^{14}N Nuclear Quadrupole Hyperfine Structure in the Microwave Spectrum of Methyl Azide, CH_3N_3

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Dedicated to Professor Helmut Dreizler on the Occasion of his 60th Birthday

The ^{14}N nuclear quadrupole hyperfine structure in the rotational spectra of three isotopic species of methyl azide, $CH_3{}^{14}N_3$, $CH_3{}^{15}N^{14}N_2$, and $CH_3{}^{14}N_2{}^{15}N$, has been resolved using microwave Fourier transform spectroscopy. The quadrupole coupling constants of ^{14}N at all three positions have been evaluated and are compared with those from an *ab initio* calculation in the literature.

Since the spectra of the substituted species have been obtained for the first time, they have provided new structural information: the rotational constants are consistent with a structure in which the NNN chain is slightly bent.

Introduction

The microwave spectrum of methyl azide, CH_3NNN, was first observed by Salathiel and Curl in 1965 [1], using a Stark modulated spectrometer. They measured both *a*- and *b*-type transitions of the normal isotopic species, and used them to evaluate the rotational constants, as well as the barrier to internal rotation of the methyl group, which turned out to be rather low (~ 714 cal mol^{-1}). They also measured both components of the dipole moment using the Stark effect. Although they pointed out that several transitions showed evidence of ^{14}N quadrupole hyperfine structure they were unable to resolve it, and accordingly reported no coupling constants. And because they observed the spectrum of only one isotopic species they could not evaluate a definitive structure, but could say only that the rotational constants were consistent with a reasonable model, which at that time was believed to have a linear NNN chain.

The recently developed technique of microwave Fourier transform (MWFT) spectroscopy has been found to have up to an order of magnitude higher resolution than Stark modulation spectroscopy. It has recently been extensively reviewed [2]. It would thus seem to be an excellent method to resolve the ^{14}N quadrupole structure of methyl azide. Since, however, there are three nitrogen nuclei in the molecule the hyperfine patterns should be rather complex, making evaluation of the coupling constants, and their assignment to particular nuclei, difficult. This was the case for cyanogen azide [3], the only other azide for which all ^{14}N coupling constants have thus far been reported. The problem could be considerably simplified by replacing at least one ^{14}N nucleus with ^{15}N.

In the work reported here we have successfully resolved the hyperfine structure of all ^{14}N nuclei in methyl azide. In order to simplify the patterns, we have prepared two different species containing ^{15}N, and have made the first measurements of their microwave spectra. It has been possible from them unambiguously to assign the coupling constants to particular nuclei. The new isotopic data have permitted us to obtain further information about the structural parameters.

Experimental Methods

Methyl azide was prepared by the reaction of dimethyl sulfate with warm, alkaline soldium azide, following the procedure of Salathiel and Curl [1]. Although different samples were found to have varying small amounts of dimethyl ether impurity, this did not interfere with our measurements. The two samples labelled with ^{15}N, $CH_3{}^{15}NNN$ and $CH_3NN^{15}N$, were synthesized in equal amounts from the same preparation, which this time used $NaNN^{15}N$ (99% ^{15}N, ICN Biochemicals).

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The spectra were measured in the frequency region 4.2–12.6 GHz using the G band (4.0–6.0 GHz) [4] and X band (8.0–12.4 GHz) [5, 6] microwave Fourier transform travelling wave spectrometers at the University of Kiel. Sample pressures were 1–3 millitorr and temperatures were ~ −50 °C. Up to 38×10^6 cycles were collected for individual transitions, covering an averaging time up to 30 min. Although the spectra were displayed by taking the Fourier transform of the decay, the final transition frequencies were evaluated from the time domain signals using the least squares fitting program written by Haekel [7].

Results and Analysis

The initial observations were of the $1_{01}-0_{00}$ transitions of the normal isotopic species. The transitions of both A and E internal rotation species were observed; those of the A species are shown in Figure 1 a. The quadrupole hyperfine structure is well resolved. However, since it was initially rather difficult to assign quantum numbers to individual lines, and hence to obtain the ^{14}N coupling constants, the rather simpler spectra of the labelled species $CH_3{}^{15}NNN$ and $CH_3NN^{15}N$ were sought.

Since there had been no previous measurements of the spectra of either labelled species their principal moments of inertia were initially predicted, using the approximate structure of Salathiel and Curl [1]. The differences between the calculated principal moments of the normal and labelled species were applied to the "Stark effect" principal moments of [1], and the resulting moments were then used to predict the rotational constants and transition frequencies. For both isotopes the $1_{01}-0_{00}$ transitions were found within a few MHz of the predictions. They were easily identified from their internal rotation and quadrupole patterns. The transitions of the A species of both isotopes are given in Figs. 1c and d. Clearly the patterns are much simpler than those of the normal species; for each it was easy to assign quantum numbers to the lines.

