exposed plates did not reveal any such group of bands.

(i) HgBr BANDS IN THE REGION 2968-2766 A°:

A group of bands lying in the region 2968-2766 A° was recorded in the second order with double passage of a plane grating spectrograph at a dispersion of 1.85 A°/mm. Ilford N40 and N50 plates were used and exposures of about fifty minutes were found adequate to record the spectra with good contrast. The spectrogram showing the bands in the region 2936-2766 A° is reproduced in Plate 4. The bands are intense and clearly degraded to violet. The bands on the longer wavelengths are sharp but those on the shorter wavelengths are diffuse in appearance and a few of them show double heads. The visually estimated intensities, wavelengths, wave numbers in vacuum and the assignments of the bands in the region 2968-2766 A° are given in Table X. The differences between the observed and the calculated wave numbers are given in the fifth column. Wave numbers reported by Krishnamurthy (1958) are included in the last column for comparison.

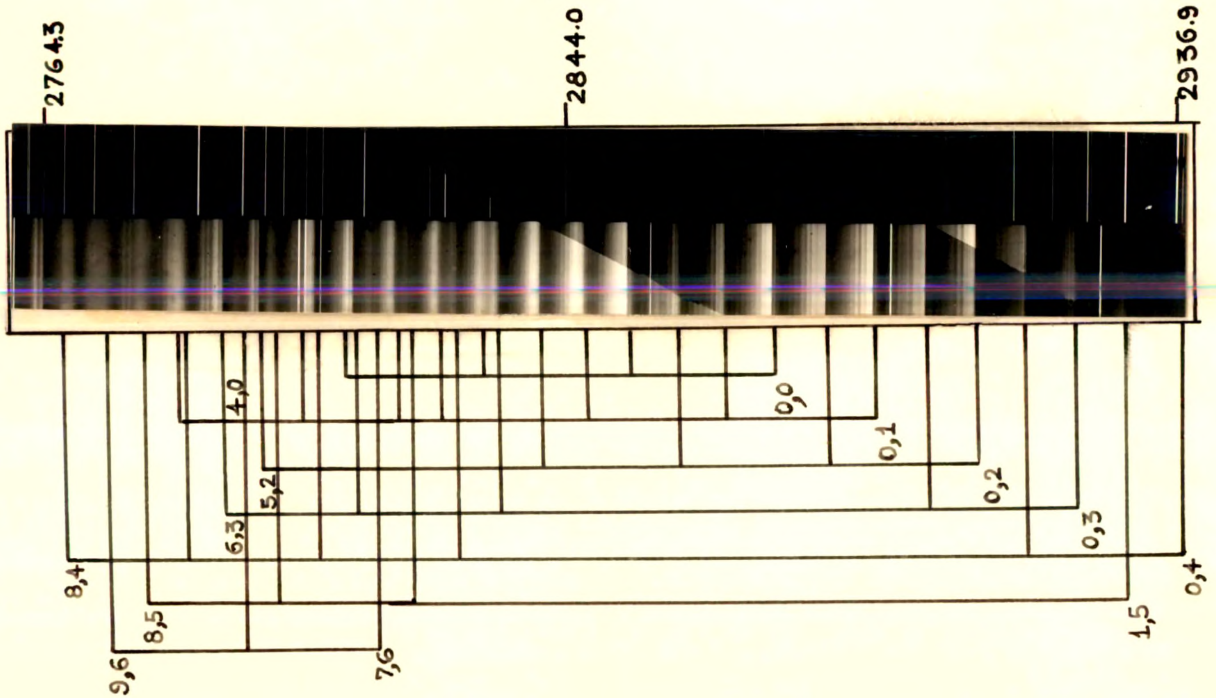

PLATE . 4 .

SPECTROGRAM OF HgBr TAKEN AT
A DISPERSION OF 1.85 Å / M. M.
C-SYSTEM.

