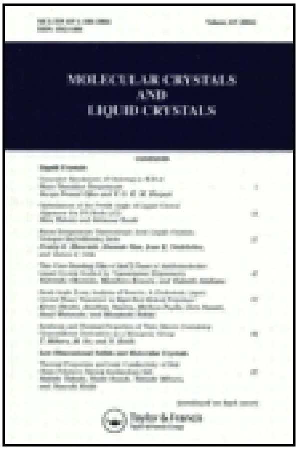

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Ultrafast Relaxation Dynamics of Excitons in One-dimensional Metal Complexes.

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Abstract Temperature dependence of the relaxation processes from the photo-excited state in Platinum dimethylglyoxime complex ($Pt(dmg)_2$) film was investigated by femtosecond pump- probe spectroscopy. Measurements were made at 300K and 80K. The exciton lifetime estimated from the decay of the excited state absorption was 21ps at both temperatures. This suggests that the thermal barrier associated with the relaxation to the ground state is very small. The intensity of bleaching of exciton absorption caused by third order nonlinear susceptibility was about ten times larger at 80K than at 300K. It suggests that an excited state with higher electronic coherence exists at lower temperatures. An ultrafast bleaching component decaying within 400fs which is observed only at 80K is considered to arise from the the electronic coherence of the excited state.

keywords: one-dimensional metal complex, exciton, femtosecond spectroscopy.

INTRODUCTION

Recently, large optical susceptibilities and its ultrafast response have been found in d^8 transition metal complexes containing dionedioximes as ligands ($M(dmg)_2$)(M denotes metal: Pt, Ni, Pd)[1-4]. These complexes have square planar configurations and are stacked face to face to form a linear metal chain in the solid state[1,2,5,6]. Linear and non-linear optical properties are considered to be due to the intermolecular delocalization of the electronic states. The electronic parameters of these metal complexes can be easily changed by changing the kind of metal ion and/or the substituents in the ligands. This enables us to fabricate various interesting photo-active structures such as the hetero-structures[7]. We have made the investigation using various experimental methods such as linear[1-3] and electromodulated[8] absorption, photoconductivity[8] and femtosecond pump-probe spectroscopy[3, 4] in order to reveal the origin of the linear and nonlinear optical properties. We have shown that the formation of one-dimentional(1-D) exciton and its ultrafast relaxation play important roles in the non-linear optical properties in this system.

In the present study, we investigate the temperature dependence of exciton relaxation dynamics in 1-D platinum complex by pump-probe spectroscopy using 150fs pulses. Excitation was made at the wavelength in the low energy region of the exciton absorption band at 80K and 300K. We found large difference in the bleaching intensity of the exciton absorption and in its behaviors at different temperatures.

Experimental

Vacuum evaporated thin films of $Pt(dmg)_2$(Platinum dimethylglyoxime complex) were prepared on a fused quartz substrates of 1mm thickness. The synthesis of the complexes and the preparation of the thin films were described in previous papers in detail[1, 2]. In the pump-probe experiments, a regenerateive amplifier system of a $Ti:Al_2O_3$ laser operating at 1kHz was employed as a light source. The wavelength, the pulse energy and the pulse width were 800nm, 1mJ and 150fs, respectively. The fundamental light of 800nm was divided into two beams. Wavelength conversion was made for one of the beams using an optical parametric generator/amplifier(OPA). The residual beam was used for generation of white-light of 400-1000nm region. This was used as a probe pulse. In this study, 840(1.48eV), and 730nm(1.69eV) pulses were used for excitation of the specimen at 80K and 300K. The energy density at the focusing spot was 0.2mJ/cm^2.

