Wave packet motion during thermalization of the relaxed excited state in the one-dimensional platinum dimethylglyoxime complex

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Pump–probe spectroscopic studies were made for a one-dimensional (1D) platinum dimethylglyoxime complex $(Pt(dmg)_2)$ under excitation in the exciton absorption band using 40 fs pulses. Oscillation with a period of 0.11 ps which is superimposed on the rise of the induced absorption due to the self-trapped exciton (STE) was found for the first time in this system. The oscillation damped with a time constant of 0.1 ps. In a previous work in which 150 fs pulses were used for excitation at various wavelengths, we found that the spectral shape of the induced absorption changed with time in 0.1–0.3 ps after instantaneous rise up. These results were reasonably explained by the formation and the thermalization of the STE. In the framework of the interpretation we have presented, the oscillation superimposed on the induced absorption is considered to originate from the wave packet motion of the STE during thermalization. © *1999 American Institute of Physics.* [S0021-9606(99)00936-8]

I. INTRODUCTION

Low-dimensional molecular aggregates have attracted much attention because of their characteristic electronic structures which are quite different from those of a bulk or an isolated molecule. They give us various features to investigate interesting photoinduced phenomena such as energy transfer and various photochemical reactions which strongly depend on the dimensionality and the size of the systems.

The 1D molecular aggregates of d^8 transition metal dimethylglyoxime complexes ($M(dmg)_2$:M denotes a metal) are known as the 1D electronic systems.[1,2] The molecules of the complex with square planar configuration are stacked face to face to form a linear metal chain in the thin film and the in the crystal. The central chain of the metal has a simpler 1D backbone compared with the main chains of other 1D systems such as polydiacetylene (PDA) and 1D halogen bridged mixed valence metal complexes (MX). (It does not have a zig–zag configuration or contain different atoms.) The measurements of photoconductivity (PC), and electroabsorption (EA) showed that the 1D exciton delocalized along the 1D chain gives a strong absorption in the visible region.[3] Large optical nonlinear susceptibilities were found around the exciton absorption band.[4]

Recently, we made femtosecond spectroscopic studies to reveal the relaxation dynamics of the 1D exciton under excitation of the exciton[5] and of the MLCT excited states.[6] Transient absorption studies using 150 fs pulses at various wavelengths showed that the relaxation to the self-trapped exciton (STE) occurs within a very short time. Instantaneous rise of the induced absorption in the lower energy side of the exciton absorption was observed, and the spectral shape of the induced absorption changed in time within 0.4 ps. To explain these spectral features, we proposed a model involving the formation and the thermalization of the STE by anal-

ogy from the case of polydiacetylene (PDA).[7] The formation and thermalization times of the STE were estimated to be <0.05 ps and 0.1–0.3 ps, respectively. This suggests that an intramolecular mode with a frequency higher than that of the intermolecular stretching mode ($80\ cm^{-1}$) drives the self-trapping process. So, the configurational distortion in the initial self-trapping process is considered to occur within the molecules. This is quite different from the case of other 1D electronic systems with strong interaction between electron and phonon such as PDA (Ref. 7) or MX (Refs. 8 and 9) in which structural change of the chain in 1D direction occurs in the primary process.

Our model consistently explained the results of the transient absorption. However, the time resolution of $\sim$180 fs in the previous work was not enough to reveal the initial relaxation processes and to confirm the presented model, since the period of the vibrations related to the formation and the thermalization of STE in $Pt(dmg)_2$ is considered to be $\lesssim$100 fs. So, measurements with higher time resolution is needed. As the first step of this course, 40 fs pulses were used in this study to measure the transient absorption. The pump–probe (transient absorption) experiment was made by exciting the 1D excition absorption.

