Excitation Photon Energy Dependence of the Relaxation Processes of the Photoexcited States in a Quasi-One-Dimensional Halogen Bridged Pt Complex

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Abstract

Excitation photon energy dependence of the relaxation processes of the photoexcited states in a quasi-one-dimensional halogen-bridged platinum complex has been investigated by femto second transient absorption measurements. In a Pt complex, \([\text{Pt(en)}_2][\text{Pt(en)}_2\text{I}_2](\text{SO}_4)_2\cdot6\text{H}_2\text{O}\) (Pt-I-SO\(_4\)), a photo-induced absorption (PA) band caused by self trapped excitons (STE’s) has been observed when the excitation photon energy is close to the peak energy, 1.44eV, of the absorption band of the one photon allowed charge transfer (CT) exciton with odd parity. In addition, a long lived PA bands caused by charged solitons (CS’s) has been observed. The intensity of these long lived CS absorption band shows quadratic excitation power dependence. This shows that CS’s pairs are not generated from odd-CT-excitons but from the higher energy two photon excited states. When the excitation photon energy is close to a half of the of the even CT- exciton energy, 1.84eV, PA bands caused by STE’s and CS’s have been observed. These states are generated from the two photon excited even CT-excitons. When the excitation photon energy is much higher than the energy of the odd CT-exciton, PA bands caused by CS’s and polarons have been observed. The intensities of these PA bands show linear excitation power dependences. Photo-generated free electron hole pairs are considered to relax into CS’s and polarons.

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One dimentional electron system; lattice relaxation; ultrafast penomena; seif-trapped exciton; soliton

1. Introduction

Optical properties of one-dimensional electron systems have been attracting much attention because of their large optical nonlinearity and novel relaxation dynamics of photo-excited states. In MX-chain compounds metal (M=Pt, Pd, or Ni) ions and halogen (X=Cl, Br, and I) ions form linear chains. The metal-halogen ion chains are surrounded by ligand molecules and by counter ions. Due to the halogen ion distortion from the center of the
neighboring metal ions, charge density waves as $M^{\rho \cdot}X-M^{\rho \cdot}X-M^{\rho \cdot}X-M^{\rho \cdot}X$ with periods of twice the metal-metal distance are formed in the chains in Pt- and Pd-complexes [1]. Some Ni-complexes have Mott insulating ground states [2]. Due to the two-fold degeneracy in the ground states, and due to the strong electron-phonon interaction, photoexcited states are considered to relax to neutral soliton (NS) pairs, charged soliton (CS) pairs, polaron pairs, or self-trapped excitons (STE’s) in Pt and Pd complexes [3-5]. Considerable amounts of studies have been made on the generation and the annihilation processes of these lattice-relaxed states. Femtosecond dynamics of the STE’s has been elucidated by the time resolved luminescence [7] and transient absorption [8] measurements. However, little attention has been paid on the dependence of the relaxation dynamics on the initial excited states. Since there is no potential barrier between free electronic states and lattice relaxed states in one dimensional electronic system, the relaxations of the excited states occur immediately after their photo generation. Therefore, lattice relaxation dynamics is considered to depend on the initial excited states. In order to elucidate the initial state dependent relaxation dynamics of the photoexcited states in MX-chain compounds, transient photo-induced absorption (PA) measurements have been made on an MX-chain compound, $[\text{Pt(en)}_2][\text{Pt(en}_2\text{I}_2](\text{SO}_4)_2\cdot6\text{H}_2\text{O (Pt-I-SO}_4)$, for several excitation photon energies.

2. Experimental

In transient photo-induced absorption (PA) measurement a 1kHz regeneratively amplified Ti: sapphire laser (RATSL), the second harmonics of RATSL, and an optical parametric amplifier (OPA) pumped by the RATSL have been used as excitation light sources. A white light continuum has been generated by collimating a part of the RATSL beam onto CCl$_4$ in a quartz flow cell and has been used as a probe and a reference light source. A 300 nm spectrometers and an InGaAs-photodiode array detector have been used to measure the probe spectra. Reference spectra have been measured by another pair. Single crystals of an MX-chain compound, Pt-I-SO$_4$, were cooled down to 100 K by a He gas flow cryostat in order to reduce the absorption tail of the odd-exciton. The time resolution of the system is in the range from 150fs to 300 fs. In all measurements the polarization of the excitation light and that of the probe light were parallel to the chain axis. Transient absorption spectra of single crystals of Pt-I-SO$_4$ have been measured by the usual pump and probe method.

