Femtosecond Transient Absorption Studies of *trans*- and *cis*-1,3,5-Hexatriene in Solution

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The electronic, vibrational and conformational relaxation of *trans*- and *cis*-1,3,5-hexatriene in solution have been investigated by femtosecond transient absorption spectroscopy. Upon excitation to the 1B state, the transient absorption is observed in the visible region, which mainly consists of an instantaneous rise (<150 fs) and a subpicosecond decay. For the trans isomer, the decay of the transient absorption signals becomes faster at longer wavelengths. On the other hand, for the cis isomer, the decay of the signals does not depend on the probe wavelength significantly. For both isomers, these temporal profiles of signals show that the internal conversion from the S_2 to S_1 state occurs within 100 fs and the lifetime of the S_1 state is less than 500 fs. The observed dependence of the decay on the probe wavelengths for the trans isomer is ascribed to vibrational energy redistribution in the S_1 state. We also measured the bleach recovery signals by the one-color pump−probe method in the UV region. The bleach recovers in several time scales. The temporal profiles of trans isomer in the first 20 ps are similar to those of cis isomer, which come from the vibrational relaxation in the ground state. However, on a longer time scale, these signals are quite different to each other. While the trans isomer takes 150−300 ps to fully recover the bleach, the cis isomer requires no more than 100 ps. These slow components are attributed to the conformational relaxation around the C−C single bond to the original forms. The different behavior between the trans and cis isomers reflects different product distributions and dynamics among the isomers around the C−C single bonds.

1. Introduction

The electronic structures and spectroscopic properties of simple linear polyenes have stimulated a great number of experimental and theoretical studies over the past two decades.[1−4] From a biological point of view, polyene derivatives such as retinal and carotenoids play important roles in vision and light-harvesting systems. In a light-harvesting complex, the efficiency of the energy transfer from carotenoids to chlorophyll is strongly affected by the nature of the excited-state dynamics in polyenes.[5] The cis−trans isomerization and photoinduced electrocyclization reactions in the polyene moiety are found in the primary event in the vision and in the photochemistry of vitamin D and its precursors.[2]

The dynamics of longer substituted polyenes such as β-carotene and its derivatives and retinal in bacteriorhodopsin have been studied by ultrafast transient absorption and fluorescence spectroscopy.[6−8] For β-carotene, after the photoexcitation to the S_2 state, internal conversion to the S_1 state occurs at around 200 fs and the lifetime in the S_1 state is $\sim$10 ps.[6,7] The rate of the internal conversion to the S_1 state, which is influenced by the structural change and solute−solvent interactions, depends on the energy gap between the S_1 and S_2 states.[7,8] For retinal in bacteriorhodopsin, the primary event in the all-trans to 13-cis photoisomerization takes place in 200 fs.[9] Both results indicate that the lifetime of the initially excited state is very short and the internal conversion to the ground state or the isomerization reaction occurs quite efficiently and dominates among the deactivation processes. In order to reveal the nature of these dynamics, it is highly desirable to investigate each step in the dynamics of smaller linear polyenes in detail. Recently, refined molecular orbital calculations and molecular dynamics simulations have been performed and are available for comparison with experiments.[10,11]

In contrast to its longer chain and substituted analogues, the excited electronic properties of smaller linear polyenes such as 1,3-butadiene and 1,3,5-hexatriene have not been well understood because of a complete lack of fluorescence and broad absorption spectra even under jet-cooled conditions and low-temperature matrices.[12] The ordering of the lowest excited states of 1,3,5-hexatriene has been a matter of debate until recently. All-trans polyenes have C_{2h} symmetry and possess two neighboring excited electronic states regardless of its chain length, namely, S_1 and S_2, with different symmetric characters, 2^1A_g and 1^1B_u, respectively. While a one-photon transition from the S_0 to S_1 state is forbidden, there is a strongly allowed transition to the S_2 state. On the other hand, the cis isomer belongs to the C_{2v} symmetry and the two low-lying excited states are the 2^1A_1 and 1^1B_2 states. When we refer to the electronic states for both isomers, we use the following symmetry notation, i.e., 2A and 1B state, for simplicity.

The two-photon absorption and two-photon excitation thermal lens method suggested that the 0−0 transition to the 2A state was located at lower energy than the 0−0 transition to the 1B state, whereas the vertical transition to the 2A state might overlap or even be located at higher energy than that to the 1B band.[13,14] For *cis*-1,3,5-hexatriene, the location of the 2^1A_1 state in the gas phase was found to be about 5000 cm^{-1} below the 1^1B_1 state by the resonance-enhanced multiphoton ionization method and laser-induced fluorescence spectroscopy.[15,16]

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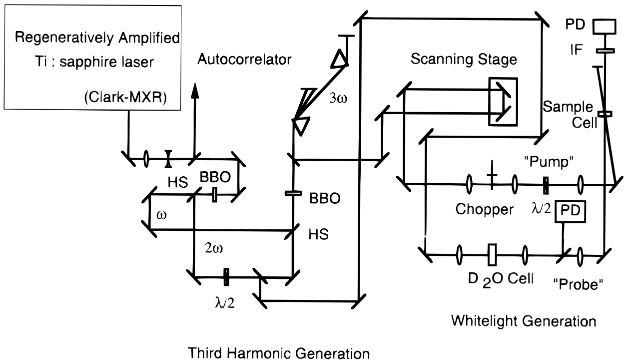

Figure 1. Schematic diagram of the apparatus for transient absorption measurement. HS, harmonic separator; PD, photodiode; IF, interference filter; $\lambda/2$, $\lambda/2$ waveplate.

The excited state absorption of 1,3,5-hexatriene was not observed by the nanosecond transient absorption spectroscopy due probably to insufficient time resolution.[17] It was suggested that the lifetime of the 2A state was below 200 ps. Recently, femtosecond spectroscopic studies of 1,3,5-hexatriene and its related compounds in the gas phase revealed that upon excitation of the 1B state the internal conversion to the 2A state occured in less than 100 fs and the vibrational energy redistribution in the S_1 state and the internal conversion to the ground-state proceeded within a subpicosecond time scale.[18] The lifetime of the 2A state for the cis isomer is about three times longer than that for trans isomer.[19,20]

In the condensed phase, resonance Raman spectroscopy and femtosecond transient absorption spectroscopy have been used to investigate the excited-state dynamics of simple polyenes.[21−27] The initial motion of the wave packet out of the Franck−Condon region occurs on 10 fs time scale and the ground-state photoproduct appears in less than 1 ps.[21−26] We also reported the transient absorption measurements of *trans*-1,3,5-hexatriene in solution and found that the decay of the population in the S_1 state was within 500 fs.[27]

In this paper, we present the results of ultrafast transient absorption experiments on the excited-state dynamics and vibrational and conformational relaxation in the ground state of *trans*- and *cis*-1,3,5-hexatriene in solution. After the photoexcitation to the 1B state, we observed the transient absorption in a very broad region (ultraviolet to visible region), which consisted of an instantaneous rise and decay in less than 500−600 fs. We also measured the bleach recovery signals by the one-color pump−probe method. The transients show an instrument-limited appearance of a bleach followed by a recovery which occurs on several time scales. These signals provide information about the vibrational relaxation in the ground state and the conformational relaxation around the C−C single bonds. The results are compared with those in the gas phase and the differences between *trans*- and *cis*-1,3,5-hexatriene are discussed.

