

FTIR and Raman Spectra Assignments and Electronic Structure Calculations for 3, 4-Difluoroaniline

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Abstract – Comprehensive investigation of geometrical and electronic structure in ground as well as the first excited state of 3, 4-Difluoroaniline (C₆H₅NF₂) was carried out. The experimentally observed spectral data (FT-IR and FT-Raman) of the title compound was compared with the spectral data obtained by Electronic structures calculations, at the RHF/6-31G* and B3LYP/6-31G* basis set has been carried out. The molecular optimized geometry parameter like bond angle, bond length, stretching and bending force constants of title molecule were calculated.

Keywords— 3, 4-Difluoroaniline, FT-IR and FT-Raman Spectra, Electronic Structure, DFT

I. INTRODUCTION

In the present study Electronic structures calculations, at the RHF/6-31G* and B3LYP/6-31G* has been carried out on 3, 4-difluoroaniline (DNA). A complete revised assignment of the experimental spectra has proposed in terms of molecular parameters and PEDs obtained from force field calculations. The electronic structure calculations have been performed using Gassian 03W⁸; the PED calculations with the MOLVIB⁹, giving optimized structures, energies harmonic vibrational frequencies, depolarization ratios, infrared intensities, Raman activities, force constants and PEDs. The proposed assignments on the basis of experimental IR and Raman spectra have been reviewed. All the computed harmonic frequencies have been scaled¹⁰.

Excellent agreement between experimental and theoretical anharmonic inversion-torsion frequencies of fundamental, overtone and combination modes in aniline has been obtained in the correlated ab initio studies, which gives a confidence to thecalculated. Potential energy surface and the evidence to a rather high nonplanarity of aniline molecule [8, 9].

Comprehensive studies of the molecular and electronic structures, vibrational frequencies and infrared and Raman intensities of the aniline radical cat-ion have been performed by using the (UB3LYP) and (UMP2) methods with the extended 6-31111G ~

df, pd basis set by Piotr etal. For comparison, analogous calculations were carried out for the closed- shell neutral aniline [10]. To assess reliability of theoretical calculations in substituted anilines we have carried out ab initio and DFT calculations on 3, 4-Difluoroaniline. 3,4-Difluoroaniline is a chemical compound which has a strong activating - NH₂ substituent and two weakly deactivating F.

II. EXPERIMENTAL STUDIES

Experimental details:

The liquid sample of 3, 4-difluoroaniline (DAN) was supplied by Aldrich Chemical Co. and was distilled in vacuum before use. The infrared (IR) spectrum of the sample in KBr pellet was recorded at room temperature on Perkin-Elmer model 377 double beam automatic Spectrophotometer. The Laser Raman Spectrum of the sample was recorded on Cary-model Laser Raman Spectrometer using Ar⁺ laser with two Czerny-Littrow monochromators.

Computational Work:

i) Electronic structure calculation methods:

The development of theoretical methods and in particularly quantum chemistry, allowed not only an

interpretation of the experimental observations, but also made it possible to predict molecular properties.

Computational chemistry is simply the application of quantum mechanical and computing skill to the solution of physical, chemical problems. Here, one uses computer softwares like GAUSSIAN to generate information such as properties of molecules or simulated experimental results. The Schrödinger equation is the basis for the computational methods.

The Born-Oppenheimer approximation is the first of several approximations made while trying to solve Schrödinger's equation for more complex systems with more than one or two electrons. A few electronic structure computation methods are discussed in brief as follows.

ii) In the *ab initio* Hartree-Fock self-consistent Field (HF-SCF) method:

The wave function is an antisymmetrized determinantal product of one-electron orbitals (the "Slater" determinant). Schrödinger's equation is transformed into a set of Hartree-Fock equations. The wave function of each electron is optimized under the mean potential averaged over all the other electrons in the system, as well as the electrostatic potential generated by the fixed nuclei.

