CHAPTER V

VIBRATIONAL ANALYSES OF IODIDES OF STRONTIUM AND BARIUM

The spectra of iodides of Strontium and Barium were first reported by Olmsted (1906) in flames and latter by Walters and Barratt (1928) in absorption. The spectrum of SrI consists of three groups in the regions $\lambda\lambda$7100-6150, 4500-4200 and 3450-3350 A°. Mesnage (1939) investigated the spectrum of SrI in emission in the range $\lambda\lambda$ 4485-4250 A° and assigned the bands to two separate systems A and B. Latter Reddy et al. (1971) reinvestigated the above group of bands at a higher dispersion (1.25 A°/mm) and assigned these

bands to a transition of a type $C^2\pi - X^2\Sigma$ and established the correlations with the corresponding systems observed in the spectra of SrF, SrCl and SrBr. They also photographed the bands of this molecule in the region λλ7100-6150 A° and assigned them to two different systems viz. $A^2\pi - X^2\Sigma$ and $B^2\Sigma - X^2\Sigma$. The group of bands of SrI molecule in the region λλ3450-3350 A° as reported by Walters and Barratt is known to consist of three bands at 3439 A°, 3406 A° and 3378 A°. No analysis has been offered for these bands. The present chapter deals with the vibrational analysis of this system.

The band spectrum of BaI has been designated as C, D and E systems in the regions λλ5650-5250 A°, 3970-3800 A° and 3800-3565 A° respectively. The systems have been reinvestigated by Patel and Shah (1970) and Reddy and Rao (1970). Again while studying these spectra some additional bands have been photographed in D and E systems of BaI. C-system has been analysed as two sub-systems arising from $^2\pi - {}^2\Sigma$ transition. In the present chapter vibrational analyses of these systems have been presented.

(1) Vibrational analysis of SrI molecule in the region λλ3560-3350 A° (D-X system)

The spectrum of SrI molecule has been excited in a high frequency discharge source of the conventional type.

A capillary discharge was found suitable. External heating was needed to maintain the red colour of discharge. The spectrum was recorded in the fourth order of a plane grating spectrograph at a reciprocal dispersion of 1.8 A°/mm. The exposure time required was about 15 to 20 minutes to get a good spectrogram. The spectrum was photographed on Ilford N-40 plates. The plates were measured with an Abbe Comparator against iron arc standard lines. The spectrogram of the group of bands in the region $\lambda\lambda$ 3500-3300 A° as seen on the negative has been reproduced in Plate 6.

The bands reveal seven sharp and single headed bands. Their visually estimated intensities, wavelengths, wave numbers in vacuum, vibrational assignments and the difference between observed and calculated wave numbers of the bands are given in Table 18. The observed bands were arranged in a Deslandres Table given in Table 19.

The most intense band at 28957.1 cm^{-1} has been taken as (0,0) band and the vibrational analysis has been carried out in the usual way. The quantum equation representing the band heads is

$$\nu_{head} = 28943.99 + 200.4(v'+\tfrac{1}{2}) - 0.5(v'+\tfrac{1}{2})^2 - 174.1(v''+\tfrac{1}{2}) + 0.35(v''+\tfrac{1}{2})^2$$

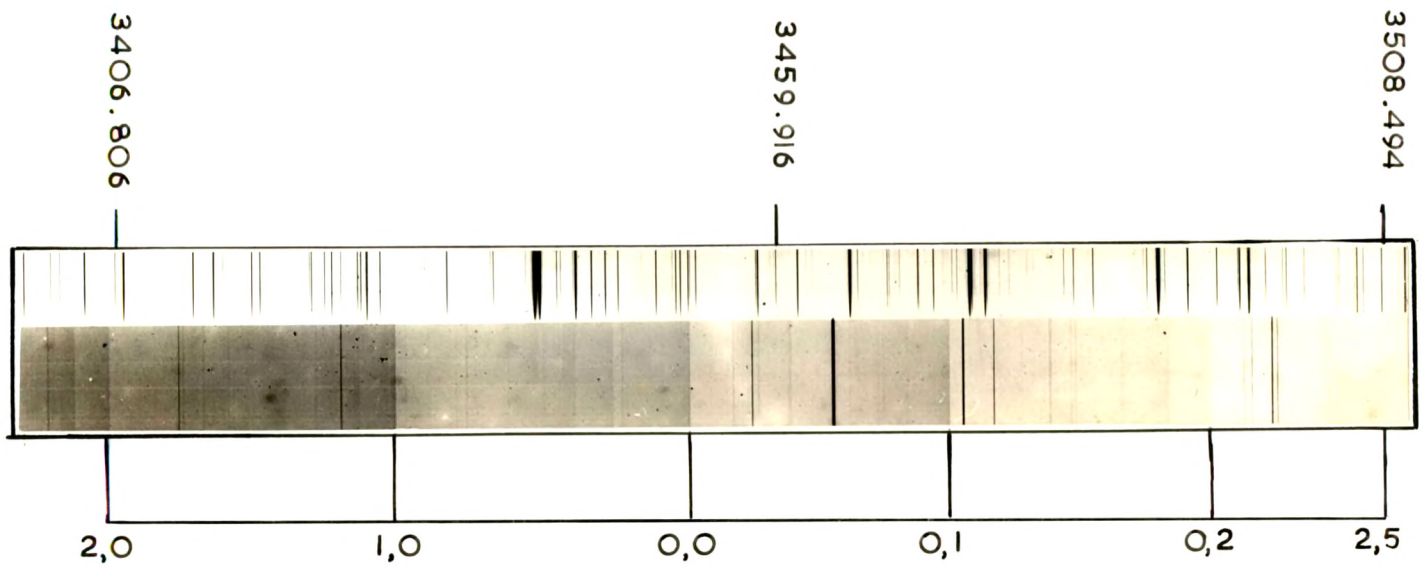

PLATE.6.

$D^2\Sigma - X^2\Sigma$ SYSTEM OF Sr^+I MOLECULE AT A DISPERSION OF 1.8 Å/mm.

TABLE 18

BAND HEAD DATA OF THE $D^2\Sigma - X^2\Sigma$ SYSTEM OF SrI MOLECULE

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v', v")	$=\nu_{obs}-\nu_{cal}$ cm^{-1}
2	3353.20	29813.5	7,3	-0.3
2	3357.13	29790.1	6,2	-2.3
3	3357.90	29771.9	5,1	1.2
4	3360.69	29747.5	4,0	-1.2
2	3375.38	29620.1	6,3	-0.3
2	3377.49	29599.4	5,2	1.4
3	3380.40	29574.0	4,1	-1.3
6	3382.80	29552.9	3,0	0.6
1	3394.73	29449.1	6,4	0.0
2	3397.25	29427.2	5,3	1.2
2	3400.05	29403.1	4,2	0.5
8	3403.90	29378.2	3,1	-0.7
8	3405.68	29354.3	2,0	-0.6
3	3417.30	29254.2	5,4	-0.5
3	3420.10	29230.7	4,3	0.1
3	3422.92	29206.4	3,2	0.2
7	3425.98	29180.7	2,1	-0.8
9	3428.70	29156.3	1,0	-0.2
2	3440.13	29060.5	4,4	1.2
5	3443.20	29034.5	3,3	0.3
7	3446.20	29009.2	2,2	0.4
2	3449.23	28983.7	1,1	0.6
10	3452.40	28957.1	0,0	0.0
1	3457.38	28915.6	5,6	1.4
2	3460.50	28889.3	4,5	0.6
2	3463.68	28862.9	3,4	-1.5

contd...

