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the liquid and solid data of the large momentum transfers give further indications of free molecular rotations in all three states. The first moment ratios for the liquid and solid at small momentum transfers differ from those of the cold gas which also gives further evidence to a new mode of excitation which has been mentioned earlier to be oscillations of the center of mass of the molecule.

ACKNOWLEDGMENTS

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Microwave Spectrum of Methyl Thionylamine*

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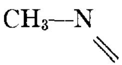
(Received 13 July 1964)

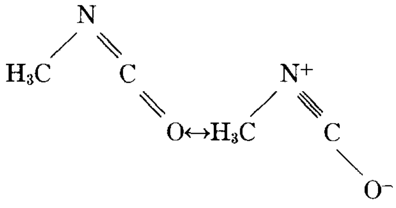
The microwave spectrum of methyl thionylamine (CH_3NSO) has been investigated. Only the *a*-type *R*-branch transitions have been identified. The components of the dipole moment parallel and perpendicular to the *a* axis have been found to be $\mu_a^2 = 2.74 \pm 0.06$, $\mu_b^2 = 0.14 \pm 0.05$. The dipole moment is 1.70 ± 0.02 D. The barrier to internal rotation of the CH_3 group in CH_3NSO has been found to be 335 ± 15 cal/mole. No nitrogen nuclear quadrupole splittings were observed.

INTRODUCTION

RECENTLY the microwave spectra of three molecules containing the group

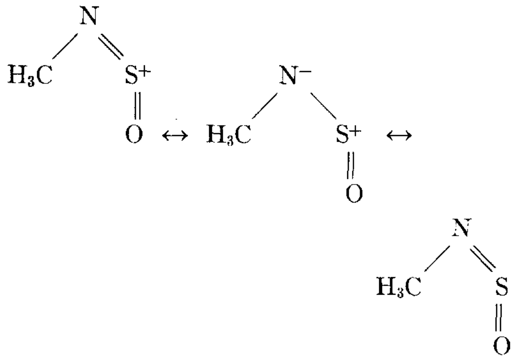


have been investigated. These are CH_3NCS,[1] CH_3NCO,[2] and CH_3NCH_2.[3] *N*-methylmethylenimine (CH_3NCH_2) shows a normal C=N bond length (1.30 Å), ∠CNC of about 117°, and a barrier to internal rotation of the methyl group of 1970 cal/mole (which is the same as that of propylene). On the other hand, the two compounds with two double bonds have short C=N bond lengths (~1.20 Å), ∠CNC near 140°, and very low barrier to internal rotation (~50 cal/mole). This may be qualitatively explained by assuming that the resonance



is large.

The investigation of the microwave spectrum of a similar molecule CH_3NSO seemed appropriate. This molecule has a more complicated type of bonding, probably a combination of the resonance structures

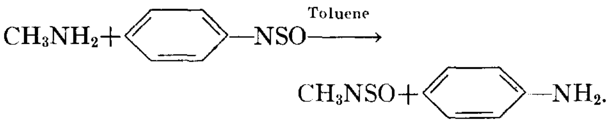


by analogy to SO_2. The third structure with two double bonds must involve the 3*d* orbitals on the sulfur.

From the microwave spectrum of CH_3NSO, it should be possible to obtain the barrier to internal rotation, the dipole moment, and some information about the structure.

EXPERIMENTAL

Methyl thionylamine was prepared from the following reaction[4]:



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* This work was supported by a grant from the Robert A. Welch Foundation and in part by a grant from the National Science Foundation NSFG-17343.

[1] S. Siegel, thesis, Harvard University, 1958.

[2] R. F. Curl, V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, J. Chem. Phys. **39**, 3335 (1963).

[3] K. V. L. N. Sastry and R. F. Curl, J. Chem. Phys. **41**, 77 (1964).

[4] A. Michaelis and O. Storbeck, Ann. Chem. **274**, 187 (1893).

