I-P Photoinduced Phase Transitions in Spin-Crossover and Charge-Transfer Complexes

Now a variety of materials show photoinduced phase transitions. Their characters depend much on the relative importance of the interactions inside the system to those between the system and the heat bath. If the former are dominant, the time evolution is deterministic allowing coherent oscillations for instance. If the latter are dominant, the time evolution is stochastic and the efficiency is generally low. These characters depend also on the time scale. For long-time properties, dissipation generally obscures the deterministic evolution. Thus we need to employ both the deterministic approach with the help of the time-dependent Schrödinger equation and the stochastic approach with the help of the master equation. The macroscopic coherent oscillation of the neutral-ionic domain walls in the TTF-CA complex needs to be described by the former approach. Meanwhile, the photoinduced neutral-to-ionic transition accompanied with ferroelectric ordering in the same material by pump light for intra-molecular excitations would be described by the latter approach. Low-spin-to-high-spin transitions in organometal spin-crossover complexes are well described by the stochastic approach because the evolution is governed by thermal processes.

I-P-1 On Thermo- and Photo-Induced Symmetry-Broken Transformation in Spin-Crossover Complex; Cooperative Activation

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[*J. Phys. Soc. Jpn.* **73**, 1237–1243 (2004)]

We study energetics of a cooperative low-spin (L) to high-spin (H) transformation in a crystal with two sublattices, where thermo- and photo-induced symmetry-broken phases have been recently observed. The model takes into account an intra-dimer antiferroic coupling and inter-dimer couplings. Cooperative activation processes for switching between LH and HL states and that from LL to HH states of a dimer are analyzed. It is shown that locally (within a dimer) preferred symmetry-broken, LH and HL, states compete with inter-dimer couplings, which stimulates dynamical disorder *via* a decrease in the energy barrier for a flip between asymmetric configurations. On the other hand, a locally non-preferred symmetric state (HH) is supported by inter-dimer interaction *via* a cooperative activation mechanism. We conclude that symmetry-broken states can form an intermediate thermo-induced phase or can be observed as a photo-induced one at low temperatures as a result of local equilibrium. The global equilibrium follows from cooperative interaction and governs the thermo-induced re-entrant phase transition.

I-P-2 Different Stabilities of the Mixed-Spin Phase in Equilibrium from That in Non-Equilibrium in a Two-Sublattice Classical-Spin Model for Spin-Crossover Complexes

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Some spin-crossover complexes show two-step transitions by changing temperature between high-spin and low-spin phases in equilibrium. In $[\mathrm{Fe(2\text{-}pic)_3}]\mathrm{Cl_2{\cdot}EtOH}$, high-spin-low-spin ordering is recently observed on the 50% plateau of high-spin fraction at intermediate temperatures. However, the time evolution of this material under continuous photoirradiation does not clearly show the high-spin-low-spin-ordered phase even transiently. We employ a two-sublattice classical-spin model, where an intra-dimer inter-sublattice anti-ferroic coupling prefers the intermediate phase while an inter-dimer intra-sublattice ferroic coupling the uniformly high-spin or low-spin phase. Although an inter-dimer inter-sublattice coupling plays the same role with the intra-dimer inter-sublattice coupling at the mean-field level, we find by Monte Carlo simulations that their effects are different especially when the material is under photoirradiation. The inter-dimer coupling so enhances the short-range spin-spin correlation as to give larger deviation from the mean-field results than the intra-dimer coupling. This effect makes the appearance of the high-spin-low-spin-ordered phase difficult in non-equilibrium conditions.

I-P-3 Inter-Chain Electrostriction and Pressure-Induced Multicriticality in Charge-Transfer Organic Complexes

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[*Proc. Int. Conf. Sci. Tech. Synth. Met.* (2004)]

Pressure-induced multicriticality in the quasi-one-dimensional mixed-stack charge-transfer complex TTF-CA is theoretically explained. We show that the inter-stack electrostriction (Coulomb-lattice coupling) is essential to cause multi-critical phase transitions among the neutral, paraelectric ionic, and ferroelectric ionic phases.

I-P-4 Stochastic Approach to Evolution of Ionicity and Ferroelectricity in Mixed-Stack Organic Charge-Transfer Complexes by the Blume-Emery-Griffiths Model

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Mixed-stack organic charge-transfer complexes show neutral-ionic and dimerization-induced ferroelectric phase transitions. In the most famous TTF-CA complex, they occur simultaneously at ambient pressure but at different temperatures under high pressure. Thus we treat both the ionicity and the dimerization using the Blume-Emery-Griffiths model. Long-time evolution is studied by solving the master equation during and after photoirradiation of the complex. As a first step, we use the mean-field approximation that does not distinguish the intra- and inter-chain couplings. The time evolution of the ionicity and that of the ferroelectricity generally take place on different time scales, allowing the transient appearance of the paraelectric ionic phase. We find photoinduced breaking of the inversion symmetry and spontaneous ordering of electric polarizations leading to the ferroelectric ionic phase after the neutral phase is photoexcited and converted into the paraelectric ionic phase. This would explain the recent experimental findings with intra-molecular excitations.

