

Isotope shift studies in the spectrum of boron monosulphide

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Abstract. The spectrum of boron monosulphide has been excited in microwave discharge and photographed at moderate dispersion. The $C^2\Pi_i-X^2\Sigma^+$, $B^2\Sigma^+-A^2\Pi_i$ and $A^2\Pi_i-X^2\Sigma^+$ band systems extending from 2100-9000 Å have been obtained for $B^{32}S$ and $B^{34}S$ species. Isotope shifts for all these band systems have been measured. Comparison of the observed isotope shifts with the theoretically calculated isotope shifts confirms the emitter as well as the vibrational assignments of all these band systems.

Keywords. Emission band spectrum; boron monosulphide; isotope shifts.

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1. Introduction

Boron monosulphide molecule has an extensive electronic band spectrum in the 2200-9000 Å region in which several band systems have been identified:

$$\begin{aligned} &A^2\Pi_i-X^2\Sigma^+ (4300-9000 \text{ Å}), \quad B^2\Sigma^+-A^2\Pi_i (4900-5050 \text{ Å}), \\ &C^2\Pi_i-X^2\Sigma^+ (2400-2900 \text{ Å}), \quad D^2\Delta_i-A^2\Pi_i (3100 \text{ Å}), \\ &F^2\Delta_i-A^2\Pi_i (4100 \text{ Å}) \quad \text{and} \quad E^2\Sigma^+-X^2\Sigma^+ (2100-2300 \text{ Å}). \end{aligned}$$

Although vibrational and rotational structure analyses of several of these band systems have been carried out, (Zeeman 1951; McDonald and Innes 1969; Singh *et al* 1971; Bell and McClean Megan 1976; Jenouvrier and Pascat 1981), extensive isotope shift studies of this spectrum have not so far been carried out. The isotope shift studies help identify the emitter of the spectrum as well as provide a check on the correctness of the vibrational assignments in various electronic band systems. We have taken up the isotope shift studies of this molecule by exciting the spectra of $B^{32}S$ and $B^{34}S$ in microwave discharge and by recording the spectrum under moderate dispersion (5.6 Å/mm). We have obtained experimental isotope shifts and compared them with the corresponding theoretical shifts for various band systems. The details of these studies are presented in this paper.

2. Experimental details

The spectra of $B^{32}S$ and $B^{34}S$ molecules have been excited by microwave discharge (200 Watt, 2450 MHz) through a sealed quartz discharge tube containing small

quantities of pure elemental sulphur (^{32}S and ^{34}S), boron and neon gas at a pressure of 2 torr. As soon as the discharge is initiated a strong spectrum of S_2 is produced. As the discharge tube warms up, the sulphur vapour reacts with boron metal to form the BS molecule. When sulphur is completely reacted the spectrum of S_2 disappears and only the spectrum of BS persists. The spectra were photographed on a 3 m Jarrell Ash grating spectrograph at a dispersion of $5.60 \text{ \AA}/\text{mm}$. The band heads were measured against iron standard lines. The accuracy of head measurement is expected to be about 0.5 cm^{-1} .

3. Results and discussion

The spectrum of BS molecule, which extends from $2200\text{--}9000 \text{ \AA}$, consists mainly of three strong band systems, namely, $C^2\Pi_r-X^2\Sigma^+$, $B^2\Sigma^+-A^2\Pi_i$ and $A^2\Pi_i-X^2\Sigma^+$. These band systems are very intense and extend over wide spectral regions. There are two more short groups of bands at around 3100 \AA and 4100 \AA which have been assigned to $D^2\Delta_r-A^2\Pi_i$ and $F^2\Delta_r-A^2\Pi_i$ transitions respectively. Recently, yet another band system was observed in the $2100\text{--}2300 \text{ \AA}$ region and assigned to $E^2\Sigma^+-X^2\Sigma^+$ transition (Bell and McClean Megan 1976). In the present studies all band systems except the $E-X$ have been photographed both for B^{32}S and B^{34}S molecules. The experimental isotope shifts have been evaluated for all these band systems and compared with the corresponding theoretical isotope shifts. We discuss below the results for each one of the systems.

