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Excited-State Dynamics of *all-trans*-1,3,5,7-Octatetraene in Solution. Direct Observation of Internal Conversion from the S_2 to S_1 State and Relaxation Processes in the S_1 State

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Femtosecond transient absorption spectroscopy was used to study the excited-state dynamics of the S_2 (1^1B_u) state *all-trans*-1,3,5,7-octatetraene in solution. The sample was excited at 267 nm and probed at eleven different wavelengths from 340 to 540 nm. Combined with the picosecond fluorescence spectroscopy, this study allows direct observation of the initial excited-state dynamics of *all-trans*-1,3,5,7-octatetraene and the subsequent relaxation process to the ground state. Transient absorption signals decaying on time scales of about 0.4 ps were seen at wavelengths longer than 480 nm. These absorptions are assigned to an S_n-S_2 transition, indicating that internal conversion from the S_2 to S_1 state takes place on a 400-fs time scale. The transient absorption signals observed at shorter wavelengths, which correspond to the S_n-S_1 transition, decay on a picosecond to subnanosecond time scale. A weak fluorescence at about 300−350 nm, originating from the S_2 state, and a strong fluorescence at about 350−500 nm, from the S_1 state, were observed. The time profile of the S_2 fluorescence signal is almost equal to the instrument response function, and the lifetime is estimated to be faster than 5 ps. This observation is consistent with the results of transient absorption signals. The S_1 fluorescence signal consists of two decay components. The average lifetimes are 0.88 ns in acetonitrile and 2.0 ns in *n*-hexane. Nonexponential decay of the fluorescence may result from an equilibrium mixture of the fluorescent state and the conformationally relaxed state. The fluorescence intensity ratio of S_2 to S_1 in solution is much different from that observed in the gas phase. This means that the efficiency of internal conversion increases significantly in solution because of the solute−solvent interactions that are absent in the gas phase. We discuss differences in the excited-state dynamics between 1,3,5-hexatriene and 1,3,5,7-octatetraene.

1. Introduction

Considerable attention is paid to the photodynamics of simple linear polyenes both experimentally and theoretically because these compounds are important chromophores in the vision, proton-pumping systems, and light-harvesting systems.[1−4] Retinal and carotenoids are examples of such chromophores. Several ultrafast spectroscopic studies have recently shown that initial relaxation processes in these chromophores occur on subpicosecond time scales.[5−7] To learn more about these biologically interesting chromophores, it is highly desirable to investigate the dynamics of shorter linear polyenes for comparison.

Studies on the excited-state dynamics of small polyenes have only recently become possible because of developments in creating the necessary ultrafast UV pulses. Several groups including our own have reported the electronic, vibrational, and conformational relaxation dynamics of 1,3,5-hexatriene in solution.[8−11] For 1,3,5-hexatriene, S_2-S_1 internal conversion is completed within 100 fs. The vibrational energy redistribution in the S_1 state and the internal conversion to the S_0 state occur within a 500-fs time scale to create a vibrationally excited product in the S_0 state. The conformational relaxation around the C−C single bond depends strongly on the internal temperature of the molecule. A small amount of s-cis conformer is trapped on a time scale of 100 ps at thermal equilibrium. Subpicosecond internal conversion and conformational relaxation around the C−C single bond were also observed in the photochemical ring-opening reaction of 1,3-cyclohexadiene, which produces *cis*-1,3,5-hexatriene.[12,13] Unlike shorter linear polyenes such as 1,3-butadiene and 1,3,5-hexatriene, 1,3,5,7-octatetraene exhibits an intense fluorescence with a relatively long excited-state lifetime in gas and condensed phases.[14]

It is well-known that two low-lying electronic states with similar energy exist in simple polyenes. These states are assigned to different symmetries in the C_{2h} point group. Transition to the 1^1B_u state is allowed, whereas transition to the 2^1A_g state is forbidden. Hudson and Kohler reported the first experimental evidence of a low-lying optically forbidden 2^1A_g state below the optically allowed 1^1B_u state in *all-trans*-diphenyloctatetraene.[15] Theoretical calculations by Schulten et al.[16] established that mixing of singly and doubly excited A_g states results in a lowering of the 2^1A_g energy below that of the 1^1B_u state. Recently, Nakayama et al. applied the multireference perturbation theory to study excited states of small linear polyenes.[17] They reported that the 2^1A_g state of *all-trans*-1,3,5,7-octatetraene is the lowest excited singlet state (S_1) according to both the 0−0 excitation energy and the vertical excitation energy. Robb and co-workers calculated the S_1 and S_0 potential energy

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surfaces of *trans*-1,3,5-hexatriene and *all-trans*-1,3,5,7-octatetraene.[18,19] They found that the barrier height of trans−cis isomerization is less than about 4 and 25 kJ/mol in the S_1 state, respectively.

