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Infrared, Raman, and Ultraviolet Absorption Spectra and Theoretical Calculations and Structure of 2,6-Difluoropyridine in its Ground and Excited Electronic States

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Abstract

The infrared and Raman spectra of 2,6-difluoropyridine (26DFPy) along with *ab initio* and DFT computations have been used to assign the vibrations of the molecule in its S_0 electronic ground state and to calculate its structure. The ultraviolet absorption spectrum showed the electronic transition to the $S_1(\pi, \pi^*)$ state to be at $37,820.2 \text{ cm}^{-1}$. With the aid of *ab initio* computations the vibrational frequencies for this excited state were also determined. TD-B3LYP and CASSCF computations for the excited states were carried out to calculate the structures for the $S_1(\pi, \pi^*)$ and $S_2(n, \pi^*)$ excited states. The CASSCF results predict that the $S_1(\pi, \pi^*)$ state is planar and the $S_2(n, \pi^*)$ state has a barrier to planarity of 256 cm^{-1} . The TD-B3LYP computations predict a barrier of 124 cm^{-1} for the $S_1(\pi, \pi^*)$ states, but the experimental results support the planar structure. Hypothetical models for the ring-puckering potential energy function were calculated for both electronic excited states to show the predicted quantum states. The changes in the vibrational frequencies in the two excited states reflect the weaker π bonding within the pyridine ring.

Keywords

vibrational spectra; ultraviolet absorption spectra; electronic excited states; molecular structure; 2,6-difluoropyridine

INTRODUCTION

We have recently reported the spectra, structures, and vibrational levels of pyridine (Py),¹ 2-fluoropyridine (2FPy),² and 3-fluoropyridine (3FPy)² in their ground and excited electronic states. We have also reported the ground state vibrational spectra of 2-chloro and 2-bromopyridine.³ All of these molecules are planar in their S_0 electronic ground states and have nearly harmonic out-of-plane ring-bending vibrational frequencies near 410 cm^{-1} . In its $S_1(n, \pi^*)$ electronic excited state pyridine¹ becomes quasi-planar and very floppy with a barrier to planarity of 3 cm^{-1} . Its out-of-plane ring-bending vibration has a mostly quartic potential energy function and has a frequency of 59.5 cm^{-1} . The two fluoropyridines remain

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Supporting Information Description

The supporting information consists of a listing of the observed ultraviolet absorption frequencies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

planar in their $S(n,\pi^*)$ states but become more floppy with vibrational frequencies of 240 cm^{-1} (calculated) and 227 cm^{-1} for the out-of-plane bending modes of 2FPy and 3FPy, respectively. In their $S(\pi,\pi^*)$ states, the molecules are also planar and floppy with bending frequencies of 163 cm^{-1} for 2FPy and 272 cm^{-1} for 3FPy. In the present study we present our results for 2,6-difluoropyridine (26DFPy). We were particularly interested in determining how the additional fluorine substitution affects the structures and low-frequency vibrations in the electronic excited states. Infrared and Raman spectra provide the ground state vibrational data and ultraviolet absorption spectra provide the data for the $S_1(\pi,\pi^*)$ state. Theoretical computations were carried out to assist in the assignment of the vibrational frequencies for both ground and excited states and also to calculate the structures for the S_0 , $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ states.

EXPERIMENTAL

2,6-Difluoropyridine (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 global light source, a KBr beamsplitter and a deuterated lanthanum triglycine sulfate (DLaTGS) detector for mid infrared. For the far-infrared region, a Mylar beamsplitter and a mercury cadmium telluride (MCT) detector 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 laser and CCD detector. The laser excitation at 532 nm provided a power of 1W for liquid samples and 6W 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.³ 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.

THEORETICAL COMPUTATIONS

The structure and vibrational frequencies of 26DFPy in its S_0 electronic ground state were calculated using the Gaussian 09 program.⁴ *Ab initio* calculations were done at the second order Moller-Plesset (MP2) level of theory with the cc-PVTZ basis set for structure optimization. The Becke and Lee-Yang-Parr exchange-correlation function (B3LYP) with the 6-311++G(d,p) basis set was utilized for the calculation of vibrational frequencies. The time-dependent B3LYP (TD-B3LYP)^{5, 6} method was used to compute the structure and vibrational frequencies of 26DFPy in its $S_1(\pi,\pi^*)$ state. A scaling 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.⁷⁻¹²

Additionally, the complete active-space self-consistent field (CASSCF) method¹³ was employed to investigate geometries and vibrational frequencies of 26DFPy in its S_0 , $S_1(\pi,\pi^*)$, and $S_2(n,\pi^*)$ states. 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), as shown in Figure 1. A scaling factor of 0.905 was used for all vibrational frequencies computed at the CASSCF level. All (TD-)B3LYP and CASSCF computations were done using the Gaussian 09⁴ and GAMESS¹⁴ program packages, respectively.