In another words, during the Hartree-Fock calculation, the electron cannot 'see' other electrons, instead of averaged 'electron gas'. The primary deficiency of Hartree-Fock method is that the correlation of electron motion cannot be accounted adequately.

iii) Density Functional Theory (DFT) method:

This method is one of the most popular approaches to quantum mechanical many-body electronic structure calculations of molecular and condensed matter systems. It has been proved that for molecules, the ground-state molecular energy is uniquely determined by the ground-state electron probability density. Therefore, all the ground-state molecular properties can be calculated from the electron density, without having to find the molecular wave function.

In addition, according to the Hohenberg-Kohn variational theorem, the true ground-state electron density minimizes the energy functional. The DFT method is variational.

A number of density functional theoretical methods have been developed, one such method is B3-LYP (Becke's three parameter mixing of exchange functional with Lee Yang Parr correlation functional).

In order to model structures and vibrational spectral properties, we performed electronic calculations with the *ab initio*,s RHF/6-31G* and hybrid DFT,s B3LYP/6-31G* using the *Gaussian 03W* suite of programs [15]. Molecular electronic energies, equilibrium geometries,

vibrational frequencies, IR intensities and Raman activities have been computed.

All the computed harmonic frequencies have been scaled with scaling factors 0.8929 (RHF) and 0.9616 (B3LYP) [17].

iv) MOLVIB:

MOLVIB is a FORTRAN program for the calculation of harmonic force-fields and vibrational modes of molecules upto 100 atoms. To aid the vibrational assignments, we carried out normal coordinate calculations using MOLVIB package [16]: force fields and PEDs have been computed for B3LYP/6-311G* results for all the compounds.

III. RESULTS AND DISCUSSION

The optimized molecular structure of the DAN is shown in Fig.7. DAN belongs to C_1 symmetry due to nonlinearity of amino group. The molecular electronic energy is -486.0607 hartrees at B3LYP/6-31G*. The experimental infrared spectrum taken from reference [14] is presented in Fig -8. We present the optimized geometrical parameters in Table - 4. The results are compared with the available experimental data [19, 20]. The Table - 5 includes stretching and bending force constants derived from a normal coordinate calculations using B3LYP/6-31G* results. Table -6 presents experimental IR and Raman (Fig-9) and theoretical fundamental vibrational frequencies with assignments (in % PED).

The observed IR and Raman vibrational frequencies were analyzed and assigned to different normal modes of the molecule. The error obtained was in general very low. The observed IR and Raman vibrational frequencies were analyzed, revised and assigned to different normal modes of the molecule.

We point out that the proposed assignments are correlated with the benzene modes, though, it is true, and several of the modes of DAN show contributions from different bond oscillators.

This correlation would serve the object of gaining an understanding as to changes in the normal modes of benzene to aniline derivatives. Characteristic benzene as well as C-X vibrations are in the correlation range [8-14].

The deformation vibrations of DAN have appeared with single dominant contribution as evident from PED. We also note that the in-plane and out-of-plane C-X bending vibrations show dominance in the region below 1000 cm^{-1} . All the assignments are in agreement with the literature [8-14]. Other general conclusions have also been deduced. There is good agreement between theory and experiment.

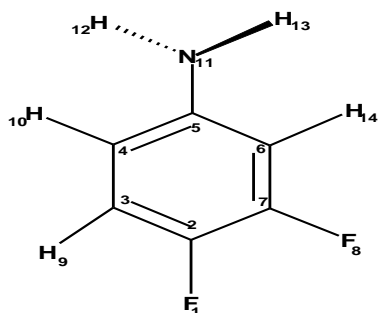


Fig.7. Molecular structure of 3, 4 – difluoroaniline

Assignments:

In the present work, vibrational assignments have been made on the basis of “Spectra-Structure Correlations”, aided by the electronic structure calculations that is, the scaled theoretical vibrational fundamental frequencies. In Table – 6 assignments of vibrational frequencies are presented with bold internal modes in PED. Assignments are discussed with experimental IR and Raman frequencies.

C-H stretching vibrations:

These vibrations show characteristic bands, as in the benzene derivatives, in the region $3100-3000\text{ cm}^{-1}$ [3-7]. These vibrations are assigned to medium strong IR/Raman bands at 3080, medium weak IR/Raman bands at 3040 and to a medium weak IR band at 3010 cm^{-1} where corresponding Raman band was not observed. These modes are predicted as weak at RHF and B3LYP levels.