TABLE 18 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v', v")	$= \nu_{obs} - \nu_{cal}$ cm^{-1}
2	3466.91	28835.9	2,3	-0.9
3	3470.00	28810.3	1,2	-0.1
9	3473.20	28783.5	0,1	-0.2
1	3478.90	28744.7	5,7	-0.3
2	3480.83	28720.5	4,6	1.7
3	3484.40	28691.1	3,5	-1.2
3	3487.40	28665.5	2,4	0.0
8	3490.88	28637.9	1,3	-0.5
7	3494.26	28610.3	0,2	-0.7
1	3498.60	28574.7	5,8	-1.8
1	3501.56	28550.6	4,7	1.0
2	3505.05	28522.4	3,6	0.0
4	3508.50	28494.1	2,5	-0.8
2	3511.90	28466.5	1,4	-0.6
2	3515.48	28437.5	0,3	-1.5
1	3522.45	28381.1	4,8	0.0
4	3526.06	28352.5	3,7	-0.7
2	3529.59	28323.9	2,6	-1.1
1	3533.00	28296.4	1,5	-0.1
1	3536.48	28268.8	0,4	1.1
1	3550.78	28154.4	2,7	-1.4
1	3554.23	28127.4	1,6	0.8
1	3558.05	28097.0	0,5	-0.1

TABLE 19

DESLANDRES TABLE FOR $D^2\Sigma - X^2\Sigma$ SYSTEM OF SrI MOLECULE

v' \ v''	0	1	2	3	4	5	6	7	8	9
	173.6	173.2	172.8	168.7	171.8					
0	28957.1	28783.5	28610.3	28437.5	28268.8	28097.0				
	199.2	200.2	200.0	200.4	197.7	199.4				
	172.6	173.4	172.4	171.4	170.1	169.0				
1	29156.3	28983.7	28810.3	28637.9	28466.5	28296.4	28127.4			
	198.0	197.0	198.9	198.0	199.0	197.7	196.5			
	173.6	171.5	173.3	170.4	171.4	170.2	169.5			
2	29354.3	29180.7	29009.2	28835.9	28665.5	28494.1	28323.9	28154.4		
	198.6	197.5	197.2	198.6	197.4	197.0	198.5	198.1		
	174.7	171.8	171.9	171.6	171.8	168.7	169.9			
3	29552.9	29378.2	29206.4	29034.5	28862.9	28691.1	28522.4	28352.5		
	194.8	195.8	196.7	196.2	197.6	198.2	198.1	198.1		
	173.5	170.9	172.4	170.2	171.2	168.8	169.9	169.5		
4	29747.5	29574.0	29403.1	29230.7	29060.5	28889.3	28720.5	28550.6	28381.1	
		197.9	196.3	196.5	193.7		195.1	194.1	193.6	
		172.5	172.2	173.0			170.9	170.0		
5		29771.9	29599.4	29427.2	29254.2		28915.6	28744.7	28574.7	
			190.7	192.9	194.9					
			170.0	171.0						
6			29790.1	29620.1	29449.1					
				193.4						
7				29813.5						

The value of lower state frequency 174.1±0.05 cm^{-1} observed agrees very well with the ground state frequency 173.9 cm^{-1} of the other system and it may therefore be attributed to the $X^2\Sigma$ state of this molecule. At the dispersion used in the present work it is not possible to resolve the rotational structure of the bands, however, the heads are single and sharp. This leads to conclusion that the upper state involved in this system may also be the type $^2\Sigma$.

The comparison of the region of occurrence of this system with $D^2\Sigma - X^2\Sigma$ systems of SrF, SrCl and SrBr molecules indicates that the system occurs in the expected region and may therefore be attributed to electronic transition of the type $D^2\Sigma - X^2\Sigma$.

(2) Vibrational analyses of BaI

The spectrum of barium iodide was obtained with the help of a medium quartz spectrograph initially. The reproduction of spectrum is given in Plate 7 where all the three (C, D and E) systems have been marked.

(a) C-X system in the region λλ 5700-5200 A°:

A pure sample of barium iodide was placed in a conventional type quartz discharge tube. The molecule was excited using a high frequency oscillator. External heating

PLATE .7.

SPECTROGRAM OF BaI MOLECULE TAKEN ON GLASS SPECTROGRAPH

was needed to maintain the characteristic bright green colour of the discharge. An exposure time of about one hour was sufficient to record the spectrum on Ilford HP_3 plates at a dispersion of 3.7 A°/mm. The overlapping spectra were selected out using a filter WG5.

The C-system has been analysed as two sub-systems $^2\Pi_{\frac{1}{2}} - {}^2\Sigma$ and $^2\Pi_{3/2} - {}^2\Sigma$. The reproductions of the $\overset{\omega}{t_0}$ components of the systems are given in Plates 8 and 9. In the case of C-system only a few sequences were developed however each sequence has large number of bands. The sequences are degraded to shorter wavelength side.

The band heads at 17815.9 cm^{-1} and 18570.8 cm^{-1} were fixed as (0,0) bands of $\Pi_{\frac{1}{2}}$ and $\Pi_{3/2}$ components due to their intensities and sharpness. The analyses have been carried out by the usual methods. The bands were fitted in Deslandre's tables which are given in Table 20 and Table 21 for $\Pi_{\frac{1}{2}}$ and $\Pi_{3/2}$ components respectively. Intensities, wavelengths, wave numbers in vacuum, assignments and $\Delta\nu$(= $\nu_{obs} - \nu_{cal}$) for both the components are given in Table 22 and Table 23.

