Boron Hyperfine Structure in Trifluorophosphine-Borane

W. Kasten and H. Dreizler
Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

R. L. Kuczkowski
Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

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We reinvestigated the microwave spectrum of trifluorophosphine-borane by microwave Fourier transform spectroscopy and determined the quadrupole coupling and centrifugal distortion constants for both isotopes ^{10}B and ^{11}B. The B–P bond order is discussed.

The microwave spectrum of trifluorophosphine-borane, PF_3BH_3, was first investigated by Kuczkowski and Lide [1]. We reinvestigated the spectrum with the higher resolution of microwave Fourier transform (MWFT) spectroscopy to resolve the boron-hfs. It is the first time that the boron-hfs of an addition compound of boron and an element of the fifth group of the periodic table has been resolved. It will be interpreted in terms of the B–P bonding.

The sample was prepared according to [1] and measured at temperatures around −50 °C and pressures around 0.5 mTorr. The MWFT-spectrometers are described in [2, 3]. The $J = 1-0$ and $J = 2-1$ transitions of the ^{10}B compound with nuclear spin $I = 3$ and of the ^{11}B compound with $I = 3/2$ were investigated in natural abundance [4]. The measurements are given in Tables 1 and 2. A recording is given in Figure 1. The frequencies were determined by a line shape analysis [5].

First the quadrupole coupling constants eqQ were determined from the $J = 1-0$ transitions. For the $J = 2-1$ transitions the assignment was complicated by the hfs and K fine structure. The two strongest components of each multiplet were assigned to the $F = 5-4$ for ^{10}B and $F = 7/2-5/2$ for ^{11}B with the $K = 0$ and $|K| = 1$ assignment unknown. Considering the squared dipole matrix elements for $K = 0$ and $|K| = 1$ transitions one gets [6]:

$$|\mu_{21}(K=0)|^2 : |\mu_{21}(|K|=1)|^2 = 4:3\,.$$

The intensity ratio is modified by the K-degeneracy and statistical spin weight to 4:5 assuming C_{3v}-symmetry of the molecule. Thereby the K assignment for ^{10}B was possible as given in Table 1. For ^{11}B the intensity argument was useless as $K = 0$, $F = 7/2-5/2$ and $F = 5/2-3/2$ overlap which gives nearly the same intensity as $K = \pm 1$, $F = 7/2-5/2$. We favoured an assignment which resulted in the

Table 1. Measured frequencies ν_{obs} of trifluorophosphine-borane-(^{10}B) refined by line shape analysis. ν_{calc} calculated with constants of Table 3. $\nu_{unsplit}$ hypothetical frequency without hfs-splitting (see text). Frequencies in MHz.

$J'-J$	K	$F'-F$	ν_{obs}	ν_{calc}	$\nu_{unsplit}$
1–0	0	3–3	7847.317	7847.317	
		4–3	7846.668	7846.668	7846.830
		2–3	7846.441	7846.441	
2–1	0	5–4	15693.564	15693.564	
		4–3	–	15693.494	15693.633
		3–3	–	15693.377	
	±1	5–4	15693.412	15693.412	
		4–3	15693.989*	15694.026	15693.609
		3–3	15693.989*	15693.980	

* not used.

Table 2. Measured frequencies of trifluorophosphine-borane-(^{11}B). See Table 1.

$J'-J$	K	$F'-F$	ν_{obs}	ν_{calc}	$\nu_{unsplit}$
1–0	0	3/2–3/2	7614.400	7614.400	
		5/2–3/2	7614.030	7614.030	7614.104
		1/2–3/2	7613.735	7613.735	
2–1	0	7/2–5/2	15228.149	15228.149	
		5/2–3/2	15228.149	15228.149	15228.180
		3/2–3/2	–	15227.884	
	±1	7/2–5/2	15228.068	15228.068	
		5/2–3/2	–	15228.438	15228.158
		3/2–3/2	–	15228.306	

Reprint requests to Prof. Dr. H. Dreizler, Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40, D-2300 Kiel.

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same sign of the centrifugal distortion parameter D_{JK} for both isotopes. By addition of the hfs-corrections to the components of the multiplets ν_{unsplit} was calculated as a mean value. These frequencies were used to determine the rotational constant B and the centrifugal distortion constants D_J and D_{JK} [7] given in Table 3 together with eqQ.

