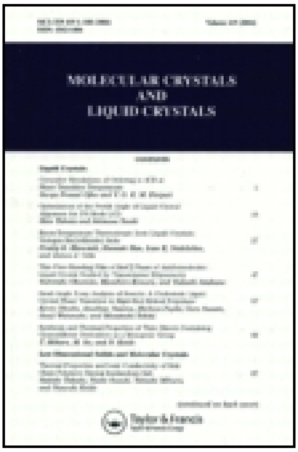

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Excitation Photon Energy Dependent Relaxation Processes of the Photoexcited States in Wide Gap MX-Chain Complexes

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EXCITATION PHOTON ENERGY DEPENDENT RELAXATION PROCESSES OF THE PHOTOEXCITED STATES IN WIDE GAP MX-CHAIN COMPLEXES

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Abstract Photo-induced absorption (PA) spectra of $[Pt(en)_2][Pt(en)_2X_2](SO_2)_2.6H_2O$ (X=Cl and Br) have been measured. Large excitation photon energy dependent changes were found in the features of the PA spectra. The excitation photon energy dependences are considered to be due to the difference between the relaxation processes of the charge transfer excitons and those of the higher energy excited states. Several new PA bands have been found.

INTRODUCTION

Recently, the relaxation processes of the photoexcited states in MX-chain complexes have gained considerable interest.[1] In MX-chain complexes alternate alignments of the metal (M=Pt, Pd, and Ni) and halogen ions (X=Cl, Br, and I) form one-dimensional linear chains. In Pt and Pd complexes, halogen ion distortions from the midpoints of the neighboring metal ions cause commensurate charge density waves (CDWs) with periods of twice the metal-metal distances as $X^--M^{2+}-X^--M^{4+}-X^--M^{2+}-X^--M^{4+}$.[2,3] In MX-chain complexes various mid-gap photo-induced absorption (PA) bands have been observed.[4-7] There are large differences between the relaxation processes of the photoexcited states in the MX-chain complexes with narrow CDW band gaps (E_{CT}<2.0eV) and those in the MX-chain complexes with wide CDW band gaps (E_{CT}>2.5eV). Here, E_{CT} is the peak energy of the charge transfer (CT) exciton absorption band.[8] In the narrow gap complexes CT-excitons are nonradiatively relax into the ground states. Polarons and charged solitons[9] are generated from the higher energy excited states.[7] On the other hand, in the wide band gap complexes CT-excitons relax into self-trapped excitons[10] and the lattice relaxed states which are observed as "A-" and "B-bands" in the PA-spectra[5]. The origin of the states is still at the stage of discussion. Additional PA-bands have also been observed in the wide gap complexes.[11,12]

In one-dimensional charge density wave (CDW) systems, lattice relaxations occur immediately after the generation of the photoexcited states. This predicts the excitation energy dependence of the relaxation processes of the photoexcited states. However, little attention has been paid to the excitation photon energy dependence of the relaxation processes of the photoexcited states in the wide gap MX-chain complexes. In order to elucidate the overall features of the excitation photon energy dependence, PA-spectra of $[Pt(en)_2][Pt(en)_2X_2]-(SO_4)_2.6H_2O$ (X=Cl, Br) have been measured for several excitation photon energies.

EXPERIMENTS

A high pressure Hg-lamp was used as an excitation light source. The light was passed through a monochromator or a narrow band pass filter, and a polarizer. The light was chopped (5Hz). The single crystals which were immersed in super-fluid liquid helium (2K) were irradiated by the light. Light from the W-lamp was passed through the crystals, a polarizer, and a monochromator. The light was detected by a photo-multiplier or by a Ge photo-detector. Both the DC and AC components were recorded. The excitation light was polarized parallel to the chain axis except for the excitation light of 4.89eV. In the excitation spectra measurements of the PA-signals and photocurrent, the excitation light was chopped (1Hz). The AC components were recorded.

RESULTS AND DISCUSSION

Fig. 1 shows the polarized PA-spectra of $[Pt(en)_2][Pt(en)_2Br_2]-(SO_4)_2.6H_2O$ ($Pt-Br-SO_4$) for the polarization parallel to the chain axis for five excitation photon energies. The PA-spectra are normalized against the maximum values. The polarized component of the imaginary part of the dielectric constant (ε_2) for the polarization parallel to the chain axis is also shown in the figure. For all excitation photon energies, the PA-bands are polarized parallel to the chain axis. The intense broad absorption band in the ε_2 spectrum is the CT-exciton absorption band.[8] In the PA-spectrum of the excitation photon energy (E_{ex}) of 2.85 eV, A- and B-bands are observed as other wide gap MX-chain complexes. Here, the initial photoexcited states are considered to be the CT-excitons. Another PA-band indicated by C is observed in the higher energy side. Such PA-bands are also detected in some wide gap MX-chain complexes.[11,12] It is seen, the relative intensity of the C-band increases compared to those of the A- and B-bands as the excitation energy increases.

