Microwave Spectrum, Dipole Moment and Quadrupole Coupling Constants of Orthofluoropyridine

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The rotational spectrum of 2-fluoropyridine has been analyzed in the region between 7—40 GHz. The rotational constants for the vibrational ground state are: $A=5870.9_0$ MHz, $B=2699.9_6$ MHz, $C=1849.2_6$ MHz. The small inertia defect indicates that the nuclear frame is planar. The two components of the electric dipole moment were obtained from Stark effect measurements: $\mu_a=2.80\pm0.06$ D, $\mu_b=1.87\pm0.05$ D. These values agree well with an INDO closed molecular orbital calculation done at T.I.F.R. From the hyperfine splittings of the rotational line the ^{14}N nuclear quadrupole coupling constant are determined. The values are:

$$\chi_{aa}=-0.02\pm0.05 \text{ MHz}, \quad \chi_{bb}=-2.80\pm0.05 \text{ MHz}, \quad \chi_{cc}=+2.82\pm0.05 \text{ MHz}.$$

The only microwave studies reported on substituted pyridines are 2-Methyl Pyridine [1] and 4-Methyl Pyridine [2]. The microwave spectrum of orthofluoropyridine (2-Fluoropyridine) has now been analyzed at the Tata Institute of Fundamental Research and the Institut für Physikalische Chemie der Universität Kiel. The preliminary values of the rotational constants had been determined at the former laboratory [3]. Since the results [4] were in good agreement with each other, it was decided to have a joint publication. No electron diffraction work on this molecule has come to our knowledge.

At the Tata Institute, the microwave measurements were carried out at dry ice temperature with a conventional 100 kHz Stark modulation microwave spectrometer in the frequency range of 8 to 18 GHz. The pressure was maintained around a micron. As described in an earlier paper [5], the spectral frequencies were measured using oscilloscope presentation and were reproducible to ±0.05 MHz. At the Kiel University the spectrum was analysed in the region 5 to 40 GHz with a Stark modulation microwave spectrograph [6, 6a] employing phase stabilised BWO's as radiation sources. The absorption cell had a length of 4.50 m with inner dimensions 4.7 cm × 1 cm. It was cooled with methanol flowing through a cooling jacket. The pressure was around a micron and temperatures around -60 °C.

The molecule exhibits a very rich spectrum showing strong a and b type transitions, many of them with resolved quadrupole hyperfine patterns due to the ^{14}N nucleus. The low J lines were identified by their clear Stark patterns and preliminary values of the rotational constants were obtained by transitions

$$2_{11}-1_{10}=3B+C, \quad 2_{12}-1_{11}=B+3C,$$
$$3_{22}-2_{21}=3(B+C), \text{ and } 2_{12}-1_{01}=A+3C.$$

The usual Q line plot further confirmed our results and assignments. The final rotational constants were obtained by a least square fit of many low J lines. Table 1 lists a few R and Q branch transitions and Table 2 gives the rotational constants. If the pyridine structure as evaluated by BAK et al. [8] is assumed, and only the CF bond length and the FCN bond angle are optimized so as to give a best fit of the rotational constants, these values turn out to be 1.300 Å and $117._4^\circ$ respectively. However, NYGAARD et al. [9] in their thorough study on fluoro-

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Table 1.

Transition	ν_{obs} [MHz]	$\nu_{obs-calc}$ [MHz]
2(0,2)−1(0,1)	8949.10[a]	0.038
	8949.05	− 0.019
2(1,2)−1(1,1)	8247.79	0.024
2(1,1)−1(1,0)	9949.14	0.051
2(2,1)−2(1,2)	12064.92⊕	− 0.05
2(2,0)−2(1,1)	9662.46	0.118
2(1,2)−1(0,1)	11418.61⊕	− 0.12
2(2,1)−1(1,0)	19461,894 ± 0.01[a]	− 0.001
3(2,2)−3(0,3)	15103.90	− 0.05
3(0,3)−2(0,2)	13078.30	− 0.06
3(1,3)−2(1,2)	12285.15 ± 0.05[a]	− 0.014
	12285.19	− 0.06
3(1,2)−2(1,1)	14820.64 ± 0.05[a]	− 0.012
	14820.60	0.06
3(2,2)−2(2,1)	13647.60	− 0.04
3(2,1)−2(2,0)	14216.93	0.0
3(2,1)−2(1,2)	26431,344 ± 0.01[a]	0.0
3(2,2)−3(1,3)	13427.38	0.02
3(2,1)−3(1,2)	9058.70⊕	0.01
3(0,3)−2(1,2)	10608.78	0.12
3(1,3)−2(0,2)	14755.00	− 0.05
4(1,3)−4(0,4)	9391,808 ± 0.01 [a],⊕	0.06
4(2,3)−4(0,4)	16266.22	0.02
4(1,3)−4(1,4)	8391.87⊕	− 0.04
4(0,4)−3(0,3)	16917.60	0.06
4(0,4)−3(1,3)	15240.90	− 0.04
4(1,4)−3(1,3)	16240.30	− 0.03
4(2,2)−3(1,3)	33503.96 ± 0.01[a]	0.001
4(3,1)−4(2,2)	16558.60	− 0.05

