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THE VISIBLE EMISSION SPECTRUM OF DIATOMIC BARIUM IODIDE

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Abstract: High resolution spectrograms of the visible emission spectrum of the diatomic barium iodide, excited in a radio-frequency discharge source, reveal the presence of two intense sequences of head-less bands in the region 5330—5620 Å. These sequences are identified as the $\Delta V = 0$ sequences of the $C^2\pi - X^2\Sigma^+$ transition of the BaI molecule. The following are the vibrational constants (cm^{-1}) of the $C^2\pi$ and $X^2\Sigma^+$ states, obtained from a vibrational analysis of the system.

1. Introduction

The first spectroscopic identification of the diatomic barium iodide was due to Olmsted[1], followed by Walters and Barratt[2], who reported the observation of bands in the regions 5610—5360 Å and 3830—3760 Å. Later, Mesnage[3], studied the bands in the visible region, in emission and analysed them as the $\Delta V = 0$ sequences of two sub-systems, designated as C_1 and C_2 with a doublet separation of about 755 cm^{-1}; however, as he observed only the $\Delta V = 0$ sequences, he could not deduce the vibrational frequencies of either of the states. In order to obtain more detailed information on the visible bands, it is felt desirable to reinvestigate the emission spectrum of BaI under high resolution.

In the present investigation, the spectrum has been studied in a R. F. discharge source, by photographing the visible bands in the first order (reciprocal dispersion; 1.25 Å/mm) of a 21 ft. concave grating spectrograph. The present paper, deals with the results and analysis of the visible bands attributed to the $C^2\pi - X^2\Sigma^+$ transition. The experimental details and analysis are described in the following Sections.

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2. Experimental procedures

The spectrum of BaI has been excited in a R. F. (40MHz) discharge source from a 500 watt oscillator, using spectroscopically pure sample of BaI_2, in a quartz transparent tube of 30 cm length, with a central capillary part, 30 mm long and 3 mm diameter. The characteristic intense green colour of the discharge was photographed in the first order of a 21 ft. concave grating spectrograph. Exposures of 10 to 20 minutes duration were found sufficient to photograph the two intense sequences using Kodak 103 a-F plates.

A DC iron arc was used for the comparison spectrum. The plates were measured on a Hilger comparator, using iron arc wavelengths taken from the MIT tables. Vacuum wave numbers were calculated using a computer program, which fits the dispersion curve to a cubic polynomial.

3. Results and analysis

High resolution spectrograms reveal the presence of two intense sequences of bands, extending to shorter wavelengths in the region 5330–5620 Å. These two sequences, are identified as the $\Delta V = 0$ sequence of two sub-systems of a $^2\pi - ^2\Sigma$ transition, with a spin doublet separation of about 755 cm^{-1}, by analogy with the visible $C^2\pi - X^2\Sigma^+$ transitions, observed in the other halides of the alkaline-earth metals. Assuming the upper $^2\pi$ state as a regular state, the sequence in the region 5624–5572 Å is identified as the $\Delta V = 0$ sequence of $C^2\pi_{1/2} - X^2\Sigma^+$ sub-system and the sequence in the high frequency side, in the region 5394–5341 Å is identified as the $\Delta V = 0$ sequence of the $C^2\pi_{3/2} - X^2\Sigma^+$ sub-system. Both these sequences are shown in Fig. 1. It is seen that each of the sequence consists of as many as 25 members. The origins are seen for most of the bands with R and P branches on either side. From the structure of the bands it is evident that the B_e values of the upper and lower states must be nearly equal.

From Fig. 1, it is seen that the bands at 5611.3 Å and 5383.0 Å are the most intense, and are identified as the (0,0) bands of the two sub-systems. The detailed vibrational assignments in both the sequences are shown in Fig. 1.

From an analysis of the ultraviolet bands (D-X and E-X systems) the ground state constants are known[4] ($\omega_e'' = 152.43$; $\omega_e'' x_e'' = 0.793$). Assuming the ground state is common for the C–X, D–X and E–X systems, the upper state constants of the C–X system are determined by a least squares fit method. The following are the vibrational constants of the upper state for the two sub-systems

$$C^2\pi_{1/2} - X^2\Sigma^+: \quad \nu_e = 17813.92, \quad \omega_e' = 158.02, \quad \omega_e' x_e' = 0.296,$$

$$C^2\pi_{3/2} - X^2\Sigma^+: \quad \nu_e = 18569.05, \quad \omega_e' = 158.10, \quad \omega_e' x_e' = 0.290.$$

