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

Yu-Hui Liu[1]*, Sheng-Cheng Lan

Department of Physics, College of Mathematics and Physics, Bohai University, Jinzhou 121013, China

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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

* Corresponding author. *E-mail:* yhliu@dicp.ac.cn Tel: +86-416-3400145; Fax: +86-416-3400149;

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.

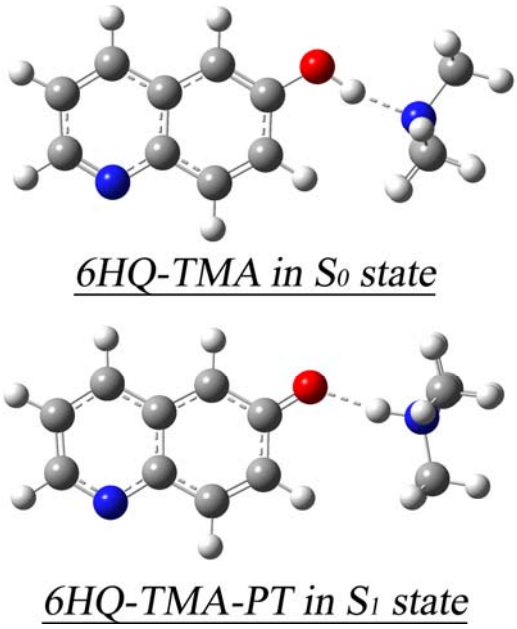

Figure 1: Optimized geometric structures of 6HQ-TMA hydrogen-bonded complex in S_0 state calculated and 6HQ-TMA-PT complex in S_1 state with the CPCM package (acetonitrile, ε=35.688)

In order to investigate the excited-state hydrogen-bonding dynamics of 6HQ-TMA complex in polar solvents (acetonitrile and toluene), we have employed DFT method to optimize the ground-state and excited-state structures of 1:1 6HQ-TMA hydrogen-bonded complex. Moreover, the bulk effects of acetonitrile and toluene solvents are introduced in the calculation with the help of COSMO package (ε=35.688 and 2.3741). The **Figure 1** shows the ground-state and excited-state structures of 6HQ-TMA complex in acetonitrile solvent. The optimization for S_1 state would lead to the 6HQ-TMA-PT structure, which means the intermolecular proton-transfer reaction from 6HQ to TMA would proceed without a barrier in potential energy surface. This result is in accordance to the experimental finding by Mehata and co-workers [36], in which they could not observe a slow rise component in their experimental results because of the barrierless proton transfer process (faster proton-transfer process than that of the instrumental time resolution of 200 ps).

The vertical excitation energies, as well as the oscillator strengths for 6HQ:TMA complex in the ground state were calculated within CPCM model and the results are given in **Table 1**. As shown, a very strong absorption for 6HQ-TMA hydrogen-bonded complex is observed corresponding to the higher electronic energy levels. However, in the long wavelength range, the calculated absorption maximum of 6HQ-TMA complex

corresponding to the S_1 state are estimated at 324 nm for both cases. Moreover, the absorption bands corresponding to the S_2, S_3 and S_5 states are shifted to red by the increased dielectric constant of solvent. On the contrary, the absorption band for S_4 state goes to blue range. It is interesting that, the $S_0 \rightarrow S_1$ absorption band is insensitive to the polarity of environment.

Table 1: Calculated Electronic Excitation Energy (EEE) with COSMO and Corresponding Oscillator Strength (OS) for Electronically Excited States for free 6HQ and 6HQ-TMA Complex in acetonitrile together with the contribution of Orbital Transition (OT) to the Electronic States.

States	Toluene		Acetonitrile	
	EEE (nm)	OS	EEE (nm)	OS
S_1	324	0.1183	324	0.1070
S_2	282	0.0024	278	0.0124
S_3	277	0.0131	276	0.0023
S_4	259	0.0000	275	0.0000
S_5	234	1.0546	233	0.9023

As reported by Mehata and co-workers [36], in presence of TMA in a solution of 6HQ in acetonitrile, an "unusual" fluorescence emission band is obtained. The dual fluorescence suggests that there are two emitting species existing in the solution, as also observed experimentally corresponding to the free 6HQ and 6HQ-TMA complex. Herein, the simulated $S_1 \rightarrow S_0$ emission spectrum for both the free 6HQ and 6HQ-TMA complex in acetonitrile solvent are shown in **Figure 2**. The emission peaks correspond to the free 6HQ and 6HQ-TMA-PT are located at 366 and 444 nm, respectively. All these results are in good agreement with the experimental results [36]. Hence, the normal fluorescence of 359 nm in experimental spectra is assigned to the free 6HQ, while the "unusual" emission of 440 nm is corresponding to the 6HQ-TMA-PT complex, which is the product of ESPT process.

Table 2: The Bond Lengths (Å) of Hydrogen-bonds and C-O bonds in optimized structures of 6HQ-TMA in S_0 state and 6HQ-TMA-PT in S_1 state for different solvents.

