^{14}N- and D-Hyperfine Structure in the Rotational Spectrum of Pyrrolidine

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We present an analysis of the rotational spectra of the normal and the N-deuterated pyrrolidine measured by microwave Fourier transform spectroscopy. The quartic centrifugal distortion constants and the ^{14}N coupling constants have been determined with higher accuracy. In addition the D hyperfine structure could be analyzed.

Introduction

Caminati et al. [1] investigated for the first time the microwave spectrum of pyrrolidine, C_4H_8N-H and C_4H_8N-D. They assigned the rotational spectra in different vibrational states which they attributed to a bent form with the hydrogen bond to the nitrogen in axial position (compare Fig. 2 of [1]). They determined also the ^{14}N hyperfine structure. We reinvestigated the rotational spectra by microwave Fourier transform (MWFT) spectroscopy [2] as we noticed that with this technique the resolution can be improved considerably. The resulting coupling constants for ^{14}N are more accurate, those for D can be determined.

Experimental

We used commercial pyrrolidine. To get the deuterated isotopomer 1 ml of pyrrolidine was mixed with 4 ml of a 40% sodium deuterooxide (NaOD) solution in D_2O (99 atom% D). After a few minutes of shaking in a separatory funnel the two phases could be separated. The upper phase containing the deuterated isotopomer was good enough to be used for our measurements.

The spectra were recorded with our MWFT spectrometers in the range from 4 to 18 GHz [3–5]. The temperature was about 220 K, the pressure between 0.5 and 4 mTorr (0.1–0.5 Pa). We confirmed the assignment of both isotopomers by double resonance experiments [6] for example with the transition $J, K_-, K_+ - J', K'_-, K'_+ = 2, 1, 1 - 1, 1, 0$ near 23921.5 MHz as pump and 1, 1, 0–0, 0, 0 as signal. Most of the measurement in the Ku band (12.4–18 GHz) were performed with double resonance technique to eliminate interfering lines.

The frequencies of the multiplet components were calculated by a least squares fit of the time domain signal [7]. Some of the measuremets are given in Tables 1 and 2.*

Analysis

The hfs analysis was based on the splittings $\Delta\nu_{\mathrm{hfs}}$ of the lines given in the complete list of measurements mentioned above by diagonalizing the hamiltonian matrix, neglecting matrix elements off diagonal in the quantum number J (programme SUZIQS [8]). For the deuterated species we used a programme based on first order theory with the coupling scheme $F_1 = J + I_1$ and $F = F_1 + I_2$ [9] (programme Q2FIT/Q2SIM [10]). The results are given in Table 3. The centrifugal distortion analysis with Watson's S reduction for the III^r representation [11] (programme ZFAP4 [12]) used the hypothetical center frequencies ν_0 of the measured transitions calculated in course of the hfs analysis by the programme SUZIQS [8]. We supplemented our measurements by those given in the appendix of [1]. Because of the lower accuracy of the Stark measurements the transitions that differ from the calculated frequencies more than three times the standard deviation have not been used in the final analysis. A typical

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* The complete list of all measurements is available under no. TNA 19 at the Universitätsbibliothek, Westring 400, D-2300 Kiel.

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Table 1. Part of the measured transitions of pyrrolidine H axial. Experimental frequency of a component ν_{obs}, hfs splitting $\Delta\nu_{hfs} = \nu_{obs} - \nu_0$, deviation of the hfs analysis $\delta\nu_{calc-obs}$, hypothetical unsplit line ν_0, deviation of the centrifugal distortion analysis $\delta\nu_{calc-obs}$.

$J, K_-, K_+ - J', K'_-, K'_+$ $F - F'$	ν_{obs}/GHz	ν_0/GHz	$\Delta\nu_{hfs}$/MHz	$\delta\nu_{calc-obs}$/kHz	$\delta\Delta\nu_{calc-obs}$/kHz
1, 0, 1 − 0, 0, 0		10.565908		0	
1 − 0	10.567607		1.699		− 4
1 − 1	10.565060		−0.848		0
1 − 2	10.566077		0.169		0
1, 1, 0 − 0, 0, 0		13.512385		−9	
1 − 0	13.512066		−0.319		6
1 − 1	13.512535		0.150		6
1 − 2	13.512356		−0.029		− 3
2, 1, 1 − 2, 1, 2		8.369359		−12	
1 − 1	8.369891		0.532		2
2 − 2	8.368825		−0.534		− 1
2 − 3	8.369724		0.365		−11
3 − 2	8.368635		−0.724		−12
3 − 3	8.369511		0.152		0
2, 2, 1 − 2, 0, 2		8.845818		−13	
1 − 1	8.844768		−1.050		4
2 − 2	8.846864		1.046		0
3 − 3	8.845520		−0.298		− 1
3, 2, 2 − 3, 0, 3		14.344695		−19	
2 − 2	14.344523		−0.172		4
3 − 3	14.344902		0.207		2
4 − 4	14.344627		−0.068		− 2
9, 8, 1 − 9, 8, 2		5.359256		− 5	
8 − 8	5.359618		0.362		0
9 − 9	5.358641		−0.615		0
10 − 10	5.359520		0.264		0
12, 11, 2 − 12, 10, 2		4.695953		−13	
11 − 11	4.695430		−0.523		− 1
12 − 12	4.696878		0.925		1
13 − 13	4.695542		−0.411		+ 1
13, 12, 2 − 13, 11, 2		5.964236		−14	
12 − 12	5.963692		−0.544		2
13 − 13	5.965204		0.968		− 1
14 − 14	5.963803		−0.433		− 1

