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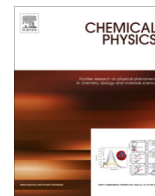**37** PUBLICATIONS **440** CITATIONS

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Infrared, Raman, and ultraviolet absorption spectra and theoretical calculations and structure of 2,3,5,6-tetrafluoropyridine in its ground and excited electronic states

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A B S T R A C T

Infrared and Raman spectra of 2,3,5,6-tetrafluoropyridine (TFPy) were recorded and vibrational frequencies were assigned for its S_0 electronic ground states. *Ab initio* and density functional theory (DFT) calculations were used to complement the experimental work. The lowest electronic excited state of this molecule was investigated with ultraviolet absorption spectroscopy and theoretical CASSCF calculations. The band origin was found to be at 35,704.6 cm^{-1} in the ultraviolet absorption spectrum. A slightly puckered structure with a barrier to planarity of 30 cm^{-1} was predicted by CASSCF calculations for the $S_1(\pi, \pi^*)$ state. Lower frequencies for the out-of-plane ring bending vibrations for the electronic excited state result from the weaker π bonding within the pyridine ring.

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1. Introduction

The vibrations of the pyridine (Py) molecule have been extensively studied in both its ground [1,2] and excited electronic states [3–5]. This molecule is rigidly planar in its ground state but becomes quasi-planar with a tiny barrier to planarity of 3 cm^{-1} in its $S_1(n, \pi^*)$ electronic excited state [5]. In order to understand what effect fluorine substitution has on the structure of this ring system in electronic excited states, in recent years we have carried out ultraviolet absorption and theoretical studies of several fluoropyridines. In 2011 we reported our results on 2-fluoropyridine (2FPy) and 3-fluoropyridne (3FPy) [6] which had previously been

studied under low resolution by Medhi and Medhi [7,8]. Our work showed that these molecules remain planar and fairly rigid in their excited states. In 2013 we published our results on 2,6-difluoropyridine (26DFPy) [9]. For the $S_1(\pi, \pi^*)$ state of this molecule the experimental results supported a planar structure although two different theoretical computations predicted conflicting results (a planar structure from CASSCF but a non-planar structure with small barrier to planarity from TD-B3LYP). The $S_2(n, \pi^*)$ state for 26DFPy has a calculated barrier to planarity of 256 cm^{-1}. In the present study we report our results for 2,3,5,6-tetrafluoropyridine (TFPy) for both its ground and first excited electronic states.
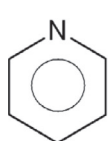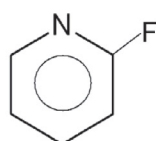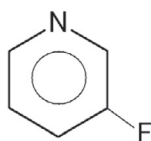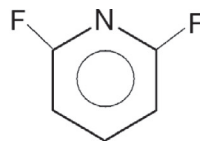

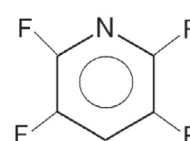Py   2FPy   3FPy   26DFPy   TFPy

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2. Experimental

2,3,5,6-Tetrafluoropyridine (99% purity) was purchased from Sigma–Aldrich. The liquid and vapor-phase infrared spectra were obtained using a Bruker Vertex 70 Fourier-transform spectrometer equipped with a globar light source, a KBr beamsplitter and a deuterated lanthanum triglycine sulfate (DLaTGS) detector for mid-infrared. A 10 cm glass cell with KBr windows and 20 Torr of sample was used. For the far-infrared region, a Mylar beamsplitter and a mercury cadmium telluride (MCT) detector and polyethylene windows for the gas cell were used. Measurements were done with 1024 scans at $0.5\ cm^{-1}$ resolution. The liquid and vapor-phase Raman spectra were collected using a Jobin–Yvon U-1000 spectrometer equipped with a frequency-doubled Nd:YAG Coherent Verdi-10 laser and CCD detector. The laser excitation at 532 nm provided a power of 1 W for liquid samples and 6 W for vapor samples. The effective resolution was $0.7\ cm^{-1}$. The vapor sample was sealed in a specially designed glass cell as described previously [10,11]. Parallel and perpendicular polarization measurements were made utilizing the standard accessory and scrambler. Ultraviolet absorption spectra of vapor samples were recorded with a Bomem DA8.02 Fourier transform spectrometer. The vapor sample was loaded into a 20 cm glass cell with quartz window and measurements were done by taking the average of 4000 scans at $1\ cm^{-1}$ resolution.

