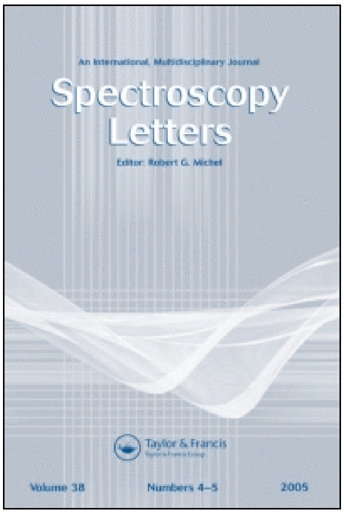

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Kushawaha, V. S.(1973) 'The $C^2\pi$ and the $X^2\sigma$ States of BaF', Spectroscopy Letters, 6: 10, 633 — 645
To link to this Article: DOI: 10.1080/00387017308060853
URL: http://dx.doi.org/10.1080/00387017308060853

SPECTROSCOPY LETTERS, 6(10), 633-645 (1973)

THE $C^2\Pi$ AND THE $X^2\Sigma$ STATES OF BaF

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ABSTRACT

An extensive calculation was carried out using the precisely measured value of the Q-band heads and the following molecular constants for the $C^2\Pi_{\frac{1}{2}}$ and the $X^2\Sigma$ states, which are responsible for the Green Band System of BaF, were determined.

Constants*	Upper State $C^2\Pi_{\frac{1}{2}}$	Lower state $X^2\Sigma$
ν_e	19993.719	0
ω_e	457.913	470.072
$\omega_e x_e$	1.559	1.717
$\omega_e y_e$	- 0.03689	- 0.03297
$\omega_e z_e$	+ 0.00116	+0.009357
B_e	0.2136	0.2164
α_e	0.0012	0.0012
r_e	2.1744	2.1601
I_e	131.033×10^{-40}	129.314×10^{-40}

* All the constants are in cm^{-1} except r_e and I_e, which are in A^o and gm cm^2 respectively.

INTRODUCTION

In the earlier communication (1), we have reported the vibrational constants ν_e , ω_e , $\omega_e x_e$, $\omega_e y_e$ and $\omega_e z_e$ for the upper ($C^2\Pi_{\frac{1}{2}}$) and the lower ($X^2\Sigma$) states involved in the transition responsible for the green band-system of BaF, using the precisely measured value of the Q_1-band heads photographed in the second-order of a 35-ft. concave grating spectrograph. Jenkins et al.(2) have shown that the state $^2\Pi_r$ splits into two components $^2\Pi_{3/2}$ and $^2\Pi_{\frac{1}{2}}$ with a separation of ~200 cm^{-1} and Mulliken (3) has shown that for a doublet state the B_v value is given by $B_{eff} = B_v \left(1 \pm \frac{B_v}{\Lambda A} \right)$ where A is the spin-orbit coupling constant and Λ is a quantum number associated with the component of the electronic angular momentum along the internuclear axis. when we were calculating the molecular constants, we used B_v' and B_v'' for determining the band-origin for various bands and then these band origin were used to derive the molecular constants for the upper and the lower states. But we ignored the splitting constant (~200 cm^{-1}) in the calculation, which contributes substantially to the values of B'_v and thus to the molecular constants.

In the present communication we report a new set of molecular constants for the upper and the lower states. These constants have been derived using the modified values of the band-origins in a least square iterative technique.

DETERMINATION OF THE MOLECULAR CONSTANTS:

As it is already stated (1) that our best attempt to resolve the bands right upto the origin was unsuccessful and therefore, it was not possible to measure the band-origins experimentally. However, it was recognized that the band origins lie very close to the Q_1-band-head. The postion of these origins were then calculated using the following expressions for the R_1 and Q_1-branches (4).

$$R_{1\text{Head}}^{(v',v'')} - Q_{1\text{Head}}^{(v',v'')} = \frac{2\,B'_{\text{eff}} \cdot B''_v}{(B''_v - B'_{\text{eff}})} \qquad \ldots (i)$$

and

$$Q_{1\text{Head}}^{(v',v'')} - \nu_0^{(v',v'')} = \tfrac{1}{4}\left[B''_v - \frac{B'_{\text{eff}}}{(B'_{\text{eff}} - B''_v)}\right] \qquad \ldots (ii)$$

where

$$B_{\text{eff}} = B_v \left(1 \pm \frac{B_v}{\Lambda A}\right) \qquad \ldots (iii)$$

