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Microwave Spectrum and Quadrupole Coupling Constants of Orthochloropyridine

F. SCAPPINI * and A. GUARNIERI

Abteilung für Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

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The rotational spectrum of 2-chloropyridine was measured in the region between 8—40 GHz. The rotational constants for the vibrational ground state are:

$A = 5872.01 \pm 0.02$ MHz, $B = 1637.82 \pm 0.02$ MHz, $C = 1280.51 \pm 0.02$ MHz.

The value 0.0385 amu·A^2 of the inertia defect indicates a planar nuclear frame. From the hyperfine splittings of the rotational lines the nuclear quadrupole coupling constants of ^{35}Cl were determined. The values are:

$\chi_{aa} = -70.79 \pm 0.17$ MHz, $\chi_{bb} = 39.01 \pm 0.45$ MHz, $\chi_{cc} = 31.78 \pm 0.62$ MHz.

Microwave Zeeman studies of ring currents induced by strong magnetic fields on ring molecules have already been made in this laboratory on 2-fluoropyridine [1] and on isotopically substituted pyridine [2], furane [3] and selenophene [4]. To support the study of the series of halogen derivatives of pyridine, we have also investigated the microwave spectrum of 2-chloropyridine.

The spectrum was analyzed in the region between 8 and 40 GHz with a conventional Stark modulation microwave spectrograph [5, 6], employing stabilized BWO's as radiation sources.

The pressure of the gas was kept around one micron and the temperature around −50 °C. The molecule exhibited a very rich spectrum showing a- and b-type transitions with resolved quadrupole patterns due to the ^{35}Cl nucleus.

The a-type lines were identified on the basis of the guessed structure, which allowed us to predict with a good approximation the sequence of the K-doublets. The characteristic quadrupole patterns were also helpful. Values of the rotational constants B and C were thus obtained. However, these lines

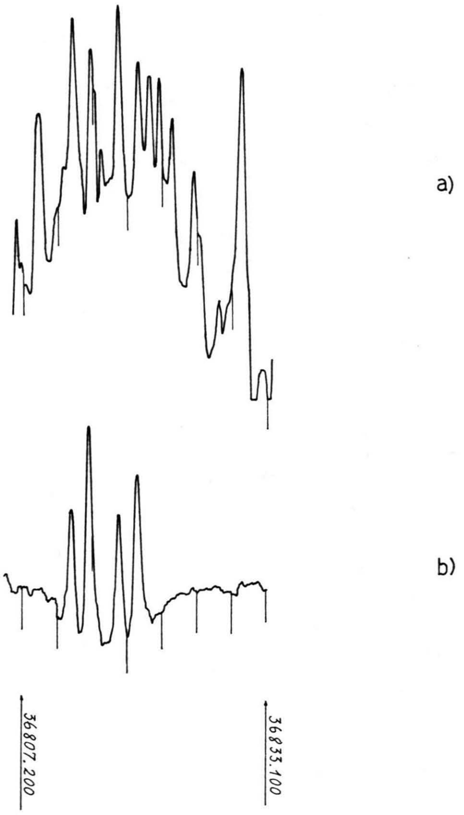

Fig. 1. Spectra of 2-chloropyridine. (a) Stark spectrum with a field strength of 200 V/cm. (b) RFMDR spectrum of the same region with a pump frequency of 23 MHz.

Reprint requests to Prof. Dr. A. GUARNIERI, Institut für Physikalische Chemie der Universität Kiel, Abt. Chemische Physik, *D-2300 Kiel*, Olshausenstraße 40—60.

* On leave from Laboratorio di Spettroscopia Molecolare, Bologna, Italy.

Table 1. Measured transitions of 2-chloropyridine. Frequencies are in MHz. Transitions labeled with ^{a} were used to obtain the rotational constants. Those labeled with ^{b} were used to obtain the quadrupole coupling constants.