STRUCTURES AND MOLECULAR ORBITALS

Figure 1 shows the calculated n , π and π^* molecular orbitals for 26DFPy. At both B3LYP and CASSCF levels, 26DFPy in its ground state has a planar structure with the C_{2v} symmetry. For the $S_1(\pi, \pi^*)$ excited state, however, whereas the CASSCF method predicted a planar structure, the TD-B3LYP method resulted in a puckered structure with a barrier to planarity of 124 cm^{-1} (52 cm^{-1} after the zero-point vibrational energy (ZPVE) correction). At the CASSCF level, the molecular structure of 26DFPy in its $S_2(n, \pi^*)$ state was predicted to be puckered with a barrier to planarity of 256 cm^{-1} (121 cm^{-1} after the ZPVE correction). Figure 2 shows the calculated structures for 26DFPy in its S_0 state from B3LYP and CASSCF calculations. The bond distances and angles can be seen to be very similar for the two different calculations. Figure 3 shows the molecular structures for 26DFPy in its $S_1(\pi, \pi^*)$ and $S_2(n, \pi^*)$ states, computed at the CASSCF/6-311++G(d,p) level. The figure also shows the structure for the TD-B3LYP calculation for the $S_1(\pi, \pi^*)$ state. The structure of 26DFPy in the $S_1(\pi, \pi^*)$ state, compared to its ground state, was characterized by increased bond lengths in the pyridine ring. The N-C, C(F)-C and C(3)-C(4) bond lengths were longer in the $S_1(\pi, \pi^*)$ state than in the ground state, by $0.032\text{ \AA}$, $0.037\text{ \AA}$, and $0.046\text{ \AA}$, respectively, reflecting the excitation of an electron from a bonding π orbital to an antibonding π^* orbital. The two determinants with the largest contribution to the CASSCF wave function for the $S_2(n, \pi^*)$ state of 26DFPy correspond to excitation from the nitrogen lone pair orbital to the π_4^* orbitals (Figure 1), which has a bonding character between the C(F) and C(H) atoms and an antibonding character between the N and C(F) atoms and between the C(H) and C(H) atoms. As a result, 26DFPy in the $S_2(n, \pi^*)$ state had a shorter C(F)-C bond length (by $0.037\text{ \AA}$) and longer N-C and C(H)-C(H) bond lengths (by $0.072\text{ \AA}$ and $0.055\text{ \AA}$, respectively) than in its ground state. Table 1 compares selected geometrical parameters of 26DFPy in its ground and excited states with those of pyridine,¹ 2FPy,² and 3FPy.² The bond length changes for 26DFPy in its $S(n, \pi^*)$ and $S(\pi, \pi^*)$ states showed a similar trend to those for the other three compounds.

SPECTROSCOPIC RESULTS

Infrared and Raman spectra

Figures 4 and 5 show the infrared and Raman spectra, respectively, for liquid and vapor samples of 26DFPy. The figures also show the computed spectra from the B3LYP calculations. The agreement between observed and calculated frequency values is excellent. The agreement for intensities is good for the most part although the ν_3 ring stretching band at 1615 cm^{-1} in the observed Raman spectrum is much weaker than predicted. The observed spectra also show a few overtone bands which are not in the calculated spectra for the fundamentals. As can be seen in Figure 4, the infrared spectra of the vapor clearly display some distinct type A (ν_{22} , ν_{24} , ν_{26} , ν_{27}), type B (ν_5 , ν_8), and type C (ν_{10} , ν_{15}) band contours which correspond for B_2 , A_1 and B_1 symmetry species, respectively. Table 2 summarizes both the experimental and calculated data. All of the vibrational assignments can be made unambiguously.

Ultraviolet absorption spectra

Figure 6 shows the ultraviolet absorption spectra of 26DFPy vapor. The band origin is at $37,820.2\text{ cm}^{-1}$ and corresponds to a transition to the $S_1(\pi, \pi^*)$ state. The CASSCF calculations predict a value of $39,191\text{ cm}^{-1}$ for this transition and a value of $42,323\text{ cm}^{-1}$ for the transition to the $S_2(n, \pi^*)$ state. In the observed spectra in Figure 6 the increasing absorption at higher frequencies results in part from the $S_2(n, \pi^*)$ absorption. Table 3 compares the transition frequencies of 26DFPy to those of pyridine, 2FPy, and 3FPy. Figure 7 shows the uv spectra in expanded form along with labels for the most significant

transitions. Table 4 presents a summary of the most significant observed uv bands. A complete list of observed bands is available in the supplementary material (Table S1). Figure 8 shows the energy diagram for the low frequency vibrations for the S_0 and $S_1(\pi, \pi^*)$ states. Table 5 presents a comparison of observed and calculated frequency for the S_0 , $S_1(\pi, \pi^*)$, and $S_2(n, \pi^*)$ states. Both excited states would have C_s symmetry if they are puckered with small barriers to planarity. However, the assignments were made according to C_{2v} symmetry which is applicable for planar structures. The data in Table 4 make it possible to assign most of the vibrational frequencies for the $S_1(\pi, \pi^*)$ state with considerable certainty.

