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First analysis of the $3\nu_9-\nu_9$ hot band of difluoroboric acid (BF_2OH). Further evidence of large amplitude effects for the OH torsion

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In honor of three great contributors and mentors of high-resolution molecular spectroscopy: Jean-Marie Flaud, Claude Camy-Peyret, and Alain Barbe
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ABSTRACT

The hot band $3\nu_9-\nu_9$ of the isotopologue $^{11}BF_2OH$ (difluoroboric acid) located at 1034.78 cm^{-1} was investigated for the first time by Fourier transform infrared spectroscopy. During previous studies both, the ν_9 mode (OH-torsion relative to the BF_2 moiety, at 522.87 cm^{-1}) and the ν_4 mode (in-plane OH bend) had been shown to exert large amplitude motion, and splittings of 0.0051 and 0.0038 cm^{-1} had been observed in the interacting $2\nu_9$ and ν_4 bands located at 1042.87 and 961.49 cm^{-1}, respectively. The present work establishes large amplitude effects also for the 9^3 excited state located at 1557.655 cm^{-1}. Numerous P and R transitions of the $3\nu_9$–ν_9 hot band were identified in the $2\nu_9$ manifold, and doublets corresponding to a torsional splitting of 0.031 cm^{-1} in the 9^3 state were observed. The vibrational assignment of the 9^3 state was confirmed by the detection of the $3\nu_9-2\nu_9$ hot band Q branch in the 19 μm region.

1. Introduction

Unlike ozone [1], for which the contribution of the three honourees is of major importance, difluoroboric acid (BF_2OH, see Fig. 1) is to our knowledge not supposed to be of atmospheric relevance. The latter molecule is a reactive intermediate formed in the hydrolysis of BF_3. The BF_2OH molecule is a planar asymmetric rotor. Its equilibrium geometry and anharmonic force field up to semidiagonal quartic terms have been calculated at the coupled cluster level of theory including a perturbational estimate of the effects of connected triple excitations [CCSD(T)] [2]. The microwave spectrum was measured several times [2–5]. The matrix infrared (IR) spectra of eight isotopologues were first observed by Jacox et al. [6]. Some of these data for the ^{11}B and ^{10}B isotopic species of BF_2OH[1] are also contained in Table 1, which otherwise quotes the available high resolution infrared data. The first high resolution gas phase IR spectrum of BF_2OH was observed by Collet et al. [7] using a Fourier transform spectrometer, and this study led to the first investigation of the ν_8 and ν_9 fundamental bands of 11B. Subsequently, the ν_5, ν_8, ν_9, and $\nu_8+\nu_9$ bands of 10B, and the ν_7, ν_5, and $\nu_8+\nu_9$ bands of 11B were investigated by high resolution [8], and only the ν_5 and ν_7 bands were found to be weakly perturbed. On the contrary, the ν_4 and $2\nu_9$ bands [9] which correspond to the OH in-plane bending mode and to the first overtone of ν_9 (OH torsion relative to the $\frac{F}{F}>B{-}O$ moiety), respectively, are strongly perturbed. Indeed, the energy levels of the 9^2 state are involved in B-type Coriolis resonances with those of the 6^19^1 dark state. Moreover,

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[1] For the $^{11}BF_2OH$ and $^{10}BF_2OH$ isotopic species we will use henceforth in the text the abbreviated notation 11B and 10B, respectively.

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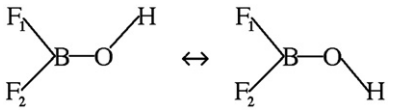

Fig. 1. Exchange of the fluorine nuclei in the large amplitude OH torsional and OH bending motions (v_9 and v_4, respectively).

Table 1
Fundamental and hot bands of BF_2OH and overtones states of interest for this study (cm^{-1}).

Vibrational assignment[a]	Description	$^{11}BF_2OH$	$^{10}BF_2OH$
v_1, A′	v (OH)	3712.5[b]	3712.5[b]
v_2, A′	v_{as}(BF)	1464.3[b]	1515.8[b]
v_3, A′	v_s(BF)	1414.9[b]	1456.9[b]
v_4, A′	δ(BOH) i.p.	961.49[d]	961.74[d]
v_5, A′	$\delta(BF_2)$ i.p.	880.74[c]	880.64[c]
v_6, A′	v (F_2BO) i.p.	479.17[c]	
v_7, A′	$\delta(F_2BO)$ i.p.	446.54[c]	
v_8, A″	$\delta(F_2BO)$ o.p.	684.16[c]	711.41[c]
v_9, A″	δ(BOH) o.p.	522.87[c]	523.04[c]
$2v_9$		1042.87[d]	1043.89[d]
$3v_9-v_9$		1034.78[e]	
$3v_9-2v_9$		514.80[e]	
9^2, A′		1042.87[d]	1043.89[d]
9^3, A″		1557.66[e]	

[a] A′ and A″ are the symmetry species in the C_s point group.
[b] Matrix band centers from Ref. [6].
[c] Gas phase band centers from Ref. [8].
[d] Gas phase band centers from Ref. [9].
[e] This work.

the 4^1 levels are perturbed by B-type Coriolis resonances with 7^19^1 levels and by C-type Coriolis and anharmonic resonances with the 6^17^1 levels. In addition to these rather "classical" perturbations, large amplitude effects emerged in the analysis of the $2v_9$ and v_4 bands and this lead to the observation of tunneling splittings of about 0.0051 and 0.0038 cm^{-1} for the 9^2 and 4^1 states, respectively.

