Coherent dynamics of photoinduced nucleation processes

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Abstract

We study the dynamics of initial nucleation processes of photoinduced structural change of molecular crystals. In order to describe the nonadiabatic transition in each molecule, we employ a model of localized electrons coupled with a fully quantized phonon mode, and the time-dependent Schrödinger equation for the model is numerically solved. We found a minimal model to describe the nucleation induced by injection of an excited state of a single molecule in which multiple types of intermolecular interactions are required. In this model coherently driven molecular distortion plays an important role in the successive conversion of electronic states which leads to photoinduced cooperative phenomena.

1 Introduction

As the recent advance in laser technology has made it possible to generate arbitrarily designed optical pulses, control of quantum mechanical states of materials with those laser pulses has become to one of the central interests of the research of future device applications. For example, study on quantum information technology[1] has opened up a new aspect of device applications, i.e., utilization of the phase(coherence) of the quantum mechanical states. In those new fields, contrary to the conventional control methods of electronic/vibrational states, it is required to
keep the coherence of the internal states of materials during control processes, which means that we need to understand the dynamics of quantum-mechanical states in coherent regime.

On the other hand, it was also found in various materials that injection of photoexcited states induces cooperative phenomena regarding with the change of structural, magnetic, or ferroelectric properties[2, 3, 4, 5, 6]. These photoinduced cooperative phenomena are considered to have a common mechanism, and many experimental and/or theoretical studies have been presented to make it clear[7, 8, 9]. In particular, when we are interested in controlling such cooperativity by designed optical pulses, it is necessary to understand the transient properties of the photoinduced cooperative phenomena more deeply. Thus, theoretical studies focused on the dynamics of the photoinduced cooperative phenomena are important at the current stage.

As we have shown in the previous papers[10, 11], nonadiabaticity of electronic transitions is a key to understand the temporal behavior of the above-mentioned phenomena. Dynamics of nonadiabatic transitions has been studied since the pioneering works by Landau[12] and Zener[13], and the bifurcation rate of wavefunction was analytically obtained in general cases[14]. These studies mainly focused on the wavefunctions before/after nonadiabatic transition, and hence the time evolution of wavefunctions itself is out of their scope. On the other hand, the dynamics of nonadiabatic processes has been considered to be important in, for example, photochemical reactions[15], and hence computational methods of the dynamics have been proposed by many authors[16]. Since, however, those methods require the atomic coordinates/momenta to be treated as classical variables due to the limited computational capacity at the present time, they could discuss the wavefunctions after decoherence of the atomic degrees of freedom takes place. As a result they mentioned the reaction yield or the absorption rate after various nonequilibrium processes. On the contrary, the initial nucleation processes in photoinduced cooperative phenomena involve consecutive switching of potential energy surfaces (PESs) relevant to the dynamics of excited states, and the coherence of the wavefunction of electrons/atoms should be taken into account. In other words, the wavefunction at every moment should be pursued to understand the dynamics of the whole processes. Hence, not only the bifurcation rate of the wavefunction after nonadiabatic transition but also the wavefunction as a function of time is required, which means that the conventional methods are not suitable for the theory of photoinduced cooperativity.

In this paper, we study the initial dynamics of the photoinduced domain growth, which is characterized by nucleation processes before decoherence of quantum-mechanical states takes place. We also focus on the photoinduced phenomena in which electron-phonon interactions play an important role and propose a minimal model to describe such cases.

The organization of the paper is as follows: in Section 2 the molecular model is introduced and the method of calculation is described. In Section 3 the calculated results are shown. Section 4 is devoted to discussion and conclusions.
2 models and method

As we discussed in our previous papers \cite{10, 11}, nonadiabatic transitions between quantized states are particularly 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 which is sufficient to describe the photoinduced nucleation processes.

In the present model we consider molecules arrayed on a square lattice. Electrons relevant to the nonadiabatic transitions are assumed to be localized in each molecule, and two electronic levels coupled with a single vibration mode is taken into account per molecule. The diabatic PESs with respect to the electronic states in each molecule cross with each other and that the nonadiabaticity in the dynamics is taken into account via “spin-flip” interaction between two electronic states. This model is known as a simplest model to discuss the relaxation dynamics of, \textit{e.g.}, photoisomerization of molecules \cite{17}. As for the intermolecular interaction, we take into account vibrational coupling and the Coulomb interaction between excited state electrons. $\beta$ affects to induce molecular distortion by the excited electrons in the adjacent molecules which is also of the same order as the other interaction terms.

