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MICROWAVE SPECTRA OF FLUOROMETHYLMETHYLETHER

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

Microwave spectra of fluoromethylmethylether and its two deuterated species were studied. This molecule is mainly in the gauche form with the skeletal dihedral angle of 69°. The CH_3 internal rotation barrier was calculated from the observed splittings of the spectra as 1500 ± 30 cal/mol and the dipole moment was determined by the Stark effect measurements of the spectra as 1.744 ± 0.029 D for the normal species.

As a part of a series of researches on the molecular structures of halomethylmethylethers,$^{1)}$ we studied recently the microwave spectra of fluoromethylmethylether and its two deuterated species (FCH_2OCD_3 and FCD_2OCH_3).

About twenty-five of the a-, b-, and c-type transitions could be assigned for each isotopic species. For the normal and FCD_2OCH_3 species, many observed spectra were doublets with small spacings due to the internal rotation of the methyl group. Since the centrifugal distortion contributions seem to be rather large for this

Table 1. Rotational Constants (MHz),$^{a)}$ Deviations,$^{b)}$ and Plausible Structure$^{c)}$

Species	A	B	C	$D_J \times 10^3$	ΔA	ΔB	ΔC
FCH_2OCH_3	17698.57(50)	5604.33(17)	4791.50(16)	6.99(758)	-5.06(-0.03)	0.45(0.01)	-6.89(-0.14)
FCH_2OCD_3	15513.80(51)	4987.58(17)	4304.90(15)	5.89(680)	-8.73(-0.06)	3.89(0.08)	-3.83(-0.09)
FCD_2OCH_3	15384.57(47)	5406.91(14)	4625.07(12)	4.43(510)	-12.47(-0.08)	8.25(0.15)	0.63(0.01)

OCH_3 transferred from $(CH_3)_2O$				FCH_2O adjusted				assumed
r(CO)	1.410 Å	α(OCH_s)	107°14'	r(CF)	1.394 Å	α(H_sCF)	105°40'	r(CH_s) = r(CH_a)
r(CH_s)	1.091 Å	α(OCH_a)	110°50'	r(CO)	1.385 Å	α(OCH_s)	112°15'	= 1.100 Å
r(CH_a)	1.100 Å	α(H_sCH_a)	109°33'	α(COC)	113°23'	α(H_sCH_a)	109°54'	α(H_sCF) = α(H_aCF)
		α(H_aCH_a)	108°44'	α(OCF)	110°30'	τ	69°	α(OCH_s) = α(OCH_a)

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

b) $\Delta R = R_{obsd} - R_{calctd}$. Figures in parentheses indicate the % deviation, $100 \times \Delta R/R_{obsd}$. R = A, B, or C. R_{calctd} is the calculated rotational constant from the structure listed.

c) H_s and H_a refer to the hydrogen atoms situated in the COC plane and out of the COC plane, respectively. τ is the skeletal dihedral angle (FCOC).

Table 2. Dipole Moment (D)[a)]

Species	$\lvert\mu_a\rvert$	$\lvert\mu_b\rvert$	$\lvert\mu_c\rvert$	$\lvert\mu_{total}\rvert$
FCH_2OCH_3	1.055(13)	0.334(99)	1.348(24)	1.744(29)
FCH_2OCD_3	1.063(7)	0.394(62)	1.340(9)	1.755(17)
FCD_2OCH_3	1.025(13)	0.408(83)	1.350(17)	1.743(26)

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

molecule, the rotational constants were obtained from about fifteen of the observed A component frequencies of the transitions with $J \leqq 3$ and $K_a \leqq 1$ so as to fit with the modified rigid rotor expression which includes only the $D_J[J(J+1)]^2$ term of the centrifugal distortion formula. The rotational constants and D_J values are shown in Table 1.

As the r_s structure of this molecule cannot be determined due to the lack of the data for a sufficient number of the isotopic species, a plausible structure was estimated from the observed rotational constants of the three isotopic species. In Table 1, the structural parameters of the OCH_3 part of the molecule were transferred from those of the reported r_s values of dimethylether,[2)] while the other parameters were determined by adjusting the parameter values so as to give the best fit of the calculated rotational constants with the observed. The deviations of the calculated rotational constants from the observed are given in Table 1.

From the observed splittings of the spectra for the normal and FCD_2OCH_3 species, the internal rotation barriers of the methyl group were calculated assuming the structure given in Table 1. The value of 1500 ± 30 cal/mol was obtained for both of the two species. The barrier of this molecule is much lower than that of chloromethylmethylether(1850 ± 49 cal/mol).[3)]

Dipole moments were determined by Stark effect measurements of ten low J transitions for the three species. They are listed in Table 2.

The direction of the dipole moment could be determined, since the deuterium substitutions rotated the inertial axes considerably. The signs of μ_b and μ_c are opposite to and same as that of μ_a, respectively. Taking this fact into account, it is concluded that the dipole moment for the normal species makes an angle of 78°49' with the $O-CH_2$ bond toward C-F direction and lies in a plane whose dihedral angles with the FCO and COC planes are 44°28' and 113°28', respectively. A comparison of the dipole moments between the normal and FCH_2OCD_3 species indicates that the CH_3 group is situated at the side of the positive pole of the dipole moment.

We are working on the other isotopic species and on the spectra due to the excited vibrational states.

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