Nitrogen and Deuterium Hyperfine Structure in the Rotational Spectra of Pyridine and [4-D]Pyridine

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We reanalysed the ^{14}N hyperfine structure in the rotational spectra of pyridine and [4-D]-pyridine with higher precision and determined the D quadrupole coupling. It is intended to provide a reference for comparison with substituted pyridines.

We investigated by microwave Fourier transform (MWFT) [1] spectroscopy the rotational spectra of a number of substituted pyridines. The aim was a study of substitutional effects reflected by the ^{14}N quadrupole coupling. Therefore, high precision was necessary to analyse the hyperfine structure (hfs) induced by the ^{14}N nucleus and other nuclei with quadrupole moments.

To base the investigation on comparable experimental methods and analyses we remeasured as reference pyridine, C_5H_6N, itself, which has been the subject of many investigations, the last by Sørensen et al. [2, 3]. In this publication we present the results for pyridine and [4-D]pyridine [3, 4], which is the molecule with the least substitutional effect. The data for the other substituted pyridines (4-chloropyridine, 4-cyanopyridine, and perfluoropyridine) will be given in forthcoming publications together with a discussion of the quadrupole coupling constants.

We used our MWFT spectrometers in the range from 5.3 to 26.4 GHz described elsewhere [5–8].

Dry pyridine, 99.5%, was purchased from Merck, Darmstadt, and used without further treatment.

[4-D]Pyridine was in our stock for more than 14 years. It was purchased from Merck, Sharp and Dohme, Canada.

The spectra of both of the pyridines were recorded at temperatures of −25 °C to −45 °C and pressures below 0.2 Pa (1.5 m Torr). The measurements are given in Tables 1 a and 1 b. The frequencies given are those resulting from line shape simulation [9] to account for interference of neighbouring lines. A sample of the measurements is given in Fig. 1 showing the nitrogen and deuterium hfs of the $4_{41} - 4_{22}$ transition of [4-D]pyridine.

A first order hfs analysis [10] proved to be sufficient. The rotational constants were taken from [3]. They are given with the determined coupling constants χ_{gg}, g = a, b, c in Table 2. For [4-D]pyridine a coupled basis: $F_1 = J + I$ (nitrogen), $F = F_1 + I$ (deuterium), J angular momentum and I spin operator, was used. For pyridine the analysis was made with the programs HT1NQ and DH14KS [11] and for [4-D]pyridine with Q2SIM [12] and Q2FIT [13].

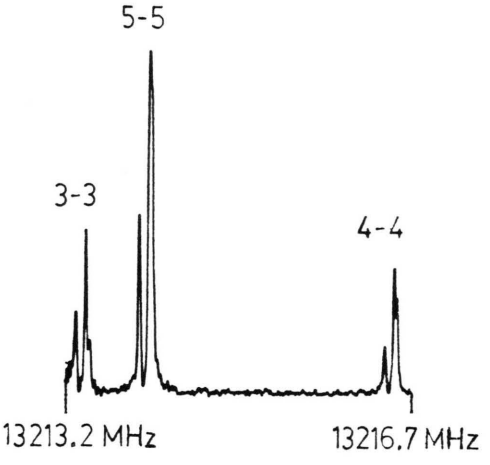

Fig. 1. Rotational transition $J_{K_-K_+} = 4_{41} - 4_{22}$ of [4-D]pyridine showing ^{14}N- and D-hfs. Range from 13213.2 to 13216.7 MHz out of a 10 MHz recording. Temperature −35 °C, pressure 0.2 mTorr, polarizing frequency 13213.2 MHz, 50 ns sampling interval, 10^7 averaging cycles, 1024 data points supplemented with 3072 zeros prior to Fourier transformation. Spectral point distance 2.5 kHz. F_1 quantum numbers are above the lines.

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$\Delta\nu$ hfs-splittings referred to the strongest multiplet component, ν_0 hypothetical unsplit lines, $\Delta(\Delta\nu) = \Delta\nu - \Delta\nu_{calc}$ deviations of the splittings, $\Delta\nu_{calc}$ splittings calculated with the constants of Table 2, $\Delta\nu_0$ deviations from rigid rotor spectrum calculated with the rotational constants of Table 2 (program DH9 [11]).

