

Structural and Conformational Properties of 1,3-Difluoropropane as Studied by Microwave Spectroscopy and *Ab Initio* Calculations

K.-M. Marstokk and Harald Møllendal*

Department of Chemistry, The University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

Marstokk, K.-M. and Møllendal, H., 1997. Structural and Conformational Properties of 1,3-Difluoropropane as Studied by Microwave Spectroscopy and *Ab Initio* Calculations. – Acta Chem. Scand. 51: 1058–1065. © Acta Chemica Scandinavica 1997.

The microwave spectrum of 1,3-difluoropropane has been investigated in the 10.0–36.0 GHz spectral region at dry-ice temperature (-79°C). Four all-staggered rotameric forms are possible for this compound. The gas phase consists almost exclusively of an equilibrium mixture of two rotameric forms of the molecule denoted *GG* and *AG* for which a total of about 2600 transitions have been assigned. The *GG* rotamer was found to be the most stable conformer and is $4.0(2) \text{ kJ mol}^{-1}$ more stable than *AG*. The dipole moment is lying along the *b*-inertial axis in the *GG* conformer for symmetry reasons and is $6.946(29) \times 10^{-30} \text{ C m}$. The dipole moment of the *AG* conformer is (same units) $\mu_a = 3.59(5)$, $\mu_b = 5.32(9)$, $\mu_c = 1.02(19)$, $\mu_{\text{tot}} = 6.50(11)$.

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/6-311++G** level. The structural parameters predicted in both these computational schemes are close to the accurate electron-diffraction values apart from the C–F bond length that is systematically too long. The relative energies computed for the different conformers were rather similar at both these levels of theory and in good agreement with experiment.

1,3-Difluoropropane represents an interesting conformational problem. Four all-staggered rotameric forms shown in Fig. 1 are possible for this compound. In the *GG* conformer the F–C–C–C links of atoms are both about 60° (clockwise rotation) (or -60°) from *syn* (0°), while these angles are approximately 60° (-60°) and -60° (60°), respectively, from *syn* in the *GG'* rotamer. One F–C–C–C dihedral angle is about 60° and the other 180° in *AG*, whereas both these dihedral angles are 180° in the *AA* form.

There has been several studies of the conformational properties of 1,3-difluoropropane. Lere-Porte *et al.*¹ using infrared spectroscopy concluded that *GG* and *AG* exist in carbon tetrachloride solution. CNDO and PCILO computations² predicted that *GG'* is about 4 kJ mol^{-1} less stable than *GG*, *AG* and *AA*, respectively, which were computed to have about the same energy. Molecular mechanics computations³ predict 31% *GG*, 45% *AG*, 17% *GG'* and 7% *AA*, respectively, in carbon tetrachloride solution. In his systematic studies of halogenated propanes, Stølevik and co-workers,⁴ also investigated 1,3-

difluoropropane. Using electron diffraction (ED), IR spectroscopy and molecular mechanics they found that the gas phase is made up of 63(4)% *GG*, 27(2)% *AG* and 10(5)% *GG'* at 20°C , while only *GG* exists in the crystalline phase.⁴

No microwave (MW) or high-level quantum chemical studies have previously been made for 1,3-difluoropropane. MW spectroscopy is ideal for investigating complicated conformational equilibria where several polar conformers are present because of its high selectivity and specificity. The four rotamers (Fig. 1) that are possible for 1,3-difluoropropane would each possess a rather large dipole moment which is a prerequisite for a strong MW spectrum. It is also an advantage that the compound is so volatile that it has a sufficiently high vapour pressure to allow a study at dry-ice temperature where intensities are significantly larger than at higher temperatures. All this makes 1,3-difluoropropane very well suited for a microwave conformational investigation.

Advanced quantum chemical computations are often found to predict rather accurate rotational constants, dipole moments and energies of the different conformers. These calculations may thus serve as useful starting

* To whom correspondence should be addressed.
E-mail: harald.mollendal@kjemi.uio.no.

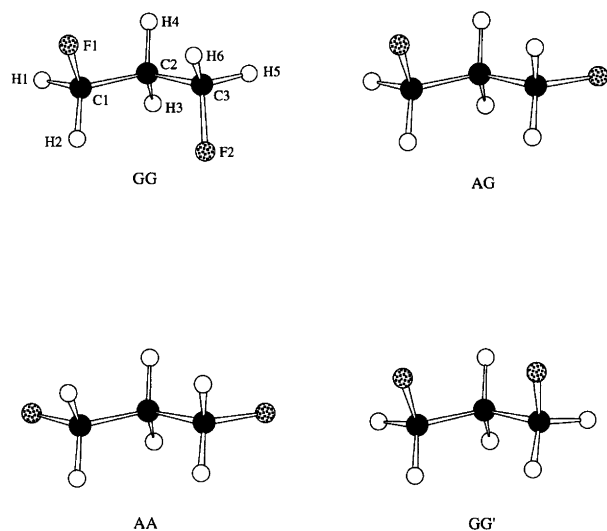


Fig. 1. The four all-staggered conformations of 1,3-difluoropropane. Atom numbering is shown on the *GG* rotamer. *GG* and *AG* were assigned in this work. These two rotamers make up most of the gas phase. *GG* is the most stable conformer. It is $4.0(2)$ kJ mol⁻¹ more stable than *AG*.

