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Quantum Mechanical Studies of Conformers, Molecular Structures and Vibrational Characteristics of Hetero-cyclic Organics: Nicotinic acid and 2-Fluoronicotinic acid

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ABSTRACT

The stabilities, optimized molecular geometries, APT charges and vibrational characteristics for the nicotinic acid (NA) and 2-fluoronicotinic acid (2-FNA) have been studied theoretically using density functional theory (DFT) methods. The E (trans) conformers of nicotinic acid are found to be more stable and less polar than their respective Z (cis) conformers. Most of the vibrational frequencies have nearly the same magnitude for the NA and 2-FNA molecules; however, significant changes are noticed in their IR intensities, Raman activities and depolarization ratios of the Raman bands.

Keywords: *ab initio* calculations; molecular geometries; atomic charges; vibrational frequencies; nicotinic acid and 2-fluoronicotinic acid.

INTRODUCTION

Nicotinic acid (Niacin here after labeled as NA) and its derivatives (i.e., 2-fluoronicotinic acid here after labeled as 2-FNA) has been the subject of investigation for many reasons. Nicotinic acid and its derivatives have good biological activities and versatile bonding modes. The structures of many of the complexes that have been reported show nicotinic acid and its derivatives acting as bridging ligands through the carboxylate group and the pyridyl N atom [1]. NA plays a nutritional role as a vitamin, deficiency of which results into pellagra. It is involved in a wide range of biological processes, including production of energy, synthesis of fatty acids and steroids, signal transduction, regulation of gene expression and maintainace of genomic integrity. It serves as precursor to various forms of coenzyme nicotinamide adenine dinucleotide and a broad spectrum lipid drug which is used to lower cholesterol [2]. NA acts as an anti-hyperlipidemic agent; promotes healthy skin, good digestion, and proper circulation, metabolism of carbohydrates, fats and protein and functioning of the nervous system; serves as origin for most of the commercial compounds, from anti bacterial and cancer drugs in the biomedical industry to pesticides and herbicides in the agrochemical industry and to charge control agent in photocopier toners [3]. It is also an important raw material and intermediate widely used in the synthesis of medicines and dyes [4].

Wright and King [5] determined crystal structure of NA by two and three dimensional X-ray methods. Inelastic neutron scattering spectrum of NA has been measured and analyzed using DFT method by Hudson et al. [6]. Wang and Berglund [7] carried out calorimetric study and thermal analysis of crystalline for the NA molecule. Vibrational investigations of NA based on ab initio molecular orbital calculations have been carried out by Sala et al. [8]. They have also studied the Raman Spectra of its aqueous solutions in the range 200-1800 cm^{-1}. Koczon et al. [9] studied the experimental and theoretical spectra of NA and obtained its two stable structures which differ in orientation of the COOH group with respect to the pyridine ring. IR spectra 3 of this compound were investigated by Taylor [10] and Wojcik and Stok [11]. Park et al. [12] investigated the adsorption of picolinic acid and NA molecule by SERS. Kumar et al. [13] investigated the experimental IR, Raman spectra and density functional theory studies of the conformers of nicotinic acid and its N-oxide.

To the best of our knowledge, neither quantum chemical calculations nor the vibrational spectra of 2-FNA have been reported up to now. This inadequacy observed in the literature encouraged us to make this theoretical vibrational spectroscopic research based on the conformers of the NA molecule to give a correct assignment of the fundamental bands in the experimental FT-IR and FT-Raman spectra. Therefore, the present study aims to give a complete description of the molecular geometry, atomic charges and molecular vibrations of the 2-FNA. And also in the present article attempt has been made to record the FT-IR and FT-Raman spectra of NA and analyze these IR and Raman spectra in light of the quantum chemical calculations and to study the stability, optimized molecular geometries, APT charges and vibrational characteristics for the four possible conformers NA using DFT method employing different basis sets. Furthermore, earlier reported vibrational spectra of NA have also been compared with that of the present investigation.

EXPERIMENTAL SECTION

The compound nicotinic acid (NA) was purchased from Sigma-Aldrich Chemical Company, (USA) with a purity ≥ 99%. This is a white solid at room temperature. It was used as such without further purification for recording the FT-IR and laser Raman spectra. The IR spectra have been recorded in KBr pellets using Perkin Elmer RX-1 spectrometer in the spectral range 50-4000 cm^{-1} with the following experimental parameters: Perkin Elmer RX-1: scans – 200; resolution – 2 cm^{-1}; gain – 50. The recorded FT-IR for the NA molecule is reproduced in Fig.-1(a).

The laser Raman spectrum of the NA molecule has been recorded using 488 nm line of an Ar^+ laser for excitation in the region 50-4000 cm^{-1}. The Raman spectrum was recorded on the Jobin Yvon HORIBA HR800 Raman spectrometer equipped with air cooled CCD and OLYMPUS microscope with the following parameters: laser spot size - 1 μm, resolution ~ 5 cm^{-1}, power at the sample < 10 mw, integration time – 10 s, accumulation – 5, time constant – 10 s, one window covers ~ 800 cm^{-1}, accuracy of measurements - 1 cm^{-1}, slit width fixed at the entrance of laser- 1 cm^{-1}. The recorded FT-Raman for the NA molecule is reproduced in Fig.-1(b).