$J_{K_-K_+}$	$J'_{K'_-K'_+}$	F	F'	ν_{exp}	$\tilde{\nu}$	$\tilde{\nu}_{\text{calc}}$	$\Delta\tilde{\nu}_{(\text{exp}-\text{calc})}$	ν_{calc}	$\Delta\nu_{(\text{exp}-\text{calc})}$
3_{21}	$2_{20}^{a,b}$	9/2	7/2	8,846.115	8,841.105	8,841.160	− 0.055	8,846.279	− 0.164
		7/2	5/2	8,828.415				8,828.411	+ 0.004
		5/2	3/2	8,841.097				8,841.103	+ 0.006
3_{12}	2_{11}^{a}	9/2	7/2	9,278.975	9,277.031	9,276.991	+ 0.040	9,278.918	+ 0.057
		7/2	5/2	9,274.555				9,274.532	+ 0.023
3_{13}	2_{12}^{a}	$\left.\begin{matrix}9/2\\3/2\end{matrix}\right\}*$	7/2 1/2	8,207.709	8,205.891	8,205.856	+ 0.035	8,207.715	− 0.006
		$\left.\begin{matrix}7/2\\5/2\end{matrix}\right\}*$	5/2 3/2	8,203.416				8,203.340	+ 0.076
3_{22}	2_{21}	9/2	7/2	8,760.150	8,755.210	8,754.993	+ 0.172	8,760.049	+ 0.101
		7/2	5/2	8,742.685				8,742.353	+ 0.332
3_{31}	$2_{20}^{a,b}$	9/2	7/2	30,808.304	30,810.674	30,810.709	− 0.035	30,808.370	− 0.066
		7/2	5/2	30,812.845				30,812.876	− 0.031
		5/2	3/2	30,815.108				30,815.126	− 0.018
		3/2	1/2	30,810.598				30,810.620	− 0.022
3_{30}	$2_{21}^{a,b}$	9/2	7/2	30,830.956	30,833.249	30,833.206	+ 0.043	30,830.901	+ 0.055
		7/2	5/2	30,835.367				30,835.287	+ 0.080
		5/2	3/2	30,837.621				30,837.622	− 0.001
		3/2	1/2	30,833.275				30,833.236	+ 0.039
4_{13}	3_{12}^{a}	11/2	9/2	12,343.143	12,342.125	12,342.054	+ 0.071	12,343.103	+ 0.040
		9/2	7/2	12,341.446				12,341.395	+ 0.051
		7/2	5/2	12,340.475				12,340.354	+ 0.121
5_{32}	$5_{23}^{a,b}$	13/2	13/2	21,537.936	21,541.577	21,541.551	+ 0.026	21,537.950	− 0.014
		11/2	11/2	21,547.358				21,547.313	+ 0.045
		9/2	9/2	21,544.707				21,544.672	+ 0.035
		7/2	7/2	21,535.346				21,535.309	+ 0.037
5_{33}	$4_{22}^{a,b}$	13/2	11/2	36,471.188	36,473.206	36,473.214	− 0.008	36,471.194	− 0.006
		11/2	9/2	36,476.864				36,476.859	+ 0.005
		9/2	7/2	36,474.722				36,474.743	− 0.021
		7/2	5/2	36,469.068				36,469.078	− 0.010
5_{32}	4_{23}	13/2	11/2	36,814.200	36,816.005	36,816.032	− 0.027	36,814.211	− 0.011
		11/2	9/2	36,819.280				36,819.330	− 0.050
		9/2	7/2	36,817.364				36,817.402	− 0.038
		7/2	5/2	36,812.276				36,812.283	− 0.007
6_{42}	5_{41}	15/2	13/2	17,586.906	17,583.828	17,584.314	− 0.486	17,587.403	− 0.497
		13/2	11/2	17,578.941				17,579.275	− 0.334
		11/2	9/2	17,581.052				17,581.678	− 0.626
6_{51}	5_{50}^{a}	15/2	13/2	17,568.983	17,564.232	17,564.267	− 0.035	17,568.929	+ 0.054
		13/2	11/2	17,556.243				17,556.253	− 0.010
		11/2	9/2	17,560.311				17,560.461	− 0.150
6_{33}	$5_{32}^{a,b}$	15/2	13/2	17,654.627	17,652.716	17,652.748	− 0.032	17,654.628	− 0.010
		13/2	11/2	17,649.974				17,650.002	− 0.028
		11/2	9/2	17,650.959				17,651.007	− 0.048
		9/2	7/2	17,655.581				17,655.633	− 0.052
6_{52}	5_{51}^{a}	15/2	13/2	17,568.983	17,564.232	17,564.259	− 0.027	17,568.922	+ 0.061
		13/2	11/2	17,556.243				17,556.246	− 0.003
		11/2	9/2	17,560.311				17,560.454	− 0.143
6_{34}	$5_{33}^{a,b}$	15/2	13/2	17,609.310	17,607.464	17,607.402	+ 0.062	17,609.263	+ 0.047
		13/2	11/2	17,604.755				17,604.683	+ 0.072
		11/2	9/2	17,605.744				17,605.679	+ 0.065
		9/2	7/2	17,610.327				17,610.259	+ 0.068
6_{43}	5_{42}	15/2	13/2	17,586.906	17,583.828	17,583.384	+ 0.444	17,586.472	+ 0.434
		13/2	11/2	17,578.941				17,578.346	+ 0.595
		11/2	9/2	17,581.052				17,580.748	+ 0.304

