Boron Nuclear Quadrupole Coupling in $BF(OH)_2$

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We investigated the nuclear quadrupole coupling of the ^{11}B and ^{10}B nuclei in fluorodihydroxy borane, $BF(OH)_2$. An analysis of the hyperfine splittings resulted in the coupling constants $\chi_{aa} = -1.414(11)$ MHz, $\chi_{bb} = -1.206(11)$ MHz, $\chi_{cc} = 2.620(11)$ MHz for ^{11}B and $\chi_{aa} = -2.872(67)$ MHz, $\chi_{bb} = -2.525(69)$ MHz, $\chi_{cc} = 5.397(69)$ MHz for ^{10}B. From these constants the ratio r of the quadrupole moments $r = Q(^{10}B)/Q(^{11}B) = 2.051(44)$ could be derived and compared to data taken from the literature.

I. Introduction

Our investigation was motivated by the search for the $BF_3 \cdots H_2O$ complex. We were not able to find transitions belonging to this complex, but we could observe the hydrolysis products BF_2OH and $BF(OH)_2$ of BF_3. The quadrupole coupling of ^{11}B in the first hydrolysis product has already been studied by Vormann and Dreizler [1] using waveguide and molecular beam Fourier transform microwave (MB-FTMW) spectroscopy. The spectrum of fluorodihydroxy borane, $BF(OH)_2$, has been studied by Kawashima et al. [2] using Stark modulation spectroscopy. For producing the latter substance in the waveguide a relatively high pressure was necessary leading to broad lines showing no quadrupole hyperfine structure. In this investigation the application of MB-FTMW spectroscopy allowed to resolve the hyperfine structure of some of the transitions reported in [2].

II. Experimental

The substance was produced by mixing water vapour and BF_3 (Merck, Darmstadt) in a bottle together with argon as carrier gas. This mixture was expanded at a backing pressure of 1 atm into our Fabry–Perot type beam spectrometers [3–5]. We recorded transitions in the frequency range between 15 and 35 GHz. For the most abundant isotopomer (^{11}B, 80.39%, nuclear spin $I = 3/2$ [6]) 6 rotational transitions with 20 hyperfine (hfs) components were observed, whereas for the less abundant isotopomer (^{10}B, 19.61%, nuclear spin $I = 3$ [6]) only two transitions with 6 hyperfine components could be identified. This relatively low number of measured lines reflects the experimental difficulties in preparing the substance by the described method.

III. Analysis

For each of the observed transitions at least three hyperfine components have been found. Their values are compiled in Tables 1 and 2 for the ^{11}B and ^{10}B isotopomers, respectively. The power spectra of the $1_{11}-0_{00}$ transitions showing all three hyperfine components are depicted in Fig. 1, for $^{11}BF(OH)_2$ on the left hand side and for $^{10}BF(OH)_2$ on the right. The quadrupole coupling constants χ_{aa} and $\chi_{\min} = \chi_{bb} - \chi_{cc}$, determined from the hyperfine splittings by diagonalization of the Hamilton matrix using the program HFS [7], are given in Table 3 together with the derived

Table 1. Transitions of $^{11}BF(OH)_2$ with hyperfine components. $\delta\nu$: hyperfine splitting with respect to the line denoted by *, $\Delta_{obs-calc}$: error of $\delta\nu$.

$J'_{K'_-K'_+} - J_{K_-K_+}$	$F'-F$	ν [MHz]	$\delta\nu$ [kHz]	$\Delta_{obs-calc}$ [kHz]
$1_{11}-0_{00}$	3/2–3/2	15 245.2734	*	*
	5/2–3/2	15 245.5808	−307.4	−5.8
	1/2–3/2	15 245.8161	−542.7	0.1
$2_{12}-1_{01}$	5/2–3/2	25 314.8461	*	*
	7/2–5/2	25 315.1479	−301.8	−0.2
	1/2–1/2	25 315.3149	−468.8	−0.9
$2_{02}-1_{11}$	5/2–5/2	25 057.9263	*	*
	5/2–3/2	25 058.2262	−299.9	1.7
	7/2–5/2	25 058.5790	−652.7	3.0
$2_{21}-1_{10}$	3/2–3/2	35 666.2295	*	*
	5/2–3/2	35 666.4878	−258.3	−5.8
	7/2–5/2	35 666.7844	−554.9	−0.9
$3_{13}-2_{02}$	5/2–3/2	35 264.1031	*	*
	7/2–5/2	35 264.1939	−90.8	−4.6
	3/2–1/2	35 264.2591	−156.0	7.3
	9/2–7/2	35 264.3501	−247.0	2.5
$3_{03}-2_{12}$	5/2–3/2	35 254.8093	*	*
	7/2–5/2	35 254.8997	−90.4	−4.7
	3/2–1/2	35 254.9727	−163.4	0.6
	9/2–7/2	35 255.0567	−247.4	2.2

