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Indian Journal of Pure & Applied Physics
Vol. 11 December 1973, pp. 923-925

Band Spectrum of CaI Molecule in the Region 6610-6175 Å (*A* and *B* Systems)

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Received 11 *June* 1973

The spectrum of calcium iodide molecule has been excited in a high frequency discharge tube source and has been photographed in the 6610-6175 Å region in the second order of a plane grating spectrograph at a reciprocal dispersion of 3·38 Å/mm The bands have been analyzed into two different systems which may be attributed to electronic transitions $A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$ and $B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$, showing the $A\ ^2\Pi$ separation of about 59 cm^{-1} and the spin splitting in the $B\ ^2\Sigma$ state of about 3 4 cm^{-1} respectively.

1. Introduction

THE SPECTRUM of CaI molecule was first reported by Walters and Barratt[1] in absorption. It consists of three groups of bands in the regions 6690-6270 Å, 4440-4410 Å and 3290-3075 Å. Hedfeld[2] investigated the spectrum of this molecule in emission in flame and reported a vibrational analysis for the bands in the region 6690-6270 Å. Mesnage[3] obtained the group of bands of this molecule in the range 4440-4410 Å in discharge. A vibrational analysis for these bands was reported and the system was assigned to the electronic transition $C \rightarrow X$. Later on, Murthy *et al*[4] reinvestigated the same group of bands in high frequency discharge and the system was ascribed to an electronic transition $C\ ^2\Pi \rightarrow X\ ^2\Sigma$. Morgan (Ref 5) in his unpublised work reinvestigated the spectrum of calcium iodide molecule in absorption and gave vibrational analyses for the bands in the region 6690-6270 Å. A few bands at 6512·43, 6487 59, 6413·26, 6389·15, 6315·17 and 6512·43 Å were analyzed and assigned by him to a transition $A\ ^2\Pi \leftarrow X\ ^2\Sigma$ Three bands at 6430·37, 6362 8) and 6267·66 Å were analyzed as belonging to $B\ ^2\Sigma \leftarrow X\ ^2\Sigma$ system.

In view of the fact that the vibrational constants have been derived from measurements of a few bands only, it was thought desirable to reinvestigate the spectrum of CaI molecule in the red region and the results obtained are presented in this paper.

2. Experimental Details

The spectrum of calcium iodide molecule has been excited in a high frequency discharge using a 500 W oscillator working in the frequency range 10-15 MHz. A pure sample of calcium iodide (E. Merck) was kept in a conventional type of quartz tube. The tube was constricted in the middle to increase the brilliance of the discharge. Strong heating was necessary to maintain a characteristic dark pink colour of the discharge in which the bands were found to develop better. The spectrum was photographed in the second order of a plane grating spectrograph at a dispersion of 3·38 Å/mm. Measurements of bandheads were made on Abbey comparator against iron-arc standards.

3. Results

The spectrum of CaI molecule in the region 6600-6200 Å is reproduced in Fig. 1. It reveals two groups of violet degraded bands. One of them having two

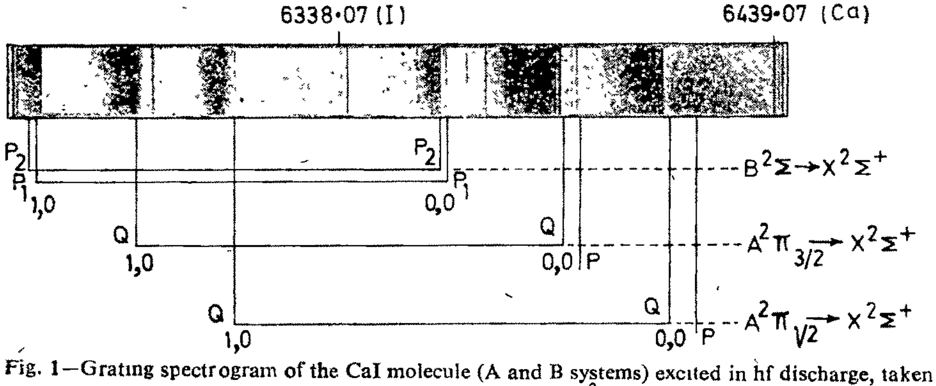

Fig. 1—Grating spectrogram of the CaI molecule (A and B systems) excited in hf discharge, taken at a dispersion of 3 38 Å/mm

