PART II

CHAPTER IV

VIBRATIONAL ANALYSES OF CALCIUM CHLORIDE, CALCIUM BROMIDE AND CALCIUM IODIDE MOLECULES

This chapter deals with the experimental observations and the study of vibrational structures of the band systems of CaCl, CaBr and CaI molecules in emission, carried out during present investigation.

A preliminery survey of the spectra of CaCl, CaBr and CaI molecules in the visible as well as in the ultra violet regions was made on an E_2-glass spectrograph and on a medium quartz spectrograph respectively. The spectra of all the three molecules were excited in a conventional type of quartz discharge tube with external electrodes by means of a high frequency oscillator. Continuous evacuation of the discharge tube by a high vacuum pump and strong external heating by a burner were found necessary to maintain the characteristic dark pink (redish) colour of the discharge. Under these conditions of excitation, the band systems for these molecules developed strong in intensity without any impurity bands. ? As the molecules under investigation are highly hygroscopic, in first few attempts impurity bands of CaH were developed. The occurrence of CaH bands was completely eliminated by using dehydrated substances. The substances were dehydrated by heating them in atmosphere. Throughout the course of present investigation dehydrated substances have been used.

Having established the conditions of excitation the spectra were photographed on a 2 meter plane grating spectrograph. Ilford N-40 and R-40 plates were employed to record the spectra in the ultra violet and visible regions respectively.. Measurements of the bands were made against iron arc lines or internal atomic lines. In what follows will now be given the details regarding the work carried out on the grating spectra of CaCl, CaBr and CaI molecules.

(1) CaCl BANDS

Bands in the region λλ6072-5810 A°:

A group of CaCl bands in the region λλ6072-5810 A° has been observed. The spectrum was photographed in the fourth order of a 2 meter plane grating spectrograph at a reciprocal dispersion of about 1.2 A°/mm. A spectrum with reasonable intensity and clarity could be recorded in about 50 to 60 minutes. The spectrum is reproduced in plates 1 and 2. Contrary to what is reported by earlier workers, it reveals the presence of four heads in each sub-group of bands. The two of the heads with approximately equal intensities and a separation of about 3.5 - 6.5 cm^{-1} wave numbers between them are identified as P_1 and P_2 heads. Visually estimated intensities, wavelengths, wave numbers in vacuum, vibrational assignments and differences between observed and calculated wave numbers ($\Delta\nu$) for P_1 heads are given in Table 7 and for P_2 heads they are given in Table 8. The isotopic shifts due to Chlorine-35 and Chlorine-37 were calculated using the usual formula

$$\begin{aligned}\Delta\nu &= (\rho-1)(\nu-\nu_e) \\ &= (\rho-1)\left\{\omega_e'(v'+\tfrac{1}{2}) - \omega_e''(v''+\tfrac{1}{2})\right\} \\ &\qquad - (\rho^2-1)\left\{\omega_e'x_e'(v'+\tfrac{1}{2}) - \omega_e''x_e''(v''+\tfrac{1}{2})^2\right\}\end{aligned}$$

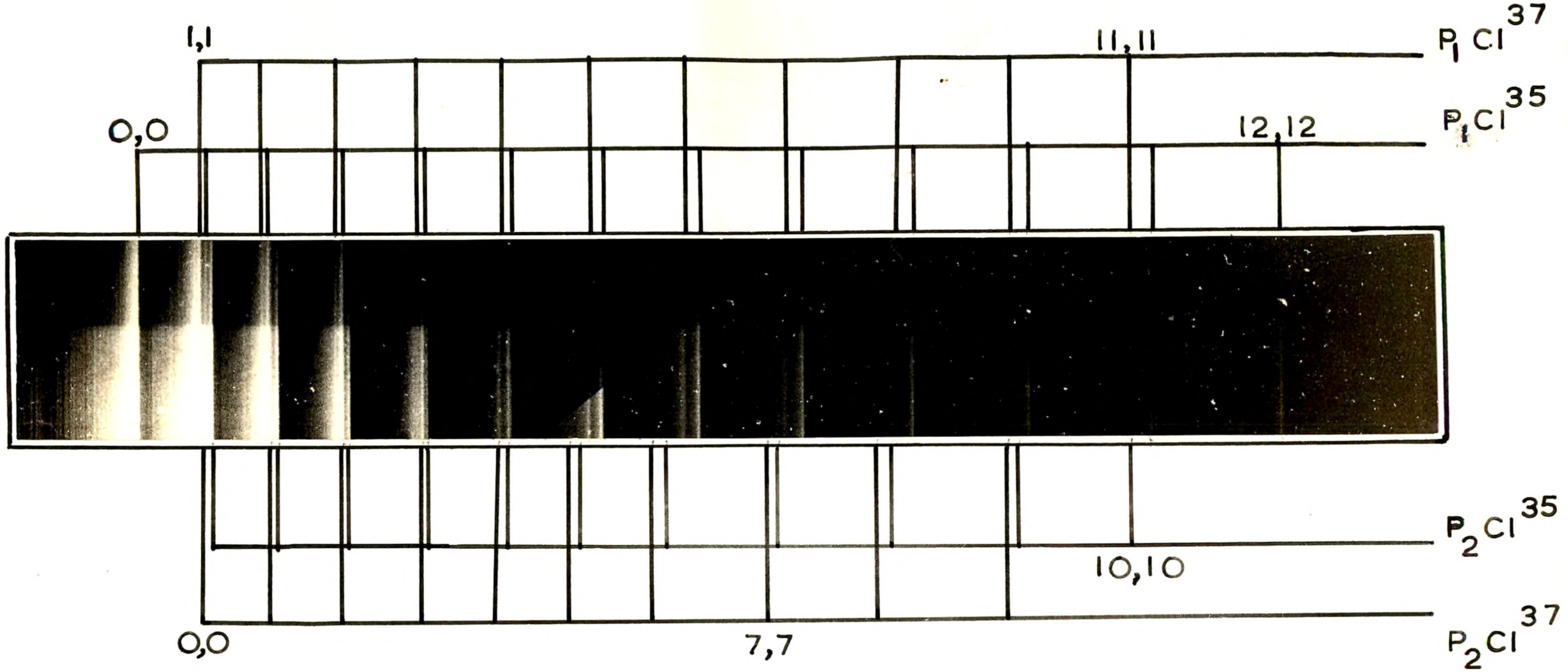

PLATE.I

$B\,^2\Sigma - X\,^2\Sigma$ SYSTEM OF CaCl MOLECULE AT A DISPERSION OF 1.2 Å/mm.