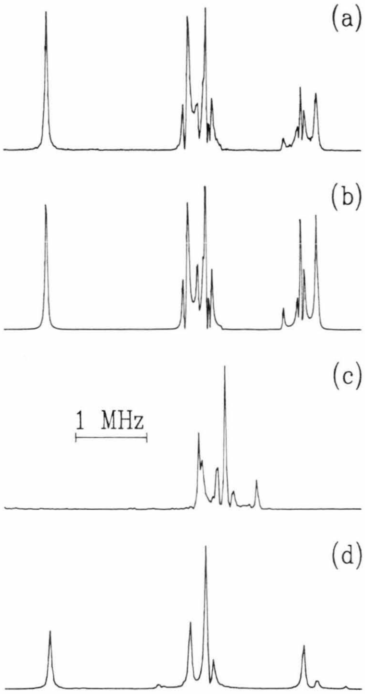

Fig. 1. The transition $1_{01}-0_{00}$ of various isotopic species of methyl azide, shown as power spectra with the centre frequencies aligned. To emphasize the resolution of the ^{14}N quadrupole hyperfine structure only the lines of the A internal rotation species are given. Identical patterns to lower frequencies are found for the E species [1]. – (a) $CH_3{}^{14}N_3$; (b) $CH_3{}^{14}N_3$, synthesized from the derived constants; (c) $CH_3{}^{15}N^{14}N^{14}N$; (d) $CH_3{}^{14}N^{14}N^{15}N$.

Because χ_{aa} is the only coupling constant obtainable from $1_{01}-0_{00}$, some a-type Q branch lines of the labelled species were also measured. For these transitions the hyperfine splitting depends only on $(\chi_{bb}-\chi_{cc})$, so all diagonal elements of the quadrupole tensor could thus be obtained. The transitions of only the A-species were sought; again they were found within a few MHz from where they predicted. Because for both species $(\chi_{bb}-\chi_{cc})$ of one nucleus was rather bigger than for the other the hyperfine structure was quite simple. This provided confirmation of the assignment.

The ^{14}N quadrupole coupling constants were then evaluated for each of the labelled species. Quantum number assignments were made in the coupling scheme $J+I_1=F_1$; $F_1+I_2=F$, using reasonable estimates of the rotational and quadrupole coupling constants both from the patterns and from values for other molecules, notably NCN_3 [3]. The transition frequencies and quantum numbers are given in Table 1. The coupling constants themselves were evaluated by a least squares fit of the coupling constants χ_{aa} and χ_{bb} to the splittings. The program used a full diagonalization of the Hamiltonian, including off-diagonal terms in F_1 but not J. This is well known to be sufficient for the small coupling constants involved.

The results of the fits are in Table 2. Since the quadrupole splittings depend on χ_{aa} and $(\chi_{bb}-\chi_{cc})$,

Table 1. Measured transition frequencies (MHz) of $CH_3{}^{15}NNN$ and $CH_3NN^{15}N$.

F_1'	F'	F_1''	F''	$CH_3{}^{15}NNN$		$CH_3NN^{15}N$	
				observed frequency	dev. [a]	observed frequency	dev. [a]
$1_{01}-0_{00}$				10 303.957 [b]		10 054.735 [b]	
0	1	1	– [c]	10 304.482	0.002	10 052.343	−0.001
2	2	1	–	10 303.930	0.000	10 054.320	−0.002
2	3	1	–	10 304.036	−0.003	10 054.546	0.001
2	1	1	–	10 304.134	0.002	10 054.628	−0.002
1	0	1	–	10 303.575	0.002	10 055.683	0.000
1	2	1	–	10 303.679	0.001	10 055.907	0.000
1	1	1	–	10 303.712	−0.002	10 056.092	−0.001
$4_{13}-4_{14}$				4 628.664 [b]		4 259.266 [b]	
4	4	4	4	4 627.534	−0.001	4 258.651	0.000
4	5	4	5	4 627.714	−0.001	4 258.805	0.000
4	3	4	3	4 627.749	0.001	4 258.853	−0.001
5	5	5	5	4 628.896	0.000	4 259.311	−0.001
5	6	5	6	4 629.076	0.000	4 259.501	−0.004
5	4	5	4	4 629.126	−0.001	4 259.536	0.004
3	3	3	3	4 629.257	−0.002	4 259.493	0.000
3	4	3	4	4 629.417	−0.004	4 259.667	0.002
3	2	3	2	4 629.472	0.000	4 259.737	0.002
$5_{14}-5_{15}$				6 942.081 [b]		6 388.136 [b]	
5	5	5	5	6 940.948	0.000	6 387.508	0.001
5	6	5	6	6 941.137	−0.001	6 387.683	0.004
5	4	5	4	6 941.170	0.001	6 387.719	0.001
6	6	6	6	6 942.328	0.001	6 388.194	0.005
6	7	6	7	6 942.515	−0.001	6 388.384	−0.001
6	5	6	5	6 942.557	0.000	6 388.413	−0.003
4	4	4	4	6 942.617	0.002	6 388.332	−0.004
4	5	4	5	6 942.796	0.003	6 388.519	−0.001
4	3	4	3	6 942.833	0.000	6 386.576	0.000

