Nitrogen and Chlorine Hyperfine Structure in the Rotational Spectra of 4-Chloropyridine

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We resolved and analysed the ^{14}N hyperfine structure in addition to the ^{35}Cl and ^{37}Cl hyperfine structure of 4-chloropyridine-[^{35}Cl] and -[^{37}Cl] to investigate substitutional effects.

The ^{14}N, ^{35}Cl, and ^{37}Cl hyperfine structure in the rotational spectra of 4-chloropyridine-[^{35}Cl] and -[^{37}Cl] has been investigated by microwave Fourier transform (MWFT) spectroscopy [1]. The aim was to study the substitutional effect produced by the chlorine atom reflected by the ^{14}N quadrupole coupling. This paper is the second in a series. In the first we presented results for pyridine and [4-D]pyridine [2], which were investigated to provide a reference.

4-Chloropyridine was first investigated by Caminati and Forti [3]. They reported the rotational constants of both isotopic forms and the ^{35}Cl quadrupole coupling constants.

Our MWFT spectrometers in the range from 5.3 to 18 GHz described elsewhere [4–6] were used.

The substance, which at room temperature tends to dimerize, was prepared by neutralisation of 4-chloropyridine hydrochloride (Fluka). It was purified by sublimation and stored below its freezing point of – 42.5 °C.

The spectra were recorded at temperatures of approximately – 35 °C and pressures between 0.2 and 1 Pa (1.5 and 7.5 mTorr).

Part of the measurements are given in Tables 1a and 1b. The complete list is available under the number TNA5 from the Universitätsbibliothek, D-2300 Kiel. The multiplets were simulated by a line contour analysis [7] to account for interference of neighbouring lines. A sample of a multiplet is presented in Fig. 1, showing the Cl and N hfs of the $4_{23}-3_{22}$ rotational transition of the ^{37}Cl-species.

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A first order hfs analysis [8] proved to be sufficient as the hfs patterns could be calculated near to the experimental uncertainty. A coupled basis $F_1 = J + I$ (chlorine), $F = F_1 + I$ (nitrogen), (J angular momentum, I spin operator), was used. The hypothetical unsplit transitions were calculated by

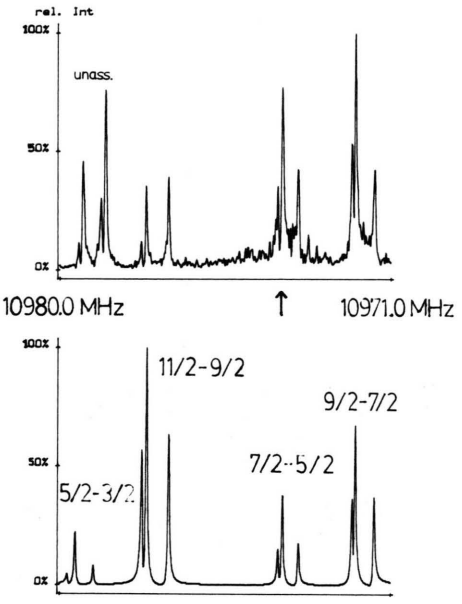

Fig. 1. Rotational transition $J_{K_-K_+} = 4_{23} - 3_{22}$ of 4-chloropyridine-[^{37}Cl] showing both chlorine and nitrogen hfs. F_1 quantum numbers are given. The components with $F_1 = 5/2 - 3/2$ could not be detected. They are overlayed by an unassigned line. In the lower trace the result of a theoretical line pattern is given. The intensities are not reproduced as the polarization conditions vary over the range of the multiplet. Range 10971–10980 MHz out of a 25 MHz recording, sampling interval 20 ns, polarizing frequency 10974 MHz (↑), temperature – 30 °C, pressure 2.7 mTorr, 10^7 averaging cycles, 1024 data points supplemented by 3072 zeros prior to Fourier transformation.