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Table 1 — Bandhead Data of the $A-X$ System of CaI Molecule

Visual intensity	Wavenumber in vacuum (cm^{-1})	Assignment v'-v''	Difference $\nu_{obs.}-\nu_{calc.}$ cm^{-1}
		$A\,^2\Pi_{3/2}\rightarrow X\,^2\Sigma^+$	
3	15173·5	0,2(Q)	−1·6
2	15179·5	1,3(Q)	−1·6
4	15198·4	4,6(Q)	−1.7
3	15212·5	6,8(Q)	+0·4
5	15410·0	0,1(Q)	−0·3
4	15415·3	1,2(Q)	+0·1
5	15419·1	2,3(Q)	−0·7
6	15425·4	3,4(Q)	+0·9
6	15429·4	4,5(Q)	+0·3
4	15434·1	5,6(Q)	+0 6
4	15436 5	6,7(Q)	−0·9
9	15647·2	0,0(Q)	0 0
5	15637·5	0,0(P)	—
8	15650·2	1,1(Q)	−0·2
4	15641 2	1,1(P)	—
7	15653 1	2,2(Q)	−0·4
4	15643·5	2,2(P)	—
6	15655·3	3,3(Q)	−1·2
6	15657 7	4,4(Q)	−1.8
8	15886·7	1,0(Q)	−0·5
6	15889·6	2,1(Q)	+0·9
4	15893·4	4,3(Q)	+1·8
3	15896·0	6,5(Q)	+1 9
4	16123·8	2,0(Q)	+1·8
2	16125·6	3,1(Q)	+0·1
2	16127·0	4,2(Q)	+1·7
		$A\,^2\Pi_{1/2}\rightarrow X\,^2\Sigma^+$	
3	15130 6	2,4(Q)	−0·7
2	15139 7	3,5(Q)	+0·5
3	15147·3	4,6(Q)	0·0
2	15155·4	5,7(Q)	−0·1
2	15164·4	6,8(Q)	+0·4
2	15351·1	0,1(Q)	−0·5
2	15356·6	1,2(Q)	−1
2	15361·5	2,3(Q)	−1·5
3	15366·5	3,4(Q)	−1·7
10	15588·5	0,0(Q)	+0 1
6	15580·1	0,0(P)	—
9	15592·9	1,1(Q)	−0 1
7	15584·4	1,1(P)	—
9	15596·4	2,2(Q)	−1·4
6	15587·2	2,2(P)	—
6	15829 4	1,0(Q)	−0·4
5	15832·9	2,1(Q)	−0·2
7	15835·9	3,2(Q)	−0·8
4	16068 3	2,0(Q)	−1·7
3	16072·4	3,1(Q)	+0 3

Table 2 — Bandhead Data of the $B\,^2\Sigma^+\rightarrow X\,^2\Sigma^+$ System of CaI Molecule

Visual intensity	Wavenumber in vacuum cm^{-1}	Assignment v', v''	Difference $\nu_{obs.}-\nu_{calc.}$ cm^{-1}
1	15246·9	3,5(P_1)	−0·3
2	15250·6	4,6(P_1)	+0·6
2	15253·1	5,7(P_1)	+0·4
1	15254·2	6,8(P_1)	−1·0
4	15257·7	7,9(P_1)	+0 2
3	15474·2	0,1(P_1)	−0·4
3	15477·6	0,1(P_2)	−0·4
2	15475·8	1,2(P_1)	−0 9
2	15479·6	1,2(P_2)	−0·5
5	15477·0	2,3(P_1)	−1·7
4	15480 6	2,3(P_2)	+1·5
4	15482·1	4,5(P_1)	−0·1
5	15484·7	5,6(P_1)	+0·9
7	15485·2	6,7(P_1)	+0·2
8	15712·4	0,0(P_1)	0·0
7	15715·8	0,0(P_2)	0·0
6	15713·4	1,1(P_1)	0 0
5	15717 0	1,1(P_2)	+0·3
7	15714·6	2,2(P_1)	+0·4
6	15718 2	2,2(P_2)	+0·5
6	15950.7	1,0(P_1)	−0·3
6	15953.6	1,0(P_2)	−0·8
6	15952·9	2,1(P_1)	+1·1
6	15955·9	2,1(P_2)	−1·6
4	16178·3	8,6(P_1)	+1.3
5	16180·7	7,5(P_1)	+0·3
2	16182·6	6,4(P_1)	+0·8
3	16184·3	5,3(P_1)	+0 6
3	16185·9	4,2(P_1)	+0 5
3	16188·0	3,1(P_1)	+0 9

