

REGULAR ARTICLE

A New Excited-State Intramolecular Proton Transfer Mechanism for C₂ Symmetry of 10-hydroxybenzoquinoline

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Abstract: The excited state intramolecular proton transfer (ESIPT) mechanisms of bis-phenol possessing C₂ symmetry of 10-hydroxybenzoquinoline (2HBQ-a) have been investigated based on the time-dependent density functional theory (TDDFT). A new ESIPT mechanism of concomitant single and double ESIPT process has been proposed, which is different from the one proposed previously (Piechowska *et al.* *J. Phys. Chem. A*, 2014, **118**, 144). The phenomenon of hydrogen bond strengthening was verified based on primary bond lengths, angles and the IR vibrational spectra. The calculated vertical excitation energies based on the TDDFT method reproduced the experimental absorbance and fluorescence emission spectra well. Three stable structures of 2HBQ-a tautomerization have been founded in the S₁ state. Intramolecular charge transfer based on the frontier molecular orbitals demonstrated the indication of the ESIPT reaction. The constructed PESs of S₀ and S₁ states based on keeping the O-H distance fixed at a series of values have been used to illustrate the ESIPT process. The values of potential barriers among these stable points in the S₁ state are less than 10 kcal/mol, which infer a concomitant single and double proton transfer mechanism. Based on the new ESIPT mechanism, we further explained the phenomenon of fluorescence quenching reasonably.

AMS subject classifications: 74E40, 78M50

Keywords: Excited-State Intramolecular Proton Transfer; Electronic Spectra; Frontier Molecular Orbitals; Potential Energy Surface;

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1. Introduction

Excited-state intramolecular proton transfer (ESIPT), as one of the most important elementary reactions in chemistry and biology [1-7], is the pioneering work of Weller *et al.* [8, 9]. A new kind of investigation, the unique observation of methyl salicylate in the field of photochemistry, was envisaged in the middle of the last century [8, 9]. Since then, extensive studies on proton transfer (PT) reactions were performed both experimentally and theoretically [10-16]. PT occurs in molecules containing both acidic and basic groups that may rearrange in the electronic excited state via transferring a proton or hydrogen atom. The strong and fast reorganization of the charge distribution derived from tautomerization makes these molecules very attractive towards the design and use of fluorescence sensors [17-22], laser dyes and LEDs [23, 24], UV filters [25-27], and molecular switches [28, 29]. In effect, the excited state intra- or inter- molecular proton transfer is one of the simplest examples of a hydrogen bond reaction that occurs in electronically excited state. Recently, the hydrogen bonds between donor and acceptor in excited state upon photo-excitation have been researched based on the time-dependent density functional theory (TDDFT) by Han and co-workers theoretically [30-35]. That is to say, to further study the PT mechanism, DFT and TDDFT methods have been the primary tool to clarify fundamental aspects concerning the different electronic states and structures.

10-Hydroxybenzo[*h*]quinoline (HBQ), as an important reagent in the preparation of optical filter agents, has been paid attention to for a long time [36, 37]. The excited-state intramolecular proton transfer (ESIPT) of HBQ is a prototypical reaction in solution [38-45]. The enol form of HBQ is stable in the S_0 state, which converts from the enol to the keto form rapidly following photoexcitation. Takeuchi *et al.* reported the rate of ESIPT and the decay times of subsequent coherent vibrational motions in cyclohexane based on the pump-probe transient absorption spectroscopy firstly [38]. The ESIPT rate was about 25 fs and the decay time of a vibrational mode was at about 250 cm^{-1} , which was faster than the decay times of higher-frequency modes [38]. Subsequently, Takeuchi *et al.* proposed that the mode at 250 cm^{-1} was correlated with the ESIPT reaction. Similar experimental results were also reported by Schriever *et al.* [39]. Chou *et al.* reported the dynamics of excited-state intramolecular enol-keto proton-transfer HBQ based on steady-state absorption and fluorescence spectroscopy, femtosecond fluorescence up-conversion combining with pump-probe transient absorption experiments in detail [40]. Various PH dependent ESIPT dynamics of HBQ have been investigated in aqueous solution [41], which demonstrated the charge transfer between hydroxyl oxygen and benzoquinolinic nitrogen acting as a driving force for the proton transfer reaction. Robert *et al.* reported the influence of organized media of HBQ