Microwave and Millimeterwave Spectrum of Monofluoracetonitrile-^{15}N ($CH_2FC^{15}N$). A Contribution to Molecular Structure

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The microwave and millimeterwave spectrum of ^{15}N-fluoracetonitrile ($CH_2FC^{15}N$) in the ground vibrational state are investigated in the region between 8 and 150 GHz. The measured transitions are fitted to a Hamiltonian with three rotational constants, five quartic and seven sextic centrifugal distortion constants in the symmetric top limit of van Eijck-Typke and in the s-reduction of Watson. The rotational constants are used to improve the calculated r_0-structure of the fluoracetonitrile molecule.

Introduction

The microwave spectra of the fluoracetonitrile isotopomers CH_2FCN, CHDFCN and CD_2FCN have been investigated by Kasten, Dreizler, Job and J. Sheridan [1]. These authors considered low J lines in the frequency range up to 30 GHz only. A further investigation in the millimeter range has been performed in this laboratory [2] to get detailed informations about quartic and sextic centrifugal distortion terms. In the present work, following similar criteria as in [2], the millimeterwave and microwave spectrum of $CH_2FC^{15}N$ has been investigated and 123 lines have been measured and assigned. These lines have been fitted using both the Hamiltonian of van Eijck-Typke and of Watson's symmetric top reduction. Rotational constants as well as quartic and sextic centrifugal distortion constants have been determined. In reference [1] a first approach to a r_0-structure had been made taking in account all rotational constants available. Additional data from the present investigation have been used with the purpose of improving the structure parameters and to give better initial constants for the calculation of the spectra of two other isotopomers with ^{13}C which are being investigated.

Experimental

The ^{15}N-fluoracetonitrile was prepared by dehydration of ^{15}N-fluoracetamide with phosphorpentoxide [3]. The ^{15}N-fluoracetamide is easily prepared from ^{15}N-ammonia and ethylfluoracetate [4]. Most of the lines were measured using source modulation. A 16.7 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 33.4 kHz and phase detected. The frequency sweep was provided by an externally controlled ramp voltage which drives the frequency decade Schomandl ND 800. The frequencies were stabilized by a Schomandl FDS 30 synchronizer. For these measurements the absorption cell was a glass cell with an inner diameter of 10 cm and a length of 150 cm.

The transitions were assigned on the basis of an 'a priori' calculation and lines pattern comparison with the normal isotopomer. In some special cases the assignment has been made using Stark modulation or microwave-millimeterwave double resonance technique (MW-MMW-DR) [5]. For the measurements with Stark modulation and MW-MMW-DR technique a conventional Stark waveguide cell was used. The microwave and millimeterwave frequencies were produced by different OKAYA klystrons either directly or by harmonic multiplication of the fundamental frequency.

All frequency measurements have been carried out using as standard frequency a 5 MHz signal derived from the 77.5 kHz signal of the broadcasting station DCF 77 (Mainflingen, Germany) with a relative accuracy of $5 \cdot 10^{-13}$.

The measurements of the lines are believed to be better than $1 \cdot 10^{-7}$.

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Table 1. Some of the 123 measured lines compared with calculated values. Frequencies are given in GHz.

J	KP	KO	J'	KP'	KO'	NUE(calc.)	NUE(exp.)	Calc. − exp. [kHz]
1	0	1	0	0	0	8.836292	8.836334	−42
2	1	2	1	1	1	17.256002	17.255970	32
2	1	1	1	1	0	18.089579	18.089530	49
3	0	3	2	0	2	26.492353	26.492370	−17
3	1	2	3	0	3	33.273787	33.273680	107
4	2	2	3	1	3	132.736607	132.736610	−3
7	0	7	6	1	6	33.767773	33.767740	33
8	0	8	7	0	7	70.346856	70.346830	26
12	5	8	11	5	7	106.114810	106.114830	−20
12	5	7	11	5	6	106.114817	106.114830	−13
15	2	14	14	2	13	132.154579	132.154630	−51
15	12	4	14	12	3	132.823486	132.823420	66
15	1	14	15	0	15	63.503785	63.503910	−125
16	2	14	15	2	13	143.314363	143.314470	−107
16	2	15	15	2	14	140.904996	140.905170	−174
16	7	9	15	7	8	141.511536	141.511620	−84
16	11	5	15	11	4	141.630362	141.630370	−8
17	1	17	16	1	16	145.951651	145.951600	51
17	0	17	16	0	16	147.354523	147.354320	203
17	1	16	17	0	17	73.843365	73.843250	115

