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Nonlinear optical excitations in femtosecond spectroscopy of conjugated polymers

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Abstract

We have investigated the optical excitation of solitons and charge transfer excitons in polymer chains by solving the equations of motion for the reduced density matrix and the lattice displacement simultaneously in time. Electron–phonon coupling leads to polaron–exciton formation which can be identified in transient pump-probe signals.

1. Introduction

Conjugated polymers show highly nonlinear optical and transport properties due to strong electron–phonon and Coulomb interactions [1]. Also, due to the weak interchain coupling, they show quasi-one-dimensional behaviour. Simulations based on the Su–Schrieffer–Heeger (SSH) model predict that charged solitons can be generated in polymer chains by optical pumping and that soliton excitations show up as midgap states in the electronic spectrum [2]. Therefore, in the last decade, many frequency-dispersed pump-probe experiments were performed, establishing the formation of solitons upon photoexcitation [3]. Moreover, using picosecond (ps) and femtosecond (fs) pump-probe and photon-echo-spectroscopy, the dynamics of photogenerated solitons were investigated [4, 5]. However, since the simulations based on the SSH model do not describe the process of optical excitation, the formation of soliton pairs out of an electron–hole pair during the excitation, and possible interactions between solitons and their decay mechanisms are not well understood.

In the present paper we address the issue whether photogeneration of charged solitons may occur within the SSH model based on a fully dynamical calculation starting from the electron–hole ground state, and tracing the time evolution of the system excited by a fs Gaussian pump pulse. Furthermore, we discuss excitonic effects due to Coulomb interaction and how the interplay of electron–phonon and Coulomb interaction affects the optical response of time-resolved pump-probe spectroscopy.

2. Theory

Conjugated polymers can be appropriately described by a one-dimensional tight-binding Hamiltonian including electron–phonon and Coulomb interaction $H = H_{SSH} + H_C + H_{ext}$. In

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the Su–Schrieffer–Heeger Hamiltonian [2],

$$\hat{H}_{\mathrm{SSH}} = \sum_{n,m=1}^{N} t_{nm}\hat{\rho}_{nm} + \sum_{n=1}^{N-1} \frac{\kappa}{2}(u_n - u_{n-1} - c)^2 + \sum_{n=1}^{N} \frac{M}{2}\dot{u}_n^2, \quad (1)$$

for a chain with N sites, the first term describes nearest neighbor electron hopping $t_{n,n+1} = \beta + \beta'(u_n - u_{n+1})$ where β is the hopping integral and β' represents the electron–phonon interaction. $\hat{\rho}_{nm} = \hat{c}_m^{\dagger}\hat{c}_n$ denotes the density operator where $\hat{c}_n^{\dagger}$ ($\hat{c}_n$) creates (annihilates) an electron at the nth site. The second and third terms in Eq. (1) describe the dynamics of the lattice where κ is the harmonic force constant between the atoms. c is the difference of the averaged actual bond length from the equilibrium bond length of the σ bonds. u_n denotes the displacement of the nth atom with respect to a reference chain with the averaged bond length.

The Coulomb interaction of the electrons is described by

$$\hat{H}_{\mathrm{C}} = \sum_n \frac{U_0}{\varepsilon}\hat{\rho}_{nn}\hat{\rho}_{nn} + \tfrac{1}{2}\sum_{n,m}^{n\neq m} V_{nm}\hat{\rho}_{nn}\hat{\rho}_{mm}. \quad (2)$$

Here, U_0 is the on-site Hubbard potential, ε the static dielectric constant, and V_{nm} the matrix element of the Coulomb potential with respect to the atomic functions. We use Ohno's expression $V_{nm} = U_0/\varepsilon\sqrt{1 + (r_{nm}/r_0)^2}$ (note that due to the zig-zag geometry, the through-space distance r_{nm} between sites n and m differs from the sum of the bond lengths).