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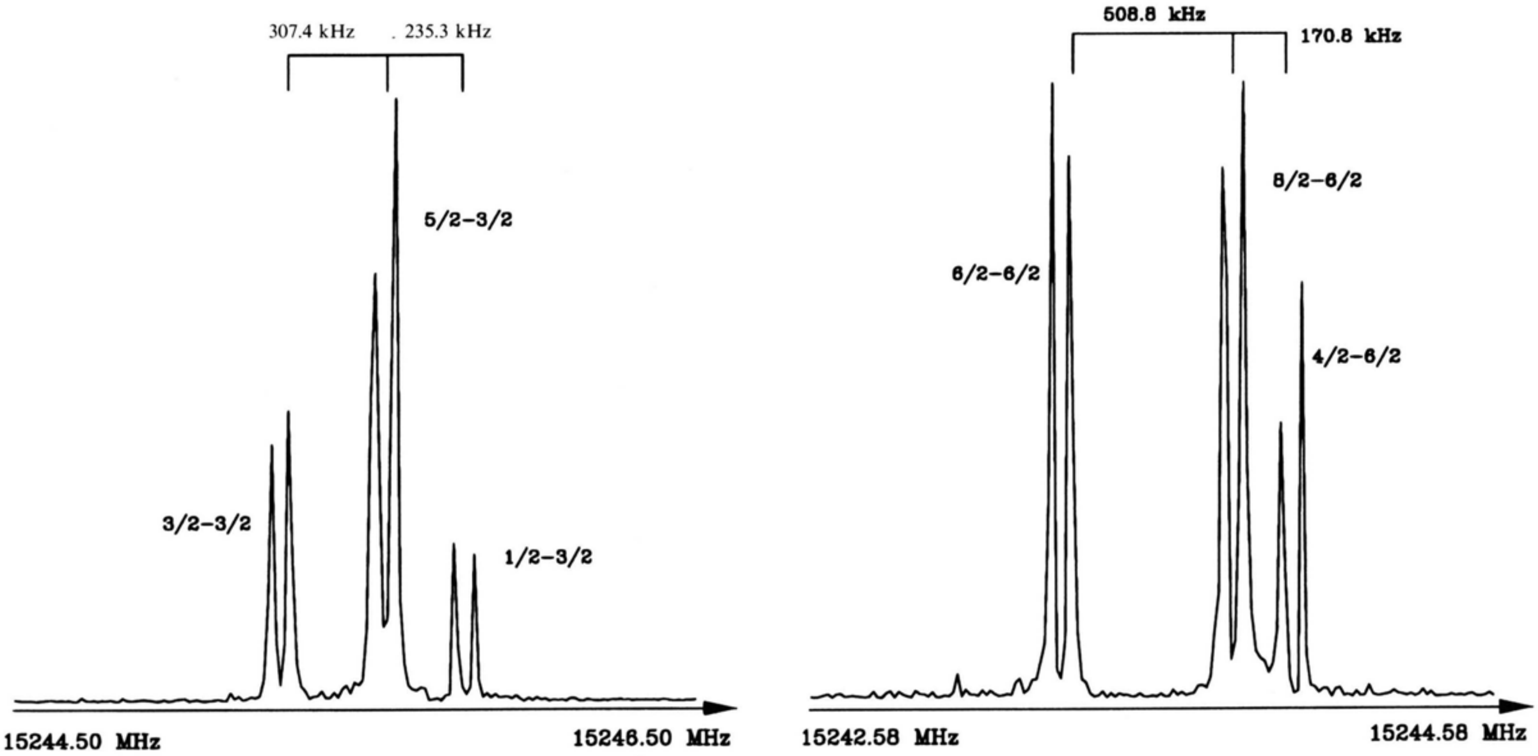

