

Studies on Ultrafast Photoinduced Relaxation Processes in Solution

Kaoru Ohta

Department of Chemistry, Graduate School of Science,
Kyoto University
and Institute for Molecular Science

Preface

The majority of interesting reactions from biological, environmental and industrial aspects occur in the condensed phase. Solvent molecules effectively work as a heat bath which accepts the excess energy from the solute. Therefore, it is very important to know how the surrounding solvent molecules affect the rate and the pathway of the chemical reaction. In parallel with it, theoretical studies of the electronic structure and the molecular dynamics have also made great a progress in revealing the underlying physical properties in the chemical reaction dynamics. Recent rapid development of the ultrafast spectroscopy has helped us to obtain comprehensive understanding of chemical reaction dynamics both in the gas and condensed phases. In a last few years, the novel solid-state laser technology, particularly development of the Kerr-lens mode-locked Ti:Sapphire laser, has brought about stable generation of ultrashort pulses and has contributed an enormous progress in a wide variety of the spectroscopic methods. These methods have been applied to various fields in physics, chemistry and biology. In the present study, we developed the femtosecond UV transient absorption and fluorescence spectroscopies based on a regeneratively amplified Ti:Sapphire laser system and used them to investigate the ultrafast photo-induced relaxation processes in solution.

This thesis consists of two topics of ultrafast molecular relaxation dynamics in solution. First, we studied the ultrafast relaxation dynamics of simple linear polyenes in solution by femtosecond UV transient absorption spectroscopy. Despite of the fundamental importance in biological systems and application to the photoconductive materials, there still remain many unresolved problems in the excited state dynamics of simple polyenes. This is due to a low fluorescence quantum yield and extremely short lifetime of the excited state. A direct ultrafast time-resolved study is required to reveal the fate of the excited state of the linear polyenes. In Chapter 1, we review the photophysical and photochemical properties of 1,3,5-hexatriene and 1,3,5,7-octatetraene as well as related compounds both in the gas and solution phases. We also mention the theoretical works on the calculation of the potential energy surface. These results give valuable information about the pathways and the energetics of the photo-initiated reaction. The

experimental method is described in Chapter 2. After describing the laser system, we explain the setup for the transient absorption measurement. We present the experimental results of trans- and cis-1,3,5-hexatriene in Chapter 3. After the internal conversion from the initially excited $1B$ (S_2) state to the $2A$ (S_1) state in less than 100 fs, the vibrational energy redistribution process in the $2A$ state and the internal conversion to the ground state occur in a subpicosecond time scale. The bleach recovery signals show that 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. We also performed the spectral simulation on the absorption spectra of the vibrationally excited photoproduct, which is created by the ultrafast internal conversion to the ground state. The agreement of the experimental results and calculation is quite good, which is also discussed in Chapter 3. In Chapter 4, the investigation on the photodynamics of 1,3,5,7-octatetraene is described and the difference in dynamics between 1,3,5-hexatriene and 1,3,5,7-octatetraene is discussed. In contrast to 1,3,5-hexatriene, the internal conversion from the S_2 to S_1 state is directly observed in the transient absorption signals which occurs in about 400 fs.

Secondly, we present the investigation on the relaxation process from a highly excited electronic state of a dye molecule in solution. Dissipation of the excess energy strongly influences the pathways and the rates of the chemical reaction. This may cause a significant difference of the reactivity between the gas and solution phases. Various techniques using ultrashort pulses have been developed in last two decades. After reviewing the previous studies on vibrational energy redistribution and relaxation processes in Chapter 5, the apparatus for the ultrafast UV fluorescence up-conversion method is described in detail in Chapter 6. The experimental results are shown in Chapter 7, which reveals that the intramolecular energy redistribution occurs in less than 100 fs and the observed dynamics is controlled by the internal conversion to the S_1 state. The model calculation on the fluorescence spectra is performed in the two limiting cases, one of which assumes the ultrafast intramolecular energy redistribution and the other assumes the selective excitation of a few particular Franck-Condon active modes. The results of the

simulation are presented in Chapter 8. The calculated results show that the shape of the fluorescence spectra strongly depends on the distribution of the population in the vibrational modes. On the other hand, we did not observe any evidence for the dramatic departures from the steady-state fluorescence spectra within a few picoseconds. This means that the intramolecular energy redistribution is completed within our instrument response function and the observed spectra are the intramolecularly relaxed ones. The summary of this study is given in Chapter 9.

In conclusion we investigated ultrafast photoinduced relaxation processes in solution and discussed the solvent effect on the photoinduced dynamics. The experimental results of simple linear polyenes show that the lifetime of the excited state in solution is slightly different from that in the gas phase. We found that the conformational relaxation around the C-C single bond for 1,3,5-hexatriene takes place in a few hundreds of picosecond and competes with the vibrational cooling. The internal conversion of a higher excited state of a dye molecule show that the intramolecular energy redistribution process occurs quite efficiently with the rate of a couple of hundred femtosecond. We can consider that these low frequency solvent motions can compensate of energy mismatch between the initial and final states of the energy transfer and thus accelerate the intramolecular energy transfer.

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Kaoru Ohta

Contents

Part I Photodynamics of Simple Linear Polyenes in Solution

Chapter 1 General Introduction

1-1 Photodynamics of simple linear polyenes	2
1-2 Photophysical properties of 1,3,5-hexatriene and its related compounds in the gas phase	8
1-3 Photophysical properties of 1,3,5-hexatriene and its related compounds in the solution phase	15
1-4 Photochemical properties of 1,3,5-hexatriene in the solution phase	20
1-5 Photochemical properties of 1,3,5,7-octatetraene	23
1-6 Theoretical works of simple polyenes	27
References and Notes	30

Chapter 2 Experimental

2-1 Laser system	36
2-2 Transient absorption spectrometer	39
2-3 Reagents	42
References and Notes	44

Chapter 3 Ultrafast Dynamics of the Photoexcited 1,3,5-Hexatriene in Solution

3-1 Introduction	46
3-2 Results	48
3-2-1 Static absorption spectra of trans- and cis-1,3,5-hexatriene	48
3-2-2 Transient absorption signals of trans- and cis-1,3,5-hexatriene in solution	49

3-2-3 Transient bleach recovery signals of trans-1,3,5-hexatriene in solution	57
3-2-4 Transient bleach recovery signals of cis-1,3,5-hexatriene in solution	61
3-3 Discussion in the transient absorption signals	64
3-3-1 Origin of the transient absorption in the visible region	64
3-3-2 Anisotropy Decay Measurement	69
3-4 Discussion in the transient bleach recovery signals	78
3-4-1 The origin of the transient bleach recovery signals within 20 ps time scale	78
3-4-2 Theoretical calculation for explaining the temporal behavior of the bleach recovery signals	81
(a) Estimation of the transient vibrational temperature	86
(b) Calculation of the absorption spectrum	90
(c) Results of the calculation	93
(d) Temporal profiles of the internal temperature	96
(e) Pitfalls of the model calculation	98
3-4-3 Conformational relaxation in the ground state	103
3-4-4 Temperature dependence of the slow component of the bleach recovery signals	105
3-5 Conclusion	105
References and Notes	107

Chapter 4 Photodynamics of 1,3,5,7-Octatetraene in Solution

4-1 Introduction	111
4-2 Results	113
4-2-1 Static absorption and fluorescence spectra of all-trans-1,3,5,7-octatetraene in solution	113
4-2-2 Transient absorption signals of all-trans-1,3,5,7-octatetraene in solution	

4-3 Discussion	122
4-4 Conclusion	126
References and Notes	127

Part II Femtosecond Relaxation Processes from a Higher Excited Electronic State of a Dye Molecule in Solution

Chapter 5 General Introduction

5-1 Propose of this study	130
5-2 Vibrational energy redistribution and relaxation processes in solution	131
5-3 What is IVR ? Definition and Background	133
5-4 Studies on the vibrational relaxation dynamics of large molecules in solution	135
5-5 Studies on the vibrational relaxation dynamics of large molecules after the photoexcitation to the higher electronic excited state	139
5-6 The concept of internal temperature	141
5-7 Vibrational cooling process	142
5-8 Slow intramolecular energy redistribution process	144
5-9 Relationship between the solvation dynamics and the vibrational relaxation	146
5-10 Summary	148
References and Notes	149

Chapter 6 Experimental

6-1 Laser system	153
6-2 Generation of the third harmonic of a Ti:Sapphire laser	154
6-3 Construction of fluorescence up-conversion spectrometer	156
6-3-1 Principle	156
6-3-2 Apparatus	158
6-3-3 Estimation of the instrument response function	161
6-4 Steady-state absorption and fluorescence spectra	163

6-5 Reagents	163
References and Notes	164

Chapter 7 Relaxation Processes from a Higher Electronic Excited State of Coumarin 481 in Cyclohexane

7-1 Steady-state absorption and fluorescence spectra	166
7-2 The temporal profiles of the fluorescence signal within a few picosecond time scale	167
7-3 Spectral narrowing in a 10 ps time scale	171
7-4 Temperature dependence of the steady-state fluorescence spectra	174
7-5 Mechanism of the ultrafast intramolecular energy redistribution process	175
7-6 Conclusion.	176
References and Notes	177

Chapter 8 Model Calculation

8-1 Introduction	179
8-2 Calculation of the fluorescence spectrum	180
8-2-1 Frequency-domain approach	180
8-2-2 Time-domain approach	182
8-2-3 Comparison with the experimental results	185
8-2-4 Ultrafast intramolecular energy redistribution	187
8-2-5 Selective excitation of a few Franck-Condon active modes	189
8-2-6 Vibrational cooling process	192
8-3 Conclusion	196
References and Notes	197

Chapter 9 Summary	198
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Acknowledgments	203
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Chapter 1

General Introduction

1-1. Photodynamics of simple linear polyenes

Linear polyenes are molecules with a chain of conjugated carbon-carbon double bonds of an unbranched π -electron system [1-3]. Detailed studies of the excited structures and dynamics of the simple linear polyenes are crucial for understanding the mechanism of the cis-trans photoisomerization process. Polyenes also give us a suitable benchmark for quantum mechanical theory and calculation because they are the first class of molecules for which the description of the lowest excited state requires the inclusion of the configurations with two excited electrons [4]. All of these make polyenes intriguing for investigation. Despite the fundamental importance of the polyene photodynamics and considerable amount of the experimental and theoretical effort that has been focused on this topic, there remain unknown characteristics, in particular, the relaxation dynamics of their excited electronic states of small polyenes.

Furthermore linear polyenes constitute a large class of molecules which play important roles in biological systems. Some of these molecules are shown in Figure 1-1. For example, carotenoids prevent the photosynthetic systems from damaging by the singlet molecular oxygen [5,6]. In purple photosynthetic bacteria, they serve to harvest light in the blue green region of the spectrum, subsequently transferring excitation energy to bacteriochlorophyll. This function increases the efficiency for collecting sun light. For another important example, retinal is included in retina and plays a key role in the vision system [7,8]. After the photoexcitation, retinal undergoes isomerization from the all-trans form to the 13-cis form which causes vision. This photoisomerization event triggers a thermally driven cycle which involves several spectroscopic distinguishable intermediates. This cycle drives the transport of protons across the membrane. Within 100 ms, the retinal isomerizes back to the all-trans form.

Long polyenes also appear in vitamins as shown in Figure 1-1. The cis-trans isomerization and photoinduced electrocyclization reactions in the polyene moiety are found in the photochemistry of vitamin D and its precursors [2]. The polymeric form, namely polyacetylene, is photoconductive. The physical properties of this polymer have been a subject of the intense research because of its practical purposes.

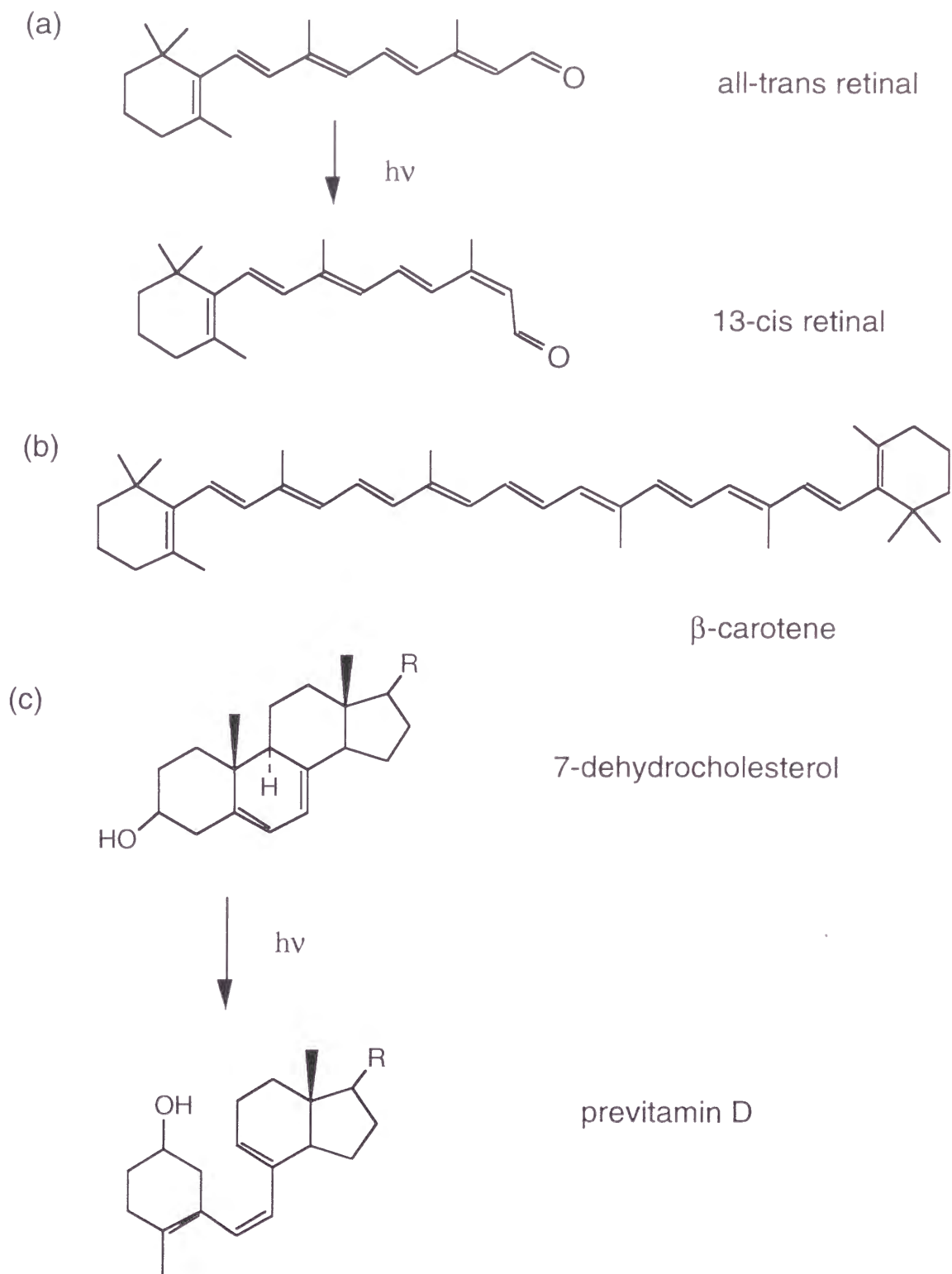


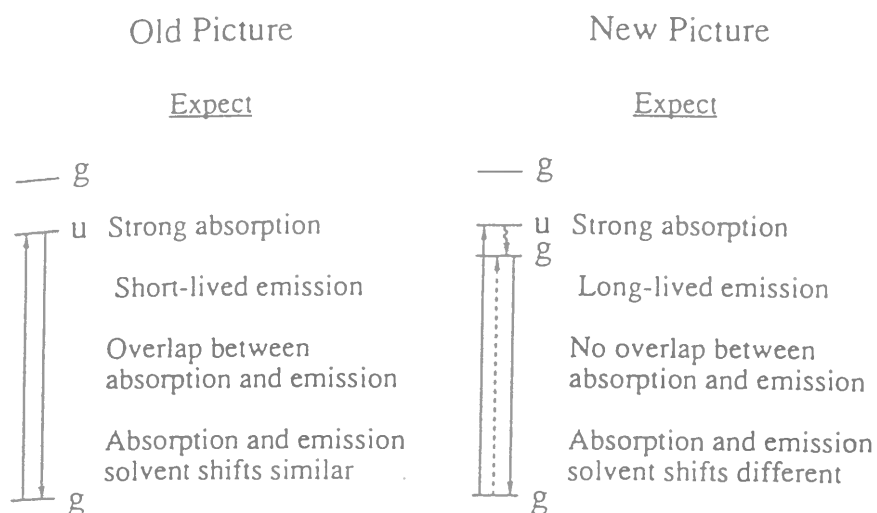
Figure 1-1. The structures and reaction schemes of (a) retinal, (b) β -carotene, and (c) 7-hydrocholesterol and previtamin D.

The photophysical and photochemical properties of linear polyenes were first studied in the 1930s [9-11]. In the earlier studies, it is revealed that there exists a strong absorption band in the ultraviolet to visible region. It comes from the allowed transition from the 1^1A_g to 1^1B_u state. Upon the light absorption, an electron is promoted from a bonding π -MO to an antibonding π^* -MO. When the number of the double bond in the polyene increases, it is well known that the absorption intensity of this band becomes greater and its 0-0 transition energy decreases [5]. By using the simple Huckel method, we can easily calculate the dependence of the chain length on the transition energy from the 1^1A_g to 1^1B_u state. It has been believed for a long time that the symmetry of the lowest electronic excited state (S_1) is $1B_u$ (π , π^*), which can be expressed by the transition of an electron from HOMO to LUMO and there does not exist any electronic state lower in energy than the 1^1B_u state (Figure 1-2a).

Hudson and Kohler for the first time pointed out that the S_1 state of linear polyenes was not the B_u state but the A_g state in 1972 based on the absorption and fluorescence spectra of 1,8-diphenyl-1,3,5,7-octatetraene [12,13]. This means that the energy level of the A_g state is lower in energy than that of the B_u state i.e., the B_u state corresponds to S_2 . The A_g state also belongs to the π - π^* transition, which is optically forbidden due to the same symmetry as in the electronic ground state. The electronic structure of simple linear polyenes is shown in Figure 1-2b. All-trans-polyenes have the 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, cis isomer belongs to the C_{2v} symmetry and the two low lying excited ones are the 2^1A_1 and 1^1B_2 states. When we refer to the electronic states for both isomer, we use the following symmetry character, i.e. 2A and 1B state, for simplicity.

(a)

Polyene Electronic Structure



(b)

Electronic structure

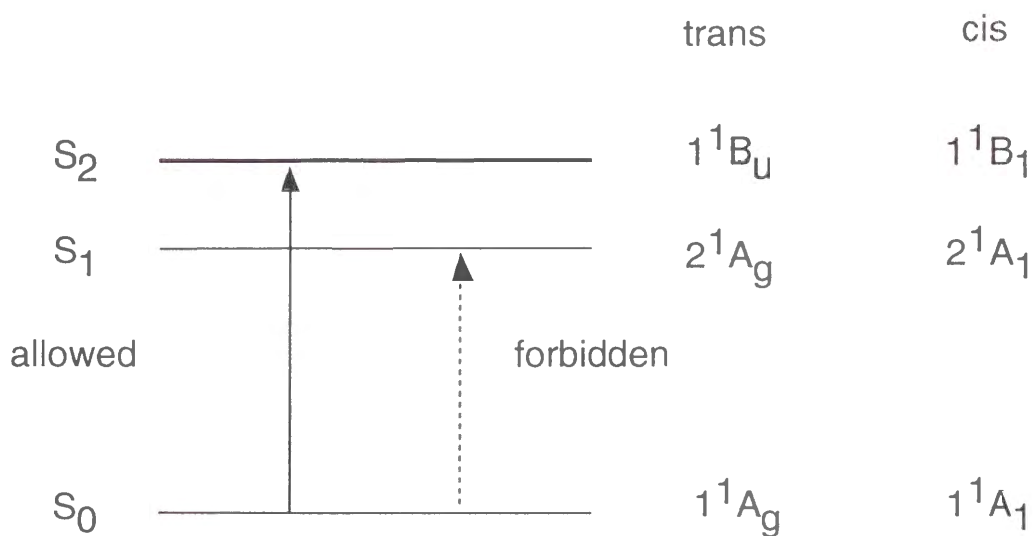


Figure 1-2. (a) Energy level diagram for linear polyenes before and after 1972. This is quoted from Ref.[58].

(b) The electronic structure and symmetry labels of simple linear polyenes.

The above prediction is based on the following experimental observations. First, there is no overlap between the absorption and fluorescence spectra. This corresponds to the large Stokes shift of the fluorescence spectrum. Second, the value of the oscillator strength has been estimated by two different methods. One of them is to use the integral value of the absorption spectra from the $1A_g$ to $1B_u$ state. The other is estimated based on the fluorescence quantum yield and lifetime. However, these values are not consistent to each other. The estimated value based on the latter method is one order magnitude smaller than that by the former method. Third, the absorption spectra from the $1A_g$ to $1B_u$ state are shifted by changing the polarity of the solvent. On the other hand, the position of the fluorescence band is not sensitive to the solvent polarity. This observation suggests that the electronic transition in the absorption spectrum is not same as that for fluorescence.

For diphenyl substituted polyenes and longer polyenes, it has been experimentally confirmed that the $2A$ state is located lower in energy than the $1B$ state [1,3]. In contrast to this, 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.

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 [14-23]. For β -carotene, after the photoexcitation to the S_2 state, the internal conversion to the S_1 state occurs at around 200 fs and the lifetime in the S_1 state is ~ 10 ps at room temperature [14-19]. 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. For retinal in bacteriorhodopsin, the primary event in the all-trans to 13-cis photoisomerization is reported to take place, that is completed as fast as 200 fs [20-23]. 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 the each step of the dynamics of smaller linear polyenes in detail.

In this chapter, we review the recent progress in the photophysical and photochemical properties of small polyenes in the both gas and solution phases.

1-2. Photophysical properties of 1,3,5-hexatriene and its related compounds in the gas phase

In 1970-80s, a number of groups have measured the absorption spectra of both trans- and cis-1,3,5-hexatriene in the gas phase. For example, Gavin and coworkers reported the absorption spectra of 1,3,5-hexatriene on a gas cell condition and analyzed the position and band width of a few Franck-Condon active modes [24,25]. Vaida and coworkers reported the direct absorption spectra under the supersonic jet expansion [26,27]. These jet absorption spectra allow more accurate determination of the Franck-Condon factors, upper-state vibrational intervals and the widths of the vibronic band. They found that the line width of the absorption spectra of 1,3,5-hexatriene as well as 1,3-butadiene did not become sharp under the jet-cooled condition compared with that on a gas cell condition at room temperature. The results of this experiment are shown in Figure 1-3. The similar band widths were observed under the low-temperature matrices. Until recently, there is no report for the observation of the fluorescence in the gas phase. The nonfluorescent feature of these shortest polyenes suggests that the observed band width is due mainly to the extremely short excited state lifetime. An upper limit of the fluorescence quantum yield is estimated to be 5×10^{-5} . An oscillator strength of 0.7 for the $1^1B_u-1^1A_g$ band of 1,3,5-hexatriene leads to a radiative lifetime of about 1.4 ns. Based on these estimations, a molecule must escape from the initially prepared excited state (Franck-Condon state) within 10^{-13} s. This value is consistent with the estimated one from the linewidths of the absorption spectra. They also found that the linewidth of the spectrum becomes broader as decreasing the chain length. The origin band of jet-cooled trans,trans-1,3,5,7-octatetraene has a full width at half-maximum intensity of 18 cm^{-1} . The corresponding lifetime is around 400 fs. The origin band of trans-1,3,5-hexatriene is about eight times broader, with a width of 155 cm^{-1} . In the 1,3-butadiene jet spectrum, 1000 cm^{-1} wide lowest energy band is observed in turn six times broader than that of 1,3,5-hexatriene. The corresponding lifetimes for 1,3-butadiene and 1,3,5-hexatriene are about less than 10 fs and 40 fs, respectively.

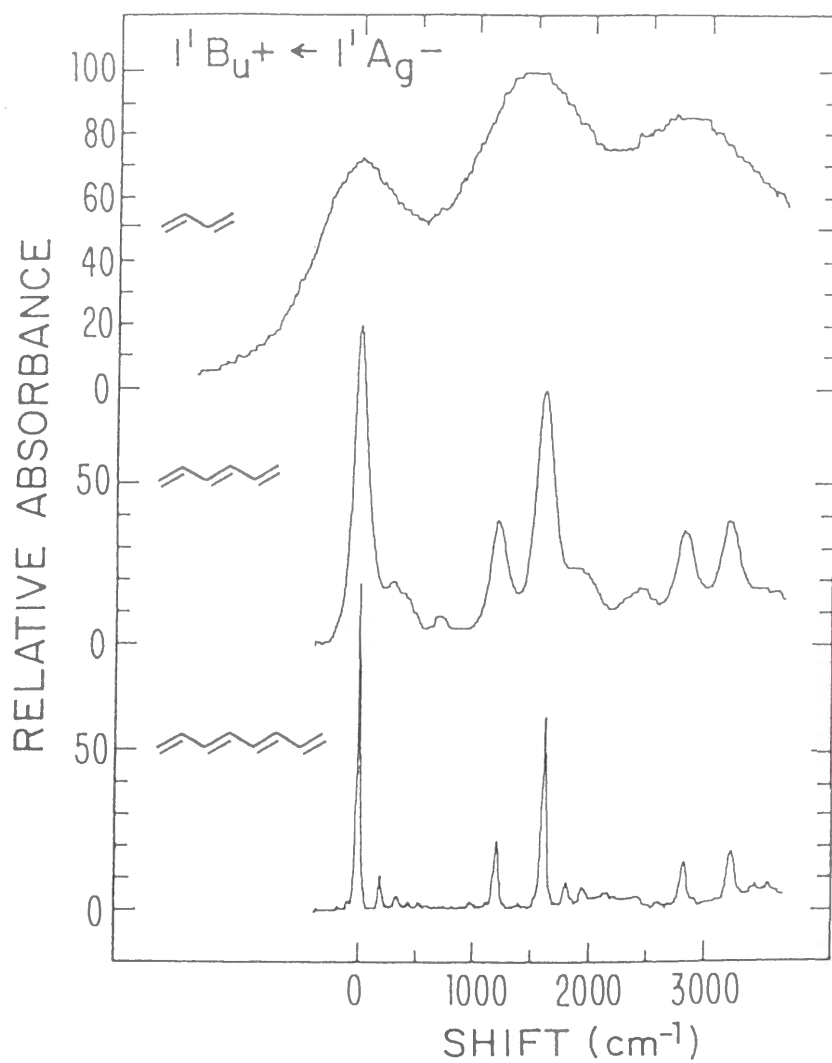


Figure 1-3. The $1^1B_u^+ \leftarrow 1^1A_g^-$ absorption spectra of jet-cooled 1,3-butadiene, trans-1,3,5-hexatriene, and trans, trans-1,3,5,7-octatetraene. This figure is a copy from Ref. [27].

The ordering of the lowest excited states of 1,3,5-hexatriene has been a matter of debate until recently. 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 1B state, whereas the vertical transition to the 2A state may overlap or even be located at higher energy than that to 1B band [28,29].

It was recently reported that the 2^1A_1 state of cis-1,3,5-hexatriene in a supersonic jet expansion was observed by using resonance enhanced multiphoton ionization spectroscopy [30]. 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. The position of the 2A state is also confirmed by resonance Raman spectrum and the direct absorption spectrum following the excitation to the 2A state [31,32]. The excitation spectrum shows that the origin of the spectrum consists of a feature that comprises two bands separated by 5 cm^{-1} . It is suggested that cis-1,3,5-hexatriene in the 2^1A_1 state deviates slightly from planarity to at least two distinct nonplanar geometries, which involves the terminal hydrogen atoms. This observation is supported by the ab-initio calculations.