Various spectroscopic techniques, including time-resolved absorption and fluorescence measurements, have been used to investigate the excited-state dynamics of 1,3,5,7-octatetraene during the past two decades. However, no ultrafast time-resolved studies have been conducted to resolve the initial step of the excited-state dynamics.[20−22] Gavin et al. measured the absorption and emission spectra of *all-trans*-1,3,5,7-octatetraene in solution.[20] They found a gap of about 3000 cm^{-1} between the absorption band of the $S_2(1^1B_u)-S_0(1^1A_g)$ transition and the onset of the emission spectrum. They concluded that the emission originates from the S_1 state in solution. They also observed the emission spectrum in the gas phase, which shows no Stokes shift, indicating that the fluorescence originates from the S_2 state.[20] Bouwman et al. observed the fluorescence spectrum from the S_2 state in the gas phase at room temperature as well as that from the S_1 state.[21] The fluorescence intensity from the S_2 state is much stronger than that from the S_1 state. The lifetime of the S_1 state was 4 ns in *n*-hexane by time-resolved fluorescence measurements at room temperature, which is much longer than that of 1,3,5-hexatriene (<500 fs).[22,23] The S_n-S_1 excited-state absorption spectrum of 1,3,5,7-octatetraene was measured by nanosecond time-resolved transient absorption spectroscopy.[23] The spectrum is broad and structureless and shows a peak at 330 nm with a long tail to the longer wavelength region. Recently, our group measured the fluorescence excitation spectra of 1,3,5,7-octatetraene after direct photoexcitation of the 2^1A_g state under jet-cooled conditions.[24] The fluorescence lifetime of 7 ns indicates an abrupt onset of nonradiative decay processes at about 2100 cm^{-1} over the 0−0 transition energy. We suggested that the decay is due to trans−cis isomerization. The rate increases with every 80 cm^{-1} in energy, reflecting the quantization of the vibrational motion orthogonal to the reaction coordinate.[25] A low-temperature study of 1,3,5,7-octatetraene in *n*-hexane indicated that the photoisomerization in the S_1 state occurs adiabatically with a ~950 cm^{-1} barrier before decaying to the ground state.[26] In contrast, our work[24] and theoretical calculations by Robb and co-workers[19] suggested that trans−cis isomerization induces the opening of an efficient nonadiabatic radiationless deactivation channel from the S_1 to S_0 state.

Internal conversion from the S_2 to S_1 state for 1,3,5,7-octatetraene is considered to occur on a much faster time scale. In a time-resolved fluorescence measurement, Kohler and coworkers showed that the fluorescence from the S_1 state rises within 10 ps in solution.[22] Heimbrook et al. measured the S_2-S_0 emission in a supersonic expansion and estimated an S_2 lifetime of 100−300 ps.[27] Leopold et al. reported a 18 cm^{-1} line width for the S_0-S_2 (0−0) transition in the gas phase.[28] This gives a nonradiative lifetime of 300 fs. Bouwman et al. measured the fluorescence spectra from both the S_2 and S_1 states in the gas phase.[21] They also estimated a lifetime of 400 fs for the zero-point level of the S_2 state based on the line width of their fluorescence spectrum. Even though there is a discrepancy in S_2 lifetimes in the gas phase, the S_1 population is created efficiently by internal conversion on a subpicosecond to picosecond time scale, and subsequent process occurs in the longer lived S_1 state. Recently, Stolow and co-workers used time-resolved photoelectron spectroscopy to investigate the ultrafast internal conversion of *all-trans*-2,4,6,8-decatetraene.[29] They found that S_2 to S_1 internal conversion in this molecule occurs within 400 fs. Using photoelectron spectroscopy, they can clearly distinguish the vibrational dynamics from the coupled electronic population dynamics in the S_2 to S_1 internal conversion.[29]

In this article, we report the ultrafast dynamics of photoexcited *all-trans*-1,3,5,7-octatetraene in solution by picosecond fluorescence spectroscopy and femtosecond transient absorption spectroscopy. After photoexcitation to the S_2 (1^1B_u) state, we measured the transient absorption in the ultraviolet to the visible region. These signals involve internal conversion from the S_2 (1^1B_u) state to S_1 (2^1A_g) state and the vibrational and conformational relaxation in the S_1 state. We also measured the time-resolved fluorescence spectrum on the picosecond time scale. These results give direct evidence for the short lifetime of the S_2 state. We compare these results with those in the gas phase and discuss the difference in dynamics between 1,3,5,7-octatetraene and shorter polyenes.

2. Experimental Section

The details of the pump−probe apparatus for the transient absorption measurement have been described elsewhere.[8,9] Pulses of 70-fs duration with 4 nJ/pulse energy at a repetition rate of 100 MHz were obtained from an argon-ion laser pumped Ti:sapphire oscillator and amplified in a Ti:sapphire regenerative amplifier (NJA-4 and CPA-1, Clark-MXR). This produced 120-fs pulses at ~800 nm, with a repetition rate of 960 Hz and a pulse energy of 900 μJ/pulse. The output of the fundamental was frequency-doubled in the first BBO crystal. The second harmonic was separated from the fundamental and divided into two beams. One of them was mixed with the remaining fundamental in the second BBO crystal. The resulting third harmonic (267 nm, 30 μJ/pulse) was used for the pump beam. A white light continuum was generated by focusing the other part of the second harmonic into a flowing cell of deuterated water. This was used as the probe beam. The absorption change was monitored by a photodiode through an interference filter [full width at half maximum (fwhm) = 10 nm]. All measurements were performed with magic-angle polarization between the pump and probe beams. The temporal width of instrument response was estimated to be 550 fs from the temporal rise of the excited-state absorption or bleach recovery of Rhodamine 6G in ethanol.

The time-resolved fluorescence spectra and their decay profiles were measured using a picosecond streak camera (Hamamatsu C4780). The third harmonic, attenuated to less than 10 nJ by a neutral density filter, was also used as an excitation light source. The fluorescence was passed through a color glass filter (UV-29, Schott) to reduce laser scatter, dispersed by a 25-cm monochromator (Chromex), and detected by a streak camera.

