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THE ULTRAVIOLET BAND SYSTEMS OF BaI MOLECULE

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ABSTRACT

The emission spectrum of the BaI molecule is excited in a R.F. discharge and photographed in the first order (reciprocal dispersion: 1.25 Å/mm) of a 21 ft. concave grating spectrograph. A comprehensive new vibrational analysis of the D–X and E–X systems of the diatomic BaI is reported. The following are the vibrational constants of the two systems.

Transition	ν_e	ω_e''	$\omega_e''x_e''$	ω_e'	$\omega_e'x_e'$
$E^2\Sigma^+ - X^2\Sigma^+$	26753.5	152.43	0.293	176.08	0.594
$D^2\Sigma^+ - X^2\Sigma^+$	25771.9	152.43	0.293	162.13	0.425

RESUMEN

Se ha obtenido el espectro de emisión de la molécula BaI -excitada por descarga R.F.- fotografiándolo en el primer orden de un espectrógrafo de red cóncava de 21 pies (dispersión recíproca: 1,25 Å/mm). Un nuevo y amplio análisis vibracional de los sistemas D–X y E–X de esta molécula diatómica ha permitido revalorar las constantes vibracionales de ambos sistemas.

1. INTRODUCTION

The band spectrum of BaI, as investigated previously by Olmsted (1) in emission, Walters and Barratt (2) and Mesnage (3) in absorption, was known to consist of groups of bands in two spectral regions 5610–5360 Å and 3830–3760 Å. However, it appears that no analysis of these bands is available until 1970, as this work seems not to have been followed up.

Recently, Reddy and Rao (4) have investigated the ultraviolet emission spectrum of BaI, excited in a high frequency discharge through a mixture of heated Barium and Iodine vapour. They photographed the ultraviolet bands in the region 3650–3950 Å on a Hilger E_1 quartz littrow spectrograph, having a dispersion of 10 Å/mm at 3800 Å. The bands are analysed and attributed to the D–X and E–X systems by analogy with similar systems in the other halides of Barium. Patel and Shah (5) have also studied independently the emission spectrum of BaI. They photographed the ultraviolet bands using a high frequency discharge at a dispersion of about 7.3 Å/mm with a plane grating spectrograph. The bands are analysed and attributed to the D and E systems of BaI, as was proposed by Reddy and Rao (4); however, it was seen from the derived constants of Patel and Shah (5) that the analysis is at variance with that of Reddy and Rao (4).

It is therefore, felt desirable to reinvestigate the band spectrum of BaI, under high resolution in order to resolve the existing ambiguity and thereby enabling us to arrive at accurate vibrational constants for the ground as well as the upper states (D and E) of the BaI molecule. Also, Dagdegian (6) recently, has drawn our attention for this study, while he is investigating the laser fluorescence spectrum of the barium iodide molecule.

In the present investigation, the spectrum has been studied in a R.F. discharge from a 500 Watt Oscillator by photographing the visible as well as the ultraviolet bands at the first order dispersion (1.25 Å/mm) of a 21 ft. concave grating spectrograph. The present paper deals with the results and vibrational analysis of the ultraviolet bands attributed to the $D^2\Sigma^+ - X^2\Sigma^+$ and $E^2\Sigma^+ - X^2\Sigma^+$ transitions. The experimental details and analysis are described in the following sections.

2. EXPERIMENTAL PROCEDURE

The light source employed in the excitation of the BaI spectrum was a high frequency 500 watt Oscillator working at a frequency of 30–40 MHz. The discharge tube was all quartz transparent tube of 30 cm in length with central capillary of length 30 mm and diameter 3 mm. A sufficient quantity of the spectroscopically pure sample of BaI_2 (supplied by B.D.H. England) 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 green. Intermittent external heating by means of a special bunsen burner was found necessary to maintain the characteristic colour of the discharge.

