

MODELING OF NON-ADIABATIC PHOTOINDUCED DYNAMICS AND ENERGY TRANSFER IN ORGANIC MOLECULES

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Introduction

The development of new materials with potential applications on light-harvesting and transport for solar cell devices represent a major task to address the global challenge on renewable and clean energy resources. Nowadays, the advances in organic synthesis can yield macromolecules with well-defined structures. In this context, it has become possible to synthesize artificial light-harvesting dendritic macromolecules with built-in energy gradients.¹ Such dendrimers are perfectly branched conjugated macromolecules with regular structures that allow a very efficient energy funneling through the molecular system.^{1,2} Here, we study the ultrafast electronic and vibrational energy transfer in a building block of a well known dendrimer (the nanostar).² The energy transfer occurs between two-, three- and four-ring linear poly-phenylene ethynylene (PPE) units separated by meta-substitutions as shown in **Fig. 1 (inset)**. We use this system as a model^{4,5} to understand the successful directional-energy transfer that takes place in more complex phenylethynyl-perylene-terminated dendrimers.

Theoretical

In this work, nonadiabatic molecular dynamics simulations is performed using the Molecular Dynamics with Quantum Transitions (MDQT) as described by Tully, which has been later successfully applied to a large variety of photochemical reaction mechanisms in organic compounds. This procedure has been recently implemented in the semiempirical NA-ESMD (Non-Adiabatic Excited State Molecular Dynamics) code^{4,5} where the electronic energies, gradients and nonadiabatic coupling vectors for the excited states are calculated on-the-fly during the molecular dynamics simulations using the Collective Electronic Oscillator (CEO) method.³ The CEO code is based on the well tested major semiempirical models combined with the time-dependent Hartree Fock (TDHF) or the Configuration Interaction Singles (CIS) formalism to describe correlated excited states, and proved to be a valuable theoretical tool to model various photo-physical dynamical processes in many organic nano-materials such as conjugated polymers and carbon nanotubes.³ Details about the method can be found elsewhere.^{3,4,5} The clear advantages of this method include its speed, scalability with number of

atoms, and more importantly, efficient calculation of analytical gradients for the excited state surfaces permitting the use of molecular dynamics very efficiently.

Results and Discussion

We have performed 500 independent MDQT trajectories of 150 fs each using a Langevin thermostat to keep the temperature constant at 10K with a friction coefficient γ of 2.0 ps⁻¹. Quite obviously, the comparison of time scales with experiments needs either a correct value of friction coefficient, or the presence of real solvent molecules. We are working on those two approaches and they will be presented in future work. The velocity Verlet algorithm was used with a time step $\Delta t = 0.05$ fs for the classical nuclei. The electronic C_I coefficients (Eq. 3) were propagated using a Gear Predictor Corrector algorithm with a times δt of 1.25×10^{-5} fs (4000 times shorter than the classical time step)

Figure 1 displays the time-dependence of the average populations of the different electronic states during the MDQT trajectories. We show results only from 0 to 80 fs, but populations follow the same trends from 80 to 140 fs. The initially excited S_4 state depopulates very rapidly to the S_3 state. The $S_4 \rightarrow S_3$ transition takes place in less than 3-4 fs after photoexcitation. However, the system remains on the same diabatic state which is spatially localized on a 2-ring unit after the crossing point almost for all trajectories. Thus we do not observe any significant direct ‘through space’ 2-to-4 ring transfer via S_4/S_3 crossing (or S_4/S_1 crossing). Consequently S_4/S_3 crossing is an example of a trivial unavoided crossing when the system remains on the same diabatic state. We further denote $S_4/S_3(2)$ and $S_4/S_3(4)$ being the diabatic states localized on the two- and four ring units. A S_4/S_3 recurrence pattern is observed during the first 10 fs, indicating that the system passes twice through the region of S_4/S_3 crossing. After that, a highly efficient, sequential $S_4/S_3(2) \rightarrow S_2 \rightarrow S_1$ mechanism of electronic energy transfer between the PPE units is observed, in agreement with the near unity values of quantum yield for energy transfer to the perylene reported in the nanostar. This unidirectional mechanism is a direct consequence of the distinct values of the nonadiabatic couplings to move to a surface below and to a surface above the present one.^{4,5}

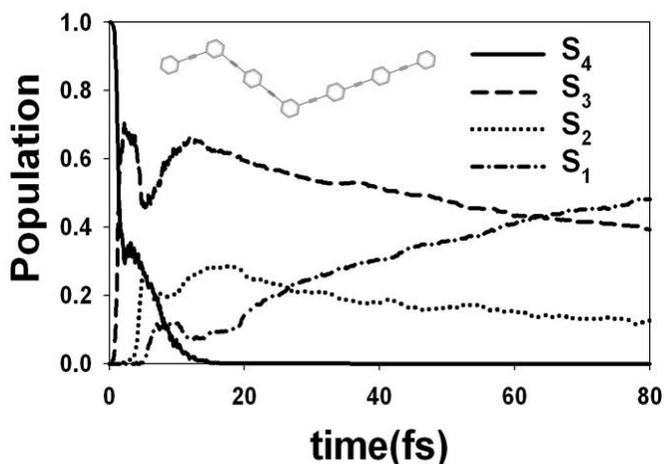


Figure 1. Population of each electronic surface as a function of time obtained from the fraction of trajectories in each state. Inset: Chemical structure of the phenylene-ethynylene (PE) building block. The molecule has two-, three-ring, and four-ring linear PE units linked by meta-substitution.

