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The Microwave Spectrum of α-Fluoropropionic Acid

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The rotational absorption lines in the microwave spectrum of α-fluoropropionic acid were shown to originate from two different molecular conformations. The rough geometries of the two conformations could be determined from the observed dipole moments and the substitution coordinates of the carboxylic hydrogen atom. In both conformations the fluorine atom is near the plane of the carboxyl group; in the conformation with the fluorine atom *trans* with respect to the hydroxyl group the carboxyl group has the usual geometry, while in the *cis* conformation the molecule is stabilized by an internal O–H · · · F hydrogen bond. By measuring the relative intensities of the absorption lines it was found that the *cis* conformer is 0.5 ± 0.2 kJ mole^{-1} lower in energy than the *trans* conformer. The barrier to internal rotation of the methyl group in the *trans* conformation was determined from *A–E* line splittings in the second excited vibrational state V_3 = 13.5 ± 0.3 kJ mole^{-1}.

INTRODUCTION

The molecular structures of propionic acid (*1, 2*) and fluoroacetic acid (*3, 4*) have been determined by microwave spectroscopy. In fluoroacetic acid the existence of two conformations was shown, both having the fluorine atom in the symmetry plane of the molecule. In the conformation with the lowest energy the chain of atoms F–C–C–O–H is zigzag, and in the second conformation the chain is cyclic. In propionic acid a structure with the methyl group *cis* with respect to the carbonyl group was found; the occurrence of a *gauche* conformation has been indicated by electron diffraction work (*5*).

A part of our research concerns the conformational behavior of disubstituted derivatives of acetic acid. Clearly there is some competition between the substituents for the energetically favored position *cis* with respect to the carbonyl group. In difluoroacetic acid (*6*) this position is occupied by the hydrogen atom and a fluorine atom, respectively, resulting in two molecular conformations with the former having the lowest potential energy. No evidence for an internal hydrogen bond has been found. In the present work we study the interplay between a methyl group and a fluorine atom as exemplified by α-fluoropropionic acid.

EXPERIMENTAL PROCEDURE

A sample of α-fluoropropionic acid was provided by Professor E. D. Bergmann, Hebrew University, Jerusalem, Israel. The deuterated form $CH_3CHFCOOD$ was prepared by exchange directly in the absorption cell which was previously conditioned with D_2O.

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The microwave spectrum was recorded at room temperature from 17.4 to 40.5 GHz at a gas pressure of about 0.07 mm Hg using a conventional 10-kHz Stark modulated spectrometer. For identification purposes and frequency measurements use was also made of modulation based upon the microwave–microwave double resonance effect. The accuracy of the measurements is expected to be 0.2 MHz and better for strong lines.

ANALYSIS

Straightforward identification of the spectrum on the basis of the Stark effect was not possible. Therefore, we tried the more powerful method of microwave–microwave double resonance. A double resonance search is feasible if the ratio between signal frequency (ν_s) and pump frequency (ν_p) is fairly independent of reasonable uncertainties in the structural parameters. It was assumed that the electronegative fluorine atom would dominate the general behavior of the potential energy function, so in α-fluoropropionic acid the same conformations are expected as in fluoroacetic acid. Following the nomenclature adopted earlier (*3*) these are called *trans* (I, $\phi \approx 240°$) and *cis* (II, $\phi \approx 60°$) (see Fig. 1). For the *trans* conformation the most promising double resonance combinations were 2_{20}–$3_{31}/3_{31}$–4_{40} with $\nu_s/\nu_p = 1.372 \pm 0.007$ and 2_{21}–$3_{30}/3_{30}$–4_{41} with $\nu_s/\nu_p = 1.351 \pm 0.010$; for the *cis* conformation the best combinations seemed to be 4_{04}–$5_{05}/5_{05}$–6_{06} and 4_{14}–$5_{15}/5_{15}$–6_{16} with frequency ratios ν_s/ν_p of 1.185 ± 0.004 and 1.189 ± 0.006, respectively. The error limits, which take into account an uncertainty of $\pm 30°$ in ϕ, are small enough to make a systematic double resonance search practicable.

This procedure proved to be very successful, and the lines were easily identified accompanied by a number of vibrational satellites. Once these transitions were found it was not difficult to identify other lines. The observed frequencies are given in Table I. As is usually the case with derivatives of acetic acid a number of excited states belonging to the torsion of the carboxylic group was observed. Spectra of the states with v up to 3 have been analyzed, where v represents the quantum number of this vibrational mode. To determine the molecular conformation unambiguously the

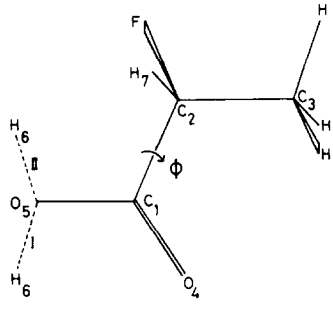

FIG. 1. Model of α-fluoropropionic acid. ϕ denotes the angle over which the carboxyl group is rotated with respect to the frame $C_1C_2C_3$; the situation in the figure corresponds to $\phi = 0°$. Two possible orientations of the hydroxyl group are indicated by I and II. For the conformation with the atoms F and O_5 *trans* the hydroxyl group has the orientation I and $\phi \approx 240°$, while for the *cis* conformer the hydroxyl group is in position II and $\phi \approx 60°$.

