The Microwave Spectrum of ^{15}N-Difluoroacetonitrile: Electric Dipole Moment and Partial r_0-Structure

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The rotational spectrum of ^{15}N-difluoroacetonitrile has been investigated in the frequency range from 8 to 18 GHz. From the measured lines with J up to 20, rotational constants and quartic centrifugal distortion constants have been determined. For some lines the Stark effect has been examined, yielding the components of the electric dipole moment along the a- and c-principal axes of inertia. The obtained rotational constants were also used together with the rotational constants of the normal isotopomer to derive a partial r_0-structure of the molecule.

Introduction

Some years ago we started a program for determining the structure and other molecular properties of fluorine derivatives of acetonitrile (CH_3CN) from the analysis of rotational spectra in the microwave range. For monofluoroacetonitrile (CH_2FCN) all possible monosubstituted isotopomers have been investigated [1–4] and the r_s-structure of the H_2CCN moiety as well as the r_0-structure of the entire molecule could be determined [4]. Furthermore, investigations of ^{14}N-quadrupole coupling [5] and the rotational Zeeman effect [6] have been performed.

The normal isotopomer of difluoroacetonitrile (CHF_2CN) has been investigated previously with studies of the ^{14}N-quadrupole hyperfine structure [1] and the rotational Zeeman effect [7]. In continuation of the project to determine the molecular structure, we give here the results of investigations on $CHF_2C^{15}N$ as a first step to the complete substitution of all possible isotopes. The electric dipole moment has also been determined from the study of Stark splittings of some lines. The analysis was particularly simple because of the lack of nitrogen quadrupole hyperfine structure.

Experimental

A conventional 100 kHz modulated Stark spectrometer with a four meter long brass cell (inner diameter 1.0 × 4.7 cm) has been used for the experiments. The microwave source oscillator was phase stabilized with reference to a frequency synthesizer which was continously monitored with the 77.5 kHz standard frequency of DCF 77 (Mainflingen, Germany). We believe that our measurements are at least as accurate as five parts in 10^7.

Difluoroacetonitrile has been prepared adding ^{15}N-ammonia in excess to ethyldifluoroacetate (Ventron, Karlsruhe) at −60 °C. Ammonia has then been removed by vacuum distillation, and the remaining amide was dehydrated with P_2O_5/SiO_2 in vacuum. The resulting difluoroacetonitrile was trapped at liquid nitrogen temperature.

Spectrum

The rotational spectrum of ^{15}N-difluoroacetonitrile was recorded in the range from 8 to 18 GHz at temperatures of about −40° to −50° C and pressures of a few mTorr. The observed lines were rather strong and could be easily identified with observation of the Stark satellite patterns and a prediction of the rigid rotor spectrum. The observed centrifugal distortion was corrected for by a first order treatment of quartic centrifugal distortion terms according to Watson's S-reduction [8] (program ZFAP4, author: V. Typke). The measured and calculated frequencies are listed in Table 1 together with the standard deviation as given by the least squares fit procedure.

The resulting molecular constants are given in Table 2 together with the corresponding correlation matrix for the fit parameters. The centrifugal distortion parameters D_J and D_K have been set equal to zero

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Table 1. Experimental and calculated line frequencies (in MHz) of ^{15}N-difluoroacetonitrile. The calculated frequencies were obtained with the constants from Table 2. $\Delta\nu = \nu_{\text{calc}} - \nu_{\text{exp}}$. The measurement error is estimated to be ± 5 kHz.

