A NEW DOMINO MECHANISM OF PHOTOINDUCED PHASE TRANSITIONS IN ONE-DIMENSIONAL SYSTEMS: EFFECT OF LATTICE OSCILLATIONS IN AN EXCITED ELECTRONIC STATE

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The photoinduced domino effect for the phase transition dynamics in one-dimensional electron-lattice systems is investigated to clarify the dependence on the friction and interaction between neighboring sites. We find a novel photoinduced domino process in the case of strong intersite interaction and weak friction. In this domino motion, the photoexcited site is still *in an excited electronic state,* which is in striking contrast to the conventional domino. This mechanism explains the photoinduced phase transitions in systems which have a large-size nucleus of the developing new phase.

Introduction

A typical cause for the phase transition development is considered to be thermal fluctuations. In recent years, however, many exotic materials are successively found, where a macroscopic phase transition is induced also by photoinjection of excitations into crystals. Such phenomena are called photoinduced phase transitions [1], which attract much attention from both the chemical and physical points of view. Such phenomena have been found in some materials with multistability, e.g., charge-transfer complexes [2, 3], π-conjugated polymers [4, 5], spin-crossover complexes [6], etc. The multistability of a system as well as the interaction among constituents is brought about by different physical mechanisms in each material, and thus the phenomena have not been understood from a unified viewpoint. One of such phenomena, which is most clearly understood on the base of the Peierls mechanism through the electron-lattice interaction, is the photoinduced structural phase transition in quasi-one-dimensional electron-lattice systems such as π-conjugated polymers [7, 8] and metal-halogen chains [9, 10].

In the recent papers [11, 12], a model of photoinduced phase transition in one-dimensional systems was proposed and investigated in detail. In the model of many atoms (molecules) with two locally-stable electronic states coupled to the lattice degree of freedom, a structural change is brought about by lattice relaxation after photoexcitation of a few sites. It is important that the energy, which is released after the lattice motion to a new stable position, is transferred to the next site to move it to a new position. This mechanism was called the 'domino process“.

In this paper, physical processes in the domino mechanism are analyzed in detail with respect to system parameters. Main attention is paid to the case of strong interaction between sites and weak friction (large energy-dissipation time). This case has not been investigated so far in detail; some results for this case were reported in [13], where the accelerated motion of the phase boundary was predicted. This parameter region might be more important in some cases. First, strong intersite interaction means that a new-phase nucleus should have large size, therefore, it is interesting to know when one-photon absorption may create a nucleus of large size of the new phase. Secondly, the case of weak friction may be often realized in nature. For example, if the atom in an excited state has a frequency of lattice oscillations of order of 10^{14} s^{-1}, the energy-dissipation rate less than 10^{12} s^{-1} can be considered as small.

1. Theoretical Model in the Adiabatic Approximation

Let us consider a one-dimensional chain of molecules with two electronic levels coupled to the classical lattice.

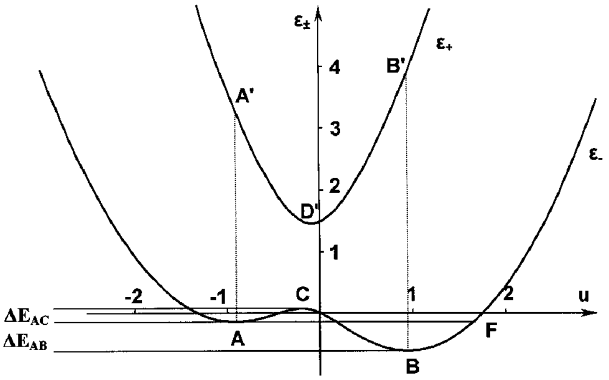


Fig.1. Local adiabatic potentials $\varepsilon_+(u)$ and $\varepsilon_-(u)$ as a function of the lattice distortion (atom position) u

In a molecule (at a site), some atoms are relevant to the phase transition but the others are irrelevan. We assume that the motion of the relevant atoms is characterized by one configurational coordinate u_j. To describe photoinduced cooperative structural changes, we must take into account both intrasite and intersite interactions. We assume that the intrasite interaction depends on local electronic states. We assume also that, at a site, there are two potential minima in the ground state and one minimum in an excited state. Such a potential of the intrasite interaction was obtained in [12] using the adiabatic approximation.