The band heads were fitted into the quantum

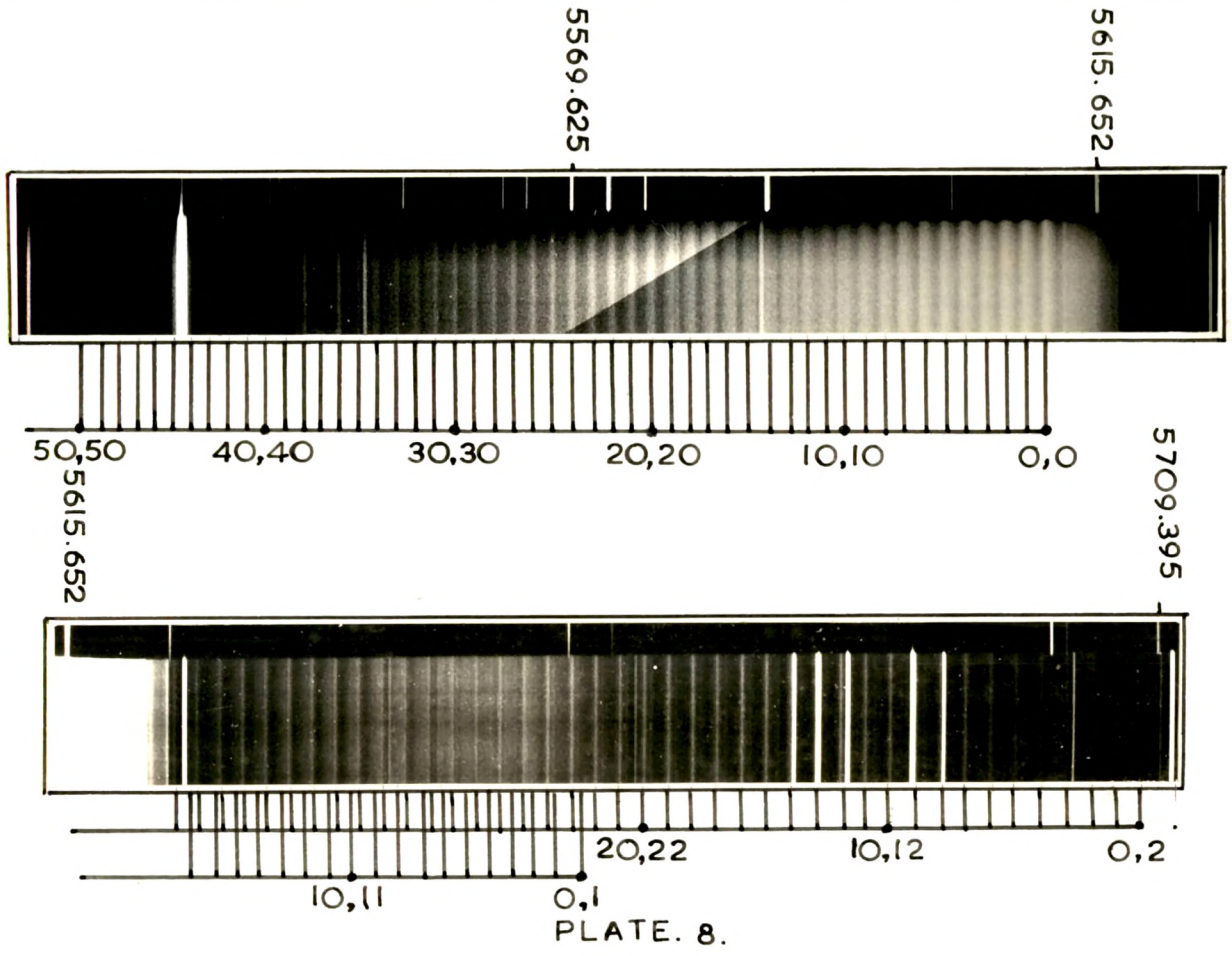

PLATE. 8.

$C\,^2\Pi_{1/2} - X\,^2\Sigma$ SYSTEM OF BaI MOLECULE AT A DISPERSION OF 3.7 Å / mm.

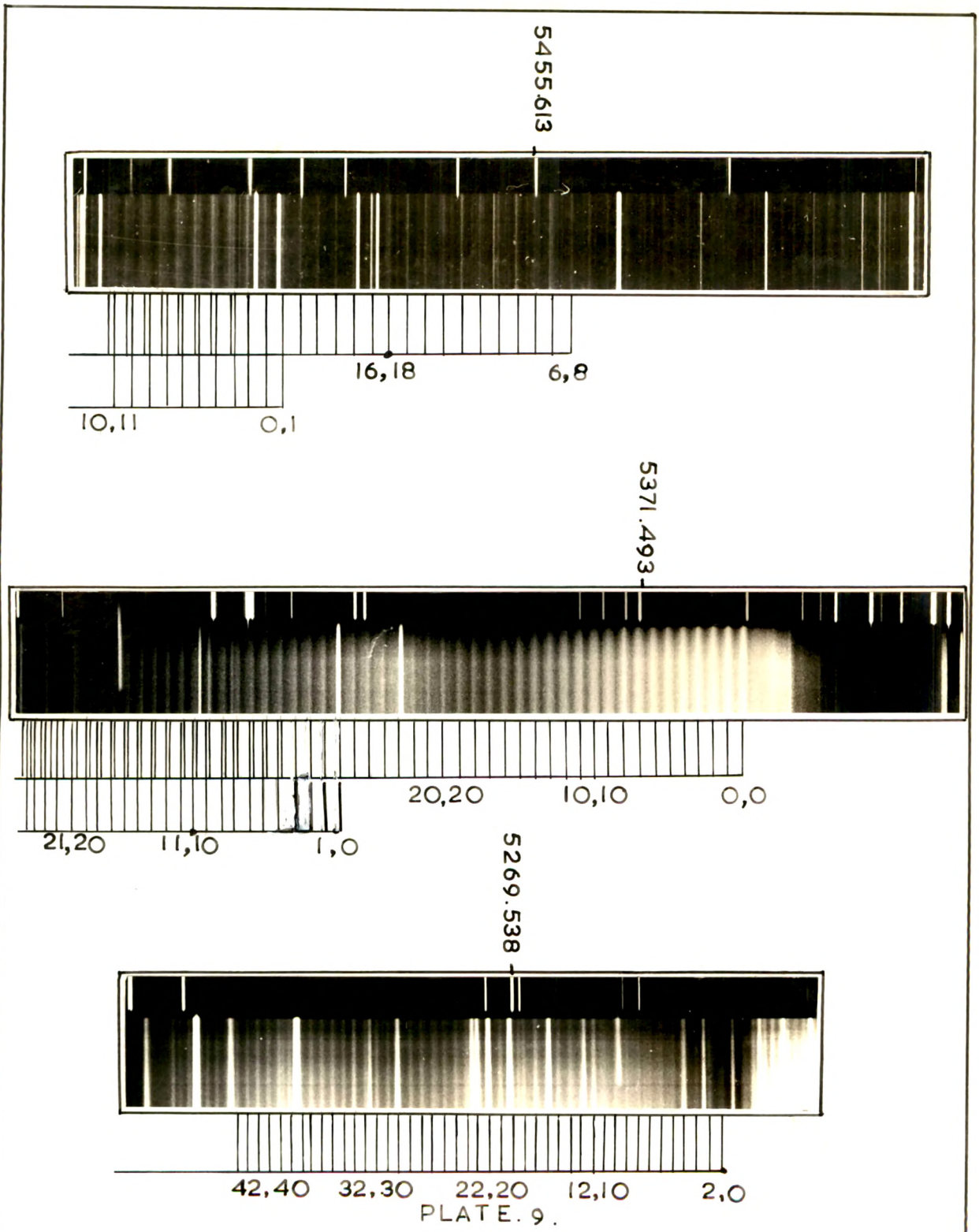

PLATE. 9.

