A Redetermination of the Barrier to Internal Rotation of 2-Fluoropropene

G. Bestmann and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

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We present the determination of the methyl barrier to internal rotation from the rotational spectrum in the ground state of 2-fluoropropene. A complete set of barrier parameters could be determined. The results are compared with those of 2-chloro- and 2-bromopropene, achieved by the same technique and evaluation method.

Recently we determined the barrier to internal rotation of the methyl group from rotational transitions in the torsional ground state of 2-chloro- and 2-bromopropene [1, 2]. Now we present a redetermination of the barrier to internal rotation of 2-fluoropropene. The measurements were made by microwave Fourier transform spectroscopy [3–6] because of the higher resolution compared to Stark spectroscopy.

2-fluoropropene, $CH_3-CF=CH_2$, was first investigated by Pierce and O'Reilly [7]. The substance was purchased from PCR Research Chemicals, Gainesville, Florida, USA, and used after vacuum distillation. The spectra between 8 and 26 GHz were recorded in the pressure range between 1 to 2 mTorr and at a temperature of approximately −30 °C. Our measurements are given in Table 1. We performed a sixth order centrifugal distortion analysis of 83 A-species lines with a standard deviation of 5 kHz. The Hamiltonian of van Eijck [8] and Typke [9] (Eq. (6)) was used. It is worth to mention, that for 2-bromopropene only one centrifugal distortion parameter δ_J' could be determined. In 2-chloropropene a fourth order analysis was possible. The results for 2-fluoropropene are given in Table 2.

The barrier V_3 was determined from 77 A–E splittings given in Table 1. The closely split doublets were corrected for effects of overlapping by a line shape analysis [10]. The internal axis method (IAM) was applied with a version of Wood's program [11–14]. Using the rotational constants of Table 2 a fit of the Fourier coefficient $w_1(s)$, s the reduced

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40, D-2300 Kiel.

Table 1. Measured transitions of 2-fluoropropene $CH_3-CF=CH_2$. Γ: symmetry species, ν_m: measured frequency, deviation from calculated frequency in brackets in units of the last digit, $\Delta\nu_m$: measured internal rotation splitting $\nu_A-\nu_E$, $\Delta\nu_c$: calculated internal rotation splitting, all frequencies in [MHz]. (****: not resolved).

J	K_-		J'	K_-'	K_+'	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
1	0	1	0	0	0	A	13968.700 (-4)	*****	0.000
						E			
1	1	1	0	0	0	A	15096.752 (0)	0.046	0.047
						E			
2	0	2	1	0	1	A	24749.032 (2)	0.031	0.031
						E			
2	1	2	1	1	1	A	23822.771 (3)	*****	0.000
						E			
2	0	2	1	1	1	A	23620.977 (2)	*****	-0.015
						E			
2	1	2	1	0	1	A	24950.833 (-4)	0.054	0.047
						E			
2	1	1	2	1	2	A	12343.558 (5)	*****	0.000
						E			
2	2	1	2	0	2	A	15929.497(-11)	0.167	0.156
						E			
2	1	1	2	0	2	A	12545.348 (11)	*****	0.017
						E			
2	2	1	2	1	2	A	15727.691 (0)	0.144	0.140
						E			
3	1	3	2	2	0	A	15208.314 (-1)	-0.103	-0.095
						E			
3	1	2	3	1	3	A	22539.450 (-4)	0.060	0.055
						E			
3	2	1	3	2	2	A	10790.888 (7)	-0.061	-0.057
						E			
3	2	2	3	0	3	A	23532.045 (-1)	0.131	0.129
						E			
3	3	1	3	1	2	A	18505.639 (-2)	0.287	0.288
						E			
3	3	0	3	2	1	A	8892.587 (-6)	0.230	0.221
						E			
3	1	2	3	0	3	A	22562.448 (-4)	0.064	0.057
						E			
3	2	1	3	1	2	A	11760.487 (8)	0.011	0.015
						E			
3	2	2	3	1	3	A	23509.053 (-7)	0.133	0.127
						E			

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Table 1 (continued)

