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Polarity Effect of Solvents on Ground- and Excited-state Hydrogen Bonds

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Abstract: The hydrogen-bonded complex formed between 6-hydroxyquinoline (6HQ) and trimethylamine (TMA) has been calculated by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP/TZVP level, to study the polarity effect of solvents on the ground- and excited-state hydrogen bonds. In grounded 6HQ-TMA complex, the hydrogen bond in O–H···N can be strengthened by the increased polarity of solvents. However, the opposite behavior presents in the excited-state hydrogen bond in O···H–N in 6HQ-TMA-PT, which is the ion-pair form generated by the excited-state proton transfer (ESPT) reaction. The increased polarity of solvent leads a much weaker hydrogen bond in S_1 state.

AMS subject classifications: 74E40, 78M50

Keyword: excited-state proton transfer; hydrogen bond; excited state; ion-pair

As a "site-specific" interaction, the phenomenon of hydrogen bonding has been recognized for its importance in understanding microscopic structures and functions in many molecular and supramolecular systems, such as hydrogen-bonded water or alcohol networks, organic compounds in solution, hydrogen-bond crystal engineering, polymers, self-assembled supramolecular architectures, proteins, and DNA [1-5]. The ground-state structures and dynamics of intermolecular and intramolecular hydrogen bond in solution are of particular interest and have been investigated extensively by diverse experimental and theoretical methods [6-15]. Upon photoexcitation of hydrogen-bonded systems, the reorganization of

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the hydrogen donor and acceptor moieties proceeds caused by the change of charge distribution in excited states, which is called excited-state hydrogen bonding dynamics (ESHBD). Until now, however, there has been very little information on the structural and relaxation dynamics of hydrogen bonds upon photoexcitation.

Recently, Zhao and Han [16–23] have determined theoretically that intermolecular hydrogen bonds between solute and alcoholic molecules can be significantly strengthened in the electronic excited state upon photoexcitation. In previous works [24–27], we have demonstrated that, the excited-state hydrogen bonding behavior would play an important role in many photochemical reactions such as fluorescence quenching [24], excited-state proton transfer [25], and tuning effects on photochemistry [26]. Novel mechanisms have been proposed and the important roles played by hydrogen bonds in these dynamic processes were demonstrated. Based on these recent advances in the excited-state hydrogen bonding dynamics, many phenomena in physics, chemistry, and biology involving exited-state hydrogen bonding need to be revisited.

As known, the solute-solvent interactions, which play a fundamental role for molecular nonequilibrium processes in liquids, have been one of the focal points of solution chemistry [28-30]. Two components are mainly contained in the solute-solvent interactions: the bulk effect of the solvent—polarity, and the site-specific interaction of solute and solvent—hydrogen bond, which have been always treated as two separated effect. However, in our previous work, the hydrogen bond can be significantly changed by the polarity of solvents, since the charge can be separated further in the polar environment. On the other hand, the changing of the hydrogen-bonding structure would effectively influence the dipole moment of the hydrogen-bonded complex. These suggest the polarity effect and hydrogen bond might be coupled, and the treating in separated way would be not reasonable.

In this work, the hydrogen-bonded complexes of 6-hydroxyquinoline (6HQ) and trimethylamine (TMA) have been chosen to study theoretically on the excited-state hydrogen-bonding dynamics in polar solvent at the time-dependent density functional theory (TDDFT) level. The geometrical configurations for complexes in vacuo and polar solvent have been globally optimized in both the ground and lowest excited singlet states. All the electronic structure calculations were carried out using the Gaussian 09 program suite [31]. The conventional DFT and TDDFT calculations using the hybrid exchange-correlation functional B3-LYP [32] was preformed, to investigate the excited-state dynamics of 6HQ-TMA cluster. The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as basis sets throughout [33]. In addition, considering the solvent effects on excited state dynamics, the polarizable conductor calculation model (CPCM) solvation model [34,35] was also used in all calculations.