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Quantum Processes of Exciton Dissociation at Organic Semiconductor Interfaces

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Abstract

Quantum processes are studied for the exciton dissociation at solar-cell-like organic semiconductor interfaces, using the time-evolution simulation of electron-hole-pair wave packet. It is shown that the dissociation probability becomes the largest at a certain value of energy-level offset at the interface, which occurs due to the competition between the exciton binding and the carrier reflection at the interface. When the exciton is exited in an applied electric field, the dissociation probability increases remarkably, but shows a reduction under a large electric field due to the Wannier-Stark localization of carriers.

1. Introduction

Solar cells made of organic solids have been studied extensively due to their fascinating features such as flexibility and low-cost production. In most solar-cell systems, the photo-generated carriers diffuse to and are dissociated at the hetero interface, thus the interface processes being one of the keys to produce the electric power. In fact, it was found that the magnification of interface area by the bulk-hetero junctions and the application of electric field are effective to enhance the efficiency of power generation [1,2]. Accordingly, a number of theoretical studies were performed to optimize such efficiency in microscopic views [3,4]. However, most these are based on the thermo-equilibrium Marcus theory, thus the application being limited to the slow carrier-generation processes. In order to understand much faster processes, non-dissipative quantum treatments are indispensable, which has never been performed. In this view, we study the quantum processes of exciton dissociation at the hetero interface, especially focusing on the effects of interface energy-level offset and the applied electric field.

2. Methodology

Since organic semiconductors are often made of molecules that are connected with each other along one direction and have isolated energy levels, we adopt the simple one-dimensional tight-binding model to represent the quantum states of exciton, as shown in Fig. 1. Here, the electron and hole carriers can transfer from one of molecular site to another site with keeping the Coulomb attractive interaction. We assume that the energy levels of molecules have the energy-height discontinuity (offset, V) at the interface.

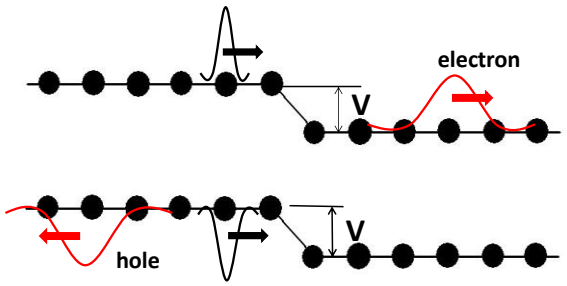

Fig. 1 Schematic view of theoretical model of interface exciton adopted in this work. Both electron and hole have energy-level offset, V, at the interface. Initial exciton is scattered at the interface and dissociated, where electron and hole are moving into right and left sides, respectively.

As shown in Fig. 1, we first prepare the exciton in the left side of the interface, and then give the velocity toward the right side. The time evolution of exciton is realized by solving the time-dependent Schroedinger equation. After the scattering to the abrupt interface, the excitonic state split into three quantum states; (1) the dissociation state where the electron and hole carriers are separated and respectively move to the right and left sides, (2) the transmission state where both electron and hole move together to the right side, and (3) the reflection state where both electron and hole reflect from the interface and move together to the left side.

3. Results and Discussion

Effect of Interface Offset

We first consider the typical behavior of scattered exciton. Figure 2 shows the probabilities of dissociation, transmission, and reflection of exciton as a function of the energy-level offset, V, at the interface. It is seen that the transmission is large in the region of small V, while the reflection becomes large in the region of large V. The exciton dissociation occurs between these regions. The dissociation probability becomes the largest at a certain value of V. This occurs due to the competition between the binding energy of exciton and the reflection movement. Since the offset supplies the energy to exciton to release the binding of electron and hole, the dissociation starts only when the offset is larger than the binding energy. On the

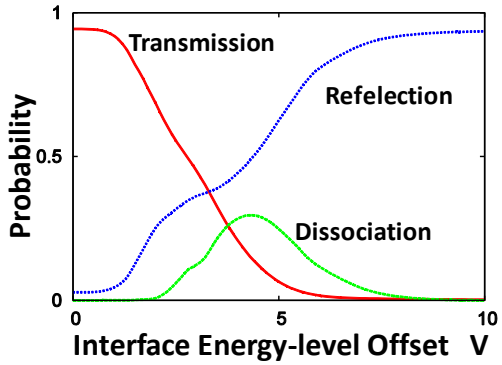

Fig. 2 Dissociation, transmission, and reflection probabilities of exciton as a function of energy-level offset at the interface.