The numbers inside bracket are relative intensities in case of frequencies and % contributions in case of the PEDs. ν -stretch, β - in-plane bending, γ - Out-of-plane bending. The predicted bands agree well with the observed ones within $\sim 1\%$ for the two methods. It may be seen that the force constants, $5.600-5.688\text{ mdyne/\AA}$, obtained from PED calculations, corresponding to C-H stretching vibrations show little changes in magnitudes compared to the known values [6, 7], suggesting the dominance of a single vibration.

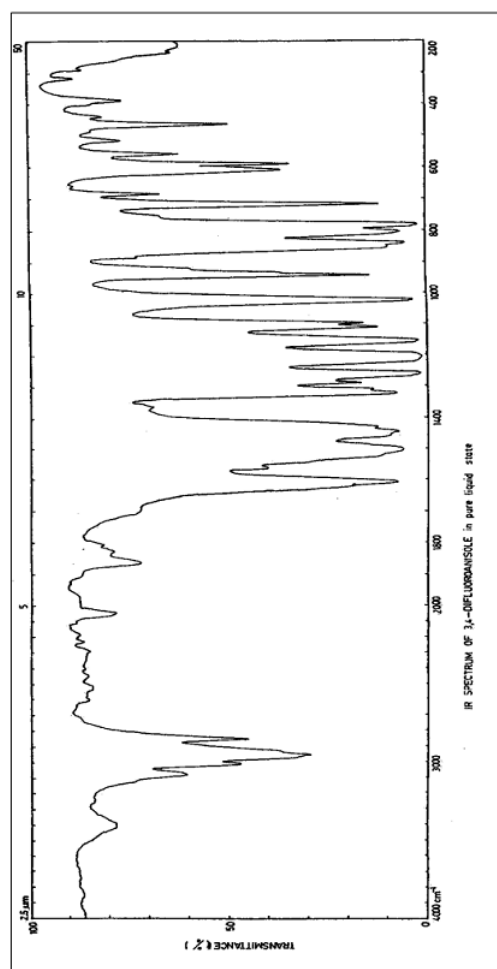


Fig -8 : Experimental IR spectrum of 3, 4 - difluoroaniline

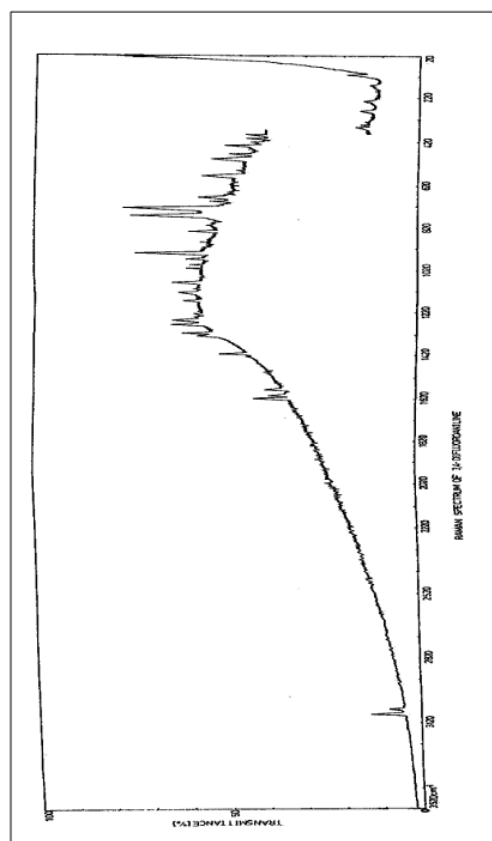


Fig -9: Experimental Raman spectrum of 3, 4 - difluoroaniline

Table.4: Optimized Geometry parameters

S.No.	Parameter	Experimental*	RHF	B3LY P
Bond length (Å)				
1	F1-C2	1.337	1.330	1.349
2	C2-C3.	1.396	1.375	1.387
3	C2-C7.	1.394	1.378	1.393
4	C3-C4.	1.394	1.385	1.395
5	C3-H9.	1.083	1.074	1.085
6	C4-C5.	1.397	1.392	1.405
7	C4-H10.	1.083	1.075	1.087
8	C5-C6.	1.397	1.393	1.406
9	C5-N11.	1.402	1.394	1.399
10	C6-C7.	1.394	1.375	1.386
11	C6-H14.	1.083	1.075	1.086
12	C7-F8	1.337	1.324	1.340
13	N11-H12	1.001	0.997	1.013
14	N11-H13.	1.001	0.997	1.013
Bond angle (°)				
15	F1-C2-C3.		120.9	121.1
16	F1-C2-C7.		119.7	119.5
17	C3-C2-C7.	118.9	119.4	119.4
18	C2-C3-C4.		120.2	120.1
19	C2-C3-H9.		118.9	118.8
20	C4-C3-H9.		120.9	121.0
21	C3-C4-C5.		120.6	120.7
22	C3-C4-H10.		119.6	119.6
23	C5-C4-H10.		119.9	119.7
24	C4-C5-C6.	119.4	118.8	118.7
25	C4-C5-N11.		120.9	120.9
26	C6-C5-N11.		120.3	120.3
27	C5-C6-C7.	120.1	119.8	119.9
28	C5-C6-H14.	119.8	121.5	121.4
29	C7-C6-H14.		118.7	118.7
30	C2-C7-C6.	120.7	121.3	121.2
31	C2-C7-F8.		119.2	119.0
32	C6-C7-F8.		119.5	119.7
33	C5-N11-H12.	115.9	114.6	114.8
34	C5-N11-H13.		114.4	114.6
35	H12-N11-H13.	113.1	110.8	111.1

Table-5: Stretching and bending force constants

