Ab initio excited-state molecular dynamics approach including spin-orbit coupling and nonadiabatic coupling effects: An application to the photodissociation of CH_3I

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Ab initio molecular dynamics (AIMD) approach has been extended to multi-state dynamics of spin-orbit-coupled electronic states that are obtained through diagonalization of the spin-orbit coupling matrix with the second-order multireference perturbation theory (CASPT2) energies in diagonal terms and the spin-orbit coupling terms at the state-averaged complete active space self-consistent field (SA-CASSCF) level in off-diagonal elements. Nonadiabatic transitions among spin-orbit-coupled states were taken into account by a surface hopping scheme with utilizing the nonadiabatic coupling terms calculated by numerical differentiation of spin-orbit-coupled wavefunctions and analytical nonadiabatic coupling terms at the SA-CASSCF level. The present method was applied to the photodissociation of methyl iodide, $CH_3I + h\nu \rightarrow CH_3 + I^*(^2P_{1/2})/I(^2P_{3/2})$, reproducing well the experimental values in the branching ratio and the energy distributions of the dissociative products.