

# Structural and Conformational Properties of 1,1,1-Trifluoro-2-propanol Investigated by Microwave Spectroscopy and Quantum Chemical Calculations

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The microwave spectrum of 1,1,1-trifluoro-2-propanol,  $\text{CF}_3\text{CH}(\text{OH})\text{CH}_3$ , and one deuterated species,  $\text{CF}_3\text{CH}(\text{OD})\text{CH}_3$ , have been investigated in the 20.0–62.0 GHz spectral region at about  $-50^\circ\text{C}$ . The rotational spectrum of one of the three possible rotameric forms was assigned. This conformer is stabilized by an intramolecular hydrogen bond formed between the hydrogen atom of the hydroxyl group and the nearest fluorine atoms. The hydrogen bond is weak and assumed to be mainly a result of attraction between the O–H and the C–F bond dipoles, which are nearly antiparallel. The identified rotamer is at least 3 kJ/mol more stable than any other rotameric form. Two vibrationally excited states belonging to two different normal modes were assigned for this conformer, and their frequencies were determined by relative intensity measurements. The microwave work has been assisted by quantum chemical computations at the MP2/cc-pVTZ and B3LYP/6-311++G\*\* levels of theory, as well as by the infrared spectrum of the O–H stretching vibration.

## Introduction

Molecules containing intramolecular hydrogen (H) bonds have for a long time been the main research interest of this laboratory. Recent studies are found in refs 1–14. Reviews are also available.<sup>15–18</sup>

The fluorine atom is an interesting proton acceptor for H-bonds, and numerous spectroscopic<sup>1,2,14–16,19–32</sup> and electron-diffraction<sup>18,33–37</sup> studies have been made of the internal H-bonding properties of this atom. These studies have shown that the fluorine atom is a rather weak proton acceptor and that the H-bonds in which it is involved are mainly dipole–dipole interactions.

Fluorine-containing alcohols such as, for example, 1,1,1-trifluoro-2-propanol,  $\text{CF}_3\text{CH}(\text{OH})\text{CH}_3$  (TF2P), have been suggested as a replacement for Freon<sup>38,39</sup> because they are thought to have preferable environmental qualities. This laboratory is involved in research focusing on the elucidation of the physical and chemical properties of fluorinated alcohols and ethers,<sup>40</sup> with the aim of developing a greater understanding of their emerging environmental importance.

Structural studies by electron diffraction and microwave (MW) spectroscopy have been carried out for several fluoro-ethanols<sup>26,32,33</sup> and fluoropropanols.<sup>14,20,24,28,36</sup> Few studies have been conducted for fluorine-substituted 2-propanols. One example is  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{F}$ .<sup>24</sup> Two H-bonded rotamers are possible in this case, but only the conformer with the methyl and hydroxyl groups in the antiperiplanar conformation was detected.<sup>24</sup>

TF2P exists in two enantiomeric configurations, which will have identical MW spectra. The conformation of the title compound is determined by the position of the hydroxyl group (see Figure 1). There are three conformers having all-staggered

atomic arrangements. These rotamers are drawn in this figure, where the R configuration is used as model.

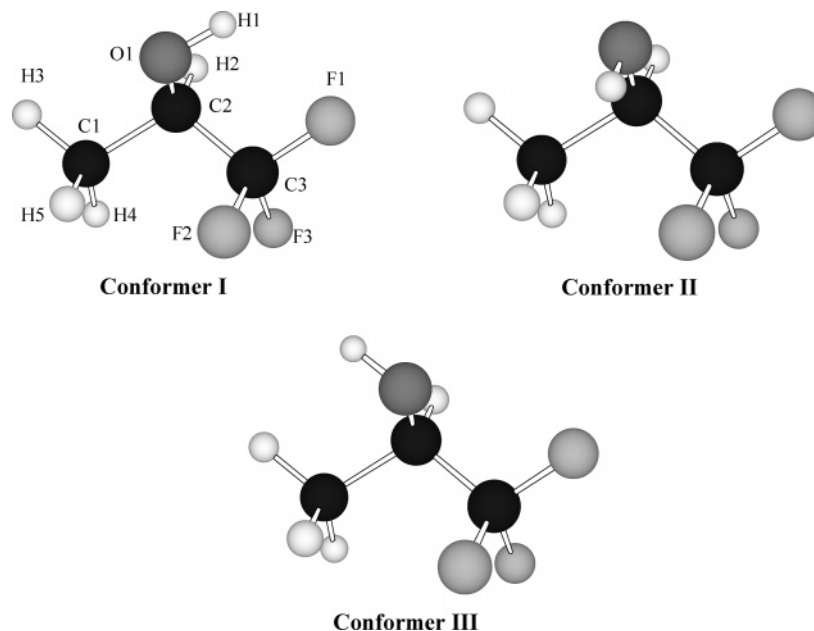
In conformer I, the H1–O1–C2–C1 link of atoms has an antiperiplanar conformation, with a dihedral angle of about  $180^\circ$  from synperiplanar (dihedral angle =  $0^\circ$  by definition), whereas this angle is +synclinal (+gauche; about  $+60^\circ$ ) in conformer II and –synclinal (–gauche; approximately  $-60^\circ$ ) in conformer III.