The $S_1(\pi, \pi^*)$ state is calculated by TD-B3LYP to be floppy but slightly puckered (Figure 3) and have a barrier to planarity of 124 cm^{-1} . This implies that this excited state should have a double-minimum potential function for the ring-puckering vibration. However, because the ring-puckering and C-F out-of-plane wagging motions of A_2 symmetry species are strongly coupled, a one-dimensional calculation of the puckering vibrational potential energy function cannot be readily applied. In fact, we have found no definitive evidence for inversion doubling in the $S_1(\pi, \pi^*)$ excited state which would have been reflected in the energy levels of ν_{17} and/or ν_{18} . Thus, the experimental results support the CASSCF calculation result that this excited state is planar. For pyridine¹ in its $S_1(n, \pi^*)$ state we did confirm with experimental data that the spectra for the ring-puckering vibration could be fit with a one-dimensional potential energy function with a tiny barrier to planarity of 3 cm^{-1} .

Theoretical Ring-Puckering Potential Energy Functions for the Electronic Excited State

Although we observed no experimental evidence for inversion doubling or a barrier to inversion for the $S_1(\pi, \pi^*)$ state, it is instructive to present a picture of what would be expected if 26DFPy were in fact non-planar in this state as well as in its $S_2(n, \pi^*)$ state. As discussed, ν_{17} , the ring-puckering, and ν_{18} , the out-of-plane, in-phase C-F wagging motions are strongly coupled in both electronic excited states so it is not expected that one-dimensional calculations of the type that we successfully carried out for pyridine¹ are feasible here. Nonetheless, we believe that the calculation of one-dimensional functions based on the *ab initio* computations will provide insight into understanding the pattern of quantum states when energy barriers are present. The TD-B3LYP *ab initio* calculations predicted a barrier of 124 cm^{-1} for the $S_1(\pi, \pi^*)$ state and a predicted ring-puckering frequency (coupled to the C-F wagging mode) of 112 cm^{-1} . The CASSCF calculation predicted a barrier of 256 cm^{-1} and a ring-puckering frequency of 69 cm^{-1} for the $S_2(n, \pi^*)$ state.

As we showed many years ago,¹⁵ for double-minimum potential energy functions with high enough barriers the separations between lowest pairs of near-degenerate levels (caused by inversion doubling) become more and more harmonic. In other words, the separation between pairs of levels can be estimated quite well using a harmonic oscillator model to approximate the shape of each potential well. This means that the predicted harmonic frequency from the *ab initio* calculation is at least a fairly good estimate of the expected energy between the lowest pairs of levels. We have demonstrated this in the past by observing experimental transitions for double-minimum potentials and finding them to be quite well estimated by DFT and *ab initio* calculations.¹⁶³² Applying this principle, we have calculated one-dimensional potential energy functions for the ring-puckering so that they match the computed barrier heights and the calculated *ab initio* frequencies. The latter were set to match the $\nu = 0 \rightarrow \nu = 3$ puckering transitions. The calculations were done with reduced coordinates¹⁵ since the reduced mass could not be reliably calculated due to the strong coupling with the C-F wagging motion. For the $S_1(\pi, \pi^*)$ the calculated function is

$$V(\text{cm}^{-1}) = 18.34(Z^4 - 5.20Z^2) \quad (1)$$

and for $S_2(n,\pi^*)$ it is

$$V(\text{cm}^{-1}) = 7.33(Z^4 - 12.6Z^2) \quad (2)$$

These functions are shown in Figures 9 and 10. The symmetry species for both sets of quantum states are A_1 for even v values and B_1 for odd values of v . Hence, electronic transitions to $v = \text{even}$ levels should only arise from A_1 vibrational levels in the electronic ground state while transitions to $v = \text{odd}$ should arise from B_1 vibrational excited state. In our experimental data for the $S_1(\pi,\pi^*)$ state, which only has a small calculated barrier to inversion of 124 cm^{-1} , we were not able to find transitions compatible with a function similar to Eq. (1). Thus, we conclude that 26DFPy is most likely planar in its $S_1(\pi,\pi^*)$ state although it is conceivable that the coupling with the C-F wagging sufficiently distorts the potential energy surface to invalidate the predicted picture. For the $S_2(n,\pi^*)$ state, however, the calculated barrier of 256 cm^{-1} is sufficiently higher that we feel it is very likely that the molecule is indeed non-planar and that the potential function shown in Figure 9 may present quite a reasonable picture of the puckering potential energy function. Unfortunately, we have not been able to obtain experimental data for that state.