2. Experimental Section

The experimental apparatus for the present measurement is schematically shown in Figure 1. A laser system was based on a self-mode-locked Ti:sapphire laser (NJA-4, Clark-MXR) pumped by a continuous wave (CW) argon ion laser (Spectra Physics 2060). The oscillator was seeded into a regenerative amplifier (CPA-1000, Clark-MXR) to provide amplified pulses of about 120 fs at 1 kHz centered at around 800 nm. The pulse energy was around 900 μJ/pulse. The fundamental pulse was doubled by a 1 mm BBO crystal (Type I). The second harmonic output selected by a harmonic separator passed through a $\lambda/2$ waveplate to rotate the polarization and was divided into two parts. One of them was used for the third harmonic generation by mixing with the remaining fundamental in a 0.5 mm BBO crystal (Type I). We used a prism pair for selecting the third harmonic from the output of the BBO crystal and compressed the pulse duration. This third harmonic was used as a pump pulse. The excitation energy incident on the sample was about 10 μJ/pulse. The other beam was focused into the H_2O or D_2O flow cell to generate the white light continuum which lay between 300 and 600 nm and was used as a probe pulse. The delay between the pump and probe pulses was achieved by a computer-controlled optical delay line. The pump and probe pulses were overlapped on the sample at a small angle and the polarization between them was set at a magic angle by inserting a $\lambda/2$ plate into the pump pulse path. The transient absorption measurements were made by monitoring the probe intensity with a photodiode as a function of delay between the pump and probe pulses. The monitored wavelengths were selected with an interference filter (Andover, fwhm = 10 nm) after a sample cell. A part of the white light continuum was detected by the other photodiode as a reference for compensation of power fluctuation of probe pulse. The absorbance change was calculated by an analogue processor and a boxcar integrator with a toggle mode where the pump pulse was chopped every other shot. The instrument response function was determined by a temporal rise of the excited-state absorption or bleach recovery of rhodamine 6G in ethanol. It was estimated to be 550−600 fs assuming a Gaussian function. We also performed a one-color pump−probe experiment to measure the bleach recovery process in the ground state by using the third harmonic as both pump and probe pulses.

1,3,5-Hexatriene was purchased from Aldrich as a mixture of two isomers. *trans*- and *cis*-1,3,5-Hexatriene were prepared as described by Moller et al.[28] The isomeric purity of the product was checked by gas choromatography, which was higher than 95% for each isomer. Cyclohexane and acetonitrile (spectrograde, Wako Chemicals) were used without further purification. The sample solution flowed through a quartz cell with a 1 mm optical path length at a flow rate fast enough to ensure that fresh solution was exposed to each laser shot. The sample of 2.4×10^{-4} M was prepared, which gave an absorbance of about 1.0 at 268 nm. For cyclohexane solutions we used a cell with a 0.1 mm optical path length to suppress the pulse-duration-limited artifact observed in a 1 mm quartz cell, which originated from the solvent. All measurements were performed at ambient temperature (293 K).

3. Results

3.1. Static Absorption Spectra of *trans*- and *cis*-1,3,5-Hexatriene in Solution. The static absorption spectra of *trans*- and *cis*-1,3,5-hexatriene in cyclohexane and acetonitrile are shown in Figure 2. This molecule has a very strong absorption band from 230 to 280 nm. The maximum molar extinction coefficient in cyclohexane is $\epsilon_{\max} = 51\,740$ M^{-1} cm^{-1} for the trans isomer[21] and 41 000 M^{-1} cm^{-1} for the cis isomer.[22] Both absorption peaks of the 0−0 band are slightly dependent on solvent polarity and are 268 nm in cyclohexane and 266 nm in acetonitrile, respectively. They are similar in shape, as reported previously.[21,22]

3.2. Transient Absorption Signals of *trans*- and *cis*-1,3,5-Hexatriene in Solution. Transient absorption data were collected for *trans*- and *cis*-1,3,5-hexatriene in cyclohexane and acetonitrile with an excitation wavelength of 268 nm, and the

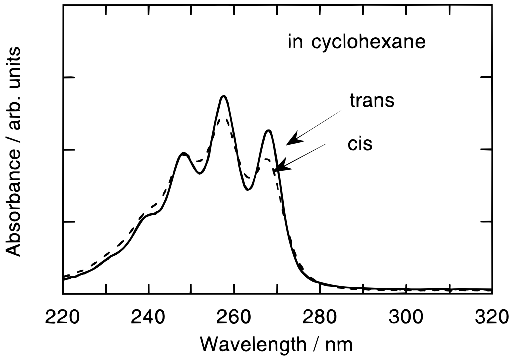

Figure 2. Static absorption spectra of *trans*-1,3,5-hexatriene (a) and *cis*-1,3,5-hexatriene (b) in cyclohexane. Each spectrum is scaled by arbitrary units.

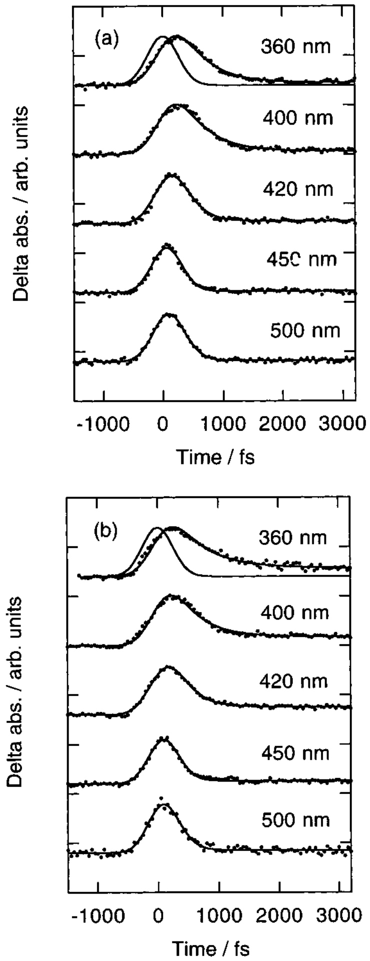

Figure 3. Transient absorption signals probed at five different wavelengths for *trans*-1,3,5-hexatriene in (a) cyclohexane and (b) acetonitrile. The instrument response function is shown in the top decay curve. The solid line represents the best fit to the data by the convolution of the instrument response function with a sum of the two exponentials.