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

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

[c] For the 0_{00} level $F''=0, 1, 2$; these levels are all degenerate.

Table 2. Spectroscopic constants of isotopically substituted methyl azide.

Parameter		$CH_3{}^{15}NNN$	$CH_3NN^{15}N$
Rotational and centrifugal distortion constants/MHz [a]			
B		5383.452	5240.366
C		4920.506	4814.368
$\delta_J \times 10^3$		0.78	0.73
^{14}*N Nuclear quadrupole coupling constants/MHz*			
N_α: [b]	χ_{aa}	–	4.744(4)
	χ_{bb}	–	−1.354(2)
N_β:	χ_{aa}	−0.950(5) [c]	−0.950(5)
	χ_{bb}	0.769(3)	0.768(3)
N_γ:	χ_{aa}	−0.585(8)	–
	χ_{bb}	2.259(4)	–

[a] The rotational constants are effective constants for the A internal rotation species only. They take no account of internal rotation. The uncertainties are ~1 in the last quoted figure.

[b] Labelling of the N atoms is in the order $CH_3N_\alpha N_\beta N_\gamma$.

[c] Quoted errors are single standard errors in units of last significant figure.

rather than χ_{aa} and χ_{bb}, χ_{aa} and χ_{bb} are connected, and there are various possible permutations of these connections. The values in Table 2 are the most reasonable in terms of internal consistency and in comparison with other molecules. Since both substituted species contain ^{14}N at the central position of the azide group the values common to both isotopic species are assigned to this nucleus (N_β). The others are assigned to the respective unsubstituted nucleus.

The rotational constants B and C were obtained for both substituted species. They were evaluated from the unsplit line frequencies, assuming that the inertial defect was unchanged from the normal isotope. A direct calculation was made of the three frequencies to B, C and the distortion constant δ_J [8]. The results are in Table 2. It is interesting that δ_J is close to that found for isoelectric FN_3 [9]. Because the fits considered the A species only, with no account taken for internal rotation, the constants are simply effective constants for this species. The uncertainties given reflect the uncertainties in the frequency measurements.

With the quadrupole coupling constants determined it now became feasible to try to account for the hyperfine patterns of the normal isotopic species, $CH_3{}^{14}N_3$. The quadrupole patterns of the transition $1_{01}-0_{00}$ mentioned above were predicted, as were those of three a-type Q branches, using the derived quadrupole constants and the rotational constants of [1]. A multinuclei quadrupole coupling program was used; it was originally written by Cook [10], and was adapted to this project during the course of this work. The program was a prediction program, written in the coupling scheme $J+I_1=F_1$; $F_1+I_2=F_2$; $F_2+I_3=F$. It included off-diagonal terms in the quantum numbers F_1 and F_2, but not J. No provision was made for least squares fitting, which in view of the complication of the pattern seemed reasonable.

The observed frequencies of the $1_{01}-0_{00}$ transitions of $CH_3{}^{14}N_3$ are given in Table 3, along with a prediction of the frequencies using the constants of Table 1. The agreement is excellent. A very slight systematic error in the value of χ_{aa} for N_α is apparent; this error is, however, of the order of magnitude of the uncertainty in Table 1. Figures 1 a and 1 b also show a com-

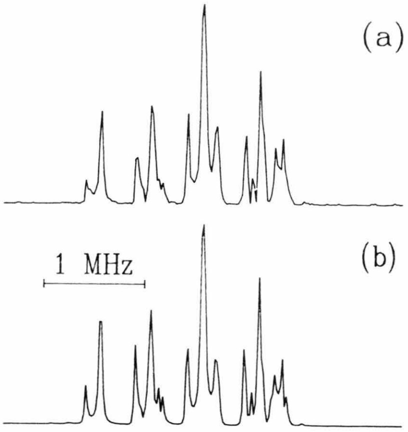

Fig. 2. The transition $7_{16}-7_{17}$ of $CH_3{}^{14}N_3$ at 12 525.4 MHz. In (a) the experimental power spectrum is shown. In (b) the power spectrum synthesized from the derived constants is given.

