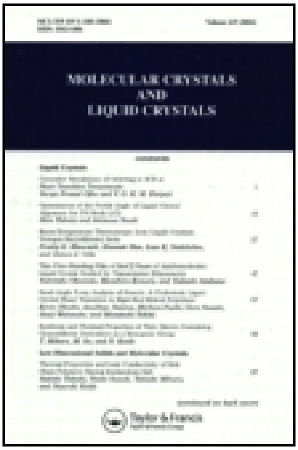

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Theory of Domino Processes in Photoinduced Cooperative Phenomena

Tetsuo Ogawa [a] [b] [c]

[a] Department of Physics, Osaka University, Toyonaka, Osaka, 560-0043, Japan

[b] Department of Physics, Tohoku University, Aoba-ku, Sendai, 980-8578, Japan

[c] "Structure and Transformation", PRESTO, JST, Japan

Version of record first published: 24 Sep 2006

To cite this article: Tetsuo Ogawa (2001): Theory of Domino Processes in Photoinduced Cooperative Phenomena, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 361:1, 199-207

To link to this article: http://dx.doi.org/10.1080/10587250108025739

Mol. Cryst. and Liq. Cryst., 2001, Vol. 361, pp. 199-207
Reprints available directly from the publisher
Photocopying permitted by license only

Theory of Domino Processes in Photoinduced Cooperative Phenomena

TETSUO OGAWA

Department of Physics, Osaka University, Toyonaka, Osaka 560–0043, Japan
Department of Physics, Tohoku University, Aoba-ku, Sendai 980–8578, Japan
"Structure and Transformation", PRESTO, JST, Japan

Photoinduced phase transitions via excited electronic states are discussed theoretically using a minimal model composed of localized electrons and one-dimensional lattices under the adiabatic and diabatic approximations. We show that the global structural transition by photoexcitation only at a site is possible, and we clarify conditions for the occurrence of such cooperative phenomena. Spatiotemporal dynamics of nonequilibrium first-order phase transitions is also investigated in terms of the domino process in photoinduced nucleations.

Keywords: photoinduced first-order phase transition; electron-lattice system; domino process; adiabatic and diabatic approximations

INTRODUCTION

Systems that show drastic changes in chromic, magnetic, dielectric, and transport properties triggered by external light stimulation[1] is an attractive target for fundamental physics and materials science[2,3]. One important strategy for developing highly responsive photo-excitation materials is to identify the photo-control of the cooperative phenomena. This exotic photo-effect is called a photoinduced phase transition (PIPT). Actually, in some organic materials such as π-conjugated polymers[4], organic charge-transfer complexes[5,6], and organo-metal spin-crossover complexes[7–9], the switching between absolutely-stable and metastable phases can be induced by local irradiation of light.

Since phenomena observed experimentally are very complicated, a simple theory and an essential mechanism help us understand them. Thus far, nevertheless, there has been little progress in theoretical study on such nonequilibrium dynamics[10,11] via excited electronic states. We need good phenomenological theories as well as microscopic calculations. Simultaneously, materials as better candidates for PIPTs are eagerly looked for. In this paper, we stress interesting and important features of the PIPTs; one of our purposes is to introduce a simple model and to discuss the dynamics of photoinduced first-order phase transitions via excited electronic states. We shall clarify qualitative differences in the domino dynamics during the phase transition in the adiabatic and diabatic regimes; both regimes yield two qualitatively different types of the domain-growing dynamics.

GENERAL FEATURES

Before discussing the spatiotemporal dynamics of the PIPTs, we shall review the general and universal features and remarks on PIPTs. (i) The "phase transitions" is originally defined under a thermally-equilibrium condition. On the other hand, the PIPT is a phenomena in a nonequilibrium situation. In this sense, the PIPT is also called "nonequilibrium phase transitions"[12]. Since the term "phase" means a global, macroscopic (not local, microscopic) state of a matter, photoinduced changes in one (or a few) molecule(s) are out of category of the PIPT. (ii) In order to yield the PIPTs, *multistabili ty* should be inherently built in the relevant materials. In other words, several local minima are necessary in their free energy. (iii) In the study of the PIPTs, spatiotemporal dynamics *during* the phase transition is of special importance. How does a local, microscopic change induced by photoexcitation develop to mesoscopic domains and to a global, macroscopic phase? This is a main problem to be solved. (iv) In the PIPT phenomena, the *cooperativity* always plays an essential role. This cooperativity results from nonlocal interactions between molecules (sites), and results in huge *nonlinearity* as a function of external stimulations or time. This nonlinearity has a great potentiality also in applications.

