Structural and Conformational Properties of 1,1,2,2-Tetrafluoroethyl Methyl Ether as Studied by Microwave Spectroscopy and Quantum Chemical Calculations

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The microwave spectrum of 1,1,2,2-tetrafluoroethyl methyl ether ($HCF_2CF_2OCH_3$) has been investigated in the 17.0–40.0 GHz spectral region at dry-ice temperature ($-79\,°C$). Five all-staggered rotameric forms are possible for this compound. The gas phase consists of an equilibrium mixture, in which two rotamers, denoted **Conformer I** and **Conformer III**, could be observed through their rotational spectra. The latter rotamer was found to be the most stable form of the molecule, being $0.8(4)$ kJ mol^{-1} more stable than **Conformer I**. The ground vibrational state and five vibrationally excited states belonging to three different normal modes were assigned for **III**, while only the ground vibrational state was assigned for **I**.

The microwave work has been assisted by *ab initio* computations at the MP2/6-311+ +G** (frozen core) level of theory, as well as density theory calculations at the B3LYP/6-31G* level. The structures and relative energies of the five conformers predicted in both these computational schemes are rather close to one another. Very good agreement with the experimental findings was found for rotamers **I** and **III**.

Compounds containing fluorine atoms often have interesting and sometimes unique structural and conformational properties. This has been a major reason why several studies of such compounds have been made in this laboratory.[1] The present study of 1,1,2,2-tetrafluoroethyl methyl ether (TFE) represents an extension of these investigations.

There is also another motivation for studying TFE. This molecule is a fluorinated ether. Such ethers have recently been suggested to replace freons[2] because they may have better environmental qualities. This laboratory is now involved in research focusing on the derivation of physical and chemical properties of fluorinated ethers with an eye to their emerging environmental importance.

The conformational properties of TFE is determined by its three internal axes of rotation, viz. the C1–C2, C2–O1 and O1–C3 axes (Fig. 1). If the conformation of the methyl group is assumed to be fixed in the position shown in the same figure, there should be nine all-staggered rotameric forms of the compound. Symmetry reduces this to five rotamers that are spectroscopically distinguishable. Representatives of these five forms are drawn in Fig. 1.

In **Conformers I** and **III** the C3–O1–C2–C1 link of atoms is in an *anti* conformation with a dihedral angle of about 180°, whereas this angle is near +*gauche* (60°) in **II** and **IV**, and −*gauche* (−60°) in **V**. The O1–C2–C1–H1 chain of atoms is *anti* in **I** and **II**, and +*gauche* in the remaining three rotamers.

No microwave (MW) or high-level quantum chemical studies have previously been made for TFE. MW spectroscopy is ideal for investigating complicated conformational equilibria where several polar conformers are present because of its high selectivity and specificity. The five rotamers (Fig. 1) that are possible for TFE would each possess a rather large dipole moment, which is a prerequisite for a comparatively strong MW spectrum. Another advantage is that the compound is so volatile that it has a sufficiently high vapour pressure to allow a study to be made at dry-ice temperature where intensities are significantly larger than at higher temperatures. All this makes TFE well suited for a microwave conformational investigation.

Advanced quantum chemical computations are often found to predict rather accurate rotational constants, dipole moments and relative energies of the different conformers. These calculations may thus serve as useful starting points in the spectral analysis. In addition, they

