Theoretical Studies on the Mechanism of Excited-State Proton Transfer in Hydrogen-Bonded Dimers and Complexes

Excited-state proton transfer plays significant roles in physics, chemistry, and biology [1]. In this thesis, I focus on mechanism of excited-state proton transfer in hydrogen-bonded dimers and complexes by applying modern quantum chemical approaches. In Chapter 1, the current status of experimental and theoretical studies for excited-state proton transfer is presented as general introduction. Through the present work, I choose 7-azaindole (7AI) as a target molecule, which contains both proton donor and proton acceptor parts, so that excited-state proton transfer can take place via self-associated hydrogen-bonded dimers and via solvent bridge relay. Excited-state double proton transfer (ESDPT) in 7AI dimer has received particular attentions, because this process can be taken as a model of the photoinduced mutation in DNA base pairs [2-4]. For 7AI dimer, one major question has been put forward through the intensive studies: Does the ESDPT follow a concerted mechanism or a stepwise mechanism? Figure 1 shows schematic pictures of the mechanisms of the ESDPT in 7AI dimer from the normal dimer (ND) to the tautomeric dimer (TD). In the concerted mechanism, two protons are simultaneously transferred through a single transition state, without forming any intermediate for single-proton-transferred (SPT) component, while, in the stepwise mechanism, an intermediate is formed by the first SPT from ND, followed by the second SPT to TD. This intermediate can have either a zwitterionic character or a neutral character. As to mechanism of the ESDPT in 7AI dimer, there is still controversy in both experiments and theoretical calculations. In Chapter 2, my theoretical calculations on the ESDPT in 7AI dimer (homodimer) and (3-methyl-7AI)-7AI complex (heterodimer) are reported and the mechanism is discussed. In this study I employ the better methodology in both ab initio and density functional theory (DFT) calculations than the previous ones; the long-range corrected time-dependent DFT (LC-TDDFT) and ab initio multireference 2nd-order perturbation theory (CASPT2) methods are used to get the reliable energy profiles of the ESDPT process along the reaction pathways for the respective dimers. The calculated potential energy profiles clearly indicate that the

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Fig. 1. Concerted mechanism vs. stepwise mechanism for ESDPT in 7AI dimer.
ESDPT reactions in both dimers take place in the locally excited state following the concerted mechanism, in which each proton-transfer process occurs simultaneously without forming any stable zwitterionic intermediate. The concerted ESDPT reactions are found to proceed asynchronously in C₄ symmetry.

In Chapter 3, my theoretical calculations on the excited-state multiple-proton transfer (ESMPT) in 7Al(H₂O)₃ cluster are reported and the mechanism is discussed. Recently, Pino et al. [5] reported experimental studies on ESMPT through the hydrogen bond networks in 7Al(H₂O)₃ cluster by resonance enhanced multi-photon ionization (REMPI) and fluorescence excitation (FE) spectra. With a help of theoretical calculations, they proposed that isomerization of hydrogen bond network in 7Al(H₂O)₃ occurs after photoexcitation, followed by ESMPT. Figure 2 shows typical equilibrium structures of two isomers, referred to as the bridged-planar and cyclic-nonplanar isomers. The potential energy profiles for 7Al(H₂O)₃ cluster in the first excited state show that the reaction path of triple proton transfer after the rearrangement of hydrogen bond structure of water molecules from a bridged-planar isomer to a cyclic-nonplanar isomer is more favorable than the reaction path of quadruple proton transfer without hydrogen bond rearrangement. The calculated results show good consistency with the experimental observations such as the electronic spectra and excited-state lifetime of 7Al(H₂O)₃ cluster [5].

![Diagram of equilibrium structures of 7Al(H₂O)₃ cluster](image)

(a) bridged-planar isomer  (b) cyclic-nonplanar isomer

Fig. 2. Equilibrium structures of 7Al(H₂O)₃ in the excited state.

In Chapter 4, a general conclusion of the present work is presented. My theoretical calculations on 7Al homodimer, heterodimer, and complexes with waters have provided consistent results in both ab initio and DFT calculations, as well as with available experimental data. It is concluded that reliable theoretical calculations can provide a strong support to understand the mechanism of ESMPT for hydrogen-bonded complexes.

References
学位論文審査の要旨

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学位論文題名

Theoretical Studies on the Mechanism of Excited-State Proton Transfer in Hydrogen-Bonded Dimers and Complex
（水素結合二量体および水素結合複合体における励起プロトン移動に関する理論的研究）

博士学位論文審査等の結果について（報告）

核酸塩基のモデル分子として取り上げられる7アザインドール(7AI)は水素結合のdonor、acceptor を有し、水素結合を通じて容易に二量体や溶媒分子との複合体を形成して、電子励起状態で多重プロトン移動を示す。近年分光実験技術の進歩により、電子励起状態における多重プロトン移動のメカニズム、ダイナミクスについても実験的に調べられるようになってきたが、従来の機構を理解する上では理論計算の果たす役割はきわめて大きい。核酸塩基対のモデルとなる7AIの二量体については、電子励起状態で二重水素移動が起こり異性化するものが示されており、そのメカニズムが段階的機構や協奏の機構かについて明らかにした。電子励起状態の理論計算にはab initio法と密度汎関数（DFT）法の2つのアプローチがあるが、ab initio法ではコストと精度の観点から、多配置SCF法で反応経路を求めて多参照構造法で経路沿ったエネルギーを計算する方が主流であった。本論文では、多大な計算コストをかけ反応経路の決定にも多参照構造法を適用したところ、従来のab initio計算の結果と異なり協奏機構を支持する結果が得られた。さらに、DFT法に長距離補正法を導入したLC-TDDFT法を適用することにより、ab initio法とDFT法が統一結果を与えることを示し、理論計算の立場から分光実験の結果を矛盾なく説明することに成功した。同じ計算手法を適用することにより、7AI二量体において一方の分子にメチル置換基を導入した誘導体においても反応機構が変化しないことや、7AIと水分子3つからなるクラスターにおける励起多重プロトン移動では水素結合の組み換えが重要であることも明らかにしている。

これを要するに、著者は、水素結合二量体および複合体の電子励起状態における多重プロトン移動について、世界的に説明を欠いた問題に真摯に応じ、高精度な理論計算に基づき従来のメカニズムを解明したものと評価でき、水素結合系の励起多重プロトン移動の従来の理解に対して貢献するところあるものがある。

よって著者は、北海道大学博士（理学）の学位を授与される資格があるものと認める。