**Computational Modeling of Photofragmentation of Gas-phase**

**Tris(isopropylcyclopentadienyl)lanthanum Complexes**

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In this study, time-dependent excited state molecular dynamics (TDESMD) is used to explore photodissociation mechanisms of tris(isopropylcyclopentadienyl)lanthanum complexes, $La(iCp)_3$. TDESMD simulations rely on molecular dynamics (MD) induced by periodic excitations and de-excitations of the electronic configuration of the model at given excitation wavelength.[1,2] A set of nuclear configurations at subsequent instants of time is generated from the initial position of a trajectory through electron hopping between potential energy surfaces of the ground state and that of the ligand-to-metal charge transfer state.[3] The TDESMD algorithm is implemented in the basis of Kohn-Sham orbitals generated on the fly at each step of first principles molecular dynamics. TDESMD simulations confirm the central role of ligand-to-metal charge transfer and metal-to-ligand charge transfer during the photodissociation process of complexes. The TDESMD simulations model the dynamical formation of several product molecules, which are consistent with fragments proposed experimentally from photoionization time-of-flight mass spectrometry (PI-TOF-MS). The computational results demonstrate that the distribution of photofragmentation products is controlled by the intensity and wavelength of the exciting laser pulse. In addition, excited state MD and thermalized MD are applied to the model, resulting in the formation of few fragments. However, the structure, composition, and molecular mass of fragments obtained without TDESMD procedure differ from the ones observed in PI-TOF-MS. Thus, the simulation results indicate that dissociation process depends on the way an excitation energy has been communicated to the molecule. This study has implications for the deposition of insulators with high dielectric constants by laser-assisted metal-organic chemical vapor deposition (LCVD).

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(2) Chen, J.; Hochstatter, A. M.; Kilin, D.; May, P. S.; Meng, Q.; Berry, M. T. *Organometallics* **2014**, *33*, 1574.
(3) Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061.