Internal coordinates	Atoms involved	Force constant
Stretching force constants (mdyne/Å)		
R1	F1-C2.	6.631
R2	C2-C3.	5.412
R3	C2-C7.	5.329
R4	C3-C4.	5.361
R5	C3-H9.	5.688
R6	C4-C5	5.114
R7	C4-H10.	5.600
R8	C5-C6.	5.122
R9	C5-N11.	6.435
R10	C6-C7.	5.486
R11	C6-H14.	5.653
R12	C7-F8.	6.691
R13	N11-H12.	7.198
R14	N11-H13.	7.198
Internal coordinates	Atoms involved	Force constant
Bending force constants (mdyne/Årad²)		
1A	F1-C2-C3	0.627
A2	F1-C2-C7.	0.619
A3	C3-C2-C7.	0.728
A4	C2-C3-C4	0.700
A5	C2-C3-H9.	0.426
A6	C4-C3-H9.	0.433
A7	C3-C4-C5.	0.712
A8	C3-C4-H10.	0.451
A9	C5-C4-H10.	0.450
A10	C4-C5-C6.	0.753
A11	C4-C5-N11.	0.673
A12	C6-C5-N11	0.672
A13	C5-C6-C7	0.700
A14	C5-C6-H14	0.433
A15	C7-C6-H14	0.428
A16	C2-C7-C6	0.735
A17	C2-C7-F8	0.639
A18	C6-C7-F8	0.652
A19	C5-N11-H12	0.533
A20	C5-N11-H13	0.531
A21	H12-N11-H13	0.311

The numbers inside bracket are relative intensities in case of frequencies and % contributions in case of the PEDs.v-stretch, β - in-plane bending, γ - Out-of-plane bending .The predicted bands agree well with the observed ones within ~1% for the two methods. It may be seen that the force constants, 5.600–5.688 mdyne/Å, obtained from PED calculations, corresponding to C-H stretching vibrations show little changes in magnitudes compared to the known

values [6, 7], suggesting the dominance of a single vibration.

C-H in-plan vibrations:

The CH in-plane bending vibrations are substitution sensitive, normally showing the bands in the region 1300-1000 cm^{-1} [6, 7]. Medium Strong IR bands at 1170, 1130, 975 cm^{-1} with corresponding medium weak Raman bands at 1165, 1125, 980 cm^{-1} are assigned to the CH in-plane bending vibrations. It is seen from the PEDs that the modes show couplings of the bond oscillators of the ring, NH₂ and fluorine. The predicted bands are medium weak at RHF and B3LYP. These frequencies agree well with the observed ones within ~1%.

