^{11}Boron Quadrupole Hyperfine Structure in the Rotational Spectrum of Hydroxydifluoroborane

Kirsten Vormann and Helmut Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

Z. Naturforsch. **44a,** 1191–1195 (1989); received October 12, 1989

The ^{11}B quadrupole hyperfine structure in the rotational spectra of three isotopic species of hydroxydifluoroborane, BF_2OH, BF_2OD, and $BF_2{}^{18}OH$ has been investigated and the quadrupole coupling constants of these species have been determined. Using the variation of the ^{11}B quadrupole coupling constants with isotopic substitution, it has been possible to evaluate the complete quadrupole coupling tensor, including the off-diagonal element χ_{ab}, for each isotopic species.

Introduction

The microwave spectra of six isotopic species of hydroxydifluoroborane have been observed and assigned by Takeo and Curl [1]. They determined the rotational constants of all isotopic species. With the assumption of equal BF bond lengths they calculated the structure of the molecule. They could not resolve the ^{11}B hyperfine structure (hfs).

Hydroxydifluoroborane is a planar near-oblate asymmetric rotor. Substitution of H with D or ^{16}O with ^{18}O causes a considerable rotation of the molecule in the principal axis system. It is thus possible to calculate the orientation of the quadrupole coupling tensor in the principal axis system and the off diagonal element χ_{ab} of each isotopomer, using the coupling constants of the three isotopic species BF_2OH, BF_2OD, and $BF_2{}^{18}OH$.

Experimental

The substance was prepared in the waveguide cell by mixing BF_3 and H_2O.

$$\begin{aligned} BF_3 \quad &+ H_2O \Leftrightarrow BF_2OH \quad + HF, \\ BF_2OH \quad &+ H_2O \Leftrightarrow BF(OH)_2 + HF, \\ BF(OH)_2 &+ H_2O \Leftrightarrow B(OH)_3 \quad + HF. \end{aligned}$$

BF_3 was obtained commercially from Fa. Merck, Darmstadt, and used without further purification. BF_2OD was prepared using D_2O instead of H_2O, and $BF_2{}^{18}OH$ using ^{18}O enriched water (30%). The spectra of BF_2OH and BF_2OD were recorded with our microwave Fourier transform (MWFT) spectrometers [2–5] in the frequency range 4.8–40 GHz at room temperature and pressures between 0.13 and 0.65 Pa (1 and 5 mTorr). The measured transitions are listed in Tables 1 a and 1 b. All frequencies were determined by a least squares fit of the multiplet signals in the time domain to minimize overlapping effects [6, 7].

Transitions of $BF_2{}^{18}OH$ were measured in a pulsed molecular beam Fourier transform microwave spectrometer [8]. The absorption-emission cell consists of a Fabry-Perot resonant cavity (mirror diameter: 16 cm, mirror curvature: 20 cm) inside a high vacuum chamber. A pulsed nozzle is used to generate a supersonic molecular beam of the substance, which is diluted with argon as carrier gas. Frequencies resulting from these measurements may not be as accurate as those from normal MWFT spectroscopy because there is no obvious fitting procedure to correct frequencies of narrow multiplets. The line shape in this type of spectroscopy is influenced by the resonance curve of the cavity. Therefore a line form analysis is difficult. The transition frequencies are listed in Table 1 c.

Results and Discussion of the ^{11}B Quadrupole Coupling

The rotational transition frequencies of the three isotopomers of hydroxydifluoroborane were predicted with the rotational constants given by Takeo and

---

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40–60, D-2300 Kiel.

0932-0784 / 89 / 1200-1191 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1 a. Measured transition frequencies [MHz] of BF_2OH with hfs-splittings. ν: measured frequency, $\Delta\nu_{hfs}$: hfs-splitting referred to the strongest component, δ_{hfs}: deviation of the experimental and the calculated splitting, ν_0: hypothetical unsplit line frequency calculated with the hfs-shift of the components provided by the evaluation program.

