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Transient photoinduced absorption of one-dimensional excitons and biexcitons during lattice relaxation

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Abstract. Transient photoinduced absorption spectra of one-dimensional excitons and biexcitons coupled with lattice vibrations are calculated with a two-band model by molecular dynamics. It is shown that the absorption peaks corresponding to the transition from photoexcited B_u excitons to A_g excitons and the lowest biexciton shift as self-trapping proceeds, where the former shifts to higher energy and the latter to lower energy. This difference is understood by means of the relaxation energy of B_u , A_g excitons and the biexciton. The transient absorbance change near the $B_u \rightarrow A_g$ peak is also discussed.

Recent progress in ultrafast spectroscopy has made it possible to observe the initial relaxation processes of photoexcited states [1]. Most notably, the dynamics of the self-trapping process of excitons in polydiacetylenes (PDA) has been investigated with ultrashort pulse lasers, and the self-trapping was found to take place typically in ~ 100 fs [2]. However, the following arguments have prevented an understanding of the dynamics of the lattice relaxation process of excitons in PDA. According to the experimental results, excitons in PDA strongly couple with the stretching mode of the $C \equiv C$ bond, for which the period of the lattice vibration is ~ 10 fs [2]. Since there is no potential barrier between a free exciton and a self-trapped exciton (STE) in one-dimensional (1D) systems [3], lattice relaxation is expected to take place within a couple of lattice vibration periods, i.e. the relaxation time of the self-trapping process is expected to be ~ 10 fs.

We have studied these features of the self-trapping process of 1D excitons and shown that the experimentally observed *long* relaxation time is due to the initial relaxation process of an exciton in a free state, interacting with the lattice vibration with the longest wavelength [4].

Transient photoinduced absorption (PA) spectra are usually observed in pump-probe experiments to investigate the evolution of electronic states as the lattice relaxation proceeds [2]. Peaks in PA spectra are assigned to transitions between two electronic states, which facilitates an understanding of the dynamical behaviour of the photoexcited states. For example, Yoshizawa and co-workers [5] assigned PA peaks in PDA-4BCM to transitions from the photoexcited B_u exciton to an A_g exciton and a biexciton state. However, those assignments have not yet been well established, partly because theoretical calculations have not been performed to confirm them. Hence, it is important to make transient PA peaks correspond to transitions between electronic states in order to understand the relaxation dynamics of photoexcited carriers or excitons.

To study the PA spectra, we should consider higher excited states than the lowest exciton, which are the final states of PA processes. Although many authors [6] have studied the energy relaxation of the lowest exciton, which is the initial state of PA processes studied in

the present paper, the behaviour of other excited states as the lattice relaxation proceeds has not been discussed. Therefore, one of the aims of the present paper is to study the relaxation of higher excited states accompanied by the self-trapping of the lowest B_u exciton.

In this paper we show the calculated results of the transient optical properties of 1D excitons in the course of self-trapping, particularly focusing on the PA spectra below the excitonic peak in the linear absorption spectra. A two-band model coupled with an optical vibration mode is employed for the present purpose. The Hamiltonian is described in standard notation by [4, 7]

$$\begin{aligned} \mathcal{H} = & -t_e \sum_{i\sigma} (a_{i+1\sigma}^\dagger a_{i\sigma} + \text{HC}) - t_h \sum_{i\sigma} (c_{i+1\sigma}^\dagger c_{i\sigma} + \text{HC}) \\ & + \sum_{\substack{i \\ \sigma\sigma'}} U(|i-j|) (a_{i\sigma}^\dagger a_{i\sigma} a_{j\sigma'}^\dagger a_{j\sigma'} + c_{i\sigma}^\dagger c_{i\sigma} c_{j\sigma'}^\dagger c_{j\sigma'} - a_{i\sigma}^\dagger a_{i\sigma} c_{j\sigma'}^\dagger c_{j\sigma'}) \\ & + \frac{1}{2} \sum_i (p_i^2 + \Omega_1^2 u_i^2 + \Omega_2^2 u_i u_{i+1}) + \sum_{i\sigma} u_i (\alpha a_{i\sigma}^\dagger a_{i\sigma} + \beta c_{i\sigma}^\dagger c_{i\sigma}) \end{aligned} \quad (1)$$

where

$$U(n) = \begin{cases} U_0 & n = 0 \\ U_1/n & n \neq 0 \end{cases} \quad U_0 > U_1 > 0. \quad (2)$$

