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MICROWAVE SPECTRA OF TRANS-METHYL(SILYLMETHYL)ETHER

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Molecular structure and dipole moment of trans-methyl(silylmethyl) ether were obtained from the observed microwave spectra of the normal and three deuterated species. From the splittings of the spectra for the normal and $SiH_3CD_2OCH_3$ species, the barrier to internal rotation of the SiH_3 or CH_3 group was discussed.

As a part of a series of researches on the molecular structure of organosilicon molecules with skeleton similar to ethylmethylether, we recently studied the microwave spectra of methyl(silylmethyl)ether($SiH_3CH_2OCH_3$) and its three deuterated species ($SiD_3CH_2OCH_3$, $SiH_3CD_2OCH_3$, $SiH_3CH_2OCD_3$). According to our preliminary measurements of the Raman spectra in the liquid state, the trans isomer was found to be dominant in the liquid state though two rotational isomers are expected. Then, the measurements of the microwave spectra were carried out for the trans isomer alone. Though a- and b-type transitions are expected for the trans isomer, only b-type transitions were measured.

For each species, about thirty b-type transitions of the types $J_{1J-1}\leftarrow J_{0J}$, $(J+1)_{1J+1}\leftarrow J_{0J}$, $(J+1)_{0J+1}\leftarrow J_{1J}$, $J_{2J-1}\leftarrow(J+1)_{1J}$, and $J_{2J-2}\leftarrow(J+1)_{1J+1}$ with $J\leq 10$ could be assigned. Some of the transitions for the normal and $SiH_3CD_2OCH_3$ species in the ground state exhibit doublet structure due to the internal rotation of either the CH_3 or SiH_3 group, while those for the deuterated species ($SiD_3CH_2OCH_3$ and $SiH_3CH_2OCD_3$) are singlet.

At first, for each species, all the observed frequencies were used in a least-squares fit of the four parameters in a modified rigid rotor expression which included the $-d_J[J(J+1)]^2$ term of the centrifugal distortion formula. The observed A-component frequencies of the doublets were used in the calculation for the normal and $SiH_3CD_2OCH_3$ species. However as the centrifugal distortion effect seems to be large, the rotational constants and the d_J constant were determined using the above formula from the observed frequencies of the transitions with $K_p=0$ and 1, which were less affected from the centrifugal distortion terms. They are given in Table 1.

In order to estimate the plausible structure, the rotational constants were calculated from a model and they are compared with the observed. In this model, the structural parameters for the SiH_3C- and $-CH_2OCH_3$ parts of the molecule were transferred from those in chloromethylsilane[1] and of trans-ethylmethylether[2], respectively, and four skeletal structural parameters [$r(O-CH_2)$, $r(O-CH_3)$, $\alpha(COC)$, and $\alpha(SiCO)$] were taken as adjustable parameters. The minimum deviations of the

calculated rotational constants from the observed for the four species were satisfactorily small (less than 0.36 %) when four adjustable parameter values were taken as those given in Table 1. For trans-methyl(silylmethyl)ether, 1) two CO bond lengths are larger than those of ethylmethylether (1.404 Å and 1.415 Å) and are nearly equal to each other. 2) α(COC) is larger than that of ethylmethylether (111°49') and 3) α(SiCO) is smaller than α(CCO) of ethylmethylether (108°09').

The dipole moment of the four species were determined by Stark effect measurements of low J transitions. For the normal and $SiH_3CH_2OCD_3$ species, some transitions useful to the determination of the dipole moment such as $2_{12}\leftarrow1_{01}$ are situated close to strong unassigned transitions. Hence, the error in the dipole moment values could not be reduced for these species at present. The results are listed in Table 2. The dipole moment of methyl(silylmethyl)ether (1.531 D) is larger than those of alkyl ethers such as dimethylether (1.302 D)[3], ethylmethylether (1.174 D), and diethylether (1.061 D)[4]. The dipole moment makes an angle of 33°13' with the "b" inertial axis and an angle of either 17°37' (Direction A) or 48°49' (Direction B) with the bisector of the COC angle, as shown in Fig. 1. Unfortunately, the rotation of the principal axes due to the isotopic substitution is so slight when compared with the experimental error of the dipole moment that the direction of the dipole moment cannot be determined uniquely from the experimental data. However, since

Table 1. Rotational Constants, d_J Constant (MHz)[a] and Structural Parameters[b]