We start with the expression of the local adiabatic potential obtained in [12]:

$$\varepsilon_\pm(u_j) = u_j^2 + \frac{\varepsilon}{2} \pm \sqrt{\left(\frac{\varepsilon}{2} - 2u_j\right)^2 + t^2}\,, \qquad (1)$$

where u_j is the configurational coordinate of the jth site. Thus, in the model used, we can imagine the behavior of a single site as the one-dimensional movement of an atom in the potential $\varepsilon_\pm(u_i)$. The sign $+\,(-)$ corresponds to the excited (ground) electronic state. In [12], ε denotes the energy difference between two potential minima, and t is the off-diagonal matrix element that affects mostly the height of a potential barrier between minima. All the values are given in dimensionless variables, which have been determined in [12].

The potential $\varepsilon_\pm(u_i)$ is presented in Fig.1 for, e.g., $\varepsilon = -0.5$ and $t = 1.1$ and shows two minima in the ground state and one minimum in the excited state. There are some important values (see Fig.1): the energy barriers $\Delta\varepsilon_{AC}(=0.038)$, $\Delta\varepsilon_{BC}(=0.45)$; the energy differences between the excited and the ground states $\Delta\varepsilon_{AA'}(=3.33)$, $\Delta\varepsilon_{DD'}(=2.21)$. The difference $\Delta\varepsilon_{AA'} - \Delta\varepsilon_{DD'}$ is the well-known Stokes shift.

The total adiabatic-potential energy of the system is determined by the intrasite interaction $\varepsilon_\pm(u_i)$ and the interaction between different i and j sites, $U(u_i - u_j)$, as

$$E_\pm(\{u_j\}) = \varepsilon_\pm(u_0) + \sum_{j\neq 0} \varepsilon_-(u_j) + \sum_{i>j} U(u_i - u_j). \qquad (2)$$

Here, the sign $+\,(-)$ on the left-hand side corresponds to the same sign on the right-hand side. The sign $+$ means the chain, in which only the zeroth site is in the excited electronic state. The E_- describes the total adiabatic energy when all molecules are in the ground state.

We take into account the intersite interaction only between a site and the nearest sites in the harmonic approximation:

$$U(u_i - u_j) = k(u_i - u_j)^2 \delta_{|i-j|,1}. \qquad (3)$$

If every atom of the chain is located at minimum A, we call the state of the system as phase A. In phase B, all atoms are localized at minimum B. Phase A is assumed here to have a larger energy than phase B; phase A is metastable and phase B is absolutely stable.

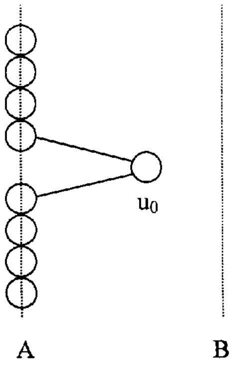
The energy barrier $\Delta\varepsilon_{AC}$ separates two potential minima A and B. But interaction (3) with neighbors prevents an atom from overcoming this barrier. This fact is illustrated in Fig.2, where the total adiabatic energy is drawn as a function of the displacement of only one atom while the other atoms are fixed at minimum A. It is seen that, depending on the interaction coefficient k, the atom may have one or two minima and is always localized at the lowest minimum.

