

Ab initio molecular dynamics approach to dissociative recombination reactions

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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 mechanism or the indirect mechanism. In the direct mechanism, the molecular system makes transitions directly from the electronic ground state of cation to the dissociative state of neutral molecule after capturing an electron. In the indirect mechanism, this transition proceeds via Rydberg states. In the interstellar medium, polyatomic ions are produced through ion-molecule reactions, and the DR process is one of the possible ways of neutralizing the ions. Through the DR reactions, polyatomic ions dissociate into different combinations of neutral atoms/molecules, and the study of the branching ratios of the DR reaction will help to understand the chemical evolution in interstellar clouds.

In order to examine the reaction mechanism and dynamics in the DR processes, we have developed an ab initio molecular dynamics (AIMD) program code for excited-state dynamics, including the Tully's surface hopping algorithm for nonadiabatic transitions between adiabatic electronic states. The code uses the adiabatic potential energy, energy gradients, and nonadiabatic coupling terms at the state-averaged complete active space multi-configurational SCF level, evaluated by the quantum chemistry program package, MOLPRO. The code has been applied to DR reactions, $\text{HCNH}^+ + e^-$ [1,2], $\text{H}_3\text{O}^+ + e^-$ [3], $\text{HD}_2\text{O}^+ + e^-$ [4], and $\text{CH}_3^+ + e^-$ to examine the tendency in the branching ratio of the dissociative products, and to investigate the dynamical processes with nonadiabatic transitions. In the application to $\text{HCNH}^+ + e^-$ [1], we found that (1) HNC and HCN are generated with almost the same ratio, (2) the products, $\text{CN} + 2\text{H}$, are also generated, and (3) the isomerization between HNC and HCN can occur while the HCNH molecule descends through the electronic excited states. In the second application [3], two Rydberg states and three valence states were included in dynamics, the surface hopping was observed in the relatively early stage less than 30 fs in most cases, and the rates of the respective dissociative products are estimated as $(\text{OH} + 2\text{H}) : (\text{H}_2\text{O} + \text{H}) : (\text{OH} + \text{H}_2) : (\text{O} + \text{H}_2 + \text{H}) = 0.87 : 0.10 : 0.015 : 0.015$, while the corresponding experimental rates were reported as $0.60 : 0.25 : 0.14 : 0.013$. The rate of exothermic products is small compared to the experimental ones, but the order in the ratio is reproduced. In the third application [4], it was shown that the dominant products, $\text{OD} + \text{D} + \text{H}$, were generated in 63% of trajectories, while the products, $\text{OH} + 2\text{D}$, were generated in only 11% of trajectories, indicating that the release of a light fragment H is favored over the release of a heavy fragment D. This result is in conformity with the observation that there is a larger amount of deuterium substituted species than the non-substituted species in the interstellar space.

References

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