

Microwave Spectrum, Intramolecular Hydrogen Bonding, Conformational Properties and Quantum Chemical Calculations for 3,3,3-Trifluoropropanol

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Marstokk, K.-M. and Møllendal, H., 1999. Microwave Spectrum, Intramolecular Hydrogen Bonding, Conformational Properties and Quantum Chemical Calculations for 3,3,3-Trifluoropropanol. – Acta Chem. Scand. 53: 202–208. © Acta Chemica Scandinavica 1999.

The microwave spectrum of 3,3,3-trifluoropropanol ($\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$) has been investigated in the 7.5–60 GHz spectral region at a temperature of approximately -30°C . Five all-staggered rotameric forms are possible for this compound. Two of these conformers denoted **Gg**– and **Aa** were assigned. **Gg**– is stabilised by a six-membered intramolecular hydrogen bond formed between one of the fluorine atoms and the hydrogen atom of the hydroxyl group. No such interaction is possible in **Aa**, in which both the O–C–C–C and H–O–C–C chains of atoms is in the *anti* conformation. The internal hydrogen bond is weak, since the **Gg**– rotamer is only $3.5(10)\text{ kJ mol}^{-1}$ more stable than **Aa**. The weak intramolecular hydrogen bond is also evident from the gas-phase infrared spectrum of the O–H stretching vibration.

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 structural parameters predicted in both these computational schemes are similar. Both methods predict that **Gg**– is several kJ mol^{-1} more stable than other rotameric forms, in agreement with the present experimental findings.

Molecules containing intramolecular hydrogen (H) bonds has for a long time been the main research interest of this laboratory.¹ The fluorine atom is an interesting proton acceptor, and several studies have been made of alcohols containing this atom. Studies² of the simplest member, 2-fluoroethanol ($\text{HOCH}_2\text{CH}_2\text{F}$), have shown that the H-bonded heavy-atom *gauche* conformer is favoured to a remarkable extent of more than 8 kJ mol^{-1} . 1-Fluoro-2-propanol³ ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{F}$), 2-fluoropropanol⁴ ($\text{CH}_3\text{CHFCH}_2\text{OH}$), 2,2-Difluoroethanol⁵ ($\text{HOCH}_2\text{CHF}_2$) and 2,2,2-trifluoroethanol⁶ (HOCH_2CF_3) are also stabilised by five-membered internal H bonds where one of the fluorine atoms is involved. H bonding alone is hardly responsible for the high stability seen for the H-bonded conformers of 2-fluoro-substituted ethanols. The so-called *gauche* effect⁷ is likely to be more important than H bonding in these compounds.²

Three different conformers were identified in the microwave spectrum of 3-fluoropropanol⁸ ($\text{HOCH}_2\text{CH}_2\text{CH}_2\text{F}$). One of these contains a six-membered intramolecular H bond. This rotamer is not

the most stable form of this molecule. In fact, a conformer not possessing internal H-bonding is favoured.⁸ This shows that the six-membered H bond in this molecule is rather weak.

In another compound, 2,2,3,3-tetrafluoropropanol ($\text{HOCH}_2\text{CF}_2\text{CF}_2\text{H}$), it is possible to form two different intramolecular H bonds, a five-membered one to one of the fluorine atoms in the 2-position, or alternatively a six-membered bond to one fluorine atom in the 3-position. It turns out⁹ that a conformer with a five-membered ring is preferred, presumably because the *gauche* effect⁷ is of overriding importance. The present study of 3,3,3-trifluoropropanol (TFP) represents an extension of these investigations of fluorinated propanols.

Fluoro-containing alcohols such as TFP are candidates that have been suggested to replace freons¹⁰ 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 alcohols and ethers¹¹ with an eye to their emerging environmental importance.