The above four items are minimum requirements for the PIPT phenomena. Another important purpose of the PIPT study is to search new phases which cannot be accessed by thermal fluctuations; we should make the best use of the higher energy of photons in comparison to the thermal energy. In other words, we are trying to find the new ground state ("true vacuum") of matters starting from a "false vacuum" (which has been considered as the true vacuum) via photoexcited high-energy states. From a viewpoint of application, the use of photon has also another advantage: the PIPT is one of *remote* controls of dramatic change of the state of matters.

Here some general features of the PIPT phenomena are listed. (a) Under a suitable condition, the PIPT is possible from a metastable state (false vacuum) to the absolutely-stable one (true vacuum) induced by pulse-light irradiation. In this case, the phase change can proceed *automatically* dissipating the energy to an environmental reservoir even after the light irradiation is turned off. On the other hand, a *photoinduced domain injection* is expected from the absolutely-stable state to a metastable one under the continuous irradiation (energy injection). In this article, we concentrate on the former case. (b) In usual PIPT phenomena, there are many different time scales. Competition among several time scales results in complex and novel dynamics of PIPTs. (c) The PIPT dynamics is strongly sensitive to characters of a reservoir. This is a consequence of nonequilibriumness of the PIPTs.

THE MINIMAL MODEL

To discuss the photoinduced structural change as the PIPT, a minimal model, a one-dimensional model is employed, each site of which is composed of a two-level localized electron and a lattice distortion[13–15]. The state of a single site is specified by the distortion u_j of the (jth) lattice, which we treat classically here, and the wavefunction of the localized electron, which we assume to be a linear combination of two states $|1\rangle_j$ and $|2\rangle_j$. Quantum nature of the lattice motion was discussed in [16].

The dimensionless Hamiltonian for this system is given by the sum of the local part $\mathcal{H}_j$ and the intersite interaction $\mathcal{H}_{\rm int}$ as $\mathcal{H} = \sum_j \mathcal{H}_j + \mathcal{H}_{\rm int}$;

$$\mathcal{H}_j = \begin{bmatrix} \epsilon_1^{\rm d}(u_j) + p_j^2 & t \\ t & \epsilon_2^{\rm d}(u_j) + p_j^2 \end{bmatrix}, \tag{1}$$

and $\mathcal{H}_{\rm int} = \sum_{i>j} k_{ij}(u_i - u_j)^2$, where the Hamiltonian $\mathcal{H}_j$ for the jth site is the operator acting on the jth electronic wavefunction with the diabatic energies: $\epsilon_1^{\rm d}(u_j) = u_j^2 - 2\gamma u_j + \epsilon$ and $\epsilon_2^{\rm d}(u_j) = u_j^2 + 2u_j$. Here γ is the electron-lattice coupling constant, p_j is the momentum of the jth lattice, ϵ is the energy difference between the potential minima, t is the coupling between the two electronic states, which is independent of u_j under the Condon approximation, and k_{ij} is the intersite interaction coefficient. The time is denoted by the dimensionless variable τ, which is normalized by the inverse Debye frequency. Here we set $\hbar = 1$.