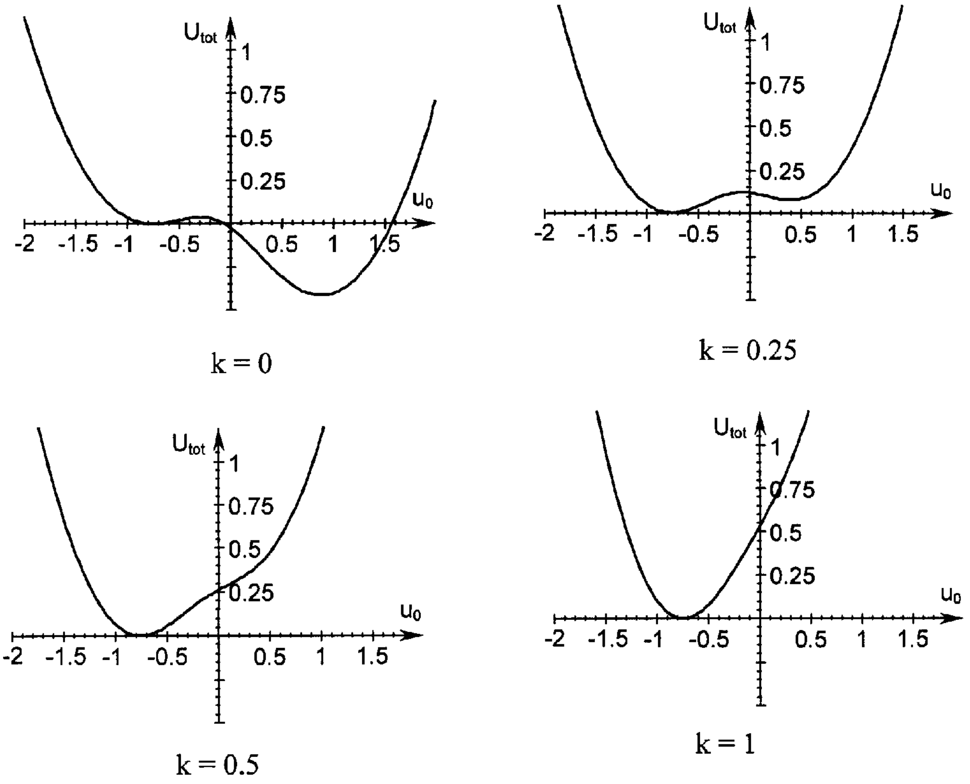
In order to start a phase transition, several atoms must be shifted from minimum A toward minimum B, i.e., a nucleus of the new phase must be created and grow. The size of a nucleus increases with the interaction strength, which reduces the probability of a thermally-activated phase transition.

2. Domino Mechanisms of Photoinduced Phase Transition

2.1. Conventional Domino Process in the Strong Friction Case

Similarly to [11 – 13], we first consider the photoinduced transition of atoms from position A to B in the case of strong friction (the overdamped case). As a result of photoabsorption only at the zeroth site, this molecule is photoexcited to the excited electronic state. According to the Franck – Condon principle, the motion of the lattice is negligible during the transition, so the transition is represented by the vertical arrows from point A to A' in Fig.1. Then the





k = 0 k = 0.25 k = 0.5 k = 1

Fi.2. Total adiabatic energy as a function of the lattice distortion of the photoexcited (zeroth) site for several values of the intersite interaction strength *k* assuming that all the other sites are in position *A*

atom relaxes in the excited state (from A' to D') releasing the intrasite energy. After that, the molecule emits spontaneously a photon and returns to the ground state. This scenario of the transition dynamics depends sensitively on the interaction between sites and the friction coefficient (energy-dissipation time). Depending on the interaction strength between sites, three qualitatively different dynamics (I, II, and III) were found [11, 12].

Region I is realized in the case of weak intersite interaction. In this case, all the atoms are almost insensitive to the movement of others. The photoexcited atom relaxes to point D' in the excited electronic state, returns to the ground state, and then relaxes to point B (see Fig.1). Other atoms do not react to this movement. Thus, the photoabsorption leads to the transition of only one atom to point B. In region I, the system is considered as a set of almost independent atoms.

