Conformational Equilibrium and Potential Energy Surface of 1-Fluorobutane by Microwave Spectroscopy and Ab Initio Calculations

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Abstract: The rotational spectra of four (GT, TT, TG, and GG) of the five possible conformers of 1-fluorobutane have been assigned by combining free jet and conventional microwave spectroscopy. The geometry optimization was performed at the MP2 (full) level of theory with the 6-31G (d) and 6-311G (d, p) basis sets and by using the B3LYP (3df, 3pd) density functional method. The relative stability of the five rotamers is calculated at the QCISD (T)/6-311G (d, p) level of theory. In spite of the fact that ab initio calculations indicated the unobserved GG′ conformer to be more stable than at least one of the observed conformers it was not possible to detect its rotational spectrum. GT and TG are the most and the least stable species, respectively. The rotational spectra of several vibrational satellites of the four conformers have been studied by conventional microwave spectroscopy. The overall conformational equilibrium is governed by the two-dimensional potential energy surface of the skeletal torsions MeC–CC and FC–CC, which have been evaluated by a flexible model analysis, based on the experimental values of the relative conformational and vibrational energy spacings, and on the shifts of second moments of inertia upon conformational change and vibrational excitation. The relative energy of the fifth stable conformer (GG′) was determined to be 333 cm^{-1} from flexible model calculations, and to be 271 cm^{-1} from the most accurate ab initio calculations.

Keywords: ab initio calculations · conformation analysis · density functional calculations · molecular dynamics · rotational spectroscopy

Introduction

Conformational equilibria of alkanes have been extensively studied and it is well known that local *gauche* and *trans* configurations are stable minima and that the torsional potential energy surfaces depend on steric and electrostatic forces.[1] Accordingly linear alkanes have a large number of conformers; the number of which rapidly increases with an increase in the length of the chain. The are already nine minima in the torsional potential energy surface for monosubstituted *n*-butanes, corresponding to five different conformers. A precise and certain identification of the five rotamers in such a complex mixture has not been reported for any of these derivatives so far.

1-Fluorobutane (FB) represents a simple and interesting model molecule for this kind of study, since it possesses a permanent dipole moment, which allows the measurements of the rotational spectra of the various conformers, and it is small enough to allow high level ab initio calculations. Figure 1 shows the five plausible conformers of 1-fluorobutane: GT, TT, TG, GG, and GG′, according to the configuration (*gauche* or *trans*) of the fluorine atom and of the methyl group, respectively. In the GG conformer the F atom and CH_3 group are on opposite sides of the plane formed by the three central carbon atoms of the molecule, while the reverse is true for the GG′ species.

In spite of the fact that 1-fluorobutane is the simplest 1-halogenated derivative of butane, its rotational spectrum has never been reported, while the microwave (MW) investigations of Cl-, Br-, and I-butane are, to different, partial extents, available in the literature. Most of the experimental data in the gas phase concern the configuration equilibrium of chlorobutane. The two most recent gas-phase electron diffraction investigations of this molecule suggest the following room temperature abundance ratios TT/GT/TG/GG/GG′: 25/50/5/15/5 (Fagerland et al. [2]), and 13/60/12/12/1 (Aarset

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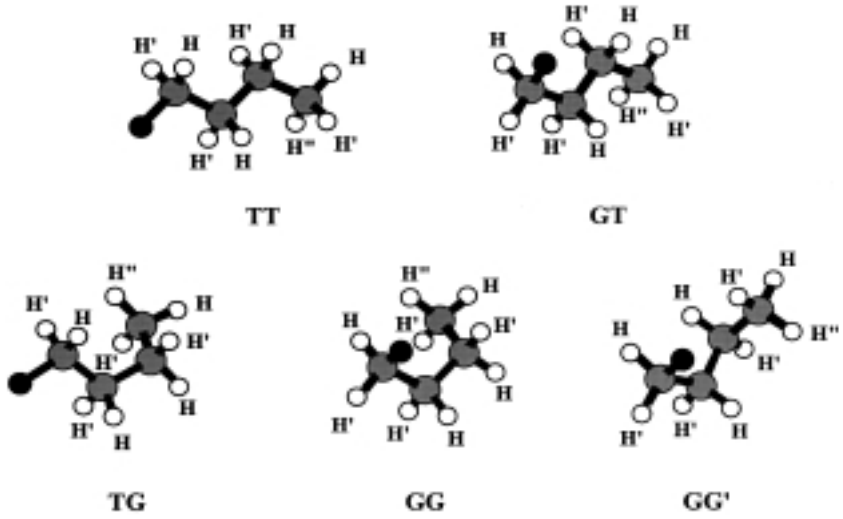

Figure 1. Draft of the five possible conformers of 1-fluorobutane.

et al.[3]), but the smaller values have a large uncertainty. We reported the rotational spectra, first of three conformers,[4] then of a fourth conformer[5] by combined free jet and conventional rotational spectroscopy. The fifth conformer, GG′, which is 600–700 cm^{-1} higher in energy than the most stable conformer (TT), escaped our investigation. We obtained information on the two-dimensional (2D) potential energy surface of the two skeletal torsions governing the conformational equilibrium from additional measurements (e.g. dipole moments, rotational spectra of several vibrational satellites, and their vibrational energies).[5] The treatment of these data with a 2D flexible model[6] allowed the determination of the conformational surface, which resulted in good agreement with the ab initio calculations. Only low-resolution MW spectra are available for the Br and I derivatives.[7]

We set ourselves the challenging goal to obtain more precise information for fluorobutane, for which it was anticipated that it should be possible to observe all the five possible conformers, especially when the suggestions given by the ab initio calculations were taken into consideration. The results of such ab initio calculations are particularly useful in assigning the microwave spectra of substituted alkanes, since they help to discriminate between the large number of features originating from the different conformers.