The conformational properties of TFP are determined by its three internal axes of rotation, viz. the C1–O1, C1–C2 and C2–C3 (Fig. 1) axes. If the conformation of

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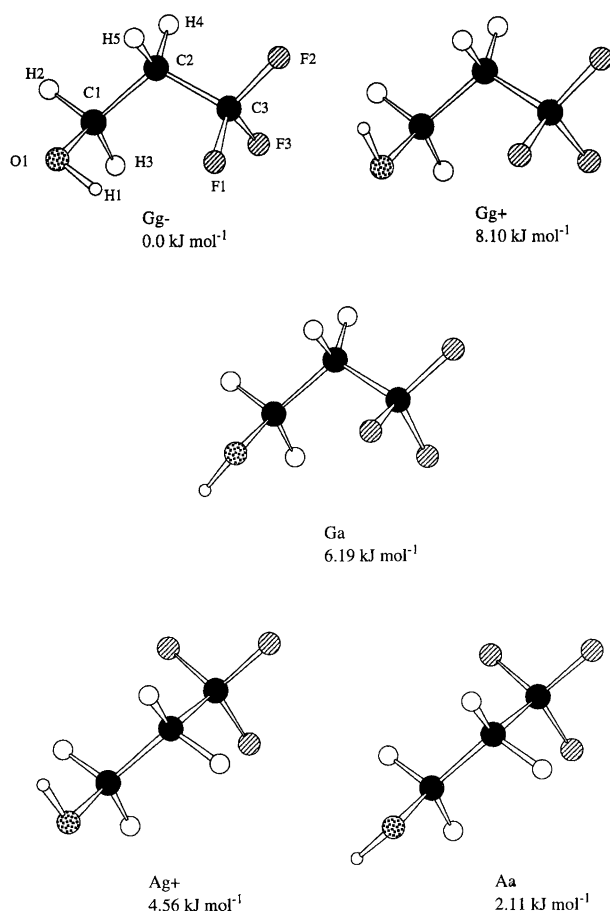


Fig. 1. The five all-staggered conformations of TFP with relative energies obtained in the MP2/6-311++G** (frozen core) computations. Atom numbering is shown on the **Gg**− conformer. The microwave spectrum of this rotamer as well as that of **Aa** was assigned. **Gg**− was found experimentally to be 3.5(10) kJ mol^{−1} more stable than **Aa**.

the CF₃ 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 **Ag**+ and **Aa** the O1–C1–C2–C3 link of atoms is in an *anti* conformation with a dihedral angle of about 180°, whereas this angle is *+gauche* (roughly +60° *syn*) in **Gg**−, **Gg**+ and **Ga**. The H1–O1–C1–C2 chain of atoms is *anti* in **Ga** and **Aa**, and *+gauche* in **Gg**+ and **Ag**+, but *−gauche* in **Gg**−. Mirror image forms exist for all rotamers except **Aa**. The H1 and F1 atoms are brought into close proximity in **Gg**−, allowing a six-membered intramolecular H bond to be formed. This interaction is of course excluded in the other four rotamers.

No microwave (MW) or high-level quantum chemical studies have previously been made for TFP. 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 TFP 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 at a relatively low temperature where intensities are significantly larger than at higher temperatures. All this makes TFP 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 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 as well.

Experimental

The sample utilised in this work was purchased from Fluorochem Ltd. It was specified to be more than 99% pure and was used as received. The MW spectrum was studied using the Oslo spectrometer which is described in Ref. 12. Most measurements were made in the 7.5–27 GHz region. Selected parts of the 27–60 GHz interval were also studied. Radiofrequency–microwave-frequency double resonance (RFMWDR) experiments were carried out as described in Ref. 13 using the equipment mentioned in Ref. 14. The microwave absorption cell was cooled to about −30 °C during the experiments. The pressure was roughly 5 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.¹⁵ The accuracy of the frequency measurements is presumed to be better than ±0.12 MHz.

The infrared spectrum was taken at room temperature using a Bruker IFS66 spectrometer. A 10-cm gas cell was employed. The pressure of the gas was roughly 600 Pa. The resolution was 1.0 cm^{−1}.

