

Theory of Photoinduced Phase Transitions

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Photoirradiation of materials usually creates electrons and holes, which are often accompanied by local structural deformation. With the help of cooperativity, the electronic and/or structural deformation can proliferate to change the physical property such as conductivity, permittivity, and magnetic susceptibility. The resultant nonequilibrium phase may not be reached by changing temperature or pressure because the energy of a photon is much higher than thermal energies. Our theoretical researches are focused on the mechanisms and dynamics of photoinduced phase transitions, how they are controlled, and how the photoinduced electron–lattice states are different from those which are realized in thermal equilibrium.¹⁾

1. Normal Mode Analysis for Intra- and Inter-Molecular Electron–Phonon Coupled Systems

The ground-state properties of a molecular compound $\text{Et}_2\text{Me}_2\text{Sb}[\text{Pd}(\text{dmit})_2]$ are theoretically studied, which shows a dimer-Mott character in $\text{Pd}(\text{dmit})_2$ layers at high temperature and charge order mainly stabilized by electron–phonon interactions at low temperature. An effective extended Peierls-Hubbard model is constructed with intra- and inter-molecular electronic and phonon degrees of freedom. Using a mean-field approximation, the energies and optimized structures are calculated for isolated neutral, monovalent, divalent $\text{Pd}(\text{dmit})_2$ dimers and their two-dimensional crystallized states. The optical conductivities of the latter are calculated by a single configuration interaction method. Through these numerical calculations, model parameters have been evaluated by comparing the theoretical and experimental ground-state properties.

Then, the normal mode analysis is performed for the intradimer C=C stretching vibrations and intradimer inter-monomer stretching vibrations. Molecular vibrations with different symmetries are coupled to different combinations of electrons and holes within a molecule, so that their frequencies depend on the molecular charge in different manners. This

information is useful to analyze photoinduced transient states, where the relation between their frequencies and the molecular charge is modified from the equilibrium counterpart.

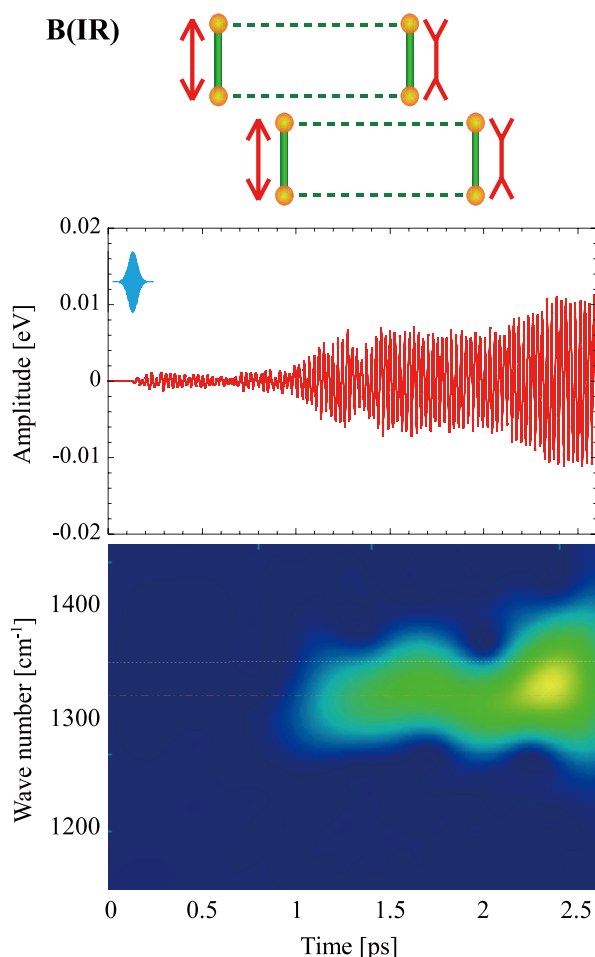


Figure 1. C=C stretching phonon mode B (infrared active) schematically represented in the upper panel. Its time evolution (middle panel) and time-frequency spectrogram (lower panel) on the initially neutral dimer are shown when the charge-separated state is photoexcited.