3: Results and Discussion

Figure 1(a),(b) shows the linear absorption spectra and transient differential absorption spectra at 0.1ps after excitation at 300K(a) and 80K(b). Yamamoto and Kamata et.al[8] have shown by measuring photo-conductivity and electro-modulated absorption spectrum that the absorption band is due to 1-D exciton. It has a binding energy ~0.7eV which is as large as half of the eigen energy of the exciton measured from grand state. The spectral structure of this absorption band strongly depends on temperature[3]. The broad absorption due to the

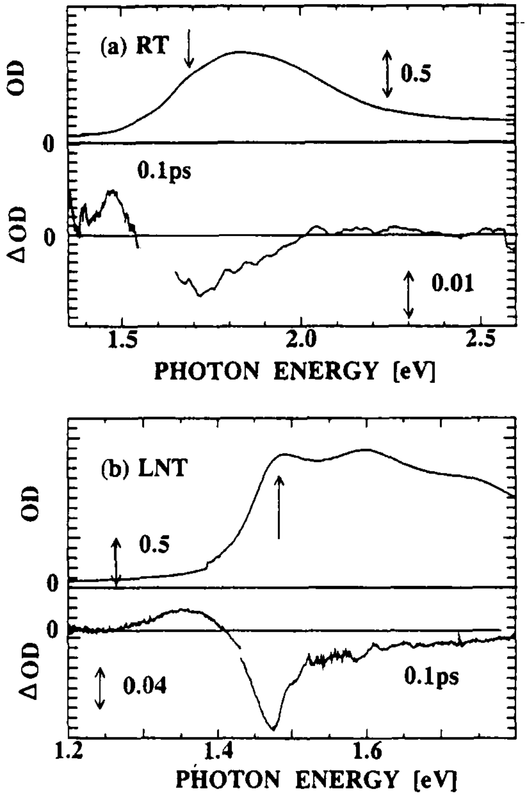

FIG.1: Absorption(upper frame) and transient differential absorption(lower frame) spectra of a ($Pt(dmg)_2$) thin films at 300K(a) and 80K(b) at 0.1ps after excitation. The arrows indicate the pumping photon energies.

exciton in $Pt(dmg)_2$ has four small structures even at 300K. This can be seen by the secondary differential spectrum(not shown). The lowest energy structure found at 1.54eV at 300K shifted toward lower energy by 60meV as the temperature was lowered to 80K. Simultaneously, the intensity of this lowest structure increased remarkably. At both temperatures, bleaching of the exciton band and the induced absorption in the lower energy side were observed. However, intensity of the absorption change and its spectral shape were rather different. At 300K, no clear structure was found in the broad bleaching band. In contrast to that, an intense peak in the bleaching was observed at 80K. The spectral peak of the bleaching was identical to the lowest peak of the linear absorption at 1.48eV. A small tail was found in the high energy side (1.55-1.8eV) of the bleaching peak. The intensity of this bleaching peak was about ten times that of the bleaching peak obserbed at 1.7eV at 300K.

Time evolutions of the transient absorption within 1.5ps are shown in fig2(a: 300K) and (b: 80K). The bleaching and the induced absorption rised up instantaneously within the time resolution of 200fs at both temperatures in any probe region. Linear dependence of the intensity of the absorption change on the excitation energy density suggests that it is caused by third order nonlinear susceptibility[4]. The instantaneous rise up of the induced absorption suggests that it is due to the transition from the excited state[4]. An ultrafast decay component which looks like a spike was observed within 400fs only around 1.48eV at 80K. It was not observed at 300K. In the behavior of the induced absorption, a similar ultrafast decay component was observed only at 1.35eV, and it was not detected at 1.24eV. The temporal behaviors of the absorption changes at longer time delays up to 40ps at 300K(a) and 80K(b) are shown in fig.3. The bleaching continues to decay until 40ps, and then grows again until ~100ps. The change in the absorption spectrum due to the rise of lattice temperature is responsible for this slow grow of the bleaching[3,4]. Therefore, the decay profile of the bleaching does not simply reflect the population dynamics of the electronic excited states.