A sample of *all-trans*-1,3,5,7-octatetraene was synthesized following the procedures described by D'Amcio et al.[30] and Yoshida et al.[31] 2,4-Hexadienal was reacted with vinylmagnesium bromide to produce 1,4,6-octatrien-3-ol. Dehydration of 1,4,6-octatrien-3-ol at 353 K using a *p*-toluene sulfonate catalysis yielded the isomerically pure all-trans isomer. Crystalline samples were dissolved in solvent to prevent polymerization. These solutions were kept at 273 K until used in the experiments. Acetonitrile and *n*-hexane (spectrograde) were purchased from Wako Chemicals and used without further purification. The sample solution was circulated through a quartz cell with a 1-mm optical path length. Under our experimental conditions, no signal was observed in neat acetonitrile. The samples were changed routinely to avoid photodegradation. The concentration of the samples was adjusted to give an absorbance of about 1.0

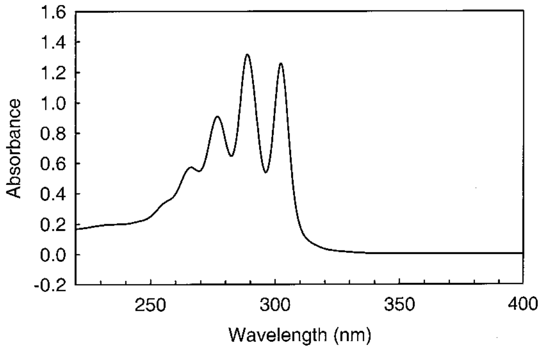

Figure 1. Static absorption spectrum of *all-trans*-1,3,5,7-octatetraene in acetonitrile.

at 267 nm for the transient absorption measurements and about 0.1 for the time-resolved fluorescence measurements. All measurements were performed at ambient temperature (293 K).

3. Results

3.1. Static Absorption Spectrum. The static absorption spectrum of *all-trans*-1,3,5,7-octatetraene in acetonitrile is shown in Figure 1. As mentioned in the Introduction, there are two closely spaced excited singlet states, 1^1B_u and 2^1A_g. The 1^1B_u state is a singly excited state with an ionic nature originating from the highest occupied molecular orbital−lowest unoccupied molecular orbital (HOMO−LUMO) one-electron transition, whereas the covalent 2^1A_g state is the doubly excited state that comes mainly from the HOMO−LUMO two-electron transition. The strong absorption band from 250 to 310 nm corresponds to the 1^1B_u (S_2) -1^1A_g (S_0) transition. Vibrational progressions result from both C−C and C═C stretching modes.[21] Our excitation wavelength is located ~4700 cm^{-1} above the 0−0 origin (32 800 cm^{-1}).

3.2. Time-Resolved Fluorescence Spectra on a Picosecond Time Scale. The time-resolved fluorescence spectra of 1,3,5,7-octatetraene in acetonitrile are shown in Figure 2. The fluorescence spectra show a peak at 420 nm, which indicates a large Stokes shift of the absorption spectra. The fluorescence spectrum integrated within 1 ns is almost the same as that observed previously,[20] which was ascribed to the fluorescence from S_1 state. In addition, we observed a weak fluorescence at 300−350 nm integrated within 100 ps, as shown in Figure 2a. We checked that this signal originated from octatetraene and was not light scattered from the solvent. No bands were detected at wavelengths shorter than 300 nm because of reduction in sensitivity of the detector system. The location of the band at 300−350 nm is in accordance with the S_2 fluorescence spectrum at longer wavelengths in the gas phase.[21] The temporal profile of the band at 300−350 nm is almost the same as the instrument response function (fwhm = 35 ps), so the decay can be estimated to be faster than 5 ps. This value does not conflict with the S_2 lifetime estimated from the line width analysis in the gas phase.[21,28]

The fluorescence signal from the S_1 state rises within the instrument response function and consists of two decaying components whose time constants are 870 ps and 2.41 ns in *n*-hexane, and 330 ps and 1.14 ns in acetonitrile, as shown in Figure 3 and Table 1. The lifetimes in acetonitrile are about half as long as those in *n*-hexane. These time constants do not depend on the wavelength.

3.3. Transient Absorption Signals from the Excited State. The transient absorption signals were measured for *all-trans*-1,3,5,7-octatetraene in acetonitrile with an excitation wavelength of 267 nm and 11 probe wavelengths from 340 to 540 nm. The results up to 3.5 ps and 35 ps are shown in Figures 4 and 5, respectively. Table 2 summarizes the results of the best-fit time constants for the transient absorption signals.

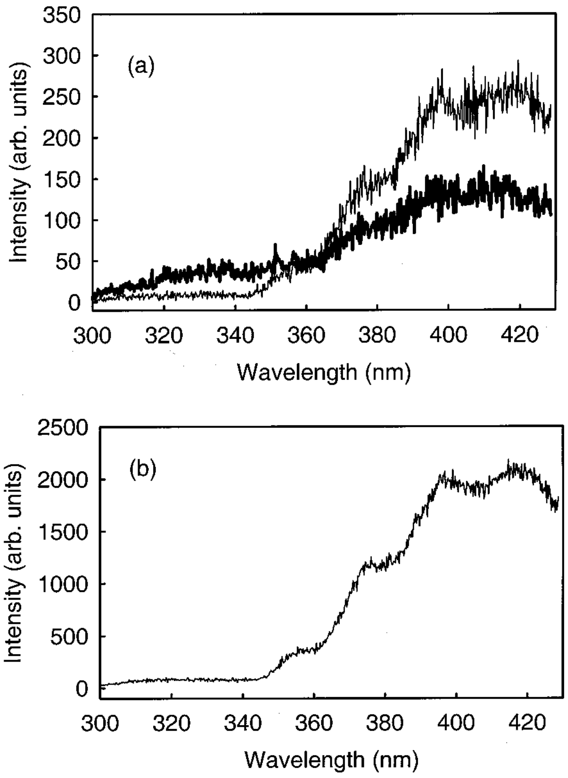

Figure 2. (a) Fluorescence spectrum of *all-trans*-1,3,5,7-octatetraene in acetonitrile integrated through the first 100-ps (thick solid line) and subsequent 100-ps (solid line) intervals, respectively. (b) Fluorescence spectrum of *all-trans*-1,3,5,7-octatetraene in acetonitrile integrated for 1 ns.

