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Vibrational spectral analysis of 2,3,4,5,6-pentafluoroaniline by density functional theory studies

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ABSTRACT

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Article history: Received: 24 May 2012; Received in revised form: 28 June 2012; Accepted: 13 July 2012; Vibrational spectral analysis of 2,3,4,5,6-pentafluoroaniline (PFA) was recorded using FT-IR and FT-Raman spectroscopic techniques in the region 4000-400 cm⁻¹ and 3500-100 cm⁻¹, respectively. The equilibrium geometry, and harmonic vibrational frequencies of PFA have been investigated with the help of HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods. The observed and calculated frequencies are found to be in good agreement.

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Keywords

FT-IR, FT-Raman, HF, DFT, 2,3,4,5,6-pentafluoroaniline.

Introduction

Aniline and its substituted derivatives are widely used in a variety of industrial and commercial purposes, including manufacturing of dyestuff, pesticide, and pharmaceuticals [1]. Some of the para- substituted derivatives of anilines are local anesthetics, and the amino group in these molecules plays an important role in the interaction with the receptor. The inclusion of a substituent group in aniline leads to the variation in charge distribution in the molecule and consequently this greatly affects the structural, electronic, and vibrational parameters [2]. Molecular geometry changes due to enhanced interaction between the aromatic ring and the amino group. The amino groups are generally referred to as electron-donating substituents in aromatic ring system [3]. The asymmetric interaction between the amino group and the aromatic ring produces a small displacement of the nitrogen atom out of the benzene ring. Aniline and its derivatives have been subjected to many different types of scientific studies up to now, and several workers [4-6] have studied the spectra of a large number of mono-, di-, tri-, and tetra-substituted aniline-related molecules.

More recently [7, 8], the experimental vibrational spectra of 3-chloro-4-methylaniline, 2,4-dichloroaniline, and 3.4dimethoxyaniline have been investigated in comparison with ab initio and DFT values. However, the detailed HF/B3LYP with 6-311++G(d,p) basis set comparative studies on the complete FT-IR and FT-Raman spectra of PFA have not been reported. In the present work, the molecular geometry, optimized parameters, and vibrational frequencies are computed, and the performance of the computational methods for HF and B3LYP at 6-311++G(d,p) basis set are compared. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules, the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional ab initio Hartree-Fock calculations. Among DFT calculation, Becke's three-parameter hybrid functions were

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combined with the Lee–Yang–Parr correlation functions (B3LYP) to predict best results for molecular geometry and vibrational wave numbers for moderately larger molecule [9]. **Experimental details**

The sample of PFA was obtained from Lancaster Chemical Company, UK, and used as such without any further purification. The FT-IR spectrum of the compound was recorded in the region 4000–400 cm⁻¹, using KBr pellet. The FT-Raman spectrum is recorded in the region 3500–100 cm⁻¹ using the 1064 nm line of a Nd:YAG laser for excitation, operating at 200mW power. Both the spectra were recorded using BRUKER IFS 66V.

Computational methods

The molecular structure optimization of the title compound and corresponding vibrational harmonic frequencies were calculated using HF and DFT with Beckee-3-Lee-Yang-Parr (B3LYP) with 6-311++G(d,p) basis set using Gaussian 09 program [10] package without any constraint on the geometry. Geometries have been first optimized with full relaxation on the potential energy surfaces at HF/6-311++G(d,p) basis set and then reoptimized at B3LYP/6-311++G(d,p) level. The optimized geometrical parameters and fundamental vibrational frequencies were calculated using the Gaussian 09 program package. By combining the results of the GAUSSVIEW [11] program with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. However, the defined coordinates form complete set and match quite well with the motions observed using GAUSSVIEW program.