The fluorescence excitation spectrum of the S_1 state of 1,3,5-hexatriene was measured by Petek and coworkers [33]. They also found that the band origin consisted of two major peaks separated by $\sim 5.7\text{ cm}^{-1}$. The rotational line shapes of the origin bands are consistent with a predominantly parallel transition. The A_1 - A_1 transition is allowed for a molecule with C_{2v} symmetry and a perpendicular band is expected. This means that the spectrum of the S_1 - S_0 transition appears to derive strength by borrowing in intensity from the strongly allowed S_2 - S_0 transition. The fluorescence intensity drops rapidly between the peaks at 71.3 and 157.7 cm^{-1} . Due to the insufficient time resolution of this experiment, this provides indirect evidence of a nonradiative decay channel that requires an activation energy between 71.3 and 157.7 cm^{-1} from the origin. They proposed that this process involved cis-trans isomerization.

Based on these observations, the dark 2A state is considered to play an important role in the ultrafast internal conversion and isomerization reaction to the ground state. However, the above observations provide only indirect evidence for the excited-state

dynamics of small linear polyenes. A direct time-resolved study is required to understand the fate of photoexcited small linear polyenes.

Very recently, femtosecond time-resolved techniques have been applied to investigate the excited-state dynamics of 1,3,5-hexatriene and its related compounds in the gas phase [32,34-37]. Hayden and coworkers used femtosecond time-resolved two-pulse photoionization techniques to study the ultrafast internal conversion in 1,3,5-hexatriene [34]. They used time-delayed single and multiple photon ionization with 350 nm and 310 nm probe pulses following the excitation of the 1^1B_u state at around 250 nm. This experiment clearly shows that while the initial step in the internal conversion of 1,3,5-hexatriene occurs in less than 100 fs, the excitation in the molecule continues to evolve for at less than 1.5 ps. The internal conversion appears to proceed through an intermediate, which may be the 2^1A_g state with its origin below 5000 cm^{-1} from the 1^1B_u state that optically excited in this experiment. The population of the apparent intermediate is observed to rise with less than a 100 fs delay and has a decay time constant of about 250 fs. They also found distinctly different dynamics for trans and cis isomers. The results are shown in Figure 1-4a. The lifetime of the 2A state for trans and cis isomers is 270 fs and 730 fs, respectively [35]. They also measured the time-resolved photoelectron spectrum. The time evolution of the spectrum in a subpicosecond time scale determines a time scale of 300 fs for the intramolecular vibrational energy redistribution within the 2A state.

Fuss and coworkers measured the lifetime of the 2^1A_1 state of cis-1,3,5-hexatriene after pumping it directly by a 250 fs pulse and probing the excited molecules by ionizing it by a delayed pulse [32]. The lifetime decreased from several ps to 730 fs, when the excess energy was increased from near 0 to 4000 cm^{-1} (Figure 1-4b). From the temperature dependence, they inferred a barrier of about 170 cm^{-1} which led to the internal conversion to the S_0 state. Furthermore, 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 [36,37]. The internal conversion from the 1^1B_2 to 2^1A_1 state completes within 100 fs. Thus the transition from the 2^1A_1 state of 1,3,5-hexatriene to the ground state is a rate determining

step with the time constant of about 600 fs [36]. These dynamics in the 2A state are general among the simple linear polyenes. They used intense-laser field ionization to observe the motion of the initially excited 1,3-cyclohexadiene. The measured $1B_2$ and $2A_1$ lifetimes are 43 fs and 77 fs, respectively, and the primary photoproduct of cis-1,3,5-hexatriene is formed within 200 fs [37]. Similar lifetimes have also been measured in two derivatives: α -terpinene and α -phellandrene.

In this research, we also focus our attention on the difference of the dynamics between the gas and the condensed phases. The experiment in the gas phase or under jet-cooled condition can provide more comprehensive information on the reaction dynamics, particularly, on the mode-specific dynamics. The vibronic transitions are well separated and different species are sometimes easy to distinguish by the photoionization method. Thanks to the results in the gas phase, we can compare the results in the condensed phase directly to reveal the role of the solvent in the reaction and relaxation processes.

(a)

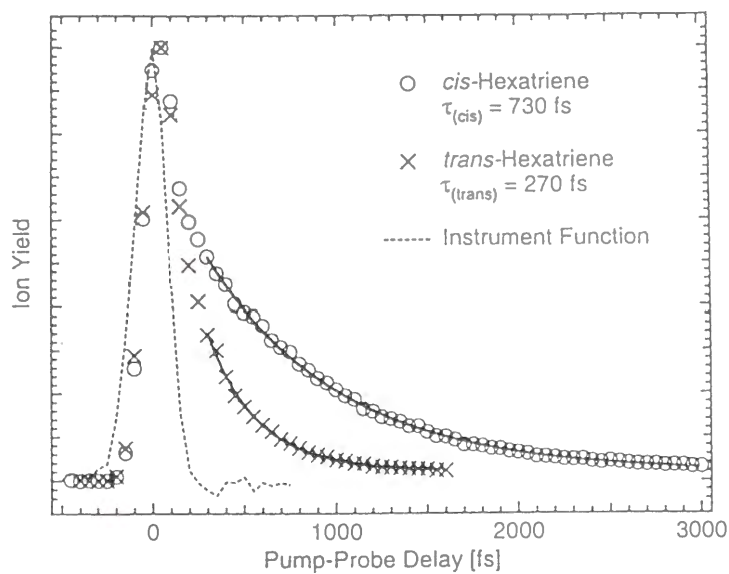
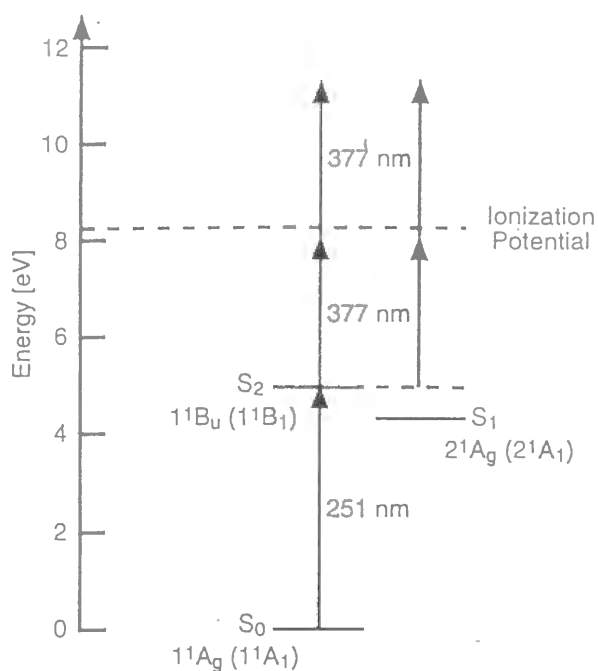


Figure 1-4. (a) (Upper) Energy level diagram of 1,3,5-hexatriene for excitation and ionization used in the femtosecond pump-probe experiment. This is quoted from Ref. [34].

(Lower) Ion yield vs pump-probe delays for both *trans*- and *cis*-1,3,5-hexatriene, with an instrument response function obtained by two photon ionizing 1,3-cyclohexadiene after excitation near 250 nm. This is quoted from Ref. [35].

(b)

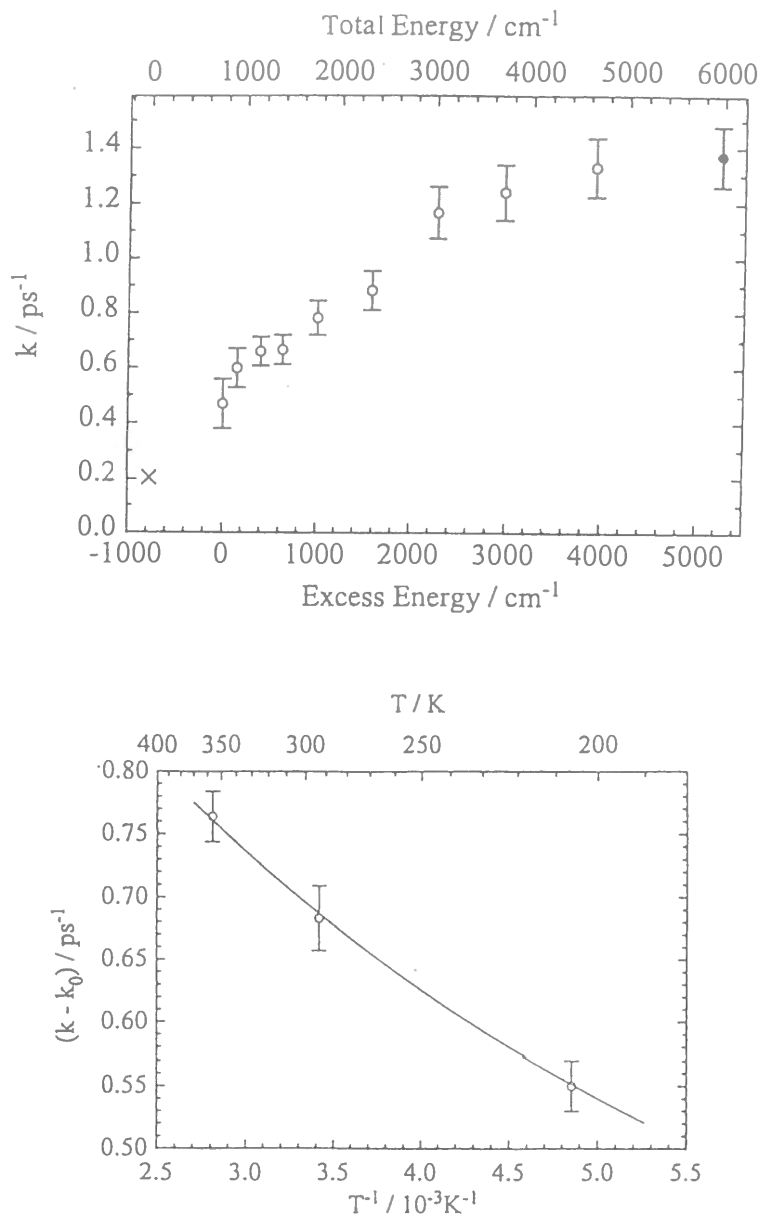


Figure 1-4 (b) (Upper) Dependence of the decay rate of the population in the 2^1A_1 state (open circles) on the excess energy and total vibrational energy. The cross is an lower limit of the rate, estimated from the linewidth of the two-photon ionization 0-0 transition. The solid circle shows the value measured by Hayden et al. This is quoted from Ref. [32].

(Lower) Dependence of the $2A_1$ decay rate (circles) on the inverse temperature. The rate of the barrierless process, k_0 , has been assumed to be 0.2 ps^{-1} . The solid line is from an RRK calculation with an activation energy of 170 cm^{-1} . This is quoted from Ref. [32].

1-3. Photophysical properties of 1,3,5-hexatriene and its related compounds in the solution phase

There are several studies of the excited-state dynamics of simple linear polyenes in the condensed phase. Kliger and coworkers have tried to measure the excited-state absorption of 1,3,5-hexatriene by nanosecond transient absorption spectroscopy [38]. The excited state absorption of 1,3,5-hexatriene in solution was not observed due probably to insufficient time resolution. It was suggested that the lifetime of the 2A state was below 200 ps.

In the condensed phase, the resonance Raman spectroscopy and femtosecond transient absorption spectroscopy have been used to investigate the excited-state dynamics of simple polyenes [39-52]. The initial motion of the reactant on the excited state potential energy surface may be probed by using the standard resonance Raman or ultrafast pump probe techniques. The Raman process can probe the motion on the excited state potential energy surface that occurs on time scales less than or equal to the electronic dephasing time. On the other hand, the femtosecond or picosecond pump-probe method is useful for examining the excited state dynamics in relatively longer time scale, particularly, for such a case that the excited electronic state persists for a substantial length of time due to a flat surface or even a minimum in the potential surface along the reaction coordinate.

Myers and coworkers have applied the steady-state resonance Raman spectroscopy to probe the excited state structure and dynamics in these small polyenes [39,40]. Quantitative modeling of the resonance Raman intensities based on the time-dependent wave packet propagation scheme provides information on the solvation effects on the excited-state potential surfaces. It was analyzed that the initial motion of the wavepacket out of the Franck-Condon region occurred on 20 fs (cis-1,3,5-hexatriene) and 40 fs (trans-1,3,5-hexatriene). It is compatible to the population decay from the 1^1B_u to 2^1A_g state on this time scale and a major source of diffuseness in the gas-phase absorption spectra.

Mathies and coworkers have applied the resonance Raman techniques to investigate the pericyclic photochemical ring opening reaction of small polyenes such as

1,3-cyclohexadiene, 1,3,5-cyclooctatriene and so on [41-47]. In particular, the photochemical ring opening reaction of 1,3-cyclohexadiene was investigated by both steady state and picosecond time-resolved resonance Raman spectroscopy. In this reaction, cis-1,3,5-hexatriene is created during the course of the reaction. The resonance Raman spectrum shows that the nuclear dynamics that occurs immediately after photoexcitation projects directly on to the conrotatory ring-opening reaction coordinate. This schematic diagram is displayed in Figure 1-5. The stereochemistry of the reaction follows the Woodward-Hoffmann rules. The basic information on the initial excited-state dynamics can be estimated by measuring the total fluorescence quantum yield. The measured fluorescence quantum yield of 2×10^{-6} can be compared with the natural radiative lifetime that is calculated from the absorption spectra. This calculation reveals that the optical lifetime (T_1) or depopulation of the initially prepared excited state is on the time scale of 10 fs. This indicates that there is a very rapid internal conversion that depopulates the initially prepared excited state.

In the picosecond time-resolved resonance Raman experiment, the appearance time of the Stokes scattering from the ground state 1,3,5-hexatriene is around 6 ps, as shown in Figure 1-5. Analysis of the photoproduct spectral evolution demonstrates that all-s-cis-1,3,5-hexatriene first appears on the ground-state surface and undergoes conformational relaxation to produce mono-s-cis isomer with a time constant of 7 ps. The anti-Stokes Raman intensities demonstrate that the vibrational relaxation in the ground state occurs with a time constant of 15 ps.

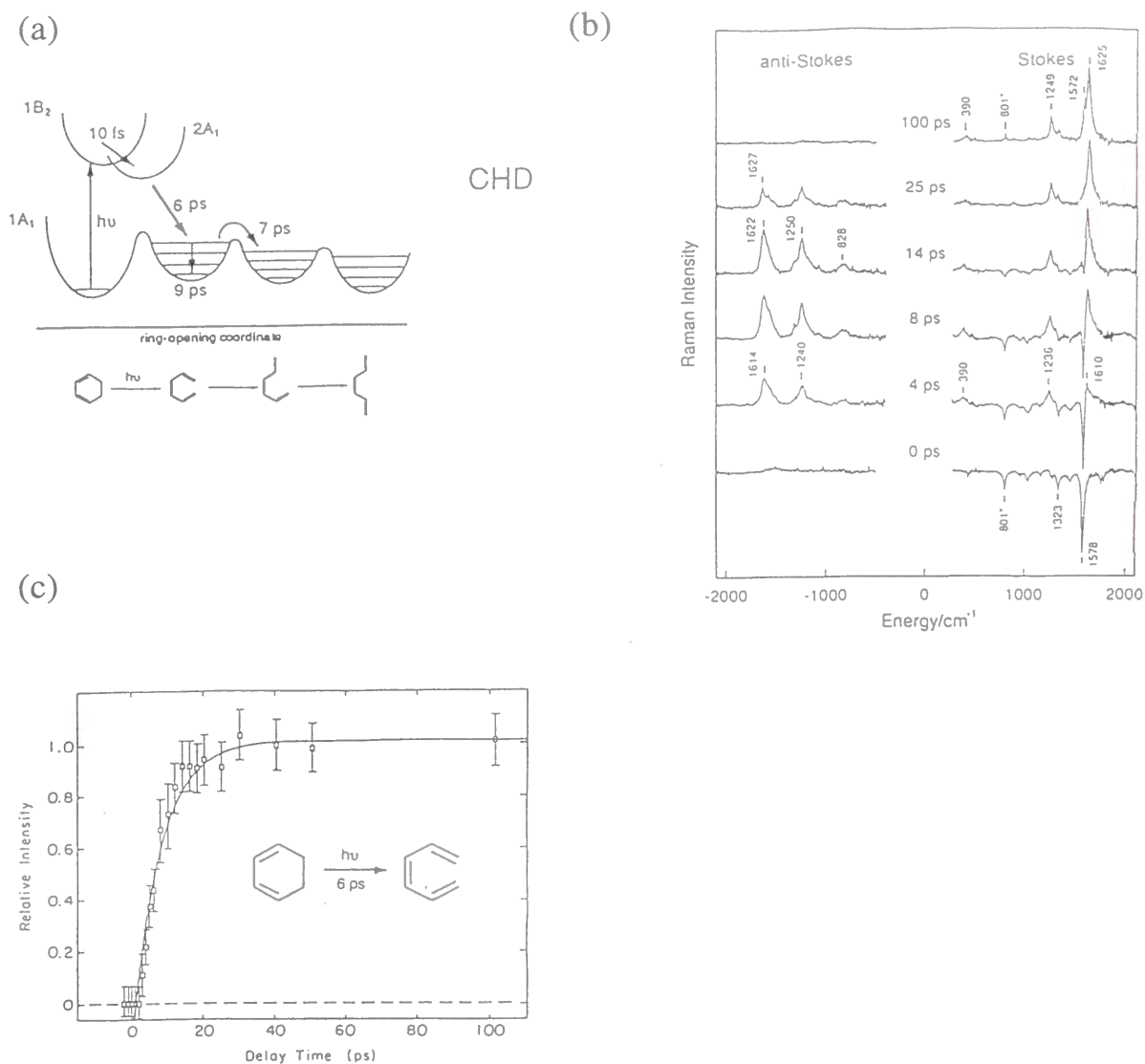


Figure 1-5. (a) Schematic reaction coordinates for the photochemical ring opening reaction of 1,3-cyclohexadiene. This is quoted from Ref. [46].

(b) Resonance Raman Stokes and anti-Stokes difference spectra of the photochemical ring opening reaction of 1,3-cyclohexadiene. The line at 801 cm⁻¹ is due to the cyclohexane solvent. This is quoted from Ref. [46].

(c) Temporal evolution of the cis-1,3,5-hexatriene Stokes ethylenic intensity. Best fit by a single exponential resulted in a ground-state appearance time of 6 ps. This is quoted from Ref. [46].

Very recent femtosecond time-resolved absorption studies indicated that the internal conversion occurred with a time constant of less than 1 ps and is solvent independent [48]. This suggests that the reaction proceeds along a near barrierless reaction coordinate. They discussed the inconsistency of their results with that by resonance Raman experiment. This probably comes from the insufficient time resolution of the picosecond time-resolved resonance Raman spectroscopy.

Fuss and coworkers studied the ring opening reaction of 7-dehydrocholesterol to previtamin D by femtosecond transient absorption spectroscopy [49]. After the photoexcitation of 7-dehydrocholesterol, which is a derivative of 1,3-cyclohexadiene, with 267 nm light, the primary product, all-s-cis conformer (previtamin D) appears with a time constant of 5.2 ps. They observed that the primary photoproduct isomerized thermally to the stable mono-s-cis conformer of previtamin D within 125 ps. They found that it depended on the solvent viscosity and temperature. The activation energy was determined to be 15.5 kJ / mol.

Until recently, there is no direct time-resolved study of the excited dynamics of 1,3,5-hexatriene in solution. Two different groups (Sension & Fuss) performed femtosecond transient absorption measurements of 1,3-cyclohexadiene and trans- and cis-1,3,5-hexatriene in solution [50-52]. They both found that the transient absorption and bleach recovery signals for trans- and cis-1,3,5-hexatriene within 20 ps time scale were similar to that for 1,3-cyclohexadiene. After the photochemical ring opening reaction of 1,3-cyclohexadiene, cis-1,3,5-hexatriene (cZc) is produced. The conformational relaxation of cZc to cZt isomer occurs with 7 ps time constant, which is in competition with the vibrational relaxation. One of them suggested that all photoproducts among these three systems appeared in the same manner. This means that the formation of s-cis isomer and the conformational relaxation around C-C single bond take place competitively with the vibrational relaxation process.

As described before, it is found that there exists quite a large difference in time between the depopulation of the initially excited state and the appearance time of the photoproduct. This means that the majority of the excited-state nuclear dynamics

evolution occurs on the optically dark state. However, the time-resolved Raman spectroscopy did not have sufficient time resolution to reveal the dynamics in the 2A state. Furthermore, the steady-state resonance Raman spectroscopy can only probe the dynamics in a few tens of femtosecond time scale. Therefore femtosecond transient absorption spectroscopy is the most suitable tool to reveal not only the excited-state but also ground-state dynamics of simple linear polyenes. With the advent of the ultrafast laser technology, it is possible to perform the deep UV transient absorption measurements by using tunable UV femtosecond pulses. We expect that these results will help us to explain the reaction dynamics in the solution phase because a reliable theoretical calculation is now available for such a small molecule.

1-4. Photochemical properties of 1,3,5-hexatriene in the solution phase

The quantum yield of the photoisomerization around the C=C double bond in solution is very low ($\phi_{\text{trans-cis}} = 0.016$, $\phi_{\text{cis-trans}} = 0.034$) [2]. The quantum yield of the intersystem crossing to the triplet state is known to be also very low [53]. There has been no report for the observation of the fluorescence in solution at room temperature. This suggests that the fluorescence quantum yield is estimated to be about or less than 10^{-6} . Most of the photoexcited 1,3,5-hexatriene molecules depopulate from the initially prepared excited state in a time scale of 10 fs and should finally return to the original stable forms.

Besides the isomer around the C=C double bonds, there exist three different C-C single-bond isomers for each trans- and cis-1,3,5-hexatriene as shown in Figure 1-6. 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.

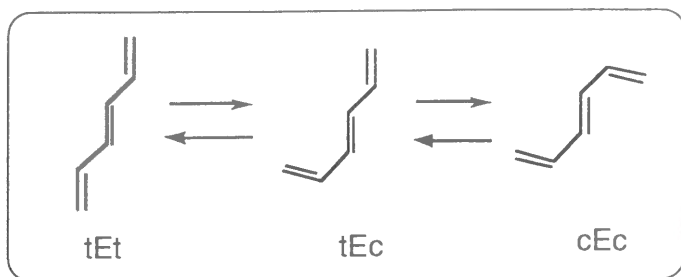
Furukawa and coworkers measured the infrared and ultraviolet absorption spectra of trans- and cis-1,3,5-hexatriene deposited in the low-temperature Ar matrices under irradiation by a Hg 253.7 nm light (Figure 1-6) [54]. In their experiment, a mixture of the sample and Ar gas was heated and deposited onto a CsI or KBr plates. The temperature of the mixture was monitored inside the nozzle. They found a new absorption band in the spectra at around 276 nm and assigned it to s-cis isomers based on the *ab-initio* MO calculation and normal mode analysis [55].

Jacobs and coworkers have investigated the photoreactivity of small polyenes in the solution phases by using various substituted polyene compounds [56,57]. They established the concept in the rationalization of triene photochemistry as follows. The composition of the photoproduct mixture will reflect the composition of the ground-state conformational equilibrium of the starting compound because the species upon the photoexcitation of the ground-state rotamers of a triene will not equilibrate during their short singlet excited-state lifetime. It is termed the Non-Equilibration of Excited Rotamers

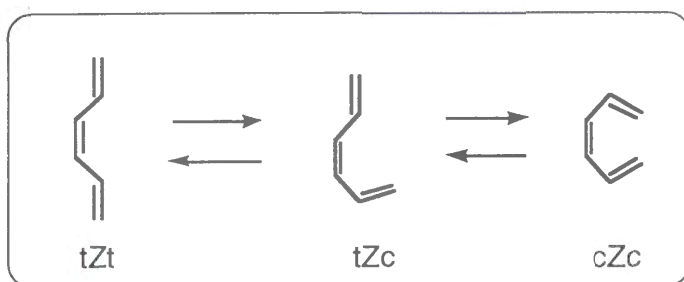
(NEER) principle [2]. Based on this principle, they investigated the stability of the ground-state isomers and its photoreactivity. They also found the creation of the s-cis isomers of dimethyl hexatrienes in Ar matrices based on the UV and IR absorption spectra. These results give a clear clue to reveal the conformational relaxation around the C-C single bond in the ground state, which will be discussed later.

(a)

trans-HT



cis-HT



(b)

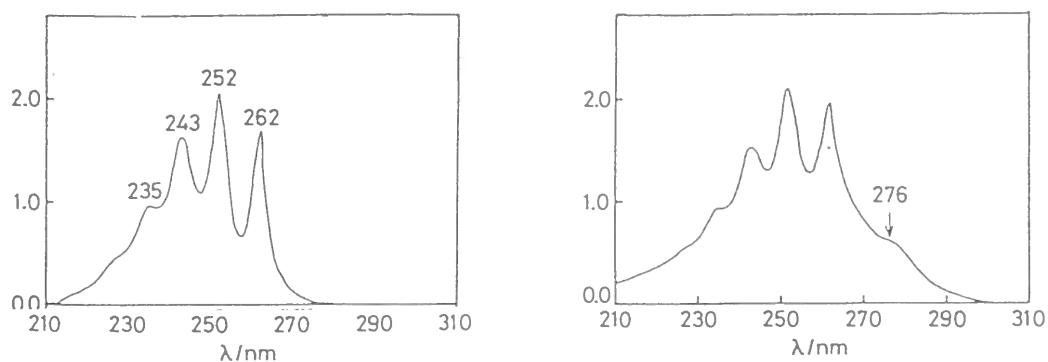


Figure 1-6. (a) The structure of the conformational isomers for trans- and cis-1,3,5-hexatriene.

(b) UV absorption spectra of trans-1,3,5-hexatriene in Ar matrices at 20 K. (1) Nozzle temperature ~ 293 K. (2) Ar matrix deposited under irradiation of Hg 253.7 light, Nozzle temperature ~ 293 K. This is quoted from Ref. [54].

1-5. Photochemical properties of 1,3,5,7-octatetraene

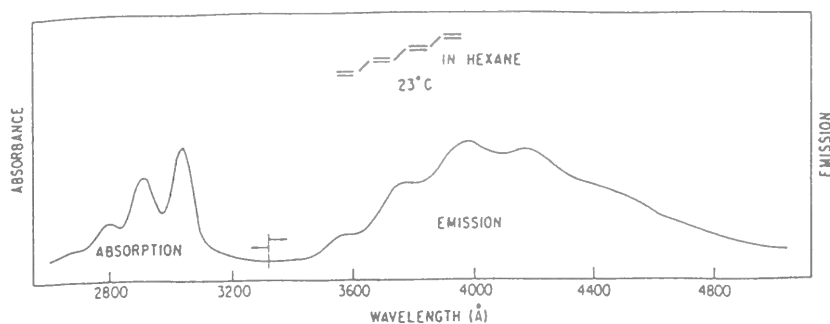
The photodynamics of 1,3,5,7-octatetraene is quite different from that of smaller polyenes such as 1,3-butadiene and 1,3,5-hexatriene [58]. Tetraenes are the shortest polyenes with significant fluorescence quantum yields in both condensed and gas phases. They are also the longest polyenes for which reliable ab-initio calculations are available. It is highly desirable to study the properties of 1,3,5,7-octatetraene because this provides an experimental benchmark for a theoretical understanding of the polyene excited-state dynamics. Here we briefly summarize the previous works of this molecules.