The spectrum was first photographed on a low dispersion Hilger medium quartz spectrograph and on a medium dispersion Hilger E_1 quartz Littrow spectrograph, using Ilford N30 plates. An exposure time of 5 minutes was found sufficient to record the bands. The bands were thereafter photographed in the first order of a 21 ft. concave grating spectrograph. Exposures of 10 to 20 minutes duration were found sufficient to obtain intense spectrograms of all the sequences using Kodak photographic plates of type 103a–0. A DC iron arc was used for the comparison spectrum. Measurements of the band heads were made on a Hilger comparator using iron arc wavelengths standards 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

High resolution spectrograms of the ultraviolet emission spectrum of BaI obtained in the present investigation reveal the presence of twelve groups of bands in the region 3650–3950 Å consisting of a total of 76 band heads. All the bands are degraded to violet. These bands are analysed and attributed to the D–X and E–X systems. We are presenting below the experimental data and vibrational analysis of the two band systems mentioned here.

3.1. The D–X system

The spectrum reveals the presence of eight groups of bands consisting of a total of 57 bands degraded towards shorter wavelength in the region 3750–3950 Å. These bands are single headed and are identified as the P heads. From sequence separations, the group at 3880 Å is identified as the $\Delta v = 0$ sequence. Other groups of bands on the longer wavelength side are identified as $\Delta v = -1$ and -2 sequences whereas those on the shorter wavelength side are identified as $\Delta v = +1, +2, +3, +4$ and $+5$ sequences. The plots of the mean values of the vibrational intervals against the corresponding $(v+1/2)_\lambda$ values for the lower and upper states of this system indicate that the vibrational terms can be expressed as

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

The slopes and intercepts of the straight line obtained by a least square fit for this system give the value $-2\omega_e x_e$ and $\omega_e - \omega_e x_e$ respectively. The band heads are represented by the following expression

$$\nu_h = 25771.9 + 162.13 \left(v' + \frac{1}{2}\right) - 0.425 \left(v' + \frac{1}{2}\right)^2 - 152.43 \left(v'' + \frac{1}{2}\right) + 0.293 \left(v'' + \frac{1}{2}\right)^2$$

As a check on the calculations and the assignments of v′ and v″, the wavenumbers of the bands are calculated by means of the above equation. The differences are shown in table 1. Except for one band, these differences are $\leqslant 0.3$ cm^{-1}.

Here it is to be noted that the (0,0) band as reported by Reddy and Rao (4) (26101 cm^{-1}) and Patel and Shah (5) (25781.8 cm^{-1}) is very close to the (2,0) and (1,1) bands respectively.

The vibrational assignments for most of the bands are shown in fig. 1. The vacuum wavenumbers of the band heads, their relative estimated intensities, and vibrational quantum numbers are listed in Table I. When the bands are arranged in a Deslandres' vibrational scheme (not shown), they fall into a narrow Franck–Condon parabola.

As some of the prominent bands of this system have also been observed by Walters and Barratt in absorption, the lower state of this system is the ground state of the BaI molecule. By analogy with the D–X systems of the other halides of Barium and from the single headed nature of the bands, it appears that these bands arise from a transition of the type $D^2\Sigma^+ - X^2\Sigma^+$.

