学位論文の要約

題目   Exciton Transfer in Organic Photovoltaic Cells: A Theoretical Study.
　　　　（有機太陽電池における励起子移動の理論的研究）

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序論

　　We theoretically investigated the exciton transfer process in the donor domain of organic photovoltaic (OPV) cells. The effect of local and nonlocal electron–phonon interactions was studied using tetracene as a reference donor molecule, where the spectral distribution functions of the local and nonlocal modes are available. Furthermore, the effect of mixed Frenkel (F) and charge transfer (CT) states on the spectral properties was studied employing perylene bisimide (PBI) derivatives. The model consisted of a system described by the Holstein–Peierls Hamiltonian coupled to multiple heat–baths for local and nonlocal molecular modes characterized by Brownian spectral distribution (BSD) functions. We employed the reduced hierarchical equations of motion (HEOM) approach to simulate the dynamics of the tetracene system under the influence of the environment as a function of the electron–phonon coupling strength and temperature. The time–evolution of the PBI system was compared to the pure F exciton cases. We also computed the absorption and time–gated fluorescence (TGF) spectra for different exciton transfer integrals and F–CT bandgap conditions. The coherence length of excitons (N_{coh}) was evaluated employing two different definitions. The results for the tetracene system indicated that the strong nonlocal electron–phonon interaction under high–temperature conditions favors the exciton transfer process and enhances the efficiency of organic photovoltaic materials, while the lifetime of the exciton becomes shorter due to a low–frequency local mode. In the PBI system, we observed the presence of an excited hot state peak whose intensity was associated with the delocalization of the excited species and ultrafast dynamics that are solely dependent on the frequency of the local bath. The results indicated that the inclusion of CT states promotes localization of the excitons, which was manifested in a decrease in the intensity of the hot state peak and the 0–1 peak and an increase in the intensity of the 0–0 emission peak in the TGF spectrum, leading to a decrease of N_{coh}.

1. Effect of local and nonlocal electron–phonon interactions in exciton transfer process in organic photovoltaic cells.

We chose tetracene as a reference donor molecule under study where the Spectral Distribution Function (SDF) of the electron–phonon coupling. In order to simulate the exciton transfer process between the molecules, we considered a three-level system described by the Holstein–Peierls Hamiltonian coupled to multiple heat–baths for local and nonlocal molecular modes characterized by Brownian spectral distribution functions, in which each state represented a dimer in the donor layer. Thus, the system was described by a single ground state and two excited states expressed as $|1\rangle$, $|2\rangle$ and $|3\rangle$, respectively. The excited states $|2\rangle$ and $|3\rangle$ interacted with the nonlocal and local modes, while the ground state $|1\rangle$ only interacted with the local mode. The local and nonlocal modes were further coupled to their own heat–bath. We then considered the transfer between the two excited states in two directions, represented by two different pair of geometry dispositions of the dimer, whose difference was described by the values of the transfer integral and the nonlocal coupling strength. We introduced the Holstein–Peierls + bath Hamiltonian in order to investigate the effects of local and nonlocal electron–phonon interactions for the exciton dynamics of organic molecules in photovoltaic cells. We employed the HEOM formalism to simulate the dynamics of excitons described by this model under various physical conditions for local and nonlocal environmental modes without employing approximations, most notably the RWA and MFP approximations. The calculated results demonstrated the effects of dynamic disorder on the order of the reported time scale of the exciton processes that were characterized by the presence of ultrafast coherent oscillations, in particular at low temperatures. We found that a stronger nonlocal electron–phonon coupling favored the exciton transfer between excited states and may be a key to enhancing the efficiency of exciton transfer processes even in materials with low excitation couplings. Moreover, the effect seemed to be favored at high temperature, while the number of low–frequency local bath modes should be suppressed.

2. Effect of mixed Frenkel and charge transfer states in time–gated fluorescence spectra of perylene bisimides H–aggregates.

We simulated the exciton transfer process in a PBI dimer using a four–level system comprising two excited F states $|F_1\rangle$ and $|F_2\rangle$, and two CT states $|CT_1\rangle$ and $|CT_2\rangle$ (2F–2CT model). In this model, each state was coupled to its own local vibrational mode, which was further coupled to the

heat–bath. We considered the frequency and the coupling strength of the vibrational modes to be identical for the two F states, but different coupling strengths for the two CT states. Moreover, we assumed that there was no interaction between the CT states. For comparison, we simulated the dynamics of a PBI tetramer including only a single F state (4F model), a dimer ignoring CT states (2F model), and a monomer (1F model). The parameters adopted in the study have been derived from literature data, and were loosely based on the Me–PTCDI molecule. However, to investigate the role of the F–CT state interaction on the dynamic behavior of the model system, we varied the system parameters. The effect of mixing of F–CT states in H–aggregates was investigated using the HEOM method for the Holstein polaron model. The effect of the coupling between the vibrational subsystem and its environment was described by the Brownian oscillator model and we considered the molecular units to be independent and all the thermal baths to be uncorrelated. The dynamics and spectroscopic properties of the model were investigated and the calculated absorption spectra were consistent with previous results. In general, compared to models that only include F states, those that include CT states caused (i) a red–shift of the spectrum, (ii) an increase and decrease in the intensity of the A_1 and A_2 absorption peaks, respectively, and (iii) the appearance of high–frequency peaks as a result of splitting caused by the F–CT interaction. TGF calculations predicted the existence of ultrafast exciton dynamics that depend only on the frequency of the local bath (high–frequency molecular mode). Furthermore, we observed the appearance of an excited hot state peak whose intensity was strongly correlated to the initial exciton delocalization, and that decayed with a constant time that was dependent on the relaxation time of the system. Finally, all our calculations indicated that the F–CT interaction promotes exciton localization, manifested in the decrease in intensity of the hot state and 0–0 peaks and the increase in intensity of the 0–1 peak, resulting in a decrease of N_{coh}. However, when the value of N_{coh} was calculated using a simplified formula based on the intensities of the peaks of the TGF spectra, the results were unphysical, and one should be cautious about using it in the case of H–aggregates.