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

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The microwave spectrum of 1,2-difluoropropane has been investigated in the 10.0–40.0 GHz spectral region at dry-ice temperature (−78 °C). Three all-staggered rotameric forms are possible for this compound. Two of these rotamers, denoted **Conformer I** and **Conformer II**, respectively, were assigned in this work. These two forms both have a F–C–C–F *gauche* atomic arrangement. The methyl group is *anti* to the C1–F bond in **Conformer I** and *gauche* to this bond in **Conformer II**. The third form, **Conformer III**, which has a F–C–C–F *anti* arrangement, is likely to be present but could not be assigned, presumably because of its small dipole moment.

Conformer II is 1.2(4) kJ mol^{-1} more stable than **I**. The dipole moments (in units of 10^{-30} C m) are $\mu_a = 5.12(4)$, $\mu_b = 8.64(8)$, $\mu_c = 0.11(2)$, and $\mu_{tot} = 10.05(8)$ for **Conformer I**, and $\mu_a = 1.108(3)$, $\mu_b = 4.46(3)$, $\mu_c = 8.30(6)$, and $\mu_{tot} = 9.49(6)$ for **Conformer II**, respectively. Three vibrationally excited states of **I** belonging to three different normal modes were assigned, while two excited states of two different normal modes were assigned for **II**. The barrier to internal rotation of the methyl group in **Conformer I** was determined from the splittings of the first excited states of the methyl group torsional vibration and is 11.88(20) kJ mol^{-1}.

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 functional theory calculations at the B3LYP/6-311++G** level. Internal energy differences between the three conformers of less than 0.5 kJ mol^{-1} were computed at both these levels of theory. The best predictions of the rotational constants were found in the MP2/6-311++G** computations which are therefore assumed to predict the most accurate geometries for the conformers. Best predictions of the dipole moment are found in the B3LYP/6-311++G** calculations.

1,2-Difluoropropane, CH_3CHFCH_2F, represents an interesting conformational problem. The three all-staggered rotameric forms shown in Fig. 1 are possible for this compound. In **Conformer I** the F1–C1–C2–F2 link of atoms is +*gauche*, about +60° from *syn* (0°); in **Conformer II** the corresponding chain of atoms is −*gauche* (approximately −60° from *syn*), while it is *anti* (ca. 180° from *syn*) in **Conformer III**. The methyl group is *anti* to the C1–F1 bond in **I**, +*gauche* in **II** and −*gauche* in **III**.

Various intramolecular forces are presumed to be in operation in 1,2-difluoropropane and their concerted interaction will determine the structure and the conformational properties of the molecule. Polarisation of the electrons of the C1–C2 bond by the strongly electronegative fluorine atoms is one effect expected to be important for the conformational preferences. This interaction leads to a preference for the *gauche* arrangement for the F1–C1–C2–F2 link of atoms (**I** and **II**) and is often termed the '*gauche* effect'.[1]

The dipole–dipole interaction between the two polar C–F bonds is another force that should be considered. This force will destabilise a F–C–C–F *gauche* arrangement (i.e. **Conformers I** and **II**) with respect to the *anti* form (**Conformer III**). There is also a close proximity between the two fluorine atoms in **I** and **II** which might lead to steric repulsion. This too would favour **III**.

In the closely related molecule 1,2-difluoroethane, CH_2FCH_2F, the *gauche* form is 2.69(33) kJ mol^{-1} more stable than the *anti* conformer.[2] This fact must mean that the *gauche* effect is rather large, prevailing over the bond–dipole as well as steric repulsive interaction in this prototype molecule.

The conformational properties of CH_3CHFCH_2F are

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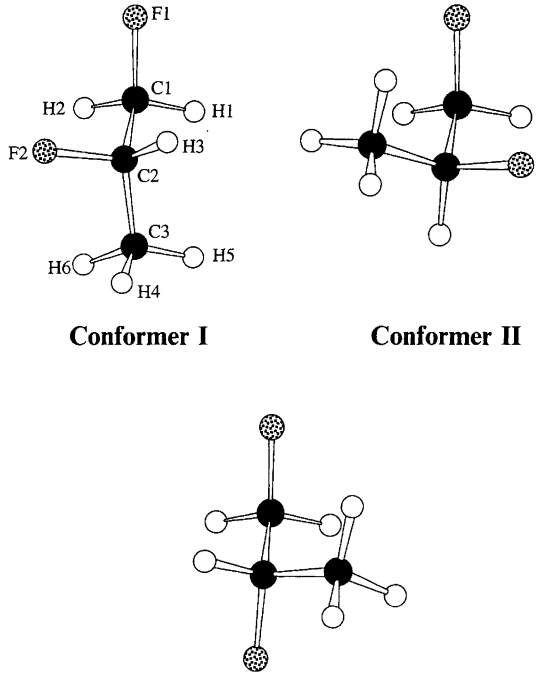

Conformer I **Conformer II**

Conformer III

Fig. 1. The three all-staggered conformations of 1,2-difluoropropane. Atom numbering is shown on **Conformer I**. **Conformers I** and **II** were assigned in this work. **II** is 1.2(4) kJ mol^{-1} more stable than **I**. **Conformer III**, which is predicted to have a small dipole moment, was not found.

more complicated than those of CH_2FCH_2F, because of the methyl group. It was expected that both the two F–C–C–F *gauche* **Conformers I** and **II** of CH_3CHFCH_2F as well as the *anti* form **III** would exist within a narrow energy range, presumably with **I** and **II** more stable than **III**, if a parallel to 1,2-difluoroethane can be drawn which seems quite plausible. The challenge that this delicate equilibrium situation poses prompted the present research.