TABLE I

Ground State Transitions (MHz) in α-Fluoropropionic Acid

Trans conformation								*Cis* conformation							
Transition						ν(obs)	Δν[a)]	Transition						ν(obs)	Δν[a)]
2	2	0	3	3	1	28624.00	0.04	4	1	3	5	1	4	28163.46	-0.00
2	2	1	3	3	0	28878.70	0.05	4	2	2	5	2	3	30529.06	-0.01
3	2	2	4	3	1	34817.10	0.01	4	3	1	5	3	2	29869.33	-0.02
3	2	1	4	3	2	33560.29	0.03	4	3	2	5	3	3	28488.09	0.14
3	3	1	4	4	0	39185.60	0.10	5	0	5	6	0	6	28602.51	-0.02
3	3	0	4	4	1	39144.80	0.13	5	1	5	6	1	6	28564.85	-0.03
5	0	5	6	1	6	28820.75	-0.09	5	1	4	6	1	5	32503.51	0.08
5	1	5	6	0	6	28590.36	-0.13	5	2	4	6	2	5	31812.13	-0.02
5	1	4	6	2	5	33774.59	-0.15	5	2	3	6	2	4	36095.08	-0.02
6	0	6	7	1	7	33263.60	-0.08	5	3	3	6	3	4	33949.08	-0.03
6	1	6	7	0	7	33173.40	-0.12	5	3	2	6	3	3	36564.22	0.06
6	1	5	7	2	6	37490.10	-0.00	5	4	1	6	4	2	35063.49	0.02
6	2	5	7	1	6	35459.80	0.16	5	4	2	6	4	3	34547.82	-0.07
7	0	7	8	1	8	37749.10	0.19	6	0	6	7	0	7	33057.16	-0.01
7	1	7	8	0	8	37715.50	-0.04	6	1	6	7	1	7	33045.40	-0.07
9	6	3	9	7	2	31711.03	-0.04	6	1	5	7	1	6	36780.25	0.03
10	6	4	10	7	3	31362.94	-0.09	6	2	5	7	2	6	36461.72	0.04
11	6	5	11	7	4	30821.38	-0.06	6	3	4	7	3	5	39162.15	-0.10
12	1	11	12	2	10	31635.35	-0.11	7	0	7	8	0	8	37521.34	0.06
13	2	11	13	3	10	29770.46	-0.02	7	1	7	8	1	8	37517.86	0.02
15	3	12	15	4	11	30765.87	-0.01	11	1	10	11	3	9	32246.87	0.07
15	7	8	15	8	7	33575.66	-0.03	11	2	10	11	2	9	32186.46	0.04
16	7	9	16	8	8	31817.10	0.01	12	2	10	12	4	9	31447.43	-0.02
17	4	13	17	5	12	31159.66	0.03	12	3	10	12	3	9	31088.63	0.04
19	5	14	19	6	13	30976.56	0.02	13	3	10	13	5	9	30700.18	-0.12
19	8	11	19	9	10	34755.60	0.14	13	5	8	13	7	7	35069.30	-0.02
20	5	15	20	6	14	35845.76	0.00	14	3	11	14	5	10	34066.86	0.06
20	8	12	20	9	11	32000.05	0.05	14	5	9	14	7	8	32880.94	0.03
21	6	15	21	7	14	30383.53	-0.00	15	4	11	15	6	10	33345.28	-0.05
21	8	13	21	9	12	29086.47	-0.07	16	4	12	16	6	11	36602.57	0.02
22	6	16	22	7	15	35497.53	0.09	17	4	13	17	6	12	40117.74	-0.02
23	7	16	23	8	15	29692.79	-0.09	17	5	13	17	5	12	39652.74	0.03
23	9	14	23	10	13	34339.78	-0.04	17	5	12	17	7	11	35992.21	-0.07
								18	5	13	18	7	12	39082.00	0.02
								18	6	13	18	6	12	37301.24	-0.05
								19	6	13	19	8	12	38686.33	-0.23
								19	7	13	19	7	12	33211.92	0.08
								20	7	13	20	9	12	40153.82	0.17
								21	8	14	21	8	13	33831.75	-0.04
								23	9	15	23	9	14	34063.23	0.02
								25	10	16	25	10	15	33906.47	0.05
								27	11	17	27	11	16	33371.07	-0.03

a) Calculated-observed frequency.

microwave spectrum of $CH_3CHFCOOD$ was also investigated. Here the measurements were confined to the ground vibrational state for both conformations.

