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Microwave Spectra and Structures of 2-fluoro-4-picoline

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Highlights

- The ground state rotational spectra of 2-fluoro-4-picoline and its mono-substituted ¹³C and ¹⁵N isotopologues were assigned.
- The V_3 barrier to the internal rotation of CH₃ has been estimated from the unexpected low values of the inertial defects
- Fluorination effect on the aromatic ring alters the geometry.

Graphical abstract

Abstract

Rotational spectra of the ground state of 2-fluoro-4-picoline and its mono-substituted ^{13}C and ^{15}N isotopologues in nature abundance have been measured and assigned using pulsed jet Fourier transform microwave spectroscopic technique. The rotational spectrum displays the features of the quadrupole coupling effect of the ^{14}N nucleus with a near-free internal rotation of CH_3 top. The V_3 barrier (16 cm^{-1}) to the internal rotation of CH_3 has been estimated from the unexpected low values of the inertial defects.

Key words: Rotational spectra; internal rotation; fluorine substitution; inertial defect

1. Introduction

Fluorination has an important role in the pharmaceuticals, agrochemicals and materials [1-3]. The presence of fluorine has the potential to influence the biophysical properties of a molecule because of its size, electronegative and low polarizability [4,5]. At the molecular level, fluorination effect is often significant in changing the conformations, molecular structures and internal dynamics, which can be accurately described from the high resolution rotational spectroscopic investigations [6-8].

According to the rotational studies of fluoropyridine [9,10], fluorobenzene [11-13], fluorocyanobenzene [14] and fluorothiophenol [15], the fluorination at the *ortho* position of the aromatic ring has the largest geometry changes with an increase in the ring angle at that site by 3-4°, and a reducing of the adjacent C-C bonds by 0.006-0.015 Å. Besides the structural changes, recent studies on 2-fluorobenzylamine [16], 2-fluorophenylethanol [17] and fluorobenzyl alcohol derivatives [18-21] have shown that fluorination can also bring great alterations to conformational preferences.

Influence of the fluorination on the large amplitude motion is another interesting rotational feature caused by a considerable change in the steric effect and the electronic potential in the substituted region. For instance, toluene and *p*-fluorotoluene have V_6 barriers to the methyl internal rotation to be 57.87337 J/mol [22,23] and 57.777 J/mol [24] respectively, which suggest that fluorination at the *para*-position does not change barrier to methyl internal rotation substantially. However, the substitution in *meta* or *para*- position may reduce the symmetry and a V_3 potential barrier appears predominantly. Thus, in *m*-fluorotoluene the V_3 barrier found to be 189.535 J/mol [25] whereas in *o*-fluorotoluene it is 2718.87 J/mol [26].

Considerable attention has been devoted in pyridine and its derivatives as the wide range of application in coordination [27] and surface chemistry [28,29], whilst the information on the methyl derivatives is scarce. Rotational study of the 2-picoline found a V_3 barrier to be 2760 GHz ≈ 1101 J/mol [30]. The structures and conformations of 3-picoline and 4-picoline were investigated by the vibrational spectra [31]. Concerning there is no rotational spectra about fluorination effect on the molecular structures and internal dynamics of picolines, herein, the rotational spectrum of 2-fluoro-4-picoline (2F4P) have been investigated using pulsed jet Fourier transform microwave (FTMW) spectroscopic technique. The results are reported below.

2. Experimental

Rotational spectra was measured by using a pulsed jet FTMW [32] spectrometer with a coaxially oriented beam-resonator arrangement (COBRA) configuration [33] built at Chongqing University [34]. The spectrometer covers the 2–20 GHz frequency range and operated with the FTMW++ set of programs. Argon as the carrier gas at a stagnation pressure of 0.01 MPa passed over the sample of 2F4P ($\geq 98\%$, commercial product from Adamas used without further purification) at 313 K and expanded through a solenoid valve (Parker-General Valve, Series 9, nozzle diameter 0.5 mm) into the Fabry-Pérot cavity ($\sim 10^{-4}$ Pa). The spectra of the mono-substituted ^{13}C and ^{15}N isotopologues were measured in natural abundance.