3.1 $A^2\Pi_i-X^2\Sigma^+$ system (4300-9000 \AA)

Zeeman (1951) was the first to photograph the $A-X$ bands in the region ($5100\text{--}9000 \text{ \AA}$) and to carry out rotational analysis of a few of them. He found good agreement between the calculated and the experimentally determined isotope shift for 4-0 band of $^{10}\text{B}^{32}\text{S}$ and $^{11}\text{B}^{32}\text{S}$ molecules. This system was further extended on the lower wavelength side to 4300 \AA by Singh *et al* (1971) who excited these bands thermally in a King furnace. A few of the typical bands of the $A-X$ system of B^{32}S and B^{34}S photographed in the present studies are shown in figure 1b. The experimental isotope shifts for B^{32}S and B^{34}S have been evaluated and presented in table 1. The theoretical isotope shifts (Δv) have been calculated from the well-known formula, viz

$$\begin{aligned} \Delta v = v - v^i = & (1 - \rho) [\omega_e(v' + 1/2) - \omega_e''(v'' + 1/2)] \\ & - (1 - \rho^2) [\omega_e'x_e'(v' + 1/2)^2 - \omega_e''x_e''(v'' + 1/2)^2] \\ & + (1 - \rho^3) [\omega_e'y_e'(v' + 1/2)^3 - \omega_e''y_e''(v'' + 1/2)^3], \end{aligned} \quad (1)$$

where $\rho = \mu/\mu^i$ and i refers to B^{34}S .

The following vibrational constants are used: for the A state, $\omega_e = 754.23 \text{ cm}^{-1}$, $\omega_e x_e = 4.85 \text{ cm}^{-1}$ and $\omega_e y_e = 0.019 \text{ cm}^{-1}$; for the X state, $\omega_e = 1179.91 \text{ cm}^{-1}$, $\omega_e x_e = 9.1 \text{ cm}^{-1}$ and $\omega_e y_e = -0.0083 \text{ cm}^{-1}$ (Jenouvrier and Pascat 1981). The computed isotope shift values are also presented in table 1. The agreement between the experimental and theoretical isotope shifts is found to be satisfactory thereby confirming the present vibrational assignments.

Table 1. Isotope shifts (in cm^{-1}) of the $A^2\Pi_r-X^2\Sigma^+$ bands of $B^{32}\text{S}$ and $B^{34}\text{S}$.

Band	$^2\Pi_{1/2}$		$^2\Pi_{3/2}$		Isotope shifts		
	$\nu(N)$	$\nu(I)$	$\nu(N)$	$\nu(I)$	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{cal}}$
					($^2\Pi_{1/2}$)	($^2\Pi_{3/2}$)	
1-1	—	—	15244.67	15249.50	—	-4.83	-4.78
2-1	16305.75	16305.05	15974.85	15975.10	+0.70	-0.23	+0.64
3-1	17039.51	17033.78	16701.22	16696.13	+5.73	+5.09	+5.92
2-0	17480.56	17472.85	17160.30	17149.52	+7.71	+10.78	+9.38
3-0	18200.74	18184.45	17872.47	17858.31	+16.29	+14.16	+14.66
4-0	18913.22	18893.41	18583.81	18563.82	+19.81	+19.99	+19.81
5-0	19628.16	19605.38	19292.34	19266.06	+22.78	+26.28	+24.81
6-0	20333.73	20307.63	19993.72	19967.48	+26.10	+26.24	+29.69
7-0	21025.94	20993.75	20678.16	20642.59	+32.19	+35.57	+34.44
8-0	21670.33	21630.62	21365.04	21331.89	+39.71	+33.15	+39.06
9-0	22531.94	22487.68	22351.76	22309.38	+44.26	+42.38	+43.55
10-0	23020.12	22978.67	22690.52	22640.11	+41.45	+50.41	+47.92

Table 2. Isotope shifts (in cm^{-1}) of the $C^2\Pi_r-X^2\Sigma^+$ bands of $B^{32}\text{S}$ and $B^{34}\text{S}$.

