Cooperative Photochemical Reaction in Molecular Crystal Induced by Intense Femtosecond Laser Excitation: Photochromism of Spironaphthooxazine[†]

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Photochromism of indolinospironaphthooxazine (SNO) microcrystalline powder was investigated by steady state and time-resolved diffuse reflectance spectroscopy using a femtosecond laser as a light source. When laser intensity is weak, the photoinduced ring-opening reaction in a picosecond time region and subsequent thermal ring-closure one in a nanosecond scale take place in the crystal, not leading to permanent photocoloration of the powder. The same sample shows photochromism upon intense femtosecond laser excitation. The absorption spectra after laser excitation are similar to those of the photocolored form in solution. The spectral shape is independent of the laser fluence, whereas the yield increases nonlinearly with the fluence. To reveal the photocoloration mechanism, we examined the excitation fluence dependence of the transient absorption spectra and elucidated the photocoloration behavior by femtosecond double pulse excitation varying the delay of the two pulses. These experimental results show that cooperative interactions between the excited states and short-lived intermediates are important to generate a long-lived photomerocyanine. Femtosecond induced photocoloration will be discussed in terms of transient and local lattice deformations, and a cooperative photochemical reaction model is proposed.

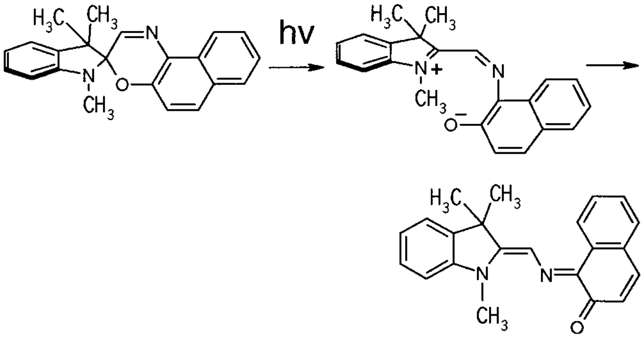
Introduction

Spiropyrans and Spirooxazines are well-known photochromic compounds that have been attracting much interest from the viewpoints of fundamental elucidation of photochemical reactions as well as from their potential applications to optical memories.[1−7] UV irradiation of the colorless spiro isomer leads to a colored open isomer called photomerocyanine (see Scheme 1). The photochromic reaction features the breakage of the spiro C−O bond producing a distribution of photomerocyanine isomers.[4−7] It is known, from time-resolved experiments, that the C−O bond breakage in the excited state occurs within 1 ps.[7−12] Subsequent rotations of carbon−carbon and/or carbon nitrogen bonds leading to transoid, planar photomerocyanines take place within 10 ps after excitation. The photomerocyanine returns back to the original spiro isomer either thermally or photochemically.

Although the photochromism in solution and in various matrixes is a well-known phenomenon,[7−12] the photochromic reactions in crystalline phase are very unusual. It was suggested that this is due to the geometrical lack of free volume in the crystal necessary for isomerization leading to trans-planar photomerocyanines. We have recently examined and directly confirmed this hypothesis for the case of SNO[13] and 6-nitrospiroindolinobenzopyran (6-nitroSP)[14] crystals using methods of ultrafast diffuse reflectance absorption spectroscopy. Specially, we showed that a C−O bond breaking in a picosecond time scale forms a short-lived, nonplanar open isomer. The open isomer does not lead to a long-lived, transoid photomerocyanine but returns back to the spiro isomer thermally within 6 ns for SNO and 400 μs for 6-nitroSP.

The photochemical properties of spiropyran and spirooxazine crystals have been out of research interests, because the crystals do not show photochromism by weak steady UV light irradiation. Recently, we have found that intense femtosecond UV pulse excitation leads to a reversible photocoloration of SNO microcrystalline powder.[13] The absorption spectrum after laser excitation showed the formation of a planar photomerocyanine isomer similar to that in solution and the thermal bleach of the photomerocyanine in a time region of several minutes at room temperature. The experimental results indicate that using an ultrashort-pulsed laser can exclusively induce the crystal state photochromism. In the previous paper,[13] the laser fluence dependence of the photomerocyanine yield showed a certain threshold above which coloration reaction was obtained. This suggested that dense formation of electronically excited molecules is necessary to induce the crystalline phase photochromism. We discussed the photocoloration mechanism in terms of photothermal effects due to intense laser excitation. However, the molecular mechanism of this event has not been cleared yet.