TABLE X

BAND HEAD DATA ON HgBr 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	2967.91	33683.9	0,6	-0.2	
3	2952.68	33857.7	0,5	-2.1	
2	2943.55	33962.8	1,6	3.9	
6	2937.59	34031.6	$0,4^{79}$	–	
0	2935.71	34053.4	2,7	-3.2	
4	2928.37	34138.7	1,5	4.1	34126.7
8	2921.41	34220.0	0,3	2.8	34215.5
5	2913.53	34310.4	1,4	-1.9	
9	2906.14	34399.8	0,2	1.1	34398.0
6	2898.80	34487.0	$1,3^{79}$	–	34487.0
4	2890.91	34581.0	$0,1(P_{12})$	–	
9	2889.61	34584.8	0,1	1.8	34581.4
8	2883.26	34672.9	1,2	-0.6	34670.0
3	2876.01	34760.3	2,3	-1.6	
6	2875.87	34761.9	$0,0(P_{12})$	–	
10	2875.39	34767.6	0,0	0.0	34768.8
6	2868.00	34857.3	1,1	-0.5	34857.3

Contd...

TABLE X (contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v', v'')	$\nu_{obs} - \nu_{cal}$	Value given by Krishnamurthy
4	2861.01	34942.7	2,2	-2.3	34942.6
2	2853.42	35035.4	3,3	4.2	35038.1
9	2852.94	35041.3	1,0	-1.0	35040.6
8	2846.22	35124.3	2,1	5.0	35120.6
6	2839.28	35210.0	3,2	-2.8	35202.2
4	2833.10	35286.7	4,3	-8.6	35280.4
6	2831.06	35312.2	2,0	-1.7	35310.3
3	2826.44	35370.3	5,4	-5.8	35359.7
4	2824.72	35391.4	3,1	-5.4	35391.6
3	2819.53	35456.9	6,5	1.7	35444.3
5	2817.87	35477.4	4,2	0.6	35477.0
2	2813.51	35532.6	7,6	0.2	
6	2811.52	35557.5	5,3	-1.7	35557.8
6	2809.50	35583.2	3,0	1.6	
5	2805.76	35630.5	6,4	-2.4	35630.0
5	2803.10	35660.3	$4,1^{79}$	-	35708.9
4	2799.10	35715.3	$7,5^{79}$	-	

Contd....

TABLE X (contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Values given by Krishnamurthy
3	2797.28	35739.1	5,2	1.9	35738.2
2	2793.82	35782.0	8,6	-0.2	35774.1
3	2791.74	35809.6	6,3	-3.0	35809.9
4	2786.11	35881.8	7,4	-4.3	35879.3
3	2782.99	35922.0	5,1	0.4	
1	2780.00	35960.6	8,5	2.7	35955.5
2	2774.65	36030.0	9,6	1.8	36029.3
1	2766.83	36131.8	8,4	-3.8	

At the outset, the (0,0) band was selected at 34767.7 cm^{-1} as proposed by Krishnamurthy (1958) and the analysis was extended further. Unlike that reported by him the regularity of intervals is better in the present case when the isotopic shifts for the bands having higher v',v" values are taken into consideration. Further, there is no justification in taking the bands at 35738.2 cm^{-1} and 35557.8 cm^{-1} respectively as the (0,0) and (0,1) bands of the other subsystem proposed by him. This has happened probably because of the poor resolution at which the spectrum was recorded by him. In the present study the band at 35738.2 cm^{-1} shows two components at 35739.1 cm^{-1} and 35747.6 cm^{-1} having equal intensity and these are assigned as the isotopic heads of the (5,2) band. In the same way the band at 35557.8 cm^{-1} has been resolved into two equally intense components at 35557.5 cm^{-1} and 35565.8 cm^{-1} and these are assigned here as the (5,3) bands of HgBr^{81} and HgBr^{79} respectively. Further, the band at 35835.6 cm^{-1} has been resolved into four components. Among these, the two on the longer wavelength side are more intense than the other two and they may be assigned as either (6,3) or (4,0) band because for both of them the calculated shift is nearly the same. However, the regularity of interval is better when they are arranged in the vibrational scheme as (6,3) band instead of (4,0) band. The remaining two less intense components are different in appearance and hence are included in the other group of bands of this molecule lying in the region 2789-2699 A°. The vibrational scheme for the bands due to $HgBr^{81}$ is shown in Table XI. The relative intensities of the bands are given in parentheses. The intensity distribution in this group of bands follows a wide Condon parabola. In the present analysis it is observed that the lower state vibrational frequency is nearly equal to the ground state vibrational frequency of the HgBr molecule. The following vibrational quantum equation derived from the analysis satisfactorily accounts all the observed bands:

$$\nu_{head} = 34772.04 + \left[278.64(v'+\tfrac{1}{2}) - 1.82(v'+\tfrac{1}{2})^2\right] - \left[187.29(v''+\tfrac{1}{2}) - 0.96(v''+\tfrac{1}{2})^2\right]$$

The wave numbers were calculated using the above equation and as seen from the Table X, they show good agreement between the observed and calculated wave numbers.