No experimental studies of the conformational properties of the title compound have been reported. However, there have been a few theoretical studies: Molecular mechanics calculations of energies and dipole moments at two different levels have been made by Hammarström *et al.*[3] In the standard MM2 procedure negligible energy differences among **I**, **II** and **III** were predicted, whereas **I** was predicted to be about 3.2 kJ mol^{-1} more stable than **III**, and 2.5 kJ mol^{-1} more stable than **II** in a modified MM2 computation. Stølevik and Bakken[4] computed the low-frequency normal vibrations using force constants derived from related molecules. The conformational energies of the three rotamers were predicted by Stølevik[5] using an empirical computational scheme. These calculations predict **Conformer II** to be the most stable rotamer, 1.7 kJ mol^{-1} more stable than **I**, and as much as 4.9 kJ mol^{-1} more stable than **III**. An INDO MO study of conformational effects upon vicinal ^{19}F–^{13}C coupling constants have also been reported.[6]

MW spectroscopy is ideal for investigating complicated conformational equilibria where polar conformers are present because of its high selectivity and specificity. Two of the three rotamers (**I** and **II**) that are possible for 1,2-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 can be studied at dry-ice temperature, where intensities are larger than at higher temperatures. All this makes 1,2-difluoropropane well suited for a MW conformational investigation.

Advanced quantum chemical computations are often found to be useful in predicting rotational constants, dipole moments and energy differences for the various conformers that are sufficiently close to the experimental ones to be really helpful 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. Such calculations are therefore of interest in their own right.

The unique effect that fluorine sometimes is seen to have on the structural and conformational properties[1] has been of interest to this laboratory.[7] 1,2-Difluoropropane was chosen for study as a continuation of our investigations of fluorine-containing molecules.

Experimental

A commercial sample was employed in this work. It was purified by preparative gas chromatography before use. The MW spectrum was studied using the Oslo spectrometer which is described in Ref. 8. The 10–40 GHz spectral region was investigated with the microwave absorption cell cooled to dry-ice temperature (194 K). The spectra were recorded at a pressure of about 2–6 Pa and stored electronically using the computer programs written by Waal.[9] The accuracy of the frequency measurements is presumed to be better than ± 0.10 MHz, and the resolution was approximately 0.5 MHz.

Results and discussion

Quantum chemical calculations. The Gaussian 94 program package[10] 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 program[10] 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 theory[11] with frozen-core electrons.[10] In the second procedure, density functional theory (DFT) calculations were carried out employing the B3LYP[12] method. Full geometry optimisation was

made in the MP2 as well as in the B3LYP computations for all three rotamers (Fig. 1) which were found to be minima ('stable') on the potential energy hyper surface, as no imaginary vibrational frequencies[13] were computed for any of them. The geometries calculated for the three conformers are given in Table 1 together with some other parameters of interest. Atom numbering is given in Fig. 1.

Some of these findings deserve comments. Both the MP2 and B3LYP methods yield rather similar and small energy differences (less than 0.5 kJ mol^{-1}) between the three conformers, with **Conformer II** as the slightly more stable form (Table 1). The fact that **III**, which has a F–C–C–F *anti* atomic arrangement, is calculated to be almost as stable as **I** and **II** is not considered to be likely, since the *anti* form of 1,2-difluoroethane is considerably less stable [by 2.69(33) kJ mol^{-1}] than *gauche*,[2] as noted above. It is thus possible that both the MP2 as well as the B3LYP procedures are not able to reproduce the energy differences accurately, but make *anti* forms more stable than they really are.

Comparatively small differences are seen for the structures computed by the two methods. Typically, the C–F bond lengths are 0.5–1.0 pm longer in the B3LYP computations. These bond lengths vary between 138.9 and 140.2 pm for the three rotamers in the MP2 calculations. The the C–F bond length determined for the closely related molecule *gauche* CH_2FCH_2F[14] is 139.4(2) pm which compares well to the MP2 values. The C1–C2 bond lengths are also calculated to be slightly longer in the B3LYP than in the MP2 computations. The substitution value in *gauche* CH_2FCH_2F[14] is 149.1(2) pm. This value is closer to the MP2 (150.9–151.9 pm) than to the B3LYP results (151.2–152.3 pm) of Table 1.

The F–C–C–F dihedral angles vary by less than 3° for the same conformer in the two computational schemes (Table 1). In the two conformers (**I** and **II**) that have a *gauche* arrangement for this angle, values of about 70° are computed. This is close to 71.3(5)° found in *gauche* CH_2FCH_2F.[14]

The rather large dihedral angle may reflect repulsion between the two C–F bond dipoles which come rather close to one another in **Conformers I** and **II.** Steric repulsion may also play a role, because the non-bonded F···F distances are computed (MP2 methods) to be 284 pm in **I** and 288 pm in **II**, respectively. This is relatively close to 270 pm, which is twice the van der Waals radius of fluorine.[15] A decrease of the F–C–C–F dihedral angle to the 'normal' value of 60° would result in a smaller distance between the two fluorine atoms, with increased dipole–dipole and steric repulsion as a likely result.

The dipole moments (Table 1) are generally computed to be smaller in the B3LYP than in the MP2 procedure by several percent.