	A	δA(%)	B	δB(%)	C	δC(%)	$d_J\times10^3$
$SiH_3CH_2OCH_3$	22992.81(23)	-0.28	2500.67(1)	-0.12	2387.23(2)	-0.11	0.85(17)
$SiD_3CH_2OCH_3$	18267.47(21)	-0.15	2312.19(1)	-0.21	2216.95(2)	-0.20	0.58(16)
$SiH_3CH_2OCD_3$	20135.75(16)	-0.25	2248.35(1)	-0.06	2157.18(1)	-0.05	0.59(12)
$SiH_3CD_2OCH_3$	18904.60(20)	-0.36	2480.78(1)	-0.10	2351.31(2)	-0.11	0.78(16)

Adjusted parameters

$r(CH_2\text{-}O)$=1.420 Å, $r(O\text{-}CH_3)$=1.420 Å, α(SiCO)=107°39', α(COC)=112°23'

Transferred parameters

SiH_3 group; r(Si-C)=1.889 Å, $r(SiH_s)$=1.477 Å, $r(SiH_a)$=1.477 Å, $\alpha(H_sSiC)$=108°20', $\alpha(H_aSiC)$=108°20', $\alpha(H_sSiH_a)$=110°36', $\alpha(H_aSiH_a)$=110°36'

CH_2 group; r(CH)=1.096 Å, α(SiCH)=110°45', α(HCH)=107°30', α(HCO)=110°04', α(HCO)=110°04'(affected by the adjusted α(SiCO) value)

CH_3 group; $r(CH_s)$=1.084 Å, $r(CH_a)$=1.100 Å, $\alpha(H_sCO)$=107°41', $\alpha(H_aCO)$=111°00', $\alpha(H_sCH_a)$=109°20', $\alpha(H_aCH_a)$=108°20'

a) Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviations. $\delta R = (R_{obsd} - R_{calctd}) \times 100/R_{obsd}$, R = A, B, and C. R_{calctd} was computed from the plausible structure. d_J represents the coefficient of the $-d_J[J(J+1)]^2$ term of the centrifugal distortion formula.

b) Transferred parameters in the SiH_3 and CH_2OCH_3 groups were taken from the reported values for chloromethylsilane and trans-ethylmethylether, respectively. H_s and H_a represent the hydrogen atoms in the molecular plane and out of the molecular plane, respectively.

the μ_a dipole component obtained is much larger than that expected from the group moment of the CH_2OCH_3 part of the molecule, the group moment of the SiH_3C part is considered to be fairly large. For dimethylsilane and disilylmethane[5], the silicon and carbon atoms are found on the sides of the negative and positive poles of the dipole moment, respectively. Then, if the situation of the present molecule is assumed to be the same as those of dimethylsilane and disilylmethane, Direction A is considered to be the correct one for methyl(silylmethyl)ether.

Though the doublet structure of the observed spectra found for the normal and $SiH_3CD_2OCH_3$ species is considered to be arising from the internal rotation of the top in the molecule, the top responsible for the doublet could not be determined easily because the corresponding transitions for both the $SiD_3CH_2OCH_3$ and $SiH_3CH_2OCD_3$ species were found as singlet. Then, the barrier to internal rotation was calculated from the splitting data in two ways; that is, one assuming the splitting due to the SiH_3 group and the other, due to the CH_3 group. The calculations were performed in the one top approximation using the quantities calculated from the plausible structure. The results are given in Table 2. The values of 1750 and 2675 cal/mol are obtained for the two cases, respectively. The expected splittings of the corresponding transitions were calculated for the $SiD_3CH_2OCH_3$ and $SiH_3CH_2OCD_3$ species assuming the barrier values obtained for the normal species. This calculation

Table 2. Dipole Moment (D)[a] and Internal Rotation[b]

	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_{total}\rvert$	$\alpha(\mu\times b)$	$\alpha(b\times bis)$	$\alpha(\mu\times bis)$ A	B
$SiH_3CH_2OCH_3$	0.839(63)	1.281(75)	1.531(74)	33°13'(6°)	15°36'	17°37'	48°49'
$SiD_3CH_2OCH_3$	0.851(14)	1.234(12)	1.499(13)	34°36'(1°)	15°48'	18°48'	50°24'
$SiH_3CH_2OCD_3$	0.858(43)	1.296(66)	1.554(62)	33°31'(5°)	15°45'	17°46'	49°16'
$SiH_3CD_2OCH_3$	0.860(13)	1.249(12)	1.517(12)	34°34'(1°)	15°47'	18°47'	50°21'

