

Microwave Spectrum, Intramolecular Hydrogen Bond, Dipole Moment and Centrifugal Distortion of 2-Fluoropropanol

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The microwave spectra of 2-fluoropropanol, $\text{CH}_3\text{CHFCH}_2\text{OH}$, and one deuterated species, $\text{CH}_3\text{CHFCH}_2\text{OD}$, have been examined in the 17.9–32.5 GHz spectral region at about -30°C . Only one conformation with an intramolecular hydrogen bond formed between the fluorine atom and the hydroxyl group hydrogen atom was assigned. This rotamer has the methyl and hydroxyl groups in *anti* positions to each other. The OCCF dihedral angle is $65(2)^\circ$, the HOCC dihedral angle is $65(3)^\circ$ and the COH angle is $101(4)^\circ$. Further conformations, if they exist, are at least 3 kJ/mol less stable. Five vibrationally excited states belonging to four different normal modes were assigned and their frequencies determined by relative intensity measurements. Force field calculations were performed using the quartic centrifugal distortion constants allowing an independent determination to be made of the heavy-atom torsional frequency as $147(7)\text{ cm}^{-1}$; a considerable improvement as compared to relative intensity measurements which yielded $140(25)\text{ cm}^{-1}$. The barrier to internal rotation of the methyl group is *ca.* 16.1 kJ/mol. The dipole moment is $\mu_a = 1.41(1)\text{ D}$, $\mu_b = 1.19(2)\text{ D}$, $\mu_c = 0.1(3)\text{ D}$, and $\mu_{\text{tot.}} = 1.85(4)\text{ D}$. Extensive centrifugal distortion analyses were carried out for the ground and the first excited states of the heavy-atom torsional mode and accurate values were determined for the quartic constants.

In 1973 Hagen and Hedberg¹ showed that the *gauche* conformation of gaseous 2-fluoroethanol possessing an intramolecular hydrogen bond is at least 11.3 kJ/mol more stable than the *anti* conformation which does not of course have this stabilizing interaction. In the closely related molecule 2-fluoropropanol, $\text{CH}_3\text{CHFCH}_2\text{OH}$, the two hydrogen-bonded rotamers of Fig. 1 were therefore expected to be several kJ/mol more stable

than further non-hydrogen-bonded conformations. The steric conditions are rather similar in both I and II. It was thought that II would be additionally stabilized as compared to I through an interaction between the methyl group and the hydroxyl group lone-pair electrons. It was thus expected that the microwave spectrum would reveal roughly equal amounts of both I and II. However, it was found that I predominates and is at least 3 kJ/mol more stable than conformation II for which no assignments could be made.

2-Fluoropropanol is the fifth of a series of related hydrogen-bonded molecules which have been investigated by microwave spectroscopy in recent years. In $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$ ² and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ³ conformations similar to both I and II of Fig. 1 were identified; in $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$ ⁴ and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{F}$ ⁵ only one rotamer similar to I was assigned in each case. These investigations may give some indication of the forces responsible for delicate equilibria of the kind shown in Fig. 1. In particular, the fluorine atom seems to play a rather unique role as pointed out in the Discussion.

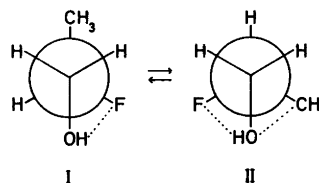


Fig. 1. Possible hydrogen-bonded conformations of $\text{CH}_3\text{CHFCH}_2\text{OH}$ viewed along the $\text{HOCH}_2\text{—CHFCH}_3$ bond. Dots indicate possible non-bonded stabilizing interactions.

Table 1. Selected transitions for the ground vibrational state of conformation I of CH₃CHFCH₂OH.