Results and discussion

Ab initio calculations. The Gaussian 94 program package¹⁶ running on the IBM RS6000 cluster in Oslo was employed in all the *ab initio* calculations. Two different computational schemes, MP2/6-311++G** and B3LYP/6-31G*, were employed.

In the first of these computational schemes, electron correlation is included using the second-order Møller–Plesset (MP2) perturbation theory¹⁷ with frozen-core electrons.¹⁶ In the second procedure, density functional theory (DFT) calculations were carried out employing the B3LYP¹⁸ method. Full geometry optimisation was made in the MP2 as well as in the B3LYP computations for all five rotamers (Fig. 1). Vibrational frequencies

Table 1. Structure,^a rotational constants, dipole moment and energy differences of conformers **Gg**−, **Gg**+, **Ga**, **Ag** + and **Aa** of CF₃CH₂CH₂OH as calculated at the MP2/6-311++G** (frozen core) level of theory.

	Gg −	Gg +	Ga	Ag +	Aa
Bond length/pm					
O1–H1	96.1	96.2	96.1	96.1	96.1
C1–O1	141.8	141.7	142.2	142.1	142.4
C1–H2	109.1	109.8	109.7	109.6	109.6
C1–H3	109.7	109.1	109.6	109.1	109.6
C1–C2	153.0	152.7	152.0	152.9	152.1
C2–H4	109.4	109.4	109.4	109.4	109.3
C2–H5	109.3	109.5	109.3	109.3	109.3
C2–C3	150.4	150.8	150.8	150.4	150.2
C3–F1	135.6	134.2	133.8	134.8	134.9
C3–F2	134.3	135.1	135.1	134.6	134.5
C3–F3	134.7	134.6	135.2	134.9	134.9
Angle/°					
H1–O1–C1	107.7	107.9	107.6	107.5	107.5
O1–C1–H2	105.6	111.3	110.9	111.3	111.1
O1–C1–H3	111.5	105.7	111.4	105.8	111.2
O1–C1–C2	113.1	113.8	108.1	110.9	105.8
C1–C2–H4	110.3	109.0	109.4	110.6	109.9
C1–C2–H5	109.6	111.1	110.0	109.7	109.9
C1–C2–C3	113.3	114.6	114.4	112.9	112.7
C2–C3–F1	111.8	112.9	113.5	111.8	111.9
C2–C3–F2	112.0	110.5	110.5	111.7	111.6
C2–C3–F3	111.7	111.7	111.3	111.7	111.9
Dihedral angle ^b /°					
H1–O1–C1–H2	177.7	−64.4	68.8	−57.0	60.6
H1–O1–C1–H3	60.7	178.6	−52.1	−174.5	−60.8
H1–O1–C1–C2	−63.9	57.9	−172.8	66.2	179.9
O1–C1–C2–H4	−162.7	−178.5	−168.5	−62.6	−59.8
O1–C1–C2–H5	−43.0	−60.0	−49.4	56.9	59.6
O1–C1–C2–C3	77.9	61.9	72.3	177.4	179.9
C1–C2–C3–F1	−55.8	−70.4	−66.3	−59.2	−60.0
C1–C2–C3–F2	−176.0	170.0	173.3	−179.4	179.9
C1–C2–C3–F3	63.5	50.9	54.8	60.7	59.9
Rotational constants/MHz					
A	4542.8	4472.8	4505.3	4999.8	5002.4
B	1778.2	1813.2	1798.6	1452.5	1467.2
C	1699.5	1727.6	1716.2	1435.2	1444.6
Dipole moment ^c components and total dipole moment/10 ^{−30} C m					
μ _a	1.10	5.57	9.84	4.27	8.07
μ _b	5.70	8.51	8.32	4.10	2.93
μ _c	0.80	7.53	1.07	4.07	0.00
μ _{tot}	5.83	12.64	12.91	7.17	8.61
Energy difference ^{d,e} /kJ mol ^{−1}					
	0.0	8.10	6.19	4.56	2.11

^aAtom numbering is given in Fig. 1. ^bMeasured from *syn* = 0°. Clockwise rotation corresponds to positive dihedral angle. ^c1 debye = 3.335 64 × 10^{−30} C m. ^dRelative to **Gg**−. ^eTotal energy obtained in the MP2/6-311++G** computations: −1 289 399.83 kJ mol^{−1}.

