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Theoretical and Experimental Studies of Vibrational Spectra of Nicotinic Acid

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ABSTRACT

Raman and FTIR spectra of nicotinic acid have been analysed using ab-initio and DFT calculations. Four stable structures were found for nicotinic acid, the structures differ in orientation of COOH with respect to the nitrogen atom. The optimized geometries, harmonic vibrational wave number, structural parameters and intensities of the nicotinic acid have been calculated using MP2/6-311++G(d,p), B3LYP/6-311++G(d,p), B3PW91/6-311++G(d,p), X3LYP/6-311++G(d,p) level of theories. Vibrational assignments have been made and calculated DFT frequencies and Raman intensities of nicotinic acid are found to be in better agreement with corresponding experimental values in comparison to previous results. Selected experimental bands were assigned based on scaled theoretical wave numbers.

Keywords: Molecular geometries, Nicotinic acid, Vibrational spectra, DFT methods, IR and Raman spectra.

INTRODUCTION

Nicotinic acid (NA) widely known as Niacin is also known as vitamin B3 and vitamin PP- is an organic compound with the formula $C_6H_5NO_2$ which is present in forty to eighty essential human nutrients. This colourless and water-soluble solid is a derivative of pyridine, with a carboxyl group (COOH) at the 3-position. Nicotinic acid (3-pyridine carboxylic acid) is a water soluble vitamin whose derivative play essential roles in energy metabolism in the living cell and DNA repair, its derivatives have been the subject of investigation for many reasons. Nicotinic acid and its derivatives have good biological activities and versatile bonding modes. It is used widely in the treatment of hyperlipoproteinemias and reduces both the cholesterol and the triglyceride concentrations in the plasma. In general, when nicotinic acid and its derivatives are used in therapy a desirable modification of the composition of the plasma lipids in the sense of an antiatherosclerotic activity can be expected. 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]. The use of nicotinic acid derivatives in the field of medicinal, biomedical industries, production of cosmetics, pesticides, agro chemical industries and its biological activities have been studied extensively over the past decades.

Various spectroscopic studies of nicotinic acid and its derivates have been reported in the literature. The crystal structure of nicotinic acid was first determined in 1953 [2] and subsequently reinvestigated [3]. Nicotinic acid has been studied extensively by optical vibrational spectroscopy in the past [4-6]. The picolinic [7], nicotinic [8] and isonicotinic acids [9] and its complexes with different metals were thoroughly investigated by different methods. Earlier, Koczon et al [10] discussed the experimental and theoretical vibrational frequency and interpreted IR and Raman spectra in the range between 1350-3437 cm^{-1} for picolinic, nicotinic and isonicotinic acids. Park et al [11] studied the adsorption of picolinic acid and nicotinic acid on a silver sol surface has been investigated over a wide range of solution of pH by surface enhanced Raman scattering. Metal halide complexes of isonicotinic acid were extensively studied by the earlier workers [12-14]. Wang [15] was carried out experimental (UV and Raman) and theoretical study (DFT) of pyridine carboxylic acid (isonicotinic acid) in aqueous solution.

Experimental and theoretical relationship between energetics and structure of nicotinic acid was studied by Goncalves et al [16]. Hudson et al [17] investigated nicotinic acid with inelastic neutron scattering spectrum and its assignments were made using density functional theory. Sala et al [18] studied the vibrational analysis of nicotinic acid in the range 400-1725 cm^{-1}. The investigation of molecular structure and vibration frequencies of 2-choloronicotinic acid and 6-chloronicotinic acid molecules with FT-IR and FT-Raman spectroscopy and quantum chemical calculations were carried out by Karabacak et al. [19-20]. Ab initio studies of molecular structures, conformers and vibrational spectra of heterocyclic organics (Nicotinamide and its N-oxide) were studied by Kumar et al [21]. Vibrational study of Nicotinic Acid complexes with different central ions were studied by Lewandowski et al [22]. Seliger et. al. [23] studied ^{14}N nuclear quadrupole resonance of picolinic, nicotinic, isonicotinic and dinicotinic acids. Experimental and theoretical UV, NMR, and vibrational features of nicotinic acid N-oxide and nicotinamide N-oxide molecules were studied by Atac et. al. [24-25].