Transition	Observed frequency ^a (MHz)	Obs. - calc. frequency (MHz)	Centrifugal distortion	
			Total (MHz)	Sextic (MHz)
<i>a</i> -type				
2 _{0,2} → 3 _{0,3}	18774.65	0.02	-0.06	
2 _{2,1} → 3 _{2,2}	19181.42	-0.02	-0.24	
2 _{2,0} → 3 _{2,1}	19588.39	-0.01	-0.27	
2 _{1,1} → 3 _{1,2}	20397.93	-0.08	-0.16	
3 _{1,3} → 4 _{1,4}	23674.04	-0.04	-0.16	
3 _{0,3} → 4 _{0,4}	24614.52	-0.01	-0.15	
3 _{2,1} → 4 _{2,2}	26454.13	-0.03	-0.46	
3 _{3,0} → 4 _{3,1}	25808.83	-0.07	-0.69	
3 _{1,2} → 4 _{1,3}	27056.10	0.09	-0.31	
4 _{1,4} → 5 _{1,5}	29445.25	-0.03	-0.29	
12 _{3,10} → 12 _{3,9}	18642.68	-0.01	-4.54	
16 _{4,13} → 16 _{4,12}	23414.91	-0.02	-10.02	0.01
23 _{6,18} → 23 _{6,17}	25078.78	0.04	-23.67	0.06
30 _{8,23} → 30 _{8,22}	24651.72	0.05	-42.36	0.24
40 _{11,30} → 40 _{11,29}	18061.85	-0.02	-63.51	0.95
49 _{13,37} → 49 _{13,36}	30883.85	-0.02	-151.36	3.72
<i>b</i> -type				
6 _{0,6} → 6 _{1,5}	18218.67	-0.15	-0.93	
8 _{0,8} → 8 _{1,7}	28044.26	0.07	-2.00	
4 _{1,4} → 4 _{2,3}	20247.53	-0.04	-0.56	
6 _{1,6} → 6 _{2,5}	25287.05	-0.08	-1.26	
5 _{2,3} → 5 _{3,2}	24178.05	-0.02	-0.98	
8 _{2,6} → 8 _{3,5}	20283.03	-0.01	-2.12	
8 _{2,7} → 8 _{3,6}	30933.20	0.01	-3.07	
10 _{3,7} → 10 _{4,6}	30384.44	0.03	-4.58	
12 _{3,9} → 12 _{4,8}	26915.69	0.03	-6.13	
14 _{3,11} → 14 _{4,10}	26558.71	-0.04	-8.63	
1 _{1,0} → 2 _{2,1}	28153.28	-0.02	-0.18	
3 _{0,3} → 4 _{1,4}	26816.31	0.01	-0.19	
6 _{3,4} → 7 _{2,5}	25321.02	0.05	-0.46	
9 _{4,5} → 10 _{3,8}	26336.24	0.03	1.07	
14 _{7,7} → 15 _{6,10}	31012.90	-0.12	2.46	0.01
21 _{12,9} → 22 _{11,12}	23108.87	0.04	12.84	0.02
21 _{12,10} → 22 _{11,11}	23108.87	-0.04	12.84	0.02
27 _{15,12} → 28 _{14,15}	30914.95	-0.05	26.15	0.07
27 _{15,13} → 28 _{14,14}	30914.95	-0.05	26.15	0.07
33 _{19,14} → 34 _{18,17}	27637.75	-0.02	51.61	0.15
33 _{19,15} → 34 _{18,16}	27637.75	-0.02	51.61	0.15
43 _{25,18} → 44 _{24,21}	29646.49	-0.03	116.47	0.44
43 _{25,19} → 44 _{24,20}	29646.49	-0.03	116.47	0.44
53 _{31,22} → 54 _{30,25}	31713.21	0.05	219.99	1.06
53 _{31,23} → 54 _{30,24}	31713.21	0.05	219.99	1.06

^a ± 0.07 MHz.

EXPERIMENTAL

2-Fluoropropanol was synthesized using the procedure of Bergmann and Cohen.⁶ The sample was purified by gas chromatography before use. $\text{CH}_3\text{CHFCH}_2\text{OD}$ was produced by direct exchange with heavy water in the wave guide. Vapour pressures in the 20–60 micron range were employed during the spectral measurements. The temperature was about -30°C . Lower temperature could not be used due to insufficient vapour pressure. Measurements were made in the 17.9–32.5 GHz spectral region.

RESULTS

Microwave spectrum and assignment of the ground state of conformation I. Preliminary rotational constants of both conformation I and the hypothetical rotamer II of Fig. 1 were computed by combining structural parameters taken from related compounds. Bond moment calculations of the dipole moment and its components along the principal axes were then performed using the values of Ref. 7. The principal axes components of the dipole moment were predicted to be $\mu_a = 1.1$ D, $\mu_b = 0.9$ D and $\mu_c = 0.2$ D for conformation I and $\mu_a = 0.3$ D, $\mu_b = 0.0$ D and $\mu_c = 1.3$ D for the hypothetical rotamer II. Each rotamer was thus predicted to possess comparatively strong and rich spectra dominated by strong Q -branch transitions.

