

THE ELECTRONIC BAND SPECTRUM OF CaI IN THE RED REGION

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The emission band spectrum of CaI is excited in a high frequency discharge and photographed in the first order (reciprocal dispersion, 1.25 Å/mm) of a 21 ft. concave grating spectrograph. High resolution spectrograms in the region 6100–6600 Å, obtained for the first time, have shown the existence of two doublet systems consisting of a number of well marked sequences of bands degraded to shorter wavelengths. The systems of double headed bands are vibrationally analysed and attributed to $A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ transitions analogous to the $A-X$ and $B-X$ systems of the other halides of calcium. The vibrational constants of the ground and excited states and the spin doublet intervals of analogous states of the isoelectronic molecules are compared. A brief discussion of the electronic states is given.

1. Introduction

The band spectrum of CaI as investigated previously [1–4] was known to consist of groups of bands in three spectral regions: 6220–6690 Å, 4110–4440 Å, and 3075–3290 Å. Murty et al. [5], reinvestigated the bands in the visible region under high resolution (1.25 Å/mm). They analysed and attributed the bands to a $C^2\Pi - X^2\Sigma^+$ transition with a doublet interval of about 428 cm^{-1} . The spectrum of CaI in the region 6270–6690 Å has been studied [6–8], and the bands were analysed on the basis of two systems $A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$. However, the band head assignments were at variance with each other, due probably to the low and medium resolutions employed.

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Therefore, following the study of visible bands [5], it was felt desirable to reinvestigate the bands in the region 6200—6600 Å under high resolution in order to provide a comprehensive vibrational analysis of these band systems. Further, the recent spectroscopic studies of some of the C—S stars [9], supported the purpose of this high resolution study.

In the present investigation, the bands in the red region have been photographed in the first order of a 21 ft. concave grating spectrograph. High resolution spectrograms obtained in the present work, have shown the existence of over 200 bands as against 76 bands observed previously [8]. A new vibrational analysis of these double headed bands is proposed. The bands are analysed and attributed to $A^2\Pi-X^2\Sigma^+$ with a spin doublet separation of 60.4 cm^{-1} and $B^2\Sigma^+-X^2\Sigma^+$ systems analogous to the $A-X$ and $B-X$ systems of CaF, CaCl, and CaBr molecules. The details of the experimental procedure and the analysis are discussed in the following sections.

2. Experimental details

The spectrum of CaI, in the red region was excited in a radio frequency discharge from a 500 watt oscillator working at 30—40 MHz. The discharge tube was an all quartz transparent tube of 30 cm length with a central capillary part, 30 mm long and 3 mm diameter. Spectroscopically pure sample of CaI_2 (supplied by E. Merck, Federal Republic of Germany) was placed in the discharge tube which was then evacuated continuously. The characteristic colour of the discharge observed in the central capillary portion of the tube was intense crimson. To maintain this intense crimson colour, intermittent external heating by means of a special Bunsen burner was found necessary.

The spectrum was first photographed under the low dispersion of a glass Littrow spectrograph. An exposure time of 5 minutes was found sufficient to record the bands. The bands were thereafter photographed under high resolution. Exposures of 20—40 minutes duration on Ilford HP_3 photographic plates were found sufficient to obtain intense spectrograms of all the sequences.

A DC iron arc was used for the comparison spectrum. Measurements of the band heads were made on a Hilger comparator using second order iron arc wavelengths taken from the MIT tables. Vacuum wavenumbers were calculated using a computer program which fits the dispersion curve to a cubic polynomial. The relative error in the wavenumbers of the intense band heads is in general less than 0.15 cm^{-1} .

3. Results and analysis

The spectrum of the CaI molecule in the region 6100—6600 Å photographed under low resolution of a glass Littrow spectrograph consists of several close groups of bands degraded to shorter wavelengths. From the high resolution spectrograms obtained, all the groups are seen to be well resolved and are identified as sequences of double headed bands of two systems designated as $A^2\Pi-X^2\Sigma^+$ and $B^2\Sigma^+-X^2\Sigma^+$. We present below the experimental data and the vibrational analyses of the two band systems.

