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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

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Online publication date: 16 December 2003

To cite this Article Bojović, V. , Antić-Jovanović, A. , Pešić, D. , Isailović, D. and Kuzmanović, M.(2003) 'Vibrational Analysis of the β System of $^{10}\text{B}^{18}\text{O}$ ', *Spectroscopy Letters*, 36: 5, 531 — 536

To link to this Article: DOI: 10.1081/SL-120026638

URL: <http://dx.doi.org/10.1081/SL-120026638>

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Vibrational Analysis of the β System of $^{10}\text{B}^{18}\text{O}$

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ABSTRACT

Ten bands of the β system ($\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$) of the $^{10}\text{B}^{18}\text{O}$ molecule have been observed for the first time. The spectrum was obtained by emission spectroscopy from a low-pressure arc, at medium dispersion, and vibrationally analyzed using isotope shift measurements. Vibrational analysis gave the constants ω_e and ω_{eXe} for both electronic states involved in the transitions.

Key Words: Boron oxide; Vibrational analysis; Isotope effect.

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INTRODUCTION

The first observation of the emission bands of the BO molecule were made by Jevons^[1] who identified two distinct systems, α (637–337 nm) and β (330–214 nm). The author measured a number of bands which were ascribed to a nitride of boron. This was a natural supposition, because the bands were developed in active nitrogen. However, a few years later, Mulliken^[2] published vibrational analysis of the same system, excited in a boron arc in air, and in active nitrogen containing a vapor of BCl_3 and a trace of oxygen, in which the bands of the isotopic ^{11}BO and ^{10}BO molecules were correctly identified; the natural abundances of the ^{11}B and ^{10}B are about 81% and 19% respectively. Mulliken's analysis is important historically because it represents the first experimental verification of the vibrational isotope effect, and the existence of zero point energy in molecules, as predicted by quantum theory.

The α system has been rotationally analyzed by Jenkins and McKeller^[3] and found to be $\text{A}^2\Pi - \text{X}^2\Sigma$, while the β system was shown by Lagerqvist et al.^[4] to be $\text{B}^2\Sigma - \text{X}^2\Sigma$. A third system, lying below 230 nm, was first observed by Chrétien^[5] and assigned to the $\text{C}^2\Pi - \text{X}^2\Sigma$ transition by Mal'tsev et al.^[6] and Kuzyakov et al.^[7] All results dealing with the emission spectrum of $^{11}\text{B}^{16}\text{O}$, can be found in Refs. [8–10].

In 1984, Coxon et al.^[11] published the results of a new rotational analysis of the A–X system of $^{11}\text{B}^{16}\text{O}$ and $^{10}\text{B}^{16}\text{O}$. Somewhat later, Mélen et al.^[12] carried out the analysis of the α and β bands of both isotopomers and determined more accurate equilibrium constants for the electronic states $\text{X}^2\Sigma$, $\text{A}^2\Pi$ and $\text{B}^2\Sigma^+$ than those obtained by Lagerqvist et al.^[4] Their results are in good agreement with those published by Coxon et al.^[11] as well as with those theoretically calculated by Karna and Grein.^[13]

Recently, Mélen et al.^[14] performed an analysis of the $^{11}\text{B}^{16}\text{O}$ and $^{10}\text{B}^{16}\text{O}$ bands of the C–X system and gave improved rotational constants for the $\text{C}^2\Pi$ state which was identified as regular state.

The lack of any data concerning the isotopic molecules $^{11}\text{B}^{18}\text{O}$ and a $^{10}\text{B}^{18}\text{O}$ is surprising in view of the astrophysical interest in the BO spectrum, and suggestions about possible lasing action of the electronic transitions of BO.^[15,16]

The objective of our study has been to provide the first spectroscopic data for BO isotopomers containing oxygen 18. In the present paper we report the results obtained from a vibrational analysis of the β bands of the $^{10}\text{B}^{18}\text{O}$ molecule detected by emission under moderate dispersion. The vibrational assignments of the bands were confirmed by isotope shift measurements.

EXPERIMENTAL

The β bands of the $^{10}\text{B}^{18}\text{O}$ molecule were measured by emission spectroscopy in a low-pressure copper arc whose lower positive electrode contained amorphous boron 10. The arc was run at a current of 6 A in an atmosphere of a (4:1) mixture of argon and oxygen 18 enriched up to 90 atom % at about 2000 Pa of total pressure. Under the appropriate conditions, the spectrum was recorded in 30 minutes on a 2.3 m Zeiss spectrograph (disp. 0.37 nm/mm) by using Ilford HP5 emulsion and a slit width of 30 μ .

The band head positions were measured on a microscope against Fe lines provided by a dc arc discharge. The accuracy of the measurements is estimated to be better than 0.5 cm^{-1} .

RESULTS AND DISCUSSION

Vibrational Analysis and Isotope Shifts

Ten B-X bands of $^{10}\text{B}^{18}\text{O}$ were obtained in the region between 220 and 300 nm. They are very similar in appearance to the red-degraded bands of $^{10}\text{B}^{16}\text{O}$. These have a single headed structure, since the R_1 and R_2 branches, which form the heads, are not resolved at low J values.