First, we mention the shortest components of the transient absorption signals. Only the signal at 340 nm contains a rise component of 260 fs. From 380 to 480 nm, the signals have small decaying components with lifetimes of 200 fs to 1.7 ps. These values depend strongly on the probe wavelengths. At wavelengths longer than 480 nm, we clearly observe subpicosecond decay components in the transient absorption signals. At 480 nm, the decay time constant is about 520 fs. At the wavelengths longer than 480 nm, the decay becomes slightly faster, with time constants of about 400 fs. We also find that the relative amplitude of the fast-decaying component becomes greater at longer wavelengths.

These transient absorption signals possess ~10 ps decay components at all probe wavelengths. From 340 to 480 nm, the decay time constants are about 5−15 ps. The transient absorption signals have a third component with time constants of 580−790 ps as listed in Table 3. The variation of these time constants comes from the limited time windows of the transient absorption signals.

4. Discussion

4.1. Origin of Weak Fluorescence. The weak and broad fluorescence spectrum measured at 300−350 nm is assigned to fluorescence from the S_2 state based on the energy and the lifetime. The time-integrated intensity of the S_2 fluorescence is much weaker than that of the S_1 fluorescence as shown in Figure 2. The S_2/S_1 ratio of the fluorescence intensity is determined to be 0.1 ± 0.05:1 from the sensitivity-corrected fluorescence

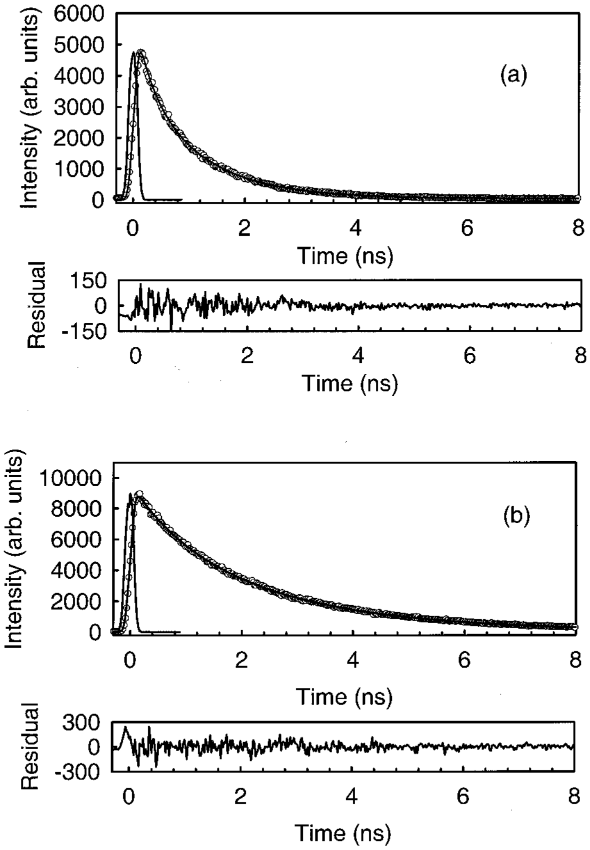

Figure 3. Time profiles of the S_1 state fluorescence signal and residuals for *all-trans*-1,3,5,7-octatetraene in (a) acetonitrile and (b) *n*-hexane along with the instrument response functions. The solid lines represent the best fits to the data by convolution of the instrument response function with a double exponential function.

TABLE 1: Best-Fit Time Constants and Average Lifetimes of Fluorescence Signals of *all-trans*-1,3,5,7-Octatetraene in Acetonitrile and n-Hexane

solvent	τ_1 (ps)[a]	τ_2 (ps)[a]	$<\tau>$ (ps)[b]
acetonitrile	330 (32.6%)[c]	1140 (67.4%)	880
n-hexane	870 (24.4%)	2410 (75.6%)	2030

[a] τ_1 and τ_2 are the first and second components, respectively, of the time-resolved fluorescence signals. [b] $<\tau>$ is the average lifetime including both components. [c] The relative amplitude of each decay component.

spectra measured by using a streak camera and static fluorescence spectrometer. On the other hand, the S_2 fluorescence spectrum in the gas phase at room temperature showed a clear mirror image of the absorption spectrum and was much stronger than that of the S_1 state, with a S_2/S_1 ratio of 16.6:1.[21] We discuss the relation between the S_2/S_1 fluorescence ratio and the lifetime of the S_2 state in a later section.

