^{11}B-Quadrupole Hyperfine Structure in the Rotational Spectrum of Phenyldifluoroborane

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We present an investigation and interpretation of the ^{11}B-quadrupole hyperfine structure (hfs) in the rotational spectrum of phenyldifluoroborane in the torsional ground state of the BF_2 group. The measurements were made with a microwave Fourier transform (MWFT) spectrometer in the frequency range between 5 and 8 GHz.

Experimental and Analysis

Both isotopic species (^{11}B, ^{10}B) of phenyldifluoroborane, $F_2B(C_6H_5)$, were first investigated and assigned by Christen, Lister and Sheridan [1]. They determined the rotational constants of the torsional ground and some excited states of the BF_2 group and the torsional potential height.

The preparation of phenyldifluoroborane was carried out in two steps. First we prepared phenyldichloroborane $Cl_2B(C_6H_5)$ by the reaction between boron trichloride and tetraphenyltin [2]. The second step was the fluorination of phenyldichloroborane with antimony trifluoride [3].

The spectra were recorded at temperatures between $-20°$ and -30 °C and pressures between 0.4 and 1 mTorr (0.052–0.13 Pa). The measured transitions are listed in Table 1. All frequencies were determined by a least squares fit of the multiplet signals in the time domain to minimize overlapping effects [4, 5]. The assignment of our transitions has been checked by a centrifugal distortion analysis including the transitions reported by Christen, Lister and Sheridan. We used the Watson A reduction of 4th order [6]. The centrifugal distortion constants Δ_{JK} and δ_J had to be fixed to zero. Because our measurements and those of [1] were of different accuracy, the deviations δ_0 of the fit were relatively high. The hfs splittings were analysed by first order approximation [7]. The rotational and centrifugal distortion constants are given in Table 2, the quadrupole coupling constants in Table 3.

Boron Coupling Discussion

We use a hybridisation analogue to pyridine, given by Gordy and Cook [8], to interpret the boron quadrupole coupling. The three valence orbitals in the molecular plane are sp^2 hybrids, the fourth orbital, perpendicular to the plane, is a pure p orbital.

$$\psi_1 = (1 - 2a_s^2)^{1/2}\ \psi_s + (2a_s^2)^{1/2}\ \psi_{p_z}, \quad \text{BC bonding orbital,}$$

$$\psi_{2,3} = a_s\psi_s - [(1-2a_s^2)/2]^{1/2}\ \psi_{p_z} \pm (1/2)^{1/2}\,\psi_{p_x}, \quad \text{BF bonding orbitals,}$$

$$\psi_4 = \psi_{p_y}, \quad \text{p orbital.} \tag{1}$$

a_s^2 represents the amount of s character in each boron bonding orbital [9].

$$a_s^2 = \cos\theta/(\cos\theta - 1) = 0.311$$

with θ the FBF angle given in [1] as $\theta = 116.0°$.

The molecular principal axes can be identified with the principal quadrupole coupling tensor axes in the following way: $z \to a$, $x \to b$ and $y \to c$. The experimental data provide two independent coupling parameters. Therefore we are able to determine two parameters: i_σ, the ionic character of the BF bond and i_π, the occupation of the pure p orbital. With the assumption of a polarized BC bond the population numbers of the molecular orbitals are

$$n(\psi_1) = 1 - [(\mathrm{EN_{Phenyl}} - \mathrm{EN_B})/2] = 1 - [(2.3 - 2.0)/2] = 1 - 0.15,$$

$\mathrm{EN_{Phenyl}}$: group electronegativity of the phenyl ring [10],
$\mathrm{EN_B}$: electronegativity of boron [11].

$$n(\psi_2) = n(\psi_3) = 1 - i_\sigma,$$
$$n(\psi_4) = i_\pi, \tag{2}$$

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Table 1. Measured transition frequencies [MHz] of phenyldifluoroborane with hfs-splittings. ν: measured frequency, $\Delta\nu_{\mathrm{hfs}}$: 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-splittings added to the frequencies of the components, δ_0 [kHz]: deviation of the calculated and the experimental centre frequency.