$J'_{\text{p}'\text{o}'}$	J_{po}	ν_{exp} [MHz]	ν_{calc} [MHz]	$\Delta\nu$ [kHz]
1_{10}	0_{00}	13 929.288	13 929.222	−66
2_{02}	1_{01}	13 780.959	13 780.940	−19
2_{11}	1_{10}	14 833.781	14 833.815	34
2_{12}	1_{11}	12 934.723	12 934.783	60
3_{03}	2_{11}	12 380.863	12 380.835	−28
3_{22}	3_{12}	16 756.347	16 756.399	52
4_{13}	4_{14}	9 446.087	9 445.764	−323
4_{23}	4_{13}	15 005.808	15 005.845	37
5_{14}	5_{15}	14 047.831	14 047.901	70
5_{24}	5_{14}	12 931.929	12 932.042	113
6_{25}	6_{15}	10 649.095	10 649.129	34
7_{25}	7_{26}	9 737.981	9 737.923	−58
8_{26}	8_{27}	14 446.230	14 446.271	41
10_{37}	10_{38}	8 619.418	8 619.331	−87
10_{38}	10_{28}	16 050.567	16 050.559	−8
11_{38}	11_{39}	13 134.397	13 134.460	63
11_{39}	11_{29}	12 622.034	12 622.033	−1
$12_{3\,10}$	$12_{2\,10}$	9 450.540	9 450.491	−49
$14_{4\,10}$	$14_{4\,11}$	10 893.322	10 893.403	81
$15_{4\,11}$	$15_{4\,12}$	16 077.479	16 077.462	−17
$15_{4\,12}$	$15_{3\,12}$	17 073.526	17 073.484	−42
$16_{4\,13}$	$16_{3\,13}$	12 960.403	12 960.304	−99
$17_{5\,12}$	$17_{5\,13}$	8 389.366	8 389.382	16
$17_{4\,14}$	$17_{3\,14}$	9 397.572	9.397.569	−3
$18_{6\,13}$	$18_{5\,14}$	12 883.958	12 883.929	−29
$20_{5\,16}$	$20_{4\,16}$	16 665.099	16 665.170	71

rms error of least squares fit procedure: 93 kHz.

Table 2. Rotational and quartic centrifugal distortion constants of ^{15}N-difluoroacetonitrile as obtained with a least squares fitting procedure from the experimental data in Table 1. The standard deviations are given in parentheses in units of the least significant figure. The principal moments of inertia, Ray's asymmetry parameter $\varkappa$, and the correlation coefficients for the fit parameters are also given.

	CHF$_2$C^{15}N		CHF$_2$CN *
A	9 983.403(22) MHz	A	9 985.938(51) MHz
B	3 945.852(10) MHz	B	4 095.116(30) MHz
C	2 996.329(10) MHz	C	3 081.427(34) MHz
D_J	0		
D_{JK}	15.928(226) kHz		
D_K	0		
d_1	−0.208(20) kHz		
d_2	−0.159(8) kHz		
I_a	50.6116(1) a.m.u.A^2		
I_b	128.0778(3) a.m.u.A^2		
I_c	168.6651(6) a.m.u.A^2		
$\varkappa$	−0.7282		

Correlation Matrix

A	1.000					
B	0.669	1.000				
C	0.426	0.936	1.000			
D_{JK}	0.637	0.219	−0.045	1.000		
d_1	0.543	0.202	−0.048	0.978	1.000	
d_2	0.461	0.169	−0.040	0.935	0.982	1.000

* Rotational constants of the normal isotopomer CHF$_2$CN as determined in [1].

because of their large standard deviations (>100%) when they were included in the fit. As a result of this choice the rms error of the fit became significantly smaller.

Electric Dipole Moment

The measurements of Stark splittings for the determination of the dipole moment have been carried out on several lines for different values of the M-quantum number and at various Stark voltages. Table 3 gives the measured and calculated Stark shifts for the investigated rotational lines. The rectangular Stark cell was calibrated by measuring Stark shifts of the $J=0$–1 rotational transition of OCS and using a value of 0.71519(1) D for the dipole moment [9], yielding a value of 0.466 ± 0.001 cm for the distance between the Stark septum and the cell wall.

Table 3. Frequency list of experimental and calculated shifts for Stark satellites of ^{15}N-difluoroacetonitrile.

