

## Centrifugal Distortion and Internal Rotation Analysis of the Rotational Spectra of *N*-Methylmethanimine $d_0$ and $d_5$

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The ground state millimeter-wave spectra of  $\text{CH}_3\text{N}=\text{CH}_2$  and  $\text{CD}_3\text{N}=\text{CD}_2$  have been measured. The rotational constants, centrifugal distortion constants, and barrier hindering internal rotation of the methyl group have been determined for both species. For the parent species  $I_a$  and  $\kappa(i, a)$  were also obtained, and for the perdeuteriated species the quadrupole coupling constants of  $^{14}\text{N}$  were determined.

### INTRODUCTION

The imines are compounds of growing usefulness and interest to chemists and biochemists, but their physical properties have been little studied because they are very reactive. The microwave spectrum of *N*-methylmethanimine ( $\text{CH}_3\text{N}=\text{CH}_2$ ) was first studied by Sastry and Curl (1). They prepared  $\text{CH}_3\text{N}=\text{CH}_2$  by dripping 1,3,5-trimethylhexahydrosymtriazine onto a bed of fused alumina and  $\text{SiO}_2$  maintained at  $450^\circ\text{C}$ . They have determined the rotational constants, the dipole moment, the quadrupole coupling constants of nitrogen, and the barrier to internal rotation of the methyl group. Later, by measuring the microwave spectra of the isotopic species  $\text{CH}_2\text{DN}=\text{CH}_2$ , Curl *et al.* (2) showed that one methyl proton eclipses the  $\text{C}=\text{N}$  double bond. Recently Bak and Svanholt (3), by measuring some new lines of  $\text{CH}_3\text{N}=\text{CH}_2$  and the microwave spectrum of  $\text{CD}_3\text{N}=\text{CD}_2$ , have determined approximate centrifugal distortion constants for these two species, which have been produced by pyrolysis of dimethylamine  $d_0$  or  $d_7$  on a quartz surface at  $950^\circ\text{C}$ .

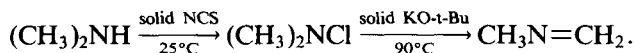
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However, these studies have been limited up to 50 GHz. As  $\text{CH}_3\text{N}=\text{CH}_2$  is relatively light ( $A \sim 52.5$  GHz), the greatest part of the strong lines are above 50 GHz.

Therefore, to predict the frequencies of the strong lines which are of great potential interest to radioastronomers, it is necessary to measure first the millimeter-wave spectrum. This was the aim of the present work, for which a very simple and efficient procedure has been used to prepare the *N*-methylmethanimine. This procedure is quite general and could be used for other molecules of the same type.

#### EXPERIMENTAL DETAILS

Reactive molecules have been recently synthesized by vacuum dynamic gas/solid phase reaction (4, 5).  $\text{CH}_3\text{N}=\text{CH}_2$  and  $\text{CD}_3\text{N}=\text{CD}_2$  have been prepared here by "one-tube" multistep sequences carried out in a single vacuum line which was pumped continuously through the absorption cell (Fig. 1). *N*-Chlorination of the dimethylamine ( $(\text{CH}_3)_2\text{NH}$  or  $(\text{CD}_3)_2\text{ND}$ ) on solid *N*-chlorosuccinimide (NCS) at room temperature is followed by an  $\alpha$ -elimination reaction of the resulting *N*-chloramine over solid potassium *tert*-butoxide ( $\text{KO}^t\text{Bu}$ ) at  $90^\circ\text{C}$ . This process can be schematically represented as



The only gaseous by-product, *t*-BuOH, was eliminated by a cold trap at  $-82^\circ\text{C}$ . A cell pressure of about 5 mTorr was maintained by cooling the dimethylamine at  $-55^\circ\text{C}$ . At the outset of this investigation the purity of the compound was checked by its low-temperature ir, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (5). The lifetime of this species in the closed cell was more than 1 min.