$J\ K_-\ K_+ - J'\ K'_-\ K'_+$	$F - F'$	ν [MHz]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]
1 1 0 – 1 1 1	5/2–5/2	5 003.895			5 004.109
	5/2–3/2	5 004.196	−0.301	2	
	3/2–5/2	5 004.558	−0.663	−5	
	1/2–3/2	5 003.656	0.239	−3	
1 0 1 – 0 0 0	5/2–3/2	15 194.451			15 194.377
	3/2–3/2	15 194.079	0.372	−3	
	1/2–3/2	15 194.742	−0.291	−5	
2 1 1 – 2 1 2	7/2–7/2	15 012.157			15 012.431
	5/2–5/2	15 013.122	−0.965	−2	
	5/2–7/2	15 012.458	−0.301	2	
	3/2–3/2	15 012.431	−0.274	−2	
	1/2–3/2	15 012.130	0.027	−4	
2 0 2 – 1 0 1	7/2–5/2	25 598.582			25 598.465
	5/2–3/2	25 598.280	0.302	−2	
	5/2–5/2	25 597.912	0.670	−1	
	3/2–3/2	25 598.762	−0.180	2	
	1/2–1/2	25 598.762	−0.180	−2	
2 1 2 – 1 1 1	7/2–5/2	25 385.025			25 384.894
	5/2–3/2	25 384.654	0.371	−1	
	3/2–1/2	25 384.592	0.433	−3	
	5/2–5/2	25 384.357	0.668	0	
	3/2–3/2	25 385.134	−0.109	1	
4 3 1 – 4 3 2	11/2–11/2	14 251.607			14 251.704
	9/2–9/2	14 251.879	−0.272	6	
	7/2–7/2	14 251.784	−0.177	4	
	5/2–5/2	14 251.514	0.093	0	
5 4 1 – 5 4 2	13/2–13/2	13 715.798			13 715.862
	11/2–11/2	13 715.965	−0.167	1	
	9/2–9/2	13 715.909	−0.120	1	
	7/2–7/2	13 715.744	0.045	2	
6 5 1 – 6 5 2	15/2–15/2	13 081.115			13 081.115
	13/2–13/2	13 081.217	−0.102	−7	
	11/2–11/2	13 081.193	−0.078	−5	
	9/2–9/2	13 081.087	0.028	−2	
7 6 1 – 7 6 2	17/2–17/2 11/2–11/2	12 355.024			12 355.062
	15/2–15/2 13/2–13/2	12 355.094	−0.070	−3	

Table 1 b. Measured transition frequencies [MHz] of BF_2OD, all symbols are used in the same way as in Table 1 a.

