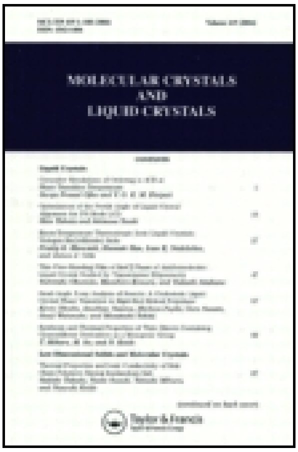

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SOLITON AND EXCITON EFFECTS IN FEMTOSECOND PUMP PROBE SPECTROSCOPY OF CONJUGATED POLYMERS

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Abstract Using a density matrix approach, the nonlinear optical response of conjugated polymers is examined taking into account many-body effects of the excitation process. The formation of charge transfer excitons and the creation of lattice distortions are studied in short polymer chains by solving the self consistent equations of motion for the reduced single electron density matrix and the lattice displacement. The coupling of electronic motions to lattice dynamics gives rise to the formation of excitonic polarons, which can be identified in the femtosecond pump-probe signal.

INTRODUCTION

The comprehensive understanding of the combined influence of lattice dynamics and Coulomb interaction in nonlinear optical experiments is still an open problem. Whereas the coupling of the electronic motion to the lattice dynamics leads to the formation of solitons which show up as in-gap states in the electronic spectrum[1], the long range Coulomb interaction between the electrons gives rise to the formation of charge transfer excitons[2]. Both types of interactions are responsible for the very large optical nonlinearities of conjugated polymers and make them interesting for special applications in optoelectronics. In this paper we investigate the interplay between lattice dynamics and Coulomb interaction in short polymer chains, and how it may be measured using coherent femtosecond pump-probe experiments. For the calculation of the nonlinear optical response we use a density matrix approach which allows to study the optical excitation process out of the ground state taking into account many-body properties of the system and which describes the effects of Coulomb interactions, lattice motions and interaction with the laser field on an equal footing[3].

Starting from a 1-dimensional tight binding model with nearest neighbor hopping, the equation of motion for the reduced single particle density matrix $\rho_{nm} \equiv \langle \hat{\rho}_{nm} \rangle$ can be written as[4]

$$\begin{aligned} i\hbar\partial_t\rho_{nm} &= \sum_j[t_{nj}\rho_{jm} - \rho_{nj}t_{jm}] + \sum_j[V_{nj} - V_{mj}][2\rho_{jj}\rho_{nm} - \rho_{nj}\rho_{jm}] \\ &- e(z_n - z_m)(E_1(t) + E_2(t - T_D))\rho_{nm}. \end{aligned} \tag{1}$$

The first term of Eq. (1) describes nearest neighbor electron hopping specified by

$$t_{nm} = \begin{cases} \beta + \beta'(u_n - u_{n+1}) & m = n+1 \\ -\sum_l V_{nl} & n = m \\ \beta + \beta'(u_{n-1} - u_n) & m = n-1 \\ 0 & otherwise. \end{cases} \tag{2}$$

Here β is the nearest neighbor hopping integral and β' represents the electron–phonon interaction. The lattice motion dynamics follows from Heisenberg's Equation

$$M\partial_{tt}u_n = -\kappa(2u_n - u_{n-1} - u_{n+1}) - \beta'(\rho_{n+1,n} + \rho_{n,n+1} - \rho_{n-1,n} - \rho_{n,n-1}). \tag{3}$$

The second term in Eq. (1) describes the Coulomb interaction in Hartree–Fock approximation where V_{nj} is Ohno's potential. The last term is the coupling of the system to the pump field E_1 and the probe field E_2 which has a time delay T_D. Linearizing the problem with respect to the probe E_2 and solving the equation of motion Eq. (1) and Eq. (3) simultaneously, we can calculate the pump–probe signal according to