SCHEME 1



This paper presents time-resolved and steady state absorption spectral studies on the femtosecond laser induced photochromism of SNO microcrystalline powder. Absorption spectral measurements with a picosecond temporal resolution were

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carried out at the excitation laser fluence below and above the threshold of photocoloration in order to get insights into the electronic structure and the lifetimes of the excited state and short-lived transients after femtosecond pulse excitation. The primary photochemical processes in the crystalline phase are discussed in this paper, in comparison with both the photoisomerization mechanism and dynamics in solution phase. Furthermore, to reveal why and how densely formed electronically excited states lead to planar photomerocyanine in the crystal, we examined here the laser fluence dependence of the steady-state absorption after femtosecond laser excitation under two excitation conditions. According to the first one, a sample was excited with 170 fs UV pulses at 390 nm with the repetition rate of 10 Hz. In the second case, the sample was excited with a pulse train of double femtosecond pulses with a determined time interval between them. The yield of the colored isomer was examined as a function of this time interval. We name here the second excitation condition as "double pulse excitation experiment". Because both lifetimes of the excited state and of the nonplanar open form are in the range of the double pulse interval, spectral studies in dependence on the later one should bring information on dynamics of the transients. In this work, we show clearly that cooperative interaction of these short-lived transients plays a key role in the photocoloration and that the contribution of photothermal effect is negligible.

On the basis of these experimental results, femtosecond induced photocoloration is discussed in terms of transient and local lattice deformations. A cooperative photochemical reaction model is proposed.

Experimental Section

Material. SNO (Aldrich) was recrystallized from *n*-hexane. Samples of microcrystalline powder were prepared by mechanical grinding of SNO crystals in a mortar till the particle size ranged from a few to several tens of microns, as estimated with an optical microscope. We filled the powder in a 1 mm quartz cell and degassed it for spectroscopic measurements.

Spectroscopy. The details of a femtosecond diffuse reflectance spectroscopic system have been reported elsewhere.[15,16] Briefly, an excitation light source consists of a cw self-mode-locked Ti:sapphire laser (Mira 900 Basic, Coherent), pumped by an Ar^+ laser (Innova 310, Coherent), and a Ti:sapphire regenerative amplifier system (TR70, Continuum) with a Q-switched Nd:YAG laser (Surelight I, Continuum). The fundamental output from the regenerative amplifier (780 nm, 3−4 mJ/pulse, 170 fs fwhm, 10 Hz) was frequency doubled (390 nm) and used as a femtosecond excitation pulse. The excitation intensity dependence was examined by adjusting the pulse intensity using a polarizer and a $\lambda/2$ plate. The residual of the fundamental output was focused into a 1 cm quartz cell containing H_2O in order to generate a white-light continuum as a probe beam. The transient absorption intensity was displayed as percentage absorption (% absorption), given by % absorption $= 100 \times (1 - R/R_0)$, where R and R_0 represent the intensity of the diffuse reflected white-light continuum of a probe pulse with and without excitation, respectively.

Photocoloration of SNO microcrystalline powder was followed with the same spectroscopic system. Namely, after excitation with femtosecond laser pulses (390 nm, 10 Hz repetition), steady state absorption spectra of the powder were measured with the femtosecond white-light continuum as a probe. In the case of double pulse excitation experiments, a femtosecond excitation pulse train was divided into two using a half mirror. Two trains were introduced to a common position of the sample with a timing determined by an optical delay unit. The time interval between two trains was varied between 40 ps and 5 ns.

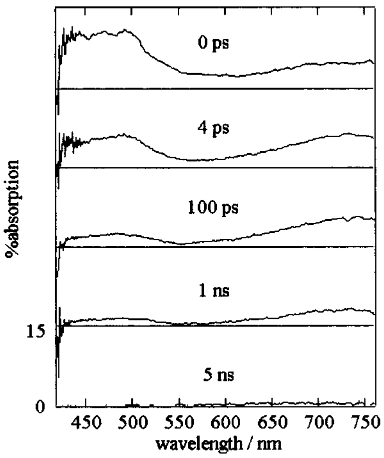

Figure 1. Transient absorption spectra of SNO microcrystalline powder monitored after excitation with a 390 nm femtosecond laser pulse at room temperature. Excitation laser fluence is 0.4 mJ/cm^2.