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Table 1a. Selection of measured rotational transitions of 4-chloropyridine-[^{35}Cl] showing ^{35}Cl (F_1 quantum numbers) and ^{14}N (F quantum numbers) hyperfine structure. The F and F_1 quantum numbers are multiplied by 2. ν measured and improved frequencies, $\Delta\nu$ hfs splittings referred to the strongest 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 the rigid rotor spectrum calculated with the rotational constants of Table 2, determined from transitions marked with *.

$J'K'_-K'_+ - J''K''_-K''_+$	$F_1'-F_1'',F'-F''$ *2	ν [MHz]	$\Delta\nu$ [MHz]	ν_0 [MHz]	$\Delta(\Delta\nu)$ [kHz]	$\Delta\nu_0$ [kHz]
2 0 2 - 1 0 1	5-3 , 5-3	5621.964	-1.149		+ 4	
	7-5 , 7-5	5622.785	-0.328		+ 7	
	7-5 , 9-7	5623.113		5621.498*	+ 4	
	7-5 , 5-3	5623.203	+0.090		+ 30	
	5-3 , 7-5	5623.410	+0.297		- 14	
2 1 1 - 1 1 0	5-3 , 3-1	5950.687	-18.676		+ 55	
	5-3 , 7-5	5951.081	-18.282		+ 19	
	5-3 , 5-3	5951.455	-17.908		+ 1	
	7-5 , 7-5	5968.287	-1.076		+ 13	
	7-5 , 9-7	5969.363		5964.664*	+ 22	
	7-5 , 5-3	5969.741	+0.378		- 24	
2 1 2 - 1 1 1	5-3 , 3-1	5299.115	-18.362		+ 47	
	5-3 , 5-3 }	5299.283	-18.194		+ 58	
	5-3 , 7-5 }					
	7-5 , 7-5	5316.248	-1.229		- 34	
	7-5 , 9-7	5317.477		5312.888*	+ 17	
	7-5 , 5-3	5317.935	+0.458		- 2	
3 0 3 - 2 0 2	5-3 , 5-3	8385.237	-0.851		- 15	
	3-1 , 5-3	8385.934	-0.154		+ 18	
	5-3 , 7-5	8386.088		8389.399*	- 2	
	5-3 , 3-1	8386.420	+0.332		- 19	
	7-5 , 7-5	8389.973	+3.885		+ 8	
	9-7 , 9-7	8390.103	+4.015		+ 10	
	9-7 , 7-5	8390.194	+4.106		+ 25	
	9-7 ,11-9	8390.290	+4.202		+ 25	
	7-5 , 9-7	8390.491	+4.403		- 4	
	7-5 , 5-3	8390.592	+4.504		+ 16	
3 1 2 - 2 1 1	5-3 , 5-3	8932.695	-0.781		+ 32	
	7-5 , 7-5	8933.065	-0.411		+ 33	
	5-3 , 7-5	8933.149	-0.327		+ 18	
3 1 3 - 2 1 2	5-3 , 5-3 }	7955.721	-5.080		- 41	
	7-5 , 7-5 }					
	7-5 , 9-7	7956.344	-4.457		- 28	
	7-5 , 5-3 }	7956.489	-4.312		+ 9	
	5-3 , 7-5 }					
	9-7 , 9-7	7960.320	-0.481		- 5	
	9-7 ,11-9 }	7960.801		7958.787*	- 7	
	9-7 , 7-5 }					
	3-1 , 5-3	7960.89	+0.089		- 11	
3 2 1 - 2 2 0	7-5 , 7-5	8513.565	-18.810		+ 19	
	7-5 , 9-7	8514.065	-18.310		- 21	
	7-5 , 5-3 }	8514.229	-18.146		+ 11	
	5-5 , 7-7 }					
	5-3 , 3-1	8526.706	-5.669		- 20	
	5-3 , 7-5	8526.821	-5.554		+ 9	
	5-3 , 5-3	8526.942	-5.433		+ 34	
	9-7 , 9-7	8531.097	-1.278		+ 7	
	9-7 ,11-9	8532.375		8526.869*	- 5	
	9-7 , 7-5	8532.827	+0.452		- 5	
	3-1 , 5-3	8544.935	+12.560		+ 45	
3 2 2 - 2 2 1	7-5 , 7-5	8444.907	-0.543		+ 14	
	7-5 , 9-7	8445.450		8458.139*	+ 2	
	7-5 , 5-3	8445.623	+0.173		+ 23	
	9-7 , 9-7	8462.295	+16.845		+ 2	
	9-7 ,11-9	8463.607	+18.157		+ 7	
	9-7 , 7-5	8464.073	+18.623		+ 14	