The conformational properties of TF2P have been studied previously with conflicting results. Murto et al.<sup>41</sup> studied the title compound using infrared (IR) spectroscopy and found that only conformer I exists. Durig et al.,<sup>42</sup> using IR and Raman spectroscopy, claimed that all three conformers coexist, with II as the most stable one, being 3.06(90) kJ/mol lower in energy than I. Recently, Schaal et al.<sup>43</sup> came to a similar conclusion as that of Murto and co-workers in their combined IR and quantum chemical (B3LYP/6-31+G\* level) study.

No microwave (MW) investigations have been previously conducted for TF2P. MW spectroscopy is ideal for investigating complicated conformational equilibria between several polar conformers because of its high specificity. The three rotamers (Figure 1) should each possess a relatively large dipole moment, which is a prerequisite for a strong MW spectrum. Moreover, the high volatility of TF2P allows it to be studied at reduced temperatures. This is advantageous since the intensities of MW transitions are proportional to  $T^{-2.5}$ , where  $T$  is the absolute temperature. The high volatility and the high polarity of its rotamers make TF2P well-suited for a microwave conformational investigation.

Advanced quantum chemical calculations have also been performed. These are able to predict to a high degree of accuracy a series of physical properties such as rotational and centrifugal distortion constants, dipole moments, and relative energies, which are useful in assisting and guiding experimental work.

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**Figure 1.** Possible rotameric forms of 1,1,1-trifluoro-2-propanol. A microwave spectrum attributable to conformer I was observed in this work. This rotamer is at least 3 kJ/mol more stable than any other form of the molecule.

### Experimental Procedures

The sample utilized in this work was purchased from Fluorochem, Ltd. It was specified to be more than 97% pure and was used as received. The deuterated species,  $\text{CF}_3\text{CH}(\text{OD})\text{-CH}_3$ , was produced in the microwave cell by admitting small quantities of heavy water together with the parent species. A rapid exchange of the hydrogen atom of the hydroxyl group with deuterium was observed. About 50% deuteration was achieved this way.

The spectra of the parent and deuterated species were studied using the Oslo spectrometer described in ref 1. Most measurements were made in the 20–48 GHz region. Selected parts of the 48–62 GHz frequency range were also studied. No impurities were seen in the spectrum of the parent species. Radio frequency microwave frequency double resonance (RFMWDR) experiments were carried out as described in ref 44 using the equipment mentioned in ref 1. The microwave absorption cell was cooled to about  $-50\text{ }^\circ\text{C}$  during the experiments, and the pressure was roughly 5 Pa. The spectra were recorded using the computer programs of Waal<sup>45</sup> and Grønås.<sup>46</sup> The accuracy of the frequency measurements is estimated to be of the order of  $\pm 0.10\text{ MHz}$  or better.

The infrared spectrum was taken at room temperature using a Bruker IFS66 spectrometer. A multiple-reflection gas cell with an optical path length of about 120 m was employed. The pressure of the gas was roughly 3–400 Pa. The resolution was  $1.0\text{ cm}^{-1}$ .

### Results and Discussion

**Quantum Chemical Calculations.** The *Gaussian 03* package<sup>47</sup> running on the HP Superdome in Oslo was employed in the quantum chemical calculations. Ab initio and density functional theory (DFT) calculations were performed.

Møller–Plesset second-order perturbation calculations<sup>48</sup> (MP2) employing a large basis set were first carried out for two reasons: first, accurate equilibrium geometries are predicted this way.<sup>49</sup> Second, there is generally a relatively small difference between the approximate equilibrium rotational constants calculated from such MP2 geometries and the effective rotational

constants obtained from MW spectra. The MP2 rotational constants are therefore useful starting points in the assignment procedure of a complicated MW spectrum, such as that expected for the title compound.

The basis set chosen in the present case was Dunning's correlation-consistent triple- $\zeta$  basis set with polarized valence electrons, cc-pVTZ,<sup>50</sup> with frozen core electrons. The fully optimized geometries and dipole moments were calculated using this extensive procedure. The MP2/cc-pVTZ geometries are listed in Table 1. Atom numbering is shown in Figure 1.

The vibrational frequencies were not calculated using the MP2 procedure, owing to constraints on computational time. Positive values for all vibrational frequencies are normally used to show that the conformation derived in the calculations represent a minimum on the energy hypersurface. This criterion cannot therefore be applied in the present case. However, it is seen (Table 1) that all the bonds in conformers I–III are staggered on adjacent atoms, as one would expect for a true minimum-energy conformation. Moreover, the conformations of I–III found in these MP2 calculations are the same as the corresponding ones obtained in the DFT calculations described next. Positive vibrational frequencies were calculated for all three conformers in the latter case.

The rotational constants calculated from the MP2 structures are listed in Table 1 together with the principal–inertial axes dipole moments and the total electronic MP2 energy differences between the three conformers.

