Millimeterwave Spectrum and Centrifugal Distortion Analysis of Fluoroacetonitrile in the Ground State

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The millimeterwave spectrum of fluoroacetonitrile (CH_2FCN) in the ground state has been investigated in the region between 50 and 150 GHz. The transitions have been fitted to a Hamiltonian using three rotational constants, five quartic and seven sextic centrifugal distortion constants in the symmetric top reduction by van Eijck and Typke and in the *s*-reduction of Watson. Further Watson's "determinable constants" have been calculated.

1. Introduction

Kasten, Dreizler, Job, and J. Sheridan [1] measured 22 rotational transitions of CH_2FCN in the microwave region, with the principal purpose of determining the quadrupole hyperfine constants of the nitrogen atom. They have been able to determine the three rotational constants and four quartic centrifugal distortion constants. The constant D'_K was fixed to zero, because there was a high correlation between this constant and the A' rotational constant. To improve the data we measured 101 lines in the millimeterwave region and fit them to the Hamiltonians of Watson's symmetric top reduction and the symmetric top reduction of van Eijck and Typke. We were able to determine all rotational, all quartic and all sextic centrifugal distortion constants, including a value for D'_K and a more precise value for the A' rotational constant.

2. Experimental Details

The fluoroacetonitrile was prepared by dehydration of fluoroacetamide with phosphorpentoxide (see [2, 3]). The fluoroacetamide was made from ethyl fluoroacetate and ammonia. The transitions were measured by two methods. Most of the lines were measured using the video-method directly. The klystrons were modulated by a sawtooth frequency between 20 and 50 Hz and the absorptions of the transitions were displayed on a control CRD. The frequency marks were produced with a conventional method. The IF-frequency obtained by mixing the overtones of a synchronizer ND 800 Schomandl with the klystron frequency was detected by a radio receiver. The following klystrons were used as fundamental microwave sources: OKI 30V12, OKI 35V12 and OKI 40V12. The millimeterwave frequencies were produced by harmonic multiplication of the fundamental frequencies. The absorption cell was a glass cell with an inner radius of 50 mm and a length of 150 cm.

The rest of the lines was measured using source modulation. A 16.65 kHz sine wave was used to modulate the standard frequency which stabilizes the klystron. After detection the modulated signal was amplified in a narrow-band amplifier at 33.3 kHz and further phase detected. The frequency sweep was provided by an externally controlled ramp voltage to the frequency decade ND 800. The klystrons were stabilized by a Schomandl FDS 30 syncriminator. The millimeterwave frequencies were produced by the klystrons OKI 90V11 and OKI 100V11. The absorption cell was a *K*-band cell of 1.5 m length.

The transitions were assigned on the basis of frequency fitting and of relative line intensities. The sample pressures were between 40 and 50 mTorr. All spectra were measured at room temperature. The accuracy of the measurements is believed to be ± 10 kHz.

3. Results

The measured lines and twelve lines measured by Kasten et al. [1] are given in Table 1. These fre-

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quencies were fitted to the symmetric top reduction Hamiltonian of van Eijck and Typke [4, 5]

$$H' = B'_x P_x^2 + B'_y P_y^2 + B'_z P_z^2 - D'_J (P^2)^2 - D'_{JK} P^2 P_z^2 - D'_K P_z^4 - \delta_J [P^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2) P^2]$$
$$- 2 R'_6 [3 (P_x^2 P_y^2 + P_y^2 P_x^2) - P_x^4 - P_y^4] + H'_J (P^2)^3 + H'_{JK} (P^2)^2 P_z^2 + H'_{KJ} P^2 P_z^4 + H'_K P_z^6$$
$$+ H'_5 (P^2)^2 (P_x^2 - P_y^2) + 1/2 H'_6 P^2 [3 (P_x^2 P_y^2 + P_y^2 P_x^2) - P_x^4 - P_y^4] + H'_{10} (P_x^2 - P_y^2)$$

and to the Watson's s-reduction Hamiltonian [6]