Table 1b. Selection of measured rotational transitions of 4-chloropyridine-[^{37}Cl] showing ^{37}Cl (F_1 quantum numbers) and ^{14}N (F quantum numbers) hyperfine structure. See also Table 1a.

J'K'$_-$K'$_+$ – J"K"$_-$K"$_+$	F_1'-F_1'',F'-F" *2	ν [MHz]	Δν [MHz]	ν_0 [MHz]	Δ(Δν) [kHz]	$\Delta\nu_0$ [kHz]
2 0 2 – 1 0 1	7-5 , 7-5	5479.261	-0.320		+ 10	
	7-5 , 9-7	5479.581		5478.287*	+ 8	
	7-5 , 5-3	5479.757	+0.176		+ 95	
	5-3 , 7-5	5479.964	+0.383		+103	
2 1 1 – 1 1 0	5-3 , 3-1	5792.165	-14.910		+ 20	
	5-3 , 7-5	5792.586	-14.489		+ 4	
	5-3 , 5-3	5792.98	-14.095		+ 1	
	7-5 , 7-5	5806.045	-1.030		+ 19	
	7-5 , 9-7	5807.075		5803.328*	+ 41	
	7-5 , 5-3	5807.416	+0.341		- 41	
2 1 2 – 1 1 1	5-3 , 7-5	5173.504	-14.410		0	
	7-5 , 7-5	5186.750	-1.164		+ 4	
	7-5 , 9-7	5187.914		5184.242*	+ 57	
	7-5 , 5-3	5188.299	+0.385		- 77	
3 0 3 – 2 0 2	5-3 , 5-3	8175.635	-4.281		- 13	
	5-3 , 7-5	8176.482	-3.434		+ 14	
	7-5 , 7-5	8179.378	-0.538		- 17	
	9-7 , 9-7	8179.529	-0.387		- 28	
	9-7 , 7-5	8179.646	-0.270		+ 15	
	9-7 ,11-9	8179.763	-0.153		+ 31	
	7-5 , 9-7	8179.916		8179.029*	- 3	
	7-5 , 5-3	8180.049	+0.133		+ 59	
3 1 3 – 2 1 2	5-3 , 5-3 7-5 , 7-5	7764.359	-4.100		+ 16	
	7-5 , 9-7 5-3 , 7-5	7764.966	-3.493		- 38	
	7-5 , 5-3	7765.083	-3.376		+ 18	
	9-7 , 9-7	7768.025	-0.434		+ 48	
	9-7 ,11-9 9-7 , 7-5 3-1 , 5-3	7768.459		7766.834*	- 13	
4 0 4 – 3 0 3	5-3 , 5-3 5-3 , 3-1 7-5 , 7-5	10833.800	-1.699		+ 82	
	5-3 , 7-5 7-5 , 5-3 7-5 , 9-7	10834.150	-1.349		+ 60	
	9-7 , 9-7 11-9 ,11-9 11-9 , 9-7	10835.499		10835.169*	- 8	
	11-9 ,13-11	10835.628	+0.129		+ 36	
	9-7 , 7-5 9-7 ,11-9	10835.784	+0.285		+ 31	
4 1 3 – 3 1 2	7-5 , 7-5	11572.598	-2.471		- 3	
	7-5 , 9-7 7-5 , 5-3	11572.953	-2.116		+ 31	
	9-7 , 9-7	11573.486	-1.583		+ 44	
	9-7 ,11-9 9-7 , 7-5	11573.691	-1.378		- 22	
	5-3 , 5-3	11573.947	-1.122		- 23	
	5-3 , 7-5 5-3 , 3-1	11574.249	-0.820		- 20	
	11-9 ,11-9	11574.860	-0.209		- 4	
	11-9 ,13-11 11-9 , 9-7	11575.069		11574.164*	- 2	
4 2 2 – 3 2 1	9-7 , 9-7	11123.715	-5.683		0	
	9-7 ,11-9	11124.153	-5.245		- 34	
	9-7 , 7-5	11124.265	-5.133		- 8	
	7-5 , 7-5	11125.763	-3.635		- 9	
	7-5 , 9-7	11126.157	-3.241		- 16	
	7-5 , 5-3	11126.31	-3.088		+ 23	
	11-9 ,11-9	11129.398		11127.714*	- 12	
	11-9 ,13-11	11129.966	+0.568		- 3	
	11-9 , 9-7	11130.084	+0.686		+ 6	
	5-3 , 5-3	11131.434	+2.036		- 18	
	5-3 , 7-5	11131.898	+2.500		- 19	
	5-3 , 3-1	11132.128	+2.730		+ 1	
4 2 3 – 3 2 2	9-7 , 9-7	10971.456	-0.521		- 5	
	9-7 ,11-9	10971.977		10975.424*	- 19	
	9-7 , 7-5	10972.065	+0.088		+ 12	
	7-5 , 7-5	10973.540	+1.563		+ 21	
	7-5 , 9-7	10973.956	+1.979		+ 10	
	7-5 , 5-3	10974.074	+2.097		+ 19	
	11-9 ,11-9	10977.050	+5.073		+ 14	
	11-9 ,13-11	10977.653	+5.676		+ 11	
	11-9 , 9-7	10977.779	+5.802		+ 18	