The excitation intensity was adjusted so that the maximum absorption was less than 25% in the measurement in both transient and steady state experiments. This guarantees a linear relation between % absorption and the concentration of absorbing species under the present experimental condition.[16,17]

Results and Discussion

Picosecond Dynamics of Microcrystalline SNO under Weak Excitation. First, we deal with photochemical dynamics of the powder in picosecond to nanosecond time regions under a weak excitation condition. As a representative example, Figure 1 shows time-resolved absorption spectra after excitation with a 0.4 mJ/cm^2 laser pulse at 390 nm. At this laser fluence, the sample powder did not show permanent photocoloration even after 300 laser shots at room temperature. An absorption band with its maximum at 495 nm can be assigned to the S_1 state of the spiro isomer. Its decay reveals that two broad long-lived spectral peaks at 460 and 760 nm remain. We consider these bands to be due to a nonplanar primary photoproduct formed after the C−O bond breaking (see Scheme 1).

Figure 2 shows the time profiles of transient absorption at 495 and 740 nm. We estimated the lifetimes of 3 ps and 2 ns for the S_1 state and the nonplanar open form, respectively. It is confirmed that the nonplanar open form returns back to the ground-state spiro isomer, not leading to a trans-planar photomerocyanine under the weak excitation condition. An experiment for a sample exposed to air gave almost the same results on the spectra and time profiles. Therefore, we considered contribution of the surface molecules of the microcrystal to be negligible in the transient absorption spectral data.

Here, we compare the transient absorption spectra in the crystal to those reported for the methylated SNO derivatives at the 2′ position of the oxazine moiety in solution.[12,18] Although nonsubstituted SNO yields only long-lived planar photomerocyanines, a short-lived nonplanar species (~1 μs lifetime) is formed as the predominant product for the 2′-methyl derivative because of hindered rotation around C(2′)−C(3′).[12,18] The absorption spectrum reported in ref 18 has two peaks at 470 and 680 nm in ethanol.[18] This is similar to spectral features of the primary photoproduct we monitored in our research in solid

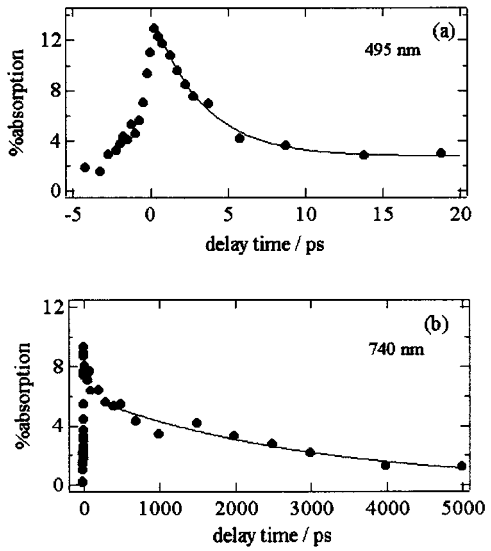

Figure 2. Temporal profiles of transient absorption of SNO microcrystalline powder observed at (a) 495 and (b) 740 nm.

state. The similarity supports the idea that the primary photoproduct is a nonplanar open form.

The nature and spectral properties of the primary photoproduct of photoisomerization of unsubstituted SNO in fluid solutions were studied by several groups, using picosecond and femtosecond absorption spectroscopies[7−10] and picosecond Raman spectroscopy.[11,12] The spectroscopic evidence on a nonplanar structure of the primary product is reported only in ref 8, where photochromism of SNO in 1-butanol was studied in a wide spectral range (420−700 nm) with a subpicosecond temporal resolution. It was shown that the decay of the S_1 state of the spiro isomer with a lifetime of 0.7 ps results in the direct formation of a nonplanar species living for 0.4 ps before the isomerization to a planar photomerocyanine isomer. Thus, the absorption of the nonplanar species has a very similar spectral character to that of the nonplanar open form observed in our studies. However, as it was shown in 1-butanol, the lifetime of the primary photoproduct is shorter than that of S_1 state. The primary product in 1-butanol undergoes conformation changes into a metastable merocyanine isomer. Thus, transient absorption represented a blue shift within 2 ps after excitation. The very rapid isomerization in solution makes it difficult to study the nature of the primary photoproduct. In the case of the crystal, any structural changes of molecules are strongly restricted in a lattice environment; we are able to confirm clearly a nonplanar nature of the photoprimary product.

