© 1999 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 72, 909—914 (1999)

Femtosecond Regular Reflection Spectroscopic Study on Ultrafast Photoinduced Heat Generation in Copper Phthalocyanine Solid

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(Received July 15, 1998)

A femtosecond regular reflection spectroscopic system was developed and applied to a β-copper phthalocyanine (β-CuPc) pellet. Transient regular reflection spectra were converted into extinction coefficient change (Δk) ones, which correspond to transient absorption spectra, by using Kramers-Kronig transformation. The Δk spectrum observed immediately after excitation was assigned to the excited state of β-CuPc solid, which relaxed by an exciton–exciton annihilation. The spectra remaining over several nanoseconds were assigned to a hot band due to a vibrationally excited state of the electronically ground state. We have clarified that a fast photothermal conversion process is induced by the exciton–exciton annihilation, which was analyzed by a simulation using a time dependent rate (proportional to $t^{-1/2}$) of the annihilation.

When an organic crystal with a high absorption coefficient is excited by an intense laser pulse, various nonlinear photophysical and photochemical dynamic processes are induced. Multiphoton absorption leading to higher excited states, simultaneous two photon absorption, ionization, mutual interactions between excited states, and so on are representative examples, while defect formation, melting, and ablation are well known as resultant morphological phenomena. Among them, exciton–exciton annihilation often plays an important role as a relaxation channel of the excited state in the early time range. Usually the penetration depth of the excitation pulse is shallow in the crystal, hence it is expected that much amount of thermal energy is generated rapidly in a small volume. The photothermal conversion upon the exciton–exciton annihilation will induce interesting thermal phenomena in such organic crystals at the later stages. The dynamics of the exciton–exciton annihilation has been investigated for various organic solid systems by using time-resolved laser spectroscopy.[1—19] Phthalocyanines (Pcs) are one of representative aromatic molecules and have been studied for their thin films,[6—13] microcrystals in polymer matrix,[14] and other relations. However, the primary heat generation processes induced by the exciton–exciton annihilation were not elucidated in detail.

To examine the photothermal conversion processes of such organic solids, we have developed transient regular reflection spectroscopy, which probes dynamic processes of their surface layers in the time domain from ps to μs, and have applied it to β-CuPc solid.[15—18] Transient extinction coefficient spectra, which give transient absorption spectra, can be estimated from regular reflection ones by using Kramers–Kronig transformation. The spectroscopy was also demonstrated to be fruitful for the dynamics at a β-CuPc/water interface.[19] The conventional transmittance mode UV absorption spectroscopy is restricted to very thin films deposited on transparent substrates. Furthermore, a spectral bend due to its reflectance change cannot be excluded in the transient absorption spectra. These problems which are sometimes involved in the transmittance mode measurements have been solved by our spectroscopic method.

In the previous work,[15—18] the time resolution of the regular reflection spectroscopy system was about 25 ps, hence dynamics and kinetics of the exciton–exciton annihilation in β-CuPc pellet sample were not measured directly. It was confirmed that the vibrationally excited state of the ground electronic state, giving a hot band, is induced by the exciton–exciton annihilation. However, the contribution of cyclic multiphotonic absorption process,[20] where once produced excited singlet and triplet states are further excited to their higher excited states, the latter relax to the original states quite rapidly, and again the recovered states absorb the photon repeatedly during the excitation pulse, was not completely neglected. Also, it was not excluded enough that the excited states come back quickly to the ground state via fast internal conversion and undergo repetitive absorption of excitation photons. Therefore, for revealing the ultrafast dynamics of the photothermal conversion process, a regular reflection measurement with higher time resolution has been needed.

In the present work, we have improved for the first time the time resolution of the regular reflection spectroscopy system to femtosecond by introducing a mode-locked Ti : sapphire laser system. The transient reflection spectra of β-CuPc are now obtained with the time resolution of about 400 fs, which is short enough compared with the photothermal conversion process. In addition, the 780 nm excitation with the Ti : sapphire laser excludes another possible photothermal conversion mechanism. The present pulse populates selectively the vibrationally lower excited states of the lowest electronically excited state. In our former picosecond experiment, the 355 nm excitation forms the electronically higher excited state of β-CuPc, hence the rapid internal conversion from the latter to the lowest excited state should also generate appreciably thermal energy. Now we can elucidate the primary processes of photothermal conversion more directly and precisely.

