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Model of transient photoinduced absorption with an exciton polaron in conjugated polymers

V. A. Shakin, S. Abe, and Y. Shimoi
Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba 305, Japan

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A theoretical description of a spin-singlet exciton polaron is given by incorporating both electron-electron and electron-lattice interactions to discuss transient photoinduced absorption in conjugated polymers. Absorption spectra with transitions from a relaxed exciton polaron state as well as from an unrelaxed Franck-Condon state to higher-lying excited states were calculated within the frozen-lattice approximation and the configuration interaction among single and double excitations for chains of up to 24 sites. Main absorption peaks are situated in the region of relatively low photon energies for both unrelaxed and relaxed lattices, although the energy levels responsible for the peaks are different. After the lattice relaxation, oscillator strength is more concentrated on a single peak. [S0163-1829(98)01512-4]

I. INTRODUCTION

The nature of photoexcited states in conjugated polymers have been the subject of intensive experimental and theoretical investigations.[1] Some polymers such as poly(paraphenylene vinylene) (PPV) exhibit strong luminescence, which is frequently attributed to excitons. In nonluminescent polymers, excitons also are primary photoexcitations, but are subject to nonradiative recombination processes. On a very short time scale, a photogenerated singlet exciton is considered to undergo lattice relaxation to form an exciton polaron. On a longer time scale such a singlet dipole-allowed exciton may be converted either to a low-lying dipole-forbidden state (the so-called $2A_g$ state) or to a triplet state. The latter state has a long lifetime and can be detected by an induced midgap absorption. A previous theoretical study confirmed that the photoinduced absorption observed at about 1.4 eV in polydiacetylene and PPV are due to the triplet exciton polaron.[2] By contrast, the present paper deals with the short-time relaxation of a singlet exciton.

To reveal the dynamics of these processes, ultrafast spectroscopic pump-probe experiments have been carried out[3,4] for various polymers including polydiacetylene and polythiophene. The observed time dependencies were interpreted in terms of a configuration coordinate diagram for the formation of a self-trapped exciton (an exciton polaron). Similar experiments in PPV (Ref. 5) revealed that there is a broad induced absorption peak around 1.8 eV, which was attributed to a transition from an exciton state to a biexciton state on the basis of a model approximate calculation within an extended Hubbard hamiltonian. However, lattice relaxation was not taken into account in that calculation.

In the present paper we calculate the induced absorption spectrum of a singlet exciton polaron, by taking both electron-electron and electron-lattice interactions into account. In the previous study for a triplet exciton polaron,[2] we used the single-excitation configuration interaction (S-CI), which was rather good approximation for the dominant triplet-triplet absorption. Recent exact calculations using a valence bond basis support this point.[6] For a singlet exciton polaron, however, the S-CI is not enough, because of relatively high contribution of double excitations to the final states of the relevant optical transitions. Therefore, we use configuration interactions among single and double excitations (SD-CI) in the present paper.

Since the induced absorption spectrum reveals transitions from the optically pumped one-photon excited state to the two-photon excited states, it is directly related to so-called extra (or additional) resonances in the two-photon absorption spectrum.[7] The extra resonance can be observed if the photon energy equals the difference between energy levels of the one-photon and two-photon excited states of a polymer molecule. As shown in Ref. 7, the extra resonances in the two-photon absorption spectra can be considerably stronger than ''classic'' two-photon resonances, which correspond to the photon energy equal to the half of the excitation energy of two-photon excited states. They occur if a material under consideration has the longitudinal relaxation time much longer than the transverse relaxation time. Some conjugated polymers are well-known representatives of such materials.[3,8] In the present paper we demonstrate a correlation between the two-photon and induced absorption spectra.

II. MODEL AND CALCULATION METHOD

We consider a finite polymer chain of N sites with N π electrons (N is even). The energy structure of the polymer molecule is described by a parametrized Pariser-Parr-Pople (PPP) Hamiltonian

$$H=H_0+H_{e-e}+E, \tag{1a}$$

$$H_0=-\sum_{n=1}^{N-1}\sum_{s} t_{n+1,n}(a^{\dagger}_{n,s}a_{n+1,s}+a^{\dagger}_{n+1,s}a_{n,s}), \tag{1b}$$