$\hat{H}_{\mathrm{ext}} = -E(t)\hat{P}$ describes the coupling to the electromagnetic field $E(t)$, assumed to be polarized along the chain, in the long wave limit with the dipole operator $\hat{P} = -e\sum_n z_n\hat{\rho}_{nn}$. From the total Hamiltonian, the Liouville equation for the single electron density matrix $\rho_{nm} = \mathrm{Tr}(\hat{W}_0\hat{\rho}_{nm})$, where $\hat{W}_0$ is the statistical operator of the initial state, was derived [6]:

$$i\hbar\partial_t\rho_{nm} = \sum_j [(t_{nj}\rho_{jm} - \rho_{nj}t_{jm}) + (V_{nj} - V_{mj})(2\rho_{jj}\rho_{nm} - \rho_{nj}\rho_{jm})] - e(z_n - z_m)E(t)\rho_{nm}. \quad (3)$$

Eq. (3) couples to the dynamics of the lattice displacement u_n via t_{nm}. Using a semiclassical approach, we solve Newton's equations of motion simultaneously [6]

$$M\partial_{tt}u_n = -\kappa(2u_n - u_{n-1} - u_{n+1}) - \beta'(\rho_{n+1,n} + \rho_{n,n+1} - \rho_{n-1,n} - \rho_{n,n-1}). \quad (4)$$

Thus we determine the dynamics of the system under optical excitation. Furthermore, various linear and nonlinear optical signals, like transient pump-probe [6] or photon echo [7], may be calculated since they can be expressed straightforwardly as functions of ρ.

3. Numerical results and discussion

First we address the question whether solitons may be excited dynamically within the SSH model, i.e., how a fs pump pulse may excite solitons in a Peierls distorted system starting from the electron–hole ground state. For that aim we start with the pure SSH model, Eq. (1). The optical excitation of this system is described by the coupled system of Eqs. (3) and (4) omitting the Coulomb interaction $V_{ij} = 0$. We used $\beta = -2.4$ eV, $\beta' = -4.437$ eV/Å, $\kappa = 21$ eV/Å^2, $c = 0.26$ Å, $M = 3000$ eV fs^2/Å^2 which correspond to polyacetylene. As initial conditions for the time integration, we used the solution of the stationary equations $\partial_t\rho_{nm} = 0$, $\partial_{tt}u_n = \partial_t u_n = 0$ which defines the ground state of the system. In this paper, we restrict ourselves to an even number N of sites. For these chains, the ground state is characterized by an alternation of the bond length (dimerization), and the lowest $N/2$ energy states are occupied by two electrons each. Occupied and virtual states are separated by an energy gap which is 1.96 eV for the above parameters. Soliton excitation due to optical pumping can be appropriately visualized by studying the time evolution of the lattice order parameter $l_n \equiv \frac{1}{4}(-1)^{n-1}/(2u_n - u_{n-1} - u_{n+1})$ as shown in Fig. (1). Although the excitation in Fig. 1 is off resonant, due to the short pulse duration, the spectral width of the pulse is large enough to excite the HOMO–LUMO transition of the chain. The pump has maximal

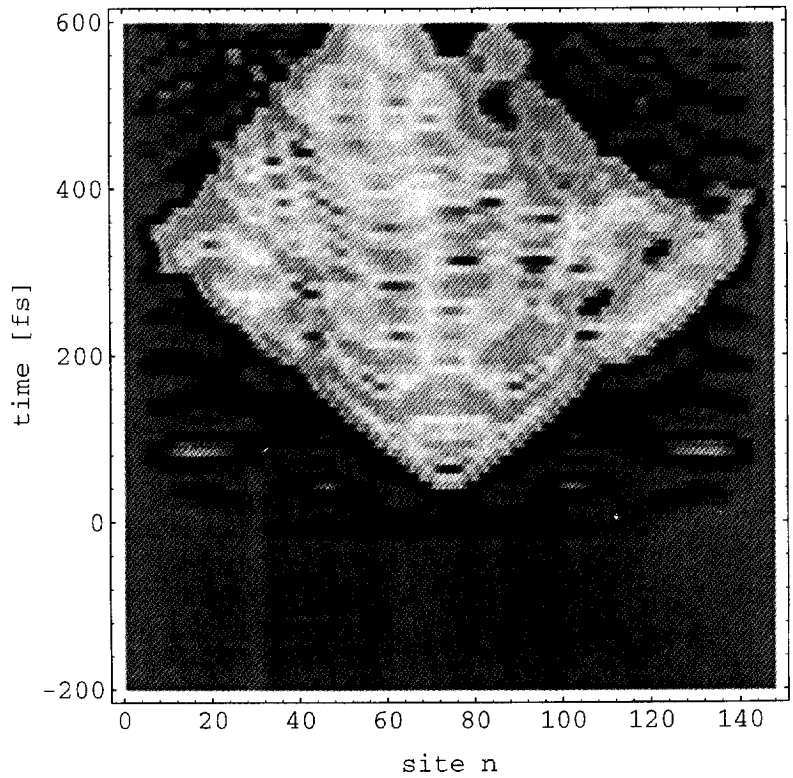

Fig. 1. Photoexcited soliton dynamics: Density plot of the lattice order parameter l_n in the SSH model. A chain of 150 atoms is excited at 0 fs by a Gaussian pump pulse of 50 fs half width energetically centered 30 meV below the energy gap ($\hbar\omega_p = 1.93$ eV). The chosen field strength 10^7 V/m of the pulse corresponds approximately to 2.5×10^7 W/cm^2. The grey scale covers the range -0.05 Å (lightest) to $+0.05$ Å (darkest grey).

