

¹⁴N Nuclear Quadrupole Coupling Constants of Acetamide and α-Fluoroacetamide

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The ¹⁴N nuclear quadrupole hyperfine structures in the rotational spectra of acetamide, CH₃CONH₂, and α-fluoroacetamide, FCH₂CONH₂, have been resolved. From the observed patterns, the quadrupole coupling constants have been determined with high precision. The results provide evidence of considerable delocalization of the nitrogen lone electron pair. For acetamide, the full coupling tensor has been determined from a combined analysis of the ground and first excited state of the methyl group internal rotation.

The spectrum of α-fluoroacetamide-[¹⁵N] has been obtained for the first time, and a refined structure is proposed.

Introduction

Although amides are the simplest molecules containing the biologically important peptide bond (characterized by R–C(=O)NR'R"; for amides, R'=R''=H), and are therefore of considerable interest, experimental data concerning the electronic situation in these molecules are relatively scarce. This is partly due to the fact that most amides are solids, making gas phase studies difficult, while in the solid state, the situation is complicated by strong intermolecular forces, mainly by hydrogen bonds.

We have now resolved the nitrogen nuclear quadrupole hyperfine structures in the rotational spectra of acetamide, CH₃CONH₂, and α-fluoroacetamide, FCH₂CONH₂, by means of microwave Fourier transform (MWFT) spectroscopy.

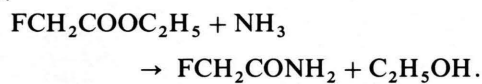
The rotational spectrum of acetamide has been assigned by Kojima et al. [1]. It is perturbed by the very low barrier to internal rotation of the methyl group, which gives rise to many lines of molecules in excited torsional states. In this work, we have confined ourselves to the ground and first excited state of the internal rotation.

The rotational spectra of α-fluoroacetamide and its N-deuterated isotopomers have been recorded by Marstokk et al. [2]. These authors have also reported ¹⁴N quadrupole coupling constants. We have now

redetermined these constants with higher precision and have additionally assigned the spectrum of the ¹⁵N-isotopomer, so that now a partial substitution structure of the amide moiety is available.

Experiment

In contrast to acetamide, α-fluoroacetamide is not commercially available. It was prepared by the ammonolysis of ethyl fluoroacetate at dry ice temperature:



α-Fluoroacetate-[¹⁵N] was prepared in the same manner, but this time using ammonia-[¹⁵N]. In both cases, all volatile side products were pumped off in vacuo after completion of the reaction.

The spectra were recorded at room temperature and pressures of rather less than 1.5 mTorr = 0.2 Pa. We used our waveguide MWFT spectrometers in the frequency range 5 to 38 GHz [3–7].

The ground state spectrum of acetamide consists mainly of ^bQ-branch transitions and several low-*J* ^bR-branch lines. We recorded transitions of both types, with *J* ranging up to 4, and found that all of these exhibited nuclear quadrupole hyperfine structures (Table 1). The nearly free internal rotation of the methyl group modifies considerably the rigid rotor energy levels in excited states of the torsion and introduces nonvanishing expectation values of the angular

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Table 1. Observed frequencies of hyperfine structure components of rotational transitions of acetamide. $m=0$ labels the ground state, $m=\pm 1$ the first excited state of the internal rotation of the methyl group. $\tau = K_a - K_c$ labels the asymmetric top levels. ν_0 hyperfine free centre frequency (in MHz), $\delta\nu_0$ observed-calculated centre frequency (in kHz), ν observed frequency (in MHz), $\Delta\nu$ quadrupole offset (in MHz), $\delta\Delta\nu$ observed-calculated offset (in kHz).