did not define the rotational constant A with enough precision to allow the b-type transitions to be found.

These transitions were identified using the radio frequency-microwave double resonance (RFMDR)[7] technique. The experimental arrangement[8] for the RFMDR consisted of a RF oscillator up to 100 MHz and a BWO for the pump and the signal radiation respectively. The amplitude modulated radio frequency field was introduced into the microwave spectrometer by applying it between septum and walls of the Stark waveguide cell. The matching with the cell was performed using different coils with ferite cores for each particular frequency range covered by the RF oscillator. A radio frequency field of the order of 4 – 10 V/cm was found to be sufficient. Because of the effectiveness of the radio frequency pumping in a quite wide frequency range[7], the RF oscillator remained fixed while the phase-locked signal BWO was swept in search of the double resonance signal.

Figure 1 shows an example of both Stark and RFMDR spectra. Table 1 lists the a-type and the b-type transition frequencies which were measured, and in Fig. 2 are shown the schemes of the levels involved in the RFMDR.

The rotational constants of Table 2 were obtained by a least square fitting procedure based on a rigid rotor model. The errors are derived from the estimated error of the lines, which is 30 KHz.

Table 2. Rotational constants of 2-chloropyridine.

Rotational constants	Moments of inertia[a]
$A = 5872.01 \pm 0.02$ MHz	$I_A = 86.0652$ amu · A^2
$B = 1637.82 \pm 0.02$ MHz	$I_B = 308.5653$ amu · A^2
$C = 1280.51 \pm 0.02$ MHz	$I_C = 394.6690$ amu · A^2
$\varkappa = -\ 0.844356$	$\Delta = I_C - I_B - I_A$ $= 0.0385$ amu · A^2

[a] Conversion factor = 505376 MHz · amu · A^2

A Watson type centrifugal distortion analysis confirmed the rotational constants within experimental errors.

In all the measured lines no splitting due to the ^{14}N nucleus was so effective as to be measured. The values for the quadrupole coupling constants of the ^{35}Cl nucleus are reported in Table 3. Since in this molecule the C – Cl bond practically coincides with the a axis (see Fig. 3), the elements of the quadrupole coupling tensor in the principal axis system and in that axis system corresponding to z along the C – Cl bond and x in the plane of the molecule are the same within experimental errors.