Gavin et al. investigated the absorption and fluorescence spectra of 1,3,5,7-octatetraene in various solutions [58]. They found that there existed a large gap of about 3000 cm^{-1} between the absorption band of the 1^1A_g - 1^1B_u transition and the onset of the fluorescence spectra as shown in Figure 1-7. The peak position of the absorption spectra depends largely on the solvent polarity, however, the 0-0 band of the fluorescence spectrum is independent of the polarity. These results supported for the conjecture of Karplus et al. that the lowest excited singlet state had the 1A_g symmetry [60]. The fluorescence quantum yield from the 2^1A_g state is 0.03 at room temperature.

Kohler and coworkers have applied nanosecond and picosecond time-resolved fluorescence spectroscopy to investigate the relaxation dynamics of the 2^1A_g state of this molecule in hydrocarbon solutions from 10 to 320 K [61]. The decay lifetime decreases with increasing temperature. At room temperature, the lifetime of the 2^1A_g state is 4.3 ns in n-hexane and 3.8 ns in cyclohexane (Figure 1-7). The temperature dependence of the fluorescence lifetime is well fitted by a simple Arrhenius formula. They obtained a barrier height of $\sim 4\text{ kcal/mol}$. They suggested that this barrier was related to the rotation about C-C single bond in the excited state.

The S_n - S_1 spectrum of 1,3,5,7-octatetraene was measured by Kliger and coworkers by nanosecond time-resolved transient absorption spectroscopy [38]. The spectrum is broad, structureless and shows a peak at 330 nm with a long tail to the red region (Figure 1-7). It shows a time dependence similar to that of the fluorescence.

(a)



(b)

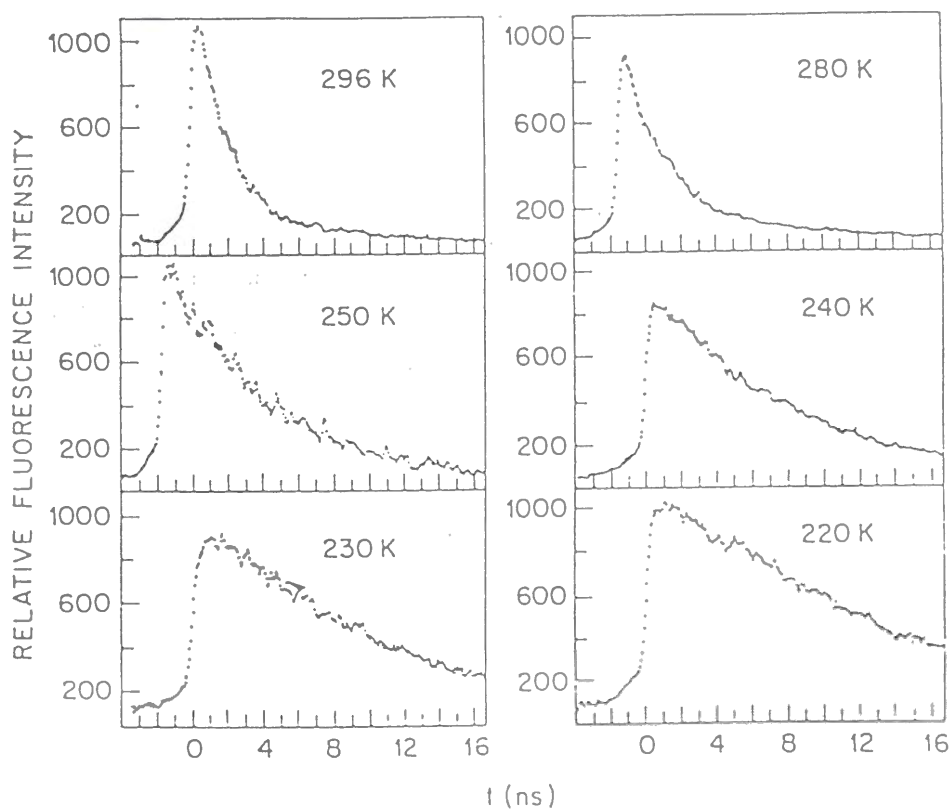


Figure 1-7. (a) Absorption and emission spectra of all-trans 1,3,5,7-octatetraene in hexane at room temperature. This is quoted from Ref.[59].

(b) Emission intensity as a function of time for all-trans 1,3,5,7-octatetraene in n-octane at various temperatures. This is quoted from Ref. [61].

(c)

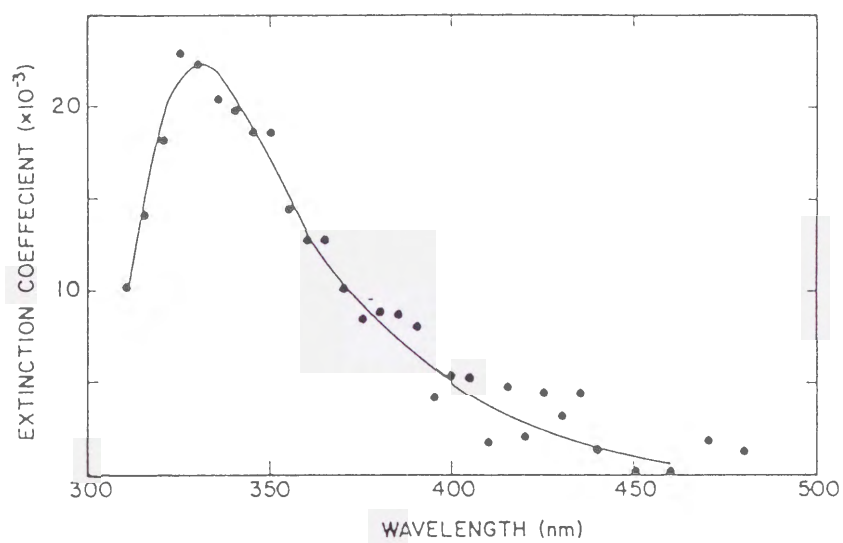


Figure 1-7. (c) The excited singlet state absorption spectrum of all-trans 1,3,5,7-octatetraene in cyclohexane. This is quoted from Ref.[38].

In the gas phase, not only the fluorescence from the S_1 state but also that from the S_2 state is easily observed. Christensen and coworkers investigated the properties of 1,3,5,7-octatetraene and its methyl substituted derivatives [62]. The ratios of the two fluorescence quantum yield (2A-1A and 1B-1A) increase significantly when terminal methyl groups are added to octatetraene. The S_2 - S_1 energy gaps are almost identical for these compounds, suggesting that the difference in the internal conversion efficiencies is due to the larger density of vibronic states in the methyl-substituted compounds. Vibronic line widths have been used to estimate a subpicosecond lifetime for the zero-point level of the 1^1B_u state and indicate the coupling between the 1^1B_u and 2^1A_g manifolds in the statistical limit.

Petek and coworkers have measured the fluorescence excitation spectra of this molecule after the direct photoexcitation to the 2^1A_g state [63,64]. They concluded that the Herzberg-Teller coupling was so strong that the forbidden 2^1A_g - 1^1A_g transition had sufficient oscillator strength to be observed in the fluorescence excitation spectra. Fluorescence lifetimes indicate abrupt onsets of nonradiative decay process at $\sim 2100\text{ cm}^{-1}$ excess energy [63]. They tentatively assigned it to trans-cis isomerization. A refined experiment shows that the decay rate increases stepwisely with increasing the excess energy [64]. This indicates the quantization of the vibrational levels of the transition state for the cis-trans isomerization around a double bond. The energy spacing of 80 cm^{-1} between the first two steps is ascribed to an in-plane bending vibration of the transition state.

1-6. Theoretical works of simple polyenes

The topology and energetics of the potential energy surface in small polyenes were calculated theoretically by Robb and coworkers [65,66]. They discussed the reactivity in terms of the conical intersection of excited- and ground-state potential energy surface. Here we briefly describe the theoretical work done by Robb and coworkers. We also mention the molecular dynamics simulation of 1,3-butadiene.

The reaction pathway of a photochemical reaction starts on the excited-state potential energy surface in the Franck-Condon region or at a spectroscopic potential minimum and ends the product potential minimum on the ground state. The internal conversion from the excited to ground state is possible to occur at a funnel. For a long time, it is believed that the crossing between the states of the same spatial symmetry or the spin multiplicity is at least weakly avoided along the single reaction coordinate due to the symmetrical restriction. (It is often called "rule of noncrossing"). However, recent theoretical works show that for a great number of chemical systems the crossings are actually unavoided and correspond to the conical intersection [67,68].

A conical intersection is defined as follows: Two state, even if they have the same symmetry, intersect along an $(F-2)$ -dimensional hyperline as the energy is plotted against the F nuclear coordinates ($F=3N-6$). The resulting energy plot will resemble two cones (one inverted on the top of the other) connected through their vertexes (Figure 1-8), and the energies of two states are the same for any point of the $(F-2)$ -dimensional intersection space. At a conical intersection, a fast radiationless decay to the ground state is possible, and the structure and energetic accessibility of the conical intersection can determine the type and yield of the possible photoproducts. In other words, since in the region surrounding a conical intersection point, there is a large probability of the decay, the molecule reaches a ground-state entrance only after this region of the excited-state surface is accessed.

For 1,3,5-hexatriene, a theoretical calculation predicts that there exist two channels 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 activation energies for double-bond and single-bond rotations are 4 and 6 kJ/mol, respectively. These conical intersections branch to the product or reactant in the ground state. Petek et al. observed the fluorescence excitation spectra of cis-1,3,5-hexatriene in a jet-cooled condition [33]. It is revealed that there exist two different radiationless decay channels. The first channel is barrierless and the second one has a barrier of about 2 kJ / mol. Although the magnitude of the estimated barriers to the two conical intersection is different from those by this calculation, the existence of these features on the excited-state potential energy surface could indeed play an important role in explaining their experimental observation and very low fluorescence quantum yield in 1,3,5-hexatriene.

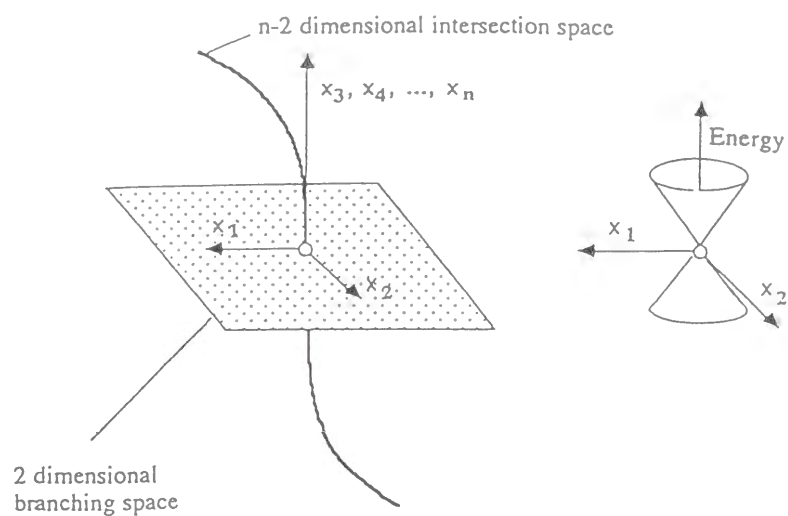
For 1,3,5,7-octatetraene, the S_1 - S_0 radiationless decay channel is found to be reached following the motion along a trans-cis isomerization path leading to a point where the S_1 and S_0 energy surfaces are conically intersecting and one of the two central C=C double bonds is ~75 degree twisted. The photoisomerization occurs non-adiabatically. The predicted barrier of about 6 kcal / mol is consistent with the experimental ones. This calculation also reproduces a 80 cm⁻¹ step in the decay rate constant of the fluorescence signals in the gas phase [66].

Itoh and Ohmine performed molecular dynamics simulation of the photoisomerization dynamics of s-trans butadiene by a semiclassical surface hopping trajectory method [69]. CASSCF/DZ+d calculation is used to evaluate the 1^1A_g and 2^1A_g potential energies at various conformations. They used the Heisenberg Hamiltonian to fit two covalent 1^1A_g and 2^1A_g states. They found that this model Hamiltonian reproduced well the structure of the potential energy surfaces of these states and the nonadiabatic coupling of the ab-initio calculation. The photoisomerization through the three partially twisted C-C conformations assisted by the CCC bendings is confirmed to a dominant channel of the internal conversion from the 2^1A_g to 1^1A_g state. The π electron energy is shown to flow to other modes before the decay of the population in the 2^1A_g state. This model calculation can explain the qualitative behavior of the excited-state dynamics of 1,3-

butadiene, even though a more elaborate model is required for quantitative analysis of the photoisomerization dynamics.

In this section we briefly discuss several theoretical works of simple polyenes. These works could predict the excited-state dynamics of simple polyene fairly well. They give us interesting conclusion as follows. It is well known that there is only one $2A$ minimum which is common to the cis and trans isomers in the case of ethylene and stilbene. This state is located at a torsion angle of the $C=C$ double bond of 90 degree and we call it a sudden polarization state. One would expect the same branching ratios for both starting compounds. In contrast to this, the triple CC torsion which leads to the conical crossing of the $2A$ to $1A$ states is the major path to yield a very fast nonadiabatic transition for linear polyenes such as 1,3-butadiene and 1,3,5-hexatriene and so on. The conical intersection proves to play an important role in the ultrafast internal conversion in simple polyenes.

(a)



(b)

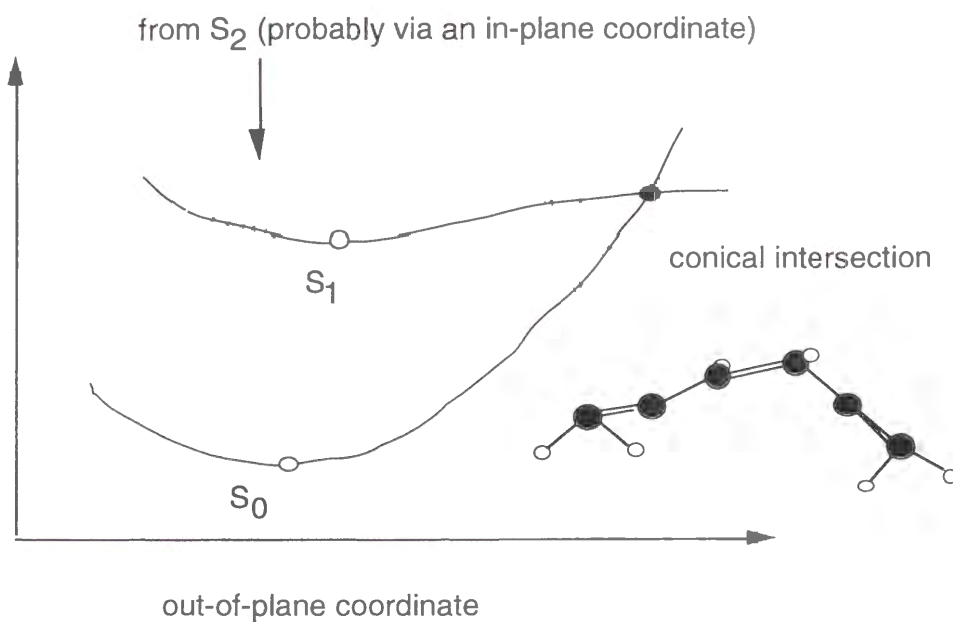


Figure 1-8. (a) Schematic representation of the conical intersection. This is quoted from Ref. [67].

(b) Schematic representation of the potential surface of 1,3,5-hexatriene. Inset shows the geometric structure of trans-1,3,5-hexatriene in the conical intersection.

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Chapter 2

Experimental

2-1. Laser system

The laser system for the present measurement is schematically shown in Figure 2-1. A laser system was based on a self mode-locked Ti:sapphire laser (NJA-5, Clark-MXR) pumped by a CW argon ion laser (Spectra Physics 2060). The oscillator was seeded into a regenerative amplifier (CPA-1000, Clark-MXR) to provide amplified pulses.

The pump laser was an argon-ion laser that operated on all lines at 4 W. The pump beam passed through a periscope arrangement to rotate the plane of polarization by 90 degree. The beam position was stabilized by using two different controllers (Beamlok and Point Master). The resulting beam was focused into the Ti:Sapphire gain medium. A Ti:Sapphire oscillator had intracavity prisms for dispersion compensation and was operated based on a Kerr-lens mode-locking. The oscillator pulse had a power of 400 mW at 100 MHz repetition rate at 800 nm. A typical pulse width was around 70 fs. For tuning purposes, the slit was placed in front of the end mirror.

In order to obtain enough power of the laser for the transient absorption measurement, we amplified the pulse from the oscillator. However, the peak power of a femtosecond pulse is high enough to damage the crystal and optics in the amplification process. It is necessary to decrease the peak intensity of the pulse before amplification. This process is achieved by the chirp pulse amplification.

The output of the oscillator was brought into the isolator to the selection of the beam pass for the incoming and outgoing to the regenerative amplifier. By using a Faraday rotator, half waveplate, and a polarizer, we controlled the polarization of the pulse to isolate it optically.

The output of pulse from the isolator was temporally stretched to ~200 ps by a pair of gratings and a concave mirror. The stretched pulses were injected into a Ti:Sapphire regeneratively amplifier (Clark CPA-1000). This was pumped by an intracavity-doubled Q-switched Nd:YAG laser at a repetition rate of 1kHz (Clark MXR, ORC-1000). The power of the second harmonics of Nd:YAG laser was 8 W. The injection and cavity damping were controlled by a Pockels cell. The amplified pulse was

selected by the timing of cavity damping among the amplified pulse train. The power of the regeneratively amplified pulse before compression was typically 1.5 W. These pulses were recompressed by a grating and mirror. A pair of the gratings and a mirror provided a negative group velocity dispersion to the input pulse. The conversion efficiency in the pulse compressor was less than 70 %. After recompression, we finally obtained an amplified pulse of 120 fs duration with an energy of 1mJ, centered at 800 nm and repetition rate of 1kHz.

Regeneratively Amplified

Ti : sapphire laser

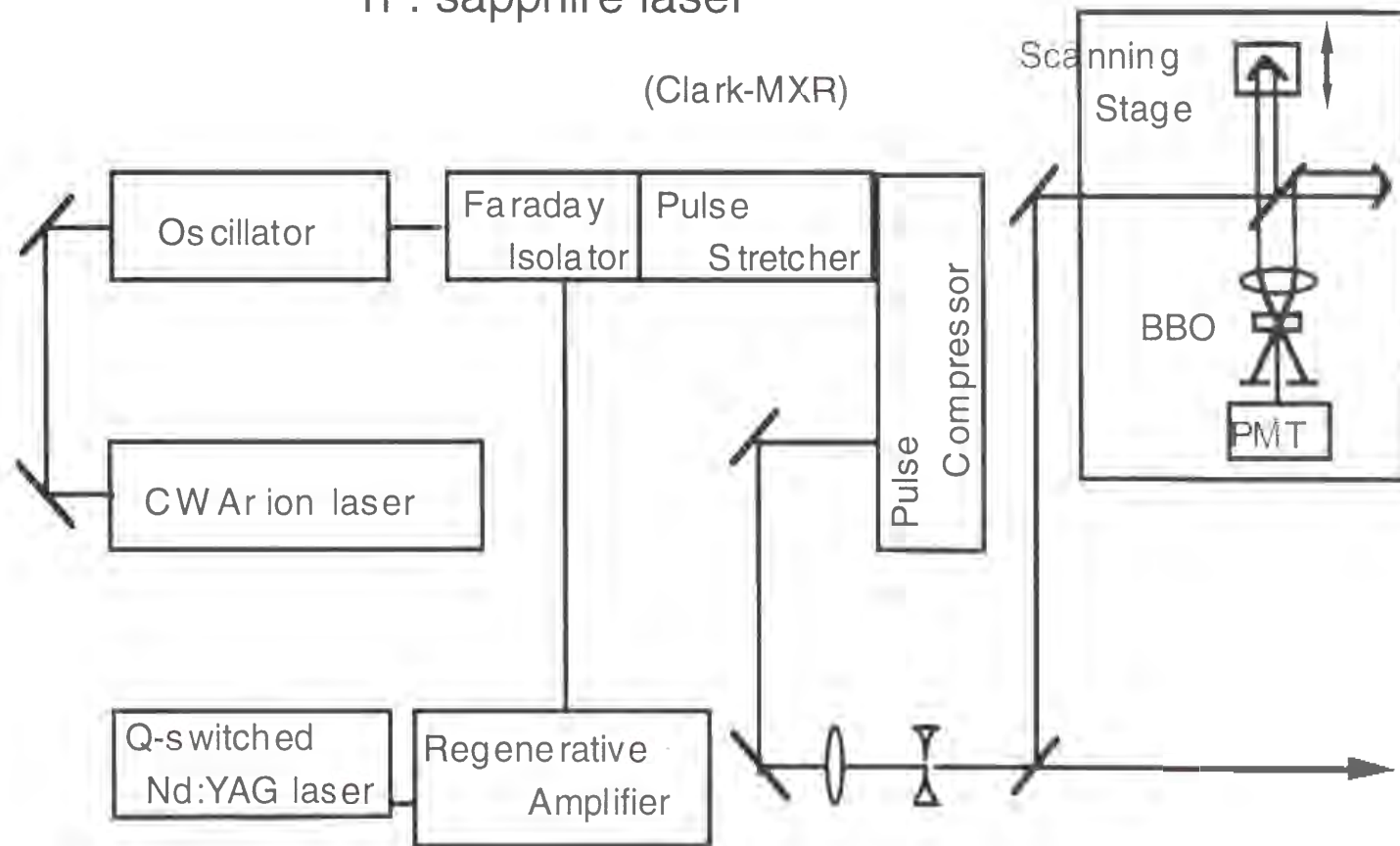


Figure 2-1. Schematic diagram of a regeneratively amplified Ti:Sapphire laser system.

2-2. Transient absorption spectrometer.

Schematic configuration for the transient absorption measurement is displayed in Figure 2-2 [1-4]. We used the third harmonic of a Ti:Sapphire laser and white light continuum for pump and probe pulses, respectively. The fundamental pulse was doubled by a 1mm 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 (267 nm) was used as a pump pulse. The excitation energy incident on the sample was about 10 $\mu\text{J}/\text{pulse}$. The other part was focused into H_2O or D_2O flow cell to generate the white light continuum which lay between 300 nm 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 optical path of pump pulse.

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 fluctuations of the probe pulse. The output of photodiodes was gated and integrated by boxcar integrators (Stanford Research Systems SR 250), and the logarithm of the ratio of the outputs of the signal and references was obtained with an analog processor. The output of the analog processor was averaged by a third boxcar that was operated in the toggle mode. The calculation of the absorbance change was performed as follows. The output of the analog processor was proportional to $\log(I_{\text{probe}}/I_{\text{ref}})$. By chopping the excitation pulses every other shots, the absorption change was obtained as follows.

$$\log\left(\frac{I_{probe'}}{I_{ref}}\right) - \log\left(\frac{I_{probe}}{I_{ref}}\right) = \log\left(\frac{I_{probe'}}{I_{probe}}\right)$$

The signals was fed into a computer and averaged.

The pulse duration 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.

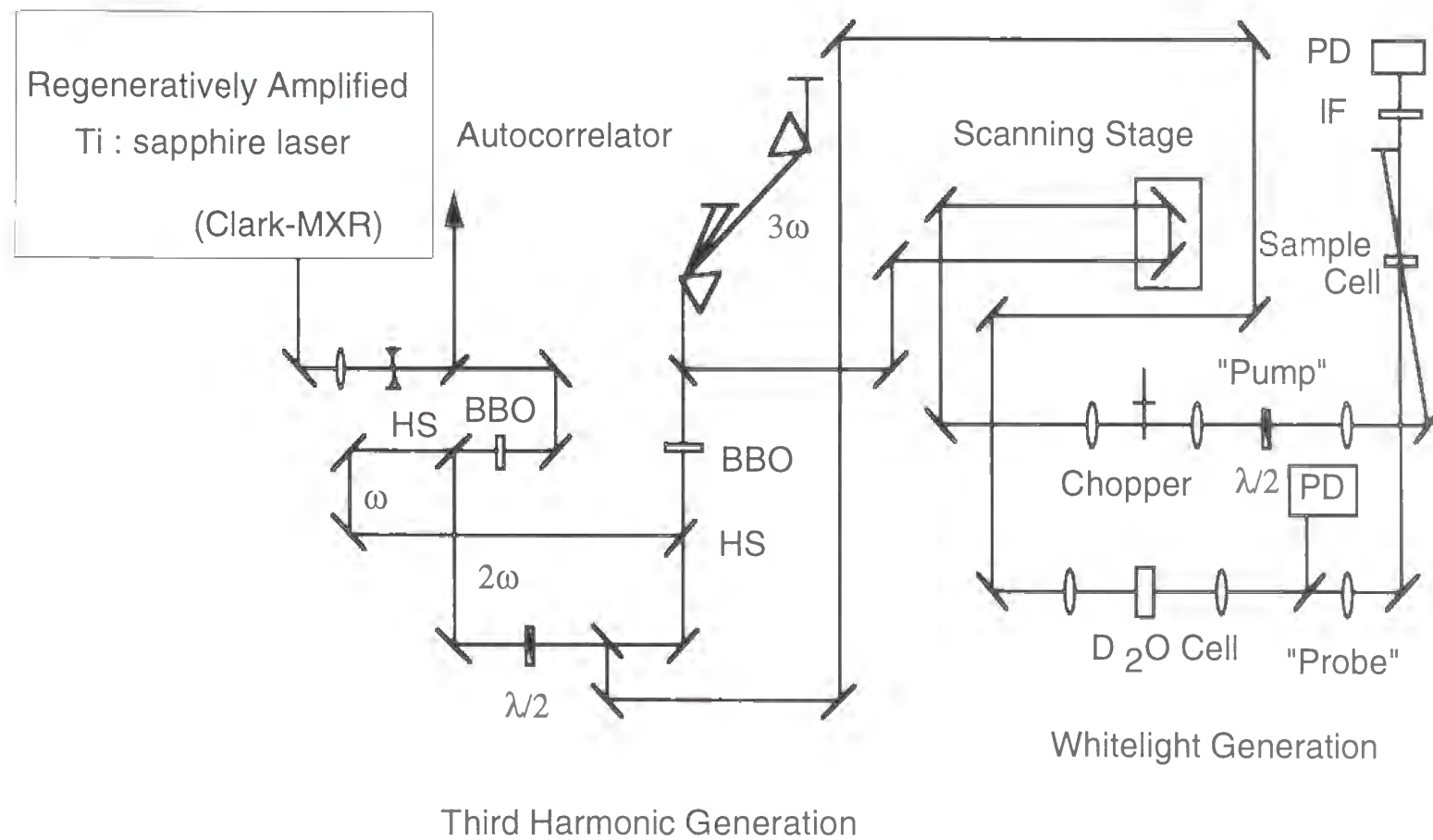


Figure 2-2. Schematic diagram of an apparatus for transient absorption measurement.

HS, Harmonic separator; PD, Photodiode; IF, Interference filter; $\lambda/2$, $\lambda/2$ waveplate.

2-3. Reagents

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. [5]. Trans-1,3,5-hexatriene was prepared by iodine-catalyzed isomerization. To a 1-2 g isomer mixture were added several crystals of iodine. The stirred and N₂-purged mixture was allowed to react about 8 hour at room temperature. The product was then transferred to a small tube on a vacuum line at room temperature. The remaining cis isomer was removed on the vacuum line at - 20 degree (dry ice in CCl₄). The sample was kept in -40 degree before use of the experiment. Cis-1,3,5-hexatriene was isolated from the mixture via Diels-Alder cycloaddition of the trans isomer to maleic anhydride. The 2 g isomer mixture were added to 4-6 g maleic anhydride. The stirred and N₂-purged mixture was allowed to react about 6-8 hour at room temperature was kept at -20 degree temperature overnight. The product was collected in a receiver cooled by liquid N₂.