Another limit is the case where the intersite interaction is strong. In this case, the atom of a photoexcited site does not not move far from point A' because unexcited neighbors hold it. After returning to the ground state, the atom relaxes back to point

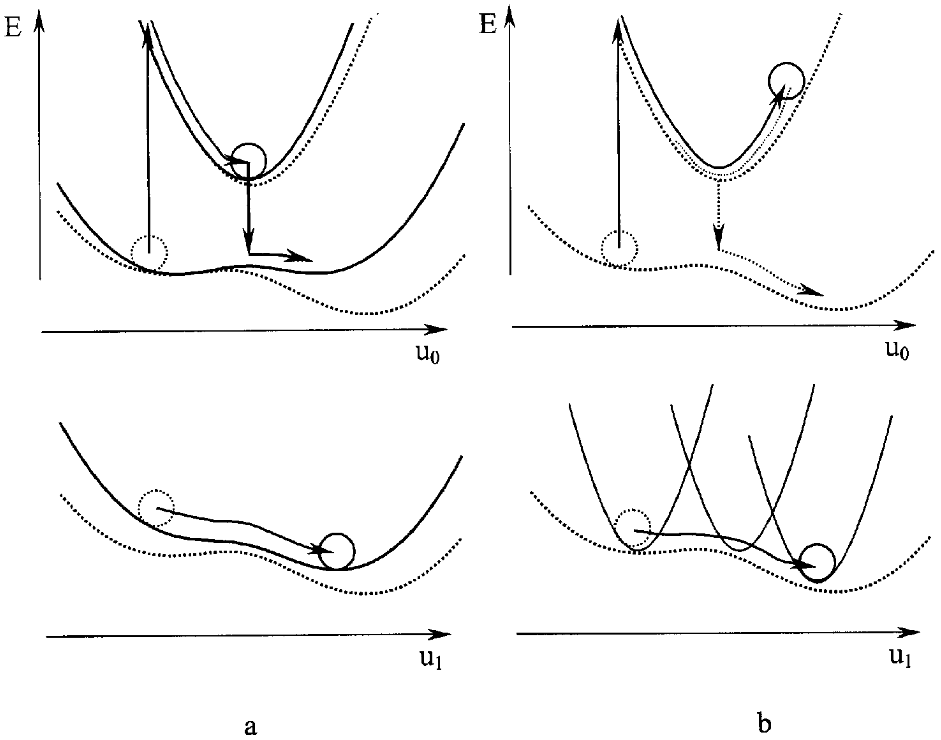


Fig.3. Qualitative picture of the lattice motion during photoinduced phase transitions: *a* ¯ Γ is large and *k* is intermediate (phase II); *b* ¯ Γ is small and *k* is large (phase IV). Solid lines show the potentials taking into account the interaction with neighbors. Dotted lines are $\varepsilon_\pm$ (u) potentials

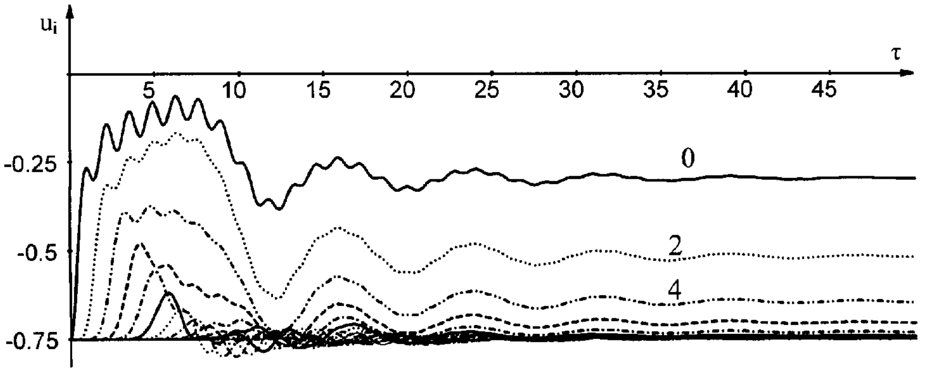
A. Thus, the one-photon absorption induces no change. This region was called region III.