Band	$^2\Pi_{1/2}$		$^2\Pi_{3/2}$		Isotope shifts		
	$\nu(N)$	$\nu(I)$	$\nu(N)$	$\nu(I)$	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{cal}}$
					($^2\Pi_{1/2}$)	($^2\Pi_{3/2}$)	
0-1	37613.63	37623.13	37730.55	37738.92	-9.50	-8.37	-9.78
0-2	36478.40	36460.12	36575.67	36592.59	-18.28	-16.92	-18.27
1-3	36195.19	36125.33	—	—	-20.14	—	-20.07
2-4	35927.71	35950.10	—	—	-22.39	—	-21.88
0-3	35317.45	35344.27	35433.48	35458.30	-26.82	-24.82	-26.58
1-4	35065.90	35094.08	—	—	-28.18	—	-28.18
2-5	34837.58	34864.19	34937.06	34963.50	-26.61	-26.44	-29.80

3.2 $C^2\Pi_r-X^2\Sigma^+$ system (2500-3400 Å)

The $C-X$ bands which are red degraded exhibit a double-headed structure. Each electronic band consists of two such double-headed bands separated by about 115 cm^{-1} , being the spin splitting in the $C^2\Pi_r$ state. Rotational structure analyses of some of the $C-X$ bands were carried out by Zeeman (1951) and recently by Jenouvrier and Pascat (1981). We have photographed the $C-X$ bands of $B^{32}\text{S}$ and $B^{34}\text{S}$ molecules which are shown in figure 1a. From these spectra the isotope shifts have been determined. Theoretical shifts have been calculated from equation (1) by using the following vibrational constants: for the C state, $\omega_e = 887.6\text{ cm}^{-1}$, $\omega_e x_e = 9.1\text{ cm}^{-1}$ and for X state, $\omega_e = 1179.91\text{ cm}^{-1}$, $\omega_e x_e = 6.25\text{ cm}^{-1}$, $\omega_e y_e = -0.0083\text{ cm}^{-1}$ (Jenouvrier and Pascat 1981). These shifts together with the experimental shifts have been given in table 2. They agree satisfactorily, confirming the vibrational assignment.