The spectral line positions were determined after Fourier transformation of the time domain signal with 8 k data points, recorded at sampling intervals of 100 ns. Due to the Doppler effect, each rotational transition is split into two component lines. The frequency is calculated from the arithmetic mean of the frequencies of the Doppler components. The accuracy of frequency measurements was better than 3 kHz and lines separated by more than 6 kHz were resolvable.

3. Results and Discussion

3.1 Theoretical calculations

To aid the analysis of rotational spectra, theoretical calculations were first performed by using the program Gaussian 09 [35]. MP2/6-311++G(d,p) level of theory was initially chosen for geometry optimization, because of its proven performance in the prediction of molecular structures and electric dipole moments, including some aromatic molecules with methyl groups, such as *o*-methyl anisole [36], *p*-methyl anisole [37] and 2,5-dimethylthiophene [38]. The molecular structure of 2F4P is shown in Fig.1, where also the principal axes and atom numbering are given. The MP2/6-311++G(d,p) calculated spectroscopic parameters are summarized in the first column of Table 1.

Fig. 1. Structure of 2F4P with principal axes and atom numbering.

The V_3 barrier to the internal rotation of methyl group has been calculated at the same level to be 43 cm^{-1} . Therefore, splittings of rotational transitions contributable to the internal rotation of methyl top might be measured. The inertial defect Δ has been also calculated from theoretical rotational constants and reported in Table 1, which is of the common value contributed by three

methyl hydrogens out of plane.

Table 1

Theoretical and experimental spectroscopic parameters of 2F4P.

	MP2	B3LYP	Exp.
A/MHz	3850.38	3887.10	3920.950(2) ^a
B/MHz	1775.37	1785.70	1788.5169(3)
C/MHz	1224.40	1232.91	1231.2030(2)
χ_{aa}/MHz	-3.105	-3.274	-3.080(3)
$(\chi_{bb}-\chi_{cc})/\text{MHz}$	-2.328	-2.472	-2.268(1)
D_J/kHz	0.063	0.065	0.051(2)
D_{JK}/kHz	0.01	0.170	0.76(1)
D_K/kHz	0.69	0.521	3.1(3)
d_1/kHz	-0.023	-0.022	-0.029(2)
d_2/kHz	-0.047	-0.27	-0.013(2)
$ \mu_a /\text{D}$	4.1	4.1	Strong
$ \mu_b /\text{D}$	0.4	0.4	Weak
$ \mu_c /\text{D}$	0.0	0.0	None
$\Delta/\text{u}\text{\AA}^2$	-3.16	-3.13	-0.98
N^b	-	-	203
σ^c/kHz	-	-	2.7

^a Errors in parenthesis are 1σ uncertainties expressed in units of the last digit.

^b Number of lines in the fit.

^c RMS error of the fit.

3.2 Rotational spectra

Following the theoretical predictions, the preliminary trial search was aimed at finding μ_a - R -branch transitions of 2F4P, which were predicted to be the most intense ones. Based on the ^{14}N ($I=1$) quadrupole hyperfine pattern, as shown in Fig. 2 for the $6_{0,6}\leftarrow 5_{0,5}$ transition for example, it was easy to assign μ_a - R -branch transitions with J_{lower} from 3 to 7 and K_a up to 4 from which the rotational constants A , B and C were well determined. The measurement was then

extended to 47 less intense μ_b -type transitions. No μ_c type transition was observed, which is in coincidence with the fact of the zero value of the μ_c dipole moment component.

In spite of a careful scan up and down about 2 GHz with respect to the frequency of several observed rotational transitions, no transition belonging to the other sub-level E -state could be assigned with unambiguity. It seems that fluorination on the 2-site of the aromatic ring can dramatically impact the internal dynamics of 4-picoline.

