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Millimeter- and submillimeter-wave spectroscopy of HBS and DBS in vibrationally excited states

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Abstract

Normal and deuterated isotopic variants of thioborine have been produced in the gas phase by a high temperature reaction between crystalline boron and hydrogen sulfide. Millimeter- and submillimeter-wave rotational spectra have been recorded in the frequency range from 75 to 730 GHz for vibrational ground and excited states of the $H^{10/11}B^{32}S$ and $D^{10/11}B^{32}S$ isotopic species. The spectra of all the excited states which lie below 1500 cm^{-1}, that are 01^10, 00^01, 02^00, and 02^20, have been observed and analyzed for each of the four isotopologues investigated. High-order Fermi resonance parameters were found important to analyze properly the spectra of the 00^01 and 02^00 interacting states. The improved rotational data in conjunction with earlier infrared spectroscopy results have been employed to calculate more precise anharmonic force constants and equilibrium bond lengths.

Keywords: Rotational spectroscopy; Thioborine; HBS; Pyrolysis; Excited states; Fermi resonance

1. Introduction

Thioborine (HBS), the first member of the X—B=S series of unstable sulphidoboron compounds, was first detected by Kirk and Timms in the mass spectrum of the products of the high temperature reaction between hydrogen sulfide and solid boron [1]. Its rotational spectrum was subsequently studied in the millimeter-wave (mm-wave) region, from 110 to 370 GHz, by Pearson and McCormick [2], who recorded and analyzed ground-state spectra for eight isotopic species ($^{1/2}H^{10/11}B^{32/34}S$) and bending excited-state spectra of four isotopic species ($^{1/2}H^{10/11}B^{32}S$). Further rotational spectroscopy investigations yielded the determination of the ^{10}B, ^{11}B and ^{33}S nuclear hyperfine coupling constants in thioborine [3,4]. The high-resolution infrared spectrum of thioborine was first studied by Sams and Maki [5], who analyzed the ν_1 vibrational fundamental for $H^{10/11}B^{32/34}S$, and the first hot band (11^10–01^10) for $H^{10/11}B\ ^{32}S$. The ν_1, ν_3, and $2\nu_2^0$ bands of $D^{10/11}B^{32}S$, and the ν_3 band of $H^{10/11}B^{32}S$ were subsequently recorded by Turner and Mills [6] with a resolution of about 0.1 cm^{-1}.

This article presents the first study of the pure rotational spectra of $H^{10/11}B^{32}S$ and $D^{10/11}B^{32}S$ in the vibrationally excited states located between 1000 and 1500 cm^{-1}, that are the 00^01, 02^00, and 02^20 states, and in addition it extends up to 730 GHz previous measurements [2,4] for the ground and 01^10 excited states of the same isotopic species. The lines measured for the 00^01 and 02^l0 states of each isotopologue have been analyzed taking simultaneously into account both *l*-type and Fermi resonance effects in order to obtain directly deperturbed spectroscopic constants. The improved rotational parameters have been used, together with the ro-vibrational data already known form previous works [5,6], to make a more precise evaluation of the anharmonic force constants of HBS up to quartic terms. The equilibrium structure of thioborine has been also refined using vibration–rotation interaction constants (α_r) predicted from the force field and experimental ground-state rotational constants (B_0) of the eight isotopic variants $^{1/2}H^{10/11}B^{32/34}S$.

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2. Experimental details

Thioborine has been produced in the gas phase by a pyrolysis reaction between hydrogen sulfide and crystalline boron in a flow reactor, as already described in [4]. Deuterated hydrogen sulfide was obtained simply mixing at room temperature H_2S and D_2O (1:10 molar ratio) in a glass bottle, from which D_2S has been then extracted by a low temperature trap-to-trap distillation. The rotational spectra of thioborine were observed in selected frequency regions between 75 and 730 GHz using a source modulation mm-wave spectrometer which employs Gunn oscillators (Farran and Carlstrom) and Klystrons (Varian) as main radiation sources to cover the fundamental frequency range 75–115 GHz. Higher frequencies were generated using three different frequency multipliers, one for the 50–75 GHz band, and a quadrupler and a sextupler (Radiometer Physics) both optimized for the 75–110 GHz band. The oscillators were phase-locked to the suitable harmonic of the fundamental frequency emitted by a cm-wave solid state source (Wavetek), which was in turn locked to a computer-controlled frequency synthesizer (Schomandl). A Schottky-barrier diode (Millitech) and a liquid-helium-cooled InSb detector (QMC) were, respectively, used to record the spectra below and above 200 GHz. The Gunn oscillators were frequency modulated at 16.7 kHz, and the detected signals were demodulated by a lock-in amplifier tuned at 33.3 kHz, so that the second derivative of the actual spectrum profile was displayed by the computer-controlled acquisition system. The accuracy of the frequency measurements was in the range 10–20 kHz depending on the signal-to-noise ratio of the recorded lines.