The values of the parameters are $t_e = t_h = 1$, $\Omega_1 = 0.15$, $\Omega_2 = 0.08$, $U_0 = 2$, $U_1 = 1.6$ and $\alpha = \beta = 0.11$. We define a dimensionless electron-phonon coupling constant as $s = \alpha^2/t_e \omega_0^2 = 0.42$, where $\omega_0^2 = \Omega_1^2 + \Omega_2^2$. Taking $t_e \sim 1$ eV, we can reproduce the experimental results of spectroscopy [2] and the calculated results of the electronic structure of PDA [8]. The unit of time τ_0 is given by $\tau_0 = \hbar/t_e$. A schematic view of the model is shown in figure 1.

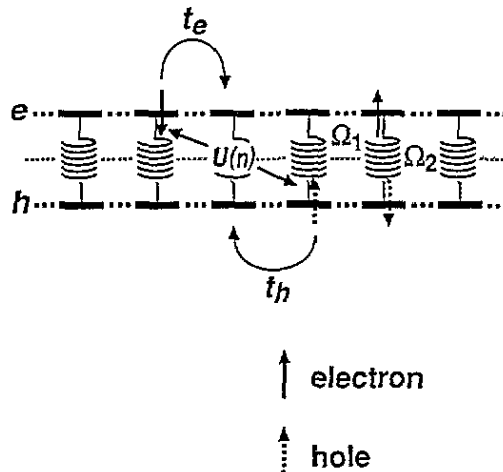


Figure 1. A schematic view of the model.

We performed a molecular dynamics (MD) simulation [9] in the one-electron-one-hole subspace with an adiabatic approximation, and calculated the dynamics of self-trapping processes of a B_u exciton [4]. We do not take into account the exchange interaction between

an electron and a hole, and thus we can regard the spin state of the electron–hole pair as a singlet state. Furthermore, since the charge transfer states were fully taken into account in the calculation, we can observe the change in both the translational motion and the relative motion of the electron and hole. In calculating PA spectra, we took a biexciton state as well as higher exciton states as the final state. The biexciton state mentioned here is the lowest state with two electrons and two holes on a deformed lattice. Since we applied the Frank–Condon principle in calculating the PA spectra, the lattice deformation does not differ between the initial state and the final state of PA, and thus the two-electron–two-hole states which are the final states are calculated with the lattice deformation fixed to that used to calculate the excitons by the Lanczos method at each MD step when the PA spectra are calculated. Since we call this two-electron–two-hole state a biexciton in this paper, it is generally different from the two-electron–two-hole state in which the lattice equilibrates with the electronic system, even when an STE is formed with the same lattice deformation. In this context we also define the ‘relaxed lattice’ as the deformed lattice which equilibrates with the lowest exciton.

The transient absorption spectra are shown in figure 2. It is seen that the PA spectrum at each time has two distinct peaks accompanied by lower one(s), where the one at lower energy (peak 1) corresponds to the transition to the biexciton state, and the one at higher energy (peak 2) appears due to the transition to an A_g exciton state. Lower peaks appearing before the lattice begins to deform correspond to the transition to the other exciton states. As the self-trapping of the lowest B_u exciton proceeds, its wavefunction becomes spatially localized. As a result, the more spatially extended the final state of photoinduced absorption is, the smaller the transition dipole moment is. Hence, the transition dipole moment to higher A_g exciton states are suppressed more than the lowest one, and thus the PA peaks corresponding to those transitions become invisible as the self-trapping proceeds and only peak 1 remains due to the sum rule for transition dipole matrix elements.

First, we discuss the temporal behaviour of peaks 1 and 2. Figure 2 shows that peak 1 shifts to higher energy when the self-trapping process takes place, while peak 2 shifts to lower energy. They both start to move after $\sim 60\tau_0$ from the photoexcitation by the pump beam, and the energy shift is completed within $\sim 20\tau_0$ except that the oscillation due to the excess energy possessed by the lattice vibration mode remains. This temporal behaviour of peaks 1 and 2 can be understood by comparing with the energy relaxation of the photoexcited B_u exciton shown in the inset of figure 2, which shows that the energy relaxation takes place through three processes [4]. When the excited B_u exciton stays free, either of peaks 1 or 2 does not move. They shift concomitantly with the lattice relaxation until the self-trapping process of the B_u exciton is completed, and vibration around an equilibrium position of each peak is then observed.