J'	τ'	J''	τ''	F'	F''	ν_0	ν	$\delta\nu_0$	$\Delta\nu$	$\delta\Delta\nu$
$m=0$										
1	0	0	0	16 672.047		201				
				2 1 16 671.948				-0.099	1.9	
				1 1 16 672.553				0.506	1.3	
				0 1 16 671.033				-1.014	-4.5	
2	-2	1	0	24 087.672		-344				
				3 2 24 087.510				-0.162	0.5	
				2 1 24 088.091				0.419	1.8	
				1 0 24 087.757				0.085	-2.6	
				2 2 24 088.692				1.020	-2.8	
				1 1 14 086.246				-1.426	0.6	
2	0	2	-2	13 107.525		-261				
				3 3 13 107.934				0.409	1.4	
				2 2 13 106.099				-1.426	0.6	
				1 1 13 108.950				1.425	-1.6	
2	1	2	-1	19 076.094		205				
				3 3 19 076.514				0.420	0.5	
				2 2 19 074.625				-1.469	-0.9	
				1 1 19 077.567				1.473	4.9	
				2 3 19 075.891				-0.203	-3.1	
				1 2 19 075.590				-0.504	0.7	
				3 2 19 075.247				-0.847	1.8	
				2 1 19 076.598				0.504	-0.7	
3	-1	3	-3	23 705.416		107				
				4 4 23 705.416				0.440	-1.3	
				3 3 23 704.092				-1.324	0.0	
				2 2 23 706.477				1.061	1.8	
3	0	3	-2	26 628.442		-288				
				4 4 26 628.848				0.406	-0.6	
				3 3 26 627.225				-1.217	-1.2	
				2 2 26 629.417				0.975	0.5	
3	1	3	-1	12 678.267		-258				
				4 4 12 678.464				0.197	-3.3	
				3 3 12 677.670				-0.597	3.9	
				2 2 12 678.747				0.480	-0.7	
3	2	3	0	22 769.635		-430				
				4 4 22 769.873				0.238	-0.4	
				3 3 22 768.925				-0.710	1.1	
				2 2 22 770.204				0.569	-1.7	
3	3	3	1	14 441.705		295				
				4 4 14 441.753				0.048	-1.0	
				3 3 14 441.563				-0.142	1.1	
				2 2 14 441.820				0.115	-1.3	
$m=\pm 1$										
1	1	1	0	20 716.965		-2294				
				2 2 20 717.128				0.163	1.0	
				1 1 20 716.161				-0.804	1.3	
				1 2 20 716.728				-0.237	-2.7	
				2 1 20 716.555				-0.410	-0.1	
				1 0 20 717.585				0.620	-2.1	

Table 1 (continued)

J'	τ'	J''	τ''	F'	F''	ν_0	ν	$\delta\nu_0$	$\Delta\nu$	$\delta\Delta\nu$
2	-2	1	-1	22 095.527		605				
				3 2 22 095.531				0.004	1.8	
				2 1 22 095.565				0.038	1.9	
				1 0 22 095.344				-0.183	-0.7	
				2 2 22 095.385				-0.142	-2.6	
				1 1 22 095.782				0.255	-1.4	
2	1	2	0	20 891.601		127				
				3 3 20 891.673				0.072	0.2	
				2 2 20 891.354				-0.247	4.4	
				1 1 20 891.849				0.248	-3.4	
3	0	2	1	24 934.506		-242				
				4 3 24 934.477				-0.029	1.2	
				3 2 24 934.601				0.095	1.7	
				2 1 24 934.426				-0.080	-1.4	
3	-1	3	-3	15 714.277		558				
				4 4 15 714.564				0.287	1.3	
				3 3 15 713.421				-0.856	1.0	
				2 2 15 714.960				0.683	-2.6	
3	0	3	-1	12 587.549		311				
				4 4 12 587.428				-0.121	1.4	
				3 3 12 587.915				0.366	-1.2	
				2 2 12 587.253				-0.296	-2.2	
3	1	3	0	20 686.106		2599				
				4 4 20 686.140				0.034	0.3	
				3 3 20 686.002				-0.104	-3.0	
				2 2 20 686.189				0.083	2.2	
4	1	4	0	18 507.374		-593				
				5 5 18 507.309				-0.065	-0.2	
				4 4 18 507.553				0.179	0.7	
				3 3 18 507.246				-0.128	-0.7	

Table 2. Rotational constants, torsional parameters (three-fold potential barrier V_3 , moment of inertia of the internal rotor I_x , and angle θ of internal rotation axis to a axis), and quadrupole coupling constants of acetamide, CH_3CONH_2 . a, b, c principal inertial axes, x, y, z principal axes of coupling tensor, $\varphi = \angle(a, z)$.

