

The Ground State Microwave Spectrum of 2-Fluoropropane

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Z. Naturforsch. **43a**, 138–142 (1988); received November 27, 1987

We determined the internal rotation barrier $V_3 = 3.285$ kcal/mol (13.74 kJ/mol) and the moment of inertia $I_x = 3.184$ amuÅ² of the methyl groups from the ground state microwave spectrum of 2-fluoropropane. Additionally the rotational constants, the quartic and some sextic centrifugal distortion constants are reported. The analysis of the Stark effect leads to the dipole moment 1.958 D.

The internal rotation of two top molecules has been studied extensively [1] but for 2-fluoropropane microwave spectroscopy provided only an approximate value of the internal rotation barrier V_3 . As the internal rotation fine structure of the ground state was not resolvable with conventional Stark spectroscopy, Griffith et al. [2] determined the barrier from the first excited states $vv' = 01$ and $vv' = 10$ with the assumption of a certain molecular structure and neglect of top-top interactions. With the aid of microwave Fourier transform (MWFT) spectroscopy [3] we resolved the fine structure of the ground state $vv' = 00$. In this state no top-top interaction is present. As further the torsion-vibration interaction is at its minimum, the ground state internal rotation analysis should lead to more reliable results.

For this molecule, far infrared spectroscopy contributed partly to barrier determinations, since the absorption of 2-fluoropropane in this spectral region is very weak [2, 4, 5]. Only Dew [6] was able to determine the barrier using this technique.

The molecular structure obtained from a joint analysis of gas electron diffraction data and microwave moments of inertia by Kakubari et al. [7] and the combined r_s/r_o -structure of Saito [8] proved to be important for our study.

The sample of 2-fluoropropane was prepared according to the procedure of Edgel and Parts [9] and purified by vacuum distillation. The spectra were recorded in the frequency range from 5 to 36 GHz using MWFT spectroscopy [10–14]. The pressure was kept below 0.1 Pa (0.8 mTorr) and the tempera-

ture between 220 and 250 K. The analysis of the narrow multiplets was refined by a lineshape analysis [15]. The frequencies of a part of the transitions are given in Table 1. A complete list has been deposited under number TNA 13 at the Universitätsbibliothek of the University of Kiel. An example of the measured spectra is reproduced in Figure 1. The resolved transitions appeared always as triplets, i.e. the internal rotation components AE and EA remained degenerate.

The internal rotation and centrifugal distortion were treated independently. An iterative procedure resulted in standard deviations of the respective least squares fits close to the experimental uncertainty. We included unsplit lines and multiplets in the sixth order centrifugal distortion analysis according to the Wat-

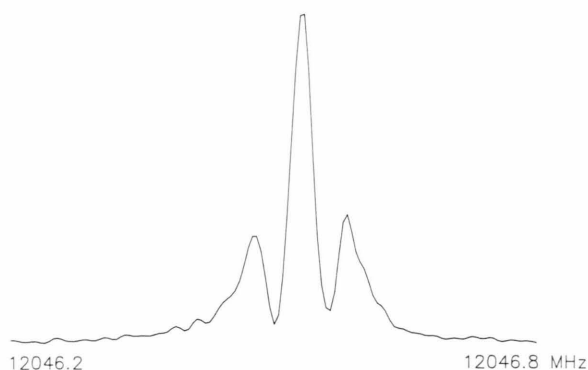


Fig. 1. Rotational transition $15_{12,4} - 15_{11,4}$ of 2-fluoropropane showing internal rotation fine structure. A 600 kHz range out of a 10 MHz scan is given. Powerspectrum, sample interval 50 ns, $13 \cdot 10^6$ averaging cycles, 1024 data points of the transient decay supplemented by 3072 zeros before Fourier transformation. Sample pressure 0.07 Pa, temperature in the waveguide cell 250 K. Calculated Doppler width 9 kHz and wall broadening width 2 kHz, experimental half width at half height of the central component 13 kHz.

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Table 1 a. Selection of transitions used for the IAM analysis. Γ : symmetry species, ν : measured frequency [MHz], δ : difference between observed and calculated splitting relative to the AA species [kHz].