$$S(\omega, T_D) = -2\,Im\{E_2(\omega)\sum_n ez_n\rho_{nn}(\omega)\}. \tag{4}$$

NUMERICAL RESULTS AND DISCUSSION

We have calculated the transient pump–probe Eq. (4) of a 30 atom polymer chain using the parameters of polyacethylene. For the excitation (pump pulse) we have assumed a Gaussian pulse $E(t) = E_0exp(-t^2/4\tau^2)$ with a temporal width of $\tau = 10fs$. Pump and Probe are resonant with the optical transition $\omega_{pump} = \omega_{probe} = 2.188\,eV$, and we have used in our calculation a phenomenological transverse relaxation time of $0.1\,eV$. Our goal is to analyze the combined influence of both the Coulomb interaction and the lattice distortion on the pump–probe signal. In order to pinpoint the roles of these various interactions we shall discuss each effect separately. In Figures 1 and 2 we show the results for the pure excitonic problem, i.e. the lattice geometry (the position of the atoms) is fixed. Therefore the lattice order parameter l_n

$$l_n(t) \equiv \frac{(-1)^{n-1}}{4}(2u_n(t) - u_{n-1}(t) - u_{n+1}(t)), \tag{5}$$

which is a measure for the magnitude of the bond length alternation, remains constant throughout the excitation process. It increases towards the ends of the chain due to the boundary conditions (Figure 1). The charge density ρ_{nm} contains a slowly varying and a fast oscillating component with respect to the lattice sites, respectively. Here we concentrate on the net charge density which is the slowly varying component given by

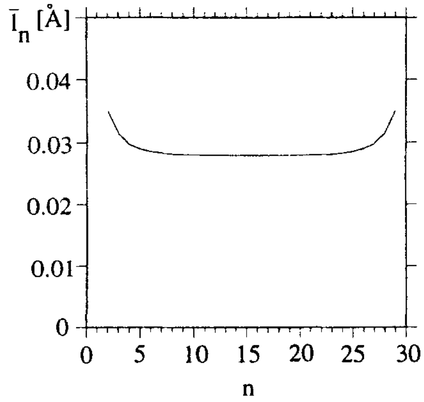

FIGURE 1 Lattice order parameter l_n for the Hartree–Fock ground state.

$$\zeta_n(t) \equiv \frac{1}{4}(2\rho_{nn}(t) + \rho_{n-1,n-1}(t) + \rho_{n+1,n+1}(t)). \tag{6}$$

This quantity contains informations about the charge distribution along the chain. As is shown for zero time delay between pump and probe ($T_D = 0$) in Figure 2a, the action of the pump pulse on the system leads to an almost uniform charge gradient along the chain. The corresponding pump-probe signal for different time delays is shown in Figure 2b. For large negative time delays (probe precedes the pump) the signal shows the excitonic absorption peak. For zero time delay we observe bleaching and a small red shift of the exciton resonance due to phase space filling and interaction of the material with the pump pulse, respectively, known as the dynamical Stark Effect. For positive time delays the pump pulse has passed and only bleaching is obtained due to phase space filling.

Now we discuss the influence of the lattice distortions (Figures. 3–5) by solving the equations of motion for u_n Eq. (3) simultaneously. The pump pulse excites electrons from the valence band to the conduction band creating an electron density (dashed curve in Figure 3) and generating a lattice distortion. The calculated lattice order parameter (Figure 3) has an soliton–antisoliton like feature. When the charge density reaches its stationary value, the lattice distortion starts to oscillate with the caracteristic time $T_l = \pi\sqrt{M/\kappa} = 31fs$ of the lattice since the electronic motion is much faster than the lattice motion. The coupling of lattice motions to the electronic part leads to changes in the electronic spectrum. Furthermore, since the lattice distortion depends on the excited charge density, we expect a significant dependence of the density matrix on time

