Resolution of the ^{14}N Nuclear Quadrupole Hyperfine Structure in the Rotational Spectrum of Hydrazoic Acid, HN_3, and Evaluation of the Rotational Constants of $H^{15}NNN$ and $HNN^{15}N$

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Microwave Fourier transform spectra have been measured for hydrazoic acid as its normal isotopomer, $H^{14}N_3$, and two substituted isotopomers, $H^{15}N^{14}N^{14}N$ and $H^{14}N^{14}N^{15}N$. The ^{14}N quadrupole hyperfine structure has been resolved in all cases, and the quadrupole coupling constants of all ^{14}N atoms have been determined. They are compared with those from *ab initio* predictions. Rotational constants A have been evaluated accurately for the first time for the two ^{15}N species, and have been used to confirm a previously published structure.

Introduction

Although the microwave spectrum of hydrazoic acid, HN_3, has been studied several times at both low and high frequencies, the hyperfine structure due to the three ^{14}N nuclei has never been completely resolved. Traditional Stark modulated and millimeter wave spectrometers do not normally have the resolving power to achieve this. Thus, although several papers reported partial resolution of the hyperfine structure [1–3], values for only two of the six quadrupole coupling constants have been measured [1]. Since these constants have been the subject of several *ab initio* predictions [4, 5], an experimental determination of all of them is certainly of interest.

The relatively new technique of microwave Fourier transform (MWFT) spectroscopy has at least an order of magnitude better resolving power than the traditional methods. It has recently been extensively reviewed [6]. It should thus seem to be an excellent technique to resolve the ^{14}N hyperfine structure in HN_3. We show in this paper that this is indeed the case, although the spectra are rather too complex for easy determination of the coupling constants.

Since the coupling patterns are very much simplified by replacing one ^{14}N by ^{15}N we have obtained the constants by instead measuring and analyzing the MWFT spectra of the two substituted species $H^{15}N^{14}N^{14}N$ and $H^{14}N^{14}N^{15}N$. Although microwave spectra of both have been previously reported [2] it is interesting that the only measured transitions were *a*-type R-branches, so that only two of the three rotational constants could be accurately determined. Only a crude value of the rotational constant A was obtained from $K_a=2$ asymmetry splittings. More recently however, Winnewisser [7] suggested some improved values for A by transferring the inertial defect from the normal species, $H^{14}N_3$, which she then used in a structural determination. It was thus a second goal of the present work to locate and measure some *b*-type transitions of these species in order to obtain accurate values for A.

Experimental Methods

The samples of HN_3 were prepared by gently heating dry sodium azide with stearic acid. The labelled species were obtained in equal amounts in a similar preparation, which this time used $NaNN^{15}N$ (99% ^{15}N, ICN Biochemicals). Because of the well known explosive nature of hydrazoic acid, the samples were stored in milligram quantities below 100 Torr in the gas phase in the dark at room temperature. They were apparently stable enough for the purpose of these experiments.

The spectra were measured using the MWFT travelling wave spectrometers in G- [8], K- [9] and V- [10] band at the University of Kiel. Sample pressures were below 2 mTorr (<0.3 Pa), and temperatures were

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about 200 K. Up to $40 \cdot 10^6$ cycles were collected for individual transitions, covering averaging times up to one half hour. Although the spectra were displayed by taking the fast Fourier transforms of the decay signals, accurate frequencies were obtained by fitting the decays in the time domain, using the program developed by Haekel and Mäder [11].

Observed Spectrum and Assignment

The first transition observed was $1_{01}-0_{00}$, in K-band, which Forman and Lide could resolve only partially [1]. For all three isotopic species studied the quadrupole hyperfine structure of all ^{14}N nuclei was resolved. The observed lines are depicted in Fig. 1 (a), (c) and (d).

Because only the coupling constants χ_{aa} could be determined with the $1_{01}-0_{00}$ transition, it was necessary to make further measurements, especially of *a*-type Q-branch transitions, to evaluate $\chi_{bb}-\chi_{cc}$. For the normal isotope they were predicted from the observations of Bendtsen and Winnewisser [3], who had previously measured some of these. For the substituted species they were predicted from the rotational constants of Winnewisser and Cook [2]. In all cases the transitions were easily located. Their assignments were confirmed with the hyperfine structure.

