Electronic and Vibrational Energy Transfer in Conjugated Dendritic Molecules

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Non-adiabatic excited-state molecular dynamics (NA-ESMD)[1,2] and excited-state Instantaneous Normal Modes (ES-INMs) analyses have been applied to describe the state-specific vibrations that participate during the unidirectional energy transfer between two-, three-, and four-ring linear polyphenylene ethynylene (PPE) chromophore units linked through meta-substitutions:

Several excited-state electronic energies, with their corresponding gradients and nonadiabatic coupling vectors were included in the simulations[3,4]. The initial laser excitation creates an exciton initially localized in the absorbing two-ring linear PPE units. Thereafter, we observe an ultrafast directional change in the spatial localization of the transient electronic transition density. The analysis of the intramolecular flux of the transition density shows a sequential through-bond two-ring→three-ring→four-ring transfer. The vibrational excitations of C≡C stretching motions change according to that. Our results reveal a unique vibrational mode that significantly matches with the corresponding nonadiabatic coupling vector $d_{n,(n-1)}$. This mode corresponds to the highest frequency ES-INM(S_n) and its lifetime is mainly restricted to times close to the electronic transitions. Furthermore, it reveals us the main role that specific-state vibrations play in the efficiency of the unidirectional $S_n \rightarrow S_{n-1}$ electronic and vibrational energy funneling in light-harvesting dendrimers. Finally, a mechanism of unidirectional energy transfer is presented based on the variation of the energy gaps between consecutive electronic excited states in response to the intramolecular flux of the transition density.

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[2] *"Nonadiabatic Excited-State Molecular Dynamics (NA-ESMD). Numerical tests of convergence and parameters".* T. Nelson, S. Fernandez-Alberti, V. Chernyak, A. E. Roitberg, and S. Tretiak, J. Chem. Phys., submitted (2011)

[3] *"Nonadiabatic molecular dynamics simulations of the energy transfer between building blocks in a phenylene ethynylene dendrimer"* S. Fernandez-Alberti, Valeria D. Kleiman, S. Tretiak, and Adrian E. Roitberg, J. Phys. Chem A, 113, 7535-7542, (2009).

[4] *"Unidirectional energy transfer in conjugated molecules: the crucial role of high frequency C(triple)C bonds"* S. Fernandez-Alberti, Valeria D. Kleiman, S. Tretiak, and Adrian E. Roitberg, J. Phys. Chem. Lett. 1, 2699-2704. (2010).