A	10 839.43(27) MHz	χ_+	-1.9368(24) MHz
B	9 285.20(12) MHz	χ_-	5.9548(36) MHz
C	5 156.15(11) MHz	χ_{ab}	-0.0998(78) MHz ^b
		χ_{aa}	1.9368(24) MHz ^c
V_3	71.284(22) cal/mol	χ_{bb}	2.0090(22) MHz ^c
I_x	3.1269(13) amu Å ²	χ_{cc}	-3.9458(22) MHz ^c
θ	11.389° ^b	χ_{xx}	1.876(6) MHz ^c
φ	-54.23° ^{b, c}	χ_{yy}	-3.9458(22) MHz ^c
		χ_{zz}	2.098(6) MHz ^c

^a Numbers in parentheses are single standard deviations in units of the last significant digits.

^b The sign of θ was defined to be positive; the sign of χ_{ab} , and likewise the sign of φ , was then found to be negative in this case.

^c Derived parameters.

Table 3. Observed frequencies of hyperfine structure components of rotational transitions of α -fluoroacetamide. ν_0 hyperfine free centre frequency (in MHz), $\delta\nu_0$ observed-calculated centre frequency (in kHz), ν observed frequency (in MHz), $\Delta\nu$ quadrupole offset (in MHz), $\delta\Delta\nu$ observed-calculated offset (in kHz).

$J' K'_a K'_c$	$J'' K''_a K''_c$	ν_0	$\delta\nu_0$	ν	$\Delta\nu$	$\delta\Delta\nu$
F'	F''					
a-type transitions						
2 0 2	1 0 1	13 835.947	-2			
	3 2	13 835.876			-0.071	-1
	2 1	13 836.065			0.118	-2
	1 0	13 836.241			0.294	-1
	2 2	13 836.565			0.618	-1
	1 1	13 835.001			-0.946	4
2 1 2	1 1 1	12 857.040	-2			
	3 2	12 856.883			-0.157	5
	2 1	12 857.451			0.411	-4
	1 0	12 857.132			0.092	-3
	2 2	12 858.067			1.027	0
2 1 1	1 1 0	15 111.435	0			
	3 2	15 111.395			-0.040	-1
	2 1	15 111.849			0.414	-1
	1 0	15 110.096			-1.339	1
	2 2	15 110.738			-0.697	-2
	1 1	15 112.871			1.436	0
3 2 2	2 2 1	20 976.235	-2			
	4 3	20 976.117			-0.118	0
	3 2	20 976.649			0.414	-1
	2 1	20 975.821			-0.414	1
3 2 1	2 2 0	21 553.175	2			
	4 3	21 553.123			-0.052	5
	3 2	21 553.417			0.242	-5
	2 1	21 552.869			-0.306	-1
5 1 4	5 1 5	16 572.727	0			
	6 6	16 573.241			0.515	-7
	5 5	16 571.373			-1.353	3
	4 4	16 573.634			0.908	4
7 2 5	7 2 6	12 841.364	0			
	8 8	12 841.716			0.352	-2
	7 7	12 840.509			-0.855	5
	6 6	12 841.890			0.526	-3
b-type transitions						
1 1 1	0 0 0	12 816.831	3			
	2 1	12 816.733			-0.098	4
	1 1	12 817.336			0.505	-5
	0 1	12 815.812			-1.019	1
2 1 2	1 0 1	18 681.733	0			
	3 2	18 681.551			-0.182	0
	2 1	18 682.244			0.511	1
	1 0	18 681.634			-0.099	-4
	2 2	18 682.743			1.010	2
	1 1	18 680.393			-1.340	0
3 0 3	2 1 2	15 553.612	3			
	4 3	15 553.639			0.027	-3
	3 2	15 553.395			-0.217	5
	2 1	15 553.973			0.361	-1