3. Observed spectra and analysis

Ground and excited state rotational spectra have been recorded and analyzed for four isotopologues: $H^{11}B^{32}S$, $H^{10}B^{32}S$, $D^{11}B^{32}S$, and $D^{10}B^{32}S$, covering the J range from 1 to 21. The excited states observed are all which lie below 1500 cm^{-1}, that are (in order of increasing energy for $H^{11}B^{32}S$): 01^10, 00^01, 02^20, and 02^00. The l-type resonances in the bending states and the Fermi resonance which couples the vibrational states 00^01 and 02^00 [6] have been taken into account using the same formalism already employed to analyze the excited-state rotational spectra of FBS [7] and FCP [8]. Briefly, using the basis functions $|v_1 v_2^l v_3; J\rangle$ a ro-vibrational energy matrix is obtained with diagonal elements of the form:

$$\begin{aligned}\left\langle v_1 v_2^l v_3; J\middle|\hat{H}\middle|v_1 v_2^l v_3; J\right\rangle = {} & G_v^0 + x_{ll} l^2 \\ & + \left[B + \gamma_{ll} l^2\right]\left[J(J+1) - l^2\right] \\ & - \left[D + y_{ll} l^2\right]\left[J(J+1) - l^2\right]^2 \end{aligned} \quad (1)$$

where G_v^0 is the unperturbed vibrational energy, with the l-dependent term excluded. The off-diagonal ($\Delta l = \pm 2$), l-type resonance terms are:

$$\begin{aligned}&\left\langle v_1 v_2^{l\pm 2} v_3; J\middle|\hat{H}\middle|v_1 v_2^l v_3; J\right\rangle \\ &\quad = \frac{1}{4}\{q + q_J J(J+1)\}\sqrt{(v_2 \mp l)(v_2 \pm l + 2)} \\ &\quad\times \sqrt{\{J(J+1) - l(l\pm 1)\}\{J(J+1) - (l\pm 1)(l\pm 2)\}}\end{aligned} \quad (2)$$

whereas the off-diagonal matrix elements for Fermi resonance have the expressions: [9,10]:

$$\begin{aligned}&\left\langle v_1 v_2^l v_3; J\middle|\hat{H}\middle|v_1 (v_2+2)^l (v_3-1); J\right\rangle \\ &\quad = \frac{1}{2}\left[W_{223} + \lambda_1 v_1 + \lambda_2 (v_2+2) + \lambda_3 (v_3 + \tfrac{1}{2}) + W_{223J} J(J+1)\right] \\ &\quad\times \sqrt{v_3\left[(v_2+2)^2 - l^2\right]}\end{aligned} \quad (3a)$$

$$\begin{aligned}&\left\langle v_1 v_2^l v_3; J\middle|\hat{H}\middle|v_1 (v_2+2)^{l\pm 2} (v_3-1); J\right\rangle \\ &\quad = \frac{1}{2\sqrt{2}} W'_{223}\sqrt{v_3 (v_2 \pm l + 2)(v_2 \pm l + 4)} \\ &\quad\times \sqrt{[J(J+1) - l(l\pm 1)][J(J+1) - (l\pm 1)(l\pm 2)]}\end{aligned} \quad (3b)$$

The leading term W_{223} is directly related to the normal coordinate cubic force constant ϕ_{223} ($W_{223} = -\phi_{223}/2\sqrt{2}$), while the high-order W'_{223}, W_{223J}, and λ_v parameters involve the contributions of several potential constants up to cubic, quartic and quintic terms, respectively [9]. Theoretical expressions for W'_{223} and W_{223J} were derived by Watson [10].

Adopting the proper Wang-type linear combinations of wave functions, the resulting ro-vibrational energy matrix can be factorized in symmetric and antisymmetric blocks so that every sublevel of a state in which the v_2 quantum number is different from zero can be identified by the absolute value of l and by a plus or minus superscript [7].

The treatment of l-type and Fermi-type resonances led us to analyze simultaneously the spectra recorded for different vibrational states. Four polyads made of the 00^01, 02^00, and 02^20 states were considered for $^{1/2}H^{10/11}B^{32}S$, whereas ground and 01^10 states of each isotopic variant were treated as isolated. In the following subsections some details are given for the analyses performed. The complete list of transition frequencies measured is available as electronic Supplementary material.

3.1. Ground and 01^10 states of $H^{10/11}B^{32}S$ and $D^{10/11}B^{32}S$

Ground-state transition frequencies up to 460 GHz were already available for the $H^{10/11}B^{32}S$ isotopologues [4], and up to 370 GHz for the $D^{10/11}B^{32}S$ isotopologues [2]. As far as the 01^10 bending state is concerned, a few transition frequencies of each isotopic variant were measured by Pearson and McCormick in the 150–260 GHz frequency range [2]. We have extended the measurements up to 730 GHz, reaching a J value as high as 21 for the deuterated species. The full set of transition frequencies have been analyzed