Similar transient absorption spectra and their temporal change were also observed at 363 and 275 K. Moreover, the temperature dependences of the lifetimes of the S_1 state and the nonplanar open form were observed. The S_1 state and nonplanar open form lifetimes are of 1.5, 3, and 4.5 ps and 0.5, 2, and 4.5 ns for 363, 295, and 275 K, respectively. The lifetime dependence on temperature indicates that both the C−O bond breaking in the S_1 state and the ring-closure reaction of the nonplanar open form are thermally activated events. It is considered that the bond breaking does not occur in the orthogonal parent geometry of the indolino and oxazine chromophers. The bond breaking process is coupled to both the intramolecular vibration motions, such as twisting around the spiro carbon, and lattice oscillations. Although the mechanism of bond cleavage in the crystalline phase is not so clear at the present stage of investigation, the temperature dependence indicates that the nonplanar open form observed here is not the geometrical structure to the parent spiro isomer. Therefore, it is considered that the photoinduced ring-opening and the subsequent ring-closure reactions cause a local and transient lattice deformation.

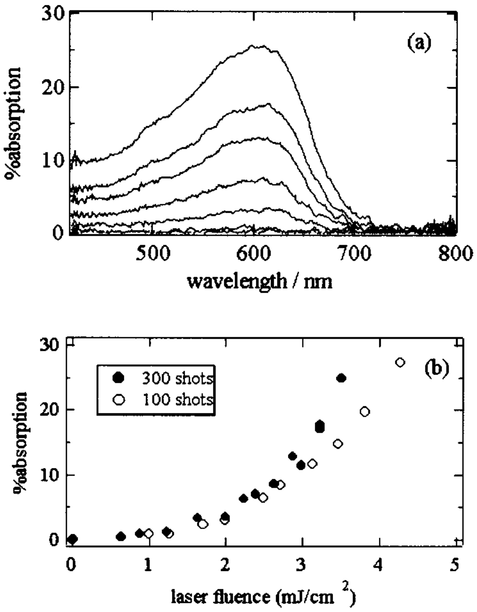

Figure 3. Laser fluence dependence of photocoloration for SNO microcrystalline powder at room temperature. (a) The steady state absorption spectra after 100 shots of irradiation of 390 nm femtosecond laser pulse. Spectral shapes are almost independent of laser fluence. (b) Plots of absorption at 610 nm after 100 shots (open circles) and 300 shots (filled circles) of laser irradiation as a function of the laser fluence.

Photocoloration by Intense Femtosecond Pulse Excitation. As described in the Introduction, SNO microcrystalline powder shows photocoloration by intense femtosecond laser excitation. The absorption spectra after 100 laser shots at various laser fluences are shown in Figure 3, where the spectral shape is almost independent of the laser fluence. A characteristic absorption spectrum with its maximum at 610 nm can be safely assigned to the photomerocyanines from the spectral similarity to that in solutions.[2] When the laser fluence was less than about 0.5 mJ/cm^2, the sample powder did not show any detectable absorption change even when excited with several thousands of shots. Above a certain laser fluence threshold, the absorption increases nonlinearly with the fluence. The absorption at the peak wavelength after 300 and 100 shots of irradiation is plotted against the laser fluence in Figure 3b. Similar spectral response was observed for other spirooxazine and spiropyran compounds. Therefore, the reported laser-induced photocoloration seems to be a common feature for this class of photochromic molecules.

The colored powder bleached thermally at room temperature, and the decoloration kinetics in Figure 4 shows a nonexponential and complex decay. The half-lifetime was estimated to be 7 min; however, the photomerocyanine was still present in the powder even after 1 h when the laser fluence was 3.6 mJ/cm^2. The lifetime obtained here is much larger than that of photomerocyanines in fluid solutions and also in polymer films at room temperature. Because the same photocoloration and thermal bleaching behavior was observed for the powder sample in air, we may neglect any specific contribution of molecules on crystalline surface in the spectral response. This is consistent with the air effect upon transient absorption spectral measurement.