Now it is reported by Barrow <u>et al</u>.(5) that for the ground state of BaF, $B_o = 0.2158\ \text{cm}^{-1}$. Using this value and the experimentally detemined values of $R_{1\text{Head}}^{(v',v'')} - Q_{1\text{Head}}^{(v',v'')}$ for the (0,0), (0,1) and (1,1) bands, B'_o, B'_1 and B''_1 were calculated to be $0.2131\ \text{cm}^{-1}$, $0.2119\ \text{cm}^{-1}$, and $0.2146\ \text{cm}^{-1}$ respectively. These constants were then used to determine the values of B_e and α_e for the upper and the lower states employing the following relation:

$$B_v = B_e - \alpha_e \left(v + \tfrac{1}{2}\right) \qquad \ldots (iv)$$

The values are :

$B'_e = 0.2136\ \text{cm}^{-1}$, $\alpha'_e = 0.0012\ \text{cm}^{-1}$

$B''_e = 0.2146\ \text{cm}^{-1}$, $\alpha''_e = 0.0012\ \text{cm}^{-1}$

These values were then used to calculate B'_v and B''_v for various vibrational levels and are given in Table I.

It will be noted that the B'_{eff} appearing in equations (1 & 2) is associated with $C^2\Pi_{\frac{1}{2}}$ component, since we could observe (1) bands belonging to $C^2\Pi_{\frac{1}{2}} - X^2\Sigma$ system only. Using therefore, the -ve sign and putting $A = 200\ cm^{-1}$ (2) and $\Lambda = 1$ in the equation (iii), the values of B'_{eff} were calculated for different vibrational levels and are given in Table I. The origin of all the bands of the $\Delta v = 0$ and $\Delta v = -1$ sequences were then calculated by substituting the values of B'_{eff} and B''_v in equation (1 & 2) and these values are given in Table II. Since the band origins have been determined from directly measured data for Q_1 - band heads, these band-origins will be referred as the "experimentally determined band-origins" here after. These band-origins were then used to evaluate the molecular constants employing a least square fit to the equation :

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

where all the symbols have their usual meaning. 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.

Calculation of r_e and I_e for the Upper and the Lower States:

The molecular constant B_e is related to the internuclear distance r_e by the following relation :

$$r_e = \frac{4.10610}{\sqrt{\mu_A \cdot B_e}} \times 10^{-8} \text{ cm} \qquad \ldots \text{(vi)}$$

Substituting the values of B'_e and μ_A (= 16.6953 a.m.u.) in the equation (vi), one readily obtains $r'_e = 2.1744$ A°. Likewise, r''_e is found to be 2.1601 A°. It will be noted that , as expected, the above value of r''_e is smaller than r''_o (= 2.163 A°) reported by Barrow <u>et</u>.<u>al</u>.(4) for the ground state of BaF. The moment of inertia I_e can easily be calculated by the following relation :

$$I_e = \mu_A \cdot r_e^2 \qquad \ldots \text{(vii)}$$

The values of I'_e and I''_e were found to be 131.033×10^{-40} and 129.314×10^{-40} gm cm^2 respectively.

RESULTS AND DISCUSSION

The vibrational and the rotational constants are reported in Table III, alongwith the constants reported earlier for the sake of comparison. The set of molecular constants determined in this work reproduce the observed band-origins with an average error of ($\nu^{(v',v'')}_{obs} - \nu^{(v',v'')}_{cal}$) equal to + 0.003 cm^{-1} and the average value of absolute error equal to 0.093 cm^{-1}, as shown in Table II.

The magnitude of $\omega_e y_e$ and $\omega_e x_e$ reported in Table III for the upper and the lower electronic states are quite small and one could argue whether these constants are of any significance. In order to test the accuracy of these constants, the following calculations were done ;

The values of ω_e and $\omega_e x_e$ for the upper and the lower states were used (living aside $\omega_e y_e$ and $\omega_e z_e$) in the quation (v) to calculate the band-origins of the various bands and the results are shown in Table IV. One can easily see that the values of ($\nu^o_{obs.}$ - $\nu^o_{cal.}$) is relatively small for bands involving lower vibrational quanta but assume unreasonably large magnitudes for bands involving higher vibrational quanta. In view of the precision of measurement reported by Kushawaha et al. (1), the magnitude of ($\nu^o_{obs.}$ - $\nu^o_{cal.}$) for bands involving higher values of v' and v", seems unreasonable. The average value of the errors ($\nu^o_{obs.}$ - $\nu^o_{cal.}$) and $|(\nu^o_{obs.} - \nu^o_{cal.})|$ turns out to be + 0.791 and 2.097 cm^{-1} respectively, which is much larger than the ones reported in Table II. It can therefore, be concluded that the set of molecular constants reported in Table III are more accurate and that the constants $\omega_e y_e$ and $\omega_e z_e$ are really quite significant.