The isomeric purity of the product was checked by gas chromatography, which was higher than 95% for each isomer. The results of the analysis are shown in Figure 2-3. Cyclohexane and acetonitrile (spectrograde, Wako Chemicals) were used without further purification. The sample solution was flowed through a quartz cell with a 1 mm optical path length at a flow rate fast enough to assure 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 solution 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 an ambient temperature (293 K).

A sample of trans,trans-1,3,5,7-octatetraene was prepared as follows: 2,4-hexadienal was reacted with vinylmagnesium bromide following the procedures described by D'Amico et al. to produce 1,4,6-octatrien-3-ol [6]. Dehydration of 1,4,6-octatrien-3-ol at 80 degree using p-toluene sulfonate catalysis following the procedure of Yoshida et al. yielded isomerically pure all trans isomer [7]. Crystalline samples were dissolved in

solvent after the distillation so as to prevent the polymerization. Solution was kept at 0 degree before using in the experiments.

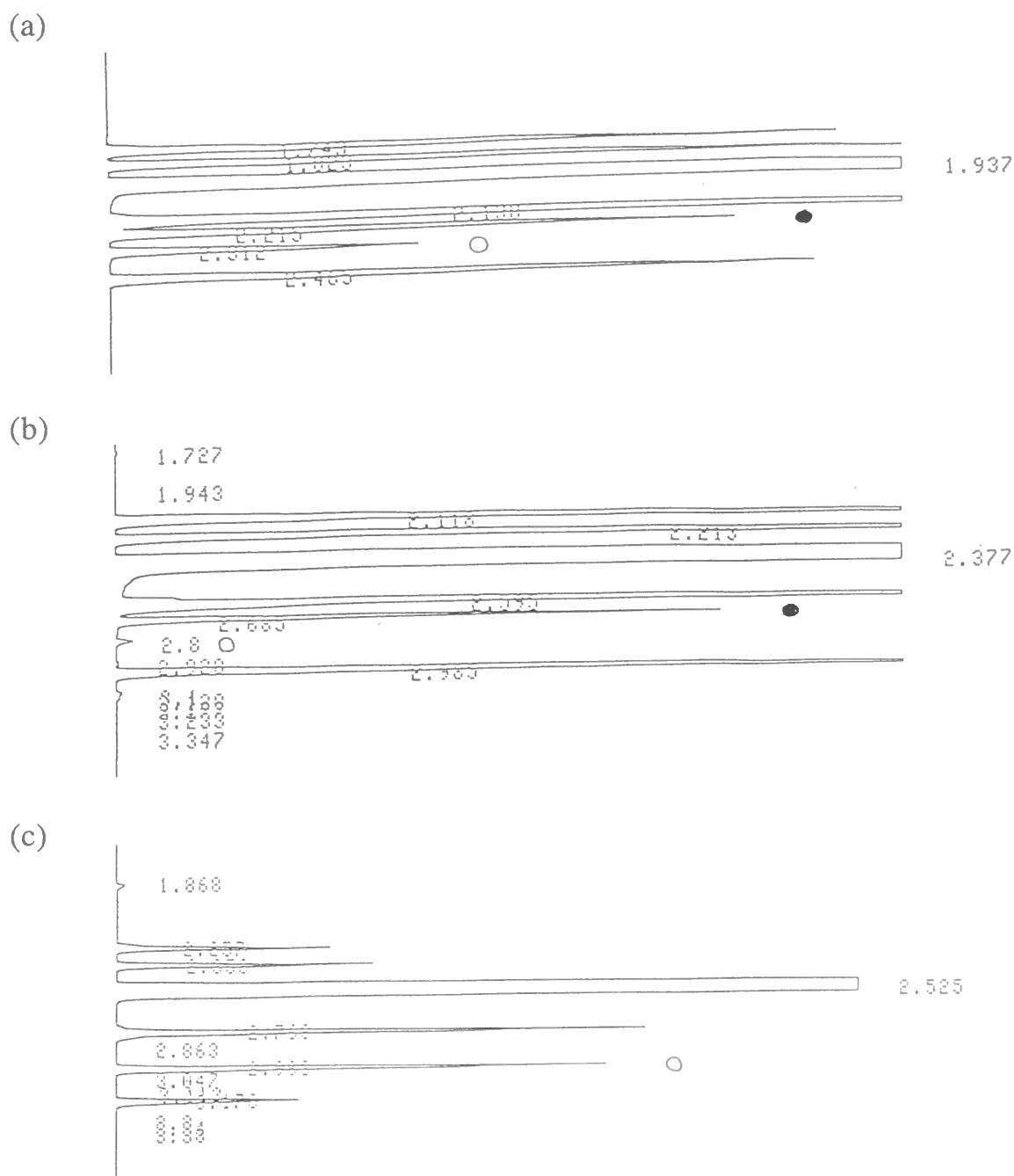


Figure 2-3. Results of the analysis by gas chromatography (a) before reaction, (b) after the iodine-catalysed reaction, (c) after the Diels-Alder reaction with maleic anhydride. The closed and open circles show the trans and cis isomers, respectively. The other peaks are impurities in the solvent.

References and Notes

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Chapter 3

Ultrafast Dynamics of the Photoexcited

1,3,5-Hexatriene in Solution

3-1. Introduction

The electronic structures and spectroscopic properties of simple linear polyenes have stimulated a great deal of experimental and theoretical studies over the past two decades [1-4]. From biological point of view, polyene derivatives such as retinal and carotenoids play important roles in the vision and light harvesting systems.

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 [5-9]. The 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 the each step in the dynamics of smaller linear polyenes in detail. Recently a refined molecular orbital calculation and molecular dynamics simulation 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 [12-17].

In this section, 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 the 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 in 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 difference between trans- and cis-1,3,5-hexatriene are discussed.

3-2. Results

3-2-1 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 3-1. This molecule has a very strong absorption band from 230 nm to 280 nm. The maximum molar extinction coefficient in cyclohexane is $\epsilon_{\text{max}}=51740 \text{ M}^{-1}\text{cm}^{-1}$ for trans isomer and $41000 \text{ M}^{-1}\text{cm}^{-1}$ for cis isomer [18,19]. The 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 [18,19].

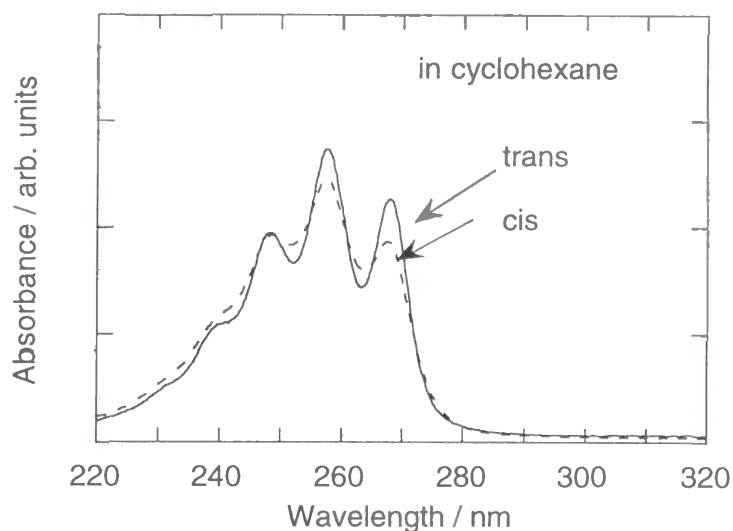


Figure 3-1. Static absorption spectra of trans-1,3,5-hexatriene (solid line) and cis-1,3,5-hexatriene (dashed line) in cyclohexane. Each spectrum is scaled by arbitrary units.

3-2-2 Transient absorption signals of trans- and cis-1,3,5-hexatriene in solution

The transient absorption data were collected for trans-1,3,5-hexatriene in cyclohexane and acetonitrile with an excitation wavelength of 268 nm and the results at five probe wavelengths ranging from 340 nm to 550 nm are shown in Figure 3-2. The time profiles of the signals are fitted to a sum of the exponential functions convoluted with the instrument response function. Table 3-1 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 3-3 displays the transient absorption data collected for cis-1,3,5-hexatriene in cyclohexane and acetonitrile at five wavelengths from 340 nm to 550 nm. These absorption signals possess an instantaneous rise and subpicosecond decay component which are rather similar to those for trans isomer, but one. 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 3-2. The contribution 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 signals decay with the time constant of 13 ps at 400 nm and 5 ps at 420 nm.

The transient absorption spectrum of trans- and cis-1,3,5-hexatriene in cyclohexane at time zero was measured as shown in Figure 3-4. 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 trans isomer is similar to that for cis isomer at time zero within our experimental uncertainty.

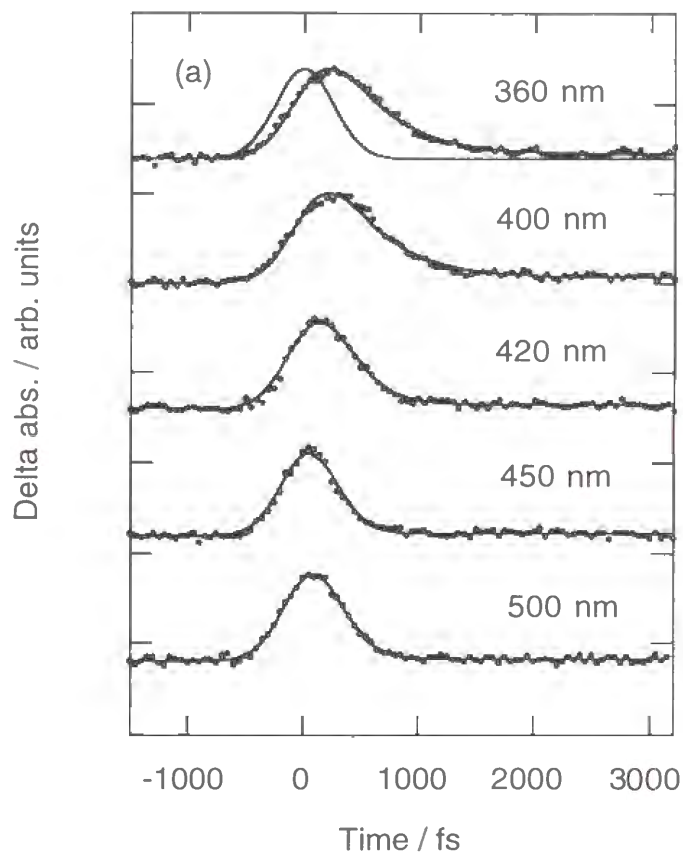


Figure 3-2. (a) Transient absorption signals probed at five different wavelengths for trans-1,3,5-hexatriene in cyclohexane. The instrument response function is shown in the top decay curve. The solid line represent the best fits to the data by the convolution of the instrument response function with a sum of the two exponentials.

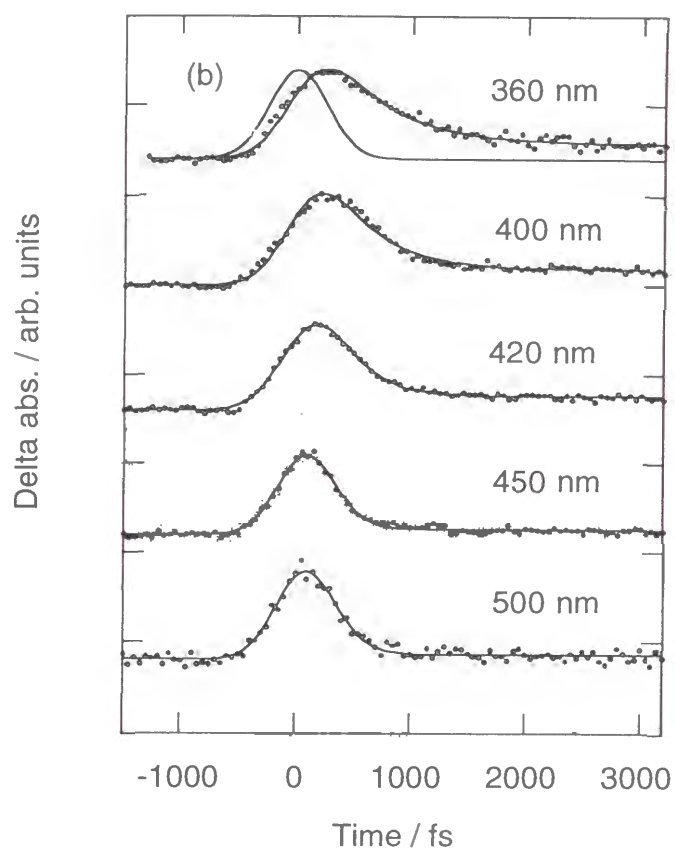


Figure 3-2. (b) Transient absorption signals probed at five different wavelengths for trans-1,3,5-hexatriene in acetonitrile. The instrument response function is shown in the top decay curve. The solid line represent the best fits to the data by the convolution of the instrument response function with a sum of the two exponentials.

Table 3-1. The 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.

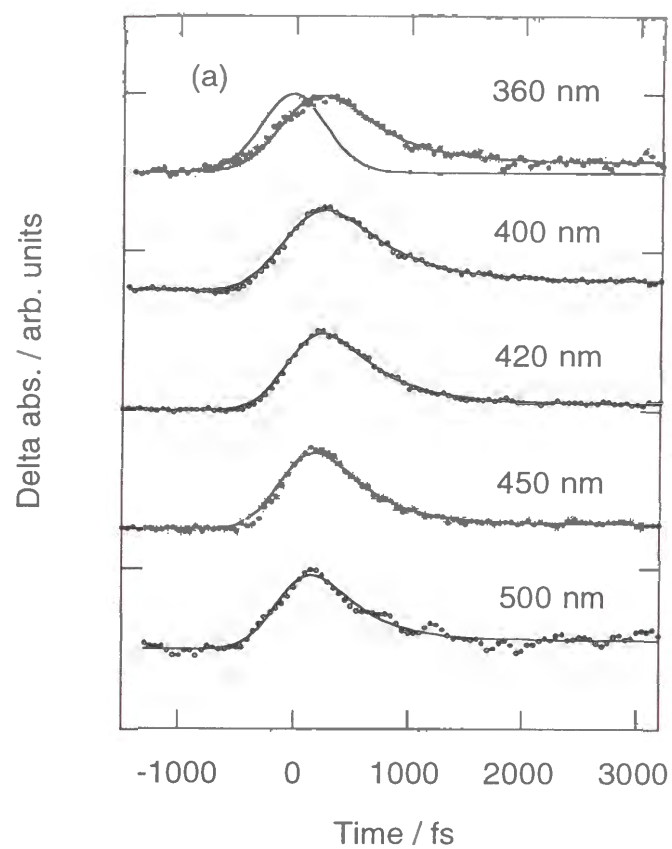


Figure 3-3. (a) Transient absorption signals probed at five different wavelengths for cis-1,3,5-hexatriene in cyclohexane.

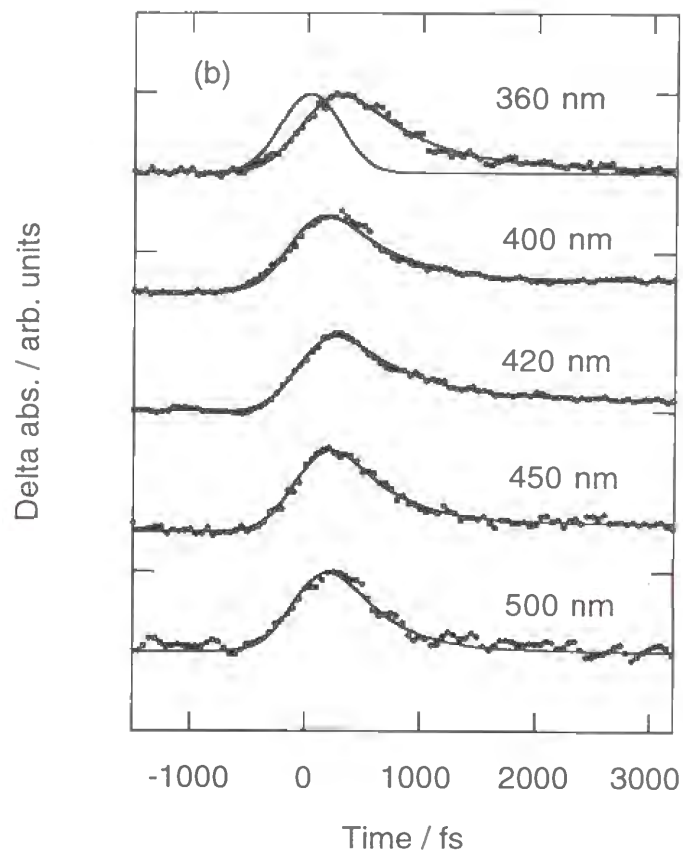


Figure 3-3. (b) Transient absorption signals probed at five different wavelengths for cis-1,3,5-hexatriene in cyclohexane.

Table 3-2. The 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.

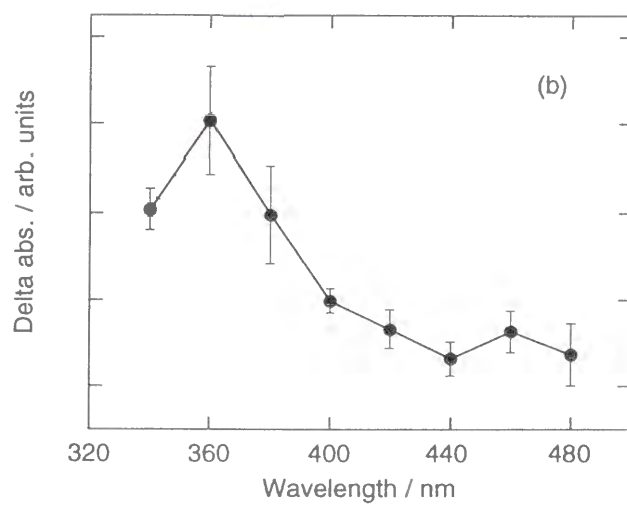
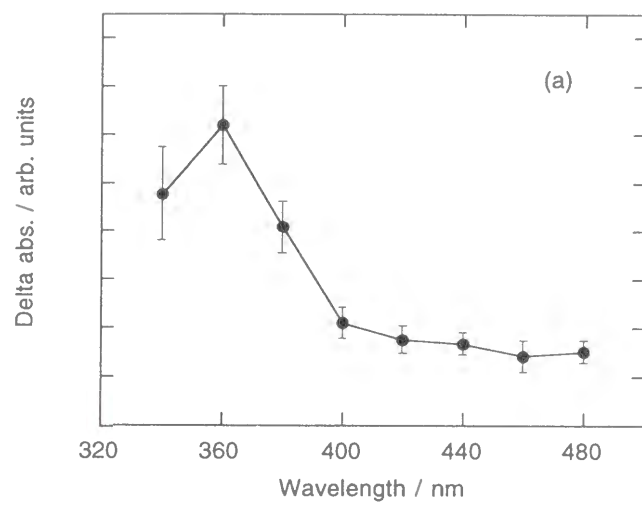


Figure 3-4. Transient absorption spectrum of (a) trans- and (b) cis- 1,3,5-hexatriene in cyclohexane observed at the zero time delay.

3-2-3 Transient bleach recovery signals of trans-1,3,5-hexatriene in solution

Figure 3-5 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 nm and 257 nm and the bottom between these peaks, 263 nm in cyclohexane. The corresponding peaks and the bottom 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 3-3.

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 ps and 150 ps. However, the transient at 262 nm recovers faster than that at 268 nm and reaches the baseline at around 20 ps, and 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 ps and 180 ps.

Figure 3-6 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 constants 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 longer recovery with the time constant of 320 ps. At 259 nm, the behavior is similar to that between 268 nm and 259 nm. The slower component recovers with the time constant of 305 ps.

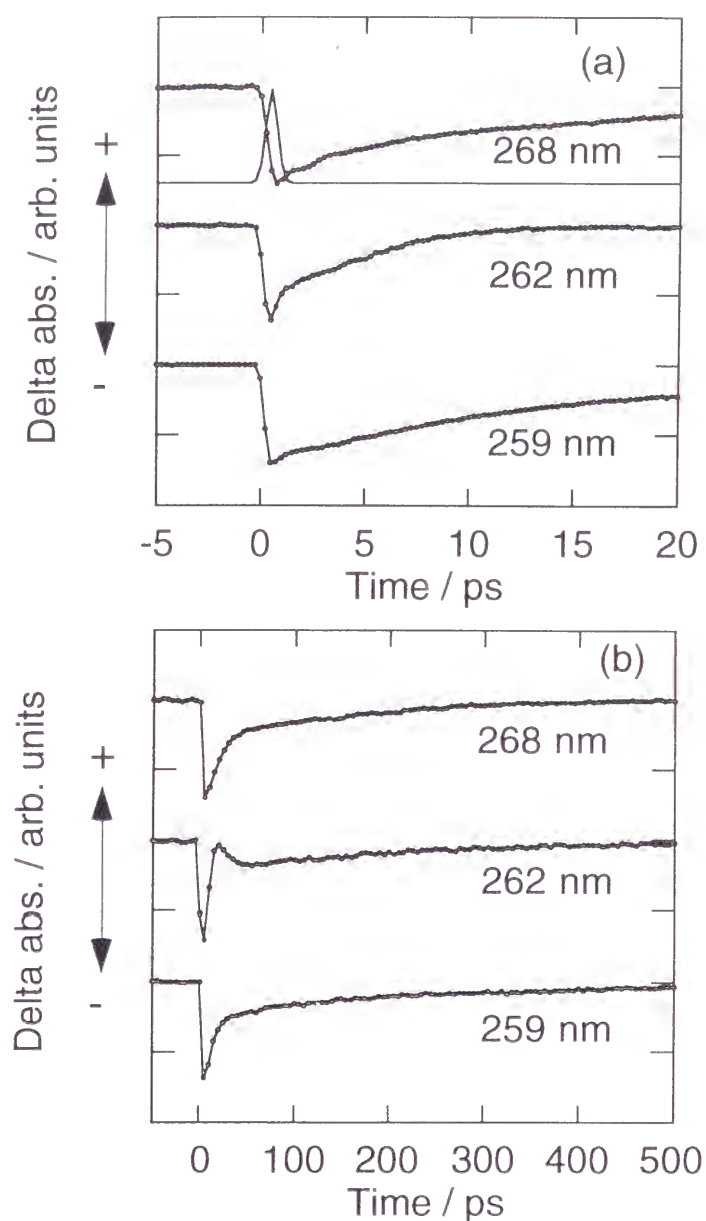


Figure 3-5. Transient bleach recovery signals (a) within 20 ps time scale and (b) subnanosecond time scale by a one-color pump-probe experiment at three different wavelengths for trans-1,3,5-hexatriene in cyclohexane. The instrument response function is shown in the top decay curve of the left figure.

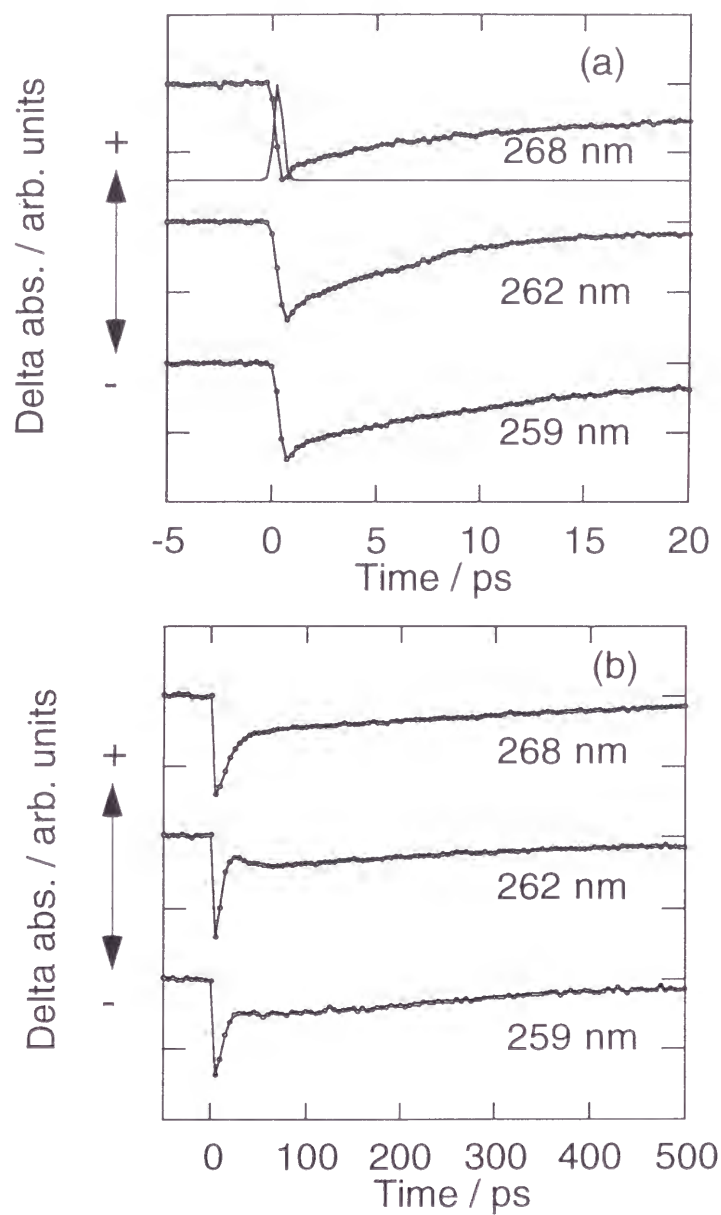


Figure 3-6. Transient bleach recovery signals (a) within 20 ps time scale and (b) subnanosecond time scale by a one-color pump-probe experiment at three different wavelengths for trans-1,3,5-hexatriene in acetonitrile.

Table 3-3. Best fit time constants of transient bleach recovery signals obtained by one-color pump-probe method. * shows the data which can not be fitted well by a sum of exponential functions.

Solute / Solvent	λ / nm	τ_1 / ps ^a	τ_2 / ps ^a	τ_3 / ps ^c
trans-HT	268	$0.8 \pm 0.1(0.38)^b$	18 ± 1 (0.62)	150 ± 10
/ cyclohexane	262	*	*	180 ± 20
	259	0.6 ± 0.2 (0.09)	13 ± 1 (0.91)	184 ± 10
trans-HT	268	$1.2 \pm 0.1(0.31)$	16 ± 1 (0.69)	325 ± 15
/ acetonitrile	262	*	*	325 ± 35
	259	*	*	305 ± 30
cis-HT	268	-----	12 ± 1	-----
/ cyclohexane	262	*	*	-----
	259	*	*	-----
cis-HT	268	-----	13 ± 1	175 ± 15
/ acetonitrile	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.

3-2-4 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 3-7. The temporal profiles of cis isomer in the first 20 ps are similar to those of 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 show 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 3-8 shows the data for 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.