Because the absorption change after one-shot excitation is very small, multishot excitation is necessary here in order to

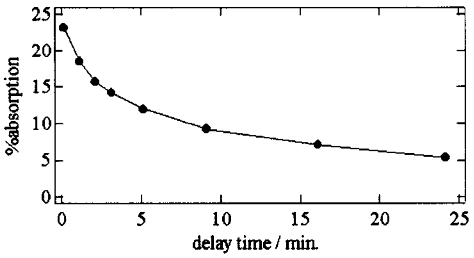

Figure 4. Thermal decay kinetics of photocolored SNO microcrystalline powder after 300 shots of the laser at the laser fluence of 3.6 mJ/cm^2.

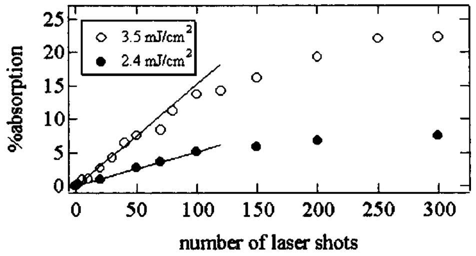

Figure 5. Dependence of the steady state absorption at 610 nm on the number of laser shots at fluence of 2.4 (open circles) and 3.5 mJ/cm^2 (filled circles) for SNO microcrystalline powder at room temperature.

get a detectable photocoloration when the laser fluence is less than 4 mJ/cm^2. Under such excitation conditions, multishot excitation effects should be considered. For example, the preceding excitation pulses may produce a variety of structural defects in the crystal lattice where later pulses would induce photoisomerization leading to trans-planar photomerocyanines. In this case, the absorption of the sample will show a nonlinear dependence on the number of invested pulses. To confirm this idea, we plot the absorption at 610 nm as a function of the number of irradiated laser shots at the fluences of 2.4 and 3.5 mJ/cm^2 in Figure 5. The absorption grows in line with the number of laser shots at first, and for further increasing, it shows a saturation tendency. Probably the saturation tendency is due to photoinduced bleaching of photomerocyanines caused by the succeeding laser pulses. The thermal bleaching during the irradiation also contributes to the saturation behavior, as a 300 shot excitation needs 0.5 min in this experiment using the 10 Hz repetition rate laser system. Therefore, we consider at the present stage of investigation that accumulation and incubation effects due to multishot excitation are not dominant in the photocoloration behavior at room temperature and that photomerocyanines are generated by one intense laser pulse.

When laser fluence was over 6 mJ/cm^2, the produced photomerocyanine absorption spectrum with its maximum at 610 nm was detected even after single laser shot excitation. The steady state absorption spectra obtained in the one-shot experiment with different excitation fluences are shown in Figure 6. The absorption increases nonlinearly with the fluence, as in the case of the multishot excitation experiment. The one-shot excitation, however, gives a sharper band of the photoproduct compared to the multishot excitation measurements. One possible explanation for the spectral difference is to assume that plural conformers are formed by multishot excitation.

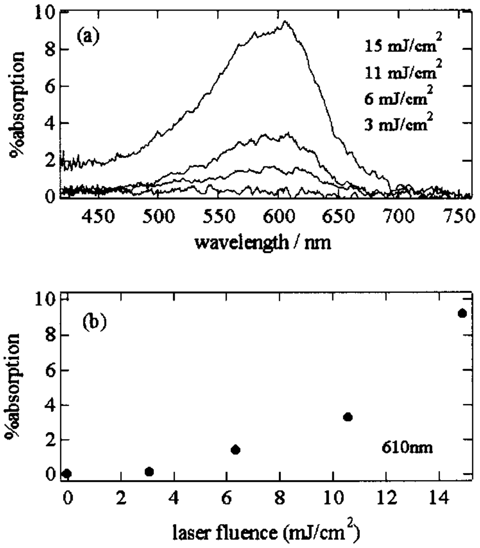

Figure 6. Laser fluence dependence of photocoloration by one-shot femtosecond laser excitation for SNO microcrystalline powder at room temperature. (a) The steady state absorption spectra after excitation of the 390 nm femtosecond laser pulse. (b) Plots of absorption at 610 nm as a function of laser fluence.