intensity at 0 fs. Thus, for large negative times, the amplitude of the pump is vanishingly small so that the chain is in the ground state corresponding to a constant l_n indicated by the homogeneous grey area in Fig. 1, where $l_n(t \to -\infty) = 0.06$ Å is given by the stationary solution of Eqs. (3) and (4). Shortly after the pulse maximum has passed, a domain wall arises which separates into two parts, one evolves to the left and the other to the right end of the chain. As discussed in Ref. [2], since the chain has a twofold degenerate ground state, the domain walls separate regions of different ground state properties or different bonding structure. The domain walls are solitonic in nature and are positively and negatively charged as can be seen by calculating the polarization along the chain. The solitons are reflected at the ends of the chain. However, this process is not perfectly accomplished since we used open boundary conditions. Next we investigated the time-dependent electronic energy spectrum by diagonalizing the SSH Hamiltonian, Eq. (1). For the two lowest transitions, $\varepsilon(t)$ is shown in Fig. 2. Around 0 fs when the pump pulse is present, the soliton generation leads to a rapid red shift of the transitions until for the lowest transition the midgap state is reached. The second and higher transitions perform irregular oscillations which are induced by the numerous lattice vibrations (see Fig. 1) superimposed onto the soliton generation.

Up to now we considered a fully coherent excitation regime, i.e. without dephasing. Now we take into account a strong dephasing of the lattice dynamics by adding a phenomenological damping term $-M\gamma\partial_t u_n$ to the right-hand side of Eq. (4). The result for $\gamma = 25$ fs is shown in Figs. 3 and 4. The lattice order parameter l_n shows quasi-stationary

behavior for a given lattice site and no soliton generation could be found. The corresponding energy states become red shifted, but no midgap state is excited indicating that soliton formation is hindered due to the strong dephasing.

Next we study the influence of both electron–phonon and Coulomb interactions upon the time-resolved response of the system. In order to calculate the transient pump-probe signal as a function of the time delay T_D [6], we divided the field $E(t)$ into pump and probe $E(t) = E^{pu}(t) + E^{pr}(t - T_D)$. We used $U_0 = 11.13$ eV, $\varepsilon = 1.5$, $r_0 = 1.29$ Å, and changed the parameters $\beta' = -3.5$ eV/Å, $\kappa = 30$ eV/Å^2 and $c = 0.14$ Å to account for renormalization effects of the Coulomb interaction [6]. As is known, the Coulomb interaction leads to a well separated excitonic peak [7, 8]. For large negative time delay (the probe pulse excites the system first), the pump-probe signal shows the excitonic absorption peak (long dashed line in Fig. 5). As pump and probe begin to overlap, lattice vibrations are generated due to the strong pump as discussed in Ref. [6], splitting the excitonic resonance (full line in Fig. 5). Furthermore, since the pump pulse saturates the transition, a strong bleaching occurs due to the Pauli exclusion principle.

In conclusion, we studied the dynamical properties of the SSH model. For fully coherent excitation, photogeneration of charged solitons may occur under excitation by a fs pump pulse. Relaxation processes of the lattice dynamics obstruct soliton generation. Incorporation of the Coulomb

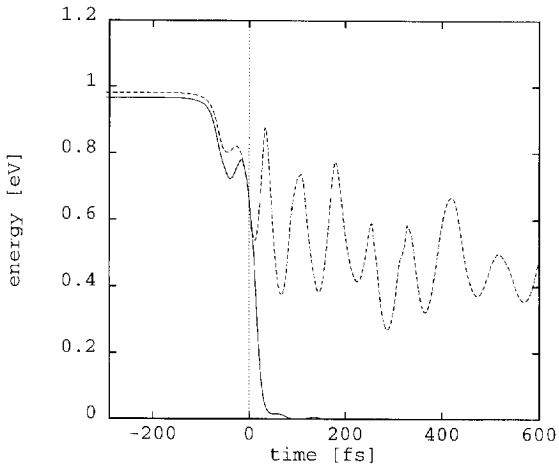

Fig. 2. Time dependence of the two lowest energy states.