MW spectrum and assignment of the ground vibrational state of ***Conformer I.*** The MW spectrum of 1,2-difluoropropane is very crowded with absorptions occurring every few MHz throughout the entire frequency range owing to the presence of at least two rotamers each with rich, perpendicular spectra.

The quantum chemical computations (Table 1) indicate that small energy differences exist among **Conformers I–III.** A search was first made for **Conformer I.** This conformer is predicted to have its largest dipole moment component 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[17a] 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 a*- and *b*-type *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 475 transitions were ultimately assigned for the ground vibrational state, 452 of which were used to determine the spectroscopic constants (*A*-reduction, I^r representation)[16] shown in Table 3. Maximum value of *J* was 76. 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. Three sextic centrifugal distortion constants were included in order to obtain a fit with a root-mean-square deviation similar to the experimental uncertainty of about ±0.10 MHz.

Vibrationally excited states of ***Conformer I.*** The ground-state transitions were accompanied by series of transitions presumably belonging to vibrationally excited states of **Conformer I.** Three excited states belonging to three different normal vibrational modes were assigned; their spectroscopic constants are listed in Tables 3 and 5.

The most intense excited state (Table 3) has about 38% of the intensity of the ground vibrational state at 194 K. Its frequency was determined to be 130(20) cm^{-1} by relative intensity measurements made largely as described in Ref. 17. This is close to 120 cm^{-1} found in the B3LYP calculations (not given in Table 1) and 117 cm^{-1} predicted by Bakken and Stølevik[4] for the first excited state of the C1–C2 torsion.

The first excited state of another fundamental (Table 3) was found to have about 18% of the intensity of the ground vibrational state. A frequency of 231(25) cm^{-1} was determined by relative intensity measurements.[17] This mode is assumed to be the lowest bending vibration. The B3LYP value for this fundamental was 249 cm^{-1}, and the force-field value[4] was 266 cm^{-1}.

The first excited state of the torsional vibration of the

* 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 1. Structure, rotational constants, dipole moment and energy differences of **Conformers I, II** and **III** of 1,2-difluoropropane as calculated at the MP2/6-311++G** (frozen core) and B3LYP/6-311++G** levels of theory. Atom numbering is given in Fig. 1.

Procedure:	MP2			B3LYP		
Conformer:	I	II	III	I	II	III
Distance/pm						
C1–F1	138.9	139.0	139.3	139.6	139.7	140.1
C1–C2	150.9	151.1	151.9	151.2	151.5	152.3
C1–H1	109.3	109.5	109.2	109.3	109.5	109.2
C1–H2	109.4	109.2	109.3	109.4	109.2	109.3
C2–F2	139.8	139.9	140.2	140.9	140.9	141.2
C2–H3	109.4	109.7	109.4	109.4	109.7	109.4
C2–C3	151.6	151.4	151.0	151.9	151.7	151.2
C3–H4	109.2	109.2	109.2	109.1	109.1	109.2
C3–H5	109.4	109.1	109.4	109.3	109.1	109.3
C3–H6	109.4	109.4	109.3	109.3	109.4	109.3
Angle/°						
F1–C1–C2	110.4	110.7	108.6	110.7	111.5	108.9
F1–C1–H1	108.1	108.1	108.5	107.8	107.6	108.1
F1–C1–H2	108.1	107.9	108.4	107.6	107.7	108.0
C1–C2–F2	108.2	108.6	105.9	108.4	108.7	105.6
C1–C2–H3	109.4	107.6	109.5	109.4	107.3	109.4
C1–C2–C3	112.1	113.9	113.5	112.7	114.7	114.3
C2–C3–H4	109.7	109.9	110.3	109.7	110.0	110.4
C2–C3–H5	110.5	110.0	110.0	111.0	110.4	110.5
C2–C3–H6	110.5	110.0	109.7	110.6	110.2	109.7
Dihedral angle[a]/°						
F1–C1–C2–F2	67.8	−71.1	175.7	69.1	−73.7	174.5
F1–C1–C2–H3	−48.0	173.8	60.5	−46.1	172.1	60.2
F1–C1–C2–C3	−172.2	50.2	−64.4	−170.6	48.3	−65.3
F2–C2–C1–H1	−51.4	169.7	56.7	−50.3	167.1	55.8
F2–C2–C1–H2	−173.0	48.3	−65.4	−172.0	45.9	−66.7
C1–C2–C3–H4	185.2	179.5	181.0	185.2	180.5	180.8
C1–C2–C3–H5	−55.2	−60.2	−58.9	−55.1	−59.1	−58.7
C1–C2–C3–H6	65.5	59.7	61.0	65.8	60.9	61.1
Rotational constants/MHz						
A	8452.6	6786.8	8082.2	8374.1	6766.1	7997.9
B	3497.1	4033.0	3546.7	3451.3	3955.8	3503.2
C	2706.8	3248.9	2687.2	2674.5	3180.8	2653.3
Dipole moment components[b] and total dipole moment/10^{-30} C m						
μ_a	6.66	1.62	0.43	6.14	1.47	0.51
μ_b	9.96	4.02	1.51	9.18	3.67	1.70
μ_c	0.26	9.86	0.24	0.13	8.91	0.28
μ_{tot}	11.98	10.77	1.64	11.04	9.75	1.80
Energy difference[c]/kJ mol^{-1}						
	0.35	0.0[d]	0.27	0.07	0.0[e]	0.10

[a]Measured from *syn*=0°. Clockwise rotation correspond to positive dihedral angle. [b]Along the principal inertial axes. [c]Relative to **Conformer II**. [d]Total energy obtained in the MP2 computations: −832 081.40 kJ mol^{-1}. [e]Total energy obtained in the B3LYP calculations: −834 164.16 kJ mol^{-1}.

methyl group was also assigned and used to determine the barrier to internal rotation of this group, as described in the next section.