[a] The frequency measured at Kiel is the weighted average frequency of the HFS multiplet [7]. Frequency uncertainties are due to finite linewidth. The frequency standard used has a long time stability better than $1:10^9$. The measurements at T.I.F.R. were made at higher pressures when the quadrupole splittings were not resolved.

⊕ These lines were not subjected to the least squares fitting procedure for the rotational constants.

benzene have concluded that the CF bond length should be 1.350 Å. Even in polyfluorocompounds like C_6F_5H [5], C_6F_5CN [10], C_6F_6 [11], C_6F_{12} [12] the value for the CF bond length is around 1.330 Å. Therefore the low value of only 1.300 Å for the CF bond length indicates, that the pyridine structure which was assumed in the calculation gets affected by fluorine substitution and a number of isotopical species will have to be studied to give a reliable structure for the molecule.

Values for the two components of the electric dipole moment were calculated from Stark effect measurements. In both laboratories the Stark cell was calibrated using OCS as a standard with

$$\mu_{OCS} = 0.71521 \text{ Debye}\ [13].$$

During the evaluation of the data, the effect of the quadrupole coupling was neglected. The field strength was increased until the calculated components of the electric dipole moment approached the values for the strong field condition. The results ($|\mu| = 3.40$ D at T.I.F.R. and $|\mu| = 3.33$ D at Kiel)

Table 2. Rotational constants and moments of inertia of 2-fluoropyridine.

Kiel [MHz]	T.I.F.R.
$A = 5870.883 \pm 0.014$	$A = 5870.921 \pm 0.007$ MHz[a]
$B = 2699.977 \pm 0.006$	$B = 2699.940 \pm 0.006$ MHz[a]
$C = 1849.246 \pm 0.004$	$C = 1849.271 \pm 0.004$ MHz[a]
	$I_a = 86.081$ amu Å^2
	$I_b = 187.180$ amu Å^2
	$I_c = 273.283$ amu Å^2
	$\Delta = 0.018$ amu Å^2
	Conversion factor = 505376 MHz amu Å^2

[a] These values are square roots of the variances.

Table 3. Electric dipole moment of 2-fluoropyridine. For comparison the values calculated with the INDO method are given too. In this calculation Bak's pyridine structure was used for the ring together with $r_{CF}=1.3$ Å and $\sphericalangle$ FCN$=117.4°$.

Transition		M	E Stark [V/cm]	$\Delta\nu_{obs}$ [MHz]	$\Delta\nu_{calc}$ [MHz]	$(\Delta\nu/E^2)_{obs}$ [MHz/(kV/cm)^2]	$(\Delta\nu/E^2)_{calc}$
2(0,2)−1(0,1)	8949.10	1	337.50	12.07	12.04_4*		
3(1,3)−2(1,2)	12285.15	0	281.2_5	8.07	8.09_8*		
3(1,2)−2(1,1)	14820.64	1	675.0_0	9.38	9.39_8*		
3(1,2)−2(1,1)	14820.60	1				21.3	21.44
2(1,1)−1(1,0)	9949.14	0				17.2	17.16
4(0,4)−3(0,3)	16917.60	2				53.8	53.75
$\|\mu_a\| = 2.78 \pm 0.05$ D*		$\|\mu_b\| = 1.84 \pm 0.05$ D*			$\|\mu\| = 3.33 \pm 0.08$ D*		
$\|\mu_a\| = 2.82 \pm 0.06$ D		$\|\mu_b\| = 1.91 \pm 0.03$ D			$\|\mu\| = 3.40 \pm 0.07$ D		
$\mu_{a\,INDO} = 2.65$ D		$\mu_{b\,INDO} = -1.83$ D			$\|\mu_{INDO}\| = 3.22$ D		

* Values obtained at Kiel.

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are given in Table 3. An INDO closed molecular orbital calculation using the program of DOBOSH [14] done at T.I.F.R. gives for the total dipole moment a value of 3.22 D, which is in good agreement with the above values (compare Fig. 1 and Table 3).