The measurements were performed with the Lille millimeter-wave spectrometer. Phase-stabilized klystrons (Varian, 68–80 GHz) supply a harmonic generator (Custom Microwave) with fundamental power. To obtain a good sensitivity, superheterodyne detection was used; the local oscillator was kept at a constant frequency difference of 600 MHz from the source oscillator. After the detection, the signal was digitally averaged and then processed by a microcomputer (ITT 2020), which calculated the line frequencies and which allowed—if necessary—digital filtering (line smoothing, baseline subtraction). For details see (6).

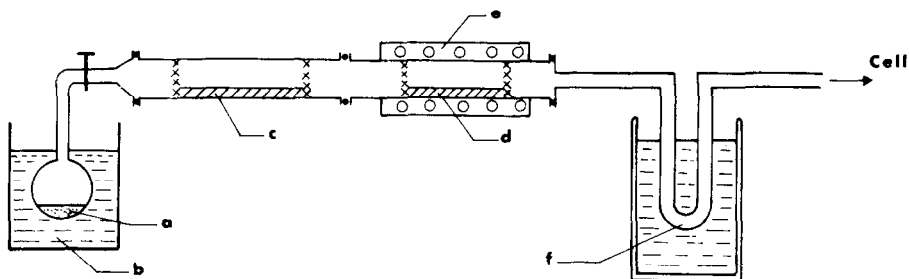
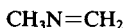


FIG. 1. Preparation of *N*-methylmethanimine: a, dimethylamine; b, methanol bath at  $-55^\circ\text{C}$ ; c, solid *N*-chlorosuccinimide; d, solid potassium *tert*-butoxide; e, furnace at  $+90^\circ\text{C}$ ; f, trap at  $-82^\circ\text{C}$ .

TABLE I  
Transition Frequencies (MHz) in  $\text{CH}_3\text{N}=\text{CH}_2$

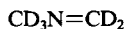
$J^1$	$K^1_a$	$K^1_c$	$J^2$	$K^2_a$	$K^2_c$	$\nu_A - \nu_E$ (calc.)	$\nu_A$ (obs.)	$\nu_A$ (calc.-obs.)	$\nu_E$ (obs.)	$\nu_E$ (calc.-obs.)
3	3	1	3	2	2	100.74	212 479.87	0.24	212 379.07	0.30
3	3	0	3	2	1	26.18	212 333.78	0.27	212 307.59	0.28
4	3	1	4	2	2	15.28	212 124.62	0.24	212 109.27	0.31
4	3	2	4	2	3	110.74	212 560.74	-0.10	212 449.46	0.43
5	3	2	5	2	3	15.39	211 713.76	0.23	211 698.28	0.32
5	3	3	5	2	4	109.53	212 722.39	0.24	212 612.82	0.28
6	3	4	6	2	5	100.40	213 004.46	0.23	212 904.00	0.29
6	3	3	6	2	4	23.18	211 009.93	0.27	210 986.71	0.31
7	3	4	7	2	5	36.10	209 915.82	0.23	209 879.69	0.25
7	3	5	7	2	6	85.93	213 450.75	0.20	213 364.78	0.24
8	3	6	8	2	7	73.11	214 109.71	0.15	214 036.52	0.23
9	3	7	9	2	8	65.31	215 032.82	0.16	214 967.43	0.24
10	1	10	9	0	9	13.69	213 612.23	-0.13	213 598.39	0.02
10	3	8	10	2	9	60.75	216 273.47	0.16	216 212.72	0.16
11	3	9	11	2	10	57.69	217 885.45	0.11	217 827.70	0.17
12	0	12	11	1	11	-7.90	219 019.19	-0.17	219 026.09	0.83
12	3	10	12	2	11	55.27	219 921.48	0.07	219 866.18	0.10
13	3	11	13	2	12	53.10	222 432.20	-0.02	222 379.06	0.02
14	1	13	13	2	12	-30.55	211 164.38	-0.12	211 194.99	-0.18
14	3	12	14	2	13	51.00	225 464.76	-0.10	225 413.75	-0.09
15	3	13	15	2	14	48.91	229 061.77	-0.04	229 012.85	-0.03
16	2	15	16	1	16	54.26	218 197.13	-0.08	218 142.57	0.22
16	3	14	16	2	15	46.80	233 260.89	-0.12	233 214.04	-0.07
17	3	15	17	2	16	44.66	238 093.15	-0.15	238 048.43	-0.08
17	2	16	17	1	17	54.91	229 347.00	-0.07	229 291.75	0.27
18	2	16	17	3	15	-42.71	212 564.39	0.09	212 607.18	0.02
19	1	18	19	0	19	41.03	220 844.88	0.07	220 803.57	0.35
19	2	17	19	1	18	18.52	144 843.84	-0.16	144 825.31	-0.15