To evaluate the rotational constant *A* for $H^{15}NNN$ and $HNN^{15}N$ some *b*-type lines had to be found. Because this constant was expected to be very large ($\sim$600 GHz) only one P, R-branch series had transitions in our frequency region. These lines were potentially very difficult to find by estimating *A* from a structure because the uncertainties could have been thousands of MHz. Fortunately the estimates made by Winnewisser [7] reduced the uncertainties to ± 300 MHz, which was relatively manageable, especially since these transitions were expected to be strong. All of them were found within this region; the assignments were again confirmed with the hyperfine structure.

Analysis of the Spectrum

To start the analysis, the ^{14}N quadrupole coupling constants were evaluated for each of the labelled species. From a prediction using crude estimates of the constants from the spectrum, quantum number assignments were made in the coupling schemes $I_1+I_2 \rightarrow I, I+J \rightarrow F$ as well as in the alternative scheme $J+I_1 \rightarrow F_1$, $F_1+I_2 \rightarrow F$. A least squares fit was then made to the quadrupole coupling constants using a program written by Böttcher [12]; it fitted shifts of the lines from the unsplit line frequency, and in the process calculated that frequency. The program used a full diagonalization of the Hamiltonian, including terms off-diagonal in *I* but not *J*. This is well known to be sufficient for the small coupling constants found here. Well resolved lines of the *a*-type R-branch and several Q-branch transitions were included in the fit. The rotational constants *B* and *C* were taken from [2], and *A* was estimated from the observed *b*-type transitions.

Table 1. Derived spectroscopic constants of $H^{15}N^{14}N^{14}N$ and $H^{14}N^{14}N^{15}N$.

Parameter		$H^{15}N^{14}N^{14}N$	$H^{14}N^{14}N^{15}N$
Rotational constants (MHz)			
A		605 583.30 (15)	610 979.7 (2)
B		11 667.5433 (15)	11 641.7764 (14)
C		11 427.8558 (15)	11 405.0788 (14)
Centrifugal distortion constants (kHz)			
D_J		4.627 (5)	4.540 (5)
D_{JK}		769.0 (8)	752.3 (8)
D_K		270 480.0[b]	270 480.0[b]
d_1		−0.0836 (15)	−0.0827 (15)
d_2		−0.023 (14)	−0.027 (13)
$10^4\ H_{JK}$		9.32[b]	9.32[b]
H_{KJ}		−0.07 (11)	−0.25 (12)
H_K		520.0[b]	520.0[b]
^{14}N nuclear quadrupole coupling constants (MHz)			
N_α[c]	χ_{aa}	–	4.727 (5)
	$\chi_{bb}-\chi_{cc}$	–	2.271 (3)
N_β	χ_{aa}	−0.819 (17)	−0.858 (8)
	$\chi_{bb}-\chi_{cc}$	0.209 (4)	0.197 (4)
N_γ	χ_{aa}	−1.224 (14)	–
	$\chi_{bb}-\chi_{cc}$	3.998 (4)	–

[a] Numbers in parentheses are one standard deviation obtained in the least squares fit, in units of the last significant figures.

[b] These constants were held fixed in the least squares fit at the values for $H^{14}N_3$ [14].

[c] The notation refers to the N atoms in the order $HN_\alpha N_\beta N_\gamma$.

The results of these fits are given in Table 1. Since both labelled species contain ^{14}N at the central position of the azide group, the values common to both isotopomers were assigned to this nucleus (N_β). The others were assigned to the unsubstituted nucleus. The agreement between the values obtained for N_β is reasonable (within 2 standard deviations).

Table 2. Observed rotational transitions (MHz) of $H^{15}N^{14}N^{14}N$.