Table 3. Observed and calculated frequencies (MHz) of the $1_{01}-0_{00}$ transition of $CH_3{}^{14}N_3$ (A species).

F_1'	F_2'	F' [a]	Frequency observed	Frequency calculated [b]
0	1	0	10 345.529	10 345.521
0	1	1		
0	1	2		
2	2	2	10 347.449	10 347.447
2	2	3	10 347.507	10 347.506
2	2	1		
2	3	3	10 347.661	10 347.657
2	1	1	10 347.735	10 347.736
2	3	4	10 347.763	10 347.761
2	3	2	10 347.804	10 347.804
2	1	2	10 347.840	10 347.840
2	1	0	10 347.988	10 347.992
1	0	1	10 348.842	10 347.845
1	2	1	10 349.047	10 349.051
1	2	3	10 349.084	10 349.086
1	2	2	10 349.126	10 347.129
1	1	2	10 349.307	10 347.312
1	1	0		
1	1	1		

[a] Only the F quantum numbers of the 1_{01} level are given. For the 0_{00} level $F_1''=1$, $F_2''=2, 1, 0$, and $F''=3, 2, 1, 0$; all these levels are degenerate.

[b] Frequency calculated using the constants of Table 2, and an unsplit frequency of 10 347.921 MHz.

parison of the measured pattern with the calculated one; again the excellent agreement is evident.

The agreement with the Q branch patterns is also excellent. Figure 2 gives a comparison of the measured pattern of the $7_{16}-7_{17}$ transition with that calculated from the derived constants. In this case the patterns are so complex that comparison of the frequencies did not appear to be fruitful.

Discussion

Methyl azide has been the subject of several recent *ab initio* calculations. Our results provide a chance of test them. Sjøgren and Nielsen [11] have calculated the structure and force field of HN_3 and CH_3N_3. For both molecules they predict a bend in the NNN chain, which they noted was in agreement with experiment for HN_3 [12]. They predicted a bend of 6° away from the methyl group in the NNN chain of CH_3N_3, but pointed out that the experimental evidence at the time could not confirm it. They also predicted a tilt of the methyl group of 4.2° away from the CN bond. In collaboration with others [13] these workers carried out further calculations as well as electron diffraction studies on several other organic azides, and found bends of 6–8° in the NNN chain for all of them.

Murgich and Aray [14] have also recently reported *ab initio* calculations for CH_3N_3. Although they do not seem to have taken into account structural variations they obtained a lower energy than did Sjøgren and Nielsen [11]. In their work the main aim of the calculations was to predict ^{14}N quadrupole coupling constants for the compounds HN_3, CH_3N_3 and NCN_3, along with the ion N_3^-. They presented quadrupole coupling constants for all ^{14}N nuclei in the azide group for each species.

We first used our new isotopic data in an attempt to improve the structural parameters. Although there are still not enough of these data to be definitive about the structure, nevertheless some useful information can be obtained. The following procedure was adopted.

Salathiel and Curl [1] presented constants for the A species only, as well as constants taking into account internal rotation. There are slight differences between them. We applied the corresponding differences to the constants of Table 1 to evaluate the ground state effective constants B_0 and C_0 for both substituted species. Using the inertial defect of [1], the corresponding values of A_0 were obtained. Then the r_s coordinates of both substituted N atoms were calculated [15, 16]. The values obtained are in Table 4; since both these atoms are well away from the inertial axes all the values are well determined.

In virtually all azides the $N_\alpha N_\beta$ distances are essentially the same, as are the $N_\beta N_\gamma$ distances [13]. From this information we can provide evidence of a bend in the NNN chain at N_β. We noticed that for HN_3 there are slight differences between the calculated lengths [16] and experimental lengths [12]. We applied the same differences to the calculated lengths of CH_3N_3. When we did this we found that the NNN chain had to have a bend of 6.9° to fit the substitution coordinates. This is in very reasonable agreement with the theoretical prediction. If we took the bond lengths to be the same as in HN_3, then this angle was larger, nearer 12°, which may be a little unrealistic. In any case it is highly likely that this chain is bent.