3. Theoretical computations

The molecular structure of TFPy in its S_0 electronic ground state were computed using the second-order Møller–Plesset (MP2) level of theory [12] with the cc-pVTZ basis set [13]. The B3LYP [14,15] density functional with the 6-311++G(d, p) [16–18] basis set was used to compute the harmonic vibrational frequencies. A scaling
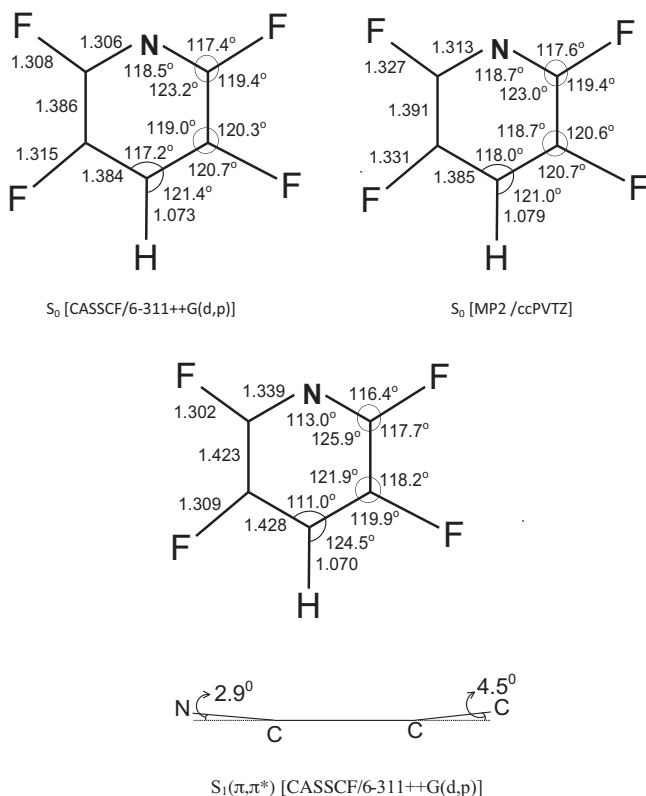
Fig. 1. Calculated structures of 2,3,5,6-tetrafluoropyridine (TFPy) in its electronic ground and excited states.
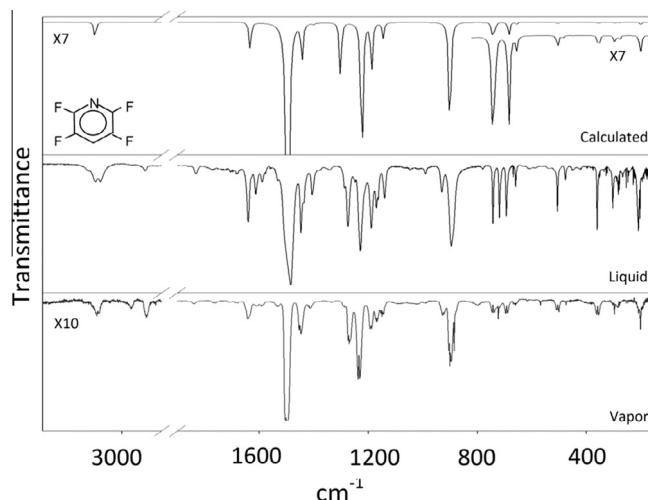
Fig. 2. Calculated and observed infrared spectra of TFPy.
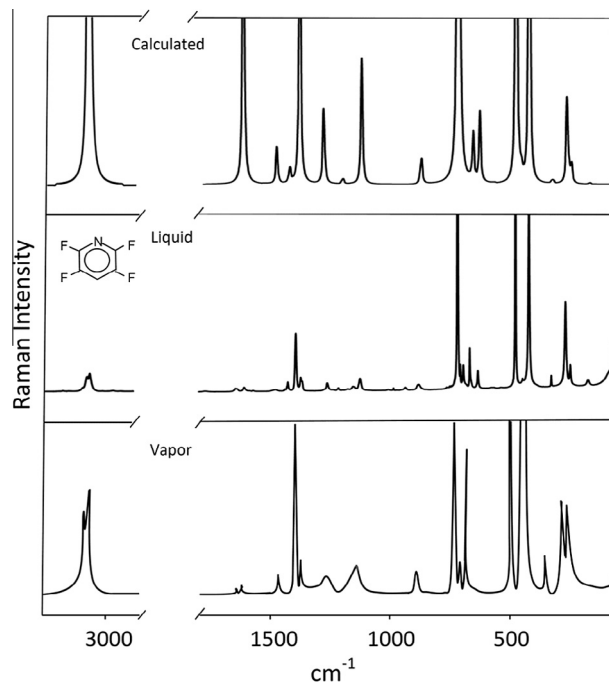
Fig. 3. Calculated and observed Raman spectra of TFPy.