TABLE 1: Best-Fitted Time Constants of the Transient Absorption Signals at Nine Different Wavelengths for *trans*-1,3,5-Hexatriene in Cyclohexane and Acetonitrile

solvent	wavelength/nm	τ_1/fs	τ_2/fs
cyclohexane	340	490 ± 20 (0.96)[a]	-[b] (0.04)
	360	440 ± 10 (0.97)	- (0.03)
	380	460 ± 20 (0.97)	- (0.03)
	400	440 ± 15 (0.97)	- (0.03)
	420	220 ± 10 (0.98)	- (0.02)
	450	<150	
	470	<150	
	500	<150	
	550	<150	
acetonitrile	340	520 ± 25 (0.96)	- (0.04)
	360	510 ± 20 (0.92)	12000 ± 5500 (0.08)
	380	410 ± 15 (0.92)	14600 ± 6000 (0.08)
	400	410 ± 15 (0.91)	13600 ± 2000 (0.09)
	420	250 ± 10 (0.94)	5200 ± 2000 (0.06)
	450	<150	
	470	<150	
	500	<150	
	550	<150	

[a] The relative amplitude of each decay component. [b] The lifetime cannot be determined.

TABLE 2: Best-Fitted Time Constants of the Transient Absorption Signals at Nine Different Wavelengths for *cis*-1,3,5-Hexatriene in Cyclohexane and Acetonitrile

solvent	wavelength/nm	τ_1/fs	τ_2/fs
cyclohexane	340	530 ± 30	
	360	440 ± 20 (0.94)	- (0.06)
	380	550 ± 10 (0.97)	- (0.03)
	400	490 ± 10 (0.94)	- (0.06)
	420	440 ± 10 (0.95)	- (0.05)
	450	400 ± 15 (0.97)	- (0.03)
	470	350 ± 10 (0.98)	- (0.02)
	500	370 ± 30 (0.94)	- (0.06)
	550	350 ± 50 (0.94)	- (0.06)
acetonitrile	340	500 ± 50 (0.95)	- (0.05)
	360	580 ± 20 (0.97)	- (0.03)
	380	450 ± 15 (0.94)	- (0.06)
	400	500 ± 20 (0.91)	13400 ± 5000 (0.09)
	420	560 ± 15 (0.91)	8300 ± 2000 (0.09)
	450	430 ± 20 (0.95)	- (0.05)
	470	490 ± 30 (0.96)	- (0.04)
	500	400 ± 40	
	550	330 ± 40 (0.95)	- (0.05)

[a] The relative amplitude of each decay component.

results at five probe wavelengths ranging from 360 to 500 nm are shown in Figure 3. The time profiles of the signals are fitted to a sum of the exponential functions convoluted with the instrument response function. Table 1 summarizes the results of the best-fit time constants of the transient absorptions. After photoexcitation, an instrument-limited rise (<150 fs) can be seen at each probe wavelength. In cyclohexane, the signal observed at 400 nm decays with the time constant of about 400 fs. The decay at 420 nm becomes faster than that at 400 nm. At both wavelengths, the signals include small remaining components in a longer time scale. At a probe wavelength longer than 450 nm, the observed signals are similar to that of the instrument response function, and we cannot resolve the decaying component unambiguously. The transient absorptions at wavelengths shorter than 400 nm also show a feature similar to that observed at 400 nm. The transient absorption signals in acetonitrile are similar to those in cyclohexane, except that the slow decaying components have a greater contribution. These signals decay with the time constants of 14 ps at 400 nm and 5 ps at 420 nm, as determined from the data measured in a longer time scale.

Figure 4 displays the transient absorption data collected for *cis*-1,3,5-hexatriene in cyclohexane and acetonitrile at five wavelengths from 360 to 500 nm. These absorption signals possess an instantaneous rise and subpicosecond decay component which are rather similar to those for the trans isomer. However, a significantly different character is that the time constant of the decaying component does not depend on the probe wavelength. The results are tabulated in Table 2. The time constant is slightly smaller at longer wavelength as well. Acetonitrile and cyclohexane give similar dynamics but the latter has smaller residual components at shorter wavelength. These

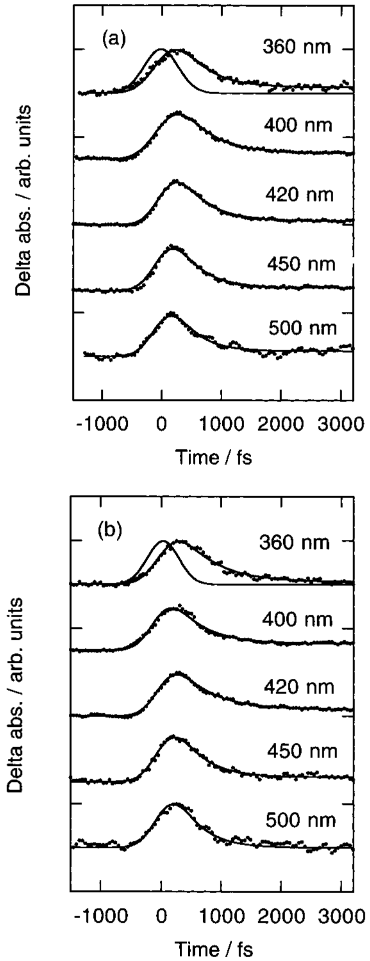

Figure 4. Transient absorption signals probed at five different wavelengths for *cis*-1,3,5-hexatriene in (a) cyclohexane and (b) acetonitrile.

signals decay with the time constant of 13 ps at 400 nm and 8 ps at 420 nm.

The transient absorption spectrum of *trans*- and *cis*-1,3,5-hexatriene in cyclohexane at time zero was constructed as shown in Figure 5. The peak position of the absorption spectrum is located at around 350 nm, and the spectrum is extended to beyond 500 nm. The spectrum for the trans isomer is similar to that for the cis isomer at time zero within our experimental uncertainty.

