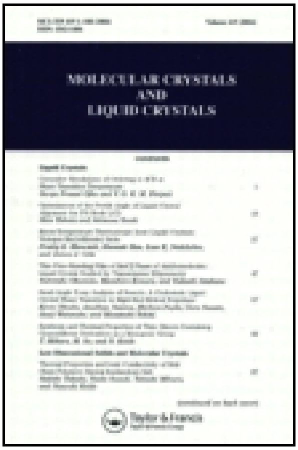

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FEMTOSECOND SPECTROSCOPY OF ONE-DIMENSIONAL METAL COMPLEXES

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Abstract We have investigated the temperature dependence of the absorption spectrum of the one-dimensional metal complex ($Pt(dmg)_2$) and the relaxation dynamics of its photo-excited states using a femtosecond pump-probe method. At lower temperature than 150K, four peaks(P1-P4) appear in the region of the absorption band due to the metal chain, where P1 and P2 are dominant components in the absorption at 90K although they are very small at 300K. In the pump and probe spectroscopy at 90K ,the bleaching first rises up very rapidly(<200fs) and decays within 1ps in the energy region of P1. This is followed by slower rise-up with the time constant of 60ps. The slow component of the bleaching is due to the increase of the lattice temperature. The relaxation processes in $Pt(dmg)_2$ are discussed.

INTRODUCTION

It is known that the d^8 transition metal complexes containing dionedioximes as ligands have square planar configuration and are stacked face to face forming a linear metal chain with large *d*-orbital overlap between metals of adjoining molecules[1]. In this system appearance of the characteristic features in optical susceptibility and electric conductivity due to the one-dimensional electronic structure can be expected. We have reported formations of linear metal chains in vacuum evaporated thin films of these metal complexes and their considerably large third-order optical nonlinearities around the energy region of the inter-metal charge transfer absorption band[2,3]. The large optical nonlinearities may originate from the electronic delocalization on the one-dimensional chain. However, the fundamental electronic structures and the dynamic properties of the photo-excited electrons remain unresolved. In this study, the temperature dependence of absorption spectra is observed and the behaviors of the transient absorption spectrum after photo-excitation are investigated by a femtosecond pump-probe method.

EXPERIMENTAL

Thin film of Pt(dmg)$_2$ was prepared by conventional vacuum evaporation onto a fused quartz substrate of 1mm thick. The synthesis of the complexes and the prepareation of the thin films have been described in the previous papers[2,3]. In the pump-probe experiments, we use an amplified Ti: Al_2O_3 laser system with pulse duration of 200fs and wavelength of 800nm. The pulse energy and the repetition rate of the pumping light are 5μJ and 1KHz, respectively. White light as a probe pulse is generated by focusing the 800nm pulses into a CH_3OH cell.

RESULTS AND DISCUSSION

FIGURE 1 shows the absorption spectra of a thin film of Pt(dmg)$_2$ at 90K. The broad absorption band peaked at 1.8eV is assigned to the 5dz-6pz transition of platinum that originates from the large *d*-orbital overlap between adjacent platinum ions in the metal chain[4,5]. An 'exciton' picture may be useful in this one-dimensional electronic structure. We call this band as metal band. Absorption spectrum at 150K,120K and 90K are illustrated in the fig.1. Four peaks as shown by triangles(open: 90K, closed: 300K) can be observed at any temperature. These peaks are located at 1.480, 1.604, 1.745 and 1.890eV at 90K, and 1.549, 1.678, 1.810 and 1.950eV at 300K (derived from second order differentiation). We refer to these peaks as P1,P2,P3 and P4, respectively, from the low energy side. The shifts of the absorption spectra were traced every 30K temperature change from 300K to 90K. The four peaks continuously move toward low energy side and the total shift of about 60-70meV is observed. The absorption strengths of P1 and P2 are remarkably enhanced upon temperature decrease. The degree of enhancement was larger in P1 than in P2 at lower temperatures. Similar result was obtained from a more precise analysis using spectral deconvolution. Transition dipoles of the P1, P2, P3 and P4 are parallel to the linear metal chain. This is suggested by the polarized absorption spectra for epitaxial films in which the metal chains are perpendicular to the KBr substrate. The origin of each peak and its temperature dependent behavior have not been understood yet. Considering the nature of this system such as the large third order optical nonlinearities or analogy from other one-dimensional exciton systems, we propose the possibility of some kind of structural phase transition and the extension of electronic coherence of the photo-excited states[6]. FIGURE 2 shows the transient absorption spectra at 90K at various delay times (t_d) between pump and probe pulses as shown in the right side of the figure. ΔOD spectra are obtained by subtracting the spectra without pumping from the spectra after pumping. In the top frame of the figure, the absorption spectrum of the metal band is shown. Within the pump pulse duration (200fs), absorption bleaching around the energy region of P1 and P2 and increase of absorption in higher energy regions are observed. At 5ps induced absorption appears in the low energy tail of P1. The bleaching in the region around P1 and P2 grows with the time until about 100ps and does not decay until at least 300ps, which is the long time limit of our measurement system. Temporal changes of the spectra at several photon energies are illustrated in FIGURE 3. a), b), c) and d) show the time evolution at 1.35, 1.44, 1.65, and 2.0eV, respectively. The energy region around a) corresponds to the induced absorption, and those around b), c) indicate the bleaching bands, and d) is located in the region of increase of absorption. Furthermore, the energies b) and c) correspond to those of P1 and P2 of linear absorption spectrum. As shown in b) the bleaching in the region of P1 has two rise-up components. It rises up within the pulse duration (fast component) and decays within 1ps. We don't mention the fast decay in this paper. This is followed by the rise-up with the time constant with 60ps(slow component) for single exponential rise-up courve. The bleaching at the energy of c) has only one fast rise-up component and a slow recovery component with a time constant of 60ps. In the energy region of d), the increase of absorption grows with the same time constant of 60ps. Furthermore, the absorption spectrum(not ΔOD spectrum)observed at t_d>100ps agrees very well with the spectrum at a higher temperature(about 240K). This indicates that the excited electron or the exciton has nonradiatively relaxed to the electronic grand state within 100ps causing the rise of the lattice temperature to 240K. The slow component is considered to be induced by the rise of the lattice temperature. Results obtained for the transient spectra can be explained as follows: The fast component of the rise-up of bleaching is considered to be due to the electronic transition induced by the femtosecond pulse. The photon energy of the pumping pulse(800nm=1.55eV) is located between P1 and P2, and the pumping pulses may bleach both peaks simultaneously. During that time the electrons or excitons are excited into the states which give P1 and P2. They nonradiatively relaxe to the ground state with the slower time constant. As the lattice temperature increases, the absorption spectrum changes to the one at about 240K. This occurs within 100ps. In the energy region of a), induced absorption rises up with a time constant of about 10ps and decays with a time constant of about 30ps. Origin of the induced absorption in the lower energy side of P1 can not be understood yet. Analogical consideration of other one-dimensional systems, it may be configurationaly relaxed excited states such as self-trapped excitons[7] or the states created by electronic interaction such as bi-exciton . Physical meanings of the linear and transient spectra have not been fully clarified yet, and more extensive and precise works should be carried out. In summary, we have investigated the relaxation dynamics of the photo-excited states in the one-dimensional metal complex($Pt(dmg)_2$) by femtosecond pump and probe method. Fast(200fs) and slow(60ps) rise-up components of the bleaching were observed in the spectral region of P1 which is predominant at temperatures below 150K. The fast component is induced by the electronic transition due to the pumping, and the slow component is due to the non-radiative relaxation into the ground state. Simultaneously the lattice temperature increases up to 240K .