$C\,^2\Pi_{3/2} - X\,^2\Sigma$ SYSTEM OF BaI MOLECULE (3.7 Å/mm)

TABLE 20

DESLANDRES TABLE $C^2\Pi_{\frac{1}{2}} - X^2\Sigma$ SYSTEM OF BaI MOLECULE

v' \ v''	0	1	2	3	4	5	6	7	8	9
0	17815.9	151.4 17664.5	151.0 17513.5							
1		157.4 17821.9	157.6 150.8 17671.1	151.8 17519.3						
2			156.3 17827.4	156.8 151.3 17676.1	149.7 17526.4					
3				157.0 17833.1	157.5 149.2 17683.9	150.7 17533.2				
4					155.6 17839.5	156.3 150.0 17689.5	149.3 17540.2			
5						155.4 17844.9	156.5 148.2 17696.7	149.5 17547.3		
6							154.5 17851.2	155.1 148.8 17702.4	148.9 17553.5	
7								154.3 17856.7	154.7 148.5 17708.2	147.9 17560.3

contd...

TABLE 20 (contd.)

v' \ v"	6	7	8	9	10	11	12	13	14	15
			153.6	154.6						
			146.9	147.5						
8			17861.8	17714.9	17567.4					
				152.9	153.2					
				147.2						
9				17867.8	17720.6					
					152.7					
					146.8	146.5				
10					17873.3	17726.5	17580.0			
						151.6	152.6			
						145.5	146.4			
11						17878.1	17732.6	17586.2		
							150.9	152.8		
							144.5	145.1		
12							17883.5	17739.0	17593.9	
								149.9	151.2	
								143.8		
13								17888.9	17745.1	
									148.9	
14									17894.0	

TABLE 21

DELANDRES TABLE FOR $C^2\Pi_{3/2}$ — $X^2\Sigma$ SYSTEM OF BaI MOLECULE

v' \ v"	0	1	2	3	4	5	6	7	8	9
	151.6									
0	18570.8	18419.2								
	156.9	158.5								
	150.0	151.7								
1	18727.7	18577.7	18426.0							
	157.3	155.3	157.2							
	152.0	149.8	150.7							
2	18885.0	18733.0	18583.2	18432.5						
		157.5	155.4	157.3						
		151.9	148.8	151.9						
3		18890.5	18738.6	18589.8	18437.9					
			157.6	154.4	157.0					
			152.0	149.3	150.2					
4			18896.2	18744.2	18594.9	18444.7				
				157.0	154.9	155.2				
				151.4	148.9	149.6				
5				18901.2	18749.8	18600.9	18451.3			
					155.7	156.0	155.1			
					148.6	150.5	149.4	145.4		
6					18905.5	18956.9	18606.4	18457.0	18311.6	
						153.2	154.7	154.6	151.9	
							149.0	149.5	148.1	147.5
7						18910.1	18761.1	18611.6	18463.5	18316.0

contd....

TABLE 21 (contd.)

v' \ v"	6	7	8	9	10	11	12	13	14	15
	153.3	154.4	154.3	155.6						
	148.4	148.2	147.0	146.6						
8	18914.4	18766.0	18617.8	18470.6	18324.0					
		153.1	153.9	153.6	152.1					
		147.4	147.1	148.5	143.7					
9		18919.1	18771.7	18624.6	18476.1	18332.4				
			152.4	153.1	153.2	150.2				
			146.4	148.4	146.7	143.8				
10			18924.1	18777.7	18629.3	18482.6	18338.8			
				151.4	152.3	152.9	148.9			
				146.9	146.7	147.8	141.5			
11				18929.1	18782.2	18635.5	18487.7	18346.2		
					151.2	152.4	153.4	149.4		
					145.5	146.8	145.3	142.7		
12					18933.4	18987.9	18641.1	18495.6	18352.9	
						149.1	152.1	152.7	148.2	
						143.8	144.9	147.2	142.1	
13						18937.0	18793.2	18648.3	18501.1	18359.0
							149.9	150.6	150.4	
							144.2	147.4		
14							18943.1	18798.9	18651.5	
								148.2	152.3	
								143.3	146.0	
15								18947.1	18803.8	18657.8

TABLE 22

BAND HEAD DATA OF THE $C^2\Pi_{\frac{1}{2}}$ — $X^2\Sigma$ SYSTEM OF BaI MOLECULE

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
5	5511.20	18139.84	60,60	-1.7
5	5513.43	18132.60	59,59	-1.8
5	5514.99	1827.3	58,58	-1.8
5	5516.17	18123.1	57,57	-0.7
5	5517.93	18117.8	56,56	-0.6
5	5519.06	18113.9	55,55	0.9
5	5520.97	18107.6	54,54	0.0
5	5522.41	18103.0	53,53	0.7
5	5523.96	18097.8	52,52	1.0
5	5525.51	18092.9	51,51	1.3
5	5527.06	18087.7	50,50	1.5
6	5528.57	18082.7	49,49	1.8
6	5530.13	18077.8	48,48	2.2
6	5531.65	18072.9	47,47	2.7
6	5533.29	18067.3	46,46	2.4
6	5535.13	18061.4	45,45	1.9
6	5536.75	18056.1	44,44	1.9
6	5538.15	18051.4	43,43	2.5
6	5539.69	18046.5	42,42	2.9
6	5541.33	18041.3	41,42	3.2
6	5543.43	18034.8	40,40	2.8
7	5544.79	18029.9	39,39	2.2
7	5546.47	18024.4	38,38	2.0
7	5547.83	18020.2	37,37	3.1
7	5549.49	18014.6	36,36	2.7

contd...

TABLE 22 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
7	5551.20	18009.1	35,35	2.4
7	5552.85	18003.9	34,34	2.7
7	5554.59	17998.1	33,33	2.0
7	5556.21	17992.9	32,32	2.0
7	5557.97	17987.1	31,31	1.5
7	5559.54	17982.2	30,30	1.8
8	5561.34	17976.4	29,29	1.2
8	5563.02	17970.9	28,28	1.1
8	5564.71	17965.4	27,27	0.7
8	5566.42	17959.9	26,26	0.5
8	5568.28	17953.8	25,25	-0.3
8	5569.96	17948.3	24,24	-0.5
8	5571.66	17942.9	23,23	-0.6
8	5573.16	17938.0	22,22	-0.4
8	5574.95	17932.6	21,21	-0.5
8	5576.55	17927.1	20,20	-0.6
8	5578.39	17921.3	19,19	-1.2
9	5580.00	17916.2	18,18	-1.0
9	5581.76	17910.4	17,17	-1.4
9	5583.63	17904.3	16,16	-2.1
9	5584.21	17902.7	15,15	1.7
9	5586.94	17894.0	14,14	-1.6
9	5588.47	17888.9	13,13	-1.2
9	5590.18	17883.5	12,12	-1.2
9	5591.89	17878.1	11,11	-1.0
9	5593.41	17873.3	10,10	-0.4

contd...