F_1'	F'	F_1''	F''	Observed Line Frequency	Dev.[a]
$1_{0,1}-0_{0,0}$				23 095.381[b]	0.000
1	0	1	–[c]	23 094.865	−0.006
1	2	1	–	23 095.011	−0.004
1	1	1	–	23 095.059	−0.003
2	2	1	–	23 095.388	−0.001
2	3	1	–	23 095.487	0.004
2	1	1	–	23 095.623	0.000
0	1	1	–	23 096.066	−0.006
$6_{1,5}-6_{1,6}$				5 033.140[b]	0.001
6	6	6	6	5 032.064	0.001
6	7	6	7	5 032.154	−0.001[d]
6	7	7	6	5 032.154	−0.002
6	5	6	5	5 032.164	−0.001
6	6	5	6	5 032.242	−0.002[d]
7	7	7	7	5 033.496	0.002
7	6	6	6	5 033.496	0.002
7	8	7	8	5 033.559	−0.002
7	6	7	6	5 033.587	−0.002
5	6	7	6	5 033.736	0.011
5	5	5	5	5 033.736	0.003
5	6	5	6	5 033.811	0.003
5	4	5	4	5 033.811	0.001
$7_{1,6}-7_{1,7}$				6 710.722[b]	0.000
7	7	7	7	6 709.647	0.001
7	7	8	7	6 709.725	−0.001
7	8	7	8	6 709.741	0.002
7	6	7	6	6 709.747	−0.001
7	7	6	7	6 709.795	0.002[d]
8	8	8	8	6 711.086	0.000
8	7	7	7	6 711.097	−0.003
8	9	8	9	6 711.153	−0.002
8	7	8	7	6 711.178	−0.003
6	6	6	6	6 711.295	0.003
6	7	8	7	6 711.295	−0.002
6	7	6	7	6 711.370	0.002
6	5	6	5	6 711.370	0.001
$12_{1,11}-12_{1,12}$				18 691.488[b]	0.000
12	12	12	12	18 690.423	0.003
12	12	13	12	18 690.488	0.019
12	13	12	13	18 690.514	0.004
12	12	11	12	18 690.514	0.003[d]
12	11	12	11	18 690.514	−0.002
13	13	13	13	18 691.876	−0.010
13	12	12	12	18 691.922	0.000
13	14	13	14	18 691.957	0.002[d]
13	12	13	12	18 691.957	−0.014[d]
11	11	11	11	18 692.006	0.003
11	12	13	12	18 692.040	−0.001
11	10	11	10	18 692.083	0.000
11	12	11	12	18 692.083	0.000
$13_{1,12}-13_{1,13}$				21 805.917[b]	−0.001
13	13	13	13	21 804.854	0.000
13	13	12	13	21 804.940	0.004[d]
13	14	13	14	21 804.940	0.000
13	12	13	12	21 804.940	−0.005
14	14	14	14	21 806.314	0.000
14	15	14	15	21 806.386	−0.002[d]
14	13	14	13	21 806.386	−0.017[d]
12	12	12	12	21 806.430	0.003
12	11	12	11	21 806.505	−0.001
12	13	12	13	21 806.505	−0.001
$17_{1,16}-17_{1,17}$				36 656.018[b]	0.001
17	17	17	17	36 654.962	0.006
17	18	17	18	36 655.044	0.002
17	16	17	16	36 655.044	−0.002
18	18	18	18	36 656.428	0.002
18	19	18	19	36 656.505	0.004
18	17	18	17	36 656.505	−0.007
16	16	16	16	36 656.505	−0.007
16	17	16	17	36 656.593	0.001
16	15	16	15	36 656.593	0.001
$22_{1,22}-23_{0,23}$				32 836.862[b]	0.001
22	23	21	22	32 836.585	−0.005[d]
22	21	21	20	32 836.585	−0.006[d]
24	23	23	22	32 836.621	0.002[d]
24	25	23	24	32 836.621	−0.003[d]
22	22	21	21	32 836.621	−0.009[d]
24	24	23	23	32 836.656	−0.005[d]
23	22	22	21	32 837.335	0.005[d]
23	24	22	23	32 837.335	0.004[d]
23	23	22	22	32 837.379	0.004[d]
$23_{1,23}-24_{0,24}$				7 114.989[b]	−0.002
23	24	22	23	7 114.718	−0.001[d]
23	22	22	21	7 114.718	−0.003[d]
23	23	22	22	7 114.753	−0.006[d]
23	24	24	23	7 114.753	0.009[d]
25	24	24	23	7 114.753	0.006[d]
25	26	24	25	7 114.753	0.002[d]
25	24	23	23	7 114.792	0.008[d]
25	25	24	24	7 114.792	0.003[d]
24	23	23	22	7 115.455	0.000[d]
24	25	23	24	7 115.455	−0.001[d]
24	24	24	23	7 115.455	−0.008[d]
24	24	23	23	7 115.497	−0.003[d]
$25_{0,25}-24_{1,24}$				18 708.263[b]	−0.001
25	25	24	24	18 707.756	0.001[d]
25	26	24	25	18 707.797	−0.001[d]
25	24	24	23	18 707.797	−0.002[d]
26	26	25	25	18 708.464	0.001[d]
26	25	24	24	18 708.464	−0.008[d]
24	24	23	23	18 708.497	0.006[d]
26	27	25	26	18 708.497	−0.002[d]
26	25	25	24	18 708.497	−0.007[d]
24	23	23	22	18 708.531	0.002[d]
24	25	23	24	18 708.531	0.001[d]