In addition to these three PA-bands, two new PA-bands indicated by D (0.86eV) and E (1.1eV) have been found in the PA-spectra for the high excitation photon energies (E_{ex}=3.71, 3.96, and 4.18eV). These two bands are not detected in the PA-spectrum for E_{ex}=2.85eV. By the high photon energy light, the higher energy excited states such as

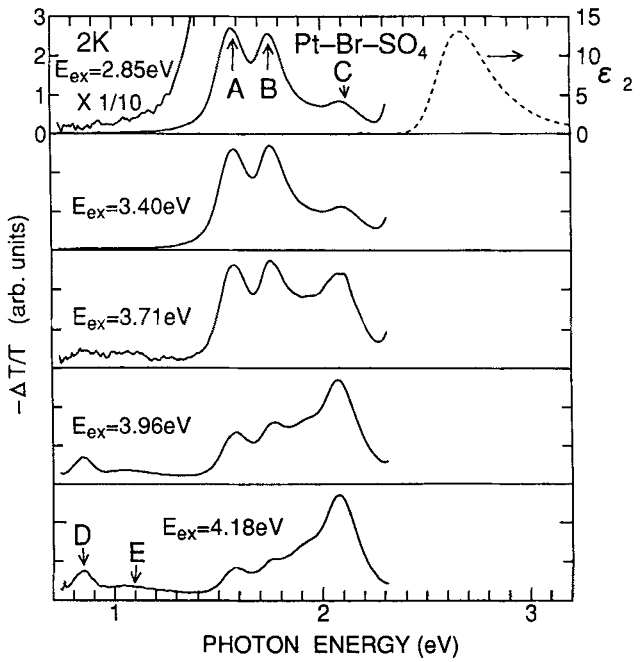

FIGURE 1 The polarized PA spectra (solid line) and polarized components of ε_2 (broken line) of Pt-Br-SO_4.

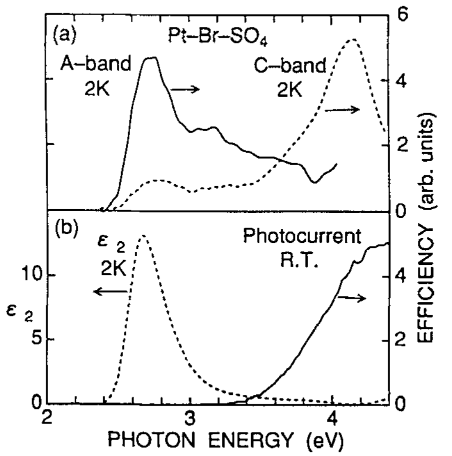

FIGURE 2 (a) The excitation spectra of PA-signals of Pt-Br-SO_4 (b) The excitation spectrum of photocurrent (solid line) and the polarized component of ε_2 (broken line) of Pt-Br-SO_4.

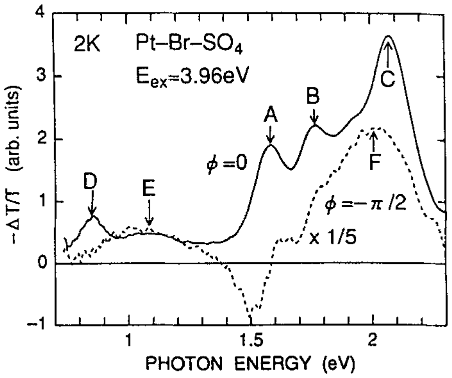

FIGURE 3 The polarized PA-spectra of Pt-Br-SO_4 at 2K for the detection phase of $\phi=0$ (solid line) and $\phi=-\pi/2$ (broken line) for E_{ex}=3.96eV.

free electron hole pairs are considered to be initially generated in addition to the CT-excitons. These results show that the D- and E-bands are generated only from the higher energy excited states. The excitation photon energy dependence of the D- and E-bands is different from that of the C-band. As seen in the PA-spectrum for E_{ex}=2.85eV, the C-band is also generated from the CT-excitons.

Fig. 2(a) shows the excitation spectra of the PA-signals detected at the peak energy of the A-band (solid line) and the C-band (broken line) of Pt-Br-SO_4 at 2K for the excitation light polarized parallel to the chain axis. Fig. 2(b) shows the excitation spectra of the photocurrent at room temperature for the excitation light polarized parallel to the chain axis (solid line) and the polarized components of ε_2 at 2K for the polarization parallel to the chain axis (broken line) of Pt-Br-SO_4. It is seen in the figure that the A-band is efficiently generated by the light with the photon energy near the peak energy of the CT-exciton absorption band. The C-band can be generated from the CT-excitons. But it is much more efficiently generated by the light with higher energy. The excitation spectrum of the photocurrent shows that the charge carriers are not generated from the CT-excitons.