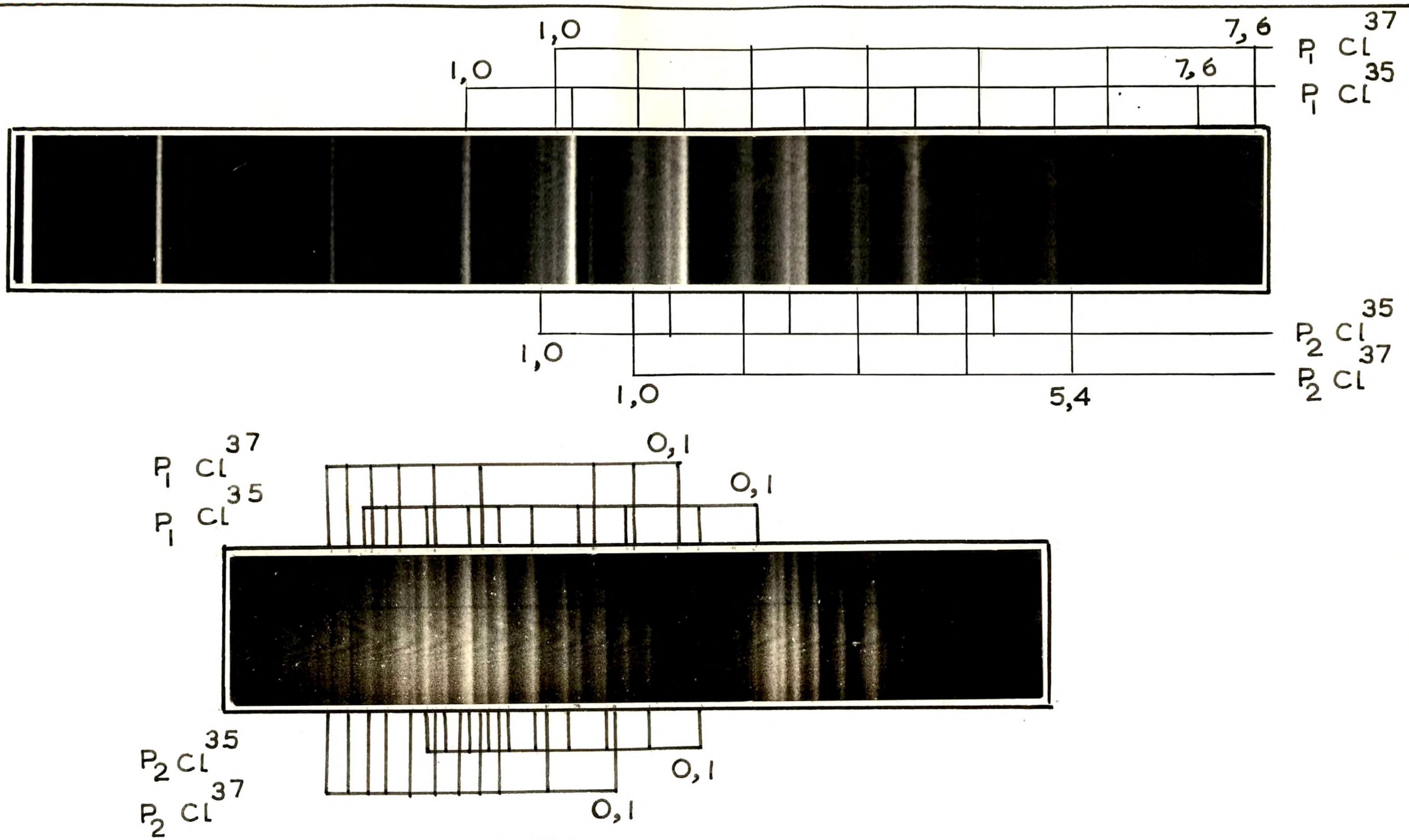

PLATE . 2 .

$B\ ^2\Sigma — X\ ^2\Sigma$ SYSTEM OF CaCl MOLECULE AT A DISPERSION OF 1.2 Å/mm.

TABLE 7

BAND HEAD DATA OF THE $B^2\Sigma^+ — X^2\Sigma$ SYSTEM OF CaCl MOLECULE

(P_1 heads)

Intensity	Wave length λ (A°)	Wave number in vacuum ν cm^{-1}	Assignment (v', v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
2	6072.39	16463.4	11,12 (35)	1.3
3	6071.28	16466.4	10,11 (35)	0.4
1	6070.88	16467.7	11,12 (37)	-
3	6069.82	16470.5	9,10 (35)	1.2
1	6069.40	16471.8	10,11 (37)	-
3	6068.89	16472.9	8,9 (35)	0.6
2	6068.26	16474.5	9,10 (37)	-
5	6068.03	16475.3	7,8 (35)	0.3
5	6067.37	16477.0	6,7 (35)	-0.5
4	6067.00	16478.1	8,9 (37)	-
4	6066.60	16479.1	5,6 (35)	-0.3
4	6066.27	16480.0	7,8 (37)	-
6	6065.87	16481.0	4,5 (35)	-0.1
4	6065.44	16482.4	3,4 (35)	-0.1
3	6065.01	16483.5	2,3 (35)	-0.1
3	6064.76	16483.8	1,2 (35)	-0.5
2	6064.57	16484.6	0,1 (35)	-0.2
1	6063.93	16486.5	4,5 (37)	-
1	6063.62	16487.3	3,4 (37)	-
1	6063.30	16488.1	2,3 (37)	-
1	5962.03	16768.3	14,14 (35)	-1.2
1	5961.28	16770.2	14,14 (37)	-
1	5959.13	16776.4	13,13 (35)	-0.8
1	5958.46	16778.1	13,13 (37)	-

contd...

TABLE 7 (contd.)

Intensity	Wave length λ (A°)	Wave number in vacuum ν cm^{-1}	Assignment (v', v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	5956.35	16784.0	12,12 (35)	-0.5
1	5955.80	16785.7	12,12 (37)	-
1	5953.81	16791.4	11,11 (35)	-0.2
1	5953.28	16792.6	11,11 (37)	-
3	5951.40	16798.1	10,10 (35)	-0.2
1	5951.25	16798.7	10,10 (37)	-
3	5949.10	16804.6	9,9 (35)	-0.1
3	5948.62	16806.0	9,9 (37)	-
4	5946.97	16810.5	8,8 (35)	-0.3
2	5946.61	16811.7	8,8 (37)	-
6	5944.93	16816.5	7,7 (35)	0.2
5	5944.62	16817.3	7,7 (37)	-
6	5943.04	16821.9	6,6 (35)	-0.1
5	5942.71	16822.7	6,6 (37)	-
6	5941.26	16826.7	5,5 (35)	-0.4
5	5941.00	16827.5	5,5 (37)	-
7	5939.39	16832.1	4,4 (35)	0.4
4	5939.27	16832.4	4,4 (37)	-
7	5937.80	16836.6	3,3 (35)	0.2
5	5937.70	16836.9	3,3 (37)	-
8	5936.32	16840.8	2,2 (35)	-0.3
5	5936.21	16841.1	2,2 (37)	-
9	5935.00	16844.5	1,1 (35)	0.1
7	5934.90	16844.8	1,1 (37)	-
10	5933.83	16847.9	0,0 (35)	0.0
1	5827.30	17155.9	7,6 (37)	-

contd...