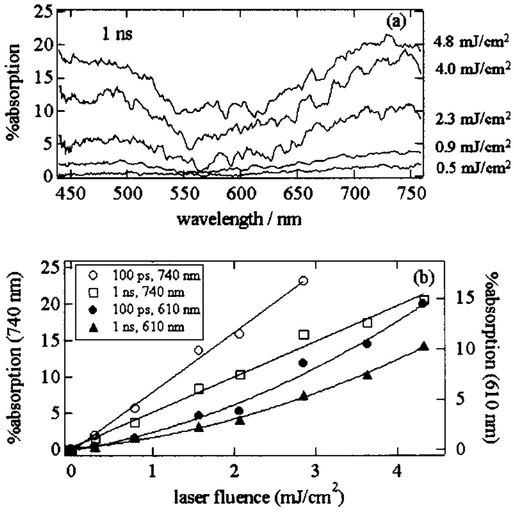

Figure 7. Laser fluence dependence of transient absorption for SNO microcrystalline powder at room temperature. (a) The transient absorption spectra at 1 ns after excitation at different laser fluence. (b) The transient absorption at 740 and 600 nm at delay times of 100 ps and 1 ns as a function of laser fluence.

Transient Absorption Spectra under an Intense Excitation Condition. Intense femtosecond laser excitation is expected to induce ionization and generation of higher excited states because of multiphoton absorption. Namely, some other transients, which are not observed under a weak excitation condition, can be formed and thus involved in the photochromic reactions. Therefore, transient absorption spectral measurements after intense laser excitation are important and indispensable for a detailed investigation of the photocoloration mechanism. As a representative example, the laser fluence dependence of transient absorption spectra at 100 ps and 1 ns after excitation is shown in Figure 7. In the lower fluence range, absorption spectra can be identified as the primary photoproduct, nonplanar open form. The increase in the laser fluence yields an additional absorption between two peaks at 480 and 730 nm. The relations between laser fluence and absorption at 740 and 610 nm for delay times of 100 ps and 1 ns are illustrated in Figure 7. The absorption band of the primary photoproduct shows a good linearity with respect to the laser fluence for each of the delay times. This indicates that main photochemical processes are independent of excitation laser fluence. On the other hand, the absorption at 610 nm shows nonlinear dependence on the excitation fluence,

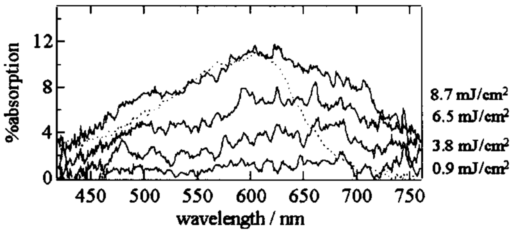

Figure 8. Laser fluence dependence of the transient absorption spectra at 10 ns after excitation with a 390 nm femtosecond laser pulse for SNO microcrystalline powder at room temperature (solid lines). The dashed line represents a steady state absorption spectrum of the permanent photoproduct.

which is consistent with the steady state absorption spectra in Figures 3 and 6. Transient species formed with high-density excitation should be responsible for an absorption peak around 600 nm corresponding to that of the permanent photoproduct.

We examined also the dependence of the transient absorption on the fluence at a delay time of 10 ns, where any transient absorption was not detected under the weak excitation condition as described above. As shown in Figure 8, a broad absorption band from 500 to 700 nm appears, and its peak shifts to shorter wavelength at higher laser fluences. At the fluence of 8.6 mJ/cm^2, the maximum value examined here, the peak is located at 600 nm, which is close to that of the permanent photoproduct. The observed laser fluence dependence of the spectra at 10 ns is quite similar to the transient absorption spectral change monitored in 1-butanol solution from 0.26 to 2 ps after excitation.[8] The later corresponds to transformation of the nonplanar primary photoproduct to metastable photomerocyanine isomers. This means that at higher laser fluences planar or near-planar photomerocyanine isomers are formed even in the crystalline phase and live for a long period compared with the nonplanar open form. Therefore, we can conclude that a molecular structural change leading to planar or near-planar photomerocyanines can take place within a nanosecond time region in the densely excited SNO crystal, although the main photochemical processes of the composed molecule are almost independent of the laser fluence.

