Nuclear Quadrupole Hyperfine Structure in the Rotational Spectrum of 3-Chloropyridine. An Application of Microwave-Microwave Double Resonance Fourier Transform Spectroscopy

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We redetermined the rotational and the chlorine-35 and nitrogen-14 nuclear quadrupole coupling constants of 3-chloropyridine. The values are $A = 5839.5330(12)$ MHz, $B = 1604.1875(6)$ MHz, and $C = 1258.3121(5)$ MHz for the rotational constants, and $\chi_{aa}(\mathrm{Cl}) = -72.255(19)$ MHz, $\chi_{bb}(\mathrm{Cl}) = +38.500(13)$ MHz, $\chi_{cc}(\mathrm{Cl}) = +33.755(23)$ MHz and $\chi_{aa}(\mathrm{N}) = -0.009(13)$ MHz, $\chi_{bb}(\mathrm{N}) = -3.473(10)$ MHz, $\chi_{cc}(\mathrm{N}) = +3.482(16)$ MHz for the chlorine-35 and nitrogen-14 nuclear quadrupole coupling constants, respectively.

Application of double resonance modulation technique is shown to greatly simplify the assignment of hyperfine structure components even of weak rotational transitions.

Introduction

The rotational spectrum of 3-chloropyridine has been the topic of several investigations [1–3]. Only Brown and Matouskova [2] determined both chlorine and nitrogen quadrupole coupling constants. In the past two years, the rotational spectra of the related compounds 2- and 4-chloropyridine have been investigated in our group [4, 5] employing the high resolution of microwave Fourier transform (MWFT) spectroscopy. The analysis clearly revealed substitutional effects reflected by the respective nuclear quadrupole coupling constants.

In the monohalopyridines, the "*a*"-principal inertia axis practically coincides with the carbon-halogen bond. For 3-chloropyridine, this leads to a relatively small value for the μ_a dipole moment component. Therefore, the spectrum is predominated by several ^{b}R- and ^{b}Q-subbranches. Only very few "*a*"-type transitions have been assigned so far, none of which could be split into the hyperfine structure components. It was a major topic of the present investigation, to employ microwave-microwave double resonance (MWFTDR) modulation to simplify or even make possible the analysis of relatively weak, but widely split low-J "*b*"-type transitions and, if possible, to detect and resolve "*a*"-type transitions.

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Experimental

Pure 3-chloropyridine is a stable, colourless liquid. The substance was purchased from Aldrich Chemie, Steinheim (chemical purity > 98%) and used without further treatment. The spectra were recorded at temperatures of 220–250 K and pressures of 0.1–1 Pa (0.7–7.5 mTorr). Data acquisition time was 20 µs/cycle in most cases, while 5–50 million experiment cycles were necessary to achieve reasonable signal-to-noise ratios. We used our MWFT-spectrometers in the signal frequency range from 5.3 to 18.0 GHz [6–8] (modified to allow for double resonance experiments) and our K-band MWFT-spectrometer (18.0– 26.4 GHz) [9]. The transition frequencies were evaluated from the time domain signals using the least squares fit program written by Haekel [10]. These frequencies are given in Table 1.

Theoretical Aspects

The analysis is based on a first order perturbation treatment employing the coupling scheme $J + I(\mathrm{Cl}) = F_1$, $F_1 + I(\mathrm{N}) = F$ with J = molecular rotation angular momentum operator, I = nuclear spin operators, F_1 = intermediate, F = overall angular momentum operator. We used our programmes Q2SIM [11] and Q2FIT [12]. The coupling constants as well as the hypothetical unsplit line frequencies were fitted to reproduce the frequencies of the hyper-

