

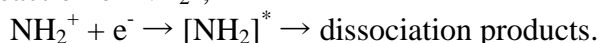
Theoretical study on dissociative recombination reaction of NH_2^+

T. Koyama, T. Akama, and T. Taketsugu

Department of Chemistry, Faculty of Science, Hokkaido University, Japan

The dissociative recombination (DR) reaction is a combination of an electron and a positive molecular ion, which is followed by the dissociation into neutral molecules. The DR reaction proceeds via the direct process or the indirect process. In the direct process, the molecule system makes transitions directly from the electronic ground state of cation to the dissociative excited state of neutral molecule after capturing an electron. In the indirect process, this transition proceeds via Rydberg states. In the interstellar space, temperature and pressure is so low that the DR reaction which proceeds with electrostatic attraction is very important.

We have studied the DR reactions of HCNH^+ [1], H_3O^+ [2], and HD_2O^+ [3], using *ab initio* molecular dynamics (AIMD) simulation with a surface hopping scheme, and discussed non-adiabatic dynamics and the branching mechanism. In the present study we investigate the mechanism of the DR reaction of NH_2^+ ,



While in the previous studies initial condition of AIMD simulation was determined by conservation of energy before and after the collision, in this study we aim to take electron dynamics into account for the initial condition. The electron dynamics can be described by real-time propagation of time-dependent density functional theory (RT-TDDFT).

For preparation of electron dynamics, geometry of positive molecular ion NH_2^+ was optimized first by the B3LYP/cc-pVTZ method. Then, excited states of NH_2 which are produced after the collision were calculated by CASPT2 and TDDFT(B3LYP) with the cc-pVTZ basis-set. The TDDFT result was very close to the highly accurate CASPT2 result, and so we decided to adopt TDDFT in the following. Because the indirect process needs the Rydberg states, TDDFT calculation including Rydberg basis-set was also carried out. The result of this calculation shows that Rydberg state lies at low level, indicating that this reaction may proceed via the indirect process. Next, we will perform electron dynamics to determine the initial distribution of electronic states just after the collision, and execute AIMD simulation.

References

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- [3] M. Kayanuma, T. Taketsugu, & K. Ishii, 2008, TCA 120, 191.