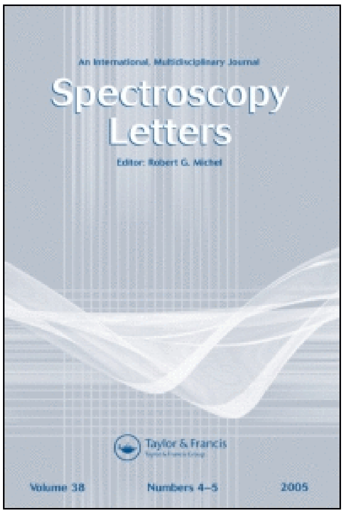

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THE GREEN BAND SYSTEM OF BaF

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ABSTRACT

The emission spectrum of the Green Band System of BaF has been photographed on a 35-feet concave grating spectrograph in the second order. Some new bands have been observed and analysed. Precise measurements of the Q_1 band-heads are used to calculate the band-origins which have led to the determination of accurate molecular constants for the upper $C\,^2\Pi_{1/2}$ and the lower $X\,^2\Sigma$ states of the molecule. The constants determined are:

Constants	Upper State $C\,^2\Pi_{1/2}$ (cm^{-1})	Lower State $X\,^2\Sigma$ (cm^{-1})
ν_e	19993.553	0
ω_e	458.814	471.116
$\omega_e x_e$	1.649	1.645
$\omega_e y_e$	-0.02635	-0.01912
$\omega_e z_e$	0.000726	0.000452

INTRODUCTION

The electronic spectra of the alkaline earth halides have been investigated by several workers (1-4). Nine electronic band system of BaF are known in the region 9000-3600Å, with the green system lying at 5139-

4842Å. The characteristic feature of the green system is that the bands from a long sequence. Johnson(5) and Harvey (6) recorded this system on a 21-ft. concave grating spectrograph in the first order. According to Harvey the electronic states involved in the transition giving rise to the green system are $^2\Pi$ (upper state) and $^2\Sigma$ (lower state). The present investigation was undertaken with the hope of resolving the rotational structure of the some of the more intense bands of the green system right upto the origin so that more accurate rotational constants could be determined. Although our attempt to resolve the rotationa structure of the bands right upto the origin, using a 35-ft. concave grating spectrograph in the second order, failed, it was possible for us to measure the Q_1 heads of the bands with a better precision. Using these precise values of the band heads it became possible for us to evaluate the molecular constants for the upper and lower states using a least square iterative technique These constants reproduce the observed frequencies well within ± 0.2 cm^{-1} and may be regarded as more accurate than the previously determined ones.

EXPERIMENTAL

The emission spectrum of the green band system of BaF was excited in a D.C. copper arc. The lower electrode of the arc was made up of copper (diameter 20 mm) and having a cylindrical cavity of 15 mm. in diameter and 10 mm. depth. The upper electrode was also made up of copper and had a diameter of about 7 mm. The lower electrode containing the cavity was charged with spectral grade BaF_2 obtained from the British Drug House, London. The emission spectrum was recorded on a 35-ft. concave grating spectrogrph in the second order at a reciprocal linear dispersion of 0.33 Å/mm. using Ilford HP-3 plates. The slit width and exposure times were 20 microns and two hours respectively. The measurements of the band heads were made on a Russian made comparator (Model No. EZA-2) using iron lines as reference. The Q_1 band heads were measured with a precision of ± 0.05 cm^{-1}. The measured wavelengths are listed in Table I.