The fourth lowest fundamental vibration was calculated to have a B3LYP frequency of 358 cm^{-1}. This corresponds to a Boltzmann factor of 0.07 at 194 K. This small value can presumably explain why this weak excited state was not found in the crowded spectrum.

*Barrier to internal rotation of the methyl group of **Conformer I**.* Several members of a third vibrationally excited state were split into two components of equal

Table 2. Selected transitions of the MW spectrum of the ground vibrational state of **Conformer I** of 1,2-difluoropropane.

Transition $J'_{K'_{-1},K'_{+1}}$	←	$J''_{K''_{-1},K''_{+1}}$	Observed frequency[a]/MHz	Obs. −calc. freq./MHz
$1_{1,1}$	←	$0_{0,0}$	11 163.54	0.10
$2_{2,1}$	←	$2_{1,2}$	17 236.68	−0.03
$3_{0,3}$	←	$2_{0,2}$	18 288.79	0.03
$3_{0,3}$	←	$2_{1,2}$	14 042.93	0.04
$4_{1,4}$	←	$3_{1,3}$	23 097.79	0.03
$4_{2,2}$	←	$4_{1,3}$	13 517.10	0.10
$5_{2,3}$	←	$5_{1,4}$	13 292.88	−0.04
$5_{4,2}$	←	$4_{4,1}$	31 250.87	0.13
$6_{1,6}$	←	$5_{0,5}$	35 949.98	−0.07
$6_{3,3}$	←	$6_{4,2}$	23 606.09	0.09
$7_{0,7}$	←	$6_{1,6}$	39 270.06	−0.01
$8_{2,7}$	←	$8_{1,8}$	31 048.15	−0.13
$9_{3,7}$	←	$8_{4,4}$	18 787.23	−0.04
$10_{4,7}$	←	$9_{5,4}$	15 537.09	−0.05
$12_{3,10}$	←	$11_{4,7}$	33 272.97	0.10
$14_{5,9}$	←	$14_{4,10}$	39 791.89	−0.10
$16_{5,11}$	←	$16_{4,12}$	35 135.84	0.11
$19_{5,14}$	←	$19_{4,15}$	33 327.68	0.18
$21_{5,16}$	←	$21_{4,17}$	38 411.21	−0.08
Coalescing *R*- and *P*-branch transitions[b]				
10_{9}	←	11_{8}	21 798.05	0.07
14_{12}	←	15_{11}	28 752.03	0.11
19_{14}	←	20_{13}	18 456.61	−0.08
25_{17}	←	26_{16}	12 538.05	−0.01
30_{15}	←	29_{16}	24 671.21	0.02
35_{17}	←	34_{18}	35 359.00	0.06
42_{28}	←	43_{27}	23 019.17	−0.02
50_{27}	←	49_{28}	22 592.58	−0.02
61_{33}	←	60_{34}	28 221.88	−0.06

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

intensity, but of two different symmetries, the non-degenerate *A*-level and the degenerate *E*-level. The separation between the two components amounted to as much as 2.84 MHz for one transition, as seen in Table 4,

Table 4. Split transitions of the first excited state of the torsional vibration of the methyl group of **Conformer I** of 1,2-difluoropropane used to determine the barrier to internal rotation of this group.

Transition $J'_{K'_{-1},K'_{+1}}$	←	$J''_{K''_{-1},K''_{+1}}$	Observed frequency[a] /MHz (*A* species)	$(\nu_E-\nu_A)$/ MHz	V_3/ kJ mol^{-1}
$9_{3,6}$	←	$9_{2,7}$	20 227.41	1.11	11.93
$8_{3,5}$	←	$8_{2,6}$	20 947.92	1.23	11.95
$14_{4,10}$	←	$14_{3,11}$	26 600.06	1.34	11.85
$13_{4,9}$	←	$13_{3,10}$	26 907.23	1.51	11.95
$12_{4,8}$	←	$12_{3,9}$	28 084.38	1.86	11.83
$7_{3,5}$	←	$7_{2,6}$	29 228.82	1.30	11.92
$11_{4,7}$	←	$11_{3,8}$	29 819.61	2.03	11.81
$10_{4,6}$	←	$10_{3,7}$	31 755.77	2.20	11.76
$18_{5,13}$	←	$18_{4,14}$	32 761.53	1.64	11.92
$17_{5,12}$	←	$17_{4,13}$	33 422.04	2.02	11.91
$16_{4,12}$	←	$16_{5,11}$	35 033.80	2.38	11.87
$22_{6,16}$	←	$22_{5,17}$	38 813.78	1.96	11.89
$14_{5,9}$	←	$14_{4,10}$	39 679.85	2.84	11.77
$21_{6,15}$	←	$21_{5,16}$	39 829.71	2.47	11.90
				Average:	11.89(20)[b]

[a] ±0.10 MHz. [b]The uncertainty is estimated to represent one standard deviation; see text.

where well resolved transitions are listed. Other lines were seen to be rather broad, and partial resolutions were also seen for some of them. Such a spectral feature is typical for the tunnelling motion of a methyl group.