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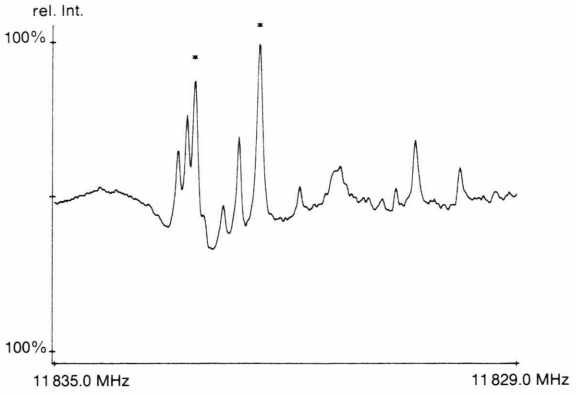
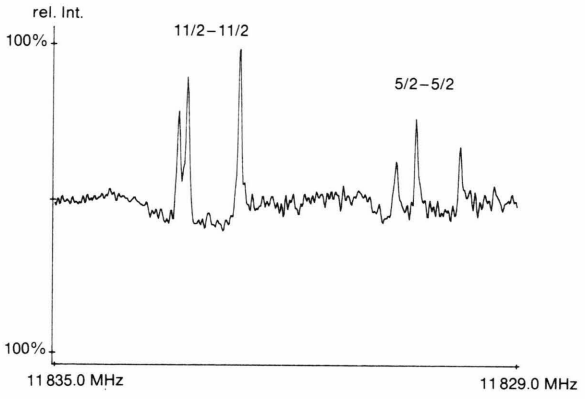
Table 1. Rotational transitions of 3-chloropyridine showing hyperfine structures. The frequencies of the unsplit lines were derived from the least-squares-fit. For all hyperfine components applies $F' - F'' = F_1' - F_1'' = J' - J''$. Centre frequencies marked with asterisks were not used for the determination of the rotational constants.