Experimental

The polycrystalline micropowder of β-CuPc (Dainippon Ink & Chemicals, Inc., Fastogen Blue TGR) was used without further purification. The polymorph of the material was confirmed by its X-ray diffraction patterns. A pellet of β-CuPc for the regular reflection spectroscopy was prepared by compressing it with a KBr pellet die (Shimadzu, a diameter of the pellet is 13 mm) at (6.1 ± 0.2) GPa for 10 min. in vacuum. For the measurement, the sample pellet was supported by a Teflon® holder in the atmosphere.

A block diagram of the femtosecond regular reflection spectroscopic system that we have developed here is presented in Fig. 1. The system is made of a femtosecond Ti : sapphire laser (Coherent Mira Basic) with a nanosecond YAG (Coherent Surelight I)-pumped regenerative amplifier (Continuum TR70-10). The fundamental light (center wavelength 780 nm, FWHM 150 fs) of the Ti : sapphire laser was used as an excitation pulse. The femtosecond white light continuum, which was generated by focusing the fundamental light of the Ti : sapphire laser into a H_2O cell, was divided into two: One was used as a probe light and the other as a reference light. The FWHM of the cross-correlation between the probe and excitation pulses was typically 400 fs. The white continuum was detected by a pair of polychromators coupled with multichannel photodiode arrays (MCPD, Hamamatsu, C4351). The probe light was introduced to the sample pellet with an angle of 4° which could be regarded as normal incidence, and the reflected femtosecond continuum was detected by MCPD1.

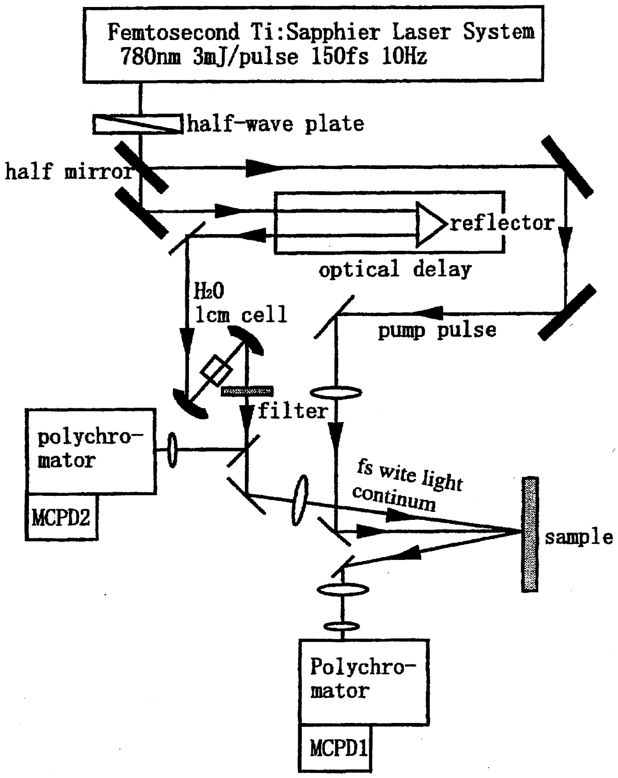

Fig. 1. A block diagram of femtosecond regular reflection spectroscopy system.

The transient reflectance change (γ) is experimentally obtained as the ratio of the signals of MCPD1 with and without excitation, whose shot-to-shot variations are corrected by using the signal of MCPD2 as a reference. The γ value was obtained by averaging 100—300 measurements. For femtosecond spectral measurement, the chirping (dispersion) of the white continuum should be considered for correct and reliable spectral analysis, whose method was established by us long ago.[21)] The dispersion of the white continuum was estimated by measuring the time correlation profile between the white continuum and the excitation light, and the γ was corrected using this time dispersion curve.[5)]

The real reflection index (n) and extinction coefficient (k) were measured for the ground state of β-CuPc by the regular reflection spectroscopic apparatus based upon Avery's method.[18)] All measurements were performed at room temperature (23 °C).