The broad lines with partially resolved *A*- and *E*-components were not used to determine the spectroscopic constants, because they are not well suited for this purpose. However, transitions with minor perturbations together with the split transitions shown in Table 4 'corrected' for tunnelling using[18] $\nu_0=(\nu_A+2\nu_E)/3$ were the ones selected to determine the best values for the spectroscopic constants of the first excited state of the methyl torsion. The results are shown in Table 5.

Table 3. Spectroscopic constants[a,b] of the ground and vibrationally excited states of the **Conformer I** rotamer of 1,2-difluoropropane.

Vibrational state:	Ground vibrational state	1st ex. C1–C2 tors. vibration	Lowest bending vibration
No. of transitions:	452	203	73
R.m.s. dev.[c]/MHz:	0.080	0.096	0.101
A_v/MHz	8454.817 2(25)	8421.324 9(40)	8437.680 7(74)
B_v/MHz	3502.816 3(11)	3500.845 6(15)	3502.760 6(45)
C_v/MHz	2708.576 7(10)	2707.311 5(14)	2707.866 3(43)
Δ_J/kHz	0.767 7(39)	0.860 5(35)	0.848(50)
Δ_{JK}/kHz	7.924(32)	8.110(41)	19.628(86)
Δ_K/kHz	0.164 2(81)	0.058(35)	0.1624[e]
δ_J/kHz	0.217 4(15)	0.198 8(28)	0.228 2(51)
δ_K/kHz	4.075(41)	4.612(63)	3.92(12)[f]
Φ_J/Hz	−0.115 8(48)	0.003 88(22)	—
Φ_{JK}/Hz	−1.616(64)	−0.084(33)[d]	—
Φ_{KJ}/Hz	−1.724(70)[d]	—	—
Max. value of *J*	61	47	18

[a] *A*-reduction, I^r-representation.[16] [b]Uncertainties represent one standard deviation. [c]Root-mean-square deviation. [d]Further sextic centrifugal distortion constants pre-set at zero. [e]Kept constant at this value in the least-squares fit. [f]All sextic centrifugal distortion constants pre-set at zero.

Table 5. Spectroscopic constants[a,b] of the first excited state of the torsional vibration of the methyl group of **Conformer I** of 1,2-difluoropropane.

No. of transitions:	59
R.m.s. dev.[c]/MHz:	0.226
A_v/MHz	8445.488(17)
B_v/MHz	3502.356 6(56)
C_v/MHz	2707.121 1(53)
Δ_J/kHz	0.767 7[d]
Δ_{JK}/kHz	6.98(13)
Δ_K/kHz	0.164 2[d]
δ_J/kHz	0.189 5(95)
δ_K/kHz	4.019(22)
Φ_J/Hz	−0.115 8[d]
Φ_{JK}/Hz	−1.616[d]
Φ_{KJ}/Hz	−1.724[d,e]
Max. value of J	22

[a–c]Comments as for Table 3. [d]Kept constant at this value in the least-squares fit. [e]Further sextic centrifugal distortion constants pre-set at zero. [f]All sextic centrifugal distortion constants pre-set at zero.

The following procedure was employed to determine the barrier height. The direction cosines (Table 6) of the methyl group (the C2–C3 bond) were taken from the MP2 structure in Table 1. The methyl group was assumed to have three-fold symmetry and its moment around the symmetry axis was assumed to be 3.20×10^{-20} u m^2. The computer program used is reported in Ref. 19. It uses second- and fourth-order perturbation treatment of the tunnelling interaction and is based on the principal axis method.[18] The barrier height was varied in a systematic manner until complete matching with the splittings was found. The barrier height determined in each such case is listed in Table 4. The barrier heights determined from the various transitions vary relatively little, as seen in the same table. The average height is found to be 11.89 kJ mol^{-1}. It is difficult to assess the accuracy of this number because of a possible interaction with other vibrational modes, as well as the simplified model used in our approach. However, a standard deviation of $\pm$0.20 kJ mol^{-1} seems reasonable. From the barrier of 11.89(20) kJ mol^{-1} a torsional frequency of 209 cm^{-1} is computed for the torsional fundamental frequency of the methyl group. The B3LYP value is 213 cm^{-1}.

The barrier of the related compound, CH_3CH_2F, is14.012(17) kJ mol^{-1}.[20] For the congener CH_3CHFCH_3 it is 13.74(10) kJ mol^{-1}.[21] Both these barriers are somewhat higher than that of the title compound.

Table 6. Parameters used to determine the barrier to internal rotation of the methyl group of **Conformer I**.[a,b]

Direction cosines with respect to the principal inertial axes of the methyl group:[c]

$\lambda_a = 0.8519$ $\lambda_b = 0.4790$ $\lambda_c = 0.2116$

Moment of inertia of the methyl group/10^{-20} μm^2:[d] $I_\alpha = 3.20$

Miscellaneous parameters:[b]

$R = 0.95534$ $F = 1.6531 \times 10^5$ $s = 80.05$

Barrier to internal rotation of the methyl group[e]/kJ mol^{-1}: $V_3 = 11.89(20)$

[a]See text. [b]Defined in Ref. 18. [c]From MP2 structure. [d]Assumed value; see text. [e]For assessment of one standard deviation; see text.

*Dipole moment of **Conformer I**.* The dipole moment was determined in the standard way by Stark effect measurements.[22] The results are shown in Table 7. The error limits of one standard deviation quoted in this table are assumed to encompass random as well as systematic errors.

