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Structural, Spectroscopic and Optical Properties of Monohydrated Adenine: A Theoretical Study

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Abstract

The structural, spectroscopic (IR, NMR and UV-Vis), electronic and optical properties of monohydrated adenine (monohydrated 6-aminopurine, $C_5H_5N_5.H_2O$) are investigated theoretically using DFT/B3LYP level of theory. Three minimum energy structures have been identified for monohydrated of adenine where H_2O molecule is doubly hydrogen bonded with adenine.^{1}H NMR analysis shows that the protons which are hydrogen bonded become deshielded and chemical shift moves to the higher frequency region.Five IR active mode of vibrations were found at 3108, 3295, 3665, 3676 and 3719 cm^{-1} which are assigned as bonded -OH vibration of H_2O, Bonded -NH vibration of NH_2, Free -NH vibration of adenine (9 N), Free -NH vibration of NH_2, Free -OH vibration of H_2O, respectively and agree well with the available experimental results. The investigation of electronic properties shows that the HOMO-LUMO band gap energy of monohydrated adenine at B3LYP level is 5.15 eV. The major electronic transition (from HOMO to LUMO (83%) ($\pi\rightarrow\pi^*$)) occurs at 258 nm (4.80 eV) with a minor transition at 237 nm (5.23 eV). Theoretically it is observed that the HOMO-LUMO band gap energy is for monohydrated adenine is lower than that of adenine.

Keywords: Monohydratedadenine, TD-DFT, IR, NMR, Electronic properties, Optical absorption

I. Introduction

Knowledge of the photophysics and photochemistry of individual nucleic acid bases or base pairs is a prerequisite for a detailed understanding of DNA photostability under ultraviolet (UV) irradiation. Because, nucleobases absorb UV light strongly and act as a primary chromophores of DNA.[1-5] Photostability of DNA bases is the essential criteria for the preservation of genetic information of DNA bases. In solvated DNA bases, understanding the role of solvent for the stability of DNA bases is very important. As we know that Hydrogen-bonds (HB) play an important role in molecular systems, particularly in biological systems, because all lives on the earth may be viewed as a matter of hydrogen-bonding supramolecular systems. Since HBs have a central role on the mechanism of life phenomena including the structure and functions, it is essential to understand the molecular-level aspects of HB systems. Besides the basic science view, molecular-level understating of HB systems is also important for synthesis and design of highly specific drugs. This is because the intermolecular interaction, controls the working activity of a drug is determined by the specific interaction and binding constant of HB complexes such as those between drugs and DNA, RNA or protein.[6-7]

Numerous experimental and theoretical studies on DNA and DNA bases have been performed to understand structural, electronic properties and excited state lifetimes.[8-11] All the calculations have been focused on the ground state to the higher electronic singlet and triplet states of the neutral molecules.

In this paper, we have performed a theoretical investigation of structural, spectroscopic, electronic and optical properties of monohydrated adenine with DFT method and compared with the available experimental data.

II. Computational Details

All the calculations have been performed using well known hybrid approach B3LYP[12] as implemented in the quantum chemistry package G09.[13] We have used 6-31G basis set in order to calculate the structure, IR,^{1}H NMR and UV–Vis spectra of monohydrated adenine in the ground state at the B3LYP level of theory. The optimized structure of monohydrated adenine in the ground state was verified by calculating vibrational frequencies to confirm that there were no imaginary frequencies. Excited state calculations have been done by TD-DFT method employing the same basis set and theory to study electronic and optical properties of monohydrated adenine. To avoid complexity, we have calculated only six excited states of monohydrated adenine.

III. Results and Discussion

Molecular Geometry and Thermodynamic parameters

The optimized structure of monohydrated adenine by B3LYP is shown in Fig. 1. In order to get optimized minimum energy structure of monohydrated adenine, at first we have done intrinsic reaction coordinate (IRC) calculation with HF/6-31G.This minimum energy structure was re-optimized using DFT/B3LYP/6-31G level of theory.

