Rotational Spectrum of Borane Monoammoniate: Boron and Nitrogen Hyperfine Structure and Vibrational Structure

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The boron and the nitrogen hyperfine structure in the rotational spectra of two borane monoammoniate isotopomers, $^{11}BH_3NH_3$ and $^{11}BH_3ND_3$ have been investigated and the quadrupole coupling constants of boron and nitrogen have been determined. It was also possible to determine the spin rotation constants C_N of boron. In the spectrum of $^{11}BH_3NH_3$ we observed additional splittings which are not caused by quadrupole coupling. In the spectra of the ammonia dimer, $(NH_3)_2$, to our opinion the same kind of splittings occur. As interpretation of this phenomenon it was proposed that two different vibrational states cause the splitting. They were called α and β. We use the same model for $^{11}BH_3NH_3$. The deuterated isotopomer $^{11}BH_3ND_3$ shows the normal spectrum of a symmetric top with two coupling nuclei, similar to the deuterated ammonia dimer $(ND_3)_2$. We obtained the following results: $^{11}BH_3NH_3$ in the α vibrational state, $1/2(B+C) = 17517.21399\,(48)$ MHz, $eQq_{aa}(^{11}B) = 2.584\,(10)$ MHz, $eQq_{aa}(^{14}N) = -2.135\,(5)$ MHz, $C_N(^{11}B) = 4.59\,(87)$ kHz, $^{11}BH_3NH_3$ in the β vibrational state, $1/2(B+C) = 17517.27706\,(52)$ MHz, $eQq_{aa}(^{11}B) = 2.583\,(8)$ MHz, $eQq_{aa}(^{14}N) = -2.132\,(5)$ MHz, $C_N(^{11}B) = 4.76\,(99)$ kHz, and $^{11}BH_3ND_3$, $1/2(B+C) = 15076.79992\,(41)$ MHz, $eQq_{aa}(^{11}B) = 2.550\,(7)$ MHz, $eQq_{aa}(^{14}N) = -2.169\,(4)$ MHz, $C_N(^{11}B) = 3.42\,(67)$ kHz.

Introduction

Borane monoammoniate is the simplest boron donor-acceptor complex, formed by electron donation from a Lewis base NH_3 to a Lewis acid BH_3. Furthermore BH_3NH_3 is isoelectronic to ethane. In opposition to CH_3CH_3, borane monoammoniate is a white solid with a low vapour pressure (<0.13 Pa at room temperature), which begins to decompose at temperatures above 90 °C. The first microwave measurements of this symmetric top molecule were made by Thorne, Suenram, and Lovas [1]. They determined the rotational and centrifugal distortion constants of nine different isotopomers, the complete r_s structure of the molecule, the dipole moment and the torsional barrier. To provide a satisfactory vapour pressure the cell was heated to 35–45 °C. Due to the limited resolution of their spectrometer they were not able to resolve the nuclear hyperfine structure cause by quadrupole coupling of the boron and the nitrogen nuclei.

The present contribution aims at the determination of the nuclear quadrupole coupling constants of both nuclei in the gas phase. This work was partially initiated by the discrepancy between the calculated and the measured quadrupole coupling constants in the solid state, which were measured by Lötz and Voitländer [2].

Experimental

Borane monoammoniate, BH_3NH_3, was obtained commercially from Fa. Alfa Products, Karlsruhe, and used without further purification. The deuterated species BH_3ND_3 was obtained by dissolving BH_3NH_3 in D_2O and then removing the D_2O by vacuum destillation. Impurities of the product were partially deuterated products. This procedure was also used by Thorne et al. [1] to prepare BH_3ND_3. Borane monoammoniate is considered to be a symmetric top molecule of the prolate type. Its molecular symmetry belongs to the point group C_{3V}.