J' K'_- $K'_+ - J''$ K''_- K''_+	$F_1-J, F-F_1$	ν/MHz	obs −calc / kHz
2 1 2 – 1 0 1	unsplit	9 614.487	*
	+3/2, 0	9 612.594	− 3
	+3/2, +1	9 613.536	+ 3
	+3/2, −1	9 613.879	− 5
	+1/2, 0	9 622.571	+10
	+1/2, +1	9 622.965	−14
	+1/2, −1	9 623.073	+11
2 2 1 – 1 1 0	unsplit	18 776.942	*
	+3/2, −1	18 772.939	− 3
	+3/2, +1	18 773.639	− 3
	+3/2, 0	18 773.917	0
	+1/2, −1	18 782.391	+ 3
	+1/2, +1	18 782.927	+ 1
	+1/2, 0	18 783.558	+ 1
2 2 0 – 1 1 1	unsplit	19 143.148	*
	+3/2, −1	19 139.384	−10
	+3/2, +1	19 139.735	− 9
	+3/2, 0	19 140.566	− 7
	+1/2, 0	19 147.670	− 1
	+1/2, +1	19 148.410	+14
	+1/2, −1	19 148.968	+16
2 2 0 – 2 1 1	unsplit	12 726.375	+ 9
	+3/2, 0	12 717.824	0
	+3/2, +1	12 718.720	+ 3
	+3/2, −1	12 718.882	− 4
3 1 3 – 2 0 2	unsplit	11 966.134	+ 2
	−1/2, 0	11 963.147	− 9
	−1/2, +1	11 963.684	−22
	−1/2, −1	11 963.887	−20
	+3/2, 0	11 964.588	+ 6
	+3/2, +1	11 965.593	+ 9
	+3/2, −1	11 965.839	+12
	+1/2, 0	11 969.781	+ 4
	+1/2, +1	11 970.541	+ 4
	+1/2, −1	11 970.703	+10
3 2 2 – 3 1 3	unsplit	14 274.825	− 4
	+3/2, −1	14 269.962	+ 9
	+3/2, +1	14 270.229	+10
	+3/2, 0	14 271.304	+ 5
	−1/2, −1	14 277.041	−12
	−1/2, +1	14 277.236	−17
	−1/2, 0	14 277.792	−11
	+1/2, −1	14 283.092	+ 7
	+1/2, +1	14 283.259	+ 5
	+1/2, 0	14 284.050	+ 5
4 1 4 – 3 1 3	unsplit	10 719.743	+ 2
	−1/2, 0	10 717.917	− 2
	−1/2, 1	10 718.237	+10
	+1/2, 0	10 718.861	−12
	+1/2, 1	10 719.092	+10
	−3/2, 0	10 719.676	−24
	−3/2, −1	–	–
	−3/2, +1	10 719.983	− 4
	+3/2, 0	10 720.717	+ 2
	+3/2, 1	10 720.821	+20
4 2 3 – 3 2 2	unsplit	11 434.178	+ 5
	+1/2, +1	11 429.599	+ 6
	+1/2, 0		
	−1/2, +1	11 432.125	+ 5
	−1/2, 0		
	+3/2, +1	11 436.788	−10
	+3/2, 0		
	−3/2, +1	–	–
	−3/2, 0		
4 2 2 – 3 1 3	unsplit	26 009.352	− 8
	−3/2, −1	26 003.516	0
	−3/2, +1	26 004.209	+ 3
	−3/2, 0	26 005.202	+ 6
	+3/2, −1	26 007.071	− 1
	+3/2, +1	26 007.406	+ 3
	+3/2, 0	26 008.850	+ 5
	−1/2, −1	26 009.245	−16
	−1/2, +1	26 009.536	−11
	−1/2, 0	26 010.356	−10
	+1/2, −1	26 012.629	0
	+1/2, +1	26 012.886	+15
	+1/2, 0	26 013.963	+ 9
4 1 3 – 4 0 4	unsplit	6 381.963	+ 9
	−3/2, −1	6 379.896	+17
	−3/2, +1	6 380.420	+27
	+3/2, −1	6 380.636	−10
	+3/2, +1	6 380.893	− 9
	−3/2, 0	6 381.594	+ 9
	−1/2, −1	6 381.861	−21
	−1/2, +1	6 382.217	− 4
	+3/2, 0	6 382.328	− 6
	+1/2, −1	6 382.507	+ 2
	+1/2, +1	6 382.796	+ 5
	−1/2, 0	6 383.273	− 8
	+1/2, 0	6 383.947	0
4 2 2 – 4 1 3	unsplit	11 836.093	− 1
	−3/2, 0	11 829.743	+ 8
	−3/2, +1	11 830.309	+ 3
	−3/2, −1	–	–
	+3/2, 0	11 832.599	+11
	+3/2, +1	11 833.272	− 1
	+3/2, −1	11 833.403	+11
	−1/2, 0	11 840.968	− 9
	−1/2, +1	11 841.504	−17
	−1/2, −1	11 841.660	− 5
5 1 4 – 5 0 5	unsplit	7 536.559	+ 1
	−3/2, −1	7 535.224	− 6
	+3/2, −1	7 535.544	− 1
	−3/2, +1	7 535.666	+ 4
	+3/2, +1	7 535.794	+ 2
	−1/2, −1	7 536.133	−13
	+1/2, −1	7 536.382	+11
	−1/2, +1	7 536.463	− 3
	+1/2, +1	7 536.652	+11
	−3/2, 0	7 537.107	− 5
	+3/2, 0	7 537.402	0
	−1/2, 0	7 537.793	−11
	+1/2, 0	7 538.057	+10



a)



b)

Fig. 1a. Frequency range from 11 835.0 MHz to 11 829.0 MHz of the rotational spectrum of 3-chloropyridine, showing part of the transition $J, K_-, K_+ = 4,2,2-4,1,3$. Phase corrected absorption spectra are presented. Polarizing frequency 11 830 MHz, cell temperature −40 °C, gas pressure 6 mTorr, $5 \cdot 10^6$ experiment cycles, delay 800 ns, sample interval 20 ns, 1024 data points supplemented by 3072 zeros prior to Fourier transformation. A perturbing doublet is marked by asterisks.

Fig. 1b. The same range under the influence of double resonance modulation. Pump frequency 26 006 MHz, pump power 100 mW, other experimental conditions as before. F_1 quantum numbers are given.

