



Research Article

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Hydrogen bonded nicotinic acid-water complexes studied by *ab-initio* and density functional theory

Achchhe Lal*, Neha Shukla and Devendra K. Singh

Department of Physics, Udai Pratap Autonomous College, Varanasi, India

ABSTRACT

Molecular structure and Vibrational spectra of Nicotinic Acid (NA)–Water (W) complexes with stoichiometric ratios ranging from 2:1 (NA₂W) to 1:3 (NAW₃) Complexes have been studied by means of quantum chemical calculations using HF and B3LYP methodology and the 6-311++G(d, p) basis set. It was found that the strength of hydrogen bond between the hydrogen and the nitrogen increases with increasing the number of water molecules. Structural parameters of the optimized geometries, total energies and dipole moment have been calculated. We show that increasing the number of water molecules strength of the binding energy as well as bond length between N and H decreases i.e. stability increases. The ring-breathing mode frequency ν_1 of the reference system NA has been chosen as a marker band to the strengths of hydrogen bonding. IR intensity and Raman activity corresponding to the ring-breathing mode frequency ν_1 have been calculated for three numbers of hydrated complexes of Nicotinic Acid.

Key words: Nicotinic acid-water complexes, Molecular Structure, ab-initio and DFT Calculations, Optimized Geometry.

INTRODUCTION

Nicotinic Acid (NA) or Niacin (3-pyridine carboxyl acid) also known as Vitamin B₃, is a water soluble vitamin and indispensable dietary factor for humans and animals [1,2]. In human, mild Nicotinic acid deficiency has been shown to slowdown metabolism and cause decreased tolerance to the cold and severe deficiency of it in the diet causes the disease pellagra, a systematic disorder. It is involved in a wide range of biological processes, including production of energy, synthesis of fatty acids and steroids, regulation of gene expression and maintenance of genomic integrity. Nicotinic acids has been used to increase levels of high-density lipoprotein (HDL) in the blood and has been found to modestly decrease the risk of cardiovascular events in a number of controlled human trials [3]. W.B. Wright et al [4] studied the crystal structure of nicotinic acid in the first time by two and three dimensional X-ray methods. A. Kuttoglu et al [5] reinvestigated the crystal structure of nicotinic acid and derived more accurate parameters as a preliminary to the study of the electron density distribution in the molecule. Sala et al [6] studied the vibrational analysis of nicotinic acid species based on ab initio molecular orbital calculations by ab initio (Hartree Fock and second-order Moller Plesset perturbation) and hybrid density functional theory calculations 6-31G** basis set. Koczon et al. [7] studied the experimental and theoretical spectra of nicotinic acid and obtained its two stable structures NA I and NA II which differ in orientation of the COOH group with respect to the pyridine ring. Hudson et al [8] proposed a study on the inelastic neutron scattering spectrum of nicotinic acid and its assignment by solid-state density functional theory. Kumar et al [9] have been recorded and analysed the FTIR and Raman spectra of nicotinic acid. The stabilities, optimized molecular geometries, APT charges and vibrational characteristics for the two possible conformers of nicotinic acid have been computed using DFT method.

Hydrogen bonding is an extensively investigated phenomenon, [10,11] especially due to its importance for biological system [12]. Quantum Chemistry provides the concepts to achieve an understanding of the fundamental nature of chemical bonds in general and hydrogen bonds in particular [13]. Structures (optimized geometries), energetics (total energies) and vibrational spectra (infrared and Raman) of hydrogen-bonded complexes can be determined via electronic structure calculations. To predict molecular properties reliably, the inclusion of electron correlation is required. Besides *ab initio* methods such as Hartree Fock (HF) theory, density functional theory (DFT) has become very popular recently owing to its good performance and reasonable computational efforts [14]. Binary ionic complexes, complexes of small organic molecules with water and some other systems have been examined [15-22]. Computer simulation of molecular structures in the Nicotinic Acid–Water and Nicotinic Acid–Water–Poly (N-vinylpyrrolidone) system was performed and IR spectra of these systems were calculated recently [23].

