Boron and Nitrogen Hyperfine Structure in the Microwave Spectrum of Trimethylamine-Borane

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We investigated the microwave spectrum of trimethylamine-borane by microwave Fourier transform spectroscopy and determined the quadrupole coupling constants of B and 14N and the rotational and centrifugal distortion constants for the 13B isotopic species. The B–N bond order is discussed and a value for εQq_{210}(14N) is determined.

We investigated the microwave spectrum of trimethylamine-borane, (CH₃)₃N–BH₃, with the higher resolution of microwave Fourier transform (MWFT) spectroscopy to resolve the nitrogen and boron hfs. Previous investigations by Schirdewahn [1], Durig et al. [2] and Cassoux et al. [3] did not obtain this information. The interpretation of the quadrupole coupling constants results in the order of the B–N bond and a value of εQq_{210}(14N) [4] under certain assumptions. Trimethylamine-borane was prepared according to

B₂H₆ + 2N(CH₃)₃ → 2(CH₃)₃N–BH₃.

In the frequency range of our MWFT spectrometer the J = 1–0 and J = 2–1 transitions of (CH₃)₃N–$^{13}$BH₃ were measured at a temperature of −50 °C and pressures of approximately 0.25 mTorr. The transitions are given in Table 1.

The multiplet patterns were assigned and analysed on the basis of a centrifugally distorted symmetric rotor with the rotational hamiltonian [5] $H_R = BP^2 + (A - B) P^2_R - D_J P^4 - D_K P^2 \mathbb{I} + \mathbb{I}_Q$, containing two coupled nuclei.

The coupling scheme $I_1(14N) + P = F_1, F_1 + I_1(13B) = F$ [6] was used. The Hamiltonian matrix of $H_R + H_Q + H_D$, with $H_Q$ the hamiltonian for the hfs diagonal in K, $I_1$, $I_2$, F, M_y and non-diagonal in J and $F_1$ was diagonalised (program SYM2Q.FOR).

As the J = 2–1 transition is not well resolved the quadrupole coupling constants εQq(13B) and εQq(14N) were calculated from the splittings of the $J = 1–0$ transition only. With fixed εQ's B, D_J, and D_K were fitted to both transitions.

The results are given in Table 2. In Tables 3 and 4 we give measurements and analysis of $J = 1–0$ transitions of two unassigned vibrationally excited states.

Table 1. Observed frequencies $v_{obs}$ [MHz] of the $^{13}$B- and $^{14}$N-hyperfine components of the $J = 1–0$ and $2–1$ transitions of trimethylamine-borane. The values $v_{calc}$ [MHz] were calculated with the parameters of Table 2. $\Delta v = v_{obs} - v_{calc}$ [MHz].

<table>
<thead>
<tr>
<th>J' – J</th>
<th>K</th>
<th>F'</th>
<th>F</th>
<th>$v_{obs}$ [MHz]</th>
<th>$v_{calc}$ [MHz]</th>
<th>$\Delta v$</th>
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</thead>
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<tr>
<td>1–0</td>
<td>0</td>
<td>1.5–0</td>
<td>1–1</td>
<td>9 031.692</td>
<td>9 031.704</td>
<td>−0.012</td>
</tr>
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<td>1–0</td>
<td>1</td>
<td>1.5–1</td>
<td>1–1</td>
<td>9 031.692</td>
<td>9 031.704</td>
<td>−0.012</td>
</tr>
<tr>
<td>1–0</td>
<td>2</td>
<td>1.5–2</td>
<td>1–1</td>
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<td>9 031.704</td>
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<tr>
<td>1–0</td>
<td>3</td>
<td>1.5–3</td>
<td>1–1</td>
<td>9 031.692</td>
<td>9 031.704</td>
<td>−0.012</td>
</tr>
<tr>
<td>2–1</td>
<td>0</td>
<td>2.5–1</td>
<td>1–0</td>
<td>18 064.625</td>
<td>18 064.589</td>
<td>0.036</td>
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<tr>
<td>2–1</td>
<td>1</td>
<td>2.5–2</td>
<td>1–0</td>
<td>18 065.239</td>
<td>18 065.275</td>
<td>−0.036</td>
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<td>2.5–3</td>
<td>1–0</td>
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<tr>
<td>± 1</td>
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<td>2–1</td>
<td>18 064.714</td>
<td>18 064.717</td>
<td>−0.003</td>
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<td>± 1</td>
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<td>3–2</td>
<td>18 065.963</td>
<td>18 065.960</td>
<td>0.003</td>
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</tr>
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</table>

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Table 2. Rotational, centrifugal, and hfs coupling constants of trimethylamine-borane, (CH₃)₃¹⁴N—¹⁰BH₃. The hfs analysis is based on J = 1–0 transition only.