TABLE 7 (contd.)

Intensity	Wave length λ (A°)	Wave number in vacuum ν cm^{-1}	Assignment (v', v")		$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	5826.10	17159.4	7,6	(35)	-1.8
2	5824.14	17165.3	6,5	(37)	-
1	5822.89	17168.8	6,5	(35)	-0.9
2	5821.18	17173.8	5,4	(37)	-
2	5819.81	17178.0	5,4	(35)	0.1
2	5818.48	17181.2	4,3	(37)	-
3	5817.31	17185.4	4,3	(35)	0.4
1	5816.11	17188.9	3,2	(37)	-
4	5814.63	17193.3	3,2	(35)	0.0
2	5813.73	17196.0	2,1	(37)	-
5	5812.30	17200.0	2,1	(35)	0.1
2	5811.77	17201.6	1,0	(37)	-
4	5809.80	17207.5	1,0	(35)	0.0

TABLE 8

BAND HEAD DATA OF THE $B^2\Sigma^+ — X^2\Sigma$ SYSTEM OF CaCl MOLECULE

(P_2 heads)

Intensity	Wave length λ (A°)	Wave number in vacuum ν cm^{-1}	Assignment (v', v'')	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	6071.55	16465.6	9,10 (35)	0.6
3	6070.30	16469.1	8,9 (35)	1.0
1	6069.90	16470.1	9,10 (37)	-
4	6069.40	16471.5	7,8 (35)	0.7
4	6068.64	16473.7	6,7 (35)	0.4
2	6068.26	16474.5	8,9 (37)	-
5	6068.03	16475.3	7,8 (35)	0.3
2	6067.48	16476.7	6,7 (37)	-
5	6067.37	16477.0	4,5 (35)	0.1
2	6066.80	16478.5	3,4 (35)	0.2
4	6066.60	16479.1	2,3 (35)	-0.3
4	6066.27	16480.0	1,2 (35)	-0.1
6	6065.87	16481.0	0,1 (35)	0.4
3	6065.62	16481.9	5,6 (37)	-
4	6065.44	16482.4	4,5 (37)	-
3	6065.01	16483.5	3,4 (37)	-
3	6064.76	16483.8	2,3 (37)	-
1	6064.40	16485.1	1,2 (37)	-
1	6063.93	16486.5	0,1 (37)	-
1	5956.00	16785.0	11,11 (35)	-2.4
1	5953.30	16792.8	10,10 (35)	-1.4
1	5951.09	16799.0	9,9 (35)	-1.4
1	5950.93	16799.5	9,9 (37)	-
3	5948.40	16806.0	8,8 (35)	-0.6

contd...

TABLE 8 (contd.)

Intensity	Wave length λ (A°)	Wave number in vacuum ν cm^{-1}	Assignment (v', v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	5948.25	16807.0	8,8 (37)	-
3	5946.40	16812.2	7,7 (35)	-0.4
2	5946.23	16812.8	7,7 (37)	-
4	5944.29	16818.2	6,6 (35)	0.5
3	5943.97	16819.0	6,6 (37)	-
5	5942.43	16823.6	5,5 (35)	0.5
4	5942.20	16824.0	5,5 (37)	-
5	5940,96	16827.5	4,4 (35)	-0.1
4	5940.90	16827.8	4,4 (37)	-
5	5939.52	16831.8	3,3 (35)	-0.6
4	5939.39	16832.1	3,3 (37)	-
6	5938.00	16836.0	2,2 (35)	-0.7
4	5937.70	16836.6	2,2 (37)	-
6	5936.41	16840.6	1,1 (35)	0.3
5	5936.32	16840.8	1,1 (37)	-
6	5935.32	16843.7	0,0 (35)	0.0
5	5935.10	16844.3	0,0 (37)	-
1	5823.47	17167.2	5,4 (37)	-
1	5821.63	17172.5	5,4 (35)	-1.3
1	5820.91	17174.7	4,3 (37)	-
2	5819.60	17178.6	4,3 (35)	-2.6
2	5818.48	17181.8	3,2 (37)	-
3	5816.99	17186.2	3,2 (35)	-2.9
2	5815.91	17189.5	2,1 (37)	-
3	5814.31	17194.2	2,1 (35)	-2.3
1	5813.50	17196.6	1,0 (37)	-
2	5811.42	17202.8	1,0 (35)	-0.5

The abundance ratio of Cl^{35} and Cl^{37} is roughly 3:1 and the calculated value of ρ is 0.014856. The observed and calculated isotopic shifts are given in Table 9.

In the present work, a fairly large number of bands have been observed in addition to those already reported by earlier workers. The group of bands at 5934 A° is seen to be very intense whereas the groups at 6072 A° and 5809 A° are relatively weak. The bands at 16847.9 cm^{-1} and 16844.3 cm^{-1}, were taken as the P_1 and P_2 heads of (0,0) band and a vibrational analysis was carried out in the usual way. The bands could be arranged to form three extensive sequences viz. (1,0), (0,0) and (0,1), having sequence degradation on the longer wavelength side. In Table 11(a,b,c & d) Deslandres tables for P_1 and P_2 heads are presented separately. The following vibrational quantum equation was obtained from these tables.

$$\nu_{head} = \begin{matrix} 16849.5(P_1) \\ \\ 16845.3(P_2) \end{matrix} + 363.0(v'+\tfrac{1}{2}) - 1.70(v'+\tfrac{1}{2})^2$$
$$- 366.2(v''+\tfrac{1}{2}) + 1.54(v''+\tfrac{1}{2})^2$$

TABLE 9

ISOTOPE SHIFTS (cm^{-1}) IN THE $B^2\Sigma$ — $X^2\Sigma$ SYSTEM OF CaCl MOLECULE

Assignment v',v"	Observed shift $\Delta\nu_{obs}=\nu^{35}-\nu^{37}$ cm^{-1}	Calculated shift $\Delta\nu_{cal}=\nu^{35}-\nu^{37}$ cm^{-1}
11,12 (P_1)	-4.3	-5.4
10,11 (P_1)	-5.4	-5.3
9,10 (P_1)	-4.0	-5.3
9,10 (P_2)	-5.1	-
8,9 (P_1)	-5.2	-5.3
8,9 (P_2)	-5.4	-
7,8 (P_1)	-4.7	-5.3
7,8 (P_2)	-5.2	-
4,5 (P_1)	-5.5	-5.2
4,5 (P_2)	-5.4	-
3,4 (P_1)	-4.9	-5.2
3,4 (P_2)	-5.0	-
2,3 (P_1)	-4.6	-5.2
2,3 (P_2)	-4.7	-
1,2 (P_2)	-5.1	-5.3
0,1 (P_2)	-5.5	-5.3
14,14 (P_1)	-1.9	-1.5
13,13 (P_1)	-1.7	-1.4
12,12 (P_1)	-1.7	-1.2
11,11 (P_1)	-1.2	-1.1
10,10 (P_1)	-0.6	-0.9
9,9 (P_1)	-1.4	-0.8
9,9 (P_2)	-0.5	-
8,8 (P_1)	-1.2	-0.7
8,8 (P_2)	-1.0	-
7,7 (P_1)	-0.8	-0.6

contd...