Abstract in Italian: *Gli spettri rotazionali di quattro (GT, TT, TG and GG) dei cinque possibili conformeri dell' 1-Fluorobutano sono stati assegnati combinando spettroscopia rotazionale in espansione supersonica e spettroscopia rotazionale convenzionale. L'ottimizzazione della geometria e' stata ottenuta al livello MP2 (full) della teoria con i set di basi 6–31G (d) e 6–311G (d, p), ed usando il metodo funzionale di densita' B3LYP (3df, 3pd). La stabilita' relativa dei cinque rotameri e' stata calcolata al livello QCISD (T)/6–311G (d, p). Malgrado i calcoli ab initio abbiano indicato che il conformero non osservato, GG′, sia piu' stabile di almeno uno dei conformeri osservati, non e' stato possibile identificare il suo spettro rotazionale. GT e TG sono la specie piu' stabile e quella meno stabile, rispettivamente. Gli spettri rotazionali di parecchi satelliti vibrazionali dei quattro conformeri sono stati studiati con la spettroscopia a microonde conventionale. L' equilibrio conformationale e' governato, nel suo complesso, dalla superficie di energia potenziale bidimensionale delle torsioni scheletali MeC-CC ed FC-CC, che sono state calcolate con un model flessibile, basandosi sui valori sperimentali delle energie relative conformazionali e vibrazionali, e sulle variazioni dei momenti planari di inerzia per effetto delle interconversioni conformazionali e delle eccitazioni vibrazionali. L' energia relativa del quinto conformero (GG′) risulta essere 333 cm^{-1} dai calcoli col modello flessibile, e 271 cm^{-1} dai calcoli ab initio piu' accurati.*

Results and Discussion

Rotational spectra

The rotational spectrum of fluorobutane recorded with a conventional spectrometer appears very crowded, due to the large number of rotamers and of low-energy vibrational satellites. Thanks to the relatively good agreement between the ab initio and the experimental rotational constant values of the GT, TT, and TG conformers (see later), the assignment of their rotational spectra was rather straightforward already at room temperature. The radiofrequency–microwave double resonance (RFMWDR) technique[10] was very useful, however, in assigning the first transitions, several μ_a-R-type doublets. Many more rotational transitions were then measured by conventional Stark modulation and by free jet absorption millimeter wave spectroscopy (FJ-AMMW). The GG conformer, whose experimental rotational constants were indeed quite far away from the preliminary ab initio calculated values, was assigned only by using the FJ-AMMW spectrometer.[8] We did not succeed, however, in spite of a long and careful search with the available techniques, in assigning the spectrum of the GG′ conformer. This fact is very puzzling because the GG′ conformer should be more stable than the TG one and it should have a high μ_b value.

The rotational spectra of several vibrational satellites were also assigned by using RFMWDR. All of them correspond to excited states of the skeletal torsions. We label τ_F and τ_{Me} the skeletal torsions of the CH_2F and CH_2CH_3 groups, respectively. Correspondingly, the notation (v_F, v_{Me}) will indicate the various excited states. Five, three, two, and two torsional satellites have been assigned for the GT, TG, TT, and GG conformers, respectively. The measured transition frequencies of all conformers and vibrational satellites are available as Supporting Information. The spectroscopic constants obtained by treating the experimental frequencies with the

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Table 1. Rotational constants, centrifugal distortion constants and inertial defect of the GT, GG, TG, and TT conformers of flurobutane in the ground and vibrational excitated states.