The rotational constants and centrifugal distortion constants are collected in Table II. For the *cis* conformation an accurate value of the constant Δ_K could only be obtained in the ground vibrational state; in the excited states Δ_K was fixed to this value. For the *cis* conformer of the deuterated species only *R*-type lines with *J* up to 8 were measured, which allowed only a determination of the constant Δ_J.

A careful search for absorption lines belonging to a conformation with the methyl group *cis* with respect to the carbonyl group, as found in propionic acid (*1*), was performed. Employing the same procedure followed for the *cis* and *trans* conformations we searched for the combination 2_{20}–3_{30}/3_{30}–4_{40} with $\nu_s/\nu_p = 1.365 \pm 0.004$. A number of resonances were found but no vibrational satellites were present, in contrast to

TABLE II

Rotational Constants (MHz) and Centrifugal Distortion Constants (kHz, Representation I^r) of α-Fluoropropionic Acid

	trans-$CH_3CHFCOOH$			
v	0	1	2	3
v'	0	0	0	0
A	5205.757(7)	5205.961(8)	5206.346(9)	5206.884(14)
B	3124.049(9)	3113.231(10)	3101.572(9)	3088.873(14)
C	2258.196(9)	2264.136(10)	2270.813(10)	2278.326(13)
Δ_J	1.90(0.09)	1.81(0.09)	2.05(0.09)	2.23(0.13)
Δ_{JK}	-4.87(0.06)	-5.24(0.06)	-5.71(0.06)	-6.42(0.09)
Δ_K	4.88(0.17)	5.26(0.18)	5.67(0.18)	6.05(0.25)
δ_J	0.571(0.007)	0.586(0.007)	0.612(0.006)	0.628(0.010)
δ_K	8.05(0.07)	8.86(0.07)	9.86(0.07)	11.39(0.10)
N_R	15	12	9	7
N_Q	18	18	18	17
J_{max}	23	23	24	24
s	0.097	0.103	0.096	0.128
	trans-$CH_3CHFCOOH$			*trans*-$CH_3CHFCOOD$
v	0	1	2	0
v'	1	1	1	0
A	5193.241(12)	5193.305(14)	5193.506(10)	5187.748(4)
B	3128.623(12)	3117.691(14)	3105.924(10)	3009.581(2)
C	2254.735(12)	2260.399(13)	2266.755(10)	2195.107(3)
Δ_J	1.93(0.10)	2.01(0.12)	2.16(0.10)	1.85(0.01)
Δ_{JK}	-4.38(0.11)	-4.82(0.09)	-5.23(0.06)	-4.46(0.02)
Δ_K	3.98(0.22)	4.31(0.25)	4.63(0.19)	4.51(0.07)
δ_J	0.588(0.014)	0.585(0.010)	0.608(0.008)	0.511(0.003)
δ_K	7.44(0.13)	8.32(0.09)	9.25(0.07)	7.97(0.03)
N_R	6	7	6	14
N_Q	15	16	15	24
J_{max}	23	23	23	22
s	0.101	0.128	0.085	0.053

what was observed for the *cis* and *trans* conformers. So these double resonances were encountered rather accidentally and did not belong to the combination searched for. In fact, an observable signal is only expected when the ground state of this possible third conformation is appreciably lower in energy than that of the observed conformers, since the relevant component of the dipole moment is estimated from bond moments (*7*) to be about only half that of the *trans* and *cis* conformers.

CH_3 INTERNAL ROTATION

A number of double resonances encountered during the search for absorption lines belonging to a third molecular conformation could be attributed to rotational tran-

TABLE II—*Continued*

	cis-$CH_3CHFCOOH$			
v	0	1	2	3
v'	0	0	0	0
A	5052.731(7)	5052.892(10)	5052.947(10)	5052.891(10)
B	3332.162(5)	3325.846(7)	3319.395(7)	3312.773(5)
C	2234.986(6)	2238.496(8)	2241.994(7)	2245.509(5)
Δ_J	1.39(0.06)	1.49(0.08)	1.45(0.07)	1.29(0.05)
Δ_{JK}	-1.33(0.07)	-1.25(0.05)	-1.05(0.05)	-1.11(0.06)
Δ_K	1.3(0.2)	1.3(ass)	1.3(ass)	1.3(ass)
δ_J	0.351(0.006)	0.341(0.009)	0.371(0.008)	0.342(0.008)
δ_K	3.95(0.04)	3.79(0.07)	3.42(0.06)	3.48(0.07)
N_R	20	19	17	16
N_Q	22	16	16	11
J_{max}	27	25	25	22
s	0.076	0.099	0.094	0.061