The observed spectrum was relatively strong with absorptions occurring every few megahertz. Assignments were readily made for low J a - and b -

type transitions of conformation I; these were lying close to their predicted frequencies. The rotational constants were then determined and used to predict the positions of further transitions which were measured and included in the least-squares fit in which centrifugal distortion was also taken into account. This procedure was repeated several times, and ultimately 143 lines of the a - and b -type varieties were assigned. No c -type transitions were definitely identified because of the small μ_c being 0.1(0.3) D (see later section). These lines thus have insufficient intensities to allow their assignments. The highest J - and K_{-1} -transitions identified belonged to the coalescing pair of $53_{31,22} \rightarrow 54_{30,20}$ and $53_{31,23} \rightarrow 54_{30,24}$. Even higher J -transitions were searched for but not found, presumably because of insufficient intensities. A portion of the ground state spectrum is shown in Table 1.*

The derived spectroscopic constants are shown in Table 2. The rotational and quartic centrifugal distortion constants are accurately determined, while the two sextic constants included have standard deviations of about 10%. Inclusion of more sextic distortion constants resulted in only a marginal improvement of the fit, high correlations among the sextic constants and associated large

* The complete list of frequencies for the ground, the vibrationally excited states, and for the ground state of $\text{CH}_3\text{CHFCH}_2\text{OD}$ is available from the authors upon request, or from the Microwave Data Center, Molecular Spectroscopy Section, National Bureau of Standards Bldn. 221, Washington D.C. 20234, U.S.A., where it has been deposited.

Table 2. Spectroscopic constants for the ground vibrational states of $\text{CH}_3\text{CHFCH}_2\text{OH}$ and $\text{CH}_3\text{CHFCH}_2\text{OD}$.^a

Species	$\text{CH}_3\text{CHFCH}_2\text{OH}$	$\text{CH}_3\text{CHFCH}_2\text{OD}$
Number of transitions	143	29
Root-mean-square dev. (MHz)	0.066	0.101
A_0 (MHz)	8461.7439(35)	8367.062(29)
B_0 (MHz)	3625.6374(14)	3538.610(17)
C_0 (MHz)	2768.2557(11)	2707.914(17)
Δ_J (kHz)	0.8611(36)	0.21(38)
Δ_{JK} (kHz)	6.007(23)	5.51(32)
Δ_K (kHz)	2.1394(97)	1.1(22)
δ_J (kHz)	0.1978(15)	0.196(17)
δ_K (kHz)	3.537(40)	3.39(33)
H_J (Hz)	0.000678(93)	— ^b
H_{JK} (Hz)	-0.0166(17)	— ^b

^aUncertainties represent one standard deviation. ^bNot determined. Assumed to be zero in least-squares fit.

Table 3. Vibrationally excited states of CH₃CHFCH₂OH.^a

Vibrational state	First ex. heavy-atom tors.	Second ex. heavy-atom tors.	Lowest bending	Highest bending	Methyl torsion
Number of transitions	68	26	33	6	19
Root-mean-square dev. (MHz)	0.102	0.083	0.093	0.641	0.098
A_v (MHz)	8418.6679(86)	8383.176(24)	8487.792(22)	8413.5(40)	8445.116(36)
B_v (MHz)	3620.0511(33)	3614.597(14)	3626.315(14)	3618.69(16)	3623.683(16)
C_v (MHz)	2765.3234(27)	2762.158(14)	2765.197(14)	2762.51(19)	2766.553(17)
Δ_J (kHz)	0.8458(97)	1.69(30)	1.27(32)	0.5(35)	0.63(40)
Δ_{JK} (kHz)	5.98(13)	6.10(46)	5.59(27)	— ^b	0.29(56)
Δ_K (kHz)	1.609(63)	−2.3(28)	6.3(18)	— ^b	11.9(35)
δ_J (kHz)	0.209(10)	0.199(19)	0.160(14)	— ^b	0.237(26)
δ_K (kHz)	3.02(21)	2.76(40)	4.69(30)	— ^b	2.80(50)
H_J (Hz)	0.0090(40)	— ^b	— ^b	— ^b	— ^b
H_{JK} (Hz)	−0.016(25)	— ^b	— ^b	— ^b	— ^b

^aUncertainties represent one standard deviation. ^bNot determined. Assumed to be zero in least-squares fit.

standard deviations. It was thus concluded that five quartic and two sextic constants give the best physical representation of the spectrum.