20	1	19	20	0	20	44.38	238 231.30	0.02	238 186.62	0.32
20	2	18	20	1	19	17.05	156 308.62	-0.18	156 291.50	-0.11
23	3	21	22	4	18	-21.20	150 088.63	0.55	150 109.69	0.69
23	4	20	23	3	21	20.77	306 595.57	-0.18	306 574.89	-0.27
24	1	23	24	0	24	57.20	306 418.83	0.25		
24	2	23	24	1	24	62.37	319 238.22	-0.02		
24	2	22	24	1	23	15.10	215 792.69	-0.09	215 777.61	-0.11
25	4	21	24	5	20	-10.69	144 901.05	0.38	144 911.46	0.67
25	2	23	25	1	24	15.54	233 256.41	-0.11	233 240.88	-0.12
25	4	22	25	3	23	14.77	313 620.01	-0.09	313 605.43	-0.28
26	3	24	26	2	25	26.40	311 650.79	-0.25		
26	4	22	26	3	23	13.68	230 913.87	-0.59	230 900.18	-0.58
26	4	23	26	3	24	11.74	318 061.27	-0.19	318 049.51	-0.17
27	4	23	27	3	24	9.48	225 228.80	-0.16	225 219.33	-0.17
28	4	24	27	5	23	-5.04	225 467.95	0.41	225 472.70	0.70
28	4	24	28	3	25	5.33	220 450.48	-0.18	220 445.13	-0.16
29	2	27	29	1	28	18.68	307 275.88	-0.04		
29	4	25	29	3	26	1.36	216 819.13	0.02	216 817.72	0.07
30	5	25	29	6	24	8.29	156 435.22	-0.49	156 426.65	-0.21
30	3	27	30	2	28	-0.24	223 847.72	-0.35		
30	4	26	30	3	27	-2.30	214 531.29	0.06		
31	4	27	30	5	26	3.73	315 976.63	0.38	214 553.56	0.10
31	4	28	30	5	25	7.78	236 456.30	0.24	315 972.77	0.51
31	3	28	31	2	29	-0.89	239 140.32	-0.18	236 448.25	0.52
32	4	28	32	3	29	-8.31	214 821.09	0.12	239 141.42	-0.38
33	5	29	32	6	26	13.12	210 735.62	-1.37	214 829.37	0.15
33	5	28	32	6	27	11.80	230 971.61	-1.30	210 722.17	-1.04
33	4	29	33	3	30	-10.50	217 637.18	0.25	230 959.42	-0.91
33	5	28	33	4	29	-15.46	303 445.12	0.38	217 647.70	0.24
34	5	30	33	6	27	14.12	231 174.88	1.63	303 460.65	0.32
34	4	30	34	3	31	-12.10	222 373.40	0.27	231 163.83	-1.43
35	4	31	35	3	32	-13.06	229 087.87	0.35	222 385.49	0.28
36	4	32	36	3	33	-13.42	237 803.32	0.38	229 100.92	0.36
									237 816.69	0.42



The rotational constants are rather large and  $\mu = \mu_b = 1.53 D (I)$ , so the lines are rather strong. First, an approximate spectrum was predicted with the constants of Bak (3). Some lines showed a rather well-resolved quadrupole hyperfine structure due to  $^{14}\text{N}$  which greatly facilitated their assignment. Then higher  $J$  transitions were assigned using the "bootstrap" method as described by Kirchhoff (7). The predicted internal rotation splitting was also of great help for the assignment. A list of measured frequencies is given in Table I. As the quadrupole hyperfine structure could be well reproduced by the constants of Sastry (1), no new determination of the quadrupole coupling constants was attempted. The hypothetical unperturbed frequencies of the split lines were calculated using the intensity-weighted mean of the multiplets (8).