Table 3 (continued)

$J' K'_a K'_c$	$J'' K''_a K''_c$	ν_0	$\delta\nu_0$	ν	$\Delta\nu$	$\delta\Delta\nu$
F'	F''					
b-type transitions						
4 1 3	3 2 2	14 003.633	-1			
	5 4	14 003.728			0.095	3
	4 3	14 003.376			-0.257	-4
	3 2	14 003.815			0.182	1
2 2 1	2 1 2	20 855.586	-2			
	3 3	20 855.970			0.384	1
	2 2	20 854.250			-1.336	4
	1 1	20 856.941			1.355	15
	3 2	20 854.772			-0.814	-7
	2 3	20 855.436			-0.150	1
	2 1	20 856.091			0.505	-5
	1 2	20 855.070			-0.515	-5
3 2 2	3 1 3	22 633.597	1			
	4 4	22 633.946			0.349	-6
	3 3	22 632.533			-1.064	0
	2 2	22 634.454			0.857	6
4 1 3	4 0 4	13 664.026	-1			
	5 5	13 664.441			0.415	-1
	4 4	13 662.885			-1.141	3
	3 3	13 664.842			0.816	-1
5 2 3	5 1 4	15 965.907	0			
	6 6	15 965.980			0.073	-1
	5 5	15 965.715			-0.192	0
	4 4	15 966.037			0.130	2
6 2 4	6 1 5	17 045.190	0			
	7 7	17 045.337			0.147	2
	6 6	17 044.825			-0.365	-2
	5 5	17 045.423			0.233	2

momentum cross-term $P_a P_b + P_b P_a$ [8]. Therefore, the hyperfine patterns and even the selection rules are completely different in the first excited state of the internal rotation and allow the determination of the off-diagonal coupling constant χ_{ab} , including its sign. A compilation of the determined parameters is given in Table 2. In the case of normal α -fluoroacetamide we concentrated on low- J transitions both of a - and b -type to resolve their hyperfine structures, whereas in the case of the ¹⁵N-isotopomer we mainly recorded higher- J , and higher- K transitions in order to precisely determine the rotational and centrifugal distortion constants (Tables 3–5).

Analysis

Nuclear quadrupole hyperfine structures were analyzed using first order perturbation theory [9] (programmes HT1NQ [10] and MIRNQ [11]). We used

Table 4. Observed frequencies of rotational transitions of α -fluoroacetamide- ^{15}N . ν_0 observed frequency (in MHz), $\delta\nu_0$ observed-calculated frequency (in kHz).

J'	K'_a	K'_c	J''	K''_a	K''_c	ν_0	$\delta\nu_0$
a-type transitions							
3	0	3	2	0	2	20 218.760	13
3	1	3	2	1	1	19 024.990	10
3	1	2	2	1	1	22 463.400	8
8	2	6	8	2	7	19 562.483	-3
14	4	10	14	4	11	20 580.428	-6
17	5	12	17	5	13	19 579.510	4
b-type transitions							
2	1	2	1	0	1	18 264.822	-4
3	1	3	2	0	2	23 554.130	-7
15	3	12	16	2	15	20 074.940	1
9	3	7	8	4	4	19 639.614	-6
15	3	13	14	4	10	23 651.216	-3
11	4	8	10	5	5	23 229.613	-7
20	4	17	19	5	14	26 110.460	2
12	5	8	11	6	5	20 010.274	-7
9	8	2	10	7	3	20 492.682	-12
9	8	1	10	7	4	20 492.876	6
10	9	2	11	8	3	25 650.280	3
10	9	1	11	8	4	25 650.280	-11
11	9	3	12	8	4	18 378.418	-4
11	9	2	12	8	5	18 378.491	-3
17	8	9	16	9	8	19 273.150	5
17	8	10	16	9	7	19 245.280	-6
12	10	2	13	9	5	23 550.082	-2
12	10	3	13	9	4	23 550.082	4
19	9	10	18	10	9	21 497.496	3
19	9	11	18	10	8	21 487.444	3
14	11	3	15	10	6	21 427.608	2
14	11	4	15	10	5	21 427.608	5
16	12	4	17	11	7	19 287.280	-10
16	12	5	17	11	6	19 287.280	-9
17	13	4	18	12	7	24 472.540	2
17	13	5	18	12	6	21 472.540	2
19	14	5	20	13	8	22 329.520	10
19	14	6	20	13	7	22 329.520	10