Calculation of the vibrational frequencies, the quartic and sextic centrifugal distortion constants of Watson,<sup>51</sup> and the vibration–rotation interaction constants, which may be available from the MW spectra for comparison, could not be performed using MP2/cc-pVTZ owing to the computational resources available in this lab. Instead, much less expensive DFT calculations were performed. The B3LYP functional of Becke et al.<sup>52</sup> and the 6-311++G\*\* basis set were employed. The structures, rotational constants, dipole moments, and total electronic energy differences are listed in Table 1 together with the corresponding MP2 predictions. In addition, the total B3LYP electronic energy differences corrected for zero-point vibrational energies are given in this table. These quantities are of course

**TABLE 1: MP2/cc-pVTZ and B3LYP/6-311++G\*\* Structures,<sup>a</sup> Rotational Constants, and Dipole Moments of Three Conformers of 1,1,1-Trifluoro-2-propanol**

conformer	I		II		III	
	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
Bond distance (pm)						
O1–H1	96.3	96.4	96.4	96.5	96.1	96.2
C2–O1	141.1	141.6	141.1	141.3	141.5	141.9
C2–H2	109.4	109.8	108.8	109.2	109.4	109.8
C1–C2	151.0	152.0	151.6	152.6	151.5	152.6
C2–C3	151.9	153.3	151.9	153.3	151.7	152.9
C1–H3	108.6	109.1	108.6	109.1	108.9	109.3
C1–H4	108.7	109.1	108.7	109.1	108.7	109.2
C1–H5	108.7	109.1	108.9	109.4	108.7	109.1
C3–F1	134.8	136.0	133.4	134.4	133.5	134.4
C3–F2	133.5	134.4	134.7	135.8	133.7	134.6
C3–F3	134.1	135.2	134.1	135.3	134.5	135.7
Angle (deg)						
H1–O1–C2	108.0	109.4	107.3	108.8	107.4	108.7
O1–C2–H2	111.6	111.0	106.0	105.6	111.2	110.7
O1–C2–C1	107.8	108.2	112.7	113.0	112.7	112.8
O1–C2–C3	110.0	110.1	109.5	109.6	110.5	105.8
C2–C1–H3	109.1	109.0	108.9	108.8	109.5	109.5
C2–C1–H4	110.9	111.0	111.4	111.3	111.2	111.2
C2–C1–H5	109.7	110.2	110.4	111.0	110.0	110.5
C2–C3–F1	110.3	110.4	112.0	112.2	111.6	112.0
C2–C3–F2	112.8	113.3	110.8	111.1	112.2	112.7
C2–C3–F3	110.9	111.1	111.2	111.4	109.8	109.8
Dihedral angle (deg)						
H1–O1–C2–H2	-56.9	-55.2	177.4	176.8	75.2	68.2
H1–O1–C2–C1	-178.4	-176.3	56.2	56.1	-49.5	-55.8
H1–O1–C2–C3	60.0	60.9	-68.2	-69.4	-170.9	-178.4
C3–C2–C1–H3	-177.5	-177.3	179.9	-179.1	-178.7	-178.1
C3–C2–C1–H4	-57.4	-57.5	-59.8	-59.2	-59.3	-59.1
C3–C2–C1–H5	63.4	63.6	60.7	61.5	61.9	62.3
C1–C2–C3–F1	-175.6	-175.5	176.4	175.5	-179.4	179.7
C1–C2–C3–F2	-55.6	-55.4	-63.7	-64.5	-58.2	-58.8
C1–C2–C3–F3	65.6	65.9	55.8	55.0	61.4	60.8
Rotational constants (MHz)						
A	3538.2	3490.2	3518.5	3473.3	3536.3	3488.0
B	2422.3	2370.8	2426.6	2376.0	2442.7	2391.7
C	1984.4	1944.8	1988.9	1950.5	1995.4	1956.4
Dipole moment <sup>b</sup> (10 <sup>-30</sup> C m)						
$\mu_a$	3.5	3.9	6.4	6.8	11.3	11.4
$\mu_b$	0.1	0.1	4.1	4.2	3.7	3.4
$\mu_c$	5.0	5.0	1.2	1.3	4.0	4.4
$\mu_{\text{tot}}$	6.1	6.3	7.8	8.0	12.5	12.7
Energy differences <sup>c</sup> (kJ mol <sup>-1</sup> )						
	0.0 <sup>d</sup>	0.0 <sup>e</sup>	2.2 <sup>d</sup>	2.5 <sup>e</sup>	9.5 <sup>d</sup>	10.5 <sup>e</sup>
		0.0 <sup>f</sup>		2.3 <sup>f</sup>		8.9 <sup>f</sup>

<sup>a</sup> Atom numbering is given in Figure 1. <sup>b</sup> 1 D = 3.33564 × 10<sup>-30</sup> C m. <sup>c</sup> Relative to conformer I. <sup>d</sup> Total electronic energy differences. Total MP2 energy of conformer I is -1290145.7 kJ/mol. <sup>e</sup> Total electronic energy differences. Total B3LYP energy of conformer I is -1292400.2 kJ/mol. <sup>f</sup> Total electronic energies corrected for zero-point vibrational energies.

not available in the MP2 case because vibrational frequencies were not calculated. The quartic centrifugal distortion constants of Watson<sup>51</sup> are listed in Table 2. It should be remarked that no correction for basis-set superposition errors was made in either the MP2 or the B3LYP calculations.