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.

The unique effect that fluorine sometimes is seen to have on the structural and conformational properties⁵ has been of interest to this laboratory.⁶ 1,3-Difluoropropane was chosen for study as a continuation of our investigations of fluorine-containing molecules.

Experimental

The sample utilised in this work was purchased from Lancaster. It was specified to be more than 97% pure, and was 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. 7. The 10–36 GHz spectral region was investigated with the microwave absorption cell cooled to dry-ice temperature (194 K). The pressure was about 2–6 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.⁸ The accuracy of the frequency measurements is presumed to be better than ± 0.10 MHz.

Results and discussion

Ab initio calculations. The Gaussian 94 program package⁹ running on the IBM RS6000 cluster in Oslo was employed in all the *ab initio* calculations. The rather large 6-311++G** basis set provided with the program⁹ was used throughout. Two different computational schemes, MP2/6-311++G** and B3LYP/

6-311++G**, were utilised, because we wanted to compare the results obtained in these two different ways.

In the first of these computational schemes, electron correlation was included using the second order Møller–Plesset (MP2) perturbation theory¹⁰ with frozen-core electrons.⁹ In the second procedure, density functional theory (DFT) calculations were carried out employing the B3LYP¹¹ method. Full geometry optimisation was made in the MP2 as well as in the B3LYP computations for all four rotamers (Fig. 1) which were found to be minima ('stable') on the potential energy hypersurface, as no imaginary vibrational frequencies¹² were computed for any of them.

The geometries calculated for the four rotamers are given in Table 1, together with some other parameters of interest. Atom numbering is given in Fig. 1. Selected structural parameters from the ED investigation⁴ are included in this table. These parameters, which represent a mean over the conformers present, are not expected to vary much between the individual rotamers. This has indeed been found for the substitution structures of the *anti* and *gauche* forms of the closely related molecule propyl fluoride, CH₃CH₂CH₂F.¹³

It is interesting to note that all distances and angles but the C–F bond length, are close to the ED values in the MP2 and as well as in the B3LYP computations (Table 1). The C–F bond length is calculated to be approximately 1 pm too long with both methods. The B3LYP C–F bond length is slightly worse (longer) than MP2 bond length. It should be mentioned for comparison that the ED value⁴ for the C–F bond of 139.1(2) pm is nearly the same as the substitution values of 140.1(3) and 139.0(5) pm determined for the congener *anti* and *gauche* propyl fluoride, respectively.¹³ The corresponding bond length (substitution value) is 140.3(20) pm in another related compound, isopropyl fluoride, CH₃CHFCH₃.¹⁴

The dihedral angles are predicted to be close to or identical with the exact staggered values in *GG*, *AG* and *AA*. A somewhat larger deviation from staggered value is calculated for the F–C–C–C dihedral angle in the *GG'* form. This dihedral angle deviates by about 10° from the 'normal' value (Table 1). This perhaps reflects repulsion of the dipole–dipole type between the two C–F bond dipoles which are quite close to one another and nearly parallel. Steric repulsion between the two fluorine atoms is not considered to be of much significance, as the non-bonded distance between them is about 291 pm (from MP2 structure), compared to 270 pm, which is twice the van der Waals radius of fluorine.¹⁵

The MP2 and B3LYP energy differences between the conformers (Table 1) are all nearly identical. *GG* is predicted to be the most stable form, in agreement with the ED and IR work.⁴ *AG* is predicted to be approximately 4 kJ mol⁻¹ less stable than *GG*, whereas *AA* and *GG'* are less stable by about 10 and 12 kJ mol⁻¹, respectively.

1,3-Dipole–dipole interaction might perhaps explain

Table 1. Structure, rotational constants and dipole moments of the *GG*, *AG*, *AA* and *GG'* rotamers as calculated at the MP2/6-311++G** (frozen core) and B3LYP/6-311++G** levels of theory.^a