		$v_F=0$, $v_{Me}=0$	$v_F=0$, $v_{Me}=1$	$v_F=1$, $v_{Me}=0$	$v_F=0$, $v_{Me}=2$	$v_F=2$, $v_{Me}=0$	$v_F=1$, $v_{Me}=1$		$v_F=0$, $v_{Me}=0$	$v_F=0$, $v_{Me}=1$	$v_F=1$, $v_{Me}=0$
A [MHz]	GT	12586.647(3)[a]	12466.38(2)	12718.60(3)	12353.67(2)	12840.18(2)	12585.86(3)	GG	8537.082(3)	8559(2)	8537.082[d]
B [MHz]		2331.9187(5)	2335.584(2)	2325.900(3)	2339.269(4)	2320.503(4)	2329.910(2)		2875.8126(9)	2884.62(3)	2868.7(1)
C [MHz]		2155.3353(4)	2159.739(2)	2150.084(3)	2164.039(4)	2145.476(5)	2154.878(2)		2678.040(1)	2679.85(3)	2669.7(1)
Δ_J [kHz]		0.8277(4)	0.87(1)	0.90(2)	0.82(4)	0.9[c]	0.834(6)		6.399(4)	5.37(4)	4.71(4)
Δ_{JK} [kHz]		−7.619(7)	−7.57(5)	−7.8(1)	−7.84(5)	−10.2(4)	−8.22(8)		−45.16(1)	−36.9(2)	−45.16[d]
Δ_K [kHz]		67.05(3)	51(4)	67(9)	59(5)	67[c]	70.0(8)		125.86(5)	386(157)	125.86[d]
δ_J [kHz]		0.1365(1)	0.1427(5)	0.1334(4)	0.1509(2)	0.1334[c]	0.1421(5)		1.7503(2)	1.4(1)	1.75[d]
δ_K [kHz]		2.29(2)	0.96(8)	2.9(1)	0[b]	0.9[c]	1.50(7)		21.37(1)	21.37[d]	21.37[d]
H_{JK} [kHz]		–	–	–	–	–	–		−0.276(7)	–	–
H_{KJ} [kHz]		–	–	–	–	–	–		−1.6(3)	–	–
H_K [kHz]		−2.2(1)	–	–	–	–	–		0[b]	–	–
h_J [kHz]		–	–	–	–	–	–		0.0333(1)	–	–
Δ_c [uÅ^2][e]		−22.3963	−22.9216	−21.9679	−23.4155	−21.5921	−22.5359		−46.2202	−45.4545	−46.0641
σ [kHz]		42	54	48	47	75	48		42	77	52
$N_{trans.}$		105	42	38	32	12	35		105	29	8
A [MHz]	TG	12555.81(1)	12577(2)	12455(2)		12355[f]		TT	19008.463(6)	18446(17)	18690(10)
B [MHz]		2287.400(2)	2286.240(4)	2287.877(4)		2289.91(1)			1934.331(1)	1936.239(4)	1934.997(3)
C [MHz]		2115.262(2)	2114.598(6)	2119.989(5)		2124.26(1)			1837.215(1)	1842.368(4)	1839.778(3)
Δ_J [kHz]		0.680(4)	0.68(3)	0.73(3)		0.71(4)			0.195(3)	0.181(7)	0.130(8)
Δ_{JK} [kHz]		−4.85(3)	−4.98(8)	−5.30(7)		−5.92(9)			−2.34(5)	−2.8(2)	8.4(3)
Δ_K [kHz]		60(1)	60[d]	60[d]		60[d]			77.3(41)	77.3[d]	77.3[d]
δ_J [kHz]		0.133(2)	0.133[d]	0.133[d]		0.133[d]			0.0168(1)	0.0168[d]	0.0168[d]
δ_K [kHz]		4.7(8)	4.7[d]	4.7[d]		4.7[d]			0[b]	0[b]	0[b]
Δ_c [uÅ^2]		−22.2706	−22.2415	−23.0832		−23.6950			−12.7762	−13.5169	−13.5226
σ [kHz]		50	57	52		56			50	24	20
$N_{trans.}$		68	25	24		20			68	82	48

[a] Standard errors in parentheses are in units of the last digit. [b] Parameter fixed to zero because not statistically significant. [c] Parameter fixed to the excited state $v_F=1$ $v_{Me}=0$ value. [d] Parameter fixed to the ground state value. [e] $\Delta_c=-I_{cc}+I_{aa}+I_{bb}$. [f] Parameter fixed to $A_{2,0}=A_{1,0}+(A_{1,0}-A_{0,0})$.

quartic Watson Hamiltonian, "A" reduction, I^r representation[11] are reported in Table 1, in which some statistical parameters of the fits are also shown.

Relative intensity measurements

Microwave relative intensity measurements have been performed in order to estimate the conformational and vibrational energies. These measurements have been made following the method of Esbitt–Wilson.[12] We needed to take quantitatively into account the fact that during the measurements the line intensity decreased sensibly. A first-order kinetic equation satisfactorily reproduces the decay of [FB], the fluorobutane concentration, according to Equation (1). The value of k was estimated to be 0.52(9) h^{-1}.

$$[FB]=[FB]_0e^{-kt} \quad (1)$$

Dipole moments

It is not easy to measure dipole moments for a complex molecular system such as fluorobutane. Nevertheless, based on some lucky circumstances and approximations, we could estimate the dipole moments of all four conformers. For example it has been possible in several cases[13] to find a few transitions having the M− dependent Stark coefficients (ΔB^g) much smaller than the coefficients (ΔA^g) which do not depend on M[14] ($g(=a, b, c)$ indicates the dipole moment component). In these cases, due to the overlapping of several Stark lobes, a single giant Stark lobe (SGSL) appears when an electric field is applied. This technique has been used here to determine the dipole moment components of two rotamers. The cell was calibrated with the 3-2 transition of OCS ($\mu=0.71521$ D[15]). The Stark coefficients and the $\Delta\nu/E^2$ slopes of the various Stark lobes are given as Supporting Information, while all experimentally estimated dipole moment components are given in Table 2.