$$\begin{aligned}H_{e-e}=&\sum_{n=1}^{N} U(a^{\dagger}_{n,\uparrow n,\uparrow}-\tfrac{1}{2})(a^{\dagger}_{n,\downarrow}a_{n,\downarrow}-\tfrac{1}{2})\\&+\frac{1}{2}\sum_{\substack{n,m\\(n\neq m)}}^{N}\sum_{s,s'} V_{nm}(a^{\dagger}_{n,s}a_{n,s}-\tfrac{1}{2})(a^{\dagger}_{m,s'}a_{m,s'}-\tfrac{1}{2}),\end{aligned} \tag{1c}$$

$$E=\frac{K}{2}\sum_{n=1}^{N-1}(u_{n+1}-u_n)^2. \tag{1d}$$

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Here, the first term in the r.h.s. of Eq. (1a), H_0, represents the transfer interaction. Operator $a^{\dagger}_{n,s}(a_{n,s})$ creates (annihilates) a π electron with spin s at the nth site. The transfer integral is defined here as

$$t_{n,n+1}=t-\alpha(u_{n+1}-u_n)+(-1)^{n-1}\delta t_{\mathrm{BK}}, \tag{2}$$

where t is the transfer integral for the mean bond length (in our calculation we use the mean bond length $a_0=1.4$ Å), u_n is lattice displacement at site n, and α is electron-lattice coupling. The last term in Eq. (2) is the symmetry-breaking Brazovskii-Kirova (BK) term, which assures the nondegeneracy of the ground state.[9] Expression (1c) corresponds to the electron-electron interaction. Here we use the Pople potential

$$V_{nm}=\frac{Va_0}{R_{nm}}, \tag{3}$$

where R_{nm} is a distance between sites n and m. Since V_{nm} varies slowly against R_{nm}, we neglect here a dependence on site displacement and assume $R_{nm}=a_0|n-m|$. U and V stand for the on-site and off-site coulomb coefficients, respectively. The last term, E, represents the elastic energy for the change of bond lengths with a force constant K. Since we consider a finite length polymer chain, the open boundary condition is imposed to the system.

A geometrical configuration of the polymer chain is determined by the value of u_n for different n. The equilibrium geometrical configuration for a particular molecular state is defined here as the one with the lowest energy of such state. For example, in the ground state such equilibrium configuration of a polymer chain with cyclic boundary condition is a perfect dimerization $u_n=(-1)^{n+1}u_0$ resulting from the Peierls instability. In the present paper we need to know the equilibrium geometrical configuration for two states: ground and lowest one-photon excited states. In general, to be consistent with a level of the CI calculation adopted here, the energy structure of a polymer molecule should be found in all cases within the SD-CI scheme. However, finding the energy structure just for a specific geometrical configuration of a molecule within the SD-CI calculation is already a very CPU time-consuming process, and we cannot afford using it for resolving the extremum problem that requires iteration processes. Therefore, for such a purpose we invoke here only the S-CI. At least for the lowest one-photon excited state, the validity of the S-CI can be justified by the fact that, according to the analysis made in Ref. 10, this state is composed mainly of singly excited states, so it can be described reliably in the framework of the S-CI. As for the ground state, we just assume for the equilibrium configuration a perfect dimerization (neglecting the chain end effect) and limit ourselves to the energy level of the Hartree-Fock (HF) ground state, which is equivalent to the S-CI ground state.

Even in the S-CI calculation, it still requires much computer time to determine a fully optimized lattice deformation in contrast to the HF calculation. Therefore we use a variational form[11] for the lattice displacement after the geometrical relaxation of a pumped molecule:

$$u_n=(-1)^{n+1}u'_n, \tag{4a}$$

$$u'_n=u_0\left\{1-Q\ \mathrm{sech}\left[\left(n-\frac{N+1}{2}\right)/\xi\right]\right\}. \tag{4b}$$

Here u_0 is a magnitude of the lattice displacement for the ideally dimerized molecule in the ground state, Q and ξ stand, respectively, for the amplitude and width of the exciton polaron, the center of which is located at the bond center between sites $N/2$ and $N/2+1$.

After fixing the geometrical configuration, the ground state and all excited states of the polymer chain are found numerically with the SD-CI calculation.[10] The molecules considered here are supposed to be symmetrical with respect to 180° rotation around the axis crossing the polymer chain perpendicularly at its center, and the assumed geometrical relaxation does not disturb this symmetry. Therefore, all the states can be divided into groups A and B, which correspond to the symmetrical and antisymmetrical states under such rotation, respectively.