Fig. 1. Power spectra of the $1_{11}-0_{00}$ transitions of $^{11}BF(OH)_2$ (left) and $^{10}BF(OH)_2$ (right). The transient signals were recorded with 256 and 1024 averaging cycles, respectively, microwave power 2 mW, microwave pulse length 0.6 µs, sample interval 10 ns, 8 K data points.

Table 2. Transitions of $^{10}BF(OH)_2$ with hyperfine components. $\delta\nu$: hyperfine splitting with respect to the line denoted by *, $\Delta_{obs-calc}$: error of $\delta\nu$.

$J'_{K'_aK'_c}-J_{K_aK_c}$	$F'-F$	ν[MHz]	$\delta\nu$[kHz]	$\Delta_{obs-calc}$ [kHz]
$1_{11}-0_{00}$	3–3	15 243.3048	*	*
	4–3	15 243.8136	508.8	−1.4
	2–3	15 243.9844	−679.6	2.2
$2_{12}-1_{01}$	4–3	25 311.8867	*	*
	3–3	25 312.0421	−155.4	−1.2
	5–4	25 312.2777	−391.0	−1.6

Table 3. The quadrupole coupling and rotational constants of the ^{11}B- und ^{10}B-isotopomers of $BF(OH)_2$ and their ratio r giving the ratio of the corresponding nuclear quadrupole moments. The rotational constants were taken from the work of Kawashima et al. [2].

	^{10}B	^{11}B	
χ_{aa} [MHz]	−2.872 (67)	−1.414 (11)	$r = 2.031$ (63)
χ_{min} [MHz]	−7.922 (71)	−3.826 (11)	$r = 2.071$ (24)
χ_{bb} [MHz]	−2.525 (69)	−1.206 (11)	
χ_{cc} [MHz]	5.397 (69)	2.620 (11)	
A [MHz]	10 209.403 (75)	10 210.696 (48)	
B [MHz]	9 962.117 (73)	9 963.203 (48)	
C [MHz]	5 034.124 (42)	5 034.759 (30)	

parameters χ_{bb} and χ_{cc} for both isotopomers. Table 3 contains also the rotational constants of Kawashima et al. [2]. Some care has to be taken in the case of ^{10}B. Here a relatively high correlation of 0.98 between the coupling constants occurs due to the low number of experimental data. Since the boron nucleus is situated nearly in the center of mass in both isotopomers, the substitution of ^{11}B by ^{10}B does not alter the orientation of the inertia axes system. Therefore the electric field gradients referred to the principal inertia axes $q_{gg} (g = a, b, c)$ in the expressions for the quadrupole coupling constants $\chi_{gg} = e\,Q\,q_{gg}$ (e: charge of the electron, Q nuclear quadrupole moment) are assumed to be the same for both isotopomers. In this case the ratio $\chi_{gg}(^{10}B)/\chi_{gg}(^{11}B)$ should give the ratio of the nuclear quadrupole moments $r := Q(^{10}B)/Q(^{11}B)$. The mean value of $r = 2.051\,(44)$, obtained as mean from the values in Table 3 agrees within the error limits with the value 2.084(2) taken from [6]. This could serve as an additional check of the determined quadrupole coupling constants.

IV. Summary

We were able to resolve the hyperfine structure of the hydrolysis product $BF(OH)_2$ of BF_3. The hfs could not be observed by Stark modulation techniques. From the ratio of the quadrupole coupling constants the ratio of the nuclear quadrupole moments could be obtained. For future investigations to improve especially the ^{10}B constants and to allow in addition an overall fit of rotational, centrifugal distortion and quadrupole coupling constants a more effective method for producing a greater amount of the sample is required.

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