To obtain molecular parameters from the observed frequencies, a least-squares program based on the Internal Axis Method was used (9). The elements off-diagonal in  $v$  were removed by a Van Vleck transformation. Then the eigenvalues of the Hamiltonian were directly calculated by matrix diagonalization. Basis functions  $\exp i\alpha(3k + \sigma)$  with  $k$  ranging from  $-9$  to  $+9$  and a Van Vleck transformation up to  $v = 2$  were sufficient to obtain stable results within a few kilohertz. As in Ref. (9), quartic centrifugal distortion terms were defined in the Principal Axis System (representation  $I'$ ), transformed to the Internal Axis System, and added to the Hamiltonian. All data of Refs. (1) and (3) and Table I were used. The determinable quantities derived from the fit to the spectrum are listed in Table II, together with their standard deviations. All the parameters are well determined. The correlation of  $I\alpha$  and  $\delta_K$  is the highest with 0.886; the standard deviation is 0.38 MHz for 87  $A$  lines and 0.43 MHz for 82  $E$  lines; the mean splitting being  $\overline{\Delta\nu} = 33.76$  MHz, and the greatest splitting 111.28 MHz for the  $4_{32} \leftarrow 4_{23}$  line.



The spectrum of  $\text{CD}_3\text{N}=\text{CD}_2$  was identified using the same method as for  $\text{CH}_3\text{N}=\text{CH}_2$ . A list of measured frequencies is given in Tables III and V. The hyperfine structure due to  $^{14}\text{N}$ -quadrupole coupling to overall rotation could be at least partially resolved for many lines. The hyperfine structure was analyzed with first-order perturbation theory. The diagonal elements  $\chi_{gg}$  of the quadrupole coupling tensor determined from the splittings of Table III are listed in Table IV, together with those of the parent species. The fitting parameters were  $\chi^+$  and  $\chi^-$ . The correlation coefficient of these two parameters is 0.131. Since the molecule has  $C_s$  symmetry the only non-zero off-diagonal tensor element is  $\chi_{ab}$ . By rotating the principal inertial axis system with isotopic substitution and combining the diagonal elements  $\chi_{gg}$  of the two isotopic species, the off-diagonal element  $\chi_{ab}$  may be, in principle, calculated. Unfortunately, in the present case the angle of rotation is practically negligible ( $\sim 0.1^\circ$ ). It explains why the quadrupole constants are nearly identical for the two molecules. The value found for the constant  $\chi_{cc} = 3.59$  (18) MHz is in good agreement with that found for the similar molecule  $\text{CH}_2=\text{NH}$ ,  $\chi_{cc} = 3.591$  (8) MHz (10).

Some lines were found split by internal rotation (Table V), but as these splittings are small and few, only  $V_3$  could be determined. The moment of inertia of the methyl top was taken to be  $I_\alpha = 6.30 \text{ u} \cdot \text{\AA}^2$  and the angle  $\theta$  (methyl top to a axis) =  $29^\circ$ .

TABLE II  
Molecular Parameters for *N*-Methylmethanimine in Representation *I'*

	CH <sub>3</sub> N = CH <sub>2</sub>	c	CD <sub>3</sub> N = CD <sub>2</sub>	d
A/MHz	52 514.711 (31)	34 579.433 (26)	34 577.460 (18)	
B/MHz	10 670.2820 (96)	8 165.012 (23)	8 161.1468 (28)	
C/MHz	9 371.4939 (99)	7 185.594 (34)	7 191.2333 (27)	
$I_{\alpha}/\text{u. A}^2$	3.1976 (23)	6.30 <sup>b</sup>	-	
$\theta/^\circ$ <sup>a</sup>	25.660 (45)	29 <sup>b</sup>	-	
$V_3/\text{cm}^{-1}$	713.71 (32)	715 (8)	-	
$\Delta_J/\text{kHz}$	7.5584 (43)	4.1348 (36)	4.1357 (23)	
$\Delta_{JK}/\text{kHz}$	-34.189 (86)	-5.83 (26)	16.772 (28)	
$\Delta_K/\text{kHz}$	639.18 (100)	148.75 (63)	122.65 (33)	
$\delta_J/\text{kHz}$	1.39557 (83)	0.69110 (37)	0.68403 (32)	
$\delta_K/\text{kHz}$	19.844 (140)	5.55 (61)	-48.464 (26)	
$H_{KJ}/\text{Hz}$			-3.22 (55)	

a)  $\theta$  denotes the angle between the *a*-axis and the internal rotation axis.

b) assumed value

c) simultaneous fit the A and E lines

d) fit of the A lines only (neglecting internal rotation).