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Conformer I
0.5 kJ mol⁻¹

Conformer II
10.6 kJ mol⁻¹

Conformer III
0.0 kJ mol⁻¹
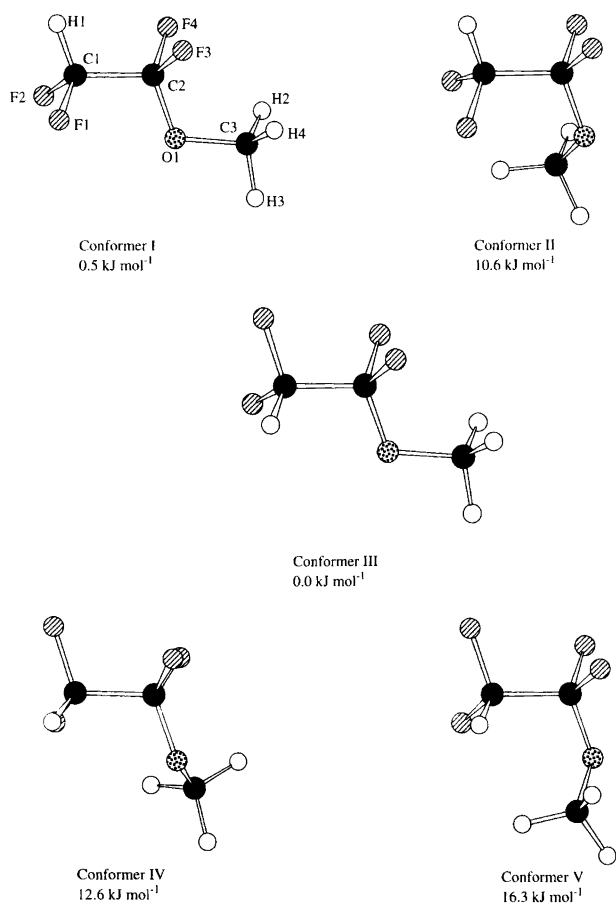
Conformer IV
12.6 kJ mol⁻¹

Conformer V
16.3 kJ mol⁻¹

Fig. 1. The five all-staggered conformations of TFE with relative energies obtained in the MP2/6-311+ +G** computations. Atom numbering is shown on **Conformer I**. The microwave spectrum of this rotamer as well as that of **Confomer III** were assigned. III was found experimentally to be 0.8(4) kJ mol⁻¹ more stable than I.

may give important information about rotamers that for whatever reason have not been assigned by MW spectroscopy, and they are therefore of interest in their own right.

Experimental

The sample utilised in this work was purchased from Fluorochem Ltd. and used as received. No impurities were seen in the MW spectrum. The MW spectrum was studied using the Oslo spectrometer, which is described in Ref. 3. The 17–40 GHz spectral region was investigated with the microwave absorption cell cooled to dry-ice temperature (194 K). The pressure was about 5 Pa when the spectra were recorded and stored electronically using computer programs written by Waal.[4] The accuracy of the frequency measurements is presumed to be better than ± 0.10 MHz. Microwave frequency – radio frequency double resonance (MWRFDR) experiments were made as outlined in Ref. 5 using the equipment described in Ref. 6.

Results and discussion

Ab initio *calculations.* The Gaussian 94 program package[7] running on the IBM RS6000 cluster in Oslo was employed in all the *ab initio* calculations. Computations were made at two different levels of theory, viz. the elaborate MP2/6-311+ +G** scheme and the much less demanding B3LYP/6-31G* level, because we wanted to compare the results obtained in these two different ways.

In the first of these computational schemes, electron correlation is included using the second-order Møller–Plesset (MP2) perturbation theory[8] with frozen-core electrons.[7] In the second procedure, density functional theory (DFT) calculations were carried out employing the B3LYP[9] method. Full geometry optimisation was made in the MP2 as well as in the B3LYP computations for all five rotamers (Fig. 1). Vibrational frequencies (not included in Table 1) were calculated only by the B3LYP procedure, because it was not possible to make MP2 computations of vibrational frequencies owing to a lack of computational resources. No imaginary vibrational frequencies were computed by the B3LYP procedure for any of the five conformers, which are thus assumed to be true minima on the potential-energy hypersurface.[10]

Only the MP2 structures (atom numbering in Fig. 1) of the five rotamers are listed in Table 1, together with some other parameters of interest. The reason for this selection is our experience that MP2/6-311+ +G** geometries and energy differences between conformers are generally found to be rather accurate.[1a] It should be mentioned, however, that the structures and relative energies obtained in the much less expensive B3LYP computations were very similar to the MP2 results.

Some of the results of this table deserve comment. **Conformers I** and **III** are predicted to be the two most stable forms of the molecule. The C3O1C2C1 link of atoms is *anti* in these two rotamers. This angle is *gauche* in **II, IV** and **V**, which would bring the lone pair electrons of O1 close to either the F3, or to the F4 atom. This might destabilise the three last-mentioned rotamers, and perhaps be a significant reason why these forms are predicted to be 10–16 kJ mol⁻¹ less stable than I and III.