factor of 0.964 was used for C—H stretching frequencies and 0.985 for frequencies below $1800\ cm^{-1}$ based on our previous work [5,6,9]. In addition, the complete active-space self-consistent field (CASSCF) method [19] were also employed to investigate the vibrational frequencies of TFPy in its S_0 and $S_1(\pi, \pi^*)$ state. The active space for the CASSCF computations consisted of eight electrons (two lone-pair electrons and six π electrons) distributed in seven orbitals (one lone-pair orbital on the nitrogen atom and six π orbitals). A scaling factor of 0.905 was used for all vibrational frequencies computed at the CASSCF level. All MP2 and B3LYP were carried out using the Gaussian 09 program package [20], and CASSCF computations were done using the GAMESS package [21,22].

4. Results and discussion

In its S_0 ground state TFPy was predicted to have a planar structure with C_{2v} symmetry. For the $S_1(\pi, \pi^*)$ excited state a puckered

Table 1
Vibrational spectra (cm^{-1}) and assignments for the electronic ground and excited states of 2,3,5,6-tetrafluoropyridine.

C_{2v}	v	Approximate description	Calculated		IR		Raman		S_1	
			v	Intensity[d]	Liquid[e]	Vapor[f]	Liquid	Vapor	Cal.	Obs.
A1	1	C–H stretch	3101	(0.4, 100)	3082 m	3091 w (B)	3080 (2)	3089 (4)	3072	–
	2	Ring stretch[c]	1632	(4, 7)	1640 s	1640 w (A/B)	1640 (0.3)	–	1554	–
	3	Ring stretch (C-F)	1443	(7, 2)	1446 s	1450 s (B)	1445 (0.2)	–	1381	1380
	4	C-F stretch	1401	(0.2, 37)	1405 m	1414 w (B)	1401 (7)	1404 (7)	1361	1358
	5	C-F stretch (ring)	1223	(30, 0.8)	1228 s	1233 s (B)	1226 (0.3)	–	1104	1100
	6	Ring breathing	746	(2, 100)	742 s	742 m (B)	742 (100)	740 (100)	690	709
	7	Ring bending (in-plane)	684	(2, 5)	693 s	692 m (B)	692 (5)	690 (6)	672	689
	8	Ring bending (in-plane)	505	(0.3, 42)	506 m	505 w (B)	505 (53)	503 (39)	451	453
	9	C-F wag (in-plane)	355	(0.3, 0.5)	360 m	358 w (B)	359 (1)	357 (1)	347	347
	10	C-F wag (in-plane)	278	(0.1, 2)	283 m	280 w (B)	282 (3)	280 sh (2)	265	280
A2	11	Ring twisting	699	(0, 0.1)	–	–	692 (5)	–	383	373
	12	C-F wag (out-of-plane)	454	(0, 17)	–	–	451 (25)	451 (10)	305	302[b]
	13	C-F wag (out-of-plane)	115	(0, 0.004)	–	–	–	–	98	84
B1	14	C-H wag	897	(4, 2)	895 s	900 s (C)	900 (0.6)	–	406	400
	15	Ring twisting	736	(2, 4)	719 s	723 m (C)	718 (3)	–	335	328
	16	Ring bending (out-of-plane)	485	(0.06, 0.9)	477 w	475 w (C)	477 (0.6)	–	108[a]	110
	17	C-F wag (out-of-plane)	296	(0.2, 9)	303 m	297 w (C)	302 (10)	301 (4)	303	302[b]
	18	C-F wag (out-of-plane)	201	(0.4, 0.1)	211 m	201 w (C)	210 (0.7)	–	198[a]	165
B2	19	Ring stretch[c]	1634	(0.7, 36)	1640 s	1640 w (A/B)	1640 (0.3)	–	1770	–
	20	Ring stretch (C-F)	1495	(100, 4)	1483 s	1500 s (A)	1482 (0.1)	–	1518	–
	21	Ring stretch	1302	(9, 9)	1274 s	1270 m (A)	1274 (0.7)	–	1385	–
	22	C-H wag	1188	(8.4, 0.02)	1189 s	1191 m (A)	1188 (0.1)	–	1151	–
	23	C-F stretch (ring)	1145	(2.5, 13)	1139 m	1149 m (A)	1139 (1)	1145 (1)	1137	–
	24	C-F stretch	901	(18, 0.9)	896 s	900 s (A)	900 (0.6)	894 (1)	825	809
	25	C-F wag (in-plane)	656	(0.3, 7)	659 m	659 w (A)	658 (2)	–	617	611
	26	Ring bend (in-plane)	448	(0.007, 16)	452 w	–	451 (25)	444 (9)	408	420
	27	C-F wag (in-plane)	299	(0.02, 0.01)	–	297 w (A)	–	299 (4)	293	290

