Model of transient cooperative phenomena triggered by THz-pulse irradiation

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Abstract. We studied the cooperative phenomena induced by injection of coherent phonons by THz optical pulses. Based on the analogy to the photoinduced phase transitions observed in various materials, we consider that cooperative interactions between electrons and coherent phonons will lead to the multiplication of excited electrons and/or growth of a transient phase, which is understood by bifurcation of quantum-mechanical wavepackets on adiabatic potential energy surfaces. Employing a model of localized electrons coupled with a quantized optical phonon mode, we discuss the dynamics of the cooperative phenomena by THz-pulse irradiation and, in particular, the role of the number and/or the initial distribution of phonons in the initial creation process of transient phases.

1. Introduction

Recent progress of intense THz-pulse generation technology has made it possible to inject coherent phonons in a macroscopic scale[1], and the lattice deformation induced by such a process will induce photoluminescence caused electronic transitions in coupled electron-phonon systems[2].

On the other hand, photoinduced cooperative phenomena have been observed in various materials, and the study of these phenomena has shed light on long-standing theoretical and experimental problems with nonequilibrium dynamics of excited states[3, 4, 5, 6]. In particular, they are concomitant with the change of crystal structure as well as the electronic transitions in coupled electron-phonon systems, which means that similar phenomena will be observed by excitation of phonons.

In this paper, we discuss the cooperative phenomena triggered by injection of coherent phonons by a model of localized electrons coupled with phonons[7]. In this case, adiabatic transition of electronic states is relevant to the cooperative phenomena, e.g., multiplication of excited electrons. In particular, nonadiabatic coupling of electrons is important in the initial relaxation dynamics as in the case of injection of electronically excited states, since nonadiabatic transition disturbs the generation of excited electrons. Thus, in considering the possibility of cooperative phenomena, we should carefully consider the dynamics of electrons where both adiabatic and nonadiabatic transition is possible.
2. Model and method

We employ a model of localized electrons coupled with an optical phonon mode which describes the general properties of the photoinduced structural change. In the present study we consider an array of molecules (unit cells) on a square lattice with two electronic levels and a single phonon mode interacting with each other, which is described by the following Hamiltonian:

\[ \mathcal{H} = \sum_{\vec{r}} \left\{ \frac{\hat{p}_{\vec{r}}^2}{2} + \frac{\omega^2 \hat{u}_{\vec{r}}^2}{2} \right\} \]

\[ + \left\{ \sqrt{2\hbar\omega^3} \hat{s}\hat{u}_{\vec{r}} + \varepsilon \hbar \omega + s^2 \hbar \omega \right\} \hat{n}_{\vec{r}} + \frac{\lambda\sigma_3}{2} \sum_{(\vec{r},\vec{r}')} \right] \]

\[ \left\{ V - W(\hat{u}_{\vec{r}} + \hat{u}_{\vec{r}'}) \right\} \hat{n}_{\vec{r}}\hat{n}_{\vec{r}'}, \]  

(1)

where \( \hat{p}_{\vec{r}} \) and \( \hat{u}_{\vec{r}} \) are the momentum and coordinate operators for the vibration mode of a molecule at site \( \vec{r} \), respectively. Two electronic states are assigned to each site \( \vec{r} \) which are denoted by \( |\downarrow\rangle_{\vec{r}} \) (ground state) and \( |\uparrow\rangle_{\vec{r}} \) (excited state). \( \sigma_i (i = x, y, z) \) are the Pauli matrices which act only on the electronic states of the molecule at site \( \vec{r} \). The nonadiabaticity in the dynamics is taken into account via “spin-flip” interaction between two electronic states as in typical organic molecules\[8\]. \( \hat{n}_{\vec{r}} \) denotes the density of the electron in \( |\uparrow\rangle_{\vec{r}} \), i.e., \( \hat{n}_{\vec{r}} = \sigma_z + 1/2 \).

The second sum which gives the intermolecular interaction is taken over all the pairs on nearest neighbor sites, and we take into account the dipole-dipole interaction between excited molecules as well as the elastic interactions. We note that this Ising-like model is similar to the one to study the thermodynamical properties of the Jahn-Teller effect\[9\], while our aim is to reveal the nonequilibrium dynamics of the excited states of the model.

The molecules that we consider have two diabatic potential energy surfaces (PESs) which cross each other, and the nonadiabatic coupling \( \lambda\sigma_3 \) acts to reorganize them into two adiabatic PESs. We assume that the quantum mechanical nature of the nuclear wavepackets on the PESs plays an important role, which is the case particularly for nonadiabaticity of the dynamics is relevant. We chose the values of the parameters as: \( \omega = 1 \), \( \varepsilon = 2.3 \), \( s = 1.4 \), \( V = 1.1 \), \( W = 0.2 \), \( \alpha = 0.1 \), \( \beta = 0.2 \), and \( \lambda = 0.2 \), and the unit of time is taken to be \( T = 2\pi/\omega \). We note that the values of the parameters do not correspond to any specific material but the order of magnitude for the parameters is estimated referring to those for typical organic materials. We numerically solved the time-dependent Schrödinger equation for the Hamiltonian (1) for systems with 128 × 48 sites in which the periodic boundary condition is taken only for the longer edge of the system, and the time-dependent wavefunction of the electron-phonon system \( |\Phi(t)\rangle \) was obtained. Detail of the method of calculations is described in Ref. \[7\] and we do not mention it further to avoid redundancy.

