Microwave Spectrum and Dipole Moment of Dimethylnitrosamine

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The microwave spectrum of the $(CH_3)_2NNO$ and $(CH_3)_2{}^{15}N^{15}NO$ species have been studied and the rotational constants evaluated. By comparison of the inertia defects of the two species it can be stated that the nuclear frame of the molecule is planar, which is in agreement with the reported electron diffraction results. The dipole moment of the $(CH_3)_2{}^{15}N^{15}NO$ species has been determined. Further studies on the internal rotation of the two methyl tops are in progress together with the analysis of the spectra of other isotopically substitued species.

The investigation of the microwave spectrum of dimethylnitrosamine provides an accurate way to evaluate its molecular structure, dipole moment, and, possibly, barrier to internal rotation of the two methyl tops.

The microwave spectrum was recorded with a conventional 100 kHz Stark modulation spectrograph, employing phase stabilized BWO's as radiation sources and an automatic system of recording the frequency markers [1, 2]. The spectrograph is operating in the range from 6 to 40 GHz. Frequency measurements are believed to be accurate within ± 0.03 MHz. The samples were prepared according to RADEMACHER [3].

The structure of gaseous dimethylnitrosamine was first investigated, using the electron diffraction method, by RADEMACHER and STØLEVIK [4]. They found that the nuclear frame is planar and gave a detailed structure.

We started from these data to predict the line frequencies of $(CH_3)_2NNO$. The assignment of the spectrum by the usual methods failed but was made possible using the radio frequency microwave double resonance (RFMDR) technique in the way described elsewhere [5–7]. The observed and calculated frequencies are listed in Table 1.

No effect due to the nuclear quadrupole moments of the two nitrogen nuclei was relevant enough to be measured for the lines listed, nor any effect due to the internal rotation.

Table 2 contains the rotational constants, the asymmetry parameter, the moments of inertia, and the inertia defect of $(CH_3)_2NNO$.

Table 1. Microwave spectrum of $(CH_3)_2NNO$. Frequencies are in MHz. A rigid rotor fitting procedure has been used. Transitions labeled with ^{a} were used to obtain the rotational constants.

$J_{K_{-1},K_1} \leftarrow$	$J'_{K'_{-1},K'_1}$	ν_{exp}	ν_{calc}	$\Delta\nu_{exp-calc}$
2_{02}	$1_{01}{}^a$	15,270.084	15,269.849	0.235
2_{12}	$1_{11}{}^a$	14,125.110	14,125.062	0.048
2_{20}	$2_{11}{}^a$	13,615.730	13,616.060	— 0.330
2_{12}	$1_{01}{}^a$	18,564.337	18,564.298	0.039
3_{21}	$2_{20}{}^a$	24,470.476	24,470.114	0.362
3_{03}	$2_{02}{}^a$	22,234.624	22,234.487	0.077
3_{13}	$2_{12}{}^a$	21,016.955	21,017.019	— 0.065
3_{12}	$2_{11}{}^a$	25,307.546	25,306.878	0.668
3_{22}	$2_{21}{}^a$	23,353.080	23,352.300	0.780
4_{31}	3_{30}	31,863.176	31,863.255	— 0.079
4_{32}	3_{31}	31,633.172	31,632.946	0.226
4_{40}	4_{31}	35,427.840	35,427.501	0.339
4_{41}	4_{32}	35,692.800	35,693.035	— 0.236
5_{41}	4_{40}	39,614.100	39,615.043	— 0.943
5_{42}	4_{41}	39,580.640	39,581.038	— 0.398

Table 2. Rotational constants, asymmetry parameter, moments of inertia and inertia defect of $(CH_3)_2NNO$. The conversion factor is 505376 MHz·amu·A².

$A = 9052.89 \pm 0.08$ MHz	$I_A = 55.8248$ amu · A²
$B = 4613.77 \pm 0.04$ MHz	$I_B = 109.5364$ amu · A²
$C = 3170.46 \pm 0.03$ MHz	$I_C = 159.4015$ amu · A²
$\varkappa = -0.509280$	$\Delta = I_C - I_B - I_A$ $= -5.9597$ amu · A²

With these new data we made a prediction of the spectrum of $(CH_3)_2{}^{15}N^{15}NO$ and, using again the RFMDR technique, we succeeded quickly in obtaining the assignment of the spectrum.

The observed and calculated frequencies are listed in Table 3. As in the previous case we did not observe, for the lines listed, any internal rotation splitting.

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Table 3. Microwave spectrum of $(CH_3)_2{}^{15}N^{15}NO$. Frequencies are in MHz. A rigid rotor fitting procedure has been used. Transitions labeled with ^{a} were used to obtain the rotational constants.