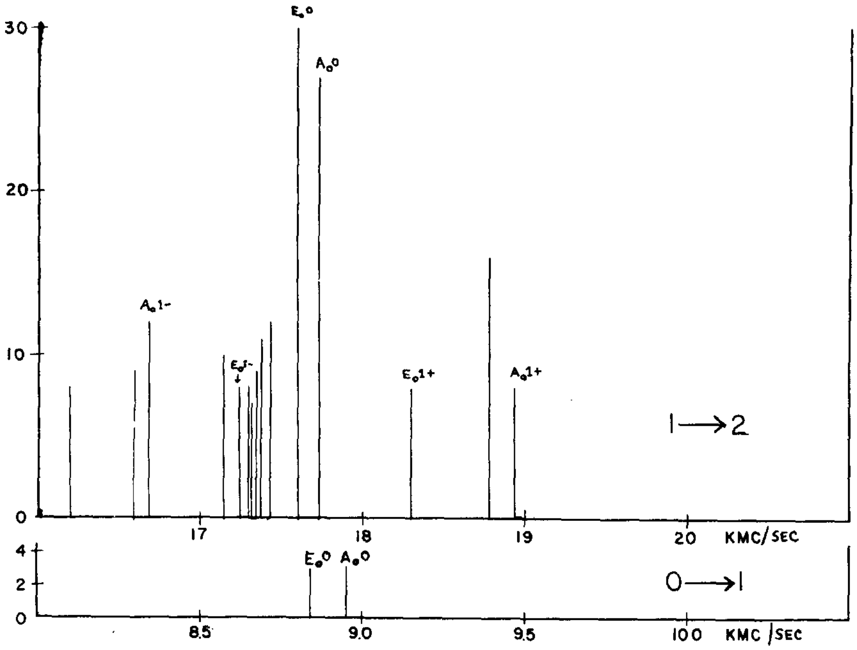

FIG. 1. The observed J:0→1 and 1→2 regions of CH_3NSO. The assigned lines are indicated. The internal-rotation symmetry is given first with the torsional level as a subscript. Then the value of K follows ($\Delta K=0$ in the transitions). For $K\neq 0$ the + sign indicates the upper level, the − sign the lower level.

Thionylaniline (C_6H_5NSO) was purchased from the Aldrich Chemical Company and was used without purification. Methylamine (98% purity) was purchased from Olin–Matheson Company. One hundred grams of C_6H_5NSO was mixed with four times its volume of toluene and cooled to dry-ice temperature. About 28 ml of CH_3NH_2 were condensed and also cooled to dry-ice temperature. The solutions were mixed, placed under reflux with dry ice and allowed to warm up to salt–ice temperature with occasional shaking. The mixture was allowed to remain at salt–ice temperature for about 5 h. It was then allowed to warm up to 0°C and then overnight to room temperature (the reflux being removed and replaced by silica-gel tube). Care was taken to keep H_2O out of the system. The solution was distilled and the 60°–80° and 80°–100° fractions retained. The 80°–100° fraction was redistilled, and the 60°–80° fraction was retained. Finally, the 60°–80° fractions were fractionally distilled, retaining that portion boiling at 58°–60°. The infrared spectrum of CH_3NSO (10% solution in CCl_4) was studied and the absorption frequencies were found to be in agreement with the literature[5] values.

The microwave spectrum was observed at dry-ice temperature with a conventional 100-kc/sec Stark modulation spectrometer. The frequencies measured were accurate to ±0.3 Mc/sec.

SPECTRUM AND ASSIGNMENT

The spectrum is very rich at room temperature with many lines observed, only a few of which have resolved Stark effect. The spectrum does not appear nearly as rich at dry-ice temperature. This might be the result of decomposition of the sample at room temperature or possibly of population of the levels of a higher-energy *trans* isomer at room temperature.

The low-energy form of CH_3NSO was guessed to be the *cis* form (CH_3 on the same side of NS bond as the oxygen atom) by analogy to HNSO.[6] The spectrum of this form was predicted for a number of CNS angles assuming the same NSO group as that of HNSO.[6]

The initial effort was directed towards finding and assigning the *a*-type *R* branch, J: 0⟶1 and 1⟶2. These were quickly located by their Stark effects. These lines are shown in Fig. 1. From the number of 1⟶2 transitions observed at dry-ice temperature, it was apparent that the barrier to internal rotation must be low. It appears that there are some lines which are stronger than some of the ground-state lines.

The regions of 0⟶1 and 1⟶2 have been thoroughly investigated. Some lines in the 2⟶3 and 3⟶4 region have been observed. The lines in the 0⟶1 region have a single second-order lobe to high frequency. The line at 8907.0 Mc/sec was assigned as $A_0K=0$ and the line 8829.15 Mc/sec to $E_0K=0$. The lines at 17 733.0 and 17 599.0 Mc/sec have a second-order lobe to low and high frequencies with almost equal speeds. The line 17 733.0 Mc/sec was assigned to $1_{01}\rightarrow 2_{02}(A_0K=0)$ and 17 599.0 Mc/sec to $E_0K=0$. The line 16 690.15 Mc/sec had a rapid second-order Stark to high and the line 18 937.1 Mc/sec had a rapid second-order Stark to low. These were assigned to $1_{11}\rightarrow 2_{12}(A_0K=1-)$ and $1_{10}\rightarrow 2_{11}(A_0K=1+)$, respectively. A first-order Stark effect with single rapid lobes to high and low frequencies and a slow lobe to high has been observed for the lines 17 238.15 and 18 304.9 Mc/sec. These lines were assigned to $E_0K=1-$ and $E_0K=1+$, respectively.