Since bromine has two isotopes Br^{79} and Br^{81} having an abundance ratio 50.57:49.43, one may expect the intensities of the corresponding heads to be nearly the same. The isotope shifts for some of the bands were observed.

TABLE XI

DESLANDRES TABLE FOR C-SYSTEM OF HgBr MOLECULE

v' \ v''	0		1		2		3		4		5		6	7
	*34761.9(6)		*34581.0(4)											
0	34767.6(10)	182.8	34584.8(9)	185.0	34399.8(9)	179.8	34220.0(8)							
	273.7		272.5		273.1									
1	35041.3(9)	184.0	34857.3(6)	184.4	34672.9(8)				34310.4(5)	171.7	34138.7(4)	175.9	33962.8(2)	
	270.9		267.0		269.8									
2	35312.2(6)	187.9	35124.3(8)	181.6	34942.7(4)	181.8	34760.3(3)							34053.4(0)
	271.0		267.1		267.3		275.1							
3	35583.2(6)	191.8	35391.4(4)	181.4	35210.0(6)	174.6	35035.4(2)							
					267.4		251.3							

The isotopic factors $(\varrho-1)$ and (ϱ^2-1) for the HgBr molecule are -0.0089 and -0.0177 respectively. Theoretical isotope shifts were calculated using the standard formula mentioned in Chapter IV. Table XII shows the agreement between the observed and calculated isotope shifts for twenty three bands of this group.

This system of HgBr molecule is considered as one of the components of a $^2\pi — ^2\Sigma$ electronic transition, the other component being in the farther ultraviolet region (2650-2470 A°). For some of the intense bands, weaker P_{12} heads were observed which supports the above consideration. With the (0,0) band of this system at 34767.7 cm^{-1}, the $^2\pi$ interval between the C and D systems of this molecule comes out to be 3852 cm^{-1} which is in good agreement with the value observed for HgCl molecule in the present investigation and also in good proximity with the theoretically predicted value.

(ii) HgBr BANDS IN THE REGION 2789-2694 A°:

This group of bands was photographed along with the above discussed group of bands at a dispersion of 1.85 A°/mm. The grating spectrogram showing the bands in the range 2789-2699 A° is reproduced in Plate 5. It reveals that most of the bands in this region are double

