

Ab Initio Molecular Dynamics of Photodissociation of Lanthanide Cyclopentadienyl-type Precursors for Laser-Assisted MOCVD

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A detailed photodissociation mechanism for laser-assisted metal-organic chemical vapor deposition (LCVD) process using lanthanide cyclopentadienyl-type precursors, is computationally simulated by ab initio molecular dynamics (AIMD).¹ The key challenge of the modeling is the strong laser field which induces periodic population-depopulation Rabi cycles.² This challenge is addressed in our plane-wave DFT modeling with electron density and nuclear potential being periodically driven. Resulting hopping between potential energy surfaces strongly affects the nuclear trajectory providing a set of nuclear configurations at subsequent instants of time $\{\bar{R}_i(t)\}$, obtained through ab-initio molecular dynamics for a time-dependent excited state. We explore trajectories obtained at several laser field frequencies, intensities, and durations. In the computed trajectories, the interatomic distances $\{\bar{\Delta}_{ij}(t) = \bar{R}_i(t) - \bar{R}_j(t)\}$ demonstrate different regimes, from small oscillations to abrupt elongations, corresponding to fragmentation of the studied compound. The computed fragments are compared with the ones elucidated experimentally using photoionization time-of-flight mass spectrometry. The collisionless environment of the molecular beam source revealed a series of unimolecular steps, starting with dissociation of an intact CP or TMCP ligand.³ The ligand-to-metal charge transfer (LMCT) process causes metal reduction and intact-ligand dissociation steps, producing neutral Ln and neutral L organic ligand. Subsequently, neutral Ln atoms undergo direct photoionization to Ln^+ . Competing with the ligand dissociation process from LnCP^+ and LnTMCP^{2+} is the photodecomposition of these complexes to form, primarily, lanthanide carbides, which is helpful in understanding the metal-carbide-formation mechanism during the LCVD process.

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