A few comments are warranted. It is seen in Table 1 that the MP2 and B3LYP structures are quite similar. All MP2 bond lengths are slightly less than their B3LYP counterparts. The largest variations are seen for the dihedral angles, which vary by up to 7° (the H1–O1–C2–H2 dihedral angle).

Interestingly, both computational procedures predict a rather small variation in the C1–C2 and C2–C3 bond lengths. The largest variation (1.3 pm) is calculated for conformer I using

**TABLE 2: B3LYP/6-311++G\*\* Quartic Centrifugal Distortion Constants (kHz)<sup>a</sup> of Three Conformers of 1,1,1-Trifluoro-2-propanol**

conformer	I	II	III
Quartic centrifugal distortion constants			
$\Delta_J$	0.272	0.272	0.270
$\Delta_{JK}$	0.396	0.483	0.501
$\Delta_K$	-0.211	-0.282	-0.291
$\delta_J$	0.0583	0.0595	0.0594
$\delta_K$	-0.823	-0.922	-1.07

<sup>a</sup> A-reduction.<sup>51</sup>

the B3LYP method. This small difference is somewhat surprising given the highly electronegative fluorine atoms attached to C3.

The dipole moments and total electronic energy differences obtained in the two procedures are also similar. Both methods predict conformer I to be about 2 kJ/mol more stable than II and roughly 10 kJ/mol more stable than III. Correction for zero-point vibrational energies, which can only be made in the B3LYP case, influence the energy difference between conformers III and I by about 1.6 kJ/mol but affects the energy difference between II and I by only 0.2 kJ/mol.

**MW Spectrum and Assignment of the Ground Vibrational State of Conformer I.** The partition function of TF2P is relatively large even at -50 °C because the rotational constants (Table 1) are comparatively small, and eight normal vibrational frequencies are less than 500 cm<sup>-1</sup> according to the B3LYP calculations (not given in Table 1). Each rotational quantum state will therefore have a low Boltzmann population. It was therefore not surprising to find that the MW spectrum was comparatively weak, even at this low temperature.

The three conformers were each predicted to have a large dipole moment component along either the *b*- or the *c*-principal inertial axis (Table 1), allowing perpendicular transitions to occur. This should result in a very dense spectrum, as was the case. In fact, absorption lines occur every few MHz throughout the entire MW range.

The quantum chemical computations described previously indicate that conformer I is the preferred form of the molecule. The largest dipole moment component of this rotamer is calculated to be  $\mu_c$  (Table 1), this being somewhat larger than  $\mu_a$ . However, the <sup>a</sup>R-transitions are often easier to assign than the *c*-type lines, as RFMWDR searches can be conveniently made for these parallel transitions. RFMWDR searches were therefore first made in the 40–60 GHz spectral region, where the strongest *a*-type R-branch transitions are located. These searches met with immediate success. The first <sup>c</sup>Q-lines were then found in the 20–30 GHz region using a trial and error procedure. The assignments were next extended to include additional *c*-type Q- and R-branch transitions. The frequencies of the *b*-type lines could now be predicted very accurately. However, no *b*-type transitions were found, presumably because they are very weak as a consequence a small value of  $\mu_b$ . This is in agreement with the predictions (Table 1) made for conformer I. A total of about 600 transitions was ultimately assigned; 577 of these with a maximum value of *J* = 67 were used to determine the spectroscopic constants (A-reduction, *I'* representation<sup>51</sup>) shown in Table 3. The centrifugal distortion effect is relatively small in this compound, even for high-*J* transitions. The quartic centrifugal distortion constants and only one sextic constant ( $\phi_J$ ) were therefore fitted. The root-mean-square of the fit (0.090 MHz) is comparable to the experimental uncertainty, which is estimated to be ±0.10 MHz. The spectrum

**TABLE 3: Spectroscopic Constants<sup>a</sup> of the Ground Vibrational State of the Parent and One Deuterated Isotopolog of Conformer I of 1,1,1-Trifluoro-2-propanol**

species	CF <sub>3</sub> CH(OH)CH <sub>3</sub>	CF <sub>3</sub> CH(OD)CH <sub>3</sub>
A (MHz)	3523.9412(13)	3434.1137(28)
B (MHz)	2404.8353(12)	2388.8274(36)
C (MHz)	1969.7318(13)	1932.0678(59)
$\Delta_J$ (kHz)	0.2747(46)	0.235(11)
$\Delta_{JK}$ (kHz)	0.3709(15)	0.415(24)
$\Delta_K$ (kHz)	-0.1807(14)	-0.247(19)
$\delta_J$ (kHz)	0.06082(17)	0.0690(20)
$\delta_K$ (kHz)	-0.7988(22)	-0.831(41)
$\phi_J^b$ (Hz)	0.0000405(95)	c
rms <sup>d</sup> (MHz)	0.090	0.091
no <sup>e</sup>	577	129

<sup>a</sup> A-Reduction I<sup>r</sup> representation.<sup>51</sup> <sup>b</sup> Further sextic centrifugal distortion constants preset at zero. <sup>c</sup> Preset at zero. <sup>d</sup> Root-mean-square deviation. <sup>e</sup> Number of transitions.

