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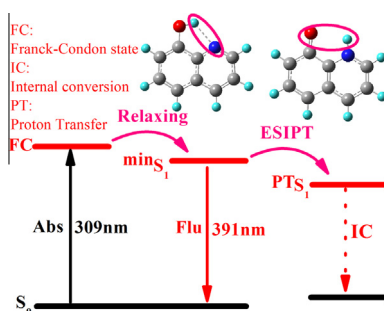
TDDFT study on the excited-state proton transfer of 8-hydroxyquinoline: Key role of the excited-state hydrogen-bond strengthening

Sheng-Cheng Lan^{a,b}, Yu-Hui Liu^{a,*}^a Department of Physics, College of Mathematics and Physics, Bohai University, Jinzhou 121013, China^b State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

HIGHLIGHTS

- DFT/TDDFT method has been performed to study the ESIPT.
- The nature of excited-state hydrogen bond dynamic has been investigated.
- ESIPT of 8-hydroxyquinoline is facilitated by strengthening of the electronic excited-state hydrogen bond.
- The radiationless deactivation via internal conversion is demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations have been employed to study the excited-state intramolecular proton transfer (ESIPT) reaction of 8-hydroxyquinoline (8HQ). Infrared spectra of 8HQ in both the ground and the lowest singlet excited states have been calculated, revealing a red-shift of the hydroxyl group (–OH) stretching band in the excited state. Hence, the intramolecular hydrogen bond (O–H···N) in 8HQ would be significantly strengthened upon photo-excitation to the S_1 state. As the intramolecular proton-transfer reaction occurs through hydrogen bonding, the ESIPT reaction of 8HQ is effectively facilitated by strengthening of the electronic excited-state hydrogen bond (O–H···N). As a result, the intramolecular proton-transfer reaction would occur on an ultrafast timescale with a negligible barrier in the calculated potential energy curve for the ESIPT reaction. Therefore, although the intramolecular proton-transfer reaction is not favorable in the ground state, the ESIPT process is feasible in the excited state. Finally, we have identified that radiationless deactivation via internal conversion (IC) becomes the main dissipative channel for 8HQ by analyzing the energy gaps between the S_1 and S_0 states for the enol and keto forms.

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Introduction

Photo-induced proton-transfer reactions are of importance in photochemical and photobiological processes. Numerous studies have been conducted by various experimental [1–4] and theoretical [5–8] methods since the first experimental observation of the

phenomenon by Weller in the middle of the last century [9]. ESIPT occurs in molecules containing both acidic and basic groups in close proximity that may rearrange in the electronic excited state through a proton or hydrogen atom transfer. The fast reorganization of the charge distribution resulting from the tautomerization renders these molecules of interest for the design and operation of fluorescent sensors [10,11], organic light-emitting diodes (OLEDs) [12,13], and molecular switches [14].

Compounds in which excited-state proton transfer could occur three categories [15]. The first group consists of compounds in

* Corresponding author. Tel.: +86 416 3400145; fax: +86 416 3400149.

E-mail address: yhliu@bhu.edu.cn (Y.-H. Liu).

which donor acidic and acceptor basic groups are in close proximity, linked by hydrogen bonds. ES IPT occurs after the excited enol form converts into the keto form. Later, the molecule returns to the electronic ground state by fluorescence or internal conversion, and the proton is finally transferred back to the initial position [16–20]. The emission spectrum of the keto form may be strongly red-shifted compared to the absorption spectrum of the enol form. Such compounds were reported by Weller in 1956 [9]. The second series of compounds are those in which the functional groups are in suitable positions to allow photo-induced tautomerization as a result of concerted double-proton transfer from a donor group to an acceptor group in a hydrogen-bonded system. This is exemplified by 7-azaindole [21]. Proton transfer can also occur through bridging solvent molecules. This occurs, for instance, in 7-hydroxyquinoline (7HQ) in ammonia clusters [22,23] and in 8HQ in aqueous solutions [24–26]. The third group of compounds are those in which the donor acidic and acceptor basic groups are far from each other; unconcerted intermolecular proton transfer is facilitated by the surrounding solvent molecules, as can occur for 6-hydroxyquinoline (6HQ) in aqueous solution [27]. In summary, hydrogen bonding plays an important role in the excited-state intramolecular proton-transfer reaction. Recently, Zhao and Han [6,7,16,28–32], using DFT and TDDFT, demonstrated the feasibility of an excited-state hydrogen-bond strengthening mechanism, as opposed to the hydrogen-bond cleavage mechanism for coumarin 102 proposed by Chudoba and co-workers in 1998 [33]. This seminal work can successfully explain many photochemical phenomena, such as internal conversion [34], intermolecular charge transfer [35], and excited-state proton transfer [36]. Due to development in experimental techniques and subsequent studies of excited-state hydrogen-bond dynamics, many photophysical and photochemical phenomena involving photo-induced excited-state reactions need to be reconsidered.