The Kramers–Kronig transformation was performed in the same manner as described in the previous paper.[15,16)] The transient extinction coefficient (Δk) is given by

$$\Delta k = \frac{2\sqrt{R_{\text{ex}}}\sin\theta_{\text{ex}}}{1+R_{\text{ex}}-2\sqrt{R_{\text{ex}}}\cos\theta_{\text{ex}}} - k, \tag{1}$$

where R_{ex} and θ_{ex} is the reflection coefficient and the phase shift with excitation, respectively. By using the Kramers–Kronig relation, R_{ex} is related to θ_{ex} as follows:

$$\theta_{\text{ex}} = 2\frac{\lambda}{\pi}P\int_0^{\infty} \mathrm{d}\lambda'\frac{\mathrm{Ln}\sqrt{R_{\text{ex}}(\lambda')}}{\lambda'^2-\lambda^2}, \tag{2}$$

where P indicates that the principal value of the integral along the wavelength λ' should be taken. And R_{ex} is given by

$$R_{\text{ex}} = \gamma\cdot R_0, \tag{3}$$

where R_0 is the reflection coefficient in the ground state, which can be determined by n and k. Of course, Δk, k, n, R_0, R_{ex}, and θ_{ex} are functions of the wavelength λ. Δk was calculated by using the experimentally determined value of R_{ex} in Eqs. 1 and 2. To perform the integration of Eq. 2, the obtained R_{ex} at the wavelength region from 460 to 750 nm was used in the calculation and that in other longer and shorter wavelength regions was estimated by an extrapolation method proposed by Roessler.[22,23)] In the estimation, the numerical integration algorithm based on the Maclaurin's formula[24)] was used. Although the calculation is based on some assumptions, the result should be reliable as the denominator of $(\lambda'^2-\lambda^2)$ in Eq. 2 is practically effective only for the wavelength range within ±30 nm.

Results and Discussion

Transient Δk Spectra: Refractive index and extinction coefficient spectra of the β-CuPc pellet, obtained by Avery's method, are shown in Fig. 2A. In the visible region, the Q-band transition with peaks at 630 and 710 nm appears, and a shoulder due to B-band transition is observed below 550 nm. The contour of the visible absorption is characteristic of the β-crystal form.[25)] Thus the preparation of the pellet by compression is considered not to modify the crystal form of β-CuPc. Figure 2B shows the γ spectrum of β-CuPc at 1 ns of the femtosecond excitation, giving a positive peak at 540 nm and two negative peaks at 560 and 720 nm. As an example, this γ spectrum was changed to the Δk spectrum in Fig. 2C,

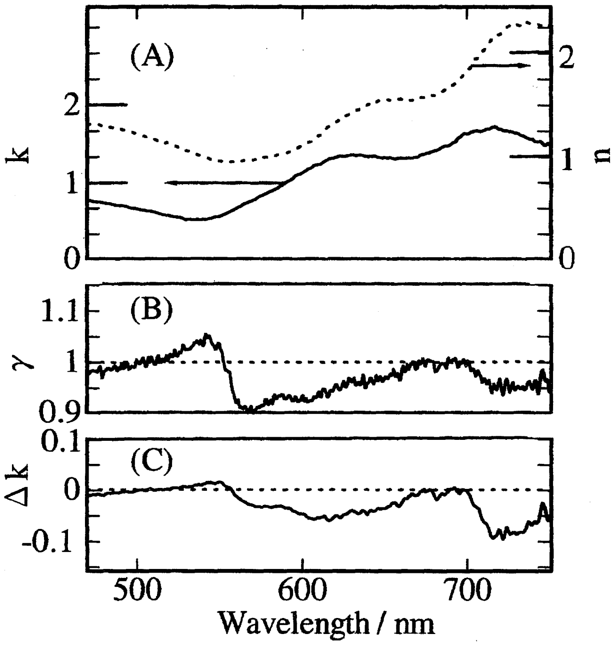

Fig. 2. (A) Refractive index (n) and extinction coefficient (k) spectra in the ground state; (B) the transient reflectance change (γ) spectrum; (C) the transient excitation coefficient change (Δk) spectrum. The delay time in (B)–(C) is 1 ns after excitation.