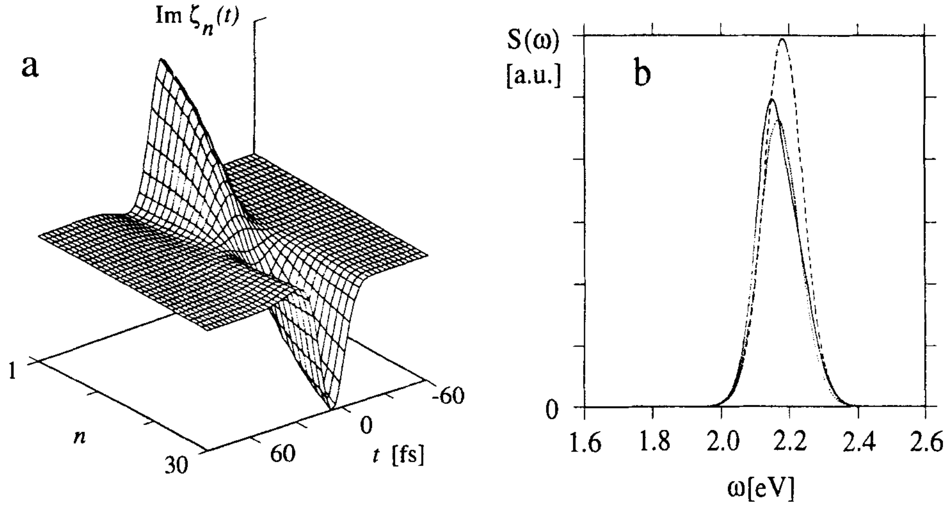

FIGURE 2 (a) Imaginary part of the net charge density $Im\zeta_n(t)$ of the excitonic problem for zero time delay and (b) the corresponding pump–probe signal $S(\omega)$.

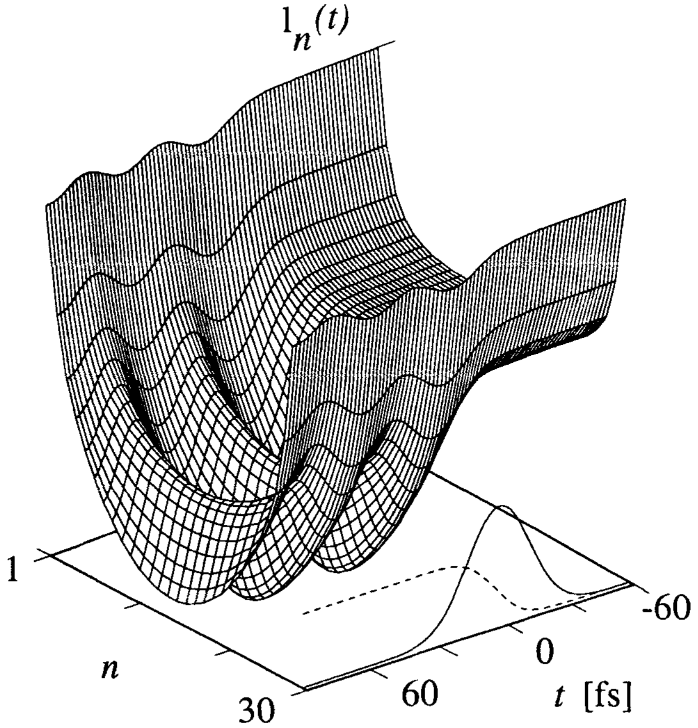

FIGURE 3 Lattice order parameter $l_n(t)$ as function of site n and time t. Solid trace: the 10 fs Gaussian pump pulse, dashed trace: excited electron density.

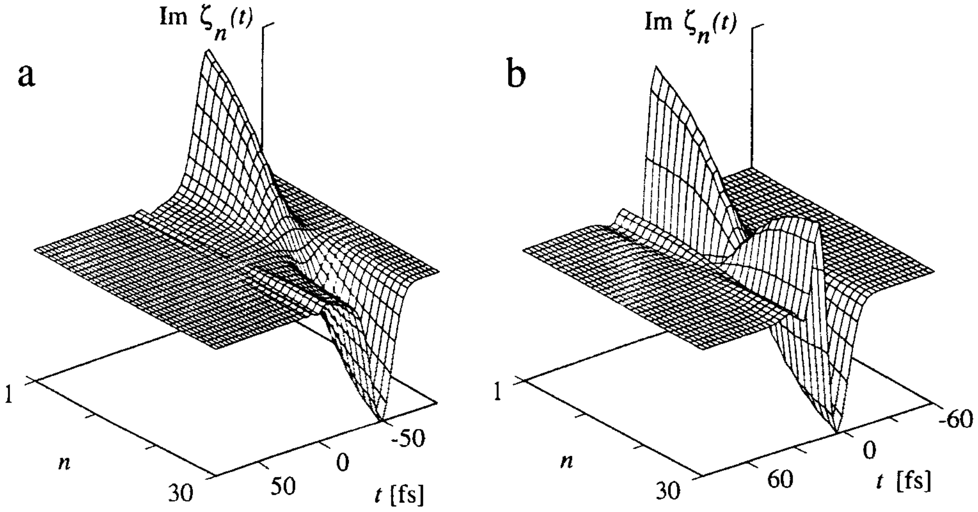

FIGURE 4 Imaginary part of the net charge density $\zeta_n(t)$ with time delay (a) $T_D = -50fs$ and (b) zero time delay as function of site n and time t.