III. RESULTS AND DISCUSSION

For the beginning we ignore the geometrical relaxation effects and consider a relation between the two-photon absorption and induced absorption spectra of an ideally dimerized polymer molecule. This means we consider, for the time being, the chain with the bond length modulation

$$y_n=u_{n+1}-u_n, \tag{5}$$

which has the same magnitude for all pairs of adjacent sites, $y_n=(-1)^n 2u_0=(-1)^n y_0$, and corresponds to a minimum of the Hartree-Fock ground-state energy. (As we mentioned already, the S-CI and HF methods both give the same energy of the ground state.) To calculate two-photon absorption spectra we use an expression for $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ based on the density matrix approach, that enables, unlike the Orr-Ward formula, to describe correctly the spectral regions around one-photon resonances as well as to take into consideration a plenty of additional resonances missed in the Orr-Ward formula.[7] The induced absorption is calculated as the linear absorption of optically pumped polymer molecule $\chi^{(1)}{}_{\mathrm{ind}}(\omega)$, assuming that the molecule is initially in the lowest one-photon excited state ($1B$ singlet). The geometrical configuration of the $1B$ state is kept the same as that of the ground state, i.e., the geometrical relaxation of the molecule after pumping to the equilibrium for the $1B$ state configuration has not yet occurred.

Figure 1 shows the calculation results for the polymer chain of $N=20$ sites with $t=1.65$ eV, $U=3t$, $V=1.3t$, $\alpha=4.2$ eV/Å, $K=50$ eV/Å^2, and $\delta t_{\mathrm{BK}}=0.05t$. For these parameters, optimized y_0 is found to be 0.0573 Å. The longitudinal damping constant Γ_1, which is the inverse of the longitudinal relaxation time, is here ten times smaller than the transverse damping constant Γ_2, and equals $0.002t/\hbar$. Such a ratio of the damping constants was chosen intentionally to make the additional resonances more pronounced. The upper line represents the imaginary part of $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ per site in units of $\chi_0^{(3)}$, and the lower line—the imaginary part of $\chi^{(1)}{}_{\mathrm{ind}}(\omega)$ per site in units of $\chi_0^{(1)}$. Normalization constants $\chi_0^{(1)}$ and $\chi_0^{(3)}$ are defined as

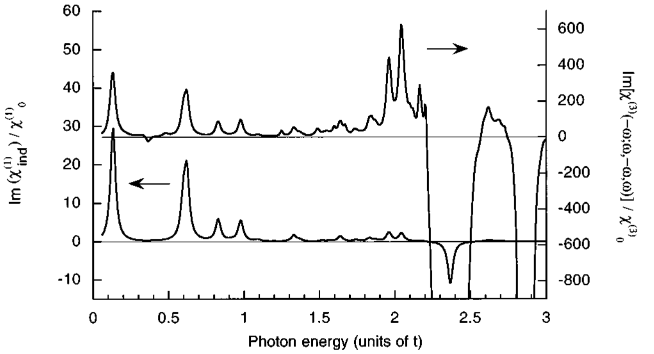

FIG. 1. The spectra of the two-photon absorption (upper plot) and induced absorption (lower plot) for the ideally dimerized polymer chain of $N=20$ sites with $t=1.65\,\mathrm{eV}$, $U=3t$, $V=1.3t$, $\alpha=4.2\,\mathrm{eV/Å}$, $K=50\,\mathrm{eV/Å}^2$ and $\delta t_{\mathrm{BK}}=0.05t$. For these parameters, a value of y_0 optimized for the ground state is found to be 0.0573 Å. The longitudinal and transverse damping constants Γ_1 and Γ_2 equal $0.002t/\hbar$ and $0.02t/\hbar$, respectively.

$$\chi_0^{(1)}=e^2a_0^2/t, \qquad\qquad (6)$$
$$\chi_0^{(3)}=e^4a_0^4/t^3,$$

where e is electron charge. It is easy to see that for every peak in the induced absorption spectrum there is a corresponding peak in the two-photon absorption spectrum. These peaks are those which we call additional or extra resonances, because they are missed in the commonly used Orr-Ward formula. Other peaks in the two-photon absorption spectrum are either ''classical'' two-photon resonances with the photon energy equal to the half of the excitation energy of the two-photon excited states or other additional resonances involving transitions from nB states with $n>1$. At the photon energy corresponding to the excitation energy of the $1B$ state, the induced absorption spectrum demonstrates a negative peak, which is related to the induced emission. It should be noted, that in the pump-probe experimental spectra such a negative part is explained mainly by a decrease of the number of molecules in the ground state after the pumping rather than by induced emission, which requires special experimental facilities to be observed.