In the present work Raman and FTIR spectra of nicotinic acid have been analyzed using ab-initio and DFT calculations. The optimized geometries, harmonic vibrational wave number, structural parameters and intensities of the nicotinic acid have been calculated using MP2/6-311++G(d,p), B3LYP/6-311++G(d,p), B3PW91/6-311++G(d,p), X3LYP/6-311++G(d,p) level of theories. Vibrational assignments have been made and calculated DFT frequencies and intensities of nicotinic acid are found to be in better agreement with corresponding experimental values in comparison to previous results. Selected experimental bands were assigned based on scaled theoretical wave numbers.

EXPERIMENTAL SECTION

The compound nicotinic acid (NA) in solid state was purchased from Sigma-Aldrich Chemical Company, USA, with a stated purity of 98% and it was used as such without further purification. The FT-IR spectra of this compound have been recorded using Perkin Elmer, USA. The scan range was from 50 – 4000 cm^{-1} with scan rate 100 cm^{-1} per second. The Raman spectra of the above compound had been taken using Renishaw in-Via spectrometer having diode laser of wavelength 432 nm in wave number range 100 – 4000 cm^{-1}. The laser spot size was 1 mm and with power 5 mW. The accuracy of the spectrometer was 1 cm^{-1}.

Computational Method

Ab-initio and density functional theory (DFT) calculations were performed for all the four conformers of Nicotinic acid NA-I, NA-II, NA-III and NA-IV to calculate the optimized molecular energies, zero point vibrational energies, dipole moments and thermodynamic functions using the Gaussian 03 software package [26] and Gaussian type basis functions. The geometries of nicotinic acid conformers were optimized by minimizing the energies with respect to all geometrical parameters without imposing any constraint. The front view of the NA-I along with labelling scheme is shown in fig. 1. Molecular structure optimization of the NA-I, NA-II, NA-III and NA-IV were done using MP2, B3LYP, X3LYP and B3PW91 methods with 6-311++G(d,p) basis sets. The stability of the optimized geometries was confirmed by wave number calculations, because values of all the wave numbers are positive. Assignments of the normal mode of vibrational frequencies were made by visual inspection of individual mode using Gaussian view software. The experimentally observed Raman and IR frequencies corresponding to fundamental modes have been correlated to the calculated fundamental frequencies of NA-I using B3LYP, X3LYP and B3PW91 methods with 6-311++G(d, p) basis sets.

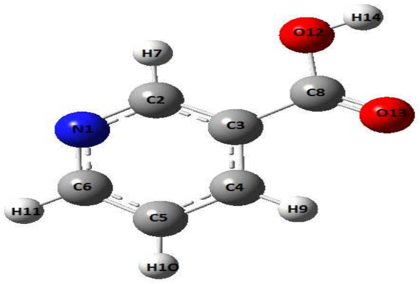


Fig.1 The optimized geometry of NA-I at MP2/6-311++G(d,p) and numbers assigned for the atoms