The final geometry corresponds to true energy minima as revealed by the lack of imaginary frequencies in the vibrational mode calculation. Several structures of monohydrated adenine have been calculated to see the hydration site of adenine. Among them, three structures (Structure I, Structure II and Structure III) are found for minimum energy which is shown in Fig. 1. The most stable structure is structure I where H_2O molecule is connected with adenine via two hydrogen bonding.

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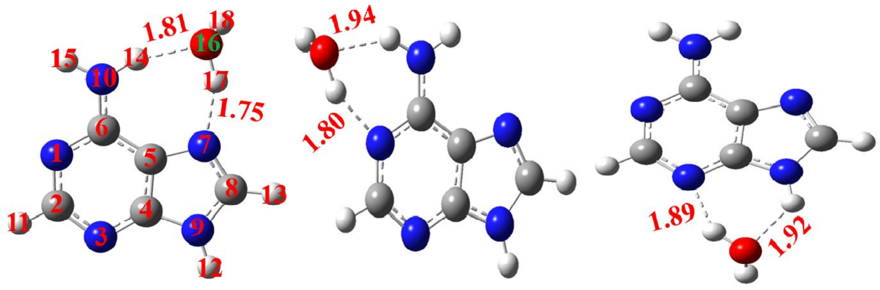

Structure I
(0 eV)

Structure II
(0.1130 eV)

Structure III
(0.1267 eV)

Fig. 1. Three optimized structures of monohydrated adenine.

One hydrogen of H_2O molecule is connected with nitrogen atom (7 position) and oxygen atom of H_2O is connected with amino group of adenine. The second most stable one is structure II where one hydrogen of H_2O molecule is connected with nitrogen atom (1 position) and oxygen atom of H_2O is connected with amino group of adenine. Structure I is more stable than structure II by 0.1130 eV. In case of structure III, one hydrogen of H_2O molecule is connected with nitrogen atom (3 position) and oxygen atom of H_2O is connected with hydrogen atom (9 position) of adenine. Structure I is more stable than structure III by 0.1267 eV.

The total energy (SCF), zero point vibrational energy (ZPVE), rotational constants, specific heat capacity(Cv) at constant volume, entropy(S) and dipole moment of monohydrated adenine for the most stable structure are provided in the Table 1.

Table 1. Calculated thermodynamic parameters of monohydrated adenine

Molecule	SCF energy/ Hatree	Z PV energy/ kcal $mole^{-1}$	Rotational constant /GHz	Specific heat(Cv)/cal mol^{-1} K^{-1}	Entropy(S)/ cal mol^{-1} K^{-1}	Dipole moment , μ /Debye
Hydrated Adenine	-543.5937	87.2050	1.52627 1.10294 0.64144	35.554	9.339	5.3917

SCF= Self-Consistent Field and ZPV= Zero Point Vibrational

^{1}HNMR spectral analysis

For structural analysis of organic compounds, NMR spectroscopy is one of the most powerful techniques. It is well-established that the combined use of experimental NMR spectroscopic technique and computational simulation methods give a powerful gadget to interpret and predict the structure of organic compound, even for the structures of large biomolecules.To get theoretical ^{1}H NMR results of monohydrated adenine, first the full geometry optimization is carried out with the B3LYP/6-31G in gas phase. After optimization, ^{1}HNMR calculations of the studied compounds are calculated by using the gauge-including atomic orbital (GIAO) method. The chemical shifts of the studied compounds are reported in ppm relative to tetramethylsilane (TMS) for ^{1}H NMR spectrum as presented in Table 2. The chemical shift of H(14), H(11), H(17), H(12)H(13), H(15) and H(18) protons (See Fig.1 for labeling) are found at 8.15, 7.84, 6.88, 6.53, 6.38, 3.43 and -0.25 ppm, respectively.