[a] Coupled vibrations.
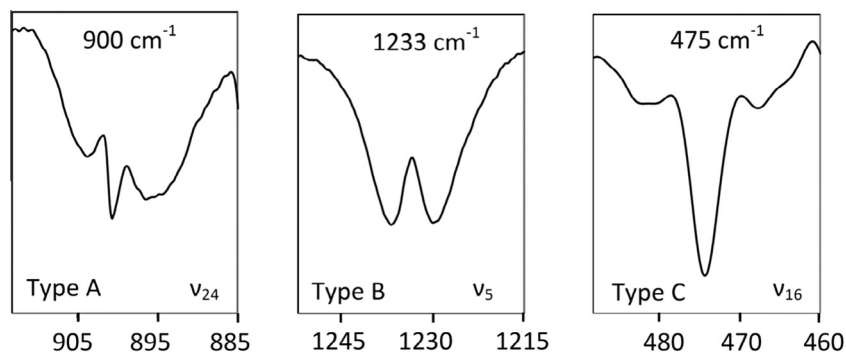[b] Assigned twice.
[c] v_2 and v_{19} overlap in the spectra; v_2 is in Fermi resonance with $v_{14} + v_{15}$ and this gives a band near 1611 cm^{-1} in the liquid and vapor infrared and Raman spectra.
[d] Relative intensities for IR and Raman.
[e] s: strong m: medium w: weak.
[f] A, B, and C in parentheses indicate the infrared band types.

Fig. 4. Examples of band types in the infrared spectrum of TFPy.

structure with a barrier to planarity of 30 cm^{-1} was predicted by CASSCF computations. The calculated structures for TFPy in its S_0 ground state and $S_1(\pi, \pi^*)$ excited state are shown in Fig. 1. As expected, the excited state has longer bond lengths in the pyridine ring as compared to the ground state due to the decrease in π bond character. The N—C, C(2)—C(3) and C(3)—C(4) bond lengths are longer in the $S_1(\pi, \pi^*)$ state by 0.033, 0.037, and 0.044 Å, respectively.

The liquid and vapor phase infrared and Raman spectra of TFPy are shown in Figs. 2 and 3, respectively, and are compared with those computed with the DFT B3LYP method using the 6-311++G(d, p) basis set. Good agreement between experimental and calculated frequency values was found. A few overtone bands were observed in the experimental liquid and vapor spectra, but

the calculated spectrum provides only the fundamental vibrational frequencies. Both the experimental and calculated frequencies for the infrared and Raman spectra are summarized in Table 1. As indicated in the table, the v_2 ring-stretching vibration is in Fermi resonance with a combination band of a C—H wag (v_{14}) and ring twist (v_{15}) which results in a band near 1611 cm^{-1} in the liquid and vapor infrared and Raman spectra. Three infrared band types (type A, type B and type C bands) were clearly observed in the infrared spectrum and examples of these are shown in Fig. 4.