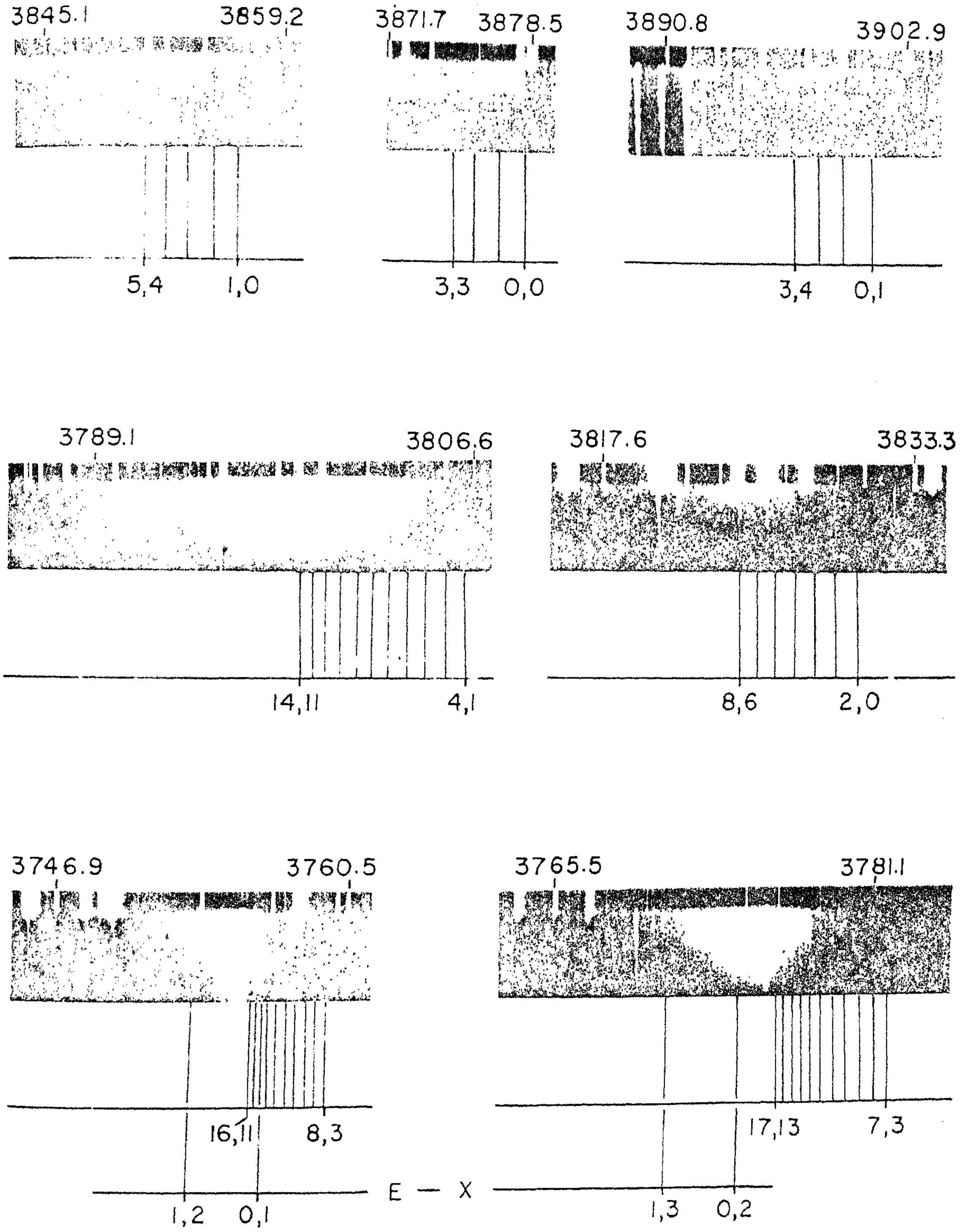

Fig. 1.— The D—X system of BaI.

