I-L  Photoinduced Phase Transitions in Molecular Materials

Photoirradiation may create electrons, holes or excitons, which are often accompanied by local structural deformation. Sometimes it causes spatially large structural transformations with the help of cooperativity possessed by interacting electrons and molecules. Thus, a nonequilibrium phase can be generated, which may not be reached by simply changing temperature or pressure because the energy of a photon is much higher than thermal energies. Such photoinduced phase transitions have been studied extensively, both experimentally and theoretically. Thanks to the great progress in laser spectroscopy techniques, charge and lattice dynamics are being clarified in many molecular materials on different time scales including ultrafast and/or coherent dynamics. Now we need to treat relevant itinerant-electron models, whose transfer integrals give transition amplitudes. This is in contrast to stochastic dynamics in classical statistical models, where transition probabilities are determined by the Boltzmann factors at finite temperatures.

I-L-1  Interchain Coupling Effects on Photoinduced Phase Transitions between Neutral and Ionic Phases in an Extended Hubbard Model with Alternating Potentials and an Electron-Lattice Coupling

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Dynamics of ionic-to-neutral and neutral-to-ionic phase transitions induced by intrachain charge-transfer photoexcitations are studied in a quasi-one-dimensional extended Hubbard model with alternating potentials and an electron-lattice coupling for mixed-stack charge-transfer complexes. For interchain couplings, we use electron-electron interactions previously estimated for TTF-CA. Photoexcitation is introduced by a pulse of oscillating electric field. The TDHF approximation is used for the electronic part, and the classical approximation for the lattice part. In the ionic-to-neutral transition, the transferred charge density is a strongly nonlinear function of the photoexcitation density, which is characterized by the presence of a threshold. With substantial interchain couplings comparable to those in TTF-CA, the interchain correlation is strong during the transition. Neutral domains in nearby chains simultaneously grow even if their nucleation is delayed by reducing the amplitude of the electric field. With weaker interchain couplings, the growing processes are in phase only when the amplitude of the electric field is large. Thus, the experimentally observed, coherent motion of a macroscopic neutral domain boundary is allowed to emerge by such substantial interchain couplings. In the neutral-to-ionic transition, by contrast, the transferred charge density is almost a linear function of the photoexcitation density. Interchain electron-electron interactions make the function slightly nonlinear, but the uncooperative situation is unchanged and consistent with the experimental findings.

I-L-2  Inter-Chain Coulomb-Lattice Relaxation and Multicriticality in Charge Transfer Organic Complexes

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We discuss the neutral-to-ionic phase transition and the emergence of multi-criticality in the quasi-one-dimensional charge-transfer salt TTF-CA under pressure. We stress that subtle interplay of Coulomb and lattice dynamics may be quite sensitive to pressure. Emergence or disappearance of the multi-critical point in a series of charge-transfer salts is understood through this interplay. What’s behind is coexistence and coupling of non-symmetry-breaking and symmetry-breaking order parameters.

I-L-3  Quantum Paraelectricity near the Neutral-Ionic Critical Point

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In a series of organic charge-transfer complexes DMTTF-QBrCl4–n, the neutral-ionic (NI) phase transition is observed in the chlorine rich complexes for n < 2.1. The neutral ground state of DMTTF-QBr4 is destabilized by applying hydrostatic pressure P, and the NI transition emerges when P exceeds P\text{c} where Tc = 0; so-called the quantum critical point (QCP). In the vicinity of the QCP, the dielectric permittivity in the neutral phase follows the Barrett formula characteristic of quantum paraelectricity, which probably originates from charge-transfer fluctuations. In the present study, we have phenomenologically dealt with the NI phase transition by a quantum version of the Blume-Emery-Griffiths (BEG) model. Applying the mean-field approximation to the QBE model, the magnitude of ferroelectricity and ionicity as well as the dielectric permittivity are calculated with changing P. The paraelectric ground state with a finite ionicity is realized with the Barrett-type permittivity, which is consistent with the experimental results. In addition, the calculated permittivity agrees well with that of DMTTF-QBr4 under various pressures including the ionic phase. What we found is that the quantum dipole-flipping term is indispensable to reproduce the experimental results within our model. Therefore, it is highly suggested that charge transfer fluctuations due to the quantum tunneling allow a finite ionicity even in the neutral phase, which realizes the quantum paraelectric ground state near the quantum critical point.
Molecular materials are used in many device structures. Charge transport is always through an interface between two materials with different electronic states and work functions. In field-effect transistors fabricated on an insulating material with coherent charge transport under electric fields, the insulator-(source/drain) electrode interface barrier potentials, known as Schottky barriers, play an important role. For band insulators, the Schottky barriers indeed govern the current-voltage characteristics. Quite recently, ambipolar characteristics are found in field-effect transistor device structures based on organic single crystals of a quasi-one-dimensional Mott insulator. Thus, we need to take correlation effects into account in dealing with charge transport through electrostatic potentials that originate from the long-range Coulomb interaction.

The characteristics of a field-effect transistor (FET) fabricated on a crystal of an organic charge-transfer complex depend on the electronic state of the crystal. Ambipolar characteristics are observed for Mott insulators, while unipolar ones for band insulators. We study them in one-dimensional models of electrons. The Hubbard model for a Mott insulator is attached to the tight-binding model for metallic electrodes. We solve the Poisson equation and add its solution for the electrostatic potential to these models in order to reproduce Schottky barriers at the interfaces. We use both the mean-field approximation and the Lanczos exact-diagonalization method in solving the time-dependent Schrödinger equation to obtain essentially the same results.

Mott insulators show ambipolar FET characteristics irrespective of the difference between the work function of the channel and that of the metallic electrodes. In order to exclude the ambiguity introduced in the one-dimensional modeling of the effect of the gate electrode and to allow the direct observation of the correlation between the electronic state in the channel and that at the interfaces, we have designed gate electrodes and employed different metals for the electrodes among which only one interface possesses a large work-
function difference. In this case, the current-voltage characteristics are almost anti-symmetric for Mott insulators and very asymmetric for band insulators. These results are also consistent with recent experiments by T. Hasegawa and coworkers. The characteristics for Mott insulators are again caused by the correlation between the electronic state in the channel and that at the interface.