Procedure:	MP2				B3LYP				Exp. ^b
	<i>GG</i>	<i>AG</i>	<i>AA</i>	<i>GG'</i>	<i>GG</i>	<i>AG</i>	<i>AA</i>	<i>GG'</i>	
Distance/pm									
C1-F1	139.9	139.9	139.4	139.1	140.7	140.7	140.2	139.9	139.1(2) ^c
C3-F2		139.6				140.3			
C1-H1	109.3	109.2	109.4	109.4	109.2	109.2	109.4	109.4	109.4(5) ^c
C3-H5		109.1				109.1			
C1-H2	109.2	109.5		109.5	109.2	109.4	109.4	109.5	
C3-H6		109.5				109.4			
C1-C2	151.5	151.4	151.7	151.7	151.8	151.7	152.0	151.9	151.3(3) ^c
C2-C3		151.6				151.9			
C2-H3	109.6	109.6	109.4	109.8	109.6	109.6	109.4	109.8	
C2-H4		109.4		109.4		109.4		109.4	
Angle/°									
F1-C1-C2	109.1	109.5	109.4	110.9	109.7	110.2	109.5	111.3	110.1(3) ^c
F2-C3-C2		109.3				109.4			
C1-C2-C3	112.5	111.9	111.4	114.8	113.6	112.8	111.9	115.9	112.9(8) ^c
H1-C1-C2	111.4	111.3	111.6	111.0	111.4	111.3	112.0	111.5	
H5-C3-C2		111.5				111.7			
H2-C1-C2	109.1	111.6		110.9	111.7	112.1		110.7	
H6-C3-C2		111.1				111.6			
C1-C2-H3	109.1	108.5	109.3	107.4	108.6	108.1	109.3	107.2	
C1-C2-H4	109.1	109.7		109.7	109.3	109.7		109.7	
Dihedral angle ^d /°									
F1-C1-C2-C3	63.5	61.7	180.0	69.9	64.7	62.3	180.0	71.5	
F2-C3-C2-C1		176.8		-69.9		177.8		-71.5	
H1-C1-C2-C3	182.0	180.5	-61.2	-171.0	183.1	181.1	-61.5	-169.7	
H5-C3-C2-C1		-64.1		49.6		-63.4		48.2	
H2-C1-C2-C3	-55.0	-57.0	61.2	-49.6	-54.0	-56.5	61.5	-48.2	
H6-C3-C2-C1		58.3		171.0		59.4		169.7	
F1-C1-C2-H3	184.7	182.0	-59.1	189.3	186.6	183.1	-58.9	190.9	
F1-C1-C2-H4	-57.5	-60.3	59.1	-54.1	-56.7	-60.1	58.9	-53.5	
Rotational constants/MHz									
<i>A</i>	9215.9	13717.8	21585.9	8007.0	9341.2	13736.9	21457.8	8044.2	
<i>B</i>	2931.0	2340.6	1914.8	3581.0	2826.4	2296.5	1898.0	3443.8	
<i>C</i>	2757.2	2155.4	1819.4	2716.0	2674.8	2120.6	1803.2	2641.3	
Dipole moments/10 ⁻³⁰ C m									
μ_a	0.0 ^e	4.23	0.0 ^e	0.0 ^e	0.0 ^e	3.71	0.0 ^e	0.0 ^e	
μ_b	8.32	5.44	7.70	14.07	7.61	5.06	7.01	12.96	
μ_c	0.0 ^e	4.08	0.0 ^e	2.66	0.0 ^e	3.77	0.0 ^e	2.30	
Energy difference/kJ mol ⁻¹									
	0.0 ^f	4.2	10.3	12.4	0.0 ^g	3.7	9.0	12.0	

^aOnly one of the two symmetry equivalent parameters are listed. *GG* has *C*₂ symmetry, *AG* has *C*₁ symmetry, *AA* has *C*_{2v} symmetry and *GG'* has *C*_v symmetry. Atom numbering is given in Fig. 1. ^bTaken from Ref. 4. ^cAverage value; see text. ^dMeasured from *syn*=0°. Clockwise rotation has positive dihedral angle. ^eFor symmetry reasons. ^fTotal energy obtained in the MP2 computations: -832 074.12 kJ mol⁻¹. ^gTotal energy obtained in the B3LYP computations: -834 157.92 kJ mol⁻¹.

in a qualitative manner many of the energy differences computed for the four rotamers. In the *GG* conformer there are two such stabilising 1,3-interactions between the C-F and C-H bond dipoles which would be nearly anti-parallel (Fig. 1). This is the most favourable position two dipoles can take. In *AG* there is only one such favourable 1,3-interaction. In *AA*, which is predicted to

be even less stable than *AG*, there are no 1,3-interactions of the stabilising kind. In *GG'* the two C-F bond dipoles would be nearly parallel, which would be most unfavourable and destabilise this rotamer, in agreement with the theoretical predictions.

Further effects, such as the polarisation of the electron clouds of the C-C bond by the strongly electronegative

fluorine atoms, could also contribute to the conformational properties, albeit in a less obvious way.

MW spectrum and assignment of the ground vibrational state of the GG conformer. The ED and IR work⁴ as well as the present quantum chemical computations indicate that the GG conformer is the preferred form of the molecule. This conformer has C_2 symmetry, and its dipole moment lies consequently exclusively along the b -axis. Searches were first made for the strong bQ -branch transitions using the rotational constants obtained in the MP2 computations as the starting point, because it is our experience that this computational scheme produces accurate rotational constants (and structures). These Q -branch transitions were soon identified close to their predicted frequencies. The same was the case with the low- J R -branch lines. The assignments were then gradually extended to high values of the J quantum number. A few selected transitions are listed in Table 2.*

A total of about 600 transitions were ultimately assigned for the ground vibrational state, 568 of which were used to determine the spectroscopic constants (A -reduction, I' representation)¹⁶ shown in Table 3. The maximum value of J was 77. 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. It is seen in Table 3 that accurate values have been obtained not only for the quartic centrifugal distortion constants, but for all the sextic as well.