Hence, the Hamiltonian in the present study is described by:

$$
\mathcal{H} = \sum_{\vec{r}} \left\{ \frac{p_{\vec{r}}^2}{2} + \frac{\omega^2 u_{\vec{r}}^2}{2} + (\sqrt{2\hbar\omega}s_\vec{r} + \epsilon\hbar\omega + s^2\hbar\omega)\hat{n}_\vec{r} + \lambda\sigma_{\vec{r}}^z \right\} + \sum_{\langle\vec{r},\vec{r}'\rangle} \left[ \alpha\omega^2(u_{\vec{r}} - \beta\hat{n}_{\vec{r}})(u_{\vec{r}'} - \beta\hat{n}_{\vec{r}'}) - \{V - W(u_{\vec{r}} + u_{\vec{r}'})\}\hat{n}_{\vec{r}}\hat{n}_{\vec{r}'} \right],
$$

(1)

where $p_{\vec{r}}$ and $u_{\vec{r}}$ are the momentum and coordinate operators for the vibration mode of a molecule at site $\vec{r}$, respectively. 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 modified by molecular distortion. The vibrational period of an individual molecule is denoted by $T = 2\pi/\omega$ in the rest of the paper.

A schematic view of the present model is shown in Fig. 1. The two diabatic PESs for an individual molecule are crossed with each other, and the nonadiabatic coupling constant $\lambda$ acts to separate them into two adiabatic PESs. We chose the values of the parameters as: $\epsilon = 1.6, s = 1.4, V = 1.1, W = 0.2, \alpha = 0.1, \beta = 0.2$, and $\lambda = 0.2$. Although those values are typical for organic molecules as for electron-vibration coupling \cite{18} and the intermolecular Coulomb interaction \cite{17}, the other parameters are not easy to determine their values either from...
theoretical calculations or experimental results. We only mention that the order of magnitude for the parameters is estimated referring to those for typical organic materials. The electronic states at site $\vec{r}$ are denoted by $| \downarrow \rangle_{\vec{r}}$ (ground state) and $| \uparrow \rangle_{\vec{r}}$ (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 $\vec{r}$. $\hat{n}_r$ denotes the density of the electron in $| \uparrow \rangle_{\vec{r}}$ which is rewritten as $\hat{n}_r = \sigma_z^r + 1/2$. The model and the notations of the parameters are schematically shown in Fig. 1.

Details of the quantization procedure of the vibration mode of each molecule will be published elsewhere. We mention that the basis set for the vibronic states is composed of the Fock states shown in Ref. [19]. The phonon dispersion relation of the vibration mode is given by

$$\Omega(\vec{k}) = \omega \sqrt{1 + 2\alpha(\cos k_x + \cos k_y)},$$

where $(k_x, k_y)$ denote the reciprocal lattice vector of the square lattice, and the lattice constant is taken to be unity. The quantized states on each diabatic PES of a single molecule are the vibronic states $| n\sigma \rangle_{\vec{r}}$ ($n = 0, 1, 2, ..., \sigma = \uparrow, \downarrow$) in the Fock representation, where the coordinate of the molecule is labelled by $\vec{r}$. $| n \uparrow \rangle$ is related with $| n \downarrow \rangle$ by

$$| n \uparrow \rangle = | \uparrow \rangle \langle \downarrow | e^{s(a^\dagger + a)} | n \downarrow \rangle,$$

where $e^{s(a^\dagger + a)}$ denotes the translation operator in the vibration coordinate space[20]. We note that this Ising-like model is similar to the one to study the thermodynamical properties of the

Figure 1: Schematic view of the model. Circles denote the molecules with two electronic states and a vibrational mode. Adiabatic potential energy surfaces for an individual molecule is shown in the inset.
Jahn-Teller effect\[21\], though the nonequilibrium dynamics of the excited states in the model has not been understood.

We obtain the numerical solution of the time-dependent Schrödinger equation for the Hamiltonian (1) by the Runge-Kutta method. In each series of calculations, one of the molecules on 128×128 lattice is initially in the Franck-Condon state, while the others are in the ground state, which corresponds to the injection of a photoexcited state to a single molecule at the origin. In solving the Schrödinger equation, we applied a mean-field approximation in which the contribution of the wavefunction at the nearest neighbor sites is substituted by the average value with respect to the wavefunction \(|\Phi(t)\rangle\). The detail of the approximation is described in the appendix. We only mention here that this approximation is equivalent to decomposing the wavefunction of the total system \(|\Phi(t)\rangle\) into a product of the wavefunctions at each molecule, i.e.,

\[
|\Phi(t)\rangle = |\phi(t)\rangle_{r_1} \otimes |\phi(t)\rangle_{r_2} \otimes \ldots |\phi(t)\rangle_{r_N},
\]

where \(N\) denotes the number of molecules in the system. Thus, we can solve the differential equation for each molecule when only the average values of the properties for adjacent molecules are provided, which means that the present calculation method is suitable for parallel computing. Hence, we have made it possible to handle more than 10000 molecules by the present method.