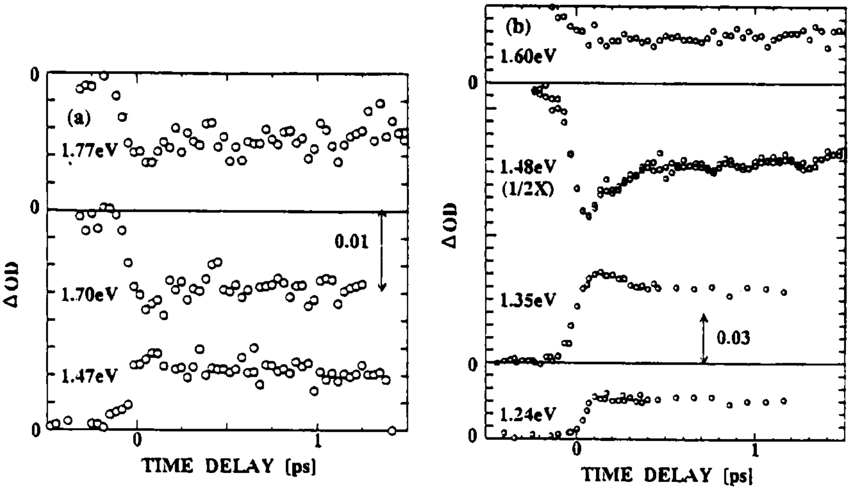

FIG.2: Time evolutions of the transient absorption within the time scale up to 1.5ps at 300K(a) and 80K(b). 1.70, 1.77eV in (a) and 1.48, 1.60eV in (b) correspond to the energy region of the bleaching. 1.47eV in (a) and 1.24, 1.35eV in (b) are located in the region of the induced absorption. The bleaching at 1.48eV in (b) is indicated after being multiplied by 0.5.

The induced absorption, on the other hand, decays with time constant of 21ps. Since the effects of the rise of lattice temperature is negligible in the energy region of the induced absorption, we can estimate the lifetime of the exciton from the decay time of the induced absorption. The same decay time (21ps) was found at both temperatures. This suggests that the thermal barrier associated with the exciton relaxation is very small.

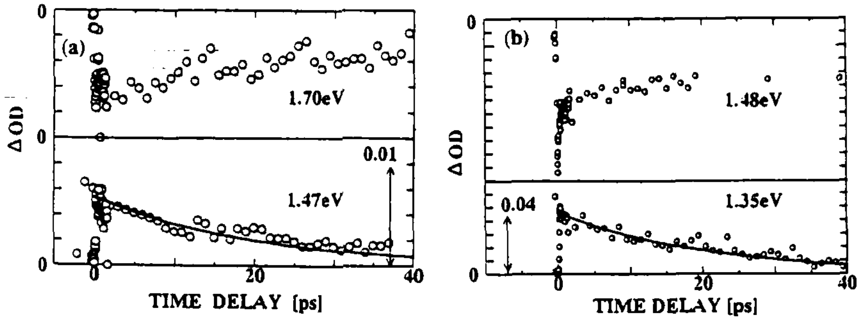

FIG. 3: Time evolutions of the transient absorption in longer time scale up to 40ps at 300K(a) and 80K(b). Solid lines in the figure show the single exponential curves with a time constant of 21ps.

In a previous study, we have investigated the dependence of the transient absorption spectra on the excitation photon energy[4]. Intensive bleaching peak and its ultrafast decay occurring within 400fs were observed only under resonant excitation at the lowest absorption peak of 1.48eV at 80K . We concluded that two kinds of electronic states(A and B) are responsible for the exciton absorption band in $Pt(dmg)_2$. The A state gives the bleaching peak at 1.48eV and B corresponds the tail up to 1.8eV, respectively, at 80K. However, virtually no component corresponding to A was detected at 300K. Therefore, the A state is predominant in the lower temperatures, which suggests the higher electronic coherence of the A state. At higher temperatures, the coherence of the system may be lowered by exciton-phonon interaction. Another possibility is the occurrence of structural phase transition(ordered at low temperature and disordered at high temperature), although the detailed investigation as to the structure should be made in the future. The origin of the ultrafast decay in the time region of 400fs has not been revealed yet. It may be caused by the electronic coherence.

SUMMARY

We have measured the transient absorption spectra at 80K and 300K. Intense bleaching around the lowest exciton absorption peak was observed only at

80K. Its decay involves an ultrafast component decaying within 400fs. This suggests that the lowest excited state is electronically highly coherent. The lifetime of the exciton estimated from induced absorption was 21ps at both temperatures, which shows that the thermal barrier associated with relaxation is very small.

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