Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 171 (2017) 305–310

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Time-dependent density functional theory study on the excited-state hydrogen-bonding characteristics of polyaniline in aqueous environment

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A R T I C L E   I N F O

Article history:
Received 14 December 2015
Received in revised form 13 August 2016
Accepted 18 August 2016
Available online 20 August 2016

Keywords:
Excited-state
First-principles
TDDFT
Hydrogen bond

A B S T R A C T

A theoretical study was carried out to study the excited-state of hydrogen-bonding characteristics of polyaniline (PANI) in aqueous environment. The hydrogen-bonded PANI-H_2O complexes were studied using first-principles calculations based on density functional theory (DFT). The electronic excitation energies and the corresponding oscillator strengths of the low-lying electronically excited states for hydrogen-bonded complexes were calculated by time-dependent density functional theory (TDDFT). The ground-state geometric structures were optimized, and it is observed that the intermolecular hydrogen bonds C—N···H—O and N—H···O—H were formed in PANI-H_2O complexes. The formed hydrogen bonds influenced the bond lengths, the charge distribution, as well as the spectral characters of the groups involved. It was concluded that all the hydrogen-bonded PANI-H_2O complexes were primarily excited to the S1 states with the largest oscillator strength. In addition, the orbital transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) involved intramolecular charge redistribution resulting to increase the electron density of the quinonoid rings.

1. Introduction

Intermolecular hydrogen bonding, a site-specific weak bond between hydrogen donor and acceptor molecules, is an important solute-solvent interaction. Ever since it was first introduced, [1] much attention has been paid to the investigation of hydrogen bonding effect based on its extremely crucial role in chemical, physical, and biological processes. [2–4] Various theoretical and experimental methods have been applied to explore its structural stability and photochemical properties. [5–9] The ground-state structures and electronic properties of hydrogen-bonded complexes have been roundly studied. Furthermore, the electronic excited-state properties of hydrogen-bonded complexes become attracted more and more attentions. [10–12] The charge distribution of hydrogen bond in different electronic excited states produces a significant change on photoexcitation. This process is known as the electronic excited-state hydrogen bonding dynamics. The relationship between electronic spectral shift and excited-state hydrogen-bonding characteristics has been demonstrated by Zhao [2,12] and showed in Fig. 1. According to the electronic spectral shift rule, during the excitation from ground state to excited state, the decreased electronic transition energy makes the related electronic spectra shift towards red as hydrogen bond strengthened in the excited state. On the contrary, hydrogen bond weakening will lead to the blue shift of corresponding electronic spectral. [2,12] In recent years, the time-dependent density functional theory has been widely used to study the hydrogen-bonding characteristics by calculating the electronic excitation energies and monitoring the spectral shifts. It is considered to be a reliable and efficient way for theoretical investigation of the excited-state hydrogen-bonding characteristics. [13–17].

PANI is considered as one of the most promising conducting polymers due to its excellent properties i.e. chemical and environmental stabilities, remarkable electrical conductivity, low cost, and the easy preparation ability. [18] The highly conducting emeraldine salt through the reversible protonic acid doping process is regarded as one of the most distinctive characteristics of PANI.

During the past decade, different theoretical calculations have been devoted to investigating the PANI structure, doping mechanism, conductivity, band structure, DOS, UV/VIS spectra, the hydrogen bonding effect, etc. [19–24] The theoretical studies on PANI-water interactions have also been carried out. [25,26] Matveeva and co-workers classified the PANI-water interaction into two certain types adsorbing on amine and imine nitrogen atoms, respectively. [25] Romanova et al. [27,28] proved that the protons bound tighter to the chains lead to stronger impact of the dopant on the structural parameters of PANI, and the charge

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http://dx.doi.org/10.1016/j.saa.2016.08.039
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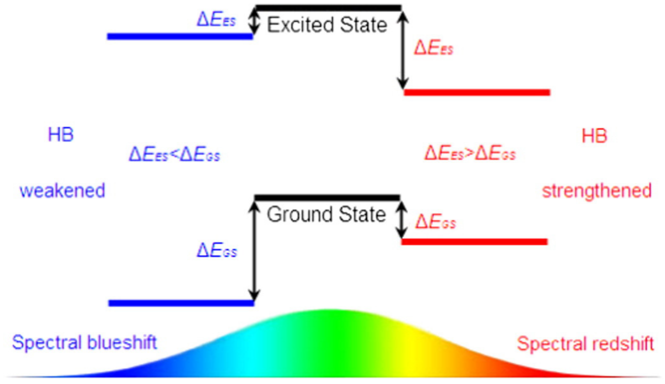

Fig. 1. The relationship between the electronic spectral shift rule and the excited-state hydrogen-bonding characteristics. Strengthened hydrogen bonds can reduce the excitation energies in their corresponding excited states and induce the electronic spectral redshift.

density distribution was more realistic in aqueous environment compared with vacuum estimates. Canales et al. [29] studied the water absorption behavior of PANI by calculating the excess chemical potential, and predicted that the maximum content of water absorbed by PANI was 15% which was consistent with the experimentally measured value (14%). Casanovas et al. [30] reported the interaction of reversible and irreversible absorbed water molecules with PANI using quantum mechanical calculations.