RESULTS AND DISCUSSION

4.1. Molecular Geometry

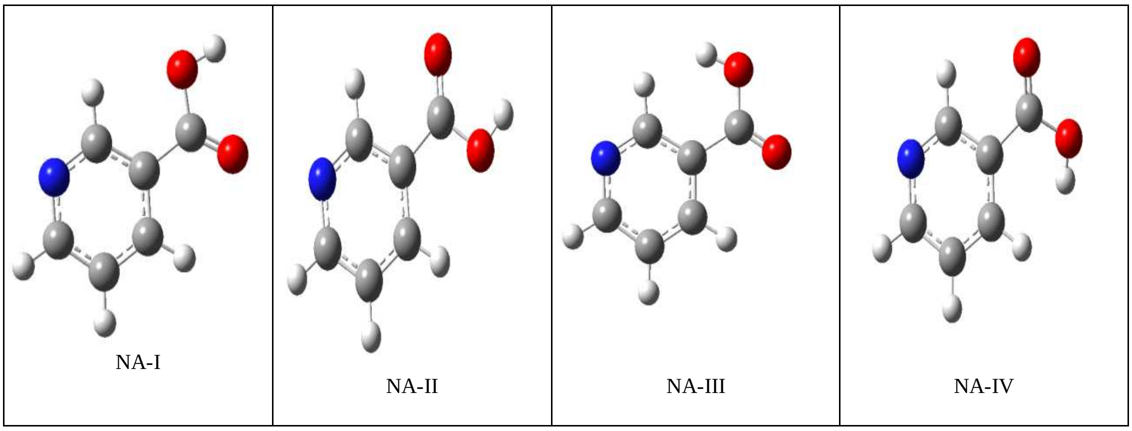
The calculated optimized molecular energies, zero point vibrational energies, dipole moments and thermodynamic functions using MP2, B3LYP, X3LYP and B3PW91 methods with 6-311++G(d,p) basis sets for all the four conformers of Nicotinic acid NA-I, NA-II, NA-III and NA-IV are shown in Table-1. As the total optimized energy is lowest for NA-I, it will be the most stable conformer. The optimized structures of all the four conformers using MP2 with 6-311++G(d, p) are shown in the fig.2.The dipole moment of NA-I is least and that of NA-IV is largest, therefore NA-IV is more polar than any other conformer.

To calculate structural parameters, APT charges at various atomic sites, fundamental vibrational wave numbers along with their corresponding intensities in IR spectrum, Raman activities and assignments of the normal mode of vibrational frequencies we have used the most stable conformer of Nicotinic Acid i.e. NA-I using MP2, B3LYP, X3LYP and B3PW91 methods and 6-311++G(d,p) basis set.

The calculated bond lengths and bond angles NA-I using MP2, B3LYP, X3LYP and B3PW91 methods and 6-311++G(d,p) basis set are reported along with the corresponding experimental values [2] in Table 3. We see that the calculated bond lengths are very close to experimental values while calculated using B3PW91/6-311++G(d,p) and bond angles are very close to experimental values while calculated using MP2/6-311++G(d,p). The APT (atomic polarizability tensor) charges at various atomic sites of NA-I using MP2, B3LYP, X3LYP, B3PW91 methods and 6-311++G(d,p) basis set are shown in Table 3.

Table 1 Calculated energies, zero-point vibrational energy, dipole moment and thermodynamic functions of the nicotinic acid and its conformers with Ab-initio and DFT methods

S. No.	Species	Total energies E(hartree)	Zero-point Vibrational energy(J/mol)	Dipole moment (Debye)	Constant volume molar heat capacity(C_v) (cal/mol K)	Entropy S(cal/mol K)
MP2/6-311++G(d,p)						
1	NA-I	-435.804103572	267840.8	0.7623	26.322	86.187
2	NA-II	-435.80373365	-	3.6502		
3	NA-III	-435.79325186	-	3.6624	-	-
4	NA-IV	-435.79288671	264621.5	5.6558	26.896	85.758
B3LYP/6-311++G(d,p)						
1	NA-I	-436.98670127	271096.5	0.7193	26.503	84.525
2	NA-II	-436.98630200	271067.5	3.4210	26.499	84.494
3	NA-III	-436.97539433	269142.4	3.1747	25.040	80.700
4	NA-IV	-436.97424917	269988.8	5.3229	26.809	85.022
X3LYP/6-311++G(d,p)						
1	NA-I	-436.80390000	271983.1	0.7158	26.397	84.903
2	NA-II	-436.80349768	271710.4	3.4250	26.439	84.449
3	NA-III	-436.79214929	268747.0	3.2081	24.932	80.306
4	NA-IV	-436.79130597	269898.9	5.2570	26.595	83.869
B3PW91/6-311++G(d,p)						
1	NA-I	-436.80923735	272148.4	0.6673	26.462	84.551
2	NA-II	-436.80891398	272134.0	3.4217	26.464	84.548
3	NA-III	-436.79765714	268815.9	3.1632	25.002	80.286
4	NA-IV	-436.79751300	270591.3	5.3307	26.796	84.357