These large amplitude effects for BF_2OH were confirmed by a careful reinvestigation of the rotational spectrum by millimeter wave techniques [5]. In this study, torsional splittings were found for most of the rotational transitions within the ground state and could be satisfactorily reproduced using the IAM (Internal Axis Method) formalism developed in Refs. [10–13]. Indeed, BF_2OH is not the first molecule for which large amplitude effects associated with the OH torsion (nv_9 mode) were observed in the IR spectrum. However, the observation of similarly large splittings in the v_4 band was rather surprising. In Ref. [5] it was possible to explain the existence of large amplitude effects both in the states 4^1 and 9^2 by using the pseudo Jahn–Teller (PJT) formalism for the description of the $4^1 \Leftrightarrow 9^1$ vibronic coupling. Using this approach, reasonable agreement between the ab initio (0.0061 and 0.0043 cm^{-1}) and experimental (0.0038 and 0.0051 cm^{-1}) tunneling splittings for the 4^1 and 9^2 states could be achieved.

It is tempting to compare difluoroboric acid (BF_2OH) with nitric acid (HNO_3) which is an isovalent molecule.

For the latter [14] the v_9 vibrational mode corresponds to the large amplitude torsional motion of the H–O bond relative to the $^{O}_{O} > N-O$ radical. This motion induces torsional splittings of the 9^n energy levels which increase with n. For the 9^1 and 9^2 excited states located at 458.2 and 896.4 cm^{-1}, respectively, these splittings amount to ~2 MHz and ~0.002 cm^{-1} (ca. 60 MHz), respectively, and are therefore only observable by microwave or millimeter wave techniques [15–19].[2] In contrast, for the 9^3 excited state located at 1288.87 cm^{-1} the torsional splittings are on the order of 0.060 cm^{-1} and should be observable by infrared technique. However, the $3v_9$ band being a dark one, its energy and tunneling splittings could only be measured by studying the hot bands $3v_9-v_9$, $3v_9-2v_9$, and $3v_9-v_5$, located at 830.6, 392.4, and 409.7 cm^{-1}, respectively [20]. No evidence of large amplitude effects, however, was found in the analysis of the v_4 infrared band of nitric acid [21].

The goal of the present study is to evident large amplitude effects in the 9^3 vibrational state of difluoroboric acid by using high resolution Fourier transform spectra [9]. As for HNO_3 [14], the $3v_9$ band of BF_2OH is a dark band, while the $2v_9$ band reveals considerable infrared intensity [9]. Therefore, the 9^3 state of BF_2OH may be reached in analogy to nitric acid via analysis of the $3v_9-v_9$ hot band since it is expected to have some infrared intensity. Possibly there may be additional information deducible from the $3v_9-2v_9$ hot band near 19 μm. These assumptions were valid both for 11B and 10B and both species are investigated although only that of 11B with success.

In Section 2 the experimental spectra used for this study will be briefly described. Section 3 outlines the analysis of the spectra, while Section 4 presents the theoretical model and reports the results. Section 5 discusses the results and draws conclusions.

2. Experimental details

Details of the synthesis of the enriched isotopologues 10B (92.4%) and 11B (99%) of BF_2OH and the recording of the high resolution FT-IR spectra were given in Table 2 of Ref. [8]. For the present study, only the 11B spectra denoted "1043c-11B" and "0522-11B" were successfully used for the investigation of the $3v_9-v_9$ and $3v_9-2v_9$ hot bands near 1030 and near 515 cm^{-1}, respectively. In addition, the "1044-10B" and "0523-10B" spectra were used for the still unsuccessful search of the $3v_9-v_9$ and $3v_9-2v_9$ hot bands for the 10B isotopologue. In order to avoid contamination by SiF_4, BF_2OH was synthesized from BF_3 and H_2O in a glass-free reactor and the IR spectrum recorded employing a stainless steel absorption tube measuring 1.5 m in length and outfitted with NaCl windows. The chosen total pressure was 250 and 100 Pa for the "1043c-11B" and "0522-11B" spectra, respectively. The Bruker IFS 120 h interferometer at Wuppertal was

[2] In fact, the v_5 mode (NO_2 in-plane bending) of nitric acid is a low amplitude motion. However, due to strong Fermi resonance coupling of the 5^1 and 9^2 energy levels, a transfer of torsional splitting from 9^2 to 5^1 was observed and theoretically modeled [16, 17, 19].