Vibrationally excited states of GG. The ground state transitions were accompanied by series of transitions presumably belonging to vibrationally excited states of GG. Six excited states belonging to three different normal vibrational modes were assigned; their spectroscopic constants are listed in Table 3.

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 $75(15) \text{ cm}^{-1}$ by relative intensity measurements made largely as described in Ref. 17. This is close to 85 cm^{-1} found in the B3LYP calculations (not given in Table 1) and 94 cm^{-1} measured for the lowest torsion of a -symmetry species.⁴

Two further successively excited states of this fundamental mode were assigned (Table 3). While the first and second excited state of this vibration could be accurately fitted to the Watson A -reduction Hamiltonian,¹⁶ problems were encountered for the third excited state. Several of the high- J Q -branch transitions could not be fitted to within the experimental uncertainty of ± 0.10 MHz. Deviations of typically 0.3–5 MHz were seen for most

Table 2. Selected transitions from the MW spectrum of the ground vibrational state of the GG conformer of 1,3-difluoropropane.

Transition		Observed frequency ^a /MHz	Obs. – calc. freq./MHz
$J'_{K'-1, K'+1}$	$\leftarrow J''_{K'-1, K'+1}$		
1 _{1,1}	\leftarrow 0 _{0,0}	12 088.45	–0.02
3 _{0,3}	\leftarrow 2 _{1,2}	10 509.69	–0.08
4 _{2,2}	\leftarrow 4 _{1,3}	18 914.65	–0.01
6 _{0,6}	\leftarrow 5 _{1,5}	28 137.97	–0.05
8 _{1,8}	\leftarrow 7 _{2,5}	21 890.32	0.01
9 _{3,6}	\leftarrow 9 _{2,7}	32 139.98	0.06
12 _{1,11}	\leftarrow 12 _{0,12}	14 690.50	0.13
13 _{3,10}	\leftarrow 12 _{4,9}	27 486.06	–0.02
18 _{2,16}	\leftarrow 18 _{1,17}	18 559.45	0.09
20 _{1,19}	\leftarrow 20 _{0,20}	30 977.77	0.07
23 _{2,21}	\leftarrow 23 _{1,22}	25 084.13	0.00
27 _{3,24}	\leftarrow 27 _{2,25}	25 866.53	–0.09
31 _{3,28}	\leftarrow 31 _{2,29}	29 747.19	0.09
34 _{4,30}	\leftarrow 34 _{3,31}	33 255.41	–0.06
37 _{4,33}	\leftarrow 37 _{3,34}	33 550.02	0.10
40 _{4,36}	\leftarrow 40 _{3,37}	35 727.56	0.01
Coalescing R - and P -branch transitions ^b			
6 ₄	\leftarrow 5 ₅	25 276.03	–0.17
11 ₅	\leftarrow 10 ₆	10 291.40	0.02
17 ₆	\leftarrow 16 ₇	10 296.49	0.05
24 ₁₁	\leftarrow 23 ₁₂	15 839.76	–0.01
27 ₁₄	\leftarrow 28 ₁₃	19 521.20	–0.01
33 ₁₇	\leftarrow 34 ₁₆	24 990.82	0.00
40 ₁₄	\leftarrow 39 ₁₅	33 852.48	0.08
47 ₁₇	\leftarrow 46 ₁₈	33 400.84	0.01
62 ₂₄	\leftarrow 61 ₂₅	24 917.57	–0.09
70 ₃₃	\leftarrow 71 ₃₂	26 575.83	–0.01
77 ₃₀	\leftarrow 76 ₃₁	28 598.89	0.03

^a ± 0.10 MHz. ^b The K_{-1} doublet coalesce for high- K_{-1} .

of them. The reason for these deviations is presumed to be higher order vibration–rotation interaction terms. The frequencies that deviated more than 0.3 MHz were omitted in the final fit, whose spectroscopic constants are listed in Table 3.

The changes of the rotational constants upon three successive excitations of this lowest torsional mode are quite constant, as can be seen in Table 3. This is typical for a harmonic mode.¹⁸

The second lowest fundamental was found to be about 25% as intense as the ground vibrational state. A frequency of $172(20) \text{ cm}^{-1}$ was determined by relative intensity measurements. The B3LYP value for the lowest bending vibration was 174 cm^{-1} . The IR value of this mode, that is of b -symmetry species, is 182 cm^{-1} (Ref. 4).

A combination mode involving the lowest torsional vibration and the lowest bending vibration was also assigned (Table 3). If the changes of the rotational constants upon excitation to these two modes are added to the rotational constants of the ground vibrational state, a set of rotational constants are obtained that are close to the observed ones. This is the basis for the present assignment.

The final excited state in Table 3 is the first excited state

* 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, Molecular Physics 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 rotamer of 1,3-difluoropropane.