Results and discussion

Molecular geometry

The molecular structure along with numbering of atoms of PFA, which has Cs point group symmetry, is shown in Fig. 1. The global minimum energies obtained by the HF and DFT are -780.170724272 hartrees -2048338.392610281 kJ/mol) and -783.992749831 hartrees (-2058373.12147984 kJ/mol), respectively. The most optimized structural parameters (bond



length and bond angle) were also calculated by HF and B3LYP with 6-311++G(d,p) basis set, and they were depicted in Table 1 and pictorial representation of bond lengths and bond angles are shown in Fig.2.



Fig. 1 Molecular structure of 2,3,4,5,6-pentafluoroaniline

The C1–C2 and C1–C6 bonds have the high bond length values as compared with the C–C bond. This may due to the effect of substitution of amino group in C1 atom. The calculated values of bond length and bond angle are slightly longer (-or-) shorter than the experimental values, and these variations may due to the substitution of NH_2 , and F groups.

The title molecule PFA has 14 atoms 36 normal vibrational modes. Assuming that the PFA defines a symmetry plane, i.e., that the molecule belongs to the Cs point group, for the atoms located in the plane of molecule, the A' vibrational displacements take place in the plane of the molecule, and the A' modes correspond to the displacement out of the plane of the molecule.

The 36 normal modes of the PFA are distributed among the symmetry species as vib=25A' (in-plane) +11A" (out-of-plane). The A' vibrations are totally symmetric and give rise to polarized Raman lines whereas A" vibrations are asymmetric and give rise to depolarized Raman lines. All vibrations are active in both the Raman scattering and infrared absorption.

The harmonic vibrational frequencies calculated for PFA at HF and B3LYP levels using the triple-split valence basis set along with the diffuse and polarization functions, 6- $311{+}{+}G(d{,}p)$, and the observed FT-IR and FT-Raman frequencies for various modes of vibrations have been presented in Table 2. Comparison of frequencies calculated at HF and B3LYP with the experimental values reveals the over-estimation of the calculated vibrational modes due to the neglect of harmonicity in real system. Inclusion of electron correlation in the density functional theory to certain extent makes the frequency values smaller in comparison with the HF frequency data. In the computed harmonic vibrations is observed, although basis set is only marginally sensitive as observed in the DFT values using 6-311++G(d,p). Any-way, notwithstanding the level of calculations, it is customary to scale down the calculated harmonic frequencies in order to agree with the experiment. The scaled calculated frequencies minimize the root- mean square difference between calculated and experimental frequencies for bands with definite identifications. The descriptions concerning the assignment have also been indicated in Table 2. The observed FT-IR and FT-Raman spectra are reported in Figs. 3 and 4, respectively.



Fig. 2 Pictorial representation of bond length and bond angles of 2,3,4,5,6-pentafluoroaniline
(a) HF/6-311++G(d,p) (b) B3LYP/6-311++G(d,p)







Fig. 3 FT-Raman spectrum of 2,3,4,5,6-pentafluroaniline *NH*₂ group vibrations

The molecule under consideration possesses one NH₂ group, and hence, six internal modes of vibrations are possible: symmetric stretching, asymmetric stretching, scissoring, rocking, wagging, and the twisting modes. Subashchandrabose *et al.* [12] assigned the 3200–3330 cm⁻¹ region for the NH₂ stretching vibration of NH₂ group. The asymmetric stretching mode was calculated at higher frequencies, 3632, 3496 cm⁻¹ than the symmetric stretching mode 3511, 3382 cm⁻¹ in HF and B3LYP and was related to the FT-IR bands observed

experimentally at 3504, 3409 cm⁻¹, and FT-Raman band observed at 3412 cm⁻¹. So, the strong intensities of the bands correspond to the deformation vibration of NH₂ and the range 1590–1650 cm⁻¹, reported for aniline by Krishnakumar et al [13,14]. Based on this, the internal deformation vibration of NH₂ as scissoring frequency observed at 1520 cm⁻¹ in FT-IR spectrum. Theoretically, the bands were calculated at 1652 cm^{-1} in HF and 1565 cm⁻¹ in B3LYP. The B3LYP method is closer to the observed value. The calculated values 1149 cm^{-1} , 1114 cm^{-1} belong to NH₂ rocking vibration by HF and B3LYP, respectively. The observed value at 1112 cm⁻¹ (FT-Raman) is assigned to NH₂ rocking mode, which is in agreement with the calculated frequency of B3LYP method. In this study, the NH₂ wagging mode was calculated at 90 cm⁻¹ in HF and 89 cm⁻¹ in B3LYP method. The weak Raman band observed at 353 cm^{-1} is assigned to NH₂ twisting mode, which is in agreement with the theoretical value 349 cm⁻¹.