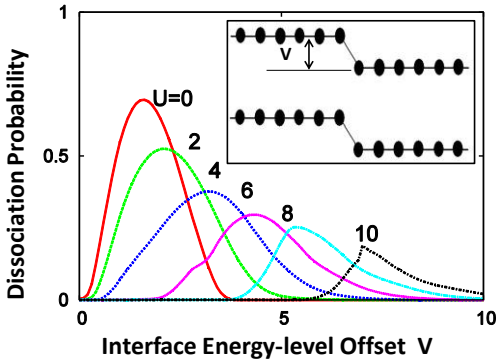

Fig. 3 Dissociation probability of exciton as a function of energy-level offset at the interface, for various values of attractive Coulomb interaction.

other hand, as the offset becomes large, the reflection by the interface increases and thus the dissociation decreases.

Then, we consider how the dissociation changes with varying the attractive Coulomb interaction, U. Figure 3 shows the dissociation probability as a function of the interface offset for various values of U. It is clearly seen that the dissociation probability becomes small together with shifting the necessary energy to unbind the exciton as increasing U.

Effect of Electric Field

Next, we consider how the dissociation is enhanced when the electric field is applied around the interface, as shown by the energy diagram in the inset of Fig. 4. In this case, we assume that the exciton is first generated in the region of electric field but has no kinetic energy. Figure 4 shows the dissociation probability of exciton as a function of the electric-field strength, E, for various values of Coulomb interaction, U.

It is seen that, as increasing the electric field, the dissociation probability first increases and then decreases. Moreover, the dissociation probability becomes small together with shifting the necessary energy to unbind the exciton as increasing U. These features are similar to the cases shown in Figs. 2 and 3. Compared to the case in Fig. 3, however, we note that the dissociation is remarkably

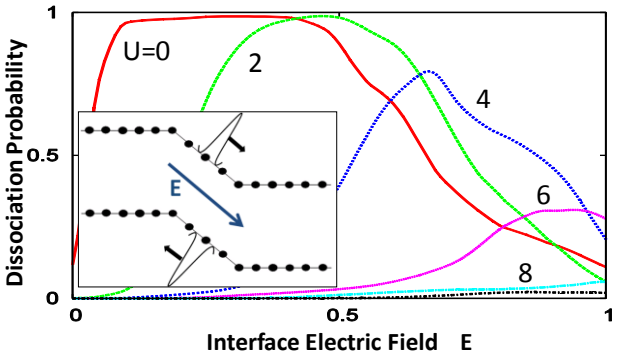

Fig. 4 Dissociation probability of exciton as a function of applied electric field strength, E, for various values of Coulomb interaction, U. Inset shows the energy diagram near the interface.

enhanced, which is in agreement with the observations [1].

Most notable feature is the sudden decrease of the probability when the electric field becomes larger than 0.7, not depending on the magnitude of Coulomb interaction. This occurs due to the appearance of Wannier-Stark effect. When the electric field becomes strong, not only electron or hole but also exciton tends to localize, which decreases the dissociation probability. In fact, we can observe the oscillation movement of exciton within a few molecules in our time-evolution simulation.

4. Conclusions

Quantum processes of exciton dissociation at the organic semiconductor hetero-interface were studied, using the time-evolution simulation of electron-hole-pair wave packet. It was shown that the dissociation becomes large when the energy-level offset is larger than the binding energy of exciton but is smaller than the reflection-dominant energy. Moreover, we found that the dissociation is remarkably enhanced when the exciton is exited in an applied electric field. On the other hand, the dissociation is largely suppressed when the electric field becomes larger than a certain value, which occurs due to the Wannier-Stark localization of exciton.

Acknowledgements

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