II. EXPERIMENT

The sample of the thin film of $Pt(dmg)_2$ (bis(dimethyl-glyoximato) platinum(II)) we used in this study is same as that used in a previous work.[5] The thickness of the film prepared on the quartz substrate is $\sim$100 nm. In the pump–probe measurement, a regenerative amplifier system of a Ti:Al$_2$O$_3$ laser (Spectra Physics Tsunami-35 fs and sub-50 fs Super Spitfire system) operating at 1 kHz was employed as a light source. The center wavelength and the spectral width of the pulses were 800 nm and 40 nm (FWHM), respectively.
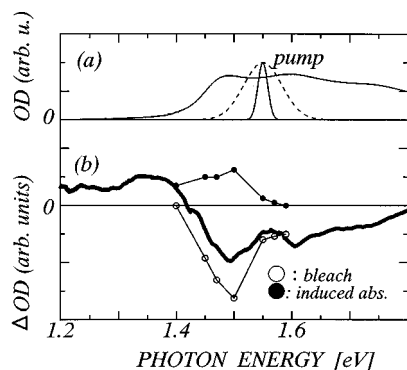
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FIG. 1. (a) Absorption spectrum of a Pt(dmg)$_2$ thin film observed at 80 K. The spectra of the 150 fs (solid line) and the 40 fs (dashed line) excitation pulses are superimposed. (b) Transient absorption spectrum of Pt(dmg)$_2$ thin film at 80 K under excitation at 1.55 eV. The pulse width and the excitation density of the pump pulse are 150 fs, and 0.1 mJ/cm^{-1}, respectively.

FIG. 2. Time evolutions of the transient absorption change($-\Delta$OD) under excitation by 40 fs, 1.55 eV pump pulse after normalization at the maximum value. The lowest frame shows the time resolved optical Kerr effect (OKE) signal of water. This can be fitted by a Gaussian function with a FWHM of 60 fs.

A quartz prism pair was used to precompensate for the chirp generated in the measurement optics before the sample. The prism distance was optimized by observing the response function using by either the cross-correlation at a BBO crystal or the optical Kerr effect (OKE) at a water cell. By this optimizing procedure, the response function with a FWHM of 60 fs was obtained at the sample position. The distance between the prisms was typically 90 cm. After the precompensation, the pulse energy was reduced to 10 μJ by spatial filters and a reflective neutral filter, and the 800 nm beam was lead into ordinary pump–probe optics.

The intensity ratio and the relative angle between the pump and the probe beams were 1000/1 and 3°, respectively. Almost the same optics was used in the pump and the probe paths in order to have the same chirp. After the sample, the probe beam with a spectral width of 40 nm was passed through a spectrometer and the resulting beam was detected by a Si-photodiode (Thorlabs DET100). The wavelength resolution of the spectrometer is 10 nm ($\sim$20 meV). The signal from the photodiode was amplified by a lock-in amplifier (Stanford Research SR830). To block the scattered pump beam, the pump and probe beams were modulated at separate frequencies (f_1, f_2) and the difference frequency ($f_1 - f_2$) was used as a reference frequency for the lock-in amplifier. Obtained signal is the difference in the transmitted probe beam intensity induced by the pump beam ($\Delta I = I - I_0$), where I_0 and I are the transmitted intensity without and with pump, respectively. Change in the optical density induced by the pump (ΔOD) is given by Eq. (1),

$$\Delta\text{OD} = -\log\left(1 + \frac{\Delta I}{I_0}\right). \tag{1}$$

Transmitted intensity of the probe beam without excitation (I_0) was measured using a reference frequency of f_2.

Transient absorption measurements using white light with $\sim$180 fs resolution were also made under excitation at the same wavelength (800 nm). The details of the setup for the measurements were described in the previous paper.[5]
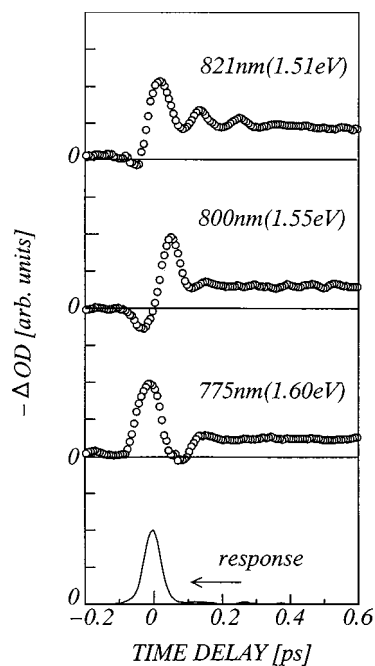
III. RESULTS