TABLE 9 (contd.)

Assignment v',v"		Observed shift $\Delta\nu_{obs} = \nu^{35} - \nu^{37}$ cm^{-1}	Calculated shift $\Delta\nu_{cal} = \nu^{35} - \nu^{37}$ cm^{-1}
7,7	(P_2)	-0.6	-
6,6	(P_1)	-0.8	-0.5
6,6	(P_2)	-0.8	-
5,5	(P_1)	-0.8	-0.4
5,5	(P_2)	-0.4	-
4,4	(P_1)	-0.3	-0.3
4,4	(P_2)	-0.3	-
3,3	(P_1)	-0.3	-0.2
3,3	(P_2)	-0.3	-
2,2	(P_1)	-0.3	-0.1
2,2	(P_2)	-0.6	-
1,1	(P_1)	-0.3	-0.08
1,1	(P_1)	-0.2	-
7,6	(P_1)	3.5	4.1
6,5	(P_1)	3.5	4.4
5,4	(P_1)	4.2	4.6
5,4	(P_2)	5.3	-
4,3	(P_1)	4.2	4.7
4,3	(P_2)	3.9	-
3,2	(P_1)	4.4	4.9
3,2	(P_2)	4.4	-
2,1	(P_1)	4.7	5.0
2,1	(P_2)	4.7	-
1,0	(P_1)	5.9	5.2
1,0	(P_2)	5.3	-

The lower state frequency of 366.2 cm^{-1} obtained from the present analysis is in agreement with the ground state frequency of CaCl molecule as reported by previous workers. Further, as the system has been observed in absorption also, it confirms that the lower state involved in this system is the ground state of CaCl molecule. The upper state shows a spin splitting of about 3.5 - 6.5 cm^{-1} wave numbers which is in accordance with the spin splitting observed in the B-systems of CaF, CaBr, CaI, BaF, SrF, SrCl, SrBr and SrI molecules. The observed spin splitting for different bands in the B system of CaCl is given in Table 10.

A comparision of the region of occurrence of this system with the $B^2\Sigma^+ — X^2\Sigma^+$ systems of similar molecules indicates that the system may be attributed to an electronic transition $B^2\Sigma^+ — X^2\Sigma^+$.

A rotational analysis of the (0,0) band of the B system of CaCl molecule is given in Chapter VI.

(2) CaBr BANDS

Bands in the region λλ 3050-3350 A°:

The band spectrum of CaBr molecule has been studied by several workers. Recently a new system of bands has been reported by Reddy and Rao (1968) in the region

TABLE 10

SPIN SPLITTING $\nu_{P_1} - \nu_{P_2}$ OBSERVED IN THE $B^2\Sigma$ — $X^2\Sigma$ SYSTEM OF CaCl MOLECULE

Assignment v',v"	$\nu_{P_1} - \nu_{P_2}$ for $CaCl^{35}$ cm^{-1}	$\nu_{P_1} - \nu_{P_2}$ for $CaCl^{37}$ cm^{-1}
9,10	4.9	3.8
8,9	3.8	3.6
7,8	3.8	3.3
6,7	3.3	-
5,6	5.8	-
4,5	4.0	4.1
3,4	3.9	3.8
2,3	4.4	4.3
1,2	3.8	-
0,1	3.6	-
11,11	6.4	-
10,10	5.3	-
9,9	5.6	5.5
8,8	3.5	4.7
7,7	4.3	4.5
6,6	3.7	3.7
5,5	3.1	3.5
4,4	4.3	4.9
3,3	4.8	4.8
2,2	4.8	4.5
1,1	3.9	4.0
0,0	3.6	-
5,4	6.5	6.6
4,3	6.8	6.5
3,2	7.1	7.1
2,1	6.5	6.5
1,0	4.7	4.2

TABLE 11(a)

DESLANDRES TABLE FOR $B^2\Sigma$ — $X^2\Sigma$ SYSTEM FOR P_1 HEADS OF $CaCl^{35}$

v" v'	0		1		2		3		4		5		6		7
		363.3													
0	16847.9		16484.6												
	359.6		359.9												
		363.0		360.7											
1	17207.5		16844.5		16483.8										
			356.2		357.0										
				359.9		357.3									
2			17200.7		16840.8		16483.5								
					352.5		353.1								
						356.7		354.2							
3					17193.3		16836.6		16482.4						
							348.8		349.7						
								353.3		351.1					
4							17185.4		16832.1		16481.0				
									345.9		345.7				
										351.3		347.6			
5									17178.0		16826.7		16479.1		
											342.1		342.8		
												346.9		344.9	
6											17168.8		16821.9		16477.0

contd...

TABLE 11(a) (contd.)

v' \ v"	6		7		8		9		10		11		12		13
	337.5		339.5												
		342.9		341.2											
7	17159.4		16816.5		16475.3										
					335.2										
						337.6									
8					16810.5		16472.9								
							331.7								
								334.1							
9							16804.6		16470.5						
									327.6						
										331.7					
10									16798.1		16466.4				
											325.0				
												328.0			
11											16791.4		16463.4		
													320.6		
12													16784.0		
13															16776.4

TABLE 11(b)

DESLANDRES TABLE FOR $B^2\Sigma — X^2\Sigma$ SYSTEM FOR P_2 HEADS OF $CaCl^{35}$

v'' v'	0		1		2		3		4		5		6		7
		363.3													
0	16844.3		16481.0												
	358.3		359.6												
		362.2		360.6											
1	17202.8		16840.6		16480.0										
			353.6		356.0										
				358.2		356.9									
2			17194.2		16836.0		16479.1								
					350.2		352.7								
						354.4		353.3							
3					17186.2		16831.8		16478.5						
							346.8		349.3						
								350.8		350.8					
4							17178.6		16827.8		16477.0				
									344.7		346.6				
										348.9		348.3			
5									17172.5		16823.6		16475.3		
													342.9		
														344.5	
6													16818.2		16473.7

contd...