Standard deviation of 123 lines: 116 kHz.

Table 2. Rotational and centrifugal distortion constants. Errors, given in parenthesis in units of the last digit, are standard errors as obtained from the least squares fitting procedure. Constant values and errors have been given up to the last digit as obtained from the computing program to allow the integral reproduction of the measured frequencies.

Watson's s-reduction			van Eijck-Typke		
$A^{(s)}$	36417.7379(1040)	MHz	A'	36417.7378(1040)	MHz
$B^{(s)}$	4626.55348(440)	MHz	B'	4626.55361(438)	MHz
$C^{(s)}$	4209.74848(401)	MHz	C'	4209.74861(405)	MHz
D'_J	2.6129(204)	kHz	D'_J	2.6132(204)	kHz
D'_{JK}	−67.4374(578)	kHz	D'_{JK}	−67.4380(578)	kHz
D'_K	−5.282(109)	MHz	D'_K	−5.2823(109)	MHz
d_1	−0.5158(163)	kHz	δ_J	0.5153(162)	kHz
d_2	0.0334(326)	kHz	R'_6	0.0334(326)	kHz
H'_J	−0.1060(409)	Hz	H'_J	−0.1066(409)	Hz
H'_{JK}	0.744(1190)	Hz	H'_{JK}	0.748(1190)	Hz
H'_{KJ}	−5.857(3760)	Hz	H'_{KJ}	−5.859(3760)	Hz
H'_K	−19.6(217)	kHz	H'_K	−19.6(217)	kHz
h_1	−0.067(36)	Hz	H'_5	−0.161(45)	Hz
h_2	−0.061(89)	Hz	H'_6	−0.244(357)	Hz
h_3	0.032(11)	Hz	H'_{10}	0.253(85)	Hz

Table 3a. Correlations between the constants calculated according to van Eijck-Typke.

A'	1.000														
B'	−0.110	1.000													
C'	−0.132	−0.077	1.000												
D'_J	−0.221	0.648	0.529	1.000											
D'_{JK}	−0.184	0.023	0.114	−0.272	1.000										
D'_K	0.891	−0.110	−0.169	−0.251	−0.237	1.000									
δ_J	0.087	0.683	−0.667	0.124	−0.114	0.054	1.000								
R'_6	0.068	−0.136	0.261	−0.015	0.053	0.103	−0.492	1.000							
H'_J	−0.163	0.594	0.431	0.973	−0.402	−0.188	0.170	−0.032	1.000						
H'_{JK}	−0.832	0.120	0.183	0.234	0.323	−0.986	−0.051	−0.100	0.157	1.000					
H'_{KJ}	0.836	−0.121	−0.174	−0.267	−0.227	0.990	0.039	0.108	−0.202	−0.995	1.000				
H'_K	0.836	−0.121	−0.171	−0.258	−0.243	0.991	0.037	0.102	−0.196	−0.995	0.998	1.000			
H'_5	0.048	0.503	−0.424	0.141	−0.090	0.005	0.691	−0.157	0.183	−0.003	−0.009	−0.013	1.000		
H'_6	−0.058	0.132	−0.264	0.007	−0.051	−0.091	0.490	−0.993	0.025	0.088	−0.096	−0.091	0.171	1.000	
H'_{10}	0.050	0.023	−0.104	−0.042	−0.019	0.055	0.146	−0.316	−0.040	−0.054	0.054	0.056	−0.600	0.303	1.000

Table 3b. Correlations between the constants calculated according to Watson's s-reduction.