[a] For the unsplit line this is the "observed" unsplit frequency minus that calculated from the derived rotational and centrifugal distortion constants. For the hyperfine components this is the observed frequency minus that calculated from the derived quadrupole coupling constants and centre frequencies.

[b] Unsplit line frequency calculated from the measured frequencies corrected for hyperfine structure.

[c] $F''=0$, 1 or 2; all levels with $J=0$ are degenerate.

[d] These transitions were not included in the least squares fit for the quadrupole coupling constants.

Table 3. Observed rotational transitions (MHz) of $H^{14}N^{14}N^{15}N$.

F_1'	F'	F_1''	F''	Observed Line Frequency	Dev.[a]
$1_{0,1}-0_{0,0}$				23 046.838[b]	0.001
0	1	1	–[c]	23 044.453	−0.005
2	1	1	–	23 046.443	0.000
2	3	1	–	23 046.646	0.002
2	2	1	–	23 046.718	0.006
1	0	1	–	23 047.804	−0.001
1	2	1	–	23 048.006	0.000
1	1	1	–	23 048.165	−0.006
$6_{1,5}-6_{1,6}$				4 970.358[b]	0.000
6	6	6	6	4 969.748	−0.001
6	7	6	7	4 969.810	0.000
6	5	6	5	4 969.821	0.000
7	7	7	7	4 970.536	0.000
7	8	7	8	4 970.610	−0.002
7	6	7	6	4 970.610	−0.002
5	5	5	5	4 970.668	−0.003[d]
5	6	5	6	4 970.731	−0.005
5	4	5	4	4 970.748	−0.003
$7_{1,6}-7_{1,7}$				6 627.012[b]	−0.001
7	7	7	7	6 626.400	−0.001
7	8	7	8	6 626.466	0.001
7	6	7	6	6 626.477	0.002
8	8	8	8	6 627.197	0.000
8	9	8	9	6 627.271	0.004
8	7	8	7	6 627.271	−0.002
6	6	6	6	6 627.311	−0.002[d]
6	7	6	7	6 627.374	−0.006
6	5	6	5	6 627.391	−0.001
$12_{1,11}-12_{1,12}$				18 458.329[b]	0.000
12	12	12	12	18 457.712	−0.002
12	13	12	13	18 457.786	0.003
12	11	12	11	18 457.786	−0.003
13	13	13	13	18 458.533	0.001
13	12	13	12	18 458.606	0.004[d]
11	11	11	11	18 458.606	0.003[d]
13	14	13	14	18 458.606	−0.002[d]
11	12	11	12	18 458.673	0.002
11	10	11	10	18 458.673	−0.005
$13_{1,12}-13_{1,13}$				21 533.909[b]	0.002
13	13	13	13	21 533.292	−0.002
13	14	13	14	21 533.366	0.002
13	12	13	12	21 533.366	−0.003
14	14	14	14	21 534.116	0.001
14	13	14	13	21 534.187	0.009[d]
12	12	12	12	21 534.187	0.002[d]
14	15	14	15	21 534.187	−0.003[d]
12	13	12	13	21 534.251	0.003
12	11	12	11	21 534.251	−0.004
$14_{1,13}-14_{1,14}$				24 845.806[b]	0.001
14	14	14	14	24 845.188	−0.003
14	15	14	15	24 845.263	0.002
14	13	14	13	24 845.263	−0.003
15	15	15	15	24 846.016	0.002
15	14	15	14	24 846.087	0.015[d]
13	13	13	13	24 846.087	0.003[d]
15	16	15	16	24 846.087	0.000[d]
13	14	13	14	24 846.146	0.003
13	12	13	12	24 846.146	−0.003
$17_{1,16}-17_{1,17}$				36 198.776[b]	0.000
17	17	17	17	36 198.157	−0.003
17	18	17	18	36 198.232	0.001
17	16	17	16	36 198.232	−0.003
18	18	18	18	36 198.991	0.004
16	16	16	16	36 199.076	0.040[d]
18	19	18	19	36 199.076	0.017[d]
18	17	18	17	36 199.076	0.013[d]
16	17	16	17	36 199.076	−0.032[d]
16	15	16	15	36 199.076	−0.036[d]
$22_{1,22}-23_{0,23}$				39 731.657[b]	0.000
21	20	22	21	39 731.524	0.024[d]
21	22	22	23	39 731.524	0.022[d]
23	22	24	23	39 731.524	0.002[d]
23	24	24	25	39 731.524	0.001[d]
21	21	22	22	39 731.524	−0.014[d]
24	24	23	23	39 731.524	−0.035[d]
22	21	23	22	39 731.922	0.013[d]
22	23	23	24	39 731.922	0.012[d]
22	22	23	23	39 731.922	−0.025[d]
$26_{0,26}-25_{1,25}$				37 497.890[b]	0.000
26	26	25	25	37 497.625	0.022[d]
26	27	25	26	37 497.625	−0.013[d]
26	25	25	24	37 497.625	−0.014[d]
27	27	26	26	37 498.024	0.036[d]
25	25	24	24	37 498.024	0.017[d]
27	28	26	27	37 498.024	−0.001[d]
27	26	26	25	37 498.024	−0.002[d]
25	26	24	25	37 498.024	−0.019[d]
25	24	24	23	37 498.024	−0.020[d]