DISCUSSION

The calculated molecular orbital pictures are shown in Figure 1 and these help to explain the observed structural changes listed in Table 1. For pyridine, 2FPy, 3FPy, and 26DFPy the bond length changes in the $S(n,\pi^*)$ and $S(\pi,\pi^*)$ states are similar. The N-C bonds increase in both excited states but the C(2)-C(3) and C(5)-C(6) bonds decrease in the $S(n,\pi^*)$ state and increase in the $S(\pi,\pi^*)$ state. The pyridine ring molecular orbitals are similar to those in benzene so the $n \rightarrow \pi^*$ transition is to an antibonding orbital which has increased bonding character between the C(2)-C(3) and between the C(5)-C(6) bonds. The orbital nodes are at the N-C bonds and C(3)-C(4) and C(4)-C(5) bonds. For both the ground and excited states it is also evident that the fluorine substitution in the carbon(s) adjacent to the nitrogen atom decreases the N-C(F) bond distances. This is due to both electrostatic effects as well as some bonding participation of the fluorine p orbitals with the ring π system.

All four of the molecules under discussion have planar and fairly rigid structures in their electronic ground states. Pyridine¹ in its $S_1(n,\pi^*)$ state becomes extremely floppy and its out-of-plane ring bending frequency drops to 57 cm^{-1} . In fact, it even has a minute barrier to planarity of 3 cm^{-1} . 2FPy and 3FPy also become floppier in their electronic excited states as reflected by their lower out-of-plane ring bending frequencies but they remain planar. 26DFPy, however, becomes puckered according to TD-B3LYP calculations in its $S_1(\pi,\pi^*)$ state and according to CASSCF in its $S_2(n,\pi^*)$ excited state. The calculated barriers to planarity are quite small (124 cm^{-1} and 256 cm^{-1} for the $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ states, respectively). The CASSCF predict the $S_1(\pi,\pi^*)$ state to be planar and we observed no experimental evidence for inversion doubling. This may be due to the coupling between the puckering and C-F out-of-plane wagging vibration, or it may simply result from the fact that the molecule is in fact only floppy but planar.

It should be noted that the TD-B3LYP and CASSCF methods gave qualitatively different descriptions of the structure of 26DFPy in the $S_1(\pi,\pi^*)$ state. In general, because TD DFT methods (including the TD-B3LYP method) use a single reference configuration of Kohn-Sham orbitals, they cannot take static electron correlation effects into account. On the

contrary, the CASSCF method, with an appropriate choice of the active space, is free from this issue, but it does not include dynamic electron correlation, which the TD-DFT method can explain. As a result, the two excited-state methods often result in qualitatively different results. For example, in computational studies by Cai and Reimers^{33,34}, the CASSCF method predicted the $S_1(n,\pi^*)$ excited state of pyridine to have a boat form with a double-well potential along the ν_{16b} mode, whereas the TD-B3LYP method predicted a planar structure with the C_{2v} symmetry. Although experimental studies by Jesson et al.³⁵ and Boopalachandran and Laane¹ supports the double-well potential of the $S_1(n,\pi^*)$ excited state of Py, which may be interpreted as in line with the CASSCF results, the observed well depth was 4 cm^{-1} and 3 cm^{-1} , respectively, much smaller than the CASSCF well depth of 90 cm^{-1} .

Table 6 summarizes the pyridine ring vibrational frequencies for all these molecules in their S_0 , $S(\pi,\pi^*)$, and $S(n,\pi^*)$ states. The table also lists the C-F stretching and wagging frequencies. The symmetry species in the table apply to pyridine and 26DFPy both of which have C_{2v} symmetry point groups. For 2FPy and 3FPy, which have C_s symmetry, the vibrations listed under A_1 and B_2 in Table 6 correspond to the in plane A' modes while A_2 and B_1 correspond to the out-of-plane A'' modes. As expected, all of the ring stretching and bending vibrations for all four molecules drop in frequency as the bonds in the excited state become weaker and the rings get floppier due to the decreased π bonding character. The C-F stretching frequencies also drop in the excited state suggesting that the fluorine atoms do participate to some extent in the π bonding. By far the most significant changes in vibrational frequencies in the excited electronic states are for the A_2 and B_1 out-of-plane ring modes and the out-of-plane C-F wags. There is significant vibrational coupling between the ring-puckering and the out-of-plane C-F wagging modes so it is somewhat overly simplistic to look at the puckering frequencies separately. In the electronic ground state all four molecules have strong π bonding and are rigid with a puckering frequency over 400 cm^{-1} . Substitution of fluorine atoms increases this value and for 26DFPy it is 460 cm^{-1} . The in-phase out-of-plane C-F wagging is at 247 cm^{-1} . In both the $S_1(\pi,\pi^*)$ and $S_2(n,\pi^*)$ states the increased anti-bonding character drops the puckering frequency below that of the C-F wagging and the motions become even more highly mixed. For 26DFPy in the $S_1(\pi,\pi^*)$ state the puckering is at 127 cm^{-1} and the wagging at 179 cm^{-1} . For $S_2(n,\pi^*)$ the frequencies are calculated to be at 69 and 288 cm^{-1} , respectively. As discussed above, if a barrier to planarity is present, a complex pattern of quantum states will be present.