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν	δ
9	9	0	9	8	1	AA	22 825.437	
						EE	22 825.405	-2
						AE, EA	22 285.369	0
9	8	2	9	7	2	AA	12 986.816	
						EE	12 986.783	1
						AE, EA	12 986.747	5
10	8	3	10	7	3	AA	6 235.072	
						EE	6 235.045	3
						AE, EA	6 235.020	4
11	10	1	11	9	2	AA	21 576.510	
						EE	21 576.475	-4
						AE, EA	21 576.436	-4
11	10	2	11	9	2	AA	20 881.580	
						EE	20 881.541	-3
						AE, EA	20 881.500	-5
12	11	1	12	10	2	AA	25 343.036	
						EE	25 342.999	-6
						AE, EA	25 342.957	-7
13	11	2	13	10	3	AA	19 766.641	
						EE	19 766.610	-4
						AE, EA	19 766.578	-8
13	11	3	13	10	3	AA	17 024.886	
						EE	17 024.841	-2
						AE, EA	17 024.794	-1
14	12	2	14	11	3	AA	23 185.915	
						EE	23 185.870	2
						AE, EA	23 185.829	-1
14	12	3	14	11	3	AA	21 436.790	
						EE	21 436.738	0
						AE, EA	21 436.688	-1
15	13	3	15	12	3	AA	25 973.300	
						EE	25 973.243	2
						AE, EA	25 973.182	9
15	12	4	15	11	4	AA	12 046.566	
						EE	12 046.522	0
						AE, EA	12 046.479	-2
16	13	4	16	12	4	AA	16 286.691	
						EE	16 286.637	2
						AE, EA	16 286.582	4
17	14	3	17	13	4	AA	24 505.396	
						EE	24 505.354	0
						AE, EA	24 505.315	-3
17	13	5	17	12	5	AA	7 198.478	
						EE	7 198.443	0
						AE, EA	7 198.407	1
17	14	4	17	13	4	AA	20 941.964	
						EE	20 941.898	8
						AE, EA	20 941.842	6
18	15	4	18	14	4	AA	25 882.559	
						EE	25 882.497	0
						AE, EA	25 882.427	9

Table 1 b. Selection of transitions used for centrifugal distortion analysis. ν : measured frequency [MHz], δ : difference between observed and calculated frequency [kHz]. For the multiplets (*) the hypothetical unsplit frequency is given (see text).

J	K_-	K_+	J'	K'_-	K'_+	ν	δ
1	1	0	0	0	0	16 796.425	4
1	1	1	0	0	0	13 482.715	2
2	2	0	1	1	0	33 664.937	-3
2	1	1	1	0	1	33 001.421	-3
2	1	1	2	0	2	10 013.343	-3
2	2	1	2	1	2	11 714.894	-2
2	0	2	1	1	1	22 396.790	3
2	1	2	1	0	1	23 060.375	3
3	3	0	3	2	2	14 791.498	-6
3	2	1	3	1	2	9 456.797	0
3	3	0	3	2	1	5 689.274	0
3	3	1	3	2	2	12 644.263	-1
3	1	3	2	0	2	32 371.889	-1
3	0	3	2	1	2	32 294.017	-3
9	8	2	9	7	2*	12 986.771	0
9	9	0	9	8	1*	22 825.392	-5
10	8	3	10	7	3*	6 235.037	1
11	10	2	11	9	2*	20 881.527	0
11	10	1	11	9	2*	21 576.461	-3
12	11	1	12	10	2*	25 342.984	1
13	11	3	13	10	3*	17 024.825	2
13	11	2	13	10	3*	19 766.599	-2
14	12	3	14	11	3*	21 436.722	2
14	12	2	14	11	3*	23 185.857	-2
15	13	3	15	12	3*	25 973.222	2
15	12	4	15	11	4*	12 046.508	1
16	13	4	16	12	4*	16 268.619	0
17	13	5	17	12	5*	7 198.431	0
17	14	4	17	13	5*	20 941.882	-5
17	14	3	17	13	4*	24 505.341	-4
18	14	5	18	13	5*	10 628.967	-4
18	15	4	18	14	4*	25 882.472	5
19	15	5	19	14	5*	14 797.338	-2
20	16	5	20	15	5*	19 576.309	-12
20	15	6	20	14	6*	5 853.235	-1
20	16	4	20	15	5*	25 918.177	-7
21	17	5	21	16	5*	24 790.880	2
22	17	6	22	16	6*	12 860.179	-4
23	18	6	23	17	6*	17 556.089	-2
24	18	7	24	17	7*	7 193.320	-6
25	19	7	25	18	7*	10 712.430	-6
26	20	7	26	19	7*	15 126.054	-8
31	24	8	31	23	8*	23 142.979	3
32	24	9	32	23	9	10 029.798	4
33	25	9	33	24	9	14 419.402	4
34	25	10	34	24	10	5 010.354	4
34	26	9	34	25	9	19 785.066	1
35	26	10	35	25	10	7 769.490	3
36	27	10	36	26	10	11 529.576	8
37	28	10	37	27	10	16 353.348	8
38	28	11	38	27	11	5 875.601	0
38	29	10	38	28	10	22 188.097	3