The only significant difference between I and III is the conformation of the HCF₂ group. In **Conformer III** the electropositive H1 atom and the electronegative O1 atom are rather close (261 pm from the structure in Table 1). This proximity may lead to electrostatic stabilisation in III making it slightly more stable than I, which does not have this favourable interaction.

The dihedral angles take their 'usual' values in all rotamers but **IV**. In this rotamer a rather unusual C3–O1–C2–C1 dihedral angle of 92.6° is seen (Table 1) instead of about 60°. This deviation of some 30° might be explained by a repulsion between the H1 and the H2 atoms calculated to be separated by 247 pm from the structure in Table 1, compared to 240 pm, which is twice the value of the van der Waals radius of hydrogen.[11]

Table 1. Structure, rotational constants, dipole moments and energy differences of **Conformers I, II, III, IV** and **V** of 1,1,2,2-tetrafluoroethylmethyl ether as calculated at the MP2/6-311+ +G** (frozen core) level of theory.

Conformer:	I	II	III	IV	V
Distance/pm					
C1–H1	109.1	109.1	109.1	109.1	109.1
C2–C1	153.0	153.9	153.0	153.4	153.8
F1–C1	135.2	135.8	135.3	135.1	135.1
F2–C1	135.2	135.3	135.2	136.0	135.5
F3–C2	136.8	134.8	136.7	135.0	137.0
F4–C2	136.8	136.8	135.7	135.5	133.8
O1–C2	133.7	134.6	134.5	135.9	135.4
C3–O1	144.0	143.9	144.0	144.0	143.4
H2–C3	109.1	109.1	109.1	109.0	109.4
H3–C3	109.1	109.1	109.1	109.1	109.2
H4–C3	108.7	108.8	108.7	108.8	108.8
Angle[b]/°					
H1–C1–C2	110.4	110.9	111.0	110.6	112.0
H1–C1–F1	109.4	109.1	109.5	109.7	108.7
C2–C1–F1	109.4	110.1	109.0	110.1	109.2
H1–C1–F2	109.4	109.5	109.6	109.3	109.2
C2–C1–F2	109.4	108.9	109.2	109.0	109.0
F1–C1–F2	108.8	108.3	108.5	108.3	108.8
C1–C2–F3	107.9	106.8	108.2	107.0	106.1
C1–C2–F4	107.9	106.4	110.0	109.2	109.5
F3–C2–F4	105.2	107.3	105.8	107.9	107.7
C1–C2–O1	110.7	117.2	108.6	112.7	115.2
F3–C2–O1	112.4	106.7	111.8	107.4	111.3
F4–C2–O1	112.4	111.9	112.5	112.4	106.9
C2–O1–C3	115.2	116.8	115.0	117.2	115.7
O1–C3–H2	110.4	110.8	110.4	110.4	110.9
O1–C3–H3	110.4	110.7	110.3	111.3	110.9
H2–C3–H3	110.6	110.5	110.6	110.4	110.8
O1–C3–H4	105.0	104.9	105.1	104.6	105.3
H2–C3–H4	110.2	110.0	110.2	110.0	109.2
H3–C3–H4	110.2	110.0	110.2	110.1	109.5
Dihedral angle[b]/°					
F3–C2–C1–H1	56.6	48.8	−63.9	−59.7	−55.3
F3–C2–C1–F1	177.1	169.6	56.7	61.6	65.1
F3–C2–C1–F2	−63.8	−71.8	−184.9	−179.8	−176.2
F4–C2–C1–H1	−56.6	−65.6	181.0	183.7	188.8
F4–C2–C1–F1	63.8	55.2	−58.3	−54.9	−50.8
F4–C2–C1–F2	−177.1	−186.2	60.0	63.6	67.9
O1–C2–C1–H1	180.0	168.4	57.6	58.1	68.3
O1–C2–C1–F1	−59.6	−70.9	178.2	179.4	188.7
O1–C2–C1–F2	59.6	47.8	−63.4	−62.0	−52.6
C3–O1–C2–C1	180.0	61.4	177.9	92.6	−57.7
C3–O1–C2–F3	−59.2	−179.0	−62.8	−149.8	63.0
C3–O1–C2–F4	59.3	−61.9	56.0	−31.4	180.4
H2–C3–O1–C2	61.3	46.0	58.6	66.5	74.5
H3–C3–O1–C2	−61.3	−76.8	−63.9	−56.4	−49.1
H4–C3–O1–C2	180.0	164.6	177.4	184.9	192.5
Rotational constants/MHz					
A	2915.1	2326.0	3324.4	2765.9	2674.9
B	1592.6	1994.1	1612.0	1895.0	1838.0
C	1537.1	1697.3	1376.5	1445.4	1520.4
Dipole moment components[c] and total dipole moment/10^{-30} C m					
μ_a	4.00	0.80	9.27	6.47	8.74
μ_b	5.10	4.83	1.76	5.37	7.91
μ_c	0.00	2.57	5.50	3.84	8.81
μ_{tot}	6.50	5.50	10.94	9.24	14.71
Energy difference[d,e]/kJ mol^{-1}					
	0.49	10.62	0.00	12.59	16.31