J'	K'_-	$K'_+ - J''$	K''_-	K''_+	$F' - F''$	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ [kHz]	$\Delta\nu_0$ [kHz]
1	0	1 - 0	0	0	1-1	8762.887	-1.477		- 5	
					2-1	8764.364		8764.118		- 5
					0-1	8766.572	+2.208		- 1	
2	0	2 - 1	0	1	1-0	14901.463	-1.544		+ 1	
					2-2	14901.810	-1.197		- 2	
					3-2	14903.007		14902.987		- 15
					2-1	14903.276	+0.269		- 9	
					1-1	14905.146	+2.139		+ 3	
2	1	1 - 1	1	0	2-1	20372.681	-1.502		+ 1	
					1-1	20373.399	-0.784		+ 2	
					2-2	20373.736	-0.447		+ 14	
					3-2	20374.183		20373.907		- 39
					1-0	20376.003	+1.820		0	
2	1	2 - 1	1	1	2-1	14681.302	-1.549		- 2	
					2-2	14681.728	-1.123		- 6	
					3-2	14682.851		14682.531		- 16
					1-1	14683.033	+0.182		- 8	
					1-0	14684.111	+1.260		- 6	
2	1	1 - 2	1	2	2-3	8536.463	-0.466		- 5	
					1-1	8536.563	-0.366		- 1	
					3-3	8536.929		8537.075		- 25
					2-2	8537.584	+0.655		- 1	
					3-2	8538.040	+1.111		- 6	
					1-2	8538.297	+1.368		- 5	
2	2	1 - 2	0	2	1-1	9251.818	-1.544		- 4	
					3-3	9253.362		9253.978		- 26
					1-2	9253.668	+0.306		- 12	
					2-1	9254.275	+0.913		- 1	
					3-2	9254.556	+1.194		- 1	
					2-3	9254.932	+1.570		- 5	
					2-2	9256.135	+2.773		+ 1	
3	1	2 - 3	1	3	2-2	14752.846	-0.444		+ 1	
					4-4	14753.290		14753.608		- 75
					3-3	14754.566	+1.276		+ 4	
3	2	1 - 3	2	2	3-3	8194.350	-0.161		+ 1	
					4-4	8194.511		8194.471		- 69
					2-2	8194.565	+0.054		- 3	
3	3	1 - 3	1	2	2-2	9667.811	-0.755		- 3	
					4-4	9668.566		9669.104		- 62
					3-3	9670.717	+2.151		+ 1	
4	2	2 - 4	2	3	3-3	14654.305	-0.151		+ 5	
					5-5	14654.456		14654.618		- 175
					4-4	14655.065	+0.609		+ 1	
4	3	1 - 4	3	2	4-4	7743.927	-0.500		- 3	
					5-5	7744.427		7744.294		- 129
					3-3	7744.549	+0.122		- 6	
4	4	1 - 4	2	2	3-3	10288.149	-0.516		+ 2	
					5-5	10288.665		10289.203		- 108
					4-4	10290.684	+2.019		+ 3	
5	3	2 - 5	3	3	4-4	14463.827	-0.048		- 9	
					6-6	14463.875		14463.929		- 297
					5-5	14464.059	+0.184		- 9	
5	4	1 - 5	4	2	5-5	7193.367	-0.654		+ 2	
					6-6	7194.021		7193.839		- 209
					4-4	7194.160	+0.139		+ 5	
5	5	1 - 5	3	2	4-4	11162.700	-0.416		+ 4	
					6-6	11163.116		11163.689		- 155
					5-5	11165.178	+2.062		+ 1	
6	4	2 - 6	4	3	6-6	14149.272	-0.104		+ 2	
					7-7	14149.376		14149.346		- 470
					5-5	14149.390	+0.014		- 4	
6	5	1 - 6	5	2	6-6	6553.758	-0.724		+ 5	
					7-7	6554.482		6554.274		- 306
					5-5	6554.606	+0.124		+ 1	
6	6	1 - 6	4	2	5-5	12340.275	-0.363		+ 5	
					7-7	12340.638		12341.261		- 200
					6-6	12342.822	+2.184		+ 4	
7	5	2 - 7	5	3	7-7	13687.498	-0.334		- 1	
					8-8	13687.832		13687.735		- 682
					6-6	13687.881	+0.049		+ 1	
7	6	1 - 7	6	2	7-7	5841.363	-0.744		+ 6	
					8-8	5842.107		5841.888		- 418
					6-6	5842.217	+0.110		+ 2	
8	6	2 - 8	6	3	8-8	13069.681	-0.502		0	
					9-9	13070.183		13070.034		- 942
					7-7	13070.243	+0.060		- 3	
8	7	1 - 8	7	2	8-8	5078.677	-0.733		- 2	
					9-9	5079.410		5079.192		- 538
					7-7	5079.498	+0.088		- 4	
9	7	2 - 9	7	3	9-9	12300.998	-0.621		- 1	
					10-10	12301.619		12301.433		-1251
					8-8	12301.689	+0.070		+ 1	
10	8	2 - 10	8	3	10-10	11397.481	-0.697		- 2	
					11-11	11398.178		11397.967		-1603
					9-9	11398.244	+0.066		- 4	
11	9	2 - 11	9	3	11-11	10382.130	-0.736		- 1	
					12-12	10382.866		10382.641		-1996
					10-10	10382.929	+0.063		- 4	
12	10	2 - 12	10	3	12-12	9282.599	-0.745		0	
					13-13	9283.344		9283.115		-2410
					11-11	9283.405	+0.061		- 1	
13	11	2 - 13	11	3	13-13	8130.497	-0.730		- 1	
					14-14	8131.227		8131.001		-2820
					12-12	8131.282	+0.055		- 1	
18	15	3 - 18	15	4	18-18	11490.952	-0.711		- 2	
					19-19	11491.663		11491.439		-8866
					17-17	11491.703	+0.040		+ 1	
19	16	3 - 19	16	4	19-19	9964.828	-0.684		0	
					20-20	9965.512		9965.295		-9759
					18-18	9965.546	+0.034		- 2	
20	17	3 - 20	17	4	20-20	8455.586	-0.641		- 2	
					21-21	8455.627		8456.424		-10439
					19-19	8456.656	+0.029		- 3	