Hydroxyquinoline is a good model molecular system for exploring proton-transfer reactions. We have previously investigated the proton-transfer reaction dynamics of 6HQ and 7HQ clusters by means of quantum chemical calculations [37–39]. However, 8HQ is different from other hydroxyquinolines because its donor acidic and acceptor basic groups are in close proximity and linked by a hydrogen bond. Thus, intramolecular and intermolecular proton-transfer reactions could occur in both the ground and excited states. In 1970, Goldman and Wehry pointed out that different solvents and temperature can directly influence the quantum yield of 8HQ [40]. Later, Bardez confirmed that the intermolecular proton-transfer process can occur in 8HQ in aqueous solution, but intrinsic intramolecular proton transfer between the hydroxyl group (–OH) and the heterocyclic ring nitrogen atom (–N–) could not be ruled out [27]. In 2007, Amati and co-workers demonstrated low fluorescence yields in aqueous and some organic solutions. They also reported on the 1:1 water–8HQ adduct and the 2:1 water–8HQ adduct on the basis of experimental measurements and theoretical methods [24]. To date, few experimental studies and quantum chemical calculations have been performed on 8HQ [24–27,40–43]. In addition, little is known about the role of the excited-state hydrogen-bond dynamics.

As mentioned above, the proton-transfer reaction occurs through hydrogen bonding, hence the role of the excited-state hydrogen-bond dynamics is very important for understanding the process. In this work, the ES IPT reaction of 8HQ has been investigated by a time-dependent density functional theory (TDDFT) method. The geometrical structures have been globally optimized in both the ground and the excited electronic states. Moreover, the steady-state absorption and fluorescence spectra of 8HQ have been simulated. The potential energy curves for the ground and excited states have also been calculated.

Theoretical methods

By means of density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods, geometry optimizations of the ground state and the excited state of the 8HQ molecule were accomplished without symmetry constraints. Frequency calculations at the same levels of theory were then performed to confirm that each optimized structure was a real minimum. In addition, potential energy curves in both the ground state and electronic excited state were calculated through optimizing the excited state by increasing the hydroxyl group (–OH) bond length in increments of 0.1 Å. Becke's three-parameter hybrid exchange functional with Lee–Yang–Parr gradient-corrected correlation (B3LYP) was used in both the DFT and TDDFT methods [44]. The triple- ζ valence quality with one set of polarization functions (TZVP) was chosen as the basis set [45]. In view of the solvent effect, dichloromethane was used as solvent in the SCRF calculations using IEFPCM throughout. All electronic structure calculations were carried out using the TURBOMOLE program suite [46,47].

Results and discussion

Optimized geometric structure in the S_0 state

8HQ has two isomeric forms in the ground state, *cis*-8HQ and *trans*-8HQ, with different geometrical configurations. The donor acidic and acceptor basic groups of *trans*-8HQ are far from each other, essentially precluding ES IPT [24]. Herein, we focus exclusively on *cis*-8HQ, since it can form an intramolecular hydrogen bond between the donor acidic and acceptor basic groups. The geometric structure was fully optimized by the DFT method. Fig. 1a shows the optimized structure of 8HQ in the ground state, which can be seen to be planar. One can note that an intramolecular hydrogen bond (O–H...N) can be formed between the proton-donating hydroxyl group (–OH) and the accepting heterocyclic ring nitrogen (–N–) atom. Table 1 lists some salient geometrical parameters, that is, bonds and angles.

The calculated absorption spectra

The electronic excitation energies and corresponding oscillator strengths of 8HQ are presented in Table 2. The result of this simulation is shown in Fig. 2, where the vertical lines denote the corresponding peaks in the experimental spectrum. A very strong absorption is observed at higher electronic energy levels. In the long-wavelength region, the calculated absorption maximum for 8HQ in dichloromethane solution is located at 329 nm, which is in good agreement with the experimental value (309 nm) [15]. From the calculated electronic excitation energies, we can expect that 8HQ may be electronically excited to the S_1 state upon photo-excitation by a laser pulse of 305 nm [15]. Thus, we consider only the S_1 state in this work.

Molecular orbital analysis

Before discussing the ES IPT dynamics, it is important to understand the nature of the excited states of the reactants and products. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 8HQ–enol and 8HQ–keto have been calculated. As shown in Fig. 3, for both complexes the π character of the HOMO and the π^* character of the LUMO reveal that the first excited state, S_1 , has $\pi\pi^*$ character. The HOMO and LUMO of 8HQ–keto are almost identical to those of 8HQ–enol. In addition, the electron density at the hydroxyl oxygen atom in the

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