TABLE 11(b) (contd.)

v' \ v"	6	7	8	9	10	11	12
		338.5					
			340.7				
7		16812.2	16471.5				
			334.5				
				336.9			
8			16806.0	16469.1			
				329.9			
					333.4		
9				16799.0	16465.6		
					327.2		
10					16792.8		
11						16785.0	

TABLE 11(c)

DESLANDRES TABLE FOR $B^2\Sigma$ — $X^2\Sigma$ SYSTEM FOR P_1 HEADS OF $CaCl^{37}$

v" v'	0		1		2		3		4		5		6		7
0															
		356.8													
1	17201.6		16844.8												
			351.2												
				354.9		353.0									
2			17296.0		16841.1		16488.1								
					347.8		348.8								
						352.0		349.6							
3					17188.9		16836.9		16487.3						
							344.3		345.1						
								348.8		345.9					
4							17181.2		16832.4		16486.5				
									341.4		341.0				
										346.3					
5									17173.8		16827.5				
											337.8				
												342.6			
6											17165.3		16822.7		

contd...

TABLE 11(c) (contd.)

v' \ v"	6		7		8		9		10		11		12		13
	333.2														
		338.6		337.3											
7	17155.9		16817.3		16480.0										
					331.7										
						333.6									
8					16811.7		16478.1								
							327.9								
								331.5							
9							16806.0		16474.5						
									324.2						
										326.9					
10									16798.7		16471.8				
											320.8				
												324.9			
11											16792.6		16467.7		
													318.0		
12													16785.7		
13															16778.1

TABLE 11(d)

DESLANDRES TABLE FOR $B^2\Sigma$ — $X^2\Sigma$ SYSTEM FOR P_2 HEADS OF $CaCl^{37}$

v" / v'	0		1		2		3		4		5		6		7
		357.2													
0	16843.7		16486.5												
	353.8		354.3												
		356.7		355.7											
1	17196.6		16840.8		16485.1										
			348.7		351.5										
				352.9		352.8									
2			17189.5		16836.6		16483.8								
					345.2		348.3								
						349.7		348.6							
3					17181.8		16832.1		16483.5						
							342.6		344.0						
								347.2		345.1					
4							17174.7		16827.5		16482.4				
									339.7		341.6				
										343.2		342.1			
5									17167.2		16824.0		16481.9		
													337.1		
6													16819.0		

contd...

TABLE 11(d) (contd.)

v'' v'	6	7		8		9		10	11	12
			336.1							
7		16812.8		16476.7						
				330.3	332.5					
8				16807.0		16474.5				
						325.0	328.8			
9						16799.5		16470.7		
10										

λλ3025-2900 A°. They have also reported some additional bands of the previously reported D- X system in the region λλ3300-3100 A°. Because of rather low dispersion employed by them, the vibrational constants for the D-system derived from the analysis give wide discrepancies in the calculated and observed wave numbers for a large number of band heads. The aim of the present study is to reinvestigate and to carry out a complete vibrational analysis of the D-X system using better dispersion and support it by vibrational isotopic effect which is measurable for most of the bands. The results obtained are presented in this section.

The spectrum of CaBr molecule was excited in a high frequency discharge and was photographed in the second and the third orders of a plane grating spectrograph at a dispersion of 3.5 A°/mm and 1.8 A°/mm respectively. Exposure time of about six hours was required to get a satisfactory spectrogram on Ilford R-40 plates. The reproductions of the spectrograms are given in Plates 3 and 4.

Sixty-three band heads have been measured out of which 28 bands are new. The bands as well as sequencies are degraded to shorter wavelength side. For most of the band heads isotopic separations have been observed and are compared with the theoretically calculated values. The

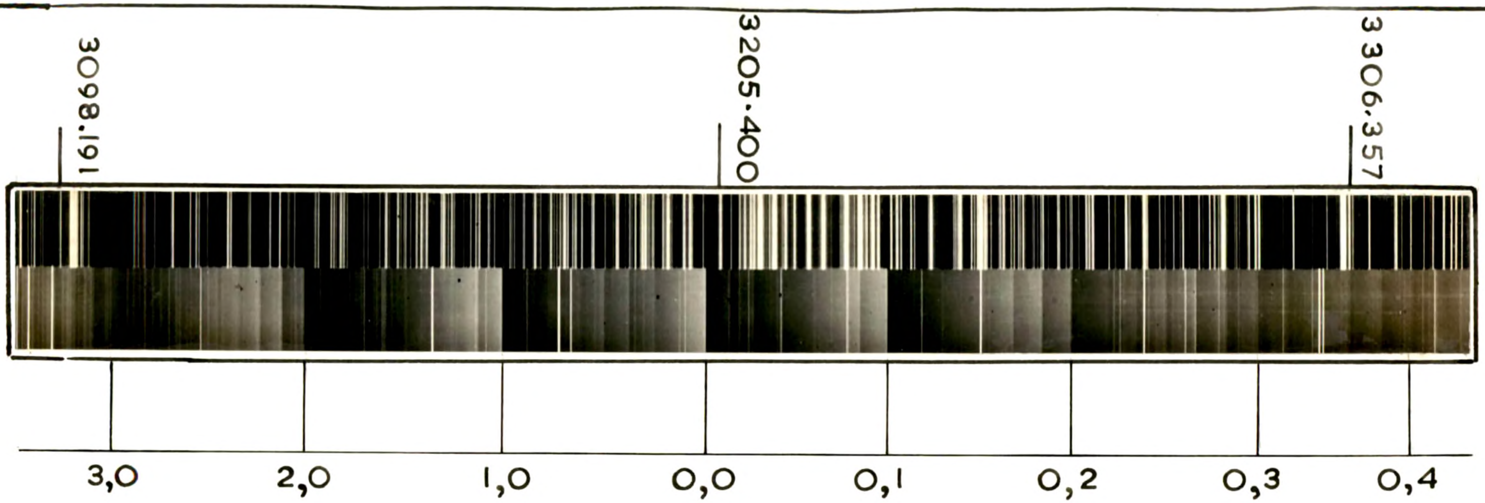

PLATE. 3.

$D^2\Sigma — X^2\Sigma$ SYSTEM OF CaBr MOLECULE AT A DISPERSION OF 3.5 Å/mm.