$$H^{(s)} = 1/2 (B_x^{(s)} - B_y^{(s)}) P^2 + [B_z^{(s)} - (B_x^{(s)} + B_y^{(s)})/2] P_z^2 + 1/4 (B_x^{(s)} - B_y^{(s)}) (P_+^2 + P_-^2) - D'_J (P^2)^2$$
$$- D'_{JK} P^2 P_z^2 - D'_K P_z^4 + d_1 P^2 (P_+^2 + P_-^2) + d_2 (P_+^4 + P_-^4) + H'_J (P^2)^3 + H'_{JK} (P^2)^2 P_z^2 + H'_{KJ} P^2 P_z^4$$
$$+ H'_K P_z^6 + h_1 (P^2)^2 (P_+^2 + P_-^2) + h_2 P^2 (P_+^2 + P_-^2) + h_3 (P_+^6 + P_-^6)$$
$$(P_\pm = P_x \pm i P_y) .$$

Table 1. Rotational Transitions of fluoroacetonitrile in the ground state (in GHz).

No.	J	K_-	K_+	J'	K'_-	K'_+	Fre. (Calc.)	Fre. (Exp.)	ΔF/kHz
1	1	0	1	0	0	0	9.120998	9.120995	3
2	1	1	0	1	0	1	32.237853	32.237880	− 27
3	2	0	2	1	0	1	18.237363	18.237460	− 97
4	2	1	1	2	0	2	32.684239	32.684160	79
5	2	1	2	1	1	1	17.800666	17.800660	6
6	3	0	3	2	0	2	27.344464	27.344390	74
7	3	1	2	3	0	3	33.362326	33.362270	56
8	3	1	3	2	1	2	26.698026	26.697990	36
9	4	0	4	3	0	3	36.437693	36.437780	− 87
10	4	1	3	3	1	2	37.357628	37.357530	98
11	4	1	3	4	0	4	34.282262	34.282280	− 18
12	4	1	4	3	1	3	35.591863	35.591890	− 27
13	5	1	4	5	0	5	35.457435	35.457440	− 5
14	6	1	5	6	1	6	9.268231	9.268240	− 9
15	7	1	6	7	1	7	12.353844	12.353850	− 6
16	7	2	6	7	1	7	102.283421	102.283420	1
17	8	1	7	8	1	8	15.876528	15.876530	− 2
18	8	2	7	8	1	8	104.083687	104.083720	− 33
19	9	1	8	9	1	9	19.833605	19.833650	− 45
20	9	1	9	8	0	8	104.787777	104.787730	47
21	9	2	8	9	1	9	106.115785	106.115830	− 45
22	10	1	9	10	1	10	24.221330	24.221380	− 50
23	10	2	9	10	1	10	108.381341	108.381350	− 9
24	11	1	10	10	1	9	102.476940	102.479650	− 10
25	11	1	10	11	1	11	29.034653	29.034570	83
26	11	2	10	11	1	11	110.881757	110.881770	13
27	11	3	9	10	3	8	100.446243	100.446200	43
28	11	8	3	10	8	2	100.437999	100.437930	69
29	11	8	4	10	8	3	100.437999	100.437930	69
30	12	1	11	12	1	12	34.266951	34.266980	− 29
31	12	2	10	11	2	9	110.471542	110.471570	− 28
32	12	2	11	11	2	10	109.235073	109.235140	− 67
33	12	3	9	11	3	8	109.650770	109.650720	50
34	12	5	7	11	5	6	109.538148	109.538170	− 22
35	12	5	8	11	5	7	109.538140	109.538170	− 30
36	12	6	6	11	6	5	109.539212	109.539170	42
37	12	6	7	11	6	6	109.539212	109.539170	42
38	12	7	5	11	7	4	109.550612	109.550580	32
39	12	7	6	11	7	5	109.550612	109.550580	32
40	12	8	4	11	8	3	109.568941	109.569000	− 59
41	12	8	5	11	8	4	109.568941	109.569000	− 59
42	12	10	2	11	10	1	109.620838	109.620850	− 12
43	12	10	3	11	10	2	109.620838	109.620850	− 12
44	13	1	12	12	1	11	120.963585	120.963590	− 5
45	13	1	13	12	0	12	133.544233	133.544230	3
46	13	2	11	12	2	10	119.838290	119.838320	− 30