However, the energy of the $1B$ singlet with an ideally dimerized configuration is not the lowest one, and this configuration cannot be considered as an equilibrium. To find the equilibrium geometrical configuration [i.e., parameters Q and ξ in Eq. (4b)] we have solved numerically the extremum problem for the absolute (but not excitation) energy of the $1B$ singlet state in the framework of the S-CI. Figure 2 shows the calculated exciton polaron parameters as functions of the number of sites in the polymer chain. Until the number of sites becomes approximately 60, the width of the exciton polaron quickly increases with N while the exciton polaron amplitude also quickly decreases. The polaron looks like spreading over the whole chain and becoming delocalized with the chain becoming longer. But in the chains with more than 80 sites the polaron is already a well-localized geometrical lattice distortion with a width of about 5 bond lengths, and it's parameters Q and ξ seem to approach asymptotically to constant values with increasing N.

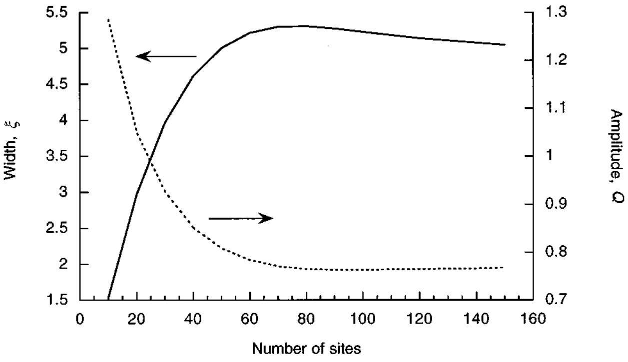

FIG. 2. The width and the amplitude of the exciton polaron as a function of the polymer chain size. The exciton polaron is situated in the center of the chain and corresponds to a minimum of the molecule energy in the $1B$ state. The chain parameters, other than N, are the same as in Fig. 1.

If a delay time between pump and probe beams is long enough for the geometrical relaxation, i.e., the creation of a polaron, to occur before the probe beam comes, the induced absorption spectrum is expected to be different from the spectrum of the ideally dimerized molecule. Figure 3 shows the induced absorption spectra of the ideally dimerized (dashed line) and relaxed (solid line) polymer chains with the same parameters as in Fig. 1. In the lower part of Fig. 3 we present as a reference the linear absorption spectrum of the ideally dimerized molecule. Figure 3(a) shows the spectra in terms of the dielectric susceptibility, while Fig. 3(b) demonstrates corresponding absorption coefficients (in arbitrary units), which are proportional to the susceptibilities multiplied by the photon energy.

The equilibrium geometrical configuration of the relaxed molecule in $1B$ state is found to be the exciton polaron with amplitude $Q=1.05$ and width $\xi=2.98$. Figure 3 clearly demonstrates that the energy difference between the $1B$ state and the ground state in the polymer chain with an exciton polaron (it corresponds to the position of the negative solid line peak) is less than the excitation energy of the $1B$ state in the unrelaxed molecule (the first peak of the linear absorption spectrum or the position of the negative dashed line peak). This should be observed as a Stokes shift of luminescence in photoluminescence experiments.

The next important feature that should be noted here is a location of main peaks in the induced absorption spectra. Both in the unrelaxed and relaxed molecules the strongest positive peaks are situated in the spectral range of rather low photon energies. Therefore, we suggest experimentalists to pay more attention to the low-energy range of the induced absorption spectra, where the strongest signal is expected, rather than to the region around the pumped one-photon resonance. Experimental evidence of a strong signal in the low-energy range of the photoinduced absorption spectra is found in Refs. 12 and 13. In Ref. 12 the oriented M-PPV [poly(2-methoxy-1,4-phenylene vinylene)] films were investigated, but unfortunately, the spectral range registered in the experiment was too narrow to capture all features of the low-energy band. More informative spectra of the induced absorption are presented in Ref. 13, which deals with DOO-PPV (dioctyloxy PPV). However, there are still very few