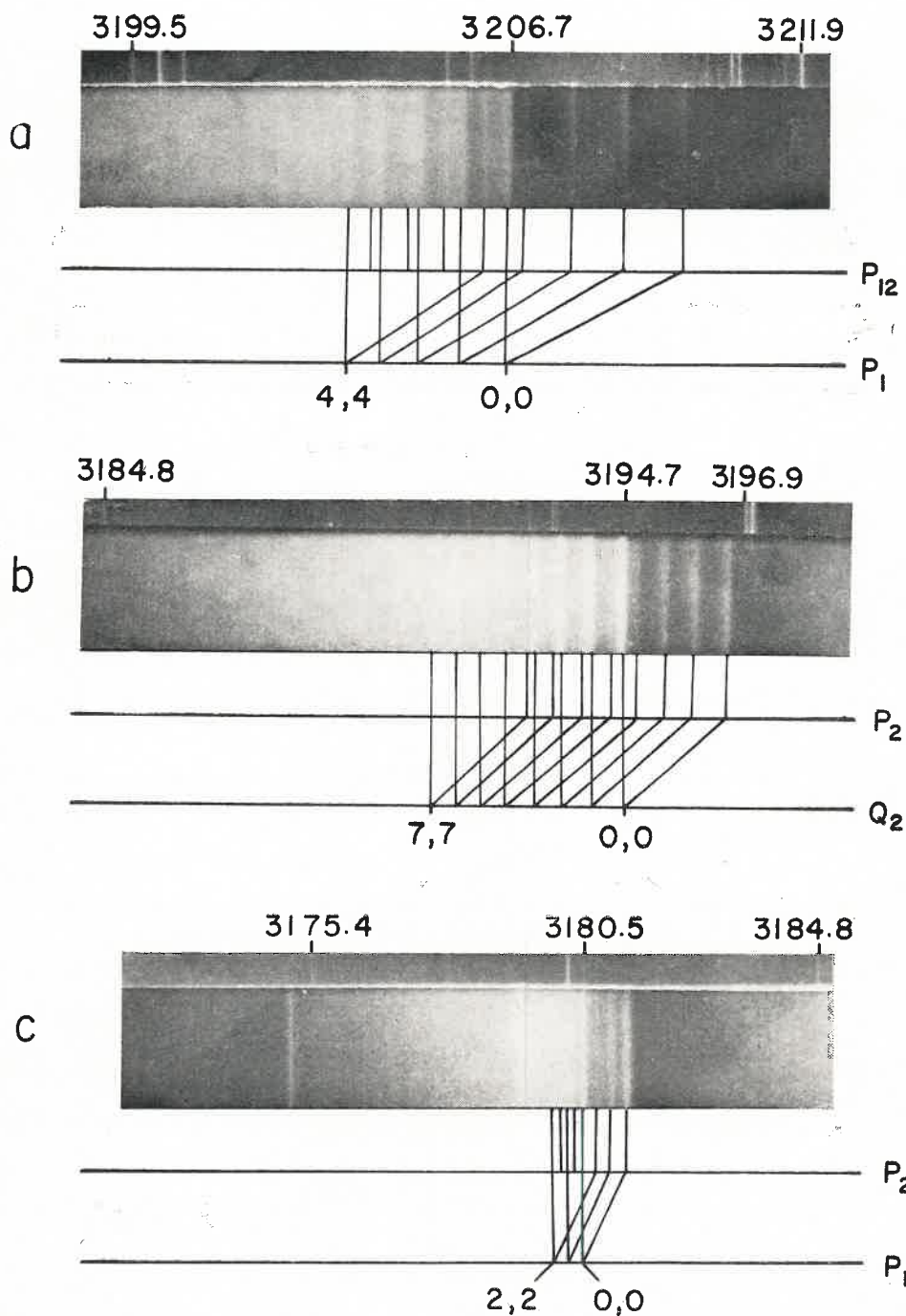


Fig. 1. The $\Delta v = 0$ sequence of the $A-X$ and $B-X$ system of CaI. a. The $\Delta v = 0$ sequence of $A^2\Pi_{1/2} - X^2\Sigma^+$. b. The $\Delta v = 0$ sequence of $A^2\Pi_{3/2} - X^2\Sigma^+$. c. The $\Delta v = 0$ sequence of $B^2\Sigma^+ - X^2\Sigma^+$. (The CaI spectrum is photographed in the 1st order. The standard iron arc spectrum is in the 2nd order)