(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.¹⁹

The MP2 and B3LYP structures were fairly similar. The largest differences were seen for the dihedral angles (up to 6°). The total dipole moments predicted by B3LYP calculations were considerably smaller than their MP2 counterparts. Both computational schemes predict that **Gg**− is the most stable form of the molecule. However, the B3LYP energy differences are 1–5 kJ mol^{−1} larger than the MP2 energy differences.

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.¹¹ This is also found in the present case (see below).

Most details of the geometries of the five rotamers in Table 1 are 'normal'. However, it should be mentioned that the C2–C3 bond length is calculated to be short (150–151 pm) in the various rotamers. This is similar to that found in H₃C–CF₃, where the C–C bond length is found experimentally to be 149.4(3) pm.²⁰

All five rotamers are computed to fall within a narrow energy range of about 8 kJ mol^{−1}. **Gg**−, containing an internal H bond, is computed to be the most stable form of the molecule. The H bond is likely to be weak, since this rotamer is calculated to be only 2.11 kJ mol^{−1} more stable than **Aa**, which is not stabilised by this interaction.

From the structure in Table 1 the non-bonded distance between the H1 and F1 atoms in **Gg**− is calculated to be 216 pm compared to 255 pm, which is the sum of the van der Waals radii of hydrogen and fluorine.²¹ The O1–H1...F1 angle is 128°, as much as 52° from the ideal linear position. The geometry of the H bond thus implies a moderate interaction.

MW spectrum and assignment of the ground vibrational state of Gg−. The MW spectrum of TFP is very dense, with lines occurring every few MHz throughout the entire MW range. The large majority of lines are comparatively weak at −30 °C 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 several low-frequency normal vibrational modes.

The quantum chemical computations above indicate that **Gg**− is the preferred form of the molecule. The largest dipole moment component of this rotamer is μ_b (Table 1). This component is calculated to be much larger than μ_a and μ_c.

Searches were first made for the relatively strong *K*_{−1} = 2 ← 1 series of *b**Q*-branch transitions occurring in the 7.5–14 GHz region using the rotational constants obtained in the MP2 computations to predict their approximate spectral positions. These transitions, which were the strongest ones in this spectral interval, were

soon identified. The frequencies of a large number of further *b*-type *Q*-branch transitions were then predicted and readily assigned. The maximum value of *J* was 71 for these transitions.

It should be possible to predict the frequencies of *c*-*Q*-branch lines accurately from the *b*-*Q*-lines. Futile searches were, however, made for the *c*-type *Q*-branch lines, presumably because they are too weak owing to a small μ_c (Table 1).

R-Branch transitions have to be assigned in order to determine all three rotational constants. It was not easy to find such lines, because there are few relatively strong low-*J* *b*-*R*-branch transitions. The first *R*-branch lines were ultimately assigned in a RFMWDR experiment by pumping the $6_{3,3} \leftarrow 6_{3,4}$ transition at about 2 MHz and observing the $7_{4,4} \leftarrow 6_{3,3}$ and $7_{4,3} \leftarrow 6_{3,4}$ pair of lines at about 43.9 GHz. A large number of *b*-*R* lines with a maximum value of *J*=58 were then assigned in a least-squares fitting procedure. *R*-Branch transitions with even higher *J* values than 58 were searched for, but could not be assigned presumably because they are too weak owing to an unfavourable Boltzmann factor. A few selected transitions are listed in Table 2.* A total of about 370 transitions were ultimately assigned, mostly in the 7.5–27.5 GHz region for the ground vibrational state; 325 of these were used to determine the spectroscopic constants (*A*-reduction, *I'* representation)²² shown in Table 3.