<table>
<thead>
<tr>
<th>J'–J</th>
<th>K</th>
<th>F'–F</th>
<th>F₁–F₁</th>
<th>v₁₀</th>
<th>v₁₁</th>
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<tr>
<td>1–0</td>
<td>0</td>
<td>1–1</td>
<td>9 026.923</td>
<td>9 026.933</td>
<td>-0.010</td>
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<td>-0.010</td>
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<tr>
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<td>1–1</td>
<td>9 027.257</td>
<td>9 027.238</td>
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<tr>
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<td>9 027.238</td>
<td>0.019</td>
<td></td>
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<tr>
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<td>1–1</td>
<td>9 027.257</td>
<td>9 027.243</td>
<td>0.014</td>
<td></td>
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<tr>
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<td>1–1</td>
<td>9 027.257</td>
<td>9 027.243</td>
<td>0.014</td>
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<tr>
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<td>9 027.983</td>
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<td>0.001</td>
<td></td>
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<td>2–1</td>
<td>9 028.098</td>
<td>9 028.097</td>
<td>0.001</td>
<td></td>
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<tr>
<td>1.5–2.5</td>
<td>2–1</td>
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<td>9 028.416</td>
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<tr>
<td>1.5–0.5</td>
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<td>9 029.452</td>
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<td>0–1</td>
<td>9 029.452</td>
<td>9 029.451</td>
<td>0.001</td>
<td></td>
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</table>

Following the procedure given in [7] we calculated from the measured quadrupole coupling constant eQq(¹⁰B) = 2.064(33) MHz the B–N bond order n_B = 0.43(1), the number of electrons donated from the nitrogen to the boron. eQq(²¹⁰B) = -5.39 MHz [8] and <NBH = 105.32(16)° [2, 3] were used. So the B–N bond can be interpreted as given in Figure 1. The low bond order correlates with estimates of the dissociation energy to BH₃ + (CH₃)₃N of 31 to 48 kcal/mol [3].

The next consideration uses the experimental value eQq(¹⁴N) to determine eQq(²¹⁰(¹⁴N)). We follow Townes and Dailey [9] and Gordy [10]. Details are given in [11].

We use
\[
eQq(¹⁴N) = - (u_p / 1 + [3(n_e - 1) - n_p] \xi_N)\]

(1)

with eQq(¹⁴N) the experimental nitrogen quadrupole coupling constant, eQq(²¹⁰(¹⁴N)) the quadrupole coupling constant induced by a 2p₂ electron, \(\xi_N = 0.3\) [12] the shielding constant of nitrogen, \(n_e\) is the mean number of electrons occupying the orbitals directed to the methyl groups, \(n_p\) the mean number of electrons donated by the nitrogen to the boron.
The number of "unbalanced" \( p \) electrons in z-direction i.e. the N-B-bond direction may be expressed by

\[
(Up_i) = - \frac{j}{2} \cdot n_c \cdot a^2_p(\psi_c) \cdot (3 \cos^2 \xi (BNC) - 1) - (2 - n_B) \cdot a^2_p(\psi_B)
\]

(2)

with \( a^2_p(\psi_c) \) the p-electron fraction of the nitrogen orbital directed to the methylcarbon and \( a^2_p(\psi_B) \) that directed to boron. Assuming hybridisation mixing of s and p functions \( \psi_c = s_c + z p_c \) one gets:

\[
a^2_p(\psi_c) = \frac{\mu^2}{1 + \mu^2} \text{ with } \mu^2 = \frac{1}{2} \cdot \cos \xi (CNC)^{-1} \]

(3)

and similar

\[
a^2_p(\psi_B) = \frac{\mu^2}{1 + \mu^2} \text{ with } \mu^2 = \frac{1}{2} \cdot \cos \xi (BNC)^{-1} \]

(4)

with the relation

\[
\cos^2 \xi (BNC) = \frac{1}{3} \left( 1 + 2 \cos \xi (CNC) \right)
\]

(5)

and

\[
a^2_p(\psi_c) = \frac{1}{1 + \mu^2}.
\]

(6)

(1) simplifies to

\[
e Q q(\text{14N}) = \frac{3 \cdot a^2_p(\psi_c) \cdot (2 - n_c - n_B)}{1 + [3(n_c - 1) - n_B] \cdot \epsilon_N} \cdot e Q q_{210}(\text{14N})
\]

(7)

Equation (7) describes for \( n_B = 0 \) the quadrupole coupling constant of trimethylamine.

For trimethylamine-borane the bond angle \( \xi \) CNC = 109.0° is known from the structure [3] and the quadrupole coupling constant \( e Q q(\text{14N}) = -2.832 \) MHz is measured in this work.

For trimethylamine the bond angle \( \xi \) CNC = 110.9° is determined by Wollrab and Laurie [14] and the quadrupole coupling constant \( e Q q(\text{14N}) = -5.47 \) MHz was measured by Lide and Mann [15].

Assuming \( n_c \) (trimethylamine) = \( n_c \) (trimethylamine-borane) equation (7) yields two equations for \( n_c \) and \( e Q q_{210}(\text{14N}) \). The results are \( n_c = 1.16 \) and \( e Q q_{210}(\text{14N}) = -9.38 \) MHz. As there are some assumptions we do not give an error limit. The value of \( e Q q_{210}(\text{14N}) \) compares well with that determined from solid nitrogen \( e Q q_{210}(\text{14N} \text{ solid}) = -9.3 \) MHz [16].

Acknowledgements

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Bibliography

[6] l.c. [4], Chapter IX.4 and 5.
[8] l.c. [4], Table 14.2.
[10] l.c. [4], Chapter XIV.
[12] l.c. [4], Table 14.3.