### 3 calculated results

We have pointed out that the population of the excited electronic state \(|\uparrow\rangle_{\vec{r}}\) is suitable for understanding the dynamics of the initial nucleation processes\[10, 11\]. Thus, we show in Fig. 2 the population of \(|\uparrow\rangle_{\vec{r}}\) for 48×48 sites around the injected excited state ("seed") defined by

\[
N(\vec{r}, t) = \langle \Phi(t)|\hat{n}_{\vec{r}}|\Phi(t)\rangle,
\]

for \(t = 0, 5T,\) and \(10T\). Figure 2 shows that the number of molecules in the excited electronic state increase surrounding the initially excited molecule. Those molecules will constitute a photoinduced domain observed in many experiments\[2, 3, 4, 5, 6\] and thus the present calculation described the initial processes of the photoinduced cooperative phenomena, i.e. photoinduced nucleation triggered by an injected excited state.

Since the population transfer is induced by adiabatic transition on the PESs in Fig. 1, molecular distortion is also relevant to the nucleation processes. Hence, molecular distortion defined by

\[
\zeta(\vec{r}, t) = \langle \Phi(t)|u_{\vec{r}}|\Phi(t)\rangle,
\]
Figure 2: Population of the excited electronic state $N(\vec{r}, t)$ on $48 \times 48$ lattice for (a) $t = 0$, (b) $t = 5T$, and (c) $t = 10T$. 
is calculated to discuss different aspects of the nucleation processes. Figure 3 shows $\zeta(\vec{r}, t)$ for $t = 0$, $5T$, and $10T$. We found that the molecular distortion is coherently driven in the system and that the vibrational energy is propagated by coherent phonons.

The elementary processes of the nucleation is understood by comparing $N(\vec{r}, t)$ and $\zeta(\vec{r}, t)$ as functions of time. Although these properties seem to have similar temporal behavior at first glance, we found that the difference in their initial growth dynamics is a key to understand the details of the nucleation processes. We show in Figs. 4-(b)-(f) $N(\vec{r}, t)$ and $\zeta(\vec{r}, t)$ as functions of time, where $\vec{r}$ corresponds to the molecular sites shown by filled circles in Fig. 4-(a). As we mentioned, the boundary between the converted (excited state) domain and the ground state domain moves to extend the former in the system. Thus the values of $N(\vec{r}, t)$ and $\zeta(\vec{r}, t)$ rise at later time as the distance to the “seed” increases. Comparing Figs. 4-(b)-(f), we found that the distance to the “seed” should refer to the Manhattan distance in discussing the time of rising of those values when $|\vec{r}|$ is small. However, as the growth process proceeds, the number of the excited molecules increases and the conversion of the electronic states takes place as in the continuous systems and the boundary between domains becomes a circle (Fig. 3-(c)). Hence, the Euclidean distance becomes appropriate for the distance between two molecules. This behavior is reminiscent of the propagation of coherent phonons, and the nucleation processes are driven by those coherent motion of the molecules.

Figures 4-(b)-(d) also show that an oscillating component in both $N(\vec{r}, t)$ and $\zeta(\vec{r}, t)$ appears before transition to $|\uparrow\rangle_{\vec{r}}$ is realized. We found that, after $N(\vec{r}, t)$ and/or $\zeta(\vec{r}, t)$ begins to grow, it takes longer time to complete electronic state conversion in the molecules close to the “seed” than in the others. To be more precise, a precursor to the electronic state conversion is observed in molecules at the nearest neighbor and the next nearest neighbor of the “seed”. This behavior is understood as a preliminary process required to overcome potential energy barrier at the beginning of nucleation. Thus, in the present model, the first process of the nucleation corresponds to making a cluster of the $\sim 10$ converted molecules around the “seed.” Then the other molecules will suffer electronic state conversion which smoothly takes place as Figs. 4-(e) and (f) show.