subheads (P_1 and P_2) with equal intensity and a separation between them of about 3·4 cm^{-1} while the other having intense Q-heads and corresponding weak P-heads with a separation between them of about 9 cm^{-1}. Visually estimated intensities, wavenumbers in vacuum, vibrational assignments and differences between observed and calculated wavenumbers of the band heads are given in Tables 1 and 2 corresponding to the A and B systems, respectively.

4. Discussion

In the present investigation a fairly large number of bands have been recorded in addition to those already reported by earlier workers[2,5]. From the group of bands having equal intensity of two subheads, the most intense bands at 15712·4 cm^{-1} and 15715·8 cm^{-1} were taken as P_1-and P_2-heads of the (0, 0) bands and a vibrational analysis was carried out in the usual way. The following vibrational quantum equation satisfactorily represents the P_1-and P_2-heads:

$$\nu_{\mathrm{head}} = \left.\begin{matrix} (P_1)\ 15711{\cdot}8 \\ (P_2)\ 15715{\cdot}2 \end{matrix}\right\} + 239{\cdot}95\,(v' + \tfrac{1}{2}) - 0{\cdot}62\,(v' + \tfrac{1}{2})^2 - 238{\cdot}8\,(v'' + \tfrac{1}{2}) + 0{\cdot}55\,(v'' + \tfrac{1}{2})^2$$

The lower state frequency of 238·8 cm^{-1} observed in the present work is in excellent agreement with the ground state frequency of 238·3 cm^{-1} of CaI molecule as reported by earlier workers. Moreover, the system has also been observed in absorption by Morgan (Ref. 5) and his report confirms that the lower state involved in this system is the ground state $X\,^2\Sigma$. The upper state shows a splitting of 3·4 cm^{-1} which may be considered as a spin splitting in the upper state $B\,^2\Sigma$. Such a spin splitting has been observed in the $B\,^2\Sigma$ states of CaF, SrF (Ref. 8), BaF (Ref. 6 and 7) and SrCl (Ref. 8) molecules. A comparison of the region of occurrence of this system with the $B\,^2\Sigma - X\,^2\Sigma$ systems of CaF, CaCl and CaBr molecules indicates that the system may be attributed to an electronic transition $B\,^2\Sigma \rightarrow X\,^2\Sigma$ showing a spin splitting of 3·4 cm^{-1} in the upper state.

The spectrogram also reveals a large number of bands having intense Q-heads and corresponding weak P-heads with a separation between them of about 9 cm^{-1}. Among these, 15647·2 cm^{-1} and 15588·2 cm^{-1} were taken as the (0, 0) bands of the subsystems $A\,^2\Pi_{3/2} \rightarrow X\,^2\Sigma$ and $A\,^2\Pi_{1/2} \rightarrow X\,^2\Sigma$ respectively and the vibrational analysis was carried out in the usual way. The following vibrational quantum equations satisfactorily represent nearly 43 Q-heads :

$$A\,^2\Pi_{3/2} \rightarrow X\,^2\Sigma : \nu_{\mathrm{head}} = 15645{\cdot}57 + 241{\cdot}69\,(v' + \tfrac{1}{2}) - 0{\cdot}83\,(v' + \tfrac{1}{2})^2 - 238{\cdot}40\,(v'' + \tfrac{1}{2}) + 0{\cdot}79\,(v'' + \tfrac{1}{2})^2$$

$$A\,^2\Pi_{1/2} \rightarrow X\,^2\Sigma : \nu_{\mathrm{head}} = 15586{\cdot}20 + 242.65\,(v' + \tfrac{1}{2}) - 0{\cdot}62\,(v' + \tfrac{1}{2})^2 - 238{\cdot}26\,(v'' + \tfrac{1}{2}) + 0{\cdot}73\,(v'' + \tfrac{1}{2})^2$$

The nature of the bands and a comparison of the region of occurrence of this system with $A\,^2\Pi \rightarrow X\,^2\Sigma$ systems of CaF, CaCl and CaBr molecules indicate that the system may be attributed to an electronic transition $A\,^2\Pi \rightarrow X\,^2\Sigma$ with $a\,^2\Pi$ separation of about 59 cm^{-1}.