[a]Atom numbering is given in Fig. 1.[6] [b]Measured from syn=0°. Clockwise rotation corresponds to a positive dihedral angle. [c]Along the principal inertial axes. 1 debye = 3.33564 × 10^{-30} C m. [d]Relative to **Conformer III**. [e]Total energy obtained in the MP2/6-311+ +G** computations: −1549 483.15 kJ mol^{-1}.

A smaller value for this dihedral angle would have brought the two hydrogen atoms into closer proximity, presumably resulting in increased repulsion.

All bond angles and all bond lengths but one have their 'normal' values in the five conformations. The exception is the O1–C2 bond length, which is as much as about 10 pm shorter than the C3–O1 bond length in each of the five rotamers. A similar finding[12] has been made for the F_3C–O and O–CH_3 bond lengths in the case of F_3COCH_3 and explained[12] as a result of the anomeric effect which produces a significant double bond character in the F_3C–O bond.

MW spectrum and assignment of the ground vibrational state of Conformer III. The microwave spectrum of TFE is dense. The large majority of lines are rather weak even at dry-ice temperature in spite of the fact that all five rotamers are predicted (Table 1) to be rather polar. The weakness is undoubtedly a result of an unfavourable Boltzmann factor for each transition, as a result of small rotational constants and many low-frequency normal vibrational modes.

The quantum chemical computations above indicate that Conformer III is the preferred form of the molecule. The largest dipole moment component of this rotamer is μ_a (Table 1). Searches were first made for the strong ^aR-branch transitions using the rotational constants obtained in the MP2 computations as the starting point. These transitions were soon identified close to their predicted frequencies.

The second largest dipole moment component is μ_c. Searches were next made for the c-type Q-branch lines which are the strongest ones of this type of transition. A series of rather weak lines were found close to their predicted frequencies and assigned as the ^cQ-transitions. A few selected transitions are listed in Table 2.*

A total of about 160 transitions were ultimately assigned for the ground vibrational state, 148 of which were used to determine the spectroscopic constants (A-reduction, I^r-representation)[13] shown in Table 3. The maximum value of J was 39. Transitions with higher J-values were searched for, but could not be assigned presumably because they are too weak owing to an unfavourable Boltzmann factor. All quartic centrifugal distortion constants as well as one sextic constant were used in the least-squares fitting procedure. No dipole moment could be determined because the low-J lines are too weak to allow quantitative measurements of the Stark effect to be made.

Vibrationally excited states of III. The a-type R-branch ground state transitions were accompanied by a series of

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*The full spectra of the two conformers assigned in this work are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Optical Technology Division, Bldg. 221, Rm B208, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 2. Selected transitions from the MW spectrum of the ground vibrational state of **Conformer III** of $HCF_2CF_2OCH_3$.