quadrupole *offsets* referred to the hypothetical unsplit line frequencies rather than quadrupole *splittings* relative to arbitrary reference components. In all cases, the linear combinations of the coupling constants $\chi_{\pm} \equiv \chi_{bb} \pm \chi_{cc}$ were used as fit parameters; for acetamide, inclusion of χ_{ab} was necessary to reproduce the observed patterns. In order to minimize overlap effects, line frequencies of multiplet components were determined by fitting to the time domain data [12].

The hyperfine free centre frequencies were then subjected to a fit of rotational constants and three torsional parameters (acetamide; programme VC3IAM [13]) or rotational and quartic centrifugal distortion constants (α -fluoroacetamide; programme ZFAP4 [14]), respectively. In the centrifugal distortion fits, Watson's A-reduction [15] was used.

Table 5. Rotational, quartic centrifugal distortion, and quadrupole coupling constants of α -fluoroacetamide and α -fluoroacetamide- ^{15}N . Watson's A-reduction was used. ϕ is the angle between the a - and z -axes.

	α -fluoroacetamide- ^{14}N	α -fluoroacetamide- ^{15}N
A/MHz	9884.3746(15) ^a	9568.06664(77)
B/MHz	4059.6776(5)	4049.89994(25)
C/MHz	2932.4746(6)	2898.94130(37)
Δ_J/kHz	0.86(2)	0.8663(13)
Δ_{JK}/kHz	3.85(6)	3.7913(67)
Δ_K/kHz	3.16(31)	2.8140(23)
δ_J/kHz	0.232(6)	0.23921(25)
δ_K/kHz	2.95(9)	2.9673(45)
χ_+/MHz	-1.6595(26)	
χ_-/MHz	5.7421(48)	
χ_{aa}/MHz	1.6595(26) ^b	
χ_{bb}/MHz	2.0413(27) ^b	
χ_{cc}/MHz	-3.7008(27) ^b	
χ_{xx}/MHz	1.657 ^b	
χ_{yy}/MHz	-3.7008(27) ^b	
χ_{zz}/MHz	2.043 ^b	
ϕ	86° assumed	

^a Numbers in parentheses are single standard deviations in units of the last significant digits.

^b Derived parameters.

Results

Our results for the torsional parameters of acetamide are very similar to those of Kojima et al. [1]; our value for the potential barrier is slightly higher, and the moment of inertia slightly smaller than their value. We used only those transitions which we have remeasured and are therefore unambiguously assignable from their hyperfine patterns. Nevertheless, the standard deviation of a simultaneous fit of the centre frequencies of both torsional states was 1.1 MHz, which would be unacceptable for a semirigid rotor spectrum. Indeed, a tentative pseudo-centrifugal distortion fit of the ground state lines alone gave a much lower residual standard deviation, but rather meaningless parameters. Obviously, model deficiencies, inherent to the treatment of the almost unhindered internal rotation, limit the analysis. On the other hand, the fit of the coupling constants to the quadrupole offsets had a standard deviation of only 2.4 kHz, which is about the present precision limit of our waveguide spectrometers (particularly those operating at higher frequencies).