To show the dynamical behaviour of the PA peaks more clearly, we show in figure 3 the transient absorbance change for $\hbar\omega = 1.05$, which corresponds to peak 1 on the completely relaxed lattice. The absorbance change does not appear for the first $60\tau_0$, which amounts to several periods of the lattice vibration. This is due to the first process of the relaxation dynamics of an exciton, in which an exciton remains free, interacting with the lattice vibration mode with the longest wavelength [4]. Then, as the local deformation of the lattice grows to form an STE, peak 1 shifts to higher energy and the absorbance change appears and saturates within a period of the lattice vibration, i.e. the change in PA spectra follows the formation of an STE. As a whole, the relaxation time of the absorbance change is observed to be $\sim 100\tau_0$. Since, however, the relaxation process is non-linear, a simple exponential form is no longer suitable for describing the dynamical behaviour of the absorbance change.

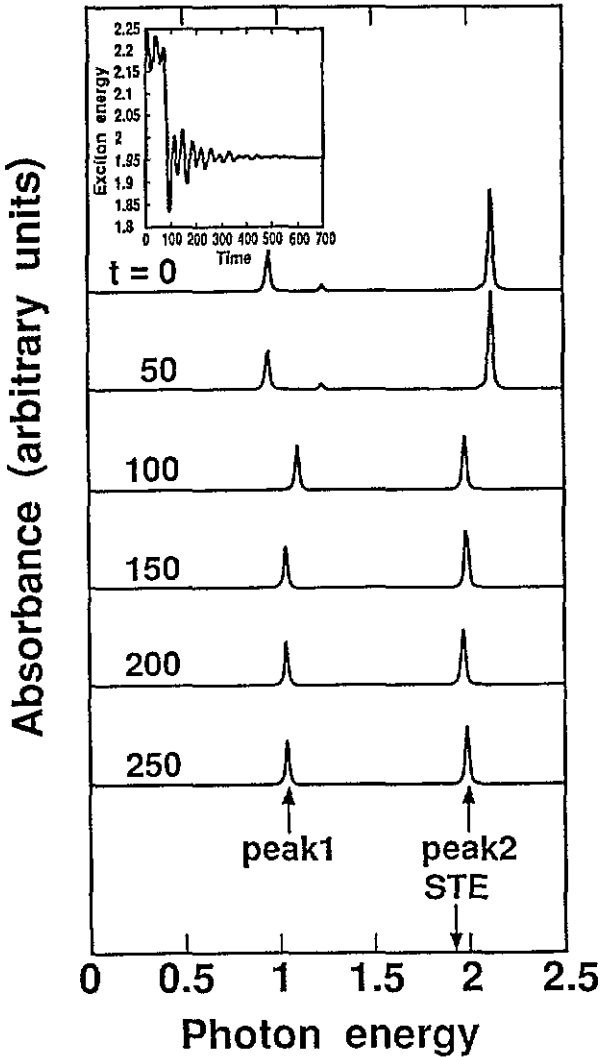


Figure 2. The transient optical absorption spectra. Peaks 1 and 2 correspond to the transition to an A_g exciton and the biexciton, respectively. The energy of an STE is indicated by an arrow. Inset: energy relaxation as a function of time (see [4]).

Evolution in experimental techniques is required to make the detailed investigation of the initial relaxation processes possible.

We now discuss the difference in the temporal behaviour of peaks 1 and 2. A distinct difference between them is that peak 1 shifts to higher energy as the lattice relaxation takes place, while peak 2 shifts to lower energy. To understand the origin of this difference, we study the energetics of exciton states and the biexciton state in self-trapping. First, we note that the difference of the relaxation energy between the initial and the final state of PA is equal to the amount of the transient peak shift, where the former corresponds to the lowest B_u exciton and the latter to an A_g exciton for peak 1 and the biexciton for peak 2. According to the calculated results, the total amount of the peak shift caused by the self-trapping is ~ 0.098 for peak 1 and ~ 0.20 for peak 2, which are smaller than the Stokes shift, $E_S(\sim 0.29)$; see the inset of figure 2. Figure 4 schematically shows the profile of the energy relaxation of the B_u and A_g exciton states and the biexciton state. We have estimated the relaxation energy of an A_g exciton, δE_1 , and that of the biexciton, δE_2 , as $\delta E_1 \sim 0.19$

