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Dynamical properties of nucleus boundaries in photoinduced structural change

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ABSTRACT

Dynamics of the boundaries of photoinduced nuclei in electron–phonon systems is theoretically studied. By regarding the spatial distribution of the excited electronic state population as a geometric pattern, we applied the multifractal analysis to it and calculated the temporal behavior of the fractal dimension $f(\alpha)$ as a function of the Lipschitz–Hölder exponent α, which is an appropriate method for understanding the cooperative relaxation process of photoexcited states. We found that the incubation period observed in various types of photoinduced cooperative phenomena corresponds to the formation of embryonic nuclei which is driven by nonadiabatic/adiabatic transition between electronic states during the relaxation of the Franck–Condon state.

1. Introduction

Recent progress on the study of photoinduced cooperative phenomena has shed light on long-standing theoretical and experimental problems with nonequilibrium dynamics of excited states [1–4]. It has been shown that many of these phenomena take place in strongly coupled electron–phonon systems, which means that they are concomitant with the change of crystal structure as well as the electronic transitions.

As we mentioned in our previous papers, we should discuss two important situations according as the itinerancy of the electrons in order to understand their mechanisms. When itinerant electrons are relevant to the cooperative phenomena, photoexcited electrons induce the instability of the crystal lattice, which leads to macroscopic structural change [5]. The second one, which we focus on in this paper, concerns the excitation of localized electrons in each molecular unit. In this case the Franck–Condon state of the system is approximately identical with an excited state of a single unit.

When multiple photons are irradiated to electronic systems, a superposition of the ground state and the Franck–Condon state is generated in general. After the light is turned off, electronic decoherence immediately takes place and the quantum-mechanical state of the system becomes a mixed state composed of the above-mentioned two states. Hence, the initial state of photoinduced cooperative phenomena is composed of randomly distributed excited units, and the statistical average of physical properties over different configurations of them corresponds to the experimental results of pump-probe spectroscopy, for example. After electronic decoherence is completed, the following relaxation process triggers the nucleation in which intermolecular interaction plays an important role. In this case, growing nuclei appear here and there in the system, which create characteristic spatial patterns composed of excited units. We note that, in various materials, there exists an incubation period which is characterized by the delay between photoexcitation and the start of the change of physical properties, and that we have demonstrated a similar feature in coupled electron–phonon systems [6]. In this paper, we study its microscopic nature and discuss the dynamics of the earliest stage of photoinduced nucleation which is understood as a mutation process of the Franck–Condon state into embryonic nuclei, nuclei which are able to grow.

Recent time-resolved x-ray or electron diffraction measurements have been shown to be promising to study the structural dynamics in ultrashort time scales [7,8]. Although the current time resolution of such experiments is at most 50 picoseconds, development of the beam sources has been recently accelerated, and, for example, x-ray free electron lasers will make it possible to observe the structural change on a time scale of lattice vibration period in the near future [9]. We stress that those ultrafast structural analyses will be used to study the initial dynamics of photoinduced nucleation, which is complementary to the conventional pump-probe experiments. For example, x-ray speckles in transient regime will give us fruitful information on the relaxation of Franck–Condon states, coalescence of photoinduced nuclei, and their growth dynamics [10].

We, however, still require more efficient methods to study the dynamics of the nucleation, since direct observation of the

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spatial patterns is unavailable in microscopic scale except for limited cases, e.g., photoinduced graphite–diamond transition [11]. Amongst various experimental techniques, recent results on cyanocomplexes have shown the possibility to reach the dynamics of nucleus boundaries in the early stage of photoinduced phase transition [12]. They probed the motion of the nucleus boundaries by transient Raman spectroscopy and estimated the timescale of the growth or the coalescence of photoinduced nuclei, which has additional information on the dynamical properties of photoinduced nuclei compared with their "bulk" properties. In discussing the interpretation or the role of their experiments, we first mention that the boundary of each photoinduced nucleus is its growth front in which nonadiabatic transition between electronic states frequently takes place. Since, as we have stressed [6,13], nonadiabatic relaxation process is a key to understand the dynamics of photoinduced nucleation particularly at its earliest stage, the measurement of the boundary dynamics will be a direct way to discuss the electronic transition in coherent regime.

We should be reminded of another important point when we pay attention to the boundaries in photoinduced nuclei, i.e., the geometrical property of their spatial patterns is a key to understand the nucleation as pattern formation dynamics. When domains or clusters grow their boundary also has a complicated structure as shown in, e.g., diffusion-limited aggregation (DLA) [14] or domain dynamics of the Ising model at the critical point [15]. Since, generally speaking, the boundaries and the domains show different geometrical features [16], we expect that we will obtain additional information on the cooperative dynamics of photoexcited states by studying the behavior of the boundaries. In this paper, we show that the multifractal analysis on the nucleation dynamics is useful to reveal the physics of photoinduced structural change particularly at the earliest stage of the relaxation processes. We note that, although the typical time-scale of the cooperative phenomena in cyanocomplexes is much longer than the coherent regime in general, it is worth while discussing the initial dynamics of the nucleus boundaries in order to prepare for future experiments on similar phenomena and/or materials.