Table 1 c. Transitions used for Stark effect analysis. E : Stark field strength [V/cm], v_0 : zero field line [MHz], $v_{St} - v_0$: Stark shift [MHz], δ : difference between observed and calculated shift.

J	K_-	K_+	J	K_-	K_+	M	E	v_0	$v_{St} - v_0$	δ
2	2	1	2	1	2	1	0.000	11 714.894	0.000	
						2	38.869		-0.194	-0.028
						1	38.689		-0.634	0.026
						1	58.300		-0.379	-0.006
						2	58.300		-1.458	-0.008
						1	77.730		-0.660	0.000
						2	77.730		-2.563	0.001
3	2	1	3	1	2		0.000	9 456.797	0.000	
						2	194.326		0.652	-0.014
						3	194.326		1.521	-0.020
						2	233.191		0.968	0.011
						3	233.191		2.221	0.010
						2	310.921		1.706	0.011
						3	310.921		3.893	-0.004
4	1	3	4	2	2		0.000	9 045.708	0.000	
						2	194.326		0.273	0.027
						3	194.326		0.573	0.005
						4	194.326		1.035	0.013
						2	233.191		0.352	0.003
						3	233.191		0.823	0.003
						4	233.191		1.482	-0.013
						2	272.056		0.433	-0.040
						3	272.056		1.148	-0.030
						4	272.056		2.045	0.044

Table 2. Rotational [MHz], quartic [kHz], and sextic [Hz] centrifugal distortion constants according to Watson's A reduction with correlation matrix. σ : standard deviation of the fit [kHz], N : number of transitions, J_m : highest J quantum number. Fixed values in square brackets.

A	8693.8573	(6)	1.00															
B	8102.5969	(6)	0.997	1.00														
C	4788.8526	(6)	0.93	0.95	1.00													
Δ_J	8.231	(28)	0.85	0.86	0.85	1.00												
Δ_{JK}	-13.9279	(32)	-0.06	-0.03	0.02	0.07	1.00											
Δ_K	6.729	(19)	0.01	0.00	0.07	-0.07	-0.88	1.00										
δ_J	0.55264	(14)	0.08	0.03	-0.05	-0.04	-0.84	0.57	1.00									
δ_K	-8.6043	(32)	-0.06	-0.03	0.02	0.02	0.72	-0.53	-0.94	1.00								
Φ_{JK}	-0.243	(12)	0.12	0.10	-0.01	0.04	-0.84	0.72	0.77	-0.74	1.00							
Φ_{KJ}	1.34	(22)	-0.13	-0.11	0.01	-0.06	0.82	0.74	-0.62	0.53	0.93	1.00						
Φ_K	-4.5	(12)	0.12	0.11	0.00	0.06	-0.82	0.77	0.59	-0.52	0.93	0.997	1.00					
ϕ_{JK}	0.0352	(60)	0.11	0.09	-0.02	0.02	-0.88	0.78	0.73	-0.65	0.97	-0.93	0.94	1.00				
ϕ_K	1.578	(81)	-0.08	-0.06	0.01	0.07	0.74	-0.67	-0.73	0.77	-0.91	0.71	-0.73	-0.89	1.00			
Φ_J	[0.0]		σ	4														
ϕ_J	[0.0]		N	121														
			J_m	38														