NA-I NA-II NA-III NA-IV

Fig. 2 Optimized geometries of all the four conformers of nicotinic acid at MP2/6-311++G(d,p) level

Table-2: Theoretical bond lengths (angstroms) and bond angles (degrees) of NA-I compared with experimental data [Ref. 2] of Nicotinic Acid

Parameters	**Experimental**	**Theoretical**			
		MP2/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)	X3LYP/ 6-311++G(d,p)	B3PW91/ 6-311++G(d,p)
Bond lengths					
C2-N1	1.336	1.343	1.334	1.334	1.332
C2-C3	1.349	1.403	1.400	1.399	1.397
C2-H7	-	1.086	1.084	1.084	1.085
C3-C4	1.388	1.399	1.397	1.396	1.395
C3-C8	1.482	1.491	1.486	1.485	1.483
C4-C5	1.378	1.394	1.387	1.387	1.385
C4-H9	-	1.086	1.083	1.083	1.085
C5-C6	1.385	1.399	1.395	1.395	1.393
C5-H10	-	1.086	1.083	1.083	1.084
C6-N1	1.343	1.344	1.337	1.336	1.334
C6-H11	-	1.088	1.086	1.086	1.087
C8-O12	1.184	1.354	1.355	1.353	1.348
C8-O13	1.338	1.212	1.208	1.207	1.206
O12-H14	-	0.968	0.968	0.968	0.967
Bond angles					
C3-C2-H7	-	120.3	120.2	120.2	120.0
C3-C2-N1	-	123.3	123.3	123.3	123.4
H7-C2-N1	-	116.4	116.5	116.6	116.5
C2-C3-C4	-	118.9	118.4	118.5	118.4
C2-C3-C8	124.0	122.5	122.7	122.7	122.7
C4-C3-C8	118.2	118.6	118.8	118.8	118.8
C3-C4-C5	119.1	118.1	118.6	118.6	118.5
C3-C4-H9	-	119.7	119.4	119.4	119.3
C5-C4-H9	-	122.2	121.9	122.0	122.2
C4-C5-C6	119.2	118.7	118.4	118.4	118.4
C4-C5-H10	-	121.1	121.2	121.3	121.2
C6-C5-H10	-	120.1	120.3	120.3	120.4
C5-C6-H10	-	120.4	120.3	120.3	120.3
C5-C6-N1	112.4	123.8	123.7	123.7	123.8
H11-C6-N1	-	115.8	115.9	115.9	115.9
C2-N1-C6	117.5	117.1	117.5	117.5	117.4
C3-C8-O12	124.0	112.4	112.9	112.9	112.9
C3-C8-O13	114.1	124.4	124.6	124.6	124.5
O12-C8-O13	121.9	123.2	122.4	122.5	122.5
C8-O13-H14	-	105.9	106.9	107.0	106.7

For atom numbering, see figure 1.

Table - 3: APT Charges at various atomic sites of NA-I

Atoms	**MP2/6-311++G(d,p)**	**B3LYP/6-311++G(d,p)**	**X3LYP/6-311++G(d,p)**	**B3PW91/6-311++G(d,p)**
N1	-0.115	-0.038	-0.039	0.012
C2	-0.327	-0.409	-0.409	-0.602
C3	0.323	0.389	0.377	0.522
C4	0.258	0.117	0.116	0.193
C5	-0.320	-0.138	-0.138	-0.157
C6	-0.307	-0.342	-0.343	-0.474
C8	-0.178	-0.221	-0.217	-0.327
O12	-0.272	-0.186	-0.187	-0.165
O13	-0.402	-0.298	-0.300	-0.284
H7	0.282	0.231	0.234	0.268
H9	0.292	0.227	0.231	0.263
H10	0.222	0.185	0.188	0.226
H11	0.227	0.188	0.191	0.268
H14	0.319	0.295	0.297	0.300