$J\ K_-\ K_+ - J'\ K'_-\ K'_+$	$F - F'$	ν [MHz]	$\Delta\nu_{hfs}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]
3 2 1 – 3 2 2	9/2–9/2	12 221.755			12 221.887
	7/2–7/2	12 222.164	−0.409	−1	
	5/2–5/2	12 221.971	−0.216	−3	
	3/2–3/2	12 221.563	0.192	−1	
3 0 3 – 2 0 2	9/2–7/2	34 417.357			34 417.271
	7/2–5/2	34 417.198	0.159	3	
	5/2–3/2	34 417.109	0.248	6	
	3/2–1/2	34 417.282	0.093	0	
3 1 3 – 2 1 2	9/2–7/2	34 306.612			34 306.523
	7/2–5/2	34 306.440	0.172	−2	
	5/2–3/2	34 306.349	0.263	−6	
	3/2–1/2	34 306.531	0.081	5	
4 3 1 – 4 3 2	11/2–11/2	10 610.288			10 610.102
	9/2–9/2	10 610.499	−0.211	−1	
	7/2–7/2	10 610.427	−0.139	1	
	5/2–5/2	10 610.212	0.076	−2	
4 2 3 – 4 0 4	11/2–11/2	34 409.926			34 410.180
	9/2–9/2	34 410.623	−0.697	−1	
	7/2–7/2	34 410.377	−0.451	−2	
	5/2–5/2	34 409.682	0.244	1	
5 3 3 – 5 1 4	13/2–13/2	34 363.985			34 364.164
	11/2–11/2	34 364.449	−0.464	−1	
	9/2–9/2	34 364.317	−0.332	−2	
	7/2–7/2	34 363.849	0.136	−5	
5 2 3 – 5 2 4	13/2–13/2	34 077.078			34 077.255
	11/2–11/2	34 077.545	−0.467	6	
	9/2–9/2	34 077.409	−0.331	0	
	7/2–7/2	34 076.942	0.136	−6	
6 3 3 – 6 3 4	15/2–15/2	33 532.447			33 532.576
	13/2–13/2	33 532.773	−0.326	3	
	11/2–11/2	33 532.697	−0.250	3	
	9/2–9/2	33 532.369	0.078	−1	
6 4 3 – 6 2 4	15/2–15/2	34 374.367			34 374.500
	13/2–13/2	34 374.695	−0.328	−5	
	11/2–11/2	34 374.617	−0.250	−4	
	9/2–9/2	34 374.282	0.085	−6	
7 5 2 – 7 5 3	17/2–17/2 11/2–11/2	17 680.145			17 680.210
	15/2–15/2 13/2–13/2	17 680.270	−0.125	1	
7 6 2 – 7 4 2	17/2–17/2	29 925.570			29 925.661
	15/2–15/2	29 925.791	−0.221	1	
	13/2–13/2	29 925.747	−0.177	1	
	11/2–11/2	29 925.528	0.042	3	
7 4 3 – 7 4 4	17/2–17/2 11/2–11/2	32 529.575			32 529.696
	15/2–15/2 13/2–13/2	32 529.809	−0.234	3	

Table 1 c. Measured transition frequencies [MHz] of BF$_2{}^{18}$OH, all symbols are used in the same way as in Table 1 a.

$J\,K_-\,K_+ - J'\,K'_-\,K'_+$	$F - F'$	ν [MHz]	$\Delta\nu_{\mathrm{hfs}}$ [MHz]	δ_{hfs} [kHz]	ν_0 [MHz]
2 0 2 − 1 0 1	7/2−5/2	24 867.540			24 867.438
	5/2−3/2	24 867.317	0.223	0	
	3/2−1/2	24 866.987	0.553	− 1	
	5/2−5/2	24 866.860	0.680	− 8	
	3/2−3/2	24 867.782	−0.242	−15	
	1/2−3/2	24 868.468	−0.928	− 2	
2 1 2 − 1 1 1	7/2−5/2	24 218.560			24 218.413
	5/2−3/2	24 218.098	0.462	−13	
	3/2−1/2	24 218.200	0.360	− 3	
	5/2−5/2	24 217.898	0.662	− 2	
	1/2−1/2	24 218.857	−0.297	− 6	
	1/2−3/2	24 219.234	−0.674	− 9	
2 1 2 − 1 0 1	7/2−5/2	24 947.704			24 947.605
	5/2−3/2	24 947.497	0.207	4	
	3/2−1/2	24 947.156	0.548	0	
	5/2−5/2	24 947.042	0.662	− 2	
	3/2−3/2	24 947.973	−0.269	8	
2 0 2 − 1 1 1	7/2−5/2	24 138.389			24 138.239
	5/2−3/2	24 137.930	0.459	3	
	3/2−1/2	24 138.029	0.360	1	
	5/2−5/2	24 137.714	0.675	− 2	
	1/2−1/2	24 138.691	−0.302	−10	