The ultraviolet absorption spectrum of TFPy vapor is shown in Fig. 5. The band origin which corresponds to a transition to the $S_1(\pi, \pi^*)$ excited state is at 35,704.6 cm^{-1}. A comparison of observed and calculated vibrational frequencies for the $S_1(\pi, \pi^*)$ excited state is presented in Table 1. A strong coupling between
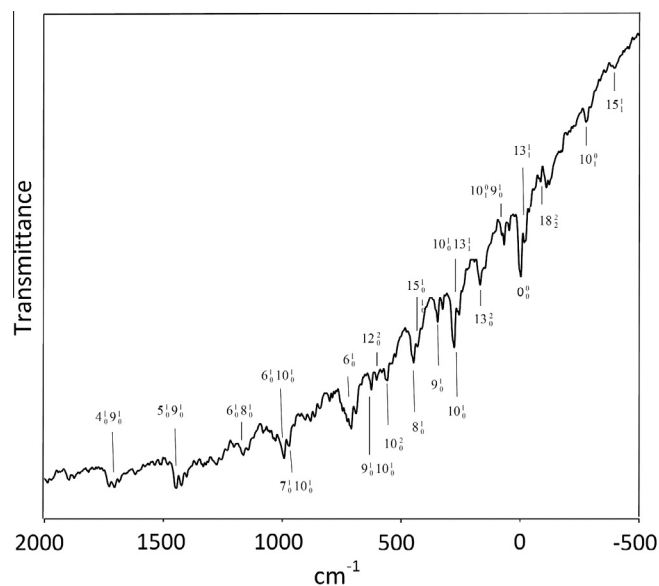
Fig. 5. Ultraviolet absorption spectra of TFPy relative to the band origin at 35,704.4 cm^{-1}.

Table 2
Ultraviolet absorption spectra (cm^{-1}) and assignments for 2,3,5,6-tetrafluoropyridine.

Observed	Peak intensity[a]	Assignment	Inferred
−784	w	$8_1^0 10_0^0$	−506−283 = −789
−763	w		
−738	m	6_1^0	−742
−675	m		
−573	w	$12_1^0 13_1^0$	−[115]−451 = −566
−504	mw	8_1^0	−505
−480	mw		
−458	w		
−438	w		
−395	m	15_1^1	328−723 = −395
−359	w	9_1^0	
−297	mw		
−280	ms	10_1^0	0.−280 = −280
−219	w	$8_1^0 10_0^1$	280−503 = −223
−211	w		
−198	w		
−178	m	$16_0^1 17_0^1$	302−475 = −173
−122	ms		
−112	ms		
−101	mw		
−87	ms	18_2^2	325−412 = −87
−38	m	18_1^1	165−201 = −36
−21	s	13_1^1	84−105 = −21
45	ms	$10_0^1 18_0^2$	325−280 = 45
67	ms	$10_1^0 9_0^1$	346−280 = 66
75	m		
101	m	$8_0^1 9_1^0$	453−357 = 96
145	m		
167	ms	13_0^2	84 × 2 = 168
172	m	$8_0^1 10_1^0$	453−280 = 173
176	m		
193	m	$14_0^1 18_1^0$	400−201 = 199
200	m		
214	ms	16_0^2	110 × 2 = 220
222	w		
234	w		
244	m		
260	s	$10_0^1 13_1^1$	280 + 84−105 = 261
275	s	$16_0^1 18_0^1$	110 + 165 = 275

Table 2 (*continued*)

Observed	Peak intensity[a]	Assignment	Inferred
280	s	10_0^1	280−0 = 280
310	mw	$25_0^1 27_1^0$	611−299 = 312
325	s	18_0^2	165 × 2 = 330
346	s	9_0^1	346−0 = 346
355	mw	$6_0^1 9_1^0$	709−357 = 52
391	m		
411	m	$7_0^1 10_1^0$	689−280 = 409
414	w	$16_0^1 17_0^1$	302 + 110 = 412
423	m		
428	m	$6_0^1 10_1^0$	709−280 = 429
435	m	$15_0^1 16_0^1$	328 + 110 = 438
446	s		
453	s	8_0^1	453−0 = 453
522	m		
535	m		
546	mw		
556	mw		
563	s	10_0^2	280 × 2 = 560
		$14_0^1 18_0^1$	400 + 165 = 565
580	m	27_0^2	290 × 2 = 580
603	m	12_0^2	302 × 2 = 604
625	s	$9_0^1 10_0^1$	346 + 280 = 626
633	m	$15_0^1 17_0^1$	328 + 302 = 630
646	m		
650	mw		
655	m	15_0^2	328 × 2 = 656
667	mw		
689	ms	7_0^1	689−0 = 689
692	m	9_0^2	346 × 2 = 692
709	s	6_0^1	710−0 = 710
726	ms	$14_0^1 15_0^1$	400 + 328 = 728
733	ms	$8_0^1 10_0^1$	453 + 280 = 733
746	ms	11_0^2	373 × 2 = 746
754	m		
768	w		
779	w		
788	w		
799	m	14_0^2	400 × 2 = 800
		$8_0^1 9_0^1$	453 + 346 = 799
841	m	26_0^2	420 × 2 = 840
862	m		
880	m		
901	m	$25_0^1 27_0^1$	611 + 290 = 901
906	m	8_0^2	453 × 2 = 906
927	mw		
949	mw		
957	mw		
969	m	$7_0^1 10_0^1$	689 + 280 = 969
991	s	$6_0^1 10_0^1$	710 + 280 = 990
1029	m	$25_0^1 26_0^1$	611 + 420 = 1031
1037	m	$7_0^1 9_0^1$	689 + 346 = 1035
1051	m		
1058	m	$6_0^1 10_0^1$	710 + 346 = 1056
1071	m		
1081	m		
1128	m		
1143	m	$7_0^1 8_0^1$	689 + 453 = 1142
1162	ms	$6_0^1 8_0^1$	710 + 453 = 1163
1204	mw		
1231	mw	25_0^2	611 × 2 = 1222
		$24_0^1 26_0^1$	809 + 420 = 1229
1247	mw		
1255	mw		
1274	mw		
1278	m		
1285	m		
1293	m		
1331	m		