	cis-$CH_3CHFCOOH$		*cis*-$CH_3CHFCOOD$
v	0	1	0
v'	1	1	0
A	5043.702(30)	5044.166(25)	4902.065(24)
B	3334.255(11)	3327.488(10)	3325.211(4)
C	2231.247(12)	2235.114(14)	2204.509(7)
Δ_J	1.20(0.10)	1.52(0.11)	1.37(0.06)
Δ_{JK}	-1.1(0.2)	-1.5(0.2)	-1.33(ass)
Δ_K	1.3(ass)	1.3(ass)	1.3(ass)
δ_J	0.36(0.03)	0.31(0.03)	0.351(ass)
δ_K	3.6(0.3)	4.1(0.3)	3.95(ass)
N_R	15	14	21
N_Q	4	4	0
J_{max}	16	16	8
s	0.112	0.097	0.057

Values in parentheses are the standard deviations in kHz.

N_R and N_Q denote the number of observed R- and Q-type transitions; J_{max} is the maximum value of J; s is the root mean square deviation in MHz.

sitions in the first excited state of a second vibrational mode, to be indicated by the quantum number v'. We also identified transitions belonging to some combination states. The derived molecular parameters are given in Table II.

Extension of the measurements to lines belonging to the $v' = 2$ state of the *trans* conformation revealed that we are dealing with the methyl torsional vibration, since these lines showed *A–E* splitting. The observed frequencies are listed in Table III.

Although the barrier hindering the CH_3 internal rotation must be high the method of calculating the barrier height from the observed differences between the rotational

TABLE III

Transition Frequencies (MHz) and Molecular Parameters (Representation I^r) in the Second Excited State of the Methyl Torsion in *trans*-$CH_3CHFCOOH$

Transition	ν_A(obs)	ν_A(calc-obs)	ν_E(obs)	ν_E(calc-obs)	$\nu_A-\nu_E$(obs)
7 1 7 8 0 8	37631.55	-0.05			
7 0 7 8 1 8	37661.87	0.05			
10 6 5 10 7 4	31141.64	-0.16			
11 6 5 11 7 4	30448.87	0.05	30485.27	0.02	-36.40
12 1 11 12 2 10	31872.04	0.03	31907.21	-0.28	-35.17
13 2 11 13 3 10	30103.92	0.04	30126.76	-0.04	-22.84
14 2 12 14 3 11	33723.24	0.05	33758.90	0.14	-35.66
14 7 7 14 8 6	34284.91	0.19	34317.17	0.05	-32.26
15 3 12 15 4 11	31236.63	0.01	31245.17	0.11	-8.54
15 7 8 15 8 7	33002.22	-0.06	33018.16	-0.02	-15.94
18 4 14 18 5 13	36186.64	-0.06	36195.92	-0.05	-9.28
18 8 10 18 9 9	36187.92	-0.07	36199.92	-0.04	-12.00
19 5 14 19 6 13	31799.67	-0.04	31795.43	0.06	4.24
19 8 11 19 9 10	33861.65	0.05	33868.72	-0.01	-7.07
20 8 12 20 9 11	31007.98	-0.02	31013.52	-0.03	-5.54
21 6 15 21 7 14	31341.91	-0.09	31335.54	-0.12	6.37
22 6 16 22 7 15	36502.40	0.09	36497.64	-0.07	4.76
22 9 13 22 10 12	36337.80	0.02	36344.90	0.10	-7.10
23 7 16 23 8 15	30679.12	0.12	30671.87	0.13	7.25
23 9 14 23 10 13	33150.74	0.16	33157.10	0.02	-6.36
24 7 17 24 8 16	35865.28	0.04	35857.72	-0.10	7.56
24 9 15 24 10 14	30199.82	0.02	30204.87	-0.08	-5.05
25 8 17 25 9 16	30162.00	-0.02	30155.21	-0.00	6.79
25 10 15 25 11 14	38581.35	0.01	38589.18	-0.02	-7.83
26 8 18 26 9 17	34937.44	-0.01	34928.52	-0.01	8.92
26 10 16 26 11 15	35133.68	-0.04	35140.67	-0.05	-6.99