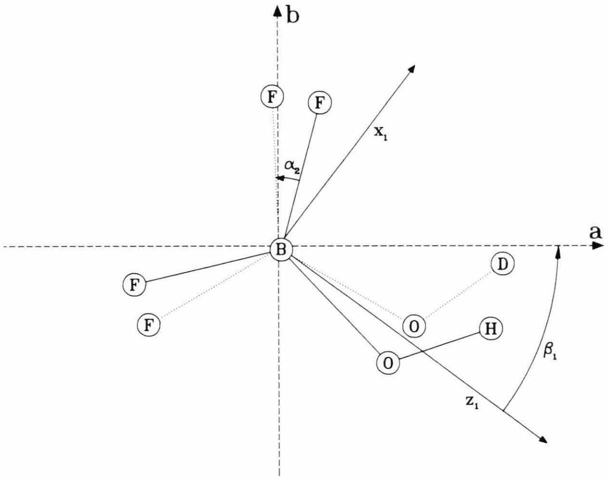

Fig. 1. BF$_2$OH and BF$_2$OD in their principal inertia axes system a, b, c. α_2 is the rotational angle caused by substitution of H and D. z_1 and x_1 are directions of the principal coupling tensor of BF$_2$OH in the molecular plane, β_1 is the angle between the z-axis and the a-axis.

Curl [1]. Centrifugal distortion effects were neglected because we were interested only in the hfs splittings. The splittings were analysed using first order theory [9]. The results of these analyses are listed in Table 2. Standard errors of the fit are given in brackets.

Because hydroxydifluoroborane is a molecule with a plane of symmetry, the axis perpendicular to the plane is a principal axis of inertia and also a principal axis of the quadrupole coupling tensor [10]. In this case the transformation equation of the quadrupole coupling tensor from the principal axis system of inertia to its own principal axis system has the form

$$\begin{pmatrix} \chi_{aa} & \chi_{ab} & 0 \\ \chi_{ab} & \chi_{bb} & 0 \\ 0 & 0 & \chi_{cc} \end{pmatrix} = S \begin{pmatrix} \chi_z & 0 & 0 \\ 0 & \chi_x & 0 \\ 0 & 0 & \chi_y \end{pmatrix} S^{-1}$$

with

$$S = \begin{pmatrix} \cos\beta_i & -\sin\beta_i & 0 \\ \sin\beta_i & \cos\beta_i & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

β_i, $i = 1$, is the angle between the z quadrupole tensor axis and the a axis of the principal inertial axis system of the isotopomer BF$_2$OH (see Figure 1). We use $i = 2, 3$ for the two other isotopomers BF$_2$OD and BF$_2{}^{18}$OH.

Table 2. ^{11}B quadrupole coupling constants and used rotational constants [1] of the three isotopomers of hydroxydifluoroborane, σ: standard deviation of the hfs analysis, $\overline{\Delta\nu}$: mean splitting.

BF_2OH:

$A = 10\,320.32$ MHz
$B = 10\,099.33$ MHz
$C = 5\,095.13$ MHz

Correlation coefficient matrix:

$\chi_+ = 1.477(5)$ MHz	1.000	
$\chi_- = -3.867(7)$ MHz	0.350	1.000

$\chi_{aa} = -1.477(5)$ MHz
$\chi_{bb} = -1.195(6)$ MHz
$\chi_{cc} = 2.672(6)$ MHz

σ: 3 kHz
$\overline{\Delta\nu}$: 278 kHz

BF_2OD:

$A = 10\,296.88$ MHz
$B = 9\,400.85$ MHz
$C = 4\,905.77$ MHz

Correlation coefficient matrix:

$\chi_+ = 1.717(9)$ MHz	1.000	
$\chi_- = -3.637(9)$ MHz	0.019	1.000

$\chi_{aa} = -1.717(9)$ MHz
$\chi_{bb} = -0.960(9)$ MHz
$\chi_{cc} = 2.677(9)$ MHz

σ: 3 kHz
$\overline{\Delta\nu}$: 238 kHz

$BF_2{}^{18}OH$:

$A = 10\,216.55$ MHz
$B = 9\,487.18$ MHz
$C = 4\,910.57$ MHz

Correlation coefficient matrix:

$\chi_+ = 1.798(9)$ MHz	1.000	
$\chi_- = -3.484(16)$ MHz	0.110	1.000

$\chi_{aa} = -1.798(9)$ MHz
$\chi_{bb} = -0.843(13)$ MHz
$\chi_{cc} = 2.641(13)$ MHz