GT conformer: It has been possible to measure the Stark shifts of some lobes of three Q-branch transitions. In addition four R-type transitions with SGSL have been individuated. The fitting of these data has allowed a relatively precise determination of the three dipole moment components, as shown in Table 2.

TG conformer: Three transitions with a SGSL have been identified. From these data we could determine μ_a and μ_c, while μ_b was fixed to zero because μ_b^2 was small and negative. These assumptions are in agreement with the results of ab

Table 2. Experimental and calculated (B3LYP/6–311G (3df, 3pd)) dipole moment components (D) for the various conformers of fluorobutane.

	Experimental values				Calculated values			
	μ_a	μ_b	μ_c	μ_{tot}	μ_a	μ_b	μ_c	μ_{tot}
GT	0.97 (1)	1.50 (2)	0.3 (1)	1.81 (3)	−0.78	1.38	0.49	1.66
TT	1.7(2)	0.93(2)	0.0[a]	1.98[b]	1.508	−1.15	0.0	1.89
GG	1.01(7)	1.10(6)	1.02(5)	1.81[b]	0.85	0.96	1.04	1.65
TG	1.9(1)	0[c]	0.51(3)	1.98(6)	−1.83	−0.04	0.42	1.88
GG′	–	–	–	–	0.20	1.69	0.28	1.73

[a] Fixed to zero by simmetry. [b] Fixed (see text). [c] Fixed to zero. See text.

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initio calculations (see later), which supply the value $\mu_b^2 = 0.00016$.

TT conformer: Two transitions with a SGSL have been found. In order to give an estimate of the μ_a and μ_b dipole moment components (μ_c is zero by symmetry), we needed, however, to assume the value of the total dipole moment to be the same as for the TG conformer, as indicated by the *ab initio* calculations (see later).

GG conformer: The dipole moment components have been estimated from relative intensity measurements of μ_a-, μ_b-, and μ_c-type transitions, assuming the overall dipole moment to have the same value as for the GT conformer as suggested by ab initio calculations. The estimated values have been obtained by averaging various measurements from different rotational lines.

Conformational equilibria

By combining microwave relative intensity measurements of several lines and the values of the dipole moment components of the various conformers it was possible to estimate the energies of the TT, GG, and TG conformers relative to GT, in the vibronic ground states, using Equation (2), where ω_{XY} is the conformational degeneracy ($\omega_{XY}=1$ for TT and $\omega_{XY}=2$ for all the other conformers). I_{XY} and $\Delta\nu_{XY}$ are the peak height and line width, $\mu_{g,XY}$ the considered dipole moment component, and γ_{XY} and ν_{XY} the line strength and frequency, respectively. The following values have been obtained: E_{TT}, E_{GG}, and $E_{TG} = 110(40)$, 170(40), and 360(50) cm^{-1}, respectively.

$$E_{XY} = KT\ln[(\omega_{XY}I_{GT}\Delta\nu_{GT}\mu^2_{g,XY}\gamma_{XY}\nu^2_{XY})/(\omega_{GT}I_{XY}\Delta\nu_{XY}\mu^2_{g,GT}\gamma_{GT}\nu^2_{GT})], \quad XY = TT, GG, TG \tag{2}$$

Two-dimensional potential energy surface of the ν_F and ν_{Me} skeletal torsions

A total of 45 experimental data, that is three conformational energies (E_{TT}, E_{GG}, and E_{TG}), nine vibrational energies of the vibrational satellites relative to the local ground states, the three planar moments of inertia of the GT ground state, and 30 shifts of second moments of inertia with respect to the GT ground state, have been used to obtain information on the 2D potential energy surface of the two torsions. Data relative to the excited states, for which some assumptions on the rotational constant were made, have not been included. Planar (or second) moments of inertia, defined and related to the rotational constants through Equation (3) represent the mass distribution along the principal inertial axes.

$$M_{aa} = \Sigma_i m_i a_i^2 = h/(16\pi^2)(-1/A + 1/B + 1/C), \text{ etc.}, \tag{3}$$

Meyer's 2D flexible model,[6] has been applied to the above-described data to determine the five parameters of the potential energy function given in Equation (4), in which x and y denote the τ_F and τ_{Me} skeletal torsions, $x=0$ and $y=0$ correspond to the values of the dihedral angles F-C-C-C and C-C-C-$CH_3 = 180^\circ$. The C-C-F [$\alpha(1)$], C-C-C [$\alpha(2)$], and C-C-CH_3 [$\alpha(3)$] valence angles, were also considered as model parameters, as well as their relaxations upon skeletal torsions, according to Equation (5).

$$V(x, y) = 1/2[V_{1x}(1-\cos x) + V_{3x}(1-\cos 3x) + V_{1y}(1-\cos x) + V_{3y}(1-\cos 3x) + V_{xy}\sin x \sin y] \tag{4}$$

$$\alpha(i) = \alpha_0(i) + \delta\alpha_x(i)(1-\cos x) + \delta\alpha_y(i)(1-\cos y) \tag{5}$$

These structural relaxations were included in the model calculations to describe the changes of the reduced mass upon torsional motions. Only the $\delta\alpha_y(2)$ and $\delta\alpha_y(3)$, could be determined, while the remaining four $\delta\alpha$ values were fixed to zero. In this way it has been possible to obtain ten parameters: five of them describing the potential energy function, three equilibrium valence angles, and two structural relaxation parameters.