CONCLUSIONS

The infrared and Raman spectra of 2,6-difluoropyridine have been readily assigned based on vapor-phase infrared band types, Raman polarization data, and DFT computations. The ultraviolet absorption spectra for the $S_1(\pi,\pi^*)$ were also assigned with the help of *ab initio* calculations. Structures for the S_0 , $S_1(\pi,\pi^*)$, and $S_2(n,\pi^*)$ states were calculated. The ground state molecule is rigidly planar while the computations at the CASSCF level predict the $S_2(n,\pi^*)$ state is puckered with a barrier to planarity of 256 cm^{-1} . The CASSCF calculation for the $S_1(\pi,\pi^*)$ state predicts a planar molecule while the TD-B3LYP computation predicts a puckered structure with a small barrier to planarity of 124 cm^{-1} . The experimental data favor the planar structure.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. CASSCF-optimized molecular orbitals for 26DFPy in the ground state, computed at the CASSCF(8,7) /6-311++G(d,p) level. Orbital symmetries in the C_{2v}/C_s point group are indicated in parentheses.

S₀ [MP2/cc-PVTZ]

S₀ [CASSCF/6-311++G(d,p)]

Figure 2.

Calculated structures of 2,6-difluoropyridine (26DFPy) in its ground electronic state.

Figure 3.
Calculated structures of 2,6-difluoropyridine (26DFPy) in its excited electronic states.

Figure 4.
Calculated and observed infrared spectra of 26DFPy.

Figure 5.
Calculated and observed Raman spectra of 26DFPy.

Figure 6.

Ultraviolet absorption spectra of 26DFPy relative to the O_0^0 band origin at 37,820.2 cm^{-1} .

Figure 7.
Ultraviolet absorption spectra of 26DFPy expanded near the band origin.

Figure 8. Energy diagram for the lower frequency vibrations of 26DFPy in its S_0 ground and $S_1(\pi, \pi^*)$ excited states.

Figure 9.
Hypothetical potential energy function for the ring puckering vibration of 26DFPy based on Eq. (1) for the $S_1(\pi, \pi^*)$ electronic excited state

Figure 10. Hypothetical potential energy function for the ring puckering vibration of 26DFPy based on Eq. (2) for the $S_2(n, \pi^*)$ electronic excited state

Table 1

Bond distances (Å) and bond angles (degrees) for pyridine and fluoropyridines^a

	S ₀					S (n, π*)					S (n, π*)					
	Py	2FPy	3FPy	26DFPy	Py	2FPy	3FPy	26DFPy	Py	2FPy	3FPy	26DFPy	Py	2FPy	3FPy	26DFPy
	TD-B3LYP CASSCF															
N-C(H)	1.340	-	1.338, 1.340	-	1.375	1.386	1.363, 1.382	-	-	1.369	1.365	1.367, 1.370	-			
N-C(F)	-	1.344	-	1.317	-	1.360	-	1.338	1.341	-	1.343	-	1.381			
C-F	-	1.313	1.340	1.333	-	1.309	1.330	1.333	1.312	-	1.316	1.322	1.309			
C(2)-C(3)	1.392	1.338	1.389	1.387	1.364	1.343	1.371	1.412	1.423	1.433	1.420	1.423	1.349			
C(3)-C(4)	1.391	1.391	1.384	1.390	1.439	1.463	1.405	1.433	1.438	1.433	1.436	1.421	1.447			
C(4)-C(5)	1.391	1.387	1.391	1.390	1.439	1.416	1.454	1.433	1.438	1.433	1.435	1.432	1.447			
C(5)-C(6)	1.392	-	1.392	1.387	1.364	1.375	1.358	1.412	1.423	1.433	1.437	1.435	1.349			
CNC angle	116.8	-	117.4	116.0	128.5	127.4	129.1	109.5	112.9	116.0	114.5	115.6	122.1			

^a Calculated using MP2/cc-pVTZ for the S₀ states and CASSCF/6-311++G(d,p) for the electronic excited states unless otherwise indicated

Table 2

Vibrational spectra (cm^{-1}) and assignments for the electronic ground state of 2,6-difluoropyridine