There is region II between the above two limits. In this region, the interaction is not strong, and so the atom of a photoexcited site shifts significantly toward point *B*. Fig.3,*a* (above) shows the potential of a photoexcited site taking into account the interaction between neighbors. After spontaneous photoemission, the zeroth atom appears in the potential well with the minimum close to position *B*. Thus, it relaxes to point *B*. This relaxation changes the potential for neighboring sites due to the intersite interaction. As a result, minimum *A* disappears and the neighboring sites come to minimum *B* (Fig.3,*a* below). These transitions cause a successive motion of the next neighbors. Thus, the one-photon absorption induces the transition of all the atoms of the system (i.e., the so-called 'deterministic domino" effect). This possibility was analyzed in detail in [12]. The 'stochastic domino" dynamics under the adiabatic approximation was given in [14].

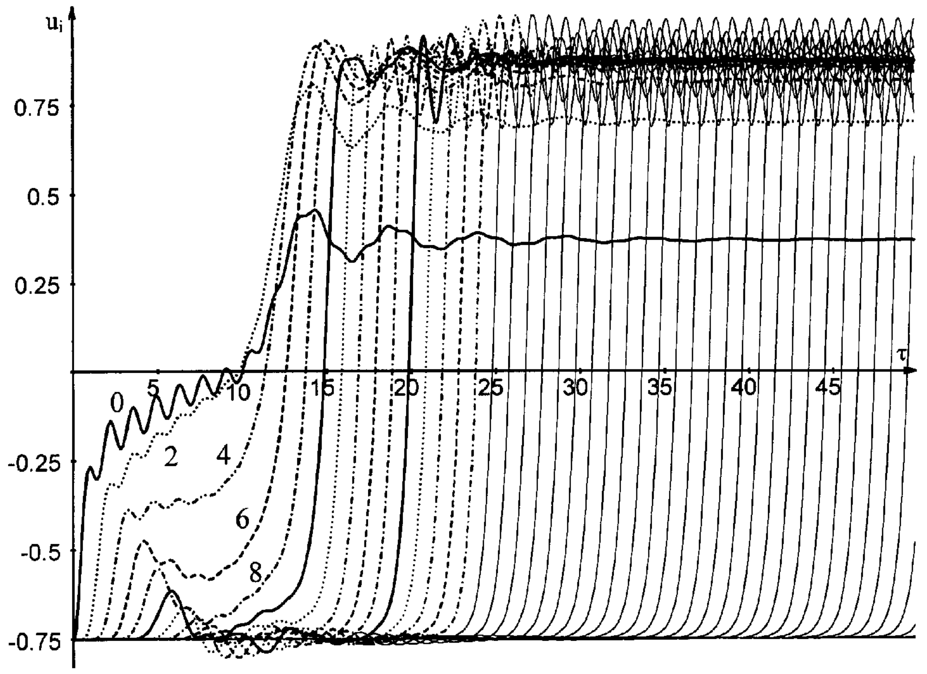
2.2. Novel Domino Process in the Friction Case

There is another possibility for photoinduced phase transitions. If the interaction is large, it holds neighboring atoms close to each other. In this case, we can describe qualitatively the atoms as moving almost synchronously in the potentials $\varepsilon_\pm$ (see Fig.3, *b*). Let us consider the case of weak friction, i.e., the relaxation time of lattice oscillations in an excited electronic state is larger than the period of oscillations (the damped oscillation case). In this case, the atom of the photoexcited (zeroth) site can go far beyond the minimum of the potential ε_+ and comes close to point *B* (Fig.3,*b* above). The atoms of neighboring sites also come close to point *B* because the strong interaction forces them to move almost synchronously with the zeroth atom. Solid lines in Fig.3, *b* (below) show the potential of the next site to the photoexcited one in different timestamps. It moves with the neighboring sites toward point *B*. Thus, a nucleus of phase *B* can be created that starts the phase transition of the whole system.

