

The C ($^2\Pi$) \rightarrow X ($^2\Sigma^+$) transition in thermal emission spectra of the diatomic alkaline earth bromides

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Abstract. The extensive thermal emission spectrum attributed to the diatomic bromides of calcium, strontium and barium has been observed in the visible region at temperatures about 2200–2400° C, using a vacuum graphite furnace. Many new bands, *viz.*, 141 in CaBr, 53 in SrBr and 68 in BaBr, have been recorded and classified. The vibrational constants agree with those determined by earlier workers and involved the ground state in each case. The transition C \rightarrow X appears in each molecule and consists of two equally intense systems, *viz.*, C₁ \rightarrow X and C₂ \rightarrow X. The general spectroscopic features of the C \rightarrow X systems of the bromides of the II A sub group of the periodic table have been compared. They exhibit a close structural similarity and furnish a good example of homologous spectra. The system C \rightarrow X in all these molecules arises from a C² π – X² Σ^+ transition where the ² π state appears to be intermediate between Hund's cases (a) and (b).

Keywords. Thermal emission; molecular spectra; alkaline earth bromides.

1. Introduction

The flame emission spectrum of the alkaline earth bromides was first observed by Olmsted (1906), and their absorption spectrum was recorded by Walter and Barratt (1928). The emission bands attributed to these molecules were reinvestigated by Hedfeld (1931) who had also proposed a vibrational quantum assignment for them. Harrington (1942) made an extensive absorption study of the diatomic bromides of calcium, strontium and barium and his analyses in many cases were substantiated by the presence of a vibrational isotope shift. Reddy and Rao (1966, 1968) have studied the ultraviolet emission of SrBr and CaBr molecules. Recently, Shah (1970) observed the D–X system of CaBr in h.f. discharge and Reddy *et al* (1970) have photographed a new visible spectrum $\lambda\lambda$ 4950–4600 Å in case of CaBr. Mishra and Majumdar (1966) observed a few additional bands in the thermal emission of barium bromide contained in a vacuum graphite furnace. They assigned these bands to D–X and E–X systems of BaBr. We investigated the thermal emission of alkaline earth bromides with a view to consolidate our knowledge of the thermal emission of alkaline earth bromides.

2. Experimental

The experimental procedure adopted for all the molecules under study was almost the same. In each case a small quantity of the pure substance (B.D.H.) was put in the experimental tube of the vacuum graphite furnace described by Saha *et al*

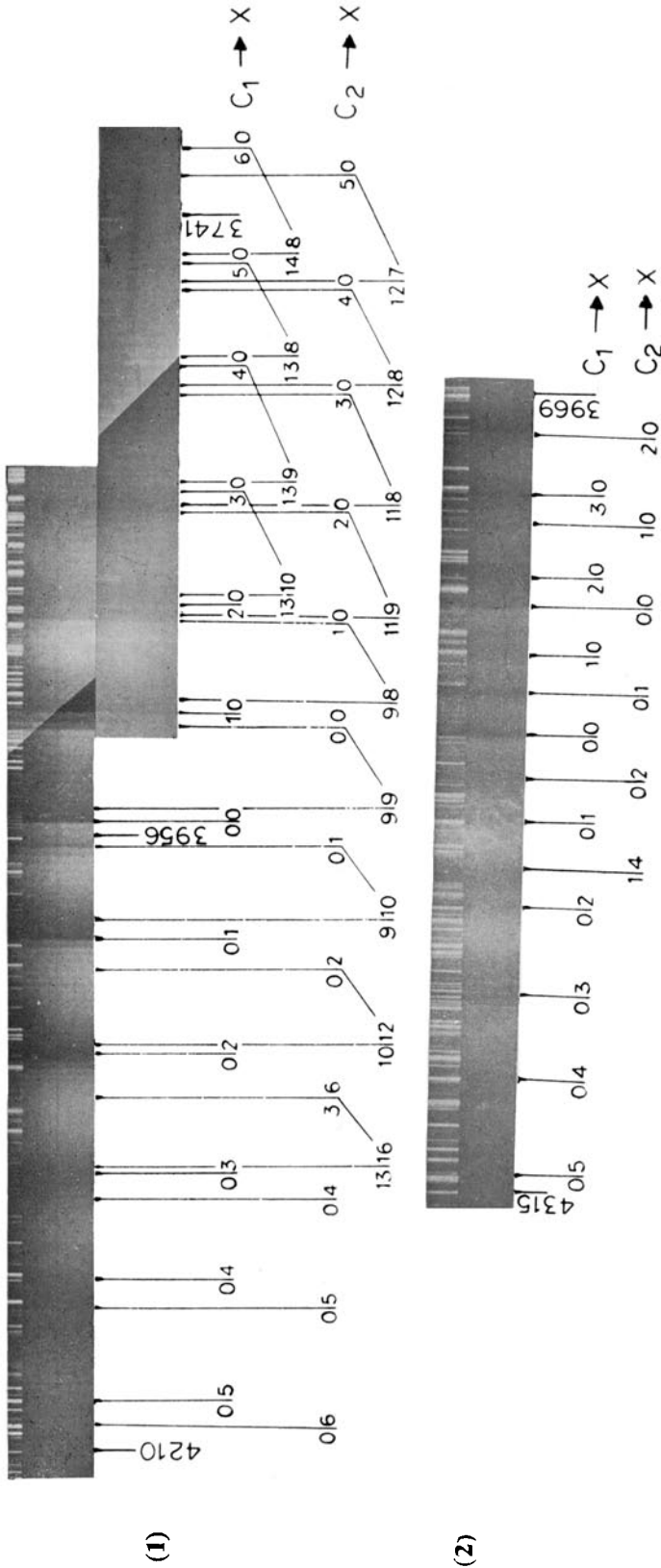
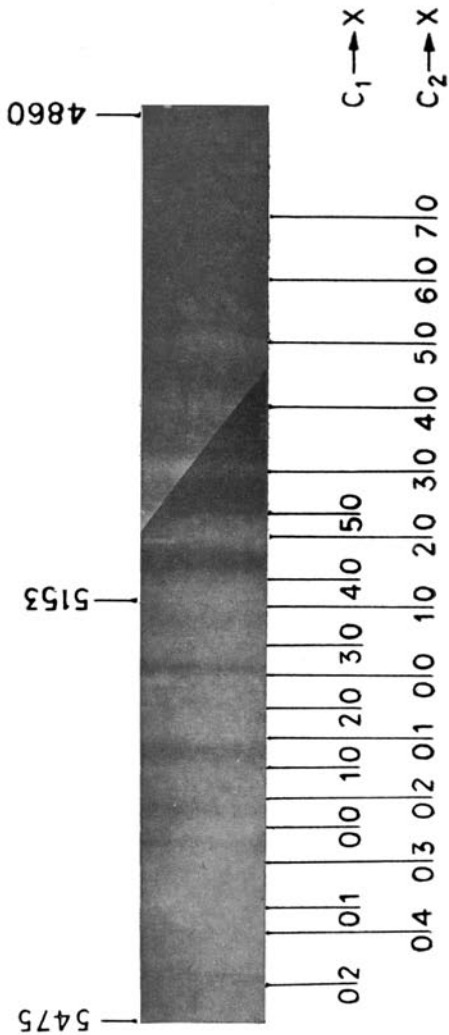