The quartic centrifugal distortion constants are quite similar to those previously determined for 1-fluoro-2-propanol.⁵ This is indicative of similar force fields and mass distribution for the two related molecules, whose rotational constants are also fairly similar.

Vibrationally excited states. The ground vibrational state transitions were accompanied by a rich satellite spectrum. The strongest of these absorption lines were about 50% as intense as the corresponding ground state transitions. They are assigned as the first excited state of the heavy-atom (OC—CF) torsional mode. A total of 68 transitions were assigned for this mode. Maximum value of J was 40 of the $40_{11,30} \rightarrow 40_{11,29}$ transition. The spectroscopic constants are shown in Table 3. They are close to their ground-state counterparts as expected, with one exception, namely Δ_K which differs by about 30% between the two states. This is about ten times the standard deviation. The reason for this is not known.

Relative intensity measurements were made observing most of the precautions of Esbitt and Wilson.⁸ The frequency was determined as 140(25) cm^{-1} . Using an alternative, completely independent force-field calculation as described below, this frequency was found as 147(7) cm^{-1} in good agreement with the relative-intensity determination. This frequency is not far from 109(10) cm^{-1} determined for the corresponding normal mode of 1-fluoro-2-propanol.⁵

The changes of the rotational constants upon excitation of this mode is close to what was found for the corresponding mode of 1-fluoro-2-propanol.⁵ Attempts to reproduce these changes by opening up the OCCF dihedral angle by 2° met with some success. This indicates that the heavy-atom torsional mode of this molecule is not strongly coupled with other normal vibrations.

The second excited state of this mode was also assigned with the spectroscopic constants determined as shown in Table 3. The intensity of these transitions is roughly 25% of their ground state counterparts as expected. However, the changes of the rotational constants upon excitation from the first to the second excited state were $\Delta A = -35.5$ MHz, $\Delta B = -5.5$ MHz, and $\Delta C = -3.2$ MHz, respectively, as compared to $\Delta A = -43.1$ MHz, $\Delta B = -5.6$ MHz and $\Delta C = -2.9$ MHz obtained upon excitation of the ground state to first excited state of this heavy-atom torsional mode. Similar findings were made for 1-fluoro-2-propanol⁵ indicating a very slight anharmonic contribution or interaction with other normal vibrations.

The third excited state transitions of this torsional mode should, in case of a near-harmonic vibration, have approximately 12% of the intensity of the ground state lines. They should thus clearly have sufficient intensities to allow definite assignments to be made. Moreover, their spectral positions should be possible to predict quite accurately since both the first and the second excited states were identified. The strongest third excited state transitions of the torsion were searched for thoroughly, but were not

found. Resonance with another normal mode is suggested as the reason for this.

The first excited state of what is assumed to be the lowest heavy-atom bending mode was assigned as shown in Table 3. The intensities of these transitions were about 30% of the corresponding groundstate lines. A frequency of 220(40) cm^{-1} was determined by relative-intensity measurements. The changes of the rotational constants upon excitation as well as the vibrational frequency of this mode is again found to correspond well with the findings for 1-fluoro-2-propanol.⁵

It is likely that the heavy-atom bending modes are strongly coupled. Despite this, attempts were made to see if this excited state could be located to either the CCC, FCC or OCC bending mode. Model calculations were made by opening up each of these angles by 0.5°. None of them reproduced the observed changes of the rotational constants very satisfactorily. However, the agreement for the CCC bending mode is much better than for the other two. We therefore believe that this mode is largely a CCC bending vibration.

Another low-frequency mode having about 15% intensity of the ground state was also assigned as shown in Table 3. The energy of this state was estimated to be roughly 320 cm^{-1} above the ground state. Again, the changes of the rotational constants closely resemble an excited state identified for 1-fluoro-2-propanol.⁵ This excited state is tentatively assigned as another bending mode of the molecule. The changes of the rotational constants upon excitation in no way resemble what was calculated by opening up the three heavy-atom angles as described above. It is therefore concluded that complex coupling must exist for this presumed bending mode.

The first excited state of what is believed to be the methyl group torsional mode was identified with the spectroscopic constants displayed in Table 3. The changes of the rotational constants once more were found to agree closely with their counterparts of 1-fluoro-2-propanol.⁵ Relative intensity measurements yielded 260(50) cm^{-1} for this mode.