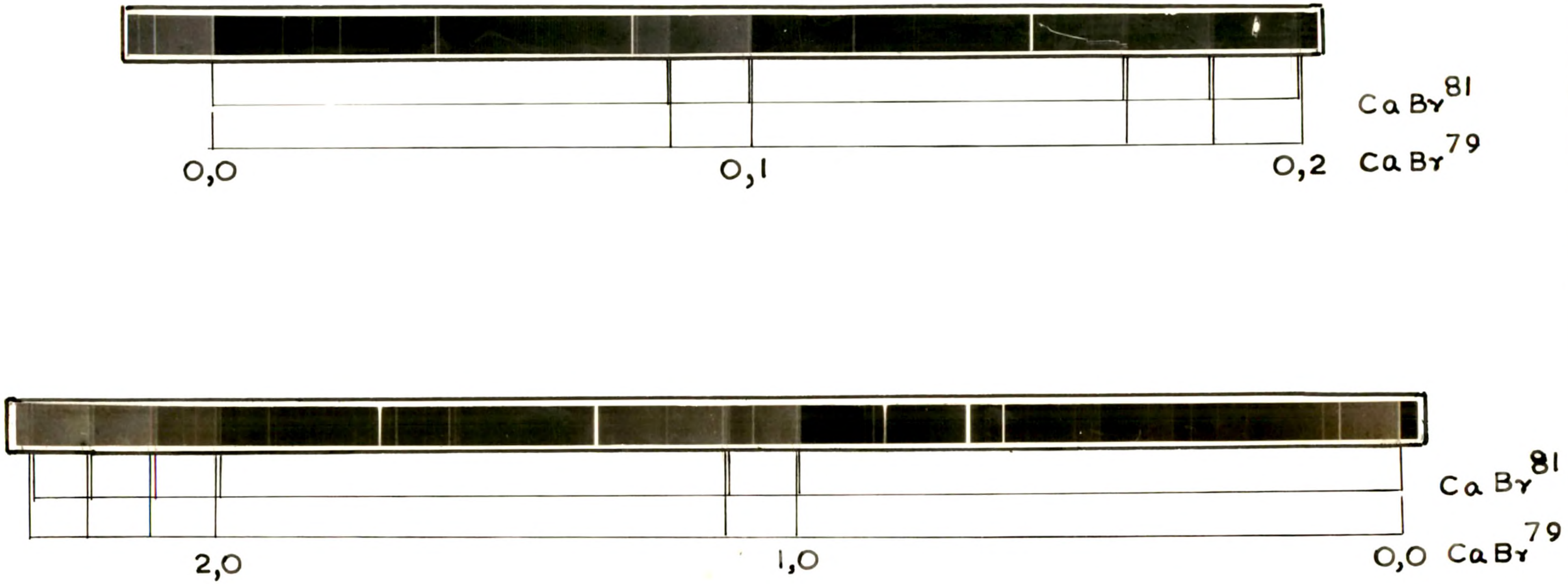

PLATE. 4.

$D\,^2\Sigma - X\,^2\Sigma$ SYSTEM OF CaBr MOLECULE REVEALING ISOTOPIC EFFECT (1.8 Å/mm.)

wave numbers of the band heads reported by the previous workers and observed during the present work along with their vibrational assignments are given in Table 12 along with calculated and observed isotopic shifts for each band. The close agreement between calculated and observed isotopic shifts confirms the correctness of the analysis.

The bands of the system have been arranged in the Deslandres Table which is presented in the Tables 13 and 14. The following band head equation was derived:

$$\nu_{head} = 30190.64 + 327.64(v'+\tfrac{1}{2}) - 1.245(v'+\tfrac{1}{2})^2$$
$$- 285.15(v''+\tfrac{1}{2}) + 0.865(v''+\tfrac{1}{2})^2$$

The lower state frequency of the system agrees with the previously reported ground state frequency of CaBr molecule. Moreover since the system has been observed in absorption, the lower state of this system is the ground state $X^2\Sigma^+$ of the CaBr molecule. The high dispersion pictures of a few bands reveal a simple rotational structure. Even though the dispersion is not enough to carry out a rotational analysis one can easily suggest that the bands arise due to a transition of the type $^2\Sigma^+ - X^2\Sigma^+$.

TABLE 12 (contd.)

Wavelength A° Present work	Wavenumber, cm^{-1}		Assignment	Isotope shift	
	Present work	Observed by earlier workers	v',v"	Obs.	Calc.
3228.00	30970.0	30970.0	1,2 (79)		
3227.91	30970.9	30970.9	1,2 (81)	0.9	0.9
3223.56	31012.7	-	2,3 (79)		
3223.45	31013.5	-	2,3 (81)	0.8	0.7
3202.99	31211.8	31211.7	0,0		
3194.59	31293.9	31293.3	2,2		
3190.55	31333.5	31333.1	3,3		
3186.13	31372.0	31371.4	4,4		
3182.67	31411.1	-	5,5		
3170.11	31535.6	31534.6	1,0 (81)		
3169.92	31537.4	31535.6	1,0 (79)	1.8	1.4
3166.21	31574.4	31573.5	2,1 (81)		
3166.06	31575.9	31575.5	2,1 (79)	1.5	1.6
3162.30	31613.4	-	3,2 (81)		
3162.15	31615.0	-	3,2 (79)	1.6	1.7
3158.62	31650.0	-	4,3 (81)		
3158.45	31652.7	-	4,3 (79)	2.7	1.9
3138.08	31857.4	31856.3	2,0 (81)		
3137.81	31860.2	-	2,0 (79)	2.8	2.7
3134.47	31894.1	31892.8	3,1 (81)		
3134.18	31897.1	31895.8	3,1 (79)	3.0	3.0
3130.93	31930.1	31929.4	4,2 (81)		
3130.62	31933.4	31932.5	4,2 (79)	3.3	3.0
3127.60	31964.2	31965.3	5,3 (81)		
3127.09	31969.4	-	5,3 (79)	5.2	5.4
3124.05	32000.1	32000.1	6,4 (81)		

contd...

TABLE 12 (contd.)

Wavelength A° Present work	Wavenumber, cm^{-1} Present work	Observed by earlier workers	Assignment v',v"	Isotope shift Obs.	Calc.
3123.79	32003.2	-	6,4 (79)	3.1	3.2
3106.82	32178.0	32175.9	3,0 (81)		
3106.40	32182.3	-	3,0 (79)	4.3	4.3
3103.70	32210.2	32210.2	4,1 (81)		
3103.30	32214.4	32214.4	4,1 (79)	4.2	4.2
3100.49	32243.7	32244.5	5,2 (81)		
3100.15	32247.3	32248.7	5,2 (79)	3.6	4.2
3097.23	32277.6	32277.8	6,3 (81)		
3096.80	32282.0	32282.0	6,3 (79)	4.4	4.4
3092.05	32314.5	32314.4	7,4 (79)		
3091.02	32342.3	32341.5	8,5 (81)		