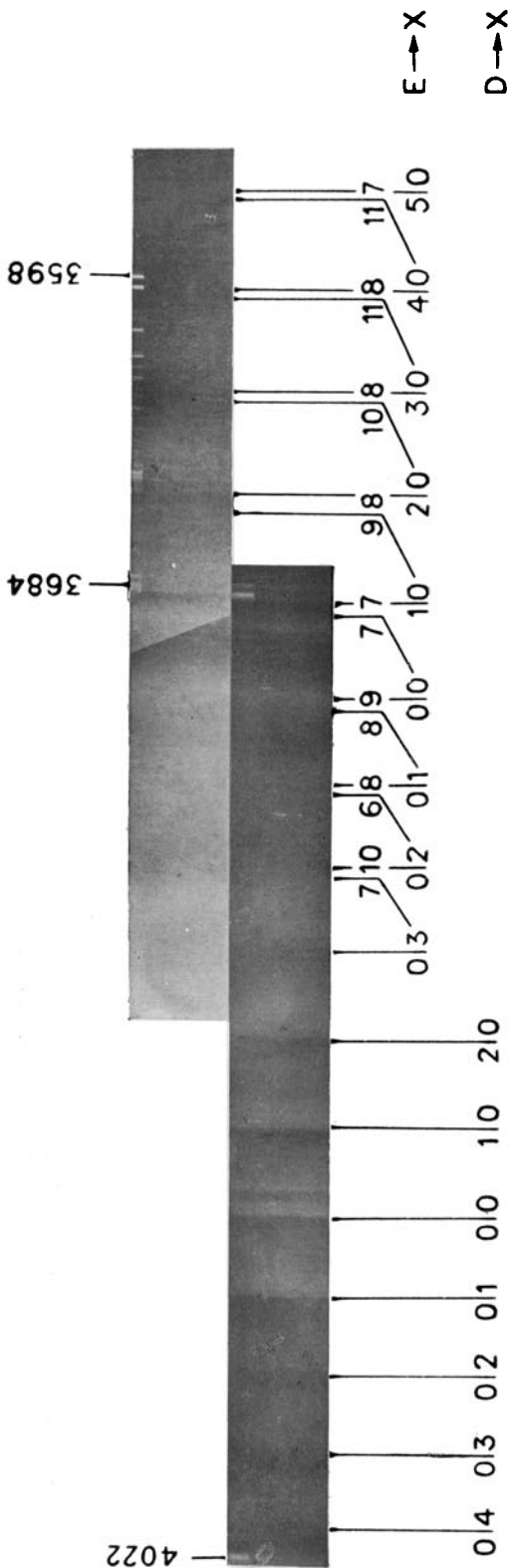
Plate 1

Figure 1. Thermal emission spectrum of CaBr molecule system $C \rightarrow X$.

Figure 2. Thermal emission spectrum of SrBr molecule system $C \rightarrow X$.



(3)



(4)

Plate 2

Figure 3. Thermal emission spectrum of BaBr molecule system C to X.

Figure 4. Thermal emission spectrum of BaBr molecule systems D to X and E to X.

(1928). The chamber of the furnace, after evacuation, was filled with pure nitrogen gas at a pressure of 45 cm of mercury. Using a Hilger E-492 large quartz spectrograph, we obtained good spectrograms at temperatures about 2200–2400° C.

Ilford R.40 panchromatic plates were used and exposure times of 2–5 min were sufficient for recording the spectra. Copper and iron arcs served as sources of comparison standard.

3. Results

3.1. *CaBr*: $C(^2\pi) \rightarrow X(^2\Sigma)$ ($\lambda\lambda$ 4200–3720 Å) system

The extensive thermal emission spectrum of CaBr recorded by us (figure 1 plate 1) reveals the presence of 141 new bands degraded to the red in addition to those observed by Harrington (1942).

All these bands have been analysed and fitted into two groups $C_1 \rightarrow X$ and $C_2 \rightarrow X$ represented by the equations:

System $C_1 \rightarrow X$ ($\lambda\lambda$ 4187–3721 Å)

$$\begin{aligned} \nu_{01} = & 25315 \cdot 1 + 265 \cdot 6 (v' + \frac{1}{2}) - 0 \cdot 90 (v' + \frac{1}{2})^2 \\ & - 286 \cdot 9 (v'' + \frac{1}{2}) + 1 \cdot 01 (v'' + \frac{1}{2})^2. \end{aligned} \quad (1)$$

System $C_2 \rightarrow X$ ($\lambda\lambda$ 4192–3726)

$$\begin{aligned} \nu_{02} = & 25537 \cdot 5 + 264 \cdot 9 (v' + \frac{1}{2}) - 1 \cdot 06 (v' + \frac{1}{2})^2 \\ & - 286 \cdot 9 (v'' + \frac{1}{2}) + 1 \cdot 01 (v'' + \frac{1}{2})^2 \end{aligned} \quad (2)$$

Out of the total of 187 bands observed, 69 have been assigned to system C_1 in the following way: 2 bands in $\Delta v = +1$ sequence, 3 bands each in $\Delta v = +2, 0$, and -5 sequences, 4 bands each in $\Delta v = -1, -3$ and -4 sequences, 7 bands in $\Delta v = -2$ sequence, 9 bands each in $\Delta v = +6$ and $+5$ sequences, 10 bands in $\Delta v = +4$ sequence and 11 bands in $\Delta v = +3$ sequence.

