COMMUNICATION

Questionable Excited-State H-Atoms Transfer Mechanism for 7-Hydroxyquinoline·(NH₃)₃ Cluster

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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·(NH₃)₃ (7HQ·(NH₃)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·(NH₃)₃ and the keto isomer (7KQ·(NH₃)₃), which obviously destroyed the symmetry. Hence, the calculated results under Cs symmetry constraint have been demonstrated to be invalidation.

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 $7HQ \cdot (NH_3)_3$ 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 $7HQ \cdot (NH_3)_3$ 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 $7HQ \cdot (NH_3)_3$ cluster have been fully optimized

in ground state at B3LYP/TZVP level. As shown in the **Figure 1**, all the heavy atoms of them are located in the plane, however, except for the middle N in the hydrogen bonded wire of $7HQ \cdot (NH_3)_3$ cluster. Hence, $7HQ \cdot (NH_3)_3$ is not a planar cluster, which suggest the calculations under Cs symmetry constraint by Leutwyler and co-workers [27] might supply an inaccurate expectations.
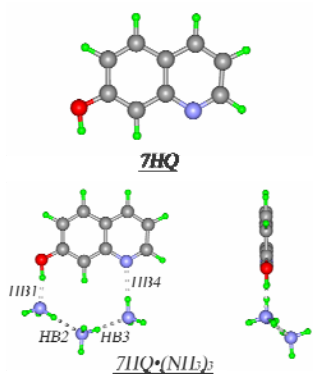

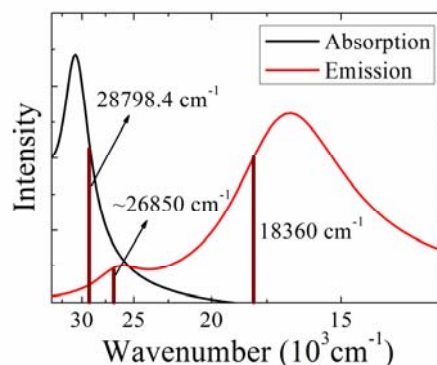**Figure 1:** Optimized geometric structure of $7HQ \cdot (NH_3)_3$ cluster in electronic ground state.

Figure 2: Simulated absorption and emission spectra of $7HQ \cdot (NH_3)_3$ cluster. Wine-red lines denote the experimental peaks [27,28].

The vertical excitation energies and oscillator strengths corresponding to the excitations and emissions are calculated. In the long wavelength range, the calculated excitation energies corresponding to maximum absorption of isolated 7HQ and $7HQ \cdot (NH_3)_3$ due to the S_1 state are located at 4.13 and 3.81 eV, respectively. Moreover, The absorption and emission spectra of $7HQ \cdot (NH_3)_3$ in gas phase have been shown in **Figure 2**. To simulate the spectra, we expanded the emission energies by Lorentzian shape and added them with weight coefficients. As shown the figure, both the calculated absorption and emission energies are in agreement with the experimental spectra [27,28], which reveals the reliability of our DFT/TDDFT calculations for $7HQ \cdot (NH_3)_3$ and $7KQ \cdot (NH_3)_3$ clusters in both the S_0 and S_1 states. Therefore, we can expect that the 7HQ chromophore can be electronically excited to the S_1 state upon excitation by the laser pulse used in the experiments [27,28].

We have performed the excited-state structure optimizations of $7HQ \cdot (NH_3)_3$ and $7KQ \cdot (NH_3)_3$ clusters in S_1 state, as well as HT1, HT2, HT3, which were proposed by Leutwyler and co-workers [27,28]. Unexpectedly, by using TDDFT methods, the structures of HT1 and HT3 is not steady in S_1 state. Hence, only three stationary structures can be optimized for $7HQ \cdot (NH_3)_3$, $7KQ \cdot (NH_3)_3$ and the transient HT2. This maybe suggest that the ESHAT is not the optimal pathway of the excited-state reaction of $7HQ \cdot (NH_3)_3$ cluster.

Table 1: The Bond Lengths of the Hydrogen Bonds and Hydrogen-Bonded Wire (the Distance Between the O to the Last N Atom along the Wire) in $7HQ \cdot (NH_3)_3$, HT2 and $7KQ \cdot (NH_3)_3$ Complexes.