TABLE 22 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
9	5595.14	17867.8	9,9	-0.4
9	5597.00	17861.8	8,8	-0.8
9	5598.61	17856.7	7,7	-0.3
9	5600.29	17851.2	6,6	0.0
10	5602.29	17844.9	5,5	-0.6
10	5604.04	17839.5	4,4	-0.1
10	5606.01	17833.1	3,3	-0.7
10	5607.79	17827.4	2,2	-0.5
10	5609.46	17821.9	1,1	0.0
10	5611.39	17815.9	0,0	0.0
3	5626.72	17767.5	17,18	-1.4
	"	"	39,41	-0.1
1	5627.78	17764.1	16,17	1.1
1	5628.79	17760.8	38,40	0.7
1	5629.78	17757.9	15,16	0.9
1	5630.73	17754.9	37,39	0.1
1	5631.78	17751.4	14,15	0.3
1	5632.82	17748.2	36,38	0.3
1	5633.80	17745.1	13,14	0.0
1	5634.77	17741.9	35,37	0.2
1	5635.75	17739.0	12,13	0.1
1	5636.69	17736.0	34,36	0.3
1	5637.78	17732.6	11,12	0.5
1	5638.87	17729.3	33,35	0.0
1	5639.70	17726.5	10,11	0.5
1	5640.60	17723.7	32,34	1.0

contd...

TABLE 22 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	5641.60	17720.6	9,10	-0.3
1	5642.65	17717.1	31,33	0.8
2	5643.38	17714.9	8,9	0.3
1	5644.78	17710.5	30,32	0.5
2	5645.55	17708.2	7,8	-0.3
1	5646.84	17704.2	29,31	0.6
2	5647.45	17702.4	6,7	0.1
1	5648.68	17698.3	28,30	1.1
2	5649.21	17696.7	5,6	0.6
1	5650.87	17691.7	27,29	0.8
2	5651.47	17689.5	4,5	-0.2
1	5652.89	17685.1	26,28	0.8
2	5653.33	17683.9	3,4	0.6
1	5654.84	17679.2	25,27	0.8
2	5655.76	17676.1	2,3	-0.7
1	5657.05	17672.3	24,26	0.8
2	5657.45	17671.1	1,2	0.6
1	5659.11	17665.8	23,25	0.7
2	5659.54	17664.5	0,1	0.6
1	5661.16	17659.2	21,23	0.4
1	5665.36	17646.1	20,22	0.1
1	5667.43	17639.9	19,21	0.4
1	5669.53	17633.3	18,20	0.3
1	5671.58	17626.8	17,19	0.2
1	5673.77	17620.6	16,18	0.5
1	5675.90	17613.5	15,17	0.0

contd...

TABLE 22 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	5678.08	17606.6	14,16	-0.4
1	5680.27	17599.8	13,15	-0.6
1	5682.24	17593.9	12,14	0.0
1	5684.47	17586.2	11,13	-1.1
1	5686.68	17580.0	10,12	-0.7
1	5689.49	17571.4	9,11	-2.7
1	5690.81	17567.4	8,10	0.0
1	5693.11	17560.3	7,9	0.7
1	5695.26	17553.5	6,8	-0.4
1	5697.34	17547.3	5,7	0.2
1	5699.63	17540.2	4,6	0.0
1	5701.86	17533.2	3,5	-0.1
1	5704.11	17526.4	2,4	0.1
1	5706.42	17519.3	1,3	-0.1
1	5708.26	17513.5	0,2	1.2

TABLE 23

BAND HEAD DATA OF THE $C^2\pi_{3/2}$ — $X^2\Sigma$ SYSTEM OF BaI MOLECULE

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	5239.02	19082.3	45,43	-0.9
1	5240.65	19076.1	44,42	-2.4
1	5241.80	19072.1	43,41	-1.5
1	5242.97	19067.8	42,40	-1.5
1	5244.26	19063.0	41,39	-1.7
1	5245.49	19058.7	40,38	-1.3
1	5246.33	19055.8	39,37	0.3
1	5247.64	19051.0	38,36	0.0
1	5248.92	19046.3	37,35	-0.1
1	5250.15	19041.6	36,34	-0.1
1	5251.33	19037.6	35,33	0.3
1	5252.48	19033.3	34,32	0.4
1	5253.92	19028.2	33,31	-0.2
1	5255.16	19023.5	32,30	-0.5
1	5256.27	19019.5	31,29	0.0
1	5257.33	19015.9	30,28	1.0
1	5258.67	19010.8	29,27	0.7
1	5260.42	19004.7	28,26	-1.4
1	5261.22	19001.8	27,25	0.2
1	5262.40	18997.5	26,24	0.3
1	5263.72	18992.8	25,23	0.0
1	5265.08	18987.7	24,22	-0.8
1	5266.16	18983.7	23,21	-0.3
1	5267.29	18979.8	22,20	-0.3
1	5268.61	18975.1	21,19	0.0

contd...

TABLE 23 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	5269.68	18971.1	20,18	-0.5
1	5271.27	18965.5	19,17	-0.7
1	5272.58	18960.7	18,16	-1.0
1	5273.60	18957.1	17,15	-0.1
1	5275.07	18951.7	16,14	-1.0
1	5276.40	18947.1	15,13	-1.2
1	5277.50	18943.1	14,12	-0.6
1	5279.15	18937.0	13,11	-2.2
1	5280.23	18933.4	12,10	-1.2
1	5281.40	18929.1	11,9	2.2
1	5282.75	18924.1	10,8	-1.2
1	5284.19	18919.1	9,7	-1.6
1	5285.48	18914.4	8,6	-1.3
1	5286.68	18910.1	7,5	-1.1
1	5288.00	18905.5	6,4	-0.8
1	5289.15	18901.2	5,3	-0.3
2	5290.56	18896.2	4,2	-0.4
2	5292.02	18890.5	3,1	-1.1
2	5293.72	18885.0	2,0	-1.6
2	5295.66	18878.0	30,29	-0.4
2	5296.74	18874.4	29,28	1.2
2	5298.06	18869.5	28,27	1.1
2	5300.14	18862.3	27,26	-1.1
2	5301.39	18857.7	26,25	-0.5
2	5302.42	18854.1	25,24	0.9
2	5304.68	18846.0	24,23	-2.3

contd...