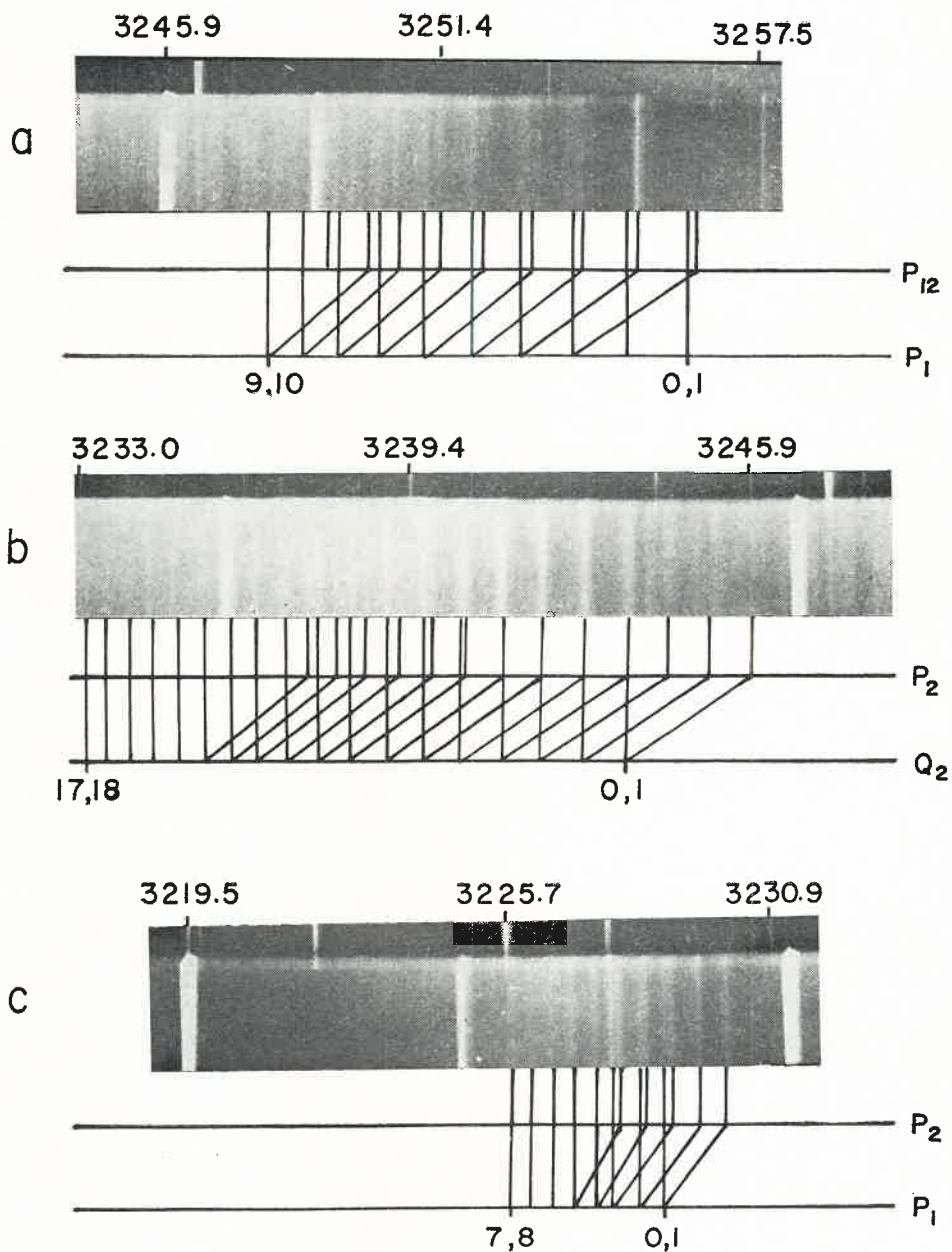


Fig. 2 The $\Delta v = -1$ sequence of the $A-X$ and $B-X$ system of CaI. a. The $\Delta v = -1$ sequence of $A^2\Pi_{1/2} - X^2\Sigma^+$. b. The $\Delta v = -1$ sequence of $A^2\Pi_{3/2} - X^2\Sigma^+$. c. The $\Delta v = -1$ sequence of $B^2\Sigma^+ - X^2\Sigma^+$. (The CaI spectrum is photographed in the 1st order. The standard iron arc spectrum is in the 2nd order)