No splittings due to internal rotation were observed for this mode or for any of the other of the excited states described above. It is believed that splittings would have been observed if they had exceeded 0.5 MHz. Computations using the computer programme MB10 described previously,⁹ and assuming splittings not exceeding 0.5 MHz, makes it possible to estimate the barrier to be at

least 14.2 kJ/mol. Using the approximation of a harmonic oscillator¹⁰ with a torsional frequency of 260 cm^{-1} yields as a result that the barrier is roughly 16.1 kJ/mol. This is in keeping with values obtained for $\text{CH}_3\text{CH}_2\text{F}$ ¹¹ (14.1 kJ/mol) and $\text{CH}_3\text{CHFCH}_3$ ¹² (14.9 kJ/mol).

Determination of the heavy-atom torsional frequency from force-field calculations. Low-frequency torsional vibrations are generally difficult to observe experimentally by Raman or IR spectroscopy. Relative intensity measurements in the microwave range with Esbitt-Wilson's procedure⁸ often give rather large uncertainties as exemplified above. An alternative method for their determination would be desirable as a supplement to these methods. Perhaps accurate centrifugal distortion constants could be used in many cases for this end.

The centrifugal distortion constants depend primarily on low-frequency normal vibrations, as the force constants enter inversely in their mathematical expressions.¹³ Moreover, the torsional modes are often well isolated from other fundamentals as in the present case where 140(25) cm^{-1} , 220(40) cm^{-1} , 260(50) cm^{-1} and ca. 320 cm^{-1} are the lowest normal vibrations. Torsional modes thus often couple little with other frequencies as is assumed to be the case for the title compound.

A simple diagonal force field as shown in Table 4 was selected from related molecules. Only the torsional force constant of the heavy-atom torsion was allowed to vary in a least-squares fitting procedure of the centrifugal distortion constants. All the remaining force constants of the simple valency force field shown in this table were kept constant at the values reported there. The programme used was NCA written by Christen.¹⁴

Quite good agreement was obtained between the observed and calculated centrifugal distortion constants, as shown in Table 4, and the torsional frequency was found as 147 cm^{-1} in good agreement with the value obtained by relative-intensity measurements [140(25) cm^{-1}]. The uncertainty of this frequency (147 cm^{-1}) is difficult to estimate since several assumptions are involved in its derivation. However, it is felt that $\pm 7 \text{ cm}^{-1}$ is a realistic error limit; a considerable improvement in comparison with the relative intensity method which yielded 140(25) cm^{-1} .

It is hoped that use of centrifugal distortion constants in this manner may have some merit as an independent way of determining the elusive torsional frequencies.

Table 4. Assumed force field, centrifugal distortion constants, and torsional frequency of $\text{CH}_3\text{CHFCH}_2\text{OH}$.

Force constants

Stretching ($\text{m dyn } \text{Å}^{-1}$)

C(1)–C(2)	4.60	C(1)–H	4.81
C–F	5.15	C–O	4.90
C(2)–C(3)	4.42	O–H	7.48
C(2)–H	4.81	C(3)–H	4.70

Bending ($\text{m dyn } \text{Å rad}^{-2}$)

C–O–H	0.76	C–C–C	1.27
H–C–O	0.70	C(3)–C(2)–F	1.08
H–C(1)–H	0.51	C(3)–C(2)–H	0.72
C–C–O	1.18	C(2)–C(3)–H	0.66
C(2)–C(1)–H	0.71	H–C(3)–H	0.49
C(1)–C(2)–F	1.01	C(1)–C(2)–H	0.81

Torsion ($\text{m dyn } \text{Å rad}^{-2}$)

C(2)–C(3)	0.13	C–O	0.053
C(1)–C(2)	0.204 ^a		

Centrifugal distortion constants

	Obs.	Calc.
Δ_J (kHz)	0.8611	0.9687
Δ_{JK} (kHz)	6.0071	6.1973
Δ_K (kHz)	2.1394	2.4715
δ_J (kHz)	0.1978	0.2020
δ_K (kHz)	3.5372	3.7146

Heavy-atom torsional frequency (cm^{-1})147^a^a Obtained from least-squares fit. $\text{H}_3\text{C}(3)–\text{C}(2)\text{HF}–\text{C}(1)\text{H}_2\text{OH}$.