The rotational constants of α -fluoroacetamide- ^{15}N and those of the singly deuterated species from [2]

Table 6. Substitution coordinates of the nitrogen atom (label N) and the amino protons (labels H_c = cis and H_t = trans with respect to the oxygen atom), and plausible structure of fluoroacetamide. Proton coordinates were evaluated with data from [2]. τ_{OCF} is the dihedral angle between the C=O and C-F bonds.

	a _s	b _s
N	54.78 pm	131.38 pm
H _c	139.28 pm	183.35 pm
H _t	32.68 pm	174.97 pm
r _{CO}	125.4 pm ^a	✕ NCO 124.5°
r _{CN}	131.9 pm ^a	✕ CCO 117.3°
r _{CC}	153.3 pm ^a	✕ CCF 109.2°
r _{CF}	140.6 pm ^a	✕ CCH 108.0°
r _{NH_c}	99.3 pm	✕ CNH _c 119.8°
r _{NH_t}	97.7 pm	✕ CNH _t 119.4°
r _{CH}	110.0 pm ^a	τ _{OCF} 180.0°

^a These bond lengths were taken from [2].

were used to calculate substitution coordinates using Kraitchman's equations [16]. We then tried to obtain bond angles which reproduce both these coordinates and the rotational constants of the parent isotopomer. In this calculation, the plausible bond lengths of [2] were used unchanged. The results are presented in Table 6.

The interpretation of the quadrupole coupling constants follows the procedure outlined for pyridine-N-oxide and picoline-N-oxide [17]. Because none of the molecules investigated in the present study possesses a C_{2v} symmetry axis, we had to make the same additional assumption of local C_{2v} symmetry at the nitrogen atom. In both acetamide and α-fluoroacetamide, one of the principal coupling tensor axes (defined as the y-axis) is necessarily perpendicular to the symmetry plane of the molecule. We assumed that in α-fluoroacetamide the second principal axis (z) bisects the HNH-angle. In the case of acetamide, we obtained the orientation of the coupling tensor from the simultaneous analysis of the ground and first excited torsional state hyperfine patterns. Introducing the angle φ between the principal inertial and assumed princi-

pal coupling axes, we have used the relations

$$(\chi_{xx} + \chi_{zz}) = -\chi_{yy} = -\chi_{cc}, \quad (1)$$

$$(\chi_{xx} - \chi_{zz}) = (\chi_{bb} - \chi_{aa})/\cos 2\varphi \quad (\alpha\text{-fluoroacetamide}), \quad (2a)$$

$$(\chi_{xx} - \chi_{zz})^2 = (\chi_{bb} - \chi_{aa})^2 + (2\chi_{ab})^2 \quad (\text{acetamide}). \quad (2b)$$

The definition of the bonding orbitals is the same as in [17]; instead of *i*₀ and *i*_c, we now use *i*₁ and *i*₂ and assume equivalence of the ψ_{2,3}-orbitals. The relations between the coupling constants and the orbital occupation numbers are then

$$(\chi_{xx} + \chi_{zz})/eQq_{210} = i_1/3 + 2i_2/3 - i_\pi, \quad (3a)$$

$$(\chi_{xx} - \chi_{zz})/eQq_{210} = i_2 - i_1. \quad (3b)$$

Since there are still three unknown quantities and only two experimental parameters, one further assumption has to be made. We assume the ionicity of the nitrogen-carbon bond to be 19% from the results for pyridine [18]. With the data for χ_{xx} and χ_{zz} and Kasten's value for *eQq*₂₁₀ [19], the results for the *i*_π's are 65% for acetamide, and 62% for α-fluoroacetamide (where a charge correction on *eQq*₂₁₀ of 6% has been introduced). The quantity *i*₁ - *i*₂ is small in both cases, 2.4% and 4.4%, respectively. The relatively low value of *i*_π found for α-fluoroacetamide, which corresponds to a relatively high amount of π-electron delocalization, can probably best be explained by the formation of an in-plane hydrogen bond to the fluorine atom. Such a bond would increase the in-plane electron density around the nitrogen nucleus and therefore support π-electron delocalization.

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