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
3	3	1	3	2	2	A E	17536.043 (-6)	0.228	0.216
4	3	1	4	3	2	A E	8855.279 (6)	-0.125	-0.122
4	2	2	4	2	3	A E	21323.134 (2)	-0.022	-0.024
4	4	1	4	2	2	A E	22664.532 (7)	0.505	0.500
4	3	2	4	1	3	A E	24168.354 (-1)	0.178	0.179
4	3	1	4	2	2	A E	11542.545(-11)	0.069	0.064
4	4	0	4	3	1	A E	12389.542 (0)	0.381	0.382
4	2	2	4	1	3	A E	21481.104 (-1)	*****	0.006
4	4	1	4	3	2	A E	19977.286 (4)	0.315	0.314
4	3	2	4	2	3	A E	24010.385 (1)	0.158	0.161
5	3	2	5	3	3	A E	19369.057 (-1)	-0.132	-0.129
5	4	2	5	2	3	A E	25551.627 (4)	0.283	0.289
5	5	0	5	4	1	A E	16984.808 (0)	0.559	0.558
5	3	2	5	2	3	A E	19977.043 (1)	-0.073	-0.063
5	4	1	5	3	2	A E	12291.698 (-5)	0.181	0.177
5	4	2	5	3	3	A E	24943.638 (6)	0.212	0.222
5	5	1	5	4	2	A E	23028.402 (3)	0.429	0.434
6	4	2	6	4	3	A E	16777.974 (4)	-0.250	-0.241
6	5	1	6	4	2	A E	14285.794 (1)	0.352	0.357
6	6	0	6	5	1	A E	22315.149 (-8)	0.714	0.708
6	4	2	6	3	3	A E	18479.540 (0)	-0.066	-0.066
6	5	2	6	4	3	A E	26421.425 (3)	0.303	0.312
7	5	2	7	5	3	A E	13753.051 (-7)	-0.331	-0.340
7	5	2	7	4	3	A E	17560.317 (2)	0.014	0.016
7	6	1	7	5	2	A E	17668.868 (-1)	0.591	0.588
8	5	3	8	5	4	A E	26309.600 (-3)	-0.316	-0.325
8	6	2	8	6	3	A E	10556.222 (-2)	-0.406	-0.405
8	7	1	8	6	2	A E	22348.635 (-3)	0.827	0.827
8	6	2	8	5	3	A E	17726.555 (0)	0.201	0.191
9	6	3	9	6	4	A E	22866.558 (-1)	-0.487	-0.490
9	7	2	9	6	3	A E	19319.144 (2)	0.445	0.447
9	6	3	9	5	4	A E	25116.583 (-3)	-0.196	-0.204

Table 1 (continued)

J	K_-	K_+	J'	K'_-	K'_+	Γ	ν_m	$\Delta\nu_m$	$\Delta\nu_c$
10	7	3	10	7	4	A E	18900.165 (4)	-0.619	-0.621
10	7	3	10	6	4	A E	23523.886 (4)	-0.099	-0.090
10	8	2	10	7	3	A E	22497.024 (4)	0.754	0.757
11	8	3	11	8	4	A E	14732.496 (0)	-0.695	-0.694
11	8	3	11	7	4	A E	23072.795 (-8)	0.154	0.146
12	9	3	12	9	4	A E	10727.492 (1)	-0.689	-0.689
12	9	3	12	8	4	A E	24182.945 (3)	0.477	0.482
13	9	4	13	9	5	A E	24322.914 (8)	-0.943	-0.935
14	10	4	14	10	5	A E	19253.228 (4)	-1.022	-1.016
15	11	4	15	11	5	A E	14325.285 (1)	-0.998	-0.995
16	12	4	16	12	5	A E	9950.055 (-2)	-0.873	-0.873
17	12	5	17	12	6	A E	24117.334 (-2)	-1.330	-1.339
18	13	5	18	13	6	A E	18294.926 (-4)	-1.296	-1.306
19	14	5	19	14	6	A E	13019.608 (-1)	-1.153	-1.151
20	15	5	20	15	6	A E	8668.186 (-4)	-0.898	-0.909
21	15	6	21	15	7	A E	22635.158 (1)	-1.597	-1.594
22	16	6	22	16	7	A E	16460.846 (0)	-1.419	-1.415
23	17	6	23	17	7	A E	11235.556 (-2)	-1.137	-1.133
25	18	7	25	18	8	A E	20278.513 (0)	-1.650	-1.642
26	19	7	26	19	8	A E	14157.112 (2)	-1.310	-1.332
27	20	7	27	20	8	A E	9307.388 (-2)	-0.977	-0.976
28	20	8	28	20	9	A E	24475.415 (-6)	-1.812	-1.814
29	21	8	29	21	9	A E	17444.901 (15)	-1.510	-1.489
30	22	8	30	22	9	A E	11726.740 (0)	-1.108	-1.108
32	23	9	32	23	10	A E	21109.122 (1)	-1.589	-1.593
33	24	9	33	24	10	A E	14487.864 (3)	-1.204	-1.202
34	25	9	34	25	10	A E	9419.103 (1)	-0.810	-0.822
35	25	10	35	25	11	A E	25157.677 (7)	-1.639	-1.639
36	26	10	36	26	11	A E	17607.977 (7)	-1.253	-1.251
37	27	10	37	27	11	A E	11678.252 (7)	-0.871	-0.867
39	28	11	39	28	12	A E	21102.458 (11)	-1.252	-1.257
40	29	11	40	29	12	A E	14265.674 (9)	-0.886	-0.881

Table 2. Rotational and centrifugal distortion constants of 2-fluoropropene $CH_3-CF=CH_2$. σ: standard deviation of the fit, standard errors in units of the last digit in brackets.