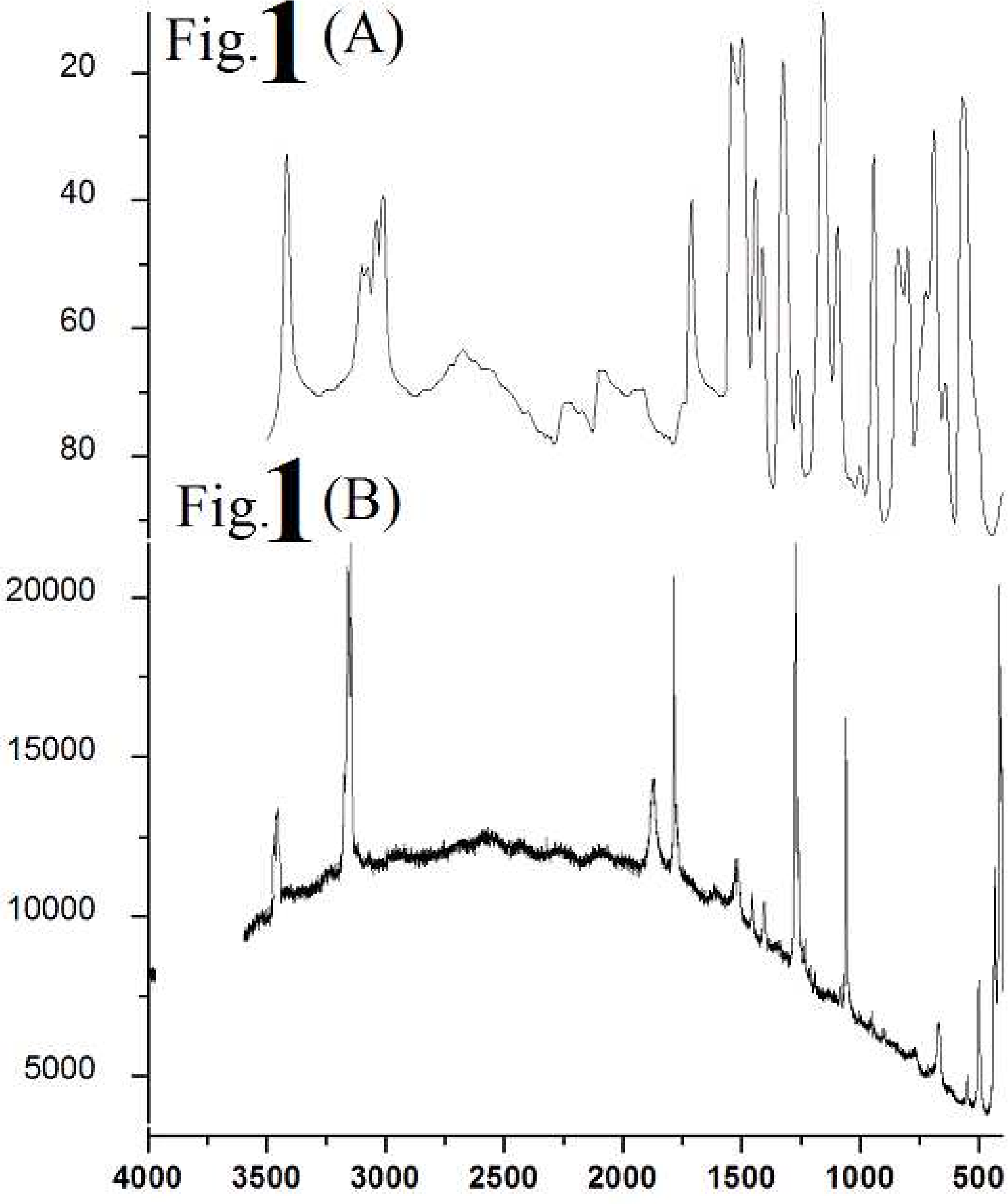

Fig.1 (A)- Experimental IR Spectra of NA
(B)- Experimental Raman Spectra of NA

Computational Details

The theoretical calculations presented in this work have been carried out to calculate the optimized molecular geometries, APT charges and fundamental vibrational wavenumbers along with their corresponding intensities in IR spectrum, Raman activities and depolarization ratios of the Raman bands for the NA molecule with its fluoro derivative molecule using Gaussian 03 [14] program package. The computations have been performed using density functional theory (DFT) [15] at the B3LYP level. The B3LYP functional, consists of Becke's three-parameter (B3) hybrid exchange functional [16] was combined with Lee-Yang-Parr correlation functional (LYP) [17] with the standard 6-311++g** basis set, accepted as a cost effective approach, for the computation of molecular structure, vibrational fundamental frequencies and energies of optimized structures. The basis set used as a Valence triple-zeta with the addition of diffuse and polarization functions for each atom in the molecules. For the NA molecule, initial parameters were taken from the work of Wright [5] while for the FNA molecule, the initial C-F bond length is taken as 0.925 Å and calculations were performed using the RHF method with the 6-31+G* basis set. The optimized geometries at the RHF/6-31+G* level were taken as the input structures for the calculations at the B3LYP/6-31+G* level. Similarly, the optimized geometries at the B3LYP/6-31+G* level were used as the input structures for the calculations at the B3LYP/6-31++G** level. Finally, the optimized geometries at the B3LYP/6-31++G** level were used as the starting geometries for the calculations at the B3LYP/6-311++G** level. For the NA-II conformer of nicotinic acid the dihedral angle $C_3C_4O_{12}H_{14}$ is changed by ~180° in the optimized geometries at the B3LYP/6-311++G** level molecule and for the NA-III conformer of nicotinic acid the dihedral angle $C_4C_3C_8O_{13}$ is changed by ~180° in the optimized geometries at the B3LYP/6-311++G** level molecule and for the NA-IV conformer of nicotinic acid the dihedral angle $C_3C_4O_{12}H_{14}$ is changed by ~180° in the optimized geometries at the B3LYP/6-311++G** level molecule and the resulting structures are taken as the input structures for the calculations at the B3LYP/6-311++G** level. It is essential to mention that for the NA-I conformer, there are four possible orientations of the COOH group but the stable one is that in which the distance between one of the H atoms of the OH group facing towards the H atom of the pyridine ring is longer. The geometries were optimized by minimizing the energies with respect to all the geometrical parameters without imposing any molecular symmetry constraints [18]. The assignments of the normal mode of vibrational frequencies were made with a high degree of accuracy along with the NA and FNA molecules are made by visual inspection of the individual mode using the Gauss View software [19]. The observed IR and Raman frequencies corresponding to the fundamental modes have been correlated to the calculated fundamental frequencies. Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics.

RESULT AND DISCUSSION

Energy analysis and Stabilities

2-FNA is substituted pyridines with two different functional groups; a F atom and COOH groups. As model system, nicotinic acid and fluorine atom are chosen. The possible stable conformers of 2-FNA and NA molecules were searched. There are four possible conformers for these molecules. The optimized geometry of the conformers and vibrational wavenumbers of 2-FNA and NA were calculated at DFT/B3LYP level of theory using the 6-311++G(d,p) basis set. The nicotinic molecule can exist as four conformers, NA1, NA2, NA3 and NA4. The calculated

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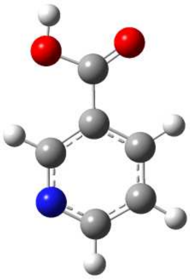
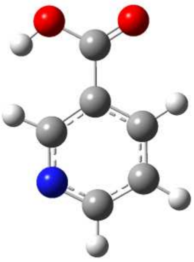
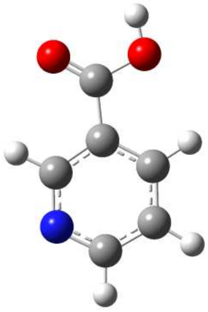
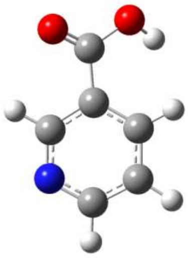
Table-1: Calculated^a total energies (TE) and relative energies ($E_{rel.)}$) for all theoretical structures of Nicotinic acid by DFT (B3LYP)

S. No.	Nicotinic Acid (NA)	Total Energy (TE)	Relative Energy $(E_{rel.})^b$ (eV)	RMS Gradient Norm (RMSGN)	Dipole Moment (DM)
1	 **(Conformation- 1) E**	-436.98679055 (-11891.021 eV)	0	0.00001621	0.7526
2	 **(Conformation- 2) Z**	-436.97647547 (-11890.740 eV)	0.281	0.00001198	3.3769
3	 **(Conformation- 3) E**	-436.98638193 (-11891.010 eV)	0.011	0.00013374	3.4266
4	 **(Conformation- 4) Z**	-436.97482801 (-11890.695eV)	0.326	0.00003235	5.3535

a: TE are measured in Hartree and eV, RMSGN are measured in a. u. and DM are measured in Debye.
b: energies of the other three conformers relative to the most stable C1 conformer.

energies and energy difference of four structures for the nicotinic acid molecule determined by B3LYP method with the 6-311++G** basis set are presented in Table-1. Many of the earlier workers have been found that the nicotinic acid molecule can exist in four conformers of the nicotinic acid molecule (see Table-1). According to the energy analysis, the present DFT calculations predicted that the (NA1) (-11891.021 eV) is more stable than (NA3) (-11891.010 eV), the (NA3) (-11891.010 eV) is more stable than (NA2) (-11890.740 eV), and the (NA2) (-11890.740 eV) is more stable than (NA4) (-11890.695 eV). The calculated dipole moments of the NA1, NA2, NA3 and NA4 conformers differ significantly in their magnitudes and hence the NA4 species is found to be more polar than the other three (NA1, NA2 and NA3) species. Calculations were done for four conformer's structure of the compounds in the ground state, and tabulated only for the most stable monomer (C1) conformers.