σ: 7 kHz
$\overline{\Delta\nu}$: 476 kHz

Solving this matrix equation, we get expressions for χ_{aa}, χ_{bb}, χ_{cc} and χ_{ab}:

$$\chi_{aai} = \chi_z \cdot \cos^2 \beta_i + \chi_x \cdot \sin^2 \beta_i\,, \tag{2.1}$$

$$\chi_{bbi} = \chi_x \cdot \cos^2 \beta_i + \chi_z \cdot \sin^2 \beta_i\,, \tag{2.2}$$

$$\chi_{cci} = \chi_y\,, \tag{2.3}$$

$$\chi_{abi} = 0.5 \cdot (\chi_z - \chi_x) \cdot \sin 2\beta_i\,, \tag{2.4}$$

$$\chi_{aai} - \chi_{bbi} = (\chi_z - \chi_x) \cdot \cos 2\beta_i\,. \tag{2.5}$$

It is a reasonable approximation in (2.1) to (2.5) for $i = 1, 2, 3$ to assume that the values of χ_x, χ_y and χ_z are independent of an isotopic substitution of nuclei other than the coupling one.

Table 3. Principal values of the ^{11}B quadrupole coupling tensor in $^{11}BF_2OH$ together with values of the off-diagonal constants χ_{ab} and β_1 for each isotopic species.

$\chi_x = -0.837(50)$ MHz $\quad \chi_z = -1.835(50)$ MHz

BF_2OH,	$\beta_1 = 36.8(8)°$:	$\chi_{ab} = -0.479(34)$ MHz
BF_2OD,	$\beta_2 = 21.4(8)°$:	$\chi_{ab} = -0.339(26)$ MHz
$BF_2{}^{18}OH$,	$\beta_3 = -0.8(8)°$:	$\chi_{ab} = 0.014(14)$ MHz

Table 4. ^{11}B quadrupole coupling constants [MHz] of some difluoroborane compounds and the principal values of their coupling tensors.

Compound	χ_{aa}	χ_{bb}	χ_{cc}	Lit.
HBF_2	$-0.75(9)$	$-2.585(55)$	$3.335(55)$	[11]
CH_3BF_2	$-2.713(21)$	$-0.695(27)$	$3.408(27)$	[12]
$C_6H_5BF_2$	$-2.589(12)$	$-0.600(15)$	$3.189(15)$	[13]
BF_2OH	$-1.477(5)$	$-1.195(6)$	$2.672(6)$	*
BF_2OD	$-1.717(9)$	$-0.960(9)$	$2.677(9)$	*
$BF_2{}^{18}OH$	$-1.798(9)$	$-0.843(13)$	$2.641(13)$	*

Compound	χ_z	χ_x	χ_y
BF_2OH	$-1.835(50)$	$-0.837(50)$	$2.672(6)$
	$\chi_z = \chi_{aa}$	$\chi_x = \chi_{bb}$	$\chi_y = \chi_{cc}$
CH_3BF_2	$-2.713(21)$	$-0.695(27)$	$3.408(27)$
$C_6H_5BF_2$	$-2.589(12)$	$-0.600(15)$	$3.189(15)$
	$\chi_z = \chi_{bb}$	$\chi_x = \chi_{aa}$	$\chi_y = \chi_{cc}$
HBF_2	$-2.585(55)$	$-0.75(9)$	$3.335(55)$

* This work.

β_2 and β_3 can be expressed as

$$\beta_i = \beta_1 - \alpha_i\,, \quad i = 2, 3\,. \tag{3}$$

α_2 is the angle between the z-axes of the principal quadrupole tensors of BF_2OH and BF_2OD, caused by the substitution of H with D; α_3 is the corresponding angle in the BF_2OH–$BF_2{}^{18}OH$ pair. These two angles are calculated from the r_s-structure of the molecule given by Takeo and Curl:

$$\alpha_2 = 15.4°\,, \quad \alpha_3 = 37.6°\,.$$

For the BF_2OH–BF_2OD pair we get for $i = 2$ and $i = 1$ with (2.5) and (3)

$$\frac{\chi_{aa2} - \chi_{bb2}}{\chi_{aa1} - \chi_{bb1}} = \frac{\cos 2(\beta_1 - \alpha_2)}{\cos 2\beta_1}\,. \tag{4}$$