4.2 Vibrational assignments:

The maximum number of potentially active vibrational modes of a nonlinear molecule which contain N atom is equal to (3N-6). Apart from these there will be three translational and three roltational degrees of freedom [27]. Hence Nicotinic acid molecule which has 14 atoms will have 36 normal modes of vibration, considered under Cs point group symmetry. For N-atomic molecules. 2N-3 of its vibrations will be planer and N-3 will be non-planer [28]. Thus, with respect to the reflection on the symmetry plane, 25 of these modes will be planar (A’) and 11 will be non planar (A”). The 36 normal modes of vibrations are distributed amongst the symmetry species as Γvib=25A’+11A”.

The detailed analysis of fundamental modes of vibrations with FTIR and FT Raman experimental frequencies, unscaled and scaled vibrational frequencies, Raman intensity, Raman activity and vibrational assignments of NA-I using B3LYP, X3LYP, B3PW91 methods with 6-311++G(d,p) basis set are listed in Table 4. Experimental FTIR and FT Raman spectra of NA are shown in fig. 3 and fig. 4 respectively.

In order to improve the calculated values in agreement with the experimental values, it is necessary to scale down the calculated harmonic frequencies. Hence harmonic frequencies calculated using B3LYP, X3LYP, B3PW91 methods with 6-311++G(d,p) basis set are scaled by 0.98.

Comparison between calculated and experimental vibrational spectra

Experimental wave numbers obtained from IR (Fig.2) and Raman spectra (Fig. 4) of nicotinic acid have been compared with the corresponding values using B3LYP, X3LYP, B3PW91 with6-311++G(d,p) basis set. The B3LYP wave numbers are more near to experimental values in comparison to X3LYP and B3PW91.

Region 4000-2000 cm^{-1}

The B3LYP calculations predict OH stretching vibrational mode at 3713 cm^{-1} in nicotinic acid and this corresponds to the observed IR band at 3434 cm^{-1}. Frequencies and intensities of vibrational modes of nicotinic acid predicted by our DFT calculations around 3128-3080 cm^{-1} attributed to CH stretching vibration are in good agreement with experimentally observed IR and Raman bands at 3060 cm^{-1} and 3069 cm^{-1} respectively (Table 4).

Table 4: Experimental and Calculated vibrational frequencies(cm^{-1}), IR Intensisity(KM/Mole), Raman activity (A^{4}amu^{-1}) of Nicotinic acid and their Vibrational Assignments