Transition:			Observed frequency[a]/ MHz	Obs. – calc. freq./ MHz
$J'_{K'_{-1},K'_{+1}}$	←	$J''_{K''_{-1},K''_{+1}}$		
$6_{1,5}$	←	$5_{1,4}$	18 397.73	−0.15
$6_{5,2}$	←	$5_{5,1}$	17 967.33	0.17
$6_{5,1}$	←	$5_{5,0}$	17 967.33	0.19
$8_{0,8}$	←	$7_{0,7}$	22 757.75	−0.15
$8_{2,7}$	←	$7_{1,7}$	32 581.10	−0.04
$8_{3,6}$	←	$7_{2,6}$	33 883.87	0.15
$9_{1,8}$	←	$8_{1,7}$	27 040.43	0.10
$9_{6,4}$	←	$9_{6,3}$	26 977.47	0.04
$9_{6,3}$	←	$9_{6,2}$	26 977.47	0.00
$10_{4,6}$	←	$9_{4,5}$	30 192.21	−0.01
$11_{1,10}$	←	$10_{1,9}$	32 517.90	−0.05
$11_{4,8}$	←	$10_{4,7}$	33 126.62	−0.04
$11_{7,4}$	←	$10_{7,3}$	32 980.48	0.00
$11_{7,5}$	←	$10_{7,4}$	32 980.48	0.01
$12_{8,4}$	←	$11_{8,3}$	35 968.00	0.02
$12_{8,5}$	←	$11_{8,4}$	35 968.00	0.02
$13_{11,2}$	←	$12_{11,1}$	38 922.61	−0.07
$13_{11,3}$	←	$12_{11,2}$	38 922.61	−0.07
$14_{9,5}$	←	$14_{8,7}$	31 182.39	0.08
$16_{9,8}$	←	$16_{8,8}$	31 087.75	0.04
$19_{6,13}$	←	$19_{5,15}$	20 109.81	0.14
$20_{10,10}$	←	$20_{9,12}$	34 607.69	−0.18
$23_{7,16}$	←	$23_{6,18}$	23 221.07	−0.08
$24_{8,17}$	←	$24_{7,17}$	25 286.79	0.20
$27_{9,18}$	←	$27_{8,20}$	29 585.10	0.18
$30_{10,21}$	←	$30_{9,21}$	32 706.28	−0.17
$34_{10,24}$	←	$34_{9,26}$	32 279.40	0.02
$39_{10,29}$	←	$39_{9,31}$	34 811.33	−0.01

[a] ±0.10 MHz.

transitions presumably belonging to vibrationally excited states of III. Five excited states belonging to three different normal vibrational modes were assigned; their spectroscopic constants are listed in Table 3. ^cQ-lines were searched for but not found, presumably because they are too weak to make definite assignments. Only Δ_J and Δ_{JK} were varied in the least squares fit in the case of the vibrationally excited states. The remaining quartic constants were kept constant at the ground-state values.

The most intense excited state has about 55% of the intensity of the ground vibrational state at 194 K. Its frequency was determined to be $81(15)\ cm^{-1}$ by relative intensity measurements made largely as described in Ref. 14. This should be compared with $61\ cm^{-1}$ found in the B3LYP calculations (not given in Table 1) for the torsion around the C1–C2 bond. Two further successively excited states of this fundamental were assigned as indicated in Table 3. The changes of the rotational constants upon successive excitations of this mode are quite constant, as can be seen in the same table. This is typical for a harmonic vibration.[15]

Another excited state (Table 3) is assumed to be the first excited state of the C2–O1 torsional vibration, or perhaps a low-frequency bending vibration. The intensity of this excited state was approximately 16% of the intensity of the ground vibrational state resulting in a

Table 3. Spectroscopic constants[a,b] of the ground and vibrationally excited states of **Conformer III** of HCF$_2$CF$_2$OCH$_3$.