**TABLE 4: Spectroscopic Constants<sup>a</sup> of Vibrationally Excited States of Conformer I of 1,1,1-Trifluoro-2-propanol**

vib. state	first ex. C-CF <sub>3</sub> torsion	first ex. C-CH <sub>3</sub> torsion <sup>a</sup>
A (MHz)	3523.1328(17)	3522.6873(86)
B (MHz)	2399.4446(17)	2403.9701(89)
C (MHz)	1969.7945(17)	1968.672(11)
$\Delta_J$ (kHz)	0.2773(92)	0.152(26)
$\Delta_{JK}$ (kHz)	0.3918(18)	0.285(24)
$\Delta_K$ (kHz)	-0.2061(20)	-0.102(21)
$\delta_J$ (kHz)	0.06030(19)	0.0480(36)
$\delta_K$ (kHz)	-0.8448(25)	-0.671(40)
$\phi_J^b$ (Hz)	0.0000294(75)	c
rms <sup>d</sup> (MHz)	0.085	0.153
no <sup>e</sup>	431	117

<sup>a-e</sup> Comments as for Table 3.

is listed in Table 1S in the Supporting Information together with derived spectroscopic constants and other relevant information.

The dipole moment could not be determined because the low-*J* lines were too weak to permit quantitative measurements of the Stark effect to be made. However, the quantum chemical calculations predict (Table 1) that  $\mu_a$  and  $\mu_c$  are similar and that  $\mu_b$  is practically zero, which is consistent with the experimental observations.

The differences between the experimental rotational constants (Table 3) and the MP2 rotational constants (Table 1) are -0.41% for A, -0.73% for B, and -0.75% for C, which is considered to be satisfactory. The corresponding values using the B3LYP rotational constants are 0.96, 1.41, and 1.27%, respectively. The agreement between the experimental and the calculated rotational constants is thus better in the MP2 case. The differences found for the centrifugal distortion constants are +7.2, -7.0, +16.8, +4.1, and +3.4% for  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$  and  $\delta_K$ , respectively. The sextic constant  $\phi_J$  is calculated to be  $7.10 \times 10^{-6}$  Hz in the B3LYP calculations, as compared to  $4.05(95) \times 10^{-5}$  Hz found experimentally (Table 3). This large discrepancy is not surprising considering the fact that the other sextic constants have been held fixed at zero in the least-squares fitting procedure.

**Vibrationally Excited States of Conformer I.** The ground-state transitions were accompanied by series of transitions that presumably belong to vibrationally excited states of conformer I. Two excited states belonging to two different vibrational modes were assigned; their spectroscopic constants are listed in Table 4. The full spectra and other relevant information are found in Supporting Information Tables 2S and 3S, respectively.

The most intense spectrum of these excited states is assigned as the first excited state of the torsional vibration of the CF<sub>3</sub>

group. A total of about 450 transitions with a maximum of *J* = 71 was assigned for this state. Relative intensity measurements performed as described in ref 53 yielded  $76(25) \text{ cm}^{-1}$  for this vibration, as compared to the unscaled frequency of  $85 \text{ cm}^{-1}$  obtained in the B3LYP calculations.

Apart from its low frequency, another criterion can be applied to assign this excited state as the first excited state of the CF<sub>3</sub> torsion. The spectroscopic vibration-rotation constant,  $\alpha_X$ , is given by  $\alpha_X = X_0 - X_1$ , where  $X_0$  is the *X* rotational constant in the ground vibrational state and  $X_1$  is the corresponding constant of the first excited vibrational state of a normal mode.<sup>54</sup> The values calculated from the entries in Tables 3 and 4 are  $\alpha_A = 0.808$ ,  $\alpha_B = 5.391$ , and  $\alpha_C = -0.063$  MHz, which compare favorably with the corresponding values, namely, 0.881, 5.199, and -0.238 MHz, obtained from the B3LYP calculations.

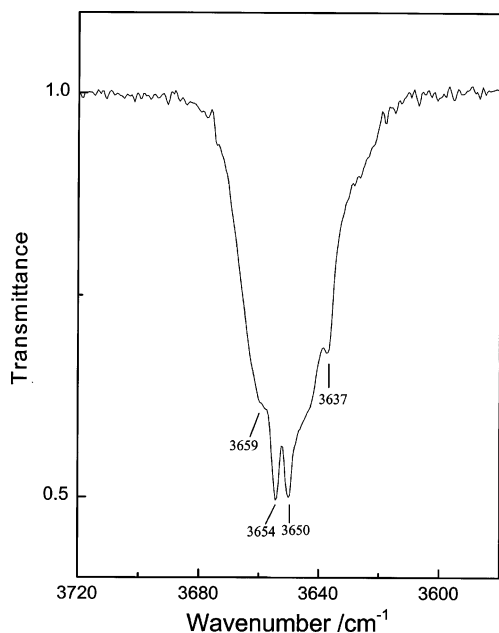
The vibrational frequency of the second excited state to be assigned was determined to be ca.  $200 \text{ cm}^{-1}$ , by means of relative intensity measurements.<sup>53</sup> A total of 117 transitions was assigned for this state with  $J_{\text{max}} = 32$  (Table 4). It is considered likely that this state is the first excited state of the torsional vibration of the methyl group, which is calculated (B3LYP) to have an unscaled frequency of  $208 \text{ cm}^{-1}$ . The values of the vibration-rotation constants for this state are now  $\alpha_A = 1.254$ ,  $\alpha_B = 0.865$ , and  $\alpha_C = 1.060$  MHz, as compared to 1.568, 1.1439, and 1.543 MHz, respectively, from the B3LYP calculations.