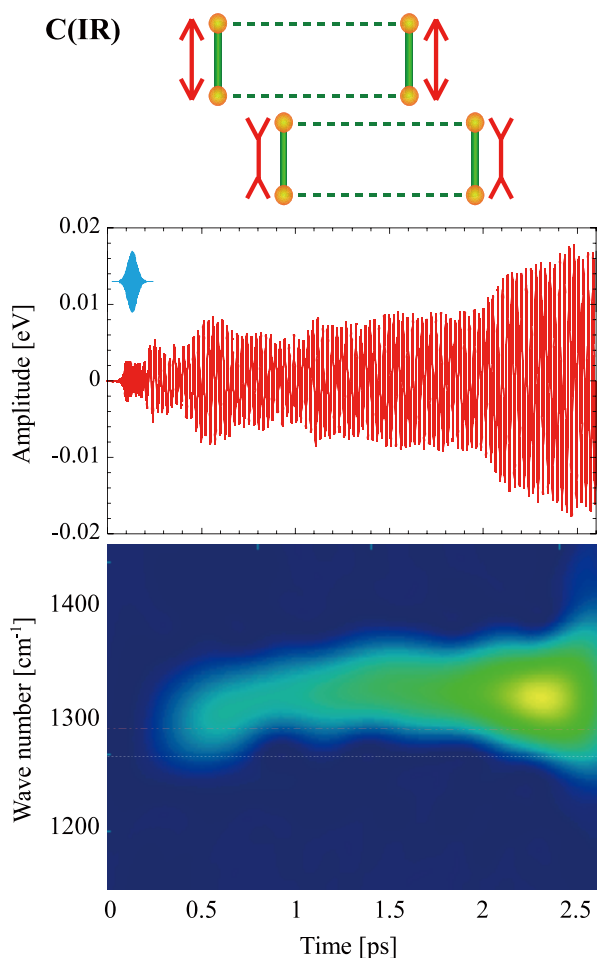


Figure 2. C=C stretching phonon mode C (infrared active) schematically represented in the upper panel. Its time evolution (middle panel) and time-frequency spectrogram (lower panel) on the initially neutral dimer are shown when the charge-separated state is photoexcited.

2. Photoinduced Dynamics in Intra- and Inter-Molecular Electron-Phonon Coupled Systems²⁾

For the photoinduced dynamics in $\text{Et}_2\text{Me}_2\text{Sb}[\text{Pd}(\text{dmit})_2]_2$, the time-dependent Schrödinger equation is numerically solved for the Hartree-Fock wave function on the cluster of sixteen dimers (eight sites in each dimer, 128 sites in total). The

classical equation of motion is solved for phonons. Photoexcitation is introduced through the Peierls phase in the transfer integrals.

We focus on intradimer C=C stretching vibrations that are infrared active and experimentally observed so far, which are schematically shown in the upper panels of Figures 1 and 2. The middle panels show the time evolution of their amplitudes on the initially neutral dimer when the charge-separated state is photoexcited. The lower panels show their time-frequency spectrograms.

The initially neutral and divalent dimers become monovalent at about 0.5 ps after photoexcitation. After 0.5 or 1 ps, their oscillations are noticeable and sinusoidal. The frequency of the B mode is actually close to that in a monovalent dimer in the equilibrium state. The B mode is coupled with the antibonding-LUMO (electron)–antibonding-HOMO (hole) excitation within the dimer. Their correlation is recovered and becomes close to that in equilibrium after 1 ps.

However, the frequency of the C mode after 1 ps is not close to that in a neutral dimer or that in a monovalent dimer, but it is rather close to the bare frequency (*i.e.*, the frequency if the couplings with electron–hole excitations are turned off) of 1331 cm^{-1} . The C mode is coupled with the antibonding-HOMO (electron)–bonding-HOMO (hole) excitation and the antibonding-LUMO (electron)–bonding-LUMO (hole) excitation within the dimer, so that it is largely softened in equilibrium. Their correlations are largely modified and far from that in equilibrium after 1 ps. This phonon mode appears to oscillate almost independently of electron–hole excitations.

Thus, a usual picture based on the adiabatic potential fails even if phonons are treated classically. The correlation between a phonon and its relevant electron–hole excitation(s) depends on the mode or on the symmetries of the vibrational pattern and the wave functions of electron(s) and hole(s). The analysis of these correlations at an early stage of photoinduced charge-order melting is essential for future manipulation of non-equilibrium phases.

References

- 1) K. Yonemitsu, *Crystals* **2**, 56–77 (2012).
- 2) K. Nishioka and K. Yonemitsu, *Phys. Status Solidi C* **9**, 1213–1215 (2012).

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