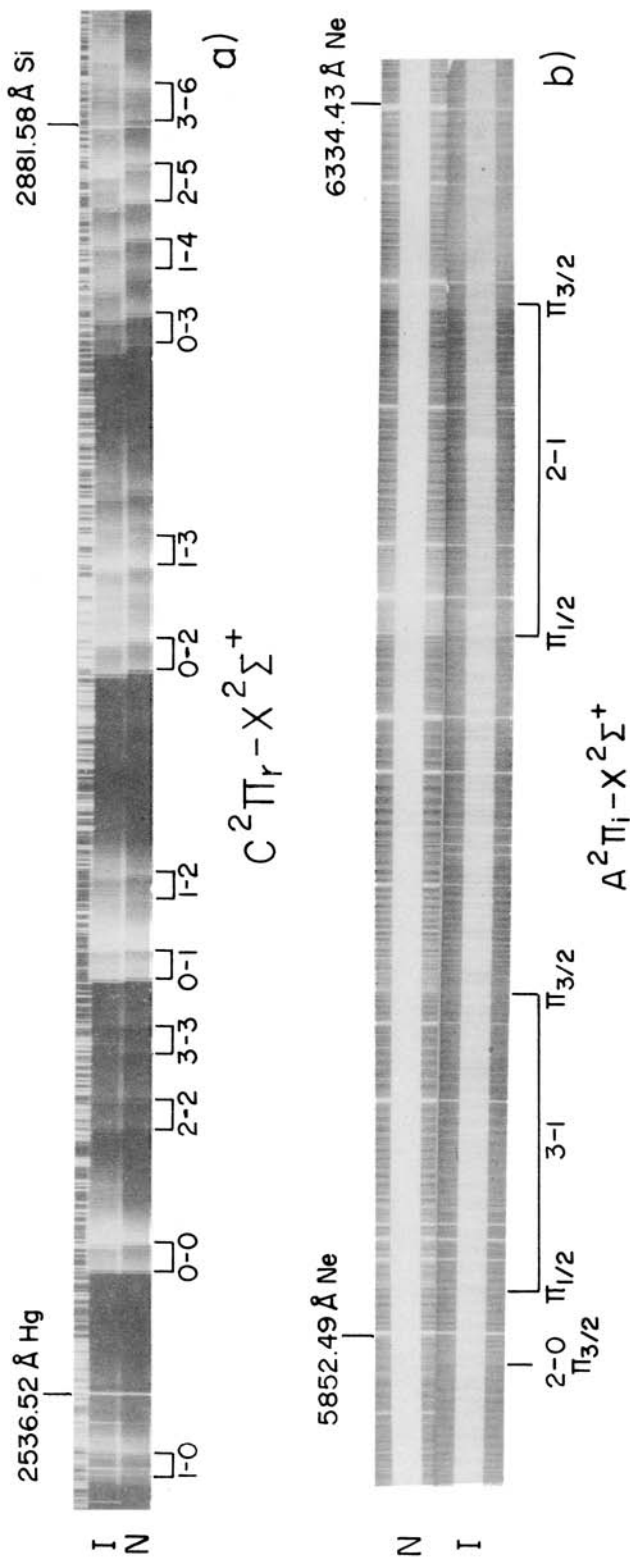


Table 3. Isotope shifts (in cm^{-1}) of the $B^2\Sigma^+ - A^2\Pi_i$ bands of $B^{32}\text{S}$ and $B^{34}\text{S}$.

Band	$^2\Pi_{1/2}$		$^2\Pi_{3/2}$		Isotope shifts		
	$\nu(N)$	$\nu(I)$	$\nu(N)$	$\nu(I)$	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{cal}}$
					($^2\Pi_{1/2}$)	($^2\Pi_{3/2}$)	
0-0	20011.70	20011.55	20348.44	20348.20	+0.15	+0.24	+0.06
0-1	20030.26	20029.89	20366.26	20365.83	+0.37	+0.43	+0.22
2-2	20050.41	20049.95	20387.62	20387.27	+0.46	+0.35	+0.40
3-3	20062.25	20061.69	20407.68	20407.20	+0.56	+0.48	+0.59
4-4	20095.10	20094.53	20431.43	20430.70	+0.57	+0.78	+0.73
2-3	—	—	19661.27	19664.85	—	-3.58	-4.88
3-4	—	—	19692.44	19696.48	—	-4.04	-4.55
4-5	—	—	19724.36	19728.69	—	-4.33	-4.23

3.3 $B^2\Sigma^+ - A^2\Pi_i$ system (4900–5050 Å)

The $B-A$ system consists of strong $\Delta V = 0$ sequence bands and very weak $\Delta V = -1$ sequence bands. McDonald and Innes (1969) confirmed by isotope substitution of ^{10}B and ^{34}S the emitter of these bands as BS molecule. We have obtained experimental isotope shifts of these bands for $B^{32}\text{S}$ and $B^{34}\text{S}$ molecules and presented them in table 3. The bands belonging to the $\Delta V = 0$ sequence are shown in figure 1c. The theoretical isotope shifts have been calculated from equation (1) using the following constants (in cm^{-1});

$$\text{for the } B \text{ state, } \omega_e = 768.71, \quad \omega_e x_e = 3.05, \quad \omega_e y_e = -0.109;$$

$$\text{for the } A \text{ state, } \omega_e = 754.23, \quad \omega_e x_e = 4.85, \quad \omega_e y_e = 0.019.$$

The agreement between the values of the experimental and theoretical isotope shifts (table 3) is found to be satisfactory. The existing vibrational assignments have thus been confirmed.

3.4 Other band systems

There are two groups of rather closely-spaced bands at 4100 Å and 3100 Å which are assigned to two band systems. In each of these systems only $\Delta V = 0$ sequence bands appear with significant intensity. The 3100 Å group was studied by McDonald and Innes (1969) and assigned to $D^2\Delta_i - A^2\Pi_i$ transition. The 4100 Å group was reported by Jenouvrier and Pascat (1981). In view of the fact that these band systems primarily consist of $\Delta V = 0$ sequences extensive vibrational and rotational analyses have not been done. We have photographed both these band systems for $B^{32}\text{S}$ and $B^{34}\text{S}$. Although we have determined experimental isotope shifts for both the groups of bands we have not considered it worthwhile to calculate the theoretical shifts because the vibrational constants are not well determined for the electronic states involved. It must also be mentioned that the $E^2\Sigma^+ - X^2\Sigma^+$ bands (2100–2300 Å) reported by Bell and McClean Megan (1976) could not be excited by the present method of excitation.

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