Figure 1 shows the linear (a) and transient absorption [bold line in (b)] spectra. In frame (a), the spectral shape of the 150 fs excitation pulse (solid line, FWHM=20 meV) and that of the 40 fs pulse (dashed line, FWHM=78 meV) are superimposed on the linear absorption spectrum. The broad absorption band observed between 1.4 and 2 eV in the linear spectrum shown in Fig. 1(a) was assigned to the 1D exciton which originates from the delocalized $d-p$ excited states of the centered metal.[1–3] The broad and structured character of this band was considered to be due to the coupling of the electronic transition with the intramolecular vibrational mode of 1140 cm^{-1} and 840 cm^{-1}.[5] The transient spectrum shown by the bold line in Fig. 1(b) was measured at 0.4 ps after excitation by the 150 fs pulses of 1.55 eV (800 nm) at 80 K. The bleaching of the exciton band and the induced absorption with a maximum at 1.35 eV were observed. According to the measurements and the analysis of the transient absorption spectrum at various excitation energies given in the previous paper,[5] the induced absorption with the maximum at 1.35 eV was due to the STE as the relaxed excited state.[10]

Figure 2 shows the time evolution of ΔOD induced by the 40 fs excitation pulses of 1.55 eV observed at 1.51, 1.55, and 1.60 eV at 80 K. ΔOD of each curve has been normalized at the maximum. The absolute values of $-\Delta$OD at the maximum are 0.014, 0.027, and 0.013 for 1.51, 1.55, and 1.60 eV, respectively. The signal due to the OKE in the water cell is shown as the instrumental response function in the bottom frame. The FWHM of the instantaneous response component was 60 fs, although the small residual component

remains at positive delay. We hereafter use Gaussian function with a FWHM of 60 fs as an instrumental response function.

In the time profile shown in Fig. 2, positive peaks were observed around $t=0$. These signals are considered to originate from the coherent transients[11] which appear in a time corresponding to the homogeneous width of the exciton (T_2).[12] The experimental setup for the pump–probe measurement used here is basically the same as that of degenerate four wave mixing (DFWM), although the intensity of the probe beam is far weaker than that of the pump beam (1/1000) and the position of the detector is different. The DFWM signal may be contained in the probe beam at the time shorter than T_2. The signal observed at negative delay are negligible at $t < -0.1$ ps. Therefore, T_2 is roughly predicted to be of the order of 0.1 ps, and the DFWM signal in the positive delay are considered to be negligible at $t > \sim 0.1$ ps. Detailed discussion needs the results of the DFWM measurement which will be made in the near future. Since the signal is partially spectrally resolved, another possible contribution to the transient absorption signal is impulsive stimulated (resonant) Raman scattering (ISRS).[13] The coherent vibrations excited by the ISRS process can persist even after T_2 and they may affect the signal after 0.1 ps. After 0.1 ps, the bleaching (positive direction in $-\Delta OD$ scale) was observed at all wavelengths observed. The magnified profiles after 0.1 ps are shown in Fig. 3(a). An oscillation with time was found in the profile observed at 1.51 eV. No oscillation was detected at 1.55 and 1.60 eV. Except for the oscillation, these profiles were reproduced well by a double-exponential [1.51 eV, $\tau_1 = 0.12$ ps (amplitude, 0.29), $\tau_2 = 26$ ps (0.71)] or a single-exponential (1.55 and 1.60 eV, 26 ps) function. The slower decay (τ_2) was determined from the profiles in the longer time region. The residual which was obtained by subtracting the calculated curves from the experimental results are shown in Fig. 3(b). The residual at 1.51 eV was fitted by a sine curve with damping, $\sin(\omega t + \phi)\exp(-t/\beta)$, where $2\pi/\omega$, ϕ and β are 0.11 ps, 0.45π, and 0.1 ps, respectively. The oscillation with the period of 0.11 ps superimposed on the profile of the bleaching at 1.51 eV is considered to originate from the wave packet motion of the ground or the excited state.