C_{2v}	V	Approximate description	Infrared		Raman		Calculated	
			Liquid	Vapor	Liquid	Vapor	ν	Intensity ^a
A ₁	1	C-H stretch	-	-	3106 (10)	3109 (21)	3114	(0, 100)
	2	C-H stretch	-	3082 w	3086 (3)	3076 (3)	3083	(100, 4)
	3	Ring stretch	1613 s	1620 s	1612 (1)	1615 (0.8)	1617	(67, 30)
	4	Ring stretch	1446 s	1458 s	1447 (0.3)	1443 (0.7)	1458	(3, 3)
	5	C-F sym. stretch	1309 s	1320 ms	1307 (12)	1318 (25)	1320	(36, 77)
	6	C-H in-plane wag	1069 m	1069 mw	1073 (8)	1072 (9)	1072	(1, 55)
	7	Ring breathing	992 s	1001 s	998 (71)	996 (82)	994	(1, 135)
	8	Ring bend	738 s	741 m	737 (100)	740 (100)	743	(5, 100)
	9	Ring bend	549 m	-	548 (19)	546 (22)	546	(0.3, 36)
A ₂	10	C-F in-plane wag	351 m	350 m	351 (1)	350 (0.9)	347	(0.4, 2)
	11	C-H out-of-plane wag	-	-	881 (0.4)	874 (1)	875	(0, 0.02)
	12	Ring twisting	-	-	660 (2)	-	672	(0, 1)
B ₁	13	C-F out-of-plane wag	-	-	-	215 (13)	211	(0, 24)
	14	C-H out-of-plane wag	993 s	999 s	982 (1)	983 (2)	987	(0.05, 1)
	15	C-H out-of-plane wag	794 s	797 s	798 (0.4)	-	804	(24, 1)
	16	Ring twisting	723 s	723 m	725 (2)	727 (1)	733	(4, 3)
	17	Ring puckering ^b	460 m	-	460 (1)	-	470	(0.03, 4)
	18	C-F out-of-plane wag ^b	249 mw	-	250 (7)	247 (2)	242	(0.1, 7)
	19	C-H antisym. stretch	3108 m	3113 w	3106 (10)	3097 (6)	3110	(29, 26)
B ₂	20	Ring stretch	1593 s	1606 s	1591 (1)	1593 (0.9)	1597	(47, 66)
	21	Ring stretch	1446 s	1461 s	1447 (0.3)	-	1461	(100, 0.2)
	22	Ring stretch	1282 s	1280 ms	1282 (3)	1285(2)	1297	(1, 12)
	23	C-H in-plane wag	1239 s	1243 s	1231 (0.3)	1253 (0.8)	1242	(39, 2)
	24	C-H in-plane wag	1143 m	1139 m	1144 (0.9)	-	1146	(2, 11)
	25	C-F anti-sym. stretch	992 s	1007 s	-	1001 sh (9)	1003	(28, 0.8)

C _{2v}	V	Approximate description	Infrared		Raman		Calculated	
			Liquid	Vapor	Liquid	Vapor	ν	Intensity ^a
	26	Ring bend	568 m	568 m	568 (6)	-	565	(2, 20)
	27	C-F in-plane wag	501 m	501 m	500 (2)	-	498	(1, 9)

^a Relative intensities for (IR, Raman);

^b Strongly coupled vibrations

Table 3Observed and calculated electronic transition frequencies (cm^{-1}).

Transition	Pyridine		2-fluoropyridine		3-fluoropyridine		2,6-difluoropyridine	
	Obs.	Calc. ^a	Obs.	Calc. ^a	Obs.	Calc. ^a	Obs.	Calc. ^a
$n \rightarrow \pi^*$	34 767	36 296	-	39 199	35 051.7	36 617	-	42 323
$n \rightarrow \pi^*$	38 350 ^b	38 312	38 030.4	38 796	37 339	38 311	37 820.2	39 191

^aCASSCF/6-311++G(d,p) level of theory^bRef[1]

Table 4Ultraviolet absorption spectra (cm^{-1}) and assignments for 2,6-Difluoropyridine