Table 2. Calculated ^{1}H NMR data of monohydrated adenine

Molecule	Protons with number	Chemical Shift (Calc.)/ppm	Chemical Shift (Expt.)/ppm
A(H_2O)	H(14)	8.15	
	H(11)	7.84	8.14
	H(17)	6.88	
	H(12)	6.53	
	H(13)	6.38	8.11
	H(15)	3.43	
	H(18)	-0.25	

We know that electron rich atom increases the shielding and moves the resonance towards lower frequency and electron-withdrawing atom can decrease the shielding and moves the resonance of attached proton towards higher frequency. Similar results were found for monohydrated adenine. Amino proton of H(14) becomes de-dshielded due to the hydrogen bond with oxygen atom of H_2O molecule. Therefore the resonance moves to the higher frequency region (8.15 ppm). On the other hand, amino proton of H(15) which is shielded and moves the resonance towards lower frequency region (3.43 ppm). Similarly H(17) of H_2O which is hydrogen bonded with N(7) atom shows chemical shift at 6.88 ppm as oxygen is more electron negative than nitrogen. The free H(18) of H_2O which is so shielded that shows chemical shift near to tetramethylsilane (TMS). The experimental ^1H NMR spectra of adenine range between 8.11–8.12 ppm in presence of water solvent.[14] Our calculated values show deviation from the experimental results, probably because lack of incorporating solvent effect in our calculations.

Vibrational spectral analysis

The assignments of the vibrational frequencies of monohydrated adenine (calculated and observed) are shown in Table 3. In the calculated spectrum of monohydrated adenine, five IR active mode of vibrations were found at 3108, 3295, 3665, 3676 and 3719 cm^{-1} which are assigned as bonded –OH vibration of H_2O, bonded -NH vibration of NH_2, Free -NH vibration of adenine (9 N), Free -NH vibration of NH_2,Free -OH vibration of H_2O, respectively. Five IR absorption bands at 3210, 3050, 3441, 3451 and 3721 cm^{-1} were also observed experimentally which are assigned as bonded -OH vibration of H_2O, Bonded -NH vibration of NH_2, Free -NH vibration of adenine (9 N), Free -NH vibration of NH_2, Free -OH vibration of H_2O, respectively.[15] Therefore we concluded that our theoretical vibrational frequencies have well agreement with the experimental data.

Table 3. IR calculated and experimental frequencies of monohydrated adenine

Molecule	IR calculated frequencies/cm^{-1}	IR experimental frequencies/cm^{-1}	IR active mode of vibration
A(H_2O)	3108	-	Bonded -OH vibration of H_2O
	3097	3050	Bonded -NH vibration of NH_2
	3445	3441	Free -NH vibration of adenine(9 N)
	3455	3451	Free -NH vibration of NH_2
	3719	3721	Free -OH vibration of H_2O

Calculated values were corrected by multiplying the frequency factor, f = 0.940

Electronic absorption and optical properties

We have used TD-DFT method for the calculations of excited state properties of monohydrated adenine. For this purpose, we have calculated six lowest singlet electronic states in the ground state of monohydrated adenine.The computed electronic values such as absorption wavelength (λ), excitation energies (E) and oscillator strengths (f) are tabulated in Table 4.

Table 4. Calculated wavelengths λ (nm), excitation energies E(eV) and oscillator strength (f) and major& minor electronic transitions of monohydrated adenine

Molecule	λ (nm)	E (eV)	f	Major and minor transitions
A(H_2O)	258	4.80	0.1504	H→L (83%), H→L+1 (10%), H-2→L (3%)&H→L+2 (2%)
	237	5.23	0.0481	H-2→L (14%),H→L (10%) H→L+1 (70%)