The remaining 118 bands have been classified in the C_2 system as, one band in $\Delta v = -6$ sequence, 8 bands in $\Delta v = +5$ sequence, 9 bands each in $\Delta v = +4, +3, +1$ sequences, 10 bands each in $\Delta v = +2, 0, -1$ sequences, 11 bands each in $\Delta v = -2, -3$ sequences with the exception of (0, 3), (1, 4), (2, 5) bands in $\Delta v = -3$ sequence, 15 bands in $\Delta v = -4$ sequence and 18 bands in $\Delta v = -5$ sequence. The maximum difference between observed and calculated values is of the order of 3 cm^{-1} for three bands which are either weak or overlapped.

Tables 1 and 2 contain the bandhead data for the systems under consideration together with a visual estimate of their intensities.

3.2. *SrBr*: $C(^2\pi) \rightarrow X(^2\Sigma)$ ($\lambda\lambda$ 4310–3880 Å) system

The spectrum of SrBr has been recorded with 53 new bands degraded to the red. The spectrogram has been displayed in figure 2 plate 1. All of them have been attributed to two groups $C_1 \rightarrow X$ and $C_2 \rightarrow X$ represented by the following expressions:

System $C_1 \rightarrow X$ ($\lambda\lambda$ 4310–3990 Å)

$$\begin{aligned} \nu_{01} = & 24343 \cdot 5 + 205 \cdot 6 (v' + \frac{1}{2}) - 0 \cdot 49 (v' + \frac{1}{2})^2 \\ & - 216 \cdot 6 (v'' + \frac{1}{2}) + 0 \cdot 51 (v'' + \frac{1}{2})^2 \end{aligned} \quad (3)$$

Table 1 Bandhead data for $C_1 \rightarrow X$ system of CaBr molecule

ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.	ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.
23,880	+1.4	2, 7*	1	25,001	+0.4	1, 2	6
23,891	+1.7	1, 6*	1	25,020	+0.4	0, 1	6
23,902	+1.7	0, 5*	1	25,263	+0.4	2, 2*	3
24,138	-0.8	3, 7*	1	25,284	+0.6	1, 1	6
24,151	-0.3	2, 6*	1	25,304	-0.5	0, 0	10
24,164	-0.1	1, 5*	1	25,546	+0.6	2, 1	4
24,178	+0.9	0, 4*	2	25,568	-0.3	1, 0	8
24,410	-1.5	3, 6	2	25,782	+0.8	4, 2	1
24,426	-0.1	2, 5*	2	25,805	-0.6	3, 1	3
24,441	+0.1	1, 4*	2	25,829	-1.3	2, 0	5
24,457	+1.1	0, 3*	3	25,835	-0.6	13, 10*	1
24,635	-2.8	6, 8*	2	25,858	+1.9	12, 9*	1
24,654	+0.2	5, 7	3	25,884	-0.8	11, 8*	1
24,670	+0.1	4, 6	3	25,910	+0.2	10, 7*	1
24,686	-0.3	3, 5	3	25,936	+1.1	9, 6*	1
24,705	+2.1	2, 4	4	25,960	-0.3	8, 5*	1
24,720	+0.3	1, 3	4	25,985	-0.9	7, 4*	1
24,738	+1.2	0, 2	4	26,011	-0.7	6, 3	2
24,963	-0.1	3, 4	5	26,037	-0.8	5, 2	2
24,983	+1.3	2, 3	6	26,064	+0.0	4, 1*	3
26,089	-1.5	3, 0*	3	26,487	+0.5	9, 4*	2
26,101	-1.3	13, 9*	1	26,517	+1.1	8, 3*	2
26,128	-0.8	12, 8*	1	26,546	+0.4	7, 2*	2
26,156	+0.4	11, 7*	1	26,575	-0.4	6, 1	2
26,183	+0.5	10, 6*	1	26,606	+0.5	5, 0*	2
26,210	+0.3	9, 5*	2	26,611	-0.4	14, 8*	1
26,240	+2.9	8, 4*	2	26,642	+0.2	13, 7*	1
26,264	-0.7	7, 3*	2	26,673	+0.7	12, 6*	1
26,292	-0.6	6, 2*	2	26,704	+0.9	11, 5*	1
26,321	+0.4	5, 1*	2	26,735	+0.9	10, 4*	1
26,347	-1.9	4, 0*	2	26,766	+0.7	9, 3*	1
26,370	-1.0	13, 8*	1	26,798	+1.2	8, 2*	1
26,399	-0.6	12, 7*	1	26,828	-0.4	7, 1*	1
26,429	+0.7	11, 6*	1	26,860	-0.3	6, 0*	1
26,458	+0.7	10, 5*	2				

* New bands observed by authors.

Table 2. Bandhead data for $C_2 \rightarrow X$ system of CaBr molecule

ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.	ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.
23,849	+1.5	0, 6*	1	24,208	-1.0	13, 17*	1
23,906	+1.9	17, 22*	1	24,226	+1.7	12, 16*	1
23,920	+2.0	16, 21*	1	24,241	+1.6	11, 15*	1
23,933	+1.4	15, 20*	1	24,253	-1.4	10, 14*	1
23,946	+0.9	14, 19*	1	24,270	+0.7	9, 13*	1
23,960	+1.5	13, 18*	1	24,285	+0.9	8, 12*	1
23,973	+1.3	12, 17*	1	24,298	-0.9	7, 11	2
23,986	+1.2	11, 16*	1	24,315	+1.5	6, 10	2
23,999	+1.2	10, 15*	1	24,328	+0.0	5, 9	2
24,012	+1.3	9, 14*	1	24,342	-0.4	4, 8	2

Table 2 (Contd.)