The vibrational assignment of the bands, supported by the observed isotope displacements, was straightforward (Table 1). The wavenumbers for

Table 1. Band heads and isotope shifts (in cm^{-1}) of the B-X system of BO molecules.

v',v''	$v_h(^{10}\text{B}^{16}\text{O})$	$v_h(^{10}\text{B}^{18}\text{O})$	$\Delta v_h(\text{obs})$	$\Delta v_h(\text{calc})$
1,0	44169.0(4)	44147.9(3)	-21.1	-20.9
0,0	42871.5(-2)	42879.3(-3)	7.8	6.7
1,1	42253.1(-6)	42273.9(-1)	20.8	20.1
2,2	41636.6(-1)	41670.3(1)	33.7	33.5
0,1	40959.2(4)	41005.6(-6)	46.4	47.4
0,2	39069.8(6)	39156.8(1)	87.0	87.6
1,3	38500.1(3)	38598.9(5)	98.8	98.8
0,3	37204.9(2)	37331.7(0)	126.8	126.4
1,4	36660.7(3)	36796.8(-2)	136.1	136.6
1,6	33056.8(2)	33265.5(1)	208.7	208.9

Numbers in parentheses denote differences $v_h(\text{obs}) - v_h(\text{calc})$ in units of 10^{-1} cm^{-1} .



the measured $^{10}\text{B}^{18}\text{O}$ band heads are given in the third column, while the second column contains Mulliken's data for the corresponding band heads of $^{10}\text{B}^{16}\text{O}$. In columns four and five, the observed and calculated band head shifts, $\Delta v_h = v_h^i - v_h$, are given, where the superscript *i* refers to heavier species. Calculation was performed using the second order vibrational isotope shift equation,^[17] reduced mass constant $\rho = (\mu/\mu^i)^{1/2} = 0.97833$ and Mélen's^[12] equilibrium vibrational constants for the B and X states. Due to the small interval between heads and origins, the contribution of the rotational isotope effect has been neglected and the electronic isotope shift was assumed to be zero. As one can see from this table, agreement between observed and calculated Δv_h values is good, supporting the previously given vibrational assignment.

Determination of the Constants

All the heads from Table 1 have been used to obtain a nonlinear least-squares fit to the constants T_e , ω_e , $\omega_e x_e$ and $\omega_e y_e$ for the upper and lower electronic states using the third order expression:

$$\begin{aligned} v_h(v', v'') = & T_e + [\omega'_e(v' + 1/2) - \omega'_e x'_e(v' + 1/2)^2 \\ & + \omega'_e y'_e(v' + 1/2)^3] - [\omega''_e(v'' + 1/2) \\ & - \omega''_e x''_e(v'' + 1/2)^2 + \omega''_e y''_e(v'' + 1/2)^3] \end{aligned}$$

The values obtained for T_e , and the vibrational constants for both the $^{10}\text{B}^{16}\text{O}$ and $^{10}\text{B}^{18}\text{O}$ isotopic molecules, are summarized in Table 2. The $\omega_e'' y_e''$ values for both species have been found to be smaller than their standard deviations and, because of this, they were neglected.

Table 2. Molecular constants for B and X states (in cm^{-1}) of BO molecules.

State	Molecule	T_e	ω_e	$\omega_e x_e$	$\omega_e y_e$	Ref.
$\text{B}^2\Sigma^+$	$^{10}\text{B}^{16}\text{O}$	43173.84(11)	1320.54(17)	12.230(84)	0.179(11)	[12]
	$^{10}\text{B}^{16}\text{O}$	43183.8(8)	1319.01(1)	12.14(6)	0.17(9)	*
	$^{10}\text{B}^{18}\text{O}$	43182.6(4)	1291.60(6)	12.20(3)	0.20(4)	*
	$^{10}\text{B}^{16}\text{O}$	0	1940.308(23)	12.4873(42)	—	[12]
$\text{X}^2\Sigma^+$	$^{10}\text{B}^{16}\text{O}$	0	1939.71(2)	12.57(2)	—	*
	$^{10}\text{B}^{18}\text{O}$	0	1897.83(3)	11.93(6)	—	*

Numbers in parentheses denote estimated standard deviations in units of the last digits.

*This work.

The constants for $^{10}\text{B}^{16}\text{O}$, thus obtained, are compared in Table 2 with those obtained by Mélen et al.^[12] With the exception of the T_e values, the other constants for this molecule, which were obtained in the present work and by previous authors,^[4] are in a reasonable agreement. The difference between our and Melen's value of T_e is caused by the fact that the latter was derived from band origins while we used the band head data.

As the head-origin separations are small and, the derived vibrational constants close to the real values, it follows that the T_e values for the B state of both isotopic molecules, estimated in this work, should be lowered by 10 cm^{-1} . The wavenumbers of the band heads calculated from the above equation, with the derived constants, agree well with those given in the second and third columns of Table 1.

The differences between measured and calculated wavenumbers, listed in parentheses in Table 1, appear free from any systematic deviation. All observed heads are reproduced within experimental uncertainties, even those in the worst case still remain within twice the error limits.

In conclusion, the present work gives the first estimates of the equilibrium vibrational constants for $\text{B}^2\Sigma$ and $\text{X}^2\Sigma$ states of $^{10}\text{B}^{18}\text{O}$. Improved values are expected from the analysis of high-resolution spectra, which are planned to be recorded in the future.

ACKNOWLEDGMENT

This work was supported by the Research Council of Serbia.

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Received March 25, 2003

Accepted September 2, 2003