Molecular structure and APT charges

The present compounds may have four possible structures. The stability of the optimized geometries was confirmed by wavenumber calculations, which gave positive values for all the obtained wavenumbers. The calculated energies and energy difference of four structures for the nicotinic acid molecule determined by B3LYP are presented in Table-1. From DFT calculations, the conformer C1 is predicted to be more stable than other conformers. As mentioned above, the results for the most stable conformer have been tabulated. The NA molecules consist of 14 atoms, and so they have 36 normal vibrational modes. On the assumption of Cs symmetry, the number of vibrational modes of the 36 fundamental vibrations is divided into 25A' + 11A". The vibrations of the A' species are in-plane modes and those of the A" species are out-of-plane modes. All fundamental vibrations are active in both IR absorption and Raman scattering. But if the molecule were of C_1 symmetry point group, there would not be any relevant distribution. The front and lateral view of the studied molecules are shown in Fig.-2. Most of the calculated crystal structure parameters for the nicotinic acid have nearly same magnitudes. However, some of the bond lengths and bond angles show significant variations in their magnitudes.

The bond lengths C_2-C_3, C_3-C_8, C_4-C_3, C_5-C_4 and C_6-C_5 in the NA molecule are calculated to be equal for the 2-FNA molecule. The bond lengths C_2–N_1 calculated to be higher in NA as compared to the 2-FNA. The four C-C bond lengths of the pyridine ring for the presently studied molecules are calculated to lie in the range 1.385 –1.401 Å for NA. The four C-H bond lengths are calculated to lie in the range 1.082 – 1.086 Å for the NA molecules. The C_3-C_8 bond length is ~ 1.485 Å and 1.492 Å for the NA and 2-FNA molecules respectively. It is found that the O-H bond length is calculated to be identical for both the molecules. The C_8=O_{12} bond lengths is slightly decreases to going from the NA to 2-FNA molecules. The C–X (F, Cl, Br, etc.) bond length indicates a considerable increase when substituted in place of C–H. The F atom is in the plane of the pyridine ring. The C–F bond length are found to be 1.336 Å (2-FNA) by using 6-311++G(d,p).

The angles C_2-C_3-C_8, C_3–C_2–N_1, C_3-C_8-O_{12}, C_4–C_3–C_8 and C_5–C_4–C_3 are calculated to be higher difference in going from the NA to 2-FNA molecule. Angle C_3–C_4–H_9, C_3–C_8–O_{13}, C_4–C_3–C_2 are calculated to be decreases in going from the NA to 2-FNA molecules. Different bond lengths, bond angles and dihedral angles along with their values are shown in figs.-3(a) and 3(b), respectively, for the both molecules. It can be seen from fig.-3(a) that there is variation in the bond lengths. However, in bond angles (Fig.-3b) variations are noticeable for many more cases.

Table-2: Calculated Optimized Geometrical Parameters[a] for the NA and 2-FNA molecules

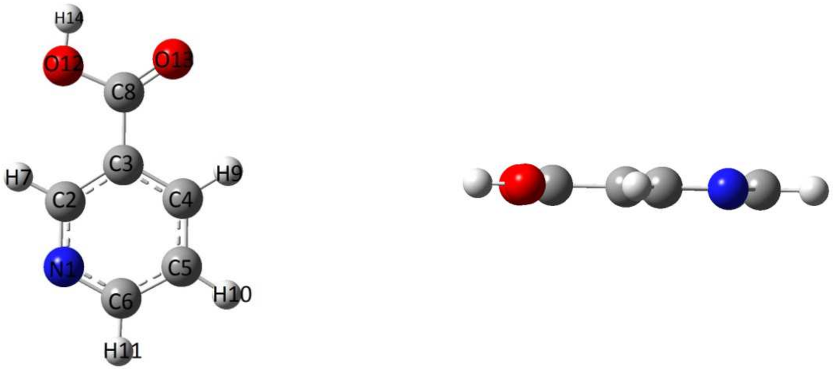
Parameters	NA		FNA
	Cal.	**Obs.[b]**	**Cal.**
r(C_2-N_1)	1.334	1.336	1.311
r(C_2-H_7/F_7)	1.084	-	1.336
r(C_3-C_2)	1.400	1.349	1.405
r(C_3-C_8)	1.486	1.482	1.491
r(C_4-C_3)	1.397	1.388	1.399
r(C_4-H_9)	1.083	-	1.083
r(C_5-C_4)	1.388	1.378	1.388
r(C_5-H_{10})	1.083	-	1.082
r(C_6-N_1)	1.337	1.343	1.337
r(C_6-C_5)	1.395	1.385	1.392
r(C_6-H_{11})	1.086	-	1.086
r(C_8-O_{12})	1.355	1.184	1.346
r(C_8-O_{13})	1.208	1.338	1.210
r(O_{12}-H_{14})	0.969	-	0.969
α(N_1-C_6-H_{11})	116.0	-	115.9
α(N_1-C_2-H_7/F_7)	116.6	-	114.9
α(C_2-C_3-C_8)	122.7	124.0	126.9
α(C_3-C_2-N_1)	123.3	-	125.0
α(C_3-C_2-H_7/F_7)	120.1	-	120.1
α(C_3-C_4-H_9)	119.4	-	118.0
α(C_3-C_8-O_{12})	112.9	124.0	114.4
α(C_3-C_8-O_{13})	124.7	114.1	123.0
α(C_4-C_3-C_2)	118.4	-	115.8
α(C_4-C_3-C_8)	118. 9	118.2	117.2
α(C_4-C_5-H_{10})	121.2	-	121.4
α(C_5-C_6-N_1)	123.7	112.4	123.1
α(C_5-C_4-C_3)	118.6	119.1	120.2
α(C_5-C_4-H_9)	122.0	-	121.8
α(C_5-C_6-H_{11})	120.3	-	121.1
α(C_6-N_1-C_2)	117.5	117.5	117.9
α(C_6-C_5-C_4)	118.4	119.2	117.9
α(C_6-C_5-H_{10})	120.3	-	120.7
α(C_8-O_{13}-H_{14})	107.0	-	106.7
α(O_{12}-C_8-O_{13})	122.4	121.9	122.6

a: Bond lengths(r) in Angstrom as (Å), bond angles(α) and dihedral angles(δ) in degrees as (°). b: [4].