The two-component decay of the bleaching around 1.5 eV was also observed in the transient absorption measurement using 150 fs pulses. In the previous paper,[5] the detailed analysis of the decay curves at 1.20–1.59 eV under excitation at 1.48 eV showed that the fast decay component $(\tau_1 \sim 0.2$ ps) of the bleaching was caused by the rise of the induced absorption. This rise component was ascribed to the thermalization of the STE on the potential surface, since its time constant agreed with the decay constant of the induced absorption observed in the lower energy region (~ 1.20 eV). In Fig. 1(b), the deconvoluted spectral components of the bleaching (open circles) and of the induced absorption (closed circles) for the transient spectra under 1.55 eV excitation are shown. To obtain each component, we use the same procedure as that of the previous paper,
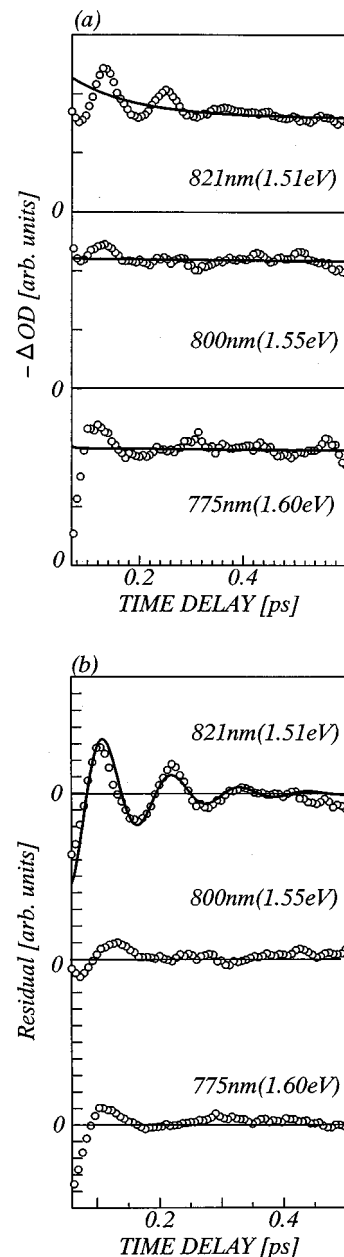

FIG. 3. (a) Magnification of Fig. 2 after 0.1 ps. The solid lines show the two-component (1.51 eV, $\tau_1 = 0.12$ ps, $\tau_2 = 26$ ps) and the one-component (1.55 and 1.60 eV, 26 ps) exponential decay functions. (b) The residuals which are obtained by subtracting the calculated curves in (a) from the observed profiles. The solid line shows $\sin(\omega t + \phi)\exp(-t/\beta)$, where $2\pi/\omega$, ϕ, and β are 0.11 ps, 0.45π, and 0.1 ps, respectively.

$$\Delta OD(E,t) = \int_{-\infty}^{l} R(t-t')\{A(E)K_{bl}(t) + B(E)K_{abs}(t)\}dt', \qquad (2)$$

where $K_{bl}(t)$ and $K_{abs}(t)$ are the kinetic function of the bleaching and the induced absorption, respectively. $A(E)$ and $B(E)$ are coefficients which depend on the observing photon energy E. $R(t)$ is the instrumental response function. A single exponential function with a time constant of 26 ps is used for $K_{bl}(t)$. $K_{abs}(t)$ is given by Eq. (3),
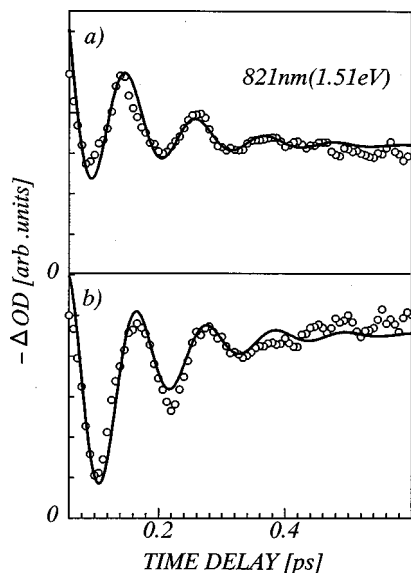
FIG. 4. (a) The time evolution observed at 1.51 eV (open circles) and the result of the fitting obtained by using Eqs. (2) and (4) (solid line, see text). (b) The component of the induced absorption which is obtained by subtracting the bleaching component from the observed profile (open circles) and from the calculated one by Eqs. (2) and (4) (solid line).

$$K_{abs}(t) = \exp\left(-\frac{t}{26}\right) - \exp\left(-\frac{t}{0.2}\right), \tag{3}$$

where t is in ps time units. $A(E)$ and $B(E)$ are plotted in Fig. 1(b) as the components of the bleaching and of the induced absorption, respectively. Almost the same deconvoluted spectra as those for the 1.48 eV excitation were obtained again in the present study (1.55 eV excitation).