3.3. Transient Bleach Recovery Signals of *trans*-1,3,5-Hexatriene in Solution. Figure 6 shows the one-color transient bleach recovery signals of *trans*-1,3,5-hexatriene in cyclohexane at three different wavelengths. As shown in Figure 2, the peaks of the first and second vibronic bands are 268 and 257 nm, and the minimum between these peaks is 263 nm, in cyclohexane. The corresponding peaks and the minimum are about 2 nm red-shifted in acetonitrile. The transients show a fast instrument-limited appearance of the bleach followed by the recovery which occurs in several time scales. We tentatively fit the experimental data by a sum of the exponential functions convoluted with the instrument response function. The results of the best fit time constants are summarized in Table 3.

The first components of the transient bleach signals in cyclohexane have recovery times of 0.8 ps at 268 nm and 0.6 ps at 259 nm, respectively. The behavior of the second components depends on the wavelength. At 268 nm, the signal recovers monotonically with the time constant of 18 and 150 ps. However, the transient at 262 nm recovers faster than that at 268 nm and reaches the baseline at around 20 ps; it then bleaches once again followed by longer recovery with the time constant of 180 ps. The transient at 259 nm is similar to that at 268 nm, but with the time constant of ca. 13 and 180 ps.

Figure 7 shows the one-color bleach recovery signals of *trans*-1,3,5-hexatriene in acetonitrile measured at three different wavelengths. In acetonitrile, the behavior of the transients is similar to that in cyclohexane. The recovery of the first components is around 1 ps at all three wavelengths. The behavior of the second component also depends on the wavelength. At 268 nm, the signal recovers with the time constant of 16 ps which is followed by a longer recovery with the time constant of 325 ps. At 262 nm, the transient recovers quickly at around 20 ps and bleaches once again followed by

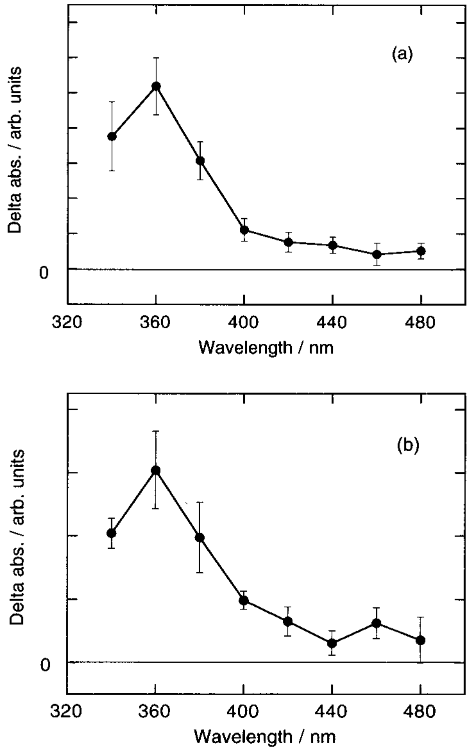

Figure 5. Transient absorption spectrum of *trans*-1,3,5-hexatriene (a) and *cis*-1,3,5-hexatriene (b) in cyclohexane observed at the zero time delay.

TABLE 3: Best-Fit Time Constants of Transient Bleach Recovery Signals Obtained by One-Color Pump−Probe Method

solute/solvent	λ/nm	τ_1/ps[a]	τ_2/ps[a]	τ_3/ps[c]
trans-HT/ cyclohexane	268	0.8 ± 0.1 (0.38)[b]	18 ± 1 (0.62)	150 ± 10
	262	*[d]	*	180 ± 20
	259	0.6 ± 0.2 (0.09)	13 ± 1 (0.91)	184 ± 10
trans-HT/ acetonitrile	268	1.2 ± 0.1 (0.31)	16 ± 1 (0.69)	325 ± 15
	262	*	*	325 ± 35
	259	*	*	305 ± 30
cis-HT/ cyclohexane	268		12 ± 1	
	262	*	*	
	259	*	*	
cis-HT/ acetonitrile	268		13 ± 1	175 ± 15
	262		7 ± 1	158 ± 20
	259	*	*	175 ± 30

[a] τ_1 and τ_2 are the first and second components, respectively, of the bleach recovery signals observed on an early time scale. [b] Relative amplitude of each bleach recovery component, determined only from the results on an early time scale. [c] The third component of the bleach recovery signal observed on a slower time scale. [d] Asterisk indicates the data which cannot be fitted well by a sum of exponential functions.

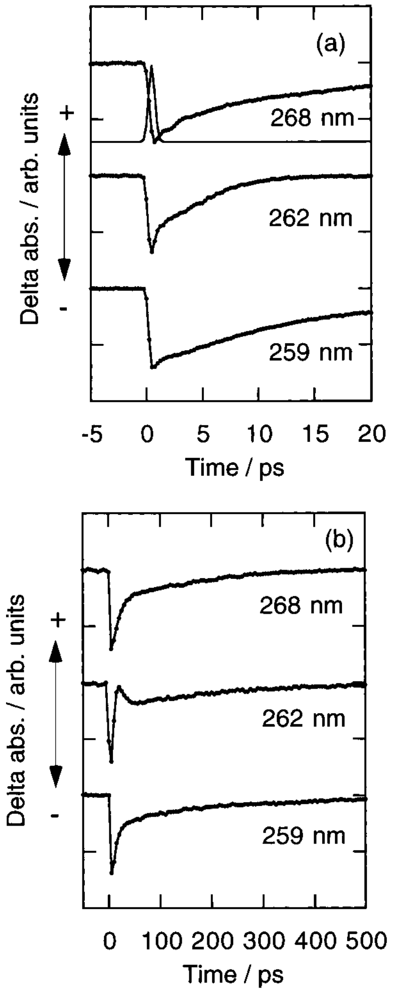

Figure 6. Transient bleach recovery signals (a) within 20 ps time scale and (b) subnanosecond time scale by a one-color pump−probe experiment at three different wavelengths for *trans*-1,3,5-hexatriene in cyclohexane. The instrument response function is shown with the top decay curve in (a).

longer recovery with the time constant of 320 ps. At 259 nm, the behavior is similar to that between 268 and 259 nm. The slower component recovers with the time constant of 305 ps.