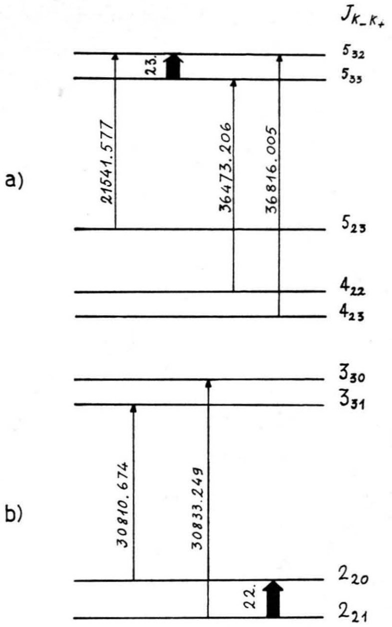

Fig. 2. Double resonance schemes (a, b) in 2-chloro-pyridine. Frequencies are in MHz. The drawings are not to scale.

Table 3. Quadrupole coupling constants of ^{35}Cl in 2-chloropyridine.

$\chi_{aa} = -70.79 \pm 0.17$ MHz
$\chi_{bb} = \ \ 39.01 \pm 0.45$ MHz
$\chi_{cc} = \ \ 31.78 \pm 0.62$ MHz
$\eta \ \ = (\chi_{xx} - \chi_{yy}) / \chi_{zz} = -0.10 \pm 0.01$

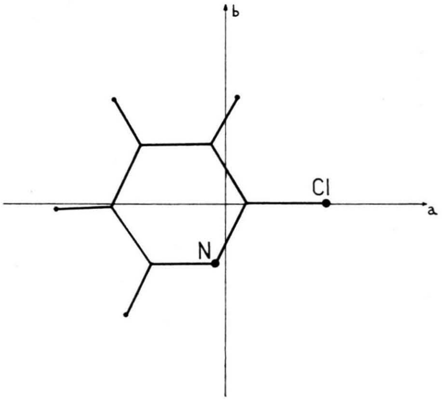

Fig. 3. Coordinates of 2-chloropyridine in the principal axis system.

The value of $U_{\mathrm{p}} = q_{\mathrm{m}} / q_{\mathrm{at}}$ expressing the number of unbalanced electrons along the bond axis[9], was found to be 0.64. The positive sign of this quantity indicates a deficit of electrons along the bond axis relative to the number of electrons in the p_x and p_y orbitals.

The amount of double bond character $\delta = \Delta_{\text{m}}/\Delta_{\text{at}}$ of the C – Cl bond, as defined by GOLDSTEIN[10], was found to be 4%.

Assuming an s – p hybridization of the Cl atom with a 20% s-contribution[11], the percentage of ionic and covalent character of the C – Cl bond were also calculated. The results are shown in Fig. 4 in which the ortho-chloropyridine is described as a resonating system among three limiting structures.

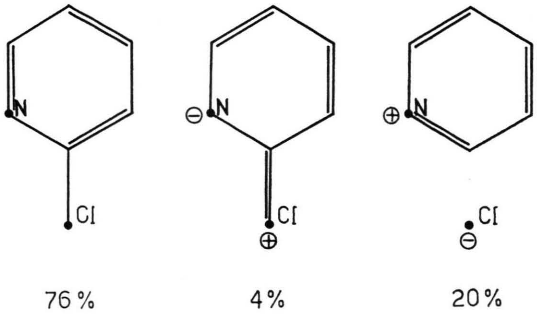

Fig. 4. Bond character in 2-chloropyridine from nuclear quadrupole coupling constants.

Table 4 gives the C – Cl bond length and the N – C – Cl angle obtained by assuming the pyridine structure[12] and fitting these parameters to the rotational constants *.

Table 4. Structural parameters determined for 2-chloropyridine. The errors indicate the limit of accuracy of the fitting procedure.

$r_{\text{CCl}} = 1.72 \pm 0.01$ Å	$\sphericalangle \text{NCCl} = 116°25' \pm 10'$

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* Note added in proof: Dr. S. DORAISWAMY of the Tata Institute, Bombay, has obtained the same rotational constants, within the experimental errors, as those given in this paper — he has also investigated the chlorine 37 species — (private communication).