All transitions $J - J' = 1 - 0$ of the isotopomers measured by Thorne et al. lie in the frequency range of our microwave Fourier transform (MWFT) spectrometer between 30 and 36 GHz. All other transitions, which have the normal selection rules of a symmetric top molecule, are in a frequency range not covered by our MWFT spectrometers. We intended to measure the main isotopomers $^{11}BH_3{}^{14}NH_3$ and $^{11}BH_3{}^{14}ND_3$. The setup of this spectrometer, which works between 26.5 and 40 GHz, is described in [3]. We were able to record the spectra at room temperature in spite of the low vapour pressure of the substance after conditioning the cell for one day. We recorded also the transitions of $^{10}BH_3NH_3$ and $^{10}BH_3ND_3$ but the quality of these spectra was not sufficient for further analysis. The frequencies of the hyperfine components are listed in Table 1a for $^{11}BH_3{}^{14}NH_3$ and in Table 1b for

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Table 1a. Rotational transition of $^{11}BH_3NH_3$, v: observed frequency of the hyperfine component, δ: difference between observed and calculated frequency of the hyperfine component. Components marked with * are not included in the fit due to their overlapping with other components.

v	J	J'	K	F	F'	F_1	F_1'	v [MHz]	δ [kHz]
α	1	0	0	0.5	0.5	1.0	1.0	35034.338	−50.1*
				0.5	0.5	2.0	1.0	35033.500	−4.7
				1.5	0.5	0.0	1.0	35035.457	−1.0
				1.5	0.5	1.0	1.0	35033.281	2.7
				1.5	0.5	2.0	1.0	35034.338	4.2
				0.5	1.5	1.0	1.0	35034.338	−50.1*
				0.5	1.5	2.0	1.0	35033.500	−4.7
				1.5	1.5	0.0	1.0	35035.457	−1.0
				1.5	1.5	1.0	1.0	35033.281	2.7
				1.5	1.5	2.0	1.0	35034.338	4.1
				2.5	1.5	1.0	1.0	35033.677	−3.4
				2.5	1.5	2.0	1.0	35034.747	0.3
				1.5	2.5	0.0	1.0	35035.457	−1.0
				1.5	2.5	1.0	1.0	35033.281	2.7
				1.5	2.5	2.0	1.0	35034.338	4.2
				2.5	2.5	1.0	1.0	35033.677	−3.4
				2.5	2.5	2.0	1.0	35034.747	0.3
				3.5	2.5	2.0	1.0	35034.216	−0.8
β	1	0	0	0.5	0.5	1.0	1.0	35034.508	7.4
				0.5	0.5	1.0	2.0	35033.677	47.3*
				0.5	0.5	2.0	1.0	35033.582	−0.7
				1.5	0.5	0.0	1.0	35035.405	0.1
				1.5	0.5	2.0	1.0	35034.461	1.2
				0.5	1.5	1.0	1.0	35034.508	−5.9
				0.5	1.5	2.0	1.0	35033.677	47.3*
				0.5	1.5	2.0	1.0	35033.511	−2.3
				1.5	1.5	0.0	1.0	35035.582	0.7
				1.5	1.5	2.0	1.0	35034.405	0.1
				2.5	1.5	1.0	1.0	35033.809	1.6
				2.5	1.5	2.0	1.0	35034.879	6.0
				1.5	2.5	0.0	1.0	35035.582	0.7
				1.5	2.5	2.0	1.0	35034.405	0.1
				2.5	2.5	1.0	1.0	35033.809	1.6
				2.5	2.5	2.0	1.0	35034.879	6.0
				3.5	2.5	2.0	1.0	35034.338	−5.1

$^{11}BH_3{}^{14}ND_3$. They were all determined by a least squares fit of the signal in the time domain to minimize overlapping effects in the frequency domain [4, 5]. Additionally we measured the transitions under different polarizing conditions, e.g. different polarizing frequencies and different delay times. The frequencies given in Tables 1a and 1b are mean values from the fitting procedures of the different decays. This procedure was necessary to get rather precise frequencies of the hyperfine components because the splitting of the components was at the limit of the resolution of our spectrometer. The frequency errors of the components due to this recording conditions were on the average about 5 kHz.

Table 1b. Rotational transition of $^{11}BH_3ND_3$, all symbols are used in the same way as in Table 1a.