3.4. Transient Bleach Recovery Signals of *cis*-1,3,5-Hexatriene in Solution. The bleach recovery signals of *cis*-1,3,5-hexatriene in cyclohexane at three different wavelengths are shown in Figure 8. The temporal profiles of the cis isomer in the first 20 ps are similar to those of the trans isomer. However, in a longer time scale, these signals show quite different behavior to each other. At 268 nm, the transient recovers completely with the time constant of 12 ps. It is clear that there is no 100 ps component within the sensitivity of our apparatus. The signal at 262 nm fully recovers at around 12 ps and shows an absorptive component, which decays completely within 50 ps. At 259 nm, the temporal profile of the signal is qualitatively similar to that at 262 nm, which also recovers within 50 ps. It is found that there exists a small absorptive component in the 15−50 ps time region.

Figure 9 shows the data for the cis isomer in acetonitrile at three different wavelengths. The behavior of the signals is different from that in cyclohexane. In addition to the 10 ps component, we observed the slow component in the signals, whose time constants are 158 ps at 262 nm and 175 ps at the other wavelengths, respectively. It should be noted that the relative amplitude of the slow 100-ps component with respect to the first 10 ps one for cis isomer is much smaller than that for trans isomer.

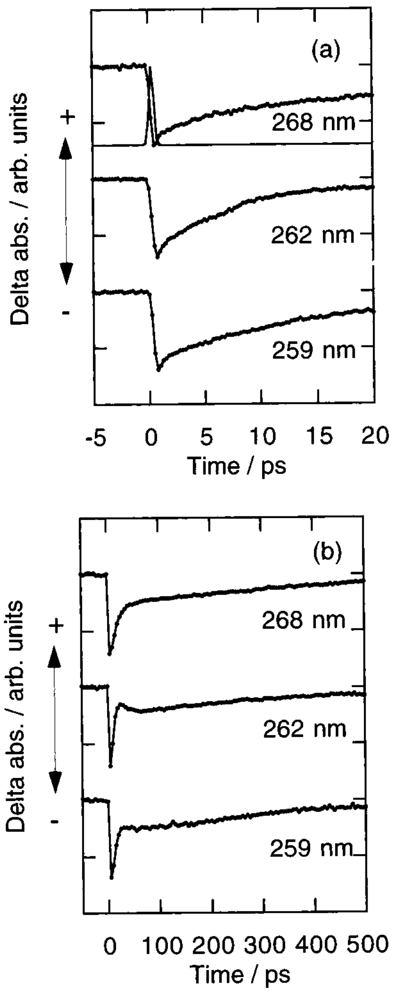

Figure 7. Transient bleach recovery signals (a) within 20 ps time scale and (b) subnanosecond time scale by a one-color pump−probe experiment at three different wavelengths for *trans*-1,3,5-hexatriene in acetonitrile.

4. Discussion

4.1. Origin of the Transient Absorption in the Visible Region. The common feature of the observed transient absorption signals is (1) an instrument-limited appearance of the transient absorption signals at all wavelengths, (2) a fast subpicosecond component, and (3) an additional picosecond component at a few wavelengths, especially in acetonitrile.

On the basis of the line shape analysis of the resonance Raman spectroscopy, the initial motion of the wave packet out of the Franck−Condon region in the 1B state occurs at 40 fs for the trans isomer and 20 fs for the cis isomer.[21,22] Vaida and co-workers estimated the time constant for the internal conversion to the 2A state to be 40 fs in the isolated molecule condition based on the line width of the absorption spectra.[12] Furthermore, the femtosecond time-delayed photoionization of 1,3,5-hexatriene in the gas phase showed that the initially excited population decayed from the 1B state in less than 100 fs.[18] By considering these observations, the internal conversion from the 1B to the 2A state for 1,3,5-hexatriene in solution is expected to occur within 100 fs for both trans and cis isomers. Therefore, the instantaneous rise observed in the transient absorption suggests that we have probed the population on the way from the 1B to the 2A state.

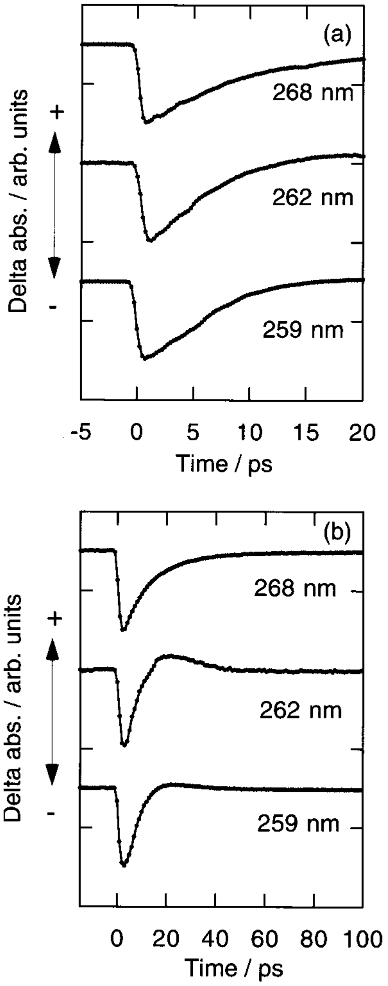

Figure 8. Transient bleach recovery signals (a) within 20 ps time scale and (b) subnanosecond time scale by a one-color pump−probe experiment at three different wavelengths for *cis*-1,3,5-hexatriene in cyclohexane.

The vibrationally excited 2A state is populated by internal conversion. In the gas phase, the lifetimes of the 2A state for trans and cis isomers are 270 and 730 fs, respectively, and the vibrational energy redistribution of the cis isomer within the 2A state occurs at around 300 fs.[19] For the trans isomer, the vibrational energy redistribution time (~300 fs) was suggested to be comparable to the lifetime of the 2A state. Our previous studies in the gas phase also provided evidence for nonradiative decay by at least two processes, one of which is independent of energy and another which requires an activation energy of <155.7 cm^{-1}.[16] Fuss and co-workers have studied the excess energy dependence of the cis isomer on the lifetime in pumping directly to the 2A state.[19] They found that the decay rate of the 2A state increased smoothly with an excess energy, converging to a value of 1.4 ps^{-1}. The temperature dependence on the lifetime of the 2A state in the gas phase gave an activation energy of about 170 cm^{-1},[20] which was consistent with our previous spectroscopic observation.[16] A theoretical calculation predicted that there existed two channels in the internal conversion from the S_1 to S_0 state.[10] These lead from the 2A state surface via two separated conical intersections to two products (double-bond and single-bond isomer). The activation energies for double-bond and single-bond rotations are estimated to be 4 and 6 kJ/mol, respectively. This prediction is consistent with the previous experimental result which suggests the existence of two decay pathways.[16] A photoexcited molecule passes through the conical intersections where the branching ratio is determined. Since the quantum yield of the photoisomerization around the C=C double bond is very small, the branching to the product of this isomerization is considered to be small.