This latter quantity was obtained from an assumed structure (*I*). The rotational constants, centrifugal distortion constants, and the barrier hindering internal rotation of the CD<sub>3</sub> group are determined using the same least-squares program as for CH<sub>3</sub>N=CH<sub>2</sub> and the experimental frequencies of Table V. When the splitting was too small to be observed, the input data is  $\nu_A^* = (\nu_A + \nu_E)/2$  (instead of  $\nu_A$  and  $\nu_E$ ). The derived constants are listed in Table II. The standard deviation of the fit is 0.21 MHz for the *A* (or *A*<sup>\*</sup>) lines and 0.23 MHz for the *E* lines. Five correlation coefficients are greater than 0.98: ( $V_3, C$ ) = 0.983; ( $V_3, \Delta_{JK}$ ) = 0.999; ( $C, \Delta_{JK}$ ) = 0.985 ( $C, \delta_K$ ) = 0.986; and ( $\Delta_{JK}, \Delta_K$ ) = 0.998.

These high correlations show that the fit is not satisfactory. Although the deuteration of the methyl group does not seem to significantly change the barrier, this good agreement is certainly accidental: for CD<sub>3</sub>N=CD<sub>2</sub>,  $I_{\alpha}$  and  $\theta$  are assumed parameters, and a small change of either  $I_{\alpha}$  or  $\theta$  changes all the other parameters by many times their standard deviation. The most sensible parameters are  $V_3$  and  $\Delta_{JK}$ . To obviate these difficulties we have simply fitted the *A* lines of CD<sub>3</sub>N=CD<sub>2</sub> to the centrifugal distorted Hamiltonian of Watson using a type *I'* representation. The derived constants

TABLE III  
Nuclear Quadrupole Hyperfine Structure of  $\text{CD}_3\text{N}=\text{CD}_2$

J'	K' <sub>a</sub>	K' <sub>c</sub>	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	F' + F''	a		b	
							$\nu_{\text{obs.}}$ (MHz)	$\Delta\nu_{\text{HFS}}$ (MHz)	obs.	calc.obs. (MHz)
1	1	0	1	0	1 <sup>c</sup>	0 1	27 383.90			
						2 2	27 385.95	-2.05	-0.05	
2	1	1	2	0	2 <sup>c</sup>	3 3	28 382.40			
						2 2	28 383.60	1.20	0.003	
3	1	2	3	0	3 <sup>c</sup>	4 4	29 925.50			
						3 3	29 926.90	1.40	0.014	
4	0	4	3	1	3 <sup>c</sup>	5 4	37 040.90			
						4 3	37 042.20	1.30	0.07	
4	1	3	4	0	4 <sup>c</sup>	5 5	32 072.60			
						4 4	32 074.10	1.50	0.07	
5	1	4	5	0	5 <sup>c</sup>	6 6	34 896.70			
						5 5	34 898.50	1.80	-0.09	
17	1	16	16	2	15	17 16	234 221.401	-0.663	-0.034	
						18 17	234 220.738			
						16 15				
17	2	16	17	1	17	17 17	157 082.883			
						18 18	157 081.318	-1.565	-0.007	
						16 16				
17	3	15	17	2	16	17 17	157 392.688 <sup>d</sup>			
						18 18	157 391.900	-0.788	0.07	
						16 16				
18	3	16	18	2	17	18 18	160 951.641			
						19 19	160 950.826	-0.815	-0.018	
						17 17				
19	1	18	19	0	19	19 19	159 331.448			
						20 20	159 329.462	-1.986	-0.028	
						18 18				
20	2	18	19	3	17	20 19	237 485.349			
						21 20	237 484.217	-1.132	0.002	
						19 18				
21	4	17	21	3	18	21 21	158 939.837			
						22 22	158 940.586	0.749	-0.007	
						20 20				
22	4	18	22	3	19	22 22	154 197.882			
						23 23	154 198.582	0.700	0.009	
						21 21				
25	1	24	25	0	25	25 25	228 208.183			
						26 26	228 206.913	-1.270	-0.149	
						24 24				
25	2	24	25	1	25	25 25	232 077.380			
						26 26	232 076.228	-1.152	-0.139	
						24 24				

