

Microwave Spectrum, Intramolecular Hydrogen Bonding, Dipole Moment and Centrifugal Distortion of 2,2-Difluoroethanol

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The microwave spectra of $\text{CHF}_2\text{CH}_2\text{OH}$ and $\text{CHF}_2\text{CH}_2\text{OD}$ have been investigated in the 18.0–37.0 GHz spectral region. Only conformation I (see Figs. 1 and 2) with an intramolecular hydrogen bond was assigned. Other conformations, if they coexist with I, are present in concentrations not exceeding $\sim 5\%$ at -25°C .

The FCCO dihedral angle is $61(2)^\circ$ and the HOCC dihedral angle is $60(4)^\circ$.

The dipole moment is $\mu_a = 0.608(7)$ D, $\mu_b = 0.282(12)$ D, $\mu_c = 0.163(40)$ D and $\mu_{\text{tot}} = 0.690(20)$ D.

Five vibrationally excited states were assigned. Three of these belong to the C–C torsional mode while the two others are attributed to low-frequency skeletal bending modes. Relative intensity measurements yielded $124(10)$ cm^{-1} for the torsional fundamental, $243(20)$ and $309(40)$ cm^{-1} , respectively, for the two bending modes.

The structure and conformational preferences of monosubstituted 2-haloethanols have in recent years attracted considerable interest. These molecules have been studied by many physical methods in all states of aggregation. Gas phase studies by electron diffraction, microwave spectroscopy, IR and Raman spectroscopy have shown that the 2-haloethanols all prefer the heavy-atom *gauche* conformation with an intramolecular hydrogen bond.¹

In contrast to the monosubstituted haloethanols, only few reports exist on the structure of 2,2-dihaloethanols. The title compound, for example, has as far as we know, been investigated only once before by spectroscopic methods by Perttilä² who examined the IR spectrum of the molecule in argon and nitrogen matrices as well as in the liquid state. A

normal coordinate analysis was also made.

Two rotamers each with an intramolecular hydrogen bond are possible in the case of 2,2-difluoroethanol. They are depicted in Fig. 1. Conformations without a hydrogen bond are of course also possible, but presumed to be several kJ/mol higher in energies since this was found by Hagen and Hedberg³ in their high-temperature electron-diffraction study of the closely related 2-fluoroethanol.

The object of this investigation has been to study the conformational preferences of the title compound and thereby perhaps obtain some indication of the role of hydrogen bonding and other forces for delicate equilibria of the kind shown in Fig. 1. Rather unexpectedly, it was found that more than about 95% of the gas consists of conformation I. No assignments could be made for II or non-hydrogen-bonded rotamers.

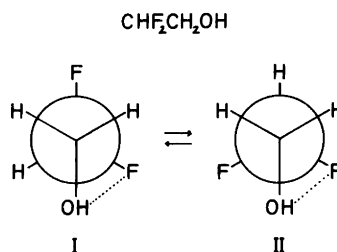


Fig. 1. Possible conformations of $\text{CHF}_2\text{CH}_2\text{OH}$ with intramolecular hydrogen bonds which are indicated by dots. Only I was assigned, while II is, if it exists, not present in concentrations exceeding $\sim 5\%$. Conformations without a hydrogen bond were also not found.

EXPERIMENTAL

2,2-Difluoroethanol was synthesized as described by Henne and Pelley.⁴ The compound was purified by gas chromatography before use. Studies were made in the 18–37 GHz spectral region on a conventional spectrometer with the cell cooled to about -25°C . Lower temperatures could not be utilized because of insufficient vapour pressure. Vapour pressures in the 5–25 micron range were employed during the spectral measurements. $\text{CHF}_2\text{CH}_2\text{OD}$ was produced by direct exchange with heavy water in the wave guide.

RESULTS

Microwave spectrum and assignment 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 moments of the two conformers were then performed using the values of Ref. 5. The dipole moment was predicted to be $\mu_a=0.8$ D, $\mu_b=0.1$ D, and $\mu_c=0.4$ D for conformation I. A rather simple and moderately strong

Table 1. Microwave spectrum of the ground vibrational state of $\text{CHF}_2\text{CH}_2\text{OH}$.