Table 3 reports the experimental vibrational and conformational energies and their values calculated with the flexible model. The ab initio results are also given for comparison. The experimental and calculated values of the planar moments of inertia of the ground state of the most stable conformer (GT), and their shifts upon conformational and/or torsional excitation are given in Table 4. They are missing for two excited states for which the assignment was based on some assumption made on their rotational constants. In Table 5 the determined parameters are shown. Flexible model calculations have been performed in the ranges $-170 < x < 50$ and $-170 < y < 50^\circ$, so as to include the four observed conformers, corresponding in first approximation to the four positions (°) (0,0 ⇒ TT), (0, ±120 ⇒ TG), (±120,0 ⇒ GT), (±120, ±120 ⇒ GG). Only the upper sign is consistent with the considered range, which has been numerically solved into 41×41 mesh points.[6] The GG′ conformer is roughly located at (±120, ±120).

Table 3. Flexible model results and comparison with experimental data and ab initio calculations in fluorobutane: vibrational energies [cm^{-1}].

	$(v_F,v_{Me}) - (v_F,v_{Me})$[a]	obs.	Flexible model	Ab initio[b]
GT	$(0,0)_{GT} - (0,0)_{GT}$	0	0	
	$(0,1)_{GT} - (0,0)_{GT}$	80(18)	84	
	$(1,0)_{GT} - (0,0)_{GT}$	120(12)	123	
	$(1,1)_{GT} - (0,0)_{GT}$	200(20)	205	
	$(0,2)_{GT} - (0,0)_{GT}$	167(10)	166	
TT	$(0,0)_{TT} - (0,0)_{GT}$	110(40)	110	157.4
	$(0,1)_{TT} - (0,0)_{TT}$	50(40)	100	
	$(1,0)_{TT} - (0,0)_{TT}$	95(30)	116	
GG	$(0,0)_{GG} - (0,0)_{GT}$	170(40)	173	154.2
	$(0,1)_{GG} - (0,0)_{GG}$	70(30)	66	
TG	$(0,0)_{TG} - (0,0)_{GT}$	360(50)	356	356.9
	$(1,0)_{TG} - (0,0)_{TG}$	105(40)	97	
	$(0,1)_{TG} - (0,0)_{TG}$	120(40)	109	
GG′			333[c]	271.0

[a] States between which the energy differences are calculated. [b] Energies of the potential minima with respect to the GT one [QCISD(T)6–311G** method]. [c] Difference between the potential energy minima of the GG′ and GT conformers.

Table 6 lists the values of the energies and of the dihedral angles at the stationary points. We can see that $E_{GG'}$, the

Table 4. Flexible model results and comparison with experimental data. Second moments of inertia M_{gg} [u Å^2] of the GT conformer and shifts of the second moments of inertia $\Delta M_{gg} = M_{gg}(v) - M_{gg}(0)$ [u Å^2].

	$(v_F,v_{Me})'$, (v_F,v_{Me})	g	Obs.	Calcd
		a	205.52	206.51
		b	28.95	29.09
		c	11.20	10.46
GT	$(0,1)_{GT},(0,0)_{GT}$	*a*	− 0.60	− 0.60
		b	0.13	0.05
		c	0.26	0.23
	$(1,0)_{GT},(0,0)_{GT}$	*a*	0.78	0.31
		b	− 0.20	− 0.14
		c	− 0.21	− 0.16
	$(1,1)_{GT},(0,0)_{GT}$	*a*	0.12	− 0.31
		b	− 0.07	− 0.08
		c	0.07	0.10
	$(0,2)_{GT},(0,0)_{GT}$	*a*	− 1.19	− 1.23
		b	0.25	0.11
		c	0.51	0.45
	$(2,0)_{GT},(0,0)_{GT}$	*a*	1.47	0.63
		b	− 0.39	− 0.29
		c	− 0.40	− 0.33
TT	$(0,0)_{TT},(0,0)_{GT}$	*a*	49.36	49.49
		b	− 8.76	− 8.98
		c	− 4.81	− 3.86
	$(0,1)_{TT},(0,0)_{TT}$	*a*	− 0.92	− 0.69
		b	0.15	0.01
		c	0.66	0.25
	$(1,0)_{TT},(0,0)_{TT}$	*a*	− 0.46	− 0.29
		b	0.08	− 0.17
		c	0.37	0.21
Gg	$(0,0)_{GG},(0,0)_{GT}$	*a*	− 52.90	− 52.76
		b	7.13	7.36
		c	11.91	12.09
	$(0,1)_{GG},(0,0)_{GG}$	*a*	− 0.16	− 0.21
		b	0.04	0.13
		c	− 0.37	− 0.39
TG	$(0,0)_{TG},(0,0)_{GT}$	*a*	4.28	4.59
		b	0.16	0.41
		c	− 0.06	0.21
	$(1,0)_{TG},(0,0)_{TG}$	*a*	− 0.45	− 0.30
		b	− 0.08	0.00
		c	0.41	0.27
	$(0,1)_{TG},(0,0)_{TG}$	*a*	0.13	0.21
		b	− 0.05	− 0.19
		c	− 0.02	− 0.17

Table 5. Flexible model parameters.