ν_{obs} cm ⁻¹	$(\nu_0 - \nu_c)$ cm ⁻¹	Anal. (ν' , ν'')	Int.	ν_{obs} cm ⁻¹	$(\nu_0 - \nu_c)$ cm ⁻¹	Anal. (ν' , ν'')	Int.
24,023	-0.5	8, 13*	1	24,356	-0.7	3, 7	2
24,036	-0.2	7, 12*	1	24,371	+0.0	2, 6	2
24,050	+1.2	6, 11*	1	24,386	+0.9	1, 5	2
24,061	-0.3	5, 10*	1	24,399	-0.1	0, 4	2
24,073	-0.7	4, 9*	1	24,463	+1.4	13, 16*	1
24,086	+0.0	3, 8*	1	24,480	+1.2	12, 15*	1
24,098	-0.2	2, 7*	1	24,497	+1.0	11, 14*	2
24,110	-0.3	1, 6*	1	24,514	+1.0	10, 13*	2
24,122	-0.3	0, 5*	2	24,530	+0.0	9, 12*	2
24,193	-0.6	14, 18*	1	24,547	+0.2	8, 11*	2
24,564	+0.5	7, 10	2	25,140	-0.2	5, 6*	2
24,581	+0.8	6, 9	2	25,162	+1.3	4, 5*	3
24,597	+0.3	5, 8	2	25,182	+0.9	3, 4*	4
24,614	+0.8	4, 7	2	25,202	+0.6	2, 3	5
24,630	+0.5	3, 6	2	25,222	+0.5	1, 2	5
24,773	-0.7	10, 12*	1	25,242	+0.4	0, 1	8
24,792	-0.6	9, 11*	2	25,326	+2.0	9, 9*	1
24,813	+1.5	8, 10*	1	25,348	+1.1	8, 8*	1
24,832	+1.8	7, 9*	2	25,371	+1.3	7, 7*	2
24,848	-0.9	6, 8*	2	25,394	+1.6	6, 6*	2
24,868	+0.5	5, 7	2	25,417	+2.0	5, 5*	3
24,885	-0.9	4, 6	2	25,438	+0.5	4, 4*	3
24,905	+0.7	3, 5	3	25,460	+0.1	3, 3*	4
24,923	+0.5	2, 4	3	25,482	-0.2	2, 2*	5
24,941	+0.3	1, 3	4	25,504	-0.4	1, 1	6
24,959	+0.2	0, 2	5	25,527	+0.5	0, 0	10
25,059	+1.7	9, 10*	1	25,594	+1.3	9, 8*	1
25,080	+1.8	8, 9*	2	25,619	+1.4	8, 7*	2
25,101	+2.0	7, 8*	2	25,644	+1.5	7, 6*	2
25,118	+1.6	6, 7*	2	25,668	+0.8	6, 5*	2
25,691	-0.8	5, 4*	3	26,251	-0.5	5, 2*	4
25,716	-0.3	4, 3*	3	26,280	-0.0	4, 1*	4
25,741	+0.3	3, 2*	4	26,309	+0.5	3, 0*	5
25,765	-0.1	2, 1	6	26,316	-1.5	12, 8*	1
25,789	-0.3	1, 0	8	26,350	+1.3	11, 7*	1
25,811	+1.7	11, 9*	1	26,382	+1.1	10, 6*	1
25,838	+1.6	10, 8*	2	26,412	+1.0	9, 5*	1
25,862	-1.5	9, 7*	2	26,443	+1.0	8, 4*	2
25,891	+0.6	8, 6*	2	26,472	-0.9	7, 3*	2
25,918	+0.8	7, 5*	2	26,505	+1.4	6, 2*	2
25,945	+1.0	6, 4*	3	26,535	+0.7	5, 1*	2
25,971	+0.4	5, 3*	3	26,564	+0.9	4, 0*	2
25,995	-0.2	4, 2	3	26,590	+1.8	12, 7*	1
26,023	-0.6	3, 1	5	26,621	-0.5	11, 6*	1
26,050	+0.1	2, 0	6	26,654	-0.7	10, 5*	1
26,077	+1.0	11, 8*	1	26,689	+1.2	9, 4*	1
26,109	+1.8	10, 7*	2	26,722	+1.2	8, 3*	1
26,137	+0.8	9, 6*	2	26,754	+0.3	7, 2*	1
26,166	+0.8	8, 5*	3	26,787	+0.5	6, 1*	1
26,196	+2.0	7, 4*	3	26,820	+0.8	5, 0*	2
26,223	+0.2	6, 3*	4				

* New bands observed by authors.

System $C_2 \rightarrow X$ ($\lambda\lambda$ 4185–3885 Å)

$$v_{Q_2} = 24665 \cdot 9 + 204 \cdot 9 (v' + \frac{1}{2}) - 0 \cdot 48 (v' + \frac{1}{2})^2 \\ - 216 \cdot 6 (v'' + \frac{1}{2}) + 0 \cdot 51 (v'' + \frac{1}{2})^2 \quad (4)$$

Out of the 129 bands observed in total for this system 70 have been analysed as system C_1 according to the scheme: 5 bands in $\Delta v = +1$ sequence, 6 bands each in $\Delta v = +2, 0, -4, -5$ sequences with the exception of 5 bands (1, 6), (2, 7) (3, 8), (4, 9) (6, 11) in $\Delta v = -5$ and 2 bands (1, 5) (2, 6) in $\Delta v = -4$ sequences, 7 bands in $\Delta v = -1$ sequence with the exception of (9, 6) 8 bands in $\Delta v = -1$ sequence, and 13 bands each in $\Delta v = -2, -3$ sequences.

The remaining 59 bands have been attributed to the C_2 system in the following way: 4 bands in $\Delta v = 0$ sequence, 6 bands each in $\Delta v = \pm 1$ sequences, 7 bands in $\Delta v = +7$ sequence, 9 bands in $\Delta v = +3$ sequence with the exception of 6 bands (3, 0), (10, 7), (11, 8) (12, 9) (14, 11), (16, 13), 13 bands in $\Delta v = -2$ sequence and 14 bands in $\Delta v = -3$ sequence with the exception of (0, 3) band. The maximum difference between observed and calculated values is of the order of 3 cm^{-1} for four bands which are weak.

Tables 3 and 4 display the bandhead data for the systems under consideration together with a visual estimate of their intensities.