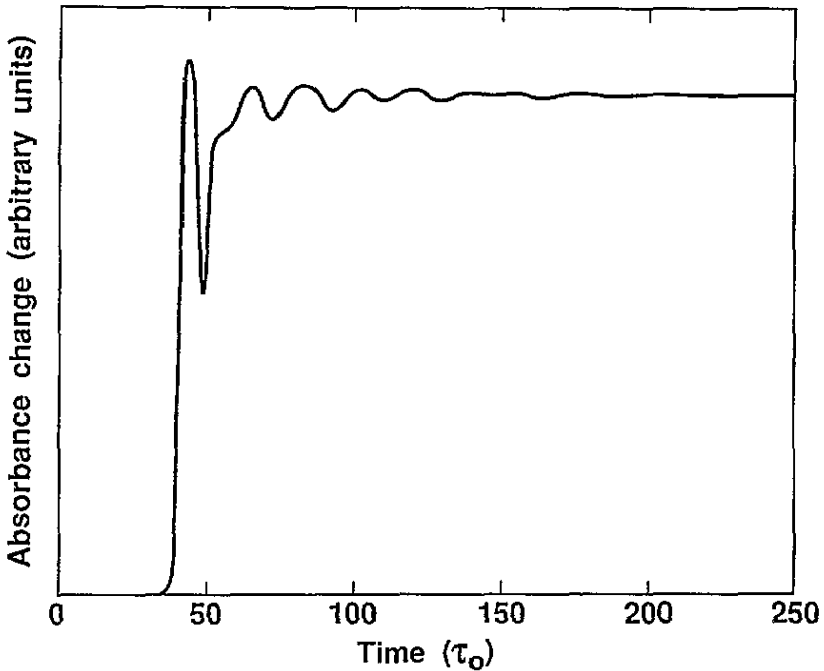


Figure 3. The time dependence of the absorbance change for $\omega = 1.05$.

and $\delta E_2 \sim 0.39$.

We can understand that $\Delta E_{PA} (\equiv E_S - \delta E_1)$, the energy shift of peak 1, is always positive, in view of the fact that the relative motion of the electron and hole of A_g states spatially extends more than that of the lowest B_u state [7]. In the present case the lattice deformation spatially extends over several sites [4], and the spatial extension of the electron-hole relative motion is much larger than that of the lattice deformation except for the lowest B_u state. On the other hand, excitons on a deformed lattice can be regarded as confined in a potential well induced by the lattice deformation, i.e. the last term of (1) can be interpreted as a potential well for the electronic system if the lattice deformation is fixed. Hence, the energy gain from the potential for the lowest B_u exciton is larger than any other excitons with spatially more extended relative motion wavefunction. In other words, the deformation of the lattice takes place so as to minimize the energy of the photoexcited B_u state, and thus the energy gain owing to the lattice deformation is largest for the lowest B_u exciton, i.e. the real excitation. Hence, the Stokes shift E_S is always larger than the relaxation energy of A_g states δE_1 , and peak 1, the peak in PA spectra corresponding to the $B_u \rightarrow A_g$ transition, always shifts to higher energy during the self-trapping process.

On the other hand, E_S is always smaller than δE_2 as explained in the following. Since there are two electrons and two holes in the biexciton state, the energy gain from the electron-phonon interaction is expected to be approximately twice as large as that for single-exciton states. To discuss whether this rough estimate is acceptable or not, we first define the binding energy of the biexciton when the electron-phonon interaction is taken into account. Usually the binding energy of a biexciton that does not interact with a lattice vibration is defined by [7]