A	5184.997 ± 0.008 MHz	ρ_a	0.0128 ± 0.0003
B	3131.229 ± 0.005 MHz	ρ_b	0.0141 ± 0.0003
C	2252.211 ± 0.006 MHz	ρ_c	0.0087 ± 0.0002
Δ_J	1.93 (ass) kHz	V_3	13.5 ± 0.3 kJ mole^{-1}
Δ_{JK}	-4.52 ± 0.04 kHz	r.m.s.	0.094 MHz
Δ_K	3.90 ± 0.10 kHz		
δ_J	0.539 + 0.004 kHz		
δ_K	7.61 ± 0.04 kHz		

constants of the A and E species by formulas given by Lin and Swalen (*8*) could not be employed, since it was not possible to reproduce the E-type frequencies with a pseudo-rigid rotor Hamiltonian. Therefore a PAM computer program which includes perturbation terms up to $n = 10$ and the denominator corrections $n = d, e, f$ was used to calculate the barrier from the observed frequencies. With this program the rotational constants, the centrifugal distortion constants and the internal rotation parameters ρ_a, ρ_b, ρ_c, V_3 (for definition of these parameters see, for instance, Ref. (*8*)) can be determined by a least-squares fitting procedure to the A and E line frequencies. The results are listed in Table III. As only two R-type transitions were measured the centrifugal distortion constant Δ_J could not be determined and its value was fixed to that of the state $v' = 1$, $v = 0$.

Using the derived internal rotation parameters it was calculated that a few lines in the $v' = 1$ states should have observable A–E splittings of about 1 MHz. Indeed,

five splittings in the $v' = 1$, $v = 0$ state could be measured confirming the results obtained for the $v' = 2$ state.

Lines belonging to the second excited state of the CH_3 torsion in the *cis* conformation could not be found, and in the $v' = 1$ states no splittings were observed. It follows that the V_3 barrier in the *cis* conformation should be at least 12.5 kJ mole^{-1}.

DIPOLE MOMENTS

The dipole moments of both conformations in the ground vibrational state were determined from the Stark effect. The frequency shifts in OCS (*9*) were used to calibrate the absorption cell.

The frequency ν can be written as a power series in E^2

$$\nu = \nu^{(0)} + c^{(2)}E^2 + c^{(4)}E^4 + \cdots \tag{1}$$

where $\nu^{(0)}$ is the zero-field frequency, the Stark coefficient $c^{(2)}$ can be expressed as $c^{(2)} = k_a\mu_a^2 + k_b\mu_b^2 + k_c\mu_c^2$, and $c^{(4)}$ can be found from a formula given in Ref. (*3*). The coefficients k_a, k_b, and k_c in the expression for $c^{(2)}$ can be calculated using nondegenerate second order perturbation theory (*10*).

After the fourth-order contribution $c^{(4)}E^4$ was subtracted from the observed frequencies ν, the zero-field frequency and the coefficients $c^{(2)}$ of the observed Stark components were determined by a least-squares procedure for various ground state transitions (Table IV). Employing the expression for $c^{(2)}$ given above μ_a, μ_b, and μ_c were obtained from the observed $c^{(2)}$ values using again the method of least squares. The results are reported in Table V (method 1), and the observed and calculated $c^{(2)}$ values are compared in Table IV. This table also contains the maximum fourth-order contribution as a fraction of the second-order contribution.

As an alternative, we also calculated μ_a, μ_b, μ_c, and the zero-field frequencies of the transitions concerned by a single least-squares procedure, i.e., without an intermediate calculation of $c^{(2)}$. The results of the two methods are compared in Table V. As can be seen from this table it was not possible to obtain a reliable result for the component μ_c of the *cis* conformer. In fact a negative value of μ_c^2 is calculated, viz., -0.023 ± 0.083 D^2 and -0.182 ± 0.054 D^2 by methods 1 and 2, respectively. Thus, the latter method really gives an impossible result. In principle, however, it should be superior as the parameters are derived directly from the observations. In the first method the frequencies are apparently better reproduced by the calculations since all $c^{(2)}$ values can be varied freely, but this results occasionally in relatively large differences $c^{(2)}_{\text{calc-obs}}$ (Table IV). However, in view of the error limits, both methods give the same results.

Not all measurements were included in the calculations: the transitions 7_{07}–8_{18}, 7_{17}–8_{08}, 6_{06}–7_{17} (*trans*), and 5_{41}–6_{42} (*cis*) were extremely perturbed by K degeneracy for $M \neq 0$. Here Eq. (1) was replaced by the usual treatment of this degeneracy (*10*). Since off-diagonal elements connecting nondegenerate levels are reduced to second order by application of a Van Vleck transformation, it was in all cases sufficient to calculate the frequencies by considering the off-diagonal element $H_{ij}^{(1)}$, which connects the two near-degenerate levels, and solving the resulting 2×2 secular equation. The

TABLE IV

Stark Coefficients (Eq. (1))