All quartic centrifugal distortion constants, as well as two sextic constants were used in the least-squares fitting procedure. No *a*- or *c*-type transitions could be assigned, although their hypothetical frequencies could presumably be accurately predicted using the spectroscopic constants in Table 3. This is in accord with the small *a*- and *c*-axis dipole moment component predicted in Table 1.

The dipole moment of this conformer could not be determined because the low-*J* lines were too weak to allow quantitative measurements.

Vibrationally excited states of Gg-. The ground-state transitions were accompanied by series of transitions presumably belonging to vibrationally excited states of *Gg*-. Two excited states belonging to the same normal vibrational mode were assigned; their spectroscopic constants are listed in Table 3.

The intensity of the first excited state was about 60% of the intensity of the ground vibrational state at 240 K. Its frequency was determined to be ca. 57 cm^{-1} by relative intensity measurements made largely as described in Ref. 23. This should be compared with 66 cm^{-1} found in the B3LYP calculations (not given in Table 1) for the lowest torsional vibration. One further excited state of

Table 2. Selected transitions from the MW spectrum of the ground vibrational state of the *Gg*- conformer of $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$.

Transition: $J_{K_{-1}, K'+1}'' \leftarrow J_{K'', K'+1}''$	Observed frequency ^a /MHz	Obs. - calc. freq./MHz
3 _{2,2} ← 2 _{1,1}	18 732.77	-0.04
5 _{2,4} ← 5 _{1,5}	9 007.18	0.07
8 _{2,7} ← 8 _{1,8}	9 864.10	0.01
10 _{1,10} ← 9 _{0,9}	35 794.53	0.03
11 _{2,10} ← 11 _{1,11}	11 104.41	0.05
14 _{3,11} ← 14 _{2,12}	12 476.33	-0.19
17 _{4,14} ← 16 _{5,11}	34 188.25	0.05
18 _{5,14} ← 18 _{4,15}	25 032.91	0.11
22 _{2,20} ← 22 _{1,21}	11 404.98	-0.01
24 _{4,20} ← 24 _{3,21}	16 435.32	-0.05
25 _{5,20} ← 25 _{4,21}	23 978.19	-0.02
29 _{4,26} ← 29 _{3,27}	21 701.42	0.21
31 _{3,29} ← 31 _{2,30}	23 701.55	0.00
34 _{2,32} ← 34 _{1,33}	24 956.12	-0.13
37 _{5,33} ← 37 _{4,34}	26 199.33	-0.20
40 _{5,36} ← 40 _{4,37}	27 353.75	0.15
46 _{5,41} ← 46 _{4,42}	23 221.07	-0.08
51 _{5,46} ← 51 _{4,47}	23 075.93	0.08
58 _{6,52} ← 58 _{5,53}	23 814.94	0.04
63 _{7,56} ← 63 _{6,57}	24 007.15	-0.15
71 _{8,63} ← 71 _{7,64}	26 719.38	-0.18
Coalescing <i>b</i> -type lines ^b		
21 ₇ ← 20 ₈	31 221.89	0.02
24 ₈ ← 23 ₉	36 081.89	0.06
27 ₁₁ ← 26 ₁₂	29 672.27	-0.16
33 ₁₄ ← 32 ₁₅	33 755.75	-0.07
41 ₁₉ ← 40 ₂₀	33 566.21	-0.02
58 ₂₉ ← 57 ₃₀	36 609.80	-0.05

^a ± 0.12 MHz. ^b The *b*-type *R*-branch pair of lines coalesce for high values of K_{-1} .

this fundamental was 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.²⁴

The next normal vibration is predicted in the B3LYP computation to have a frequency of 163 cm^{-1} and a Boltzmann factor of about 0.38 at the same temperature. Attempts to find this excited state were, however, unsuccessful, presumably because of low intensity.