3. Calculated results

Since the penetration of THz pulses is limited due to high absorption ratio of organic materials, we consider that the lattice deformation induced by those pulses is limited to the molecules in the vicinity of the surface of samples. Hence, as an initial condition of calculations, we consider that only five molecules closest to either of the longer edges of the system were excited, where the wavefunction of those molecules is given by a coherent state of phonons

\[ |a \downarrow\rangle_{\vec{r}} = e^{-\frac{|\omega|^2}{2}} \sum_{n=0}^{\infty} \frac{a^n}{\sqrt{n!}} |n \downarrow\rangle_{\vec{r}}. \]  

(2)

The other molecules are considered to stay in the ground state at \( t = 0 \).
Figures 1-(a)-(c) show the spatial distribution of the population of excited electrons $\tilde{n}(\vec{r},t)$ for $t = 10T$, $25T$, and $50T$ for $a = s$. When phonons are excited in a molecule, a wavepacket described by Eq. (2) starts to move on the ground state PES, and when it approaches the crossing point of the grounds state PES and the excited state PES, the electronic interaction $\lambda \sigma_{\vec{r}}^\xi$ induces electronic transition between $|\downarrow\rangle_{\vec{r}}$ and $|\uparrow\rangle_{\vec{r}}$. Hence, $\tilde{n}(\vec{r},t)$ increases only in the initially phonon-excited molecules as shown in Fig. 1-(a).

On the other hand, the electronic transition also affects the PES at the nearest neighbor molecules through the intermolecular interaction in Eq. (1), which causes the transition from $|\downarrow\rangle_{\vec{r}}$ to $|\uparrow\rangle_{\vec{r}}$ in those molecules. Thus, as the energy dissipation proceeds by the propagation of phonons in the system, the number of excited molecules increases, and all the molecules are in a superposition of $|\downarrow\rangle_{\vec{r}}$ and $|\uparrow\rangle_{\vec{r}}$ as shown in Figs. 1-(b) and (c).

In order to show that the increase of the excited state molecules corresponds to the multiplication of excited electrons, we calculated the sum of the population in the excited electronic state $N(t) = \sum_{\vec{r}} \tilde{n}(\vec{r},t)$ divided by the number of the initially phonon-excited molecules $n_i$. As shown in Fig. 2, $N(t)/n_i$ starts to increase at $t \sim 3$, which is reminiscent of the incubation period observed in photoinduced cooperative phenomena[7]. During this period, even the electrons at the initially phonon-excited molecules tend to stay in the ground state $|\downarrow\rangle_{\vec{r}}$ although the electronic interaction $\lambda \sigma_{\vec{r}}^\xi$ works. Thus, the origin of the incubation period in this case is the nonadiabaticity of the electron dynamics, which disturbs the adiabatic transition between $|\downarrow\rangle_{\vec{r}}$ and $|\uparrow\rangle_{\vec{r}}$.

Since, however, the electronic population gradually transfers to the excited electronic state, $\tilde{n}(\vec{r},t)$ also gradually increases, and the PES of the molecules at the ground state deforms.
Figure 2. Sum of the population in the excited electronic state $N(t)$ divided by the number of the initially phonon-excited molecules $n_i$. When $N(t)/n_i > 1$, the multiplication of electrons in the excited states takes place.

Hence, the molecules in the vicinity of initially phonon-excited molecules starts to deform and the multiplication of excited electrons is triggered by this process, though the electronic transition is slower than that in the photoexcited case[7].

4. Summary
We calculated the dynamics of coupled electron-phonon system excited by THz optical pulses. We found that the electronic transition between the ground state and an excited state is induced by the propagation of phonons, and the region of excited molecules extends over the whole system, although initial deformation of the lattice is limited to the molecules in the vicinity of the surface of samples. As a result, the population of excited electrons increases, which shows that the multiplication of excited electrons is possible by the injection of phonons. Although these features are similar to the photoinduced cooperative phenomena, we also found a certain difference between “electron-excited” cases and “phonon-excited” cases, i.e., the rate of the increase of $N(t)$ is larger in former case. The origin of the difference is that the excitation energy given to the system is larger in the former case than in the latter, since the electronic excitation energy is larger than phonon energy in typical semiconductors and insulators. It is, however, still interesting that the irradiation of intense THz-pulses are effective to induce the multiplication of excited electrons in various systems, and thus it will be another method to reveal the dynamics of excited states.

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