Observed	Peak intensity ^a	Assignment	Inferred
-547	s	9_1^0	$0-546 = -546$
-487	w	18_2^0	$0-494 = -494$
-383	s	10_2^1	$318-700 = -382$
-348	s	10_1^0	$0-350 = -350$
-331	w	16_1^1	$395-723 = -328$
-302	w	12_1^1	$372-668 = -296$
-245	w	$17_0^2 18_2^0$	$254-494 = -240$
-215	m	$10_1^0 17_1^3$	$-350-247+381 = -216$
-202	w	$13_2^2 17_1^1$	$472-677 = -205$
		$9_1^0 13_0^2$	$345-546 = -201$
-171	s	$13_2^0 17_0^2$	$-430+254 = -176$
-161	s	$13_1^1 17_1^1$	$301-462 = -161$
-120	mw	$17_0^1 18_1^0$	$127-247 = -120$
-95	w	$10_1^0 17_0^2$	$-350+254 = -96$
-87	mw	13_2^2	$345-430 = -85$
-75	s	9_1^1	$474-546 = -72$
-49sh	m	27_1^1	$455-501 = -46$
-41	s	13_1^1	$174-215 = -41$
-31	s	10_1^1	$318-350 = -32$
-18	w	$18_2^0 9_0^1$	$474-494 = -20$
10	s	$13_1^2 17_1^1$	$472-462 = 10$
46	w	$13_2^0 9_0^1$	$474-430 = 44$
72	w	12_1^2	$744-668 = 76$
143	ms	$16_0^1 18_1^0$	$395-247 = 148$

Observed	Peak intensity ^a	Assignment	Inferred
156	s	$12_0^1 13_1^0$	$372-215=157$
254	m	17_0^2	$127 \times 2 = 254$
300	s	$17_0^1 18_0^1$	$179+127=306$
		13_1^3	$516-215=301$
318	s	10_0^1	$318-0=318$
345	s	13_0^2	$174 \times 2 = 348$
358	s	18_0^2	$179 \times 2 = 358$
474	s	9_0^1	$474-0=474$
508	m	18_0^4	$508-0=508$
522	w	$16_0^1 17_0^1$	$127+395=522$
549	mw	$12_0^1 13_0^1$	$372+174=546$
572	w	$16_0^1 18_0^1$	$395+178=573$
627	mw	$15_0^1 17_0^1$	$503+127=630$
637	w	10_0^2	$318 \times 2=636$
682	s	8_0^1	$680-0=680$
713	s	$18_0^4 ?$	$358 \times 2 = 716$
745	m	12_0^2	$372 \times 2 = 744$
782	w	$14_0^1 17_0^1$	$653+127=780$
791	w	16_0^2	$395 \times 2 = 790$
		$9_0^1 10_0^1$	$474+317=791$
885	w	7_0^1	$885-0=885$
909	m	27_0^2	$455 \times 2 = 910$
952	s	9_0^2	$474 \times 2 = 948$
961	s	6_0^1	$961-0=961$
1000	s	$8_0^1 10_0^1$	$680+318=998$
		26_0^2	$496 \times 2 = 992$

Observed	Peak intensity ^a	Assignment	Inferred
1006	m	15_0^2	$503 \times 2 = 1006$
1058	m	$11_0^1 12_0^1$	$680 + 372 = 1052$
1091	w	$12_0^2 13_0^2$	$744 + 345 = 1089$
1148	w	5_0^1	1167 cal
		$8_0^1 9_0^1$	$680 + 474 = 1154$
1201	ms	$7_0^1 10_0^1$	$885 + 318 = 1203$
1264	w	$15_0^2 17_0^2$	$1006 + 254 = 1260$
1282	mw	$6_0^1 10_0^1$	$961 + 318 = 1279$
1292	ms	4_0^1	$1289 - 0 = 1289$
1351	mw	11_0^2	$680 \times 2 = 1360$
1395	m	$25_0^1 26_0^1$	$877 + 496 = 1373$
1428	m	3_0^1	$1424 - 0 = 1424$
1438	w	$6_0^1 9_0^1$	$885 + 474 = 1435$
1464	w	$5_0^1 10_0^1$	$1147 + 318 = 1465$
1671	w	$14_0^2 18_0^2$	$1306 + 358 = 1664$
1678	m	$22_0^1 26_0^1$	$1191 + 496 = 1687$
1715	mw	25_0^2	$858 \times 2 = 1716$
1755	vw	25_0^2	$877 \times 2 = 1754$
1768	w	7_0^2	$885 \times 2 = 1770$
1902	w	$3_0^1 9_0^1$	$1424 + 474 = 1898$
1948	w	$23_0^1 25_0^1$	$1071 + 877 = 1948$
1963	w	$4_0^1 8_0^1$	$1289 + 680 = 1969$
2006	w	24_0^2	$1003 \times 2 = 2006$
2060	w	$22_0^1 25_0^1$	$1191 + 877 = 2068$
2104	w	$11_0^2 12_0^2$	$1360 + 744 = 2104$
2142	w	23_0^2	$1071 \times 2 = 2142$

Observed	Peak intensity ^a	Assignment	Inferred
2243	w	$4_0^1 6_0^1$	$1289+961 = 2250$
2382	w	22_0^2	$1191 \times 2 = 2382$

^a s-strong, m-medium, w-weak, v-very

Table 5

Observed and calculated vibrational frequencies (cm^{-1}) for 2,6-difluoropyridine in its ground and excited electronic states