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[a] For the unsplit line this is the "observed" unsplit frequency minus that calculated from the derived rotational and centrifugal distortion constants. For the hyperfine components this is the observed frequency minus that calculated from the derived quadrupole coupling constants and centre frequencies.

[b] Unsplit line frequency calculated from the measured frequencies corrected for hyperfine structure.

[c] $F'' = 0$, 1 or 2; all levels with $J = 0$ are degenerate.

[d] These transitions were not included in the least squares fit for the quadrupole coupling constants.

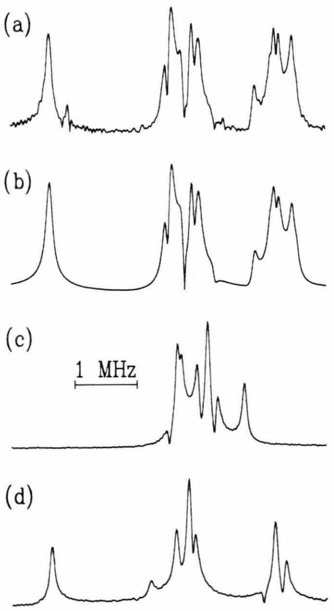

Fig. 1. The transition $1_{01}-0_{00}$ of various isotopic species of HN_3, shown as amplitude spectra with the centre frequencies aligned. (a) $H^{14}N_3$, (b) $H^{14}N_3$ synthesized from the observed constants and an assumed linewidth, (c) $H^{15}N^{14}N^{14}N$, (d) $H^{14}N^{14}N^{15}N$.