As shown in Fig. 3(a), the fast decay component was observed at 1.51 eV but not at 1.55 and 1.60 eV. This is consistent with a deconvoluted spectra in Fig. 1(b). The overlapping of the induced absorption is negligible at the observing photon energies higher than 1.55 eV. The oscillation with a period of 0.11 ps shown in Fig. 3 was observed only at 1.51 eV, where the fast decay component exists. This strongly suggests that the oscillation is related to the induced absorption due to the relaxed excited state. Furthermore, there is no peak around 291 cm^{-1} (corresponding to 0.11 ps oscillation) in the Raman spectrum.[14] So, in the following analysis, we assume that the oscillation is superimposed on the induced absorption and not on the bleaching. Equation (4) will be used instead of Eq. (3) to take into account the oscillation,

$$K_{abs}(t) = \exp\left(-\frac{t}{26}\right) - \exp\left(-\frac{t}{r}\right)$$
$$+ D \exp\left(-\frac{t}{\tau_{damp}}\right) \sin(\omega t + \varphi), \tag{4}$$

where, r, D, ϕ, ω, and τ_{damp} are the rise time of the induced absorption (not including the oscillation), initial amplitude, phase, frequency and the damping time of the superimposed oscillation, respectively. The result of the fitting by using Eq. (4) is shown in Fig. 4(a) [$r = 0.1$ ps, $\omega = 2\pi/(0.11$ ps), $\phi = 0.45\pi$, $\tau_{damp} = 0.1$ ps]. The calculated curve reproduced
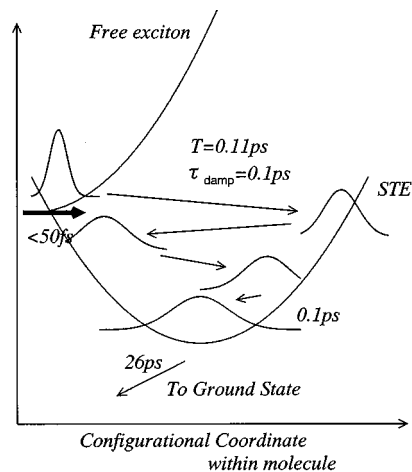

FIG. 5. Schematic illustration of the wave packet motion and the thermalization process of the relaxed excited state on the adiabatic potential surface.

the experimental result, which indicates that the observed oscillation is reasonably considered to be due to the induced absorption. Figure 4(b) shows the component of the induced absorption which was obtained by subtracting the component of the bleaching from the observed signal in the framework of the analysis using Eqs. (2) and (4).

IV. DISCUSSION

Previously,[5] we ascribed the rise up of the induced absorption which is overlapped on the bleaching to the thermalization process of the STE. In this study, we found that the oscillation with a period of 0.11 ps was superimposed on the rise of the induced absorption. In the framework of the previous scenario, the oscillation is considered to originate from the wave packet motion[15] on the potential surface of the STE (Refs. 18 and 16) during thermalization as shown in Fig. 5.

Here, to confirm this interpretation qualitatively, we make simulation of the wave packet motion. We use classical and phenomenological model, although the quantum mechanical treatment may be needed for quantitative discussions. To describe the wave packet motion under thermalization on the potential surface, the harmonic oscillator model of Brownian particles is used.[17] The Langevin equation of the Brownian oscillator is given by Eq. (5),

$$\frac{d^2x(t)}{dt^2} + \gamma\frac{dx(t)}{dt} + \omega_0 x(t) = R_D(t), \tag{5}$$

where $\omega_0 = (k/m)^{1/2}$, k is the force constant, and γ is the friction. $R_D(t)$ denotes the random force. The population density $P(x,t)$ is given by Eqs. (6) and (7) in the Gaussian process,[18]

$$P(x,t) = \int_{-\infty}^{\infty} p(x,t|x_0,0)P(x_0,0)dx_0, \tag{6}$$

$$p(x,t|x_0,0) = \frac{1}{\sqrt{2\pi(\langle x(t)^2\rangle - \langle x(t)\rangle^2)}}$$
$$\times \exp\left[-\frac{(x(t) - \langle x(t)\rangle)^2}{2(\langle x(t)^2\rangle - \langle x(t)\rangle^2)}\right]. \tag{7}$$
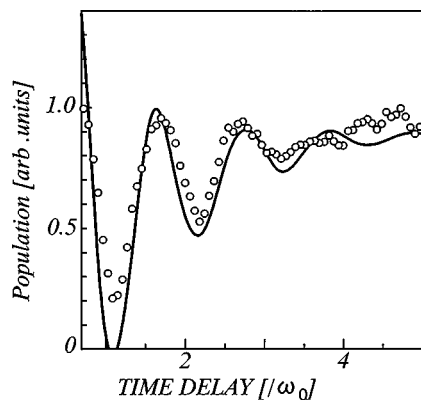
FIG. 6. The component of the induced absorption (open circles) which was obtained by subtracting the bleaching component from the observed profile [Fig. 4(b)], and the result of the fitting by Eqs. (5)–(9) ($k_BT=0.2m\omega_0^2$, $\beta=0.37\omega_0$, $a=3/\omega_0$).

