# MILLIMETER AND SUBMILLIMETER SPECTRA OF $HN_2^+$ AND $DN_2^+$

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Millimeter and submillimeter rotational transitions of the molecular ions $HN_2^+$ and $DN_2^+$ have been measured and analyzed. The determined spectral constants in MHz are $B_{000}$ = 46586.863(15) and $D_{000}$ = 0.08750(53) for $HN_2^+$ and $B_{000}$ = 38554.717(14) and $D_{000}$ = 0.06081(37) for $DN_2^+$.

## 1. Introduction

The $J = 0 \to 1$ transitions of $HN_2^+$ and $DN_2^+$ have been measured in the laboratory by Woods and coworkers [1,2]. In addition, these microwave spectra have been detected in a variety of interstellar sources [3,4]. In this letter, we report spectra of $HN_2^+$ and $DN_2^+$ in the shorter millimeter and submillimeter regions. Our measured transitions extend through $J = 4 \to 5$ for $HN_2^+$ and $J = 5 \to 6$ for $DN_2^+$. These measurements, corrected for ion drift velocities, yield accurate rest frequencies and rotational constants for these molecular ions.

## 2. Experiment and analysis

The species $HN_2^+$ and $DN_2^+$ were produced in a pyrex glow discharge cell 1 m in length and 10 cm in diameter which cooled to liquid-nitrogen temperature. The total pressure was optimized at ≈80 mTorr with an $N_2/H_2$ or $N_2/D_2$ molar ratio of 1 : 6. Discharge currents of 350–500 mA reduced the pressure on the pump end of the cell to ≈60 mTorr. The millimeter and submillimeter radiation used was produced by crystal harmonic generators driven by 50 GHz phase-locked klystrons and focused through the cell via quasi-optical techniques [5]. The radiation was detected by a 1.5 K InSb detector [5] and the lines recovered via lock-in detection with a time constant of 1 s. The observed signal-to-noise ratios were comparable with, but somewhat smaller than, those measured by us for $HCO^+$ and $DCO^+$ [6].

The measured spectra correspond to rotational transitions of $HN_2^+$ and $DN_2^+$ in their ground (000) vibrational states. Our measured frequencies and quantum assignments are listed in table 1. The frequencies have been shifted in a manner discussed previously [6] to cancel the measured Doppler shift caused by the drift velocity in the glow discharge cell. Under sufficiently high resolution, the observed spectral lines would be split by the outer nitrogen quadrupolar coupling constant $eqQ_{N_o}$ of −5.666(12) MHz, to a lesser extent by the inner nitrogen quadrupolar coupling constant $eqQ_{N_i}$ of −1.426(21) MHz, and also by spin–rotation interactions [3]. With our Doppler widths (fwhm) of $\approx(1-2) \times 10^{-6}\, \nu$, where $\nu$ is the frequency, we were not able to detect any quadrupolar structure. The measured transitions have been corrected to include

Table 1
Observed rotational transitions of $HN_2^+$ and $DN_2^+$ (MHz)

| | Transition $J'' \to J'$ | Observed a) | Corrected b) | Corrected – calculated |
|---|---|---|---|---|
| $HN_2^+$ | $1 \to 2$ | 186344.874(100) | 186344.771 | 0.118 |
| | $2 \to 3$ | 279511.671(50) c) | 279511.701 | −0.028 |
| | $3 \to 4$ | 372672.497(50) | 372672.509 | 0.003 |
| | $4 \to 5$ | 465824.941(250) | 465824.947 | 0.064 |
| $DN_2^+$ | $1 \to 2$ | 154217.199(150) | 154217.096 | 0.174 |
| | $2 \to 3$ | 231321.635(50) | 231321.665 | −0.069 |
| | $3 \to 4$ | 308422.210(50) | 308422.222 | 0.055 |
| | $4 \to 5$ | 385516.756(100) | 385516.762 | −0.001 |
| | $5 \to 6$ | 462603.931(200) | 462603.932 | −0.130 |

a) Includes shift to cancel Doppler effect caused by ion drift velocity.
b) Corrected to remove quadrupolar contribution. See text.
c) Erickson et al. [7] have obtained an astronomical frequency of 279513 MHz in 10 sources.

Table 2
Spectral constants of $HN_2^+$ and $DN_2^+$

| | $B_{000}$(MHz) | $D_{000}$(kHz) |
|---|---|---|
| $HN_2^+$ | 46586.863(15) | 87.50(53) |
| $DN_2^+$ | 38554.717(14) | 60.81(37) |

the unresolved, blended hyperfine components in the following manner: the strong, closely spaced inner components of each $J'' \to J'$ transition have been weighted according to their theoretical intensities and an average deviation from the center of gravity of the multiplet computed. This average weighted deviation was then subtracted from the measured frequency of the transition. Only for the $J = 1 \to 2$ transition was the deviation (+103 kHz) competitive in size with our assigned uncertainty in frequency.

The corrected frequencies have been used to derive the spectral constants $B_{000}$ and $D_{000}$ for $HN_2^+$ and $DN_2^+$ shown in table 2. The spectral constants for $HN_2^+$ can be compared with the value for $B_{000} - 2D_{000}$ of 46586.696(16) MHz derived by Thaddeus and Turner [3] from high-resolution astronomical observations. Our value of $B_{000} - 2D_{000}$, 46586.688(15) MHz, is in excellent agreement with this. For $DN_2^+$, our spectral constants used in conjunction with the value of −5.666 MHz for $eQq_{N_0}$ [3] reproduce the measured $J = 0 \to 1$ frequencies obtained by Anderson et al. [2] who were only able to resolve hyperfine stucture due to the outer nitrogen quadrupolar interaction.

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