Potential energy parameter		Structural parameter	
V_{3x} [cm^{-1}]	990(25)[a]	$\alpha_o(1)$ [°]	111.8(6)
V_{1x} [cm^{-1}]	− 140(10)	$\alpha_o(2)$ [°]	113.6(4)
V_{3y} [cm^{-1}]	790(25)	$\delta\alpha_y$ (2) [°]	1.4(3)
V_{1y} [cm^{-1}]	340(20)	$\alpha_o(3)$ [°]	110.7(5)
V_{xy} [cm^{-1}]	− 212(50)	$\delta\alpha_y$ (3) [°]	1.5(4)

[a] Errors in parentheses are expressed in units of the last digit.

Table 6. Values of the energies [cm^{-1}] and dihedral angles [°] at the minima of the potential energy function.

Conformer	x [°]	y [°]	V(x,y) [cm^{-1}]
GT	− 120.8	− 1.4	− 106.5
TT	0.0	0.0	0.0
GG	− 120.2	− 116.9	65.2
TG	− 1.2	− 117.6	250.9
GG′	− 121.4	118.3	226.7

energy value of the GG′ conformer, extrapolated from experimental data relative to the other four local minima, is relatively close to the most accurate ab initio values, which are there reported, as discussed in the following section.

The potential energy surface is plotted in Figure 2. The four minima, whose energies relative to the most stable conformer are 0, 107, 172, and 357 cm^{-1}, correspond to GT, TT, GG and TG, respectively. The energy of GG′ has been extrapolated to be 333 cm^{-1}.

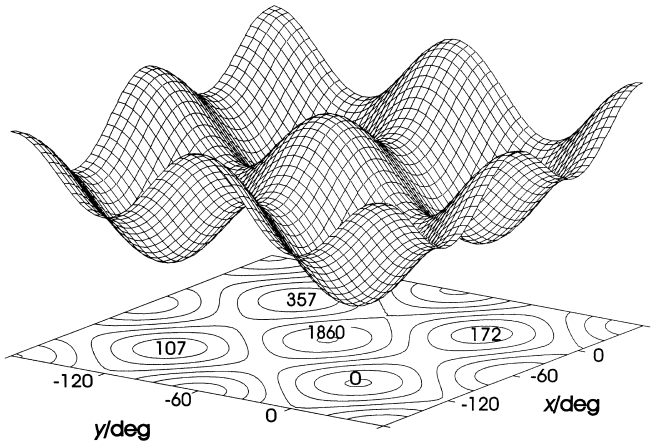

Figure 2. The 2D potential energy surface of the v_F (x) and v_{Me} (y) skeletal torsions in 1-fluorobutane referred to the most stable GT conformer. GT, TT, GG, and TG correspond to the local minima identified by the energy values 0, 107, 172, and 357 cm^{-1}, respectively. The contours are drawn every 300 cm^{-1} starting from 40 cm^{-1}.

Ab initio calculations

Our investigation of 1-chlorobutane,[5] performed at the MP2(full)/6-31G (d) level of the theory[16–18] showed that this method was reliable to estimate the rotational constants of the four rotamers observed in the microwave spectral region with a difference of at most 1.5 % from their experimental values. An excellent agreement among the calculated and experimental relative energies was found using the quadratic configuration interaction approach with single, double, and a perturbational estimate of the triple excitations[19] with the 6-311G(d, p) basis set,[20] namely the QCISD(T)/6-311G** method.

In the present case of fluorobutane, the ab initio calculations,[21] performed at the same level of the theory using the Gaussian 98 suite of programs,[22] produced rotational constants, which deviate from the corresponding experimental values by up to 7 % for the GG rotamer. Although the ab initio and experimental rotational constants are related to structures with a different meaning (r_e and r_0, respectively), such a discrepancy is larger than that usually observed. The experimentally determined rotational constants represent a thorough test on the accuracy of the calculated molecular geometry. The molecular orbitals were examined by using the Mulliken population analysis.[23]

The difficulty encountered in calculating the geometry of the five rotamers with the same accuracy arises from the delicate balancing between the electronegativity effects of the fluorine atom on the carbon chain and the long-range F – H interactions. Therefore, an accurate estimate of these effects

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turns out to be crucial for the calculation of the most stable geometry of each rotamer. For this reason the flexibility of the basis set in the valence region was increased and diffuse and polarization functions were included to account for long-range intramolecular interactions, which contribute to stabilizing the various rotamers. The geometry optimizations for the larger basis set were performed using the B3LYP[24] density functional method, requiring less computational effort than the MP2(full) method. It is known, in fact, that the hybrid functional B3LYP is adequate to accurately calculate the molecular geometries.[25] This is confirmed for fluorobutane by tests on the basis set convergence using the B3LYP density functional method, which also showed a good agreement with the rotational constants estimated by the MP2(full) method for calculations using the same basis set.