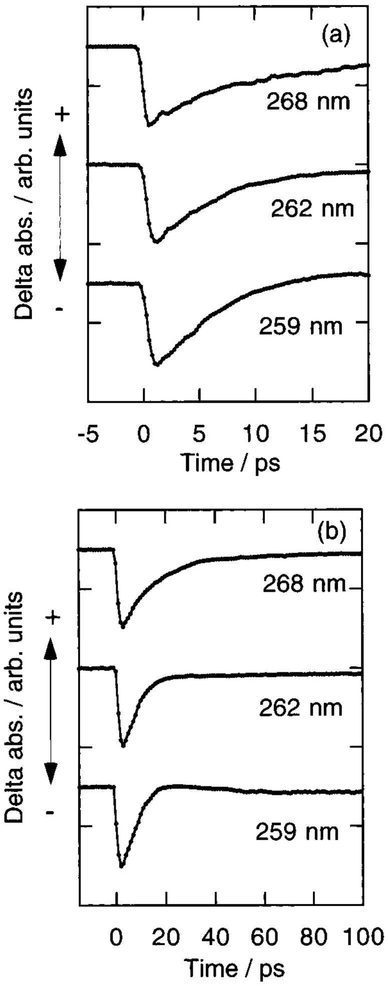

Figure 9. Transient bleach recovery signals (a) within 20 ps time scale and (b) subnanosecond time scale by a one-color pump−probe experiment at three different wavelengths for *cis*-1,3,5-hexatriene in acetonitrile.

The decay of the transient absorption signals corresponds to the internal conversion to the ground state which occurs at around 500 fs. The vibrational energy redistribution is expected to compete with the internal conversion to the ground state, which occurs in a similar time scale for both isomers. The evolution of the population in the 2A state can be probed via the S_n−S_1 transition, as illustrated in Figure 10. The difference of the behavior in the transient absorption signals between trans and cis isomers may be due to the different couplings of the potential surface between the 1A and 2A states.[10]

For the trans isomer, the decay of the transient absorption signals depends on the probe wavelengths. This suggests that the efficiency of the internal conversion is significantly different among the vibrational levels in the potential energy surface of the 2A state. The faster decay of the signal corresponds to the faster decrease of population in the vibrationally excited 2A state through the internal conversion to the ground state, which is dominant for the trans isomer. In contrast to the trans isomer, the efficiency of the internal conversion does not depend on the vibrational levels in the 2A state for the cis isomer.

Another explanation for this observation may exist. The different decay rates in the transient absorption signals may

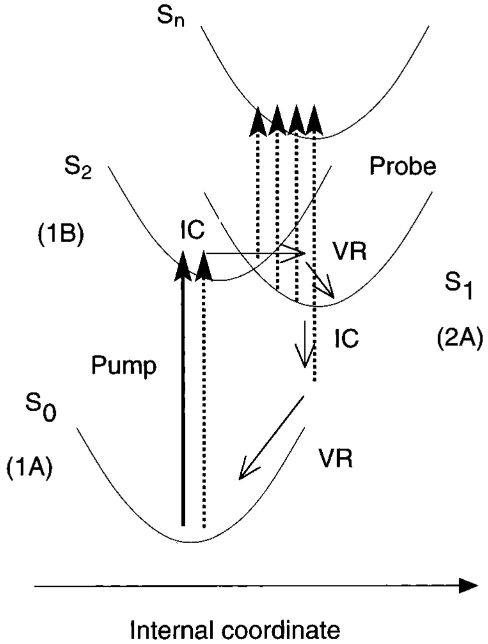

Figure 10. Schematic representation of the potential energy diagram of 1,3,5-hexatriene following the photoexcitation to the 1B state. IC and VR denote internal conversion and vibrational relaxation, respectively.

come from the rates of the vibrational energy redistribution at different energy levels within the 2A potential. The vibrational energy redistribution proceeds with keeping the total energy constant within the solute, however, its rate is level-dependent in the vibrational manifold due to different vibrational couplings. The vibrationally excited state can be probed initially at longer wavelengths. The redistribution process goes on, and the population of the vibrationally relaxed 2A state is produced on a subpicosecond time scale. At shorter wavelengths, we can probe this relaxed state.

In the gas phase, the lifetime for the cis isomer is three times larger than that for trans isomer, however the lifetimes in the liquid phase are similar to each other. This may be due to a change of the coupling between the potential energy surfaces induced by the interaction with the solvent. However, since the lifetime of the 2A state is similar in between the gas and liquid phases, we consider that these processes in solutions are governed mainly by the intrinsic nature of the excited state rather than the solvent-induced interaction and the energy transfer between the solute and solvent. The photochemical ring-opening reaction of 1,3-cyclohexadiene, which leads to *cis*-1,3,5-hexatriene, in the gas phase was investigated by the femtosecond time-resolved photoionization method.[30,31] The measured 1^1B_2 and 2^1A_1 lifetimes are 43 and 77 fs, respectively. Hexatriene is produced in the ground state within 200 fs.[31] The ultrafast internal conversion from the 2A to 1A state is typical of simple linear polyenes.[26,30] The observed ion signals in the gas phase do not contain any slow components as observed in our transient absorption signals. It is suggested that the Franck−Condon factors from the ground state to the energetically accessible ion states are very small in the femtosecond time-resolved photoionization experiment.[19] On the basis of this observation, the slow 5−15 ps component in our signals is most probably attributed to the vibrationally excited ground state.

4.2. The Origin of the Transient Bleach Recovery Signals within 20 ps Time Scale. The first components of the transient bleach signals in cyclohexane and acetonitrile have recovery time constants of ca. 1 ps. These components are only observed in the trans isomer. However, Sension and co-workers found that these 1 ps components were observed in both isomers.[32] This difference may be attributed to the observation that the recovery time constant for the cis isomer is smaller than that for the trans isomer. In our apparatus, we cannot clearly resolve this component for the cis isomer. After photoexcitation, the internal conversion from the 2A to the 1A state occurs within 500 fs and vibrationally excited products are created. When the population in the vibrationally excited 1A state relaxes to some extent and the transition from the 1A state (S_0) to the highly excited state (S_n) and/or the 1B state (S_2) matches the probe wavelength, we can detect the vibrationally excited 1A state as the fastest bleach recovery.