Vibrational state:	Ground vibrational state	1st ex. lowest C–C tors. vibration	2nd ex. lowest C–C tors. vibration
No. of transitions:	568	484	315
R. m. s. dev. ^c /MHz:	0.058	0.060	0.086
<i>A_v</i> /MHz	9362.122 5(22)	9392.695 0(25)	9422.651 3(44)
<i>B_v</i> /MHz	2886.899 41(70)	2897.298 30(78)	2906.650 8(14)
<i>C_v</i> /MHz	2726.398 05(72)	2727.754 64(79)	2728.289 2(13)
Δ_J /kHz	4.497 1(14)	4.603 6(16)	4.702 0(34)
Δ_{JK} /kHz	−31.516(12)	−32.281(13)	−32.320(29)
Δ_K /kHz	91.162 1(26)	92.864 8(44)	92.803 5(76)
δ_J /kHz	0.942 54(21)	0.974 61(25)	0.999 66(62)
δ_K /kHz	13.075(19)	13.857(24)	13.979(58)
Φ_J /Hz	0.032 12(59)	0.028 45(74)	0.0284(17)
Φ_{JK} /Hz	0.147(11)	−0.028(13)	0.134(47)
Φ_{KJ} /Hz	−0.973 4(81)	−0.868(12)	−1.143(32)
Φ_K /Hz	3.197 3(66)	3.069(12)	3.266(47)
ϕ_J /Hz	0.014 29(12)	0.011 05(18)	0.01259(73)
ϕ_{JK} /Hz	−0.398 7(54)	0.107(15)	−0.079(97)
ϕ_K /Hz	2.049(39)	−1.26(12)	7.56(62)
Max. value of <i>J</i>	77	68	58
3rd ex. lowest C–C tors. vibration ^d	1st ex. lowest bending vibration	1st ex. second lowest C–C tors. vibration	Lowest C–C tors. and bend. comb. mode
77	310	133	127
0.087	0.074	0.077	0.086
9450.493(16)	9479.918 2(35)	9351.905 6(45)	9518.539 7(58)
2914.756 7(41)	2852.521 5(11)	2886.658 8(13)	2863.596 8(16)
2727.934 1(42)	2703.8567(11)	2724.1139(13)	2706.050 0(17)
4.836(20)	4.370 6(23)	4.388 7(18)	4.427 2(27)
−33.14(13)	−33.130(19)	−30.380(14)	−35.553(24)
79.4(14)	101.385 5(93)	89.525(75)	103.188(75)
1.000 88(44)	0.924 26(39)	0.932 95(52)	0.981 48(33)
13.085(48)	14.849(44)	13.714(51)	16.247(30)
0.3212 ^e	0.025 01(92)	0.032 12 ^e	0.032 12 ^e
0.147 ^e	−0.131(21)	0.147 ^e	0.407(18)
−197(12)	−1.093(41)	−0.973 4 ^e	−0.973 4 ^e
3.197 3 ^e	3.752(46)	4.39(44)	5.54(43)
0.014 29 ^e	0.009 46(39)	0.013 13(54)	0.012 92(22)
−0.3987 ^e	0.367(59)	−0.211(61)	2.049 ^e
2.049 ^e	−7.71(53)	2.049 ^e	40
25	53	39	

^aA-reduction, *I*-representation.¹⁶ ^bUncertainties represent one standard deviation. ^cRoot-mean-square deviation. ^dSelected lines omitted from the least-squares fit; see text. ^eKept constant at this value in the least-squares fit.

of the second lowest torsional mode. Its intensity is about 17% of the ground state intensity at dry-ice temperature. Its frequency was determined to be 232(25) cm^{−1} by relative intensity measurements. The B3LYP value was 241 cm^{−1} for this vibration, while 252 cm^{−1} was measured for this fundamental frequency of the *b*-species.⁴ The close proximity of the experimental and theoretical frequency is the reason for this assignment.

The fourth lowest fundamental vibration was calculated to have a B3LYP frequency of 413 cm^{−1}: 416 cm^{−1} is found experimentally.⁴ This corresponds to a Boltzmann factor of 0.05 at 194 K. This small value can presumably explain why this weak excited state was not found in the very crowded spectrum.

Dipole moment of GG. The dipole moment was determined in the standard way.¹⁹ Only the component along the *b*-axis is different from zero because the *GG* con-

former has *C*₂ symmetry. The results are shown in Table 4.

Both the B3LYP and the MP2 values listed in Table 1 are seen to be about 9 and 20%, respectively, higher than the experimental dipole moment found in Table 4. This confirms that the 6-311++G** basis set, designed to give good energy values and structures at a reasonable cost, may lead to comparatively poor predictions of electric properties.

Bond moment computations using the values of Ref. 20 and the MP2 structure yielded a dipole moment of 6.0 × 10^{−30} C m, which is about 13% too low.

MW spectrum and assignment of the ground vibrational state of AG. The *ab initio* calculations above indicate that *AG* is the second most stable form of 1,3-difluoropropane being ca. 4 kJ mol^{−1} less stable than *GG*. *AG* is

Table 4. Stark coefficients^a and dipole moment^a of the GG conformer of 1,3-difluoropropane.