The MP2 value (Table 1) for the total dipole moment is 11.98×10^{-30} C m, which is 19% to high. The B3LYP value is (same units) 11.04, which is 9% too high. 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.

*MW spectrum and assignment of the ground vibrational state of **Conformer II**.* The quantum chemical calculations (Table 1) as well as Stølevik[5] predict that **Conformer II** is the most stable one of the three rotamers possible for this compound. This conformer is predicted to have a sizeable component of the dipole moment along the c-axis. Searches were therefore first made for the c-type Q-branch transitions which were predicted to be the strongest ones of this rotamer, using the MP2 rotational constants as starting points. These lines were soon found. Additional Q-branch transitions of the b- and c-varieties were then successively included in a least-squares proced-

Table 7. Stark coefficients[a] and dipole moment[a] of **Conformer I** of 1,2-difluoropropane.

Transition			$\lvert M\rvert$	$\Delta\nu\, E^{-2}/10^{-6}$ MHz V^{-2} cm^2 Obs.	Calc.
$7_{3,5}$	←	$7_{2,6}$	7	−57.7(6)	−55.3
			6	−42.0(5)	−40.3
			5	−27.4(2)	−27.6
			4	−16.3(2)	−17.2
$8_{3,6}$	←	$8_{2,7}$	8	−16.1(2)	−15.6
			7	−11.9(1)	−11.8
			6	−8.72(10)	−8.54
			5	−5.56(7)	−5.78
			4	−3.35(5)	−3.52
$7_{2,5}$	←	$7_{1,6}$	7	2.78(3)	2.75
			6	1.91(2)	1.90
			5	1.16(1)	1.17
			4	0.615(8)	0.579
$6_{2,5}$	←	$6_{1,6}$	6	2.13(2)	2.31
			5	1.32(1)	1.25

Dipole moment/10^{-30} C m

$\mu_a = 5.118(39)$ $\mu_b = 8.642(78)$ $\mu_c = 0.112(19)$

$\mu_{tot} = 10.045(78)$

[a]Uncertainties represent one standard deviation. 1 Debye = $3.33\,564 \times 10^{-30}$ C m.

ure. Finally, low-J b-and c-type R-branch lines were identified and included in the fit. A total of about 330 transitions were ultimately assigned with a maximum value of $J=72$. A few representative transitions are listed in Table 8. The spectroscopic constants derived from 314 transitions are shown in Table 9. One sextic centrifugal distortion constant had to be included in the least-squares fit in order to obtain a root-mean square deviation comparable to the experimental uncertainty of ± 0.10 MHz.

Table 8. Selected transitions of the MW spectrum of the ground vibrational state of **Conformer II** of 1,2-difluoropropane.

Transition $J'_{K'_{-1},K'_{+1}}$	←	$J''_{K''_{-1},K''_{+1}}$	Observed frequency[a]/MHz	Obs. − calc. freq./MHz
$1_{1,1}$	←	$0_{0,0}$	10 038.77	−0.01
$2_{2,0}$	←	$1_{1,0}$	23 779.72	0.14
$3_{0,3}$	←	$2_{1,1}$	16 766.61	−0.17
$3_{3,0}$	←	$2_{2,0}$	37 578.87	0.16
$4_{0,4}$	←	$3_{1,3}$	26 435.45	−0.07
$4_{3,2}$	←	$4_{2,3}$	16 259.01	−0.06
$5_{3,2}$	←	$5_{2,3}$	13 405.37	0.03
$6_{2,5}$	←	$6_{1,6}$	18 283.97	0.14
$6_{6,0}$	←	$6_{5,2}$	34 448.98	−0.07
$7_{4,4}$	←	$7_{3,4}$	19 403.93	−0.01
$8_{3,6}$	←	$8_{2,7}$	21 401.56	−0.01
$8_{6,2}$	←	$8_{5,4}$	34 183.59	0.00
$9_{4,6}$	←	$9_{3,6}$	15 067.31	0.00
$10_{1,9}$	←	$10_{0,10}$	30 333.30	−0.16
$11_{7,4}$	←	$11_{6,5}$	39 984.24	−0.09
$12_{5,8}$	←	$12_{4,8}$	19 062.57	−0.03
$13_{2,11}$	←	$13_{1,12}$	35 311.12	0.07
$15_{5,10}$	←	$15_{4,11}$	19 870.92	0.05
$16_{4,12}$	←	$16_{3,13}$	31 146.75	0.07
$17_{5,12}$	←	$17_{4,13}$	25 260.70	−0.05
$18_{6,13}$	←	$18_{5,13}$	11 245.53	0.08
$20_{7,13}$	←	$20_{6,13}$	26 305.09	−0.01
$23_{8,15}$	←	$23_{7,16}$	29 925.85	−0.14
$26_{8,18}$	←	$26_{7,19}$	33 601.46	−0.06
$28_{10,19}$	←	$28_{9,19}$	34 792.75	0.06
$33_{11,22}$	←	$33_{10,23}$	39 432.47	0.11
$40_{13,28}$	←	$40_{12,28}$	25 336.35	0.00
$50_{16,35}$	←	$50_{15,35}$	27 015.58	0.04
$60_{19,42}$	←	$60_{18,42}$	27 707.57	0.05
$72_{22,51}$	←	$72_{21,51}$	12 969.41	0.04

[a] ± 0.10 MHz.