Expression (4) can be solved for β_1:

$$\beta_1 = \tfrac{1}{2} \cdot \arctan \frac{[(\chi_{aa2} - \chi_{bb2})/(\chi_{aa1} - \chi_{bb1})] - \cos 2\alpha_2}{\sin 2\alpha_2}\,. \tag{5}$$

The same mathematical formalism for the BF_2OH–$BF_2{}^{18}OH$ pair leads to another equation for β_1:

$$\beta_1 = \frac{1}{2} \cdot \arctan \frac{[(\chi_{aa3} - \chi_{bb3})/(\chi_{aa1} - \chi_{bb1})] - \cos 2\alpha_3}{\sin 2\alpha_3}. \quad (6)$$

Expressions (5) and (6) allow us to calculate β_1.

BF_2OH–BF_2OD pair:

$$\beta_1 = 37.2^\circ,$$

BF_2OH–$BF_2{}^{18}OH$ pair:

$$\beta_1 = 36.4^\circ.$$

The mean is

$$\bar{\beta}_1 = 36.8(8)^\circ.$$

For the calculations of χ_x, χ_z and χ_{ab} of the three isotopomers we use the mean value $\bar{\beta}_1$. We assume the error of $\bar{\beta}_1$ to be equal to the difference of the two β_1 values. Results of these computations are given in Table 3. The standard errors of the coupling constants have been calculated using Gaussian error propagation.

In Table 4 we list the quadrupole coupling constants of some difluoroborane compounds. With the assumption that the bonding orbitals of all listed compounds are sp^2-hybrids, the orbital perpendicular to the sp^2-plane is a pure p orbital. The size of the coupling constants χ_{cc} gives us an approximate idea of the occupation of orbital caused by back donation of electrons from the bond partners of boron. The coupling constant by a single p-electron of boron is $eQq_{210} = -5.39$ MHz [14]. HBF_2 and CH_3BF_2 have the highest positive χ_{cc} values, that means the lowest occupation of the p-orbital. The χ_{cc} value of $C_6H_5BF_2$ is slightly lower caused by interactrion with the π-system of the phenyl group, but we believe that the main part of the occupation is produced by the fluorine atoms [13]. Consequently the χ_{cc} values of the BF_2OH isotopomers are the lowest ones because the BF and BO bonds are quite similar.

We thank members of our group for help and discussion, Prof. Dr. M. C. L. Gerry, Vancouver, for carefully reading the manuscript, the Deutsche Forschungsgemeinschaft, the Land Schleswig-Holstein and the Fonds der Chemie for funds. The calculations were made at the computer center of the university.

[1] H. Takeo and R. F. Curl, J. Chem. Phys. **56,** 4314 (1972).
[2] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35a,** 392 (1980).
[3] G. Bestmann and H. Dreizler, Z. Naturforsch. **37a,** 58 (1982).
[4] W. Stahl, G. Bestmann, H. Dreizler, U. Andresen, and R. Schwarz, Rev. Sci. Instrum. **56,** 1759 (1985).
[5] Ch. Keussen, N. Heineking, and H. Dreizler, Z. Naturforsch. **44a,** 215 (1989).
[6] I. Merke and H. Dreizler, Z. Naturforsch. **43a,** 196 (1988).
[7] J. Haekel and H. Mäder, Z. Naturforsch. **43a,** 203 (1988).
[8] W. Stahl et al., to be published.
[9] W. Gordy and R. L. Cook, Microwave Molecular Spectra, John Wiley, New York 1984, Chapt. IX 4.
[10] loc. cit. [9], 419ff.
[11] N. P. C. Westwood, W. Lewis-Bevan, and M. C. L. Gerry, J. Mol. Spectrosc. **106,** 227 (1984).
[12] L. Engelbrecht, Diss. 1975, University Kiel.
[13] K. Vormann and H. Dreizler, Z. Naturforsch. **44a,** 84 (1989).
[14] loc. cit. [9], Chapt. XIV, Table 14.2.