It should be noted that, under synchronous movement, several atoms have to overcome the barrier between the minima, so the barrier for the whole system is increased. But if the difference of energies at points A' and D' (the lattice relaxation energy) is large enough, some atoms may overcome the barrier with the best use of the lattice relaxation energy. We called this region of parameters as region IV. It is similar to phase II, but the phase



$\Gamma = 0.20$



$\Gamma = 0.19$

Fig.4. Temporal evolution of the lattice distortion for $k = 5$. Top — $\Gamma = 0.20$ and bottom — $\Gamma = 0.19$

transition starts while the photoexcited atom is in the excited state yet. Conditions for appearing this region are the large interaction between neighboring atoms and the weak friction. This type of dynamics in the photoinduced phase transition has not been found yet.

3. Numerical Results and Discussion

To confirm the above schematic picture, we carry out numerical calculations of the following basic equations. We assume that the energy exchange in the process of intersite collisions is much larger than the phonon energy. In this case, the dynamics of sites can be investigated using the classical equations of motion:

$$\frac{d^2u_i(\tau)}{d\tau^2} = -\frac{\partial}{\partial u_i}E_{\pm}(\{u_j\}) - \Gamma\frac{du_i}{d\tau}. \qquad (4)$$

We should consider an open, dissipative system because the energy released during the phase transition dissipates to a reservoir due to the interaction with other degrees of freedom. This dissipation is taken

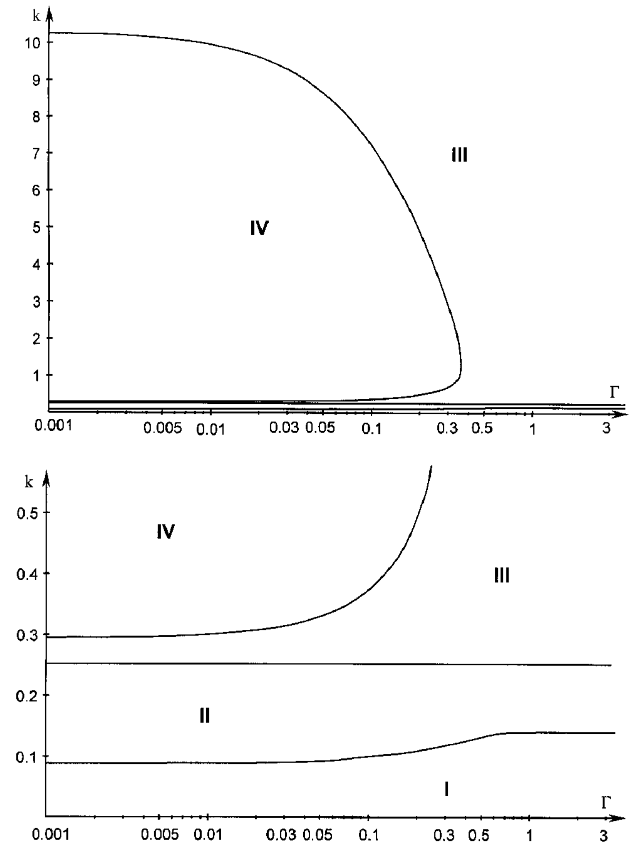


Fig.5. Phase diagram on the plane of Γ and k. Bottom is an enlargement of the small k region

into account phenomenologically by introducing the friction coefficient Γ in Eq.(4). At an initial moment, the system is in the metastable phase, i.e., all the atoms are in position A. Only the zeroth site is excited by a photon at time $\tau = 0$. Before the spontaneous emission of a photon, the system dynamics is described with the adiabatic potential $E_+(\{u_j\})$. The coupled equations (4) were solved numerically.