Conformation	Transition	M	n[a)]	$c^{(2)}_{obs}$	$c^{(2)}_{calc-obs}$	y_{max} [b)]
trans	$3_{21}-4_{32}$	0	10	5.00 ± 0.06	-0.05	0.00
		1	10	-13.2 ± 0.1	0.2	0.03
		2	15	-66.8 ± 0.6	0.0	0.02
		3	9	-156 ± 2	0	0.02
	$3_{22}-4_{31}$	1	16	10.45 ± 0.07	0.09	0.04
		2	20	43.4 ± 0.3	-0.2	0.04
		3	11	97.4 ± 0.8	0.3	0.04
	$5_{14}-6_{25}$	0	8	1.19 ± 0.02	-0.01	0.00
		1	15	4.36 ± 0.02	0.07	0.02
		2	10	13.93 ± 0.05	0.27	0.01
		3	10	29.9 ± 0.2	0.6	0.01
	$6_{15}-7_{26}$	0	10	1.406 ± 0.005	-0.014	0.00
		1	10	4.04 ± 0.02	-0.10	0.01
		2	10	11.60 ± 0.03	0.01	0.01
		3	19	24.4 ± 0.2	0.0	0.00
		4	11	42.3 ± 0.4	-0.1	0.00
		5	7	65.0 ± 0.6	0.3	0.00
	$7_{17}-8_{08}$	0	8	15.7 ± 0.3	-0.4	0.09
cis	$4_{31}-5_{32}$	1	11	-63.2 ± 0.6	-2.1	0.02
		2	10	-265 ± 1	-2	0.04
		3	6	-594 ± 3	-11	0.04
	$4_{32}-5_{33}$	0	10	1.97 ± 0.02	-0.03	0.00
		1	13	68.8 ± 0.6	0.5	0.02
		2	12	270.6 ± 0.8	0.7	0.06
		3	9	610 ± 2	-2	0.08
	$4_{22}-5_{23}$	0	8	-0.242 ± 0.002	0.002	0.04
		1	15	-3.12 ± 0.02	-0.01	0.00
		2	19	-11.78 ± 0.04	0.00	0.01
		3	8	-26.4 ± 0.2	0.2	0.01
	$5_{32}-6_{33}$	0	6	0.479 ± 0.004	-0.028	0.00
		1	18	-6.64 ± 0.07	-0.01	0.01
		2	13	-27.9 ± 0.2	-0.1	0.02
		3	18	-63.7 ± 0.3	0.3	0.02
		4	9	-112.2 ± 0.7	-1.0	0.01
	$5_{41}-6_{42}$	0	10	1.64 ± 0.02	-0.02	0.00

a) Number of observed frequencies.

b) Maximum value of $y = |c^{(4)}E^4 / c^{(2)}E^2|$.

Units are: ν in MHz, E in V cm^{-1}, μ in Debye (D) (1 D = 3.33564×10^{-30} C.m).

Conversion factor $\mu E = 0.50344$ MHz.cm.D^{-1}.V^{-1}.

resulting root mean square deviation of the frequencies was 0.17 MHz (*trans*) and 0.18 MHz (*cis*). This is a severe test for the reliability of the values of μ_c (*trans*) and μ_a (*cis*), which determine the matrix elements $H^{(1)}_{ij}$.

MOLECULAR STRUCTURE

With the data available only little information about the molecular structure can be obtained. However, one thing we still have to make sure is, Do the absorption lines definitely originate from the *trans* and *cis* conformations we have assumed, or are there more possibilities? To answer this question we have to determine the angle ϕ (Fig. 1) and the orientation of the hydroxyl group from the experimental data.

TABLE V

Comparison of the Dipole Moments (D) Calculated by the Two Methods Mentioned in the Text

Conformation	Method	μ_a	μ_b	μ_c	$s^{a)}$
trans	1[b)]	0.588 ± 0.004	2.986 ± 0.012	0.529 ± 0.004	0.16
	2[c)]	0.588 ± 0.002	2.997 ± 0.006	0.527 ± 0.002	0.19
cis	1[b)]	2.895 ± 0.006	0.28 ± 0.08	(0.2 ± 0.3)i	0.11
	2[c)]	2.905 ± 0.004	0.10 ± 0.13	(0.43 ± 0.07)i	0.14

a) Root mean square deviation of the frequencies (MHz).
b) Calculation from the $c_{obs}^{(2)}$-values (Table IV).
c) Calculation via a single least-squares procedure.