Table 2 (*continued*)

Observed	Peak intensity[a]	Assignment	Inferred
1364	m		
1401	m		
1422	m	$6_0^2 24_0^1 25_0^1$	$710 \times 2 = 1420$
			$809 + 611 = 1420$
1446	m	$5_0^1 9_0^1$	$1100 + 346 = 1446$
1511	w		
1619	m	24_0^2	$809 \times 2 = 1618$
1705	m	$4_0^1 9_0^1$	$1358 + 346 = 1704$
1726	m	$3_0^1 9_0^1$	$1380 + 346 = 1726$
1877	mw		
1895	mw		
1987	mw		
2091	mw		
2134	m		
2153	m		
2367	mw		
2415	m		
2600	w		
2699	w		
2796	w		
2824	mw		
3106	mw		

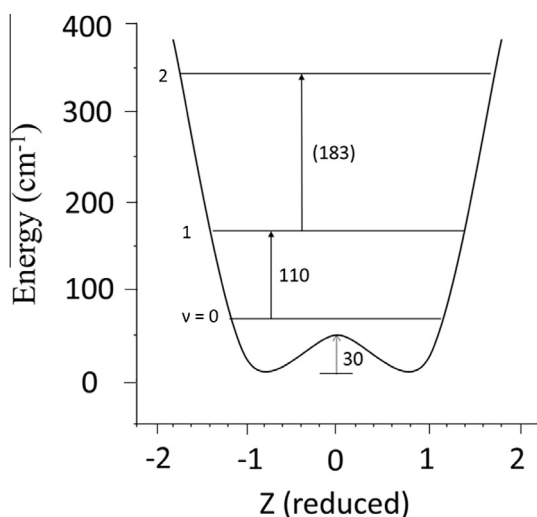[a] s – strong, m – medium, w – weak, v – very.

Fig. 6. Calculated ring-bending potential energy function of TFPy in reduced coordinates. The 110 cm^{-1} transition was observed while the 183 cm^{-1} transition was calculated.

the out-of-plane ring bending and out-of-plane C—F wag was observed. A listing of the observed ultraviolet bands and the assignments for the excited state vibrational transitions are shown in Table 2. Examination of Tables 1 and 2 shows that the lower frequency A_1 vibrations ($v_6 - v_{10}$) in the electronic excited state were observed directly. For the non-totally symmetric vibrations many of the overtones were observed. For example, transition 13_0^2 at 167 cm^{-1} shows v_{13} in the excited state to be at about 84 cm^{-1}. As expected due to the decreased π bonding character in the $S_1(\pi, \pi^*)$ state, essentially all of the vibrational frequencies in the excited state have lower values than the corresponding modes in the S_0 ground state.

