



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Review Article

Hydrogen bond strengthening between *o*-nitroaniline and formaldehyde in electronic excited states: A theoretical study

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ARTICLE INFO

Article history:

Received 29 January 2018

Received in revised form 16 March 2018

Accepted 23 March 2018

Available online 24 March 2018

Keywords:

Hydrogen bonds

TD DFT

Vibrational spectra

Blue shifted

Excited states

ABSTRACT

To study the hydrogen bonds upon photoexcited, the time dependent density function method (TD DFT) was performed to investigate the excited state hydrogen bond properties of between *o*-nitroaniline (ONA) and formaldehyde (CH₂O). The optimized structures of the complex and the monomers both in the ground state and the electronically excited states are calculated using DFT and TD DFT method respectively. Quantum chemical calculations of the electronic and vibrational absorption spectra are also carried out by TD DFT method at the different level. The complex ONA···CH₂O forms the intramolecular hydrogen bond and intermolecular hydrogen bonds. Since the strength of hydrogen bonds can be measured by studying the vibrational absorption spectra of the characteristic groups on the hydrogen bonding acceptor and donor, it evidently confirms that the hydrogen bonds is strengthened in the *S*₁/*S*₂/*T*₁ excited states upon photoexcitation. As a result, the hydrogen bonds cause that the CH stretch frequency of the proton donor CH₂O has a blue shift, and the electron excitations leads to a frequency red shift of N=O and N–H stretch modes in the *o*-nitroaniline(ONA) and a small frequency blue shift of CH stretch mode in the formaldehyde(CH₂O) in the *S*₁ and *S*₂ excited states. The excited states *S*₁, *S*₂ and *T*₁ are locally excited states where only the ONA moiety is excited, but the CH₂O moiety remains in its ground state.

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Contents

1. Introduction	194
2. Computational Details	195
3. Results and Discussion	196
3.1. Geometric Structures in the <i>S</i> ₀ , <i>S</i> ₁ , <i>S</i> ₂ and <i>T</i> ₁ States	196
3.2. Electronic Spectra	196
3.3. Frontier Molecular Orbitals	197
3.4. Natural Bond Orbital and AIM Analyses	197
3.5. Vibrational Absorption Spectra	198
3.6. Hydrogen Bond Strengthening	199
4. Conclusion	200
Appendix A. Supplementary Data	200
References	200

1. Introduction

Noncovalent interactions play a fundamental role in study of the physical and chemical properties of the complex systems. It still currently attracts a considerable attention. Among the noncovalent

interactions, hydrogen bonding acts as an important factor in several fields, ranging from chemistry to biochemistry and biophysics, and plays a critical role in the configurations of proteins, DNA and RNA [1–11]. Hydrogen bonding is composed of the proton donor and acceptor, and is also a fundamental type of solute-solvent interaction [9–13]. Up to now, the nature of hydrogen bonds in the ground state and excited states is a subject of intense contemporary research interest [4–17].

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Upon photoexcitation of hydrogen-bonded systems, the hydrogen bonds are easy to change. The hydrogen donor and acceptor molecules need to reorganize because of the difference in the charge distribution of electronic states. This process is considered as electronic excited-state hydrogen bonding dynamics (ESHBD) [4,14,17,18]. In this process either hydrogen donor or acceptor, or the whole hydrogen bonding complex is photoexcited to its electronic excited state [14,17]. ESHBD is mainly studied by vibrational properties of hydrogen-bonding acceptor and donor groups. The formation of hydrogen bonds can mainly lead to spectral shifts of some hydrogen-bonded groups [19,20]. Various electronic structure methods have been explored to study the nature of the electronic excited state. Time-dependent density functional theory (TD DFT) is the most widely used alternative to explore the excited states of molecules. Since TD DFT is low computational cost and moderate efficiency a great many of excited state properties based on the TD DFT method have been performed. TD DFT method can obtain reasonable absorption spectra. Consequently, TD DFT has been successfully applied to study the spectra and the transition natures of the excited states [19,21].

There has been significant effort in past decade to study the excited-state for understanding many physical, chemical, and biological phenomena both experimentally and computationally, such as hydrogen-bonded water or alcohol networks, organic compounds in solution, hydrogen band DNA and proteins [22,23]. A detailed understanding of the properties and dynamics of the excited states is very important because of their scientific significance. The compounds studied in the excited states are characterized by the possession of electron acceptor and electron donor substituents connected by a π -system [24]. The studies were already performed for some nitroaromatic and nitro-polyaromatic compounds including *o*-nitroaniline (oNA), *m*-nitroaniline (mNA) and *p*-nitroaniline (pNA) [24–26]. Nitroaniline, served as a simple model compound of important nitroaromatics is significant to explore the nature of the excited states. Nitroaniline as a desired chromophore has some characteristically spectroscopic properties. The active N=O group involved in nitroaniline plays a key role in the spectroscopy and the excited states dynamics. So far, for the individual nitroaniline, vertical and adiabatic excitation energies, conical intersection structures, and relaxation pathways have been calculated at various levels of theories and experiments, and some excited-state simulations have been performed as well [31–35]. Meanwhile, the hydrogen-bonding complexes of nitroaniline with several water molecules have been represented for studying the effect of hydrogen-bonding interactions [27–30].

