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The high-resolution infrared spectrum of $^{11}BF_3$ from 400 to 1650 cm^{-1}

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Abstract

High-resolution infrared spectra of boron trifluoride, enriched to 99.5 at. % ^{11}B, have been measured from 400 to 1650 cm^{-1}. In that region we have identified and analyzed 16 absorption bands attributed to the three fundamental bands, two combination bands, 10 hot bands, and one difference band. All possible states were accessed in this region through direct transitions either from the ground state or as hot bands from thermally populated levels. The spectral resolution of the measurements varied from 0.0015 to 0.0020 cm^{-1}. An improved set of ground state rotational constants and rovibrational constants for the infrared-active fundamental vibrations have been determined from over 32 000 assigned transitions. This study resulted in the first direct characterization of the infrared-inactive ν_1 state of $^{11}BF_3$ leading to values for ν_1, α_1^B, and α_1^C of 885.843205(24), 0.000678548(53), and 0.000337564(66) cm^{-1}, respectively. The Fermi resonance perturbation between the E' states ν_3 and $3\nu_4(l=\pm1)$ was further elucidated by observation of hot band transitions to both the $3\nu_4(l=\pm1)$ and $3\nu_4(l=\pm3)$ states. Several other resonances were also found including the weak rotational interaction, between the A_1' state $2\nu_2$ and the E' state of $\nu_1+\nu_4$.

Keywords: Infrared spectroscopy; Rovibrational spectrum; High resolution; Boron trifluoride; Boron-11

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1. Introduction

Boron trifluoride (BF_3) is a highly toxic, colorless gas that fumes in the presence of moist air and hydrolyzes to form hydrogen fluoride. It is used in the semiconductor industry where it serves as a feed gas to create boron species in ion implanters. BF_3 is also widely used as a catalyst in many chemical operations due to its ability to act as a strong Lewis acid. This ability is due to an empty valence orbital that readily accepts a donated electron pair. The molecular structure of BF_3 is dictated by this empty orbital, making it one of the classic examples of a molecule possessing D_{3h} symmetry. The strength of BF_3 as a Lewis acid is somewhat counterintuitive when compared to other boron halides. Based on electronegativity and steric hindrance properties, one would expect the acidic strength of the boron halide compounds to fall as the fluorine ligand is replaced by a chlorine and then a bromine. However, just the opposite trend in Lewis acidity is observed for boron trihalides when complexed with weak Lewis bases [1,2], leading to many investigations of those complexes through various methods of spectroscopic and computational studies [1–11]. In particular, the HF–BF_3 complex has received considerable attention [8–12] because of the superacidity exhibited by BF_3 when dissolved in HF solution.

High-resolution spectroscopy on the $^{11}BF_3$ isotopomer has been limited to the tunable diode laser experiments of Yamamoto [13–15]. Though diode laser experiments have exquisite sensitivity, they are hampered by non-linearity and reduced spectral range. Because of these limitations, and a desire to extend the analysis to include the ν_4 fundamental vibration and a variety of never-before-studied hot bands and combination bands, we have conducted a high-resolution infrared analysis on isotopically enriched $^{11}BF_3$ between 400 and 4600 cm^{-1}. This paper will detail the re-

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sults of the analysis for those states whose band origins fall below 1650 cm^{-1} which includes all of the fundamental vibrations. In total, the three fundamental infrared-active bands, two combination bands, 10 hot bands, and one difference band were identified and analyzed. In addition, we were able to significantly improve upon the precision of the constants for previously analyzed vibrational states and for the ground state. The vibrational energy levels and transitions examined in this work are displayed in Fig. 1. The infrared-inactive ν_1 symmetric-stretching mode was characterized directly for the first time in $^{11}BF_3$ through three different routes; one using the transitions 110^00^0–000^00^0 A_2''–A_1' and 110^00^0–100^00^0 A_2''–A_1', one using the transitions 001^10^0–000^00^0 E'–A_1' and 001^10^0–100^00^0 E'–A_1', and the last using the transitions 100^01^1–000^00^0 E'–A_1' and 100^01^1–100^00^0 E'–A_1'.

