

# Dynamics of Photoexcited Charges in Organic Heterojunctions – Insights from Theory and Simulation

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**Abstract**—The process of exciton splitting at heterojunctions of two organic semiconductors in organic photovoltaic devices was investigated. Theoretical model is based on a Hamiltonian taking into account the effects of electronic coupling, interaction of carriers with external electromagnetic field, Coulomb interaction between electrons and holes and carrier-phonon interaction. Exciton dynamics at subpicosecond timescales was investigated within density matrix theory complemented with the dynamics controlled truncation scheme. Our results indicate that the efficiency of charge separation on subpicosecond timescales is low and that the majority of space-separated charges that occur on these timescales are directly optically generated. Next, we investigated charge separation process on longer timescale by considering it as a sequence of phonon-assisted transitions between electron-hole pair states at the interface. We found that donor exciton separation yields larger than 90% can be achieved in agreement with experimentally observed internal quantum efficiencies close to 100% in most efficient organic photovoltaic devices.

## I. INTRODUCTION

Significant research attention in the last two decades was devoted to the development of photovoltaic devices based on organic semiconductors which offer the advantage of easy and cheap processing. Nevertheless, understanding of the details of the processes that take place in a solar cell device is still limited. It is well understood that binding between an electron and a hole that are created by an incident photon is sufficiently strong to form a bound electron-hole pair (exciton). For this reason, efficient devices can be obtained only if they are composed of (at least) two semiconductors (donor and acceptor) whose band edge alignment is chosen to energetically allow the dissociation of an exciton into an electron in the acceptor and a hole in the donor. A simple picture of photon-to-charge conversion process suggests that it takes place by photon absorption that creates an exciton, exciton diffusion to an interface between the two materials, exciton separation to charges at opposite sides of an interface, and charge transport from an interface to external contacts [1, 2].

To better understand the mechanism of exciton splitting at the interface, several ultrafast spectroscopy studies that probe the dynamics at subpicosecond timescales have been performed in the last decade [3, 4, 5, 6]. These studies

typically register response signals with subpicosecond decay times, which are often interpreted to originate from ultrafast separation of donor excitons into space-separated charges. Nevertheless, the nature of exciton evolution on these timescales and the mechanism of its possible separation remains unclear.

In this presentation, we will review our recent results on exciton dynamics at photoexcited organic heterojunctions [7-9].

## II. METHODS

We model the heterojunction of two organic semiconductors using a microscopic Hamiltonian that takes into account the effects of electronic coupling, interaction of carriers with external electromagnetic field, attractive Coulomb interaction between electrons and holes and interaction of charges with lattice vibrations. We consider a one-dimensional model of a semiconductor in which it is represented using a lattice of sites. Each site provides at least one electron and at least one hole level from which the conduction and valence band of the material are derived. Interaction with phonons is modeled using local Holstein interaction, while electron-hole interaction is modeled in the lowest monopole-monopole approximation with the Ohno interaction potential between the charges.

The parameters of the model – electronic coupling between the sites, site energies, electron-phonon interaction parameters, on-site Coulomb interaction parameter – were chosen to yield values of band gaps, band offsets, bandwidths and exciton binding energies that are representative of typical organic photovoltaic materials.

To model exciton dynamics on ultrafast timescales, we use the density matrix theory along with the dynamics controlled truncation scheme. We consider the case of low excitation field and low carrier densities when it is appropriate to work in the subspace of single electron-hole excitations. The carrier branch of the hierarchy of equations in density matrix approach was truncated by keeping the contributions up to second order in the excitation field. The phonon branch is truncated in such a way to ensure the conservation of particle number and energy [7].

### III. RESULTS

Our results indicate that space-separated charges present around 100 fs after the optical excitation, originate mainly from direct optical generation. There is also a certain degree of donor exciton population transfer but it is not the main source of space-separated charges, see Figs. 1(a) and (b). We also find that such a conclusion is insensitive to the values of model parameters since similar behavior is obtained when material parameters were changed within reasonable limits [8].

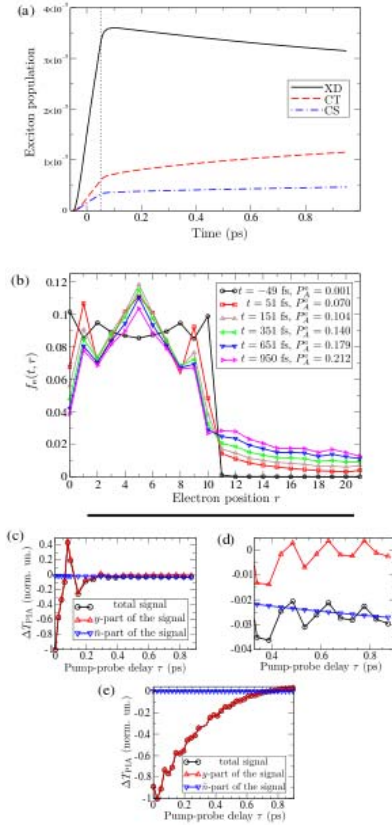


Fig. 1. (a) Dependence of the number of incoherent excitons in donor (XD), charge transfer (CT) and charge separated (CS) states. Optical excitation is centered at photon energy of 1500 meV and lasts from -50 to 50 fs. (b) Time evolution of spatial electron probability distribution. (c) and (d) Simulated photoinduced absorption signal from space separated states after pumping at photon energy of 1500 meV. (e) Simulated PIA signal from donor states after pumping to lowest donor state.

Our analysis indicates that microscopic mechanism responsible for direct optical generation of space-separated charges is resonant mixing between donor states and states of space-separated charges. We find that the efficiency of charge separation at these time scales is quite low, as can be seen for example in Fig. 1(a).

Next, within our theoretical approach we simulate the photoinduced absorption (PIA) signal obtained in ultrafast pump-probe experiments [3]. Our results indicate that for interpretation of PIA signal it is of essential importance to

consider not only the excitonic populations, but also the coherences between the exciton and ground state, as well as the coherences between exciton states. Calculated signals presented in Figs. 1(c)-(e) qualitatively agree with experimental signals obtained in [3]. In the case of excitation well above the lowest donor exciton, PIA signal from space-separated states [labeled as total signal in Figs. 1(c) and (d)] is initially dominated by the contribution of coherences between the exciton and ground state [labeled as  $y$ -part of the signal in Figs. 1(c) and (d)], while at longer times the contribution of excitonic populations dominates [labeled as  $\bar{n}$ -part of the signal in Fig. 1(d)]. On the other hand, in the case of excitation to the lowest donor exciton, PIA signal completely originates from the contribution of coherences between the exciton and ground state, see Fig. 1(e). Therefore, such a signal does not originate from ultrafast transfer of donor excitons to states of space-separated charges, but rather from relatively slow conversion from coherences to populations of lowest donor state.

Overall, our simulations at subpicosecond timescale do not show that there is ultrafast charge transfer and cannot explain high internal quantum efficiencies observed in best solar cell devices. For this reason, we investigated charge separation process on longer timescale by considering it as a sequence of phonon-assisted transitions between electron-hole pair states at the interface. Our preliminary results indicate that donor exciton separation yields larger than 90% can be achieved in agreement with experimentally observed internal quantum efficiencies close to 100% in most efficient organic photovoltaic devices.

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