a) A-species unless otherwise stated

b) Splitting with respect to first component

c) Taken from the thesis of H. SVANHOLT (15)

d) E-species

TABLE III—Continued

$J'$	$K'_a$	$K'_c$	$\leftarrow J''$	$K''_a$	$K''_c$	$F' \leftarrow F''$	$\nu_{\text{obs.}}$ (MHz)	$\Delta\nu_{\text{HFS}}^{\text{obs.}}$ (MHz)	$\Delta\nu_{\text{HFS}}^{\text{calc.}-\text{obs.}}$ (MHz)
26	1	25	26	0	26	26 26	239 123.221	-1.318	-0.032
						27 27	239 121.903		
						25 25			
28	3	26	28	2	27	28 28	232 651.499	-1.140	0.098
						29 29	232 650.359		
						27 27			
30	2	28	30	1	29	30 30	238 382.522	-1.326	0.006
						31 31	238 381.196		
						29 29			
30	4	27	30	3	28	30 30	231 783.958	-0.728	0.045
						31 31	231 783.230		
						29 29			
34	4	30	34	3	31	34 34	158 477.900	-0.808	0.019
						35 35	158 477.092		
						33 33			
35	3	32	35	2	33	35 35	238 537.583	-1.328	0.048
						36 36	238 536.255		
						34 34			

are shown in the third column of Table II. The standard deviation of the fit is then only 186 kHz and the highest correlation ( $\Delta_K, \delta_K$ ) = 0.964.

## CONCLUSION

The results of the present analysis are sufficient for the prediction of all strong transitions of  $\text{CH}_3\text{N}=\text{CH}_2$  throughout the microwave and millimeter-wave ranges.

TABLE IV

 Nitrogen Quadrupole Coupling Constants of *N*-Methylmethanimine (MHz)

	$\text{CD}_3\text{N} = \text{CD}_2$	$\text{CH}_3\text{N} = \text{CH}_2^a$
$X^+ = X_{bb} + X_{cc}$	-1.28(37)	
$X^- = X_{bb} - X_{cc}$	-8.460(79)	
<u>derived constants</u>		
$X_{aa}$	1.28(37)	1.9(3)
$X_{bb}$	-4.87(19)	-5.1(2)
$X_{cc}$	3.59(18)	3.2(2)

a) from ref. (1)