TABLE 13

DESLANDRES TABLE FOR $D^2\Sigma$ — $X^2\Sigma$ SYSTEM FOR $CaBr^{79}$ MOLECULE

v' \ v"	0		1		2		3		4		5		6		7
0	31211.8	284.8	30927.0	282.8	30644.2	281.7	30362.5								
	325.6				325.8		326.1								
1	31537.4				30970.0	281.4	30688.6	279.9	30408.7	277.8	30130.9				
	322.8				323.9		324.1		324.0		323.3				
2	31860.2	284.3	31575.9	282.0	31293.9	281.2	31012.7	280.0	30732.7	278.5	30454.2	275.8	30178.4		
	317.8		321.2		321.1		320.8				320.8		321.1		
3	32178.0	280.9	31897.1	282.1	31615.0	281.5	31333.5				30775.0	275.5	30499.5	275.1	30224.4
			317.3		318.4		319.2								318.9
4			32214.4	281.0	31933.4	280.7	31652.7	280.7	31372.0						30543.3
			310.3		323.9		313.7								
5			32524.7	267.4	32257.3	290.9	31966.4				31411.1				
					300.7		315.6								
6					32558.0	276.0	32282.0	278.8	32003.2						
									311.2						
7									32314.4						

TABLE 14

DESLANDRES TABLE FOR $D^2\Sigma — X^2\Sigma$ SYSTEM FOR $CaBr^{81}$ MOLECULE

v' \ v"	0		1		2		3		4		5		6		7
		283.9		281.5		280.5									
0	31211.8		30927.9		30646.4		30365.9								
	323.8				324.5		325.1								
						279.9		279.1		277.7					
1	31535.6				30970.9		30691.0		30411.9		30134.2				
	321.8				323.0		322.5		322.8		323.6				
		283.0		280.5		280.4		278.8		276.9		275.3			
2	31857.4		31574.4		31293.9		31013.5		30734.7		30457.8		30182.5		
	320.6		321.7		319.5		320.0				319.1		319.8		
		281.9		282.7		279.9						274.6		274.0	
3	32178.0		31896.1		31613.4		31333.5				30776.9		30502.3		30228.3
			314.1		316.7		316.5								316.8
				280.1		280.1		278.0							
4			32210.2		31930.1		31650.0		31372.0						30545.1
			314.5		313.6		313.2								
				281.0		280.5									
5			32524.7		32243.7		31963.2				31411.1				
					314.3		314.4								
						280.4		277.5							
6					32558.0		32277.6		32000.1						
									310.1						
7									32310.2						

(3) CaI BANDS

Bands in the region λλ 4950-4600 A°:

The spectrum of CaI molecule has been studied by various workers and consists of four band systems viz. A-X, B-X, C-X and D-X. The ground state of the molecule is a $X^2\Sigma^+$ state. The A and C levels are $^2\Pi$ states analogous to the A and C systems of the remaining halides of molecules belonging to group II(a). In most of the monohalides of this group a few more systems in the visible region were observed by various workers and hence a similar system was expected in CaI also. The spectrum of CaI molecule in the visible region was reinvestigated and the results obtained are reported here.

The spectrum of CaI molecule was excited taking a pure sample of CaI_2 and keeping it in a conventional type of quartz discharge tube (diameter about 3 mm). External heating with a burner was required to maintain the bright red colour of the discharge. The spectrum was photographed on Illford R-40 plates in the first order of a two meter plane grating spectrograph at a reciprocal dispersion of about 7.3 A°/mm. An exposure of about 30 minutes was enough to get sufficiently good spectrogram. A reproduction of the bands is given in Plate 5. The measurements of the band heads were made on an Abbe Comparator using the standard atomic lines of iron arc spectrum.

In the spectrogram a number of violet degraded bands were observed. The most intense band at 21149.2 cm^{-1} was taken as (0,0) band. Bands corresponding to $\Delta v = 0$, ± 1, ± 2 and -3 were observed with strong Q and corresponding weak P heads. The bands were analysed to form two sub-systems arising from a transition of the type $^2\Delta - {}^2\Sigma$. For the $^2\Delta - {}^2\Pi_{3/2}$ component the higher members could not be clearly recognised due to the overlapping with the members of $^2\Delta - {}^2\Pi_{\frac{1}{2}}$ components. The difference between the system origins was found to be 57 (cm^{-1}) wave numbers which is quite close to the doublet splitting of A level (59 cm^{-1}) observed by earlier workers.

Band head data of bands of this new system of CaI molecule in the region λλ 4980-4580 A° is given in Table 15.

The bands of the system have been arranged in the Deslandres Table which is given in Tables 16 and 17. The identity of the emitter was established using the standard methods. The Q heads of the bands were satisfactorily fitted in the quantum equations given below.

$$\nu_{Q_2} = 21070.1 + 287.2(v'+\tfrac{1}{2}) - 0.80(v'+\tfrac{1}{2})^2 - 241.7(v''+\tfrac{1}{2}) + 0.50(v''+\tfrac{1}{2})^2$$

TABLE 15

BAND HEAD DATA OF THE NEW SYSTEM OF CaI MOLECULE

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v'')	= $\nu_{obs}-\nu_{cal}$ cm^{-1}
1	4951.9	20188.7	0,4 (Q_1)	-0.2
1	4940.6	20234.9	1,5 (Q_1)	1.5
1	4894.6	20425.0	0,3 (Q_1)	-2.2
1	4882.6	20475.2	1,4 (Q_1)	1.1
1	4871.0	20521.4	2,5 (Q_1)	1.0
2	4850.2	20612.0	0,2 (Q_2)	-0.2
2	4837.0	20668.2	0,2 (Q_1)	1.3
1	4826.6	20712.7	1,3 (Q_1)	-0.1
1	4816.6	20755.8	2,4 (Q_1)	-2.3
4	4794.3	20852.2	0,1 (Q_2)	0.1
4	4781.6	20907.7	0,1 (Q_1)	0.1
2	4771.2	20953.2	1,2 (Q_1)	0.7
1	4761.4	20996.4	2,3 (Q_1)	-0.4
10	4739.6	21092.8	0,0 (Q_2)	0.0
10	4727.0	21149.2	0,0 (Q_1)	0.0
2	4719.6	21182.2	2,2 (Q_2)	0.4
2	4717.1	21193.2	1,1 (Q_1)	0.0
1	4709.8	21226.4	3,3 (Q_2)	-0.7
1	4707.6	21236.5	2,2 (Q_1)	0.0
1	4698.0	21279.7	3,3 (Q_1)	0.5
8	4676.2	21378.8	1,0 (Q_2)	-0.4
8	4664.0	21434.8	1,0 (Q_1)	0.0
2	4655.3	21474.9	2,1 (Q_1)	-2.2
1	4645.8	21518.8	3,2 (Q_1)	-0.1
5	4614.8	21663.3	2,0 (Q_2)	0.9
5	4603.1	21718.3	2,0 (Q_1)	-0.5
1	4595.1	21756.2	3,1 (Q_1)	-3.4