Vibrationally excited states of ***Conformer II.*** It can be seen in Table 9 that two vibrationally excited states have been assigned. Relative intensity measurements[17] yielded 131(20) cm^{-1} for the first fundamental which is assumed to be the first excited state of the C1–C2 torsional vibration. The B3LYP value (not given in Table 1) for the C1–C2 vibration is 120 cm^{-1}, and the force-field value is 125 cm^{-1}.[4]

The second excited state is assumed to be the lowest bending vibration. Relative intensity measurements yielded 223(25) cm^{-1} for this mode, compared to 245 cm^{-1} computed using the B3LYP methods, and 249 cm^{-1} predicted by Stølevik and Bakken.[4] No splittings were seen for the transitions of this excited state, and this is one important reason for not assigning it as the first excited state of the torsional motion of the methyl group which is predicted to have split lines provided the barrier to internal rotation is similar to that of **Conformer I**.

Futile searches for the first excited state of the methyl torsion were made in spite of the fact that its frequency is predicted (B3LYP) to be only 231 cm^{-1}. The transitions of this excited state are predicted to have somewhat larger splittings than those seen above (Table 4) for **Conformer I** provided their barriers were similar. Their intensities would then be reduced to half the value of the intensities of unsplit lines (about 9% of the intensity of the ground-state lines). The reduced intensities, in combination with the crowded nature of this spectrum, are presumed to be the reason why we were unsuccessful in our attempts to find this excited state.

Dipole moment of ***Conformer II.*** The dipole moment of **Conformer II** was determined in the same manner as that of **I**, as described above. The results are shown in Table 10. Both theoretical methods (MP2 and B3LYP, Table 1) predict dipole moments which are larger than

Table 9. Spectroscopic constants[a,b] of the ground and vibrationally excited states of the **Conformer II** rotamer of 1,2-difluoropropane.

Vibrational state:	Ground vibrational state	1st ex. C1–C2 tors. vibration	Lowest bending vibration
No. of transitions:	314	248	90
R.m.s. dev.[c]/MHz:	0.087	0.087	0.123
A_v/MHz	6797.784 2(37)	6811.006 2(75)	6787.914(14)
B_v/MHz	4028.633 7(36)	4030.836 7(75)	4031.754(14)
C_v/MHz	3240.929 4(36)	3233.803 8(75)	3242.206(14)
Δ_J/kHz	2.380(54)	2.30(21)	2.380[e]
Δ_{JK}/kHz	8.094 1(96)	8.253(11)	8.437(48)
Δ_K/kHz	−6.516(31)	−6.596(37)	−6.58(12)
δ_J/kHz	0.242 05(59)	0.246 82(69)	0.243 5(37)
δ_K/kHz	3.218 1(99)	3.360(12)	3.676(59)
Φ_{JK}/Hz	0.003 87(14)[d]	−0.000 65(19)[d]	0.003 87[e]
Max. value of J	72	66	37

[a–e] Comments as for Table 3.

Table 10. Stark coefficients[a] and dipole moment[a] of **Conformer II** of 1,2-difluoropropane.

Transition			|M|	$\Delta\nu\, E^{-2}/10^{-6}$ MHz V^{-2} cm^2 Obs.	Calc.
$2_{2,0}$	←	$1_{1,0}$	0	−19.4(2)	−19.4
			1	3.86(4)	3.86
$10_{5,6}$	←	$10_{4,6}$	10	−10.5(1)	−10.7
			9	−8.66(8)	−8.69
			8	−6.83(6)	−6.86
			7	−5.39(7)	−5.26
			6	−3.85(5)	−3.85
			5	−2.69(5)	−2.68

Dipole moment/10^{-30} C m
$\mu_a = 1.108(3)$ $\mu_b = 4.458(27)$ $\mu_c = 8.302(59)$
$\mu_{tot} = 9.488(58)$

[a]Comments as for Table 7.

the experimental one. The MP2 total dipole moment is too large by about 13%, whereas the B3LYP value for the total dipole moment is too large by approximately 3%.

Searches for ***Conformer III.*** This rotamer is predicted to be only slightly less stable than **I** and **II** in the quantum chemical computations above (Table 1), whereas Stølevik[5] predicts **III** to be as much as 5.0 kJ mol^{-1} less stable than **II**. **Conformer III** undoubtedly has a small dipole moment (Table 1), which would make it hard to find in a dense spectrum such as the present one even if had been the most stable conformer. If Stølevik's prediction[5] were correct, it would be almost impossible to assign its MW spectrum because in this case only a few per cent of the gas composition would be **Conformer III** with a small dipole moment and an extremely weak MW spectrum.

The above assignments include a total of about 1500 transitions in the 10–40 GHz region. All the strongest transitions seen in the MW spectrum, the majority of the lines of intermediate intensity, as well as many weak lines have been assigned. Unsuccessful attempts were made to assign unidentified transitions of weak or intermediate intensities to **Conformer III**. The starting points in these searches were the MP2 rotational constants and the B3LYP dipole moment components given in Table 1.

Energy differences. The internal energy difference between **Conformers I** and **II** was determined by relative intensity measurements observing the precautions of Ref. 17. A value of 1.2(4) kJ mol^{-1} was found with **II** as the more stable. The uncertainty given here is one standard deviation.

This energy difference is in reasonable agreement with the theoretical values given in Table 1 and in good agreement with Stølevik's prediction[5] (1.7 kJ mol^{-1}). The reason why **II** is more stable than **I** is not obvious. A weak stabilising interaction between the C1–F1 bond and the methyl group may be of importance. This stabilisation is possible in **Conformer II**, but not in **I** and could be the major cause why **II** is preferred.