We propose to study the structures and spectra of possible hydrogen bonded nicotinic acid-water complexes, such as NA_2W , NAW , NAW_2 , NAW_3 . In this paper the *ab-initio* and DFT derived optimized geometries and vibrational spectra of the several nicotinic acid-water complexes are presented and the change in the structures and spectral features within this group has been discussed. The optimized geometry, total energies and ring breathing vibration ν_1 of the nicotinic acid-water complexes has been characterized theoretically for the first time using comparative study of *ab-initio* (HF) and DFT calculations (B3LYP) with 6-311++G(d, p) basic set.

Computational Methodology:

The ground state geometries and vibrational spectra for free Nicotinic Acid (NA) and its hydrogen-bonded complexes with three molecules of water have been optimized and corresponding ring breathing vibration ν_1 were calculated using *ab initio* method:-(i) Hartree–Fock (HF) [24] and hybrid density functional theory (DFT) methods-(ii) B3LYP which uses Becke’s three-parameter functional with nonlocal correlation provided by Lee–Young–Parr expression [25, 26] with 6-311++G(d, p) basic set. All calculations have been performed using the GAUSSIAN 03 (revision D.01) package of programs [27] without any constraint on the geometry. It has already been shown that this level of theory is sufficient to reliably predict molecular geometries as well as vibrational spectra of hydrogen bonded systems [28]. Geometries have been first optimized with full relaxation on the potential energy surfaces. The optimized geometrical parameters (bond length and bond angles), total energies [29], ring breathing vibration ν_1 , IR intensity, Raman activity and dipole moment have been calculated for nicotinic acid and nicotinic acid-water complexes and compared.

RESULTS AND DISCUSSION

The optimized geometries of several Nicotinic Acid (NA)-water(W) complexes with different stoichiometric ratios ranging from 2:1 (NA_2W) to 1:3 (NAW_3) are shown in Figure 1a-d. Geometry optimizations were performed without any constraints. In Table 1, some selected inter- and intra molecular structural data for the different species mentioned above, calculated at the HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) level, are listed. From Table 1, it can clearly be seen that in the series: $NA_2W \rightarrow NAW \rightarrow NAW_2 \rightarrow NAW_3$ the hydrogen bond $N_a \cdots H_a$ between Nicotinic Acid and water is successively shortened and the bond angle $N_a \cdots H_a - O$ increased which indicate the formation of stronger hydrogen bond. In the case of NA_2W , NAW , NAW_2 and NAW_3 the strengthening of the hydrogen bond causes an elongation of the covalent O– H_a bond in the water molecule. The same effect on the other covalent bond (O– H_b) of the same water molecule is much less pronounced. For the NA_2W complex, however, the inter atomic distances for the covalent bonds O₁– H_a and O₁– H_b as well as the hydrogen bonds $N_a \cdots H_a$ and $N_b \cdots H_b$ are practically the same. This is quite expected since the two Nicotinic acid rings linked with water are symmetrically placed on both sides of the water molecule. The bond lengths O₂– H_c and O₂– H_d of the second water molecule in the NAW_2 complex are quite close to those of the first water molecule, O₁– H_a and O₁– H_b , respectively. The lengths of the two covalent O–H bonds, however, do not match precisely. This is because of the fact that in NAW_2 , although both water molecules are hydrogen-bonded, their environment is different- the first water molecule being bonded to the N-atom of Nicotinic acid ($N \cdots H$), while the second water molecule is bonded to the O-atom of the first water molecule ($O \cdots H$). The water-water hydrogen bond (O₁– H_c) is slightly longer than the Nicotinic acid-water hydrogen bond ($N \cdots H_a$). With the addition of a third water molecule yielding the NAW_3 complex, the water-water hydrogen bond (O₁– H_c) distance increases. The adjacent covalent bond O₂– H_c is slightly shortened, whereas the effect on the O₂– H_d (O₃– H_f) distance is negligible. This is quite reasonable since these two O–H bonds are open-ended at the H-atom, and are not expected to be appreciably affected by hydrogen bonding. The quite symmetrical structure of the NAW_3 complex is revealed by nearly identical bond distances of the covalent bonds O₂– H_c / O₃– H_c and hydrogen bonds O₁– H_c / O₁– H_e , in which both the second and the third water molecule are involved.