The paper is organized as follows: in Section 2, our model of localized electrons used in the present study is introduced. We describe and discuss the calculated results in Section 3, and Section 4 is devoted to discussion and conclusions.

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) [17] on a square lattice with two electronic levels and a single phonon mode interacting with each other, which is described by the following Hamiltonian:

$$\begin{aligned}\mathcal{H} = \sum_{\vec{r}} \left\{ \frac{\hat{p}_{\vec{r}}^2}{2} + \frac{\omega^2 \hat{u}_{\vec{r}}^2}{2} + \left(\sqrt{2\hbar\omega^3} s \hat{u}_{\vec{r}} + \varepsilon\hbar\omega + s^2\hbar\omega\right)\hat{n}_{\vec{r}} + \lambda\sigma_x^{\vec{r}} \right\} \\ - \sum_{\langle\vec{r},\vec{r}'\rangle} \big[\alpha\omega^2(\hat{u}_{\vec{r}} - \beta\hat{n}_{\vec{r}})(\hat{u}_{\vec{r}'} - \beta\hat{n}_{\vec{r}'}) \\ + \{V - W(\hat{u}_{\vec{r}} + \hat{u}_{\vec{r}'})\}\hat{n}_{\vec{r}}\hat{n}_{\vec{r}'}\big], \qquad (1)\end{aligned}$$

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). $\sigma_i^{\vec{r}}$ $(i = x, y, z)$ 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 [18]. $\hat{n}_{\vec{r}}$ denotes the density of the electron in $|{\uparrow}\rangle_{\vec{r}}$, i.e., $\hat{n}_{\vec{r}} = \sigma_z^{\vec{r}} + 1/2$. 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 [19], 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 $\lambda\sigma_x^{\vec{r}}$ acts to reorganize them into two adiabatic PESs. Although all of the material parameters have not been successfully obtained either theoretically or experimentally, we have some clues to estimate them by referring to the experimental data on spin-crossover complex in which photoinduced cooperativity has been experimentally observed. First, ε is estimated by the results of calorimetric measurements and typically is 5–20 kJ/mol [20], and spectroscopic data on the vibrational frequency shows us that ω is 200–2000 cm^{-1} [21]. The Huang–Rhys factor s is ~ 1, since we assume that the quantum mechanical nature of the nuclear wavepackets on the PESs plays an important role. Though the other parameters are not easily accessible, we consider that they are small compared with the above-mentioned ones. In this way 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 numerically solved the time-dependent Schrödinger equation for the Hamiltonian (1) for systems with 128 × 128 sites with the periodic boundary condition in order to obtain the time-dependent wavefunction of the electron–phonon system $|\Phi(t)\rangle$. As for the initial condition, we set a certain number of molecules determined by the excitation ratio ρ to the Franck–Condon state, while the rest of them are set to the ground state. Detail of the method of calculations is described in Ref. [22] and we do not mention it further to avoid redundancy. Here we only note that the nucleation process in the present model appears as the growth of "islands" of molecules in the excited electronic states $|{\uparrow}\rangle_{\vec{r}}$, and that it is driven by the propagation of coherent phonons [6].

3. Calculated results

3.1. Distillation of the nucleus boundaries

When spatial patterns are defined by a binary function $y(\vec{r})$, we generally are able to extract their boundaries by tracing the locations of the jump of $y(\vec{r})$. The classical Ising models and/or the DLA corresponds to this case. However, our interest lies in more complicated cases, i.e., the spatial patterns of photoinduced nuclei are characterized by the distribution $n(\vec{r},t) = \langle\Phi(t)|\hat{n}_{\vec{r}}|\Phi(t)\rangle$, which takes any value between 0 and 1. This feature notifies us that we should consider the definition of the boundaries between the nuclei and the background ground-state region.

Thus, before we discuss the boundary properties with respect to $n(\vec{r},t)$, we introduce a method to "distill" the boundaries out of the entire system. We point out that a clue to define the method of distillation lies in the $\vec{r}$-dependence of $n(\vec{r},t)$. To be more precise, the value of $n(\vec{r},t)$ rapidly changes in the vicinity of boundaries, and thus we define the set of sites in the boundaries by means of the maximum value of the difference of $n(\vec{r},t)$ from those in the adjacent sites. For this purpose we introduce $k(\vec{r},t) = \min_{\vec{r}'} |n(\vec{r}',t) - n(\vec{r},t)|$ where $\vec{r}'$ runs over the nearest neighbor sites of $\vec{r}$. Although $k(\vec{r},t)$ has a large value at boundaries, we also should note that various geometrical patterns are observed also inside the nucleus [6]. This feature means that the value of $k(\vec{r},t)$ is large even for the sites inside the nucleus. and that we need an additional criterion for boundaries with respect