The identity of the emitter of the band systems was confirmed by standard methods which leads us to believe that the bands in the region 6610—6175 Å observed in the present investigation belong to the CaI molecule.

Acknowledgement

The authors are thankful to Prof. N. S. Pandya for his keen interest in the work. They are also thankful to Dr M. M. Patel for suggesting the problem and for useful discussions.

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P. Younger and Winans[5], 1960). Analysis of (0, 1) band at 4072·7 Å was carried out by comparing the combination relations for the common upper and lower state respectively of (0, 0) band at 4098·5 Å. The rotational constants for the three bands of A → X system obtained in the present work are given below:

Band	ν cm^{-1}	B′ cm^{-1}	B″ cm^{-1}	D′ cm^{-1}	D″ cm^{-1}
(1, 0)	24548·535	$0{\cdot}0374_2$	$0{\cdot}0368_1$	$0{\cdot}12 \times 10^{-7}$	$0{\cdot}087 \times 10^{-7}$
(0, 0)	24393·853	$0{\cdot}0377_2$	$0{\cdot}0368_2$	$0{\cdot}087 \times 10^{-7}$	$0{\cdot}075 \times 10^{-7}$
(0, 1)	24216·705	$0{\cdot}0376_1$	$0{\cdot}0364_1$	$0{\cdot}1 \times 10^{-7}$	$0{\cdot}06 \times 10^{-7}$

Molecular constants of InI molecule obtained from the present analysis are given below along with the microwave data.

State	B_e cm^{-1}	r_e Å	$\Delta G_{1/2}$ cm^{-1}	α_e cm^{-1}
$A^3\Pi_0$	$0{\cdot}0376_2$	$2{\cdot}710_2$	$155{\cdot}7_2$	$0{\cdot}6 \times 10^{-4}$
$X^1\Sigma^+$	$0{\cdot}0362_2$	$2{\cdot}770_1$	$176{\cdot}1_3$	$1{\cdot}3 \times 10^{-4}$
	*0·0368	*2·754	—	$1{\cdot}04 \times 10^{-4}$

The ground state configuration of Indium monoiodide molecule can be written as $z\sigma^2\ y\sigma^2\ w\pi^4\ x\sigma^2$ analogous to those of halides of the same group (InCl, InBr, InF) giving rise to $^1\Sigma^+$ ground state. The excited electron configuration is $z\sigma^2 y\sigma^2 w\pi^4 x\sigma v\pi$ which gives rise to $^1\Pi$ or $^3\Pi$ state. $^1\Pi - {}^1\Sigma^+$ transition is attributed to C → X system which is analogous to those of similar molecules. However $^1\Pi$ state is repulsive in the case of InI molecule which gives a continuum at 3180 Å. The $^3\Pi$ state belongs to Hund's case (*a*) due to its large coupling constant (648·9 cm^{-1}). Hence $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$ states are analogous to $^1\Sigma$, $^1\Pi$ and $^1\Delta$ states respectively. $^3\Pi_2 \rightarrow X^1\Sigma^+$ transition is a forbidden one whereas $^3\Pi_1 \rightarrow {}^1\Sigma^+$ has been ascribed to the B → X system. Hence $^3\Pi_0 \rightarrow {}^1\Sigma^+$ transition may be attributed to the A – X syxtem of InI molecule. The appearance of single P and R branches in case of (0, 0), (0, 1) and (1, 0) bands confirms this assignment.

The authors are thankful to Prof. M. M. Patel for his keen interest and useful discussions during the course of this work.

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*Microwave data (1958).