correlation gives Table 4. It may be observed that the value of $\chi_{bb}(N)$ of the two isotopomers agree within the error limits. Our coupling constants are at least by a factor 10 more precise.

As the deuteration changes the orientation of the molecule in its inertia axes system an estimate of the principal axis components of the coupling tensor can be calculated [13]. As the structure of pyrrolidine is not known precisely we used the structure of cyclopentane given in [14] as approximation. This gives a rotation by $\Delta\varphi = 2.0°$. The principal axis tensor components are $\chi_{xx} = 1.37$ MHz, $\chi_{yy} = \chi_{bb} = 2.7642(23)$ MHz, $\chi_{zz} = -4.13$ MHz with the z axis inclined by 21.5° from the a inertia axis and the y axis parallel to the b inertia axis. The off diagonal element $\chi_{ac} = -1.88$ MHz. As these χ values and $\Delta\varphi$ are influenced by the estimated structure we do not give error limits.

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Table 2. Part of the measured transitions of pyrrolidine D axial. Experimental frequency of a component ν_{obs}, hfs splitting with respect to the strongest hfs component $\Delta\nu_{hfs}=\nu_{obs}-\nu'_{obs}$, deviation of the hfs analysis $\delta\Delta\nu_{calc-obs}$, hypothetical unsplit line ν_0, deviation of the centrifugal distortion analysis $\delta\nu_{calc-obs}$.

$J, K_-, K_+ - J', K'_-, K'_+$ $F_1, F-F'_1, F'$	ν_{obs}/ GHz	ν_0/ GHz	$\Delta\nu_{hfs}$/ MHz	$\delta\nu_{calc-obs}$/ kHz	$\delta\Delta\nu_{calc-obs}$/ kHz
4, 4, 1 − 4, 2, 2		10.092303		−2	
3, 2 − 3, 2	10.091437		−0.420		−3
3, 4 − 3, 4					
3, 3 − 3, 3	10.091472		−0.384		−2
5, 4 − 5, 4	10.091846		−0.010		2
5, 6 − 5, 6	10.091856				
5, 5 − 5, 5	10.091893		0.036		0
4, 3 − 4, 3	10.093489		1.633		−4
4, 5 − 4, 5	10.093495		1.639		−2
4, 4 − 4, 4	10.093523		1.667		2
5, 5, 1 − 5, 3, 2		11.353332		−4	
4, 3 − 4, 3	11.352417		−0.385		5
4, 5 − 4, 5					
4, 4 − 4, 4	11.352454		−0.348		−5
6, 5 − 6, 5	11.352802				
6, 7 − 6, 7					
6, 6 − 6, 6	11.352833		0.031		−3
5, 4 − 5, 4	11.354684		1.882		−6
5, 6 − 5, 6					
5, 5 − 5, 5					
6, 4, 2 − 6, 4, 3		12.467147		−4	
6, 5 − 6, 7	12.466710		−0.595		3
6, 7 − 6, 5					
6, 6 − 6, 6	12.466749		−0.555		−12
7, 6 − 7, 6	12.467305				
7, 8 − 7, 8					
7, 7 − 7, 7	12.467338		0.033		−6
5, 4 − 5, 4	12.467409		0.104		−3
5, 6 − 5, 6					
5, 5 − 5, 5	12.467435		0.130		−4
7, 5, 2 − 7, 5, 3		11.745064		2	
7, 6 − 7, 6	11.744565		−0.706		−1
7, 8 − 7, 8					
7, 7 − 7, 7					
8, 7 − 8, 7	11.745271				
8, 9 − 8, 9					
8, 8 − 8, 8					
6, 5 − 6, 5	11.745358		0.087		9
6, 7 − 6, 7					
6, 6 − 6, 6	11.745382		0.111		3
9, 8, 2 − 9, 7, 2		5.679555		−4	
8, 7 − 8, 7	5.679005		−0.147		−1
8, 9 − 8, 9					
8, 8 − 8, 8					
9, 8 − 9, 8	5.679152				
9, 10 − 9, 10					
9, 9 − 9, 9					
7, 6 − 7, 6	5.680490		1.337		−1
7, 8 − 7, 8					
7, 7 − 7, 7					
13, 11, 2 − 13, 11, 3		4.825770		−15	
13, 12 − 13, 12	4.825348		−0.061		1
13, 14 − 13, 14					
13, 13 − 13, 13					
14, 13 − 14, 13	4.825959				
14, 15 − 14, 15					
14, 14 − 14, 14					
12, 11 − 12, 11	4.826006		0.047		0
12, 13 − 12, 13					
12, 12 − 12, 12					
13, 10, 3 − 13, 10, 4		13.864593		0	
13, 12 − 13, 12	13.864088		−0.730		1
13, 14 − 13, 14					
13, 13 − 13, 13					
14, 13 − 14, 13	13.864818				
14, 15 − 14, 15					
14, 14 − 14, 14					
12, 11 − 12, 11	13.864878		+0.060		−1
12, 13 − 12, 13					
12, 12 − 12, 12					