As the dynamical processes, we consider the motion of the lattices and the absorption and emission of the photons according to the Franck-Condon principle. Though not explicitly shown in the Hamiltonian, the

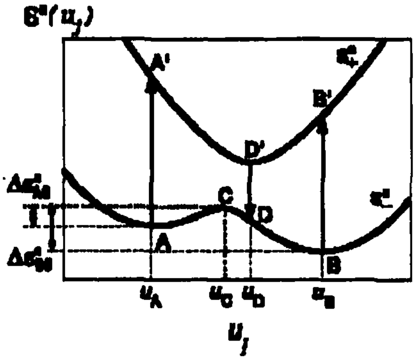

Figure 1: The local adiabatic potential $\epsilon^a_\pm(u_j)$ for the $\epsilon < 0$ case as a function of the local lattice distortion u_j in the jth unit cell. Here u_A and u_B (u_C) are the position of the local minima (maximum) of $\epsilon^a_-(u_j)$, and u_D is the position of the local minimum of $\epsilon^a_+(u_j)$. The upward (downward) arrow represents the electronic transition with absorption (emission) of a photon. $\Delta\epsilon^a_{AC} = \epsilon^a_-(u_C) - \epsilon^a_-(u_A)$ and $\Delta\epsilon^a_{BC} = \epsilon^a_-(u_C) - \epsilon^a_-(u_B)$ are the potential barriers.

lattices are coupled to the reservoir composed of other phonon and photon modes. Thus the system is an open one, and therefore the total energy dissipates during the lattice relaxation. Throughout this paper, we assume the case of strong dissipation (large friction).

We first investigate $\mathcal{H}_j$ neglecting the intersite interaction $\mathcal{H}_{\rm int}$. It is well known that the lattices should be regarded to move in the diabatic potentials $\epsilon^d_{1,2}(u_j)$ if they move fast, while they should be regarded to move in the adiabatic potentials $\epsilon^a_\pm(u_j)$ if they move slowly; the adiabatic potentials are defined as

$$\epsilon^a_\pm(u_j) = u_j^2 + (1-\gamma)u_j + \frac{\epsilon}{2} \pm \left\{\left[\frac{\epsilon}{2} - (1+\gamma)u_j\right]^2 + t^2\right\}^{1/2} . \qquad (2)$$

The + (−) sign corresponds to the higher (lower) electronic state. The adiabatic and diabatic regimes are justified under $t \gg S^{-1/2}$ and $t \ll S^{-1/2}$, respectively. Here S is the Huang-Rhys factor. We restrict our investigation to these two limiting cases. Crossover between these limits ($t \sim S^{-1/2}$) has been studied in[16].

The system can be bistable only under an appropriate choice of the single-site parameters ϵ, γ, and t; in the A (B) structure, the electronic state is almost $|2\rangle_j$ ($|1\rangle_j$) and the distortion $u_j = u_A$ ($u_j = u_B$). In the following, we treat mainly the case of $\epsilon < 0$, *i.e.*, the A (B) structure is the metastable (stable) structure. We can find four local structures A, B, C, and D′ in Fig. 1. Among these structures, A and B are stable at zero temperature, while D′ is unstable even at zero temperature due to the radiative decay to D. The electronic transition between the ground and excited states occurs accompanied by absorption or emission of a photon. The equation of motion for the lattice in a unit cell is given, *e.g.*, in the adiabatic regimes as $d^2u_j/d\tau^2 = -\partial\epsilon^{\mathbf{a}}_{\pm}(u_j)/\partial u_j - \Gamma du_j/d\tau + \eta_j(\tau)$, where Γ is the friction constant, and η_j is the thermal fluctuating force.

The local structural transition between A and B occurs through three different processes. (a) One is the *thermal* process along only the potential surface $\epsilon^{\mathbf{a}}_{-}$. (b) Second is the *quantum* tunneling process, which we neglect here. (c) The last is of importance here, the *optical* process, which is triggered by absorption of a photon. If the state is in the A structure at the moment of absorption, it will probably take the path of $\mathrm{A} \Rightarrow \mathrm{A}' \rightarrow \mathrm{D}' \Rightarrow \mathrm{D} \rightarrow \mathrm{B}$, where $\Rightarrow$ represents a path accompanied by absorption or emission of a photon; the first $\Rightarrow$ means the photoexcitation of an electron and the second one represents the spontaneous emission (SE). On the other hand, if the initial state is the B structure, the probable path is $\mathrm{B} \Rightarrow \mathrm{B}' \rightarrow \mathrm{D}' \Rightarrow \mathrm{D} \rightarrow \mathrm{B}$. Here we take into account the fact that the lattice relaxation $\mathrm{A}' \rightarrow \mathrm{D}'$ ($\mathrm{B}' \rightarrow \mathrm{D}'$) finishes within the time of order Γ^{-1} or the lattice vibration time τ_{vib}, which is usually much smaller than the SE (radiative) lifetime τ_{SE}.