TABLE I

Band head data of the D–X system of BaI

Wavenumber (cm^{-1})	Intensity[a]	Classification (v', v'')	$\nu_{obs} - \nu_{cal}$ (cm^{-1})	Wavenumber (cm^{-1})	Intensity[a]	Classification (v', v'')	$\nu_{obs} - \nu_{cal}$ (cm^{-1})
25464.6	m	1,3	0.4	26283.9	s	7,4	−0.1
25494.9	vs	2,4	0.3	26289.9	s	8,5	0.1
25624.9	vs	0,1	0.0	26295.4	s	9,6	0.0
25635.1	s	1,2	0.2	26300.5	s	10,7	−0.2
25644.5	[illegible]	2,3	−0.2	26305.6	s	11,8	−0.1
25654.1	s	3,4	−0.1	26310.2	m	12,9	−0.3
25770.7	s	0,0	0.0	26315.2	w	13,10	0.2
25780.2	m	1,1	0.0	26319.3	w	14,11	0.1
25795.5		2,2	0.2	26433.9	w	7,3	−0.2
25804.1	[illegible]	3,3	−0.1	26439.3	w	8,4	0.0
25936.0	[illegible]	1,0	0.0	26444.3	w	9,5	0.0
25946.6	[illegible]	2,1	0.0	26449.0	m	10,6	0.0
25954.[illegible]		3,2	−0.1	26453.3	m	11,7	−0.2
25962.9	m	4,3	−0.1	26457.6	m	12,8	0.0
25970.5	m	5,4	−0.3	26461.4	s	13,9	−0.2
25978.4	s	6,5	0.1	26465.3	s	14,10	0.1
25985.4	vw	7,6	−0.2	26468.5	s	15,11	−0.1
25992.4	vw	8,7	0.1	26471.6	m	16,12	−0.1
26098.5	w	2,0	0.1	26474.4	w	17,13	−0.2
26106.2	w	3,1	0.0	26589.3	w	8,3	−0.1
26113.7	m	4,2	0.1	26593.9	w	9,4	0.1
26120.9	s	5,3	0.1	26597.9	w	10,5	0.0
26127.9	m	6,4	0.1	26601.9	m	11,6	0.1
26134.5	w	7,5	0.0	26605.5	m	12,7	0.1
26140.9	vw	8,6	0.0	26608.6	w	13,8	−0.1
26147.0	vw	9,7	0.0	26611.5	w	14,9	−0.3
26264.9	m	4,1	0.0	26614.5	vw	15,10	−0.1
26271.7	s	5,2	0.2	26617.1	vw	16,11	0.0
26277.9	s	6,3	0.0				

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

3.2. The E–X system

Four groups of single headed bands degraded to violet are observed in the region 3650–3750 Å. These bands are analysed as belonging to a separate system as they do not form an extension of the D–X system. The $\Delta G''$ intervals of this system agrees very well with the corresponding values of the lower state of the D–X system. Hence the lower state of this system is also the ground state of the molecule. The band heads of this system could be fitted into the following quantum formula

$$\nu_h = 26753.5 + 176.68\left(v' + \frac{1}{2}\right) - 0.594\left(v' + \frac{1}{2}\right)^2 - 152.43\left(v'' + \frac{1}{2}\right) + 0.293\left(v'' + \frac{1}{2}\right)^2$$

As the bands are single headed, they appear to arise from a transition of the type $^2\Sigma^+ - {}^2\Sigma^+$. The vibrational assignments for most of the prominent bands are shown in Figure 2. The detailed classifications of the band head data of the system is given in Table II. The differences $\nu_{obs} - \nu_{cal}$ are shown in the last column of Table II. Except for two bands, those differences are $\leqslant 0.3$ cm^{-1}.

4. CONCLUSION

The ground state of this molecule can be assigned to a $X^2\Sigma^+$ state analogous to those of BaF, BaCl and BaBr and other related molecules. From a comparison of the vibrational constants of the D–X and E–X systems of the BaI with those of the other halides of Barium, the two systems are attributed to $D^2\Sigma^+ - X^2\Sigma^+$ and $E^2\Sigma^+ - X^2\Sigma^+$. It is claimed that the vibrational constants obtained from the D–X and E–X systems in the present work are the most accurate available so far for these systems. It is concluded that the analysis proposed by Reddy and Rao is incorrect, while that of Patel and Shah is close to the present study.

Dissociation energies of the ground $X^2\Sigma^+$ and excited $D^2\Sigma^+$ states are estimated to be 19825 cm^{-1} and 15497 cm^{-1} respectively using the relation

$$D_e = \omega_e^2/4\omega_e x_e$$

The estimated values are reasonably in good agreement with values estimated by Birge–Sponer extrapolation (19601 and 15451 cm^{-1} respectively). However, it is to be noted that the values obtained from B–S extrapolation are not reliable in the case of ionic molecules.