3. Results and discussion

Fig. 1 shows excitation energy density dependence of the time evolution of the intensity of PA for excitation photon energy ($E_{\text{ex}}$) of 1.55eV. The energy is close to the peak energy of the optically allowed CT-exciton with odd parity. Here, the detection energy ($E_{\text{det}}$) is 0.80eV. It is seen that the relative intensity of the long lived component increases as the increase of the excitation energy density. The short lived component which decays within several ps is considered to be STE absorption band. The STE absorption band is considered to be caused by the electron excitation from the STE’s to the excited states of the STE’s. The dependence of the intensity of PA on the excitation laser energy density is shown in Fig. 2. Here, a square dot shows the difference between the intensity of PA at 1.6ps and that at 2.5ps. This value corresponds to the intensity of the short lived component. A circular dot shows the intensity of PA at 14ps. This corresponds to the intensity of the long lived component. It is seen that the intensity of the short lived component has linear dependence on the excitation energy density. On the other hand, the intensity of the long lived component shows quadratic excitation energy density dependence. This shows that the states which cause the long lived component are not generated from the photogenerated CT exciton but from the higher energy two photon excited states. The peak energy of the long lived PA absorption band is about 0.83eV. In MX-chain, pinned soliton absorption bands [4, 5] are observed at energies close to a half of the CT-exciton. Since the long lived component is not generated from CT-excitons [5], the long lived absorption band is considered to be a charged soliton (CS) absorption band.

When the excitation photon energy was 1.28eV, time dependent energy shift of the transient STE absorption band to the higher energy was observed. The excitation energy corresponds to the low energy side of the CT-exciton absorption band. The time evolution of the PA for $E_{\text{ex}}=1.28$eV is shown in Fig. 3. In this case the efficiency of the two photon generation of the long lived CS’s is smaller than that for $E_{\text{ex}}=1.55$eV. Finite rise times are observed in the curves. It is found that the delay time of the maximum of the STE absorption increases as the increase of the detection energy. Such time evolution is considered to caused by the relaxation of the STE’s to the
minimum of the potential surface. Due to the large decrease in the energy of the STE’s by the lattice relaxation to the potential minimum, the energy separation between the STE’s and the electronic excited states of the STE’s increases. [10]

When the excitation photon energy is 0.83eV which is close to a half of the peak energy, 1.84eV, of the even CT-exciton [8, 9] two photon absorption band, two photon absorption, photo-induced SET absorption, and photo-induced CS absorption were observed. The dependence of the intensity of PA on the excitation energy density is shown in Fig. 4. The square dot, the circular dot, and the triangular dot corresponds to the intensity of two photon absorption at 1.00eV, that of photoinduced STE absorption at 1.00eV, and that of photoinduced CS absorption at 0.90eV, respectively. The intensity of the STE absorption and that of the CS absorption show quadratic dependence. This shows that STE’s and CS’s are generated from the two photon excited even CT-excitons. This is different from the relaxation processes of the odd CT-excitons. CS’s are not generated from the odd exciton. Transient absorption spectra for E_ex=1.77eV have also been measured. The excitation photon energy corresponds to the high energy side of the odd CT-exciton absorption band and is larger than the twice the excitation photon energy, 2E_ex=1.66eV, of the above case. However, the relaxation process are
the same as that in the case of $E_{ex}=1.55\text{eV}$. This seems to indicate that the relaxation process of CT-excitons are not mainly determined by the energy but by their wave functions.

Transient absorption spectra for $E_{ex}=3.10\text{eV}$ have also measured. Free electron–hole pairs are generated at the excitation photon energy. A photoinduced CS absorption band and photoinduced polaron absorption bands were observed. Their intensities have linear excitation energy density dependences. The decay time of the CS absorption band is about 400ps. This is much longer than the life time, about 40ps, of the CS absorption band in the case of $E_{ex}=1.55\text{eV}$. In this case CS’s are generated from the two photon excited state. Although the energy of the initial exited state, $2E_{ex}=3.10\text{eV}$, is same as the case of $E_{ex}=3.10\text{eV}$, the life times of CS’s are much different. By the photoexcitation, CS - anti-CS pairs are generated. The CS’s are annihilated by the geminate recombination of CS’s and anti-CS’s in photogenerated pairs. The decay rate of the CS’s is considered to depend on the initial separation length between CS’s and anti-CS’s in the pairs. Since the lifetime of the CS’s for $E_{ex}=3.10\text{eV}$ is larger than that for $E_{ex}=1.55\text{eV}$, the initial CS - anti-CS separation length for $E_{ex}=3.10\text{eV}$ is considered to be larger than that for $E_{ex}=1.55\text{eV}$. The difference may be due to the initial state dependent relaxation processes of the photoexcited states to the CS pairs.

### 4. Conclusion

STE’s are generated from odd CT-excitons. Solitons and Polarons are not generated from odd CT-excitons. Energy shift of the STE absorption band to the higher energy has been observed. This is considered to be due to the relaxation of STE’s to the minimum of the potential surface. STE’s and CS’s are generated from two photon generated even CT-excitons. On the other hand, by the one photon excitation with excitation photon energy close to the peak energy of the even CT-exciton absorption band, CS’s were not generated. The life time of the CS’s generated from the two photon excited states is shorter than the lifetime of the CS’s generated from one-photon excited free electron-hole pair. This is considered to be due to the difference in the separation length of CS - anti-CS in a pair.

### 5. References