Nicotinic acid I														
Exptl. Wave Numbers (cm^{-1})		Theoretical Wave Numbers (cm^{-1})												Approximate description of vibration
		B3LYP/6-311++G(d,p)				X3LYP/6-311++G(d,p)				B3PW91/6-311++G(d,p)				
FTIR	Raman	$\nu_{cal.}$ unscaled	ν_{cal} scaled	IR Int.	Raman Activity	$\nu_{cal.}$ unscaled	ν_{cal} scaled	IR Int.	Raman Activity	$\nu_{cal.}$ unscaled	ν_{cal} scaled	IR Int.	Raman Activity	
3430	-	3789	3713	104	136	3791	3715	107	134	3796	3720	108	133	ν OH
-	3069	3192	3128	6	150	3194	3130	5	150	3211	3146	5	150	ν CH
-	-	3178	3114	4	94	3180	3116	3	95	3197	3133	3	89	ν CH
3060	-	3171	3107	4	52	3174	3110	3	52	3190	3126	3	52	ν CH
-	-	3143	3080	14	117	3145	3082	14	117	3162	3098	13	114	ν CH
1700	1684	1800	1764	398	79	1801	1764	402	78	1810	1773	394	77	ν C=O
1610	-	1642	1609	62	61	1644	1611	63	61	1646	1613	64	59	ν C=C
-	1593	1619	1586	11	5	1621	1588	11	5	1624	1591	11	5	ν C=C
1595	-	1515	1484	4	2	1517	1486	4	2	1511	1480	5	3	ν C=N
1490	-	1456	1426	31	2	1458	1428	32	2	1454	1424	28	2	ν C-C
1420	-	1382	1354	132	10	1384	1356	131	9	1383	1355	145	11	β OH
1305	1310	1363	1335	14	1	1365	1337	13	1	1352	1324	11	1	ν C-C
1300	-	1307	1280	0	3	1305	1278	0	3	1319	1292	0	3	ν C-N
1250	-	1232	1207	31	6	1233	1208	35	6	1228	1203	29	6	β CH
1185	1182	1209	1184	146	20	1211	1186	147	20	1208	1183	151	21	ν C-O
1140	-	1138	1115	0	4	1139	1116	0	4	1134	1111	4	3	β CH
1105	-	1126	1103	184	0	1128	1105	182	0	1126	1103	169	0	ν (COOH)
1070	-	1062	1040	3	35	1063	1041	3	35	1063	1041	3	32	β CH
-	1036	1042	1021	11	11	1044	1023	11	11	1038	1017	11	11	β CH
1020	-	1015	994	0	0	1019	998	0	0	1008	987	0	0	γ CH
1000	-	996	976	0	0	999	979	0	0	990	970	0	0	γ CH
940	-	963	943	0	0	966	946	0	0	956	936	0	0	γ CH
840	-	845	828	3	0	848	831	3	0	845	828	2	0	γ CH
800	809	794	778	11	15	795	779	11	15	793	777	12	15	ν C-COOH
730	-	758	742	78	0	761	745	79	0	760	744	78	0	β C=O of COOH
-	-	714	699	11	0	716	701	11	0	715	700	16	0	ϕ Ring
-	-	660	646	42	1	661	647	42	1	658	644	42	1	β (COOH)
-	635	628	615	11	5	629	616	10	5	623	610	9	5	β Ring
620	-	563	551	96	2	568	556	96	2	580	568	96	2	γ OH
490	-	494	484	10	1	495	485	10	1	494	484	9	1	β C-COOH
420	-	421	412	0	0	424	415	0	0	423	414	0	0	γ C=O of COOH
395	-	388	380	6	4	388	380	6	4	385	377	6	4	γ C-O of COOH
380	380	380	372	7	0	384	376	7	0	380	372	6	0	γ (COOH)
205	-	206	201	3	0	208	203	3	0	207	202	3	0	β C-OH of COOH
140	-	146	143	0	1	149	146	0	1	155	151	0	1	γ C-COOH
60	-	40	39	3	0	51	49	3	0	61	59	3	0	τ C-COOH

Scale factor of 0.98 for calculated wavenumbers

Abbreviations used: ν-stretching, β-In-plane-bending, γ –Out-of-plane-bending, ϕ-non-planar ring deformation, τ-Twisting

Region 2000-1000 cm^{-1}

The C-O stretching frequency predicted by B3LYP calculations at 1764cm^{-1} corresponds to observed IR and Raman bands at 1700 cm^{-1} and 1684 cm^{-1} respectively. The C-C stretching frequency predicted by B3LYP calculations at 1335cm^{-1} corresponds to observed IR and Raman bands at 1305 cm^{-1} and 1310 cm^{-1} respectively. The C-O stretching frequency predicted by B3LYP calculations at 1184cm^{-1} corresponds to observed IR and Raman bands at

1185 cm^{-1} and 1182 cm^{-1} respectively. Other bands observed in this region in IR and Raman spectra of Nicotinic acid are also well predicted and assigned by DFT Calculations.

Region below 1000 cm^{-1}

In this region, the C-COOH stretching frequency is calculated to be 778 cm^{-1} which is in good agreement with the observed IR and Raman bands at 800 cm^{-1} and 809 cm^{-1} respectively. Other bands observed in this region in IR and Raman spectra of Nicotinic acid are also well predicted and assigned by DFT Calculations.