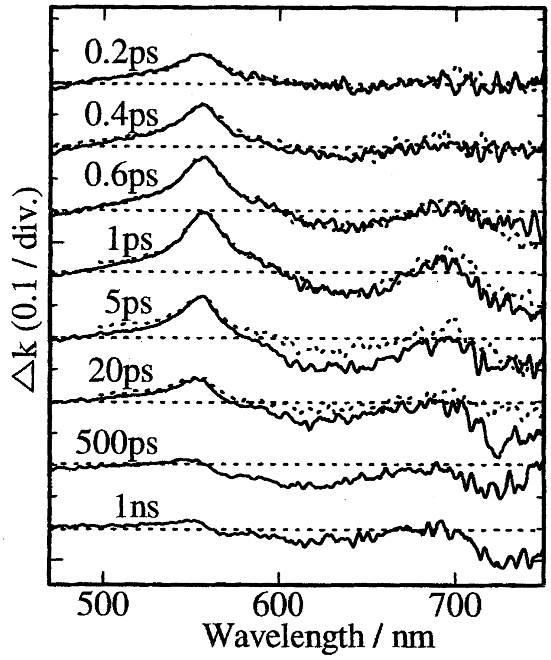

Fig. 3. Time-resolved extinction coefficient change (Δk) spectra excited at 4.5 mJ cm^{-2} (solid line) and those at 1.3 mJ cm^{-2} (broken line). The latter are normalized to the former at 550 nm.

which was obtained by the Kramers–Kronig transformation. Roughly, the spectral shape of Δk is similar to that of γ in the examined wavelength range, and indeed it is mathematically verified that the Δk spectrum coincides nearly with the γ one under the condition that the γ signal is not so strong.

Similarly Δk spectra of β-CuPc solid were obtained at each delay time. Their evolution is summarized in Fig. 3, where the spectra obtained with different excitation intensities are normalized. The positive Δk band at the 555 nm was observed at 0.2 ps immediately after excitation, while negative absorption was additionally obtained around 640 and 740 nm at late stages. The decay and spectral deformation continue almost up to a few hundreds ps. It is worth noting that the relative contribution of the negative absorption is decreased without any appreciable spectral change, when the excitation intensity is reduced. Corresponding to the decay of the 555 nm band, its absorption edge in the long wavelength side shifts to blue but the intensity of the negative bands increased. After most of the decay of the positive band, the weak Δk spectrum still remained, and its shape and intensity were almost constant over several ns.

Assignment of Transient Species: Now we assign these spectra and discuss their temporal characteristics. Firstly, the present Δk spectrum at 1 ns is considered. It reminds us of our previous picosecond regular reflection spectroscopic result that a hot band is produced within 20 ps.[15] Namely, vibrationally excited states of the electronically ground state are populated, giving an intensity decrease of the Q-band peaks, although the decrease is not appreciable between the peaks. To confirm this assignment in the present spectroscopic system, extinction coefficient spectra were measured at various temperatures and the obtained temperature difference spectra were compared with each other. It was practically confirmed that the difference increases with temperature elevation but its spectral shape depends little on the temperature. Figure 4 shows one example of the difference obtained by subtracting the extinction coefficient spectrum at 22 °C from that at 62 °C. The difference spectrum arises from intermolecular (phonon mode) or intramolecular (local mode) vibrational excitation of the electronically ground state. As shown in

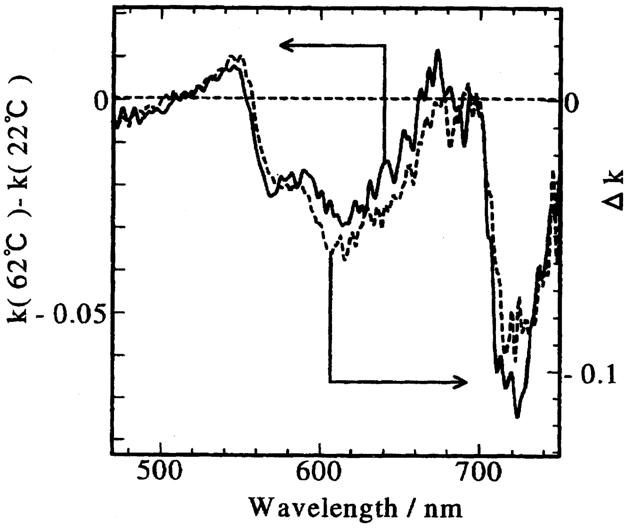

Fig. 4. A difference spectrum (solid line) obtained by subtracting an excitation coefficient spectrum at 22 °C from that at 62 °C, and an extinction coefficient change (Δk) spectrum (broken line) at 1 ns after excitation with 4.5 mJ cm^{-2} pulse.