J K_- K_+ – J' K'_- K'_+	F – F'	ν [MHz]	$\Delta\nu_{\mathrm{hfs}}$ [MHz]	δ_{hfs} [MHz]	ν_0 [MHz]	δ_0 [kHz]
3 2 1 – 2 2 0	9/2–7/2	5909.789			5909.626	–20
	7/2–5/2	5909.200	0.589	–0.003		
	5/2–3/2	5909.644	0.145	–0.003		
	3/2–1/2	5910.230	–0.441	–0.003		
3 0 3 – 2 0 2	9/2–7/2	5770.316			5770.263	–19
	7/2–5/2	5770.252	0.064	–0.003		
	5/2–3/2	5770.111	0.205	–0.002		
3 1 2 – 2 1 1	9/2–7/2	6206.962			6206.911	–27
	7/2–5/2	6206.790	0.172	0.004		
	5/2–3/2	6206.911	0.051	0.006		
	3/2–1/2	6207.086	–0.124	0.005		
14 3 11 – 14 3 12	31/2–31/2	5759.333			5759.521	72
	29/2–29/2	5759.754	–0.421	0.004		
	27/2–27/2	5759.712	–0.379	0.006		
	25/2–25/2	5759.291	0.042	0.001		
18 4 14 – 18 4 15	39/2–39/2	5236.624			5236.768	8
	37/2–37/2	5236.933	–0.309	–0.002		
	35/2–35/2	5236.906	–0.282	–0.004		
	33/2–33/2	5236.598	0.026	–0.001		
19 4 15 – 19 4 16	41/2–41/2	7054.497			7054.660	–17
	39/2–39/2	7054.843	–0.346	–0.005		
	37/2–37/2	7054.816	–0.319	–0.004		
	35/2–35/2	7054.475	0.022	0.005		

Table 2. Rotational and centrifugal distortion constants of phenyldifluoroborane, Δ_{JK} and δ_J fixed to zero. The standard deviation of the fit is 58 kHz, highest correlation coefficient $|(\Delta_K, \delta_K)| = 0.923$.

A	3686.278 (47)	MHz	[Δ_{JK}	0.0	kHz]
B	1099.4297 (16)	MHz	[δ_J	0.0	kHz]
C	847.1989 (13)	MHz	δ_K	1.21 (35)	kHz
Δ_J	0.0392 (85)	kHz			
Δ_K	14.7 (58)	kHz			

Table 3. Quadrupole coupling constants [MHz] of phenyldifluoroborane, $F_2{}^{11}B(C_6H_5)$. $|\chi^+, \chi^-)|$ correlation coefficient. The standard deviation of the hfs analysis of 17 splittings is 4 kHz, the mean splitting is 232 kHz.

χ^+	2.589 (12)	χ_{aa}	–2.589 (12)
χ^-	–3.788 (17)	χ_{bb}	–0.600 (15)
$\|(\chi^+, \chi^-)\|$	0.143	χ_{cc}	3.189 (15)

We get from (1) with the orthonormality of the orbitals for the occupation of the orbitals of boron

$$\begin{aligned} n(\psi_{p_x}) &= 1 - i_\sigma, \\ n(\psi_{p_y}) &= i_\pi, \\ n(\psi_{p_z}) &= (1 - 0.15)\,(2a_s^2) \\ &\quad + 2(1 - i_\sigma)\,[(1 - 2a_s^2)/2], \\ n(\psi_s) &= 1 - 0.15 + 2a_s^2(0.15) - i_\sigma). \end{aligned} \tag{3}$$

The coupling constants χ_{xx} and χ_{yy} may be expressed as

$$\begin{aligned} \chi_{xx} &= [n(\psi_{p_x}) - (n(\psi_{p_y}) + n(\psi_{p_z}))/2] \\ &\qquad eQq_{210}(1 + c^+\varepsilon), \\ \chi_{yy} &= [n(\psi_{p_y}) - (n(\psi_{p_z}) + n(\psi_{p_x}))/2] \\ &\qquad eQq_{210}(1 + c^+\varepsilon). \\ c^+ &= 0.15 + 2i_\sigma - i_\pi, \\ eQq_{210} &= -\,5.39\ \mathrm{MHz}\ [12]. \end{aligned} \tag{4}$$

c^+ is the positive charge on the boron and $\varepsilon = 0.5$ is the charge screening correction [13]. With $\chi_{xx} = -\,0.600$ MHz and $\chi_{yy} = 3.189$ MHz we get from (3) and (4) values for i_π and i_σ.

$$i_\sigma = 43.8\%, \quad i_\pi = 22.7\%.$$

For comparison the corresponding calculation is performed with the coupling constants and the bond angle θ of CH_3BF_2, given in [14].

$$\begin{aligned} \chi_{xx} &= -2.713\,(21)\ \mathrm{MHz}, \\ \chi_{yy} &= -\,0.695\,(27)\ \mathrm{MHz}, \\ \chi_{zz} &= 3.408\,(27)\ \mathrm{MHz}, \\ \theta &= 116.8^\circ. \end{aligned}$$

The result is

$$i_\sigma = 43.5\%, \quad i_\pi = 20.4\%.$$

The values of i_σ are nearly equal, as expected. We assume that the errors, caused by the model, are minimized by comparison of the two similar molecules. Therefore we believe that the difference of the i_π values is significant although it is small. The larger i_π for phenyldifluoroborane may be caused by interactions with the π system of the phenyl ring. In our opinion the main part of the occupation of the p_y orbital is produced by back donation of electrons by the fluorine atoms.

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