TABLE V  
Transition Frequencies (MHz) in  $\text{CD}_3\text{N}=\text{CD}_2$

J'	K' <sub>a</sub>	K' <sub>c</sub>	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	$\nu_A - \nu_E$ (calc.)	$\nu_A$ (obs.)	$\nu_A$ (calc.-obs.)	$\nu_E$ (obs.)	$\nu_E$ (calc.-obs.)
2	1	1	2	0	2	0.34	28 382.64	0.20	28 382.24	0.26
3	1	2	3	0	3	0.34	29 925.90	0.11	29 925.50	0.17
4	0	4	3	1	3	-0.29	37 041.20	0.10	37 041.60	-0.02
4	1	3	4	0	4	0.35	32 073.00	0.26	32 072.70	0.21
5	1	4	5	0	5	0.36	34 897.30	0.08	34 896.80	0.22
6	1	5	6	0	6	0.37	38 481.70	0.16	38 481.30	0.20
11	5	6	11	4	7	-0.42	241 520.87	0.31	241 521.62	-0.02
11	5	7	11	4	8	-0.09	241 560.10	0.26		
12	5	8	12	4	9	-0.17	241 385.19 *	0.21		
12	5	7	12	4	8	-0.31	241 307.36 *	0.26	241 307.93	-0.00
15	5	10	15	4	11	-0.21	240 182.41 *	-0.02		
16	1	16	15	0	15	0.04	237 756.53 *	0.05		
16	0	16	15	1	15	0.01	232 782.44 *	0.08		
16	5	11	16	4	12	-0.20	239 569.34 *	-0.01		
17	1	16	16	2	15	-0.01	234 220.96 *	-0.08		
17	2	16	17	1	17	0.77	157 081.84	0.22	157 080.85	0.45
17	3	15	17	2	16	0.22	156 392.50	0.16	156 392.17	0.27
17	5	12	17	4	13	-0.19	238 784.77 *	-0.01		
17	5	13	17	4	14	-0.19	239 937.37 *	-0.02		
18	3	16	18	2	17	0.16	160 951.10 *	0.23		
18	5	14	18	4	15	-0.19	239 562.10 *	-0.07		
19	1	18	19	0	19	0.82	159 330.12	0.21	159 329.17	0.34
19	5	15	19	4	16	-0.19	239 185.12 *	-0.11		
20	2	18	19	3	17	0.11	237 484.59 *	-0.12		
20	5	16	20	4	17	-0.19	238 827.14 *	-0.12		
21	4	17	21	3	18	-0.23	158 940.34 *	0.07		
21	5	17	21	4	18	-0.19	238 514.13 *	-0.20		
22	4	18	22	3	19	-0.30	154 198.35 *	-0.02		
22	5	18	22	4	19	-0.20	238 276.78 *	-0.16		
23	5	19	23	4	20	-0.21	238 150.85 *	-0.23		
24	5	20	24	4	21	-0.22	238 175.81 *	-0.28		
25	1	24	25	0	25	0.95	228 207.26	0.03	228 206.06	0.28
25	2	24	25	1	25	0.85	232 076.54	-0.01	232 075.47	0.22
25	5	21	25	4	22	-0.24	238 394.48 *	-0.30		
26	1	25	26	0	26	0.95	239 122.34	-0.17	239 121.09	0.12
26	5	22	26	4	23	-0.25	238 851.84 *	-0.32		
27	5	23	27	4	24	-0.27	239 593.77 *	-0.29		
28	3	26	28	2	27	-0.25	232 650.74 *	-0.25		
28	5	24	28	4	25	-0.29	240 665.96 *	-0.28		
29	2	27	29	1	28	0.02	225 996.85 *	-0.19		
29	3	27	29	2	27	-0.19			158 583.69	-0.06
29	4	26	29	3	27	-0.51	225 506.02	-0.13	225 506.74	-0.35
30	2	28	30	1	29	-0.03	238 381.64 *	-0.36		
30	4	27	30	3	28	-0.52			231 783.47	-0.31
31	4	28	31	3	29	-0.53	238 555.20	-0.26	238 555.82	-0.35
32	5	27	31	6	26	-0.06	228 266.94 *	0.01		
33	4	29	33	3	30	-0.37	150 887.70	-0.03	150 888.15	-0.11
34	4	30	34	3	31	-0.31	158 477.01 *	0.01	158 477.37	-0.04
35	3	32	35	2	33	-0.13	238 536.70 *	-0.34		
37	6	31	37	5	32	-0.07	238 501.77 *	0.25		
38	6	32	38	5	33	-0.08	231 433.81 *	0.44		
40	4	36	40	3	37	0.02	229 890.91 *	0.45		