MW spectrum and assignment of Aa. The *ab initio* calculations above indicate that *Aa* is the second most stable form of TFP. *Aa* is likely to have a sizeable components of the dipole moment along the *a*-inertial axis (Table 1). It is also almost a symmetrical top ($\kappa = -0.98$).

Searches were therefore first made for the characteristic *a*-*R* pile-ups occurring in the 25–40 GHz region at a low Stark voltage (ca. 100 V cm^{-1}). These pile-up lines were soon found using the *ab initio* rotational constants (Table 1) to predict their positions. Several assignments were then confirmed using the RFMWDR technique.^{13,14} It was difficult to assign the low- K_{-1} lines because they are comparatively weak and are frequently overlapped

* 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 3. Spectroscopic constants^{a,b} of the ground and vibrationally excited states of the **Gg**– conformer of CF₃CH₂CH₂OH.

Vibrational state:	Ground vibrational state	1st ex. tors. vibration	2nd ex. lowest. tors. vibration
No. of transitions:	325	285	180
R.m.s. dev. ^c /MHz:	0.093	0.110	0.115
A_v /MHz	4542.867 7(25)	4536.227 7(28)	4529.555 3(69)
B_v /MHz	1780.871 2(10)	1782.388 9(11)	1783.922 6(59)
C_v /MHz	1701.443 9(10)	1705.029 5(11)	1708.660 7(59)
Δ_J /kHz	0.355 2(11)	0.367 58(98)	0.327(37)
Δ_{JK} /kHz	2.435 9(23)	2.526 9(28)	2.662 6(40)
Δ_K /kHz	–1.643 1(91)	–1.743 9(76)	–2.34(15)
δ_J /kHz	0.030 069(29)	0.029 929(34)	0.029 660(46)
δ_K /kHz	–1.632 8(35)	–1.703 4(44)	–1.799 0(56)
Φ_J /Hz	0.000 640(92)	0.000 23(14)	0.0 ^d
Φ_{JK} ^e /Hz	0.009 07(55)	0.011 34(63)	0.011 98(84)
$J_{Q_{max}^f}$	71	71	71
$J_{R_{max}^g}$	58	55	9

^aA-reduction, I^r representation.²² ^bUncertainties represent one standard deviation. ^cRoot-mean-square deviation. ^dKept constant at this value in the least-squares fit. ^eFurther sextic centrifugal distortion constants pre-set at zero. ^fMaximum value of J for the Q -branch transitions. ^gMaximum value of J for the R -branch transitions.

by transitions belonging to the rich spectrum of **Gg**–. Selected transitions are listed in Table 4. 102 transitions were used to derive the spectroscopic constants shown in Table 5.

Two pile-up series presumably belonging to successively vibrationally excited states of the lowest torsional

Table 4. The MW spectrum of the ground vibrational state of the **Aa** conformer of CF₃CH₂CH₂OH.