Photocoloration by Intense Femtosecond Double Pulse Excitation. Figure 9 shows the steady state absorption spectrum after 100 shots of 10 Hz repetition femtosecond double pulses with the same fluence for the two pulses and a time interval of 40 ps, as a representative example of the double pulse excitation experiment. For the comparative purpose, in this figure, we show also the spectra colored by 100 shots of single excitation pulses with a 10 Hz repetition rate at laser fluences of 1.7 and 3.4 mJ/cm^2. Because the absorption spectra recorded in both experiments have similar shapes, we anticipate the same trans-planar photomerocyanine isomers to be formed under given excitation conditions. However, the yield of a photocoloration reaction strongly depends on the excitation condition. It is smaller in the double pulse experiment than that determined in the single pulse experiments, thought the total excitation laser fluence is the same.

The time interval dependence of the photocoloration yield in the double pulse excitation experiment is summarized in Figure 9. The steady state absorption after double pulse excitation (1.7 and 1.7 mJ/cm^2) is plotted against the time interval between two excitation pulses. The initial steep decreasing of the absorption is followed by its slow decrement with the linear increase in the time interval. Namely, femtosecond excitation events by the first and the delayed second pulses correlate to each other with respect to trans-planar photomerocyanine formation. We found two correlation times on the photocoloration; one is less than 10 ps and another is about 600 ps. A comparison between the correlation time profile and the transient absorption data in Figure 2 strongly suggests that the fast component is related to that between the S_1 states and the slow one is the nonplanar primary photoproduct. We consider that the mutual interactions between the S_1 states and the nonplanar open forms give the result in Figure 9 and are responsible for the photocoloration.

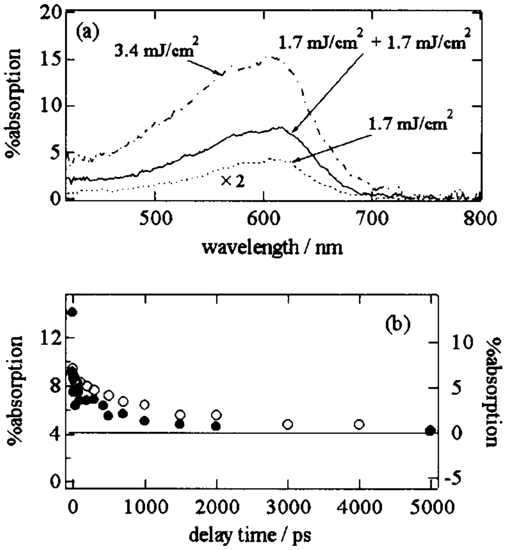

Figure 9. Steady state absorption spectra in a double pulse excitation experiment for SNO microcrystalline powder at room temperature. (a) The solid line represents the spectrum after 100 shots of 10 Hz repetition femtosecond double pulses with the same laser fluence of 1.7 mJ/cm^2 and with 40 ps interval between the two pulses. Broken and dotted lines represent the steady state absorption spectra after 100 shots of 10 Hz repetition femtosecond single pulse with the laser fluence of 3.4 and 1.7 mJ/cm^2, respectively. (b) The dependence of absorption at 610 nm on the time interval between two excitation pulses (filled circles). The absorbance at the interval of 0 ps is that recorded by single pulse excitation at the fluence of 3.4 mJ/cm^2. Open circles represent the temporal profile of the nonplanar open form, as shown in Figure 2b.

When the time interval is larger than 3 ns, the absorption obtained in the double pulse experiment became just a sum of the absorption in the single pulse excitation at a laser fluence of 1.7 mJ/cm^2. This means that photochemical and photophysical processes induced by the first femtosecond pulse excitation are not correlated to those by the second excitation when these two excitation events are separated for a time of longer than several nanoseconds. The result is consistent with the results and discussions on the shot number dependence of the photocoloration.