3.1. $A^2\Pi - X^2\Sigma^+$ system

From intensity considerations the sequences at 6413.4 Å and 6389.4 Å are easily identified as $\Delta v = 0$ sequences of the two subsystems. Sequences $\Delta v = \pm 1$ and ± 2 are also identified. The $\Delta G(v)$ intervals of the common lower state of the two sub-systems agree very closely with the corresponding intervals of the lower state of the $C^2\Pi - X^2\Sigma^+$ system analysed by Murty et al. [5]. It is therefore concluded that the lower states are the same, most probably the ground state of the molecule. The double headed nature of the bands is ascribed to the spin-splitting of the $A^2\Pi$ state.

The high resolution spectrograms of $\Delta v = 0$ and -1 sequences of the $A^2\Pi - X^2\Sigma^+$ systems are shown in Figs. 1 and 2. From the nature of a $^2\Pi - ^2\Sigma$ transition, for bands degraded to shorter wavelengths, we expect the following head forming branches: P_{12} and P_1 for $^2\Pi_{1/2} - X^2\Sigma$ and P_2 and Q_2 for $^2\Pi_{3/2} - X^2\Sigma$, assuming $^2\Pi$ as a regular state. Thus each band with a particular value of v' and v'' is expected to consist of two heads in each sub-system. The detailed classification of band heads is shown in Figs. 1 and 2.

The vibrational constants of the upper and lower states of the system are obtained by plotting the mean values of the vibrational intervals $\Delta G(v+1/2)$, against the corresponding $v+1/2$ values. From these plots, it is inferred that in order to obtain a satisfactory fit, the vibrational terms $G(v)$ should be represented as

$$G(v) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3.$$

The vibrational quanta $\Delta G(v+1/2)$ are represented by

$$\Delta G(v+1/2) = G(v+1) - G(v) = a - b(v+1/2) + c(v+1/2)^2, \quad (1)$$

where

$$a = \omega_e - \omega_e x_e + \omega_e y_e, \quad b = 2\omega_e x_e - 3\omega_e y_e \quad \text{and} \quad c = 3\omega_e y_e.$$

Using the second order polynomial fit given by equation (1), the values of the constants a , b and c for each of the electronic states of the $A - X$ system are obtained. These values are then used to calculate the vibrational constants of the system. The following are the vibrational constants (in cm^{-1}) for the strong P_1 and Q_2 heads of the two sub-systems:

$$\begin{aligned} P_1: v_e = 15585.2; \quad \omega'_e = 243.4; \quad \omega'_e x'_e = 0.81; \\ \omega''_e = 238.37; \quad \omega''_e x''_e = 0.648; \quad \omega''_e y''_e = -0.0017. \\ Q_2: v_e = 15645.6; \quad \omega'_e = 241.31; \quad \omega'_e x'_e = 0.725; \quad \omega'_e y'_e = 0.0024; \\ \omega''_e = 238.37; \quad \omega''_e x''_e = 0.648; \quad \omega''_e y''_e = -0.0017. \end{aligned}$$

As a check on the calculations and the assignments of v' and v'' , the wavenumbers of the bands are calculated by using the above constants. The agreement between the observed and calculated values of the band heads as seen from the last column of Tables I