Vibrational state:	Ground vibrational state	1st excited C–C tors. vibration	2nd excited lowest C–C tors. vibration	3rd excited C–C tors. vibration	1st excited C2–O1 tors. vibration[f]	1st excited low bending vibration[f]
No. of transitions:	136	64	66	58	63	27
R.m.s. dev.[c]/MHz:	0.104	0.094	0.111	0.096	0.103	0.139
A_v/MHz	3337.909 9(48)	3334.67(11)	3331.52(15)	3328.58(13)	3329.775(89)	3350.06(19)
B_v/MHz	1609.088 1(19)	1605.974 5(38)	1603.060 4(59)	1600.102 7(48)	1609.901 4(34)	1608.332 1(69)
C_v/MHz	1376.283 6(19)	1376.586 8(45)	1376.895 5(63)	1377.265 7(55)	1376.791 8(39)	1375.615 7(78)
Δ_J/kHz	0.156 5(79)	0.161 0(94)	0.184(12)	0.153(10)	0.141(11)	0.100(28)
Δ_{JK}/kHz	0.298(12)	0.304(18)	0.289(23)	0.286(20)	0.261(21)	0.198(62)
Δ_K/kHz	0.531(29)	0.531[d]	0.531[d]	0.531[d]	0.531[d]	0.531[d]
δ_J/kHz	0.0103(13)	0.0103[d]	0.0103[d]	0.0103[d]	0.0103[d]	0.0103[d]
δ_K/kHz	−0.151(40)	−0.151[d]	−0.151[d]	−0.151[d]	−0.151[d]	−0.151[d]
Φ_{JK}[e]/Hz	0.0284(86)	0.0[d]	0.0[d]	0.0[d]	0.0[d]	0.0[d]

[a] A–reduction, I[r]–representation.[16] [b] Uncertainties represent one standard deviation. [c] Root-mean-square deviation. [d] Kept constant at this value in the least-squares fit. [e] Further sextic constants preset at zero. [f] Tentative assignment.

frequency of 208(30) cm^{-1}. The final excited state is assumed to be a low-frequency bending mode. It frequency was determined to be ca. 243 cm^{-1} by relative intensity measurements.

MW spectrum and assignment of the ground vibrational state of I. The *ab initio* calculations above indicate that **Conformer I** is the second most stable form of TFE predicted to be 0.5 kJ mol^{-1} less stable than **III**. **Conformer I** is likely to have sizeable components of the dipole moment along *a*- and *b*-inertial axes (Table 1).

Searches were first made for the $J = 10 \leftarrow 9$ and $J = 9 \leftarrow 8$ ^aR pile-ups at a low Stark voltage (ca. 100 V cm^{-1}). These rather weak pile-up lines were immediately found using the *ab initio* rotational constants (Table 1) to predict their positions. A full assignment was made using the MWRFDR technique.[5,6] Searches for *b*-type lines were then made, but they were not found presumably because they are too weak. The spectrum is shown in Table 4. Twenty-seven transitions were used to derive the spectroscopic constants shown in Table 5. It was not possible to make definite assignments of vibrationally excited state in this weak spectrum.

Searches for further conformations. The above assignments include a total of about 500 transitions in the 17–40 GHz region. All the strongest transitions seen in the MW spectrum, the majority of the lines of intermediate intensity, as well as many weak lines have been assigned.

The fact that each of these five rotamers are predicted to possess sizeable dipole moments (Table 1) as well as the observation that no strong unassigned lines remain, is evidence that additional polar unassigned forms must have relatively high energies compared to the energy of **III**. Our conservative estimate is that further conformer(s), i.e. **II**, **IV** and **V**, are at least 3 kJ mol^{-1} less stable than **III**. This estimate agrees with the theoretical predictions in Table 4, which in fact give a considerably higher energy difference (10–16 kJ mol^{-1}).

Table 4. The MW spectrum of the ground vibrational state of **Conformer I** of HCF$_2$CF$_2$OCH$_3$.