Fig. 2. Record $6_{06}-5_{05}$ rotational transition of 2F4P showing the ^{14}N nuclear quadrupole hyperfine structure ($F' \leftarrow F''$). Each line appears as a doublet (indicated by square bracket) due to the instrumental Doppler effect.

The measured transition frequencies were fitted with Pickett's SPFIT program [39], according to the following Hamiltonian:

$$H = H_R + H_{CD} + H_Q \quad (1)$$

where H_R represents the rigid rotational parts of the Hamiltonian. The centrifugal distortion contributions (analyzed by using the S reduction and I^r representation) [40] are represented by

H_{CD} . H_Q is the operator associated with the ^{14}N nuclear quadrupolar interaction. The obtained rotational, centrifugal distortion and quadrupole coupling constants are listed in the third column of Table 1.

After a first structural adjustment, it was possible to assign rotational spectra of all mono-substituted ^{13}C and ^{15}N ($I = 1/2$) isotopologues in natural abundance. All the corresponding spectroscopic parameters are summarized in Table 2. Since much smaller number of lines could be observed, the centrifugal distortion constants cannot be well-determined and are all fixed at the values obtained for the parent species.

Rotational transition frequencies measured for all 8 isotopologues are summarized in the Supplementary Materials.

Table 2

The experimental spectroscopic constants of all measured isotopologues of 2F4P.^a

	$^{15}\text{N}1$	$^{13}\text{C}2$	$^{13}\text{C}3$	$^{13}\text{C}4$	$^{13}\text{C}5$	$^{13}\text{C}6$	$^{13}\text{C}7$
A/MHz	3889.800(6) ^b	3918.801(3)	3891.530(3)	3919.063(3)	3882.371(3)	3832.570(3)	3895.567(3)
B/MHz	1779.1878(3)	1781.1176(3)	1788.5301(3)	1778.2012(3)	1779.6552(3)	1788.5095(3)	1745.8755(3)
C/MHz	1223.7113(3)	1227.4873(1)	1228.3013(1)	1226.1263(1)	1223.1964(1)	1222.3462(2)	1208.4110(1)
χ_{aa}/MHz	-	-3.05(5)	-3.09(5)	-3.05(5)	-3.03(5)	-3.08(5)	-3.15(5)
$(\chi_{bb}-\chi_{cc})/\text{MHz}$	-	-2.260(8)	-2.272(8)	-2.256(8)	-2.368(8)	-2.260(8)	-2.172(8)
$\Delta/\text{u}\text{\AA}^2$	-0.986	-0.987	-0.988	-0.987	-0.986	-0.984	-0.984
N^c	23	51	54	51	54	51	54
σ^d/kHz	2.2	2.3	3.3	3.3	2.7	3.3	3.0

^a Centrifugal distortion constants have been fixed to those of normal species.

^b Errors in parenthesis are 1σ uncertainties expressed in units of the last digit.

^c Number of lines in the fit.

^d RMS error of the fit.

3.3 Internal dynamics

The experimental values of the inertial defects Δ , for all seven isotopologues, were

calculated from rotational constants and are summarized in Table 1 and 2. They are all much smaller in absolute values than that within the rigid approximation ($\Delta = -3.16 \text{ u}\text{\AA}^2$) which can be interpreted by a low barrier to internal rotation of the CH_3 group. The low-barrier to internal rotation of CH_3 modifies the rotational constants of the A -state with respect to the “rigid” value and, consequently, the inertial defects of all isotopologues. This can be explained qualitatively if taking into account the effective rotational constants of the ground state, $v=0$, $\sigma=0$ ($\sigma = 0, \pm 1$ for A and E species, respectively), as discussed in $\text{CF}_3\text{Cl-CH}_3\text{F}$ [41], $\text{CF}_3\text{Cl-CH}_2\text{O}$ [42] and $\text{CH}_3\text{Cl-H}_2\text{O}$ [43], according to:

$$\begin{aligned} A_{00} &= A_r + W_{00} F \rho_a^2 \\ B_{00} &= B_r + W_{00} F \rho_b^2 \\ C_{00} &= C_r + W_{00} F \rho_c^2 \end{aligned} \quad (2)$$

in which A_r , B_r and C_r are the rigid rotational constants, while F is the “reduced” rotational constant of the methyl top. W_{00} are the Herschbach’s barrier dependent perturbation sums relative to the sublevels of the A -symmetry ($\sigma = 0$) species of the torsional ground state ($v = 0$). $\rho_g = \lambda_g I_\alpha / I_g$ ($g = a, b, c$), where I_α is the moment of inertia of the methyl top, while I_g is the structural moments of inertia components of the molecule and λ_g is the direction cosines between the internal rotation axis α and principal axis g ($v = 0$). Values of the W_{00} as a function of the reduced barrier s are available [44]. The parameter s is, in turn, related to the V_3 barrier according to $V_3 = 0.215sF$.

As indicated in Fig.1, the c -axis is perpendicular to the internal rotation axis of the CH_3 top. Therefore λ_c , ρ_c and $F\rho_c$ are zero, and the rotational constant C is not affected by the internal rotations of CH_3 . In the contrast, the rotational constants A is strongly affected by the barrier to

the internal rotation of CH_3 due to the almost co-linearity of the a -axis with the C4C7 bond. As a consequence, experimental rotational constants A and B cannot be used directly for the structure fit. In order to know better the structure of 2F4P, geometry optimizations were carried out at various levels of theory (see in Supplementary Materials). The predicted rotational constant C calculated at the B3LYP/6-311++G(df,p) level (see in the second column of Table 1) matches best the experimental one, with the discrepancy of 0.2%. B3LYP/6-311++G(df,p) geometry is then chosen, from which $F\rho_a = 76.126$ MHz and $F\rho_b = 4.311$ MHz. By applying the differences between the model calculated and the experimental values of A and B to eq.(2), all seven isotopologues give $W_{00}=0.44$, which corresponds to a rather small internal rotational barrier $V_3 \approx 16 \text{ cm}^{-1}$, smaller than that expected from theoretical calculations. This very low barrier is responsible of larger splittings. In 2-butynoic acid, the barrier height is $1.00900(42) \text{ cm}^{-1}$ [45] while the splitting can reach a few hundred MHz even at low J values.

3.4 Molecular structure

Fig. 3. The geometry of 2F4P and 4-picoline.

Full geometry of 2F4P is available calculated at B3LYP/6-311++G(df,p) level of theory.

The geometry of 4-picoline is also calculated at the same level for comparison. As indicated in Fig. 3, the theoretical values show significant deviation from the nonsubstituted molecule. Upon the fluorination at the 2-site of the aromatic ring, the N1–C2 bond is shortened by ~ 0.028 Å and the N1C2C3 angle increased 2.3° . This kind of variation, as discussed in 2-fluoropyridine and 3-fluoropyridine [9], is contributable to the electron withdrawing nature of fluorine. The valence angle centered at the fluorinated carbon atom increases $\sim 3^\circ$ with respect to pyridine.

To better reveal the alteration of electron distribution caused by fluorine substitution, molecular electrostatic surface potentials (MESP) of 4-picoline and 2F4P were performed at the B3LYP/6-311++g(df,p) level of theory, as shown in Fig. 4. The electron density shared between N1 and C2 shows a noticeable increase upon the fluorine substitution, while the other hydrogens become more acidic.

Fig. 4. The MESP of 2F4P and 4-picoline.

4. Conclusion

The rotational spectrum of 2F4P have been investigated by using the pulsed jet Fourier transform microwave technique, which displays the features of the quadrupole coupling effect of

the ^{14}N nucleus with the near-free internal rotation of CH_3 top. The V_3 barrier (16 cm^{-1}) to the internal rotation of CH_3 has been estimated from the unexpected low values of the inertial defects. It seems that fluorination at the 2-site of the aromatic ring alters not only the geometry but also the internal dynamics of 4-picoline.

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