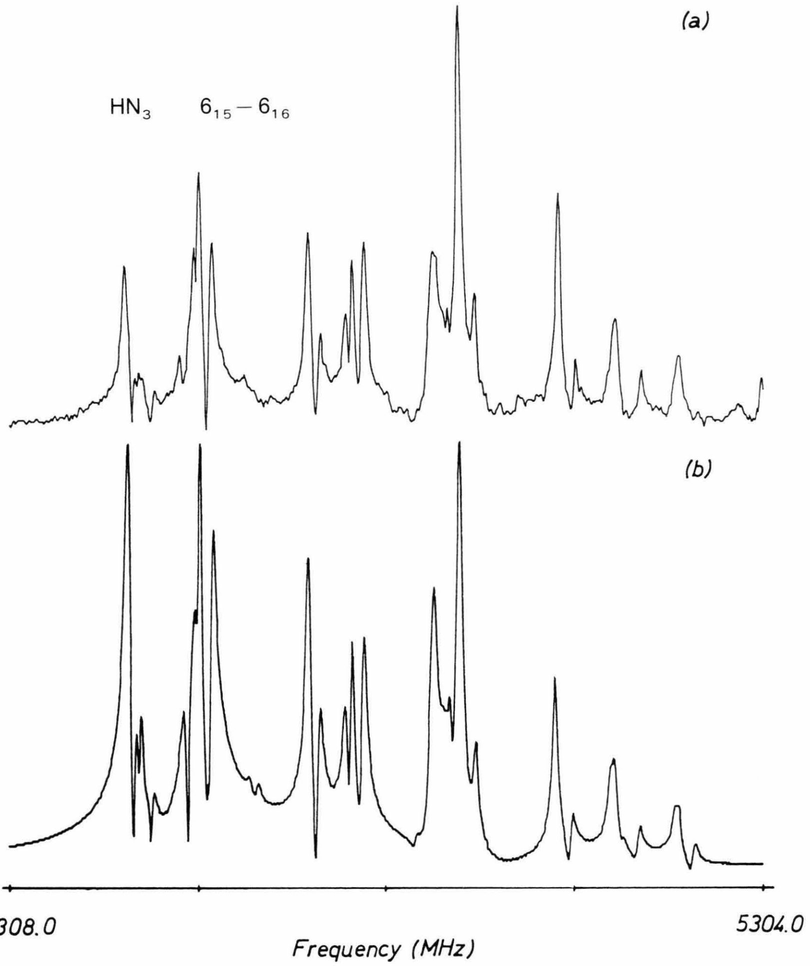

Fig. 2. The transition $6_{15}-6_{16}$ of $H^{14}N_3$. In (a) the experimental amplitude spectrum is shown. In (b) the amplitude spectrum synthesized from the derived constants and an assumed linewidth is given.

The rotational and centrifugal distortion constants for the two labelled species were then obtained by a least squares fit. The frequencies used were the unsplit line frequencies (with the hyperfine structure subtracted off) of the transitions measured here, along with the corresponding measurements with $K_a \leqq 3$ in [2]. The data were weighted in inverse proportion to their estimated experimental uncertainty. The model followed the S-reduction Hamiltonian [13] of Cheung and Merer [14] used for the normal isotopic species. This in turn was similar to one introduced earlier to account for the microwave spectrum of isoelectronic HNCO [15]. Because we could observe only one *b*-type branch it was necessary to fix values of several constants, namely D_K, H_K and H_{JK} to the values of $H^{14}N_3$ [14].

The results of the fits are in Table 1. Good values of the rotational constants, D_J, D_{JK} and d_1, have been obtained. The rotational constants B and C are in good agreement with those of [2]. The distortion constants d_2 and H_{KJ} are barely determined, if that. They were retained as fitting parameters for consistency with earlier work [15], and because the standard deviation of the fit deteriorated if they were omitted.

Tables 2 and 3 contain all the transition frequencies measured here for $H^{15}N^{14}N^{14}N$ and $H^{14}N^{14}N^{15}N$, respectively. Because for both of these isotopomers one set of quadrupole coupling constants was bigger

Table 4. Frequencies and assignments of the $1_{0,1}-0_{0,0}$ rotational transition of $H^{14}N_3$.

F_1'	F_2'	F'[a]	Frequency (MHz)	
			Observed	Dev.[b]
$1_{0,1}-0_{0,0}$			23 815.631[c]	
0	1	0	23 813.222	0.039
0	1	2	23 813.222	0.006
0	1	1	23 813.222	−0.016
2	2	2	23 815.076	0.000
2	2	3	23 815.154	0.007
2	2	1	23 815.154	−0.016
2	3	3	23 815.352	0.000
2	1	1	23 815.417	−0.003
2	3	4	23 815.504	0.006
2	3	2	23 815.573	0.017
2	1	2	23 815.573	−0.016
2	1	0	23 815.815	−0.017
1	0	1	23 816.466	0.001
1	2	1	23 816.746	−0.002
1	2	3	23 816.795	0.003
1	2	2	23 816.851	0.002
1	1	0	23 817.097	0.015
1	1	2	23 817.097	−0.004
1	1	1	23.817.140	−0.003

[a] Only the quantum numbers of the $1_{0,1}$ level are given. For the $0_{0,0}$ level $F_1''=1$, $F_2''=2, 1, 0$ and $F''=3, 2, 1, 0$; all these levels are degenerate.