PANI oligomers absorb water molecules through hydrogen bonding, which has been investigated through theoretical methods. [31,32] Results showed that hydrogen bonding interaction between water and PANI reduces the scattering cross section for defects and forms a conductive network for increased conductivity of PANI. The effect of water which acted as H-donor in the hydrogen-bonding has been proved significant. [33–36] Our previous work [37] studied the hydrogen bond in the camphorsulfonic (CSA) acid-doped polyaniline system. In the acid-doped system, S═O···H—N type intermolecular hydrogen bonds were formed, and its effect on the structure, electronic properties and excited-state characteristics were investigated. Herein, plenty of researches have been devoted to the PANI-water ground state hydrogen bonding. To the best of our knowledge, till now less information has been reported on the excited state hydrogen-bonding characteristics of PANI with water. Therefore, in this study the excited-state hydrogen-bonding characteristic of PANI under the aqueous environment was investigated using TDDFT method.

2. Theoretical method and structural model

The ground-state geometric optimization of the isolated PANI monomer and the hydrogen-bonded PANI-H_2O complexes were predicted using DFT with Becke's three-parameter hybrid exchange function using Lee-Yang-Parr gradient-corrected correlation functional (B3LYP hybrid functional). Considering the geometric optimisation of the monomer and complexes, the charge distribution and infrared spectra were predicated using DFT with B3LYP hybrid functional. The electronic transition energies and corresponding oscillator strengths of the complexes in their low-lying electronically excited states were calculated using TDDFT with B3LYP hybrid functional. The implicit water environment was taken into account. Moreover, it has been already demonstrated that the use of Polarized Continuum Model (PCM) is indispensable for theoretical treatment of PANI complexes and substantially improves the accuracy of the calculated charge distribution. [27–28] The 6-31G+(d, p) was chosen as basis set throughout the process, and all the electronic structure calculations were carried out using the Gaussian 09 program suite. [10–12].

The hydrogen bond is the interaction between electron-deficient hydrogen and a region of high electron density. The most common hydrogen bond is the X—H···Y type, where X and Y are electronegative elements and Y possesses one or more lone electron pairs. The study is focused on the emeraldine base which is a member of PANI family, and the PANI is used to represent the emeraldine base model in this study. There are two distinct nitrogen environments coexisting in the PANI: amine and imine nitrogen. As introduced above, the mechanism of water presented in PANI sample has been proposed, and the reversible absorption of water molecules were divided into two models, i.e. interaction with amine and imine nitrogen atom of AM and IM unit, respectively. [25] Considering the previous study on the varied nitrogen environment, the hydrogen-bonded PANI-H_2O complexes were built according to the water absorption degree, and the possible conformations were showed in Fig. 2. For comparison, the isolated PANI and H_2O monomers were also constructed for theoretical study.

3. Results and discussion

3.1. Ground state geometries

The fully optimized geometric structures of the hydrogen-bonded PANI-H_2O complexes in the ground state are displayed in Fig. 3. The vibrational analysis of the complexes shows that the imaginary frequency is nonexistent, which indicates that all of the optimized geometries are at the minimum energy. For comparison, the geometric optimization of the isolated PANI monomer is also calculated. The important structure parameters of the PAIN monomer and the hydrogen-bonded PANI-H_2O complexes in the ground states are calculated and presented in Table 1. The bond lengths of free O—H in isolated H_2O molecule are calculated to be the same values (0.967 Å) which are not listed in the table. It's noteworthy that the intermolecular hydrogen bond can be formed between the N3 atom of PANI and H21 atom of H_2O molecule as shown in Fig. 3(b), which is denoted as PANI-1H_2O. The bond length of the C6—N3···H21—O1 hydrogen bond is 1.864 Å. The bond lengths of N3-C6 and N3-C8 in the PANI-1H_2O complex are 1.397 Å and 1.315 Å, respectively, which are both elongated compared with the PANI monomer. Meanwhile, the bond length of O1—H21 is increased by 0.024 Å in the complex. The varied bond lengths can be explained as that the formation of hydrogen bond increases the elongation of

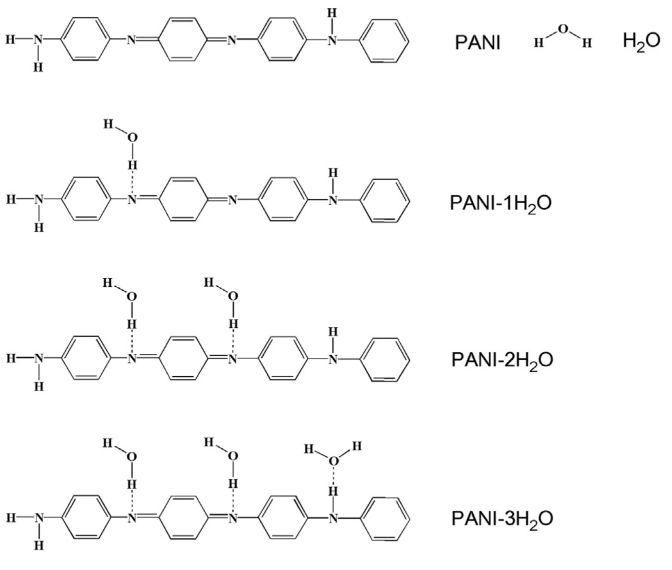

Fig. 2. The molecular models of PANI and H_2O monomers as well as the hydrogen-bonded PANI-H_2O complexes. The different absorption degrees of water molecules are taken into account, and the dotted lines represent the intermolecular hydrogen bonds.