J	J'	K	F	F'	F_1	F_1'	v [MHz]	δ [kHz]
1	0	0	0.5	0.5	1.0	1.0	30153.641	32.0*
			0.5	0.5	2.0	1.0	30152.743	3.8
			1.5	0.5	0.0	1.0	30154.696	−0.4
			1.5	0.5	1.0	1.0	30152.504	−3.0
			1.5	0.5	2.0	1.0	30153.584	20.4*
			0.5	1.5	1.0	1.0	30153.641	32.0*
			0.5	1.5	2.0	1.0	30152.743	3.8
			1.5	1.5	0.0	1.0	30154.696	−0.4
			1.5	1.5	1.0	1.0	30152.504	−3.1
			1.5	1.5	2.0	1.0	30152.584	20.4*
			2.5	1.5	1.0	1.0	30152.901	1.6
			2.5	1.5	2.0	1.0	30153.970	−0.0
			1.5	2.5	0.0	1.0	30154.696	−0.4
			1.5	2.5	1.0	1.0	30152.504	−3.0
			1.5	2.5	2.0	1.0	30153.584	20.4*
			2.5	2.5	1.0	1.0	30152.901	1.6
			2.5	2.5	2.0	1.0	30153.970	−0.0
			3.5	2.5	2.0	1.0	30153.445	−0.5

Results and Discussion of the Hyperfine Structure Analysis

In the beginning of our investigation of $^{11}BH_3{}^{14}NH_3$ we expected the normal spectrum of a rigid symmetric top rotor with two coupling nuclei, that means in this case a hyperfine pattern of the $J-J'=1-0$ transition consisting of eight components. Therefore our first calculation of the spectrum was based on the rotational parameters given in [1] and the nuclear quadrupole coupling constants listed in [2]. We used the following coupling scheme:

$$J+I_1=F_1, \quad F_1+I_2=F.$$

In case of BH_3ND_3 this model fits with modified quadrupole coupling constants but for BH_3NH_3 exist additional splittings. We believe that this kind of splittings is due to two different vibrational states α and β. The same phenomenon appears in the rotational spectrum of the ammonia dimer [6]. Nelson et al. interpreted the origin of the doubled set of hyperfine components to be due to two different vibrational states. The spectrum of $(ND_3)_2$ is the normal spectrum of a molecule with two coupling nuclei.

We fit our spectra in case of BH_3NH_3 with a "symmetric" top model and two sets of molecular constants, one set for the α state and one for the β state. We used a Hamiltonian similar to (1) and (2) of [6].

$$\boldsymbol{H}_v = \frac{(B+C)_v}{2}\,\boldsymbol{J}^2 - D_J\,\boldsymbol{J}^4 + (\boldsymbol{H}_{Q1})_v + (\boldsymbol{H}_{Q2})_v, \quad v=\alpha,\beta, \tag{1}$$

Table 2. Results of the fits of the rotational hyperfine structure of borane monoammoniate, $1/2(B+C)$: rotational constants, $eQq_{aa}(^{11}B)$: quadrupole coupling constant of boron, $C_N(^{11}B)$: spin-rotation coupling constant of boron, $eQq_{aa}(^{14}N)$: quadrupole coupling constant of nitrogen, N: number of components used for the fit, σ: standard deviation of the fit, the errors of the molecular constants are given in units of the last digits. The centrifugal distortion constants D_J had to be fixed to the values listed in [1]. All constants and σ in MHz.