[b] Observed frequency minus that calculated using the derived constants and centre frequencies.

[c] Unsplit line frequency calculated from the measured frequencies corrected for the hyperfine structure.

than the other, the quantum numbers are given in the coupling scheme $I_1+J \rightarrow F_1$, $F_1+I_2 \rightarrow F$. The excellence of the fit is clearly demonstrated by the small values of the deviations.

The quadrupole hyperfine patterns of $H^{14}N_3$ were then predicted using the derived quadrupole constants. For N_β, the central N atom, the averages of the values in Table 1 were used. The calculation used a multinuclei program written originally by Cook [16], and adapted in Kiel to this project. The program was written in the coupling scheme $J+I_1 \rightarrow F_1$, $F_1+I_2 \rightarrow F_2$, $F_2+I_3 \rightarrow F$; it included off-diagonal terms in the quantum numbers F_1 and F_2, but not J.

The measured frequencies of the $1_{01}-0_{00}$ transition of $H^{14}N_3$ are given in Table 4. Quantum numbers are assigned in the scheme described above, with the assignments $I_1=I_\alpha$, $I_2=I_\gamma$ and $I_3=I_\beta$. The table also shows the deviations between the observed and calculated frequencies, and it is clear from them that the prediction is excellent. Figures 1(a) and (b) show a comparison of the observed pattern with the calculated one; the agreement is again apparent.

Because the pattern for $1_{01}-0_{00}$ depends only on χ_{aa}, the patterns of the Q-branches were also predicted, in order to check the values for $\chi_{bb}-\chi_{cc}$. One such pattern, that of $6_{15}-6_{16}$, is given in Figure 2. The agreement between the observed and calculated patterns is rather good, and provides confirmation of the derived constants. Because the patterns are so complex, no attempt was made to compare observed and calculated frequencies.

Discussion

This work has demonstrated, once again, the very high resolution achievable with microwave Fourier transform spectroscopy. The ^{14}N quadrupole hyperfine structure of NH_3 has been fully resolved, and all the coupling constants have been evaluated. The transitions, especially the $6_{15}-16_{16}$ transition in Fig. 2, are some of the most complex thus far observed and accounted for by this technique. It is still nevertheless the case that assignment of quantum numbers to such transitions is very difficult, if not impossible, without some reasonable prior knowledge of the coupling constants. These are still best obtained by simplifying the spectrum with isotopic substitutions of the type described in this paper.

Table 5 contains a comparison of the measured coupling constants with those measured previously, with those obtained in several *ab initio* predictions, and with those of the two other azides whose ^{14}N coupling constants are all known. The two constants measured previously by Forman and Lide [1] are in excellent agreement with those measured here, though the precision in the present work is very much better.

There are two sets of *a priori* predictions of the ^{14}N coupling constants, by Palmer [4], and by Murgich and Aray [5]. Palmer's constants are given in the principal intertial axis system, and a direct comparison can be made with the experimental values. There is clearly good agreement for N_α; it is slightly less good for N_γ. For the central atom, N_β, the agreement is fairly poor for χ_{bb} and χ_{cc}. Murgich and Aray unfortunately do not state their axis systems precisely, and since the constants are often sensitive functions of angle there is little point in making a detailed comparison. However, because of the plane of symmetry the χ_{cc} components can be compared. In this case there is

Table 5. Comparison of experimental ^{14}N nuclear quadrupole constants of HN_3 with *ab initio* values and with those of other azides.