The above properties are relevant to the mechanism of the photoinduced cooperative phenomena, i.e., each molecule in the ground state receives energy through the vibrational coupling $\alpha$ first and the molecule begins to vibrate. Then, the nonadiabatic coupling $\lambda$ induces population transfer with the assistance of the Coulomb interaction $V$, and thus the molecule turns to belong to the converted domain. Once each molecule belongs to the converted domain, motion of $N(\vec{r}, t)$ and $\zeta(\vec{r}, t)$ almost disappear and it does not return to the ground state during the current simulation, since intermolecular interactions make it remain in the excited state domain. We also point out that the intermolecular Coulomb interaction $V$ enhances the population transfer rate particularly when the number of adjacent molecules in the excited state increases.
Figure 3: Molecular distortion $\zeta(\vec{r}, t)$ on $48 \times 48$ lattice for (a) $t = 0$, (b) $t = 5T$, and (c) $t = 10T$. 
Figure 4: Time-dependence of $N(\vec{r}, t)$ and $\zeta(\vec{r}, t)$. $\vec{r}$ for each figure corresponds to the filled circles in the top figure, and the “seed” is denoted by the shaded circle.
Figure 5: $N_{\text{total}}(t)$ as a function of time. The dotted line proportional to $t^{2.3}$ is drawn as a guide for the eyes.

Figure 4-(b) also shows that the molecular distortion does not grow for $\sim 3T$ after photoexcitation. Hence, it takes $\sim 4T$ for the population transfer to be completed even for the molecules in the nearest neighbor sites. Since the population transfer reflects on the electronic/optical properties of the molecules, the change of those physical properties takes place $\sim 400 - 800$ fsec ($T$ is $\sim 100 - 200$ fsec in typical organic molecular systems) after photoexcitation.

The sum of the excited state population $N_{\text{total}}(t) = \sum_{\vec{r}} N(\vec{r}, t)$ indicates the measure for the growth rate of the photoinduced domain. Figure 5 shows that $N_{\text{total}}(t)$ increases as $\sim t^{2.3}$, except in the very first stage of the domain growth. As a result we obtain that the radius of the photoinduced domain behaves as $\sim t^{1.2}$, which is understood by the picture that the growth of the domain is predominantly driven by propagation of coherent phonons rather than diffusion processes. As the vibrational coherence is lost, diffusion process becomes more important and the domain growth will slow down to make the radius of the domain increase as $\sim \sqrt{t}$. Since vibrational coherence survives for a few psec in typical organic molecules[18], the present calculation is valid only in the time range studied in this paper, and the decoherence of the vibrational states should be taken into account to study the growth dynamics of the photoinduced domain in a longer time scale.
4 discussion and conclusions

In this paper we study the coherent dynamics of photoinduced nucleation processes in organic molecular systems. When a single molecule excited to the Franck-Condon state, it induces distortion of adjacent molecules, and the excitation energy is transferred to the other molecules coherently. Once the molecules start to vibrate, the electronic state conversion from $| \downarrow \rangle_{\vec{r}}$ to $| \uparrow \rangle_{\vec{r}}$ takes place and thus photoinduced domain grows. This is the basic scenario of the initial photoinduced nucleation processes where coherent phonons play an important role. In fact, the size of the converted domain (diameter) is almost linearly increases as the nucleation proceeds, which shows that energy diffusion is subsidiary in the initial processes. However, as the decoherence of vibrational states takes place, excitation energy propagation in the system will be dominated by diffusion processes, and hence the growth rate will be $\propto \sqrt{t}$ after all. We mention that these properties will be reflected on the time-resolved spectra of e.g., reflectance, absorbance, or Raman scattering intensity and that the ultrafast spectroscopy will give a key to understand the coherent nature of the nucleation processes.

We stress that, contrary to the one-dimensional case, the domain growth by successive conversion of the molecules does not take place in higher dimensional cases if intermolecular interactions other than vibrational coupling $\alpha$ is neglected. This is a particular property in higher dimensional systems, since it was pointed out that the converted domain grows only by the intermolecular interaction between molecular distortion. In general, the value of $\alpha$ should be less $1/M$ where $M$ is the coordination number of the lattice. Hence, the maximum value of $\alpha$ is smaller as the dimensionality of the system is higher. The present study shows that, even in two-dimensional systems, $\alpha$ is not sufficient to induce cooperative phenomena, and thus other interactions such as Coulomb interaction between electrons are necessary. Since $M$ is larger in higher dimensional systems, this result is applicable to three-dimensional systems, and thus we conclude that the photoinduced nucleation processes are realized by cooperation of various types of intermolecular interactions in general cases. We mention that the results described in this paper are independent of the model and the values of the parameters for which the nucleation takes place.