Transition	M	$\Delta\nu E^{-2}/10^{-5} \text{ MHz V}^{-2} \text{ cm}^2$	
		Obs.	Calc.
4 _{2,2} ← 4 _{1,3}	4	-4.00(5)	-3.95
	3	-2.72(3)	-2.66
	2	-1.80(2)	-1.74
9 _{1,8} ← 9 _{0,9}	9	4.75(4)	4.81
	8	3.80(4)	3.82
	7	2.82(3)	2.92
	6	2.19(3)	2.14
	5	1.46(2)	1.49

Dipole moment/ 10^{-30} C m
 $\mu_b = 6.946(29)$

^aUncertainties represent one standard deviation. 1 D = $3.33564 \times 10^{-30} \text{ C m}$.

predicted to have sizeable components of the dipole moment along all three inertial axes (Table 1). However, the fact that this is a high-energy form of the molecule makes transitions belonging to this rotamer comparatively weak.

Searches were first made for the $J=8 \leftarrow 7$ and $J=7 \leftarrow 6$ *R*-pile ups at a low Stark voltage (ca. 20 V cm^{-1}). These lines were immediately found. Additional transitions of the *a*-, *b*- and *c*-varieties were then successively included in a least-squares procedure. Ultimately, a total of about 350 transitions were assigned with a maximum value of $J=79$. A few representative transitions are listed in Table 5. The spectroscopic constants derived from 335 transitions are shown in Table 6. All sextic centrifugal distortion constants had to be included in the least-squares fit in order to obtain a root-mean square deviation comparable to the experimental uncertainty of $\pm 0.10 \text{ MHz}$.

Vibrationally excited states of AG. It can be seen in Table 6 that one vibrationally excited state has been assigned, while a tentative assignment was derived for another excited state. Relative intensity measurements yielded $111(15) \text{ cm}^{-1}$ for the first of these two excited states. The B3LYP value (not given in Table 1) for the lowest C–C torsional vibration is 93 cm^{-1} , in fair agreement with the experimental value. No value is available for this vibration from the IR work.⁴ The second excited state, for which only a tentative assignment could be made, is assumed to be the second excited state of the same torsional vibration.

Dipole moment of AG. The dipole moment of the AG rotamer was determined in the same manner as for the GG conformer, as described above. The results are shown in Table 7. Both theoretical methods (MP2 and B3LYP, Table 1) predict dipole moments which are larger than that presented in Table 7. The prediction of μ_c is particularly poor.

Table 5. Selected transitions from the MW spectrum of the ground vibrational state of the AG conformer of 1,3-difluoropropane.

Transition	Observed frequency ^a /MHz	Obs. – calc. freq./MHz
$J_{K'-1, K'+1} \leftarrow J_{K'-1, K'+1}$		
2 _{1,2} ← 1 _{0,1}	20 164.81	-0.06
3 _{1,2} ← 2 _{1,1}	13 737.01	-0.11
4 _{1,4} ← 3 _{0,3}	28 517.92	0.03
5 _{4,1} ← 4 _{4,0}	22 452.59	-0.05
5 _{4,2} ← 4 _{4,1}	22 452.59	-0.05
7 _{0,7} ← 6 _{0,6}	31 306.42	0.00
12 _{1,11} ← 12 _{0,12}	19 977.94	0.00
14 _{2,12} ← 14 _{1,13}	28 970.83	0.03
16 _{2,15} ← 15 _{3,13}	12 976.08	-0.08
19 _{2,17} ← 19 _{3,16}	35 550.23	-0.02
21 _{3,18} ← 20 _{4,17}	16 421.55	0.04
31 _{3,29} ← 31 _{2,29}	28 879.31	0.03
40 _{3,38} ← 40 _{2,38}	12 598.83	-0.01
50 _{4,47} ← 50 _{3,47}	22 116.38	0.02
63 _{5,59} ← 63 _{4,59}	26 769.68	-0.05
71 _{5,67} ← 71 _{4,67}	10 975.40	-0.06

Coalescing *R*- and *P*-branch transitions^b

31 ₈ ← 32 ₇	27 576.32	0.10
35 ₉ ← 36 ₈	32 498.08	0.02
44 ₁₀ ← 45 ₉	14 706.41	-0.03
52 ₁₂ ← 53 ₁₁	24 677.09	-0.03
63 ₁₁ ← 62 ₁₂	20 821.32	-0.04
71 ₁₂ ← 70 ₁₃	33 908.46	-0.08
79 ₁₄ ← 78 ₁₅	23 437.54	-0.06

^{a,b}Comments as for Table 2.

The bond moment computations²⁰ yielded (in units of 10^{-30} C m): $\mu_a = 3.2$, $\mu_b = 4.2$, $\mu_c = 3.7$, and $\mu_{\text{tot}} = 6.4$, respectively. Accurate prediction of μ_c is again seen to be problematic, while better agreement is found for the two other dipole moment components.