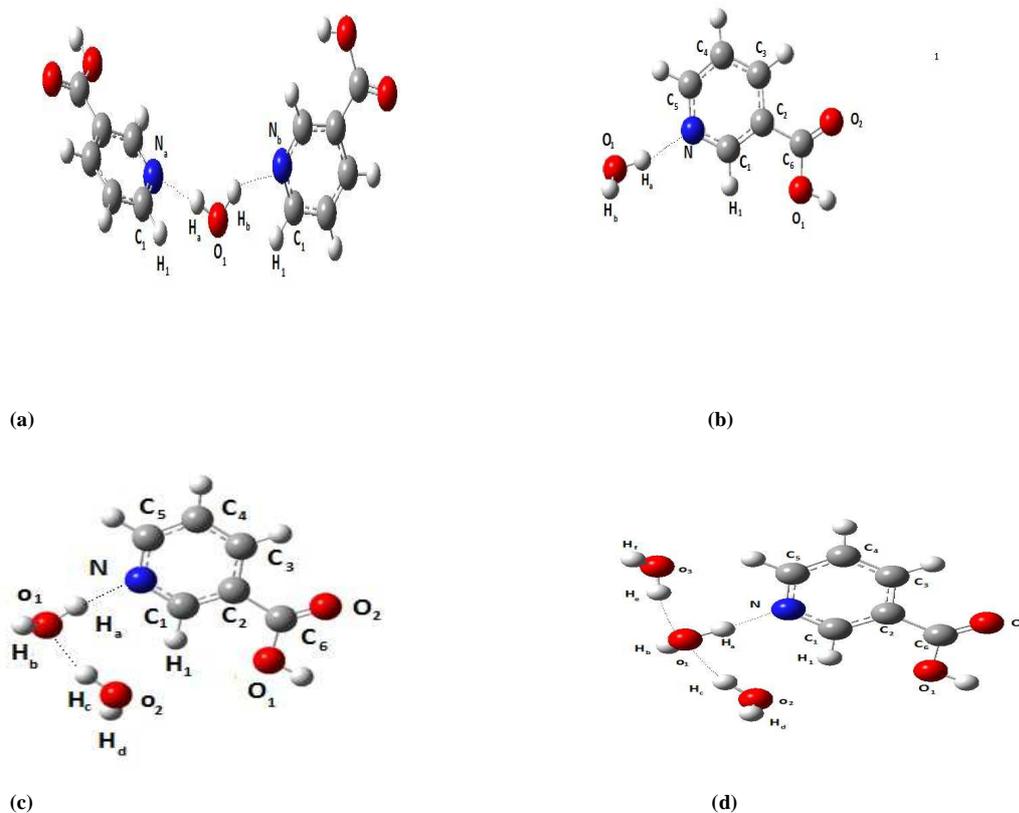


Fig. 1. Optimized geometries of Nicotinic acid-Water complexes (a) NAW (b) NA₂W (c) NAW (d) NAW₂ (e) NAW₃ at B3LYP/6-311++G(d,p)

Table1: Selected calculated structural parameters of Nicotinic acid-Water Complexes at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory

Bond distances (Å ⁰)	HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
	NA ₂ W	NAW	NAW ₂	NAW ₃	NA ₂ W	NAW	NAW ₂	NAW ₃
N _a -H _a	2.1608	2.1287	2.0535	1.9399	2.0004	1.9569	1.8662	1.7440
N _b -H _b	2.2627	-	-	-	2.0904	-	-	-
O ₁ -H _a	0.9462	0.9476	0.9519	0.9577	0.9725	0.9757	0.9853	0.9997
O ₁ -H _b	0.9445	0.9404	0.9404	0.9423	0.9689	0.9610	0.9615	0.9633
O ₁ -H _c	-	-	1.9955	2.0781	1.8508	-	1.8505	1.9226
O ₁ -H _e	-	-	-	2.5378	-	-	-	1.9397
O ₂ -H _c	-	-	0.9482	0.9469	0.9766	-	0.9766	0.9742
O ₃ -H _e	-	-	-	0.9463	-	-	-	0.9731
O ₂ -H _d	-	-	0.9405	0.9405	0.9609	-	0.9609	0.9610
O ₃ -H _f	-	-	-	0.9405	-	-	-	0.9610
Angles(deg)	NA₂W	NAW	NAW₂	NAW₃	NA₂W	NAW	NAW₂	NAW₃
H ₁ -C ₁ -N _a	115.5	116.7	116.6	116.0	115.8	116.7	116.4	115.7
H ₁ -C ₁ -N _b	115.5	-	-	-	115.5	-	-	-
C ₁ -N _a -H _a	106.4	134.9	115.5	119.3	111.9	129.5	115.8	119.4
C ₁ -N _b -H _b	97.5	-	-	-	98.6	-	-	-
N _a -H _a -O ₁	162.7	163.1	168.1	174.7	169.2	169.0	168.6	174.6
N _b -H _b -O ₁	144.6	-	-	-	147.5	-	-	-
H _a -O ₁ -H _b	106.9	-	106.9	106.6	106.3	-	106.3	106.3
O ₁ -H _c -O ₂	-	-	160.4	156.2	-	-	-	157.4
O ₁ -H _e -O ₃	-	-	-	153.9	-	-	-	155.5
H _c -O ₂ -H _d	-	-	106.5	106.7	-	-	105.7	105.9
H _e -O ₃ -H _f	-	-	-	106.7	-	-	-	105.9