3.3. *BaBr* : $C({}^2\pi) \rightarrow X({}^2\Sigma)$, $D({}^2\Sigma) \rightarrow X({}^2\Sigma)$ and $E({}^2\Sigma) \rightarrow X({}^2\Sigma)$ systems

The thermal emission spectrum of BaBr stretches from λ 5472 to 3565 Å and the bands have been classified into the following three distinct systems:

(a) $C({}^2\pi) \rightarrow X({}^2\Sigma)$ ($\lambda\lambda$ 5472–4862 Å) system

Nineteen additional bands have been recorded (figure 3 plate 2) and fitted into two groups $C_1 \rightarrow X$ and $C_2 \rightarrow X$ which can be represented by the equations:

System $C_1 \rightarrow X$ ($\lambda\lambda$ 5472–5093 Å)

$$v_{Q_1} = 18650 \cdot 9 + 197 \cdot 0 (v' + \frac{1}{2}) - 0 \cdot 41 (v' + \frac{1}{2})^2 \\ - 193 \cdot 8 (v'' + \frac{1}{2}) + 0 \cdot 41 (v'' + \frac{1}{2})^2 \quad (5)$$

System $C_2 \rightarrow X$ ($\lambda\lambda$ 5425–4862 Å)

$$v_{Q_2} = 19193 \cdot 0 + 197 \cdot 9 (v' + \frac{1}{2}) - 0 \cdot 41 (v' + \frac{1}{2})^2 \\ - 193 \cdot 8 (v'' + \frac{1}{2}) + 0 \cdot 41 (v'' + \frac{1}{2})^2 \quad (6)$$

Out of the 68 bands observed 39 have been classified as one band each in $\Delta v = +5, +4, +3$ sequences, two bands in $\Delta v = +2$ sequence, 5 bands in $\Delta v = -2$ sequence with exception of band (3, 5), 7 bands in $\Delta v = +1$ sequence with the exception of six bands (3, 2), (5, 4) (7, 6) (9, 8), (10, 9), (12, 11), 10 bands in $\Delta v = -1$ sequence except (2, 3) (6, 7) (8, 9) (11, 12), (13, 14), (14, 15) bands, and 12 bands in $\Delta v = 0$ sequence except (2, 2), (5, 5) (8, 8), (10, 10) (12, 12) (14, 14) (16, 16) (18, 18) bands in the C_1 system.

The remaining 29 bands have been analysed as system C_2 in the following manner: One band each in $\Delta v = +7, +6, +5, \pm 4, \pm 3, \pm 2$ sequences, 5 bands in $\Delta v = +1$ sequence with the exception of (4, 3) band; 6 bands in $\Delta v = -1$ sequence with the exception of (4, 5) band; and 9 bands in $\Delta v = 0$ sequence with the exception of the four bands (5, 5), (8, 8), (10, 10), (11, 11).

Table 3. Bandhead data for $C_1 \rightarrow X$ system of SrBr molecule

ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.	ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.
23,212	-1.6	10, 15*	1	23,662	-1.0	4, 7	2
23,220	+0.9	9, 14*	1	23,671	+0.3	3, 6	2
23,226	+1.5	8, 13*	1	23,678	-0.6	2, 5*	2
23,230	-0.1	7, 12*	1	23,686	-0.4	1, 4*	2
23,243	+1.6	5, 10*	1	23,695	+0.7	0, 3*	3
23,271	+0.7	0, 5*	1	23,802	-1.6	12, 14*	1
23,435	+0.5	7, 11*	1	23,812	-0.0	11, 13*	1
23,442	+0.9	6, 10*	1	23,820	-0.5	10, 12	1
23,447	-0.8	5, 9*	1	23,827	-2.0	9, 11	1
23,455	+0.5	4, 8*	2	23,836	-1.6	8, 10	1
23,461	-0.3	3, 7*	2	23,845	-1.3	7, 9	2
23,483	+1.2	0, 4*	1	23,854	-0.9	6, 8	2
23,602	-0.3	12, 15	1	23,862	-1.7	5, 7	2
23,610	+0.3	11, 14	1	23,871	-1.4	4, 6	2
23,616	-1.2	10, 13	1	23, 880	-1.2	3, 5	2
23,621	-1.6	9, 12	1	23,889	-1.1	2, 4	3
23,633	+0.8	8, 11	1	23,899	+0.1	1, 3	3
23,640	+0.1	7, 10	2	23,908	+0.1	0, 2*	4
23,648	+0.5	6, 9	2	24,052	-1.7	7, 8*	1
23,656	+0.8	5, 8	1	24,062	-1.4	6, 7*	1
24,072	-1.1	5, 6*	2	24,531	+0.3	2, 1	4
24,082	-0.9	4, 5	2	24,543	+0.4	1, 0	6
24,093	+0.3	3, 4	2	24,681	-1.1	7, 5	1
24,102	-0.6	2, 3	3	24,695	+0.2	6, 4	1
24,112	-0.5	1, 2	4	24,706	-1.6	5, 3	2
24,123	+0.6	0, 1	7	24,721	+0.5	4, 2	2
24,282	-1.6	5, 5*	1	24,734	+0.7	3, 1	3
24,293	-1.4	4, 4*	2	24,746	-0.3	2, 0*	4
24,304	-1.2	3, 3*	2	24,854	+1.5	10, 7*	1
24,316	-0.1	2, 2	4	24,867	-0.9	8, 5*	1
24,327	+0.0	1, 1	5	24,878	-1.8	7, 4*	1
24,338	+0.0	0, 0	10	24,907	-0.3	6, 3*	1
24,494	-1.1	5, 4*	1	24,922	+0.8	5, 2*	1
24,506	-0.9	4, 3	2	24,936	+1.0	4, 1*	2
24,517	-1.8	3, 2	2	24,948	-0.9	3, 0*	2

* New bands observed by authors.

Table 4. Bandhead data for $C_2 \rightarrow X$ system of SrBr molecule

ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.	ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.
23,901	-0.5	14, 17*	1	24,174	+1.0	6, 8	2
23,912	+2.7	13, 16	1	24,184	+1.7	5, 7	2
23,919	+1.9	12, 15	1	24,193	+1.4	4, 6	2
23,926	+1.0	11, 14	1	24,200	-1.0	3, 5	2
23,935	+2.0	10, 13	1	24,211	+0.3	2, 4	3
23,943	+1.9	9, 12	1	24,221	+0.7	1, 3	4
23,950	+0.8	8, 11	1	24,230	+0.1	0, 2*	5
23,958	+0.7	7, 10	1	24,393	+1.3	5, 6*	1
23,967	+1.5	6, 9	2	24,401	-1.1	4, 5	1
23,972	-1.8	5, 8	2	24,412	+1.3	3, 4	2

Table 4 (Contd.)