C-F vibrations

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations is possible due to the presence of heavy atoms on the periphery of the molecule [15]. In PFA, the C–F stretching vibrations appeared at 1311, 1217 and 1170 cm⁻¹ in FT-Raman and 1100 and 998 cm⁻¹ in IR spectra. The C–F in-plane bending vibrations were found at 706, 622, 610, 312 and 291 cm⁻¹ in FT-Raman spectrum. The C–F out-of-plane bending mode is recorded at 341, 263, 247, 131 and 100 cm⁻¹ in FT-Raman. The calculated values of C–F stretching, in-plane bending and outof-plane bending modes are found to be at 767, 689, 678, 326, and 312 cm⁻¹ in HF/6-311++G(D,P) and 354, 280, 274, 142 and 140 cm⁻¹ in B3LYP/6-311++G(d,p).

C_N vibrations

The calculation of C–N stretching frequency is rather difficult task since there are problems in identifying these frequencies from other vibrations [16]. The assigned C–N stretching vibrations in the present work, a strong IR band, is observed at 932 cm⁻¹ due to the stretching vibration between carbon and nitrogen atoms which is in line with the literature [17, 18]. The band observed at 688 cm⁻¹ in IR and 283 cm⁻¹ in Raman spectra are assigned to C–N in-plane bending vibration and the C–N out-of-plane bending vibration, respectively. This implies that the C–N vibrations are not much influenced by other substitutions in the ring, and also, these vibrations are not influenced by amine. It should be highlighted that the frequency calculated with the B3LYP/6-311++G(d,p) method for the C–N in-plane bending mode at 672 cm⁻¹ is in agreement with experimental value 688 cm⁻¹.

C-C vibration

In our present study, the frequencies observed in the FT-IR spectrum at 1680, 1612, 1351 and 1300 cm⁻¹ and in the FT-Raman at 1681, 1614, and 1483 cm⁻¹ are assigned to C–C stretching vibrations. The theoretically calculated C–C stretching vibrations by B3LYP/6-311++G(d,p) method at 1626–1285 cm⁻¹ show good agreement with recorded spectrum as well as literature data [14].

Conclusion

The FT-IR and FT-Raman spectra have been recorded and the detailed vibrational assignment is presented for PFA. The equilibrium geometries, harmonic vibrational frequencies, and IR and Raman spectra of PFA are determined and analyzed by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory. The vibrational frequency analysis by B3LYP method agrees satisfactorily with experimental results. Therefore, the assignments made at higher level of theory with lower basis set with only reasonable deviations from the experimental values, seem to be correct. We have clearly shown the relevant role played by the molecular frame where π - electron delocalization takes place.

