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Journal of Molecular Structure 742 (2005) 3–20
Journal of MOLECULAR STRUCTURE
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The high-resolution infrared spectrum of $^{10}BF_3$ from 400 to 4600 cm^{-1}

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Received 3 September 2004; revised 15 November 2004; accepted 22 November 2004
Available online 14 March 2005

This paper is dedicated to Dr Walter Lafferty, a long-term friend and colleague of one of the authors (A. Maki). For over 40 years we have witnessed the development of many improvements in the measurement, interpretation, and application of high-resolution infrared spectroscopy. Dr Lafferty has made, and continues to make, important contributions to the study and understanding of molecular structure

Abstract

High-resolution infrared spectra of boron trifluoride, enriched to 99.5 at.% ^{10}B, have been measured from 400 to 4600 cm^{-1}. In that region we have identified and analyzed 17 absorption bands including three fundamentals. In addition, three hot bands associated with ν_2 were analyzed, seven hot bands associated with ν_4, two with $\nu_1+\nu_4$ and one hot band each associated with the ν_3 and $\nu_1+\nu_2$ bands. The spectral resolution of the measurements varied from 0.0015 cm^{-1} at the lowest wavenumber to 0.0035 cm^{-1} at the highest wavenumber. This study resulted in the first direct characterization of the ν_1 state via two routes, one through the combined analysis of the 110^00^0–000^00^0 and 110^00^0–100^00^0 vibrational transitions and the other through the analysis of the 001^10^0–000^00^0 and 001^10^0–100^00^0 transitions. All of the quadratic vibrational anharmonic constants have been determined except x_{23}. An improved set of ground state rotational constants has been determined for $^{10}BF_3$. With corrections through most but not all of the quadratic rotational terms, we have found that $B_e=0.346170\pm0.000003$ cm^{-1} and $C_e=0.173038\pm0.000006$ cm^{-1}. These give a B–F bond distance of $r_e=130.731\pm0.010$ pm. The effects of *l*-type resonance were used to locate certain vibrational states that could not be directly observed through infrared transitions from the ground state. The splitting of the A'_1 and A'_2 components of $\nu_3+\nu_4$ was found to be quite large, 6.131 ± 0.007 cm^{-1}. Several other resonances were also found including the weak vibrational interaction, which had been overlooked by earlier workers, between $2\nu_2$ and the A'_1 vibrational state of $3\nu_4$.

Keywords: Infrared spectroscopy; Spectrum; Boron trifluoride; Molecular structure

1. Introduction

The first spectroscopic study of boron trifluoride (BF_3) with sufficient resolution to observe the rotational structure and consequently to experimentally determine the rotational constants for BF_3 was conducted by Nielsen [1] in 1954. That work was subsequently improved by Ginn et al. [2] in a series of papers by Overend and his co-workers that presented the first detailed survey of the infrared spectrum of BF_3 [2–7]. As part of that study, many of the overtone and combination bands of $^{10}BF_3$ and $^{11}BF_3$ were observed with low resolution and assigned by Brown and Overend [5]. A few bands were measured with sufficient resolution (0.03–0.05 cm^{-1}) to partially resolve the rotational fine structure, but the analysis, while state of the art for the time, was not up to present day standards.

Since then, there have been many improvements in spectroscopic equipment, most notably the development of tunable diode lasers and high-resolution Fourier transform spectrometers. Beginning in 1985 Yamamoto et al. [8–11] published several papers that used a tunable diode laser to study the rotational structure of two fundamental bands, ν_2 and ν_3, of $^{10}BF_3$ and $^{11}BF_3$. They also combined their tunable diode laser with a microwave spectrometer to make infrared–microwave double resonance measurements that gave very precise measurements of certain rotational transitions [8–10]. Their measurements were essential for determining the ground state constants C_0 and D_0^K.

The most recent high-resolution infrared measurements on BF_3 were reported by Zeisberger and Ruoff [12,13]. They

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doi:10.1016/j.molstruc.2004.11.089

only looked at the spectrum below 1600 cm^{-1}, but their analysis of over 12,000 transitions of $^{10}BF_3$ represents the most thorough study yet published on that molecule. Their ground state constants were used throughout most of the present study and it was only near the end of the present work that a new set of ground state constants was determined and used.

Of peripheral interest, one should mention that Oldani and Bauder [14] have measured the pure rotational spectrum of $^{11}BF_3$. Their analysis gives all the ground state rotational constants through the H terms although the H_K term was determined from the planarity condition. Since the boron atom is at the center of mass of the molecule and therefore is on all the rotational axes, the ground state rotational constants for $^{10}BF_3$ will be almost the same as for $^{11}BF_3$.