PHOTOINDUCED DOMINO PROCESSES

In the Adiabatic Regime: Deterministic Domino.

Now we start investigating the structural change from the metastable A structure ($u_j = u_{\mathrm{A}}$ for all j) taking account of the intersite interaction $\mathcal{H}_{\mathrm{int}}$. As the most simple case of the photoinduced dynamics, we focus on the case that a single photon is absorbed at a certain site, which we call the zeroth site. Because our main interest lies in the photoinduced dynamics, we consider only the case that the lattice temperature is absolute zero. For simplicity, we hereafter assume that the intersite interaction can be parameterized by the total strength k and the force range μ as $k_{ij} = (k/2)(1 - \epsilon^{-1/\mu})\exp[-(|i-j|-1)/\mu]$. In the limit of $\mu \rightarrow 0$, it approaches the nearest-neighbor interaction $k_{ij} = \frac{k}{2}\delta_{|i-j|,1}$.

We shall discuss the dynamics under the adiabatic picture. In the following, we consider only the case of $\gamma = 1$. When the zeroth site in this system is excited at $\tau = 0$, the lattices start to relax from the initial position $\{u_j\} = u_{\mathrm{A}}$ during $0 < \tau < \tau_{\mathrm{SE}}$ toward a relaxed lattice

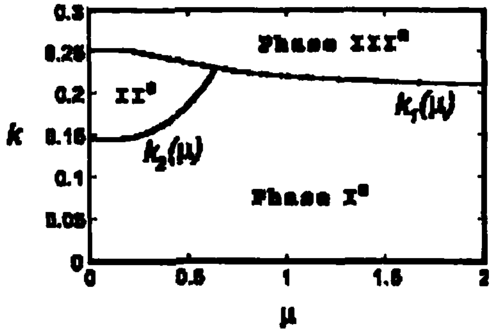

Figure 2: The phase diagram on the (μ, k) plane in the adiabatic regime with the single-site parameters $\epsilon = -0.5$, $\gamma = 1$, $t = 1.1$, and the friction $\Gamma = 1$ (large Γ). Only under the appropriate choice of ϵ and t, the phase II^a exists on the (μ, k) plane.

configuration $\{\bar{u}_j^{a1}\}$. After this first relaxation, the zeroth site is still unstable against the SE, and in the time order of $\tau_{\rm SE}$, it decays to the ground state ($D' \Rightarrow D \rightarrow B$). Then the lattices start to relax again from $\{\bar{u}_j^{a1}\}$. At this stage, we can observe the following three qualitatively different cases; (a) only the excited (zeroth) site makes a structural change to B (phase I^a, "frozen local distortion"), (b) every site yields a structural change to B (phase II^a, "domino") as the time goes by, and (c) every site goes back to the A structure (phase III^a, "restoration"). In the phase II^a for the case of strong dissipation (large Γ), the region of the B structure extends step by step with a constant velocity (called the "deterministic domino" process).

In Fig. 2, the phase diagram is drawn on the (μ, k) plane with other parameters fixed, which diagram is divided into three phases (I^a, II^a, and III^a). Some of the features can be understood qualitatively. (i) In the limit of weak interaction $k \rightarrow 0$, every site behaves independently, and only the excited site makes a structural change from A to B. Thus the phase I^a appears in the region of small k. (ii) On the other hand, in the limit of strong interaction $k \rightarrow \infty$, even the excited site cannot be distorted largely enough to satisfy $\bar{u}_0^{a1} > u_{\rm C}$ in the first relaxation stage because of the large cost of the elastic energy. Obviously, every site goes back to A. Thus the phase III^a appears in the region of large k. (iii) The most interesting phase is the phase II^a, where a global structural change occurs by only one-site excitation. The phase II^a appears in the small μ region in Fig. 2. The reason is that the region of the B structure extends step by step through the domino effect, which can be more effectively induced in the case that the local structural change around the excited site exerts strong influence upon the neighboring sites than in the case that it exerts weak influence upon many remote sites. There exists energy difference between the two structures, and a single boundary moves by itself at its intrinsic velocity.