Table - 3: Calculated APT Charges at various atomic sites for the NA and 2-FNA molecules

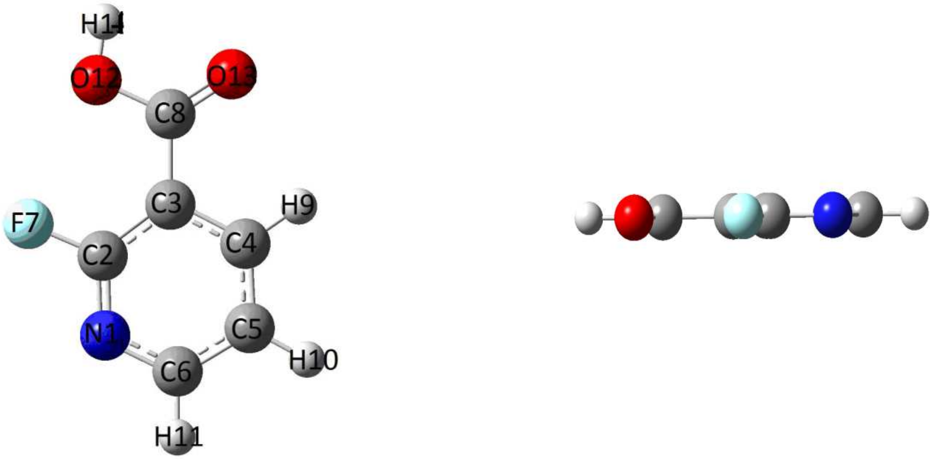
Atoms	NA	FNA
N_1	-0.4449	-0.5067
C_2	0.2211	0.8371
C_3	-0.2920	-0.3637
C_4	0.1100	0.1549
C_5	-0.1541	-0.2102
C_6	0.2439	0.3002
H_7/F_7	0.0602	-0.5423
C_8	1.3555	1.3672
H_9	0.0850	0.0981
H_{10}	0.0455	0.0552
H_{11}	0.0276	0.0381
O_{12}	-0.7547	-0.7243
O_{13}	-0.8123	-0.8126
H_{14}	0.3093	0.3088

The APT charges for the NA and 2-FNA molecules calculated using the method B3LYP/6-311++G ** are collected in Table-3. The calculated atomic charges at different atomic sites are plotted in Fig.-4 for both neutral molecules. The magnitudes of the charges at the different atomic sites remain almost same for the NA and 2-FNA molecules except at the sites N_1, C_2, C_3, C_4, C_5, C_6, C_8 and F_7/H_7. The magnitude of charge decreases at the N_1, C_3 and C_5 site and increases at the C_2, C_4, C_6 and C_8 site in going from the NA to 2-FNA molecules.



Front view of NA

Lateral view of NA



Front view of 2-FNA

Lateral view of 2-FNA

Figs. – 2 : Front and Lateral view of the Nicotinic acid and 2-fluoronicotinic acid

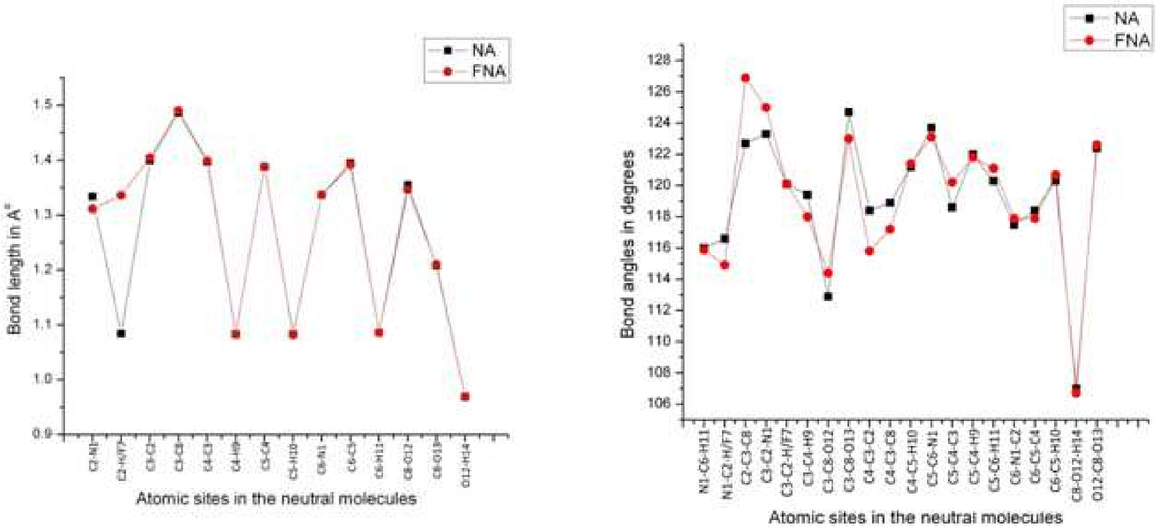


Fig.-3(a)

Fig.-3(b)

Figs.-3(a-b): The bond lengths and bond angles differences from theoretical approaches of the neutral NA and 2-FNA molecules.

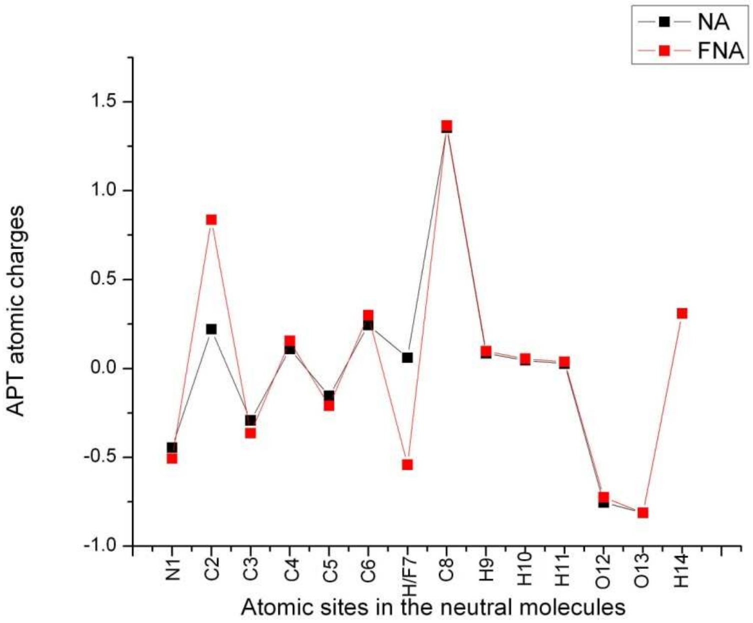


Fig.-4: APT atomic charges at various atoms of the NA and 2-FNA molecules.

Vibrational Characteristics

The calculated fundamental vibrational frequencies, IR intensities, Raman activities and depolarization ratios of the Raman bands for the NA and 2-FNA molecules using the B3LYP/6-

311++G** method are calculated in Table – 4 which also includes the experimental fundamental frequencies for the NA molecule only. All the calculated modes are numbered from the smallest to the biggest wavenumber within each fundamental vibration in the second column of the Tables. The calculated harmonic force constants and wavenumbers are usually higher than the corresponding experimental quantities because of the combination of electron correlation effects and basis set deficiencies. Nevertheless, after applying a uniform scaling factor, the theoretical calculation reproduces the experimental data well. The observed slight disagreement between theory and experiment could be a consequence of the anharmonicity and the general tendency of the quantum chemical methods to overestimate the force constants at the exact equilibrium geometry. Therefore, it is customary to scale down the calculated harmonic wavenumbers in order to improve the agreement with the experiment. In our study, we have followed two different scaling factors, i.e. 0.983 up to 1700 cm^{-1} and 0.958 for greater than 1700 cm^{-1}[20].