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[5] W. K. Glass and A. D. E. Pullin, Trans. Faraday Soc. **57**, 546 (1961).

[6] E. B. Wilson, Jr., Pure Appl. Chem. **7**, 23 (1963).

TABLE I. Observed lines of CH_3NSO.

Assignment				ν_{obs} (Mc/sec)	ν_{calc} (Mc/sec)	Intensity
		K				
$0\rightarrow1$						
	E_0	0		8 829.15	8 827.93	3
	A_0	0	$(0_{00}\rightarrow1_{01})$	8 907.00	8 906.30	3
$1\rightarrow2$						
				16 205.25		8
				16 598.95		9
				16 680.00		2
	A_0	1−	$(1_{11}\rightarrow2_{12})$	16 690.0	16 689.00	12
				17 154.00		10
	E_0	1−		17 238.15[a]	17 240.74	8
				17 300.00		8
				17 321.00		7
				17 346.50		9
				17 383.80		11
				17 430.80		12
	E_0	0		17 599.00	17 597.44	30
	A_0	0	$(1_{01}\rightarrow2_{02})$	17 733.00	17 731.40	27
	E_0	1+		18 304.90[a]	18 307.14	8
				18 785.50		16
	A_0	1+	$(1_{10}\rightarrow2_{11})$	18 937.10	18 935.49	8
$2\rightarrow3$						
	A_0	1−	$(2_{12}\rightarrow3_{13})$	24 986.60	24 984.50	
				25 035.60		
	E_0	1−		25 302.30[a]	25 305.63	
				25 884.00		
				25 984.90		
	E_0	0		26 240.10	26 241.23	
	A_0	0		26 398.30	26 396.87	
	A_0	2−		26 719.6	26 716.86	
	E_0	2+		26 763.3[a]	26 771.97	
	E_0	2−		26 824.2[a]	26 827.00	
	A_0	2+		27 040.2	27 038.72	
	E_0	1+		27 872.90[a]	27 875.14	
	A_0	1+	$(2_{11}\rightarrow3_{12})$	28 352.80	28 350.44	
$3\rightarrow4$						
	A_0	1−	$(3_{13}\rightarrow4_{14})$	33 229.80	33 226.15	
	E_0	1−		33 348.20[a]	33 353.07	
	E_0	0		34 689.80	34 690.35	
	A_0	0	$(3_{03}\rightarrow4_{04})$	34 838.60	34 837.49	
	E_0	3−		35 714.30[a]	35 713.78	
	A_0	3−	$(3_{31}\rightarrow4_{32})$	35 777.60	35 770.84	
	E_0	1+		37 312.80[a]	37 315.08	
	A_0	1+	$(3_{12}\rightarrow4_{13})$	37 699.50	37 696.79	

[a] These lines appeared to have a first-order Stark effect.

Table I gives the frequencies of all assigned lines, with their assignments.

It was not possible to resolve the quadrupole splittings of any lines.

BARRIER TO INTERNAL ROTATION

The spectrum in the $0\rightarrow1$ and $1\rightarrow2$ regions was predicted as a function of the barrier.[7] For these predictions a computer program described previously,[2] which assumes a rigid methyl group connected to a rigid frame, was used. The CH_3NSO geometrical structure which gave the best fit to the A_0 lines was assumed.

The observed and predicted spectra were found to match fairly well at a barrier of about 335 cal/mole. This was particularly true of the ground-torsional-state lines which are expected to be least affected by the nonrigidity of the molecule. The pattern of the ground-torsional-state lines corresponds to the high-barrier case in contrast to CH_3NCO.

After assigning the ground-torsional-state $0\rightarrow1$ and $1\rightarrow2$ lines, these eight lines were least-squares fitted with the parameters I_a, I_b, C, λ_a, I_α, V_3 on which the spectrum depends. The rigid molecule assumption was again made. The fit was very good, as might be expected with eight observations and six parameters. The results are shown in Table II. Unfortunately, I_α is unreasonably large being 3.47 amu·Å^2 as compared to a maximum reasonable value of about 3.24 amu·Å^2. Furthermore, the quantity $I_a+I_b-I_c$ was 2.96 amu·Å^2 which is almost unreasonably small.