H = HOMO & L = LUMO

The major transition with highest oscillator strength for monohydrated adenine is at 258 nm (4.80 eV). The major transition occurs from HOMO to LUMO (83%) ($\pi \rightarrow \pi^*$) with a minor transitions from HOMO to LUMO+1 (10%), HOMO-2 to LUMO (3%) and HOMO to LUMO +2 (2%). The HOMO and LUMO that participate in the lowest electronic transitions of monohydrated adenine are presented in Fig. 2

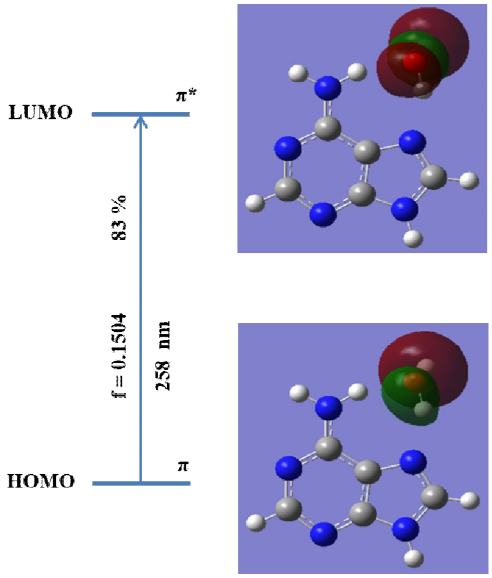

Fig. 2. Transition of HOMO → LUMO of monohydrated adenine.

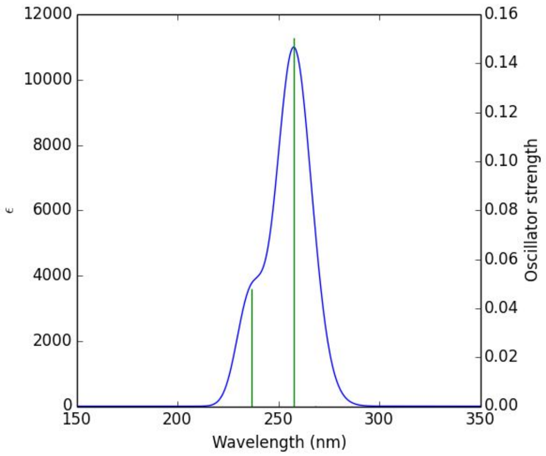

Fig. 3. Calculated UV-Visible absorption spectrum of adenine.

In the present study, the FMO energy gap is calculated as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as follows:

$\text{HOMO}_{\text{energy}}$ (B3LYP) = -6.02eV,

$\text{LUMO}_{\text{energy}}$ (B3LYP) = -0.87eV

HOMO –LUMO energy gap (B3LYP) = 5.15eV

Therefore the energy gap of FMO of monohydrated adenine is 5.15 eV.

Previously we studied pure adenine[16] and found the energy gap of FMO of is 5.35 eV whereas 5.15 eV for monohydrated adenine. Therefore we can conclude that hydration decreases HOMO-LUMO energy gap and makes electronic transition easier.

IV. Conclusion

The effect of hydration on the structural, thermodynamics, spectroscopic and electronic properties of adenine has been studied theoretically. Density Functional Theory (DFT) calculations have been performed with Gaussian 09W program at B3LYP/6-31G levels of theory and excited state calculations have been performed by Time-Dependent Density Functional Theory (TD-DFT). Three minimum energy structures have been found for monohydrated adenine where H_2O molecule is doubly hydrogen bonded with adenine. H(14) & H(17) protons become de-shielded due to the hydrogen bonding and hence resonance frequency moves to higher frequency region.The calculated IR active mode of vibrations and their assignments are in reasonable agreement with the available experimental data. The investigation of electronic properties shows that the HOMO-LUMO energy band gap of monohydrated adenine at B3LYP level is 5.15 eV. The calculation of optical properties at excited states shows that the major transition (from HOMO to LUMO (83%) (π→π*) occurs at 258 nm (4.80 eV) with a minor transition at 237 nm (5.23 eV).

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