J_{po}	$J'_{\text{p}'\text{o}'}$	M	U_{St} [V]	**1** [MHz]	**2** [MHz]	**3** [kHz]	**4** [MHz]
0_{00}	1_{10}	0	200	9.507	9.530	−23	13 938.795
1_{01}	2_{02}	0	350	−2.801	−2.803	2	13 778.158
		1	200	7.225	7.171	55	13 788.184
4_{13}	4_{23}	2	300	−6.698	−6.732	34	14 999.110
		3	300	−12.769	−12.752	−18	14 993.039
6_{15}	6_{25}	3	250	2.632	2.570	63	10 651.727
		4	250	4.399	4.443	−44	10 653.494
		5	250	6.831	6.852	−21	10 655.926
		6	250	9.841	9.797	44	10 658.936
7_{16}	7_{26}	3	250	3.304	3.263	41	8 321.979
		4	250	5.814	5.792	22	8 324.489
		5	250	9.070	9.043	27	8 327.745
		6	250	12.986	13.017	−30	8 331.661
		7	250	17.683	17.713	−30	8 336.358

1 Experimental displacement of the satellite.
2 Calculated displacement of the satellite.
3 Difference between experimental and calculated displacement.
4 Microwave frequency of the satellite.

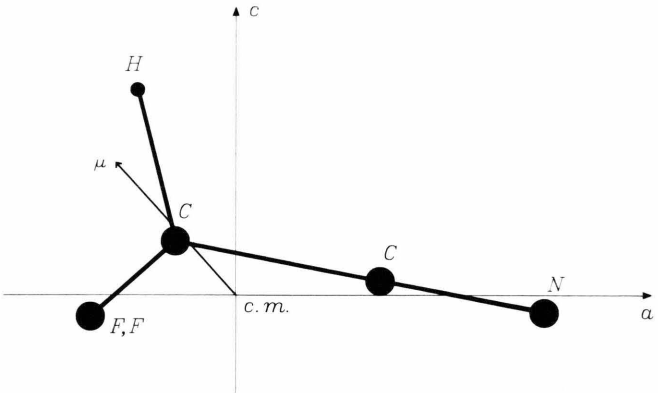

Fig. 1. ^{15}N-difluoroacetonitrile in its principal axis system as obtained from data of this work, with most probable orientation of the dipole moment $\boldsymbol{\mu}$.

Table 4. Electric dipole moment components and total dipole moment of ^{15}N-difluoroacetonitrile. The list of dipole moments of acetonitrile and its fluorine derivatives shows a decrease of the dipole moment with the number of fluorine atoms.

	Molecule	μ [D]	Literatur
$\mu_a = 1.634(2)$ D	CH_3CN	3.925	[17]
$\mu_c = 1.836(1)$ D	CH_2FCN	3.43	[18]
$\mu = 2.458(2)$ D	CHF_2CN	2.458	this work
	CF_3CN	1.262	[19]

The obtained (absolute) values for the dipole moment and its components along the *a*- and *c*-principal axes of inertia are given in Table 4. For comparison the dipole moments of acetonitrile and its fluorinated derivatives are also given in the Table.

The direction of the dipole moment can not be determined by Stark effect measurements due to the quadratic dependence of the frequency shifts on the dipole moment components. Considering the polarities of the bonds, the dipole vector should point along the positive *c*-axis ($\mu_c > 0$), but the sign of μ_a is not directly obvious, corresponding to two possible orientations (1st and 2nd quadrant in Figure 1). In order to obtain more information about its direction, one may simply assume that the total dipole moment is composed additively from contributions of partial moments of molecular subunits. With a proper choice of molecules with known dipole moments and identical subunits one may then derive a value for the dipole moment provided that the values of the partial moments are not influenced by the rest of the molecule.