Table 1 (continued)

No.	J	K_-	K_+	J'	K'_-	K'_+	Fre. (Calc.)	Fre. (Exp.)	ΔF/kHz
47	14	0	14	13	1	13	109.229599	109.229650	− 51
48	14	1	14	13	0	13	140.674733	140.674740	− 7
49	15	1	14	14	1	13	139.362840	139.362800	40
50	15	1	15	14	0	14	147.835759	147.835680	79
51	15	2	14	14	2	13	136.378850	136.378740	110
52	15	3	12	14	3	11	137.219526	137.219570	− 44
53	15	3	13	14	3	12	137.041635	137.041680	− 45
54	15	4	11	14	4	10	136.995462	136.995480	− 18
55	15	4	12	14	4	11	136.990498	136.990560	− 62
56	15	5	10	14	5	9	136.947436	136.947440	− 4
57	15	5	11	14	5	10	136.947366	136.947440	− 74
58	15	6	9	14	6	8	136.936657	136.936720	− 63
59	15	6	10	14	6	9	136.936656	136.936720	− 64
60	15	7	8	14	7	7	136.943744	136.943800	− 26
61	15	7	9	14	7	8	136.943744	136.943800	− 26
62	15	8	7	14	8	6	136.962109	136.962090	19
63	15	8	8	14	8	7	136.962109	136.962090	19
64	15	9	6	14	9	5	136.988592	136.988600	− 8
65	15	9	7	14	9	6	136.988592	136.988600	− 8
66	15	10	5	14	10	4	136.021634	137.021660	− 26
67	15	10	6	14	10	5	136.021634	137.021660	− 26
68	15	11	4	14	11	3	136.060335	137.060360	− 25
69	15	11	5	14	11	4	136.060335	137.060360	− 25
70	15	12	3	14	12	2	136.104150	137.104160	− 10
71	15	12	4	14	12	3	136.104150	137.104160	− 10
72	15	13	2	14	13	1	136.152724	137.152710	14
73	15	13	3	14	13	2	136.152724	137.152710	14
74	16	2	15	15	2	14	145.403987	145.404040	− 53
75	16	4	12	15	4	11	146.149360	146.149280	80
76	16	4	13	15	4	12	146.141523	146.141460	63
77	16	9	7	15	9	6	146.120268	146.120230	38
78	16	9	8	15	9	7	146.120268	146.120230	38
79	16	10	6	15	10	5	146.154606	146.154590	16
80	16	10	7	15	10	6	146.154606	146.154590	16
81	17	0	17	16	1	16	140.065389	140.065420	− 31
82	18	2	17	18	1	18	134.984228	134.984200	28
83	18	3	15	18	2	16	147.898967	147.898960	7
84	19	2	18	19	1	19	139.354169	139.354130	33
85	19	3	16	19	2	17	145.715433	145.715400	33
86	20	1	19	20	0	20	96.599443	96.599450	− 7
87	20	3	17	20	2	18	143.399422	143.399430	− 8
88	21	1	20	21	0	21	104.971989	103.971980	9
89	21	3	18	21	2	19	140.988446	140.988500	− 54
90	22	3	19	22	2	20	138.325778	138.525840	− 62
91	22	6	17	23	5	18	141.000708	141.000720	− 12
92	23	3	20	23	2	21	136.059328	136.059271	57
93	24	3	21	24	2	22	133.640406	133.640370	36
94	25	1	24	25	0	25	136.292433	136.292450	− 17
95	25	2	23	24	3	22	106.958672	106.958640	32
96	26	1	25	26	0	26	144.863448	144.863440	8
97	27	2	25	26	3	24	134.315297	134.315240	57
98	27	2	25	27	1	26	102.020741	102.020660	81
99	28	2	26	28	1	27	107.926533	106.926550	− 17
100	30	2	28	30	2	29	96.359220	96.359270	− 50
101	30	3	27	30	2	28	123.107290	123.107290	0
102	31	3	28	31	2	29	122.482972	122.482920	52
103	32	3	29	32	2	30	122.297179	122.297200	− 21
104	33	2	31	33	1	32	139.072949	139.072840	109
105	33	3	30	33	2	31	122.584293	122.584360	− 67
106	34	2	32	34	1	33	146.862649	146.862740	− 91
107	34	3	31	34	2	32	123.374586	123.374570	16
108	39	3	36	39	2	37	135.653598	135.653600	− 2
109	40	3	37	40	2	38	139.872972	139.872980	− 8
110	40	4	36	39	5	35	102.745460	102.745700	− 240
111	41	3	38	41	2	39	144.691166	144.691160	6
112	41	4	37	40	5	36	115.455264	115.455060	204
113	49	5	44	48	6	43	118.567510	118.567510	0