TABLE I

Band head data of the sub-system $A^2\Pi_{1/2} - X^2\Sigma^+$

$\nu_{\text{obs}}(\text{cm}^{-1})$	Rel. int. ^a	Band head	ν', ν''	$\nu_{\text{obs}} - \nu_{\text{calc}}$
15130.2	m	P_1	2, 4	1.3
15135.8	m	P_1	3, 5	0.3
15141.2	w	P_1	4, 6	-0.4
15145.6	w	P_1	5, 7	-1.8
15350.8	w	P_1	0, 1	0.2
15356.5	m	P_1	1, 2	-0.1
15361.5	m	P_1	2, 3	-0.7
15349.9	vw	P_{12}	2, 3	
15367.2	s	P_1	3, 4	-0.3
15355.5	vw	P_{12}	3, 4	
15371.7	s	P_1	4, 5	-0.7
15360.3	w	P_{12}	4, 5	
15376.0	m	P_1	5, 6	-0.9
15365.0	w	P_{12}	5, 6	
15380.3	m	P_1	6, 7	-0.8
15369.4	m	P_{12}	6, 7	
15383.9	w	P_1	7, 8	-0.9
15373.6	m	P_{12}	7, 8	
15387.4	w	P_1	8, 9	-0.7
15377.5	m	P_{12}	8, 9	
15389.8	w	P_1	9, 10	-1.2
15380.5	w	P_{12}	9, 10	
15384.3	w	P_{12}	10, 11	
15587.8	vs	P_1	0, 0	0.1
15572.2	s	P_{12}	0, 0	
15592.6	s	P_1	1, 1	0.2
15578.0	s	P_{12}	1, 1	
15396.5	s	P_1	2, 2	0.2
15582.6	m	P_{12}	2, 2	
15600.3	m	P_1	3, 3	-0.4
15586.9	w	P_{12}	3, 3	
15603.0	m	P_1	4, 4	-1.4
15590.8	w	P_{12}	4, 4	
15594.4	w	P_{12}	5, 5	
15597.4	vw	P_{12}	6, 6	
15601.2	vw	P_{12}	7, 7	
15829.6	vw	P_1	1, 0	0.1
15832.4	w	P_1	2, 1	-0.1
		P_1	17, 16	0.1
15835.7	w	P_1	3, 2	0.4
		P_1	16, 15	0.3
15837.4	w	P_1	4, 3	-0.3
		P_1	15, 14	-0.6
15839.4	w	P_1	5, 4	-0.3
		P_1	14, 13	-0.7

TABLE I (continued)

$\nu_{\text{obs}}(\text{cm}^{-1})$	Rel. int. ^a	Band head	ν', ν''	$\nu_{\text{obs}} - \nu_{\text{calc}}$
15841.8	m	P_1	6, 5	0.4
		P_1	13, 12	0.0
15842.9	m	P_1	7, 6	-0.3
		P_1	12, 11	-0.1
15843.2	m	P_1	8, 7	-0.3
		P_1	11, 10	-0.5
15844.4	m	P_1	9, 8	0.4
		P_1	10, 9	0.3
16069.7	m	P_1	2, 0	0.1
		P_1	11, 9	0.0
16071.4	m	P_1	3, 1	0.3
		P_1	10, 8	0.2
16072.5	m	P_1	4, 2	0.4
		P_1	9, 7	0.1
16073.2	w	P_1	5, 3	-0.2
16068.7	m	P_1	12, 10	1.0
16066.0	m	P_1	13, 11	0.7
16062.7	m	P_1	14, 12	0.2
16058.8	m	P_1	15, 13	-0.4
16054.7	m	P_1	16, 14	-0.7
16050.0	m	P_1	17, 15	-1.2
16046.0	m	P_1	18, 16	-0.6
16042.1	m	P_1	19, 17	-0.8
16036.9	m	P_1	20, 18	-1.2

^a Abbreviations used: vs, s, m, w, and vw denote, very strong, strong, medium, weak, and very weak, respectively.

TABLE II

Band head data of the sub-system $A^2\Pi_{3/2} - X^2\Sigma^+$

$\nu_{\text{obs}}(\text{cm}^{-1})$	Rel. int. ^a	Band head	ν', ν''	$\nu_{\text{obs}} - \nu_{\text{calc}}$
15184.1	m	Q_2	2, 4	-0.5
15189.2	m	Q_2	3, 5	-0.5
15195.8	m	Q_2	4, 6	1.3
		P_2	7, 9	
15199.6	m	Q_2	5, 7	0.4
		P_2	8, 10	
15186.4	w	P_2	5, 7	
15203.9	m	Q_2	6, 8	0.1
15191.0	w	P_2	6, 8	
15208.9	m	Q_2	7, 9	0.7
15212.7	m	Q_2	8, 10	0.3

TABLE II (continued)