C_{2v}	ν	Approximate description	S_0	$S_1(\pi, \pi^*)$		$S_2(n, \pi^*)$	
				Obs.	Calc.	Obs.	Calc.
A_1	1	C-H stretch	3109	-	3114	2954	3077
	2	C-H stretch	3082	-	3083	2889	3055
	3	Ring stretch	1620	1424	1617	1409	1525
	4	Ring stretch	1458	1289	1458	1296	1364
	5	C-F sym. stretch	1320	1147	1320	1167	1260
	6	C-H in-plane wag	1069	960	1072	948	935
	7	Ring breathing	1001	885	994	877	923
	8	Ring bend	741	682	743	688	684
	9	Ring bend	546	474	546	476	466
	10	C-F in-plane wag	350	318	347	314	329
A_2	11	C-H out-of-plane wag	874	676	875	680	573
	12	C-F out-of-plane wag	660	372	672	377	380
	13	Ring twist	215	173	211	163	89
B_1	14	C-H out-of-plane wag	999	653	987	653	547
	15	C-H out-of-plane wag	797	502	804	502	434
	16	Ring twist	723	395	733	405	349
B_2	17	Ring pucker	460	127	470	112	158
	18	C-F out-of-plane wag	247	179	242	174	217
	19	C-H anti-sym. stretch	3113	-	3110	2892	3059
	20	Ring stretch	1606	-	1597	1328	1752
	21	Ring stretch	1461	-	1461	1268	1481
	22	Ring stretch	1280	-	1297	1205	1354
	23	C-H in-plane wag	1243	-	1242	1080	1192
	24	C-H in-plane wag	1139	-	1146	1001	1103
	25	C-F antisym. stretch	1007	858	1003	877	895
	26	Ring bend	568	500	565	493	515
							488

C_{2v}	v	Approximate description	S_0	$S_1 (\pi, \pi^*)$		$S_2 (n, \pi^*)$	
				Obs.	Calc.	Obs.	Calc.
	27	C-F in-plane wag	501	498	455	450	458
							464

Table 6

Selected vibrational frequencies (cm^{-1}) of pyridine and fluoropyridines

Sym. ^a		Description		S ₀	S (π, π*)					S (n, π*)				
		Py	2FPy	3FPy	26DFPy	Py	2FPy	3FPy	26DFPy	Py	2FPy	3FPy	26DFPy	
A ₁	Ring stretch	1584	1605	1594	1620	(1499) ^b	1690	(1699)	1424	(1507)	(1586)	1532	(1580)	
	Ring stretch	1483	1478	1480	1458	(1394)	1453	1488	1289	(1379)	(1381)	1320	(1354)	
	Ring breathing	1031	997	1022	1001	(878)	946	(874)	885	(857)	(879)	790	(899)	
	Ring bend	991	842	816	741	(883)	797	690	680	(885)	(789)	737	(705)	
	Ring bend	654	620	613	546	(577)	532	500	474	636	(554)	540	(542)	
A ₂	C-F stretch	-	1266	1227	1320	-	1243	1206	1147	-	(1168)	1132	(1270)	
	C-F in-plane wag	-	433	398	350	-	396	316	317	-	(380)	383	(356)	
	Ring twisting	375	518	507	660	(434)	432	(387)	372	(476)	(454)	425	(378)	
	C-F out-of-plane wag	-	226	231	215	-	163	272	173	-	(240)	227	(125)	
	Ring twisting	700	733	701	723	(260)	322	298	395	326	(380)	305	(454)	
B ₁	Ring puckering	403	414	412	460 ^c	(244)	96	118	127 ^c	60	(40)	107	(69) ^c	
	C-F out-of-plane wag	-	226	231	247 ^c	-	163	272	179 ^c	-	(240)	227	(288) ^c	
	Ring stretch	1576	1593	1588	1606	(1680)	1489	(1512)	-	(1453)	(1438)	1519	(1515)	
B ₂	Ring stretch	1442	1439	1426	1461	(1476)	1353	(1385)	-	(1314)	(1327)	1309	(1356)	
	Ring stretch	1227	1286	1249	1280	(1310)	1220	(1265)	-	(1185)	(1210)	1199	(1292)	
	Ring bend	601	554	533	568	(509)	493	426	496	543	(494)	517	(488)	
	C-F stretch	-	1266	1227	1007	-	1243	1206	877	-	(1168)	1132	(950)	
	C-F in-plane wag	-	433	398	501	-	396	316	455	-	(380)	383	(464)	

^a Symmetry species apply to Py and 26DFPy. For 2FPy and 3FPy the C-F vibrations are listed twice and the A₁ and B₂ symmetry species correspond to A' for 2FPy and 3FPy while A₂ and B₁ correspond to A''

^b Frequencies in parentheses are calculated values

^c Strongly coupled vibrations