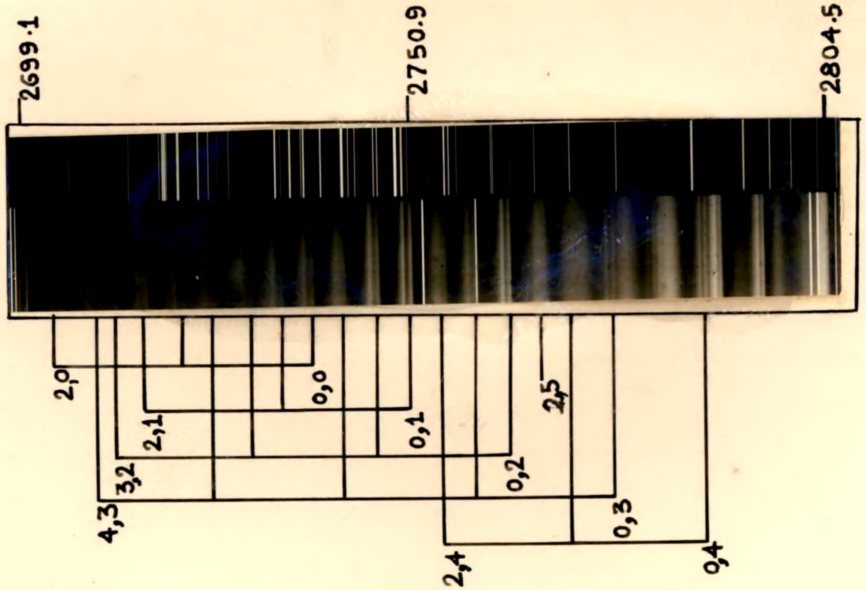

PLATE . 5

SPECTROGRAM OF HgBr TAKEN AT
A DISPERSION OF 1.85 Å/ M. M.
D'-SYSTEM

TABLE XII

VIBRATIONAL ISOTOPE SHIFT IN HgBr BANDS

Assignment (v',v")	$\Delta\nu = \nu^{79} - \nu^{81}$	
	observed shift cm^{-1}	Calculated shift cm^{-1}
0,6	- 8.3	- 9.6
0,5	-11.4	- 7.9
1,6	- 5.8	- 7.1
2,7	- 5.4	- 6.3
1,5	- 6.9	- 5.4
0,3	- 5.3	- 4.6
1,4	- 5.0	- 3.8
0,2	- 2.8	- 2.9
1,0	4.5	2.9
2,1	4.7	3.8
3,2	5.6	4.5
4,3	6.7	5.3
3,1	8.3	6.2
6,5	7.3	7.0
4,2	6.1	7.0
5,3	8.3	7.8
3,0	10.1	7.8
5,2	8.5	9.5
6,3	13.2	10.3
7,4	11.8	11.1
8,5	9.2	11.9
9,6	9.0	12.7
8,4	16.7	13.6

headed. An almost constant separation of about 15 cm^{-1} among their two components was observed. The relative intensities, wavelengths, wave numbers in vacuum and the vibrational assignments of the bands are given in Table XIII. Wave numbers reported by Krishnamurthy(1958) are included in the table for comparison. Taking the (0,0) band at 36506.6 cm^{-1} a tentative analysis for this group of bands was carried out. A vibrational scheme of these bands is given in Table XIV. The intensities estimated visually are given in parentheses. Vibrational analysis of this group of bands shows that the lower state frequency is nearly equal to the ground state frequency of the HgBr molecule. The following vibrational quantum equation represents the observed bands:

$$\nu_{head} = 36482.05 + \left[233.80(v'+\tfrac{1}{2}) - 1.68(v'+\tfrac{1}{2})^2\right] - \left[184.05\ (v''+\tfrac{1}{2}) - 1.15(v''+\tfrac{1}{2})^2\right]$$

This system of bands is designated as the D' system of HgBr molecule which may be attributed to a probable electronic transition $^2\Sigma \rightarrow {}^2\Sigma$.

(iii) HgBr BANDS IN THE REGION 2710-2470 A°:

The D system of mercury bromide molecule extending from 2710 A° to 2470 A° was recorded at a dispersion of

TABLE XIII

BAND HEAD DATA ON HgBr MOLECULE (D'-SYSTEM)

Intensity	Wavelength λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	Value given by Krishnamurthy
4	2789.33	35836.5	0,4	35835.6
4	2788.51	35850.9	0,4	
5	2777.24	35996.3	0,3	35990.4
5	2776.33	36008.0	0,3	36002.1
4	2772.39	36059.3	1,4	
4	2771.36	36072.7	1,4	
5	2768.95	36104.1	2,5	36106.1
5	2767.54	36122.5	2,5	36119.8
9	2763.76	36171.9	0,2	36166.1
9	2762.59	36187.0	0,2	36180.6
8	2759.70	36225.1	1,3	36223.8
7	2758.59	36239.7	1,3	36238.3
6	2755.70	36277.7	2,4	36277.7
6	2754.74	36290.3	2,4	36292.2
10	2751.34	36335.2	0,1	36335.7
9	2750.30	36348.9	0,1	36350.3
10	2747.04	36392.1	1,2	36391.3
9	2745.74	36409.3	1,2	36405.9

Contd...

TABLE XIII (Contd.)

Intensity	Wavelength λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	Value given by Krishnamurthy
10	2742.77	36448.6	2,3	36451.0
9	2741.60	36464.3	2,3	36465.6
8	2738.05	36506.6	0,0	36506.6
7	2737.39	36520.4	0,0	36520.4
7	2734.33	36561.2	1,1	36560.3
6	2733.27	36575.4	1,1	36575.0
4	2730.06	36618.4	2,2	36613.9
3	2728.81	36635.0	2,2	36628.6
3	2727.30	36655.5	3,3	
3	2726.36	36668.1	3,3	
4	2720.45	36747.8	1,0	
3	2719.44	36761.4	1,0	
2	2716.66	36799.0	2,1	
2	2715.53	36814.3	2,1	
3	2714.04	36834.5	3,2	
3	2712.44	36856.3	3,2	
2	2703.76	36974.6	2,0	
2	2702.42	36992.9	2,0	
2	2695.60	37086.5	5,3	
2	2694.30	37104.4	5,3	