When the friction Γ is small, on the other hand, the domino dynamics is quite different from the above deterministic domino; an *accelerated motion* of the domain walls is possible[17]. In the case of small Γ, there is another mechanism of inducing the domino; the lattice relaxation energy between A′ and D′ is effectively used to triggering the domino process at the neighbor sites. Thus, the domino starts during an electronic excited state before the SE. This novel domino mechanism is investigated in detail and the results will be published elsewhere[18].

In the Diabatic Regime: Stochastic Domino.

In the diabatic regime ($t \ll S^{-1/2}$), on the other hand, the system relaxes in a qualitatively different way. When the zeroth site is photoexcited, the system starts to relax to the relaxed lattice configuration $\{\bar{u}_j^{\mathrm{d1}}\}$. After the first relaxation, the system may still have the instability against the SE. The stability against the SE is determined by the relative location between the crossing point $u_{\mathrm{X}} (= \epsilon/4)$ of the two diabatic potentials and the relaxed position $\bar{u}_j^{\mathrm{d1}}$ of the lattice. There are three types of situation[19].

(i) First, we discuss the case of $u_{\mathrm{X}} < \bar{u}_0^{\mathrm{d1}}$ and $\bar{u}_j^{\mathrm{d1}} < u_{\mathrm{X}}$ for $j \neq 0$, which occurs when the intersite interaction is weak (small k). Every site is in the lower electronic state, and stable against the radiative decay. This local distortion does neither grow nor disappear, which we hereafter call the phase $\mathrm{I^d}$ (frozen local distortion). (ii) Next, we discuss the case of $\bar{u}_j^{\mathrm{d1}} < u_{\mathrm{X}}$ for all j, which occurs when the intersite interaction is strong (large k). Only the zeroth site is in the higher electronic state and unstable against the radiative decay. It will decay radiatively to the other electronic state in the time order of τ_{SE}. After emission of the photon, the system starts relaxation again and returns to the initial A structure. We call this case the phase $\mathrm{III^d}$ (restoration). (iii) Finally, we discuss the case of $u_{\mathrm{X}} < \bar{u}_j^{\mathrm{d1}}$ not only for $j = 0$ but also for $j = \pm 1$. In this case, the ±1st sites are in the higher electronic state, and have the possibility of SE. Because the SE from these sites is a stochastic process, we cannot predict which site emits a photon earlier. After all, the region of the B structure extends rather slowly through such a stochastic sequence of the SEs; the region of the B structure extends step by step with an irregular velocity (called the "stochastic domino" process), which we call the phase $\mathrm{II^d}$. The condition

Table 1: Comparison between the domino dynamics under the adiabatic (for large Γ case) and diabatic regimes after photoexcitation of the zeroth ($j = 0$) site. The total number of sites is N.

Regime	Adiabatic	Diabatic
Condition	$t \gg S^{-1/2}$	$t \ll S^{-1/2}$
Domino phase	II^{a}	II^{d}
SE at $j = 0$	Occur	None
SE at $j \neq 0$	None	Occur
Total number of emitted photons	1	$N - 1$
Domino type	Deterministic	Stochastic
Time scale of domino	$\tau_{\mathrm{vib}} \sim 10^{0\sim1}$	$\tau_{\mathrm{SE}} \sim 10^{4\sim5}$

for the existence of the phase II^{d} is given by $-4 < \epsilon < 4(5 - 4\sqrt{2})$.

REMARKS

We have discussed two kinds of domino dynamics in the adiabatic and diabatic limits, which are summarized in Table 1. These are typical spatiotemporal dynamics of a photoinduced nucleation in one dimension, which are quite different from those in higher-dimensional cases discussed with the mean-field approximation[20–22]. The crossover between these two limits is also interesting. We have proposed a new method to treat the lattice relaxation based on the diabatic picture, taking into account the nonradiative (nonadiabatic) electronic transition[16].