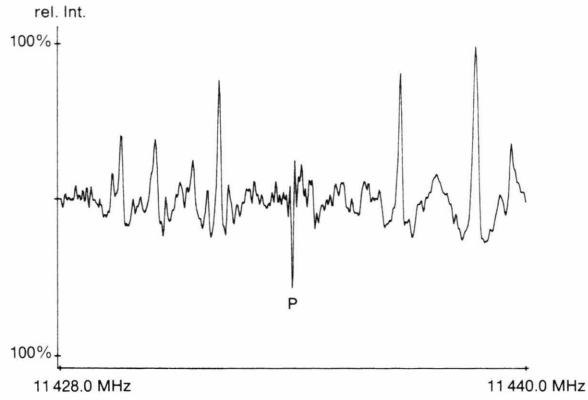
fine components. The centre frequencies were then used to refine the rotational constants in the rigid rotor approximation. The influences of nuclear quadrupole coupling tensor elements off-diagonal in the principal inertial axis system as well as spin-rotation coupling are neglected. The interpretation of the coupling constants thus obtained follows the Townes-Dailey approach [13]. A compilation of the determined parameters is given in Table 2 together with a comparison to earlier values.

Double Resonance Modulation Experiments

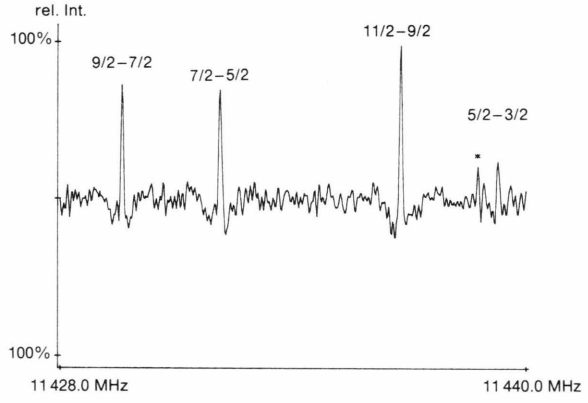
Most of the recorded hyperfine multiplets are overlayed by high-J-transitions of the vibrational ground state and, probably, excited states. Examples are given in Fig. 1a and 2a: Fig. 1a shows part of the transition $J, K_-, K_+ = 4,2,2-4,1,3$ with $F_1 = 11/2-11/2$ and $5/2-5/2$, and an unassigned, strong doublet (*). Figure 2a shows the "a"-type transition $J, K_-, K_+ = 4,2,3-3,2,2$ and a number of comparably strong perturbing lines. However, many of the low-J transitions have one energy level in common with other transitions considerably higher in frequency, so that the double resonance modulation technique [14] is applicable. Although this technique is inherently less sensitive, we were able to detect several weak "a"-type transitions showing hyperfine structures and unambigously assign the hyperfine components. The Fig. 1b and 2b show the double resonance effects: In Fig. 1b, the transition $J, K_-, K_+ = 4,2,2-3,1,3$, $F_1 = 11/2-9/2$ and $5/2-3/2$ near 26 006.0 MHz was pumped. In Fig. 2b, the pump frequency was set to 23 634.0 MHz, were the transition $J, K_-, K_+ = 4,2,3-3,1,2$ is expected. In this case, one of the overlaying lines is also slightly affected by the pump radiation resulting in a small residual peak. These spectra are given in the

	This work	[1]	[2]	[3]
A	5839.5330(12)	5839.448(27)	5839.53 (3)	5839.652 (15)
B	1604.1875 (6)	1604.152 (5)	1604.19 (1)	1604.392 (7)
C	1258.3121 (5)	1258.327 (4)	1258.31 (1)	1258.531 (7)
χ_{aa}(Cl)	−72.255 (19)	−70.04 (38)	−72.15	−71.58 (102)
χ_{bb}(Cl)	+38.500 (13)	+36.58 (19)	+38.68(19)	+37.63 (145)
χ_{cc}(Cl)	+33.755 (23)	–	+33.66(10)	+33.95 (102)
χ_{aa}(N)	−0.009 (13)	–	−0.08	–
χ_{bb}(N)	−3.473 (10)	–	−3.41(10)	–
χ_{cc}(N)	+3.482 (16)	–	+3.49(10)	–