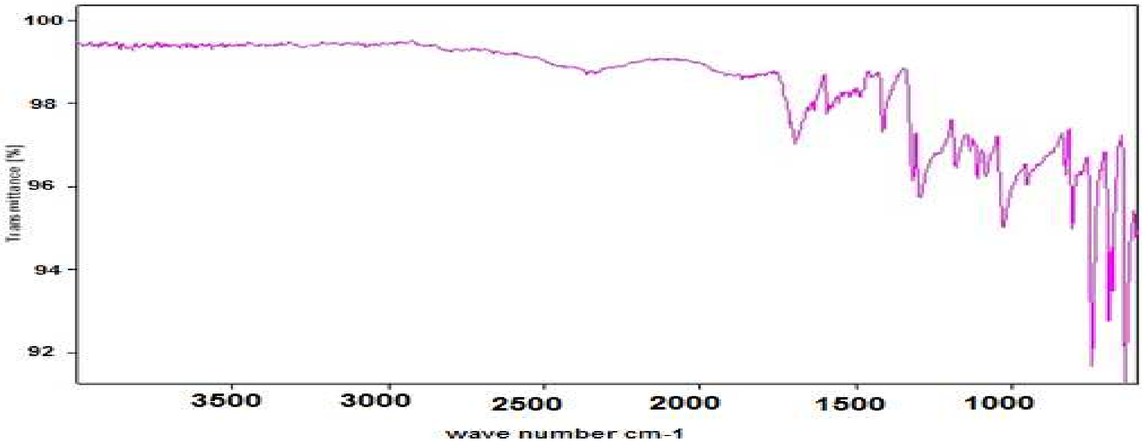


Fig.3 Experimental FTIR spectra of Nicotinic Acid

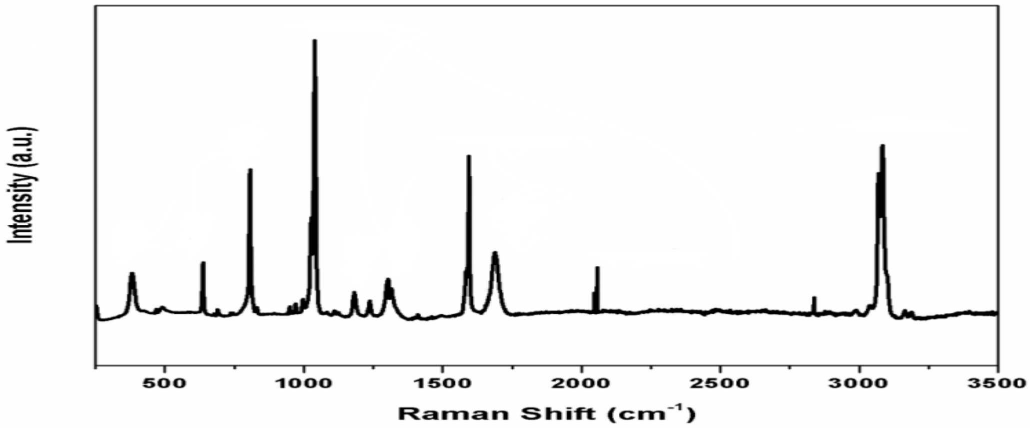


Fig.4 Experimental Raman spectra of nicotinic acid

CONCLUSION

In the present paper attempt have been made for the proper vibrational assignments for Nicotinic acid from FTIR and Raman specta. The equilibrium geometries, harmonic frequencies and FTIR, FT Raman spectra of the Nicotinc acid were obtained and analysed at MP2, B3LYP, X3LYP and B3PW91 methods utilizing 6-311++G(d,p) basis set. Comparison between the calculated vibrational frequencies and experimental values indicates that the FTIR and Raman Spectra can be well predicted by DFT methods. In particular, the results of the B3LYP method indicate better agreement to experimental one.

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