To achieve this assumptions about the rest of the molecular structure have to be made: a planar arrangement of the carboxyl group was assumed, so the hydroxyl group can have only two orientations, indicated by I and II in Fig. 1. With the hydroxyl group in position I the bond lengths and bond angles were taken over from propionic acid (*2*) and *trans* fluoroacetic acid (*4*) for the appropriate parts of the molecule; comparable values were averaged. When the hydroxyl group is in position II the geometry of *cis*-fluoroacetic acid (*4*) was taken over, completed with that of propionic acid for the remaining part of the molecule. Finally the angle C_3–C_2–F was taken to be tetrahedral and the three bond angles involving the atom H_7 were assumed to be equal. Now, apart from the orientation of the hydroxyl group, the dihedral angle ϕ is the only unknown structural parameter.

The substitution coordinates of the carboxylic hydrogen atom H_6 were determined from the observed ground state moments of inertia of the species $CH_3CHFCOOH$ and $CH_3CHFCOOD$: for the *trans* conformer a = 2.475 Å, b = 0.583 Å, c = 0.172 Å, and for the *cis* conformer a = 0.418 Å, b = 1.720 Å, c = 0.372 Å. These coordinates were also calculated from the model as a function of the angle ϕ for the two possible orientations of the hydroxyl group. From Fig. 2 it is immediately seen that our assumption about the orientation of the hydroxyl group in the two conformations (*trans* → I and *cis* → II) was valid indeed. But, as shown by the broken lines in the figure, for the angle ϕ two possible values remain for both conformations, viz., $\phi \approx 250$ or 350° (*trans*) and $\phi \approx 60$ or 175° (*cis*).

A comparison of calculated and observed moments of inertia is not helpful, since this leads to the same values for ϕ together with two additional possibilities. However, a unique choice of ϕ can be made when the observed values of the dipole moment components (Table V) are compared with the values estimated from the model using bond moments (*7*) for the two possible values of ϕ (Table VI). Although the agreement between estimated and observed dipole moments is not very good, it is clear that for the *trans* conformer $\phi \approx 250°$ and for the *cis* conformer $\phi \approx 60°$, which are about the values we wanted to confirm. For the *trans* conformation ϕ also follows uniquely from a comparison of the observed values of the internal rotation parameters ρ_a, ρ_b, ρ_c (Table III) with those calculated from the model (Table VI).

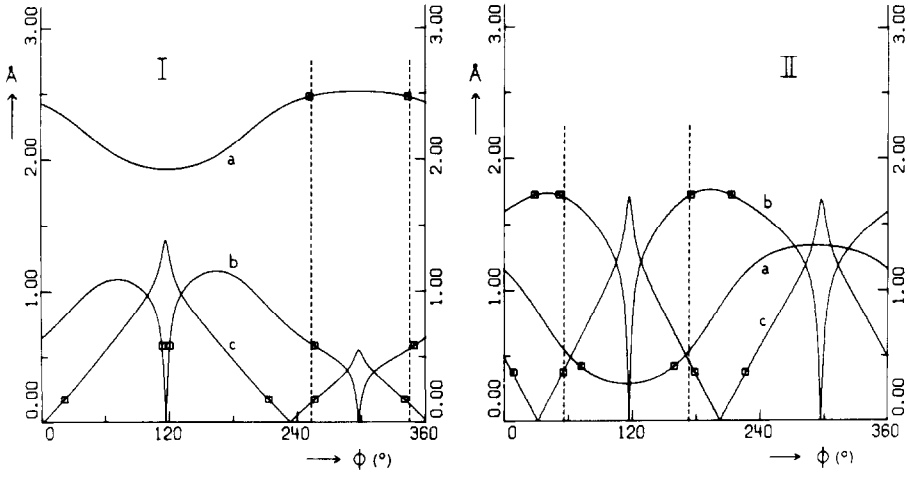

FIG. 2. Dependence of the coordinates of atom H_6 on the angle ϕ for the two possible orientations of the hydroxyl group (I and II). The observed r_s coordinates are marked. The possible values of ϕ are indicated by the broken vertical lines.

INTENSITY MEASUREMENTS

To estimate the *cis-trans* energy difference and the vibrational level spacings for both conformations, the peak intensities of absorption lines belonging to the two different conformers in the various vibrational states were measured. The measurements were performed on *trans b*-type and *cis a*-type lines at room temperature (295 ± 3 K) using Stark modulation. For a number of transitions the line width was measured. It turned out that lines of the different conformers and vibrational states had about equal width. Therefore the peak intensity I was assumed to be independent of the linewidth, and we can write

$$I = C\nu^2 S_g \mu_g^2 f_{v,v'} e^{-E_{rot}/kT} \tag{2}$$

where most symbols are explained in Ref. (*11*); C is a proportionality constant which depends only on the temperature. The symbol $f_{v,v'}$ represents the fraction of molecules in a certain vibrational state v, v', and from $f_{v,v'}$ the vibrational energies can be obtained

TABLE VI

Estimated Dipole Moments (D) and Internal Rotation Parameters for the Two Possible Values of ϕ

Conformation	ϕ(°)	μ_a	μ_b	μ_c	ρ_a	ρ_b	ρ_c
trans	250	0.79	2.53	0.62	0.0129	0.0143	0.0085
	350	0.41	0.23	1.60	0.0201	0.0160	0.0006
cis	60	2.38	0.48	0.25	0.0149	0.0152	0.0076
	175	2.39	3.34	0.98	0.0151	0.0188	0.0015

using Boltzmann's distribution law. The dipole moments are assumed not to depend on the vibrational quantum numbers v and v'.