Table 2. Comparison of the molecular parameters (in MHz) of 3-chloropyridine determined in this work with those of other authors.



a)



b)

Fig. 2a. Frequency range from 11 428.0 MHz to 11 440.0 MHz showing the transition $J, K_-, K_+ = 4,2,3-3,2,2$. Polarizing frequency 11 434 MHz, sample interval 10 ns, other conditions as in Figure 1a. P = coherent perturbation.

Fig. 2b. The same range with a pump radiation of frequency 23 634 MHz and power 100 mW. F_1 quantum numbers are given. The distorted line marked by an asterisk does not belong to the hyperfine pattern.

form of phase-corrected absorption spectra [15]. The phase correction parameters were adjusted in order to give symmetric line shapes for the lines of interest. This technique clearly shows the phase of the extra-peak (*), not perfectly suppressed by double resonance modulation, to be severely distorted, thus giving a dispersion-like line shape.

Discussion

In Table 3, the nuclear quadrupole coupling constants of 3-chloropyridine are compared to those of 2- and 4-chloropyridine, and chlorobenzene and pyridine, respectively. Because of the differing orientation of the nitrogen bonds with respect to the principal inertia axis systems, the χ_{aa} and χ_{bb} constants of nitrogen-14 are not directly comparable. However, the fact that the χ_{cc}(N) coupling constants of pyridine and 3-chloropyridine are equal within the error limits, indicates that in 3-chloropyridine there is no detectable effect due to chlorine substitution. This is in contrast to the results for 2- and 4-chloropyridine [4, 5]. With the assumption that the nitrogen nuclear quadrupole coupling tensors of pyridine and 3-chloropyridine differ only in orientation, the angle enclosed by the "z"-principal axis of the coupling tensor and the "a"-principal inertia axis can be determined using [16]

$$\cos^2\varphi = \frac{1}{2}\left(\frac{\chi'_{aa} - \chi'_{bb}}{\chi_{aa} - \chi_{bb}} + 1\right)$$

(primed: constants of 3-chloropyridine, unprimed: constants of pyridine [17]). The result, $\varphi = 61.65$ deg, is in agreement with the plausible structure given in [1]. On the other hand, the chlorine-35 coupling constants of

Table 3. Comparison of quadrupole coupling constants, ionic i_δ and double i_π bond characters of carbon-chloride bonds.

	2-	4-	3-	chlorobenzene
	chloropyridine			
χ_{aa}(Cl)/MHz	−70.42(4)	−71.65 (3)	−72.255(19)	−71.09 (10)
χ_{bb}(Cl)/MHz	+39.69(2)	+39.25(22)	+38.500(13)	+38.18 (49)
χ_{cc}(Cl)/MHz	+30.73(4)	+32.40(22)	+33.755(23)	+32.91 (50)
i_σ/%	21.3	20.7	20.9	21.9
i_π/%	5.4	4.2	2.9	3.2
				pyridine
χ_{aa}(N)/MHz	−0.09(2)	−4.81 (3)	−0.009(13)	−4.908 (5)
χ_{bb}(N)/MHz	−2.94(2)	+1.64 (7)	−3.473(10)	+1.434 (5)
χ_{cc}(N)/MHz	+3.03(3)	+3.17 (8)	+3.482(16)	+3.474 (5)

3-chloropyridine are in rough agreement with those of chlorobenzene [18]. Thus, it is confirmed that there is no noticable interaction between the nitrogen and chlorine nuclei via molecular orbitals. With the common assumption of 15% s-character ($a_s^2 = 0.15$) of the carbon-chlorine bond [13] and the formula given in [5], the ionic and the double bond character of this bond can be evaluated to $i_\sigma = 20.9\%$ and $i_\pi = 2.9\%$, respectively.

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