As the Gaussian 03 program calculates the Raman activities (S_i) at different frequency shifts (ν_i), the Raman intensities (I_i) are calculated by using the relation [21]

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i[1-\exp(-hc\nu_i/kT)]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where ν_0 is the exciting laser light frequency (in cm^{-1}); ν_i is the vibrational frequency (in cm^{-1}) of the i^{th} normal mode; h, c, T and k are the Planck constant, the speed of light temperature and the Boatman constant, respectively and f is some suitably chosen scaling factor common for all the peak intensities. The Raman spectrum was recorded using Ar^+ laser line (λ_0 = 488 nm). The corresponding excitation wavenumber (20492 cm^{-1}) was used in calculations of the stimulated Raman intensity. The computed IR and Raman spectra for the NA and 2-FNA molecules are shown in Figs.-5-6 respectively. In this section we discuss the vibrational assignments for the NA and 2-FNA molecules. The present calculations force us to make reassignments for some of the earlier assigned fundamental vibrational modes.

(a) C-COOH Modes

The C-COOH group gives rise to the three types of vibrational modes namely, γ(C-COOH) υ_2, β(C-COOH) υ_3 and υ(C-COOH) υ_{15}. The γ(C-COOH) and β(C-COOH) modes are found to be pure modes while υ(C-COOH) mode is strongly coupled with planar ring deformation and angle bending of COH mode. The calculated frequencies for the γ(C-COOH) mode decreases from 156 to 120 cm^{-1} in going from the NA to 2-FNA molecules. The experimental FT-Raman band is observed at 145 cm^{-1} for the NA molecule. The NA and 2-FNA molecules have nearly the same magnitude (210 cm^{-1}) for the β(C-COOH) mode. IR intensities and Raman activities are calculated to be very weak for γ(C-COOH) and β(C-COOH) modes. Hence the strong bands at 206 cm^{-1} in FT-Raman solid phase spectrum is assigned to the β(C-COOH) mode. The C-COOH stretching frequency is observed at 809 cm^{-1} by Sala et al. [8] for the NA molecule. In the present study it is calculated to be 760 cm^{-1} and is in good agreement with the earlier work. In the present case the υ(C-COOH) modes is calculated to have medium IR and Raman intensities with the corresponding frequency is found to be decreases from 790 to 747 cm^{-1} in going to the NA to 2-FNA molecules. The FT-Raman band experimental observation is assigned at 750 cm^{-1} for the NA molecule.

(b) COOH Modes

The COOH group has a modes as: 3 modes due to the OH group namely, ν(O-H), α(C-OH) and τ(OH) and 6 modes due to the COOH moiety, namely, ν(C=O), ν(C-OH), σ(COOH), ρ(COOH), ω(COOH) and τ(COOH). The band corresponding to the O-H stretching vibrations is observed in the region 3300-3700 cm^{-1} [22]. This mode is found to be pure and highly localized mode for the nicotinic acid molecule. For ethanoic acid and its derivatives, the O-H stretching frequency was found at ~ 3760 cm^{-1} [23]. The present calculation places this mode at nearly same frequency for the NA molecule. For the NA molecule Koczon et al. [9] observed a medium IR intensity at 3447 cm^{-1}, which could be correlated to the above frequency. The NA and 2-FNA molecules have nearly the same magnitude (~1785 and ~3765 cm^{-1}) for the C=O and O-H stretching mode (ν_{34} and ν_{39}) with very strong IR intensity and medium strong intensity of the Raman activity and the FTIR/FT-Raman bands experimentally observations at 1711/1695 and 3414/- cm^{-1}. Out of nine modes of the COOH group three modes, ω(COOH), ρ(COOH) and σ(COOH) are found to decreases by ~15, ~115 and ~20 cm^{-1} in going from the NA to 2-FNA molecules. IR intensities are very strong and Raman activity weak for ω(COOH) mode but IR and Raman activity are weak for ρ(COOH) and σ(COOH) modes. The ω(COOH) and ρ(COOH) of NA gives bands at 471, 720 cm^{-1} in the IR spectrum and ρ(COOH) of NA gives bands at 725 cm^{-1} in the Raman spectrum. Yadav et al. [24] found that for COOH group, the scissoring frequency is at higher magnitude than its rocking frequency. But in the present study, it is found that for the NA molecule, rocking frequency of the COOH group is at higher magnitude than the scissoring frequency. For the NA molecule, assignment of the COOH scissoring mode is in agreement with Sala et al. [8]. The frequency of the τ(COOH) modes shifts towards the lower wavenumber side by ~35 cm^{-1} for the 2-FNA molecule with very weak IR intensity as well as Raman activity. Modes τ(O-H), ν(C-OH) and α(C-O-H) (ν_{10}, ν_{22} and ν_{29}) increases by ~20 cm^{-1}, ~25 cm^{-1} and ~15 cm^{-1} in going from the NA to 2-FNA molecules. The C-OH stretching and the C-OH angle bending modes strongly mix with each other and are expected to lie in the region 1150- 1450 cm^{-1} [24]. Generally the C-OH stretching mode appears at lower frequency than the C-O-H angle bending mode. For the NA molecule, the angle bending of C-OH is calculated to be 1310 cm^{-1} whereas the COH stretching good agreement with Sala et al. [8] be highly coupled with C-OH angle bending mode. The calculated is found to be very weak Raman activity and very strong IR intensity for τ(O-H), ν(C-OH) and α(C-O-H) modes respectively. The FTIR/FT-Raman bands are observed 545/-, 1035/1044 and 1325/1320 cm^{-1} corresponding to the ν_{10}, ν_{22} and ν_{29} modes respectively.

(c) C–H/C-F Modes

In hetro-aromatic structure shows the presence of C–H stretching vibration appear in the range 3100-3000 cm^{-1} which is the characteristic region for the ready identification of C–H stretching vibration [25]. In the region the bands are not affected appreciably by the nature of substituents. The C-H stretching frequencies are observed in the range 3030-3095 cm^{-1} for the pyridine molecule [26]. Accordingly, in the present study, the three adjacent hydrogen atoms right around the ring of 2-FNA give rise to three C–H stretching (ν_{38}, ν_{37} and ν_{35}), which correspond to stretching modes of C_4–H_9, C_5–H_{10} and C_6–H_{11} units whereas in case of NA, there are four C–H stretching vibration i.e, the three adjacent hydrogen atoms right around the ring of NA give rise to three C–H stretching (ν_{38}, ν_{37} and ν_{35}) and an one adjacent hydrogen atoms left around the ring of NA give rise to three C–H stretching (ν_{36}), which correspond to stretching modes of C_2–H_7, C_4–H_9, C_5–H_{10} and C_6–H_{11} units. The aromatic C–H stretching of NA gives bands at 3013, 3040, 3075, 3099 cm^{-1} in the IR spectrum and at 3041, 3073, 3089 cm^{-1} in the Raman spectrum. These modes are calculated from 3200 to 3155 cm^{-1} for the NA molecule, which are in good agreement with the earlier works [9] and from 3205 to 3170 cm^{-1} for the 2-FNA molecule. As expected, these four modes are pure stretching modes. In the IR spectrum, C–H peaks were observed in the 3042–3104 cm^{-1} range for NA by Koczon et al.[8]. In present work frequencies are not much deference's to going from the NA to 2-FNA molecules. All these four of CH stretching mode, IR intensities is weak and Raman activities is strong to be calculated. The present calculations predict the C-F stretching vibration at 1254 cm^{-1} (ν_{26}) with medium intensity IR and medium Raman activity for the 2-FNA molecule.