Fig. 4, the Δk spectrum at 1 ns of the femtosecond excitation is in good agreement with the temperature difference spectrum; hence the Δk spectrum at late stages can be assigned to the hot band and the long-lifetime species should be the inter- or intramolecular vibrationally excited state.

Secondly, we consider the results at early stages. The Δk spectrum at 0.2 ps should be ascribed to an electronically excited state. The population of the excited state should be accompanied with the negative absorption around 640 and 740 nm due to the ground state depopulation, as proved clearly in the ns time region. However, no bleaching around those wavelengths was detected. For β-CuPc solid, absorption spectra of an electronically and vibrationally excited state are known to have broad bands extending into the visible-near IR region.[10] Therefore, it is considered that the positive absorption band of the excited state is overlapped with the bleaching of the Q-band at 0.2—0.4 ps and that the negative band is completely compensated by the positive band. The fast spectral change from 0.2 to 1 ps indicates that a very quick relaxation takes place in the excited state, which is discussed below.

One possible interpretation is due to intersystem crossing of β-CuPc molecules. It is rather strange to assume subps intersystem crossing, but an interaction with Cu atom may have an important role. An unpaired copper d-electron in CuPc molecule is considered to couple weakly to the normal molecular singlet and triplet states. Then singlets become doublets (^{2}S), and triplets split into doublets (^{2}T) and quartets (^{4}T).[26] Since the relaxation from ^{2}S to ^{2}T is now a spin allowed process, it is faster than an ordinary intersystem crossing. Consequently, the absorption spectra at subps and 1 ps can be assigned to ^{2}S and ^{2}T, respectively, including the corresponding ground state bleaching. As supporting data, it was reported that the relaxation from ^{2}S to ^{2}T and ^{4}T of vanadyl Pc (VOPc) solid takes place with the time constant of 0.7 ps.[11]

There is another possibility that the early change is due to vibrational relaxation in an initial electronically excited state. In solution and in a polymer matrix, this relaxation process of electronically ground state takes place in the time range of a few ps. If this time scale is also applicable to the electronically excited state of a molecular crystal, the sub ps spectral change is too fast to occur in CuPc solid.

The other possible interpretation for the rapid spectral change within 1 ps is due to spectral overlap of a transient species formed only under high intensity excitation. However, since Δk spectral shapes were almost independent of the excitation intensity in this time range, the nonlinear processes characteristic of high intensity excitation will not be involved.

Furthermore it is discussed frequently that coherent coupling effects are not negligible when the pump and the probe pulses are temporally overlapped with each other. The standard Kramers–Kronig transformation can be applied to pump-probe measurements, only when the overlap duration of these pulses is enough long compared with the dephasing time.[27,28] We have to say that the early spectral change may be caused by coherent coupling effects. On the other hand, a very rapid energy redistribution has been reported in some Pc solids with the time region of about a few tens fs,[9,12] which is faster than the present time resolution by one order of magnitude. Therefore, it is considered that the dephasing in CuPc takes place within the present temporal resolution, but its effect upon optical shape is not so large. Of course some ambiguity still remains for the spectral assignment around zero delay time.

Thirdly, Δk spectral change from 1 to 500 ps is considered. The maximum position of the positive absorption shifts from 550 nm to the blue by a few nm and its red-edge also shifts to the blue. In addition, the clear negative absorptions similar to the hot band are observed, but its intensity is larger than that of the hot band. However, this negative absorption in the present time range cannot be assigned to the hot band, as the heat dissipation leading to special changes dose not take place in thirty or forty ps. Namely, the ^{2}T absorption is overlapped with bleaching of the ground state absorption band at 1 ps, and the absorption decays and the bleaching is replaced by the hot band with time.