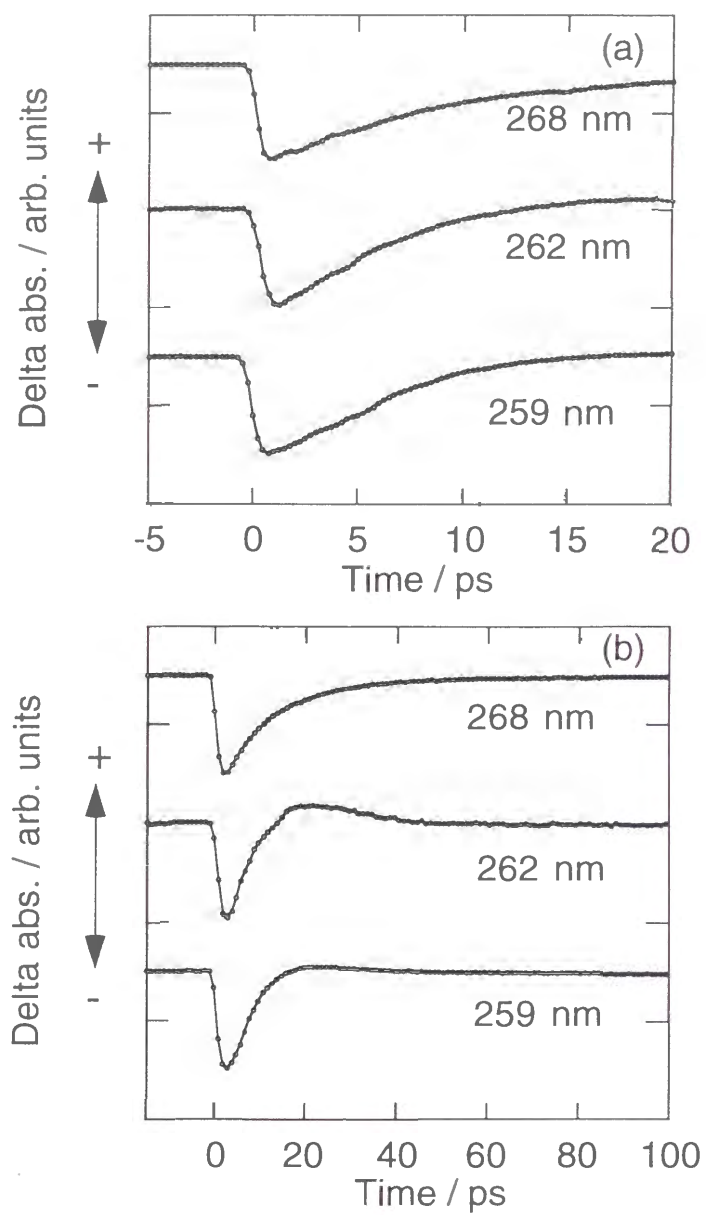


Figure 3-7. Transient bleach recovery signals (a) within 20 ps time scale and (b) subnanosecond time scale by a one-color pump-probe experiment at three different wavelengths for cis-1,3,5-hexatriene in cyclohexane.

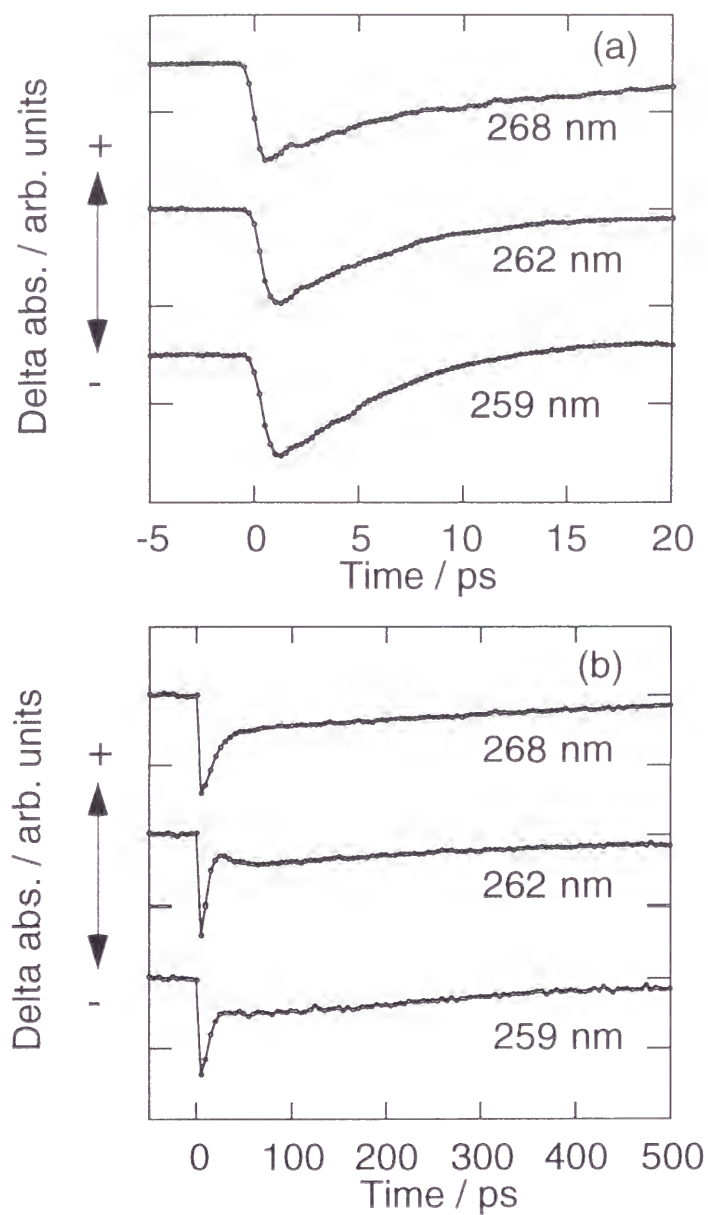


Figure 3-8. Transient bleach recovery signals (a) within 20 ps time scale and (b) subnanosecond time scale by a one-color pump-probe experiment at three different wavelengths for cis-1,3,5-hexatriene in acetonitrile.

3-3. Discussion in the transient absorption signals

3-3-1. 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.

Based on the lineshape analysis of the resonance Raman spectroscopy, the initial motion of the wavepacket out of the Franck-Condon region in the 1B state occurs at 40 fs for trans isomer and 20 fs for cis isomer [18,19]. For the photochemical ring opening reaction of 1,3-cyclohexadiene and related compounds, Mathies and coworkers suggested that this time scale was consistent with the depopulation time of the 1B state from the fluorescence quantum yield measurement [20,21]. Vaida and coworkers estimated the time constant for the internal conversion to the 2A state to be 40 fs in the isolated molecule condition based on the linewidth of the absorption spectra [12]. Furthermore, 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 and the internal conversion proceeded through the 2A state, in which population decays with the time constant of about 250 fs [22]. 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.

By internal conversion, the vibrationally excited 2A state is populated. In the gas phase, the lifetimes of the 2A state for trans and cis isomers are 270 fs and 730 fs, respectively [23]. The time-delayed photoelectron spectra showed that the vibrational energy redistribution of cis isomer within the 2A state occurred at around 300 fs [24]. For 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 was independent of energy, and another which required an activation energy of $<155.7 \text{ cm}^{-1}$ [16]. Fuss and coworkers have studied the excess energy dependence of cis isomer on the lifetime in pumping directly to the 2A state [24]. 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} . This is identical with the rate which was found when it is pumped to the 1B state. A theoretical calculation predicts that there exist 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). Since the quantum yield of the photoisomerization around C=C double bond is very small, a photoexcited molecule passes through the latter conical intersection where a fast radiationless decay is possible. The barrier height for the conical intersection between the S_0 and S_1 state is less than 4 kJ / mol . The population can reach this point easily even with a low excess energy of less than 4 kJ / mol .

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 competes 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 3-9. 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 1A and 2A state.

For trans isomer, we observed that the decay of the transient absorption signals depended on the probe wavelengths. This reflects that the efficiency of the internal conversion is significantly different among the vibrational levels in the potential energy surface of the 2A state. After creating the population in the vibrationally excited 2A state, the internal conversion to the ground state occurs directly before the vibrational energy redistribution completes. 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 trans isomer.

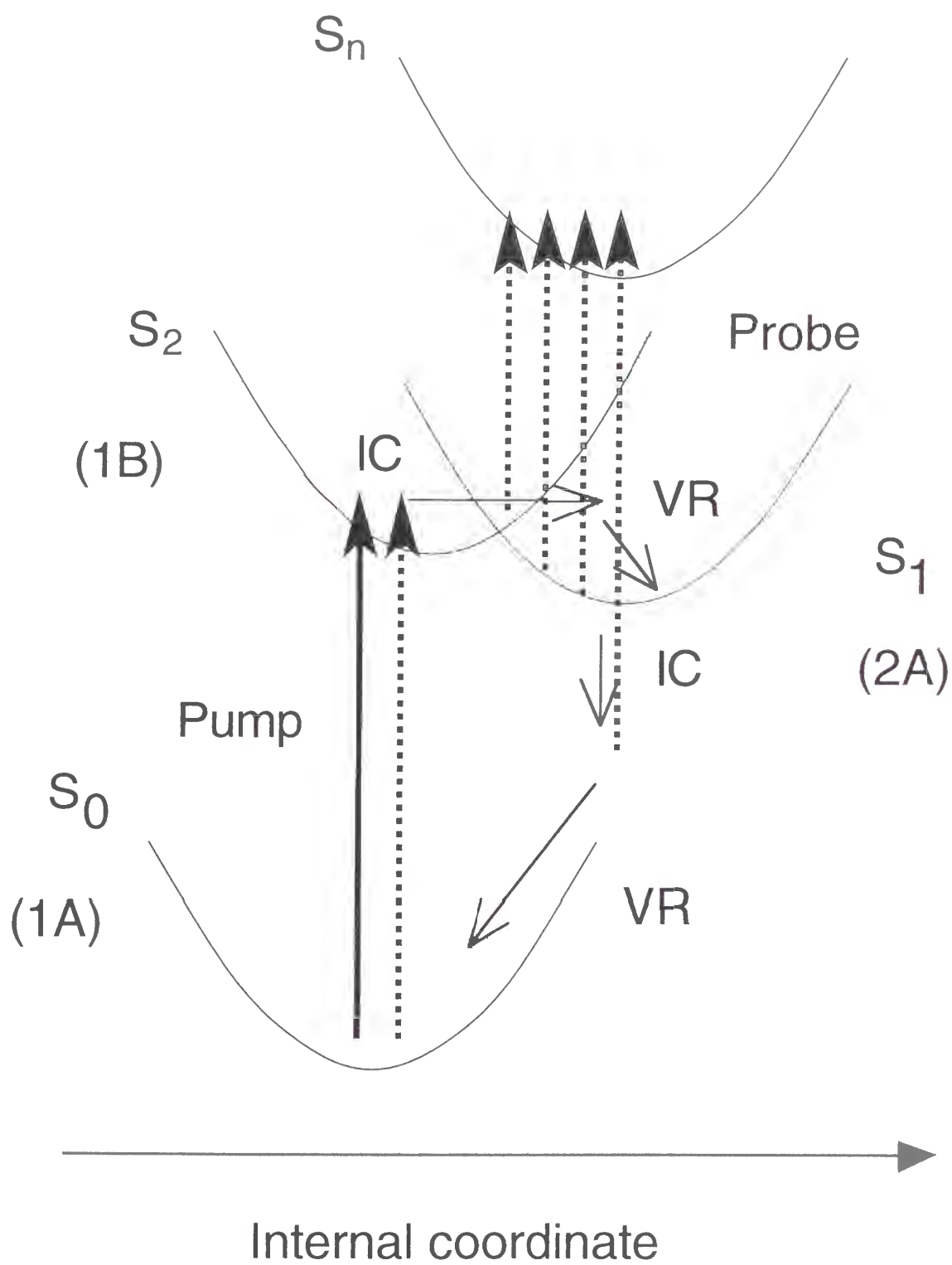


Figure 3-9. Schematic representation of the potential energy diagram of 1,3,5-hexatriene following the photoexcitation to the 1B state. IC and VR denote internal conversion and vibrational relaxation, respectively.

In contrast to trans isomer, the efficiency of the internal conversion does not depend on the vibrational levels in the 2A state for cis isomer.

Another explanation for this observation may exist. The difference in the decay rates may reflect the rates of the vibrational energy redistribution at different energy levels within the 2A potential. 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. It is considered that the rates of the vibrational energy redistribution are different among different energy levels for trans isomer and are independent of the energy levels for cis isomer.

In the gas phase, the lifetime for cis isomer is three times larger than that for trans, however the lifetime in the liquid phase is 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. For cis isomer, this change induces the acceleration of the internal conversion to the ground state. On the other hand, for trans isomer, it induces deceleration. However, since the lifetime of the 2A state has similar time scale between the gas and liquid phase, 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 [25]. The internal conversion from the 1^1B_2 to 2^1A_1 state completes within 100 fs. Thus the transition from the 2^1A_1 state of 1,3,5-hexatriene to the ground state is a rate determining step with the time constant of about 600 fs. These dynamics in the 2A state are general among the simple linear polyenes [26]. 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 [23]. Based on this observation, the slow 5-15 ps

component in our signals is most probably attributed to the vibrationally excited ground state.

3-3-2. Anisotropy Decay Measurement

Time-resolved anisotropy of the transient absorption can provide a direct probe of the molecular motion and the other relaxation process [27,28]. If the transition dipole moments of target molecules for excitation and probe processes are μ_e , μ_p , respectively, the anisotropy is given by

$$r(t) = \frac{2}{5} \langle P_2[\mu_e(0) \cdot \mu_p(t)] \rangle = \frac{2}{5} \langle P_2[\cos\theta(t)] \rangle \quad (1)$$

where $P_2(x)$ is the second Legendre polynomial and the angle brackets denote the ensemble average. $\theta(t)$ is the angle between μ_e and μ_p . If the directions of the transition dipole moments for excitation and probe processes are parallel to each other, $r(t)$ becomes 0.4. If perpendicular, $r(t)$ becomes -0.2.

The anisotropy decay is experimentally obtained from the transient absorption signals measured under the two different configurations for laser polarizations.

$$r(t) = \frac{I_{para}(t) - I_{perp}(t)}{I_{para}(t) + 2I_{perp}(t)} \quad (2)$$

where I_{para} and I_{perp} are the signals obtained using the parallel and perpendicular polarization conditions for excitation and probe pulses, respectively. However, in our case, the decay of the transient absorption signals is comparable to the instrument response function so that the substitution of the raw data to eq. (2) can not lead to the real feature of the time dependent anisotropy, $r(t)$. It is necessary to properly convolute the polarization-dependent signals with the instrument response function. We use the method by Cross et al. for analysis of the experimental data [27].

The observed polarized absorption signals are related to the true decay function, $i_{para}(t)$ and $i_{perp}(t)$, by convolution with the instrument response function, $g(t)$

$$I_{para}(t) = \int_0^t g(t - \tau) i_{para}(\tau) d\tau \quad (3)$$

$$I_{perp}(t) = \int_0^t g(t - \tau) i_{perp}(\tau) d\tau \quad (4)$$

The signal at magic angle condition, $K(t)$ and the anisotropy decay function, $r(t)$ are given by the following equations.

$$K(t) = \frac{1}{3}(i_{para}(t) + 2i_{perp}(t)) \quad (5)$$

$$r(t) = \frac{i_{para}(t) - i_{perp}(t)}{i_{para}(t) + 2i_{perp}(t)} \quad (6)$$

The decay functions in the parallel and perpendicular configurations are expressed by using $K(t)$ and $r(t)$ as follows.

$$i_{para}(t) = K(t) \times [1 + 2r(t)] \quad (7)$$

$$i_{perp}(t) = K(t) \times [1 - r(t)] \quad (8)$$

There are two methods to analyze the data.

1. Method 1 --- Global Fitting Procedure

The anisotropy data are analyzed by simultaneous iterative reconvolution and nonlinear least-squares fitting routines of the parallel and perpendicular decay signals [27]. This method of simultaneous fitting acts directly on the raw data, taking into account the common parameters that exist between parallel and perpendicular data such as eq. (3) and (4). In this method, we optimize the fitting parameters of two signals at the parallel and perpendicular configurations by using the common lifetime and anisotropy decay function simultaneously.

2. Method 2

1. The magic angle data are fitted by a single exponential function convoluted with the instrument response function.

$$K'(t) = \int_0^t g(t - \tau) K(\tau) d\tau \quad (9)$$

$$K(t) = A_1 \exp\left(-\frac{t}{\tau}\right) + A_2 \quad (10)$$

2. Using the parameters which are obtained by procedure 1, the difference signal between parallel and perpendicular data is fitted by the following relation.

$$i_{diff}(t) = i_{para}(t) - i_{perp}(t) = 3 \times K(t) \times r(t) \quad (11)$$

$$I_{diff}(t) = \int_0^t g(t - \tau) i_{diff}(\tau) d\tau \quad (12)$$

The transient absorption signals at 400 nm with the parallel and perpendicular

polarization geometry for trans and cis isomers are shown in Figure 3-10. In this figure, the anisotropy decay is calculated by eq. (2). The population decay in the excited state for trans isomer is quite similar to that for cis isomer, however, we can clearly see the difference of the anisotropy decay between trans and cis isomers. By using the method 2, we analyzed the anisotropy data of the transient absorption signals at 400 nm.

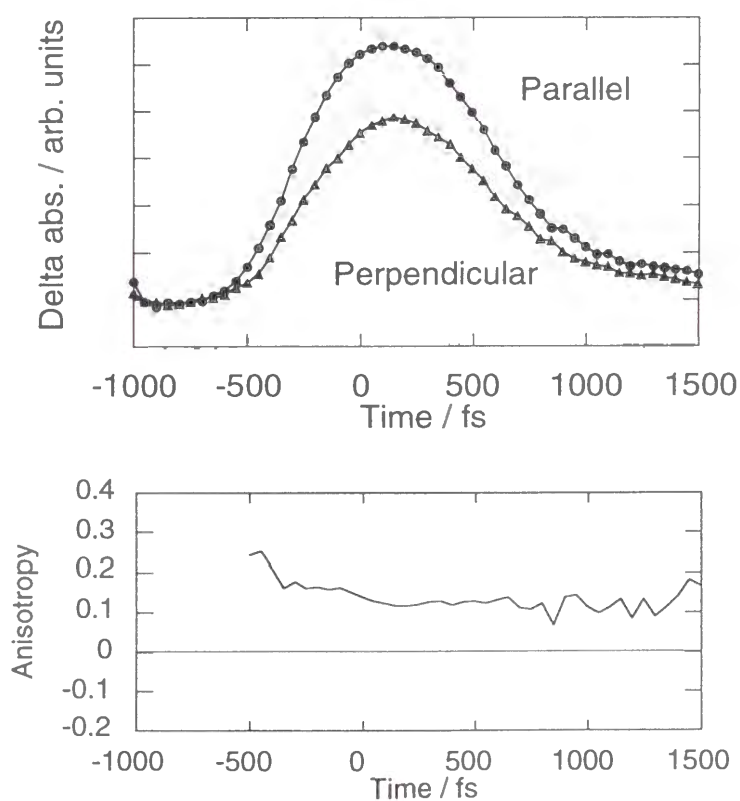


Figure 3-10(a). Transient absorption signals at 400 nm for trans-1,3,5-hexatriene in cyclohexane with the parallel and perpendicular polarization conditions and the anisotropy decay.

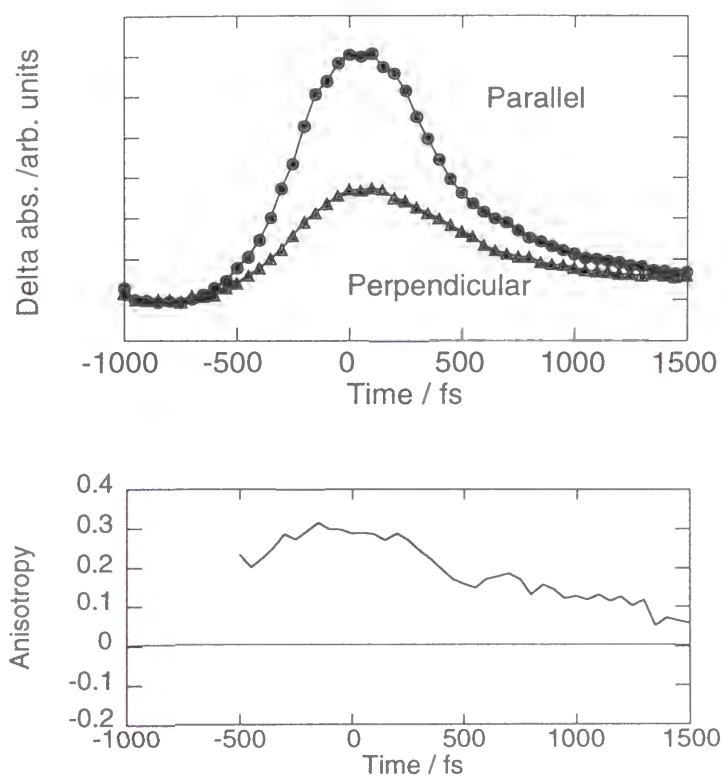


Figure 3-10(b). Transient absorption signals at 400 nm for cis-1,3,5-hexatriene in cyclohexane with the parallel and perpendicular polarization conditions and the anisotropy decay.

Figure 3-11 and 3-12 show the results of the fitting of magic angle data to a single exponential function convoluted with the instrument response function. Next we fit the difference of the signals between the parallel and perpendicular polarization condition by using eq. (12). Here we assume the anisotropy decay follows the single exponential function. The results of the fitting are shown in Figure 3-11,3-12. For trans isomer, the initial anisotropy is 0.18 and is nearly constant within our observed time scale. The anisotropy changes around 0.11 at all the time. In contrast to trans isomer, the anisotropy of cis isomer decays from 0.37 to 0.0 with the time constant of about 1.2 ps.

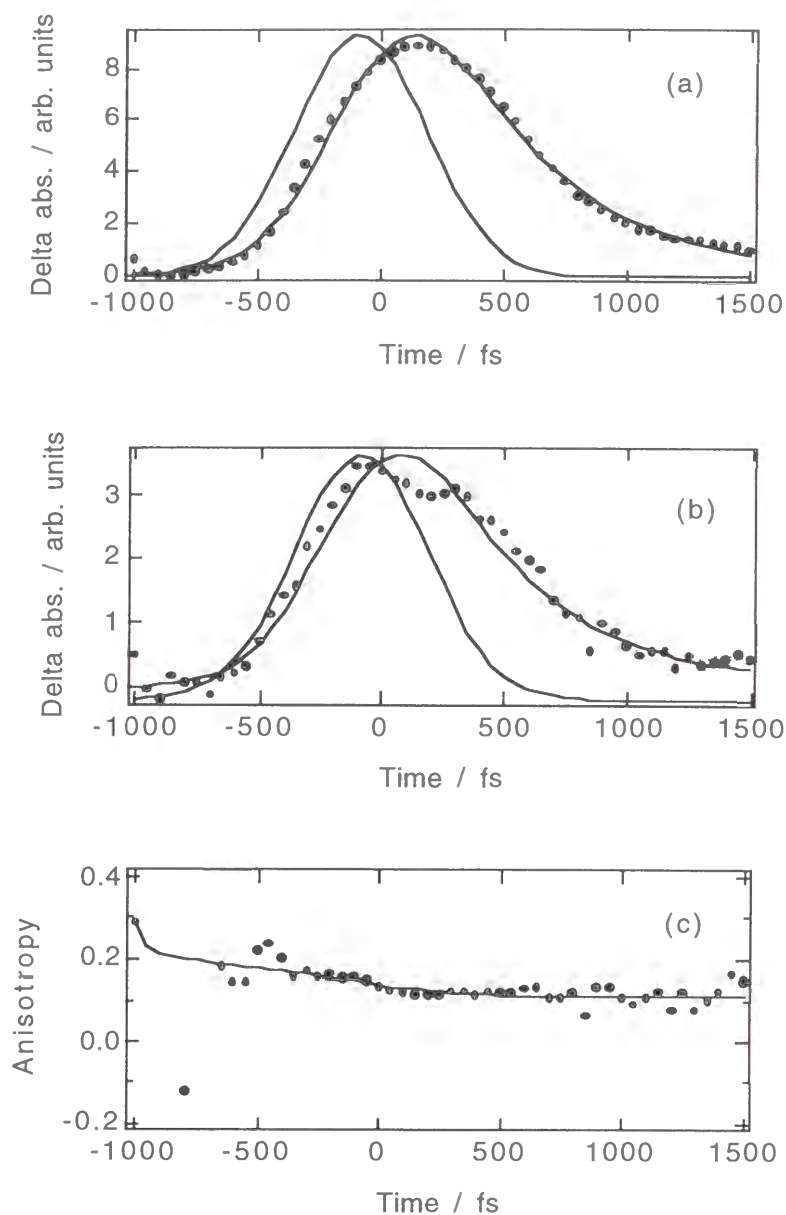


Figure 3-11. The results of the fitting of the magic angle data (a) and the difference between the parallel and perpendicular polarization conditions for trans-1,3,5-hexatriene (b). The instrument response function is shown in each figure. The solid line represents the best fits to the data by the convolution of the instrument response function. (c) Comparison of the resulting calculated anisotropy decay curves (solid line) with the experimental data (closed circles).

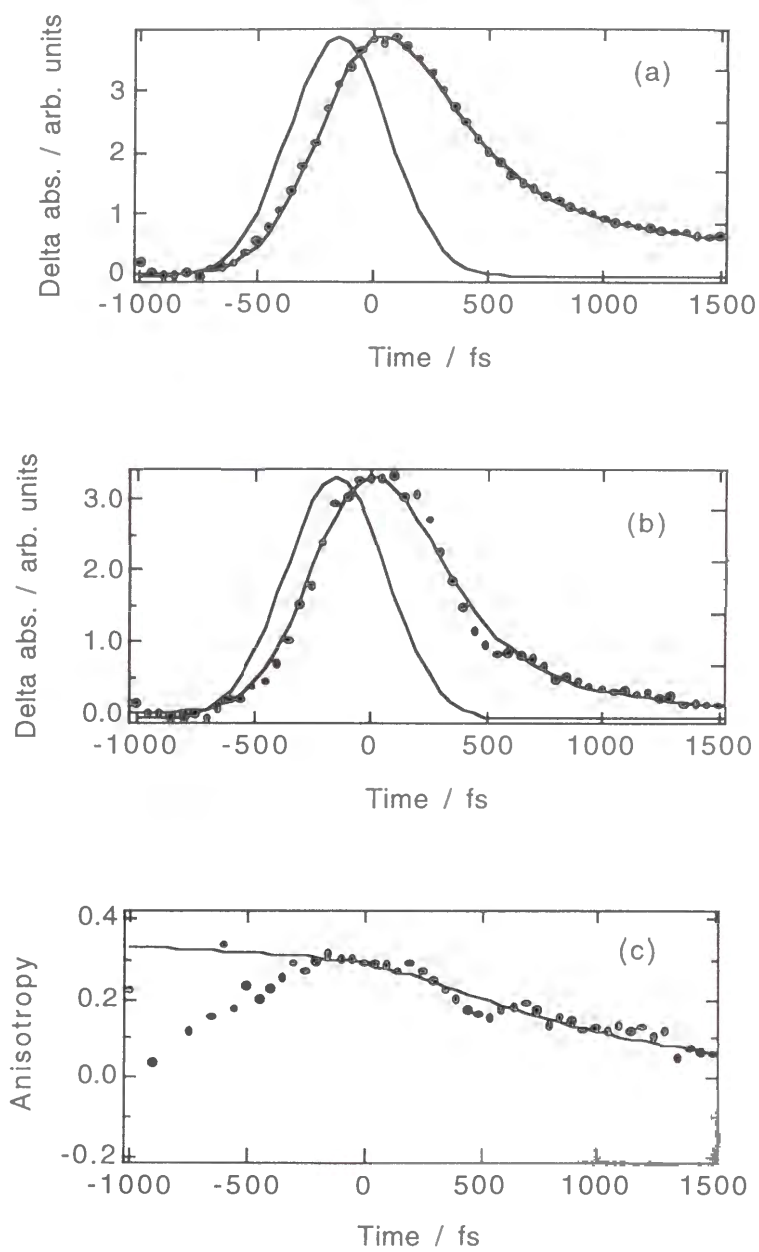


Figure 3-12. Same as Figure 3-11 except for cis-1,3,5-hexatriene.

Fuss and coworkers measured the anisotropy decay of cis-1,3,5-hexatriene in the gas phase after pumping it directly by femtosecond pulse [24]. The data is fitted by a single exponential function with a rate of 3.65 ps^{-1} . They assume that the anisotropy decay comes from free rotation of a molecule and derives a value of $38 \text{ amu \AA}^2$ for the moment of inertia. This value is close to the smallest moment of inertia around the long molecular axis. Therefore, the transition dipole moment of 1A-2A bands directs along the C_2 axis, perpendicular to the molecular axis. In contrast to this, the transition dipole moment of 1A-1B band is directed along a molecular axis. It is perpendicular to the direction of 1A-2A band.