The in-plane aromatic CH bending vibration occurs in the region 1300-1000 cm^{-1}[27], the bands are sharp but weak intensity. The four C–H in-plane bending (ν_{28}, ν_{25}, ν_{24} and ν_{23}) for the NA molecule and the three C–H in-plane bending (ν_{25}, ν_{24} and ν_{23}) for the 2-FNA molecule. The wavenumbers 1155 and 1090 cm^{-1} (ν_{24} and ν_{23}) and 1185 and 1303 cm^{-1} (ν_{25} and ν_{28}) are assigned for C–H in-plane bending in IR and Raman bands respectively for NA, which are in good agreement with values given in literature [8]. The calculated wavenumbers ~1225 cm^{-1} are assigned for C–H in-plane bending for both NA and 2-FNA molecules with very strong IR intensity and weak intensity in the Raman activity. The calculated frequencies decreases ~20 cm^{-1} (ν_{25}) and increases ~75 cm^{-1} (ν_{28}) in going from the NA to 2-FNA molecules are in-plane CH bending mode respectively. The in-plane C-F bending mode frequencies are calculated to be at 557 cm^{-1} (ν_9) for 2-FNA.

The CH out-of-plane deformation modes are vibrations in the range 1000-750 cm^{-1} [22]. In the present study, the three adjacent hydrogen atoms right around the ring of 2-FNA give rise to three C–H out-of-plane deformation modes (ν_{19}, ν_{18} and ν_{16}), which correspond to out-of-plane deformation modes of C_4–H_9, C_5–H_{10} and C_6–H_{11} units whereas in case of NA, there are four C–H out-of-plane deformation modes i.e, the three adjacent hydrogen atoms right around the ring of NA give rise to three C–H out-of-plane deformation modes (ν_{19}, ν_{18} and ν_{16}) and an one adjacent hydrogen atoms left around the ring of NA give rise to three C–H out-of-plane deformation modes (ν_{17}), which correspond to out-of-plane deformation modes of C_2–H_7, C_4–H_9, C_5–H_{10} and C_6–H_{11} units. The peaks seen at 972, 941 and 800 cm^{-1} (ν_{19}, ν_{18} and ν_{16}) in the IR spectrum and at 976, 952, 918 and 811 cm^{-1} (ν_{19}, ν_{18}, ν_{17} and ν_{16}), in the Raman spectrum are the corresponding aromatic C–H out-of-plane deformation vibrations of NA. The calculated wavenumbers ~1010, 990 and 840 cm^{-1} are assigned for γ(C–H) for both NA and 2-FNA molecules with very weak IR intensity as well as weak intensity in the Raman activity. The present calculations predict the γ(C–F) at 540 cm^{-1} (ν_8) with weak intensity IR as well as weak Raman activity for the 2-FNA molecule.

(d) Ring Modes

The heterocyclic ring of NA and 2-FNA is similar to that of pyridine ring. Therefore, it is expected that the vibrational frequencies corresponding to the NA and 2-FNA rings should match with those of the pyridine rings. The six ring stretching frequencies of the pyridine molecule are observed in the range 990-1585 cm^{-1} by Wilmshurst and Bernstein [28]. The present calculation predicts the corresponding ring stretching vibration (ν_{33} and ν_{32}) have nearly the same magnitude (~1635 and 1610 cm^{-1}) for the ν(ring) modes while the FTIR/FT-Raman experimental observations are found to be at -/1590 and 1540/- cm^{-1} respectively. The calculated frequency for the ring stretching vibrations (ν_{30}, ν_{27} and ν_{21}) are found to be increases by ~13, ~15 and ~20 cm^{-1} in going from NA to 2-FNA molecules. The same vibration in experimentally observed at 1407, 1250 cm^{-1} in the IR spectra for the (ν_{30} and ν_{27}) and at 1390, 1243, 1030 cm^{-1} (ν_{30}, ν_{27} and ν_{21}) in the FT-Raman spectra for the NA molecule. The ring stretching mode (ν_{31}) is calculated is found to be decreases from 1508 to 1488 cm^{-1} in going from the NA and 2-FNA molecules. The present assignments of the ring stretching frequencies for NA are found to be in agreement with those of Koczon et al. [9]. The observed IR band corresponding to the ν(ring) mode is found to be at 1440 cm^{-1}.

The planar ring deformation modes for pyridine are observed at 605, 652 and 1030 cm^{-1} by Wilmshurst and Bernstein [28]. The present calculations place the corresponding modes (ν_{20} and ν_{12}) shifts towards the lower wavenumber side by ~ 160 cm^{-1} and ~ 80 cm^{-1} respectively, in going from the NA and 2-FNA molecules. The observed IR band corresponding to the α(ring) mode is found to be at 996 and 635 cm^{-1} and the FT-Raman experimental observations at 1002 and 635 cm^{-1} for the ν_{20} and ν_{12} modes respectively. The calculated wavenumbers corresponding to the α(ring) mode (ν_{11}) is found to have increases by ~15 cm^{-1} in going from the NA to 2-FNA molecules. For the same vibration the FTIR/FT-Raman bands observed at 570 and 570 cm^{-1} respectively.

Wilmshurst and Bernstein [28] observed three non-planar ring deformation modes of the pyridine ring at 374, 405 and 749 cm^{-1} respectively. The calculated frequencies for the ϕ(ring) (ν_{13} and ν_{6}) are found to be increases by ~76 and ~10 cm^{-1} in going from NA to 2-FNA molecules. The observed IR band corresponding to the ϕ(ring) mode is found to be at 680 and 418 cm^{-1} and the FT-Raman experimental observations is assigned at 690 cm^{-1} for the ν_{13} mode. The present calculations place the corresponding mode ν_{4} shifts towards the higher wavenumber side by ~ 140 cm^{-1} in going from the NA and 2-FNA molecules. The observed FT-Raman band experimental is found to be 380 cm^{-1} for the ν_{4} mode.