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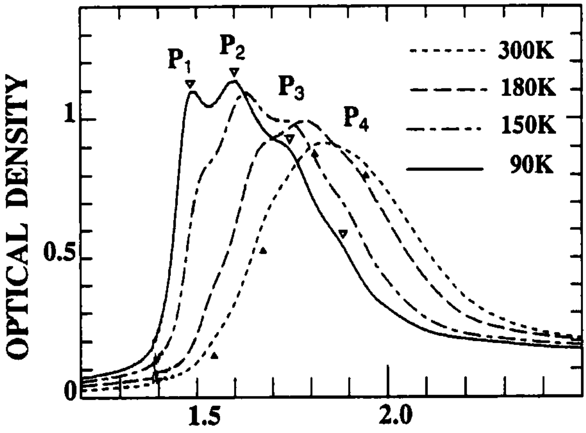

FIGURE 1. Absorption spectra of $Pt(dmg)_2$ at various temperatures between 90K and 300K. The energies of P1, P2, P3 and P4 are indicated by the closed and open triangles, respectively, in the 300K and the 90K spectra.

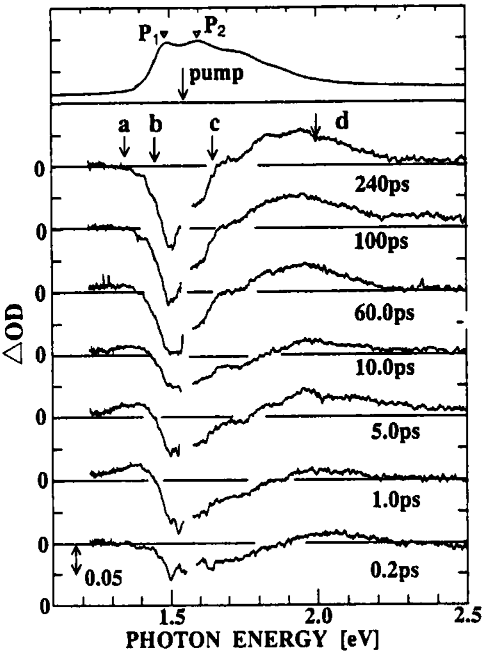

FIGURE 2. Transient absorption spectra of $Pt(dmg)_2$ at 90K. The absorption spectum at 90K is shown in the top frame. ΔOD spectra are obtained by sabtracting the spectra without excitation from the spectra after excitation. Delay times of the probe pulses after excitations are shown in the figure.

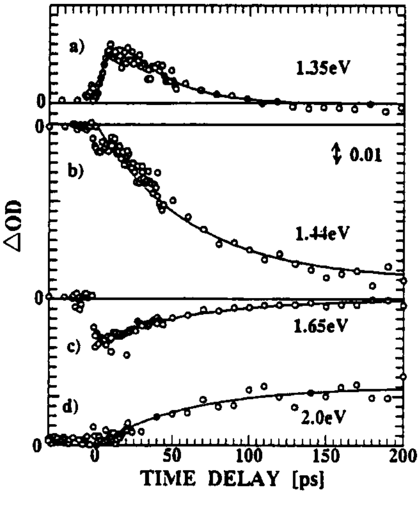

FIGURE 3. Time evolution of the transient absorption at several photon energies. a),b),c) and d) illustrate the time-profiles at 1.30, 1.44, 1.65 and 2.0eV, respectively.