

MICROWAVE SPECTRA OF METHYLSILYLSULFIDE

Yoshiko SHIKI, Tomoyuki OHTA, Jun NAKAGAWA, and Michiro HAYASHI
Department of Chemistry, Faculty of Science, Hiroshima University
Higashi-sendamachi, Hiroshima 730

Microwave spectra of methylsilylsulfide and its deuterated species were measured. A plausible structure was estimated from the observed rotational constants. Dipole moments were determined by Stark effect measurements of the two species. From the observed A-E splittings of the spectra, the barrier to methyl internal rotation was determined.

We have recently studied the microwave spectra of methylsilylsulfide and its deuterated species (CH_3SSiD_3) in order to compare the molecular structure with that of methoxysilane¹⁾. For each species, about fifteen b-type transitions with $J \leq 9$ were assigned. They exhibit doublet structures due to methyl internal rotation. As the centrifugal distortion effect seemed to be large, the rotational constants were determined by a least-squares fit of the observed A component frequencies with $J \leq 7$ with a modified rigid rotor expression which included the first two terms $-d_J[J(J+1)]^2$ and $-d_{JK}J(J+1)\langle P_z^2 \rangle$ of the centrifugal distortion formula. The rotational constants thus obtained are listed in Table 1.

The plausible structure was estimated from the observed rotational constants as follows. First, the $\alpha(\text{H}_\text{S}\text{CS})$ and $\alpha(\text{H}_\text{a}\text{CS})$ values were estimated from the internal rotation analysis described later and second the skeletal parameter values [$r(\text{CS})$, $r(\text{SSi})$, and $\alpha(\text{CSSi})$] were adjusted so as to well reproduce the observed rotational constants, using the transferred values of the other parameters from those of disilylsulfide²⁾ and dimethylsulfide³⁾. The parameter values and the differences between the observed and calculated rotational constants are given in Table 1. For the present molecule, $r(\text{CS})$ and $r(\text{SSi})$ are larger than those of dimethylsulfide (1.802 Å) and disilylsulfide (2.129 Å), respectively, and $\alpha(\text{CSSi})$ is smaller than $\alpha(\text{CSC})$ of dimethylsulfide ($98^\circ 52'$) and $\alpha(\text{SiSSi})$ of disilylsulfide ($98^\circ 35'$). Though the $\alpha(\text{COSi})$ value of methoxysilane was reported by LeCroix et al¹⁾ to be irregularly large (120°), the corresponding $\alpha(\text{CSSi})$ value of the present molecule is not irregular but ordinary.

The dipole moment and its direction were determined by Stark effect measurements of low J transitions. The results are listed in Table 1. The dipole moment of the present molecule has the value between those of dimethylsulfide (1.500 D) and disilylsulfide (0.896 D) and makes angles of $13^\circ 51'$ and $12^\circ 56'$ with the b-inertial axis for the normal and deuterated species, respectively. Since the b-inertial axis of the deuterated species rotates by $44'$ from that of the normal species, the direction of the dipole moment can be easily determined as case(a) which makes an angle of $30^\circ 34'$ with the bisector of the CSSi angle inclining towards the CS bond.