Transition: $J'_{K_{-1},K_{+1}}$	←	$J''_{K_{-1},K_{+1}}$	Observed frequency[a]/ MHz	Obs.–calc. freq./ MHz
$6_{1,6}$	←	$5_{1,5}$	18 607.17	0.12
$7_{1,6}$	←	$6_{1,5}$	22 061.55	−0.09
$8_{0,8}$	←	$7_{0,7}$	24 916.29	0.08
$8_{1,7}$	←	$7_{1,6}$	25 204.33	−0.13
$8_{2,6}$	←	$7_{2,5}$	24 713.52	−0.08
$8_{2,7}$	←	$7_{2,6}$	25 127.09	0.24
$8_{5,3}$	←	$7_{5,2}$	25 037.37	−0.19
$8_{5,4}$	←	$7_{5,3}$	25 037.37	−0.18
$9_{2,7}$	←	$8_{2,6}$	28 289.70	0.03
$9_{2,8}$	←	$8_{2,7}$	28 132.96	0.00
$9_{6,3}$	←	$8_{6,2}$	28 166.28	−0.01
$9_{6,4}$	←	$8_{6,3}$	28 166.28	−0.01
$10_{1,9}$	←	$9_{1,8}$	31 477.17	0.09
$10_{2,8}$	←	$9_{2,7}$	31 456.05	0.22
$10_{2,9}$	←	$9_{2,8}$	31 251.11	−0.01
$10_{3,7}$	←	$9_{3,6}$	31 331.37	0.08
$10_{5,5}$	←	$9_{5,4}$	31 300.36	−0.03
$10_{5,6}$	←	$9_{5,5}$	31 300.36	−0.02
$10_{7,3}$	←	$9_{7,2}$	31 295.03	−0.06
$10_{7,4}$	←	$9_{7,3}$	31 295.03	−0.06
$11_{2,9}$	←	$10_{2,8}$	34 623.49	−0.05
$11_{3,8}$	←	$10_{3,7}$	34 476.75	0.12
$11_{5,6}$	←	$10_{5,5}$	34 432.83	0.19
$11_{5,7}$	←	$10_{5,6}$	34 432.83	0.21
$12_{4,8}$	←	$11_{4,7}$	37 577.39	−0.13
$12_{6,7}$	←	$11_{6,6}$	37 559.93	0.08
$12_{6,7}$	←	$11_{6,6}$	37 559.93	0.08

[a] Comments as for Table 2.

Energy differences. The energy difference between the ground vibrational states of **I** and **III** was found to be 0.8(4) kJ mol^{-1} (with **III** as the more stable) by relative intensity measurements which were made as described in Ref. 14. The uncertainty given here is one standard deviation, which has been estimated taking experimental uncertainties as well as the uncertainty of the dipole moments into consideration. The B3LYP dipole moment components $\mu_a = 3.74$ and $\mu_a = 7.47 \times 10^{-30}$ C m for **I**

Table 5. Spectroscopic constants[a,b] of the ground vibrational state of **Conformer I** of $HCF_2CF_2OCH_3$.

Vibrational state:	Ground vibrational state
No. of transitions:	58
R.m.s. dev.[c]/MHz:	0.122
A_v/MHz	2928.66(67)
B_v/MHz	1590.2537(60)
C_v/MHz	1538.6061(61)
Δ_J/kHz	0.163(15)
Δ_{JK}[d]/kHz	0.404(36)

[a-c]Comments as for Table 2. [d]Further centrifugal distortion constants pre-set at zero.

and III, respectively, were employed, because the B3LYP procedure usually gives more reliable dipole moments than the MP2 procedure.[1a,b] The statistical weight of III was assumed to be twice that of I because a mirror image form exists for the former rotamer. The experimental energy difference is in excellent agreement with the MP2 value (0.5 kJ mol^{-1}; Table 1) as well as with the B3LYP result (0.7 kJ mol^{-1}; not given in Table 1).

Structure. The observed (Tables 3 and 5) and MP2 rotational constants (Table 1) of **Conformers I and III** are in excellent agreement. It is believed that this is not fortuitous, but in fact reflects the fact that the MP2/6-311 + +G** calculations are capable of predicting accurate molecular geometries. The structures of **I** and **III** given in Table 1 are therefore suggested as *plausible* structures for these two conformers of TFE. Any full experimental structures that might be determined in the future are expected to be very close to those shown in Table 1.

References

1. Recent examples include: (a) 1,2-difluoropropane; Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand.* 52 (1988) 296; (b) 1,3-difluoropropane; Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 51* (1987) 1058; (c) 2(fluormethyl)pyridine; C. Moberg, H. Adolfsson, K. Wärnmark, P.-O. Norrby, K.-M. Marstokk and Møllendal, H. *Chem. Eur. J. 2* (1996) 516; (d) oxalyl fluoride; Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 49* (1995) 172; (e) 2,2,3,3,-tetrafluoro-1-propanol; K.-M. Marstokk and Møllendal, H. *Acta Chem. Scand. 47* (1993) 281.
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