To summarize, the most interesting and important point in this article is the fact that the possibility of the global structural change by one-site excitation (the phases II^{a} and II^{d}) is confirmed under both the adiabatic and diabatic approximations. Although the present theory does not include all the actual details, we believe that these findings hold universally in photoactive electron-lattice systems and will be of great significance in the interpretation of experimental results. In addition, this theory will offer a guiding principle in the materials design for exhibiting PIPTs.

Acknowledgements

The author is grateful to Dr. K. Koshino and Prof. V. I. Sugakov for discussion and collaboration. This work is partly supported by a Grant-in-Aid for Scientific Research on Priority Areas, "Photoinduced Phase

Transitions and Their Dynamics," from the Ministry of Education, Science, Sports and Culture of Japan.

References

[1] K. Nasu (Ed.), *Relaxations of Excited States and Photo-Induced Structural Phase Transitions,* (Springer, Berlin, 1997).

[2] T. Ogawa and Y. Kanemitsu (Eds.), *Optical Properties of Low-Dimensional Materials,* (World Scientific, Singapore, 1995).

[3] T. Ogawa and Y. Kanemitsu (Eds.), *Optical Properties of Low-Dimensional Materials,* Volume 2, (World Scientific, Singapore, 1998).

[4] S. Koshihara, Y. Tokura, K. Takeda, and T. Koda, *Phys. Rev. Lett.* **68,** 1148 (1992).

[5] S. Koshihara, Y. Takahashi, H. Sakai, Y. Tokura, and T. Luty, *J. Phys. Chem. B* **103,** 2592 (1999).

[6] K. Koshino and T. Ogawa, *Phys. Rev. B* **61,** 12101 (2000).

[7] K. Koshino and T. Ogawa, J. *Phys. Soc. Jpn.* **68,** 2164 (1999).

[8] Y. Ogawa, S. Koshihara, K. Koshino, T. Ogawa, C. Urano, and H. Takagi, *Phys. Rev. Lett.* **84,** 3181 (2000).

[9] K. Koshino and T. Ogawa, *J. Lumin.* **87–89,** 642 (2000).

[10] J. D. Gunton and M. Droz, *Introduction to the Theory of Metastable and Unstable States,* (Springer-Verlag, Berlin, 1983).

[11] E. Hanamura and N. Nagaosa, *J. Phys. Soc. Jpn.* **56,** 2080 (1987).

[12] J. Marro and R. Dickman, *Nonequilibrium Phase Transitions in Lattice Models,* (Cambridge University Press, Cambridge. 1999).

[13] K. Koshino and T. Ogawa, *J. Phys. Soc. Jpn.* **67,** 2174 (1998).

[14] K. Koshino and T. Ogawa, *Phys. Rev. B* **58,** 14804 (1998).

[15] T. Ogawa, *Phase Transitions* (in print).

[16] K. Koshino and T. Ogawa, *J. Korean Phys. Soc.* **34,** S21 (1999).

[17] V. V. Mykhaylovskyy, V. I. Sugakov, K. Koshino, and T. Ogawa, *Solid State Commun.* **113,** 321 (1999).

[18] V. V. Mykhaylovskyy, V. I. Sugakov, and T. Ogawa, (unpublished).

[19] K. Koshino and T. Ogawa, *J. Phys. Chem. Solids* **60,** 1915 (1999).

[20] N. Nagaosa and T. Ogawa, *Phys. Rev. B* **39,** 4472 (1989).

[21] T. Ogawa and N. Nagaosa, in K. Nasu (Ed.), *Relaxations of Excited States and Photo-Induced Structural Phase Transitions,*(Springer, Berlin, 1997), pp. 45.

[22] T. Ogawa and K. Koshino, in *Physics and Chemistry of Solids,* Proc. 11th Seminar on Phase Transitions and Critical Phenomena, (Poland, 1998), pp. 131.