It will be noted that the calculations of the molecular constants reported in this work primarily depend upon the determination of B_v value for the various vibrational levels. The precision of measurement claimed by Kushwaha et al.(1) is ± 0.05 cm^{-1}. Thus one can expect a maximum error of 0.10 cm^{-1} in the measurement of $R_{1Head}^{(v',v")} - Q_{1Head}^{(v';v")}$. This error produces a very insignificant change in the calculated values of B_v'' . For example, substituting the values of 34.360 and 34.460 cm^{-1} for the $R_{1Head}^{(v',v")} - Q_{1Head}^{(v',v")}$ for the (0,0) band, one obtains the value of B_0' as 0.21312 and 0.21313 cm^{-1} respectively.

According to Pekeris (6), if an electronic state follows the Morse Potential Function, the value of α_e for the state is given by :

$$\alpha_e = \frac{6\sqrt{\omega_e x_e B_e^3}}{\omega_e} - \frac{6B_e^2}{\omega_e} \qquad \ldots \text{(viii)}$$

Substituting the values of ω_e , $\omega_e x_e$ and B_e in the above equation for the $^2\Pi_{\frac{1}{2}}$ (upper) and $^2\Sigma$ (ground) states reported in this work, one obtains the following values for α_e' and α_e'' .

$$\alpha_e'(^2\Pi_{\frac{1}{2}}) = 0.00115 \text{ cm}^{-1}$$

and

$$\alpha_e''(^2\Sigma) = 0.00116 \text{ cm}^{-1}$$

The values can be compared with those reported in Table III, which have been determined rather experimentally ($\alpha_e' = 0.0012$ cm^{-1} and $\alpha_e'' = 0.0012$ cm^{-1}). Since the above values match very well, it can be inferred that the upper electronic state $C^2\Pi_{\frac{1}{2}}$ as well as the lower state $X^2\Sigma$ follow the Morse Potential Function.

TABLE-I

Rotational constant B_v for the upper ($C^2\Pi_{\frac{1}{2}}$) and the Lower $X^2\Sigma$ States of the Green Band System of BaF

V	B'_v (cm^{-1})	B'_{eff} (cm^{-1})	B''_v (cm^{-1})
0	0.2131	0.21287	0.2158
1	0.2119	0.21167	0.2146
2	0.2107	0.21048	0.2134
3	0.2095	0.20928	0.2122
4	0.2083	0.20808	0.2110
5	0.2071	0.20688	0.2098
6	0.2059	0.20568	0.2086
7	0.2047	0.20449	0.2074
8	0.2035	0.20329	0.2062
9	0.2023	0.20209	0.2050
10	0.2011	0.20089	0.2038
11	0.1999	0.19970	0.2026
12	0.1987	0.19850	0.2014
13	0.1975	0.19730	0.2002
14	0.1963	0.19610	0.1990
15	-	-	0.1978
16	-	-	0.1966

TABLE-II

Observed and calculated band-origins of the $C^2\Pi_{\frac{1}{2}}-X^2\Sigma$ Band-System of BaF Using ν_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, and $\omega_e z_e$ from the present work.

(v',v")	Observed Frequencies (cm^{-1})	Calculated Frequencies (cm^{-1})	$\nu_{obs.} - \nu_{cal.}$ (cm^{-1})
(0,1)	19520.92	19521.14	-0.22
(1,2)	19513.03	19512.99	+0.04
(2,3)	19505.30	19505.28	+0.02
(3,4)	19498.17	19497.97	+0.20
(4,5)	19491.17	19491.04	+0.13
(5,6)	19484.48	19484.44	+0.04
(6,7)	19478.17	19478.16	+0.01
(7,8)	19472.28	19472.17	+0.11
(8,9)	19466.32	19466.47	-0.15
(9,10)	19460.89	19461.03	-0.14
(10,11)	19455.84	19455.85	-0.01
(11,12)	19450.86	19450.94	-0.08
(12,13)	19446.43	19446.28	+0.15
(13,14)	19442.31	19442.32	-0.01
(0,0)	19987.85	19987.68	+0.17
(1,1)	19975.91	19975.82	+0.09
(2,2)	19964.18	19964.26	-0.08
(3,3)	19952.82	19952.96	-0.14
(4,4)	19941.79	19941.93	-0.14
(5,5)	19931.06	19931.15	-0.09
(6,6)	19920.77	19920.62	+0.15
(7,7)	19910.26	19910.35	-0.09
(8,8)	19900.35	19900.34	+0.01

TABLE-II (Contd.)