In this experiment, pump and probe pulses are connected by the S_2 - S_0 and S_n - S_1 transitions, respectively, as shown in Fig. 3-9. Anisotropy measurement gives us information about the relative angle of the transition dipole moments between these two transitions. We could calculate this angle by using the following expression.

$$r(t) = \frac{2}{5} \left\langle \frac{1}{2} (3 \cos^2 \theta - 1) \right\rangle \quad (13)$$

For the trans isomer, the initial value of the angle yields $\theta=44$ degree. For cis isomer, it is equal to $\theta=13$ degree.

The interpretation of the anisotropy decay for 1,3,5-hexatriene is not simple because we probe the population in the different state from that prepared by pump pulse. We excite the molecules to the 1B state, however, the probe transition comes from S_n - S_1 transition. If we probe the parallel transition to the initial state, the initial value of the anisotropy should be equal to 0.4 and the time dependence of the anisotropy may come from the internal conversion to the 2A state. The observed initial value of the anisotropy, which is somewhat lower than 0.4, means that we mainly probe the S_1 (2A) state and the internal conversion from the 1B to 2A state occurs within our instrument response function.

The anisotropy decay leads to information about the change of direction in the dipole moment by not only the rotational diffusion but also the structural change in the S_1 state during the vibrational energy redistribution process. Although it is difficult to

identify the contributions in the anisotropy change only based on this experiment, we clearly observed the different initial values of the anisotropy and different time dependence between the trans and cis isomers. This means that 1,3,5-hexatriene has different potential minima and different intermediate geometries in the S_1 state for each isomer. If this is correct, this difference may provide information about the shape of the potential energy curves in the S_1 state for each isomer. Support for the two different potential minima can also be derived from the low isomerization yields around the C=C double bond. If there were a common minimum in the S_1 state with one conical intersection as an exit, one would expect the same branching ratio for starting compounds; in other words, the sum of the quantum yields for trans-cis and cis-trans isomerization should be unity. Actually, these yields are 0.034 and 0.016, respectively [2]. This is opposite situation for olefins such as ethylene and simple derivatives such as stilbene, have a common minimum of the first excited state which is located at a torsion angle of the double bond of 90 degree. This leads to a mutual isomerization between trans and cis isomers [28].

3-4. Discussion in the transient bleach recovery signals

3-4-1. The origin of the transient bleach recovery signals within 20 ps time scale

The first component of the transient bleach signals in cyclohexane and acetonitrile has the recovery time constant of ca. 1 ps. This component is only observed in trans isomer. However, Sension and coworkers found that this 1 ps component was observed in both isomers [29]. This difference may be attributed to the observation that the recovery time constant for cis isomer is smaller than that for trans isomer. In our apparatus, we cannot clearly resolve this component for cis isomer. After photoexcitation, the internal conversion from the 2A to 1A state occurs within 500 fs and vibrationally excited states of 1A are created. When the population in the vibrationally excited 1A state relaxes to some extent and the energy difference between the 1A state (S_0) and the highly excited state (S_n) matches the probe wavelength, we can probe the population in 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. Generally, the vibrational relaxation of large organic molecules in solution is known to occur in tens of picoseconds [30]. In the picosecond time-resolved resonance Raman measurements of the photochemical ring opening reaction of 1,3-cyclohexadiene in solutions [20], the vibrational relaxation of the photoproduct, i.e., hot cis-1,3,5-hexatriene, occurs with the time constant of 9 ps. Based on these observations, we assign the second components to the vibrational relaxation in the ground state. Details will be discussed in Section 3-4-2.

The wavelength-dependent bleach recovery on the different wavelengths observed in 20-ps time scale is attributed to the spectral broadening and shift of the absorption band to longer wavelengths. It is considered to be originated from the vibrationally excited products and transient s-cis 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 [30], stilbene [28] and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole [31], after the ultrafast internal conversion to the ground state. At longer than 10 ps the intramolecular vibrational distribution is well characterized by a vibrational temperature. The population in the vibrationally excited state decreases in 10-ps time region by the energy transfer from solute to solvent.

The spectral broadening reduces by the vibrational relaxation process and the transient absorption band converges to the static one. The schematic representation of this phenomena is shown in Figure 3-13. 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 bottom position. At the wavelengths of 268 nm 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 one. The vibrational relaxation is observed as the bleach recovery in 10-ps time scale because the absorbance becomes larger with the vibrational relaxation. On the other hand, at the wavelength of 262 nm, which corresponds to the bottom 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 the 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 of the signal, which corresponds to the transient absorption component in the signal. This decays up to 20 ps by vibrational relaxation process.

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

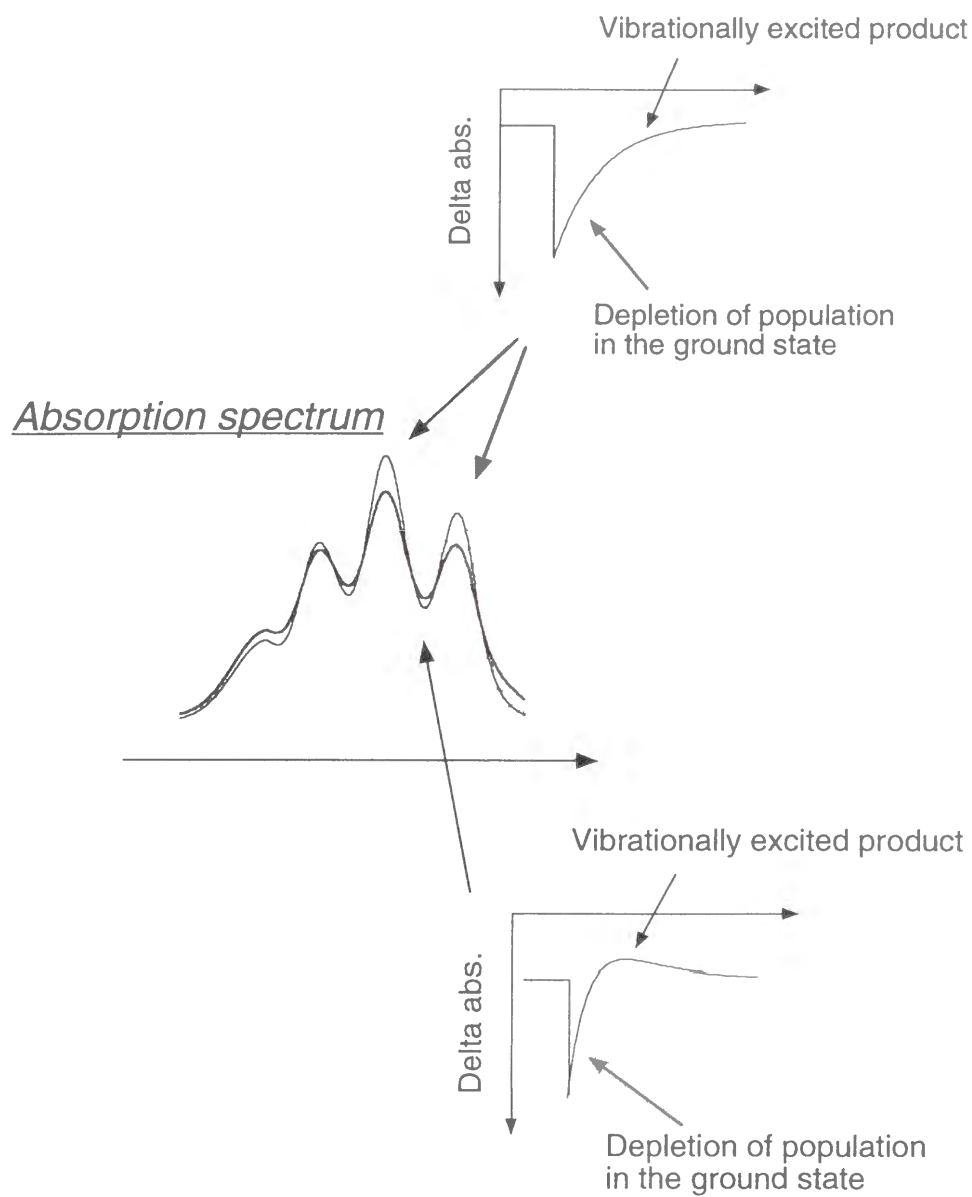


Figure 3-13. Schematic representation of the absorption spectra for vibrationally excited (thick line) and relaxed (thin line) products, and behavior of the temporal profiles of the transient bleach recovery signals.

3-4-2. Simulation for temporal behavior of bleach recovery signals

In the following we present a qualitative analysis of the transient S_2 - S_0 absorption spectra of 1,3,5-hexatriene. After the ultrafast internal conversion to the ground state, the vibrationally excited product is created. In this case, excess energy is distributed within the vibrational manifolds nonthermally. The intramolecular energy redistribution (IVR) causes dissipation of the energy from an initially nonthermal energy distribution to a fully statistically thermalized state [30]. All vibrational modes are populated according to a thermal Boltzmann factor and a vibrational temperature can be defined (“molecular thermometer”). The intermolecular energy transfer from the solute to solvent occurs successively. The rate of this process depends on the mode density of both solute and solvent and the excess energy. We assume that the intramolecular vibrational energy redistribution occurs much faster than intermolecular energy transfer.

In this calculation, we first estimate the transient temperature if the excess energy is distributed into all vibrational modes of 1,3,5-hexatriene statistically. Next we calculate the absorption spectra as a function of the transient temperature. By assuming the time dependence of the internal temperature of 1,3,5-hexatriene, which is caused by the intermolecular energy transfer to the solvent, we simulate the time dependence of the bleach recovery signals at several wavelengths.

3-4-2. (a) Estimation of the transient vibrational temperature.

The transient vibrational temperature is estimated on the assumption that the excess energy is statistically distributed among all the intramolecular vibrational modes. The relationship between the excess energy and the transient vibrational temperature T_i is given by the following equation.

$$\Delta E = \sum_{i=1}^{3N-6} \frac{\hbar\omega_i \exp\left(-\frac{\hbar\omega_i}{kT_i}\right)}{1 - \exp\left(-\frac{\hbar\omega_i}{kT_i}\right)} - \sum_{i=1}^{3N-6} \frac{\hbar\omega_i \exp\left(-\frac{\hbar\omega_i}{kT_r}\right)}{1 - \exp\left(-\frac{\hbar\omega_i}{kT_r}\right)} \quad (1)$$

where k , h , and T_r denote the Boltzmann and the Dirac constant and the room temperature (293K), respectively. 1,3,5-Hexatriene has 36 vibrational modes and these frequencies are taken from the literature [32]. The values of the frequencies for both isomers are shown in Table 3-4 and 3-5. The results of the relation between the excess energy and the transient vibrational temperature are displayed in Figure 3-14. The excitation pulses at 259, 262 and 268 nm provide photon energies of 38610, 38170, 37310 cm^{-1} , respectively. The excess energy profiles v.s. temperature for trans isomer are similar to those for cis isomer. From Figure 3-14, we obtain the maximum transient vibrational temperature of about 2200-2300 K for both isomer.

Table 3-4.

Observed and calculated vibrational frequencies of the tTt conformer of 1,3,5-hexatriene

Mode	Frequency (cm ⁻¹)			Assignment ^d	
	Obs. ^{a,b} (ρ^c)		Calc.		
a_g	ν_1	3089	R,m (0.57)	3097	$\nu_a(\text{CH}_2)$ 96
	ν_2	—		3022	$\nu_s(\text{CH}_2)$ 50 $\nu(\text{C}_2\text{H})$ 46
	ν_3	3000	R,m (0.07)	3012	$\nu(\text{C}_2\text{H})$ 36 $\nu(\text{C}_3\text{H})$ 34
	ν_4	2992	R,m (0.08)	3008	$\nu(\text{C}_3\text{H})$ 66 $\nu_s(\text{CH}_2)$ 18
	ν_5	1626	R,vs (0.25)	1649	$\nu(\text{C}_3=\text{C}_3')$ 39 $\nu(\text{C}_1=\text{C}_2)$ 26
	ν_6	1576	R,w (0.12)	1558	$\delta_s(\text{CH}_2)$ 38 $\nu(\text{C}_3=\text{C}_3')$ 25
	ν_7	1399	R,m (0.29)	1405	$\delta_s(\text{CH}_2)$ 52 $\delta(\text{C}_2\text{H})$ 22
	ν_8	1288 ^e	R,w	1298	$\delta(\text{C}_2\text{H})$ 40 $\delta(\text{C}_3\text{H})$ 18
	ν_9	1283 ^e	R,w } (0.19)	1275	$\delta(\text{C}_3\text{H})$ 34 $\nu(\text{C}_3=\text{C}_3')$ 30
	ν_{10}	1191	R,s (0.35)	1197	$\nu(\text{C}_2-\text{C}_3)$ 32 $\delta_r(\text{CH}_2)$ 18
	ν_{11}	932	R,w (0.46)	930	$\delta_r(\text{CH}_2)$ 60 $\nu(\text{C}_2-\text{C}_3)$ 20
	ν_{12}	443	R,w (0.10)	429	$\delta(\text{C}_2\text{C}_3\text{C}_3')$ 46 $\nu(\text{C}_2-\text{C}_3)$ 24
	ν_{13}	353	R,w (0.35)	344	$\delta(\text{C}_1\text{C}_2\text{C}_3)$ 88 $\delta(\text{C}_2\text{C}_3\text{C}_3')$ 12
a_u	ν_{14}	1009	IR,vs	1018	$\gamma_t(\text{CH}_2)$ 40 $\gamma_w(\text{C}_2\text{H})$ 24
	ν_{15}	941	IR,m	939	$\gamma_w(\text{C}_3\text{H})$ 30 $\tau(\text{C}_3=\text{C}_3')$ 23
	ν_{16}	900	IR,vs	903	$\gamma_w(\text{CH}_2)$ 82
	ν_{17}	682	IR,m	672	$\gamma_w(\text{C}_2\text{H})$ 44 $\gamma_t(\text{CH}_2)$ 36
	ν_{18}	248 ^e	IR,vw	246	$\tau(\text{C}_3=\text{C}_3')$ 42 $\tau(\text{C}_2-\text{C}_3)$ 26
	ν_{19}	94 ^e	IR,vw	98	$\tau(\text{C}_2-\text{C}_3)$ 64 $\gamma_w(\text{C}_3\text{H})$ 26
b_u	ν_{20}	3091	IR,m	3097	$\nu_a(\text{CH}_2)$ 96
	ν_{21}	3039	IR,m	3022	$\nu(\text{C}_2\text{H})$ 50 $\nu(\text{C}_3\text{H})$ 30
	ν_{22}	3008	IR,m	3017	$\nu_s(\text{CH}_2)$ 66 $\nu(\text{C}_3\text{H})$ 34
	ν_{23}	2969	IR,w	3006	$\nu(\text{C}_2\text{H})$ 48 $\nu(\text{C}_3\text{H})$ 36
	ν_{24}	1624	IR,s	1618	$\nu(\text{C}_1=\text{C}_2)$ 62 $\delta_s(\text{CH}_2)$ 22
	ν_{25}	1429	IR,m	1444	$\delta_s(\text{CH}_2)$ 70 $\delta(\text{C}_2\text{H})$ 16
	ν_{26}	1294	IR,w	1293	$\delta(\text{C}_2\text{H})$ 46 $\nu(\text{C}_1=\text{C}_2)$ 22
	ν_{27}	1255	IR,w	1251	$\delta(\text{C}_3\text{H})$ 80 $\delta_r(\text{CH}_2)$ 10
	ν_{28}	1128	IR,w	1125	$\nu(\text{C}_2-\text{C}_3)$ 44 $\delta_r(\text{CH}_2)$ 20
	ν_{29}	964	IR,vw	955	$\delta_r(\text{CH}_2)$ 48 $\nu(\text{C}_2-\text{C}_3)$ 34
	ν_{30}	541	IR,w	533	$\delta(\text{C}_1\text{C}_2\text{C}_3)$ 60 $\delta(\text{C}_2\text{C}_3\text{C}_3')$ 22
	ν_{31}	152 ^e	IR,w	145	$\delta(\text{C}_2\text{C}_3')$ 88 $\delta(\text{C}_1\text{C}_2\text{C}_3)$ 34
b_g	ν_{32}	986	R,vw(dp)	991	$\gamma_t(\text{CH}_2)$ 58 $\gamma_w(\text{C}_2\text{H})$ 40
	ν_{33}	903	R,w (0.70)	913	$\gamma_w(\text{CH}_2)$ 88
	ν_{34}	868	R,vw (0.76)	858	$\gamma_w(\text{C}_3\text{H})$ 82 $\gamma_w(\text{CH}_2)$ 10
	ν_{35}	615 ^f	vw	589	$\gamma_w(\text{C}_2\text{H})$ 40 $\gamma_t(\text{CH}_2)$ 38
	ν_{36}	215 ^e	vw	221	$\tau(\text{C}_2-\text{C}_3)$ 84 $\gamma_w(\text{C}_2\text{H})$ 12

^aUnless otherwise noted, the observed data were obtained in the present study for the liquid state. R, Raman; IR, infrared. ^bIntensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. ^cDepolarisation degree. p, polarised; dp, depolarised. ^d ν , stretch; ν_a , symmetric stretch; ν_{as} , antisymmetric stretch; δ , bend; δ_s , scissor; δ_r , rock; γ_t , twist; γ_w , wag; τ , torsion. The numbers indicate the values of potential energy distribution (PED). For tTt and tCt, the sum of PEDs for the two equivalent coordinates in the left and right halves of the molecule is indicated. ^eTaken from Ref. 10. ^fObserved in the solid state at low temperature.

This is quoted from Ref. [32].

Table 3-5.

Observed and calculated vibrational frequencies of the tCt conformer of 1,3,5-hexatriene

Mode	Frequency (cm ⁻¹)			Assignment ^d	
		Obs. ^{a,b} (ρ^c)	Calc.		
<i>a</i> ₁	ν_1	3090	R,w(0.54)	3097	$\nu_a(\text{CH}_2)$ 92
	ν_2	—		3051	$\nu(\text{C}_2\text{H})$ 88
	ν_3	3011	R,m(0.07)	3032	$\nu(\text{C}_3\text{H})$ 94
	ν_4	2995	R,m(0.06)	3014	$\nu_s(\text{CH}_2)$ 98
	ν_5	1626	R,vs(0.16)	1649	$\nu(\text{C}_3=\text{C}_3')$ 37 $\nu(\text{C}_1=\text{C}_2)$ 30
	ν_6	1580	R,vw(p)	1548	$\delta_s(\text{CH}_2)$ 40 $\nu(\text{C}_3=\text{C}_3')$ 32
	ν_7	1397	R,m(0.25); IR,vw	1405	$\delta_s(\text{CH}_2)$ 46 $\delta(\text{C}_2\text{H})$ 26
	ν_8	1318	R,m(0.19); IR,w	1317	$\delta(\text{C}_2\text{H})$ 40 $\nu(\text{C}_1=\text{C}_2)$ 24
	ν_9	1247	R,s(0.31)	1254	$\delta(\text{C}_3\text{H})$ 56 $\nu(\text{C}_2-\text{C}_3)$ 16
	ν_{10}	1084	R,w(0.52); IR,vw	1080	$\delta_r(\text{CH}_2)$ 44 $\delta(\text{C}_3\text{H})$ 24
	ν_{11}	883	R,w(0.60)	862	$\nu(\text{C}_2-\text{C}_3)$ 48 $\delta_r(\text{CH}_2)$ 34
	ν_{12}	392	R,m(0.12)	383	$\delta(\text{C}_1\text{C}_2\text{C}_3)$ 58
	ν_{13}	166	R,w(0.47)	164	$\delta(\text{C}_2\text{C}_3\text{C}_3')$ 68 $\delta(\text{C}_1\text{C}_2\text{C}_3)$ 20
<i>a</i> ₂	ν_{14}	(990)	R,vw	1007	$\gamma_w(\text{C}_3\text{H})$ 30 $\tau(\text{C}_3=\text{C}_3')$ 19
	ν_{15}	953	R,w(0.74)	962	$\gamma_w(\text{C}_3\text{H})$ 32 $\gamma_w(\text{C}_2\text{H})$ 32
	ν_{16}	905	R,w(0.73)	908	$\gamma_w(\text{CH}_2)$ 90
	ν_{17}	705	R,w(0.73)	701	$\gamma_w(\text{C}_2\text{H})$ 34 $\gamma_t(\text{CH}_2)$ 32
	ν_{18}	331	R,w(0.75)	324	$\tau(\text{C}_3=\text{C}_3')$ 50 $\gamma_w(\text{C}_3\text{H})$ 40
	ν_{19}	155 ^e	R,vw(dp)	148	$\tau(\text{C}_2-\text{C}_3)$ 98 $\tau(\text{C}_3=\text{C}_3')$ 12
<i>b</i> ₁	ν_{20}	3089	IR,s	3096	$\nu_a(\text{CH}_2)$ 96
	ν_{21}	3045	IR,m	3033	$\nu(\text{C}_2\text{H})$ 90
	ν_{22}	3014	IR,m	3015	$\nu_s(\text{CH}_2)$ 84 $\nu(\text{C}_3\text{H})$ 16
	ν_{23}	2979	IR,w	3007	$\nu(\text{C}_3\text{H})$ 82 $\nu_s(\text{CH}_2)$ 12
	ν_{24}	1616	IR,s	1611	$\nu(\text{C}_1=\text{C}_2)$ 62 $\delta_s(\text{CH}_2)$ 24
	ν_{25}	1449	IR,s; R,vw(0.73)	1456	$\delta_s(\text{CH}_2)$ 58 $\delta(\text{C}_3\text{H})$ 20
	ν_{26}	1355	IR,vw	1347	$\delta(\text{C}_3\text{H})$ 62 $\delta_s(\text{CH}_2)$ 14
	ν_{27}	1279	IR,w	1284	$\delta(\text{C}_2\text{H})$ 46 $\nu(\text{C}_1=\text{C}_2)$ 20
	ν_{28}	1185	IR,w; R,w(0.71)	1189	$\nu(\text{C}_2-\text{C}_3)$ 30 $\delta_r(\text{CH}_2)$ 20
	ν_{29}	950	IR,m; R,w(0.74)	944	$\delta_r(\text{CH}_2)$ 54 $\nu(\text{C}_2-\text{C}_3)$ 28
	ν_{30}	(675)	R,vw	675	$\delta(\text{C}_2\text{C}_3\text{C}_3')$ 52 $\nu(\text{C}_2-\text{C}_3)$ 18
<i>b</i> ₂	ν_{31}	356	IR,w; R,vw(0.72)	346	$\delta(\text{C}_1\text{C}_2\text{C}_3)$ 80 $\delta(\text{C}_2\text{C}_3\text{C}_3')$ 44
	ν_{32}	989	IR,s	994	$\gamma_t(\text{CH}_2)$ 60 $\gamma_w(\text{C}_2\text{H})$ 38
	ν_{33}	906	IR,vs	915	$\gamma_w(\text{CH}_2)$ 96
	ν_{34}	815	IR,m	789	$\gamma_w(\text{C}_3\text{H})$ 60 $\gamma_w(\text{C}_2\text{H})$ 16
	ν_{35}	590	IR,s	576	$\gamma_w(\text{C}_2\text{H})$ 40 $\gamma_t(\text{CH}_2)$ 38
	ν_{36}	100 ^e	IR	101	$\tau(\text{C}_2-\text{C}_3)$ 76 $\gamma_w(\text{C}_3\text{H})$ 16

^{a-c}See corresponding footnotes for Table 2.

This is quoted from Ref. [32].

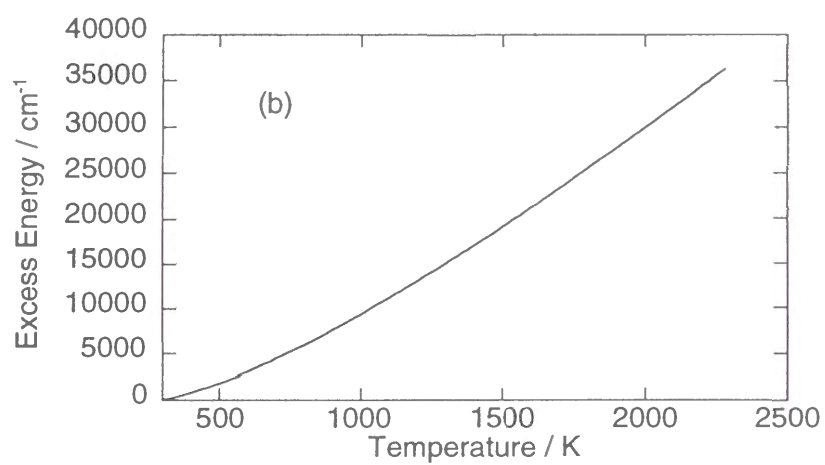
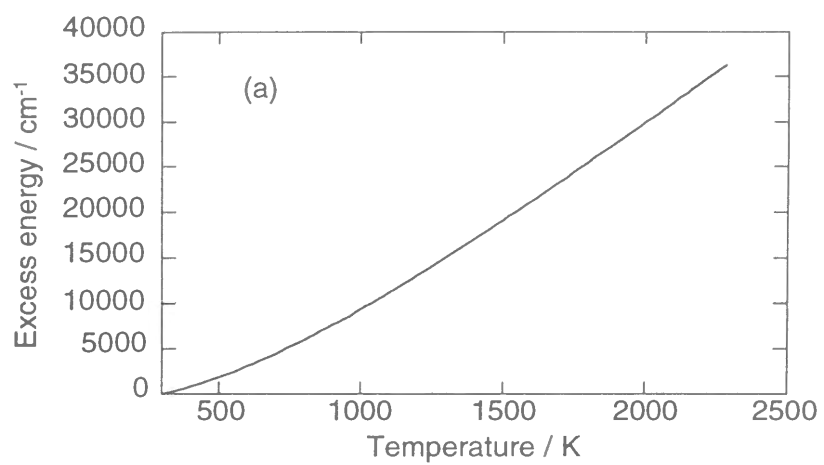


Figure 3-14. Excess energy vs temperature for (a) trans- and (b) cis-1,3,5-hexatriene.

3-4-2. (b) Calculation of the absorption spectrum

We performed the calculation of the absorption spectra for the trans and cis isomer based on the time-dependent wave packet propagation method, which is formulated by Lee and Heller [33-36]. Here we assume the harmonic potentials for ground and excited state potential surfaces. The absorption cross section is given by

$$\sigma_A(E_L) = \frac{4\pi e^2 M^2 E_L}{6\hbar^2 c n} \sum_i P_i \int_{-\infty}^{\infty} d\delta G(\delta) \text{Re} \int_{-\infty}^{\infty} dt \langle i|i(t)\rangle \exp[i(E_L + \delta + \varepsilon_i)t/\hbar - g(t)] \quad (1)$$

where M is the electronic transition length, n is the solvent refractive index, E_L is the excitation photon energy, ε_i is the vibrational energy of the state $|i\rangle$, P_i is the Boltzmann population of the state $|i\rangle$, $|i(t)\rangle = \exp(-iHt/\hbar)$, where H is the excited-state Hamiltonian. $G(\delta)$ is the inhomogeneous broadening function, taken to be a normalized Gaussian with standard deviation θ . The electronic dephasing is given by $\exp[-g(t)]$.