Searches for further conformations. The above assignments include a total of about 2600 transitions in the 10–36 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. Numerous unsuccessful attempts were made to assign unidentified transitions of weak or intermediate intensities to each of unassigned *AA* and *GG'* conformers. The starting points in these searches were the rotational constants and dipole moment components given in Table 1.

The fact that each of these conformations is predicted to possess sizeable dipole moments 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 *GG*. Our conservative estimate is that *AA* and *GG'* each is at least 4 kJ mol^{-1} less stable than *GG*. This estimate agrees with the theoretical predictions in Table 4.

The most likely explanation for the comparatively weak and numerous unassigned transitions is that they

Table 6. Spectroscopic constants^{a,b} of the ground and vibrationally excited states of the AG rotamer of 1,3-difluoropropane.

Vibrational state:	Ground vibrational state	1st ex. lowest C–C tors. vibration	2nd ex. lowest. C–C tors. vibration ^f
No. of transitions:	335	104	11
R. m. s. dev. ^c /MHz:	0.065	0.092	0.086
A_v /MHz	13 701.199 8(37)	13 547.573(12)	13 239(31)
B_v /MHz	2 334.821 20(62)	2 339.251 7(18)	2 334.942(21)
C_v /MHz	215 4.565 29(59)	2 159.446 3(18)	2 172.558(18)
Δ_J /kHz	0.909 7(11)	0.992 2(61)	0.910 ^e
Δ_{JK} /kHz	−9.057(18)	−9.106(39)	−9.06 ^e
Δ_K /kHz	86.280(46)	95.8(15)	86.28 ^e
δ_J /kHz	0.156 13(12)	0.164 84(28)	0.156 ^e
δ_K /kHz	4.512(42)	3.604(92)	4.51 ^e
Φ_J /Hz	0.001 19(75)	0.001 19 ^e	— ^g
Φ_{JK} /Hz	0.167(19)	−0.087(97)	—
Φ_{KJ} /Hz	−1.030(70)	40.9(52)	—
Φ_K /Hz	2.93(53)	−157(32)	—
ϕ_J /Hz	0.000 265(53)	−0.001 64(38)	—
ϕ_{JK} /Hz	−0.069(31)	1.20(11)	—
ϕ_K /Hz	9.68(95)	9.68 ^e	—
Max. value of J	79	71	7

^{a–e}Comments as for Table 3. ^fTentative assignment; see text. ^gSextic centrifugal distortion constants pre-set at zero.

Table 7. Stark coefficients^a and dipole moment^a of the AG conformer of 1,3-difluoropropane.

Transition	$ M $	$\Delta v E^{-2}/10^{-5} \text{ MHz V}^{-2} \text{ cm}^2$	
		Obs.	Calc.
4 _{1,3} ← 4 _{0,4}	4	4.71(5)	4.45
5 _{1,4} ← 5 _{0,5}	5	4.20(4)	4.00
	4	2.18(3)	2.30
7 _{1,6} ← 7 _{0,7}	7	3.15(3)	3.30
	6	1.05(2)	1.04
8 _{2,6} ← 8 _{1,7}	8	2.04(2)	2.09
	7	1.13(4)	1.08
Dipole moment/ 10^{-30} C m			
$\mu_a = 3.59(5) \quad \mu_b = 5.32(9) \quad \mu_c = 1.02(19) \quad \mu_{\text{tot}} = 6.50(11)$			

^aComments as for Table 4.

mainly belong to unassigned vibrationally excited states of *GG*, and/or *AG*. Small fractions of further rotamers cannot, however, be completely ruled out, nor can of course impurities.

Energy differences. The energy differences between the two conformers assigned in this investigation were made by relative intensity measurements observing the precautions of Ref. 17. The statistical weight of the *AG* conformer was assumed to be twice that of the *GG* rotamer. The statistical weights of the individual rotational levels are different in the *GG* and *AG* forms. All levels have the same statistical weight in *AG* because of its symmetry (C_1). However, *GG* contains a two-fold axis of symmetry. A 180° rotation interchanges four pairs of fermions (the hydrogen and fluorine atom pairs) and one pair of bosons (the carbons in the 1 and 3 position). The nuclear statistical weights are hence 136 for symmetrical rota-

tional energy levels and 120 for anti-symmetrical levels.²¹ These statistics were taken into account in the derivation of the energy difference between the ground vibrational states which was found to be 4.0(2) kJ mol^{−1} with *GG* as the more stable. The uncertainty given here is one standard deviation.

This energy difference is in excellent agreement with the theoretical values given in Table 1. It is about twice as large as the energy difference between *gauche* and *anti* propyl fluoride²² (1.97 kJ mol^{−1}). It is harder to compare our results quantitatively to those of the ED and IR investigation⁴ because our results refers to the internal energy difference of the ground vibrational states, while their results⁴ actually represent the Gibbs energy differences between the conformers at 20 °C.