Table-4: Calculated^{p} and experimental fundamental frequencies for the NA and 2-FNA molecules

S.No.	NA				FNA		Mode^{t}
	Cal.		Obs.		Cal.		
	Unscaled wavenumbers	Scaled wavenumbers	FTIR^{q}	FT-Raman^{r}	Unscaled wavenumber	Scaled wavenumber	
ν_1	63 (3,0.33) 0.75	62	-	-	30 (4, 0.20) 0.75	29	τ(COOH)
ν_2	156 (0.04,2) 0.75	135	-	145w	120 (0.14,1) 0.75	118	γ(C-COOH)
ν_3	211 (3,0.13) 0.68	207	-	206s	210 (5,0.02) 0.65	206	β(C-COOH)
ν_4	385 (6,0.14) 0.68	378	-	380m	245 (2, 1) 0.75	241	ϕ(ring)
ν_5	386 (6,4) 0.25	379	-	-	366 (0.87,3) 0.19	360	σ(COOH)

ν_6	426 (0.01,0.47) 0.75	419	418vw	-	435 (0.36, 0.63) 0.75	428	**ϕ(ring)**
ν_7	494 (10,1) 0.60	486	471vw	-	381 (4,2) 0.59	375	**ρ(COOH)**
ν_8	-	-	-	-	540 (3,0.71) 0.75	531	**γ(C-F)**
ν_9	-	-	-	-	557 (9,3) 0.73	548	**β(C-F)**
ν_{10}	576 (97,2) 0.75	566	545vs	-	596 (95,2) 0.75	586	**τ(O-H)**
ν_{11}	627 (10,5) 0.7465	616	570vs	570w	639 (39,2) 0.75	628	**α(ring)**
ν_{12}	660 (40,1) 0.15	649	635m	635vw	583 (13, 4) 0.48	573	**α(ring)**
ν_{13}	715 (15,0.17) 0.75	703	680vs	690vw	791 (78,0.27) 0.7498	778	**ϕ(ring)**
ν_{14}	757 (77,0.01) 0.7499	744	720s	725w	744 (13, 0.18) 0.7499	731	**ω(COOH)**
ν_{15}	790 (10,16) 0.11	777	-	750vw	747 (24,20) 0.07	734	**ν(C-COOH)**
ν_{16}	843 (3,0.50) 0.75	829	800s	811vs	835 (3,0.45) 0.75	821	**γ(C-H)**
ν_{17}	957 (0.22,0.27) 0.75	941	-	918vw	-	-	**γ(C-H)**
ν_{18}	991 (0.72,0.06) 0.7491	974	941vs	952w	987 (0.02,0.01) 0.7458	970	**γ(C-H)**
ν_{19}	1010 (0.08,0.03) 0.7465	993	972vw	976w	1006 (1,0.11) 0.7498	989	**γ(C-H)**
ν_{20}	1040 (13,9) 0.07	1032	996m	1002w	880 (25,3) 0.22	865	**α(ring)**
ν_{21}	1056 (5,37) 0.05	1038	-	1030vs	1076 (17,21) 0.07	1058	**ν(ring)**
ν_{22}	1114 (194,0.94) 0.45	1095	1035s	1044vs	1138 (146,7) 0.26	1119	**ν(C-OH)**
ν_{23}	1133 (5,4) 0.15	1114	1090vs	1117w	1113 (11,3) 0.17	1094	**β(C-H)**
ν_{24}	1204 (142,21) 0.21	1184	1155vs	1160w	1205 (159,10) 0.28	1185	**β(C-H)**

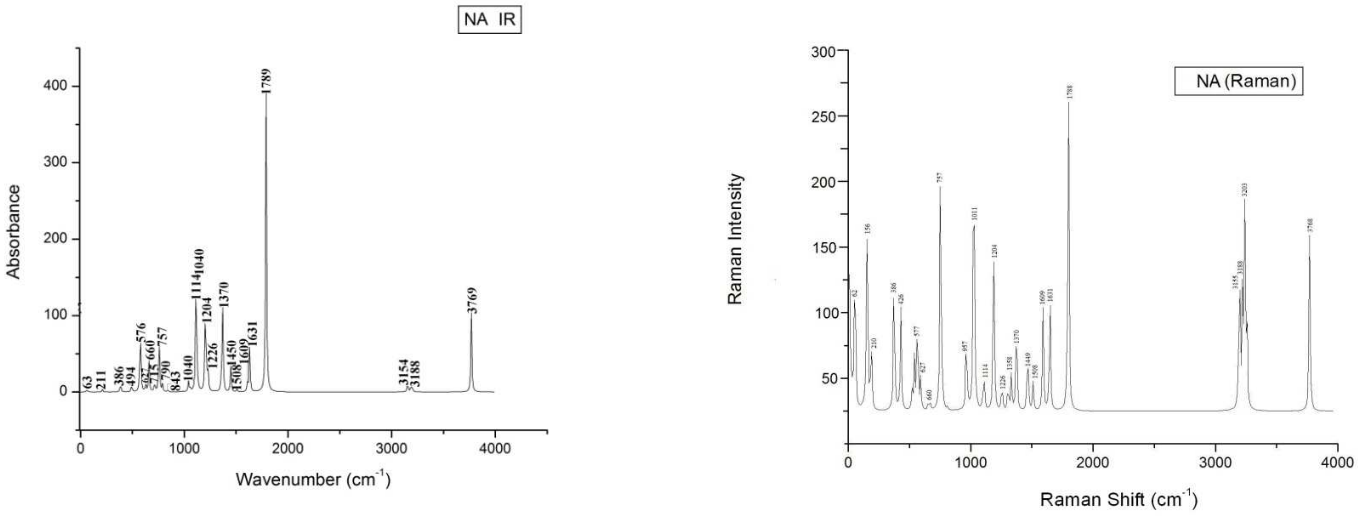
ν_{25}	1226 (38,7) 0.67	1205	-	1185m	1301 (35,9) 0.21	1279	**β(C-H)**
ν_{26}	-	-	-	-	1254 (53,28) 0.14	1233	**ν(C-F)**
ν_{27}	1292 (0.58,4) 0.7479	1270	1250w	1243m	1316 (1,4) 0.67	1294	**ν(ring) Kekule**
ν_{28}	1359 (21,2) 0.40	1336	-	1303m	-	-	**β(C-H)**
ν_{29}	1370 (108,9) 0.23	1347	1325vs	1320m	1386 (140,6) 0.27	1362	**α(C-O-H)**
ν_{30}	1450 (34,3) 0.35	1425	1407s	1390vw	1463 (178, 2) 0.72	1438	**ν(ring)**
ν_{31}	1508 (4,3) 0.31	1482	1440vs	-	1488 (42,5) 0.23	1663	**ν(ring)**
ν_{32}	1609 (11,6) 0.51	1582	1540vs	-	1606 (55,5) 0.36	1579	**ν(ring)**
ν_{33}	1631 (61,62) 0.54	1603	-	1590vs	1639 (143, 65) 0.52	1611	**ν(ring)**
ν_{34}	1789 (398,81) 0.27	1714	1711vs	1695s	1778 (403,66) 0.25	1703	**ν(C=O)**
ν_{35}	3154 (13,114) 0.41	3022	3013m	-	3167 (10,114) 0.38	3033	**ν(C-H)**
ν_{36}	3185 (6,21) 0.34	3051	3040m	3041vw	-	-	**ν(C-H)**
ν_{37}	3188 (3,144) 0.35	3054	3075m	3073vs	3197 (2, 64) 0.56	3063	**ν(C-H)**
ν_{38}	3202 (5,135) 0.13	3068	3099m	3089vs	3209 (5,149) 0.13	3074	**ν(C-H)**
ν_{39}	3769 (105,138) 0.26	3611	3414s	-	3759 (103,136) 0.26	3601	**ν(O-H)**

p: The first and second numbers within each bracket represent IR intensity(Km/mol) and Raman activity(Å^4/amu) while the number above and below each bracket represent the corresponding calculated frequency(cm^{-1}) and depolarization ratios of the Raman band respectively.

s: strong, m: medium, w: weak, vs: very strong, vvs: very very strong. t: ν=stretching, ω=wagging, τ=twisting, ρ=rocking, σ=scissoring, δ= deformation, γ=out-of-plane deformation, β=in-plane deformation, α=angle bending, α= in–plane ring bending, ϕ=out-of-plane ring bending.