Optimized energy and dipole moment are calculated at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) level. The results are shown in Table 2. According to energy analysis, the calculations predict that NA_2W is most stable than the other nicotinic-water complexes, this is quite expected since the two Nicotinic acid rings linked with water are symmetrically placed on both sides of the water molecule. In $\text{NAW} \rightarrow \text{NAW}_2 \rightarrow \text{NAW}_3$ that stability of nicotinic-water complexes increases with number of water molecules. The calculated dipole moment of NA_2W , NAW , NAW_2 , and NAW_3 differ significantly in their magnitudes and we find that NA_2W is more polar than other three complexes.

Table2: Calculated total energies and dipole moments for nicotinic acid-water complexes

	HF/6-311++G(d,p)		B3LYP/6-311++G(d,p)	
	Total energy (a.u)	Dipole moment (Debye)	Total energy (a.u)	Dipole moment (Debye)
NA_2W	-944.915268	3.563	-950.437852	3.347
NAW	-510.491986	2.3982	-513.455253	2.842
NAW_2	-586.556173	2.203	-589.928213	2.460
NAW_3	-662.618085	1.375	-666.397456	0.606

The ring-breathing mode frequency ν_1 of the reference system NA has been chosen as a marker band to the strengths of hydrogen bonding. IR intensity and Raman activity corresponding to the ring-breathing mode frequency ν_1 have been calculated for three numbers of hydrated complexes of Nicotinic Acid. The results are shown in Table 3. We see that the ring breathing mode frequency and corresponding Infrared intensity, Raman scattering activity has changed with the addition of water.

Table3: Ring breathing mode frequencies, Infrared Intensities and Raman Scattering Activities of Nicotinic acid and Nicotinic acid-water complexes

	HF/6-311++G(d,p)			B3LYP/6-311++G(d,p)		
	Frequency (cm^{-1})	Infrared Intensities (Km/Mole)	Raman Activity (A^4/AMU)	Frequency (cm^{-1})	Infrared Intensities (Km/Mole)	Raman Activity (A^4/AMU)
NA_2W	1119.32	11.6073	29.7786	1056.23	7.7121	39.5547
NAW	1119.68	10.8436	27.9939	1045.35	14.0519	21.2601
NAW_2	1119.76	7.9898	23.3141	1045.55	12.3421	33.2182
NAW_3	1119.46	13.3175	35.3882	1045.4	12.2484	45.1602

CONCLUSION

The optimized geometries and vibrational spectra of four hydrogen-bonded nicotinic acid-water complexes with different stoichiometric ratios were calculated employing ab-initio with HF and DFT with the hybrid functional B3LYP, using the 6-311++G- (d,p) basis set. Ab-initio and Density Functional Theory of hydrogen bonded Nicotinic Acid –Water Complexes shows that NA_2W is most stable than the other nicotinic-water complexes. In $\text{NAW} \rightarrow \text{NAW}_2 \rightarrow \text{NAW}_3$ that stability of nicotinic-water complexes increases with number of water molecules. The calculated dipole moment of NA_2W , NAW , NAW_2 , and NAW_3 differ significantly in their magnitudes and we find that NA_2W is more polar than other three complexes. We see that the ring breathing mode frequency of the reference system NA has changed with the addition of water.

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