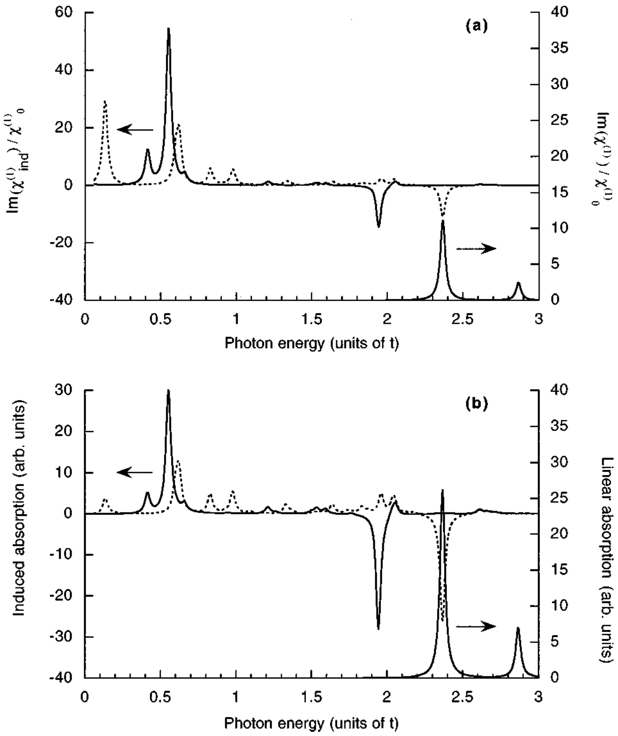

FIG. 3. The induced absorption spectra of the ideally dimerized polymer chain, i.e., before the geometrical relaxation (dashed line) and that of the molecule with the exciton polaron created, i.e., after the geometrical relaxation (solid line). In the lower part we present as a reference the linear absorption spectrum of the ideally dimerized molecule. (a) shows the spectra in terms of the dielectrical susceptibility, and (b) demonstrates absorption coefficients, that differ from the corresponding susceptibilities by factor of photon energy. The chain parameters are the same as in Fig. 1.

experimental data for the low-energy region, and we hope in future much more experimental spectra will be available for a theoretical analysis.

Before we discuss the structure of the low-energy region in detail, it is important to remember that the molecular energy levels are obtained here within the framework of the SD but not full CI calculation, because the latter cannot be realized for systems of such size even by using modern computers. However, we believe that the size of the polymer chains considered here is not too large and enables us to capture a general picture correctly, while some circumstances might be different from results of the full CI calculation, which is the only one among other CI calculations that is size consistent. For details see, for example, Ref. 10.

As one can see in Fig. 3, the spectra for the unrelaxed and relaxed molecules differ significantly. In the unrelaxed molecule there are few peaks distributed over relatively wide spectral region (about $2t$), while for the exciton polaron there is a single strong resonance peak accompanied by a pair of much smaller peaks situated in its vicinity. The nature of the peaks is different as well. For the unrelaxed molecule, the two strongest peaks at $0.13t$ and $0.62t$ are due to transitions from the $1B$ state to the $2A$ and $6A$ states, respectively, and the contribution of double excitations to these states (a strict definition of such contribution is given in Ref. 10) is, respectively, 28% and 38% (their contribution to the $1B$ state is only 4%). In the case of the relaxed molecule, the two strongest peaks are situated at $0.41t$ and $0.55t$ and correspond to the $3A$ and $5A$ states, respectively, and the second is much stronger than the first. Double excitations become drastically important after the lattice relaxation, because their contribution to these states is 52% and 67%, respectively (the contribution to the $1B$ state is still very small—only 5%). We do not show here the photon energy region close to zero (<0.1 eV), because it is out of practical interest, but for the sake of completeness we should note that the $2A$ peak is situated at $0.008t$ with intensity about half of the $3A$ peak in the susceptibility spectrum and is negligibly small in the spectrum of the induced absorption coefficient.

