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Dynamical simulation of exciton dissociation in poly(para-phenylenevinylene) systems

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Abstract

We report results from simulations of field-induced exciton dissociation in poly(para-phenylenevinylene) (PPV). The simulations were performed by solving the time-dependent Schrödinger equation and the lattice equation of motion simultaneously and non-adiabatically. The electronic system and the coupling of the electrons to the lattice were described by an extended three-dimensional version of the Su–Schrieffer–Heeger (SSH) model. The dissociation time is shown to depend strongly on the field strength as well as on the excitation energy and the lattice energy. The separation process is highly non-adiabatic and involves a significant rearrangement of the electron distribution.

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1. Introduction

Polymers and molecules with an extended π-conjugated electronic system show high electroluminescence as well as photovoltaic properties [1]. In combinations with potentially good charge transport properties they constitute an excellent platform for many applications such as organic light emitting diodes [2] (OLED) and solar cells [3,4]. While the OLEDs have already entered the market, organic solar cells still have a power conversion efficiency that is too low compared to the inorganic devices [5]. This is partly due to low intrinsic charge carrier mobilities which leads to current losses via recombinations. To increase the efficiency of this type of device it is necessary to perform more profound studies of the processes that limit the power conversion. These processes include exciton generation and relaxation, charge separation and charge transport. In this work we report results from studies of field induced exciton dissociation and charge separation. In order to study the effect of an increased temperature on the charge separation process we have also performed

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simulations after adding lattice energy to the system.

It is well known from combined experimental and theoretical studies that the lowest excited state in PPV (as well as in many other conjugated polymers) is a polaron exciton, i.e. a bound electron–hole pair dressed by a deformation of the lattice [6]. Time-resolved studies of field-induced dissociation of the polaron exciton have been performed in order to get information about, e.g. the binding energy of the exciton. In particular, it has been shown that the field-induced dissociation is ultrafast and leads to the creation of a pair of oppositely charged polarons on separate chains [7–10]. The initial phase of charge transport following electron–hole separation is also included in our simulations. This initial phase involves intra-chain polaron drift. More extensive studies of inter molecular transport processes were reported previously [11] and will be discussed in connection with the results obtained in this study.

2. Methodology

The Su–Schrieffer–Heeger (SSH) model [12] is the most commonly used theoretical model for describing carbon based π-conjugated systems. Here we have used an extended version of the SSH-model which includes a three-dimensional (3D) description of the system based on internal coordinates (bond distances, bond angles [13,14] and dihedral angles). Since the changes in the geometrical variables following excitations or charge transport are small, these changes can be approximated with linear terms for π-electron hopping and classical harmonic terms for the potential energy of the σ-system.

The SSH Hamiltonian with an additional term describing the external electric field has the form

$$H(t) = H_{\mathrm{el}} + H_{\boldsymbol{E}} + H_{\mathrm{latt}}, \tag{1}$$

where the electronic part is defined as

$$\begin{aligned} H_{\mathrm{el}} &= -\sum_{\langle nn' \rangle} \hat{c}_n^{\dagger} \beta_{nn'} \hat{c}_{n'} \\ &= -\sum_{\langle nn' \rangle} \hat{c}_n^{\dagger} [\beta_0 - \alpha(r_{nn'} - a)] \hat{c}_{n'}. \end{aligned} \tag{2}$$

All summations are over nearest neighboring carbon atoms, here denoted by $\langle nn' \rangle$, $\beta_{nn'}$ is the hopping integral between nearest neighbor carbon atom n and n' and β_0 is the hopping at a reference distance a. The actual interatomic distances are denoted $r_{nn'} \equiv |\mathbf{r_n} - \mathbf{r_{n'}}|$ and α is the electron–phonon coupling constant.

The external electric field, **E**, is accounted for by adding the following term to the electronic part of the Hamiltonian:

$$H_{\boldsymbol{E}} = -e \sum_n \mathbf{r_n} \cdot \mathbf{E} (\hat{c}_n^{\dagger} \hat{c}_n - 1). \tag{3}$$

The field is constant both spatially and in time after a smooth turn on [11].

The interactions from the σ-orbitals are described classically as [12]

$$\begin{aligned} \hat{H}_{\mathrm{latt}} = \frac{K_1}{2} \sum_{\langle nn' \rangle} (r_{nn'} - a)^2 + \frac{K_2}{2} \sum_n (\phi_n - \phi_0)^2 \\ + \frac{K_3}{2} \sum_n (\theta_n - \theta_0)^2. \end{aligned} \tag{4}$$

Here K_1, K_2 and K_3 are harmonic spring constants accounting for σ-bond forces, ϕ_n denotes an angle in which atom n participates and θ_n is a dihedral angle to which atom n contributes. All summations are over unique distances and angles to avoid double counting of these energy contributions. The angles ϕ_0 and θ_0 are those of the "relaxed" ground state geometry (see further below).

The equation of motion for the atoms is

$$M \ddot{\mathbf{r}}_n = -\nabla_{\mathbf{r}_n} \langle \Psi | H | \Psi \rangle, \tag{5}$$

where M is the mass of a CH-group. The electronic wave functions, $\Psi(t)$, are the solutions to the time-dependent Schrödinger equation:

$$i\hbar |\dot{\Psi}(t)\rangle = (H_{\mathrm{el}} + H_{\boldsymbol{E}}) |\Psi(t)\rangle. \tag{6}$$

The values used for the parameters entering the equations have been introduced elsewhere [11] and are here presented in Table 1. In principle, the parameter values should be different for different types of bonds in PPV [15]. However, for simplicity the same values of β_0 and α were used for the different bonds in PPV.

When optimizing the starting geometries of the molecules we minimized the total energy with respect to the atomic positions in all three