A Time-dependent Excited-state Molecular Dynamics Study of Lanthanide Cyclopentadienyl Complexes for Laser-assisted Metal-Organic Chemical-Vapor Deposition

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Laser assisted metal-organic chemical-vapor deposition (LCVD) has many applications including preparation of high quality thin films.[1] In order to engineer the metal-organic precursors and to optimize the thin films prepared by LCVD, it is important to study the photofragmentation mechanisms of gas-phase metal-organic complexes in a laser field. A computational description of this process should focus on coupled dynamics of electrons and nuclei.[2] Theoretically, time-dependent excited state molecular dynamics algorithm (TDESMD)[3] has been used to explore and compare photodissociation mechanisms of tris(cyclopentadienyl)lanthanum, $La(Cp)_3$ and tris(isopropylcyclopentadienyl)lanthanum, $La(iCp)_3$. Quantum evolution of electronic states is coupled to evolution of nuclei in a classic path approximation. Specifically, optical driven electron hopping between the ground state and the ligand-to-metal charge transfer state facilitate dissociative evolution of nuclei. The simulation relies on first principles molecular dynamics perturbed by the periodic excitations and de-excitations of the model, during which the molecules could accumulate enough kinetic energy and overcome dissociation barrier. This algorithm is implemented in the basis of Kohn-Sham orbitals generated at each step of first principles molecular dynamics. The simulation produces atomic models of several products such as smaller molecules LaC_3H_3 and C_2H_2 upon photofragmentation during the given time of evolution. The simulation results agree well with the photofragmentation mechanisms proposed experimentally through photoionization time-of-flight mass spectrometry.[4] Such simulations will help to interpret and predict photofragmentation of a broad class of metal-organic compounds for LCVD technique.

Reference:

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