Excitation Intensity Dependence: In Fig. 3, the time-resolved Δk spectra of β-CuPc solid excited at 1.3 and 4.5 mJ cm^{-2} are normalized at 555 nm. At 5 and 20 ps after excitation, transient spectra show excitation intensity dependence. While the 555 nm is assigned to an exciton due to ^{2}T, the difference spectra obtained by subtracting the Δk spectrum at 1.5 mJ cm^{-2} from that at 4.5 mJ cm^{-2} is similar to the hot band. This means that the hot band is observed more strongly at high intensity excitation. Figure 5 shows excitation intensity dependencies of Δk decay profiles. The decay kinetics of the 550 nm at the excitation intensity of 1.3 mJ cm^{-2} was slower than that of 4.5 mJ cm^{-2}. If one as-

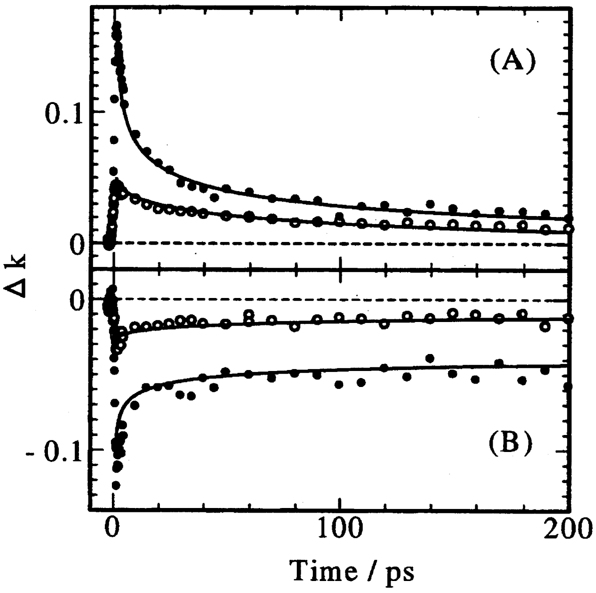

Fig. 5. Normalized time profiles of transient excitation coefficient change (Δk) at 550 nm (A) and 625 nm (B) excited at 4.5 mJ cm^{-2} (●) and 1.3 mJ cm^{-2} (○). Solid lines are curves calculated by using Eq. 4.

sumes that the Lambert–Beer equation holds, the skin depth of β-CuPc crystal at the excitation wavelength is estimated to be 100 nm. When the pellet was excited at 4.5 mJ cm^{-2}, which is the highest excitation intensity in the present experiments, the maximum (initial) exciton density is calculated to be 1.1×10^{21} molecules cm^{-3}. Under this condition, since the molecular density is 1.7×10^{21} molecules cm^{-3}, about half of the molecules are excited from the ground to the excited states. As the excitons are created so densely, efficient interactions between them are induced, leading to the present excitation intensity dependence.

Exciton–Exciton Annihilation Leading to Heat Generation: When exciton–exciton annihilation occurs, the dynamics of exciton density N will be expressed by the following rate equation,

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -K(t)N - \Gamma(t)N^2, \tag{4}$$

where $K(t)$ and $\Gamma(t)$ are the linear and nonlinear decay rates. Here, we choose the following decay rates:

$$\begin{aligned} K(t) &= K_0, \\ \Gamma(t) &= \Gamma_0 t^{-1/2}. \end{aligned} \tag{5}$$

The time-dependent nonlinear decay rate ($t^{-1/2}$) is derived by assuming the annihilation due to three-dimensional Förster-type dipole–dipole interaction between excitons or via one-dimensional exciton diffusion. It is known that β-CuPc crystal takes a columnar-like stacked structure and the distance between stacked molecules in one direction is 1.5—2 times smaller than in the others. As the Förster-type energy transfer rate depends on intermolecular distance with the six power law, the rate along the column is faster than that of other directions by 10—60 times. Therefore it is considered that the Förster-type mechanism also results in a one-dimensional process. As the present spectral data is not good enough to confirm whether the Förster-type energy transfer along one-dimensional has a main role or not, we analyze the exciton–exciton annihilation with Eq. 5. In this model, the decay of the exciton density is derived from Eq. 4 as follows:

$$N(t) = N_0 \frac{\exp(-K_0 t)}{1 + \{2N_0\Gamma_0/K_0^{-1/2} erf\ [(K_0 t)^{1/2}]\}}, \tag{6}$$

where N_0 is the initial exciton density, and $erf\ (x) = \int_0^x \exp(-u^2)\mathrm{d}u$. A similar analysis has already been applied by us to a 50 nm thin film of β-CuPc, by using transient grating spectroscopy.[13] Also Gulbinas et al. reported on similar excited state dynamics of vanadyl and lead phthalocyanine (VOPc and PbPc) films.[10]