**Deuterated Species.** The assignment of the spectrum belonging to CF<sub>3</sub>CH(OD)CH<sub>3</sub> was straightforward. The first assignments were made for the <sup>a</sup>R-lines, which were predicted by adding the differences of the rotational constants calculated from the structure in Table 1 to the experimental constants in Table 3. The *c*-type lines were included next. The spectrum consisting of 129 transitions is listed in the Supporting Information, Table 4S, and the spectroscopic constants are listed therein, as well as in Table 3.

It is possible to calculate the principal-axes coordinates of the H atom of the hydroxyl group (H1) from the rotational constants of the parent and deuterated species by using Kraitchman's equations.<sup>55</sup> The substitution coordinates of H1 calculated in this manner, using the spectroscopic constants and their standard deviations given in Table 3, are  $|a| = 112.18(2)$ ,  $|b| = 193.61(1)$ , and  $|c| = 29.40(8)$  pm, respectively. The corresponding values calculated from the MP2 structure in Table 1 are  $|a| = 109.1$ ,  $|b| = 193.2$ , and  $|c| = 28.4$  pm and are therefore in excellent agreement with the experimental values. Any confusion with conformer II is not possible because the corresponding coordinates of the H1 atom in this rotamer as calculated from the structure in Table 1 are  $|a| = 158.7$ ,  $|b| = 118.1$ , and  $|c| = 90.9$  pm. In conformer III, the coordinates obtained in the same manner are  $|a| = 240.0$ ,  $|b| = 119.8$ , and  $|c| = 12.9$  pm, thus excluding this conformer as well.

**Searches for Conformers II and III.** The previous assignments account for approximately 1200 transitions. Nearly all the more prominent lines have been assigned. However, a large number of less intense transitions remain unassigned. Many of these undoubtedly belong to unassigned vibrationally excited states of conformer I.

Conformers II and III are each predicted to have a  $\mu_a$  value that is much larger than the corresponding dipole moment component of conformer I; see Table 2. RFWDR and ordinary Stark experiments were carried out in an attempt to find <sup>a</sup>R-type transitions belonging to II or III, but no assignments could be made. It is felt that these transitions would have been identified, if the energy difference between either of them and



**Figure 2.** Gas-phase infrared spectrum of 1,1,1-trifluoro-2-propanol in the O–H stretching region.

conformer I was less than 3 kJ/mol. This is consistent with the quantum chemical calculations that predict I to be the preferred form. It was claimed by Murto et al.<sup>41</sup> that conformer I is the only rotamer present in TF2P. Schaal et al.<sup>43</sup> came to a similar conclusion, which is in agreement with the present findings.

**Structure.** The observed (Table 3) and MP2 rotational constants (Table 1) of conformer I are in excellent agreement. The same is found for the substitution coordinates of H1. It is believed that this is not fortuitous but in fact reflects that the present MP2 calculations have indeed predicted an accurate molecular geometry for this rotamer, in accord with previous claims.<sup>49</sup> The MP2 structure given in Table 1 is suggested to be a plausible structure for conformer I. Any experimental structure that might be determined in the future is expected to be close to the one shown in Table 1.

**Strength of the H-Bond.** Evidence for a weak H-bond in TF2P is seen from the infrared stretching vibration of the gas shown in Figure 2. This band has maxima at 3654 and 3650  $\text{cm}^{-1}$  and shoulders at 3659 and 3637  $\text{cm}^{-1}$ . This fine structure is presumed to be rotational in origin.

The two maxima at 3654 and 3650  $\text{cm}^{-1}$  should be compared to 3682  $\text{cm}^{-1}$  seen for gaseous methanol,<sup>56</sup> which of course has no H-bond. A red-shift of the O–H stretching vibration of roughly 30  $\text{cm}^{-1}$  that is inferred from this comparison is indicative of a rather weak H-bond.

There is additional evidence in favor of weak internal H-bonding. The nonbonded distance between the nearest fluorine atom (F1) and the H atom of the hydroxyl group (H1) is calculated to be 240 pm from the MP2 structure in Table 2. The B3LYP distance is similar (244 pm). This distance is thus about 15 pm shorter than the sum of the van der Waals radii of hydrogen and fluorine (255 pm).<sup>57</sup> The MP2 O1–H1...F1 angle is 101°, far from the ideal linear or near-linear arrangement (180°).