TABLE XIV

DESLANDRES TABLE FOR D'-SYSTEM OF HgBr BANDS

v'' / v'	0		1		2		3		4		5
		171.4		164.1		175.6		159.9			
0	36506.6(8)		36335.2(10)		36171.9(9)		35996.3(5)		35836.5(4)		
		171.5		161.8		179.0		157.1			
	36520.4(7)		36348.7(9)		36187.0(9)		36008.0(5)		35850.9(4)		
	241.2		236.0		220.2		229.8		222.8		
	241.0		236.7		222.3		231.7		221.8		
		186.6		169.1		167.0		165.8			
1	36747.8(4)		36561.2(7)		36392.1(10)		36225.1(8)		36059.3(4)		
		186.0		166.1		169.6		165.0			
	36761.4(3)		36575.4(6)		36409.3(9)		36239.7(7)		36072.7(4)		
	226.8		227.8		226.3		223.5		218.4		
	231.5		228.9		222.7		224.6		217.6		
		175.6		180.6		169.8		170.9		173.6	
2	36974.6(2)		36799.0(2)		36618.4(4)		36448.6(10)		36277.7(6)		36104.1(5)
		178.6		179.3		170.7		174.0		167.8	
	36992.9(2)		36814.3(2)		36635.0(3)		36464.3(9)		36290.3(6)		36122.5(2)
					216.1		206.9				
					221.3		203.8				
						179.0					
3					36834.5(3)		36655.5(3)				
						188.2					
					36856.3(3)		36668.1(2)				

1.85 A°/mm. Ilford N40 and N50 plates were employed to record the spectra and exposures of about an hour were found enough to obtain good spectrograms. The grating spectrogram revealed well developed violet degraded bands. The isotope effects of bromine as well as mercury was observed. This band system was attributed to one of the components of a $^2\pi — ^2\Sigma$ electronic transition by Howell (1943). In the present study a few more bands were observed which could also be analysed in the vibrational scheme suggested by Wieland (1929). The data on these additional bands is displayed in Table XV. The theoretically calculated wave numbers and the observed ones are in close agreement as seen from the table.

(iv) HgBr BANDS IN THE REGION 2470-2440 A°:

A group of bands, designated as the E system of mercury bromide molecule was photographed on a Hilger medium quartz spectrograph and in the second order of a plane grating spectrograph at a dispersion of 3.69 A°/mm. The reproduction of this group of bands recorded on the prism spectrograph is given in Plate 1(b). The bands were very close and weak in intensity. While recording the grating spectrum filters were found necessary to be used to avoid the overlapping of the other order spectra.

TABLE XV

ADDITIONAL BANDS OF D-SYSTEM OF HgBr MOLECULE

Intensity	Wavelength λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$
1	2710.21	36894.2	$1,11^{79}$	5.8
1	2708.84	36905.4	$1,11^{81}$	3.3
1	2705.41	36950.8	$2,12^{79}$	-0.2
1	2704.31	36967.0	$2,12^{81}$	2.1
1	2697.89	37053.3	$1,10^{79}$	1.1
2	2696.97	37067.0	$1,10^{81}$	0.1
2	2692.84	37124.5	$2,11^{81}$	-2.3
2	2690.06	37162.9	$0,8^{79}$	0.0
2	2689.31	37175.2	$0,8^{81}$	-0.5
3	2685.95	37226.3	$1,9^{79}$	3.8
3	2684.48	37233.6	$1,9^{81}$	0.0
2	2681.30	37284.3	$2,10^{79}$	3.2
2	2680.45	37295.4	$2,10^{81}$	3.8
3	2677.74	37334.0	$0,7^{79}$	-2.0
3	2676.70	37348.4	$0,7^{81}$	2.0
3	2673.55	37392.4	$1,8^{79}$	-0.1
3	2672.47	37407.0	$1,8^{81}$	4.7
2	2669.42	37450.2	$2,9^{79}$	1.0
2	2668.69	37460.4	$2,9^{81}$	2.1

Since the available filters were having very low transmittance around 2400 A° and the bands were very weak in intensity it was found difficult to obtain the spectrum with good contrast. However, it was possible to carry out the measurements on them. The visual estimation of the intensities, wavelengths, wave numbers in vacuum and the assignments of the bands of E system are given in Table XVI. The values of ($\nu_{obs.} - \nu_{cal.}$) are given in the table. The wave numbers reported by Rao and Rao (1944) are included in the last column for comparison.

