

The weakening or enhancing of N-H...O intermolecular hydrogen bond in different solvents revealed by density functional calculations

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Abstract. Time-dependent density functional theory (TDDFT) method has been performed to investigate the properties of $N_1-H_1 \cdots O_1$ hydrogen bond of N-methylaniline-DMSO complex (complex I) and N-methylaniline-acetone complex (complex II) in the excited state. The infrared spectra are in good agreement with the experiment data. The analysis of the bond length and AIM (atoms in molecules) demonstrated that the $N_1-H_1 \cdots O_1$ hydrogen bond is weakening from DMSO to acetone in the ground state. That is to say, the intermolecular hydrogen bond $N_1-H_1 \cdots O_1$ between N-methylaniline and solvent molecular is stronger with the polarity of solvent stronger. Upon photoexcitation, the analysis of AIM implies that the intermolecular complex II is enhanced. Interestingly, the hydrogen bond $N_1-H_1 \cdots O_1$ of complex I is weakened. The analysis of molecular orbital also support the results that the intermolecular hydrogen bond $N_1-H_1 \cdots O_1$ of complex I is weakened whereas it of complex II is enhanced.

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Key words: hydrogen bond; electrostatic potential; AIM; N-methylaniline; DFT.

1 Introduction

Hydrogen bonding has been studied by diverse experimental and theoretical methods because it is central to understanding the microscopic structure and the function of many molecular systems, such as proteins and DNA building blocks of the life [1-7]. As a site-specific solute-solvent interaction, the intermolecular hydrogen bonds between hydrogen donor and acceptor have a remarkable influence on the photophysics and photochemistry of chromophores in the hydrogen-bonding surroundings [8-12]. The hydrogen

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bonding is also associated with many process including the internal conversion (IC), photoinduced electron transfer (PET), fluorescence quenching (FQ), intramolecular charge transfer (ICT) and so on [13].

Nibbering *et al.* investigated the nature of N-H \cdots O hydrogen bond in DMSO and acetone solvents, and experimentally observed the notion of weakening the N-H \cdots O hydrogen bond from DMSO to acetone in the ground state [14]. However, the nature of hydrogen bond and its impact factors upon photoexcitation have not been explained. As we all know, the excited state hydrogen bond strengthening theory has been used to explain many photochemistry and photophysics reactions, such as fluorescence quenching, intermolecular charge transfer, and so forth. It is well known that theoretical calculation for excited states is a reliable tool to study the excited state hydrogen bonding dynamics. Therefore, the detailed investigations of N-H \cdots O hydrogen bond of complexes I and II in the S₁ state have been performed in this work.

In this work, the geometry structures of complexes I and II have been optimized both in the ground and excited states. The analysis of electrostatic potential is performed to confirm the reasonableness of the composed conformations and to determine the reactive sites of the reactants. The electronic excitation energies, oscillation strengths and infrared spectra of the electronically excited states are investigated to deeply analyze the nature of hydrogen bond. More importantly, the detailed theoretical investigations of the molecular structure, spectral properties and frontier molecular orbital of complexes I and II are performed. In addition, the AIM analysis has been performed to investigate the strength and types of hydrogen bonds.

2 Theoretical methods

The geometry optimizations for the ground state and the first singlet electronic excited state were performed using density functional theory (DFT) and TDDFT methods, respectively [15-17]. B3LYP functional (Becke's three-parameter hybrid exchange functions with Lee-Yang-Parr gradient-corrected correlation functional) was used in both the DFT and TDDFT methods. The TDDFT/B3LYP was used to calculate the excited states with the 6-311++G(d,p) basis set [18, 19]. All the electronic structure and spectra calculations were carried out using the G09 program suit. To account for the solvent effects, the equilibrium continue polarizable continuum model (CPCM) is used.

Bader's quantum theory of atoms in molecules (QTAIM) is an effective method for the analysis of electron density distribution in molecular systems [20]. The descriptors of charge density ($\rho(r)$), Laplacian of the charge density ($\nabla^2\rho(r)$) and potential energy density ($V(r)$) not only can be used to assess the interaction strength but also can be used to distinguish between different kinds of non-covalent interactions. Hunt and co-workers have proposed the different sets of hydrogen bonding criteria and types [21]. AIM analysis is also carried out at the B3LYP/6-311++G(d,p) level.