Transition	Observed frequency ^a (MHz)	Obs. – calc. frequency (MHz)	Centrifugal distortion (MHz)
<i>a</i> -Type			
$2_{1,2} \rightarrow 3_{1,3}$	18413.86	0.00	-0.06
$2_{0,2} \rightarrow 3_{0,3}$	19407.01	0.07	-0.06
$2_{2,1} \rightarrow 3_{2,2}$	19806.57	-0.04	-0.24
$2_{2,0} \rightarrow 3_{2,1}$	20206.44	0.03	-0.28
$2_{1,1} \rightarrow 3_{1,2}$	21071.10	-0.02	-0.18
$3_{1,3} \rightarrow 4_{1,4}$	24448.61	0.06	-0.15
$3_{0,3} \rightarrow 4_{0,4}$	25459.72	-0.12	-0.15
$3_{2,2} \rightarrow 4_{2,3}$	26329.02	-0.03	-0.39
$3_{3,1} \rightarrow 4_{3,2}$	26592.46	0.13	-0.71
$3_{2,1} \rightarrow 4_{2,2}$	27277.60	-0.06	-0.48
$3_{1,2} \rightarrow 4_{1,3}$	27957.42	0.00	-0.32
$4_{1,4} \rightarrow 5_{1,5}$	30414.03	0.00	-0.30
$4_{0,4} \rightarrow 5_{0,5}$	31280.05	-0.02	-0.30
$4_{2,3} \rightarrow 5_{2,4}$	32784.16	0.02	-0.59
$4_{3,2} \rightarrow 5_{3,3}$	33290.47	-0.07	-1.01
$4_{3,1} \rightarrow 5_{3,2}$	33441.59	-0.03	-1.04
$4_{2,2} \rightarrow 5_{2,3}$	34511.55	0.07	-0.77
$4_{1,3} \rightarrow 5_{1,4}$	34703.97	0.02	-0.54
$5_{1,5} \rightarrow 6_{1,6}$	36312.87	0.06	-0.52
$5_{0,5} \rightarrow 6_{0,6}$	36955.37	-0.06	-0.52
<i>b</i> -Type			
$6_{2,4} \rightarrow 6_{3,3}$	25275.87	0.07	-4.38
$7_{2,5} \rightarrow 7_{3,4}$	23750.63	0.01	-4.73
$8_{2,6} \rightarrow 8_{3,5}$	22466.43	-0.07	-5.12
$9_{2,7} \rightarrow 9_{3,6}$	21783.39	0.00	-5.57
$11_{2,9} \rightarrow 11_{3,8}$	23328.44	-0.08	-6.79
$13_{2,11} \rightarrow 13_{3,10}$	29686.96	0.01	-8.93
$6_{2,5} \rightarrow 6_{3,4}$	30504.16	0.02	-4.89
$10_{3,7} \rightarrow 10_{4,6}$	33924.38	-0.04	-13.22
$13_{3,10} \rightarrow 13_{4,9}$	28879.50	0.05	-14.78
$16_{3,13} \rightarrow 16_{4,12}$	32575.30	0.01	-16.75

^a ± 0.07 MHz.

spectrum dominated by *a*-type *R*-branch transitions was thus expected for this rotamer.

The spectrum of conformation II was predicted to be very much different from that of I since the dipole moment components were predicted to be $\mu_a=0.1$ D, $\mu_b=1.1$ D, and $\mu_c=2.3$ D, respectively. A strong, dense spectrum dominated by *c*-type *Q*-branch transitions was thus predicted for the hypothetical conformer II. Furthermore, the *b*-type lines were presumed to be combined rotation-vibration transitions caused by tunnelling of the hydroxyl group hydrogen as there are two equivalent hydrogen-bonded forms of II. This perturbation was expected to be a prominent feature of the *b*-type transitions of this conformation.

The observed spectrum was weak and comparatively simple. Assignments were made readily of *a*-type *R*-branch and some weak *b*-type *Q*-branch transitions. No *c*-type, *a*-type *Q*-branch, or *b*-type *P* or *R*-branch lines were definitely identified owing to the small dipole moment components. The ground state spectrum is shown in Table 1.* The derived spectroscopic constants displayed in Table 2 agree to within a few per cent of those originally predicted for conformer I.