Dipole moment. Stark coefficients of low J transitions were used to determine the dipole moment. A d.c. voltage was applied between the Stark septum and the cell with the modulating square wave voltage superimposed. The d.c. voltage was calibrated using the OCS $J=1\rightarrow 2$ transition with $\mu_{\text{OCS}}=0.71521$ D.¹⁵ Each second order coefficient shown in Table 5 was assigned a standard deviation. A least squares fit using a diagonal weight matrix was performed. The weights were chosen as the inverse squares of the standard deviations appearing in Table 5. This table also gives the total dipole moment and its components along the principal axes. It is seen that there is reasonable agreement between the observed dipole moment and that calculated by the bond-moment method as described above.

Table 5. Stark coefficients and dipole moment^a of $\text{CH}_3\text{CHFCH}_2\text{OH}$.

Transition		$\Delta v/E^2$ (MHz V ⁻¹ cm ²) × 10 ⁶	
		Obs.	Calc.
$2_{0,2} \rightarrow 3_{0,3}$	$ M =2$	16.24(6)	15.96
	$ M =1$	2.12(1)	2.15
	$M=0$	–2.43(2)	–2.45
$2_{1,1} \rightarrow 3_{1,2}$	$ M =2$	–24.10(90)	–25.35
	$ M =1$	–5.36(9)	–5.55
	$M=0$	1.04(1)	1.04
$3_{1,3} \rightarrow 3_{2,2}$	$ M =3$	–227(2)	–232

^a $\mu_a=1.41(1)$ D; $\mu_b=1.19(2)$; $\mu_c=0.1(3)$ D; $\mu_{\text{tot}}=1.85(4)$.

Table 6. Plausible structural parameters^a and observed and calculated rotational constants of CH₃CHFCH₂OH and CH₃CHFCH₂OD.

Assumed structural parameters			
H ₃ C—C (pm)	150.5	∠CCO (°)	112.0
HOH ₂ C—C (pm)	150.3	∠CCF (°)	109.7
C—O (pm)	141.1	∠CCC (°)	112.4
C—H (pm)	109.3	∠CCH (°)	111.0
O—H (pm)	96.6		
C—F (pm)	139.5		
Fitted structural parameters			
∠COH (°)	101(4)		
∠OCCF (°)	65(2)	from <i>syn</i>	
∠HOCC (°)	65(3)	from <i>syn</i>	
Kraitchman's coordinates for the hydroxyl hydrogen			
	a	b	c
Obs. (pm)	184.502(19)	83.090(44)	13.716(263)
Calc. (pm)	183.9	83.1	23.9
Hydrogen bond parameters			
H...F (pm)	248	∠O—H...F (°)	104
F...O (pm)	287	∠C—F...H (°)	76
		∠C—F, O—H (°) ^b	4
Sum of van der Waals radii ^c			
H...F (pm)	255	O...F (pm)	275
Rotational constants			
CH ₃ CHFCH ₂ OH			
	Obs.	Calc.	Diff. (%)
A ₀ (MHz)	8461.74	8428.43	0.39
B ₀ (MHz)	3625.64	3636.18	0.29
C ₀ (MHz)	2768.26	2774.78	0.24
CH ₃ CHFCH ₂ OD			
	Obs.	Calc.	Diff. (%)
A ₀ (MHz)	8367.06	8329.36	0.45
B ₀ (MHz)	3538.61	3548.23	0.27
C ₀ (MHz)	2707.91	2714.43	0.24

^a See text. ^b Angle between C—F and O—H bonds. ^c See Ref. 20.

Deuterated species. The deuterated species CH₃CHFCH₂OD was studied mainly to determine accurately the position of the hydroxyl hydrogen. The spectrum was readily assigned and its spectroscopic constants are listed in Table 2. The position of the hydroxyl hydrogen atom was computed using Kraitchman's equations¹⁶ with the result shown in Table 6.

Searches for further conformations. A total of 295 transitions were assigned for conformation I. This includes all the strongest lines, the majority of the medium intensity transitions as well as many weak ones. Careful Stark effect studies were made for all the unassigned lines of medium intensity. None of them displayed any splitting. Low *J* *R*-branch lines of the *c*-type variety were predicted to be among the

strongest of the hypothetical conformation II. Careful searches were made for several of these transitions, but none were found. In addition to these lines, medium and high J c -type Q -branch transitions were predicted to be relatively strong, numerous and form a distinct spectral pattern. This feature was not recognizable.

