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MICROWAVE SPECTRA OF DISILYLMETHANE

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Microwave spectra of disilylmethane[$(SiH_3)_2CH_2$] and its deuterated species[$(SiD_3)_2CH_2$] were measured. A plausible structure of the molecule was estimated from the rotational constants determined. Dipole moments were determined by Stark effect measurements. They were 0.813 ± 0.013 D for the normal species and 0.802 ± 0.010 D for the deuterated species. From the observed splittings of the spectra for the normal species, the barrier to SiH_3 internal rotation was determined to be 1210 ± 20 cal/mol by neglecting the two top coupling terms.

In order to compare the molecular structure with those of dimethylsilane$^{1)}$ and ethylsilane,$^{2)}$ we studied recently the microwave spectra of disilylmethane[$(SiH_3)_2CH_2$] and its deuterated species[$(SiD_3)_2CH_2$]. The spectra for the normal species in the ground state exhibit triplet structures due to the internal rotation of two SiH_3 groups, while those for the deuterated species were singlets. For each species, about twenty b-type spectra of the types $J_{1J-1} \leftarrow J_{0J}$, $(J + 1)_{1J+1} \leftarrow J_{0J}$, and $(J + 1)_{0J+1} \leftarrow J_{1J}$ with $J \leqq 10$ were assigned. As the centrifugal distortion effect seems to be large, the rotational constants and the coefficient of the $-D_J[J(J+1)]^2$ term in the centrifugal distortion formula were obtained by a least-squares fit of the observed frequencies with $J \leqq 7$. For the normal species, the observed frequencies of A_1A_1 components$^{1)}$ of the triplets were used. The rotational constants and the D_J constant, which were determined, are given in Table 1.

In order to estimate the plausible structure, a set of the structural parameters transferred from those of ethylsilane were adjusted so as to reproduce the observed rotational constants. The minimum deviations of the calculated rotational constants from the observed for two species could be reduced to less than 0.04 % by the adjusted parameters which are given in Table 1.

It is noted that the SiC bond of disilylmethane(1.871 Å) is longer than those of ethylsilane(1.866 Å) and dimethylsilane(1.867 Å) and the skeletal angle α(SiCSi) (114°26') is much larger than those of dimethylsilane(110°59'), propane(112°24'),$^{3)}$ and ethylsilane(113°11').

The dipole moments were determined by Stark effect measurements of three low J transitions. They are given in Table 1. The dipole moment of disilylmethane(0.813 D) is larger than that of dimethylsilane(0.75 D) despite of its larger skeletal angle.

Table 1. Rotational Constants (MHz), Structure, Dipole Moments (D) and Internal Rotation of Disilylmethane[a)]

Rotational Constant	A	$\delta A^{b)}$	B	$\delta B^{b)}$	C	$\delta C^{b)}$	$D_J \times 10^{3\,c)}$
$(SiH_3)_2CH_2$	18449.80(25)	-0.01	2941.88(3)	0.00	2739.60(4)	0.00	2.72(52)
$(SiD_3)_2CH_2$	13114.63(11)	0.03	2482.94(1)	0.02	2344.03(1)	0.04	1.23(23)
Plausible Structure							
r(SiC) = 1.871 Å,	r(SiH) = 1.480 Å,		r(CH) = 1.095 Å				
α(SiCSi) = 114°26',	α(HCH) = 104°30',		$\alpha(H_sSiC)$ = 111°3',		$\alpha(H_aSiC)$ = 109°53',		$\alpha(H_aSiH_a)$ = 108°53'
Dipole Moment		$(SiH_3)_2CH_2$	0.813(13) D,		$(SiD_3)_2CH_2$		0.802(10) D
Internal Rotation of the SiH_3 Group[d)]							
I_α = 5.852 amu·Å^2,	$(\lambda_a, \lambda_b, \lambda_c)$ = (0.8384, 0.5451, 0),			F = 105.74 GHz,		V_3 = 1210(20) cal/mol	

a) Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviations.

b) $\delta R = 100 \times (R_{obsd} - R_{calctd})/R_{obsd}$, R = A, B, and C. R_{calctd} was computed from the plausible structure.

c) The coefficient of the $-D_J[J(J+1)]^2$ term.

d) Two-top coupling terms were entirely neglected in the calculation. I_α and $(\lambda_a, \lambda_b, \lambda_c)$ were calculated from the plausible structure.

From the observed splittings of the spectra for the normal species, the barrier to SiH_3 internal rotation was determined to be 1210 ± 20 cal/mol by the standard principal axis method.[4)] The parameters used in the calculation were computed from the plausible structure and the two top coupling terms were entirely neglected.[1)]

The barrier obtained is higher than that of SiH_3SiH_2F(1048 cal/mol)[5)] but much lower than that of ethylsilane(2043 cal/mol, recalculated by neglecting the two top coupling terms).

We are working on the other isotopic species of disilylmethane in order to get the r_s structure and on the excited torsional states in order to know the coupling effect of the two SiH_3 groups.

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