Vibrationally excited states. The ground state lines were accompanied by several vibrationally excited state transitions. Five excited states were ultimately assigned as shown in Table 3. The strongest of these absorption lines were about 50 %

*The microwave spectra of the excited states of $\text{CHF}_2\text{CH}_2\text{OH}$ and the ground state of $\text{CHF}_2\text{CH}_2\text{OD}$ are available from the authors upon request, or from the Microwave Data Center, Molecular Spectroscopy Section, National Bureau of Standards, Washington D.C. 20234, U.S.A., where they have been deposited.

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

Species	$\text{CHF}_2\text{CH}_2\text{OH}$	$\text{CHF}_2\text{CH}_2\text{OD}$
Number of transitions	31	14
rms (MHz)	0.06	0.06
A_O (MHz)	9069.926(16)	8953.16(24)
B_O (MHz)	3745.2704(54)	3640.0796(79)
C_O (MHz)	2857.0128(52)	2785.9475(104)
Δ_J (kHz)	0.945(95)	0.46(14)
Δ_{JK} (kHz)	5.84(43)	9.21(78)
Δ_K (kHz)	50.0(21)	^b
δ_J (kHz)	0.116(22)	^b
δ_K (kHz)	7.51(56)	^b

^aUncertainties represent on standard deviation. rms is the root-mean-square deviation. The rotational constants are those obtained from the least squares fit without correcting for centrifugal distortion. ^bFixed at zero in least-squares fit.

as strong as the corresponding ground state transitions. Relative intensity measurements made largely as prescribed by Esbitt and Wilson⁶ yielded 124(10) cm^{-1} for this mode. This is very close to 126 cm^{-1} calculated by Perttilä² for the C–C torsional mode of the matrix isolated molecule. The observed changes of the rotational constants upon excitation of this mode are $\Delta A = -39.06$ MHz, $\Delta B = -6.21$ MHz and $\Delta C = -2.14$ MHz, respectively. These changes are only partly reproduced by opening up the $F_a-C-C-O$ dihedral angle of our molecular model (see below) by 2°, as the calculated values were $\Delta A = -20.1$ MHz, $\Delta B = -10.19$ MHz and $\Delta C = -4.12$ MHz, respectively. This indicates that

Table 3. Rotational constants for vibrationally excited states^a of $\text{CHF}_2\text{CH}_2\text{OH}$.

Vib. state	First ex. C–C tors.	Second ex. C–C tors.	Third ex. C–C tors.	Low skeletal bending modes	
A_v (MHz)	9030.87(24)	9004.54(50)	8983.8(45)	9083.10(28)	9028.24(48)
B_v (MHz)	3739.0625(70)	3733.969(20)	3729.18(14)	3746.7274(94)	3732.143(15)
C_v (MHz)	2854.8745(95)	2852.196(23)	2849.74(30)	2854.770(12)	2853.045(22)
Δ_J (kHz)	0.95(12)	1.0(3)	-5.2(36)	0.66(16)	0.0(28)
Δ_{JK} (kHz)	7.57(81)	4.5(16)	^b	8.6(85)	^b
Number of transitions	18	12	6	15	9
rms (MHz)	0.06	0.12	0.49	0.07	0.09

^aUncertainties represent one standard deviation. Δ_K , δ_J and δ_K fixed at zero in least-squares fit. ^bFixed at zero in least squares fit.

Table 4. Stark coefficients and dipole moment of CHF₂CH₂OH.^a

Transition		$\Delta\nu/E^2$ (MHz V ⁻² cm ²) × 10 ⁶	
		Obs.	Calc.
3 _{2,2} → 4 _{2,3}	M = 1	4.51(5)	4.47
	M = 2	17.8(2)	17.9
	M = 3	40.1(6)	40.3
3 _{1,2} → 4 _{1,3}	M = 0	-0.098(2)	-0.096
	M = 1	-0.183(2)	-0.184
	M = 2	-0.430(4)	-0.446
	M = 3	-0.948(12)	-0.882

$\mu_a = 0.608(7)$ D; $\mu_b = 0.282(12)$ D; $\mu_c = 0.163(40)$ D; $\mu_{tot} = 0.690(20)$ D

^aUncertainties represent one standard deviation.

the C–C torsion is somewhat more complicated than a simple rotation about the C–C bond.