However, both methods agree that *GG* is clearly the most stable form of the molecule with *AG* as the second most stable form. While the stable existence of *GG'* cannot be ruled out, it is impossible that as much as 10% is present at dry-ice temperature (−79 °C), because this rotamer would have had a large dipole moment (Table 1) resulting in a spectrum roughly as intense as that of *AG*. Such an intense spectrum would not have been overlooked. A 10% presence is also inconsistent with the *ab initio* results shown in Table 1, which predicts an energy difference of about 12 kJ mol^{−1}. This large difference would produce much less than 10% *GG'* at −79 °C in agreement with our finding.

Structure. The observed and calculated rotational constants of both *GG* and *AG* are compared in Table 8. It is seen that the MP2 rotational constants on the average are in slightly better agreement with the experimental ones than the B3LYP constants are. Both these theoretical structures are in good agreement with the ED result,⁴

Table 8. Experimental^a and theoretical^b (6-311 + +G** basis set) rotational constants/MHz.

	Exp.	MP2	Diff. (%)	B3LYP	Diff. (%)
GG					
A	9362.1	9215.9	1.6	9341.2	0.2
B	2886.9	2931.0	-1.5	2826.4	2.1
C	2726.4	2757.2	-1.1	2674.8	1.9
AG					
A	13547.6	13717.8	-1.3	13736.9	-1.4
B	2339.2	2340.6	0.0	2296.5	1.8
C	2159.4	2155.4	0.2	2120.6	1.8

^aTaken from Tables 2 and 5 above. ^bSee text.

although the C-F bond length is problematic for both computational procedures, as remarked above. It is our feeling that the bond lengths are best determined in the ED work, while angles and dihedral angles perhaps are most accurate in the theoretical computations. The MP2 and B3LYP computational procedures seem to offer predictions of about the same high quality.

Conclusions

This study has again⁴ demonstrated that gaseous 1,3-difluoropropane consists of an equilibrium mixture of GG and AG. These two rotamers make up almost the whole gas phase at 194 K. There is very little of any further conformers. GG is the most stable form of the molecule 4.0(2) kJ mol⁻¹ more stable than AG. There is reasonably good agreement between the present work and the combined ED and IR work.⁴ Good predictions of the structures of the different conformers as well as the energy differences between them are found using the 6-311 + +G** basis set in MP2 and B3LYP calculations. The conformational preferences of 1,3-difluoropropane can be explained qualitatively as resulting largely from 1,3 bond-dipole interactions.

Acknowledgement. Mrs. Anne Horn is thanked for art work. This work has received support from The Research Council of Norway (Programme for Supercomputing) through a grant of computer time.

References

- Lere-Porte, J. P., Petrissans, J. and Gromb, S. *J. Mol. Struct.* 40 (1977) 159.
- Lere-Porte, J. P. and Petrissans, J. *J. Mol. Struct.* 48 (1978) 289.
- Meyer, A. Y. *J. Mol. Struct.* 49 (1978) 383.
- Klæboe, P., Powell, D. L., Stølevik, R. and Vorren, Ø. *Acta Chem. Scand., Ser. A* 36 (1982) 471.
- Wolfe, S. *Acc. Chem. Res.* 5 (1972) 102.
- Recent examples includes: (a) 2(Fluormethyl)pyridine; Moberg, C., Adolfsson, H., Wärnmark, K., Norrby, P.-O., Marstokk, K.-M. and Møllendal, H. *Chem. Eur. J.* 2 (1996) 516; (b) oxalyl fluoride; Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand.* 49 (1995) 172; (c) 2,2,3,3-tetrafluoro-1-propanol; Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand.* 47 (1993) 281.
- Guirgis, G. A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand.* 45 (1991) 482.
- Waal, Ø. (1994) *Personal communication*.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. and Pople, J. A. *Gaussian 94, Revision B.3*, Inc., Pittsburgh, PA 1995.
- Møller, C. and Plesset, M. S. *Phys. Rev.* 46 (1934) 618.
- Becke, A. D. *J. Chem. Phys.* 98 (1993) 5648.
- Hehre, W. J., Radom, L., Schleyer, P. v. R. and Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, New York 1985, p. 227.
- Hayashi, M. and Fujitake, M. *J. Mol. Struct.* 146 (1986) 9.
- Hayashi, M. and Ikeda, C. *J. Mol. Struct.* 223 (1990) 207.
- Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, New York 1960, p. 260.
- Watson, J. K. G. In: Durig, J. R., Ed., *Vibrational Spectra and Structure*, Elsevier, Amsterdam 1977, Vol. 6, p. 1.
- Esbit, A. S. and Wilson, E. B. *Rev. Sci. Instrum.* 34 (1963) 901.
- Herschbach, D. R. and Laurie, V. W. *J. Chem. Phys.* 37 (1962) 1668.
- Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand., Ser. A* 36 (1982) 517.
- Smyth, C. P. *Dielectric Behavior and Structure*, McGraw-Hill, New York 1955, p. 244.
- Townes, C. H. and Schawlow, A. L. *Microwave Spectroscopy*, McGraw-Hill, New York 1955, p. 104.
- Hirota, E. *J. Chem. Phys.* 37 (1962) 283.

Received February 21, 1997.