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Reprinted from "Curr. Sci.", July 20, 1977, Vol. 46, No. 14, 486-487

ROTATIONAL ANALYSIS OF THE $A^3\Pi_{0^+} \rightarrow X^1\Sigma^+$ SYSTEM OF InI MOLECULE

THE spectrum of Indium monoiodide in the region λλ 3948 – 4293 Å was studied at low dispersion by Wehrli[1] (1934) and Wehrli and E. Miescher[2] (1934). Barrett and Mandel[3] (1958) studied the spectrum of InI molecule in the microwave region in absorption and obtained the rotational constants for the ground state of the molecule. The present work was undertaken to study the exact nature of the excited state involved in the emission of A → X band system of the molecule and to determine the rotational constants of the excited state. Rotational analysis of (0, 0), (0, 1) and (1, 0) bands of the A → X system has been carried out and results obtained are reported here.

The spectrum of Indium monoiodide was excited in a high frequency discharge by keeping pure Indium metal in the presence of iodine vapours in a conventional type of a quartz discharge tube. The spectrum was photographed on Ilford N–40 plates in the seventh order of a two meter plane grating spectrograph (Carl–Zeiss) at a resolution of about 3 × 10^5 and a reciprocal dispersion of 0·35 Å/mm. Exposure time of about five hours for a slit-width of 15 microns was adequate to record the spectra of sufficient intensity. Measurements were made on Abbe Comparator using iron-arc standards.

In the A – X system of InI molecule, (0, 0), (0, 1) and (1, 0) bands degraded to violet were analysed. These bands reveal the presence of single P and R branches of which P is the head forming branch (Fig. 1). The rotational analysis has been carried out by standard methods (Herzberg[4], 1955 and

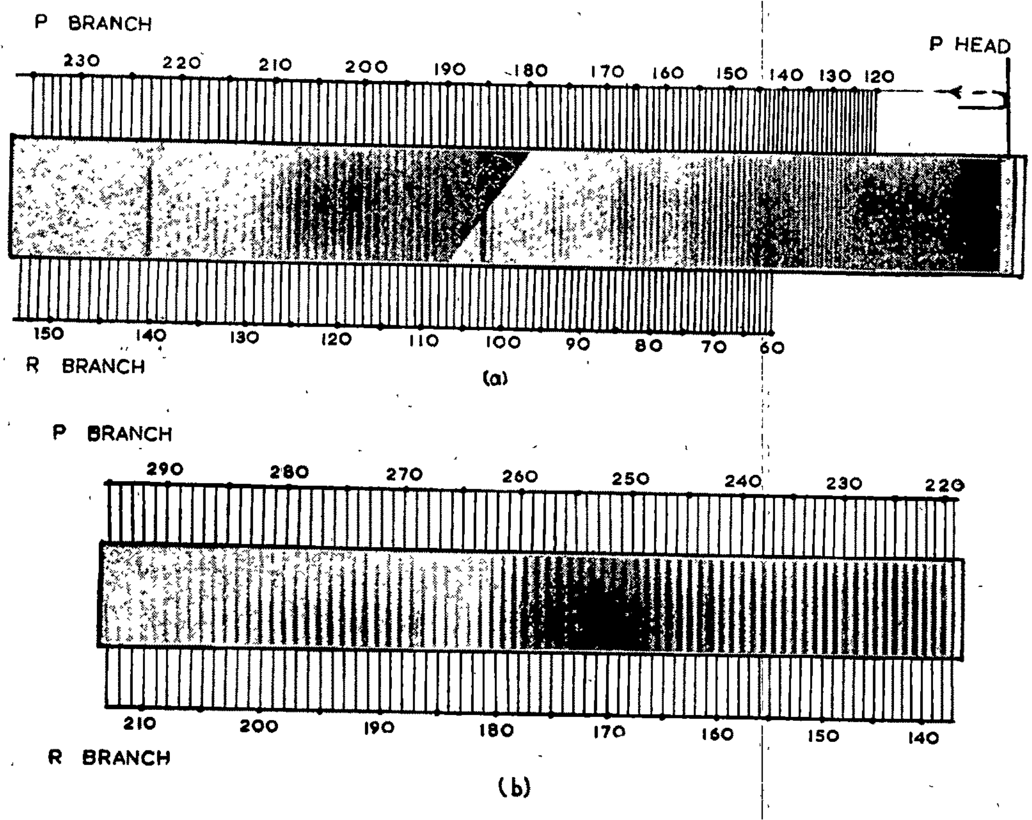

FIG. 1.

FIG. 1 (*a*) and (*b*). Rotational structure of (0, 0) band A → X system of InI molecule taken at a dispersion of 0·35 Å/mm.