The second and third excited states of the C–C torsional mode were also identified. The progressive changes of the rotational constants upon excitation are quite smooth indicating that this mode is fairly harmonic.

The two excited states of columns 5 and 6 of Table 3 are presumably low-frequency bending modes involving the heavy atoms as rather large changes of the rotational constants occur upon excitation as compared with the ground state. The frequencies determined by relative intensity measurements were 243(20) cm⁻¹ for the state displayed in column 5 and 309(40) cm⁻¹ for that of column 6. In the IR-work,² a frequency of 240 cm⁻¹ was assigned as the strongly coupled C–F rocking mode, while a frequency of 296 cm⁻¹ was attributed to the C–O torsional mode. Model calculations assuming either a pure C–F rocking mode, a pure CCF bending vibration, or a pure CCO bending frequency did not in any case reproduce the observed changes of the rotational constants. It is therefore presumed that rather extensive coupling between the low-frequency skeletal modes exists in this molecule.

Dipole moment. Stark coefficients of the transitions shown in Table 4 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 within $\mu_{OCS} = 0.71521$ D.⁷ The inverse squares of the standard deviations of the Stark coefficients of Table 4 were used as weights in the least squares fit. The

results are shown in this table.

The dipole moment components agree rather well with the predictions made above using the bond-moment method. This is independent evidence of the fact that the identified rotamer is indeed conformation I of Fig. 1. The total dipole moment of 0.690(20) D is less than 0.9 D predicted by the bond-moment method. No appreciable dipole moment enhancement as a result of hydrogen bonding is thus indicated in this case.

Searches for further conformations. After the completion of the assignment of conformation I of Fig. 1, it was noted that there was a rather rich background of unassigned very weak transitions. Some few medium intensity lines were also seen. The Stark effects of these last-mentioned absorptions were studied throughly and were found to be unresolved in all cases. Most of these transitions were modulated at comparatively low voltages indicating a sizeable dipole moment. In order to see if these lines might be impurities, gas chromatography of the sample was repeated but these transitions remained. It is therefore possible that they indeed belong to one or more unassigned high-energy conformations of the molecule, but they can, of course, also be impurities.

The fact that the hypothetical conformation II of Fig. 1 is predicted to have rather large components of the dipole moment along the *b*- and *c*-axes, spurred us to search particularly carefully in regions where intense low *J* *R*-branch *b*- and *c*-type transitions were predicted since these lines were presumed to have characteristic Stark effects and be relatively insensitive to errors of the estimated rotational

constants. No such absorptions were found. The even stronger, typical *Q*-branch series whose predicted positions in the spectrum are more dependent on accurate rotational constants, were also completely missing. Comparisons of intensities of assigned and unassigned transitions, combined with dipole moment and intensity estimates, make us conclude that there is definitely less than 10 % of conformation II and it is very probable that there is even less than 5 % of this rotamer. Conformation I is thus more stable than II by at least 6 kJ/mol. Rotamers within no hydrogen bond are presumably even less stable than the hypothetical II conformation.

Deuterated species. The deuterated species, CHF₂CH₂OD, was studied mainly to determine definitely the existence of a hydrogen bond in this

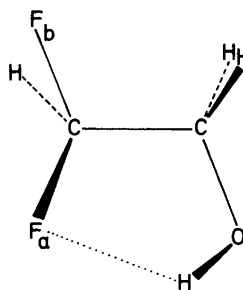


Fig. 2. Molecular model of the identified conformation I. Dots indicate hydrogen bond.

molecule. Using Kraitchman's equation,⁸ with the rotational constants of CHF₂CH₂OH and CHF₂CH₂OD, it is thus possible to locate the

Table 5. Plausible structural parameters^a and observed and calculated rotational constants of CHF₂CH₂OH and CHF₂CH₂OD.