son A-reduction [16, 17]. In the latter case we used the internal rotation parameters to calculate the deviations from the hypothetical unsplit lines. We subtracted these deviations from the observed frequencies in Table 1 a and evaluated the hypothetical unsplit lines as an average. A part of the lines used for the centrifugal distortion analysis is given in Table 1 b. The results of the analysis are summarized in Table 2.

The sextic centrifugal distortion constants Φ_J and ϕ_J were restricted to zero because they could not be determined from the transitions within the frequency range of our spectrometers. Besides Q-branch transitions there exist only R-branch transitions of low J values in the range. We propose a further investigation in the millimeter wave region for completion of the analysis.

The rotational and quartic centrifugal distortion constants were used as fixed values in the internal rotation analysis according to the internal axis method (IAM) of Woods [18, 19]. The angles between the internal rotation axes i and the inertia axes a, b, c of the molecule were insensitive to the observed splittings and could not be determined. We calculated them using the r_s -parameters of the methyl groups $r(\text{C}-\text{H}) = 1.092(9) \text{ \AA}$, $\angle \text{HCH} = 108.9(12)^\circ$ (mean values) and the r_o -parameters $r(\text{C}-\text{F}) = 1.407(5) \text{ \AA}$, $r(\text{C}-\text{C}) = 1.515(3) \text{ \AA}$, $r(\text{C}-\text{H})_{\text{sec}} = 1.096(4) \text{ \AA}$ (sec = secondary hydrogen), $\angle \text{CCC} = 114.0(3)^\circ$, $\angle \text{CCF} = 108.1(3)^\circ$, $\angle \text{CCH}_{\text{sec}} = 108.6(15)^\circ$ and $\angle \text{FCH}_{\text{sec}} = 109.4(29)^\circ$ [8]. The value of the moment of inertia I_x and the Fourier coefficient $w_1(s)$, s the reduced barrier, could

be determined from the observed spectra. The results of the IAM analysis and derived parameters are given in Table 3.

As expected, the barrier due to internal rotation $V_3 = 3.285 \text{ kcal/mol}$ is somewhat higher than $V_3 = 3.166 \text{ kcal/mol}$ of propane [20]. The moments of inertia $I_x = 3.184 \text{ amu\AA}^2$ of the IAM analysis and $3.182 \text{ amu\AA}^2$ resulting from the r_s parameters of 2-fluoropropane are almost the same, whereas the joint analysis of diffraction data and moments of inertia [7] leads to $I_x = 3.45 \text{ amu\AA}^2$, which is unusually large.

For further comparison we quote the effective barrier of related molecules investigated by far infrared (FIR), Raman (Ra) spectroscopy and neutron incoherent inelastic scattering (NIIS) in Table 4. The effective barrier corresponds to the energy required to rotate one top about 60° from the equilibrium position. With exception of the earlier results affected with large errors the data appear in correct order of magnitude and sequence. The microwave barriers are somewhat smaller than those from FIR/Ra investigations. However we do not expect exact agreement. The differences might arise from structural assumptions, that have to be made especially for the evaluation of FIR/Ra spectra, whereas the structural parameters can be obtained from the microwave spectra in favourable cases like propane. On the other hand the coupling parameters belonging to the domain of

Table 3. Internal rotation parameters of 2-fluoropropane. $w_1(s)$: Fourier coefficient, I_x : moment of inertia of the methyl groups, $\angle g, i$: angle between the inertia axes $g = a, b, c$ and the inertial axis i calculated from the structure [8], s : reduced barrier height, F : reduced rotational constant of the internal rotation, V_3 : barrier hindering internal rotation of the methyl groups, Δv : mean experimental splitting, σ : standard deviation of the fit, N : number of transitions, $(w_1(s), I_x)$: correlation coefficient, standard errors in brackets.