Moreover, the absolute intensities of the spectral lines depend on the fraction of the gas belonging to a specific conformation.¹⁷ Absolute intensities are hard to determine accurately. This makes it somewhat difficult to use this property to determine exactly how large a fraction of a gaseous mixture belongs to a particular conformation. In spite of this difficulty, absolute intensity estimates were made. It was again found that conformation I predominates. No indications for the existence of further rotamers were obtained from the absolute intensity studies.

From these studies it is concluded that conformation I predominates. It is conservatively estimated that at least 80% of the gas consists of this conformation at -30°C . It is even likely that more than 90% of the gas consists of I. This conformation is thus at least 3 kJ/mol more stable than II or any other non-hydrogen-bonded rotamer. A computer-drawn model of the identified rotamer I is shown in Fig. 2.

Structure. Only six moments of inertia were determined for conformation I. Consequently, a full molecular structure cannot be determined. Instead, we restricted ourselves to fitting the OCCF, HOCC dihedral angles, and the COH angle, because these parameters are sensitive to the experimental data at hand and because they are considered to be chemically interesting. The remaining bond lengths and angles were kept constant in the fit at the values shown in Table 6. These parameters were selected from recent, accurate studies of related compounds.

The OCCF dihedral angle was just fitted until a satisfactory agreement between the observed and

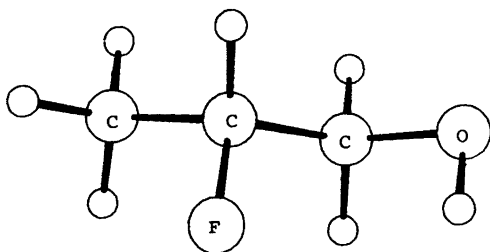


Fig. 2. Computer-drawn model of $\text{CH}_3\text{CHFCH}_2\text{OH}$.

calculated rotational constants was found. This occurred with $65(2)^\circ$. The dihedral angle $\angle\text{HOCC}$ and the angle $\angle\text{COH}$ were then fitted to Kraitchman's coordinates for the hydroxyl group hydrogen atom. $\angle\text{HOCC}$ was found to be $65(3)^\circ$, and $\angle\text{COH}$ to be $101(4)^\circ$.

Table 6 shows that good agreement exists between the observed and calculated rotational constants. Kraitchman's coordinates of the hydroxyl hydrogen atom are also well reproduced. The error limits of the three fitted parameters are assumed to encompass not only random errors but uncertainties of the assumed structural parameters as well.

The hydrogen bond parameters as shown in Table 6 are indicative of a strained hydrogen bond. This situation resembles very much what has previously been found for $\text{CH}_2\text{FCH}_2\text{OH}$,^{1,18} $\text{CHF}_2\text{CH}_2\text{OH}$ ¹⁹ and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{F}$.⁵ The major stabilizing interaction is perhaps the near-ideal bond-dipole interaction between the O-H and C-F bonds which are almost parallel. Covalency is hardly of much significance for the hydrogen bond of this molecule as the non-bonded $\text{H}\cdots\text{F}$ distance is almost equal to the sum of the corresponding van der Waals radii.²⁰

It is noteworthy that the OCCF dihedral angle takes a value of $65(2)^\circ$. This is $3-6^\circ$ more than in the three above-mentioned compounds. No obvious explanation for this can be given.

DISCUSSION

The conformational behaviour of $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{NH}_2$,⁴ $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$ ² and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ³ can be understood at least qualitatively within the framework of existing theories of steric interaction, hydrogen bonding and dipole interaction. This is hardly the case for $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{F}$ ⁵ and the title compound, $\text{CH}_3\text{CHFCH}_2\text{OH}$. The fact that neither of these have conformations similar to II with energies roughly the same as for I cannot be explained using only the popular theories of steric, hydrogen bonding, or dipole interactions. Some additional effect must be operative for these two molecules containing the fluorine atom.

$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{F}$ and $\text{CH}_3\text{CHFCH}_2\text{OH}$ are not the only known examples of small aliphatic molecules containing fluorine and also displaying unique conformational properties, e.g., $\text{CH}_2\text{FCH}_2\text{F}$ ^{21,22} takes the *gauche* conformation as

its preferred form. In $\text{CHF}_2\text{CH}_2\text{OH}$ only one of the two possible hydrogen-bonded rotamers makes up more than 95% of the gas. It appears that theoretical work is needed to explain the conformational behaviour of alifatic molecules containing the "troublesome" fluorine atom.

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