Table-6. Experimental and Theoretical frequencies (cm^{-1}) with assignments

S.No	IR	Raman	RHF	B3LYP	A	Assignments PEDs(%)
V1	3440ms	---	3475(5)	3507(3)	67.68	$\nu_{\text{as}}\text{NH}_2$ (100)
V2	3375ms	---	3386(7)	3413(5)	165.9	$\nu_{\text{s}}\text{NH}_2$ (100)
V3	3080ms	3080ms	3035(1)	3098(1)	137.4	νCH (99)
V4	3040mw	3040w	3024(1)	3086(1)	72.90	νCH (99)
V5	3010mw	---	3008(4)	3069(4)	70.88	νCH (99)
V6	1620m	1620m	1632(29)	1634(34)	31.25	ScissoringNH ₂ (61), $\nu\text{C}(\text{C}13)\nu\text{C}-\text{NH}_2(11)$
V7	1605m	1600m	1635(4)	1618(1)	8.110	$\nu\text{CC}(37)$, ScissoringNH ₂ (19)
V8	1575mw	1570m	1617(22)	1594(15)	1.930	$\nu\text{CC}(69)$, $\nu\text{C}-\text{F}$ (5)
V9	1480vs	---	1529(100)	1514(100)	0.754	$\nu\text{C}(30)$, $\beta\text{CH}(14)$, $\nu\text{C}-\text{F}(12)$
V10	1430vs	1420m	1453(7)	1448(5)	0.354	$\nu\text{C}(38)$, $\beta\text{CH}(18)$, $\nu\text{C}-\text{F}(12)$
V11	1340m	1330m	1313(9)	1319(5)	8.964	$\nu\text{C}-\text{NH}_2(32)$, $\nu\text{C}(22)$, $\nu\text{C}-\text{F}(21)$
V12	1315vs	1320ms	1263(17)	1312(10)	2.393	νCC (86)
V13	1285ms	1285m	1212(27)	1254(19)	2.608	$\beta\text{CH}(48)$, $\nu\text{C}-\text{F}(28)$, $\nu\text{C}(7)$
V14	1245vs	1250m	1185(13)	1206(26)	0.388	$\beta\text{CH}(45)$, $\nu\text{C}-\text{F}(19)$, $\nu\text{C}-\text{N}(6)$
V15	1170ms	1165mw	1156(8)	1161(14)	0.635	$\nu\text{C}-\text{F}(36)$, $\beta\text{CH}(21)$, $\nu\text{C}-\text{N}(17)$
V16	1130ms	1125mw	1091(10)	1113(7)	0.582	$\beta\text{CH}(44)$, $\nu\text{C}(\text{C}16)$, $\beta\text{C}-\text{NH}_2(8)$
V17	1070s	1075m	1047(4)	1071(2)	0.678	rocking NH ₂ (44), $\nu\text{C}(19)$
V18	975ms	980mw	945(1)	940(6)	0.109	$\nu\text{C}(\text{C}34)$, $\nu\text{C}-\text{F}(10)$, $\nu\text{C}(\text{C}10)$, $\beta\text{CC}(9)$, $\beta\text{CH}(7)$
V19	940s	945s	937(6)	884(1)	1.765	γCH (89)
V20	860s	865m	849(23)	801(19)	2.990	γCH (75)
V21	770vs	770s	820(15)	777(8)	4.887	γCH (77)
V22	735vs	735vs	765(9)	766(10)	15.43	$\nu\text{C}-\text{F}(30)$, $\nu\text{CC}(28)$, $\beta\text{CC}(15)$
V23	715s	710mw	723(6)	723(2)	11.86	$\beta\text{CC}(35)$, $\nu\text{C}-\text{F}(11)$, $\nu\text{C}-\text{N}(10)$
V24	680s	680ms	674(9)	642(21)	1.473	waggingNH ₂ (55)
V25	605s	600s	647(56)	612(51)	2.554	$\beta\text{C}-\text{NH}_2$ (58)
V26	520m	515ms	593(53)	575(65)	3.746	γCCN (73)
V27	470m	475mw	571(3)	568(3)	5.602	$\beta\text{C}-\text{F}(40)$, $\nu\text{C}(10)$, $\beta\text{CC}(9)$
V28	450vs	445s	492(0)	492(0)	4.606	$\beta\text{CC}(18)$, $\beta\text{C}-\text{F}(15)$, $\beta\text{C}-\text{N}(11)$
V29	405ms	410m	453(2)	441(2)	0.209	γCC (61)
V30	390s	395ms	430(0)	430(0)	3.438	$\beta\text{CC}(48)$, $\beta\text{C}-\text{N}(13)$
V31	330w	335w	360(2)	348(2)	2.767	γCC (53), $\gamma\text{C}-\text{NH}_2(16)$
V32	270w	280w	311(0)	312(0)	0.709	$\beta\text{C}-\text{NH}_2(57)$, $\beta\text{C}-\text{F}(14)$
V33	230w	240mw	272(0)	269(1)	0.219	$\beta\text{C}-\text{F}(53)$, $\gamma\text{C}-\text{NH}_2(18)$
V34	---	224ms	230(1)	262(7)	0.391	torsionNH ₂ (88)
V35	---	160mw	213(8)	223(1)	3.689	$\gamma\text{C}-\text{F}$ (54), $\gamma\text{C}-\text{NH}_2(10)$
V36	---	110m	148(0)	144(0)	1.254	$\gamma\text{C}-\text{F}$ (34), $\gamma\text{C}-\text{NH}_2(19)$

