Ab initio Study of Photodimerization of Cyclohexasilane

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In this study, density functional theory (DFT) based time-dependent excited-state molecular dynamics (TDESMD) calculations are performed to study photoinduced reactions of a pair of cyclohexasilane (CHS) monomers. In TDESMD trajectories, one observes vivid reaction events including dimerization and fragmentation. A postprocessing technique is applied on instantaneous configurations sampled from TDESMD trajectories to remove structural ambiguity and to facilitate property analysis. A general reaction pathway is identified as (i) ring-opening formation of dimer, (ii) rearrangement induced by bond breaking, and (iii) decomposition through elimination of small fragments. The identified pathway supports the chemistry proposed for the fabrication of silicon-based materials using CHS as precursors. In addition, we find dimers have smaller HOMO-LUMO gaps and exhibit a red shift and line width broadening in the computed photoluminescence spectra compared to a pair of CHS monomers. We also compute mass spectra to capture possible fragments formed in postprocessed trajectories. This study suggests TDESMD technique has potentials to model polymerization processes induced by photons.

References

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