To understand the reasons leading to this behavior we explore the role of the nuclear differential motion onto the different potential energy surfaces. **Figure 2** displays histograms for the energy gap $\Delta E_{(n+1)-n}$ between the $S_{(n+1)}$ and S_n ($n=3-1$) states. The value of $\Delta E_{(n+1)-n}$ is smaller when the nuclei move on the potential energy surface of the $S_{(n+1)}$ state than when they move on the S_n state. That is, while the nuclear motion is on the $S_{(n+1)}$ state, the $S_{(n+1)}$ and S_n states get closer in energy, but as the nuclei move on the S_n state the energy gap increases, separating the surface. Since the nonadiabatic couplings $d_{(n+1)-n}$ are proportional to $1/\Delta E_{(n+1)-n}$ according to the Hellmann-Feynman theorem, the nuclear motion on the $S_{(n+1)}$ surface couples the $S_{(n+1)}$ and S_n states, while the motion on the S_n surface decouples them. Therefore, the difference in the nuclear dynamics on the $S_{(n+1)}$ and S_n state enhances the funneling signature of the energy transfer mechanism in this molecule. During the nonadiabatic molecular dynamics simulations, the system visits regions of strong coupling between states, in a sequential manner, involving only one pair of states at the time. While the system passes through one of these regions, the transfer of electronic population between both states occurs with higher probability.

Conclusion

In summary, in this letter we simulate the highly efficient sequential $S_4/S_3(2) \rightarrow S_2 \rightarrow S_1$ mechanism of electronic energy transfer between phenylene-ethynylene building blocks using nonadiabatic molecular dynamics simulations.^{4,5} The mechanism was shown to be a sequential passage of the system

through regions with differential relative values of the nonadiabatic couplings. A progressive delay to reach the regions of large nonadiabatic couplings is observed.^{4,5} The system undergoes strong coupling between states in a sequential order and the couplings involve only one pair of states at the time. Electronic energy transfer is concomitant to intramolecular vibrational energy redistribution with the nuclear motions in the direction of the ethynylene bonds playing a critical role in the process.^{4,5}

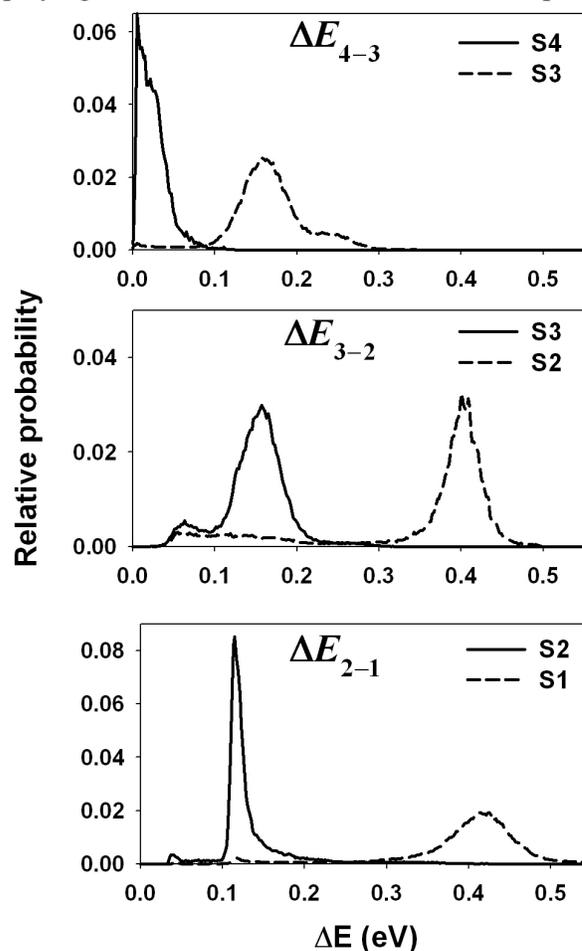


Figure 2. Histograms of the energy gap $\Delta E_{(n+1)-n}$ between the $S_{(n+1)}$ and S_n ($n=3-1$) states. Solid lines correspond to the energy gaps while nuclei are moving on the $S_{(n+1)}$ potential energy surface and dashed lines correspond to the gaps while the nuclei move on the S_n state.

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