Assuming orthogonal harmonic potential surfaces, the time-dependent overlaps can be expressed for each vibrational mode as follows.

$$\langle i|i(t)\rangle = \prod_{k=1}^{3N-6} \langle i_k|i_k(t)\rangle \quad (2)$$

In this calculation, we assumed that the vibrational frequency in the electronic ground state is same as that in the excited state and there is no Duschinsky rotation for simplicity. This vibrational correlation function of a harmonic oscillator for mode k can be calculated by

$$\begin{aligned} \langle i_k|i_k(t)\rangle &= \exp\{s_k(2\bar{n}_k + 1)[\cos(\omega_k t) - 1] - is_k \sin(\omega_k t)\} \\ \bar{n}_k &= [\exp(\hbar\omega_k / kT) - 1]^{-1} \end{aligned} \quad (3)$$

where $s = \Delta^2/2$ and Δ is the dimensionless displacement between the ground- and excited-state potential surfaces [36]. In solution, the stochastic model for the solvent-induced broadening gives $g(t)$ as

$$g(t) = \left(\frac{D^2}{\Lambda^2} \right) \left[\exp\left(-\frac{\Lambda t}{\hbar} \right) - 1 + \frac{\Lambda t}{\hbar} \right] \quad (4)$$

where D and $\Lambda/\hbar$ represent the magnitude and inverse time scale, respectively, of the solvent-induced fluctuations in the electronic zero-zero energy. This dephasing function approaches an exponential in time (giving a Lorentzian line shape of HWHM $\Gamma=D^2/\Lambda$) for fast modulation limit ($\Lambda \gg D$) and approaches a Gaussian in time (giving a Gaussian line shape of standard deviation D) for slow modulation limit ($\Lambda \ll D$).

Myers and coworkers reported the frequencies and displacements of several Franck-Condon active modes for both trans and cis isomers to reproduce the absorption spectra and resonance Raman intensities of these modes [18,19]. In this calculation, we use the same parameters as theirs. For trans isomer, we consider 12 Franck-Condon active modes and these values as well as the other parameters such as zero-zero energy and the homogenous and inhomogenous linewidth are shown in Table 3-6a. For the linebroadening function, we use the following simpler form according to Myer's treatment.

$$g(t) = \exp\left(-\frac{\Gamma t}{\hbar}\right) \quad (5)$$

For cis isomer, we consider 14 Franck-Condon active modes and the parameters are tabulated in Table 3-6b.

Table 3-6 (a) Potential parameters of trans-1,3,5-hexatriene in cyclohexane solution

Mode	Frequency / cm^{-1}	Displacement
ν_5	1635	1.32
ν_6	1581	0.409
ν_7	1403	0.113
ν_8 and ν_9	1290	0.444
ν_{10}	1192	-0.767
ν_{11}	934	0.137
ν_{12}	444	0.212
ν_{13}	354	0.334
ν_{17}	686	0
ν_{18}	246	0
ν_{19}	93	0

Homogeneous linewidth $\Gamma=246 \text{ cm}^{-1}$, inhomogeneous Gaussian standard deviation $\theta=170 \text{ cm}^{-1}$, and zero-zero energy $E_0=37315 \text{ cm}^{-1}$.

These values are taken from Ref. [18].

Table 3-6 (b) Potential parameters of cis-1,3,5-hexatriene in cyclohexane solution

Mode	Frequency / cm^{-1}	Displacement
ν_5	1634	1.390
ν_6	1575	0.391
ν_7	1402	0.177
ν_8	1320	0.344
ν_9	1250	0.750
ν_{10}	1082	0.169
ν_{14}	1032	0.076
ν_{15}	954	0.077
ν_{11}	883	0.124
ν_{17}	714	0.078
ν_{12}	392	0.694
ν_{18}	332	0
ν_{13}	177	0.164
ν_{19}	157	0.150

Broadening parameters $D=852 \text{ cm}^{-1}$, $\Gamma=2343 \text{ cm}^{-1}$, and zero-zero energy $E_0=37300 \text{ cm}^{-1}$. Inhomogeneous Gaussian standard deviation $\theta=283 \text{ cm}^{-1}$. These values are taken from Ref. [19].

3-4-2. (c) Results of the calculation

Figure 3-15 displays the calculated absorption spectra of trans-1,3,5-hexatriene at several temperatures. As the temperature increases, the spectrum becomes broader. At 268 nm and 259 nm, which correspond to the peaks of the vibronic bands, the absorbance decreases from 293 K to 2000 K continuously. The absorbance of the vibrationally excited product is smaller than that of the vibrationally relaxed one. On the other hand, at the wavelength of 262 nm, which corresponds to the valley between the first and second absorption bands, the absorbance becomes larger from 293 K to 1000 K and then smaller to 2000 K. From 1000 K to 2000 K, the integral intensity of the absorption spectra decreases. This behavior can be explained quantitatively by the following way. The population in the lower vibrational manifolds moves to the higher state as increasing temperature. In the higher state, the Franck-Condon overlaps become smaller than that in the lower state so that the absorbance at 262 nm decreases.

Figure 3-16 shows the absorption spectra of cis-1,3,5-hexatriene at various temperatures. Similar behavior is observed in this spectrum. Only remarkable difference is that the spectra of cis isomer has less structure than that for trans isomer.

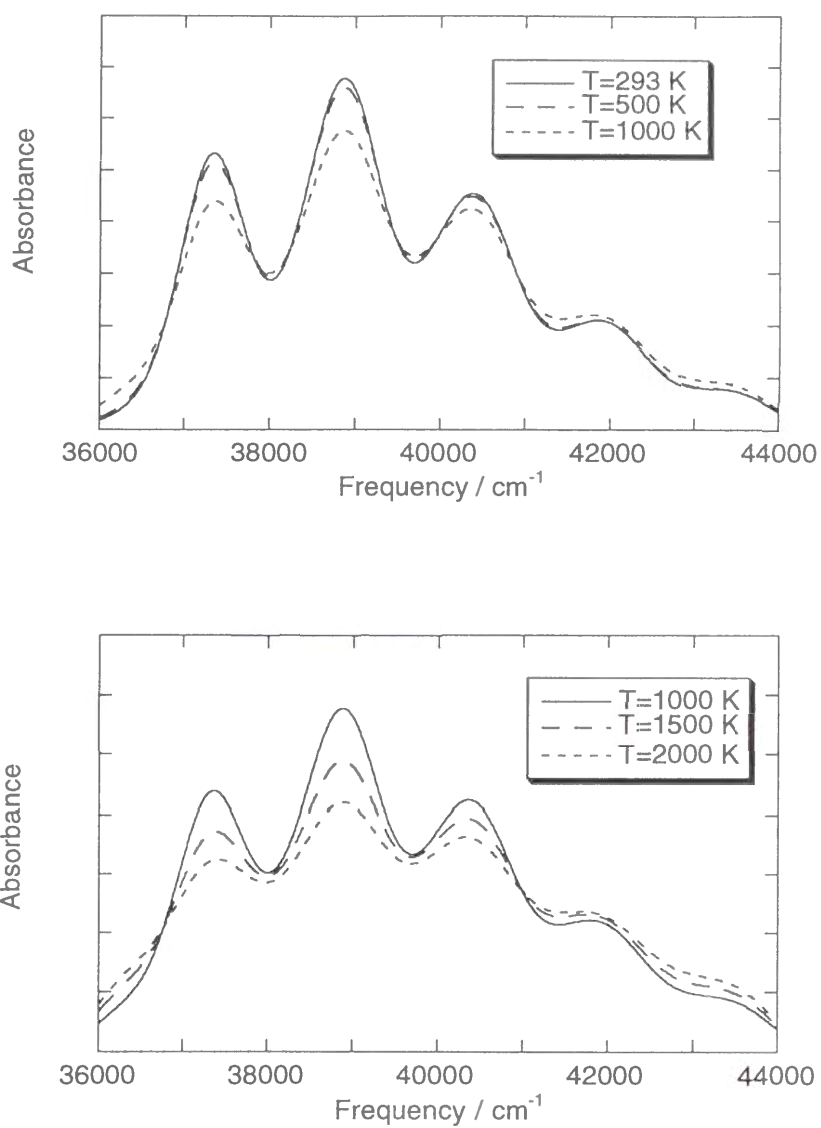


Figure 3-15. Calculated absorption spectra of trans-1,3,5-hexatriene at different temperatures.

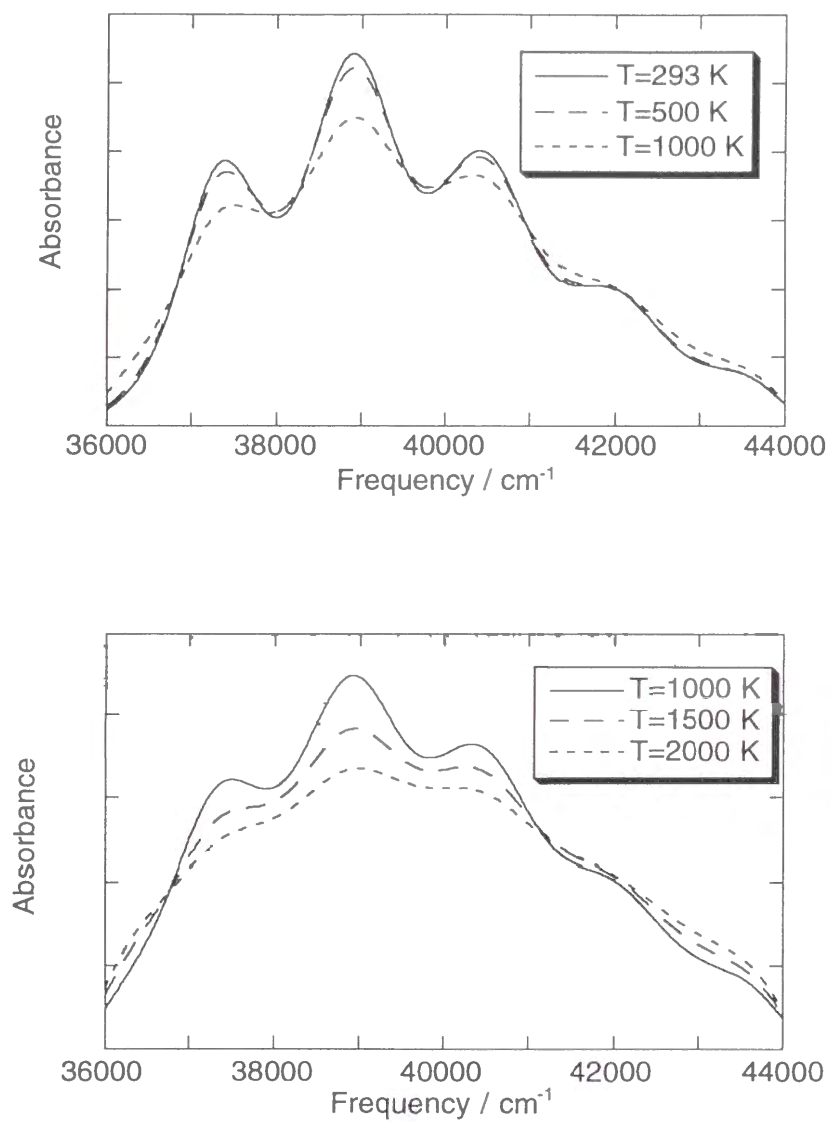


Figure 3-16. Calculated absorption spectra of cis-1,3,5-hexatriene at different temperatures.

3-4-2. (d) Temporal change in the internal temperature

We assume the time-dependent internal molecular temperature to the following simple single exponential decay.

$$T(t) - T_r = (T_m - T_r) \times \exp\left(-\frac{t}{\tau_v}\right) \quad (6)$$

where T_m is the molecular temperature at zero time and τ_v is a temperature decay. For simplicity, we also assume that intramolecular vibrational equilibration occurs instantaneously, allowing for a statistical temperature at zero time. We set T_m and τ_v to 2200 K and 15 ps, respectively.

In the photochemical ring opening reaction of 1,3-cyclohexadiene, Reid et al. measured the anti-Stokes Raman scattering and estimated the molecular temperature of photoproduct of cis-1,3,5-hexatriene at several time delays [37]. They determined the initial molecular temperature and temperature relaxation time by fitting eq. (6). Best fit to the temperature evolution resulted in a temperature relaxation time of ~ 15 ps with an initial molecular temperature of 1900 K. Our used values are similar to theirs and it is reasonable assumption.

The temporal profiles of the bleach recovery signals are calculated as follows and the results are shown in Figure 3-17 and 3-18.

$$\Delta A(t) = A(T = T(t)) - A(T = 293K) \quad (7)$$

At 268 nm and 259 nm, the bleaches recover monotonically. At 262 nm, the signals recovers faster and show an absorptive component, which decays completely within 50 ps. These calculated results are in qualitatively agreement with the experimental ones. (0 ~ 50 ps) Within this framework, we can reproduce the temporal behaviors of the bleach recovery signals at three different wavelengths such as 268, 262, 259 nm.

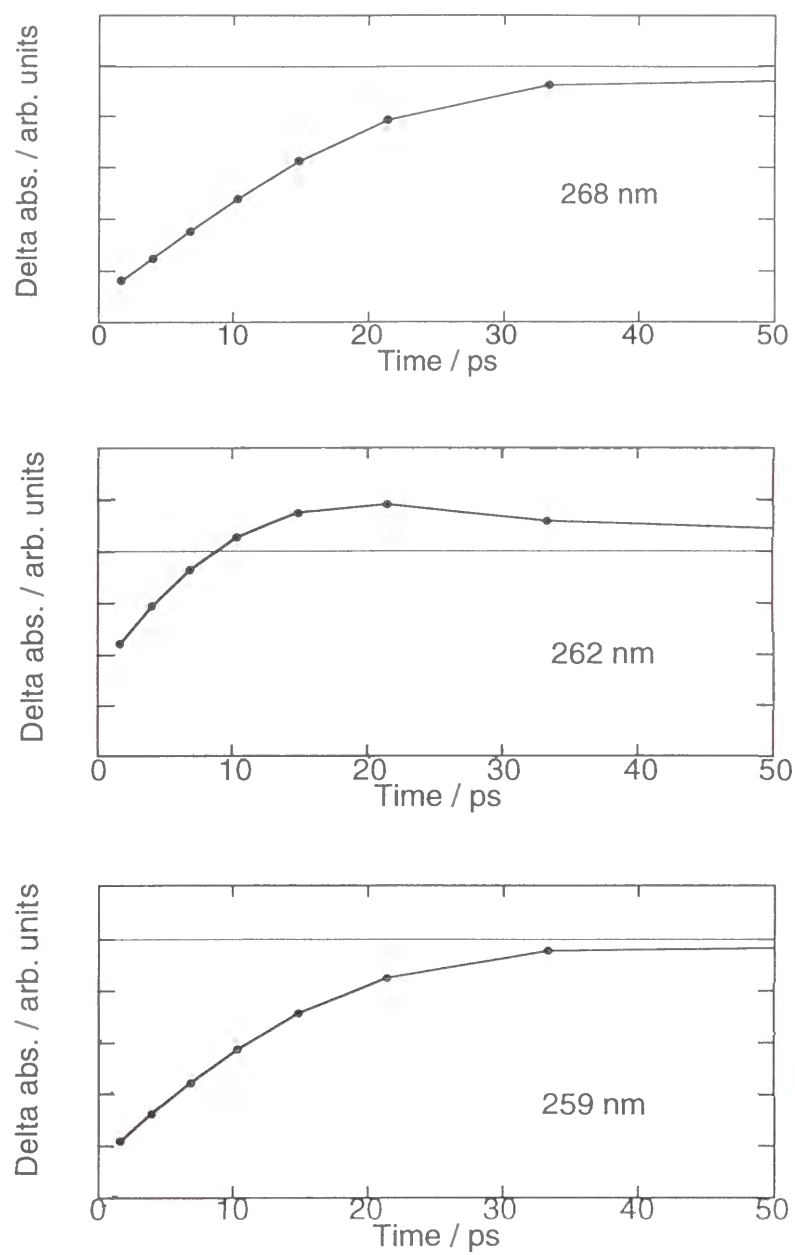


Figure 3-17. Calculated temporal profiles of the transient bleach recovery signals of trans-1,3,5-hexatriene at three different wavelengths.

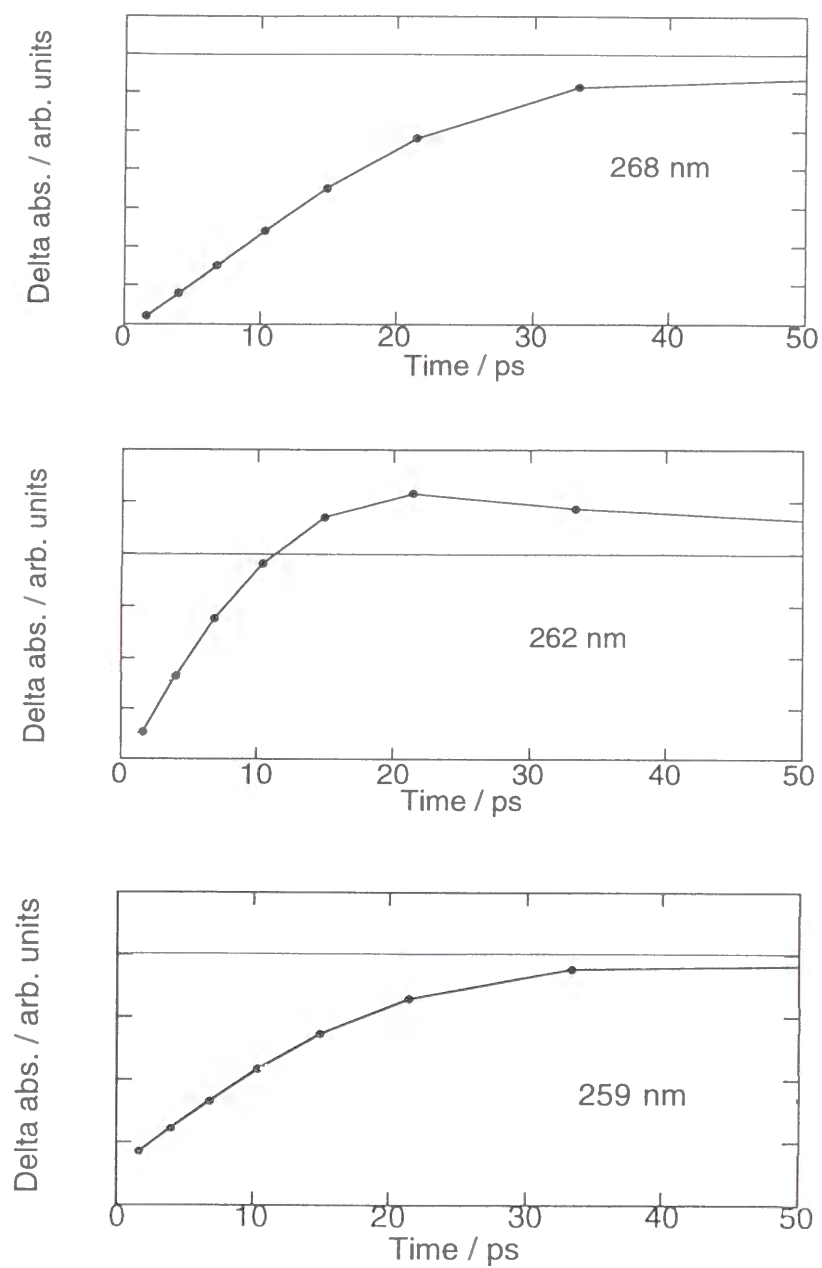


Figure 3-18. Calculated temporal profiles of the transient bleach recovery signals of cis-1,3,5-hexatriene at three different wavelengths.

3-4-2. (e) Pitfalls of the model calculation

In this model, we made the three assumptions. First, the intramolecular vibrational energy redistribution (IVR) occurs instantaneously in the ground state after the ultrafast internal conversion from the 2A state. Kaiser and coworkers investigated the vibrational relaxation processes of many organic molecules and established that the IVR occurred much faster than intermolecular energy transfer.

However, recent refined experiments show that IVR in the electronic ground state is not necessarily fast even in the case of large molecule such as stilbene [28] and TINUVIN (2-(2'-hydroxy-5'-methylphenyl)benzotriazole) [31]. These observations suggest that IVR does not complete within 10 ps time scale and competes with the reaction. Therefore the above statement is not still clear and needs further experimental verification. 1,3,5-Hexatriene contains only 14 atoms, which is relatively small, so that the density of vibrational state is not large. In this case, it can be considered that IVR does not occur fast compared with the vibrational relaxation process and conformational relaxation process around the C-C single bond. Therefore, IVR should alter the temporal behavior of the bleach recovery signals at an earlier time scale. However, after completing the IVR process, the transient bleach recovery signals in a 10-ps time scale are mainly controlled by the vibrational relaxation and can be explained by this model.

Second, we have to consider the anharmonicity of the potential energy surface in this calculation. In a higher vibrational state, the spacing between two adjacent states becomes smaller and the anharmonicity plays an important role in the population distribution. Myers and coworkers considered the anharmonicity of the central C=C double bond torsion for reproducing the overtone scattering intensity of this mode in their experiment [19]. If the IVR process is fast, the initial population is mainly located in the lower vibrational level so that the effect of the anharmonicity is not serious for the calculation of the absorption spectra.

Third, we neglect the contribution of the formation process of s-cis isomers in the ground state. The theoretical calculation predicts that there exist two channels which

lead from the 2A state surface via two conical intersections to two products (double-bond and single-bond isomer) and they have small barriers, as mentioned in Section 3-3-1. The temperature dependence on the lifetime of the 2A state in the gas phase gives an activation energy of about 170 cm^{-1} , which is consistent with our previous spectroscopic observation and theoretical prediction [10]. The two processes are ascribed to the isomerization process around the C-C single bond and the C=C double bond, respectively. Therefore, we consider that formation process of s-cis isomers completes during the internal conversion to the ground state. The distribution among these isomers may change by the vibrational relaxation process to produce a new equilibrium. This also should affect the temporal profiles of the bleach recovery signals. Fuss and coworkers suggested that the molecule had an excess energy of about 450 kJ/mol just after the internal conversion to the ground state. This excess energy is much greater than the barrier for the single-bond isomerization. The s-cis and s-trans isomers are mutually interconverted and the distribution among these isomers is considered to establish within a few picosecond time scale followed the vibrational cooling in the ground state [38]. For s-cis isomers, similar temporal behavior of the transient bleach signals at three different wavelengths is expected to appear and this does not affect our conclusion of the model calculation.

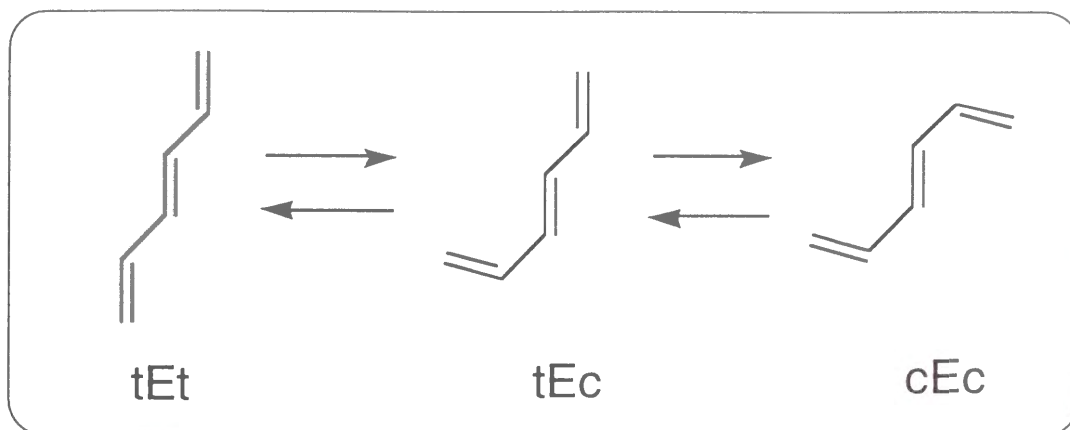
In this section, we performed the model calculation to explain the temporal profiles of the transient bleach recovery signals. We succeeded in reproducing them, although we have made several assumptions in this calculation. Time resolved transient absorption spectra in 250-300 nm region should be helpful for us to give valuable information to resolve the vibrational and conformation relaxation process in the ground state for 1,3,5-hexatriene.

3-4-3 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 hundreds of picoseconds. The quantum yield of the photoisomerization around the C=C double bond in solution is very low ($\phi_{\text{trans-cis}}=0.016$, $\phi_{\text{cis-trans}}=0.034$) [2]. 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 [39]. One plausible explanation for the slow component is that the conformational isomers around C-C single bond are produced on the way of relaxation process and the signals contain the contribution about a conformational relaxation to the original stable form.

There exist three different C-C single-bond isomers for each trans- and cis-1,3,5-hexatriene as shown in Figure 3-19. It is well known that the stable form at room temperature is the all s-trans one. After photoexcitation, the system undergoes by full or partial rotation about the single bond in the S_2 , S_1 state and/or 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 isomers to the original stable s-trans isomer at room temperature. The theoretical calculation predicts that there exist two channels which lead from the 2A state surface via two conical intersections to two products (double-bond and single-bond isomer) and they have small barriers, as mentioned in Section 4-1 [10]. The temperature dependence on the lifetime of the 2A state in the gas phase gives an activation energy of about 170 cm^{-1} [24], which is consistent with our previous spectroscopic observation [16] and theoretical prediction [10]. The two processes are ascribed to the isomerization process around the C-C single bond and C=C double bond.

trans-HT



cis-HT

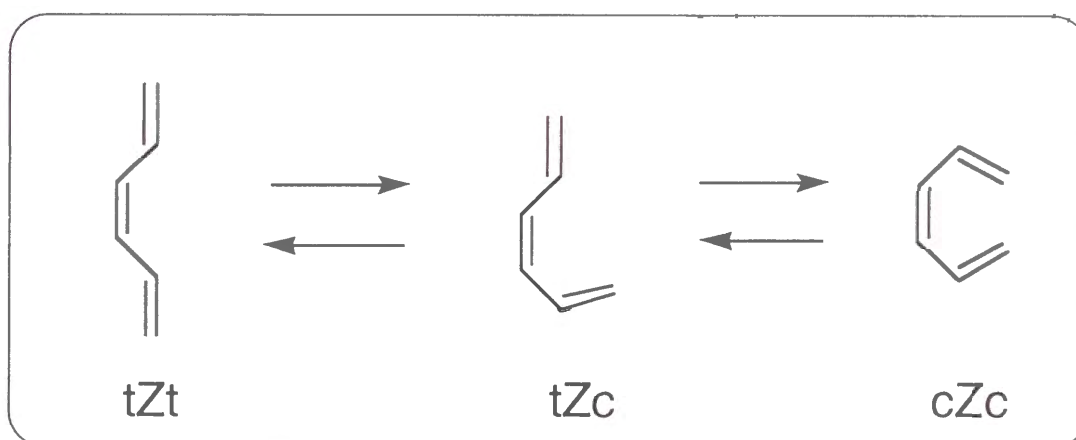


Figure 3-19. Three different conformers of trans- and cis-1,3,5-hexatriene.

Furukawa and coworkers 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 [39]. They found a new absorption band in the spectra at around 276 nm and assigned them to s-cis isomers based on the *ab-initio* MO calculation and normal mode analysis [32]. Furthermore, Brouwer and Jacobs found the s-cis isomers of dimethyl hexatrienes in Ar matrices based on the UV and IR absorption spectra [40,41]. Therefore, it is expected that the s-cis isomers can be produced on the way of relaxation in the solution phase. Very recently, two different groups performed femtosecond transient absorption measurements of 1,3-cyclohexadiene and trans- and cis-1,3,5-hexatriene in solution [29,42]. They both found that the transient absorption and bleach recovery signals for trans- and cis-1,3,5-hexatriene within 20 ps time scale were similar to that for 1,3-cyclohexadiene. After the photochemical ring opening reaction of 1,3-cyclohexadiene, cis-1,3,5-hexatriene (cZc) is produced. The conformational relaxation of cZc to cZt isomer occurs with 7 ps time constant, which is competition with the vibrational relaxation. One of them suggested that all photoproducts among these three systems appeared in the same manner. This means that the formation of s-cis isomer and the conformational relaxation around C-C single bond take place competitively with the vibrational relaxation process [29].