\* These lines are found not split and are in fact  $(\nu_A + \nu_E)/2$

TABLE VI  
Predicted Frequencies for CH<sub>3</sub>NCH<sub>2</sub>

J'	K' <sub>a</sub>	K' <sub>c</sub>	J''	K'' <sub>a</sub>	K'' <sub>c</sub>	$\nu_A$ (σ <sub>A</sub> ) <sup>a</sup>	$\nu_E$ (σ <sub>E</sub> ) <sup>a</sup>	S <sub>A</sub> <sup>b</sup>	E <sub>k</sub> (cm <sup>-1</sup> ) <sup>c</sup>
5	0	5	4	1	4	63 207.415(47)	63 224.717(48)	2.309	7.68
7	1	6	7	0	7	63 298.364(58)	63 277.248(62)	5.975	18.60
8	1	7	8	0	8	70 154.234(76)	70 132.715(79)	6.312	23.87
9	1	8	9	0	9	78 262.516(98)	78 240.518(101)	6.518	29.78
9	1	8	8	2	7	80 208.304(100)	80 251.082(110)	1.991	29.71
2	1	2	1	0	1	80 657.196(41)	80 637.311(46)	1.495	0.67
6	0	6	5	1	5	85 584.198(56)	85 600.511(57)	3.012	11.12
10	1	9	10	0	10	87 682.840(123)	87 660.238(126)	6.609	36.32
11	1	10	11	0	11	98 435.545(150)	98 412.156(153)	6.606	43.49
3	1	3	2	0	2	98 777.828(51)	97 758.324(56)	2.001	2.60
10	1	9	9	2	8	105 868.847(112)	105 909.460(121)	2.412	35.71
11	2	9	11	1	10	106 586.219(52)	106 549.102(52)	8.872	46.77
12	2	10	12	1	11	106 799.238(48)	106 764.585(62)	9.899	54.97
10	2	8	10	1	9	107 324.505(58)	107 285.057(72)	7.804	39.24
13	2	11	13	1	12	108 108.972(50)	108 076.851(62)	10.844	63.83
7	0	7	6	1	6	108 119.042(66)	108 134.213(67)	3.778	14.99
9	2	7	9	1	8	108 848.432(63)	108 806.853(78)	6.736	32.39
12	1	11	12	0	12	110 494.416(178)	110 469.992(182)	6.535	51.28
14	2	12	14	1	13	110 641.795(63)	110 612.219(71)	11.670	73.34
8	2	6	8	1	7	110 973.800(67)	110 930.369(82)	5.703	26.21
7	2	5	7	1	6	113 503.531(69)	113 458.635(83)	4.732	20.71
15	2	13	15	1	14	114 507.105(84)	114 480.033(88)	12.350	83.52
4	1	4	3	0	3	116 302.193(61)	116 283.114(66)	2.548	4.01
6	2	4	6	1	5	116 236.631(70)	116 190.854(84)	3.836	15.89
5	2	3	5	1	4	118 978.572(69)	118 933.010(83)	3.019	11.76
4	2	2	4	1	3	121 550.977(69)	121 508.351(80)	2.271	8.32
13	1	12	13	0	13	123 784.946(207)	123 759.179(211)	6.425	59.70
3	2	1	3	1	2	123 799.083(68)	123 767.713(78)	1.570	5.56

a) Calculated frequency in MHz and statistical uncertainty (one standard deviation), A = A species, E = E species

b) Line strength for the A species

c) Energy of the lower level for the A species.

But, the differences between calculated and observed frequencies (Table I) are greater than the experimental accuracy (about 30 kHz), especially for the high-*J* lines. This result seems quite general and probably shows that the rigid frame-rigid top model with one torsional degree of freedom is failing for the high-*J* transitions (11, 12).

The experimental value of the potential barrier  $V_3 = 2040.65$  (91) cal/mol is in rather good agreement with the value found previously by Bak,  $V_3 = 2007$  cal/mol (3), assuming  $\angle(i, a) = 27.52^\circ$ . The moment of inertia,  $I_\alpha$ , of the methyl group could be accurately determined from the internal rotation analysis,  $I_\alpha^{\text{ir}} = 3.1976 \text{ u} \cdot \text{\AA}^2$ .  $I_\alpha$  may be determined quite independently using the inertial defects of the normal and deuteriated species (13):

$$\begin{aligned} I_\alpha &= -[\Delta(\text{CD}_3\text{N}=\text{CD}_2) - \Delta(\text{CH}_3\text{N}=\text{CH}_2)] \\ &= 3.119\text{u} \cdot \text{\AA}^2. \end{aligned}$$

We note that  $I_\alpha < I_\alpha^{\text{ir}}$ . This behavior is rather general, as may be seen from an inspection of Table V of Ref. (14).

A list of predicted transitions is given in Table VI. The frequencies in this table include all transitions with sufficient intensity over the range 60–130 GHz. The line strength of each transition is given only for the *A* species because it is not significantly different for the *E* species. Further predictions may be obtained upon request from the authors.

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