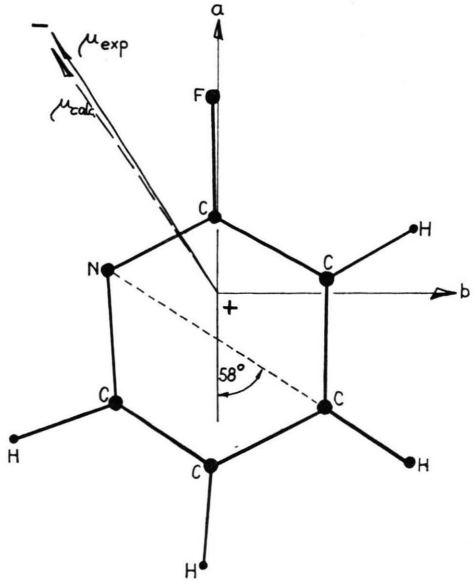

Fig. 1.

Using the usual first order theory (see for instance [15, 16]) the quadrupole coupling constants of the N^{14} nucleus were calculated. The measurements at T.I.F.R. were done at lower resolution and the $F = J+1 \rightarrow J+1$ and $F = J-1 \rightarrow J-1$ components given in Table 4a could be resolved only partly. The values for the quadrupole coupling constants are given in Table 5. In Table 6 the coupling constants are compared with those of pyridine [18]. For this purpose the coupling tensor was transformed into the pyridine principal axis system through a rotation of 31° 56′ and it was assumed that the off-diagonal element χ_{xy} caused by the fluorine substitution is sufficiently small to be neglected. In columns 2 and 4 of Table 6 coupling constants as obtained from NQR measurements in the solid state are listed for comparison. Using relations derived

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Table 4. Quadrupole hyperfine splittings.

4a) (T.I.F.R.).

$J_{K-K+} - J'_{K'-K'+}$	$\Delta\nu_{obs}$ [MHz]	$(\Delta\nu_{obs} - \Delta\nu_{calc})$ [MHz]
$3_{22} - 3_{13}$	0.99	− 0.02
$4_{23} - 4_{14}$	1.08	0.02
$5_{14} - 4_{23}$	0.60	0.01
$5_{14} - 5_{05}$	1.59	− 0.01
$6_{15} - 6_{06}$	1.55	0.03
$7_{25} - 7_{26}$	1.24	− 0.03
$7_{25} - 7_{16}$	0.96	0.05
$8_{26} - 8_{17}$	1.04	− 0.02
$10_{37} - 10_{28}$	0.64	0.01
$10_{37} - 10_{38}$	0.97	− 0.05
$19_{613} - 19_{614}$	0.72	0.02

$\Delta\nu = \nu_{J\rightarrow J} - \nu_{J+1\rightarrow J+1}$ for Q-branch lines,
$= \nu_{J\rightarrow J-1} - \nu_{J+1\rightarrow J}$ for R-branch lines.

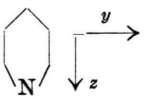
4b) (KIEL).

$J_{K-K+} \rightarrow J'_{K'-K'+}$ $\bar{\nu}_{obs}$ [MHz]	$F \rightarrow F'$	$(\nu_{F\rightarrow F'} - \bar{\nu})_{obs}$ [MHz]	$(\nu_{F\rightarrow F'} - \bar{\nu})_{calc}$ [MHz]
$1_{11} \rightarrow 2_{12}$	$2 \rightarrow 3$	+ 0.051	+ 0.055
8247.689	$1 \rightarrow 2$		+ 0.002
	$0 \rightarrow 1$	− 0.689	− 0.706
	$2 \rightarrow 2$	− 0.840	− 0.843
	$1 \rightarrow 1$	+ 1.391	+ 1.406
$4_{04} \rightarrow 4_{13}$	$4 \rightarrow 4$	+ 1.137	1.133
9391.808	$4 \rightarrow 5$		0.392
	$5 \rightarrow 4$		0.329
	$4 \rightarrow 3$		0.177
	$3 \rightarrow 4$		0.123
	$5 \rightarrow 5$	− 0.403	− 0.412
	$3 \rightarrow 3$	− 0.823	− 0.809
$1_{10} \rightarrow 2_{11}$	$2 \rightarrow 2$	0.777	0.844
9949.190	$0 \rightarrow 1$		0.700
	$1 \rightarrow 2$	− 0.049	+ 0.002
	$2 \rightarrow 3$		− 0.061
	$1 \rightarrow 1$	− 1.401	− 1.406
$1_{01} \rightarrow 2_{12}$	$0 \rightarrow 1$	0.711	0.706
11418.604	$1 \rightarrow 1$		0.700
	$2 \rightarrow 3$	0.204	0.201
	$2 \rightarrow 2$	− 0.713	− 0.702
	$1 \rightarrow 2$		− 0.704
$3_{12} \rightarrow 4_{22}$*	$4 \rightarrow 5$	− 0.443	− 0.450
33503.960	$3 \rightarrow 4$	+ 1.299	+ 1.300
	$2 \rightarrow 3$	− 0.998	− 0.993
$2_{12} \rightarrow 3_{21}$*	$3 \rightarrow 4$	− 0.329	− 0.327
26431.344	$2 \rightarrow 3$	+ 1.085	+ 1.081
	$1 \rightarrow 2$	− 1.007	− 1.005
$1_{10} \rightarrow 2_{21}$*	$2 \rightarrow 3$	+ 0.142	+ 0.141
19461.894	$1 \rightarrow 2$	− 0.704	− 0.703
	$0 \rightarrow 1$	+ 1.406	+ 1.406