For F$_2$HCCN the molecules F$_2$HCH and HCN have been chosen since the total dipole moments (and their directions) are well known to be $\mu(CH_2F_2) = 1.96$ D [13] and $\mu(HCN) = 2.968$ D [14]. Assuming that the total dipole moment for both molecules results from vector addition of contributions from partial moments of the CH-group and the rest group, we have

$$\boldsymbol{\mu}(F_2HCH) = \boldsymbol{\mu}(F_2HC) + \boldsymbol{\mu}(CH);$$
$$\boldsymbol{\mu}(HCN) \quad = \boldsymbol{\mu}(HC) + \boldsymbol{\mu}(CN).$$

For difluoroacetonitrile we may write accordingly

$$\boldsymbol{\mu}(F_2HCCN) = \boldsymbol{\mu}(F_2HC) + \boldsymbol{\mu}(CN),$$

which gives

$$\boldsymbol{\mu}(F_2HCCN) = \boldsymbol{\mu}(F_2HCH) - \boldsymbol{\mu}(CH) + \boldsymbol{\mu}(HCN) - \boldsymbol{\mu}(HC).$$

With the assumption of a tetrahedral structure of the F$_2$HC-group and that $-\boldsymbol{\mu}(CH) = \boldsymbol{\mu}(HC)$, one gets for the component of $\boldsymbol{\mu}(CHF_2CN)$ along the CCN-bond direction a value of $\mu_{\|} = -1.85$ D, and $\mu_{\perp} = 1.60$ D for the component perpendicular to it. This corresponds to the orientation shown in Figure 1.

The total dipole moment then takes the value of $\mu = 2.45$ D, and the components $\mu_a = -1.50$ D and $\mu_c = 1.93$ D along the principal axes of inertia if one refers to the molecular structure discussed in the next section. These values are surprisingly near to the experimental values (see Table 4) which might be considered a fortunate coincidence.

Information about the dipole moment has also been obtained by semiempirical quantum chemical CNDO calculations which give $\mu_a = -0.69$ D and $\mu_c = 1.80$ D for the dipole moment components. Although the agreement with the experimental results is rather poor, this result may be seen to confirm the previous consideration about the orientation of the dipole moment.

Molecular Structure

The rotational constants of the normal isotopomer CHF$_2$CN have been determined elsewhere [1], and together with the new constants (see Table 2) there are now six pieces of information which can be used for the determination of a partial r_0-structure. Because of the C$_s$-symmetry of the molecule, a total of eight parameters (bond distances r_{CN}, r_{CC}, r_{CH}, r_{CF}; bond angles ∢CCN, ∢CCH, ∢CCF; dihedral angle ∢CCH/CCF) describe the complete molecular structure.

A fit of more than three structural parameters was precluded because of high correlation, and the remaining structural parameters had to be fixed for the fit. We have thus chosen fixed values for the bond distances r_{CN} and r_{CC} which were obtained as mean values from r_0-structural data of the molecules CH$_3$CN [15], (CH$_3$)$_3$CCN [16], CCl$_3$CN [17], CH$_2$(CN)$_2$ [18] and CF$_3$CN [19] as follows

$$r_{CN} = 115.8 \pm 0.2 \text{ pm},$$
$$r_{CC} = 146.0 \pm 0.4 \text{ pm}.$$

A value for the CH-bond distance was obtained by using the fact that the wave numbers of CH-stretching vibrations are in good approximation proportional to CH-distances (r_0-structure) [20]. A wavenumber of $\nu_{CH} = 2995.38$ cm^{-1} for the CH-stretching vibration of CHF$_2$CN was obtained from investigation of the IR-spectrum employing a PE 325 grating spectrometer. With use of this result and the correlation between r_{CH} and ν_{CH} [20], a value of

$$r_{CH} = 109.2 \text{ pm}$$

was obtained and kept fixed in the structure fit.