Ginn et al. [6] used the measurements made up to that time to calculate the force constants for BF_3 and then went on to calculate the anharmonic constants and rovibrational interaction constants. That work has been superceded by an ab initio calculation by Pak and Woods [15]. The work of Ginn et al. showed the expected shifts between $^{10}BF_3$ and $^{11}BF_3$ while Pak and Woods only calculated the constants for $^{11}BF_3$.

We have used a Fourier transform spectrometer to measure the spectrum of isotopically enriched $^{10}BF_3$ between 400 and 4600 cm^{-1}. All of the vibrational transitions observed in that span have been analyzed. A number of hot bands have also been measured in the region of the ν_2, ν_3, and ν_4 bands as well as the $\nu_1+\nu_2$ and $\nu_1+\nu_4$ bands. Fig. 1 indicates the energy levels and transitions observed in this work for those levels below 1610 cm^{-1}. In total 34 vibrational states have been studied (counting $l_i=0$ and $l_i=2$ as two different states) including the four fundamentals and the ground state.

With a few exceptions, the major complications noted were due to the effects of (rotational) l-type resonance and vibrational l-type resonance. One exception was the vibrational interaction between the A'_1 vibrational states $2\nu_2$ and $3\nu_4(l=-3)$. This was further complicated by the l-type resonance within $3\nu_4$. Some bands showed minor complications such that the higher rotational transitions systematically deviate from the calculated positions. In some cases, the small deviations can be eliminated by adding higher order constants to the Hamiltonian. Such higher order constants are probably effective constants needed to simulate the perturbing effects of other levels.

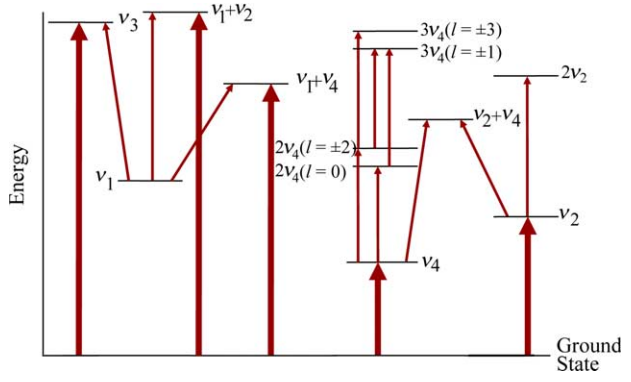

Fig. 1. The vibrational energy levels for $^{10}BF_3$ below 1610 cm^{-1}. The arrows indicate the observed infrared transitions.

Over 52,000 transitions were used in the least-squares analysis of the spectrum of $^{10}BF_3$. For these bands, the rms deviation of the fit was 0.0005 cm^{-1} or better. Had the weaker transitions been omitted, the rms deviation for most bands would have been more like 0.0002 cm^{-1} or better, but the weaker transitions are often important for determining the higher order constants.

2. Experimental details

The infrared spectra were recorded with a Bruker IFS 120 HR Fourier transform spectrometer at the PNNL facilities. Optical, electronic, and digital filters were used to limit the spectral window. The entire optical pathlength, except for the absorption cell, was evacuated for the measurements. All spectra were recorded in transmittance mode. The interferograms were collected single-sided and with both forward and backward scans. Boxcar apodization was used. A globar light source was used along with either a KBr or CaF_2 beamsplitter. The pressures used varied from 0.034 to 5.0 Torr, and either a 20 cm cell or a White cell was used for the measurements. The 20 cm cell was constructed with a double jacket that runs the length of the cell and is filled with a water/ethylene glycol mix circulated through a temperature bath that is regulated at 25.00 ± 0.02 °C. The White cell pathlengths varied from 3.2 to 38.4 m and the White cell measurements were conducted at room temperature. Both CsI and AgCl windows were used. The spectral resolution varied from 0.0015 to 0.0035 cm^{-1}. Table 1 gives a few parameters for each of the spectra used in this analysis.

The BF_3 samples, isotopically enriched to 99.5 at.% ^{10}B, were purchased from Voltaix, Inc. and were stated to be 99.9% chemically pure. In the spectra we found many spectral bands due to $^{10}BF_2OH$ [16] which was probably formed by reaction with H_2O adsorbed on the cell walls. The amount of $^{10}BF_2OH$ observed in the spectra increased steadily over time so the sample cells were thoroughly flushed and evacuated between measurements. The spectra were calibrated by means of absorption features due to H_2O, CO_2, CO, N_2O, or OCS which were either present in trace amounts in the evacuated optical pathlength or introduced into the sample cell before or after the BF_3 spectra were measured. The gas and reference used for the wavenumber calibration of each spectrum is given in Table 1. In addition to the statistical uncertainties given in the tables, the vibrational term values are believed to be accurate to