Table 3. Rotational constants A, B, C, quartic centrifugal distortion constants of Watson's S reduction D_J, D_{JK}, D_K, d_1, d_2, Ray's asymmetry parameter $\varkappa$, number of fitted lines N_L, standard deviation of the fit of the centrifugal distortion analysis σ_{cd}, quadrupole coupling constants χ, number of fitted hfs components N_c, mean splitting $\Delta\nu_{hfs}$, standard deviation of the fit of the quadrupole coupling analysis σ_{hfs}, correlation of the quadrupole coupling constants $|(\chi^+, \chi^-)|$. Standard errors in parenthesis (in units of the least significant digit).

C_4H_8N-H		C_4H_8N-D	
A/GHz	6.8345324(79)	A/GHz	6.7073675(76)
B/GHz	6.6778513(79)	B/GHz	6.4037931(76)
C/GHz	3.8880602(81)	C/GHz	3.8345331(80)
D_J/kHz	1.86(32)	D_J/kHz	1.49(34)
D_{JK}/kHz	−2.3320(30)	D_{JK}/kHz	−1.756(13)
D_K/kHz	0.983(38)	D_K/kHz	0.595(63)
d_1/Hz	13.23(29)	d_1/Hz	19.9(18)
d_2/Hz	19.67(14)	d_2/Hz	12.7(10)
$\varkappa$	0.893648	$\varkappa$	0.788659
N_L	35	N_L	20
N_L [1]	85	N_L [1]	72
σ_{cd}/kHz	70	σ_{cd}/kHz	69
χ^+(N)/MHz	3.3904(14)	χ^+(N)/MHz	3.253(9)
χ^-(N)/MHz	2.1381(31)	χ^-(N)/MHz	2.267(25)
χ_{aa}(N)/MHz	−3.3904(14)	χ_{aa}(N)/MHz	−3.253(9)
χ_{bb}(N)/MHz	2.7642(14)	χ_{bb}(N)/MHz	2.760(9)
χ_{cc}(N)/MHz	0.6262(20)	χ_{cc}(N)/MHz	0.493(17)
N_c	107	χ^+(D)/MHz	0.117(8)
$\Delta\nu_{hfs}$/kHz	539	χ^-(D)/MHz	−0.305(25)
σ_{hfs}/kHz	2.7	χ_{aa}(D)/MHz	−0.117(8)
$\|(\chi^+, \chi^-)\|$	0.452	χ_{bb}(D)/MHz	−0.094(11)
		χ_{cc}(D)/MHz	0.211(15)
		N_c	70
		σ_{hfs}/kHz	6.1

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Table 4. Correlation matrices for values of Table 3. a) For the rotational and centrifugal distortion constants of C_4H_8N-H. b) For the nuclear quadrupole coupling constants of C_4H_8N-D.

A	1.000							
B	0.998	1.000						
C	0.942	0.945	1.000					
D_J	0.902	0.903	0.908	1.000				
D_{JK}	−0.021	−0.010	0.049	0.034	1.000			
D_K	−0.094	−0.090	0.198	0.053	−0.224	1.000		
d_1	−0.034	0.011	0.016	0.007	0.405	−0.029	1.000	
d_2	−0.012	0.008	0.002	0.003	0.426	−0.086	0.865	1.000
χ_{aa}(N)	1.000							
χ_{bb}(N)	0.612	1.000						
χ_{aa}(D)	0.109	0.052	1.000					
χ_{bb}(D)	−0.058	0.072	0.154	1.000				