I_α and I_a are not well determined by the data. I_a is not well determined because it is insensitive to the

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[7] For a discussion of internal rotation see C. C. Lin and J. D. Swalen, Rev. Mod. Phys. **31**, 841 (1959).

lines observed; I_α is not well determined because, for the lines observed, I_α and V_3 are scarcely independent. Therefore, I_α was made as large as was felt tolerable (3.24 u·Å²), and I_a was made as small as was felt tolerable corresponding to $I_a+I_b-I_c=3.0$ u·Å². Then the spectrum was refitted and the final parameters obtained. These are given in Table II. The calculated frequencies are compared to the observed in Table I.

DIPOLE MOMENT

The Stark effect for the A_0 lines $0\rightarrow 1 M=0$; $1_{11}\rightarrow 2_{12} M=0$, 1; $1_{01}\rightarrow 2_{02} M=0$, 1; and $1_{10}\rightarrow 2_{11} M=0$, 1 was measured. The results are shown in Table III.

Since no computer program was available which treated the Stark effect in the presence of internal rotation, the Stark effects were calculated considering the molecule as a rigid rotor. The rotational constants used were: $A=16\,140.00$ Mc/sec, $B=5015.0$ Mc/sec, $C=3892.0$ Mc/sec. The components of the dipole moment were found to be $\mu_a{}^2=2.74\pm.06$ and $\mu_b{}^2=0.14\pm0.05$. Therefore, there is little possibility of observing *b*-type transitions. The quoted uncertainties are large because the rigid molecule approximation necessary for the calculations is not trusted.

The assignment of the $E_0K=1$ lines was checked by computation of the first-order Stark coefficient for these lines. This was done by introducing the Stark effect matrix elements which are diagonal in *JMK* into the *E* level matrices and then diagonalizing. It was found that for the parameters of Table II all these lines should have first-order Stark effects with Stark coefficients about the same as the correponding symmetric top. The observed lines had first-order Stark effects.

TABLE II. Fitting the ground-torsional-state lines for J:$0\rightarrow1$ and $1\rightarrow2$.

	Adjusting all parameters	Adjusting four parameters
I_a	31.669 ± 0.15[a]	31.7154 amu·Å² [b,c]
I_b	101.221 ± 0.004	101.2087 ± 0.0166[a] amu·Å²
C	3890.83 ± 0.19	3890.75 ± 0.8 Mc/sec
λ_a	0.649 ± 0.004	0.646 ± 0.004
I_α	3.47 ± 0.04	3.24 amu·Å² [b]
V_3	$314.11\pm4.$	335.46 ± 1.5 cal/mole
S	0.12	2.13
Number of lines	8	8

[a] The estimate uncertainties quoted here are determined from the matrix of covariances and $S=[(\nu_{\text{obs}}-\nu_{\text{calc}})^2/(n_{\text{obs}}-n_{\text{par}})]^{\frac{1}{2}}$. The S found when all parameters were adjusted was too low. In estimating uncertainties $S=0.5$ was used here. Even so, the estimated uncertainties are probably not realistic in either case.

[b] The fit adjusting all parameters gave unreasonable values of these quantities. The values of the quantities used here were assigned by the reasoning described in the text.

[c] Conversion factor 5.05531×10^5 Mc/sec amu·Å².

TABLE III. Dipole moment.

Transition[a]	M	$\Delta\nu/E^2\times10^4$ D²(Mc/sec)⁻¹
$0_{00}\rightarrow1_{01}$	0	1.641 (0.013)
$1_{11}\rightarrow2_{12}$	0	0.403 (−0.001)
	1	6.150 (+0.009)
$1_{01}\rightarrow2_{02}$	0	−0.446 (−0.003)
	1	0.413 (+0.002)
$1_{10}\rightarrow2_{11}$	0	0.359 (+0.001)
	1	−5.674 (+0.014)
$\mu_a{}^2=2.74$ D²	$\mu_b{}^2=0.14$ D²	

[a] All measured lobes were for A_0 states.

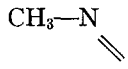
[b] The figures in parentheses after the observed Stark coefficients are the calculated coefficients from the dipole moment minus the observed coefficients.

STRUCTURE

The information obtainable from one isotopic species is, of course, insufficient for a complete determination of the geometrical structure of the molecule. The moments of inertia and λ_a given in Table II are approximately consistent with a C–N bond distance of 1.47 Å, a ∠CNS of 122°, and the NSO group found by Kirchoff[6] (N=S=1.51 Å, ∠NSO=121°, SO=1.45 Å).