Transition:		Observed frequency ^a /MHz	Obs.–calc. freq./MHz
$J_{K'-1,K'+1}^{\leftarrow}$	$J_{K''-1,K''+1}^{\leftarrow}$		
10 _{2,8}	\leftarrow 9 _{2,7}	29 079.01	–0.17
13 _{5,8}	\leftarrow 12 _{5,7}	37 784.98	0.18
13 _{5,9}	\leftarrow 12 _{5,8}	37 784.98	0.18
14 _{1,14}	\leftarrow 13 _{1,13}	40 524.91	–0.01
16 _{3,13}	\leftarrow 15 _{3,12}	46 512.69	–0.20
16 _{3,14}	\leftarrow 15 _{3,13}	46 510.31	0.00
17 _{6,11}	\leftarrow 16 _{6,10}	49 409.90	0.09
17 _{6,12}	\leftarrow 16 _{6,11}	49 409.90	0.09
17 _{12,5}	\leftarrow 16 _{12,4}	49 401.81	0.06
17 _{12,6}	\leftarrow 16 _{12,5}	49 401.81	0.06
19 _{1,19}	\leftarrow 18 _{1,18}	54 985.51	0.06
19 _{3,16}	\leftarrow 18 _{3,15}	55 239.38	0.24
19 _{3,17}	\leftarrow 18 _{3,16}	55 232.79	–0.26
19 _{8,11}	\leftarrow 18 _{8,10}	55 219.42	–0.14
19 _{8,12}	\leftarrow 18 _{8,11}	55 219.42	–0.14
19 _{11,8}	\leftarrow 18 _{11,7}	55 214.95	–0.04
19 _{11,9}	\leftarrow 18 _{11,8}	55 214.95	–0.04
19 _{14,5}	\leftarrow 18 _{14,4}	55 219.42	–0.20
19 _{14,6}	\leftarrow 18 _{14,5}	55 219.42	–0.20
20 _{5,15}	\leftarrow 19 _{5,14}	58 131.95	–0.02
20 _{5,16}	\leftarrow 19 _{5,15}	58 131.95	–0.02
20 _{7,13}	\leftarrow 19 _{7,12}	58 127.57	0.11
20 _{7,14}	\leftarrow 19 _{7,13}	58 127.57	0.11
20 _{10,10}	\leftarrow 19 _{10,9}	58 122.47	–0.05
20 _{10,11}	\leftarrow 19 _{10,10}	58 122.47	–0.05
20 _{14,6}	\leftarrow 19 _{14,5}	58 115.26	–0.04
20 _{14,7}	\leftarrow 19 _{14,6}	58 115.26	–0.04
20 _{17,3}	\leftarrow 19 _{17,2}	58 108.67	–0.08
20 _{17,4}	\leftarrow 19 _{17,3}	58 108.67	–0.08

^aComment as for Table 2.

Table 5. Spectroscopic constants^{a,b} of the ground and vibrationally excited states of the **Aa** conformer of CF₃CH₂CH₂OH.

Vibrational state:	Ground vibrational state
No. of transitions:	102
R.m.s. dev. ^c /MHz:	0.117
A_v /MHz	4991(10)
B_v /MHz	1464.306 1(60)
C_v /MHz	1442.230 2(50)
Δ_J /kHz	0.098 3(29)
Δ_{JK} ^d /kHz	1.700 0(43)

^{a-c}Comments as for Table 2. ^dFurther centrifugal distortion constants pre-set at zero.

mode of this conformer were assigned. The sum of the B and C rotational constants were $B + C = 2908.7$ MHz for the first excited state, and $B + C = 2910.2$ MHz for the second excited state of this mode. The B3LYP value is 76 cm^{-1} for this vibration. Semi-quantitative relative intensity measurements made for the ^a R pile-ups are in agreement with this frequency.

Searches for further conformations. The above assignments include a total of about 1000 transitions. However, a much larger number of lines were observed. Many of these unassigned lines undoubtedly belong to vibrationally excited states of **Gg**– in particular, and to a lesser extent to **Aa**.

Each of the three remaining rotamers **Gg**+, **Ga** and **Ag**+ are predicted to possess sizeable dipole moment components along the a -axis and to be rather prolate asymmetrical tops. The spectrum of each of them was predicted using the rotational constants appearing in Table 1. Rather extensive searches were carried out for them in the 35–60 GHz region using Stark spectroscopy as well as the RFMWDR technique, however with a negative result. It is felt that any one of these three

hypothetical rotamers has considerably higher energies than those of **Gg**– and **Aa**, in agreement with the MP2 and B3LYP predictions.