Solvents	ε	Ground-state 6HQ-TMA		Excited-state 6HQ-TMA-PT	
		$L_{H\cdots N}$	$L_{C\text{-}O}$	$L_{O\cdots H}$	$L_{C\text{-}O}$
Toluene	2.3741	1.74499	1.35129	1.52791	1.29127
Acetonitrile	35.688	1.68174	1.35014	1.69362	1.28113

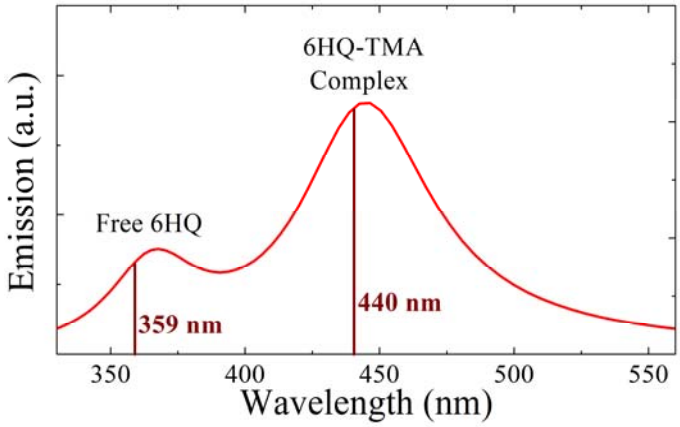

Figure 2*:* The simulated emission spectra of free 6HQ and 6HQ-TMA-PT hydrogen-bonded complexes in acetonitrile. This is produced by expanding the calculated emission energies in Lorentzian shape and added with them with artificial coefficients. The vertical lines denote the corresponding peaks in experiments [36].

Table 2 shows the primary bond lengths in ground-state 6HQ-TMA and excited-state 6HQ-TMA-PT complexes when 6HQ-TMA was dissolved in both acetonitrile and toluene solvents. On increasing solvent polarity, for the ground-state 6HQ-TMA, the hydrogen-bond length in O–H···N becomes shorter from 1.74 Å in toluene to 1.68 Å in acetonitrile. On the other hand, the hydrogen-bond length in O···H–N formed in excited S_1 state of 6HQ-TMA-PT complex becomes longer form 1.53 Å in toluene to 1.69 Å in acetonitrile. One can expect that, the polarity of solvent would promote effectively the excited-state proton transfer reaction.

As known, intermolecular hydrogen bonding interactions can be monitored via changes in the stretching vibrational frequency of the donor monomer. Herein, to confirm the weakening of the excited-state hydrogen bond in 6HQ-TMA-PT complex by polarity of solvents, the excited-state vibrational frequencies of the stretching vibrations of N-H group in H-TMA moiety have been calculated in both acetonitrile and toluene solvents, and shown in **Figure 3**. According to our results, the vibrational frequency of N-H group in toluene solvent is 2310.5 cm^{-1}, which is much lower than that in acetonitrile solvent for 543.7 cm^{-1}. This means the H atom in N-H bond of 6HQ-TMA-PT complex in acetonitrile solvent would be bound tighter to the N atom, than that in toluene solvent. Hence, it is confirmed that, the excited-state hydrogen bond in O···H–N could be weakened by the increasing dielectric constant of environment.

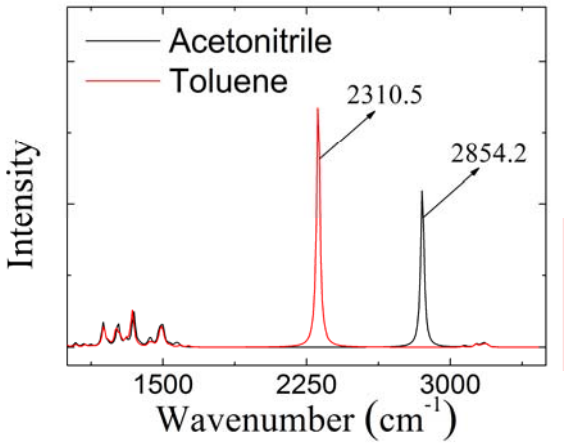

Figure 3: Vibrational absorption spectra calculated for 6HQ-TMA-PT complexes in acetonitrile and toluene solvents in the spectral region for N-H stretching.

In this work, polarity effect on both ground- and excited-state hydrogen bonds in the 6HQ-TMA complexes has been theoretically study at TDDFT level. It is interesting to note that the behavior of hydrogen-bond in the S_0 and S_1 states demonstrates opposite trend with increasing polarity of the solvents. On increasing solvent polarity, for the ground-state 6HQ-TMA, the hydrogen-bond length in O–H···N becomes shorter and hence the hydrogen-bonding becomes stronger. On the other hand, the strength of hydrogen-bond in O···H–N formed in excited S_1 state of 6HQ-TMA-PT complex becomes weaker. This suggests the couple of bulk effect and site-specific interaction is very complicated.

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