Interestingly, the O1–H1 and C3–F1 bonds are about 5° from being parallel according to the MP2 calculations. The corresponding bond dipole moments are therefore approximately 5° from being antiparallel. This is an ideal configuration for a dipole–dipole interaction assumed to be a major stabilizing force in conformer I.

## Discussion

The energy difference between II and I is larger than 3 kJ/mol, as stated previously. The conformational distinction between these two forms is just the same as the distinction between the synclinal (gauche) and the antiperiplanar forms of ethanol, where an energy difference of 0.49(6) kJ/mol has been determined,<sup>58</sup> far from >3 kJ/mol found previously for the title compound. Obviously, energy differences between these two similar conformational equilibria are not transferable.

It is apparent that several competing intramolecular forces exist in this compound. Weak internal five-membered H...F hydrogen bonds are possible both in conformers I and in II, whereas III has no such bond.

The lone electron pairs of the oxygen atom are likely to interact with their neighbors. Maximum repulsion between these lone pairs and the fluorine atoms seems to exist in III, where the two lone pairs come into close contact with two fluorine atoms (F1 and F2, respectively). Only one of the lone electron pairs experiences a similar destabilization in I (with F2), as well as in II (with F1). This repulsive effect should destabilize conformer III more than either I or II.

Attraction between these lone pairs and both the H3 and the H5 atoms is possible in I, while a similar stabilizing effect exists between one of the lone pairs and H3 in conformer II. Conformer I appears to be the most stable form because intramolecular interactions are more favorable in this conformer than in either II or III. Conformer III definitely has the least favorable intramolecular interactions.

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**Supporting Information Available:** MW spectra of the two species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

- 1-Fluorocyclopropanecarboxylic acid: Møllendal, H.; Leonov, A.; de Meijere, A. *J. Phys. Chem. A* **2005**, *109*, 6344.
- (1-Fluorocyclopropyl)methanol: Møllendal, H.; Leonov, A.; de Meijere, A. *J. Mol. Struct.* **2004**, *695–696*, 163.
- 3-Buteneselenol: Petitprez, D.; Demaison, J.; Wlodarczak, G.; Guillemin, J.-C.; Møllendal, H. *J. Phys. Chem. A* **2004**, *108*, 1403.
- Glyceraldehyde; 1,3-dihydroxy-2-propanone; 2-hydroxy-2-propen-1-al: Lovas, F. J.; Suenram, R. D.; Plusquellic, D. F.; Møllendal, H. *J. Mol. Spectrosc.* **2003**, *222*, 263.
- Formylhydrazine: Samdal, S.; Møllendal, H. *J. Phys. Chem. A* **2003**, *107*, 8845.
- 2-Bicyclopropylidenemethanol: Møllendal, H.; Kozhushkov, S. I.; de Meijere, A. *Asian Chem. Lett.* **2003**, *7*, 61.
- Allylphosphine: Møllendal, H.; Demaison, J.; Guillemin, J.-C. *J. Phys. Chem. A* **2002**, *106*, 11481.
- Glycolaldehyde: Butler, R. A. H.; De Lucia, F. C.; Petkie, D. T.; Møllendal, H.; Horn, A.; Herbst, E. *Astrophys. J., Supp. Ser.* **2001**, *134*, 319.
- 1-Ethynylcyclopropan-1-ol: Leonov, A.; Marstokk, K.-M.; de Meijere, A.; Møllendal, H. *J. Phys. Chem. A* **2000**, *104*, 4421.
- 1-Amino-1-ethynylcyclopropane: Marstokk, K.-M.; de Meijere, A.; Møllendal, H.; Wagner-Gillen, K. *J. Phys. Chem. A* **2000**, *104*, 2897.
- Propargylphosphine: Demaison, J.; Guillemin, J.-C.; Møllendal, H. *Inorg. Chem.* **2001**, *40*, 3719.
- 1-Amino-1-ethynylcyclopropane: Marstokk, K.-M.; de Meijere, A.; Wagner-Gillen, K.; Møllendal, H. *J. Mol. Struct.* **1999**, *509*, 1.
- Dicyclopropylketimine: Songe, P.; Marstokk, K.-M.; Møllendal, H.; Kolsaker, P. *Acta Chem. Scand.* **1999**, *53*, 291.
- 3,3,3-Trifluoropropanol: Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1999**, *53*, 202.
- Møllendal, H. *J. Mol. Struct.* **1983**, *97*, 303.