Energy differences. It was not easy to find relatively strong and isolated transitions belonging to **Aa** that could be used for intensity comparison with strong and isolated transitions of **Gg**–. It was therefore not possible to determine accurately the energy difference between **Aa** and **Gg**–. However, some semi-quantitative measurements could be made as described in Ref. 23. The energy difference between the ground vibrational states of **Gg**– and **Aa** was found to be 3.5 kJ mol^{-1} , with **Gg**– as the most stable. One standard deviation was estimated to be $\pm 1.0 \text{ kJ mol}^{-1}$, taking uncertainties of the dipole moment and other factors into account. The statistical weight of **Gg**– was assumed to be twice that of **Aa**. The experimental energy difference is in agreement with the MP2 value (2.11 kJ mol^{-1}), but somewhat lower than the B3LYP result (6.86 kJ mol^{-1}).

Infrared spectrum and the strength of the H bond. Independent evidence for a weak H bond in **Gg**– is seen from the infrared stretching vibration of the gas shown in Fig. 2. This band has some fine structure that may be ascribed to rotational fine structure, or to the presence of more than one conformer. The maximum of this band falls at about 3672 cm^{-1} , compared to 3682 cm^{-1} seen for gaseous methanol,²⁵ which of course has no H bond.

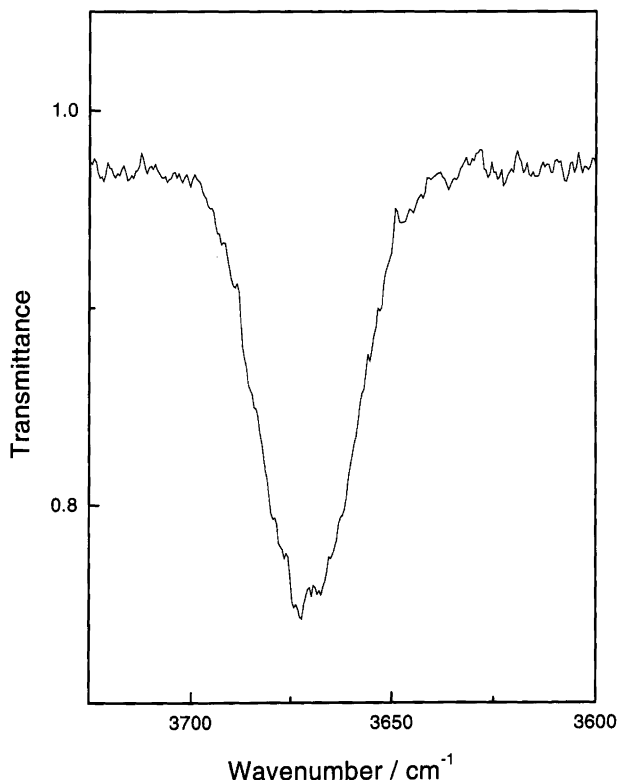


Fig. 2. The infrared spectrum of gaseous TFP in the O–H stretching region.

The typical increase in intensity and the red-shift of the O–H stretching band seen for H-bonded molecules are practically absent for the title compound. This is classical evidence for a weak internal H bond, corroborating the MW findings.

Structure. The observed (Tables 3 and 5) and MP2 rotational constants (Table 1) of **Gg**– and **Aa** 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.¹¹ The structures of **Gg**– and **Aa** given in Table 1 are suggested as plausible structures for these two conformers of TFP. Any experimental structures that might be determined in the future are expected to be close to those shown in Table 1.

Conclusions

TFP is present in the gas phase mainly as two conformers **Gg**– and **Aa**, with the former rotamer as the most stable form of the molecule. The presence of further rotameric forms cannot be completely ruled out, but large fractions of any such forms are quite unlikely.

Gg– is stabilised by a six-membered intramolecular H bond that is so weak that it represents a borderline case. This finding parallels that found for 3-fluoropropanol.⁸

MP2/6-311++G** computations are again¹¹ found to predict rotational constants for **Gg**– and **Aa** that are in excellent agreement with experiment, presumably because this computational procedure is capable of producing accurate molecular geometries.

Acknowledgements. Anne Horn is thanked for the artwork and for assistance. This work has received support from The Research Council of Norway (Programme for Supercomputing) through a grant of computer time, and from the Environment Programme of the University of Oslo.

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Received August 21, 1998.