ν_{obs} cm^{-1}	$(\nu_0 - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.	ν_{obs} cm^{-1}	$(\nu_0 - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.
23,981	-1.2	4, 7	2	24,423	-0.2	2, 3	3
23,989	-1.6	3, 6*	2	24,434	+0.2	1, 2	5
23,999	-0.2	2, 5*	3	24,445	+0.6	0, 1	7
24,008	+0.3	1, 4*	3	24,625	-0.3	3, 3*	1
24,121	+2.6	12, 14	1	24,637	+0.2	2, 2	2
24,129	+1.6	11, 13	1	24,647	-1.4	1, 1	4
24,138	+1.6	10, 12	1	24,660	0.0	0, 0	10
24,146	+0.6	9, 11	1	24,800	-1.3	6, 5*	1
24,156	+0.5	8, 10	1	24,812	-1.9	5, 4*	1
24,165	+1.3	7, 9	2	24,824	-2.3	4, 3	1
24,838	-0.8	3, 2	2	25,073	+2.1	17, 14*	1
24,851	-0.4	2, 1	2	25,097	-1.5	15, 12*	1
24,864	+0.1	1, 0	4	25,125	-1.2	13, 10*	1
24,988	+1.7	8, 6*	1	25,184	+1.5	9, 6*	1
24,998	-1.5	7, 5	1	25,198	+1.3	8, 5*	1
25,014	+1.0	6, 4	2	25,210	-1.2	7, 4*	1
25,025	-1.4	5, 3	2	25,224	-1.6	6, 3*	1
25,038	-1.9	4, 2	2	25,241	+1.0	5, 2*	2
25,052	-1.4	3, 1	2	25,255	+0.6	4, 1*	2
25,066	-0.9	2, 0*	3				

* New bands observed by authors.

Table 5. Bandhead data for $C_1 \rightarrow X$ system of BaBr molecule

ν_{obs} cm^{-1}	$(\nu_0 - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.	ν_{obs} cm^{-1}	$(\nu_0 - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.
18,270	+2.6	0, 2*	4	18,675	+0.1	7, 7	2
18,274	+1.8	1, 3*	3	18,682	+0.7	9, 9	2
18,278	+1.0	2, 4*	4	18,689	+1.3	11, 11	2
18,285	-1.7	4, 6*	1	18,695	+0.9	13, 13	1
18,290	-1.6	5, 7*	1	18,699	-1.5	15, 15	1
18,458	-1.5	0, 1	5	18,707	+0.1	17, 17	1
18,464	+0.5	1, 2	4	18,714	+0.7	19, 19	1
18,470	-1.6	3, 4	3	18,848	-0.7	1, 0	6
18,476	+0.4	4, 5	2	18,852	+0.9	2, 1	4
18,481	+1.4	5, 6	2	18,856	+0.2	4, 3	3
18,487	-0.7	7, 8	1	18,861	+0.4	6, 5	2
18,494	-1.7	9, 10	1	18,866	+0.7	8, 7	2
18,500	+0.3	10, 11	1	18,872	-0.5	11, 10	1
18,509	+1.2	12, 13	1	18,878	+0.8	13, 12	1
18,520	+0.2	15, 16	1	19,043	-1.0	2, 0*	4
18,653	+0.5	0, 0	10	19,047	+1.4	3, 1*	2
18,657	+1.3	1, 1	6	19,240	+1.4	3, 0*	2
18,661	-1.1	3, 3	5	19,433	+0.3	4, 0*	1
18,665	-0.3	4, 4	4	19,626	+0.3	5, 0*	1
18,670	-0.7	6, 6	3				

* New bands observed by authors.

The maximum difference between observed and calculated values is of the order of 3 cm^{-1} for one band which is overlapped. The bandhead data and the visual estimate of the intensities have been collected in tables 5 and 6.

Table 6. Bandhead data for $C_2 \rightarrow X$ system of BaBr molecule

ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.	ν_{obs} cm^{-1}	$(\nu_o - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.
18,428	+ 0.0	0, 4*	2	19,225	+ 1.3	7, 7	2
18,617	- 1.5	0, 3*	4	19,233	+ 1.1	9, 9	2
18,810	+ 0.1	0, 2*	6	19,246	+ 1.9	12, 12	1
19,001	- 1.0	0, 1	8	19,391	- 1.1	1, 0	7
19,008	+ 1.1	1, 2	5	19,396	+ 0.6	2, 1	4
19,013	+ 1.1	2, 3	3	19,400	+ 1.4	3, 2	3
19,018	+ 1.2	3, 4	2	19,406	+ 0.8	5, 4	2
19,025	- 1.6	5, 6	1	19,410	+ 1.5	6, 5	1
19,033	+ 1.4	6, 7	1	19,590	+ 1.7	2, 0*	6
19,195	+ 0.0	0, 0	10	19,785	+ 1.2	3, 0*	4
19,198	- 1.1	1, 1	6	19,980	+ 1.6	4, 0*	3
19,202	- 1.2	2, 2	5	20,171	- 1.2	5, 0*	2
19,206	- 1.3	3, 3	4	20,367	+ 1.8	6, 0*	2
19,212	+ 0.6	4, 4	4	20,559	+ 1.6	7, 0*	1
19,221	+ 1.4	6, 6	3				

* New bands observed by authors.

(b) $D (^2\Sigma) \rightarrow X (^2\Sigma)$ ($\lambda\lambda$ 4015–3820 Å) and $E (^2\Sigma) \rightarrow X (^2\Sigma)$ ($\lambda\lambda$ 3825–3565 Å) system of BaBr

We have recorded 49 new violet degraded bands in the region $\lambda\lambda$ 4015–3565 Å. The spectrogram has been reproduced in figure 4 plate 2. All of them are single headed and can be satisfactorily assigned to the $D \rightarrow X$ and $E \rightarrow X$ systems of BaBr molecule according to the following equations :

System $D \rightarrow X$ ($\lambda\lambda$ 4015–3820 Å)

$$\begin{aligned} \nu = 25670.4 + 209.0 (\nu' + \frac{1}{2}) - 0.53 (\nu' + \frac{1}{2})^2 \\ - 193.8 (\nu' + \frac{1}{2}) + 0.41 (\nu' + \frac{1}{2})^2 \end{aligned} \quad (7)$$

System $E \rightarrow X$ ($\lambda\lambda$ 3825–3565 Å)

$$\begin{aligned} \nu = 26865.9 + 220.0 (\nu'' + \frac{1}{2}) - 0.35 (\nu'' + \frac{1}{2})^2 \\ - 193.8 (\nu'' + \frac{1}{2}) + 0.41 (\nu'' + \frac{1}{2})^2 \end{aligned} \quad (8)$$

Out of the 140 bands observed in all, 68 have been assigned to system D in the following way: 7 bands in $\Delta\nu = +2$ sequence, 8 bands each in $\Delta\nu = 0, -4$ sequences, 11 bands each in $\Delta\nu = +1, -2, -3$ sequences and 12 bands in $\Delta\nu = -1$ sequence.