Table 1 b. Measured rotational transitions of [4-D]pyridine showing ^{14}N (F_1 quantum numbers) and D hyperfine structure (F quantum numbers). See also Table 1 a.

J' K'_- $K'_+ - J''$ K''_- K''_+	$F'_1 - F''_1$, $F' - F''$	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ [kHz]	$\Delta\nu_0$ [kHz]
1 0 1 - 0 0 0	1-1 , 1-0	8274.637	-1.492		- 3	
	1-1 , 1-1					
	1-1 , 1-2					
	1-1 , 2-1	8274.668	-1.461		- 3	
	1-1 , 2-2					
	1-1 , 0-1	8274.711	-1.418		- 4	
	2-1 , 1-0	8276.107	-0.022		- 4	
	2-1 , 1-1					
	2-1 , 3-2	8276.129		8275.894	- 5	
	2-1 , 2-1	8276.173	+0.044		0	
	2-1 , 2-2					
	0-1 , 1-1	8278.345	+2.216		- 2	
	0-1 , 1-2					
2 0 2 - 1 0 1	1-0 , 1-1	14505.901	-1.476		+ 1	
	1-0 , 2-1					
	3-2 , 3-2					
	3-2 , 4-3	14507.377		14507.331	- 3	
	3-2 , 2-1					
	2-1 , 1-0	14507.48	+0.103		+ 8	
	2-1 , 3-2	14507.52	+0.143		- 9	
	2-1 , 2-1	14507.58	+0.203		- 1	
	1-1 , 2-2	14509.576	+2.199		+ 6	
2 1 2 - 1 1 1	2-1 , 1-1					
	2-1 , 1-0	13986.304	-1.532		- 1	
	2-1 , 3-2					
	2-1 , 2-1					
	3-2 , 2-1	13987.836		13987.535	+ 7	
	3-2 , 4-3					
	3-2 , 3-2	13987.892	+0.056		- 1	
	1-1 , 2-2	13988.018	+0.182		- 22	
	1-0 , 1-1	13989.113	+1.277		- 13	
	1-0 , 2-1					
2 2 1 - 2 0 2	1-1 , 1-2					
	1-1 , 2-2	9646.384	-1.623		+ 8	
	1-1 , 2-1					
	3-3 , 3-3	9647.916	-0.091		+ 4	
	3-3 , 4-4	9648.007		9648.623	- 30	
	3-3 , 2-2	9648.042	+0.035		+ 3	
	1-2 , 2-3	9648.425	+0.418		- 2	
	2-3 , 3-4	9649.575	+1.568		- 2	
	2-2 , 2-2	9650.837	+2.830		+ 6	
	2-2 , 3-3	9650.892	+2.885		+ 8	
	2-2 , 1-1	9650.918	+2.911		+ 4	
3 2 2 - 3 0 3	2-2 , 2-2	14435.321	-0.579		- 3	
	2-2 , 3-3	14435.360	-0.540		- 1	
	2-2 , 1-1	14435.382	-0.518		+ 1	
	4-4 , 4-4	14435.852	-0.048		+ 1	
	4-4 , 5-5	14435.900		14436.260	- 67	
	4-4 , 3-3					
	3-3 , 3-3	14437.382	+1.482		+ 8	
	3-3 , 4-4	14437.420	+1.520		+ 6	
	3-3 , 2-2					
3 3 1 - 3 1 2	2-2 , 2-2	11013.860	-0.938		+ 9	
	2-2 , 3-3	11013.937	-0.861		+ 9	
	2-2 , 1-1	11013.974	-0.824		+ 4	
	4-4 , 4-4	11014.701	-0.097		- 4	
	4-4 , 5-5	11014.798		11015.389	- 65	
	4-4 , 3-3	11014.823	+0.025		+ 2	
	3-3 , 3-3	11017.185	+2.387		+ 3	
	3-3 , 4-4	11017.260	+2.462		+ 4	
	3-3 , 2-2	11017.291	+2.493		+ 9	
4 3 2 - 4 1 3	3-3 , 3-3	14744.174	-0.328		+ 3	
	3-3 , 4-4	14744.215	-0.287		+ 6	
	3-3 , 2-2					
	5-5 , 5-5	14744.461	-0.041		- 1	
	5-5 , 6-6	14744.502		14744.790	-136	
	5-5 , 4-4					
	4-4 , 4-4	14745.603	+1.101		+ 2	
	4-4 , 5-5	14745.639	+1.137		+ 2	
	4-4 , 3-3					
4 4 1 - 4 2 2	3-3 , 3-3	13213.311	-0.734		+ 1	
	3-3 , 4-4	13213.401	-0.644		- 1	
	3-3 , 2-2	13213.440	-0.605		+ 6	
	5-5 , 5-5	13213.943	-0.102		- 3	
	5-5 , 6-6	13214.045		13214.682	-118	
	5-5 , 4-4	13214.065	+0.020		- 3	
	4-4 , 4-4	13216.441	+2.396		- 2	
	4-4 , 5-5	13216.528	+2.483		- 5	
	4-4 , 3-3	13216.552	+2.507		- 4	
5 4 2 - 5 2 3	4-4 , 4-4	15412.473	-0.259		+ 2	
	4-4 , 5-5	15412.51	-0.222		+ 2	
	4-4 , 3-3	15412.53	-0.202		+ 12	
	6-6 , 6-6	15412.689	-0.043		0	
	6-6 , 7-7	15412.732		15413.016	-214	
	6-6 , 5-5					
	5-5 , 5-5	15413.769	+1.037		+ 3	
	5-5 , 6-6	15413.807	+1.075		+ 1	
	5-5 , 4-4					
5 5 1 - 5 3 2	4-4 , 4-4	16374.937	-0.646		+ 1	
	4-4 , 5-5	16375.050	-0.533		+ 10	
	4-4 , 3-3	16375.076	-0.507		+ 9	
	6-6 , 6-6	16375.477	-0.106		+ 13	
	6-6 , 7-7	16375.583		16376.270	-210	
	6-6 , 5-5					
	5-5 , 5-5	16378.08	+2.497		+ 4	
	5-5 , 6-6	16378.187	+2.604		+ 11	
	5-5 , 4-4	16378.208	+2.625		+ 10	
6 5 2 - 6 3 3	5-5 , 5-5	16658.099	-0.248		+ 2	
	5-5 , 6-6	16658.155	-0.192		+ 8	
	5-5 , 4-4					
	7-7 , 7-7	16658.295	-0.052		- 2	
	7-7 , 8-8	16658.347		16658.668	-285	
	7-7 , 6-6					
	6-6 , 6-6	16659.486	+1.139		+ 2	
	6-6 , 7-7	16659.532	+1.185		0	
	6-6 , 5-5					