Cooperative Photochemical Model. On the bases of the above results and discussions, we now consider the mechanisms of femtosecond laser induced photochromism of SNO crystals. First, we here mention the facts that trans-planar photomerocyanines after a large structural change from the initial spiro form result in the photocoloration and that dense electronic excitation of the crystal is necessary to generate long-lived trans-planar photomerocyanines. As photocoloration needs some free volume, we assume that the high density of the excited states creates space in a crystal lattice.

One idea is a cooperative photochemical reaction model. The present transient absorption experiment indicates that SNO molecules in the crystal undergo a very rapid and highly efficient photoinduced bond breaking between spiro-carbon and oxygen

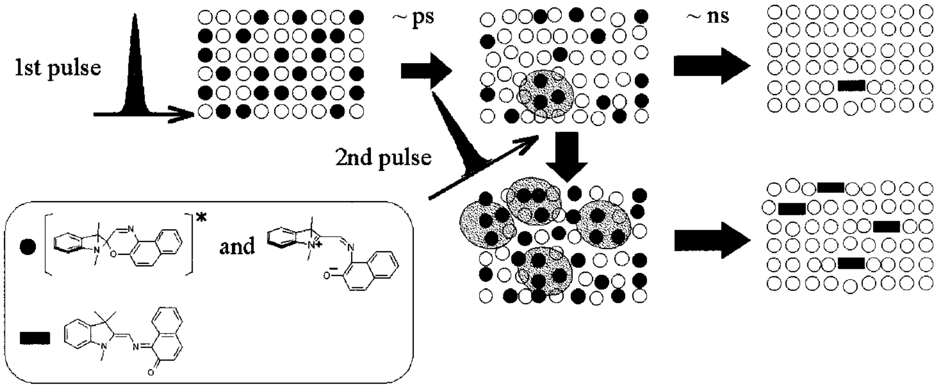

Figure 10. Schematic illustration of the cooperative photochemical reaction model. The open circles represent the ground-state spiro isomer, the filled ones represent the S_1 states and/or the nonplanar open forms, and the filled rectangles represent the trans-planar photomerocyanines.

and that the nonplanar open form goes back to the original spiro form in a nanosecond time region. It is also suggested that the photoinduced bond breaking and the ring-closure reactions generate some local lattice disorder in the crystal. When the crystal is excited by intense femtosecond light, the S_1 state and the nonplanar open form generate densely in the crystal, and the photochemical reactions of the plural transient species in the neighbor will create a free volume in crystalline lattice. Therefore, some of the plural transient species would undergo isomerization leading to trans-planar photomerocyanines.

Figure 10 shows a schematic illustration for explaining the cooperative photochemical reaction model and the double pulse excitation effect on the photocoloration. This model leads to a conclusion that the yield of the photocolored form relates directly to the concentrations of the S_1 state and the nonplanar open form at a certain delay time. If we can assume that femtosecond laser excitation creates the electronically excited molecules and the nonplanar open forms randomly in crystal, the lattice site where plural transient species exist at a certain time after excitation increases with the excitation fluence. This is consistent with the photocoloration experiment both by femtosecond single and double pulse excitation experiments.

Another possible idea is a photothermal reaction model. High temperatures are attained immediately after organic solids are excited with an intense short-pulse laser. It was proved for some organic crystals by picosecond and femtosecond transient absorption spectroscopy.[19−23] Ultrashort laser excitation of organic solids leads to significant heat generation because of various nonradiative decay channels of the electronically excited state. In the case of the SNO crystal, the photoinduced bond breaking and the subsequent ring-closure reaction convert electric excitation energy into heat within a nanosecond time scale, resulting in a rapid temperature elevation of the crystals. At high temperature, molecular vibrations and lattice motions should facilitate the primary photoproduct to undergo a conformational change to a stable and planar merocyanine even in crystalline phase. However, this model does not explain well the results in Figure 9 obtained by femtosecond double pulse excitation. A crystal surface layer, once excited by a laser pulse and thus heated, would show slow temperature decays through thermal diffusion. Because this cooling time is estimated to be of a microsecond order, two excitation events by the first and second pulses should be correlated to the photocoloration yield at the time interval of longer than 10 ns. Therefore, we conclude that photothermal effects are not dominant in the photocoloration behavior, and the cooperative photochemical reaction model is proposed for the crystalline phase molecular photochromism.

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