Theoretical study on the coherent nonlinear dynamics of photoinduced structural change

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Abstract. We study the dynamics of initial nucleation processes in localized electronic systems. We employ a model of electrons coupled with a quantized phonon mode and solved the time-dependent Schrödinger equation numerically. We calculated correlation functions to reveal the dynamical properties of the relaxation process, and the initial dynamics of the photoinduced structural change is discussed from the viewpoint of pattern formation.

1. Introduction
The initial nucleation process of the photoinduced cooperative phenomena is one of the keys to understand their dynamical properties. Since, in particular, the vibrational coherence of photoexcited states survives for several periods of lattice vibration, the coherent properties of the wave-packet dynamics on excited-state potential energy surfaces are important to reveal the mechanism of the photoinduced structural change. Thus, we have studied the dynamics of photoexcited states of electron-phonon systems in coherent regime and found that the nucleation process is driven by the propagation of coherent phonons[1]. We showed that the nonlinearity of the nucleation dynamics is ascribed to the interaction between the clusters of excited molecules which are generated by successive conversion of the electronic states[2,3]. This feature also means that the spatial fluctuation of photoexcitation energy determines the domain structure, which agrees with the experimental results on polydiacetylenes[4].

In this paper we theoretically study the nonlinear dynamics of the photoinduced nucleation employing a model of arrayed molecules with localized electrons coupled with a quantized vibration mode. We show that the nucleation dynamics is characterized as quantum pattern formation, which is understood by investigating the dynamical behavior of correlation functions.

2. Model and method
As we discussed in our previous papers[1-3], nonadiabatic transitions between quantized states are important to study the dynamical aspects of photoinduced cooperative phenomena. In this paper, we focus on the initial dynamics of a photoexcited state in interacting molecules, fully quantizing the relevant vibration modes. However, the dimension of the Hilbert space for the whole system increases drastically by quantizing atomic variables, which means that numerical calculation on those systems...
requires lots of computational resources. Thus, we employ a simplest model that is sufficient to
describe the photoinduced nucleation processes.

The Hamiltonian of the model is described by

\[
H = \sum_r \left[ \frac{p_r^2}{2} + \frac{\omega^2_u}{2}u_r^2 + \left( \sqrt{2\hbar\omega} + \frac{\varepsilon}{\hbar}\omega + s^2\hbar\omega \right)\tilde{n}_r + \lambda \sigma^z_r \right]
\]

where \( p_r \) and \( u_r \) are the momentum and coordinate operators for the vibration mode of a molecule at site \( r \), respectively. The electronic states at site \( r \) are denoted by \( |\downarrow_r\rangle \) (ground state) and \( |\uparrow_r\rangle \) (excited state) and \( \sigma^i_r \) \((i=x,y,z)\) are the Pauli matrices which act only on the electronic states of the molecule at site \( r \). \( \tilde{n}_r \) denotes the density of the electron in \( |\uparrow_r\rangle \), which is rewritten as \( \tilde{n}_r = \sigma^z_r + 1/2 \). The second sum which gives the intermolecular interaction is taken over all the pairs on nearest neighbor sites, where the Coulomb interaction between excited state electrons are modulated by molecular distortion. The vibrational period of an individual molecule is denoted by \( T = 2\pi / \omega \) in the rest of the paper. We note that this Ising-like model is similar to the one to study the thermodynamical properties of the Jahn-Teller effect[5].

Detail of the Hamiltonian (1) is discussed in Refs. [1-3]. We only mention that the nonadiabaticity in the relaxation dynamics is taken into account via “spin-flip” interaction between two electronic states, i.e., the interaction strength between two electronic levels are assumed to be a constant.

We chose the values of the parameters as: \( \varepsilon=2.3, s=1.4, V=1.1, W=0.2, \alpha=0.1, \beta=0.2, \) and \( \lambda=0.2 \), which are typical for organic molecules.

The time-dependent Schrödinger equation for the Hamiltonian (1) is numerically solved, and the time evolution of photoexcited states is calculated.

3. Calculated results

In the present model three or more molecules in nearest neighbor sites must be simultaneously excited by photons in order to trigger the nucleation process[3]. We take the initial condition of the calculation as randomly distributed excited sites with a fixed value of excitation ratio \( \rho \). In this case the average growth rate of the islands of excited molecules, for example, reveals a characteristic property of the dynamics of the initial nucleation process. Figure 1 shows the rate of formation of excited state clusters \( r(t; \rho) \) which is defined by

\[
r(t; \rho) = \left\langle \frac{dN}{dt} \right\rangle ,
\]

**Figure 1.** The rate of cluster formation \( r(t; \rho) \) as a function of \( t \) for \( \rho=0.03, 0.05, \) and 0.1.
for \( \rho = 0.03, 0.05, \) and 0.1. \( N(t) \) denotes the population of the excited electronic state in the system. All the lines show that the oscillation of the rate of cluster formation is observed for \( t < 5T \) in accordance with the vibration of individual molecules. \( N(t) \) does not increase over this period, which shows that the nucleation process is not triggered. At this stage of the relaxation process each cluster of excited molecules hesitates to grow. However, after such an "incubation period", \( r(t; \rho) \) behaves in different ways according as \( \rho \) is varied. For \( \rho = 0.1 \) the oscillation of the growth rate ceases and it is stabilized at a positive finite value, which shows that the domain growth rapidly progresses merging the islands and the domains of excited molecules cover the whole system.

On the contrary, for \( \rho = 0.03 \) or 0.05, the oscillation of \( r(t; \rho) \) remains for \( t>5T \), and \( r(t; \rho) \) has a lowest (negative) value at \( t \approx 6 \) in both cases. This means that the excited molecules start to turn back to the ground state, and that the nucleation process is not triggered after all. For \( \rho = 0.05 \), \( r(t; \rho) \) decreases and thus the prominent domain growth still does not take place.

In summary, we point out that \( r(t; \rho) \) shows the dynamics of the nucleation process clearly even when multiple clusters of excited molecules are put in the system. This aspect of the nucleation process also shows us that the analysis with statistical methods will be useful to reveal the dynamics of photoinduced nucleation.

### 4. Concluding remarks

In this paper we study the nucleation dynamics of photoinduced nucleation processes accompanied by structural change of the system. We found that quantum pattern formation is observed in the photoinduced nucleation process. When the irradiated photons induce excitation energy fluctuation in the system, there appear photoinduced nuclei which grow from clusters of excited molecules. The growth mechanism of such spatio-temporal patterns is purely quantum mechanical and nonadiabatic transition between two electronic states plays an important role.

In particular, the rate of cluster formation \( r(t; \rho) \) shows that the nucleation process is similar for various values of \( \rho \) for the first several periods of molecular vibration. Then the effect of nucleation becomes apparent and \( r(t; \rho) \) becomes almost constant when domain growth rapidly proceeds. This feature will be discussed in relation to the nonequilibrium critical phenomena which have been extensively studied[6].

We also mention that the present results will give a perspective to the future experimental studies on the coherent dynamics of photoinduced structure change by time-resolved X-ray diffraction measurement. Since strong coherent X-ray sources are under development[7], it will be possible to observe the dynamics of the nucleation process and pattern formation process in coherent regime with femtosecond resolution, and the present results will be compared with them to understand the physics of photoinduced cooperativity.

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