TABLE 23 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
2	5306.01	18841.1	23,22	-2.3
2	5306.87	18838.2	22,21	-0.1
2	5308.21	18833.5	21,20	-0.3
2	5309.49	18828.9	20,19	0.6
2	5309.93	18827.4	45,45	-0.6
2	5310.70	18824.7	19,18	1.4
2	5311.50	18821.9	44,44	-0.2
2	5312.26	18819.0	18,17	0.8
2	5313.19	18815.9	43,43	-0.4
2	5313.66	18814.1	17,16	1.1
2	5314.70	18810.5	42,42	-0.1
2	5315.02	18809.5	16,15	1.4
2	5315.85	18806.4	41,41	2.2
2	5316.58	18803.8	15,14	0.7
2	5317.40	18801.0	40,40	1.9
2	5318.03	18798.9	14,13	0.9
2	5319.51	18793.4	39,39	0.1
2	5319.55	18793.2	13,12	0.3
2	5321.10	18787.9	12,11	0.1
4	5321.32	18787.1	38,38	-0.4
2	5322.75	18782.2	11,10	-0.4
4	5322.85	18781.6	37,37	-0.2
5	5324.26	18776.7	36,36	0.5
2	5324.53	18775.7	10,9	1.3
2	5325.72	18771.7	9,8	-0.5

contd...

TABLE 23 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
5	5326.10	18770.3	35,35	-0.2
3	5326.45	18769.0	8,7	-1.0
6	5327.43	18765.5	34,34	0.9
3	5328.71	18761.1	7,6	-0.4
6	5328.79	18760.8	33,33	1.7
3	5329.90	18756.9	6,5	0.6
6	5330.46	18754.9	32,32	1.4
3	5331.92	18749.8	5,4	-1.1
6	5332.36	18748.2	31,31	0.3
7	5333.49	18744.2	4,3	-1.3
	"	"	30,30	1.9
7	5335.14	18738.6	3,2	-1.5
	"	"	29,29	2.1
7	5336.69	18733.0	2,1	1.6
	"	"	28,28	1.9
7	5338.32	18727.7	1,0	-1.3
	"	"	27,27	2.1
6	5340.00	18721.4	26,26	1.5
6	5342.01	18714.4	25,25	0.1
7	5343.16	18710.2	24,24	1.5
7	5345.15	18703.2	23,23	0.0
7	5346.57	18698.3	22,22	0.6
8	5348.20	18692.7	21,21	0.6
8	5349.80	18687.1	20,20	0.7
8	5351.52	18681.2	19,19	0.2
8	5353.18	18675.2	18,18	-0.1

contd...

TABLE 23 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
8	5354.86	18670.0	17,17	0.3
9	5356.38	18664.1	16,16	0.0
9	5358.16	18657.8	15,15	-0.7
9	5360.00	18651.5	14,14	-1.4
9	5361.50	18646.3	13,13	-0.9
9	5363.03	18641.1	12,12	-0.4
9	5364.57	18635.5	11,11	-0.4
9	5366.37	18629.3	10,10	-0.8
9	5367.93	18624.6	9,9	-0.3
9	5369.72	18617.8	8,8	-0.8
9	5371.48	18611.6	7,7	-0.2
10	5373.20	18606.4	6,6	-0.5
10	5374.62	18600.9	5,5	-0.1
10	5376.27	18594.9	4,4	-0.1
10	5377.76	18589.8	3,3	0.8
10	5379.95	18583.2	2,2	0.2
10	5381.27	18577.7	1,1	0.8
10	5383.23	18570.8	0,0	0,0
1	5398.72	18517.8	37,39	-1.9
3	5400.56	18511.3	36,38	-1.5
	"	"	15,16	-0.7
1	5402.43	18505.2	35,37	-0.8
2	5403.64	18501.1	13,14	-0.9
1	5404.45	18498.1	34,36	-1.1
2	5405.21	18495.6	12,13	-0.3
1	5406.50	18491.1	33,35	-0.3

contd...

TABLE 23 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	= obs − cal cm^{-1}
2	5407.45	18487.7	11,12	-1.9
1	5408.38	18484.6	32,34	-0.7
2	5409.01	18482.6	10,11	-0.7
1	5410.26	18478.2	31,33	-0.5
2	5410.95	18476.1	9,10	-0.9
3	5412.23	18471.6	30,32	-0.3
	5412.45	18470.8	8,9	-0.1
2	5414.09	18465.2	29,31	0.0
2	5414.61	18463.5	7,8	-0.9
1	5415.92	18459.0	28,30	0.6
2	5416.49	18457.0	6,7	-1.0
3	5417.88	18452.2	27,29	0.5
	5418.19	18451.3	5,6	-0.2
3	5419.80	18445.7	26,28	0.8
	5420.10	18444.7	4,5	-0.3
1	5421.77	18438.9	25,27	0.7
2	5422.13	18437.9	3,4	-0.6
3	5423.74	18432.5	24,26	1.1
	"	"	2,3	0.6
3	5425.64	18426.0	23,25	1.3
	"	18426.0	1,2	0.6
3	5427.62	18419.2	22,24	1.2
	"	"	0,1	0.5
1	5429.63	18412.4	21,23	0.9
1	5431.50	18406.0	20,22	1.3
1	5433.44	18399.6	19,21	1.7

contd...

TABLE 23 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	5435.40	18392.8	18,20	1.7
1	5437.97	18384.0	17,19	-0.5
1	5439.43	18379.3	16,18	1.6
1	5441.38	18372.5	15,17	1.5
1	5443.26	18366.1	14,16	1.9
1	5445.36	18359.0	13,15	1.6
1	5447.23	18352.9	12,14	2.3
1	5449.25	18346.2	11,13	2.3
1	5451.39	18338.8	10,12	1.7
1	5453.33	18332.4	9,11	2.2
1	5455.80	18324.0	8,10	0.7
1	5458.23	18316.0	7,9	-0.5
1	5459.54	18311.6	6,8	1.9
1	5462.10	18302.9	5,7	0.3
1	5464.00	18296.5	4,6	0.9

equations

$C^2\Pi_{\frac{1}{2}} - X^2\Sigma$

$$\nu_{head} = 17812.90 + 158.7(v'+\tfrac{1}{2}) - 0.29(v'+\tfrac{1}{2})^2 + 0.0006(v'+\tfrac{1}{2})^3 - 0.0000035(v'+\tfrac{1}{2})^4 - 152.6(v''+\tfrac{1}{2}) + 0.255(v''+\tfrac{1}{2})^2$$

$C^2\Pi_{3/2} - X^2\Sigma$

$$\nu_{head} = 18567.70 + 158.8(v'+\tfrac{1}{2}) - 0.2856(v'+\tfrac{1}{2})^2 + 0.0006(v'+\tfrac{1}{2})^3 - 0.0000035(v'+\tfrac{1}{2})^4 - 152.6(v''+\tfrac{1}{2}) + 0.255(v''+\tfrac{1}{2})^2$$

(b) <u>D-X and E-X systems of BaI in the region λλ 3970-3800 A° and λλ 3800-3565 A°</u>:

In the region λλ 3970-3560 A° Barium iodide has two systems D and E as reported by Patel and Shah (1970) and Reddy and Rao (1970). An attempt was made to reanalyse these systems. Taking a small quantity of BaI_2 in a narrow quartz tube and using high frequency oscillator the molecule was excited. External heating was required to maintain the colour of the discharge. Ilford N-40 plates were used to get a satisfactory spectrogram of second order with a dispersion 3.7 A°/mm. The time of exposure was about an hour. Sequences are degraded to shorter wavelength side.