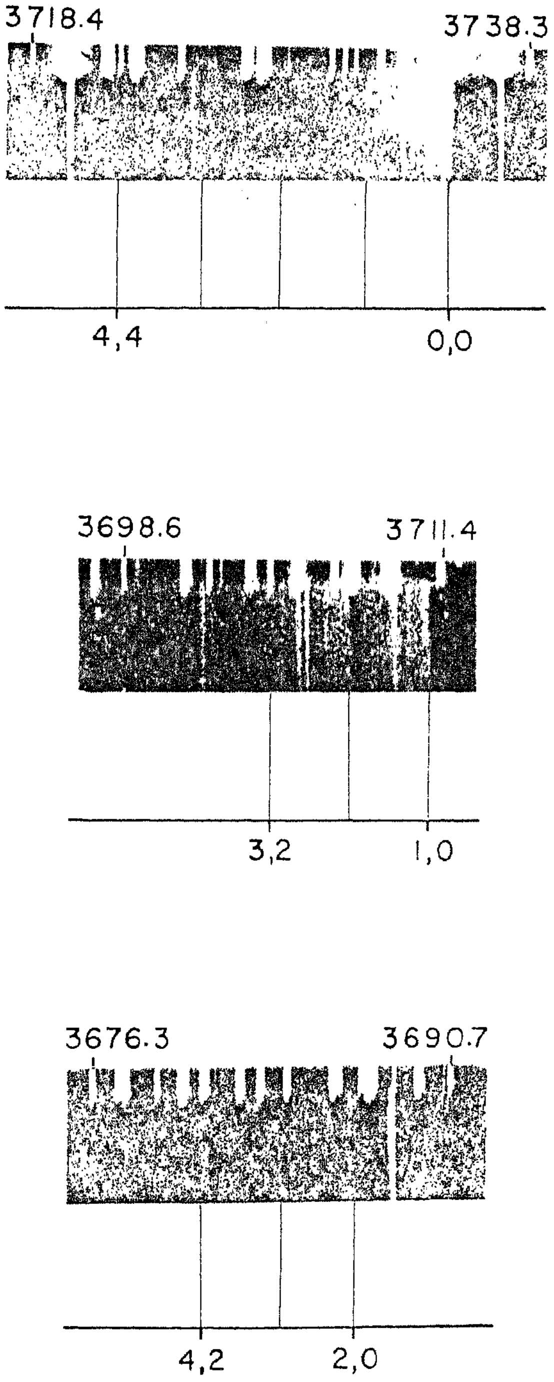

Fig. 2.– The E–X system of BaI.

TABLE II

Band head data of the E–X system of BaI

Wavenumber (cm^{-1})	Intensity[a]	Classification (v′, v″)	$\nu_{obs} - \nu_{cal}$ (cm^{-1})
26462.7	m	0,2	0.3
26487.6	w	1,3	0.3
26613.7	m	0,1	0.0
26638.2	w	1,2	0.3
26765.5	m	0,0	0.0
26789.2	m	1,1	0.0
26812.4	m	2,2	−0.1
26834.9	m	3,3	−0.2
26856.7	w	4,4	0.2
26878.2	w	5,5	0.4
26941.0	m	1,0	0.0
26963.6	m	2,1	−0.2
26985.6	w	3,2	0.2
27006.8	w	4,3	0.2
27115.0	m	2,0	−0.3
27136.6	m	3,1	0.0
27157.7	m	4,2	0.3
27327.6	w	5,2	−0.4
27347.2	vw	6,3	0.3

[a] See Table I, for abbreviations used.

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REFERENCES

1. C.M. OLMSTED: *Z. Wiss. Photogr.*, **4**, 255 (1906).
2. O.H. WALTERS and S. BARRATT: *Proc. Roy. Soc.*, **118**, 120 (1928).
3. P. MESNAGE: *Ann. de Phys.*, **12**, 5 (1939).
4. B.R.K. REDDY and P.T. RAO: *J. Phys. B.*, **3**, 1008 (1970).
5. M.M. PATEL and S.G. SHAH: *Ind. J. Pure and Appl. Phys.*, **8**, 681 (1970).
6. P.J. DAGDEGIAN: Private communication.

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