$\nu_{\text{obs}}(\text{cm}^{-1})$	Rel. int. ^a	Band head	ν', ν''	$\nu_{\text{obs}} - \nu_{\text{calc}}$
15216.9	w	Q_2	9, 11	0.4
15206.3	w	P_2	9, 11	
15220.6	w	Q_2	10, 12	0.1
15210.8	w	P_2	10, 12	
15224.6	w	Q_2	11, 13	0.2
15214.7	w	P_2	11, 13	
15228.3	w	Q_2	12, 14	0.2
15218.9	vw	P_2	12, 14	
15231.8	w	Q_2	13, 15	0.1
15223.0	vw	P_2	13, 15	
15235.1	vw	Q_2	14, 16	-0.1
15410.0	s	Q_2	0, 1	0.0
		P_2	3, 4	
15399.4	w	P_2	0, 1	
15414.1	s	Q_2	1, 2	0.1
		P_2	4, 5	
15401.5	w	P_2	1, 2	
15418.1	s	Q_2	2, 3	0.1
		P_2	5, 6	
15406.1	m	P_2	2, 3	
15421.8	s	Q_2	3, 4	-0.1
		P_2	6, 7	
15425.6	s	Q_2	4, 5	0.3
15429.2	m	Q_2	5, 6	0.4
15432.5	m	Q_2	6, 7	0.4
15435.8	m	Q_2	7, 8	0.5
15425.2	w	P_2	7, 8	
15438.6	m	Q_2	8, 9	0.3
15428.4	w	P_2	8, 9	
15441.8	m	Q_2	9, 10	0.5
15431.6	w	P_2	9, 10	
15444.4	m	Q_2	10, 11	0.3
15434.4	w	P_2	10, 11	
15447.0	m	Q_2	11, 12	0.3
15437.2	vw	P_2	11, 12	
15449.2	w	Q_2	12, 13	-0.1
15439.8	vw	P_2	12, 13	
15452.1	w	Q_2	13, 14	0.3
15454.7	w	Q_2	14, 15	0.6
15456.5	w	Q_2	15, 16	0.2
15458.6	vw	Q_2	16, 17	0.1
15460.3	vw	Q_2	17, 18	-0.2
15646.7	vs	Q_2	0, 0	-0.4
15636.9	s	P_2	0, 0	
15649.7	vs	Q_2	1, 1	-0.1
15639.8	s	P_2	1, 1	
15652.5	s	Q_2	2, 2	0.0

TABLE II (continued)

$\nu_{\text{obs}}(\text{cm}^{-1})$	Rel. in. ^a	Band head	v', v''	$\nu_{\text{obs}} - \nu_{\text{calc}}$
15642.8	m	P_2	2, 2	
15655.2	s	Q_2	3, 3	0.2
15645.7	m	P_2	3, 3	
15657.7	m	Q_2	4, 4	0.4
15648.1	w	P_2	4, 4	
15660.0	m	Q_2	5, 5	0.4
15650.6	w	P_2	5, 5	
15662.3	m	Q_2	6, 6	0.7
15653.1	vw	P_2	6, 6	
15663.7	w	Q_2	7, 7	0.1
15655.7	vw	P_2	7, 7	
15887.1	w	Q_2	1, 0	0.2
15888.4	w	Q_2	2, 1	0.1
15889.7	w	Q_2	3, 2	0.2
15890.4	m	Q_2	4, 3	-0.2
15891.3	m	Q_2	5, 4	-0.3
15892.0	m	Q_2	6, 5	0.4
16125.0	w	Q_2	2, 0	-0.3
16123.9	m	Q_2	7, 5	0.0

^a See Table I for abbreviations used.

nad II can be regarded as satisfactory. For at least 93% of the band heads of these two sub-systems, the differences $\nu_{\text{obs}} - \nu_{\text{calc}}$ are $\leq 1 \text{ cm}^{-1}$. The vacuum wavenumbers of the bandheads, their relative intensities, and the vibrational assignments are included in Tables I and II for the two sub-systems of the $A^2\Pi - X^2\Sigma^+$ transition.