Table 7 compares the rotational constants calculated for the TT, TG, GT, GG, and GG′ rotamers of fluorobutane (see Figure 1) using the MP2(full) method with the 6-31G(d) (set I) and the 6-311G(d, p) (set II) basis sets along with those obtained with the B3LYP/6-311G (3df, 3pd)[26] density functional method (set III). The difference between the experimental and the calculated value is reported within parentheses. The agreement between the calculated and experimental values of the *A* rotational constants improves, in going from set I to set II, for all the observed rotamers but the TT one. Moreover, the rotational constants of the GG rotamer are still affected by large deviations from their experimental values. The B3LYP/6-311G (3df, 3pd) density functional method shows an impressive improvement of the estimated rotational constants of the GT and GG rotamers, while the calculated values of the *A* rotational constants of both the TT and TG rotamers are worsened. A comparison of the geometrical parameters of the five rotamers calculated by the different methods indicates that the largest differences are in the estimates of the C-C-C-C skeleton angles; for instance, the dihedral angles of the TG, GG, and GG′ rotamers can change by up to 8°. The optimized bond length and angles of the five rotamers of fluorobutane calculated using the B3LYP/6-311G (3df, 3pd) and the MP2(full)/6-311G (d, p) methods, MP2(full)/6-31G (d) for the TT rotamer are available as Supporting Information.

The B3LYP/6-311G (3df, 3pd) geometry sets the distance of the C_2H and C_2H' hydrogen atoms from the fluorine atom (see Figure 1) both at 2.61 Å for TT and at 2.57 and 2.62 Å for TG, respectively. That of the GT, GG, and GG′ rotamers with the neighboring C_2H hydrogen atom is set at 2.63 Å, 2.63 Å, and 2.61 Å, respectively. In addition, the fluorine atom of the GT rotamer is 2.62 Å from the C_3H hydrogen, while that of the GG rotamer is close to the C_3H' hydrogen atom (2.61 Å), and that of the GG′ rotamer is close to the C_4H' hydrogen (2.46 Å).

In Table 8 the energy differences for the five rotamers, calculated by using the optimized geometry of the different methods neglecting the zero-point correction, are reported with reference to the energy of the most stable GT rotamer. The results indicate that the B3LYP/6-311G(3df, 3pd) method tends to overestimate the differences, up to 100 cm^{-1} for the GG rotamer, with respect to the energies calculated with the accurate QCISD(T)/6-311G** method using the B3LYP/6-311G (3df, 3pd) geometries for all the rotamers. The relative energies calculated with the QCISD(T)/6-311G** method using the MP2(full)/6-311G(d, p)-optimized geometries indicate a lowering of energy differences for all the rotamers but the TT, with the largest variation for GG, of 30 cm^{-1}. The QCISD(T)/6-311G** difference between the energy of the GT rotamer, calculated by using its B3LYP/6-311G(3df, 3pd)-optimized geometry, and that of the TT and TG rotamers, calculated by using the geometries obtained with the

Table 7. *A*, *B*, and *C* rotational contants (in MHz) of 1-fluorobutane calculated with the I) MP2(full)/6–31G (d) method, II) MP2(full)/6–31G (d, p) method, III) B3LYP/6–311G (3df, 3pd) method. The differences between the calculated and the experimental value are given in parentheses.

		TT	TG	GT	GG	GG′
I)	*A*	18994.33(−14.13)	12676.85(121.04)	12383.39(−203.26)	7995.47(−541.61)	7313.13
	B	1940.14(5.81)	2294.03(6.63)	2383.82(−51.90)	3124.53(248.72)	3641.90
	C	1840.96(3.75)	2118.15(2.89)	2186.88(31.54)	2812.06(134.02)	2702.82
II)	*A*	19145.48(137.02)	12563.69(7.88)	12495.00(−91.65)	8045.70(−491.38)	7343.05
	B	1939.03(−4.70)	2319.22(31.82)	2366.46(−34.54)	3104.08(228.27)	3620.31
	C	1841.60(−4.39)	2130.47(−15.21)	2179.38(24.04)	2800.74(122.70)	2696.67
III)	*A*	19169.64(161.18)	12763.40(207.59)	12586.43(−0.22)	8631.40(94.32)	7404.98
	B	1927.96(−6.37)	2262.92(−24.48)	2330.99(-0.93)	2837.21(−38.60)	3506.08
	C	1831.08(−6.13)	2097.85(−17.41)	2152.64(2.69)	2651.75(−26.29)	2639.89

Table 8. Energy differences for the five rotamers of fluorobutane with respect to the energy of the GT rotamer. Under the column labeled geometry optimization is specified the method used to calculate the equilibrium geometry. The energy differences are calculated with I) the B3LYP/6–311G(3df,3pd) method and II) the QCISD(T)/6–311G** method.