4.2. Internal Conversion from the S_2 to S_1 State. In the transient absorption signals, the decay time constants of the fast components observed at the longer wavelengths are 400 fs. Nanosecond flash photolysis has shown that the intensity of the S_n-S_1 excited-state absorption is very small at wavelengths longer than 460 nm.[23] These observations suggest that the transient absorption measured at longer wavelengths originates not from the S_1 state, but from the S_2 state. The fast-decay components at longer wavelengths reflect internal conversion from the S_2 to S_1 state. The transient absorption bands are shifted to the blue side on a subpicosecond time scale. Theoretical calculations support this assignment,[23] predicting that the allowed transitions from the 1^1B_u (S_2) state to the 5^1A_g and 6^1A_g states are located at 549 and 425 nm, respectively. These are also long time scale absorption components. There nonzero transient absorption signals at long times are assigned to S_1 absorption. Population in the S_1 state is created on a 400-fs time scale. However, we cannot clearly observe the rise of the transient absorption signals at shorter wavelengths, which come

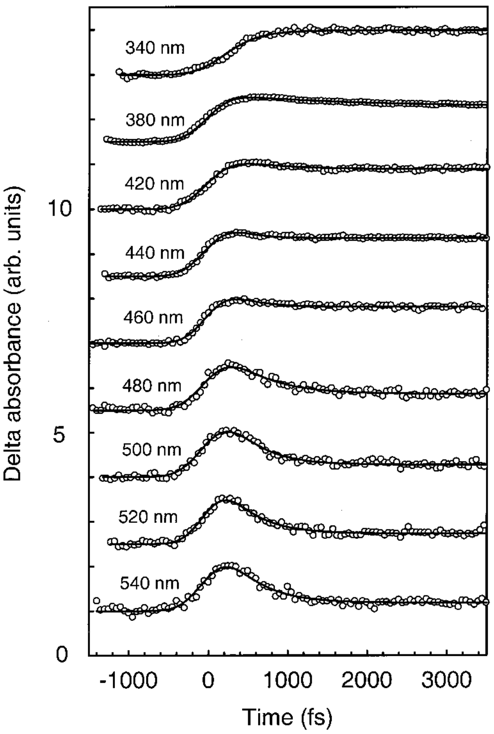

Figure 4. Transient absorption signals for *all-trans*-1,3,5,7-octatetraene in acetonitrile probed at nine different wavelengths over 3.5 ps. The solid lines represent the best fits to the data by convolution of the instrument response function with exponential functions.

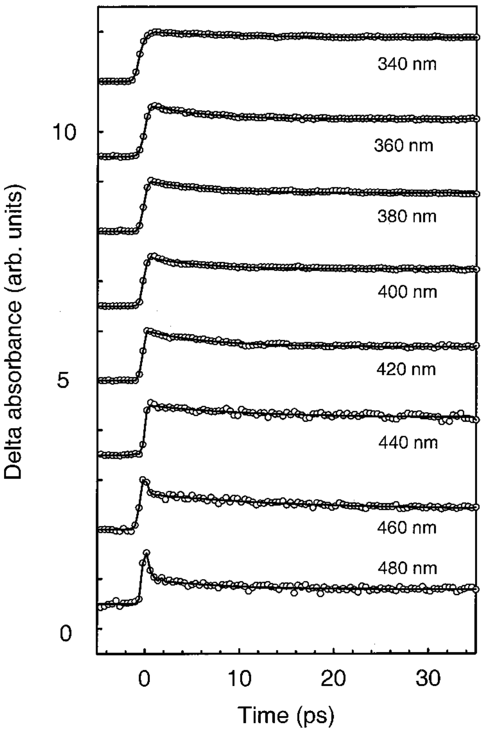

Figure 5. Transient absorption signals for *all-trans*-1,3,5,7-octatetraene in acetonitrile probed at eight different wavelengths over 35 ps.

TABLE 2: Best-Fit Time Constants for Transient Absorption Signals of *all-trans*-1,3,5,7-Octatetraene in Acetonitrile

λ (nm)	τ_1 (ps)[a]	τ_2 (ps)[a]
340	0.27[b]	9.4
360	–[c]	6.0
380	1.7	6.4
400	2.0	5.8
420	0.62	6.7
440	0.23	11.2
460	0.35	16.4
480	0.52	7.9
500	0.39	–
520	0.40	–
540	0.42	–

[a] τ_1 and τ_2 are the first and second components, respectively, of the transient absorption signals observed on a short time scale. [b] The data are fitted by an exponential rise. [c] There is no fast-decaying component.

TABLE 3: Best-Fit Time Constants for the Slowest Components for Transient Absorption Signals of *all-trans*-1,3,5,7-Octatetraene in Acetonitrile

λ (nm)	τ (ps)
340	790
360	606
380	577
400	710
420	670

from accumulation of the population through S_2 to S_1 internal conversion. This may be due to an overlap of excited-state absorption between the S_n-S_2 and S_n-S_1 transitions in the visible region. Stimulated emission from the S_2 state also appears in the shorter wavelength regions. The delayed response of the transient absorption observed at 340 nm may be attributed to a contribution of negative absorption from stimulated emission, which is overlapped with the rise component of the transient absorption signal from the S_1 state.

Ultrafast internal conversion from the S_2 to S_1 state has been observed directly for several polyene systems. For example, the lifetime of the S_2 state of β-carotene has been measured by femtosecond transient absorption and fluorescence up-conversion spectroscopies.[32,33] This lifetime is approximately 200 fs in various solvents. Furthermore, the excited-state dynamics of diphenylpolyenes have been investigated. Diphenylhexatriene (DPH) and diphenylocatetraene (DPO) are from a family of diphenylpolyenes whose dynamics have been investigated extensively.[34–36] The ordering of the electronic states is the same as that of *all-trans*-1,3,5,7-octatetraene, and the lifetime of the S_1 state of DPO is 6.2 ns. Transient absorption and fluorescence measurements of DPH have shown that the initially formed 1B state relaxes to the equilibrium 1B/2A mixture within 10 ps.[37] Bachilo and Gilbro observed a very weak ultrafast emission of DPO originating from the S_2 state.[38] They estimated an S_2 lifetime of about 70 fs based on the fluorescence quantum yield. Recently, Yee et al. reported femtosecond transient absorption measurements of DPO and DPH in solution.[39,40] They found decay components of 470–600 fs at 780 nm, which corresponds to the red edge of the S_n-S_1 transient absorption band. They assigned these components to internal conversion from the S_2 to S_1 state. The existence of the optically forbidden S_1 state, which is located close to the S_2 state, is considered to be responsible for the initial ultrafast excited-state dynamics. It was recently reported that the decay of the transient absorption from the S_2 state becomes faster at longer wavelengths.[40] The authors suggested that vibrational relaxation in the S_2 state occurs in competition with internal conversion from the S_2 to S_1 state. In contrast, we do not observe a clear wavelength dependence of the fast transient absorption decay components within our experimental sensitivity. This means that the vibrational relaxation process in the S_2 state does not contribute to the transient absorption signals. Hirata et al. also investigated the S_2 to S_1 internal conversion of α,ω-diphenylpolyenes ($N = 3-8$) in solution.[41] Internal conversion occurs in about 400–600 fs in all polyenes.