In the lock-in detection of the AC components of the PA-spectra for higher E_{ex}s (E_{ex}=3.71, 3.96, 4.18eV), energy dependent phase shifts of the signals have been observed. Fig. 3 shows the PA-spectrum where the phase of the lock-in amplifier was tuned so that the PA-signal at the peak energy of the A-band becomes the maximum (ϕ=0, solid line) and the PA-spectrum ($\phi=-\pi/2$, broken line) detected at the phase $\pi/2$ smaller than the last one. Two broad PA-bands are seen in the $\phi=-\pi/2$ spectrum at about 1.0eV and 2.0eV (indicated by F). The 1.0eV band is considered to be identical with the E-band. No structure corresponds to the C- or D-band is seen in the spectrum. These results show that the E-bands decays more slowly than the A-, B-, C-, and D-bands and that there is a PA-band at about 2.0eV which decays also more slowly than the A-, B-, C-, and D-bands and which overlaps with these PA-bands in the ϕ=0 PA-spectrum.

The results are summarized in Table I. Here "○","△","X", and "-" mean "detected", "detected but the intensity is weaker than that of the other E_{ex}", "not detected", and "not measured", respectively. From the excitation photon energy dependences, the PA-bands are divided into three groups. The A- and B-bands are efficiently generated from the CT-excitons. The C-band is generated from the CT-excitons. But it is much more efficiently generated from the higher energy excited states. The D- and E-band are only generated from the higher energy excited states. This is the same as the excitation photon energy dependence of the generation of the photocurrent. In MX-chain complexes, the CT-excitons have large electron-hole binding energy.[13] Little has been elucidated about the higher energy excited states of the MX-chain complexes. However, the electron-hole biding energies of then are considered to be much smaller than those of the CT-excitons.

TABLE I The excitation photon energy dependence of the PA-bands at 2K and the photocurrent at room temperature in Pt-Br-SO_4.

PA-band	Peak Energy	E_{ex}=2.85eV	E_{ex}=3.96eV	Decay
A	1.59eV	○	△	Fast
B	1.77eV	○	△	Fast
C	2.08eV	△	○	Fast
D	0.86eV	X	○	Fast
E	1.1 eV	X	○	Slow
F	2.0 eV	-	○	Slow
Photocurrent		X	○	-

The electron-hole binding energies may play an important role in the relaxation processes.

Fig. 4 shows the PA-spectra at 2K and polarized reflection spectrum at room temperature of $[Pt(en)_2][Pt(en)_2Cl_2](SO_4)_2.6H_2O$ (Pt-Cl-SO_4) for the polarization parallel to the chain axis. Here, the 4.89eV

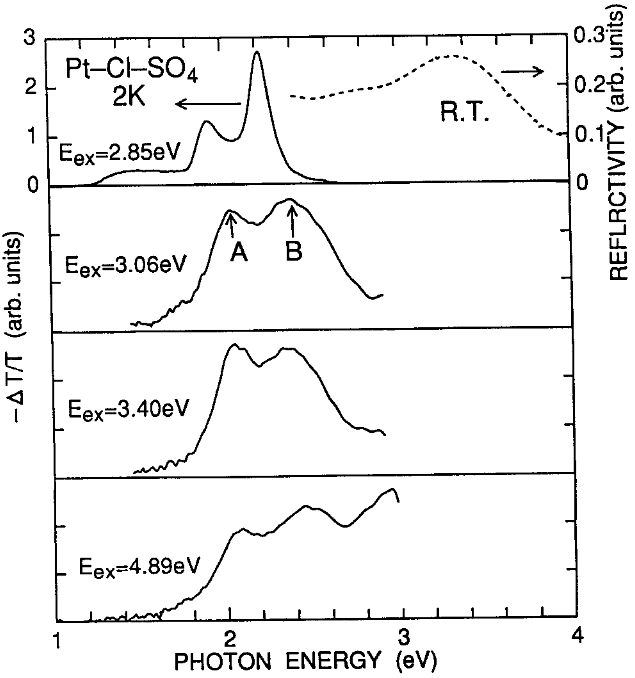

FIGURE 4 The polarized PA-spectrum (solid line) and the polarized reflection spectrum (broken line) of Pt-Cl-SO_4 .

excitation light is not polarized. In the PA spectra for E_{ex}=3.40eV and E_{ex}=3.96eV, A- and B-bands are also seen. In the PA-spectrum for E_{ex}=4.89eV, a new absorption band is observed in the high energy side. Such excitation photon dependent change of the PA spectra seems to be quite similar to that of Pt-Br-SO_4. This seems to suggest the existence of the common mechanism in the relaxation processes of the photoexcited states in the wide gap MX-chain complexes.

The PA-spectrum for E_{ex}=2.85eV is quite different from the PA-spectra for higher E_{ex}s. The photon energy corresponds to the tail of the CT-exciton absorption band. The initial states may be localized CT-excitons.

In summery, Marked excitation photon energy dependent changes of the features of the PA-spectra have been found in Pt-Br-SO_4 and Pt-Cl-SO_4. Such excitation photon energy dependent changes are interpreted by the difference between the relaxation processes of the CT-excitons and those of higher energy excited states.

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