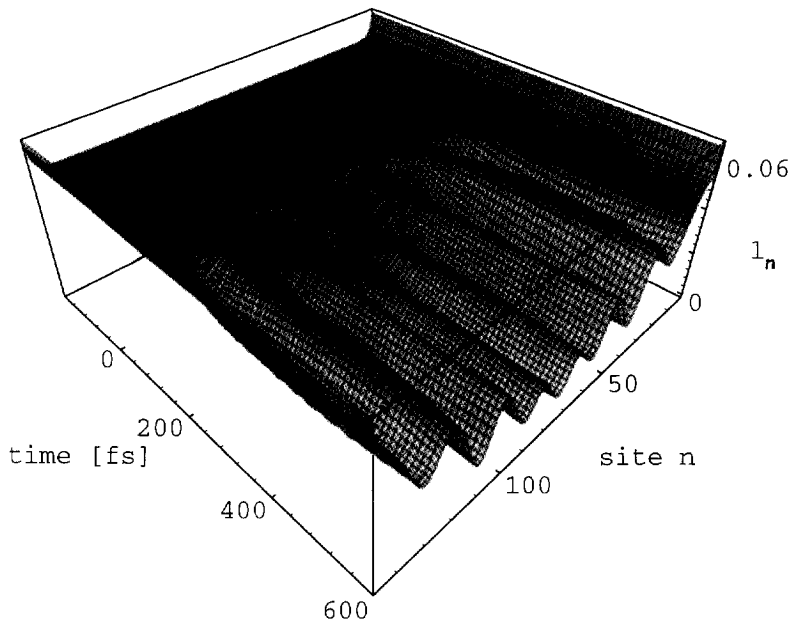

Fig. 3. Lattice order parameter l_n (in Å) for a chain consisting of 150 atoms and for strong damping of the lattice dynamics.

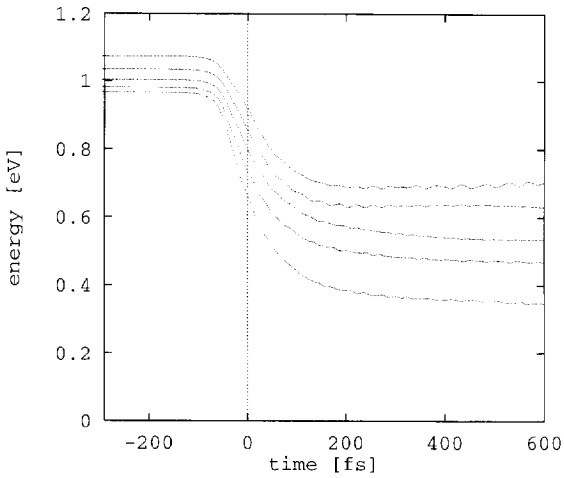

Fig. 4. Time dependence of the five lowest energy states for strong damping of the lattice dynamics.

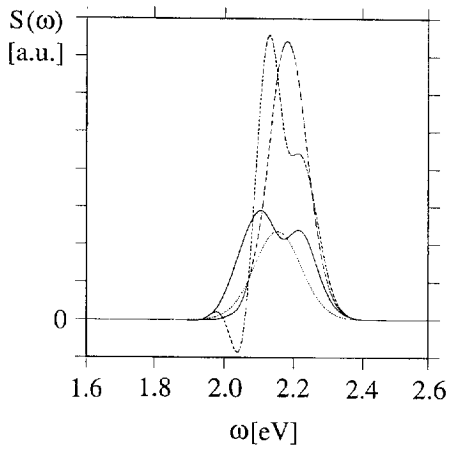

Fig. 5. Transient pump-probe signal of a 30 atom chain at different time delays T_D: $T_D = -50$ fs (long dashed), $T_D = -20$ fs (short dashed), $T_D = 0$ (solid), $T_D = +50$ fs (dotted). Excitation by 50 fs Gaussian pump and probe pulses, both centered 30 meV below the lowest excitonic transition.

interaction leads to a strong excitonic peak well below the band edge in the linear absorption spectrum. In fs pump-probe spectroscopy, lattice vibrations are generated if pump and probe do overlap, leading to polaron–exciton formation which can be identified by a splitting of the excitonic resonance.

Acknowledgements

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