Further, assuming a linear CCN-chain (∢CCN = 180°) and a dihedral angle ∢CCH/CCF = 120°, the remaining structural parameters r_{CF}, ∢CCH and ∢CCF were determined from the fit analysis. The results are summarized in Table 5. The Table also shows for both isotopomers the differences between the experimental and the calculated rotational constants which were obtained from the presented structure.

A comparison among the r_0-structure data of similar molecules is given in Table 6. It is evident from the Table that the largest discrepancies concern the angle ∢HCC which appears to be too large for difluoroacetonitrile. This may be due to the fact that some of the used assumptions about the structure are not very reliable. Thus, for example, the CCN-chain might be

Table 5. Partial r_0-structure of ^{15}N-difluoroacetonitrile obtained for three fit parameters (r_{CF}, ∢ FCC, ∢ HCC) from the six experimental rotational constants given in Table 2. Errors in parentheses are twice the standard deviations and given in units of the least significant figure. Structure parameters in parentheses were kept fixed in the fit. Values for angles FCF and HCF were obtained from fitted angles FCC and HCC and the fixed dihedral angle HCC/FCC. The calculated constants for both isotopomers are compared with the measured ones as given in Table 2.

r_{CF}	= 135.28(1)	pm	∢FCC	= 110.75(1)	deg
(r_{CH}	= 109.2	pm)	∢HCC	= 114.16(32)	deg
(r_{CC}	= 146.0	pm)	(∢HCC/FCC	= 120.0	deg)
(r_{CN}	= 115.8	pm)	(∢CCN	= 180	deg)
			∢FCF	= 108.16(4)	deg
			∢HCF	= 106.36(20)	deg

	CHF$_2$CN * [kHz]	CHF$_2$C^{15}N [kHz]
$A_{exp} - A_{calc}$	−410	76
$B_{exp} - B_{calc}$	57	7
$C_{exp} - C_{calc}$	118	10

* Experimental data from [1].

Table 6. Comparison of structural data for some molecules (r_0-structures according to quoted references). Fixed values are given in parentheses.

Molecule	Literatur	r_{CH}	r_{CF}	r_{CC}	∢HCC	∢FCF	∢HCF	∢FCC
CH$_3$CN	[15]	109.4	–	145.96	110.01	–	–	–
CH$_2$FCN	[1, 4]	109.0	137.8	(145.9)	109.96	–	109.34	111.2
CF$_3$CN	[1]	–	(133.5)	(145.9)	–	107.55	–	111.3
CH$_2$F$_2$	[21]	109.2	135.8	–	–	108.28	–	–
CHF$_3$	[22]	110.2	133.26	–	–	108.66	–	–
CH$_3$F	[23]	109.47	138.9	–	–	–	108.45 [26]	–
CH$_3$CHF$_2$	[24]	–	134.5	–	–	109.13	–	109.43
CF$_3$CHF$_2$	[25]	–	134.5	–	–	109.06	–	109.58
CHF$_2$CN	this work	(109.2)	135.28	(146.0)	114.16	108.16 *	106.36 *	110.75

* Values obtained with fixed dihedral angle ∢HCC/FCC.

slightly bent away from the two fluorine atoms. A small bend angle of the CCN-moiety has already been found in the case of monofluoroacetonitrile (2°) [5] from analysis of the observed ^{14}N-nuclear quadrupole coupling constants for the normal and deuterated isotopomer. In order to confirm a similar behaviour for difluoroacetonitrile, further isotopomers with D or ^{13}C must be studied, which should also improve other data on the molecular structure.

Summary

The microwave spectrum of ^{15}N-difluoroacetonitrile has been recorded and assigned. Rotational constants as well as quartic centrifugal distortion constants have been determined. An investigation of the Stark splittings of some lines has led to the determination of the dipole moment components μ_a and μ_c. The direction of the dipole moment was determined by using simple considerations about partial moments of related molecules. A partial r_0-structure was determined under a number of restrictive conditions, which suggests the need for further studies.

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