Table 2. Rotational and quadrupole coupling constants [MHz] of 4-chloropyridine-[^{35}Cl] and -[^{37}Cl] determined from all measured transitions. σ standard deviation of the fit in kHz, $|(B, C)|$ maximum correlation coefficient. Single standard errors in brackets. Derived parameters below the line.

4-chloropyridine-[^{35}Cl]		4-chloropyridine-[^{37}Cl]	
A	6019.0(4)	A	6019.1(7)
B	1572.631(2)	B	1528.210(5)
C	1246.748(2)	C	1218.659(6)
σ	14	σ	31
$\|(B, C)\|$	0.792	$\|(B, C)\|$	0.833
$\chi_{aa}(^{35}\mathrm{Cl})$	− 71.65(2)	$\chi_{aa}(^{37}\mathrm{Cl})$	− 56.4(1)
$\chi_{bb}(^{35}\mathrm{Cl})$	+ 39.25(11)	$\chi_{bb}(^{37}\mathrm{Cl})$	+ 30.8(3)
χ_{aa}(N)	− 4.81(1)	χ_{aa}(N)	− 4.7(1)
χ_{bb}(N)	+ 1.64(4)	χ_{bb}(N)	+ 1.5(1)
σ	15	σ	34
$\|(\chi_{aa}(\mathrm{Cl}), \chi_{bb}(\mathrm{Cl}))\|$	0.197	$\|(\chi_{aa}(\mathrm{N}), \chi_{bb}(\mathrm{N}))\|$	0.303
$\chi_{cc}(^{35}\mathrm{Cl})$	+ 32.40(11)	$\chi_{cc}(^{37}\mathrm{Cl})$	+ 25.6(3)
χ_{cc}(N)	+ 3.17(4)	χ_{cc}(N)	+ 3.2(1)

adding the hfs corrections to the frequencies of the strongest multiplet components. The transitions marked by asterisks were used for a rigid rotor analysis to refine the rotational constants. This refinement did not influence the hfs analysis.

The rotational and quadrupole coupling constants are given in Table 2. The standard errors of the rotational constants of the ^{37}Cl-species are higher as lines with higher J had to be included in the fit.

The coupling constants of the ^{37}Cl isotopomer are determined less precise. This reflects the lower isotopic abundance. Within the single standard error there is a rough agreement of the nitrogen coupling constants. We used the programs Q2SIM [9] and Q2FIT [10] for the hfs and DH9 [11] for the rotational analysis. The results for the nitrogen coupling will be discussed in a forthcoming paper.