In the present paper, we assume that only a single relevant vibration mode exists in each molecule. However, the nonadiabatic transition within a single molecule is strongly affected by the structure of the PESs. In particular, when multiple vibration modes are taken into account, the dynamics of the nucleation processes depends on the topological structure of the intersections of the PESs, e.g., existence of conical intersections. Hence, ab initio electronic-structure calculations of specific materials are important for a detailed discussion of such material-dependent features of the nucleation processes, and the dynamics calculation in the present paper should be combined with those electronic-structure calculations in the future. We, however, stress that the present results give the basic properties of the nucleation dynamics in
coherent regime and that the qualitative feature of the domain growth is sufficiently discussed in this paper.

In order to control the nucleation dynamics by outer field, e.g., laser pulses, we should estimate the effect of decoherence of the quantum-mechanical states. We point out that it is possible to take into account the decoherence by embedding the system in a large ’reservoir’ and by tracing out the dynamical variables regarding with the reservoir. We also stress that such studies will contribute to realizing the coherent control of the photoinduced domains, which will be important both from a physical point of view and device applications\cite{22}.

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A equations of motion for numerical calculations

The Schrödinger equation for the system is written by

\[ i \frac{\partial}{\partial t} |\Phi(t)\rangle = \mathcal{H}|\Phi(t)\rangle. \] (7)

When the wavefunction $|\Phi(t)\rangle$ is decomposed by those for individual molecules as shown in Eq. (4), each component $|\phi(t)\rangle_{\vec{r}}$ obeys the following equation:

\[ i \frac{\partial}{\partial t} |\phi(t)\rangle_{\vec{r}} = \left( \frac{p_{\vec{r}}^2}{2} + \frac{\omega^2 u_{\vec{r}}^2}{2} + (\sqrt{2} \hbar \omega^3 s q_{\vec{r}} + \epsilon \hbar \omega + \hbar \omega s) \hat{n}_{\vec{r}} + \lambda \sigma_{x} \hat{n}_{\vec{r}} \right) |\phi(t)\rangle_{\vec{r}} + \sum_{\vec{r}'} \left[ \alpha \omega^2 (u_{\vec{r}} - \beta \hat{n}_{\vec{r}})(u_{\vec{r}'} - \beta \hat{n}_{\vec{r}'}) - \{V - W (u_{\vec{r}} + u_{\vec{r}'}) \hat{n}_{\vec{r}} \hat{n}_{\vec{r}'} \} |\phi(t)\rangle_{\vec{r}} \right] \] (8)

where the sum is taken over the nearest neighbor sites of $\vec{r}$.

We apply a mean-field approximation to Eq. (8), i.e., the effects of molecules in the nearest neighbor sites are substituted by their average values. Hence, after canonical quantization of the $p_{\vec{r}}$ and $u_{\vec{r}}$, the following equations of motion for each molecule are derived:

\[ i \frac{\partial}{\partial t} |\phi(t)\rangle_{\vec{r}} = \hbar \omega [a_{\vec{r}}^\dagger a_{\vec{r}} + \{ s (a_{\vec{r}}^\dagger + a_{\vec{r}}) + \epsilon + s^2 \} \hat{n}_{\vec{r}} + \lambda \sigma_{x} ] |\phi(t)\rangle_{\vec{r}} + \sum_{\vec{r}'} \left[ \alpha \omega^2 \{ \gamma (a_{\vec{r}}^\dagger + a_{\vec{r}}) - \beta \hat{n}_{\vec{r}} \} \{ \langle u_{\vec{r}} \rangle - \beta \langle \hat{n}_{\vec{r}} \rangle \} \right. \\
- \left. \{ V - W \{ \gamma (a_{\vec{r}}^\dagger + a_{\vec{r}}) + \langle u_{\vec{r}} \rangle \} \} \hat{n}_{\vec{r}} \langle \hat{n}_{\vec{r}} \rangle \} |\phi(t)\rangle_{\vec{r}} \right], \] (9)
where $a^{(t)}_{\vec{r}}$ denotes the annihilation (creation) operator of the vibration mode and $\gamma = \sqrt{\hbar/2\omega}$. Intermolecular interaction is taken into account through the average value over the decomposed wavefunction and

$$\langle X_{\vec{r}} \rangle_{\varphi} = \langle \phi(t) | X_{\vec{r}} | \phi(t) \rangle_{\varphi}. \quad (10)$$

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