Table 2. Rotational and quadrupole coupling constants [MHz] of pyridine and [4-D]pyridine. Assumptions of the analysis in square brackets. σ standard deviation of the fit in kHz, $|(\chi_+, \chi_-)|$ maximum correlation coefficient. Single standard errors in brackets. Derived parameters below the line.

Pyridine		[4-D]Pyridine	
A	[6039.2516(6)][3]	A	[6038.9967(10)][3]
B	[5804.9116(6)]	B	[5420.0697(9)]
C	[2959.2117(6)]	C	[2855.8194(8)]
$\chi_+ = \chi_{bb} + \chi_{cc}$	4.908(3)	$\chi_{aa}(^{14}\mathrm{N})$	−4.907(3)
$\chi_- = \chi_{bb} - \chi_{cc}$	−2.041(5)	$\chi_{bb}(^{14}\mathrm{N})$	1.442(5)
		$\chi_{aa}(\mathrm{D})$	0.196(4)
		$\chi_{bb}(\mathrm{D})$	−0.090(8)
σ	4	σ	6
$\lvert(\chi_+, \chi_-)\rvert$	0.13	$\lvert(\chi_{aa}(\mathrm{N}), \chi_{bb}(\mathrm{N}))\rvert$	0.22
χ_{aa}	−4.908(3)	$\chi_{cc}(^{14}\mathrm{N})$	3.465(5)
χ_{bb}	1.434(3)		
χ_{cc}	3.474(3)	$\chi_{cc}(\mathrm{D})$	−0.106(8)

Our values for pyridine and [4-D]pyridine show standard errors which are by a factor 3 less than those from previous measurements [2, 4]. The ^{14}N quadrupole coupling constants of the two isotopomers agree roughly within the error limits. The D quadrupole coupling constants agree with values calculated with an ab initio SCF method by Huber [14].

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