Commun. Comput. Chem.
doi: 10.4208/cicc.2013.v1.n1.1

Vol.**1**, No.1, pp.1-7
January 2013

COMMUNICATION

Questionable Excited-State H-Atoms Transfer Mechanism for 7-Hydroxyquinoline·$(NH_3)_3$ Cluster

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Received 15 December 2012; Accepted (in revised version) 18 January 2013

Special Issue: Guo-Zhong He Festschrift

Abstract: Previously, an excited-state H-atoms transfer (ESHAT) in stepwise fashion have been proposed basing on the calculations within Cs symmetry constraint by Leutwyler and co-workers (Science, 302 (2003), 1736). To justify the rationality of this symmetric approximation, time-dependent density functional theory (TDDFT) calculations without any symmetry constraint was performed to investigate the excited-state proton transfer (ESPT) dynamics of 7-hydroxyquinoline·$(NH_3)_3$ (7HQ·$(NH_3)_3$) cluster. As results, a wagging motion of hydrogen-bonded wire has been proposed by comparing the position of the wire in HT2 with those in 7HQ·$(NH_3)_3$ and the keto isomer (7KQ·$(NH_3)_3$), which obviously destroyed the symmetry. Hence, the calculated results under Cs symmetry constraint have been demonstrated to be invalidation.

AMS subject classifications: 74E40, 78M50

Key words: Time-dependent density functional theory, excited-state proton transfer, hydrogen bond, wagging motion

The proton-transfer/hydrogen-atom transfer reaction has an important role in a variety of chemical and biological processes. Recent years, many developments of the mechanism of excited-state proton transfer (ESPT) reaction have been performed by studying on the excited-state dynamics of photoacids in protic solvents [1-7]. However, the proton transfer

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via hydrogen-bonded wire in many important biological proteins remained poorly understands so far due to their complex environment, such as the green fluorescent protein (GFP) [8]. The guide for our understanding of the proton hopping in hydrogen-bonded systems is still the skeletal mechanistic picture proposed by Grotthuss [9,10]. Recent years, Zhao and Han, who theoretically demonstrated the strengthening of hydrogen bond in excited state [1,11-20], have made a large progress in the aspect of excited-state hydrogen-bonding dynamics, which has been demonstrated the importance in the photophysics and photochemistry [11]. By utilizing this viewpoint, they have explained many important phenomena in photochemical reactions such as intermolecular charge transfer [21], fluorescence quenching [22], excited-state proton transfer [23,24], tuning effects on photochemistry [25], and internal conversion (IC), intersystem crossing (ISC), twisted intramolecular charge transfer (TICT) and so forth [26]. According to these recent advances in the excited-state hydrogen bonding dynamics, the mechanism of ESPT should be renewed also.

7-Hydroxyquinoline (7HQ), containing both proton-donating (-OH) and -accepting groups (-N-), have been extensively studied on the excited-state multiple proton transfer (ESMPT) dynamics [27-31]. The excited-state H-atom transfer (ESHAT) mechanism has been proposed basing on CIS and CASSCF calculations (under Cs symmetry constraint) by Leutwyler and co-workers [27-29]. According to calculated results, three transient species (denoted by HT1, HT2 and HT3) in excited-state reaction have been found, which are the local minima in the potential energy curve of S_1 state. However, there is no signal in corresponding emission spectrum. To explain this phenomenon, they believe the fluorescence emission of the three transient species is forbidden due to the Cs symmetry. However, with the same symmetry, the fluorescence from both the cationic and anionic forms of 6HQ have been observed in emission spectra [32,33]. Hence, the it is failed to explain the absence of the signals for transient species in experimental spectra, which break the creditability of the calculations and the ESHAT mechanism of 7HQ·$(NH_3)_3$ cluster.

In present work, all the electronic structure calculations were carried out using the TURBOMOLE program suite [34-38]. The conventional DFT and TDDFT calculations using the hybrid exchange-correlation functional B3-LYP [35] were preformed, to investigate the excited-state dynamics of 7HQ·$(NH_3)_3$ cluster. The triple-ζ valence quality with one set of polarization functions (TZVP) was chosen as basis sets throughout [36]. Fine quadrature grids 4 were also employed [37]. And no symmetry constraint is contained in our calculations. As results, the HT1 and HT3 are revealed to be instability in S_1 state. Moreover, a distinct wagging motion of the hydrogen-bonded wire has been found.

The isolated 7HQ and hydrogen-bonded 7HQ·$(NH_3)_3$ cluster have been fully optimized