I-P-5 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: I. Threshold Behavior in Ionic-to-Neutral Transition

YONEMITSU, Kenji

[*J. Phys. Soc. Jpn.* **73**, 2868–2878 (2004)]

Photoinduced dynamics of charge density and lattice displacements is calculated by solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating potentials for the mixed-stack organic charge-transfer complex, TTF-CA. A pulse of oscillating electric field is incorporated into the Peierls phase of the transfer integral. The frequency, the amplitude, and the duration of the pulse are varied to study the nonlinear and cooperative character of the photoinduced transition. When the dimerized ionic phase is photoexcited, the threshold behavior is clearly observed by plotting the final ionicity as a function of the increment of the total energy. Above the threshold photoexcitation, the electronic state reaches the neutral one with equidistant molecules after the electric field is turned off. The transition is initiated by nucleation of a metastable neutral domain, for which an electric field with frequency below the linear absorption peak is more effective than that at the peak. When the pulse is strong and short, the charge transfer takes place on the same time scale with the disappearance of dimerization. As the pulse becomes weak and long, the dimerization-induced polarization is disordered to restore the inversion symmetry on average before the charge transfer takes place to bring the system neutral. Thus, a paraelectric ionic phase is transiently realized by a weak electric field. It is shown that infrared light also induces the ionic-to-neutral transition, which is characterized by the threshold behavior.

I-P-6 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: II. Linear Behavior in Neutral-to-Ionic Transition

YONEMITSU, Kenji

[*J. Phys. Soc. Jpn.* **73**, 2879–2886 (2004)]

Dynamics of charge density and lattice displacements after the neutral phase is photoexcited is studied by solving the time-dependent Schrödinger equation for a one-dimensional extended Peierls-Hubbard model with alternating potentials. In contrast to the ionic-to-neutral transition studied previously, the neutral-to-ionic transition proceeds in an uncooperative manner as far as the one-dimensional system is concerned. The final ionicity is a linear function of the increment of the total energy. After the electric field is turned off, the electronic state does not significantly change, roughly keeping the ionicity, even if the transition is not completed, because the ionic domains never proliferate. As a consequence, an electric field with frequency just at the linear absorption peak causes the neutral-to-ionic transition the most efficiently. These findings are consistent with the recent experiments on the mixed-stack organic charge-transfer complex, TTF-CA. We artificially modify or remove the electron-lattice coupling to discuss the origin of such differences between the two transitions.

I-P-7 Phase Transition in a One-Dimensional Extended Peierls-Hubbard Model with a Pulse of Oscillating Electric Field: III. Interference Caused by a Double Pulse

YONEMITSU, Kenji

[*J. Phys. Soc. Jpn.* **73**, 2887–2893 (2004)]

In order to study consequences of the differences between the ionic-to-neutral and neutral-to-ionic transitions in the one-dimensional extended Peierls-Hubbard model with alternating potentials for the TTF-CA complex, we introduce a double pulse of oscillating electric field in the time-dependent Schrödinger equation and vary the interval between the two pulses as well as their strengths. When the dimerized ionic phase is photoexcited, the interference effect is clearly observed owing to the coherence of charge density and lattice displacements. Namely, the two pulses constructively interfere with each other if the interval is a multiple of the period of the optical lattice vibration, while they destructively interfere if the interval is a half-odd integer times the period, in the processes toward the neutral phase. The interference is strong especially when the pulse is strong and short because the coherence is also strong. Meanwhile, when the neutral phase is photoexcited, the interference effect is almost invisible or weakly observed when the pulse is weak. The photoinduced lattice oscillations are incoherent due to random phases. The strength of the interference caused by a double pulse is a key quantity to distinguish the two transitions and to evaluate the coherence of charge density and lattice displacements.

I-P-8 Theory of Optical Phase Control in Charge-Transfer Complexes

YONEMITSU, Kenji

[*Proc. Int. Conf. Sci. Tech. Synth. Met.* (2004)]

Concerning the paraelectric ionic phase in the mixed-stacked organic charge-transfer TTF-CA complex, which needs high pressure to realize in thermal equilibrium or some particular photoexcitation to transiently realize at ambient pressure and low temperatures, we theoretically point out that photoexcitations with appropriate strength and duration can generally produce this phase. Photoinduced charge-lattice dynamics is calculated in a one-dimensional extended Peierls-Hubbard model with alternating potentials during and after a pulse of oscillating electric field. When the field is so weak and long that the supplied energy does not directly transfer charge in the ionic phase, the dimerization-induced charge polarizations are disordered first to restore the inversion symmetry on average before the neutral phase appears. The interference effect observed after a double pulse due to the charge-lattice coherence is accordingly weakened.

I-P-9 Theory of Photoinduced Phase Dynamics in Organic Charge-Transfer Complexes

YONEMITSU, Kenji

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In the quasi-one-dimensional mixed-stack organic charge-transfer complex, TTF-CA, photoirradiation is known to trigger transitions between the neutral and ionic phases. Here we use a one-dimensional extended Peierls-Hubbard model with alternating potentials and calculate the mean-field dynamics of charge density coupled with that of lattice displacements. We show qualitative differences between the photoinduced ionic-to-neutral and neutral-to-ionic transitions, which are consistent with recent experimental findings. Namely, the ionic-to-neutral transition proceeds cooperatively, characterized by threshold behavior, while the neutral-to-ionic transition proceeds uncooperatively, characterized by linear behavior. The threshold absorption in the former depends on the strength or the duration of the pulse. The coherence during the transition dynamics is also different between the two transitions. In the ionic-to-neutral transition, a clear interference effect is observed as a function of the interval when the pulse is spilt into two.