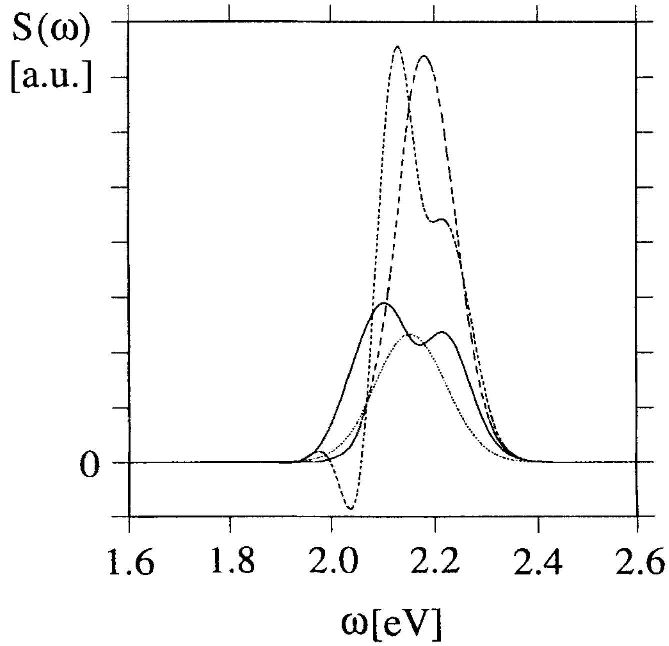

FIGURE 5 Pump-Probe signal $S(\omega)$ at different time delays. $T_D = -50fs$ (long dashed), $T_D = -20fs$ (short dashed), $T_D = 0$ (solid), $T_D = +50fs$ (dotted).

delay. For negative delays ($T_D = -50fs$) no appreciable charge density is excited in the system and therefore no lattice distortion is generated at that time. Consequently, the net charge density (Figure 4a) is dominated by excitonic effects (cp. Figure 2a). For zero time delay, the lattice distortion leads to temporal oscillations in the net charge density (Figure 4b). Since both the Coulomb interaction and the lattice distortion contribute to the lineshape, we call this feature excitonic polaron. The temporal oscillation of the charge density results in a splitting of the excitonic transition in the pump–probe signal for zero time delay (full curve of Figure 5), whereas for positive time delay $+50fs$ (dotted curve in Figure 5) a strong bleaching can be observed due to the saturation of the transitions. Furthermore, since the time delay is larger than the lifetime of the transient grating which is determined by the transverse relaxation time, the transient grating is almost destroyed at that time, and the influence of lattice distortions on electronic motions cannot be resolved by the grating. For this two reasons, the pump–probe signal shows a strong bleaching for positive time delays and the double peak structure induced by the excitonic polaron disappeares.

In conclusion, we have presented calculations of coherent femtosecond pump–probe signals of conjugated polymers in the half-filled case, using a density matrix approach and the time-dependent Hartree–Fock approximation. Electron–hole attraction results in the formation of charge–transfer excitons whereas the coupling of the electronic motion to lattice dynamics results in soliton like effects. For overlapping pulses the interplay between Coulomb interaction and lattice distortions results in the formation of excitonic polarons which show up as an additional feature in the femtosecond pump–probe signal for zero time delay. The method developed in this paper is applicable to a broad variety of nonlinear optical signals such as incoherent time resolved spectroscopy, photon echo techniques or continuous wave excitation.

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REFERENCES

1. W.-P. Su and J.R. Schrieffer, Proc. Natl. Acad. Sci. USA 77, 5626 (1980).
2. S. Abe, M. Schreiber and W.-P. Su, Chem. Phys. Lett. 192, 425 (1992).
3. M. Hartmann and S. Mukamel, J. Chem. Phys. 99, 1597 (1993).
4. M. Hartmann and S. Mukamel, submitted to J. Chem. Phys.