- (16) Wilson, E. B.; Smith, Z. *Acc. Chem. Res.* **1987**, *20*, 257.
- (17) Møllendal, H. *NATO ASI Ser., Ser. C* **1993**, *410*, 277.
- (18) Bastiansen, O.; Kveseth, K.; Møllendal, H. *Top. Curr. Chem.* **1979**, *81*, 99.
- (19) (2-Fluoromethyl)pyridine: Moberg, C.; Adolfsen, H.; Waernmark, K.; Norrby, P.-O.; Marstokk, K.-M.; Møllendal, H. *Chem.—Eur. J.* **1996**, *2*, 516.
- (20) 2,2,3,3-Tetrafluoro-1-propanol: Marstokk, K. M.; Møllendal, H. *Acta Chem. Scand.* **1993**, *47*, 281.
- (21)  $\alpha$ -Fluoropropionic acid: van Zoeren, E.; van Eijck, B. P. *J. Mol. Spectrosc.* **1984**, *103*, 75.
- (22) Difluoroacetic acid: van Eijck, B. P.; Maagdenberg, A. A. J.; Janssen, G.; Van Goethem-Wiersma, T. J. *J. Mol. Spectrosc.* **1983**, *98*, 282.
- (23) 2,2-Difluoroethylamine: Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1982**, *A36*, 517.
- (24) 2-Fluoropropanol: Braathen, O. A.; Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1982**, *A36*, 173.
- (25) 2-Fluoroethylamine: Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 15.
- (26) 2,2-Difluoroethanol: Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand., Ser. A* **1980**, *A34*, 765.
- (27) 2-Fluoroacetamide and 2-chloroacetamide: Samdal, S.; Seip, R. *J. Mol. Struct.* **1979**, *52*, 195.
- (28) 1-Fluoro-2-propanol: Marstokk, K.-M.; Møllendal, H. *J. Mol. Struct.* **1977**, *40*, 1.
- (29) 2-Fluoroacetamide: Marstokk, K.-M.; Møllendal, H. *J. Mol. Struct.* **1974**, *22*, 287.
- (30) Fluoroacetic acid: van Eijck, B. P.; van der Plaats, G.; van Roon, P. H. *J. Mol. Struct.* **1972**, *11*, 67.
- (31) Fluoroacetic acid: van Eijck, B. P. *J. Mol. Spectrosc.* **1968**, *27*, 55.
- (32) 2,2,2-Trifluoroethanol: Xu, L.-H.; Fraser, G. T.; Lovas, F. J.; Suenram, R. D.; Gillies, C. W.; Warner, H. E.; Gillies, J. Z. *J. Chem. Phys.* **1995**, *103*, 9541.
- (33) 2-Fluoroethanol: Huang, J.; Hedberg, K. *J. Am. Chem. Soc.* **1989**, *111*, 6909.
- (34) 2,2-Difluoroacetamide: Gundersen, S.; Samdal, S.; Seip, R.; Shorokhov, D. J. *J. Mol. Struct.* **1999**, *477*, 225.
- (35) 2,2,2-Trifluoroacetamide: Gundersen, S.; Samdal, S.; Seip, R.; Shorokhov, D. J.; Strand, T. G. *J. Mol. Struct.* **1998**, *445*, 229.
- (36) 3-Fluoropropan-1-ol: Richardson, A. D.; Hedberg, K. *J. Mol. Struct.* **2001**, *567–568*, 187.
- (37) 4-Fluorobutan-1-ol: Traetteberg, M.; Richardson, A. D.; Hedberg, K.; Winter, R. W.; Gard, G. L. *J. Phys. Chem. A* **2001**, *105*, 9587.
- (38) Christidis, N.; Hurley, M. D.; Pinnock, S.; Shine, K. P.; Wallington, T. J. *J. Geophys. Res.* **1997**, *102*, 19597.
- (39) Fisher, D. A.; Hales, C. H.; Wang, W. C.; Ko, M. K. W.; Sze, N. D. *Nature (London)* **1990**, *344*, 513.
- (40) Marstokk, K.-M.; Møllendal, H. *Acta Chem. Scand.* **1998**, *52*, 1307.
- (41) Murto, J.; Kivinen, A.; Edelmann, K.; Hassinen, E. *Spectrochim. Acta, Part A* **1975**, *31A*, 479.
- (42) Durig, J. R.; Cox, F. O.; Groner, P.; van der Veken, B. J. *J. Phys. Chem.* **1987**, *91*, 3211.
- (43) Schaal, H.; Haerber, T.; Suhm, M. A. *J. Phys. Chem. A* **2000**, *104*, 265.
- (44) Wodarczyk, F. J.; Wilson, E. B., Jr. *J. Mol. Spectrosc.* **1971**, *37*, 445.
- (45) Waal, Ø. Personal communication, 1994.
- (46) Grønås, T. Personal communication, 2003.
- (47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (48) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (49) Helgaker, T.; Gauss, J.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1997**, *106*, 6430.
- (50) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
- (51) Watson, J. K. G. *Vibrational Spectra and Structure*; Elsevier: Amsterdam, 1977; Vol. 6.
- (52) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (53) Esbitt, A. S.; Wilson, E. B. *Rev. Sci. Instrum.* **1963**, *34*, 901.
- (54) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra (Technique of Organic Chemistry, Vol. 9: Chemical Application of Spectroscopy, Pt. 2)*; Interscience: New York, 1970.
- (55) Kraitchman, J. *Am. J. Phys.* **1953**, *21*, 17.
- (56) Richter, W.; Schiel, D. *Ber. Bunsen-Ges.* **1981**, *85*, 548.
- (57) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: New York, 1960.
- (58) Kakar, R. K.; Quade, C. R. *J. Chem. Phys.* **1980**, *72*, 4300.