$A^{(s)}$	1.000														
$B^{(s)}$	−0.112	1.000													
$C^{(s)}$	−0.134	−0.080	1.000												
D'_J	−0.222	0.648	0.530	1.000											
D'_{JK}	−0.183	0.019	0.117	−0.273	1.000										
D'_K	0.891	−0.113	−0.174	−0.252	−0.236	1.000									
d_1	−0.087	−0.694	0.657	−0.132	0.122	−0.055	1.000								
d_2	0.070	−0.165	0.231	−0.033	0.069	0.103	0.494	1.000							
H'_J	−0.163	0.592	0.435	0.973	−0.403	−0.188	−0.170	−0.033	1.000						
H'_{JK}	−0.832	0.123	0.188	0.236	0.321	−0.986	0.052	−0.100	0.156	1.000					
H'_{KJ}	0.836	−0.123	−0.179	−0.268	−0.225	0.990	−0.039	0.108	−0.201	−0.995	1.000				
H'_K	0.836	−0.124	−0.176	−0.260	−0.242	0.991	−0.037	0.102	−0.195	−0.995	0.998	1.000			
h_1	0.103	0.655	−0.606	0.146	−0.135	0.054	−0.984	−0.471	0.192	−0.051	0.037	0.034	1.000		
h_2	−0.060	0.161	−0.234	0.024	−0.067	−0.092	−0.493	−0.993	0.026	0.088	−0.096	−0.091	0.477	1.000	
h_3	0.049	0.032	−0.095	−0.036	−0.024	0.054	−0.156	−0.316	−0.035	−0.054	0.054	0.056	0.134	0.301	1.000

Table 4. Watson's determinable parameters obtained from both sets of centrifugal distortion constants. Errors, given in parenthesis in units of the last digit, are derived from standard errors of the least squares fitting procedure as in Table 2.

	Watson's s-reduction	van Eijck-Typke	
A	36417.7434(1040)	36417.7434(1040)	MHz
B	4626.49037(438)	4626.49037(438)	MHz
C	4209.68743(405)	4209.68743(407)	MHz
τ_{AAAA}	21.390(438)	21.390(436)	MHz
τ_{BBBB}	−14.311(360)	−14.308(355)	kHz
τ_{CCCC}	−6.058(238)	−6.063(239)	kHz
τ_1	237.59(84)	237.59(83)	kHz
$\tau_2/(A+B+C)$	15.259(634)	15.258(633)	Hz
Φ_{AAA}	−19.63(2168)	−19.61(2170)	Hz
Φ_{BBB}	−0.299(236)	−0.137(234)	Hz
Φ_{CCC}	−0.159(156)	−0.320(176)	Hz
Φ_1	−11.47(306)	−11.47(387)	Hz
$\Phi_2+\Phi_3/(A+B+C)$	−0.215(633)	−0.212(544)	Hz
$\Phi_2-\Phi_3/(A+B+C)$	0.766(224)	0.652(544)	Hz
$\Phi_4/(A+B+C)$	−1.252(52)	−1.252(51)	kHz

Results

Table 1 gives only a small part of the lines measured. A complete list of lines can be obtained from the author or the Central Library of the University of Kiel under the number TNA 10. The frequencies have been fitted to the symmetric top limit Hamiltonian of van Eijck [6] and Typke [7]