The remaining 72 bands have been fitted in system E as 4 bands each in $\Delta\nu = +5, -4$ sequences except (0, 4) (1, 5) in $\Delta\nu = -4$ sequence; 7 bands each in $\Delta\nu = -1, -2, -3$ sequences; 8 bands each in $\Delta\nu = 0, +1$ sequences; and 9 bands each in $\Delta\nu = +2, +3, +4$ sequences in E→X system.

The maximum difference between observed and calculated values is of the order of 3 cm^{-1} for six bands which are weak or overlapped.

The relevant bandhead data and the visual estimate of the intensities of the bands belonging to systems $D \rightarrow X$ and $E \rightarrow X$ are presented in tables 7 and 8 respectively.

Table 7. Bandhead data for $\rightarrow X$ system of BaBr molecule

ν_{obs} cm^{-1}	$(\nu_0 - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.	ν_{obs} cm^{-1}	$(\nu_0 - \nu_c)$ cm^{-1}	Anal. (ν', ν'')	Int.
24,909	-2.0	0, 4*	2	25,309	-0.5	1, 3	4
24,928	-1.2	1, 5*	3	25,326	+0.2	2, 4	3
24,946	-1.2	2, 6*	3	25,342	+0.1	3, 5	2
24,964	-1.0	3, 7*	2	25,357	-0.8	4, 6	2
24,981	-1.5	4, 8*	1	25,373	-0.5	5, 7	1
24,999	-0.8	5, 9*	1	25,388	-0.9	6, 8*	1
25,016	-0.8	6, 10*	1	25,404	-1.0	7, 9*	1
25,033	-1.6	7, 11*	1	25,418	-2.9	8, 10*	1
25,101	-0.5	0, 3	3	25,437	+0.4	9, 11*	1
25,119	+0.1	1, 4	3	25,449	-3.0	10, 12*	1
25,136	-0.1	2, 5	3	25,486	+1.0	0, 1	6
25,153	-0.1	3, 6	2	25,502	+1.2	1, 2	6
25,170	+0.2	4, 7	2	25,517	+0.7	2, 3	5
25,185	-1.2	5, 8*	1	25,530	-1.6	3, 4	4
25,202	-0.4	6, 9*	1	25,546	-0.7	4, 5	2
25,218	-1.4	7, 10*	1	25,560	-1.5	5, 6	2
25,235	-1.2	8, 11*	1	25,576	-0.1	6, 7*	1
25,251	-1.7	9, 12*	1	25,590	-1.4	7, 8*	1
25,268	-0.9	10, 13*	1	25,605	-1.5	8, 9*	1
25,293	+0.1	0, 2	5	25,620	-1.4	9, 10*	1
25,635	-1.0	10, 11*	1	25,941	+0.9	5, 4	2
25,650	-0.4	11, 12*	1	25,954	+1.0	6, 5*	1
25,679	+1.0	0, 0	10	25,966	-0.7	7, 6*	1
25,694	+1.0	1, 1	8	25,978	-2.2	8, 7*	1
25,707	-0.7	2, 2	6	25,993	-0.4	9, 8*	1
25,723	+0.7	3, 3	4	26,006	-0.4	10, 9*	1
25,736	-0.4	4, 4	2	26,019	-0.1	11, 10*	1
25,751	+0.6	5, 5	1	26,094	+1.2	2, 0	5
25,765	+0.9	6, 6*	1	26,106	+0.4	3, 1	5
25,778	-0.7	7, 7*	1	26,118	-0.3	4, 2	3
25,887	+1.1	1, 0	7	26,130	-0.6	5, 3	2
25,900	+0.2	2, 1	6	26,143	+0.3	6, 4*	2
25,914	+0.5	3, 2	4	26,155	-0.6	7, 5*	1
25,927	+0.1	4, 3	4	26,168	-0.2	8, 6*	1

* New bands observed by authors.

4. Discussions

The thermal emission of the diatomic alkaline earth bromides, *viz.*, CaBr, SrBr, and BaBr has yielded a large number of new bands. All the new bands have been satisfactorily explained by the expressions (1) to (8). It may be mentioned that these expressions are in close agreement with those which were first proposed by Harrington (1942) on the basis of absorption studies. From the distribution of intensity in various spectrograms (figures 1 and 2 plate 1, and figures 3 and 4 plate 2) it is evident that in each case the most intense bands lie on well-formed parabola whose shape conforms to the nature of the vibrational constants of the concerned molecule. In view of the above facts it appears that the bands have been rightly attributed to the diatomic alkaline earth bromides. While $D \rightarrow X$ and $E \rightarrow X$ systems in BaBr have been recorded the same have failed to appear in case of CaBr and SrBr. This is presumably due to the fact that systems $D \rightarrow X$ and $E \rightarrow X$ for the two molecules lie farther in ultraviolet and hence it is energetically difficult to excite them thermally.