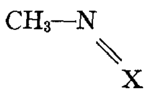
DISCUSSION

The four molecules (CH_3NCS, CH_3NCO, CH_3NCH_2, CH_3NSO) containing the

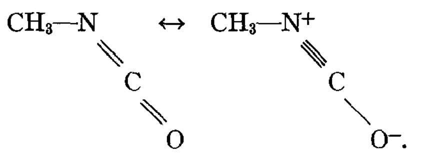


group which have now been studied are a remarkable group. Almost all cases of internal rotation problems involving a single threefold rotor are found. There are two low barrier cases (CH_3NCS and CH_3NCO), a high barrier case (CH_3NCH_2), and now an intermediate barrier case.

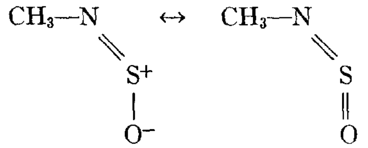
The barrier for the bonding



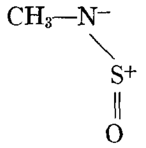
can be considered to be about 2000 cal/mole as in CH_3NCH_2. The low barrier cases may then be explained by introducing the resonance:



Now the intermediate barrier of CH_3NSO needs to be understood. In addition to an explanation similar to the above, it is possible to suggest that the intermediate barrier arises from cancellation of the barriers in the structures



in which the methyl group eclipses the N–S bond and the structure



in which the methyl group staggers the N–S bond. The barrier may also be affected by steric interaction between the CH_3 group and the oxygen atom. For a reasonable structure the closest approach of the methyl H to the O is 2.48 Å.

It may be possible to determine the equilibrium conformation of the methyl group by study of the microwave spectrum of CH_2DNSO or CHD_2NSO.

The apparent structure obtained here shows a slight opening of the HNSO bond angle (116° Ref. 6) on substitution of a methyl group to $\angle CNS = 122°$. This change is smaller than that of HNCO ($\angle HNC = 128.5°$) going to CH_3NCO ($\angle CNC \cong 140°$).

ACKNOWLEDGMENT

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Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient*

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(Received 20 July 1964)

A derivation is given of the effect of a time-dependent magnetic field gradient on the spin-echo experiment, particularly in the presence of spin diffusion. There are several reasons for preferring certain kinds of time-dependent magnetic field gradients to the more usual steady gradient. If the gradient is reduced during the rf pulses, H_1 need not be particularly large; if the gradient is small at the time of the echo, the echo will be broad and its amplitude easy to measure. Both of these relaxations of restrictions on the measurement of diffusion coefficients by the spin-echo technique serve to extend its range of applicability. Furthermore, a pulsed gradient can be recommended when it is critical to define the precise time period over which diffusion is being measured.

The theoretical expression derived has been verified experimentally for several choices of time dependent magnetic field gradient. An apparatus is described suitable for the production of pulsed gradients with amplitudes as large as 100 G cm^{-1}. The diffusion coefficient of dry glycerol at 26°±1°C has been found to be $(2.5\pm0.2)\times10^{-8}$ cm^2 sec^{-1}, a value smaller than can ordinarily be measured by the steady gradient method.

INTRODUCTION

ONE of the most satisfactory methods for measuring self-diffusion coefficients is the spin-echo method of Hahn,[1] as developed by Carr and Purcell and others,[2,3] particularly so because of the negligible extent to which the diffusing molecules are perturbed by this method. However, there are experimental limitations in the ordinary spin-echo experiment arising from the magnetic field gradient, which must be present at all times. As the gradient is increased to make possible the observation of smaller and smaller values of the diffusion coefficient, the nuclear magnetic resonance linewidth also increases, with a corresponding decrease in the duration of the free induction decay following the first (90°) pulse in the spin-echo sequence and a decrease in the width of the echo following the second (180°) pulse. There is thus a decrease in the information available from the echo. As the gradient is increased further the bandwidth of the detection system will have to be increased in order to improve its transient response, a procedure which will admit more noise. Finally, with increasing linewidth, the power output of the pulse transmitter will have to be increased to keep the rf field amplitude H_1 greater than the line-

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[1] E. L. Hahn, Phys. Rev. **80**, 580 (1950); Phys. Today **6**, No. 11, 4 (1953).

[2] H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954); and, for example, D. E. Woessner, J. Chem. Phys. **34**, 2057 (1961), which includes an extensive bibliography of the theory of the spin-echo experiment.

[3] D. W. McCall, D. C. Douglass, and E. W. Anderson, Ber. Bunsenges. Physik. Chem. **67**, 336 (1963).