3.2. $B^2\Sigma^+ - X^2\Sigma^+$ system

The intense sequence at 6361.0 \AA is identified as the $\Delta v = 0$ sequence of the system. Along with it, the $\Delta v = \pm 1$ and ± 2 sequences are also observed. The $\Delta G(v)$ intervals of the lower state again agree with those of the $X^2\Sigma^+$ state of the CaI molecule. The double headed nature of the bands could be attributed to the transition $B^2\Sigma^+ - X^2\Sigma^+$ analogous to the $B^2\Sigma^+ - X^2\Sigma^+$ transition of other alkaline earth halides. The double heads are taken as the P_1 and P_2 heads. The separation of about 4.2 cm^{-1} between P_1 and P_2 heads, is due to the large spin splitting in the upper state.

The detailed classification of the band heads of $\Delta v = 0$ and -1 sequence is also shown in Figs. 1 and 2. The vacuum wavenumbers, relative intensities and vibrational quantum numbers are included in Table III. The method of obtaining the vibrational constants of the upper and lower states of this system is essentially the same as the one described for the $A - X$ system. It is to be noted here that the ground state constants are chosen as the mean of the average $\Delta G(v+1/2)$ values of the $A - X$ and $B - X$ systems. The following are the constants (in cm^{-1}) for the P_1 and P_2 heads.

TABLE III

Band head data of the system $B^2\Sigma^+ - X^2\Sigma^+$

$\nu_{\text{obs}}(\text{cm}^{-1})$	Rel. int. ^a	Band head	v', v''	$\nu_{\text{obs}} - \nu_{\text{calc}}$
15246.8	m	P_2	2, 4	-0.4
15250.5	m	P_2	3, 5	-0.6
15252.7	w	P_1	2, 4	1.3
15254.3	m	P_2	4, 6	-0.6
15256.3	vw	P_1	3, 5	1.0
15257.6	m	P_2	5, 7	-1.0
15259.5	vw	P_1	4, 6	0.4
15261.2	w	P_2	6, 8	-0.7
15262.9	vw	P_1	5, 7	0.1
15264.3	w	P_2	7, 9	-0.7
15266.1	vw	P_1	6, 8	0.0
15267.9	vw	P_2	8, 10	0.1
15475.0	m	P_2	0, 1	0.1
15480.4	m	P_1	0, 1	1.3
15477.6	m	P_2	1, 2	-0.1
15483.0	m	P_1	1, 2	1.1
15480.2	m	P_2	2, 3	-0.2
15485.2	m	P_1	2, 3	0.6
15482.7	m	P_2	3, 4	-0.4
15487.3	m	P_1	3, 4	0.0
		P_2	5, 6	-0.7
15484.9	s	P_2	4, 5	-0.8
15489.4	m	P_1	4, 5	-0.5
		P_2	6, 7	-0.6
15491.5	w	P_1	5, 6	-0.8
		P_2	7, 8	-0.7
15493.1	w	P_1	6, 7	-1.4
		P_2	8, 9	-0.6
15494.9	w	P_1	7, 8	-1.5
		P_2	9, 10	0.0
15712.0	s	P_2	0, 0	0.0
15716.2	s	P_1	0, 0	0.0
		P_2	3, 3	0.2
15713.5	m	P_2	1, 1	0.0
15717.8	m	P_1	1, 1	0.1
15715.0	m	P_2	2, 2	0.0
15719.6	w	P_1	2, 2	0.4
		P_2	6, 6	-0.2
15717.4	w	P_2	4, 4	-0.3
15718.8	w	P_2	5, 5	-0.1
15950.7	w	P_2	1, 0	0.2
		P_2	4, 3	-0.3
		P_2	5, 4	-0.2
15954.8	w	P_1	1, 0	0.1
		P_1	2, 1	-0.2

TABLE III (continued)

$\nu_{\text{obs}}(\text{cm}^{-1})$	Rel. int. ^a	Band head	ν', ν''	$\nu_{\text{obs}} - \nu_{\text{calc}}$
15951.2	w	P_2	2, 1	0.4
		P_2	3, 2	0.3
15955.3	w	P_1	3, 2	0.2
		P_1	4, 3	0.1
15949.8	vw	P_2	6, 5	-0.8
16188.0	w	P_2	2, 0	0.1
		P_1	5, 3	-0.4
16186.1	w	P_2	3, 1	-0.6
		P_1	6, 4	-0.7
16185.6	w	P_2	4, 2	0.1
16189.7	w	P_1	4, 2	0.0
16184.5	w	P_2	5, 3	0.3
		P_1	7, 5	-0.5
16182.8	m	P_2	6, 4	0.2
		P_1	8, 6	-0.1
16181.0	m	P_2	7, 5	0.2
16178.6	m	P_2	8, 6	-0.1
16176.5	m	P_2	9, 7	0.2