Table 1. Results for Methylsilylsulfide

Rotational Constant (MHz)								
	A	$\Delta A(\%)$	B	$\Delta B(\%)$	C	$\Delta C(\%)$	d_J	d_{JK}
CH ₃ SSiH ₃	13820.98(45)	0.20	4316.28(5)	0.03	3489.16(4)	-0.06	0.015(12)	-0.16(2)
CH ₃ SSiD ₃	11876.41(44)	-0.06	3898.61(5)	0.32	3207.64(4)	0.14	0.010(5)	-0.12(2)
Structural Parameters								
Adjusted; $r(\text{CS})=1.816 \text{ \AA}$, $r(\text{SSi})=2.132 \text{ \AA}$, $\alpha(\text{CSSi})=98^\circ 02'$								
Determined from Internal Rotation Analysis; $\alpha(\text{H}_\text{S}\overset{\circ}{\text{C}}\text{S})=105^\circ 48'$, $\alpha(\text{H}_\text{A}\text{CS})=111^\circ 05'$								
Transferred; $r(\text{CH}_\text{S})=r(\text{CH}_\text{A})=1.091 \text{ \AA}$, $\alpha(\text{H}_\text{S}\text{CH}_\text{A})=109^\circ 36'$, $\alpha(\text{H}_\text{A}\text{CH}_\text{A})=109^\circ 32'$,								
$r(\text{SiH}_\text{S})=1.483 \text{ \AA}$, $r(\text{SiH}_\text{A})=1.480 \text{ \AA}$, $\alpha(\text{H}_\text{S}\text{SiS})=108^\circ 04'$, $\alpha(\text{H}_\text{A}\text{SiS})=111^\circ 03'$								
$\alpha(\text{H}_\text{S}\text{SiH}_\text{A})=109^\circ 09'$, $\alpha(\text{H}_\text{A}\text{SiH}_\text{A})=108^\circ 20'$								
Dipole Moment (D)								
	$ \mu_\text{a} $	$ \mu_\text{b} $	$ \mu_\text{total} $	$\alpha(\text{b}\times\text{bis})$	$\alpha(\mu\times\text{b})$	$\alpha(\mu\times\text{bis})$		
						Case (a)	Case (b)	
CH ₃ SSiH ₃	0.330(9)	1.340(7)	1.380(8)	16°43'	13°51'	30°34'	2°52'	
CH ₃ SSiD ₃	0.310(16)	1.348(11)	1.383(12)	17°27'	12°56'	30°23'	4°31'	
Internal Rotation of the CH ₃ group								
CH ₃ SSiH ₃	$(\lambda_\text{a}, \lambda_\text{b}, \lambda_\text{c}) = \{ (0.5875, -0.8092, 0) \}$			$F(\text{GHz}) = \{ 165.80 \}$	$V_3(\text{cal/mol}) = \{ 1100 \pm 7 \}$		$S = \{ 30.92 \}$	
CH ₃ SSiD ₃	$(\lambda_\text{a}, \lambda_\text{b}, \lambda_\text{c}) = \{ (0.5794, -0.8150, 0) \}$			$F(\text{GHz}) = \{ 164.67 \}$	$V_3(\text{cal/mol}) = \{ 1093 \pm 8 \}$		$S = \{ 30.94 \}$	

From the observed splittings of the spectra for the two species, the barriers to methyl internal rotation were determined to be 1100 ± 7 and 1093 ± 8 cal/mol for the normal and deuterated species, respectively, in the one top approximation by the standard principal axis method. In the analysis, the direction cosines of the methyl top axis were also determined so as to well reproduce the observed splittings. Since the $\alpha(\text{HCH})$ values were fixed to the transferred values in the structure determination, the direction cosines of the top axis could be used for the estimation of the $\alpha(\text{HCS})$ angle values. The barrier obtained is much lower than that of dimethylsulfide (2132 cal/mol). The methyl group of the present molecule is found to be more tilted ($3^\circ 45'$) than that of dimethylsulfide ($2^\circ 30'$) towards the lone pair electrons on the sulfur atom. As for the silyl group, the barrier may be higher than 1400 cal/mol since the splittings due to silyl internal rotation could not be observed at present.

The works on methylsilylsulfide are still in progress for the determination of the reliable structure and the barrier to internal rotation.

References

- 1) C. D. LeCroix, R. F. Curl, P. M. McKinney and R. J. Myers, *J. Mol. Spectrosc.*, **53**, 250 (1974).
- 2) K. F. Dössel and D. H. Sutter, *Z. Naturforsch.*, **33a**, 300, 1190 (1978).
- 3) L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961).

(Received February 14, 1980)