$J_{K-1,K1}$ ←	$J'_{K'-1,K'1}$	ν_{exp}	ν_{calc}	$\Delta\nu_{exp-calc}$
2_{02}	$1_{01}{}^a$	15,170.380	15,169.962	0.418
2_{11}	$1_{10}{}^a$	16,911.919	16,911.416	0.503
2_{12}	$1_{11}{}^a$	14,030.725	14,030.421	0.304
3_{21}	$2_{20}{}^a$	24,333.050	24,332.509	0.541
3_{12}	$2_{11}{}^a$	25,155.446	25,154.852	0.593
3_{13}	$2_{12}{}^a$	20,874.082	20,873.707	0.375
3_{31}	3_{22}	25,651.084	25,651.198	− 0.114
3_{13}	$2_{02}{}^a$	24,110.162	24,109.772	0.390
3_{22}	$2_{11}{}^a$	36,332.200	36,333.196	− 0.996
4_{31}	3_{30}	31,676.592	31,676.552	0.040
4_{32}	3_{31}	31,441.976	31,441.807	0.169
4_{41}	4_{32}	35,236.140	35,235.705	0.434
5_{41}	4_{40}	39,377.850	39,378.601	− 0.751
5_{42}	4_{41}	39,343.100	39,343.548	− 0.449

Table 4. Rotational constants, asymmetry parameter, moments of inertia and inertia defect of $(CH_3)_2{}^{15}N^{15}NO$. The conversion factor is 505376 MHz·amu·A².

$A = 8963.17 \pm 0.07$ MHz $\quad I_A = 56.3836$ amu · A²
$B = 4588.06 \pm 0.03$ MHz $\quad I_B = 110.1503$ amu · A²
$C = 3147.59 \pm 0.03$ MHz $\quad I_C = 160.5597$ amu · A²
$\varkappa = -0.504616 \quad \Delta = I_C - I_B - I_A = -5.9742$ amu · A²

Table 4 contains the rotational constants, the asymmetry parameter, the moments of inertia, and the inertia defect of $(CH_3)_2{}^{15}N^{15}NO$.

By comparison of the inertia defects of the parent molecule and of the isotopically substituted one, it is possible to confirm the planar skeleton, which resulted from the electron diffraction analysis. The two methyl tops are, therefore, non-equivalent. See Figure 1.

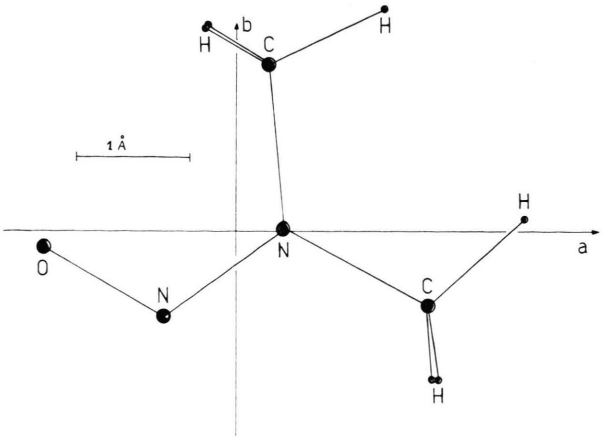

Fig. 1. Coordinates of dimethylnitrosamine in the principal axis system.

The dipole moment components and the total dipole moment were determined using the Stark effect on several lines of the $(CH_3)_2{}^{15}N^{15}NO$, as can be seen in Table 5. The Stark cell was calibrated using OCS as a standard, with $\mu_{OCS} = 0.71521$ D [8].

Table 5. Measured and calculated Stark displacements $\Delta\nu$ (MHz) as a function of the electric field strength ε (V·cm^{-1}) for $(CH_3)_2{}^{15}N^{15}NO$. Values for the two components and for the total electric dipole moment (Debye).

$J_{K-1,K1}$ ←	$J'_{K'-1,K'1}$	M	ε	$\Delta\nu_{exp}$	$\Delta\nu_{calc}$
2_{02}	1_{01}	0	169.125	− 2.057	− 2.074
			225.500	− 3.604	− 3.684
			338.250	− 8.211	− 8.265
		1	112.750	1.054	1.079
			169.125	2.346	2.428
			225.500	4.216	4.317
3_{03}	2_{02}	1	667.176	2.024	2.052
			902.451	4.025	4.035
			1127.951	7.268	7.273
		2	338.926	5.037	4.953
			407.478	7.268	7.193
			451.225	8.878	8.855
3_{12}	2_{11}	1	362.829	− 2.964	− 2.923
			451.225	− 4.576	− 4.522
			632.302	− 8.918	− 8.887
		2	362.829	−11.076	−10.869
			451.225	−16.926	−16.762
			542.778	−24.128	−24.165

Dipole moment components and total dipole moment:
$|\mu_a| = 3.97 \pm 0.02$, $|\mu_b| = 1.43 \pm 0.02$, $|\mu_{tot}| = 4.22 \pm 0.02$.

The present investigation is not sufficient for the determination of a structure. Further work on isotopic species, internal rotation, direction of the dipole moment and hyperfine structure is in progress.

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