$\bar{\nu}_0$ is the weighted average frequency [7] of the transition. Only the transitions denoted with * have been used for the least squares fit of the coupling constants.

by LUCKEN [17, 19] it is possible to calculate electron occupation numbers for the nitrogen π- and σ-bonding molecular orbitals:

$$\begin{aligned} -1/2\,a - 1/6\,b &= \chi_{zz}/\chi_p - 4/3\,, \\ (3\eta - 9)\,a + (\eta + 9)\,b &= 8\eta\,, \\ \eta &= (\chi_{yy} - \chi_{xx})/\chi_{zz} \end{aligned}$$



Here a is the occupation number of the p_x-orbital perpendicular to the plane of the ring, which contributes to the π-system. b is the occupation number of each of the two σ-bonds (sp^2-hybridization is assumed for the nitrogen molecular orbitals).

$$\chi_p = -e^2 Q \int \psi_p \frac{3\cos^2\Theta - 1}{r^3} \psi_p \, d\tau = -10\ \text{MHz}\ [20].$$

From the above equations one gets for 2-fluoropyridine:

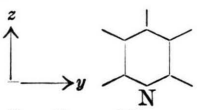
$$\begin{aligned} a &= 1.29 \pm 0.02 + 0.07\,|\,\Delta\chi_p\,|\,), \\ b &= 1.36 \pm (0.01 + 0.06\,|\,\Delta\chi_p\,|) \end{aligned}$$

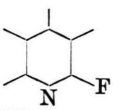
where $\Delta\chi_p$ is the uncertainty of χ_p. The values for pyridine calculated from the gas phase coupling constants [18] are: $a = 1.23$, $b = 1.37$. Thus the in plane electron density represented by b (which gives a positive contribution to the coupling constant χ_{cc} perpendicular to the ring) remains essentially unchanged, while the π-electron density represented by a (which gives a negative contribution to χ_{cc}) is slightly increased in 2-fluoropyridine when compared with pyridine. This is consistent with the decrease of χ_{cc} when going from pyridine to 2-fluoropyridine. One should however keep in mind that the interpretation of the coupling constants within the frame given above is based upon rather crude assumptions as is discussed in detail in the papers of SCHEMP and BRAY [17] and BONACCORSI, SCROCCO and TOMASI [21].

Table 5. Quadrupole coupling constants. The errors are twice the standard deviations.

T.I.F.R.	Kiel
$\chi_{aa} = -0.04 \pm 0.05$ MHz	$+0.01 \pm 0.04$ MHz
$\chi_{bb} = -2.78 \pm 0.05$ MHz	-2.82 ± 0.03 MHz
$\chi_{cc} = +2.83 \pm 0.05$ MHz	$+2.81 \pm 0.03$ MHz

Table 6. Comparison of the N^{14} coupling constants for pyridine and 2-fluoro-pyridine as obtained from the hyperfine splittings of the rotational transitions of free molecules (microwave data) and from direct transitions between the quadrupole hyperfine levels in a molecular crystal (NQR data). Although the accuracy of the microwave results is considerably less than that of the NQR data, the differences clearly indicate that the nitrogen bonds get affected in the molecular crystal.





Coupling const. (MHz)	Microwaves [18] (gas phase)	NQR [17] (solid state)	Microwaves (gas phase	NQR [17] (sol. state)
χ_{xx}	+3.45	+3.200	$+2.82 \pm 0.05$	+2.59766
χ_{yy}	+1.43	+1.384	$+1.81 \pm 0.05$	+1.60465
χ_{zz}	−4.88	−4.5845	-4.62 ± 0.05	−4.20231

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