The second time constants of the bleach recovery of the transients in cyclohexane and acetonitrile are 5−20 ps, which depend on the observed wavelength. The vibrational relaxation of *cis*-1,3,5-hexatriene occurs with the time constant of 9 ps after the photochemical ring-opening reaction of 1,3-cyclohexadiene.[23] We assign the second components to the vibrational relaxation in the ground state.

The wavelength-dependent bleach recovery on the different wavelengths observed in the 20 ps time scale is attributed to the spectral broadening and shift of the absorption band to longer wavelengths. It is considered to originate from the vibrationally excited products and transient conformational isomers in the ground state. After the internal conversion to the ground state, the population in the vibrationally excited state is created, whose distribution is different from that in the vibrationally relaxed state. This causes the change of the absorbance at each wavelength. Similar behavior in the absorption spectrum is observed in several systems such as azulene,[33] stilbene,[34] and 2-(2′-hydroxy-5′-methylphenyl)benzotriazole[35] after the ultrafast internal conversion to the ground state. At times longer than 10 ps the intramolecular vibrational distribution is well characterized by a vibrational temperature. The population in the vibrationally excited state decreases in the 10 ps time region by energy transfer from solute to solvent.

The transient spectrum narrows by the vibrational relaxation process, and the transient absorption band converges to that observed in static absorption. The schematic representation of this phenomena is shown in Figure 11. It is expected that the broadening induces the decrease of the absorbance at the peak position of the static absorption band and the increase at the trough position. At the wavelengths of 268 and 259 nm, which correspond to the peaks of the vibronic bands, the absorbance of the vibrationally excited product is expected to be smaller than that of the vibrationally relaxed product. The vibrational relaxation is observed as the bleach recovery in a 10 ps time scale because the absorbance increases with vibrational relaxation. On the other hand, at the wavelength of 262 nm, which corresponds to the minimum between the first and the second absorption bands, the absorbance is larger than that of sample at room temperature. The initial bleach of the signal is ascribed to the decrease of the population in the ground state upon photoexcitation, which recovers by internal conversion to the ground state. It is similar to that observed at 268 nm. However, the appearance of the vibrationally excited product causes the opposite behavior, which corresponds to the transient absorption component. This decays up to 20 ps by vibrational relaxation process.

The difference between cyclohexane and acetonitrile could be ascribed to the small peak shift on the solvent polarity, the collision-induced relaxation process, the distribution of vibrationally excited state, and so on. It should be noted that the

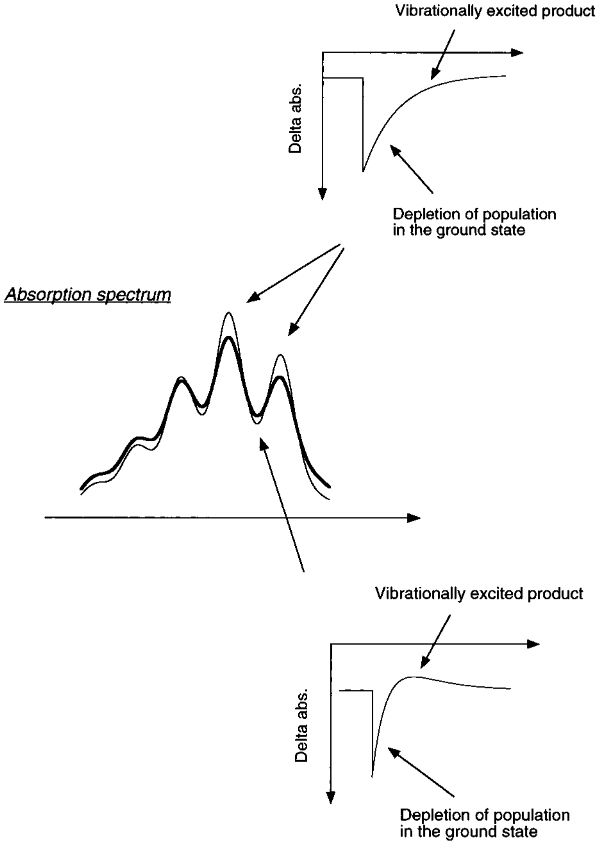

Figure 11. Schematic representation of the absorption spectra for vibrationally excited (thick line) and relaxed (thin line) products and behavior of the temporal profiles of the transient bleach recovery signals.

signals on this time scale also contain the contribution of the different conformers which will be discussed later.

4.3. Conformational Relaxation in the Ground State. The transient bleach signal contains a 150−300 ps additional component except for *cis*-1,3,5-hexatriene in cyclohexane. Some transients may decay with the lifetime of a few hundred picoseconds. The quantum yield of the photoisomerization around the C═C double bond in solution is very low ($\phi_{\mathrm{trans-cis}} = 0.016$, $\phi_{\mathrm{cis-trans}} = 0.034$).[3] This means that the most of the photoexcited 1,3,5-hexatriene molecules should finally return to the original stable forms. The quantum yield of the intersystem crossing to the triplet state is known to be also very low.[36] One plausible explanation for the slow component is that the conformational isomers around the C−C single bond are produced as part of the relaxation process and the signals contain the contribution about a conformational relaxation to the original stable form.

There are three different C−C single-bond isomers each for *trans*- and *cis*-1,3,5-hexatriene as shown in Figure 12. Here, the trans and cis forms about the C−C single bond are denoted as t and c, respectively, and those about the C═C double bond as E and Z, respectively. If we refer to the trans and cis isomers around the C−C single bond, we use the following terms, s-trans and s-cis, respectively.

It is well known that the stable form at room temperature is all-s-trans. After photoexcitation, the system undergoes partial rotation about the single bond during the internal conversion to the S_0 state. We consider that the slow component may be due to the recovery process from a mixture of the s-cis isomer to the original stable s-trans isomer at room temperature. Theoretical calculations predict that there exist two channels which lead from the 2A state surface via different conical intersections to two products (double-bond and single-bond isomer), and they have small barriers, as mentioned in section 4.1.[10]

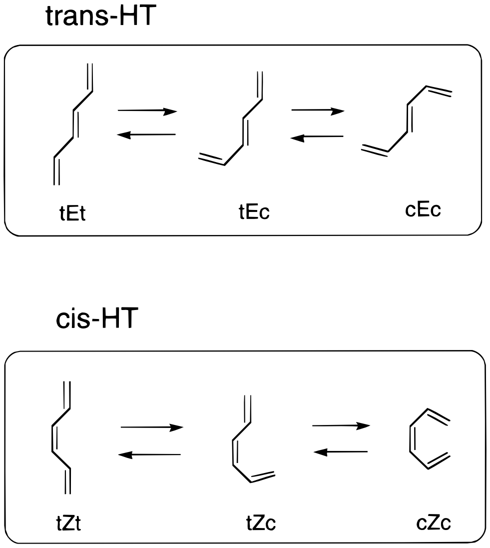

Figure 12. Conformers of *trans*- and *cis*-1,3,5-hexatriene.