This group of bands was previously studied by Rao and Rao (1944). The (0,0) band was selected by them at 40711 cm^{-1} and the analysis was carried out by forming the close sequences of the bands. However, it was found that the vibrational quantum equation reported by them could not represent all the observed bands satisfactorily. For some of the bands the difference between the observed and calculated wave numbers was larger than the separation between the consecutive sequence members. In the present case, the (0,0) band was selected at 40626 cm^{-1} and the analysis was extended further by rearranging the bands into close sequences. The following

TABLE XVI

BAND HEAD DATA ON HgBr MOLECULE (E-SYSTEM)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v', v'')	$\nu_{obs} - \nu_{cal}$	Value given by Rao & Rao
0	2469.57	40480.7	12,12	2.9	40481
					40493
2	2468.43	40499.3	10,10	1.8	40501
2	2467.84	40509.0	9,9	0.9	40509
4	2467.20	40519.1	8,8	-0.1	40518
					40525
2	2466.40	40533.0	7,7	2.2	40533
2	2465.55	40546.6	6,6	3.7	
2	2464.80	40559.0	5,5	3.5	
3	2463.93	40579.9	3,3	2.3	
3	2462.55	40596.0	2,2	-0.3	
3	2461.67	40610.5	1,1	-0.4	
4	2460.79	40626.0	0,0	0.0	
1	2459.34	40648.4	11,10	-3.9	40646
1	2458.68	40660.6	10,9	-3.7	40663
3	2457.80	40675.0	9,8	-1.0	40675
					40687
2	2456.78	40691.4	8,7	1.5	40693
2	2456.06	40703.3	7,6	0.1	
2	2455.06	40719.9	6,5	2.2	40711
3	2454.37	40731.8	5,4	-0.1	

Contd....

TABLE XVI (Contd.)

Intensity	Wave length λ A°	Wave number in vacuum ν cm^{-1}	Assignment (v',v")	$\nu_{obs} - \nu_{cal}$	Value given by Rao & Rao
3	2453.65	40744.9	4,3	-2.0	
3	2452.41	40763.9	3,2	1.4	40764
3	2451.58	40777.7	2,1	-0.8	40784
3	2450.51	40795.5	1,0	-0.5	40799
3	2448.91	40822.1	11,9	3.0	40824
4	2448.27	40832.8	10,8	0.3	40835
3	2447.39	40847.5	9,7	0.0	40846
2	2446.47	40862.8	8,6	0.4	40862
1	2445.78	40874.4	7,5	5.5	40873
1	2444.83	40889.9	6,4	-3.8	
2	2443.46	40913.1	5,3	2.8	
1	2442.41	40930.8	4,2	3.6	
0	2441.57	40944.8	3,1	-0.2	
0	2440.49	40963.0	2,0	-0.8	
					41010

vibrational quantum equation satisfactorily represents all the observed bands of this system:

$$\nu_{\text{head}} = 40633.74 + \left[170.42(v'+\tfrac{1}{2}) - 0.71(v'+\tfrac{1}{2})^2\right] - \left[186.02(v''+\tfrac{1}{2}) - 0.96(v''+\tfrac{1}{2})^2\right]$$

The wave numbers were calculated using the above expression and they are in close agreement with the observed ones. The vibrational scheme of the E system of HgBr molecule is given in Table XVII. The relative intensities of the bands are given in parentheses. The intensity distribution among the bands shows that the Condon parabola is very narrow and is developed along the diagonal of the Deslandres table. As suggested by Rao and Rao (1944) the system may be assigned to an electronic transition $^2\Sigma \longrightarrow {}^2\Sigma$.

TABLE XVII

DESLANDRES TABLE FOR E-SYSTEM OF HgBr BANDS

v' \ v''	0		1		2		3		4		5		6
0	40626.0(4)												
	169.5												
1	40795.5(3)	185.0	40610.5(3)										
	167.5		167.2										
2	40963.0(0)	185.3	40777.7(3)	181.7	40596.0(3)								
			167.1		167.9								
3			40944.8(0)	180.9	40763.9(3)	184.0	40579.9(3)						
					166.9		165.0						
4					40930.8(1)	185.9	40744.9(3)						
							168.2						
5							40913.1(2)	181.3	40731.8(3)	172.8	40559.0(2)		
									158.1		160.9		
6									40889.9(1)	180.0	40719.9(2)	173.3	40546.6(2)