^a See Table I for abbreviations used.

$$P_1, P_2: \nu_e = 15715.4 \text{ and } 15711.2;$$

$$\omega'_e = 239.86; \quad \omega'_e x'_e = 0.62; \quad \omega'_e y'_e = -0.0065;$$

$$\omega''_e = 238.37; \quad \omega''_e x''_e = 0.648; \quad \omega''_e y''_e = -0.0017.$$

The close agreement between the observed and calculated values of the P_1 and P_2 heads can be regarded as satisfactory as seen from the last column of Table III. It is seen that the differences $\nu_{\text{obs}} - \nu_{\text{calc}}$, for at least 92% of the band heads of this system, are $\bar{\leq} 1 \text{ cm}^{-1}$.

4. Discussion

The vibrational constants of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of CaF, CaCl, CaBr and CaI molecules are compared in Table IV. The constants of the $A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ systems of the CaI molecule obtained in the present work, are entirely in line with those of the $A^2\Pi - X^2\Sigma^+$ and $B^2\Sigma^+ - X^2\Sigma^+$ systems of the remaining molecules.

Dissociation energies of the excited $A^2\Pi$ and $B^2\Sigma^+$ states are estimated to be 19077 cm^{-1} and 23199 cm^{-1} respectively, using the relation

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}.$$

The estimated value of the ground state ($X^2\Sigma^+$) dissociation energy 21920 cm^{-1} (2.7 eV) is in reasonably good agreement with the values (2.5 eV) given by Gaydon. [10]. However,

TABLE IV

Comparison of the vibrational and spin-orbit coupling constants of the $A^2\Pi$ and $B^2\Sigma^+$ states of calcium monohalides (in cm^{-1})

Molecule	State	ν_e	ω_e	A
CaF	$B^2\Sigma^+$	18844.4	566.7	
	$A^2\Pi$	16557.2	592.7*	+75.1
		16482.1		
CaCl	$X^2\Sigma^+$	0.0	587.1	
	$B^2\Sigma^+$	16850.6	358.8	
	$A^2\Pi$	16162.8	364.9*	+69.5
CaBr		16093.3		
	$X^2\Sigma^+$	0.0	369.8	
	$B^2\Sigma^+$	16380.0	284.6	
CaI	$A^2\Pi$	15985.8	288.1*	+63.3
		15922.5		
	$X^2\Sigma^+$	0.0	285.3	
CaI	$B^2\Sigma^+$	15715.4	239.9	
	$A^2\Pi$	15645.6	242.2*	+60.4
		15585.2		
	$X^2\Sigma^+$	0.0	238.4	

* Average value for the two $^2\Pi$ components.

it is to be noted that the values obtained from $B-S$ extrapolation are not reliable in the case of ionic molecules.

The $^2\Sigma^+$ ground state configuration of the alkaline earth halides [11, 12] is

$$\dots (z\sigma)^2 (y\sigma)^2 (w\pi)^4 x\sigma.$$

The first and second excited states (A and B) may be attributed to the following electronic configurations and term types respectively,

$$\dots (z\sigma)^2 (y\sigma)^2 (w\pi)^4 (v\pi) \dots A^2\Pi$$

$$\dots (z\sigma)^2 (y\sigma)^2 (w\pi)^4 (u\sigma) \dots B^2\Sigma^+.$$

The above electron configurations indicate that the promotion of an electron from non bonding ($x\sigma$) orbital to non bonding ($v\pi$) or ($u\sigma$), should result in small difference in ω'_e values relative to ω'_e value, as judged from the derived vibrational frequencies.

The regular (or inverted) nature of the $A^2\Pi$ state, can be established only from a study of the rotational structure of the bands. In this connection it is of interest to note the recent work [12] on the diatomic calcium fluoride, which established the advantages of laser fluorescence studies, over the conventional experimental techniques, for the high resolution studies of the electronic spectra of heavy diatomics.

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