It is interesting to compare the present results with those found for the isoelectronic compounds $CH_3CH(OH)CH_2F$[23] and CH_3CHFCH_2OH.[24] In both these cases[23,24] only rotamers similar to **Conformer I** were found. Other rotamers were estimated to be at least 3 kJ mol^{-1} less stable. This is another demonstration that similar substituents influence the conformational properties in rather different and unpredictable ways.

Structure. The observed and calculated rotational constants of **I** and **II** are compared in Table 11. It is seen that the MP2 rotational constants are in very good agreement with the experimental ones, while the B3LYP constants are in somewhat poorer agreement. The MP2 structures (Table 1) are therefore suggested as plausible structures for **Conformers I** and **II**, and also for the hypothetical **Conformer III**. It is expected that any full experimental structures that is determined in the future for these three forms will be very close to the MP2 structures.

Conclusions

This study has demonstrated that gaseous 1,2-difluoropropane consists of an equilibrium mixture of **Conformers I** and **II**. Whether **Conformer III** co-exists with the other two rotamers cannot be answered, presumably because

Table 11. Experimental[a] and theoretical[b] (6-311++G** basis set) rotational constants/MHz.

	Exp.	MP2	Diff./%	B3LYP	Diff./%
Conformer I					
A	8454.8	8452.6	0.02	8374.1	0.95
B	3502.8	3497.1	0.16	3451.3	1.47
C	2708.6	2706.8	0.07	2674.5	1.26
Conformer II					
A	6797.8	6786.8	0.16	6766.1	0.46
B	4028.6	4033.0	−0.11	3955.8	1.81
C	3240.9	3248.9	−0.25	3180.8	1.85

[a]Taken from Tables 3 and 9 above. [b]Taken from Table 1.

of its low dipole moment and hence low intensity of its MW transitions. **Conformer II** is more stable than **I** by 1.2(4) kJ mol^{-1}.

Both conformers have a *gauche* arrangement for the F–C–C–F chain of atoms. The presence in the gas of large fractions of **I** and **II** is evidence that the *gauche* effect is of considerable importance for the conformational make-up of this compound.

Good predictions of the structures of the two conformers as well as the energy differences between them are found using the 6-311++G** basis set in the MP2 as well as in the B3LYP calculations. However, the MP2 methods is presumed to be slightly superior to the B3LYP computations in predicting the structures of the two conformers, while the MP2 calculations are inferior to the B3LYP methods in predicting correct dipole moments.

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References

1. Wolfe, S. *Acc. Chem. Res. 5* (1972) 102.
2. Durig, J. R., Liu, J., Little, T. S. and Kalasinsky, V. F. *J. Phys. Chem. 96* (1992) 8224, and references cited therein.
3. Hammarström, L.-G., Liljefors, T. and Gasteiger, J. *J. Comput. Chem. 9* (1988) 424.
4. Stølevik, R. and Bakken, P. *J. Mol. Struct. 245* (1991) 231.
5. Stølevik, R. *J. Mol. Struct. 291* (1993) 59.
6. Wray, V. *J. Am. Chem. Soc. 103* (1981) 2503.
7. Recent examples include: (a) 1,3-difluoropropane; Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 51* (1997) 1058; (b) 2(fluormethyl)pyridine; Moberg, C., Adolfsson, H., Wärnmark, K., Norrby, P.-O., Marstokk, K.-M. and Møllendal, H. *Chem. Eur. J. 2* (1996) 516; (c) oxalyl fluoride; Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 49* (1995) 172; (d) 2,2,3,3,-tetrafluoro-1-propanol; Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 47* (1993) 281.
8. Guirgis, G. A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand. 45* (1991) 482.
9. Waal. Ø. (1994) *Personal communication.*
10. 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.
11. Møller, C. and Plesset, M. S. *Phys. Rev. 46* (1934) 618.
12. Becke, A. D. *J. Chem. Phys. 98* (1993) 5648.
13. Hehre, W. J., Radom, L., Schleyer, P. v. R. and Pople, J. A. *Ab Initio Molecular Orbital Theory,* Wiley, New York 1985, p. 227.
14. Takeo, H., Matsumura, C. and Morino, Y. *J. Chem. Phys. 84* (1986) 4205.
15. Pauling, L. *The Nature of the Chemical Bond,* 3rd Edn., Cornell University Press, New York 1960, p. 260.
16. Watson, J. K. G. In: Durig, J. R., Ed. *Vibrational Spectra and Structure*, Elsevier, Amsterdam 1977, Vol. 6, p. 1.
17. Esbitt, A. S. and Wilson, E. B. *Rev. Sci. Instrum. 34* (1963) 901.
18. Herschbach, D. R. *J. Chem. Phys. 31* (1959) 91.
19. Marstokk, H. and Møllendal, H. *J. Mol. Struct. 32* (1976) 191.
20. Fliege, E., Dreizler, H., Demaison, J., Boucher, Bevrie, J. and Dubrulle, A. *J. Chem. Phys. 78* (1983) 3541.
21. Meyer, M. and Dreizler, H. *Z. Naturforsch., Teil A 43* (1988) 138.
22. Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand., Ser. A 36* (1982) 517.
23. Marstokk, K.-M. and Møllendal, H. *J. Mol. Struct. 40* (1977) 1.
24. Braathen, O.-A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand., Ser. A 36* (1982) 173.

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