Using the molecular dynamical method, we investigated the system dynamics after photoabsorption for various values of the interaction strength k and the friction coefficient Γ. We observe that, for suitable parameters, the phase transition can start during the vibration period of a photoexcited atom, i.e., before the transition of this atom back to the ground state.

Fig.4 demonstrates the appearance of the photoinduced phase transition of a new type with decreasing of the friction coefficient. This figure shows the temporal dependence of u_i for $i = 0, 2, 4,$ and so on for two values of Γ. At $\tau = 0$, the atom of $i = 0$ (thick solid lines) comes to the excited state and starts to relax toward point D'. The atoms in the vicinity of the zeroth one move from their original positions due to the intersite interaction. In Fig.4,*a*, the dissipation coefficient is too large and the domino effect cannot take place. We can see that a nucleus of the new phase almost overcomes the potential barrier because the period of the first oscillation is significantly longer than the further ones. This means that, during the first oscillation, the atoms balance near the potential maximum between two wells deciding where to fall. During the second oscillation, the large part of the energy dissipates and the atoms do not come closely to the maximum of the potential. After the excited molecule returns to the ground state, all the atoms come back to position A. Thus, these parameter values correspond to region III.

The dissipation coefficient used in Fig. 4,*b* is slightly smaller than that in Fig.4,*a*. The atoms that are close to the photoexcited ($i = 0$) one obtain enough energy and overcome the potential barrier. We see that the domino movement takes place in this case. At the parameters used in Fig.4 at $\tau = 50$ (right edge of the plot), about 80 atoms have been displaced. It should be noted that a stationary position of the zeroth atom and its neighbors is between $u = d$ and $u = b$. In this case, the phase transition starts and develops while the photoexcited atom is in the excited electronic state yet. This is in striking contrast to the conventional domino in region II [11, 12]. Thus, these parameter values correspond to the new region IV.

In the system with $k = 5$, the Stokes shift energy is enough to form a nucleus of the new phase. The implementation of the photoinduced phase transition in such a system means that the absorption of only one photon can produce a nucleus that contains several atoms. One can see from Fig. 4,*b* that the several atoms shift almost synchronously toward minimum B due to the intersite interaction, as we have discussed above.

Fig.5 shows the phase diagram on the plane of the interaction strenght k and friction coefficient Γ. In regions II (conventional 'deterministic domino“) and IV (unconventional domino), one-photon absorption causes the transition of all the atoms of the system. The noticeable feature is that the border between regions III and IV depends sensitively on Γ. This is well understandable from the qualitative picture of the processes in region IV: if Γ is large (energy dissipates fast), the atom will not accumulate enough energy and will not transfer it to the neighboring atoms. On the other hand, the border between regions II and III does not depend on Γ. This results from the fact that, before the spontaneous emission, the Stokes shift energy, which was released to the lattice after photoabsorption, dissipates, no matter quickly or slowly. Another interesting feature is that phase II and phase IV are separated by the region of phase III (at the considered values of parameters) for any Γ. This means that the nature of photoinduced phase transitions in these II and IV regions is qualitatively different. We stress again that phase IV exists only for $\Gamma < 0.36$.

Conclusions

The photoinduced phase transition called the 'domino effect“ is realized in one-dimensional electron-lattice systems, in which the adiabatic potential has two minima in the ground state and one minimum in an excited state. In this paper, we find a new type of the domino process, where a photoexcited site can induce the phase transition during its relaxation in the excited state. This novel domino dymanics takes place in the case of the strong intersite interaction, large value of the Stokes shift energy, and weak friction in the excited state. In this case, only one photon can create a nucleus of the new phase domain with many sites.

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