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Tuste 1. optimized geometrical parameters of 2,0,1,0,0 pentamoroumine										
	Bond ler	ıgths (Å)	Parameters	Bond angles (⁰)						
Parameters	HF/6-	B3LYP/6-		HF/6-	B3LYP/6-					
	311++(d,p)	311++(d,p)		311++(d,p)	311++(d,p)					
R(1,2)	1.3862	1.400	A(2,1,6)	116.58	116.32					
R(1,6)	1.3861	1.399	A(2,1,7)	121.71	121.84					
R(1,7)	1.3644	1.368	A(6,1,7) 121.71		121.84					
R(2,3)	1.3737	1.386	A(1,2,3)	122.02	122.24					
R(2,10)	1.3231	1.351	A(1,2,10)	118.46	118.14					
R(3,4)	1.3769	1.391	A(3,2,10)	119.53	119.62					
R(3,11)	1.3098	1.337	A(2,3,4)	120.18	120.08					
R(4,5)	1.3768	1.391	A(2,3,11)	119.89	119.94					
R(4,12)	1.3143	1.340	A(4,3,11)	119.93	119.98					
R(5,6)	1.3738	1.386	A(3,4,5)	119.04	119.05					
R(5,13)	1.3098	1.337	A(3,4,12)	120.48	120.48					
R(6,14)	1.323	1.351	A(5,4,12)	120.48	120.48					
R(7,8)	0.990	1.004	A(4,5,6)	120.18	120.08					
R(7,9)	0.990	1.004	A(4,5,13)	119.94	119.98					
			A(6,5,13)	119.89	119.94					
			A(1,6,5)	122.02	122.24					
			A(1,6,14)	118.46	118.14					
			A(5,6,14)	119.52	119.62					
			A(1,7,8)	120.35	120.34					
			A(1,7,9)	120.35	120.34					
			A(8,7.9)	119.30	119.31					

Table 1. Optimized geometrical parameters of 2,3,4,5,6-pentafluoroaniline

Table 2 – Vibrational assignments of 2,3,4,5,6-pentafluoroaniline

S.No. Species		Observed frequencies (cm ⁻¹)		Calculated frequencies (cm ⁻¹)				
			()	Unscaled		Scaled		Vibrational Assignments
		FT-IR	FT-Raman	HF	B3LYP	HF	B3LYP	
				/6-311++(d,p)	/6-311++(d,p)	/6-311++(d,p)	/6-311++(d,p)	
1	A'	3504		3991	3760	3632	3496	NH ₂ asymmetric stretching
2	A'	3409	3412	3858	3637	3511	3382	NH ₂ symmetric stretching
3	A'	1680	1681	1854	1694	1724	1626	CC stretching
4	A'	1612	1614	1829	1653	1701	1587	CC stretching
5	A'	1520	1521	1776	1630	1652	1565	NH ₂ scissoring
6	A'		1483	1698	1545	1579	1483	CC stretching
7	A'	1351		1687	1538	1569	1476	CC stretching
8	A'		1311	1642	1502	1527	1442	CF stretching
9	A'	1300		1448	1339	1347	1285	CC stretching
10	A'		1217	1311	1311	1219	1258	CF stretching
11	A'		1170	1276	1174	1187	1127	CF stretching
12	A'	1112		1235	1161	1149	1114	NH ₂ rocking
13	A'	1100		1188	1119	1105	1074	CF stretching
14	A'	998		1104	1013	1027	972	CF stretching
15	A'	932		1031	941	959	903	CN stretching
16	A'		706	825	757	767	727	CF in-plane bending
17	A'	688		781	700	726	672	CN in-plane bending
18	A'		622	740	658	688	632	CF in-plane bending
19	A'	608	610	729	645	678	619	CF in-plane bending
20	A'	575		646	603	601	579	Ring in-plane bending
21	A'		560	607	562	565	539	Ring in-plane bending
22	A'		446	489	451	455	433	Ring in-plane bending
23	A'	411		487	450	453	432	CC stretching
24	A''		401	455	408	423	392	Ring out-of-plane bending
25	A''		353	416	364	387	349	NH ₂ twisting
26	A''		341	381	342	354	328	CF out-of-plane bending
27	A'		312	351	322	326	309	CF in-plane bending
28	A'		291	336	308	312	296	CF in-plane bending
29	A''		283	308	283	286	272	CN out-of-plane bending
30	A''		263	301	275	280	264	CF out-of-plane bending
31	A''		247	295	269	274	258	CF out-of-plane bending
32	A''		212	240	210	223	202	Ring out-of-plane bending
33	A''		164	207	188	193	180	Ring out-of-plane bending
34	A''		131	153	137	142	132	CF out-of-plane bending
35	A''		100	151	135	140	130	CF out-of-plane bending
36	A''			97	88	90	84	NH ₂ wagging