Table 8. Bandhead data for E → X system of BaBr molecule

ν_{obs} cm ⁻¹	$(\nu_0 - \nu_c)$ cm ⁻¹	Anal. (ν' , ν'')	Int.	ν_{obs} cm ⁻¹	$(\nu_0 - \nu_c)$ cm ⁻¹	Anal. (ν' , ν'')	Int.
26,172	+0.7	2, 6*	3	26,740	-0.4	2, 3	5
26,202	+0.8	3, 7	2	26,768	+0.2	3, 4	4
26,233	+1.9	4, 8	2	26,796	+0.7	4, 5	3
26,264	+2.8	5, 9	1	26,823	+0.1	5, 6	2
26,302	-0.5	0, 3	5	26,853	+2.3	6, 7	1
26,331	-0.3	1, 4	5	26,879	+0.0	0, 0	8
26,360	-0.2	2, 5	4	26,905	-0.3	1, 1	6
26,390	+0.8	3, 6	3	26,931	-0.8	2, 2	5
26,419	+0.6	4, 7	2	26,958	-0.3	3, 3	4
26,450	+2.4	5, 8	1	26,985	+0.0	4, 4	3
26,479	+2.0	6, 9*	1	27,011	-0.8	5, 5	2
26,494	+0.1	0, 2	6	27,038	-0.7	6, 6	1
26,522	+0.2	1, 3	5	27,065	-0.8	7, 7	1
26,550	+0.1	2, 4	4	27,098	-0.3	1, 0	6
26,579	+0.9	3, 5	4	27,124	+0.1	2, 1	6
26,608	+1.6	4, 6	3	27,150	+0.3	3, 2	5
26,636	+1.1	5, 7	2	27,176	+0.5	4, 3	4
26,666	+2.6	6, 8*	1	27,201	-0.5	5, 4	4
26,686	+0.0	0, 1	7	27,227	-0.6	6, 5	3
26,713	-0.2	1, 2	6	27,254	+0.2	7, 6	2
27,281	+0.8	8, 7	1	27,682	+0.1	9, 6	2
27,317	+0.1	2, 0	5	27,708	+1.1	10, 7	1
27,342	+0.2	3, 1	5	27,733	+1.1	11, 8*	1
27,366	-0.9	4, 2	4	27,751	-1.0	4, 0	2
27,392	+0.0	5, 3	4	27,776	+0.5	5, 1	2
27,416	-1.3	6, 4	3	27,798	-1.2	6, 2	2
27,443	+0.3	7, 5	3	27,822	-0.9	7, 3	3
27,468	-0.2	8, 6	2	27,848	+1.2	8, 4	2
27,493	-0.9	9, 7*	1	27,879	-1.8	9, 5	2
27,519	-0.6	10, 8*	1	27,896	+1.1	10, 6*	1
27,535	+0.2	3, 0	3	27,920	+0.8	11, 7*	1
27,560	+1.0	4, 1	4	27,944	+0.5	12, 8*	1
27,583	-0.4	5, 2	4	27,969	+0.5	5, 0*	1
27,609	+1.2	6, 3	3	27,990	-1.3	6, 1*	2
27,631	-1.4	7, 4	3	28,015	+0.7	7, 2*	2
27,755	-2.1	8, 5	3	28,038	+0.7	8, 3*	1

* New bands observed by authors.

Table 9. Spectral data of alkaline earth bromides

	MgBr	CaBr	SrBr	BaBr
ω_e'' cm ⁻¹ (X)	373.2	286.9	216.6	193.8
ω_e' cm ⁻¹ (C)	(222.5)*	265.3	205.2	197.4
ν_e cm ⁻¹ (C ₂)	39309	25537	24666	19193
ν_e cm ⁻¹ (C ₁)	39200	25315	24343	18651
Doublet separation cm ⁻¹	109	222	323	542
ω_e'/ω_e''	(0.60)*	0.92	0.95	1.02
D_0^0 (eV)	(3.36†)	2.54	2.86	2.85

* Value uncertain.

† From predissociation observed in A ← X system (Harrington 1942).

The II A subgroup of the periodic table consists of six elements, viz., Be, Mg, Ca, Sr, Ba and Ra. The diatomic bromides of each one of them, except that of Ra, have been investigated spectroscopically and save for BeBr, the transition $C \rightarrow X$ has been observed in each case. The salient features of this transition in these molecules provide an example of homologous spectra. This transition is characterised by well-marked sequences and two equally intense systems which appear to arise from the doublet components of the upper electronic state. Table 9 incorporates the relevant data for these molecules with reference to system $C \rightarrow X$. The ω'_e/ω''_e and D_0^0 values for MgBr have been calculated on the basis of the molecular constants taken from Rosen (1970).

The behaviour of the ground state vibrational frequencies is quite satisfactory and the plot of number of electrons (n_e) against ω''_e values is a smooth curve (figure 5). Further, it can also be noticed from table 9 that the doublet separation in the two components of the upper electronic state increases quite regularly from MgBr ($\sim 109 \text{ cm}^{-1}$) to BaBr ($\sim 542 \text{ cm}^{-1}$). According to Howell (1936), the similarity of the ratio ω'_e/ω''_e in such cases indicates that the same type of relative loosening takes place in the molecular binding on excitation. That a similar situation exists in present case also can be readily inferred from table 9, where the ratio ω'_e/ω''_e is strikingly similar, except for MgBr. This discrepancy is, however, accounted for by the fact that the ω'_e value for MgBr is not reliably known and consequently that ratio becomes uncertain. The heat of dissociation D_0^0 has been calculated for these molecules with the help of the vibrational constants. Since very high vibrational quanta have been observed in the ground state the extrapolated values described in table 9 appear to be reasonably accurate. These values also show a similarity in behaviour.

From rotational studies in CaF the $C-X$ system for this molecule has been established as a ${}^2\Pi - {}^2\Sigma^+$ transition (Jevons 1932). Although no rotational data exist for the bromides under discussion, on comparing the similarity of features of $C-X$ system in CaF with that in CaBr, it is easy to infer that both of them involve similar electronic states.

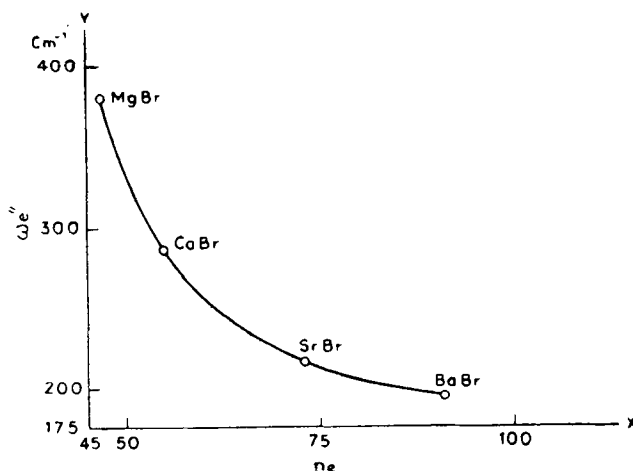


Figure 5. Variation of ω''_e of II A subgroup bromides with n_e .

Since there exists a close structural parallelism between the corresponding systems of SrBr and BaBr with the C — X system of CaBr, it is natural to interpret that presumably all of them arise from the similar $2\pi - 2\Sigma^+$ transition. Harrington (1942) has reported the presence of four heads, viz., R_1 , Q_1 , R_2 and Q_2 with Q_1 and Q_2 being comparatively more intense. The existence of four bandheads and the order of magnitude of the doublet separation observed for the state indicate that in all probability the 2π state in question is intermediate between Hund's is Grateful to coupling cases (a) and (b).

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