$w_1(s)$	$-0.6273(39) \cdot 10^6$
I_x [amu\AA ²]	3.184 (25)
$\angle a, i$ [°]	[33.00]
$\angle b, i$ [°]	[63.80]
$\angle c, i$ [°]	[71.41]
s	91.466 (65)
F [GHz]	167.5 (13)
V_3 [kcal/mol]	3.285 (27)
V_3 [kJ/mol]	13.74 (11)
Δv [kHz]	75
σ [kHz]	5
N	29
$(w_1(s), I_x)$	0.08

Table 4. Effective barriers V_{eff} of 2-fluoropropane and related molecules. The values were calculated from the respective torsional potential functions if not stated in the original studies ($1 \text{ cm}^{-1} = 2.8591 \text{ cal/mol}$).

Molecule	V_{eff} [kcal/mol]	Method	Reference
$(\text{CH}_3)_2\text{CH}_2$	3.400 (230)	NIIS	[21]
	3.257 (29)	Ra	[22]
	3.166 (27)	MWFT	[20]
$(\text{CH}_3)_2\text{CHF}$	3.42	FIR	[6]
	3.560 (300)	MW	[2]
	3.285 (27)	MWFT	this work
$(\text{CH}_3)_2\text{CF}_2$	3.42	FIR	[23]
	3.45	FIR	[6]
	3.45 (3)	FIR/Ra	[24]
	no finestructure resolved	MW	[24]

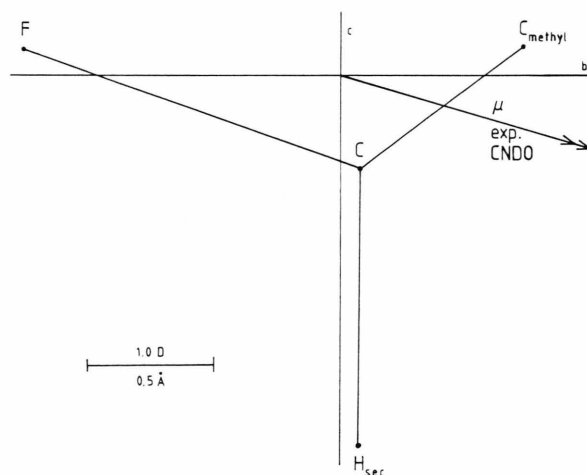


Fig. 2. Projection of a partial structure of 2-fluoropropane in the bc plane of symmetry with the most probable alignment of the dipole moment vector. The hydrogen atoms of the methyl groups have been omitted since the angular position of the methyl groups is not known.

FIR/Ra spectroscopy are difficult to treat in microwave spectroscopy [25].

We reinvestigated the Stark effect of the rotational spectrum of 2-fluoropropane. A typical set-up of the spectrometer for this experiment is given in [26]. Compared with a normal X-band cell the measurements required an increased number of averaging cycles due to the higher attenuation of the Stark cell. The calibration was accomplished with the OCS transition $J - J' = 1 - 0$ using the dipole moment $0.71519(3)$ D [27].

The analysis of the experimental splittings was performed by diagonalizing the energy matrix [28], since this led to more accurate results than the usual second order perturbation treatment. The determined components $|\mu_b| = 1.880(1)$, $|\mu_c| = 0.547(1)$

and $\mu = 1.958(1)$ D are more accurate than the values obtained by conventional Stark spectroscopy [2]. The dipole moment is aligned nearly parallel to the C–F bond in the bc plane. The direction of the dipole moment vector is not deducible from our measurements since the sign of the components is unknown. A CNDO/2 procedure [29] with the quoted structure as input predicts $\mu_b = 2.01$, $\mu_c = -0.58$ and $\mu = 2.09$ D and the direction shown in Figure 2.

We gratefully acknowledge the help of Professor Dr. S. Saito of Nagoya University, who provided the molecular structure. The work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemie. The calculations were performed at the computer center of the University Kiel.

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