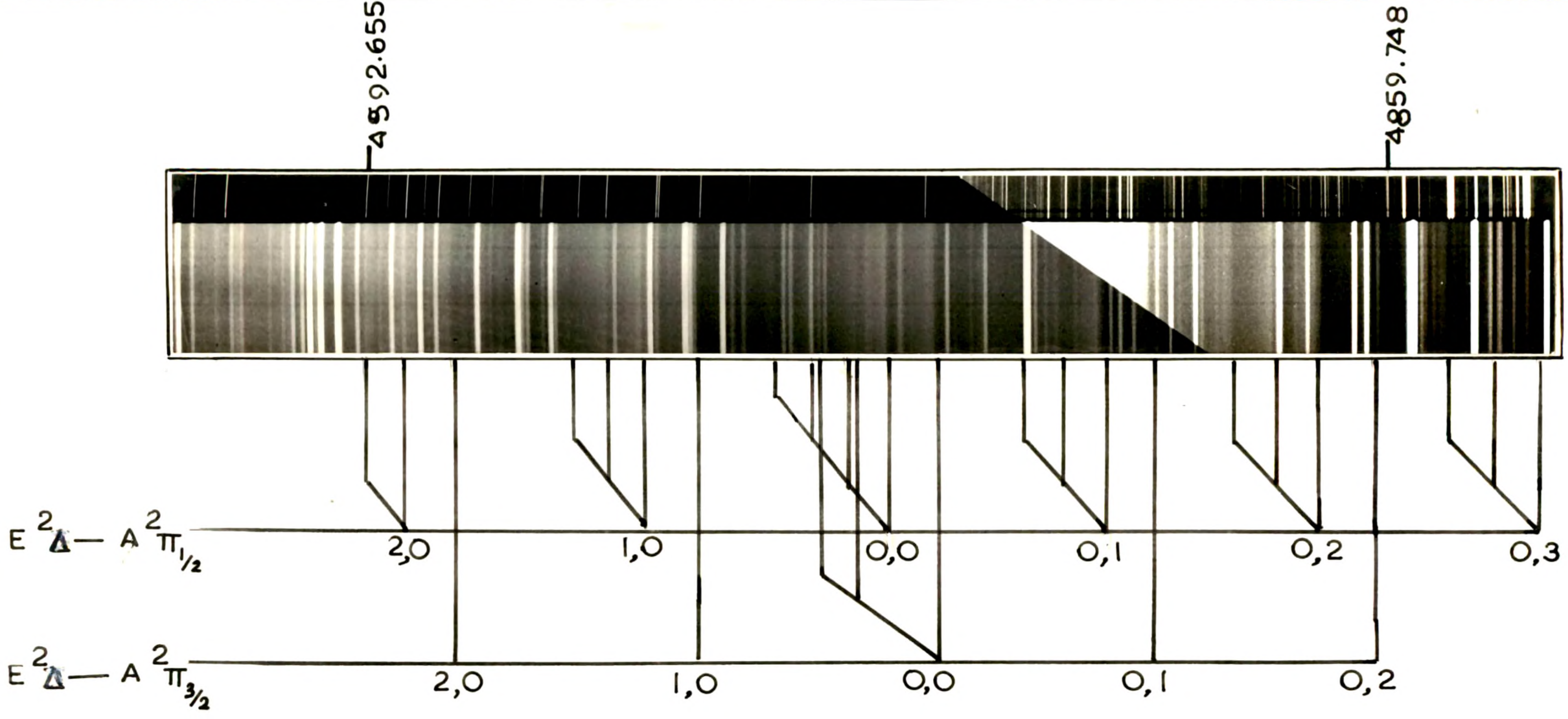

PLATE 5

$E\,{}^2\Delta - A\,{}^2\Pi$ SYSTEM OF CaI MOLECULE AT A DISPERSION OF 7.3 Å/mm.

TABLE 16

DESLANDRES TABLE FOR $E^2\Delta - A^2\Pi_{1/2}$ SYSTEM OF CaI MOLECULE

v'' v'	0		1		2		3		4		5
		241.5		239.5		243.2		229.8			
0	21149.2		20907.7		20668.2		20425.0		20188.7		
	285.6		285.5		285.0		287.7		286.5		
		241.6		240.0		240.5		237.5		240.3	
1	21434.8		21193.2		20953.2		20712.7		20475.2		20234.9
	284.0		281.7		283.3		283.7		280.6		286.1
		243.9		238.4		240.1		240.6		234.8	
2	21718.8		21474.9		21236.5		20996.4		20755.8		20521.0
			281.3		282.3		283.3				
				237.4		239.1					
3			21756.2		21518.8		21279.7				

TABLE 17

DESLANDRES TABLE FOR $E^2\Delta - A^2\Pi_{3/2}$ SYSTEM OF CaI MOLECULE

v'' v'	0		1		2		3		4		5
		240.6		240.0							
0	21092.8		20852.2		20612.2						
	286.0										
1	21378.8										
	284.5										
2	21663.3				21182.2						
3							21226.4				

$$\nu_{Q_1} = 21127.1 + 287.2(v'+\tfrac{1}{2}) - 0.80(v'+\tfrac{1}{2})^2 - 242.7(v''+\tfrac{1}{2}) + 0.50(v''+\tfrac{1}{2})^2.$$

The analysis reveals that the bands observed belong to two sub-systems of a $^2\Delta - {}^2\Pi$ transition. The lower state vibrational frequency does not agree with the ground state frequency of CaI molecule (238.2 cm^{-1}) reported by earlier workers. However it nicely agrees with the vibrational frequency of the A level (241.69 cm^{-1} and 242.65 cm^{-1}) observed by previous workers. The separation between the band origins observed in the present analysis nearly agrees with the reported doublet separation of the A levels. Hence it is suggested that the lower level involved in this transition is not the ground state but the first excited state viz. $A^2\Pi$ state. The upper state frequency of 287.2 cm^{-1} is much higher than any one of the observed levels in this molecule. For the analogous molecules one observes that for levels other than C, the vibrational frequency of the levels usually increases for higher excited states. The vibrational frequency observed in this case is higher than that of the other observed levels. The reason may be that the upper level of the system under investigation may be lying well above the previously observed levels. If one takes $A^2\Pi$ state as the lower state of this system, the upper state may lie at about 36715 cm^{-1}. The structure of these bands shows that the upper level may be a $^2\Pi$ state analogous to the $^2\Delta$ state of CaCl molecule. The doublet separation in the Δ state may be about 2 cm^{-1}. However, the correct assignment can be done by a rotational analysis only.