Py, 2FPy, 3FPy, 26DFPy and TFPy all have planar and rigid structures in their electronic ground states. Py is extremely floppy in its $S_1(n, \pi^*)$ excited state and its out-of-plane ring bending frequency drops from 403 to 60 cm^{-1} [5]. It has a tiny barrier to planarity of 3 cm^{-1}. Despite their planar structures, 2FPy, 3FPy, and 26DFPy all become floppier in their excited states with significant drops in their ring puckering frequencies from 414, 412 and 460 cm^{-1} to 96, 118 and 127 cm^{-1}, respectively [6,9]. A slightly puckered structure is predicted by CASSCF calculations for TFPy with a barrier to planarity of 30 cm^{-1}. This indicates that TFPy also has a floppier structure in the excited state and this is confirmed by the lowering of out-of-plane ring bending frequency from 475 cm^{-1} in the electronic ground state to 110 cm^{-1} in the $S_1(\pi, \pi^*)$ excited state. A strong coupling between the out-of-plane ring bending and the out-of-plane C-F wag motions was also observed. In fact, the out-of-plane ring bending frequency even drops below the out-of-plane C-F wag due to the increased antibonding character in the excited state.

Although the out-of-plane ring bending vibration of TFPy is coupled to the C-F out-of-plane wagging motion, we can approximate the ring-bending potential energy function for the excited $S_1(\pi, \pi^*)$ state based on the experimental data and theoretical calculations. Previously we carried out a similar calculation for 26DFPy [9]. For TFPy we utilized the calculated barrier of 30 cm^{-1} and the observed ring-bending frequency of 110 cm^{-1}. The resulting potential energy function in reduced coordinates [23] is shown in Fig. 6. Because of the coupling of the bending with the C-F wagging, a meaningful reduced mass for the motion could not be calculated thus requiring the use of reduced coordinates. It is notable that while there is a small barrier to planarity, the lowest quantum state lies above the barrier so we describe this molecule as quasi-planar, similar to pyridine itself.

Table 3 summarizes the excited state results for pyridine and the four fluoropyridines that we have studied. All of these molecules are rigid in their ground electronic states but become less rigid in their $S(n, \pi^*)$ and $S(\pi, \pi^*)$ states. For the excited states the barriers to planarity, if present, are small. As seen in the table, fluorinating the pyridine ring increases the frequency of the $\pi \to \pi^*$ transition and this indicates that the fluorine atom somewhat increases the π bond stabilization. However, the addition of four fluorine atoms to the pyridine ring in TFPy curiously has less of

Table 3
Excited state barrier to planarity and puckering angles of pyridine and fluoropyridines in their excited states.

Molecules	State	Band origin (cm^{-1})	Barrier (cm^{-1})	Puckering angle[a]	Method	Reference
Py	$S_1 (n, \pi^*)$	34,767.0	3	Quasi-planar	Experiment	1
	$S_2 (\pi, \pi^*)$	38,350.0	–	–	Experiment	15
2FPy	$S_1 (\pi, \pi^*)$	38,030.4	0	Planar	CASSCF/6-311++G(d, p)	2
	$S_2 (n, \pi^*)$	39,199 (Calc.)	0	Planar	CASSCF/6-311++G(d, p)	2
3FPy	$S_1 (n, \pi^*)$	35,051.7	0	Planar	CASSCF/6-311++G(d, p)	2
	$S_2 (\pi, \pi^*)$	37,339.0	0	Planar	CASSCF/6-311++G(d, p)	2
26DFPy	$S_1 (\pi, \pi^*)$	37,820.2	124	11.2°/22.7°	TD-B3LYP/6-311++G(d, p)	3
	$S_1 (\pi, \pi^*)$	37,820.2	0	Planar	CASSCF/6-311++G(d, p)	3
	$S_2 (n, \pi^*)$	42,323 (Calc.)	256	38.9°/25.9°	CASSCF/6-311++G(d, p)	3
TFPy	$S_1 (\pi, \pi^*)$	35,704.6	30	2.9°/4.5°	CASSCF/6-311++G(d, p)	This work

[a] The two values for the puckering angle refer to the out-of-plane angles from the ring to the N atom and the C atom directly opposite, respectively.

an effect than adding one or two fluorine atoms for 2FPy, 3FPy, and 26DFPy. It is also not clear why 2FPy and 3FPy remain planar in their excited states while pyridine, 26DFPy, and TFPy show more of a tendency to become non-planar.

5. Conclusions

TFPy has a rigid planar structure in its electronic ground state and the structure becomes floppier in the excited state with a small barrier to planarity of 30 cm^{-1}. The infrared, Raman and ultraviolet absorption spectra were recorded and the vibrational frequencies were assigned for both ground and excited states with the aid of theoretical calculations. A potential energy function based on experimental and theoretical results was calculated.

Conflict of interest

The authors declare that there is no conflict of interest.

Acknowledgments

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