Furukawa and co-workers measured the infrared and ultraviolet absorption spectra of *trans*- and *cis*-1,3,5-hexatriene deposited in the low-temperature Ar matrices under irradiation by a Hg 253.7 nm light.[37] They found a new absorption band in the spectra at around 276 nm, and assigned it to the s-cis isomer based on the ab initio molecular orbital calculation and normal-mode analysis.[38]

It is most plausible that the C−C single bond rotates through the internal conversion from the 2A to the 1A state. After internal conversion to the ground state, the molecule possesses about 450 kJ/mol of excess energy which is large enough to overcome the barrier for single-bond rotation. It is considered that this isomerization takes place on a subpicosecond time scale based on the recent gas-phase experiement. During the vibrational relaxation in the ground state, the single rotation becomes slower and a distribution of each conformer is created. The conformational relaxation around the C−C single bond to a stable all-s-trans form follows in a slower time scale.

In general, the absorption cross section of the s-cis isomer is smaller than that of the s-trans isomer, which is suggested by the ab initio calculation and the experimental observation of substituted hexatriene derivatives.[25,39,40] However, the absolute value of the oscillator strengths for three different conformers of *trans*- and *cis*-1,3,5-hexatriene is difficult to calculate accurately because this calculation requires large basis sets and configuration interactions among the electronic states. It is only confirmed that an expected trend of magnitude for the oscillator strengths is as follows. For the cis isomer, cZc < tZc < tZt and, for the trans isomer, cEc < tEc <tEt.[25] Therefore, the existence of s-cis isomers in the product state appears as a bleach in the transient signal after completing the vibrational relaxation in the ground state.

To confirm the single-bond isomerization, we measured the temperature dependence on the recovery times of the 100 ps component. It shows that the recovery time constant decreases by about a factor of 2.5 upon changing temperature from 286 to 326 K. The rate constant depends on the solvent viscosity and temperature and is frequently expressed by the following Arrhenius-type equation:

$$k = \frac{A}{\eta^{a}} \exp\left(-\frac{\Delta E}{k_{\mathrm{B}}T}\right) \qquad (1)$$

where η is the viscosity, A is the prefactor, ΔE is the activation energy, k_B is the Boltzmann constant, and a is an empirical parameter ($0 \le a \le 1$). The temperature dependence on the recovery time constant is well fitted by eq 1. The activation energy is estimated to be 10−20 kJ/mol, which depends significantly on the value of a. The barrier for the isomerization about single bonds in polyenes has been determined to be about 1400 cm^{-1} (17 kJ/mol) in the ground state.[42,43] The value obtained in this study thus is in good agreement with the previous work. Further details of the results will be presented elsewhere.

Picosecond time-resolved Raman and nanosecond FT-IR studies of the photochemical ring-opening reaction of 1,3-cyclohexadiene suggest that the time scale from the tZc to tZt isomerization of *cis*-1,3,5-hexatriene is longer than 200 ps and less than 20 ns.[23,44] In a recent study of the ring-opening reaction of dehydrocholesterol to previtamin D, which are derivatives of 1,3-cyclohexadiene and *cis*-1,3,5-hexatriene, single-bond isomerization occurs in 125 ps in ethanol.[45] The time scale of the third component observed in our study matches these time constants of molecules having similar structures. In our case, we can consider that it takes 150−300 ps to undergo single-bond isomerization of hexatriene in the ground state. These time constants depend on solvent.

The different time profile observed in the slow component of bleach recovery for each *trans*- and *cis*-1,3,5-hexatriene may reflect different product distributions and dynamics among three conformational isomers. After the internal conversion, the conformational relaxation around the C−C single bond occurs faster than or is compatible with the rate of the vibrational relaxation because the molecule has large enough excess energy to overcome the barrier for single-bond rotation.[46] For the trans isomer, a certain amount of s-cis isomers are trapped in the ground state so that the third bleach components have an amplitude as sufficient as the transient absorption change in a subnanosecond time scale. On the other hand, for the cis isomer, the main product is considered to be attributed to s-trans isomer. The cZc isomer should have a relatively high barrier due to the steric hindrance. This produces less distribution of cZc isomer and induces a rapid relaxation even if it is produced. The stable tZt isomer is formed predominantly within 20 ps and we could not expect to clearly observe any components slower than 100 ps. Since we observed a very small slow component in acetonitrile, there may still exist a small amount of residual mixture of s-cis isomer after completing the vibrational relaxation process.

5. Conclusion

We performed femtosecond transient absorption measurements of *trans*- and *cis*-1,3,5-hexatriene in cyclohexane and acetonitrile solutions. After the rapid internal conversion from the initially excited 1B state to the 2A state, the vibrational energy redistribution process in the 2A state and the internal conversion to the ground state occur in a subpicosecond time scale. The similarity with the results of the isolated system suggests that relaxations proceed based on the intrinsic nature of 1,3,5-hexatriene and are not much affected by solvent interactions. For the trans isomer, we observed that the decay of the transient absorption signals depends on the probe wavelengths. This reflects that the efficiency of the internal conversion significantly depends on the vibrational levels in the potential energy surface of the 2A state.

From the bleach recovery, the vibrational relaxation in the ground state is found to occur in 10−20 ps, which is followed by the single-bond isomerization in the subnanosecond time scale. The complex dynamics at different wavelengths within 50 ps is mainly ascribed to the spectral broadening in the absorption spectrum by the vibrationally excited products. The difference between *trans*- and *cis*-1,3,5-hexatriene in a subnanosecond time scale may reflect different s-cis isomer distributions and dynamics among s-cis isomers, namely conformational relaxation around the C−C single bonds. For the trans isomer, a significant amount of the s-cis isomer is created, and the bleach recovery in a subnanosecond time scale is attributed to the single-bond relaxation. On the other hand, for the cis isomer, the majority of the ground-state product is considered to be all-s-trans isomer so that there is minor contribution of s-cis isomer in the signal. Another explanation might be the conformational relaxation from the s-cis to the all-s-trans isomer which occurs faster than vibrational relaxation process. The all-s-trans isomer is formed predominately within 20 ps.

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