	N_α			N_β			N_γ		
	χ_{aa}	χ_{bb}	χ_{cc}	χ_{aa}	χ_{bb}	χ_{cc}	χ_{aa}	χ_{bb}	χ_{cc}
Obs.[a]	4.727 (5)	−1.228 (3)	−3.499 (3)	−0.84(3)	0.52 (2)	0.32 (2)	−1.224 (14)	2.611 (7)	−1.387 (7)
Obs.[b]	4.85 (10)			<0.7[c]			−1.35 (10)		
Calc.[d]	4.249	−1.653	−2.596	−0.768	−0.223	0.992	−0.758	2.708	−1.950
Calc.[e]			−1.722			0.122			3.055
Calc.[f]			−1.884			0.302			3.310
CH_3N_3[g,i]	4.744 (4)	−1.354 (2)	−3.390 (4)	−0.950 (5)	0.768 (3)	0.182 (6)	−0.585 (8)	2.259 (4)	−1.674 (9)
NCN_3[h,i]	4.82 (2)	−0.70 (8)	−4.12 (10)	−0.85 (7)	0.70 (8)	0.15 (15)	−0.75 (7)	1.55 (5)	−0.80 (12)

[a] Present work.
[b] Ref. [1].
[c] This is an upper bound to the absolute value of χ_{aa}.
[d] Palmer, Ref. [4].
[e] Ref. [5], 6–31G** calculations.
[f] Ref. [5], Dunning polarization.
[g] Ref. [17].
[h] Ref. [18].
[i] Comparison of values of χ_{aa} and χ_{bb} amongst the different azides is not entirely valid because the *a*- and *b*-inertial axes are rotated from molecule to molecule.

Table 6. Comparison of present and previously reported rotational constants (MHz) of $H^{15}N^{14}N^{14}N$ and $H^{14}N^{14}N^{15}N$.

		$H^{15}N^{14}N^{14}N$	$H^{14}N^{14}N^{15}N$
A	present work	605 583.30 (15)	610 979.7 (2)
	Ref. [5]	605 378.1[a]	610 931.1
	Ref. [2]	619 916	616 868
B	present work	11 667.5433 (15)	11 641.7764 (14)
	Ref. [2]	11 667.54	11 641.76
C	present work	11 427.8558 (15)	11 405.0788 (14)
	Ref. [2]	11 427.86	11 405.08

[a] For the previously measured constants the figures given here are those of the original authors. The implied uncertainties of the *A* constants are too small (see text).

moderately good agreement for N_β, and poor agreement for N_α. There is a total disagreement for N_γ; it is not clear why this should be so. The same problem was found for both CH_3N_3 [17] and NCN_3 [18]. However Murgich and Aray state strongly that the *z*-principal quadrupole axis is essentially perpendicular to the $N_\beta - N_\gamma$ internuclear axis. If they have interchanged the *z*- and *y*-axes much of the disagreement would be removed.

In comparing the experimental constants of HN_3 with those of CH_3N_3 and NCN_3, also in Table 5, one must remember that the angles between the NN axes and the inertial axes vary from molecule to molecule. Again the only really valid comparison is between the χ_{cc} values. It would seem that although there are some variations, they are relatively minor.

In Table 6 there is a comparison of the present and earlier rotational constants of the two ^{15}N isotopomers. For the constants *B* and *C* there is essentially precise agreement, which is hardly surprising since the constants of the present work depend largely on the data of [2]. The precision reported here cannot be considered absolute, since it is dependent on the model used in fitting to the rotational and distortion constants. What is encouraging, however, is that the fits to the rotational constants included the *b*-type transitions; the fact that *B* and *C* do not change is a strong confirmation of the assignment of the lines.

The value of d_1 of the two substituted species was obtained almost entirely from the *a*-type Q-branches measured here. They agree well between themselves, and moderately well with δ_J of the normal species [3]. The improved precision in the present work is probably a reflection of the improved accuracy of MWFT over Stark modulated spectroscopy.

For the *A* constants the agreement between the present values and those of [7] can be considered something of a triumph. The latter were obtained by assuming that the inertial defects of all H-containing isotopic species should be equal. Comparison with isoelectronic HNCO [15, 19] confirms this assumption, but gives an estimated uncertainty in *A* of ±300 MHz. In this limit there is agreement between the two sets of constants. Even more to the point is that Winnewisser [7] used her constants to estimate the structure of HN_3. Our results confirm that structure.

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