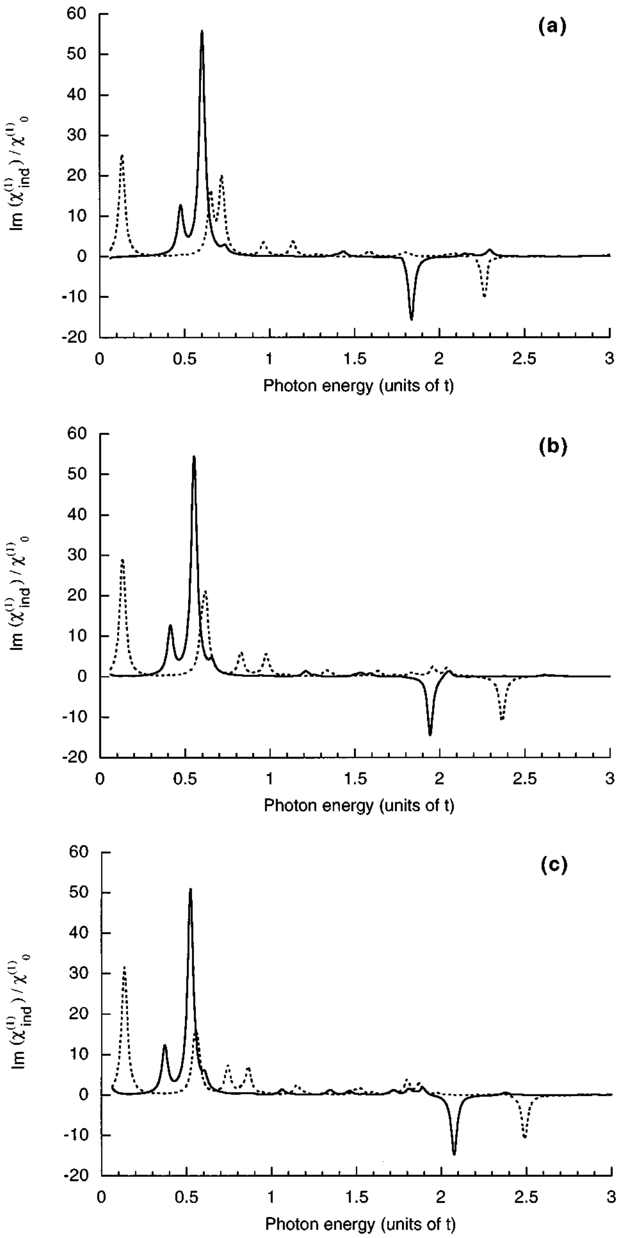

FIG. 4. The induced absorption spectra for the polymer chains of (a) $N=16$, (b) $N=20$, and (c) $N=24$ sites before (dashed) and after (solid) geometrical relaxation. Parameters of the chains, other than N, are the same as in Fig. 1.

Of course, the structure of the induced absorption spectrum described above can be a specific feature of a certain molecule. To be able to make a kind of generalization we should vary some parameter of the chain (for example, the number of sites). In Fig. 4 we present calculation data on the induced absorption spectra for three polymer chains distinguished only by the number of sites in the chain. Those are (a) $N=16$, (b) $N=20$, (c) $N=24$. All other parameters are the same as in Fig. 1. It is easy to see that the localization of main peaks is not affected to a great extent by changing the number of sites in the polymer chain. From Fig. 4, the low-energy region seems to be the most interesting spectral range in the pump-probe experiments with conjugated polymers. Another important feature is the position of the largest peak in the induced absorption spectra of relaxed molecules. It is hardly affected by changing the number of sites; therefore the inhomogeneous broadening due to a variation of the chain length is not expected to be a serious problem here. Another feature practically independent of the size of the molecule is a value of the Stokes shift. The distance between the solid and dashed negative peaks is almost the same for all three Figs. 4(a)–4(c), in spite of the fact that the polaron shape is rapidly varying in this range of N (see Fig. 2).

IV. CONCLUSIONS

We have theoretically studied photoinduced absorption spectra of polymer chains with up to 24 sites. The spectra have been calculated for both the unrelaxed and relaxed geometrical configurations of the excited molecule. The general feature common for both cases is the location of the main absorption peaks in the spectral region corresponding to relatively low photon energy. However, the origin of those peaks is slightly different. The contribution of double excitations to the relevant two-photon excited states is drastically increased after relaxation, demonstrating the importance of biexcitonic states in the process of photoinduced absorption for polymers with an exciton polaron created. Within the model considered here, the main absorption peak position and the Stokes shift are not sensitive to the chain length.

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