With the NNN parameters determined above we then calculated reasonable values of the remaining parameters by reproducing the observed rotational constants. With assumed CH lengths of 1.079 Å the HCH out of plane angle was found to be 106.8° in order to reproduce the inertial defect. The remaining parameters (∠CNN, ∠HCN and r(CN)) were then adjusted to try to reproduce the observed rotational constants; the results are also in Table 4. With these parameters all the B_0 and C_0 values are reproduced to within less than 0.7 MHz, and the A_0 values to within less than 17 MHz. The CN length and CNN angle are close to the theoretical values (1.503 Å and 112.6°, respectively) [11]. In addition, there is a tilt for the methyl group away from the CN bond, also in good agreement with the prediction.

Murgich and Aray [14] seem to be the only group to have published calculated ^{14}N quadrupole coupling constants in methyl azide. A comparison between our values and theirs is rather difficult. They calculated principal values of the quadrupole tensor; we, on the other hand, have obtained the components along the principal inertial axes, and there are not enough data to equate the two sets of values. Murgich and Aray do give some diagrams showing rather roughly the directions of the principal axes relative to the structure. However, since the constants are often rather sensitive functions of angle there seems little purpose in making a detailed comparison.

However, because the molecule has C_s symmetry the out-of-plane components can reasonably be compared. This is done in Table 4. A similar comparison is also given for NCN_3. It is clear that for both N_α and N_β there is moderate agreement between observed and calculated values. For N_γ there is total disagreement. It is not at all clear why. However, Murgich and Aray point out strongly that the z-principal quadrupole axis of this nucleus is essentially perpendicular to the $N_\beta N_\gamma$ bond. If they have interchanged the z and y axes the disagreement would largely disappear.

Table 4. Derived structural information on methyl azide.

Substitution coordinates (Å) [a]

	$\lvert a_s \rvert$	$\lvert b_s \rvert$
N_α	0.5020	0.6112
N_γ	1.6937	0.2639

Structural parameters [b]

r(CH)	1.079 Å	$\angle(H_0CH_0)$	106.8°
		$\angle(H_0CN_\alpha)$	112°
$r(CN_\alpha)$	1.483 Å	$\angle(H_iCN_\alpha)$	109°
$r(N_\alpha N_\beta)$	1.231 Å	$\angle(CN_\alpha N_\beta)$	113.85°
$r(N_\beta N_\gamma)$	1.137 Å	$\angle(N_\alpha N_\beta N_\gamma)$	173.1°

Rotational constants (MHz) [a]

	CH_3N_3		$CH_3{}^{15}NNN$		$CH_3NN^{15}N$	
	observed	dev.	observed	dev.	observed	dev.
A_0	43 953.6	−16.7	42 601	−7.4	43 702	−16.8
B_0	5 395.66	−0.40	5 381.45	−0.33	5 238.37	−0.53
C_0	4 848.04	−0.56	4 918.59	−0.38	4 812.45	−0.67

[a] The coordinates of N_α and N_β have opposite signs.
[b] H_i, H_0 are in and out of the CNNN plane, respectively.
[c] A_0, B_0, and C_0 are the ground state effective rotational constants derived as decribed in the text for the structural calculations. The deviations are the observed rotational constants minus those calculated from the derived structure.

Table 5. Comparison of experimental and *ab initio* out-of-plane components (MHz) of the ^{14}N quadrupole tensors of CH_3N_3.

		N_α	N_β	N_γ
CH_3N_3	(obs.) [a]	−3.390	0.182	−1.674
	(calc.) [b]	−2.143	0.120	3.030
	(calc.) [c]	−2.065	0.237	3.313
	(calc.) [d]	−2.367	0.137	3.265
NCN_3	(obs.) [e]	−4.12	0.15	−0.80
	(calc.) [b]	−1.39	0.01	2.91
	(calc.) [e]	−4.26	−0.28	−2.66

[a] Present work. – [b] Ref. [13], 6–31 G** calculation.
[c] Ref. [13], Dunning polarization.
[d] Ref. [13], 4–31 G* calculation. – [e] Ref. [3].

Conclusions

Microwave Fourier transform spectroscopy has been found to be an excellent technique to resolve the ^{14}N quadrupole hyperfine structure in methyl azide.

In order to evaluate the coupling constants it has been convenient to measure the spectra of two ^{15}N-containing species, whose spectra are very much simpler. The technique is generally available for other azides, including HN_3, whose spectra we have also resolved, and will report in a forthcoming article. The derived constants provide a very sensitive test of *ab initio* calculations.

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