Each observed peak intensity was divided by the calculated peak intensity, which contains all quantities occurring in Eq. (2) except $f_{v,v'}$ and C. The resulting quantity indicated by $f'_{v,v'}$ is directly proportional to $f_{v,v'}$. Values of $f'_{v,v'}$ were averaged for every vibrational state, and the quantity $A_{v,v'}$ was calculated:

$$A_{v,v'} = -kT \ln f'_{v,v'} = E_{v,v'} + B \tag{3}$$

where $E_{v,v'}$ is the vibrational energy of state v, v' relative to a scale quantity B. When the potential energy curve is assumed to be harmonic we can write for the vibrational energy

$$E_{v,v'} = E^0 + (v + \tfrac{1}{2})h\omega + (v' + \tfrac{1}{2})h\omega'. \tag{4}$$

The six unknown parameters, viz., B, ω_{trans}, ω'_{trans}, ω_{cis}, ω'_{cis}, and the energy difference $E^0_{trans} - E^0_{cis}$ were determined from the observations by a least-squares procedure. The results are given in Table VII together with the observed A values. For this table the scale of the intensity measurements has been adjusted, so that $E^0_{cis} + B = 0$.

From the values of $h\omega'_{trans}$ and $h\omega'_{cis}$ reported in Table VII the V_3 barriers to internal rotation of the methyl group are calculated to be 12.6 ± 0.8 kJ mole^{-1} (*trans*) and 10.5 ± 1.8 kJ mole^{-1} (*cis*). Comparison of these values with those determined from the observed A–E splittings (*trans*, 13.5 ± 0.3 kJ mole^{-1}) or the absence of line

TABLE VII

Results of the Intensity Measurements (kJ mole^{-1})

Conformation	v	v'	n[a)]	A_{obs}	$A_{calc-obs}$
cis	0	0	21	1.47 ± 0.09	0.03
	1	0	18	2.28 ± 0.11	-0.07
	2	0	19	2.85 ± 0.14	0.07
	3	0	16	3.66 ± 0.18	-0.04
	0	1	12	3.92 ± 0.21	-0.12
	1	1	7	4.39 ± 0.21	0.12
trans	0	0	125	2.01 ± 0.06	0.04
	1	0	121	2.66 ± 0.06	-0.02
	2	0	105	3.15 ± 0.09	0.07
	3	0	109	3.90 ± 0.08	-0.09
	0	1	80	4.65 ± 0.09	-0.08
	1	1	66	5.23 ± 0.09	-0.07
	2	1	65	5.51 ± 0.12	0.24
$h\omega_{cis}$				0.71 ± 0.07	
$h\omega'_{cis}$				2.3 ± 0.2	
$h\omega_{trans}$				0.59 ± 0.04	
$h\omega'_{trans}$				2.53 ± 0.08	
$E^0_{trans}-E^0_{cis}$				0.5 ± 0.2	

a) Number of lines measured.

splittings (*cis*, >12.5 kJ mole^{-1}) may be an indication of the reliability of the energies obtained from the relative intensity method.

DISCUSSION

A comparison of the results of α-fluoropropionic acid with those of fluoroacetic acid is of interest. The molecular conformations found are quite similar for the two molecules. However, the *trans-cis* energy differences in the two molecules are completely different: 0.5 ± 0.2 kJ mole^{-1} for α-fluoropropionic acid and −2.47 ± 0.12 kJ mole^{-1} for fluoroacetic acid. We did not expect that the substitution of a hydrogen atom by a methyl group would have such dramatic effects on the potential energy. An ab initio calculation might reproduce this effect correctly, but one would prefer to acquire a more simple, intuitive understanding of such observations. At present not even a rule of thumb can be given.

In 3-fluoro-1-propanol (*12*) two conformers without and one conformer with an internal O–H · · · F hydrogen bond were observed. The ground state energy of the hydrogen bonded conformer is about in the middle of that of the other two, and 1.7 ± 0.8 kJ mole^{-1} above that of the conformer with the lowest ground state energy. This observation was used as evidence for the weakness of the O–H · · · F hydrogen bond. However, the results of the present study, namely that in α-fluoropropionic acid the hydrogen bonded conformer has the lowest potential energy, do not support this argument.

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