Relaxation of excited states in energized PAHs

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The Tully's fewest switches surface hopping algorithm [1] is implemented within the framework of the Time-Dependent Density Functional based Tight Binding method (TD-DFTB) [2] in the deMon-Nano code [3] to simulate the energy relaxation following absorption of a UV photon by Polycyclic Aromatic Hydrocarbons (PAHs). This approach is used to study the size effect on the ultrafast dynamics in excited states for a special class of PAH species called polyacenes. We determine and discuss the dynamical relaxation times and mechanisms. Our results show that there is an alternation in decay times of the brightest singlet states for neutral polyacenes with n=3–6 of aromatic cycles. This alternation is associated with energy gaps between this initial excited state and the state lying just below in energy. The calculated decay times range in between 10 and 100 fs.

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