A = 10169.70848(108) MHz	D_J' = 2.440(89) kHz	H_J' = 0.000 fixed
B = 9041.63008(109) MHz	D_{JK}' = 12.997(13) kHz	H_{JK}' = −3.80(619) Hz
C = 4927.06935(109) MHz	D_K' = −4.813 (9) kHz	H_{KJ}' = 4.37(140) Hz
	δ_J' = 1.643(12) kHz	H_K' = −2.37 (72) Hz
	R_6' = −0.830 (6) kHz	H_5' = −0.79 (33) Hz
		H_6' = 3.88(145) Hz
	σ = 5 kHz	H_{10}' = −1.98 (70) Hz

Correlation coefficients

1.00													
0.99	1.00												
0.91	0.92	1.00											
0.85	0.86	0.89	1.00										
0.11	0.17	−0.09	0.04	1.00									
0.08	0.02	−0.06	−0.05	−0.46	1.00								
0.13	0.18	−0.10	0.05	0.89	−0.07	1.00							
0.10	0.15	−0.07	0.07	0.88	−0.16	0.98	1.00						
−0.08	−0.02	0.06	0.09	0.42	−0.48	0.40	0.56	1.00					
0.08	0.01	−0.06	−0.08	−0.38	0.44	−0.37	−0.53	−0.99	1.00				
−0.08	0.01	0.05	0.07	0.32	−0.32	0.35	0.49	0.92	−0.97	1.00			
−0.03	0.01	0.04	0.09	0.51	−0.35	0.56	0.70	0.95	−0.91	0.82	1.00		
0.06	0.01	−0.06	−0.09	−0.44	0.45	−0.45	−0.60	−0.99	0.97	−0.90	−0.98	1.00	
−0.09	−0.02	0.07	0.08	0.38	−0.51	0.34	0.50	0.99	−0.99	0.93	0.92	−0.98	1.00

Table 3. Internal rotation parameters of 2-fluoropropene, $CH_3-CF=CH_2$. $w_1(s)$: Fourier coefficient, $\measuredangle(a, i)$: angle between the inertia axis a and the internal rotation axis i, I_α: moment of inertia of the methyl group, $(\cdots)$: correlation coefficient, σ: standard deviation of the fit, $\Delta\nu$: mean experimental splitting, s: reduced barrier height, F: reduced rotational constant of the internal rotation, V_3: barrier to internal rotation, N: Number of splittings, standard errors in units of the last digit in brackets.

$w_1(s)$	$-0.9256(93)\cdot 10^{-5}$
$\measuredangle(a, i)$ [°]	5.84(75)
I_α [amuÅ^2]	3.177(18)
$(w_1(s), \measuredangle(a, i))$	−0.995
$(w_1(s), I_\alpha)$	0.970
$(\measuredangle(a, i), I_\alpha)$	−0.980
σ [kHz]	7
$\Delta\nu$ [kHz]	583
s	65.41(9)
F [GHz]	169.929(96)
V_3 [kcal/mol]	2.384(17)
N	77

barrier, $\measuredangle(a, i)$, the angle between the inertia axis a and the internal rotation axis i and I_α, the moment of inertia of the methyl group, converged to reasonable values as given in Table 3. For this molecule the value of $I_\alpha = 3.177(18)$ amuÅ^2 could be fitted, which is near to the value of $I_\alpha = 3.167$ amuÅ^2 for 2-chloropropene derived in [1] from a complete r_s-structure [15].

Table 5 of [2] may now be completed with measurements taken by the same technique and evaluated by the same method. The comparison is given in Table 4. The general trend in variation of the barrier height V_3 is like for CH_3CH_2X, X = F, Cl, and Br. V_3 increases from F to Cl and Br.

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Table 4. Comparison of potential barriers V_3 and related parameters of 2-halopropenes $CH_3-CX=CH_2$, X = F, Cl and Br. Assumptions in square brackets.

X	F	^{35}Cl	^{37}Cl	^{79}Br	^{81}Br
V_3 [cal/mol]	2384(17)	2568(10)	2582(12)	2571(49)	2558(74)
$\measuredangle(a, i)$ [°]	5.84(75)	59.78(84)	61.28(108)	56.8(34)	56.9(48)
I_α [amuÅ^2]	3.177(18)	[3.167]	[3.167]	[3.167]	[3.167]
F [GHz]	169.93(96)	165.91	165.69	164.64	164.72
s	65.41(9)	72.15(29)	72.63(35)	72.8(14)	72.4(21)
	this work	[1]	[1]	[2]	[2]

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