学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Theoretical Studies of Excited State Reactions Using Surface Hopping Molecular Dynamics and Reduced-Dimensionality Methods
（状態遷移分子動力学と次元縮約法を用いた励起状態反応の理論研究）

Excited state reactions encompass a wide range of phenomena, such as photochemical reactions and excited state dissociation reactions. When a chemical reaction involves electronic excited states, the nonadiabatic process leads to the transition of electronic state between different potential energy surfaces (PESs), corresponding to a breakdown of the Born-Oppenheimer approximation and demanding a treatment of both the nuclei and the electrons. There are a large number of chemical problems that involve excited electronic states, from photo-chemistry to chemical synthesis. Therefore, it is a major challenge in the theoretical field to describe the behavior of both electrons and nuclei in the context of nonadiabatic effects and excited state chemical reactions. The trajectory surface hopping (TSH) dynamics can meet the challenge of simulating dynamics beyond the Born-Oppenheimer approximation, in which the electron is described under the quantum mechanic's framework, and nuclei are treated classically. The trajectories propagate on multi-state PESs, resulting in complex changes in reaction processes along different degrees of freedom in geometries. This complexity makes it challenging to gain a deep understanding of the nature of excited state reactions and can lead to the omission of several crucial details of the dynamic processes. The classical Multi-dimensional Scaling (CMDS) method is a kind of dimensionality reduction method that can be applied to analyze the trajectories of TSH to gain a deeper understanding of dynamic processes.

Chapter 1 provides a general introduction, outlining the background of this thesis. In Chapter 2, I present the fundamental theory and concepts of excited state reaction dynamics simulation and the CMDS method.

In Chapter 3, the complete reaction route map of $SiCH_4$ in the ground state is explored by the ADDF method, identifying two new dissociative reaction paths at the B3LYP/def2-SVP level. Ab initio molecular dynamics (AIMD) program based on Zhu-Nakamura method has been developed, and it is applied for the investigation of photodynamic of $SiCH_4$ at the MS-CASPT2/def2-SVP level. The resulting branching ratio of the dissociative products and proton-transfer products shows different reaction paths, which can deepen the insight and understanding of the photodynamic process of $SiCH_4$.

In Chapter 4, the complete picture of the excited state chemical reaction of light-driven molecular rotary is obtained by a systematic theoretical study. According to the dynamic simulation results, I have advanced the field of light-driven molecular rotary motors (LDMRMs) by achieving two pivotal goals: lowering the thermal helix inversion (THI) barrier and extending the absorption wavelength into the visible spectrum. This redesigned motor stands

out with its two photoisomerization stages and two thermal helix inversions, featuring exceptionally low THI barriers (4.00 and 2.05 kcal/mol at the OM2/MRCI level for the EM → EP and ZM → ZP processes, respectively). Moreover, it displays absorption wavelengths in the visible light range (482.98 and 465.76 nm for the EP and ZP isomers, respectively, at the TD-PBE0-D3/6-31G(d,p) level), surpassing its predecessors in efficiency, as indicated by the narrow HOMO-LUMO energy gap. Ultrafast photoisomerization kinetics (approximately 0.8-1.6 ps) and high quantum yields (around 0.3-0.6) are observed through TSH simulations.

In Chapter 5, the direct process of the NH_2^+ DR mechanism is studied, which is an essential process in the evolution of ionization and chemistry in astrophysical environments. Consequently, understanding the evolution of interstellar molecular species requires studying the branching ratios of the NH_2^+ DR reaction. The dynamics of NH_2^+ dissociative recombination (DR) was explored using surface-hopping AIMD (SH-AIMD) simulations at the state-averaged complete activate space self-consistent field (SA-CASSCF) level. This study incorporates the Zhu-Nakamura formalism to describe the potential energy curves crossing (nonadiabatic transitions between adiabatic electronic states) nature between the electronic states of the ground and excited states of NH_2. The resulting branching ratio of the dissociative products, namely N + H + H and NH + H, shows a qualitative agreement with the experimental observations. The momentum at the hopping points of all trajectories is then analyzed using CMDS to explore the relationship between the momentum distribution and the vibrational mode, revealing the momentum at the hopping point is critically influenced by the vibrational mode and enhancing our comprehension of the DR reaction.

Chapter 6 provides a general conclusion of this thesis. In this thesis, I develop the SH-AIMD simulation program based on the Zhu-Nakamura algorithm. It is applied to investigate the photodynamics of $SiCH_4$ and the dynamics of NH_2^+ dissociative recombination. Additionally, the momentum of NH_2^+ along the trajectory is investigated using the CMDS method. Furthermore, a new type of molecular motor is proposed, and its performance is evaluated through theoretical calculations.