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MICROWAVE SPECTRA OF ETHYLFLUOROSILANE

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Microwave spectra of the trans and gauche isomers of ethylfluorosilane ($CH_3CH_2SiH_2F$) were measured and the rotational constants were determined for the ground and several excited vibrational states. The dipole moments were determined by Stark effect measurements to be 1.74 ± 0.02 D for trans and 1.71 ± 0.17 D for gauche. The observed splittings of the spectra in the first excited methyl torsional state of the gauche isomer gave the methyl internal rotation barrier as 2890 ± 60 cal/mol.

Recently we studied the microwave spectra of ethylfluorosilane in order to compare its molecular structure, dipole moment, and barrier to internal rotation with the results for propyl fluoride reported by Hirota.1)

About thirty of a- and b-type transitions with $J \leqq 10$ for the gauche isomer, and about twenty of a-type transitions with $J \leqq 6$ for the trans isomer were assigned. Rotational constants were obtained by a least-squares fit of the observed frequencies of relatively low J transitions. They are given in Table 1. The rotational constant

Table 1. Rotational Constants (MHz) and Dipole Moment (D)a)

isomer	stateb)	ν(cm^{-1})c)	A	B	C
trans	Ground	——		2871.62(14)	2619.43(14)
	Skeletal torsion	90		2869.79(13)	2625.26(12)
	CH_3 torsion	170		2873.29(14)	2618.75(20)
	CSiF deformation	250		2876.24(13)	2619.95(12)
gauche	Ground	——	10253.34(27)	3614.97(14)	3031.06(14)
	Skeletal torsion	75	10315.37(154)	3603.66(21)	3027.41(19)
	CH_3 torsion	140	10287.24(118)	3612.63(16)	3028.20(14)

isomer	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_c\rvert$	$\lvert\mu_{total}\rvert$	$\alpha(\mu \times a)$d)	$\alpha(\mu \times SiF)$e)
trans	1.73(1)	0.07(28)	————	1.74(2)	~2°	~30°
gauche	1.36(1)	1.04(13)	0.07(47)	1.71(17)	37°	26°

a) Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviation.
b) Tentative assignments are given for some of the excited states.
c) Obtained from rough intensity measurements of the spectra.
d) The angle between the dipole moment and the a-inertial axis.
e) The angle between the dipole moment and the SiF bond toward the bisector of the HSiH angle.

A for the trans isomer could not be determined from the observed a-type transitions, since this isomer is a nearly prolate symmetric top.

The observed rotational constants for the trans and the gauche isomers agreed with those estimated by a set of structural parameters transferred from those of ethylsilane[2)]and fluoromethylsilane (CH_3SiH_2F)[3)]with the root mean square deviations of less than 1.5 % where the dihedral angles were taken as 180° for the trans isomer and 60° for the gauche isomer. The dipole moments were determined by Stark effect measurements of four low J transitions for the gauche isomer and of three low J transitions for the trans isomer. They are given in Table 1 with the estimated angles which the dipole moments make with the a-inertial axis and the SiF bond in the molecule. The dipole moments of the two isomers are essentially equal to each other within the experimental error.

The intensities of the observed spectra for the trans isomer in the dry ice temperature were about one-half of those of the corresponding spectra for the gauche isomer so that the energy difference between the two isomers should be very small.

For the gauche isomer, two sets of weak spectra due to the excited vibrational states were observed near the ground state spectra. From rough measurements of relative intensities of the spectra, they were presumed to be due to the first excited skeletal and methyl torsional states, respectively.

The b-type Q branch transitions in the first excited methyl torsional state exhibited doublet structures due to the internal rotation of the methyl group. The barrier was calculated to be 2890 ± 60 cal/mol from the observed splittings of the spectra by the standard principal axis method.[4)]

For the trans isomer, three sets of weak spectra due to the excited vibrational states were found. They were presumed to be due to the first excited skeletal torsional, methyl torsional and CSiF deformation vibration states from relative intensity measurements of the spectra. Though some of the spectra due to the first excited methyl torsional state exhibited doublet structures predictable by assuming the barrier lower than that of the gauche isomer by about 100 cal/mol, the assignments of the E components of the doublets are not certain at present because so many spectra crowded around the assigned spectra.

We are working on the other isotopic species in order to get more reliable structural parameters of the molecules.

References

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