Here we comment briefly on the lifetimes of the S_2 state and the S_2/S_1 fluorescence intensity ratio in the gas and solution phases. According to analysis of the line widths of the absorption and fluorescence excitation spectra in the gas phase, the lifetime of the S_2 state is estimated to be about 0.3–0.4 ps.[21,28] These values seem nearly equal to the rate of internal conversion measured by transient absorption. On the other hand, there is a large discrepancy in the S_2/S_1 ratio of fluorescence intensity in the gas and solution phases. Because fluorescence lifetimes in the S_1 state with enough vibrational energy are similar, a few nanoseconds in both phases, the fluorescence quantum yields would be almost equivalent. Accordingly, we can attribute the discrepancy to the fluorescence quantum yield of the S_2 state. In 2,4,6,8-decatetraene, a time-resolved photoelectron spectroscopy has recently revealed that the lifetime of the S_2 state is 0.4 ps, which is similar to the lifetime of 0.25 ps estimated from the line width.[29] Although the line width of 2,4,6,8-decatetraene is similar to that of 1,3,5,7-octatetraene, the S_2/S_1 ratio of fluorescence intensity, 1.4:1, is 10 times smaller than that of 1,3,5,7-octatetraene. This means that the efficiency of internal conversion in 1,3,5,7-octatetraene is 1 order of magnitude smaller than that in 2,4,6,8-decatetraene. Therefore, the line width does not reflect the rate of the internal conversion from the S_2 to S_1 state. Significantly different from the gas phase, internal conversion in solution occurs exclusively among various relaxation processes from the S_2 state, which may be accelerated because of the solute–solvent interaction. This efficient internal conversion causes the extensive reduction of fluorescence intensity from the S_2 state and greater population transfer to the S_1 state. The estimated lifetime of 0.3–0.4 ps in the gas phase may correspond to an escape from the initially excited vibrational state, such as the vibrational relaxation in the S_2 state, and not internal conversion. Fluorescence from the relaxed S_2 state can give a clear mirror image of absorption.

4.3. Vibrational Relaxation in the S_1 State. We ascribe the 5–15 ps transition absorption decay components to vibrational relaxation in the S_1 state. After internal conversion to the S_1 state, a vibrationally excited population is created. Thermal equilibrium is then achieved through intramolecular energy redistribution. At this stage, we can define a mode-independent vibrational temperature, which is much higher than that of the surrounding solvents. The vibrational energy also dissipates via intermolecular energy transfer from solute to solvent. The vibrationally excited population gives a broad transient absorption spectrum that is initially located at longer wavelengths. The 5–15 ps decay component arises from spectral narrowing of the absorption band. However, the signal at the peak of the S_1 absorption band (340 nm) does not have a picosecond rise component. This may be due to a very small amplitude rise component being overlapped with subnanosecond decay components.

In general, vibrational relaxation of large organic molecules in solution occurs on a 10-ps time scale.[42] In particular, the excited-state dynamics of *trans*-stilbene has been extensively studied by picosecond time-resolved resonance Raman spectroscopy.[43,44] Vibrational relaxation in the S_1 state occurs on a

10-ps time scale. In 1,3,5-hexatriene, internal conversion to the ground state occurs in less than 1 ps, which is too fast to observe the corresponding vibrational relaxation in the S_1 state.[8,9] The large difference between the S_2 and S_1 lifetimes in 1,3,5,7-octatetraene allows us to directly detect internal conversion from the S_2 to S_1 state and observe vibrational relaxation in the S_1 state.

4.4. Excited-State Dynamics in the S_1 state on a Subnanosecond Time Scale. We observed nonsingle-exponential behavior of the fluorescence signal from the S_1 state. The average time constants in acetonitrile are consistent with that of the slowest decay components in the transient absorption signals. In previous studies, Kohler and co-workers measured the fluorescence decay of 1,3,5,7-octatetraene from the S_1 state.[22] The signal was fitted by a single exponential, and the time constants depended on temperature. The signal-to-noise ratio of their fluorescence signal was not good enough to resolve nonexponentiality. This may be a reason for the discrepancy between Kohler's observations and ours. The lifetimes of the two decay components are sensitive to the solvent.