The averaged value and the dispersion of $x(t)$ is given by Eqs. (8) and (9), respectively,

$$\langle x(t)\rangle = \left\{\cos(\omega t)+\frac{\gamma}{2\omega}\sin(\omega t)\right\}\exp\left(-\frac{\gamma t}{2}\right)x(0), \qquad (8)$$

$$\langle x(t)^2\rangle - \langle x(t)\rangle^2$$

$$=\frac{2\gamma k_BT}{m}$$

$$\times\left\{\frac{1}{2\gamma\omega_0^2}+\frac{-\omega_0^2+\gamma^2\cos(2\omega t)-2\gamma\varpi\sin(2\omega t)}{8\gamma\omega_0^2\omega^2\exp(\gamma t)}\right\}, \qquad (9)$$

where, $\omega^2=\omega_0^2-(\gamma/2)^2$. $P(x_0,0)$ is the initial distribution at $t=0$. As $P(x_0,0)$, we use a Gaussian function centered at $x_0=a$ and with a width (FWHM) of $5.46\,k_BT/m\omega_0^2$. $P(x,t)$ satisfies the Boltzmann distribution as an equilibrium condition at $t=\infty$. The curve calculated by Eq. (6) is shown in Fig. 6 ($x=0$, $k_BT=0.25m\omega_0^2$, $\gamma=0.37\omega_0$, $a=3/\omega_0$). This curve represents the population density at the minimum of the potential surface. It qualitatively agrees with the component of the induced absorption shown in Fig. 4(b), although the model is too simple to discuss quantitatively the physical meaning of the adjustable parameters.

According to the previous study,[5] the spectral change of the induced absorption with time indicates that STE thermalizes to the quasiequilibrium state in 0.1–0.3 ps. In this study, the oscillation with the period of 0.11 ps was observed using 40 fs pulses in the time profile of the transient absorption. The oscillation was observed only in the spectral region where the induced absorption due to STE overlaps. Therefore, the oscillation is considered to be superimposed on the induced absorption and not on the bleaching. The rise of the induced absorption with the oscillation is explained by a model involving the wave packet motion during thermalization on the adiabatic potential surface of the STE as shown in Figs. 5 and 6. In this interpretation, the electronic transition which gives the induced absorption couples with one of the dominant vibrational modes of STE. The frequency of the mode was estimated to be 290 cm^{-1} from the period of the

oscillation (0.11 ps). Initial relaxation of the exciton is considered to occur in the following way: At first, the unthermalized STE is formed within 50 fs. After that, the excess energy of STE is accepted by a mode with a frequency of 290 cm^{-1} coherently, which is followed by the energy diffusion to other lower frequency modes.

In this study, we observed the underdamped oscillation in the time profile of the transient absorption. This oscillation is considered to be due to the wave packet motion of STE under thermalization. However, the ultrashort pulse of 800–2 μm wavelength region is needed in order to reveal the formation dynamics of unthermalized STE in 1D Pt(dmg)$_2$. Refinement of the light source is now in progress.

V. CONCLUDING REMARKS

We have investigated the thermalization dynamics of the self-trapped exciton in 1D Pt(dmg)$_2$ by pump–probe spectroscopy using 800 nm, 40 fs pulses. The underdamped oscillation was observed in the time profiles of the transient absorption. The oscillation was ascribed to the wavepacket motion of the STE in the potential surface during thermalization. The frequency of the vibrational mode related to the STE of 290 cm^{-1} was obtained.

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[10] We have not obtained the direct evidence for the assignment such as the large Stokes-shifted intrinsic emission with the same decay as that of the induced absorption. However, the transient absorption spectra at various excitation energies showed that the induced absorption did not originate from the free exciton state. The bleaching spectrum under excitation at 1.48 and 1.55 eV consists of the components of the excited state occupation and of the ground state depletion. On the other hand, we did not find the component of the excited state occupation under excitation in the higher energy region, although the induced absorption was observed as in the case of 1.48 and 1.55 eV excitation. This strongly suggests that the induced absorption is due to the relaxed exciton and not to free exciton. Furthermore, we found the spectral change with time which was explained

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by the thermalization of the STE in the 0.1–0.3 ps time region. This spectral behavior was very similar to that in PDA (Ref. 7).

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