		correlation coefficients			
$^{11}BH_3NH_3$ in the α state:					
$1/2(B+C)$:	17517.21399(49)	1.000			
$eQq_{aa}(^{14}N)$	−2.135(5)	0.217	1.000		
$eQq_{aa}(^{11}B)$	2.584(10)	0.162	0.689	1.000	
$C_N(^{11}B)$	0.00459(87)	0.274	−0.272	−0.501	1.000
σ:	0.0035				
N:	16				
$^{11}BH_3NH_3$ in the β state:					
$1/2(B+C)$:	17517.27706(52)	1.000			
$eQq_{aa}(^{14}N)$	−2.132(5)	0.042	1.000		
$eQq_{aa}(^{11}B)$	2.583(8)	−0.103	0.498	1.000	
$C_N(^{11}B)$	0.00476(99)	0.353	0.070	−0.013	1.000
σ:	0.0038				
N:	16				
$^{11}BH_3ND_3$:					
$1/2(B+C)$:	15076.79992(41)	1.000			
$eQq_{aa}(^{14}N)$	−2.169(4)	0.145	1.000		
$eQq_{aa}(^{11}B)$	2.550(7)	0.104	0.691	1.000	
$C_N(^{11}B)$	0.00342(67)	0.324	−0.280	−0.503	1.000
σ:	0.0026				
N:	13				

where $\boldsymbol{H}_{Q1}$ is the nuclear interaction operator of boron and $\boldsymbol{H}_{Q2}$ is the nuclear interaction operator of nitrogen.

$$(\boldsymbol{H}_{Q1})_v = \frac{-eQq_{aa}(^{11}B)}{2I_1(2I_1-1)(2J-1)(2J+3)} \cdot [3(\boldsymbol{I}_1\cdot\boldsymbol{J})^2 + 1.5(\boldsymbol{I}_1\cdot\boldsymbol{J}) - \boldsymbol{I}_1^2\boldsymbol{J}^2] + \left[C_N + (C_K - C_N)\frac{K^2}{J(J+1)}\right]\boldsymbol{I}\cdot\boldsymbol{J}, \tag{2}$$

$$(\boldsymbol{H}_{Q2})_v = \frac{-eQq_{aa}(^{14}N)}{2I_2(2I_2-1)(2J-1)(2J+3)} \cdot [3(\boldsymbol{I}_2\cdot\boldsymbol{J})^2 + 1.5(\boldsymbol{I}_2\cdot\boldsymbol{J}) - \boldsymbol{I}_2^2\boldsymbol{J}^2]. \tag{3}$$

The centrifugal distortion constants D_J for both molecules $^{11}BH_3NH_3$ and $^{11}BH_3ND_3$ were fixed to the values determined by Thorne et al. In case of boron we had to consider in all cases boron spin rotation interaction [7], which is included in $\boldsymbol{H}_{Q1}$ in opposition to the operator (2) used in [6]. The $J-J'=1-0$ transition contains only information about one constant, C_N, as can be seen from (2). The results are listed in Table 2.

The difference between the rotational constants of the α state and the β state is 63 kHz and smaller than the difference between the rotational constants of $(NH_3)_2$, which is 152 kHz. The quadrupole coupling constants of both states are equal within their standard errors. But the coupling constants in the gas phase are nearly twice as large as the coupling constants in solid state which were reported to be $|eQq_{aa}(^{11}B)| = 1.504\,(10)$ MHz and $|eQq_{aa}(^{14}N)| = 1.253\,(13)$ MHz [2]. Ab initio calculations provide $eQq_{aa}(^{11}B) = 2.492$ MHz and $eQq_{aa}(^{14}N) = -2.034$ MHz [8] for the coupling constants, in excellent agreement with our measurements. For comparison we present the corresponding quadrupole coupling constants of the similar molecule trimethylamine borane, $BH_3N(CH_3)_3$ [9]. These values are $eQq_{aa}(^{11}B) =$ 2.064(33) MHz and $eQq_{aa}(^{11}B) = -2.832(15)$ MHz. They have the same order of magnitude and the same sign as the coupling constants of BH_3NH_3.

The coupling constants of $^{11}BH_3ND_3$ are slightly different from the coupling constants of $^{11}BH_3NH_3$, especially the coupling constants of the nitrogen nuclei. On the other hand, the nitrogen coupling constants have nearly the same values within three times their standard deviation. Perhaps the difference is artificial and caused by our recording conditions at the resolution limit of our spectrometer and the following decay fitting procedure. Therefore we do not want to interpret this slight difference.

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