Assumed structural parameters					
C-F (pm)	135.0	CCF(°)	109.0		
C-O (pm)	141.5	FCF(°)	109.94		
C-C (pm)	152.0	CCO(°)	112.5		
O-H (pm)	95.0	CCH(°)	109.48		
C-H (pm)	109.3	F _a CH(°)	109.71		
Fitted structural parameters					
F _a CCO(°)	61(2) from <i>syn</i>				
CCOH(°)	60(4) from <i>syn</i>				
Kraitchman's coordinates for the hydroxyl hydrogen					
	a	b	c		
Observed (pm)	195.725(10)	83.991(26)	24.505(88)		
Calculated (pm)	193.7	84.3	20.9		
Hydrogen bond parameters					
H···F _a (pm)	247.9	O···F _a (pm)	282.4		
O-H···F _a (°)	101.35	H···F _a (°)	79.02		
C-F _a O-H (°) ^b	0.40				
Sum of van der Waals radii ^c					
H···F (pm)	255	O···F (pm)	275		
CHF ₂ CH ₂ OH			CHF ₂ CH ₂ OD		
Obs.	Calc.	Diff. (%)	Obs.	Calc.	Diff. (%)
A ₀ (MHz)	9069.926	0.19	8953.160	8970.500	0.19
B ₀ (MHz)	3745.270	0.03	3640.080	3643.697	0.10
C ₀ (MHz)	2857.013	0.28	2785.948	2779.858	0.22

^aSee text. ^bAngle between C-F_a and O-H bonds. ^cSee Ref. 9.

hydroxyl hydrogen with high precision and thereby provide unique proof for the existence of a hydrogen bond.

14 transitions were measured for this molecule and the spectroscopic constants of Table 2 were determined. Kraitchman's coordinates for the hydroxyl hydrogen are shown in Table 5 and found to be in good agreement with those calculated for a model possessing an intramolecular hydrogen bond as depicted in Fig. 2.

Structure. Only six moments of inertia were determined for the conformation shown in Fig. 2. Consequently, a full molecular structure cannot be determined. Instead we restricted ourselves to fitting the $F_a\text{CCO}$ and HOCC dihedral angles. The remaining bond lengths and angles which were kept constant in the fit, were selected from recent accurate studies of related compounds as shown in Table 5. The $F_a\text{CCO}$ dihedral angle was first fitted until a satisfactory agreement between the observed and calculated rotational constants were found. The HOCC dihedral angle was then adjusted until the large *a*- and *b*-Kraitchman coordinates were satisfactorily reproduced. The $F_a\text{CCO}$ and HOCC dihedral angles were found to be 61(2) and 60(4)°, respectively. Table 5 shows that good agreement exists between the observed and calculated rotational constants. Kraitchman's coordinates of the hydroxyl hydrogen are also quite well reproduced. The error limits of the fitted dihedral angles are assumed to encompass not only random errors but uncertainties of the assumed structural parameters as well.

The hydrogen bond is characterized by having the O—H and C— F_a bonds nearly parallel which is favourable for an electrostatic stabilization between the O—H and C— F_a bond dipoles. The distance between the hydrogen atom and the fluorine atom is slightly shorter than the sum of their corresponding van der Waals radii.⁹ The $\text{H}\cdots\text{F}_a\text{C}$ angle of approximately 79° is presumably very unfavourable for covalent interaction and the O— $\text{H}\cdots\text{F}_a$ angle is about 75° from being linear which is generally preferred in intermolecular hydrogen-bonded systems. These findings for $\text{CHF}_2\text{CH}_2\text{OH}$ are very similar to the counterparts in $\text{CH}_2\text{FCH}_2\text{OH}$ ^{3,10} and $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{F}$.¹¹

DISCUSSION

The fact that rotamer I is more stable than II by more than 6 kJ/mol comes rather unexpectedly. Steric factors are hardly responsible for this since the non-bonded oxygen-fluorine distances of the hypothetical conformation II were calculated to be about 281 pm which is slightly longer than the sum of the van der Waals radii (275 pm).⁹ Dipole repulsion between the O—H bond dipole and the C—F bond dipole of the carbon-fluorine bond not involved in hydrogen bonding are presumed to be of moderate importance in II both because of their distance and the fact that they are predicted to be approximately 68° from being parallel. The C—O and C—F bond dipoles of II are also not expected to repel each other very much for similar reasons. A primitive model based on steric factors and bond dipole interactions is thus unable to explain the conformational preferences of 2,2-difluoroethanol.

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