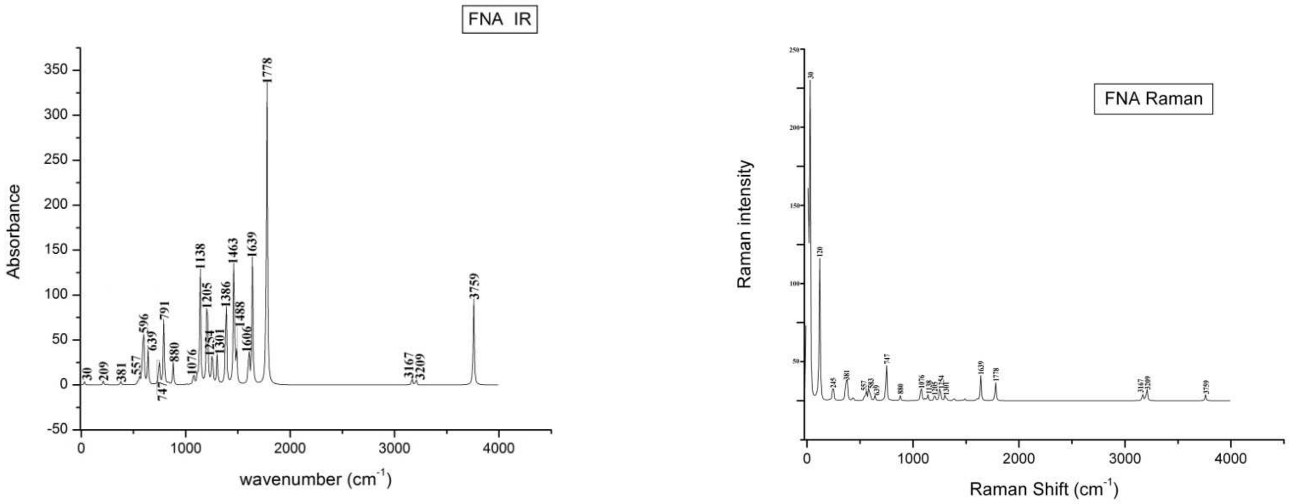
q: From solid state FT-IR spectra in KBr pellet.

r: Observed frequencies in the FT-Raman spectrum taken in solid form.



Calculated IR spectrum of NA **Calculated Raman spectrum of NA**

Figs.-5 : Calculated IR and Raman Spectra of Nicotinic acid



Calculated IR spectrum of 2-FNA **Calculated Raman spectrum of 2-FNA**

Figs.-6 : Calculated IR and Raman Spectra of 2-fluoronicotionic acid

Thermodynamical Properties

The output files of the Gaussian 03 programs provide the various thermo-dynamical properties of the studied molecules and are collected in Table-5. It is calculated that the total energy of the 2-FNA molecule is less than that of the NA molecule by 99.270 Hartrees which suggests that the 2-FNA molecule is thermodynamically more stable than the NA molecule. The magnitudes of the zero point vibrational energy (ZPVE) and the thermal energy correction decrease slightly by 5.064 and 4.564 Kcal/Mol, respectively, due to the replacement of H7 atom in the NA by an F atom.

The molar heat capacity of a molecule is defined as the amount of heat required to change the temperature of that molecule by 1 C. The molecules with larger molecular mass need more heat than the smaller ones [29]. The molecular mass of 2-FNA is more than NA and thus, the heat capacity of 2-FNA is calculated to be greater than that of NA. According to the similarity principle [30], higher the similarity among the system, higher the value of the entropy will be and higher the stability will be. Replacement of the H7 atom by a F atom in the NA molecule increases the magnitude of entropy suggesting that 2-FNA is more stable as compared to the NA molecule. The magnitudes of the rotational constant are almost equal for the NA and 2-FNA molecules.

Table-5: Calculated Thermo-dynamical Properties^d for the NA and 2-FNA molecules

Parameters		**NA**	**FNA**
Total energy(E)		-436.987	-536.257
Zero point vibrational energy(ZPVE)		64.799	59.735
Contribution to the thermal energy correction (TE)		69.239	64.675
Constant volume molar heat capacity(CV)		26.498	29.186
Entropy (S)		84.477	89.824
Rotational Constant (RC)	**a**	3.956	2.349
	b	1.242	1.226
	c	0.945	0.806

d: E are measured in Hartrees, ZPVE & TE are measured in Kcal/Mol, CV & S are measured in Cal/Mol-Kelvin and RC is measured in GHZ.

CONCLUSION

The nicotinic molecule can exist as four conformers, NA1, NA2, NA3 and NA4. The energy analysis, the present DFT calculations predicted that the (NA1) (-11891.021 eV) is more stable than (NA3) (-11891.010 eV), the (NA3) (-11891.010 eV) is more stable than (NA2) (-11890.740 eV), and the (NA2) (-11890.740 eV) is more stable than (NA4) (-11890.695 eV).

The bond lengths C_2–N_1 calculated to be higher in NA as compared to the 2-FNA. The four C-C bond lengths of the pyridine ring for the presently studied molecules are calculated to lie in the range 1.385 –1.401 Å for NA. The four C-H bond lengths are calculated to lie in the range 1.082 – 1.086 Å for the NA molecules. The C_8=O_{12} bond lengths is slightly decreases to going from the NA to 2-FNA molecules. The angles C_2-C_3-C_8, C_3–C_2–N_1, C_3-C_8-O_{12}, C_4–C_3–C_8 and C_5–C_4–C_3 are calculated to be higher difference in going from the NA to 2-FNA molecule. Angle C_3–C_4–H_9, C_3–C_8–O_{13}, C_4–C_3–C_2 are calculated to be decreases in going from the NA to 2-FNA molecules. The magnitudes of the charges at the different atomic sites remain almost same for the NA and 2-FNA molecules except at the sites N_1, C_2, C_3, C_4, C_5, C_6, C_8 and F_7/H_7.

The calculated frequencies for the γ(C-COOH) mode decreases from 156 to 120 cm^{-1} in going from the NA to 2-FNA molecules. The calculated frequencies decreases ~20 cm^{-1} (ν_{25}) and increases ~75 cm^{-1} (ν_{28}) in going from the NA to 2-FNA molecules are in-plane CH bending mode respectively. The present calculations place the corresponding modes (ν_{20} and ν_{12}) shifts towards the lower wavenumber side by ~ 160 cm^{-1} and ~ 80 cm^{-1} respectively, in going from the

NA and 2-FNA molecules. The present calculations place the corresponding mode ν_4 shifts towards the higher wavenumber side by ~ 140 cm^{-1} in going from the NA and 2-FNA molecules. The calculated total energy of the 2-FNA molecule is less than that of the NA molecule by 99.270 Hartrees which suggests that the 2-FNA molecule is thermodynamically more stable than the NA molecule. The magnitudes of the zero point vibrational energy (ZPVE) and the thermal energy correction decrease slightly by 5.064 and 4.564 Kcal/Mol, respectively, due to the replacement of H7 atom in the NA by an F atom. Replacement of the H7 atom by a F atom in the NA molecule increases the magnitude of entropy suggesting that 2-FNA is more stable as compared to the NA molecule. The magnitudes of the rotational constant are almost equal for the NA and 2-FNA molecules.

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