Calculated frequencies are based on the constants of Table 2.

Table 2. Rotational and centrifugal distortion constants of fluoroacetonitrile in the ground state (standard deviations are given in parentheses in units of the last digit).

Typke, van Eijck			Watson's s-red.		
A'	36578.6697(98)	Mhz	$A^{(s)}$	36578.6695(98)	MHz
B'	4781.28470(90)	MHz	$B^{(s)}$	4781.28483(90)	MHz
C'	4339.72461(91)	MHz	$C^{(s)}$	4339.72474(91)	MHz
D'_J	2.7828(17)	kHz	D'_J	2.7828(17)	kHz
D'_{JK}	− 69.327(22)	kHz	D'_{JK}	− 69.327(22)	kHz
D'_K	1228.7(12)	kHz	D'_K	1228.7(12)	kHz
δ_J	0.58268(41)	kHz	d_1	− 0.58268(41)	kHz
R'_6	− 0.03214(22)	kHz	d_2	− 0.03214(22)	kHz
H'_J	0.0167(12)	Hz	H'_J	0.0168(12)	Hz
H'_{JK}	− 0.267(27)	Hz	H'_{JK}	− 0.267(27)	Hz
H'_{KJ}	− 3.10(10)	Hz	H'_{KJ}	− 3.10(10)	Hz
H'_K	542(22)	Hz	H'_K	542(22)	Hz
H'_5	0.00334(25)	Hz	h_1	0.00363(39)	Hz
H'_6	0.0015(11)	Hz	h_2	0.00037(28)	Hz
H'_{10}	0.00077(64)	Hz	h_3	0.000096(80)	Hz
Standard deviations of the fits:					
	57 kHz			57 kHz	

Table 3. Determinable constants of Watson. $\mathscr{M} = \mathscr{A} + \mathscr{B} + \mathscr{C}$.

$\mathscr{A}$	36578.6749(98)	MHz
$\mathscr{B}$	4781.21978(91)	MHz
$\mathscr{C}$	4339.66202(92)	MHz
τ_{aaaa}	− 4648.8(46)	kHz
τ_{bbbb}	− 16.1(46)	kHz
τ_{cccc}	− 6.7269(82)	kHz
τ_1	244.69(10)	kHz
$\tau_2/\mathscr{M}$	17.182(14)	kHz
Φ_{aaa}	539(22)	Hz
Φ_{bbb}	0.0250(11)	Hz
Φ_{ccc}	0.0100(23)	Hz
Φ_1	− 11.48(49)	Hz
$\Phi_2 + \Phi_3/\mathscr{M}$	− 0.0332(23)	Hz
$\Phi_2 - \Phi_3/\mathscr{M}$	− 0.0084(11)	Hz
$\Phi_4/\mathscr{M}$	− 64.91(16)	Hz

The computer programm ZFAP6.FOR (author: Typke) was used for the fitting. The resulting rotational and centrifugal distortion constants are shown in Table 2. The "determinable constants" of Watson [6], calculated from the constants of Table 2, are shown in Table 3. Table 4 gives the correlation matrices of the fits. The correlation between the A' rotational constant and the D'_K centrifugal distortion constant amounts to 0.753. All correlations are smaller than 0.99 except the correlation between the D'_K and the H'_K centrifugal distortion constants, which amounts to 0.992.