Next we interpret the quadrupole coupling constants in terms of the bond order following Townes and Dailey [8] and Gordy [9]. For details see [4]. The following equation is used

$$eQq = -(\mathrm{Up})_z \cdot \frac{eQq_{210}}{1+(n-3i_\sigma)\cdot\varepsilon},$$

where eQq is the measured quadrupole coupling constant, $eQq_{210}(^{10}\mathrm{B}) = -11.83$ MHz, $eQq_{210}(^{11}\mathrm{B}) = -5.39$ MHz [10] are the quadrupole coupling constants induced by a $2p_z$-electron, $\varepsilon = 0.5$ [11] is the shielding constant for boron, $i_\sigma = \frac{1}{2}|EN(\mathrm{H}) - EN(\mathrm{B})|$ is the ionic character of the B–H bond calculated from the electronegativities $EN(\mathrm{H}) = 2.15$ and $EN(\mathrm{B}) = 2.0$ [12], $(\mathrm{Up})_z$ is the number of "unbalanced" p-electrons in z direction, i.e. the B–P bond direction and n is the number of electrons donated by the phosphorus to boron; n is the aim of this interpretation. $(\mathrm{Up})_z$ may be calculated from

$$(\mathrm{Up})_z = -\tfrac{3}{2}(1-i_\sigma)\cdot a_p^2(\psi_H) \cdot (3\cos^2(\measuredangle(\mathrm{PBH})) - 1) - n\cdot a_p^2(\psi_p),$$

where $a_p^2(\psi_H)$ is the p-electron fraction of the boron orbital directed to the hydrogen occupied by $(1-i_\sigma)$ electrons, $a_p^2(\psi_p)$ is the fraction of the boron orbital ψ_p directed to the phosphorus occupied by n electrons and $\measuredangle(\mathrm{PBH}) = 103(1)°$ is the bond angle known from the structure [1].

Approximating $\psi_H = s_H + \lambda p_H$ by a hybridisation mixing of s and p functions [13] results in $a_p^2(\psi_H)$ as:

$$a_p^2(\psi_H) = \frac{\lambda^2}{1+\lambda^2}; \quad \lambda^2 = -\{\cos(\measuredangle(\mathrm{HBH}))\}^{-1},$$

where $\measuredangle(\mathrm{HBH}) = 115(1)°$ from the structure [1].

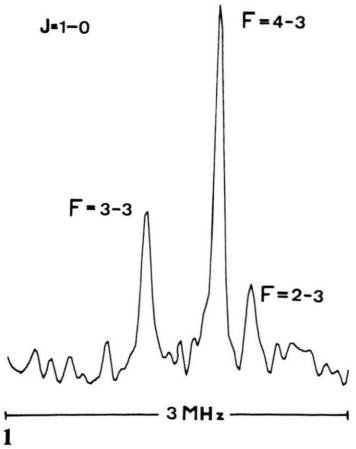
In a similar way

$$a_p^2(\psi_p) = \frac{\mu^2}{1+\mu^2}; \quad \mu^2 = \{\lambda\cdot\cos(\measuredangle(\mathrm{PBH}))\}^{-2}.$$

The information is sufficient to determine for both isotopes the bond order $n = 0.57$ (see Fig. 2), which is the first determined by microwave spectroscopy for a III–V addition compound and similar to the value 0.53 determined for BH_3CO [9].

Table 3. Rotational, centrifugal distortion and quadrupole coupling constants of trifluorophosphine-borane-(^{10}B) and -(^{11}B). Standard deviation in brackets in units of the last digit. For B, D_J, and D_{JK} no error calculation is possible as only three frequencies are available.

$PF_3{}^{10}BH_3$		[1]
B = 3923.4173	MHz;	3923.389(50) MHz
D_J = 1.13	kHz	
D_{JK} = 6.03	kHz	
eQq = 3.2445(7)	MHz	
$PF_3{}^{11}BH_3$		[1]
B = 3807.0543	MHz;	3807.067(50) MHz
D_J = 1.15	kHz;	1.1(8) kHz
D_{JK} = 5.68	kHz	
eQq = 1.478(3)	MHz	



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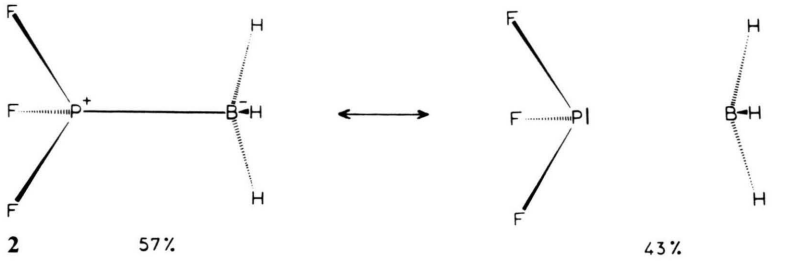

Fig. 1. $J = 1-0$ transition of $PF_3{}^{10}BH_3$ measured in natural abundance (19%). A section of 3 MHz out of a 50 MHz range of the power spectrum is given. Sample interval 10 ns, 12800 k cycles, 1024 data points supplemented by 3072 zeros, pressure 0.8 mTorr, temperature −45 °C.

Fig. 2. Relative weight of the principal structures, which contribute to the ground state of trifluorophosphine-borane.

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