To fit the present model to our experimental data, we must also consider the dynamics of the hot band, as both the ^{2}T and the hot bands are overlapped with each other in the observed wavelength region. Exciton–exciton annihilation produces an electronically higher excited state and an electronically ground state from a pair of excitons. The higher excited state relaxes to the lower excited state upon internal conversion and the excess energy should distribute in intra- and intermolecular vibrational modes in a very short time scale. Then, assuming that the hot band was generated immediately after exciton–exciton annihilation, the time profile of Δk is expressed as follows:

$$\Delta k^{\mathrm{obsd}}(t) = \Delta k_0^{2T} N(t)/N_0 + \Delta k_0^{\mathrm{hot}}(1 - N(t)/N_0), \tag{7}$$

where Δk_0^{2T} is the extinction coefficient of ^{2}T immediately after excitation and, $\Delta k_0^{\mathrm{hot}}$ is that of the hot band relaxed completely from ^{2}T to the ground state.

Table 1. Parameters Characterizing the Exciton Relaxation as Obtained from a Best Fit Procedure to the Exciton–Exciton Annihilation Data

Excitation intensity	K_0^{-1}	$\{N_0\Gamma_0\}^{-1}$	Γ_0
mJ cm^{-2}	s	s$^{1/2}$	cm^3 s$^{-1/2}$
4.5	200×10^{-12}	3.5×10^{-6}	2.7×10^{-16}
1.3	200×10^{-12}	14×10^{-6}	2.3×10^{-16}

The solid lines of both 550 and 625 nm shown in Fig. 5 are curves calculated by using Eq. 7. The curve fitting of the Δk decay at 4.5 mJ cm^{-2} was performed by using data observed after 5 ps, within which time period another fast relaxation may be completely finished, and changing extensively K_0^{-1} from 100 to 2000 ps and $\{N_0\Gamma_0\}^{-1}$ from 1×10^{-6} to 20^{-6} s$^{1/2}$. The decay at 1.3 mJ cm^{-2} can be reproduced within the experimental error by decreasing $N_0\Gamma_0$, Δk_0^{2T} and $\Delta k_0^{\mathrm{hot}}$, which are proportional to exciton density, linearly with the excitation intensity. Thus obtained decay parameters are listed in Table 1. These calculated curves are well fitted to the observed data in the time region from a few ps to 200 ps. For Γ_0, we obtained 2.5×10^{-16} cm^3 s$^{-1/2}$ as an average, which is in the same order of magnitude for β-H$_2$Pc and VOPc.[11] Thus, it is concluded that local temperature elevation takes place in the time range upon the exciton–exciton annihilation.

Conclusion

The femtosecond regular reflection spectroscopy is developed for investigating excitation energy relaxation dynamics of β-CuPc solid. Reflection spectra obtained by this measurement were converted into transient extinction coefficient (Δk) spectra by the Kramers–Kronig transformation and the decay kinetics of Δk spectra was analyzed. The temporal evolution within 1 ps of Δk spectra was interpreted to be controlled by internal conversion from ^{2}S to ^{2}T. The exciton–exciton (^{2}T–^{2}T) annihilation takes place efficiently, which was explained by assuming one-dimensional exciton diffusion. The hot band of the ground state was observed upon the exciton–exciton annihilation, meaning rapid heat generation. The exciton decay rate via bimolecular annihilation process was determined to be about 2.5×10^{-16} cm^3 s$^{-1/2}$. We conclude that a rapid temperature rise is induced upon the exciton–exciton annihilation and its time scale is a few tens ps under the excitation condition of a few mJ cm^{-2}.

We are grateful to Mr. Shyouji Funakura of Dainippon Ink & Chemicals, Inc. for providing samples of β-CuPc.

The cost of this work is partly defrayed by a Grant-in-Aid for Scientific Research No. 09304067 from the Ministry of Education, Science, Sports, and Culture and by Special Coordination Funds for Promoting Science and Technology from the Science and Technology Agency.

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