(9,9)	19890.61	19890.61	+0.00
(10,10)	19881.27	19881.16	+0.11
(11,11)	19872.14	19872.02	+0.12
(12,12)	19863.22	19863.22	+0.00
(13,13)	19854.66	19854.77	-0.11

Average Error:

$(\nu_{obs.} - \nu_{cal.}) = +0.003$

$|(\nu_{obs} - \nu_{cal})| = 0.093$

TABLE-III

Molecular constants for the $C^2\Pi_{\frac{1}{2}}$ and $X^2\Sigma$ states of BaF

Molecular* Constants	Present Work		From Ref.(1)	
	Ground State (cm^{-1})	Excited State (cm^{-1})	Ground State (cm^{-1})	Excited State (cm^{-1})
ν_e	0	19993.719	0	19993.553
ω_e	470.072	457.913	471.116	458.314
$\omega_e x_e$	1.717	1.559	1.845	1.649
$\omega_e y_e$	- 0.03297	- 0.03689	- 0.01912	- 0.02635
$\omega_e z_e$	+ 0.009357	+ 0.001116	+ 0.000452	+ 0.000726
B_e	0.2164	0.2136	-	-
α_e	0.0012	0.0012	-	-

TABLE III (cont'd)

r_e	2.1601	2.1744	-	-
I_e	129.314×10^{-40}	131.033×10^{-40}	-	-

* All the constants are in cm^{-1} except r_e and I_e, which are in A^o and gm cm^2 respectively.

TABLE-IV

Observed and Calculated Band Origins of the $C^2\Pi_{\frac{1}{2}}-X^2\Sigma$ Band-System of BaF Using ν_e, ω_e, $\omega_e x_e$ from this work.

(v',v")	Observed Frequencies (cm^{-1})	Calculated Frequencies (cm^{-1})	$\nu_{obs} - \nu_{cal}$ (cm^{-1})
(0,1)	19520.92	19521.05	-0.13
(1,2)	19513.03	19512.63	+0.40
(2,3)	19505.29	19504.54	+0.75
(3,4)	19498.17	19496.70	+0.70
(4,5)	19491.17	19489.30	+0.87
(5,6)	19484.47	19482.16	+2.31
(6,7)	19478.17	19475.33	+2.84
(7,8)	19472.28	19468.81	+3.47
(8,9)	19466.32	19462.62	+3.70
(9,10)	19460.89	19456.74	+4.15
(10,11)	19455.84	19451.17	+4.67
(11,12)	19450.86q	19445.92	+4.94
(12,13)	19446.43	19440.99	+5.44
(13,14)	19442.31	19436.37	+5.94

TABLE-IV (Contd.)

(0,0)	19987.85	19987.68	+0.17
(1,1)	19975.91	19975.83	+0.08
(2,2)	19964.18	19964.31	-0.13
(3,3)	19952.82	19953.10	-0.28
(4,4)	19941.79	19942.20	-0.41
(5,5)	19931.06	19931.62	-0.56
(6,6)	19920.77	19921.36	-0.59
(7,7)	19910.26	19911.41	-1.15
(8,8)	19900.35	19901.78	-1.43
(9,9)	19890.61	19892.47	-1.86
(10,10)	19881.27	19883.47	-2.20
(11,11)	19872.14	19874.78	-2.64
(12,12)	19863.22	19866.42	-3.20
(13,13)	19854.66	19858.37	-3.71

Average Error: $(\nu_{obs.} - \nu_{cal.}) = +0.791$

$|(\nu_{obs.} - \nu_{cal.})| = 2.097$

ACKNOWLEDGMENT

The author is thankful to Dr. C.M. Pathank for valuable suggestions and discussions. The financial support from the C.S.I.R., India, during the period of this work is gratefully acknowledged.

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Received May 16, 1973

Accepted August 29, 1973