	I_α(amu·Å^2)	(λ_a, λ_b, λ_c,)	F(GHz)	V_3(cal/mol)
Assumed the spectral splittings arising from the SiH_3 group				
$SiH_3CH_2OCH_3$	5.943	(-0.9210, -0.3897, 0)	116.58	1750(25)
$SiH_3CD_2OCH_3$	5.943	(-0.9222, -0.3868, 0)	108.71	1700(40)
Assumed the spectral splittings arising from the CH_3 group				
$SiH_3CH_2OCH_3$	3.203	(0.9623, 0.2721, 0)	191.83	2675(50)
$SiH_3CD_2OCH_3$	3.203	(0.9631, 0.2691, 0)	183.26	2625(35)

a) μ_c is identically zero from symmetry. $\alpha(\mu\times b)$ represents the angle between the dipole moment and the "b" inertial axis. $\alpha(b\times bis)$ represents the angle between the "b" inertial axis and the bisector of the COC angle. $\alpha(\mu\times bis)$ indicates two possible angles (A and B) between the dipole moment and the bisector of the COC angle. Figures in parentheses indicate the uncertainties attached to the last significant figures unless otherwise noted.

b) I_α: moment of inertia of the top around the internal rotation axis. (λ_a, λ_b, λ_c): direction cosines of the internal rotation axis. F: rotational constant of the top. These quantities were calculated from the plausible structure.

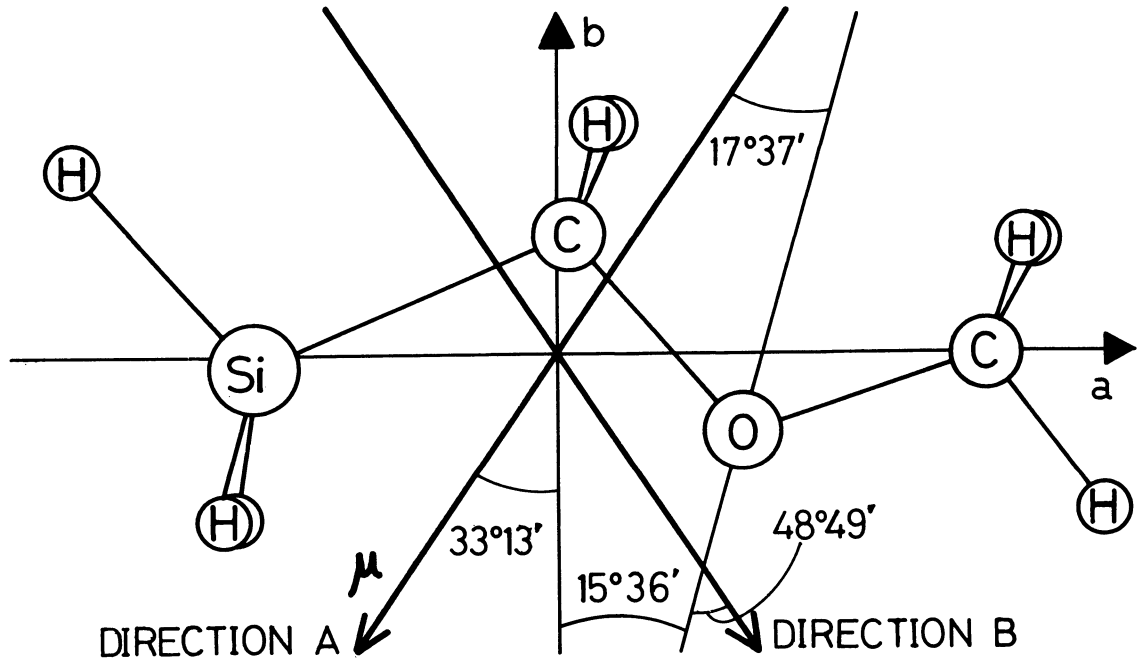

Fig. 1. Direction of the Dipole Moment

indicates that the splittings of the spectra are also expected to be of resolvable amounts for these species in contrast with the experimental results unless the barrier values are assumed to be much larger than those for the normal species. Then, it seems to us at present that the barrier value may be changed by some reasons such as the change in the coupling effect of two tops and so on when the hydrogen atoms in one of the tops are replaced by deuterium atoms. The reported values for the SiH_3 group are different for every molecule so that we cannot give any inference to the value of 1750 cal/mol. And though the value of 2675 cal/mol is close to those of the OCH_3 group in dimethylether (2720 cal/mol)[6] and ethylmethylether (2550 cal/mol) obtained in the similar approximation, we cannot conclude that the doublet is arising from the OCH_3 group.

We are working on the isotopic species in order to determine the r_s structure and are also measuring the far-infrared spectra of this molecule. Furtheremore, similar works on ethoxysilane are in progress.

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