	Geometry optimization	TT	TG	GT	GG	GG′
I)	B3LYP/6–311G (3df ,3pd)	183.98	490.08	0.00	254.12	358.10
II)	B3LYP/6–311G(3df, 3pd)	181.36	407.97	0.00	154.18	271.05
	MP2(full)/6–311G**	187.94	399.81	0.00	124.21	258.58
	MP2(full)/6–31G*(TT) B3LYP/6–311G(3df, 3pd)(GT)	157.35				
	MP2(full)/6–311G**(TG) B3LYP/6–311G(3df, 3pd)(GT)		356.87			

MP2(full)/6-31G(d) and MP2(full)/6-311G(d, p) methods, respectively, are also reported. A comparison of the calculated and experimental relative energies is presented in Table 3 and shows the excellent agreement with the relative energies calculated with the QCISD(T)/6-311G** method, using the geometrical parameters corresponding to the rotational constants which better compare with the experimental data of each rotamer. Relying on the previous results we can expect that the GG′ rotamer is 271 cm^{-1} higher in energy than the GT rotamer.

It is well-known that a high energy conformer can relax to a more stable one during a supersonic expansion, provided that the interconversion barrier is not much higher than kT, where T is the temperature before of the expansion.[27] To check if such a phenomenon could explain the nonobservability of the GG′ species, a further investigation was performed to calculate the interconversion barriers of the GG′ rotamer to the more stable GT and GG rotamers. We optimized the geometry of the transition states with the B3LYP/6-311G (3df, 3pd) method, and calculated the energy differences using the QCISD(T)/6-311G** method. Torsional barriers of 696 cm^{-1} and 1541 cm^{-1} were obtained, respectively; they are much too high to account for a conformational relaxation.

In Table 2 the dipole moments obtained with the B3LYP/6-311G (3df, 3pd) (set I) and QCISD(T)/6-311G** (set II) methods calculated at the optimum geometries of each rotamer are compared to the experimentally estimated values.

Conclusion

The rotational spectra of four conformers of fluorobutane have been assigned combining conventional and free jet microwave spectroscopy. This represents, to our knowledge, a shared "record" as regards the number of rotamers assigned with microwave spectroscopy for a given molecule. Several torsionally excited states have also been analyzed. From experimental data, the 2D potential energy surface of the two skeletal torsions that generate the conformational equilibria have been determined by using a flexible model approach. The quality of the fitting, and even the choice of the potential energy function, would be improved if precise vibrational spacings became available, either from far infrared or single vibronic fluorescence levels experiments. These data are, however, difficult to obtain due to the presence of numerous species in the complex equilibrium mixture.

By combining the experimental and the theoretical ab initio approaches we were able to perform a thorough investigation on the conformational dynamics and energetics of all the five rotamers of fluorobutane. The different techniques employed, on the one hand substantiated the results obtained by giving complementary information, on the other hand they allowed better assessment of the accuracy of the theoretical methods used. In fact, initially the ab initio calculations performed at the MP2(full) level of theory with the 6-31G(d) and 6-311G(d, p) basis sets supported the assignment of the rotational spectra of the GT, TT, and TG rotamers. Subsequently, the comparison with the experimental data revealed that the nonbonded F – H interactions were not properly accounted for and that more polarization functions had to be included in the basis set of the GT, GG, and GG′ rotamers. Moreover, using the B3LYP/6-311G (3df, 3pd) method, it was revealed that accurate results are obtained from a delicate balancing of the description of the electronegativity effects and of the nonbonded F – H interactions of the fluorine atom.

The assignment of the rotational spectrum of the GG′ conformer would have given completeness to this investigation. Unfortunately, we were unable to record it. A combination of factors such as a higher conformational energy with respect to the ab initio value and a predominant *b*-type spectrum could explain this failure. Only a few of its weaker transitions are suitable to be observed with the RFMWDR technique in the frequency range available to our conventional spectrometer. Some of these could fall, as predicted by the calculated rotational constants, in a frequency range crowded with much more intense signals belonging to other conformers. As to the jet conditions, only a few calculated doublet transitions looked promising for the assignment of the GG′ spectrum, but we could not identify them.

The relative energies of the observed conformers obtained in this work show that the order of stability of the various conformers changes considerably with respect to chlorobutane; the order of increasing energy is TT, GT, GG, TG, GG′ for chlorobutane, and GT, TT, GG, GG′, TG for fluorobutane.

Experimental Section

Chemicals: 1-Fluorobutane was prepared from 1-bromobutane and potassium fluoride in sulfolane at 200 °C. A stirred solution of 1-bromobutane (67 g, 0.49 mol; Aldrich) in dry sulfolane (600 mL) was heated with dry potassium fluoride (70 g, 1.2 mol) to 180 – 200 °C under nitrogen for 5 h. The 1-fluorobutane was collected in a trap at − 78 °C and distilled over a Vigreux column; b.p. 32.5 °C; yield 26 g (69 %).

Microwave spectrometers: The microwave spectra were recorded with a free jet millimetre wave spectrometer[8] (FJ-AMMW) in the frequency ranges 60 – 78 GHz and with a conventional Stark modulated microwave spectrometer[9] in the frequency ranges 26 – 40 GHz. In the latter case the cell was kept cold at about − 40 °C. The jet was obtained by expanding a mixture of the sample in argon (ca. 2 %) at a stagnation pressure of 0.2 atm at room temperature, to a final pressure of 10^{-3} Torr. The nozzle diameter was 0.35 mm.

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