The reproduction of D and E systems are given in Plates 10 and 11.

The most intense bands at 25777.2 cm^{-1} and 26765.5 cm^{-1} were taken as (0,0) bands of D and E systems respectively. In both the systems sequences with $\Delta v = +4, +3, \pm 2, \pm 1, 0$ were developed. The vibrational analyses were carried out by usual methods. Intensities, wavelengths, wave numbers in vacuum, assignment and difference in wave number $\Delta\nu (= \nu_{obs} - \nu_{cal})$ for bands of $^2\Lambda$ D and E systems are given in Table 24 and Table 25.

The observed bands were arranged in Deslandres tables and are given in Table 26 and Table 27.

The bands were fitted in the following equations:-

$D^2\Sigma - X^2\Sigma$

$$\nu_{head} = 25773.75 + 161.10(v'+\tfrac{1}{2}) - 0.33(v'+\tfrac{1}{2})^2 - 152.15(v''+\tfrac{1}{2}) + 0.31(v''+\tfrac{1}{2})^2$$

$E^2\Sigma - X^2\Sigma$

$$\nu_{head} = 26753.6 + 176.4(v'+\tfrac{1}{2}) - 0.3(v'+\tfrac{1}{2})^2 - 152.7(v''+\tfrac{1}{2}) + 0.35(v''+\tfrac{1}{2})^2.$$

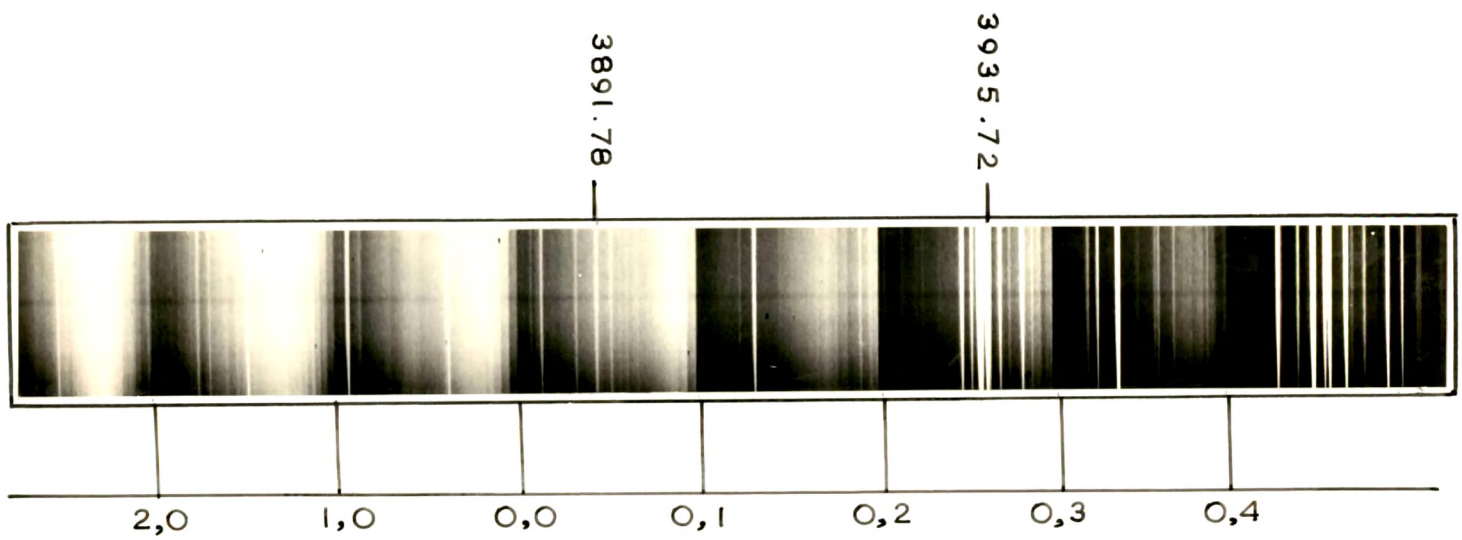

PLATE.10.

$D\,^2\Sigma - X\,^2\Sigma$ SYSTEM OF BaI MOLECULE AT A DISPERSION OF 7.3 Å/mm.

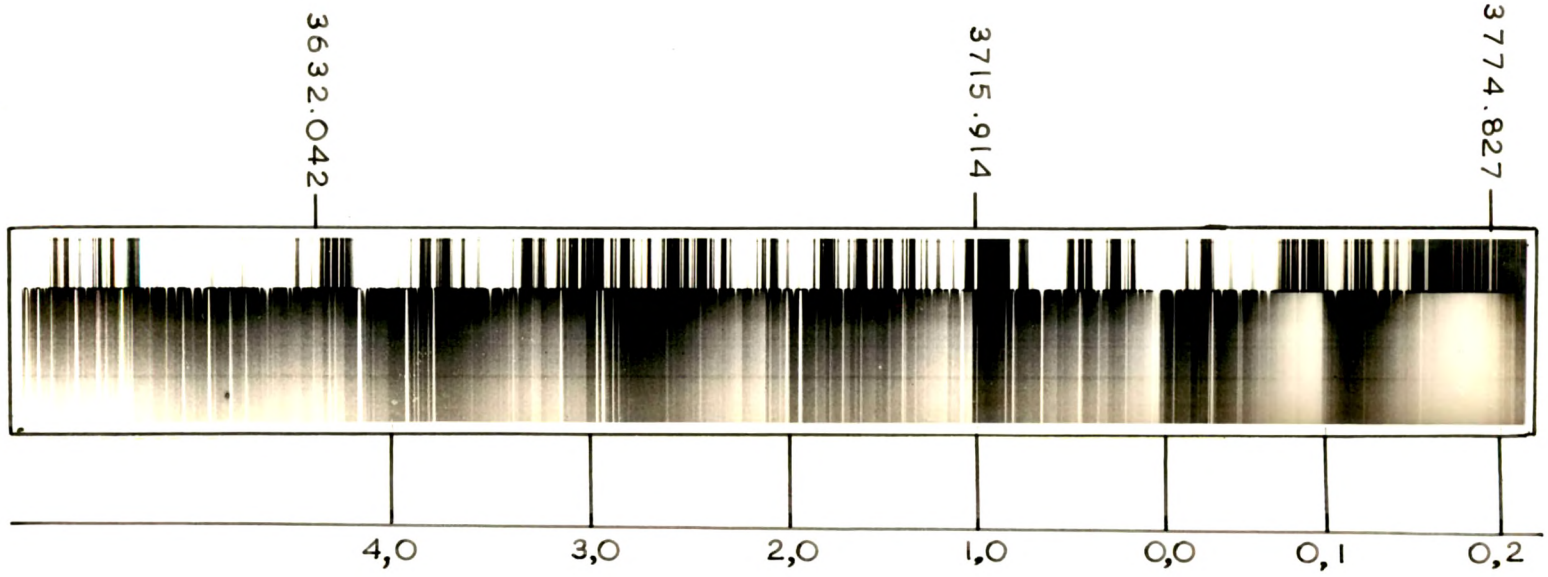

PLATE.II.