Recently, in [16] we presented the results of a new analysis of the infrared spectra of the fundamental vibrations, hot bands, and combination bands of the $^{10}BF_3$ isotopomer. With the exception of a vibrational interaction between the A_1' vibrational states of $2\nu_2$ and $3\nu_4$ ($l = -3$), the major complication in the $^{10}BF_3$ analysis was due to rotational l-type interactions. Isotopic substitution of ^{11}B for ^{10}B at the center of mass for BF_3 shifts the band origins such that significant perturbations arise from interactions between entirely different states. The strongest perturbation encountered below 1650 cm^{-1} is due to the Fermi resonance interaction that takes place between the E' states ν_3 and $3\nu_4(l = \pm1)$. A normal $\Delta k = \pm2$, $\Delta l = \pm2$ l-type interaction among the levels $3\nu_4(l = \pm1)$ and $3\nu_4(l = \pm3)$ served to further complicate the analysis of this region. In this work, a much weaker interaction has been found between the $2\nu_2$ and $\nu_1 + \nu_4$ states. These states are coupled through a $\Delta k = \pm2$, $\Delta l = \mp1$ matrix element.

The most extensive ab initio calculation on $^{11}BF_3$ was performed by Pak and Woods [17] who reported on its anharmonic force field and rovibrational properties using the coupled cluster method [CCSD(T)] of calculation. In our next publication we will report on all of the measurable anharmonic constants determined for $^{11}BF_3$. Consequently, an evaluation of the majority of the theoretical work of Pak and Woods will not be included in this paper, but some comparisons will be made for parameters determined for the fundamental vibrational states.

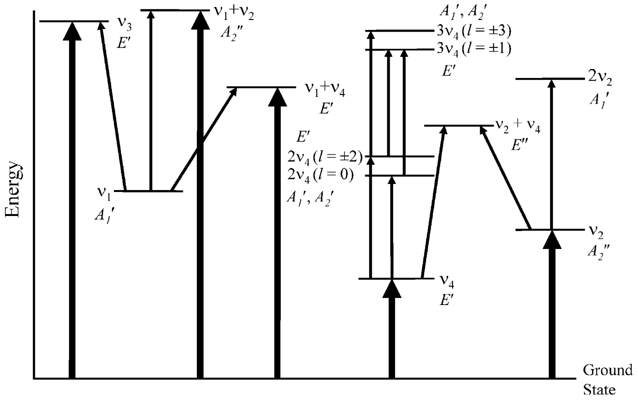

Fig. 1. The vibrational energy levels for $^{11}BF_3$ below 1650 cm^{-1}. The arrows indicate the observed infrared transitions.

2. Experimental

Due to the similarities of the vibrational bands of both isotopomers, data collection for both $^{10}BF_3$ and $^{11}BF_3$ was performed consecutively. Figs. 2 and 3 give an overview of the three infrared-active fundamental bands and two combination bands analyzed in this paper. The experimental conditions that were used in obtaining the spectra are described in detail in [16]. Briefly, the spectra were recorded at the PNNL facilities using a Bruker IFS 120HR Fourier transform spectrometer. Two different sample cells were used during the course of the measurements. The stronger bands were recorded using a gold plated sample cell with a 19.95 ± 0.01 cm pathlength that was temperature stabilized to 25.00 ± 0.02 °C. To bring out the weaker hot band transitions buried within the fundamental transitions and to extend the analysis of the stronger bands to higher J/K levels, a variable pathlength White cell was employed. Specific parameters for a given spectral region are listed in Table 1. The spectrometer was evacuated during the measurements and only minute amounts of CO_2 and H_2O persisted. The latter conveniently served as a method of absolute wavelength calibration for the lowest wavenumber region. The sample, purchased from Voltaix, was isotopically enriched to 99.5% $^{11}BF_3$. The main contamination in the majority of the spectra, however, was from $^{10}BF_3$ that had remained in both the sample cells and in the gas manifold from previous measurements. Another contaminant, $^{11}BF_2OH$ [21], was likely produced when $^{11}BF_3$ reacted with residual water in the sample cells. To reduce the amount of contamination from both of these species, the sample cells were flushed and evacuated between measurements. The resolution of the measurements ranged from 0.0015 to 0.0020 cm^{-1}. The spectra were calibrated with the reference gases listed in Table 1 resulting in an absolute wavelength calibration on the order of ±0.0002 cm^{-1}.

3. Analysis of the spectrum

3.1. Some general considerations

BF_3 belongs to the D_{3h} point group, in which only two of the six possible symmetry types allow for a dipole transition directly from the A_1' ground state. The four vibrational modes are shown in Fig. 4. Only the ν_1 vibrational mode fails to produce a change in the dipole moment of the molecule and is thus infrared-inactive. The three fundamental infrared-active vibrational absorption bands, ν_2, ν_3, and ν_4, are shown in Fig. 2. The symmetries of many of the combination and overtone states made them infrared-inactive as direct transitions from the ground state. Fortunate-