TABLE I

Wavelengths in (Å), and the Vibrational Assignment of the New and the Known Bands of the (0,0) and (0,1) Sequences of the Green System of BaF

(0,0) Sequence

v',v")	R_{21}-Head		R_2-Head		R_1Head		Q_1-Head	
	Present Work	Ref. (6)	Present Work	Ref. (6)	Present Work	Ref. (6)	Present Work	Ref. (6)
(0,0)	4937.35	4937.34	4950.74	4950.75	4992.08	4992.08	5000.08	5000.60
(1,1)	38.82	38.74	52.53	52.57	94.94	94.68	63.66	03.50
(2,2)	40.16	40.06	54.28	54.30	97.71	97.70	06.61	06.56
(3,3)	41.42	41.33	55.87	55.91	5000.49	5000.45	09.47	09.42
(4,4)	42.62	42.53	57.44	-	03.14	03.05	12.25	12.23
(5,5)	43.79	43.60	58.89	58.93	05.71	-	14.96	14.92
(6,6)	44.71	44.63	60.29	60.33	08.16	08.10	17.61	17.60
(7,7)	45.54	45.55	61.60	61.66	10.63	10.53	20.22	20.16
(8,8)	46.55	46.34	62.90	62.87	12.89	12.89	22.73	22.71
(9,9)	47.78	47.25	64.08	64.05	15.21		25.20	25.13
(10,10)	48.80		65.19	65.11	17.63		27.57	27.53
(11.11)	49.81		66.17	67.03	19.52		29.89	29.86
(12,12)			67.67		21.52		32.16	32.14
(13,13)			68.71		23.90		34.34	
(14,14)			69.44		25.85		36.36	
(15,15)			70.03		27.78		38.59	
(16,16)			70.69		30.19		40.58	

TABLE I (Contd.)

(17,17)	71.19	32.32	-
(18,18)	71.79	35.31	45.05

(0.1) Sequence

(0,1)	-	Diffuse edge at 19736.4 cm^{-1}, minimum at 19715.8 cm^{-1}	-	5102.67	5119.54	5119.05
(1,2)				04.73	21.63	21.20
(2,3)				06.58	23.68	23.25
(3,4)				08.16	25.57	25.12
(4,5)				09.58	27.43	27.17
(5,6)					29.21	29.01
(6.7)					30.89	30.73
(7,8)					32.46	32.38
(8,9)					34.05	33.99
(09,10)					35.50	35.52
(10,11)					36.85	36.94
(11,12)					38.25	38.21
(12,13)					39.37	
(13,14)					40.95	

EVALUATION OF THE MOLECULAR CONSTANTS

Since the rotational structure of the bands could not be resolved, it was not possible to measure the origin of the various bands directly. However, it was recognised that the band origin would lie quite close to the Q_1 head and the position of this origin for various bands were calculated as follows:

Using the expressions for the rotational lines of the Q_1 and R_1 branches (7), one readily obtains.

$$\nu_{R_1}^{(v',v'')}(\text{Head}) - \nu_{Q_1}^{(v',v'')}(\text{Head}) = \frac{2B'_v B''_v}{(B''_v - B'_v)} \quad \ldots (1)$$

and

$$Q_1^{(v',v'')}(\text{Head}) - \nu_0^{(v',v'')} = \frac{1}{4}\left[B''_v - \frac{B'^{2}_v}{(B'_v - B''_v)}\right] \quad \ldots (2)$$

where

$\nu_0^{(v',v'')}$ stands for the band origin and the other terms have their usual meaning.

Barrow et al (8) have reported the value of B_0 (=0.2158 cm^{-1}) for the ground state of BaF. Using this value and the experimentally determined values of $\nu_{R_1}^{(v',v'')}(\text{Head}) - \nu_{Q_1}^{(v',v'')}(\text{Head})$ for the (0,0), (0,1), and (1,1) bands, B'_0, B'_1, and B''_1 were calculated, which were used to obtain the values of B_e and α_e for the lower and upper states. Using these values, B'_v & B''_v for various vibrational levels were determined employing the relation:

$$B_v = B_e - \alpha_e\,(v + 1/2) \quad \ldots (3)$$

The origin of various bands was then calculated by substituting the values of B'_v and B''_v in Eq. (2).