Species	State	HB1	HB2	HB3	HB4	HB-wire
$7HQ \cdot (NH_3)_3$	S_0	1.735 Å	2.047 Å	2.109 Å	2.141 Å	12.124 Å
	S_1	1.555 Å	1.963 Å	2.051 Å	2.045 Å	11.773 Å
HT2	S_1	1.877 Å	1.729 Å	1.658 Å	1.875 Å	11.394 Å
$7KQ \cdot (NH_3)_3$	S_1	2.018 Å	2.087 Å	2.043 Å	1.854 Å	12.132 Å

Studying on excited-state hydrogen bonding dynamics is the key to understand the proton transfer via hydrogen-bonded wire. To exhibit the excited-state behavior of hydrogen bonds in proton transfer process, We have listed the lengths of hydrogen bonds in the $7HQ \cdot (NH_3)_3$, HT2 and $7KQ \cdot (NH_3)_3$ complexes in **Table 1**. By comparing the hydrogen bond of $7HQ \cdot (NH_3)_3$ in S_0 and S_1 states, all the hydrogen bonds are strengthened in S_1 state. And the length of the hydrogen-bonded wire has been strongly shortened from 12.124 Å in ground state to 11.773 Å in S_1 state, which would promote the proton transfer proceeding in excited state. For HT2, the wire length is the shortest (11.394 Å) in these four species. When $7KQ \cdot (NH_3)_3$ is formed in S_1 state after the PT reaction, the wire length is increased to 12.132 Å, closing to that of ground-state $7HQ \cdot (NH_3)_3$.
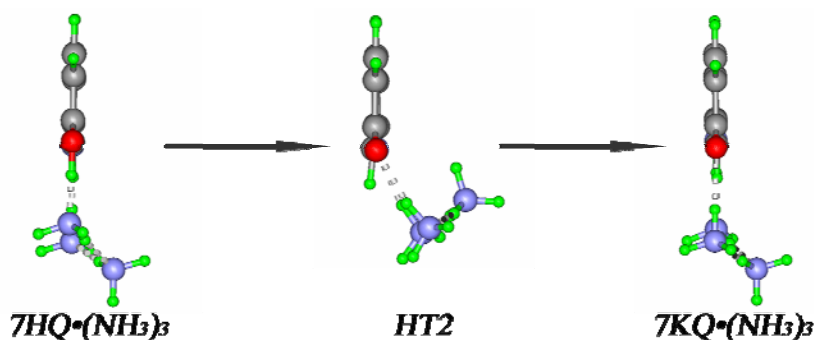
Figure 3: Optimized geometric structures of $7HQ \cdot (NH_3)_3$, HT2 and $7HQ \cdot (NH_3)_3$ clusters in S_1 state.

Interestingly, a wagging motion has been found in the ESMPT (or ESHAT) process, by observing the structure of transient HT2 in compare with those of $7HQ \cdot (NH_3)_3$ and $7KQ \cdot (NH_3)_3$, as shown in **Figure 3**. Obviously, there is a really large angle between the NH_3 wire and the molecular plane in HT2 cluster. While for $7HQ \cdot (NH_3)_3$ and $7KQ \cdot (NH_3)_3$, only a small angle has been presented, as the previous discussions on the ground-state optimizations. The large angle might be caused by the conforming of the NH_4^+ in the hydrogen-bonded wire, which requires the different bond angles. This means the whole ESMPT (or ESHAT) process of $7HQ \cdot (NH_3)_3$ cluster combined with a wagging motion of

hydrogen-bonded wire. However, the calculations within Cs symmetry constraint would be obviously failed to characterize this hydrogen-bonding dynamics. Hence, the mechanism of ESHAT process, which is proposed basing on Cs symmetric calculations, should be doubted.

In this work, the mechanisms of the proton transfer dynamics of $7HQ \cdot (NH_3)_3$ cluster upon photoexcitation has been justified by theoretical calculations. A wagging motion of hydrogen-bonded wire has been found along with the proton transfer of $7HQ \cdot (NH_3)_3$ cluster proceeding in the excited state, due to the formation of the NH_4^+ in the wire of transient HT2 structure. In other words, the Cs symmetry of the hydrogen-bonded system is obviously broken. Therefore, the ESHAT mechanism of $7HQ \cdot (NH_3)_3$ cluster, which is proposed basing on the calculations with Cs symmetry constraint by Leutwyler and co-workers [27,28], should be doubted. Further researching is requested to reveal the more detailed mechanism of the excited-state reaction of $7HQ \cdot (NH_3)_3$ cluster.

Acknowledgments

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