C-H out-of-plane vibrations:

Bands involving the out – of – plane C-H vibrations appear in the range 1000-675 cm^{-1} [6, 7]. These vibrations are assigned to strong IR bands at 940, 860, 770 cm^{-1} . The corresponding strong Raman bands are at 945, 865, 770 cm^{-1} .

The frequencies with RHF level agree well with the observed ones within ~2%, whereas B3LYP level deviates by ~5 %.

C-C stretching vibrations:

The C-C stretching vibrations occur in a wider spectral range covering 1650-650 cm^{-1} [3-7]. The five medium weak to strong IR bands at 1605, 1575, 1430, 1315, 735 cm^{-1} with the corresponding medium to strong Raman bands at 1600, 1570, 1420, 1320, 735 cm^{-1}

and a very strong IR band at 1480 cm^{-1} with corresponding Raman band not observed, are assigned to the C-C stretching vibrations. As the bands corresponding to 1575, 1315 cm^{-1} are nearly pure the force constants values fall in the known interval, 5.114 - 5.412 mdyne/Å [3, 6].

The bands at 1529 (RHF), 1514 (B3LYP) cm^{-1} are predicted as very strong where experimental IR band is also very strong. It is seen from the PED that the bands observed at 1480, 1430, 735 cm^{-1} are mixed with contributions from C-X (X= NH₂, F) vibrations. The predicted frequencies agree well with the observed ones within ~3% error.

C-C in-plane bending vibrations:

Three strong IR bands at 715, 450, 390 cm^{-1} with corresponding medium weak to strong Raman band at 710, 445, 395 cm^{-1} are assigned to CC in-plane-bending vibrations. The above bands are in the expected range, as in similar systems [6-8]. The three predicted weak bands agree well with the observed ones within ~3%.

C-C out-of-plane bending vibrations:

In the substituted benzenes, CC out-of -plane vibrations are expected in the range 730-425 cm^{-1} [6-9].

Three weak to strong IR bands at 520, 405, 330 cm^{-1} with corresponding weak to strong Raman bands at 515, 410, 335 cm^{-1} are assigned to the CC out-of-plane vibrations. These frequencies agree well with the observed ones within ~3%.