$E\,^2\Sigma$ — $X\,^2\Sigma$ SYSTEM OF BaI MOLECULE AT A DISPERSION OF 7.3 Å/mm.

TABLE 24

BAND HEAD DATA OF THE $D^2\Sigma - X^2\Sigma$ SYSTEM OF BaI MOLECULE

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
2	3778.59	26457.3	12,8	-1.2
2	3779.13	26453.8	11,7	1.3
1	3779.75	26449.6	10,6	
1	3780.38	26444.7	9,5	-1.8
2	3781.12	26439.9	8,4	-0.5
2	3781.87	26434.3	7,3	0.0
3	3782.53	26430.1	6,2	1.9
3	3784.1	26418.9	5,1	-3.1
3	3802.68	26289.7	8,5	-1.7
4	3803.49	26284.1	7,4	-0.6
4	3804.38	26277.9	6,3	0.0
4	3805.24	26272.4	5,2	1.3
6	3806.23	26265.5	4,1	1.2
3	3807.15	26258.6	3,0	1.2
3	3827.27	26120.7	5,3	-0.1
3	3828.29	26113.9	4,2	0.5
4	3829.33	26107.1	3,1	1.2
4	3830.51	26098.9	2,0	0.6
5	3850.35	25964.0	4,3	0.9
5	3851.54	25956.6	3,2	1.7
6	3852.87	25947.1	2,1	0.3
5	3854.15	25939.1	1,0	0.5
7	3869.26	25837.2	7,7	-2.2
7	3870.36	25829.8	6,6	-1.0

contd...

TABLE 24 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
7	3871.41	25823.2	5,5	1.1
8	3872.74	25814.5	4,4	1.1
8	3874.10	25805.2	3,3	0.5
8	3875.29	25797.2	2,2	1.3
10	3878.30	25778.2	0,0	0.0
3	3898.03	25646.9	2,3	1.3
3	3899.74	25635.8	1,2	-0.4
3	3901.17	25625.9	0,1	-0.8
3	3918.14	25515.4	4,6	-0.5
4	3919.59	25505.6	3,5	-0.3
3	3921.10	25495.8	2,4	-0.1
4	3922.68	25486.1	1,3	0.2
4	3924.14	25476.4	0,2	-0.6
2	3944.36	25345.2	2,5	-1.7
2	3945.14	25340.7	1,4	4.5

TABLE 25

BAND HEAD DATA OF $E^2\Sigma - X^2\Sigma$ SYSTEM OF BaI MOLECULE

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
1	3619.86	27617.2	11,7	0.3
1	3622.73	27595.9	10,6	0.9
1	3625.55	27573.8	9,5	0.8
1	3628.36	27552.5	8,4	1.3
1	3631.31	27530.5	7,3	1.0
2	3634.13	27509.3	6,2	1.3
2	3651.30	27379.7	7,4	0.1
2	3654.29	27357.3	6,3	0.0
2	3657.21	27335.6	5,2	0.4
2	3660.12	27313.9	4,1	0.9
4	3663.04	27292.3	3,0	2.3
3	3677.52	27184.7	5,3	0.2
3	3680.44	27163.3	4,2	1.5
4	3683.60	27139.7	3,1	0.6
4	3686.81	27116.1	2,0	-0.3
5	3691.47	27081.6	7,6	-0.4
5	3694.73	27058.1	6,5	-0.1
5	3697.93	27034.7	5,4	0.1
6	3700.83	27013.5	4,3	2.4
5	3704.56	26985.8	3,2	-2.1
6	3707.53	26964.7	2,1	0.3
6	3710.72	26941.5	1,0	0.3
8	3718.31	26886.4	5,5	1.0

contd...

TABLE 25 (contd.)

Intensity	Wave length A°	Wave number in vacuum cm^{-1}	Assignment (v',v")	$\Delta\nu = \nu_{obs} - \nu_{cal}$ cm^{-1}
8	3721.69	26861.8	4,4	0.6
9	3725.08	26837.3	3,3	0.1
9	3728.42	26813.3	2,2	0.1
10	3735.12	26765.5	0,0	0.0
3	3742.56	26711.8	4,5	-0.2
3	3752.87	26638.5	1,2	0.5
4	3756.45	26613.0	0,1	-0.2
2	3770.75	26512.8	2,4	0.2
3	3773.90	26490.2	1,3	2.9
4	3777.50	26464.9	0,2	2.7

TABLE 26

DESLANDRES TABLE FOR $D^2\Sigma - X^2\Sigma$ SYSTEM OF BaI MOLECULE

v' \ v"	0	1	2	3	4	5	6	7
		152.3	149.5					
0	25778.2	25625.9	25476.4					
	160.9		159.4					
				149.7	145.4			
1	25939.1		25635.8	25486.1	25340.7			
	159.8		161.4	160.8	155.1			
		151.8	149.9	150.3	151.1	150.6		
2	26098.9	25947.1	25797.2	25646.9	25495.8	25345.2		
	159.2	160.0	159.4	158.3		160.4		
		151.5	150.5	151.4				
3	26258.6	26107.1	25956.6	25805.2		25505.6		
		158.4	157.3	158.8				
			151.6	149.9	149.5			
4		26265.5	26113.9	25964.0	25814.5		25515.4	
		158.5	158.5	156.7				
			151.6	151.7				
5		26418.9	26272.4	26120.7		25823.2		
			157.7	157.2				
				152.2				
6			26430.1	26277.9			25829.8	
				156.4				
					150.2			
7				26434.3	26284.1			25837.2
					155.8			
						150.2		
8					26439.9	26289.7		
						155.0		
9						26444.7		
10							26449.6	

TABLE 27

DESLANDRES TABLE FOR THE $E^2\Sigma$ — $X^2\Sigma$ SYSTEM OF BaI MOLECULE

v' \ v"	0	1	2	3	4	5	6	7
		152.5	148.1					
0	26765.5	26613.0	26464.9					
	176.0		173.6					
				148.3				
1	26941.5		26638.5	26490.2				
	174.6		174.8					
		151.4		151.4				
2	27116.1	26964.7	26813.3		26512.8			
	176.2	175.0	172.2					
		152.6	154.2	148.2				
3	27292.3	27139.7	26985.5	26837.3				
		174.2	177.8	176.2				
			150.6	149.8	151.7	150.0		
4		27313.9	27163.3	27013.5	26861.8	26711.8		
			172.3	171.2	172.9	174.6		
				150.9	150.0	148.3		
5			27335.6	27184.7	27034.7	26886.4		
			173.7	172.6		171.7		
				152.0				
6			27509.3	27357.3		27058.1		
				173.2				
					150.8			
7				27530.5	27379.7		27081.6	
					172.8			
8					27552.5			
9						27573.8		
10							27595.9	
11								27617.2