We think that the triplet state is not involved in the transient absorption signals. The energy difference between the 1^1A_g state and 1^3A_g state is about 7000 cm^{-1}. Therefore, the equilibrium between the singlet and triplet states does not account for the nonexponentiality.[17] The quantum yield of triplet formation is small. We suggest that the nonexponential decay of the S_1 fluorescence reflects the equilibrium between the fluorescent S_1 state and the conformationally relaxed dark state. It is well-known that the excited-state dynamics of tetraphenylethylene exhibit a dual fluorescence and nonexponential decay kinetics in nonpolar solvents.[45-47] Barbara and co-workers suggested that the three-state model accounts for the observed dynamics around the central C═C double bonds.[45] Zimmt and co-workers assigned the three states to the vertically excited state, the conformationally relaxed state, and the twisted excited state, which they interpreted as a zwitterionic state.[46] In 1,3,5,7-octatetraene, the conformationally relaxed state is considered to be nonfluorescent, and the energy difference between the fluorescent state and the conformationally relaxed state is sufficiently small to create an equilibrium between these states. This therefore causes a nonexponential decay of the S_1 fluorescence signal. In acetonitrile, the average lifetime of the fluorescence decay is about half as long as that in *n*-hexane. The barrier height for the conformational relaxation could affect the faster nonradiative relaxation from the S_1 to S_0 state, because the energy of the fluorescence state and nonemitting state (the conformational relaxed state and/or the twisted excited state) is stabilized by the solvent polarity. The temperature and solvent dependence of the two different fluorescence decay constants would give more detailed information on the dynamics of these states.

4.5. Comparison of the Excited-State Dynamics of 1,3,5-Hexatriene and 1,3,5,7-Octatetraene. In this section, we discuss differences in the photophysical properties of 1,3,5-hexatriene and 1,3,5,7-octatetraene. The excited-state dynamics on both compounds are summarized in Figure 6. Regarding the S_2 state dynamics, resonance Raman studies suggest that internal conversion from the S_2 to S_1 state of 1,3,5-hexatriene occurs in about 20−40 fs.[48,49] In transient absorption measurements of 1,3,5-hexatriene, a lifetime of less than 150 fs has been estimated from the instrument-limited rise component of the S_1 state.[10-12] Recently, Anderson et al. determined the S_2 lifetime directly using transient absorption spectroscopy with sub-50-fs pulses.[50] The lifetime is 55 ± 20 fs in *trans*-1,3,5-hexatriene and <50 fs in *cis*-1,3,5-hexatriene. We found a 400-fs lifetime of the S_2 state for 1,3,5,7-octatetraene. This lifetime is 1 order of magnitude greater than that of 1,3,5-hexatriene.[48,49] The difference between the S_2 lifetime of 1,3,5-hexatriene and 1,3,5,7-octatetraene could be caused by the difference in vibronic coupling strength between the S_2 and S_1 state, depending on the energy gap and the position of the S_2/S_1 crossing point. A theoretical calculation shows that the energy difference between the S_2 and S_1 states for 1,3,5-hexatriene is 0.01 and 0.67 eV for the vertical and 0−0 excitation energies, respectively.[17] On the other hand, for 1,3,5,7-octatetraene, the difference is estimated to be 0.19 and 0.84 eV for the vertical and 0−0 excitation energies, respectively.[17] It can be assumed that the coupling strength between the S_2 and S_1 states in 1,3,5-hexatriene is greater than that in 1,3,5,7-octatetraene. The potential energy surface calculated by Robb and co-workers showed that the S_2/S_1 crossing point in 1,3,5-hexatriene is located in the vicinity of the Franck−Condon region, and that internal conversion proceeds along the totally symmetric deformation of the molecular backbone.[18] The information of the S_2/S_1 crossing point in 1,3,5,7-octatetraene is not available at this time. Moreover, it must be considered that the crossing point is strongly influenced by solute−solvent interactions, which produces the difference in the S_2/S_1 fluorescence ratio in the gas and solution phases.

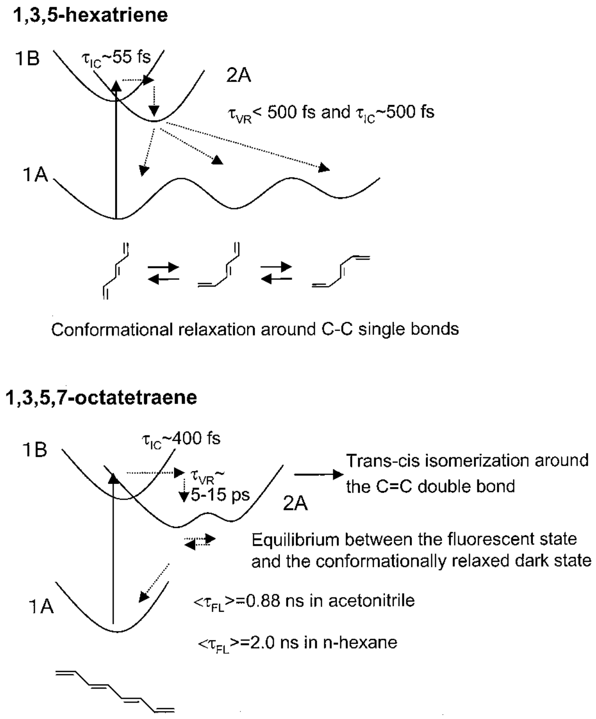

Figure 6. Schematic representation of excited-state relaxation for *trans*-1,3,5-hexatriene and *all-trans*-1,3,5,7-octatetraene. For *trans*-1,3,5-hexatriene, internal conversion from the 1B to 2A state occurs in about 55 fs. Vibrational energy redistribution in the 2A state and internal conversion to the 1A state occur within 500 fs to create the vibrationally hot product. Conformational relaxation around the C−C single bond proceeds to create a small amount of the s-cis conformer, which is trapped at thermal equilibrium on a time scale of 100 ps. For *all-trans*-1,3,5,7-octatetraene, internal conversion from the 1B to 2A state takes place in ~400 fs followed by vibrational relaxation in the 2A state (5−15 ps). The fluorescence signal from the 2A state has two different decay time constants which depend on the solvent. We suggest that the nonexponential decay results from the equilibrium between the 2A fluorescence state and the conformationally relaxed dark state. Information about conformational relaxation around the C−C single bonds for *all-trans*-1,3,5,7-octatetraene does not exist at present.