C-X vibrations(X= NH₂, F)

In aniline [19] a strong IR and at 1282 cm^{-1} was assigned to C- NH₂ stretching vibration. We have assigned this band to a medium IR band at 1340 cm^{-1} and to a medium Raman band at 1330 cm^{-1} . In aniline [19], C- NH₂ in-plane bending vibration was assigned to a weak IR band at 390 cm^{-1} and we assigned this band to a strong IR and at 605 cm^{-1} with a strong Raman band at 600 cm^{-1} . In aniline [19], C- NH₂ out-of-plane bending vibration is assigned to a weak IR band at 217 cm^{-1} and we assigned this band to a weak IR band at 230 cm^{-1} with a medium weak Raman band at 240 cm^{-1} . The errors for predicted C-NH₂ vibrations are as much as 8%.

C-F vibrations:

Aromatic fluorine compounds give stretching bands in the region 1270-1100 cm^{-1} [2]. Strong IR bands at 1285, 1245 cm^{-1} with corresponding medium Raman bands at 1285, 1250 cm^{-1} are assigned to C-F stretching vibrations. The $\nu\text{C}-\text{F}$ vibrations are mixed with νCC , $\nu\text{C}-\text{NH}_2$ and βCH vibrations. The predicted

band corresponding to observed band at 1104 cm^{-1} deviates by $\sim 6\%$. C-F in-plane bending vibrations are expected in the general range $420\text{--}375\text{ cm}^{-1}$ [2].

In 2,6-difluorobenzonitrile, these bands are assigned at $289, 254\text{ cm}^{-1}$ [21]; in this work, a medium IR band at 470 cm^{-1} with corresponding medium weak Raman band at 475 cm^{-1} ; a weak IR band at 270 cm^{-1} with corresponding weak Raman band at 280 cm^{-1} ; are assigned to C-F in-plane bending vibrations. In 4-Fluorobenzaldehyde [22] C-F out-of-plane bending vibration was assigned to a Raman band at 336 cm^{-1} . In 2,6-difluorobenzonitrile, these bands are assigned at $520, 101\text{ cm}^{-1}$ [21]; two medium Raman bands at $160, 110\text{ cm}^{-1}$ are assigned to C-F out-of-plane vibrations. The errors for predicted C-F vibrations below 400 cm^{-1} are as much as 20% .

NH₂ group vibrations:

For the aniline, Pavel Hobza et al observed two absorption bands of approximately equal infrared intensities, positioned at 3508 and 3422 cm^{-1} . They assigned these bands to the NH_2 antisymmetric and symmetric stretching vibrations, respectively [10]. In this work, two medium strong IR band at 3440 and 3375 cm^{-1} with corresponding Raman bands not observed, are assigned to the NH_2 antisymmetric and symmetric stretching vibrations, respectively.

The NH_2 scissoring vibration in the aniline contributes to two modes, these modes have been assigned to the bands at 1608 and 1618 cm^{-1} , in the IR spectrum of aniline in argon matrix [10]. We assigned this vibration to a medium IR/Raman band at 1620 cm^{-1} IR spectroscopic studies of aniline show two bands, at 1054 and 1115 cm^{-1} , involve NH_2 rocking vibration [10]. We assigned this vibration to a strong IR band at 1070 cm^{-1} with corresponding medium Raman band at 1075 cm^{-1} .

The NH_2 wagging vibration in aniline was assigned to a strong IR band at 541 cm^{-1} [10].

In this work, strong IR/Raman bands at 680 cm^{-1} are assigned to NH_2 wagging vibration. NH_2 torsional vibration in aniline, assigned to a medium IR band at 277 cm^{-1} . We assigned this vibration to a medium strong Raman band at 224 cm^{-1} . These frequencies agree well with the observed ones within $\sim 5\%$.

CONCLUSIONS:

A complete vibrational assignment for 3,4-difluoroaniline has been proposed for the experimental IR and Raman spectra, aided by the *ab initio* (RHF), hybrid density functional methods (B3LYP) using 6-31G* basis set and PED analysis.

A B3LYP/6-31G* optimization leads to stable form with C_1 symmetry. Characteristic benzene as well as C-X vibrations is in the correlation range. The C-F

stretching vibrations are mixed with CC stretching and CH in-plane bending vibrations.

We also note that the in-plane and out-of-plane C-X bending vibrations show dominance in the region below 700 cm^{-1} . All the assignments are in agreement with the similar systems.

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