Table 4. Correlation matrices.

Typke and van Eijck

A'	1.000																							
B'	0.482	1.000																						
C'	0.517	0.850	1.000																					
D'_J	0.639	0.815	0.881	1.000																				
D'_{JK}	0.416	0.564	0.602	0.574	1.000																			
D'_K	0.753	0.162	0.204	0.466	− 0.057	1.000																		
δ_J	− 0.037	0.320	− 0.191	− 0.045	− 0.035	− 0.036	1.000																	
R'_6	− 0.098	0.399	0.018	0.092	− 0.125	− 0.145	0.829	1.000																
H'_J	0.542	0.261	0.486	0.605	0.656	0.475	− 0.414	− 0.569	1.000															
H'_{JK}	0.433	0.292	0.386	0.489	0.800	0.288	− 0.124	− 0.367	0.902	1.000														
H'_{KJ}	0.248	0.492	0.476	0.425	0.797	− 0.295	0.043	0.111	0.233	0.353	1.000													
H'_K	0.714	0.139	0.188	0.447	− 0.055	0.992	− 0.052	− 0.182	0.505	0.320	− 0.326	1.000												
H'_5	0.126	0.233	− 0.193	− 0.005	0.125	0.169	0.876	0.551	− 0.057	0.232	− 0.010	0.173	1.000											
H'_6	0.084	− 0.412	− 0.039	− 0.120	0.056	0.121	− 0.847	− 0.977	0.503	0.257	− 0.121	0.152	− 0.610	1.000										
H'_{10}	− 0.211	0.356	0.067	0.067	− 0.162	− 0.267	0.665	0.912	− 0.655	− 0.465	0.134	− 0.305	0.297	− 0.923	1.000									

Watsons's s-reduction																							
$A^{(s)}$	1.000																						
$B^{(s)}$	0.483	1.000																					
$C^{(s)}$	0.517	0.850	1.000																				
D_J'	0.639	0.815	0.881	1.000																			
D_{JK}'	0.416	0.564	0.602	0.574	1.000																		
D_K'	0.753	0.162	0.204	0.467	− 0.057	1.000																	
d_1'	0.038	− 0.319	0.191	0.045	0.035	0.037	1.000																
d_2'	− 0.098	0.398	0.017	0.092	− 0.125	− 0.145	− 0.831	1.000															
H_J'	0.543	0.262	0.487	0.606	0.656	0.476	0.415	− 0.568	1.000														
H_{JK}'	0.434	0.293	0.386	0.489	0.800	0.288	0.126	− 0.367	0.903	1.000													
H_{KJ}'	0.248	0.492	0.475	0.425	0.797	− 0.295	− 0.044	0.111	0.233	0.353	1.000												
H_K'	0.714	0.139	0.189	0.448	− 0.055	0.992	0.053	− 0.182	0.506	0.320	− 0.326	1.000											
h_1'	− 0.051	0.364	− 0.080	0.037	− 0.022	− 0.059	− 0.958	0.906	− 0.438	− 0.141	0.076	− 0.080	1.000										
h_2'	0.084	− 0.411	− 0.038	− 0.119	0.057	0.122	0.848	− 0.977	0.503	0.258	− 0.122	0.153	− 0.950	1.000									
h_3'	− 0.211	0.355	0.066	0.066	− 0.162	− 0.267	− 0.667	0.912	− 0.654	− 0.465	0.135	− 0.305	0.802	− 0.924	1.000								

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