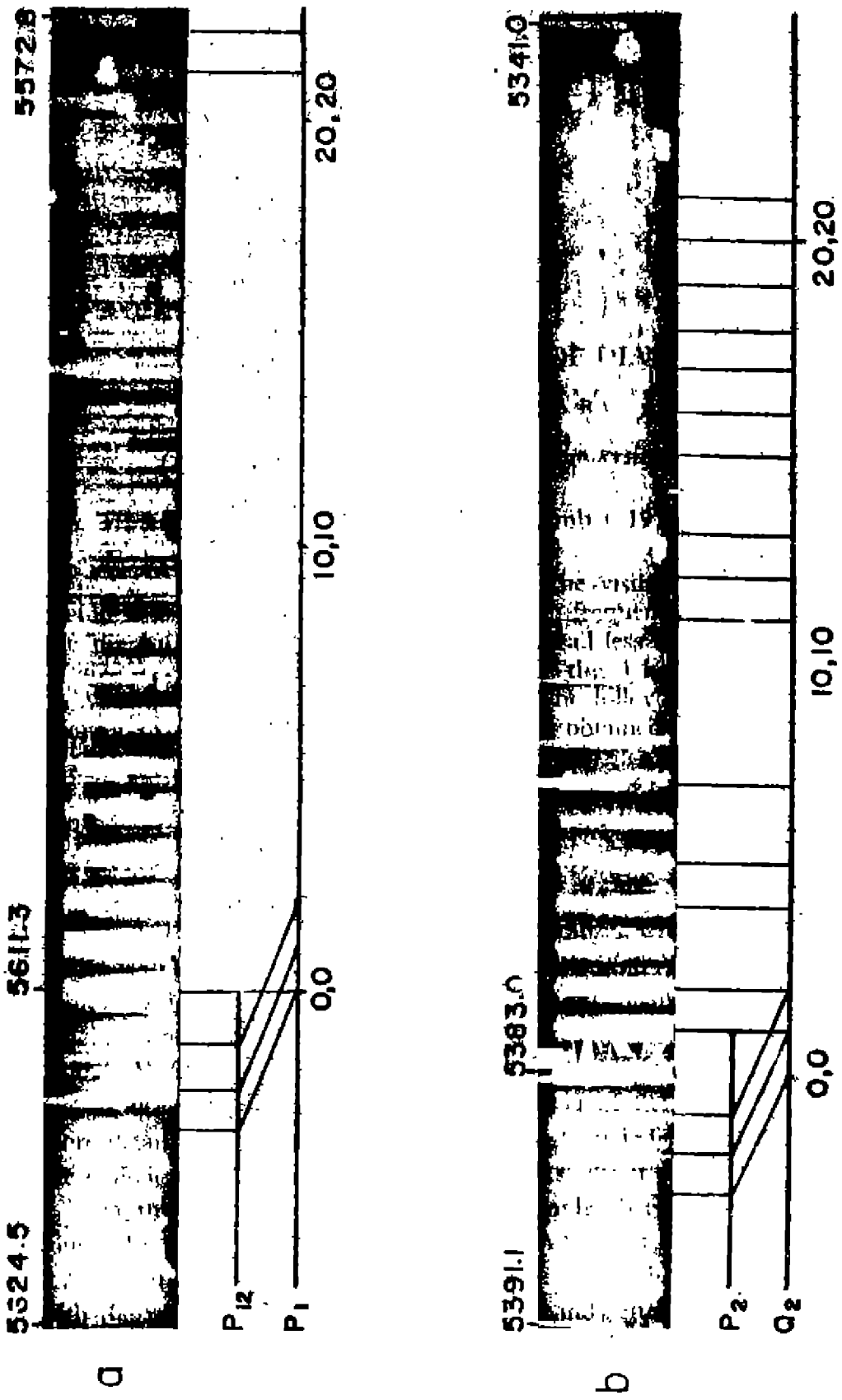

Fig. 1.: The $\Delta V = 0$ sequences of the $C^2\pi - X^2\Sigma^+$ systems. a: The $\Delta V = 0$ sequence of the $C^2\pi_{1/2} - X^2\Sigma^+$. b: the $\Delta V = 0$ sequence of the $C^2\pi_{3/2} - X^2\Sigma^+$.

The vacuum wave numbers of the band origins, the visual estimates of their intensities and vibrational quantum numbers for both the sub-systems are given in Table 1 and Table 2.

TABLE 1*).

Assignments of the bands of the $C^2\pi_{1/2} - X^2\Sigma^+$ sub-system.

ν_{obs}	Intensity*)	V', V''	$\nu_{obs} - \nu_{calc}$
17798.8	vw	0,0 P_{12}	
17803.9	m	1,1	
17810.5	s	2,2	
17816.1	vs	0,0 P_1	—0.6
17821.8	vs	1,1	—0.5
17827.7	vs	2,2	—0.2
17833.5	vs	3,3	—0.1
17839.1	vs	4,4	0.1
17843.8	vs	5,5	—0.8
17850.1	s	6,6	0.0
17856.1	s	7,7	0.4
17861.2	s	8,8	0.0
17866.9	s	9,9	0.1
17872.5	s	10,10	0.2
17877.9	s	11,11	0.1
17882.9	s	12,12	—0.4
17888.5	s	13,13	—0.3
17894.9	s	14,14	0.6
17899.2	s	15,15	—0.6
17904.9	m	16,16	—0.4
17910.4	m	17,17	—0.4
17916.3	m	18,18	0.0
17921.6	m	19,19	—0.2
17927.7	m	20,20	0.4
17932.2	m	21,21	—0.5
17938.1	m	22,22	—0.1
17943.6	w	23,23	0.0

The agreement between the observed and calculated values of the wave numbers of the bands can be regarded as satisfactory as seen from the last column of the Tables 1 and 2.

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*) Abbreviations used in the Table 1 and 2: vs, s, m, w, vw denote very strong, strong, medium, week, and very weak respectively.