Aromatic amines are very important in biology and chemical industry. Among many molecules, *o*-nitroaniline (oNA) is an ideal model system for the study of the nature of the electronic properties since it is disubstituted benzenes and contains the proton donor amine group ($-\text{NH}_2$) and the acceptor the nitro group ($-\text{NO}_2$) [30–32]. The excited state is associated with an intramolecular charge transfer from the amino group to the nitro group across the phenyl ring. *o*-Nitroaniline (ONA) is an important donor- π -acceptor chromophore and has been the subject of many theoretical and experimental studies. Donor- π -acceptor molecules are stabilized in polar solvents through solvent interactions such as the hydrogen bonding [24,28,32–34]. ONA in the excited states is dynamically quenched through nonradiative deactivation, and it progresses very fast by intersystem crossing (ISC) from the singlet excited state to triple excited state and by internal conversion (IC) from the fluorescent state to the ground state. The intersystem crossing (ISC) is found to depend strongly on the protic solvents. The nitroaromatic compounds have significantly different ISC behaviors in different protic solvents. Instead, a characteristic feature of ONA is the absence of any measurable fluorescence [25,27,35]. Recently theoretical investigations of ONA in different solvents have been reported [32,34,35]. The intramolecular hydrogen transfer of ONA was already studied by Zhang et al. using infrared spectroscopic and quantum chemistry methods [25,36].

And, the behavior of the excited states has been addressed for ONA interacting with several water molecules. In this work, we study the intramolecular and the intermolecular hydrogen bonds in the complex $\text{ONA}\cdots\text{CH}_2\text{O}$ between ONA and CH_2O . It is an ideal model that we choose the N=O (ONA) group and C=O (CH_2O) group as the electron acceptors. Meanwhile, the N—H (ONA) group and C—H (CH_2O) group are the electron donors.

Nitroaniline is an important donor- π -acceptor chromophore and has been the subject of many theoretical and experimental studies. The availability of the carefully assigned experimental and theoretical frequencies for isolated ONA-water complexes in the spectral range of NH and NO stretching vibrational frequencies allows one to assess the influence of excited states and the formed hydrogen bond [32–37]. The NH and NO stretches in ONA are sensitive vibrational modes to monitor ESHBD with frequencies red shift in H-bonds. It is beneficial to the formation of hydrogen bonds. Moreover, it is worth noting that the CH bond in formaldehyde can also participate in a hydrogen bond $\text{X}\cdots\text{H}-\text{C}$ and its stretch frequency is usually blue shifted as the proton acceptor is not very strong, since in CH_2O there is a strong intramolecular hyperconjugation $n(\text{O}) \rightarrow \sigma^*(\text{CH})$ which couples with the intermolecular hyperconjugation $n(\text{X}) \rightarrow \sigma^*(\text{CH})$ [17,38]. Therefore, we observed for the first time the $\text{ONA}\cdots\text{CH}_2\text{O}$ system. It attracts us a lot of interest for forming a large conjugated system including intramolecular and intermolecular hydrogen bonds. ONA can serve as the proton acceptor using the N=O group in one hydrogen bond and as the proton donor using its NH group in the other intermolecular hydrogen bond. From the computational point of view, these systems are small enough to allow the use of accurate quantum mechanical (QM) methods for studying the effect of hydrogen-bonding interactions and excited states on physicochemical properties. It is quite remarkable effect of the intramolecular and intermolecular hydrogen bonds and excited states on the nature of $\text{ONA}\cdots\text{CH}_2\text{O}$ system.

This work is organized as follows. We aim to perform a systematic study on the hydrogen bond $\text{ONA}\cdots\text{CH}_2\text{O}$ in the excited states using TD DFT method theoretically. We calculated the geometric configurations and the molecular properties including the vibrational frequencies and IR intensities, the vertical transition energies in some excited states, the adiabatic transition energies and adiabatic geometry in the electronically excited states S_1 , S_2 and T_1 for the isolated ONA, formaldehyde and their complexes. Similar to the monomers ONA and CH_2O , the hydrogen bonding complexes both in the ground state and the T_1 excited state have planar geometry, but ONA has a nonplanar structure in the S_1 and S_2 states, as shown in Fig. 1. The hydrogen bond energies in different electronic states were calculated, we obtain that the hydrogen bonds are strengthened in the excited states S_1 , S_2 and T_1 . The details of computations and results are presented below.

2. Computational Details

Electronic excitation is studied with the time-dependent DFT (TD DFT) method, which is an efficient tool to offer the vibrational spectra for an understanding of the electronic excitation process. Time-dependent density functional method has been widely used in theoretical chemistry for studying electronically excited states and evaluating vibrational spectra in electronically excited states [39–41]. In this work, geometry optimization and the calculations of the properties including the vertical and adiabatic transition energies, vibrational spectra, and electronic absorption in different excited states were carried out at the B3LYP/aug-cc-pVDZ level of theory [42,43]. Natural bond orbital (NBO) analyses were performed using NBO5.0 program [44,45]. The electron density topological analysis in the theory of Atom in Molecule (AIM) was performed using the AIMALL program [46], which presents useful information about intermolecular interactions and characterization of bonds. These calculations were carried out employing the Gaussian 09 package in the gas phase [47].

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