The lifetime of the S_1 state of 1,3,5,7-octatetraene is a few nanoseconds. This is 4 orders of magnitude greater than that of 1,3,5-hexatriene, which is less than 0.5 ps. The difference between the S_1 state lifetimes in 1,3,5-hexatriene and 1,3,5,7-octatetraene could be due to a large difference in the barrier heights between the bottom of the S_1 state and S_1/S_0 crossing point. The nonradiative decay of 1,3,5,7-octatetraene was measured in condensed phases as a function of temperature.[22] The temperature dependence of the lifetimes has two regions, which both depend on the environment. (i) In cyclohexane, the lifetime decreases gradually from 126 to 90 ns between 10 and 179 K. (ii) At higher temperatures, a precipitous drop of the lifetime occurs, and it decreases to 2.5 ns at 320 K. The low-temperature behavior has been ascribed to adiabatic isomerization around C═C double bonds on the S_1 surface over a barrier of about 950 cm^{-1} to form electronically excited *cis*, *trans*-1,3,5,7-octatetraene before decaying to the ground state.[26] A barrier of 1400 cm^{-1} was determined for a higher-temperature nonradiative decay pathway, but the mechanism remains ambiguous. In the gas phase, a stepwise increase in the nonradiative decay rates was observed at around 2100 cm^{-1}, which was ascribed to trans−cis isomerization.[24] A similar behavior in the nonradiative decay rates was observed for *trans*-stilbene under isolated conditions.[51] The origin of the isomerization barrier for *trans*-stilbene is believed to be a crossing between the S_1 and S_0 surfaces occurring at large ethylene torsional angles.[51] Robb and co-workers computed the low-lying transition states and minimum energy paths of an isolated *all-trans*-1,3,5,7-octatetraene.[19] These calculations showed that initial trans−cis isomerization motion leads to a point where the S_1 and S_0 energy surfaces are conically intersecting, which makes fully efficient radiationless decay possible. These theoretical calculations support our previous interpretation of gas-phase results. The predicted barrier of about 25 kJ/mol is also consistent with experimental values. This large barrier is responsible for the slow relaxation dynamics of 1,3,5,7-octatetraene in the S_1 state. On the other hand, the barrier height in the S_1 state for 1,3,5-hexatriene was estimated to be less than 4 kJ/mol.[18] Two channels exist in the internal conversion from the S_1 to S_0 state. These lead from the 2A state surface via two separated conical intersections to two products (double-bond and single-bond isomer). The nonradiative decay from the S_1 to S_0 state occurs along the nontotally symmetric deformation of the molecular backbone with a nearly barrierless path. Our previous spectroscopic observations and other work suggest an activation energy of about 170 cm^{-1}, which is less than this theoretical prediction.[52] Comparing the theoretical calculation for 1,3,5-hexatriene and 1,3,5,7-octatetraene reveals that the magnitude of the barrier along asymmetric deformation, which leads to internal conversion to the ground states, accounts for the difference between subpicosecond and nanosecond lifetimes.

5. Concluding Remarks

We investigated the excited-state dynamics of 1,3,5,7-octatetraene in solution by femtosecond transient absorption spectroscopy and picosecond fluorescence spectroscopy. After photoexcitation to the $1B_u$ state, we observed transient absorption over a broad wavelength region. The dynamics depend on the probe wavelength. The subpicosecond decay components of 0.4 ps dominate at wavelengths longer than 480 nm. The signals contain a 10-ps decay component at all wavelengths observed. The subpicosecond decay components at the longer wavelengths reflect internal conversion from the S_2 to S_1 state, and the absorption bands are shifted to shorter wavelengths within this time scale. We also measured the time-resolved fluorescence spectra using a streak camera. In addition to the fluorescence from the S_1 state, we observed a weak fluorescence originating from the S_2 state. The weak S_2 fluorescence is in contrast to gas phase results. This means that the relaxation from the initially excited S_2 state is strongly influenced by solute−solvent interactions, which increase the efficiency of internal conversion in solution.

A 5−15 ps decay component observed in the transient absorption signal is ascribed to vibrational relaxation in the S_1 state. The fluorescence signal from the S_1 state has two different decay time constants which depend on the solvent. We suggest that the nonexponential decay of the fluorescence signal is related to the equilibrium between the fluorescent S_1 state and the conformationally relaxed dark state. The solvent dependence of the lifetime comes from the polarity dependence of the barrier height on the nonradiative process.

The photophysical differences between 1,3,5-hexatriene and 1,3,5,7-octatetraene are discussed in terms of internal conversion efficiencies. The lifetime of the S_2 state of 1,3,5,7-octatetraene is 1 order of magnitude longer than that of 1,3,5-hexatriene. This may result from differences in vibronic coupling between the S_2 and S_1 states. The average S_1 state lifetimes of 1,3,5,7-octatetraene are 0.88 ns in acetonitrile and 2.0 ns in *n*-hexane, which are 4 orders of magnitude longer than the lifetime of 1,3,5-hexatriene (<0.5 ps). The difference in the S_1 state lifetimes is due to a large difference in the barrier heights. Theoretical calculations by Robb and co-workers suggested that the S_1−S_0 radiationless decay channel is caused by the non-adiabatic trans−cis isomerization.[19] The longer lifetime of the S_1 state in 1,3,5,7-octatetraene allows us to observe S_2−S_1 internal conversion and decay processes of the S_1 state separately.

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