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

and to the Watson's s-reduced Hamiltonian [8]

$$\begin{aligned} H^{(s)} = {} & \tfrac{1}{2}(B_x^{(s)} - B_y^{(s)}) P^2 + [B_z^{(s)} - (B_x^{(s)} + B_y^{(s)})/2] P_x^2 \\ & + \tfrac{1}{4}(B_x^{(s)} - B_y^{(s)}) (P_+^2 + P_-^2) - D'_J (P^2)^2 \\ & - D'_{JK} P^2 P_z^2 - D'_K P_z^4 - d_1 P^2 (P_+^2 + P_-^2) \\ & + d_2 (P_+^4 + P_-^4) + H'_J (P^2)^3 + H'_{JK} (P^2)^2 P_z^2 \\ & + H'_{KJ} P^2 P_z^4 + H'_K P_z^6 + h_1 (P^2)^2 (P_+^2 + P_-^2) \\ & + h_2 P^2 (P_+^2 + P_-^2) + h_3 (P_+^6 + P_-^6) ; \end{aligned}$$

$(P_\pm = P_x \pm i P_y)$.

To fit the rotational and centrifugal distortion constants the computer program ZFAP6 (author: Typke) has been used. The resulting parameters are listed in Table 2. The corresponding correlation matrices are listed in Table 3a and 3b. For comparison, Watson's determinable parameters were calculated from both sets of constants [9] (see Table 4).

Fitting of the Structure

A preliminary r_0 structure of CH_2FCN has already been given in [1], where several parameters were fixed to literature values. With the three rotational constants of $CH_2FC^{15}N$ we should be able to give a r_0-structure using a smaller number of fixed structural parameters. For the fit the rotational constants of $CH_2FC^{14}N$, CHDFCN, CD_2FCN and $CH_2FC^{15}N$ have been used. The rotational constants of the double hydrogen substituted isotopomer, CD_2FCN, really give no further informations on the coordinates of the hydrogen atom, nevertheless they have been used as additional secondary information. It was not possible to fit more than five structure parameters with these twelve constants, so that r(C−N) [10−13] and r(C−C) [10, 12−14] or r (C−F) [15−17] were assumed

Table 5. Partial r_0-structure of CH_2FCN calculated from twelve rotational constants. Assumptions in brackets. a) r(C−C) and r(C−N) have been held fixed as in [1]. b) r(C−C) and r(C−F) have been held fixed, taking in account that substitution of H and N gives informations on the coordinates of these nuclei. c) r(C−N) and r(C−F) have been held fixed. The last three angles are derived from the fitted values. Errors given in units of the last digit are obtained from the least squares fitting procedure or are deviations from the mean value of the parameters assumed from related compounds.

	a)	b)	c)
r(C−N)	(1.158(1) A)*	1.15(9) A	(1.158(1) A)*
r(C−C)	(1.460(1) A)**	(1.460(1) A)**	1.45(8) A
r(C−H)	1.09(25) A	1.08(23) A	1.09(26) A
r(C−F)	1.38(6) A	(1.381(7)A)***	(1.381(7) A)***
∢ HCC	110.8(6)°	109.2(7)°	110.6(6)°
∢ FCC	111.2(0)°	111.3(0)°	111.3(0)°
∢ CCN	(180°)	(180°)	(180°)
∢ CCF/CCH	121.3(2)°	121.6(2)°	121.3(2)°
∢ CCH/CCH	117.3°	116.7°	117.3°
∢ HCH	106.0°	107.1°	106.2°
∢ CN, a	19.6°	19.8°	19.8°

* Average value from CH_3CN [10], $(CH_3)_3CCN$ [11], CCl_3CN [12] and NC−CH_2−CN [13].
** Average value from CH_3CN [10], CCl_3CN [12], NC−CH_2−CN [13], and CF_3CN [14].
*** Average value from CH_3F [15], CH_2BrF [16], CH_2ClF [17].

from known geometries of related molecular structures. The CCN group was supposed to be linear. For comparison a fit with six or more free parameters has been carried out. The correlation values between the constants were then extremely high and the resulting atomic distances and angles were very different from the values of comparable molecules. Therefore only five structure parameters have been fitted and the result is listed in Table 5. The spectrum of two ^{13}C isotopomers is now under investigation in order to give a better r_0-structure.

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