The band origins obtained by the method described above were then used to evaluate the molecular constants for the upper and lower states states by an iterative technique employing a least square fit to the equation:

$$\nu_0^{(v',v'')} = \nu_e + \left[\omega'_e(v'+1/2) - \omega'_e x'_e(v'+1/2)^2 + \omega'_e y'_e(v'+1/2)^3 + \omega'_e z'_e(v'+1/2)^4\right]$$
$$-\left[\omega''_e(v''+1/2) - \omega''_e x''_e(v''+1/2)^2 + \omega''_e y''_e(v''+1/2)^3 + \omega''_e z''_e(v''+1/2)^4\right] \quad \ldots (4)$$

The calculations were carried out on an IBM-7044 computer using a program which provides a linear least square fit of the band origins by an iterative procedure.

The molecular constants obtained from our calculation are given in Table II together with the constants reported earlier. These constants reproduce the band origins of the observed bands with an average error of ($\nu_{obs}^{(v',v'')} - \nu_{calc}^{(v',v'')}$) equal to -0.0047 cm^{-1} as shown in Table III. The absolute value of the average error $|\nu_{obs}^{(v',v'')} - \nu_{calc}^{(v',v'')}|$ was found to be 0.079 cm^{-1}.

TABLE II

Molecular Constants for the $C^2\Pi_{1/2}$ & $X^2\Sigma$ state of BaF

Molecular Constants	Present Work		From Ref. (6)	
	Ground state (cm^{-1})	Excited state (cm^{-1})	Ground state (cm^{-1})	Excited state (cm^{-1})
ν_e	0	19993.553	0	19998.2
ω_e	471.116	458.814	469.1	455.9
$\omega_e x_e$	1.845	1.649	1.80	1.65
$\omega_e y_e$	-0.01912	-0.02635	-	-
$\omega_e z_e$	0.000452	0.000726	-	-

TABLE III

Calculated and Observed Band-Origins of the Green System of BaF

Bands	Observed Frequency (cm^{-1})	Calculated Frequency (cm^{-1})	Error (cm^{-1})
(0,1)	19519.942	19520.083	-0.141
(1,2)	19512.058	19511.999	0.059
(2,3)	19504.334	19504.343	-0.009
(3,4)	19497.223	19497.074	0.149
(4,5)	19490.231	19490.155	0.076
(5,6)	19483.549	19483.561	-0.012
(6,7)	19477.250	19477.269	-0.019
(7,8)	19471.372	19471.265	0.107
(8,9)	19465.422	19465.540	-0.118
(09,10)	19460.005	19460.093	-0.088
(10,11)	19454.970	19454.929	0.041
(11,12)	19450.000	19450.059	-0.059
(12,13)	19445.580	19445.500	0.080
(0,0)	19987.525	19987.448	0.077
(1,1)	19975.587	19975.516	0.071
(2,2)	19963.861	19963.917	-0.056
(3,3)	19952.508	19952.623	-0.115
(4,4)	19941.487	19941.609	-0.122
(5,5)	19930.755	19930.858	-0.103
(6,6)	19920.465	19920.360	0.105
(7,7)	19909.960	19910.111	-0.151
(8,8)	19900.055	19900.113	-0.058
(9,9)	19890.317	19890.376	-0.060
(10,10)	19880.985	19880.916	0.070
(11,11)	19871.857	19871.754	0.103
(12,12)	19862.936	19862.920	0.016
(13,13)	19854.378	19854.448	-0.071

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REFERENCES

1. C.M. Olmsted, Z. Wiss. Photogr., 4, 255 (1906).
2. S. Datta, Proc. Roy. Soc. A99, 436 (1921).
3. O.H. Walters, and S. Barrat, Proc. Roy. Soc., 118, 120 (1928).
4. T.E. Nevin, Proc. Phys. Soc., 43, 554 (1931).
5. R.C. Johnson, Proc. Roy. Soc. A122, 161 (1929).
6. F.A. Jenkins and A. Harvey, Phys., Rev., 39, 922 (1932).
7. G. Herzberg, "Spectra of Diatomic Molecules" Van Nostrand, Princeton, N.J., 1950.
8. R.F. Barrow, M.W. Bastin, and B. Lengborough, Proc. Phys. Soc. 92, 518 (1967).

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