Chlorine Coupling Discussion

The interpretation of the chlorine quadrupole coupling constants is guided by the Townes-Dailey approach [12]. It is assumed that the C−Cl bond is formed by a partially s-hybridized $3p_z$ orbital, the two counterhybridized lone pair orbitals in the molecular plane being equivalent. The p_y orbital perpendicular to the pyridine ring is further supposed to interfere with the π orbitals of the aromatic system, lowering its occupation and forming a partial double bond.

The ionic character i_σ of the C−Cl bond and the double bond charater i_π serve as determinable variables. The hybridization parameter a_s^2 is assumed to be 15% [13] for the C−Cl bond.

The four valence orbitals are described by

$$\psi_1\,(\sigma\text{ bond}) = a_s\,\psi_s + (1 - a_s^2)^{1/2}\,\psi_{p_z},$$

$$\psi_{2,3}\,(\text{lone pair orbitals}) = (\tfrac{1}{2} - \tfrac{1}{2}\,a_s^2)^{1/2}\,\psi_s \pm (\tfrac{1}{2})^{1/2}\,\psi_{p_x} - (\tfrac{1}{2}\,a_s^2)^{1/2}\,\psi_{p_z},$$

$$\psi_4\,(\pi\text{ bonding orbital}) = \psi_{p_y}. \qquad (1)$$

The occupation numbers are

$$n_1 = 1 + i_\sigma,$$
$$n_2 = n_3 = 2,$$
$$n_4 = 2 - i_\pi. \qquad (2)$$

From (1) and (2)

$$n_x = 2,$$
$$n_y = 2 - i_\pi,$$
$$n_z = 1 + i_\sigma + a_s^2\,(1 - i_\sigma), \qquad (3)$$

result.

The independent coupling constants may then be expressed by

$$\chi_{zz} = \chi_{aa} = [(i_\sigma - 1)\,(1 - a_s^2) + \tfrac{1}{2}\,i_\pi]\,eQq_{310},$$
$$\chi_{xx} = \chi_{bb} = [-\tfrac{1}{2}\,(i_\sigma - 1)\,(1 - a_s^2) + \tfrac{1}{2}\,i_\pi]\,eQq_{310}. \qquad (4)$$

It should be noted that the C−Cl bond is parallel to the principal inertia axis a. From (4) we get

$$i_\pi = \frac{2}{3}\,\frac{(\chi_{aa} + 2\chi_{bb})}{eQq_{310}},$$
$$i_\sigma = 1 + \frac{2}{3}\,\frac{(\chi_{aa} - \chi_{bb})}{eQq_{310}\,(1 - a_s^2)}. \qquad (5)$$

With the experimental data of Table 2 and

$$eQq_{310}(^{35}\mathrm{Cl}) = + 109.74\text{ MHz}$$

and

$$eQq_{310}(^{37}\mathrm{Cl}) = + 86.51\text{ MHz} \quad [14]$$

the double bond characters amount to

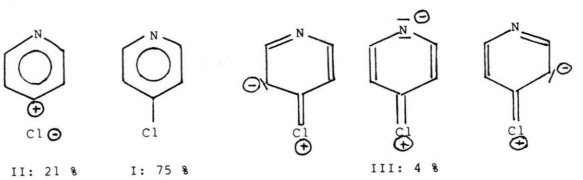
$$i_\pi = 4.2\% \quad \text{and} \quad i_\pi = 4.0\%$$

for the ^{35}Cl and ^{37}Cl species respectively. The ionic characters are

$$i_\sigma = 20.7\% \quad \text{and} \quad i_\sigma = 20.9\% .$$

As we are aware of the approximative nature of this model, no standard errors are given.

The corresponding mesomeric structures and their importance are:



The contribution of III is higher in 4-chloropyridine than in chlorobenzene (3.3% [15]) or 3-chloropyridine (2.9% [16]) but less than the value for 2-chloropyridine (5.4% [17]).

Acknowledgement

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