$$E_B^0 = 2E_{ex}^0 - E_{biex}^0 \quad (3)$$

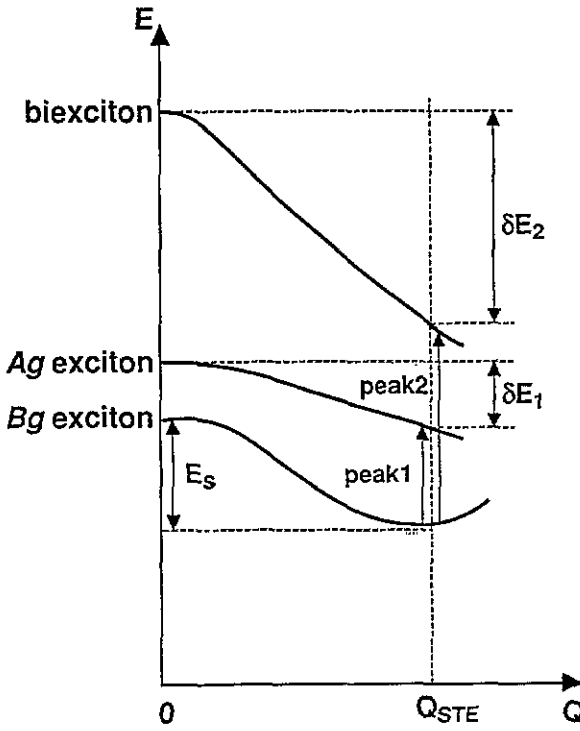


Figure 4. A schematic view of the relaxation energy of the B_u and A_g excitons and the biexciton. $\Delta E_{PA} (= E_S - \delta E_1)$ and $\Delta E_{PA}^{biex} (= E_S - \delta E_2)$ are equal to the shifts of peaks 1 and 2 shown in figure 2, respectively.

where E_{ex}^0 and E_{biex}^0 represent the energy of the lowest exciton and a biexciton, respectively.

When the electronic system is interacting with phonons, we should carefully treat (3) to discuss the binding energy of a biexciton. Since the deformation of the lattice which equilibrates with the electronic system is different for a single exciton and a biexciton, it does not make sense to discuss the binding energy of a biexciton as a static property, i.e. either a single exciton state or a biexciton state is always in non-equilibrium with the lattice for any deformation of the lattice. However, for the sake of convenience in the discussion below, we define the binding energy of a biexciton interacting with phonons E'_B as

$$E'_B(\{u_i\}) = 2E_{ex}(\{u_i\}) - E_{biex}(\{u_i\}) \tag{4}$$

where the lattice deformation is taken to be the same for a single exciton state and a biexciton state in calculating the right-hand side of the equation.

$E'_B(\{u_i\})$ originates from the exchange interaction between electrons or holes as in the biexcitons without electron-phonon interactions [7], and from the deformation of the wavefunction due to the electron-phonon interaction. In the present case, however, the latter effect is negligible, as explained below, and $E'_B(\{u_i\})$ is comparable to E_B^0 . Thus (3) and (4) lead to the following equation for δE_2 :

$$\delta E_2 = E_{biex}^0 - E_{biex}(\{u_i\}) \sim 2E_S. \tag{5}$$

In the present case, $E_B = 0.094$ [7] and $\delta E_2 \sim 1.8E_S$.

The binding energy of the biexciton on the relaxed lattice $E'_B(\{u_i^{relaxed}\})$ is ~ 0.13 , which is larger than E_B^0 . Thus biexcitons are easier to observe on a deformed lattice, i.e. the transient photoinduced absorption spectra are a more appropriate property to detect

biexcitons than the usual two-photon absorption spectra, particularly when the electron-phonon interaction is strong. To understand the increase in the binding energy of the biexciton, we first compare the spatial extension of the lattice and the hole-hole correlation function (the size of the biexciton) in the free biexciton [7]. Since in the present case they are comparable, the binding energy of the biexciton is not reduced by the deformation of the wavefunction, which increases the loss of kinetic energy. On the contrary, since the energy gain from electron-lattice interaction effectively reduces the repulsion between electrons (holes), the four fermions become more tightly bound, and $E'_B(\{u_i\})$ increases. Nevertheless, we stress that the results obtained in this paper are general and are not restricted to the study of polydiacetylenes as long as the s is not too strong to deform the exciton wavefunction considerably. If, however, the electron-lattice interaction is so strong that the lattice deformation is less extended than the hole-hole correlation function, the wavefunction of the biexciton is shrunk by the lattice deformation and the energy loss due to the kinetic energy and the Coulomb energy is no longer negligible. This problem will be studied elsewhere.

In summary, we have calculated the transient photoinduced absorption spectra corresponding to the transition from the photoexcited B_u exciton to A_g excitons and the biexciton. The PA peak corresponding to the $B_u \rightarrow A_g$ transition always shifts to higher energy as the lattice relaxation proceeds, reflecting the fact that the lattice deformation takes place so as to maximize the energy gain of the lowest B_u state. Since ΔE_{PA} is still finite, the peak shift in PA spectra is smaller than the Stokes shift, for example $\Delta E_{PA} \sim 0.34 E_S$. On the other hand, the PA peak due to the transition from the lowest B_u exciton to the biexciton shifts to lower energy as an STE is formed. The energy gain for the biexciton is $\sim 1.8 E_S$. The transient absorbance change at the energy of the PA peak (due to the $B_u \rightarrow A_g$ transition) after relaxation was also calculated, to reveal the dynamical behaviour of the PA spectra.

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