It is most plausible that s-cis isomers are produced through the internal conversion from the 2A to 1A state. The small barrier among the three different conformers makes a rapid transformation possible among s-cis isomers. During the vibrational relaxation in the ground state, a distribution of each conformer is created. The conformational relaxation around C-C single bond to a stable all s-trans form follows in a slower time scale.

In general, the absorption cross section of s-cis isomers is smaller than that of s-trans isomer which is suggested by the *ab-initio* calculation and the experimental observation of substituted hexatriene derivatives [32,39-41]. 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 many

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 cis isomer, $cZc < tZc < tZt$ and, for trans isomer, $cEc < tEc < tEt$ [43]. 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.

Picosecond time-resolved Raman and nanosecond FT-IR studies of photochemical ring opening reaction of 1,3-cyclohexadiene shows 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 [20,44]. 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 1,3,5-hexatriene in the ground state. These time constants depend on solvent.

The different time profile observed in slow component of bleach recovery for each trans- and cis-1,3,5-hexatriene may reflect different product distribution and dynamics among three conformational isomers. For trans isomer, a certain amount of s-cis isomers are produced in the ground state so that the third bleach components have a sufficient amplitude as the transient absorption change in a subnanosecond time scale. On the other hand, for cis isomer, 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 as observed in the photochemical ring opening reaction of 1,3-cyclohexadiene. This isomer does not contribute to the signal in a slower time scale. Moreover, a ratio of product for tZc to tZt isomers is expected to be small because the transient bleach recovery signals in 100-ps time scale have very small amplitude.

Another explanation is possible for the different behavior between the trans and cis isomers in 100-ps time scale [38]. The conformational relaxation from a mixture of

three different isomers to tZt isomer mainly occurs faster than or compatible to the vibrational relaxation process. It comes from the instability of s-cis isomers because of the steric hindrance. In this case, the stable tZt isomer is formed predominately 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 vibrational relaxation process.

3-4-4. Temperature dependence of the slow component of the bleach recovery signals

In order 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 about a factor of 2.5 by changing temperature from 286 K to 326 K. Figure 3-20a shows the transient bleach recovery signals of trans-1,3,5-hexatriene in cyclohexane at two different temperature. The bleach recovers faster at higher temperature. The rate constant depends on the solvent viscosity and temperature. It is frequently expressed by the following Arrhenius-type equation [45].

$$k = \frac{A}{\eta^a} \exp\left(-\frac{\Delta E}{k_b T}\right) \quad (1)$$

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 ($0 \leq a \leq 1$). The temperature dependence on the recovery time constant is well fitted by eq 1. Figure 3-20b shows the temperature dependence for trans-1,3,5-hexatriene in cyclohexane by assuming that a is 1. In this case the activation energy is equal to 7.6 kJ / mol, however this gives the lower limit of the value. The activation energy is ranging 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 [46,47]. The obtained value is in good agreement with the previous one.

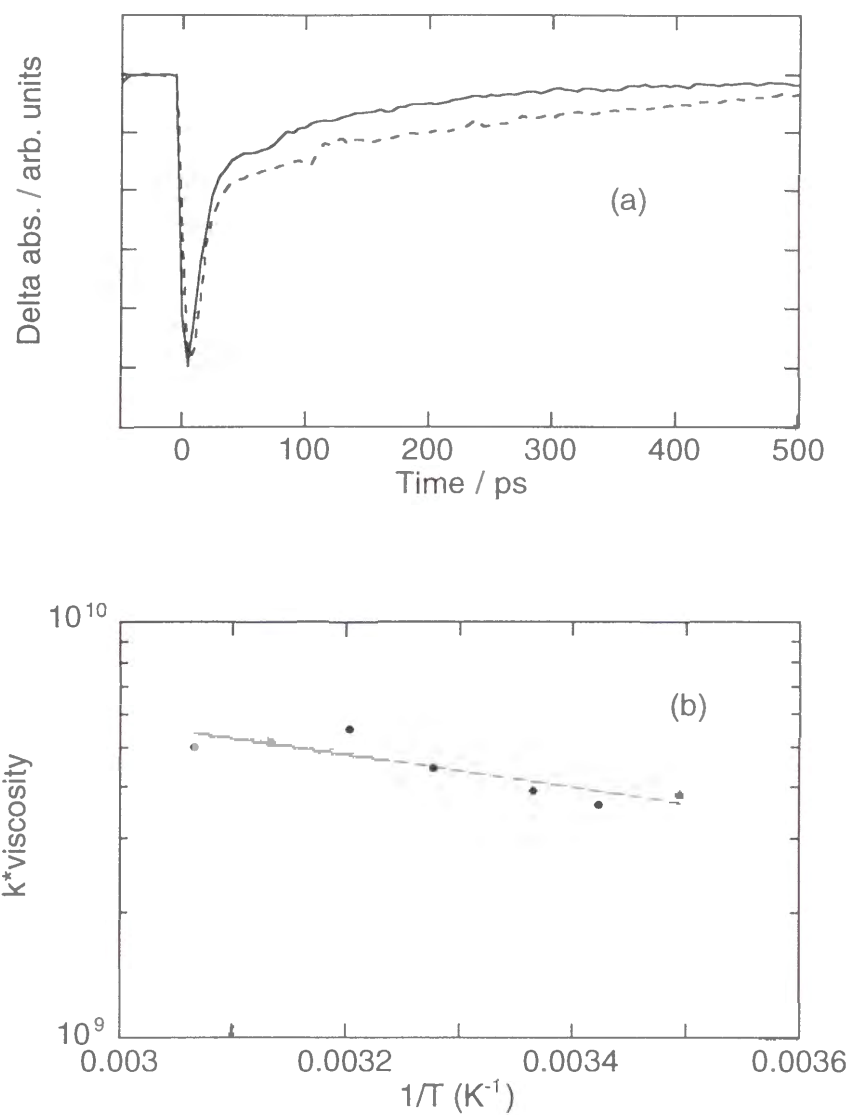


Figure 3-20 (a) Transient bleach recovery signals at 276 K (dotted line) and 327 K (solid line) for trans-1,3,5-hexatriene in cyclohexane.
 (b) Temperature dependence for trans-1,3,5-hexatriene in cyclohexane.

3-5. 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 occurs 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 not much assisted 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.

The anisotropy change of the transient absorption signals at 400 nm for trans isomer clearly shows the different time dependence from that for cis isomer. For trans isomer, the initial anisotropy is 0.18 and is nearly constant within our observed time scale. The anisotropy is around 0.11 at the all time. In contrast to trans isomer, the anisotropy of cis isomer decays from 0.37 to 0.0 with the time constant of about 1.2 ps. The anisotropy decay leads to information about the change of direction in the dipole moment between S_n - S_2 and S_n - S_1 transition or the structural change in the S_1 state during the vibrational energy redistribution process. Although it is difficult to identify the origin of the anisotropy change only based on this experiment, we clearly observed the different initial values of the anisotropy and different time dependence between the trans and cis isomers. This means that 1,3,5-hexatriene has different potential minima and different intermediate geometries in the S_1 state for each isomer.

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 model calculation based on the time-dependent wave-packet propagation scheme supports this idea. We succeeded in reproducing the

temporal behaviors of the transient bleach recovery signals at three different wavelengths, although we have made several assumptions in this calculation.

The different behavior 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, the conformational relaxation around C-C single bond. For trans isomer, a significant amount of s-cis isomers is created and the bleach recovery in a subnanosecond time scale is attributed to the single bond relaxation. On the other hand, for 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 s-cis to all-s-trans isomer which occurs faster than vibrational relaxation process. All-s-trans isomer is formed predominately within 20 ps. From the temperature dependence on the bleach recovery signals, the activation energy is estimated to be 10-20 kJ / mol. 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. The obtained value is in good agreement with the previous one.

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Chapter 4

Photodynamics of 1,3,5,7-Octatetraene in Solution

4-1. Introduction

The photodynamics of simple linear polyenes has considerable attention both experimentally and theoretically because these compounds serve as model systems in the chromophore of visual pigments [1-4]. Unlike shorter linear polyenes such as 1,3-butadiene and 1,3,5-hexatriene, 1,3,5,7-octatetraene exhibits a significant fluorescence quantum yield in both gas and condensed phases [5]. Many time-resolved spectroscopic techniques have been applied to investigate the excited-state dynamics of this compound over the last two decades [6-8].

Hudson and Kohler first demonstrated that the lowest electronic excited state of linear polyenes was an optically forbidden 2^1A_g state rather than an optically allowed 1^1B_u state in all-trans-diphenyloctatetraene [9,10]. The theoretical calculation by Shulten, Ohmine and Karplus established that the mixing of singly and doubly excited A_g configuration resulted in a lowering of the 2^1A_g energy below that of 1^1B_u state [11]. The state ordering of 1,3,5,7-octatetraene is identical with simple linear polyenes such as 1,3,5-hexatriene and 1,3,5,7-octatetraene. Recently, our group has measured the fluorescence excitation spectra of this molecule after the direct photoexcitation to the S_1 (2^1A_g) state [12]. It was concluded that the Herzberg-Teller coupling was so strong that the forbidden 2^1A_g - 1^1A_g transition had sufficient oscillator strength to be observed in the fluorescence excitation spectra. The lifetime of the S_1 state in 1,3,5,7-octatetraene was found to be an order of nanosecond, which was much longer than that of 1,3,5-hexatriene [6,7]. The wavelength dependent fluorescence lifetimes gave an abrupt onset of nonradiative decay process at $\sim 2100\text{ cm}^{-1}$ excess energy. This is ascribed to the transition state of trans-cis isomerization [12].

The internal conversion from the S_2 to S_1 state is considered to occur in a much faster time scale. However, there is no report on the dynamics in a subpicosecond-picosecond time scale. From the linewidth of the absorption spectra in the gas phase, it is estimated that the lifetime of the S_2 state is about 400 fs [13,14]. It was considered that the population in the $2A$ state was efficiently created by the internal conversion on a subpicosecond time scale and subsequent chemistry occurred in the longer lived $2A$ state.

Therefore it is highly desirable to conduct the femtosecond transient absorption measurement of 1,3,5,7-octatetraene in solution to reveal the dynamics in the early time region directly.

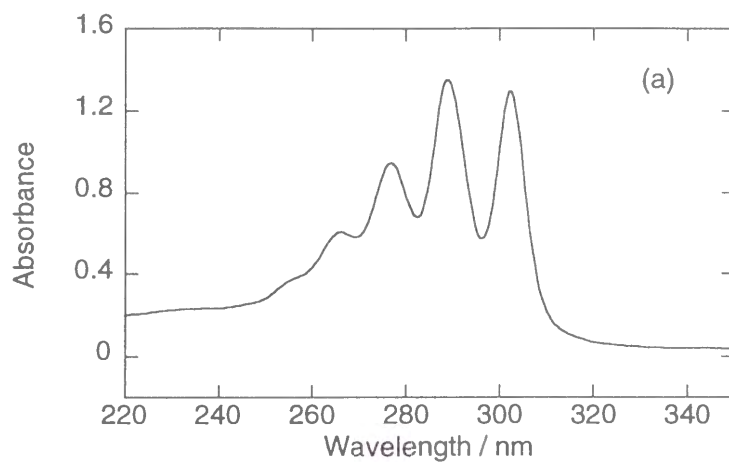
In this section, we present the results of the ultrafast transient absorption experiments on the excited-state dynamics of 1,3,5,7-octatetraene in solution. After the photoexcitation to the 1B state, we observed the transient absorption in the very broad spectral region (ultraviolet to visible region). The dynamics significantly depends on the probe wavelength. The subpicosecond decay component dominates at the wavelengths longer than 500 nm. The signals contain a 10 ps decay component at all wavelengths. These signals provide information about the internal conversion from the S_2 (1^1B_u) state to S_1 (2^1A_g) state and the vibrational relaxation in the S_1 state. The results are compared with those in the gas phase and the difference between 1,3,5,7-octatetraene and shorter ones is discussed.

4-2. Results

4-2-1 Static absorption and fluorescence spectra of all-trans 1,3,5,7-octatetraene in solution.

The static absorption spectrum of all-trans-1,3,5,7-octatetraene in acetonitrile is shown in Figure 4-1a. This molecule has a very strong absorption band from 250 nm to 310 nm. This strong absorption comes from the $1^1B_u-1^1A_g$ transition. The static fluorescence spectrum in acetonitrile is also shown in Figure 4-1b. The fluorescence band is located from 360 to 480 nm, whose peak is around 400 nm. There is a large gap between the absorption and fluorescence spectra. Gavin et al. investigated the absorption and fluorescence spectra of 1,3,5,7-octatetraene in various solutions [6]. They found that there existed a large gap of about 3000 cm^{-1} between the first band of the $1^1B_u-1^1A_g$ transition and the onset of the fluorescence spectra as observed in Figure 4-1. This means that the fluorescent state is different from that where the strong absorption is observed, i.e. the lowest excited singlet state has 1A_g symmetry. The fluorescence quantum yield from the 2^1A_g state is reported to be 0.03 at room temperature [6].

(a)



(b)

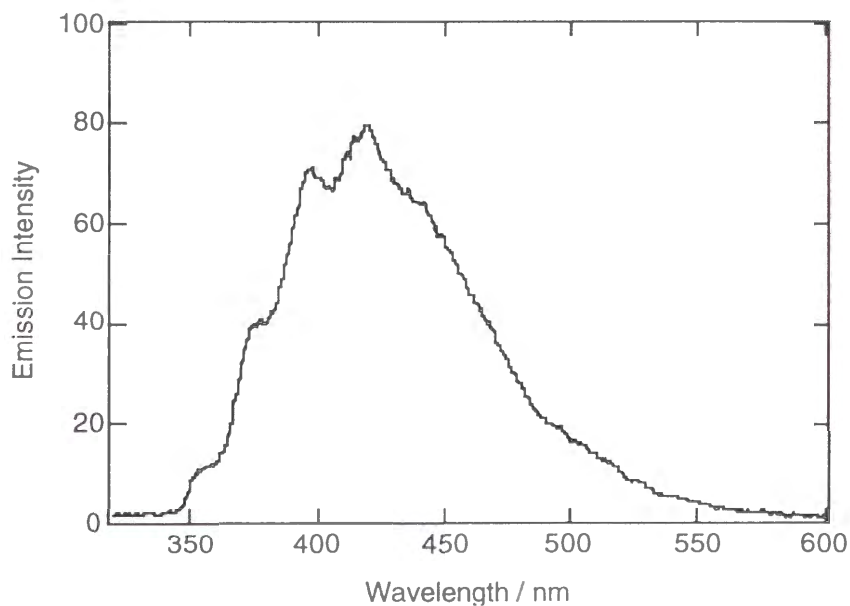


Figure 4-1. (a) Static absorption spectrum of all trans-1,3,5,7-octatetraene in acetonitrile. (b) Static fluorescence spectrum of all trans-1,3,5,7-octatetraene in acetonitrile. Excitation wavelength is 303 nm. Each spectrum is scaled by arbitrary units.

4-2-2 Excited-state dynamics of all-trans 1,3,5,7-octatetraene in solution.

The transient absorption signals within a few picosecond time scale were measured for all-trans 1,3,5,7-octatetraene in acetonitrile with an excitation wavelength of 268 nm and eleven probe wavelengths from 340 nm to 540 nm. The results are shown in Figure 4-2. Table 4-1 summarizes the results of the best-fit time constants of the transient absorption signals. The time profiles of the signals are tentatively fitted to a single exponential decay except that at 340 nm. The signal at 340 nm contains a rise component so that we fit to a single exponential rise. After the photoexcitation, the 270 fs rise of the signal is observed without any decay in this time scale. From 360 nm to 460 nm, the signals have small decaying components with the lifetime of 200 fs to 1.7 ps. The values obtained are scattered due to a very small amplitude. At the wavelengths longer than 480 nm, we clearly observed the subpicosecond decay components in the transient absorption signals. At 480 nm, the decay time constant is about 520 fs. At the wavelengths longer than 500 nm, the decay becomes slightly faster, whose time constants are around 400 fs. We also found that the relative amplitude of the fast decaying component becomes larger at the longer wavelength.

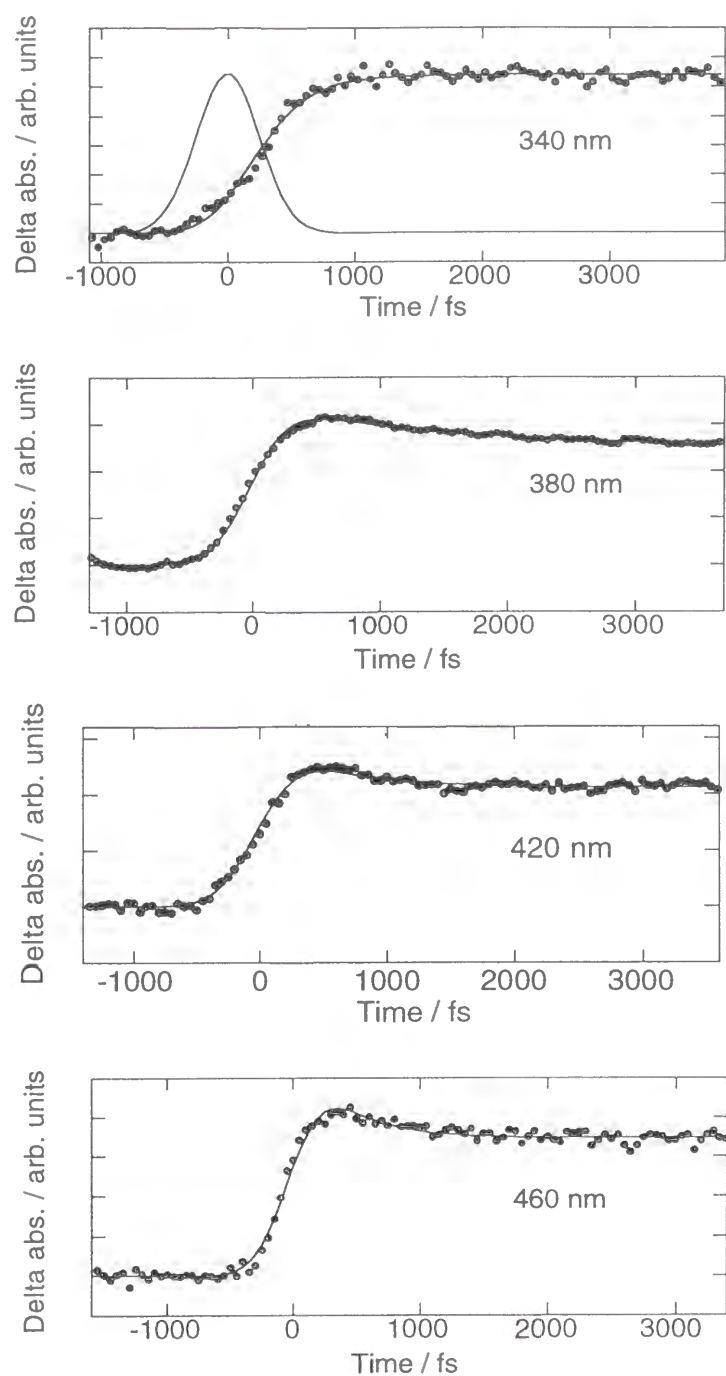


Figure 4-2 (a). Transient absorption signals probed at four different wavelengths for all trans-1,3,5,7-octatetraene in acetonitrile within a few picosecond time scale. The instrument response function is shown in the top decay curve. The solid line represents the best fits to the data by the convolution of the instrument response function with a single exponential function.

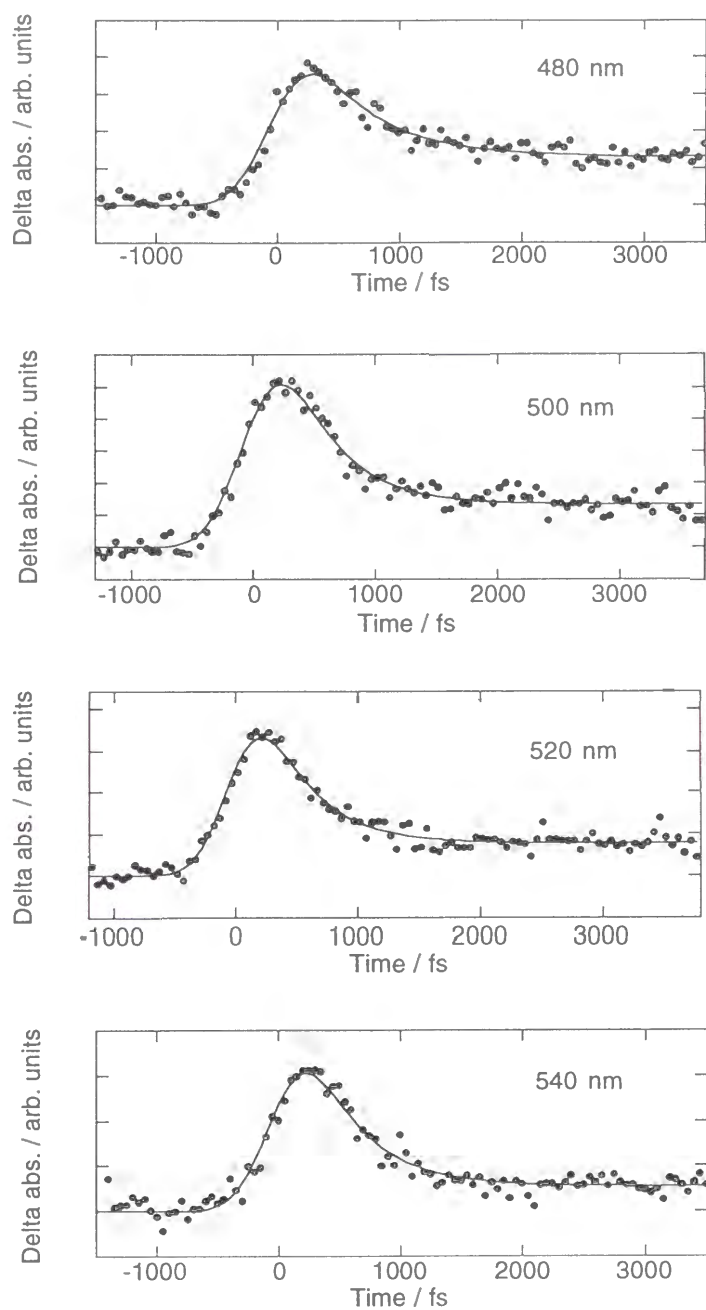


Figure 4-2b. Transient absorption signals probed at four different wavelengths for all trans-1,3,5,7-octatetraene in acetonitrile within a few picosecond time scale. The solid line represents the best fits to the data by the convolution of the instrument response function with a single exponential function.

Table 4-1. Best fit time constants of transient absorption signals of all-trans 1,3,5,7-octatetraene in acetonitrile. The asterisk shows the data which is fitted well by a single exponential rise.

λ / nm	τ_1 / ps ^a	τ_2 / ps ^a	τ_3 / ps ^b
340	$0.27 \pm 0.01^*$	9.4 ± 0.9	790 ± 8
360	-----	6.0 ± 0.3	606 ± 8
380	1.7 ± 0.2	6.4 ± 0.2	577 ± 6
400	2.0 ± 0.3	5.8 ± 0.4	710 ± 8
420	0.62 ± 0.09	6.7 ± 0.4	670 ± 10
440	0.23 ± 0.02	11.2 ± 2.7	-----
460	0.35 ± 0.04	16.4 ± 3.4	-----
480	0.52 ± 0.04	7.9 ± 2.5	-----
500	0.39 ± 0.02	-----	-----
520	0.40 ± 0.02	-----	-----
540	0.42 ± 0.03	-----	-----

^a τ_1 and τ_2 are the first and second components, respectively, of the transient absorption signals observed on an early time scale.

^b The third component of the transient absorption signal observed on a slower time scale.

The results of transient absorption signals in 30-ps time scale are displayed in Figure 4-3. The time profiles of the signals are also fitted to a single exponential decay with an offset. Table 4-1 summarizes the results of the best-fit time constants of the transient absorption signals. These transient absorption signals possess a 10 ps decay component at all probe wavelengths. From 360 nm to 460 nm, the decay time constants are around 6-16 ps.

The temporal profiles of the 100-ps time scale of the transient absorption signals are shown in Figure 4-4. The decay time constants of the slower component are 600-800 ps.

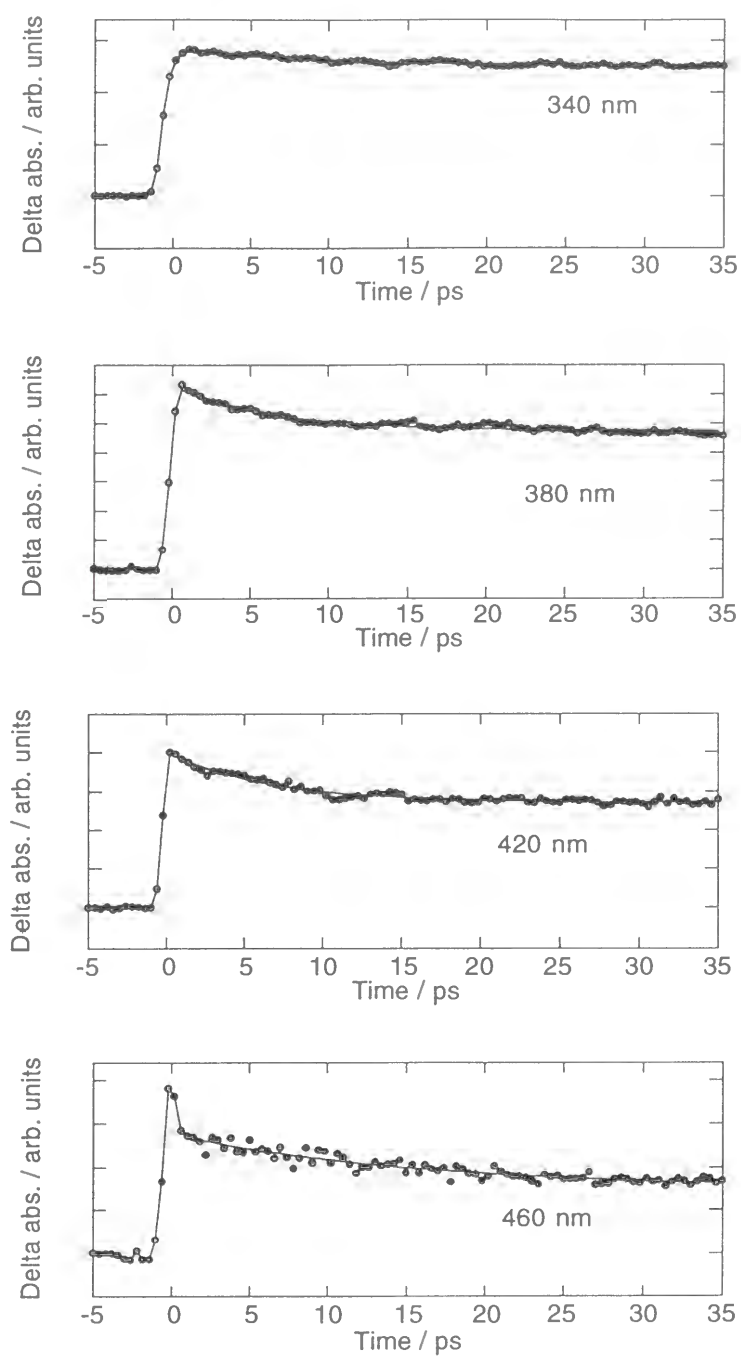


Figure 4-3. Transient absorption signals probed at four different wavelengths for all trans-1,3,5,7-octatetraene in acetonitrile in a 10 ps time scale.

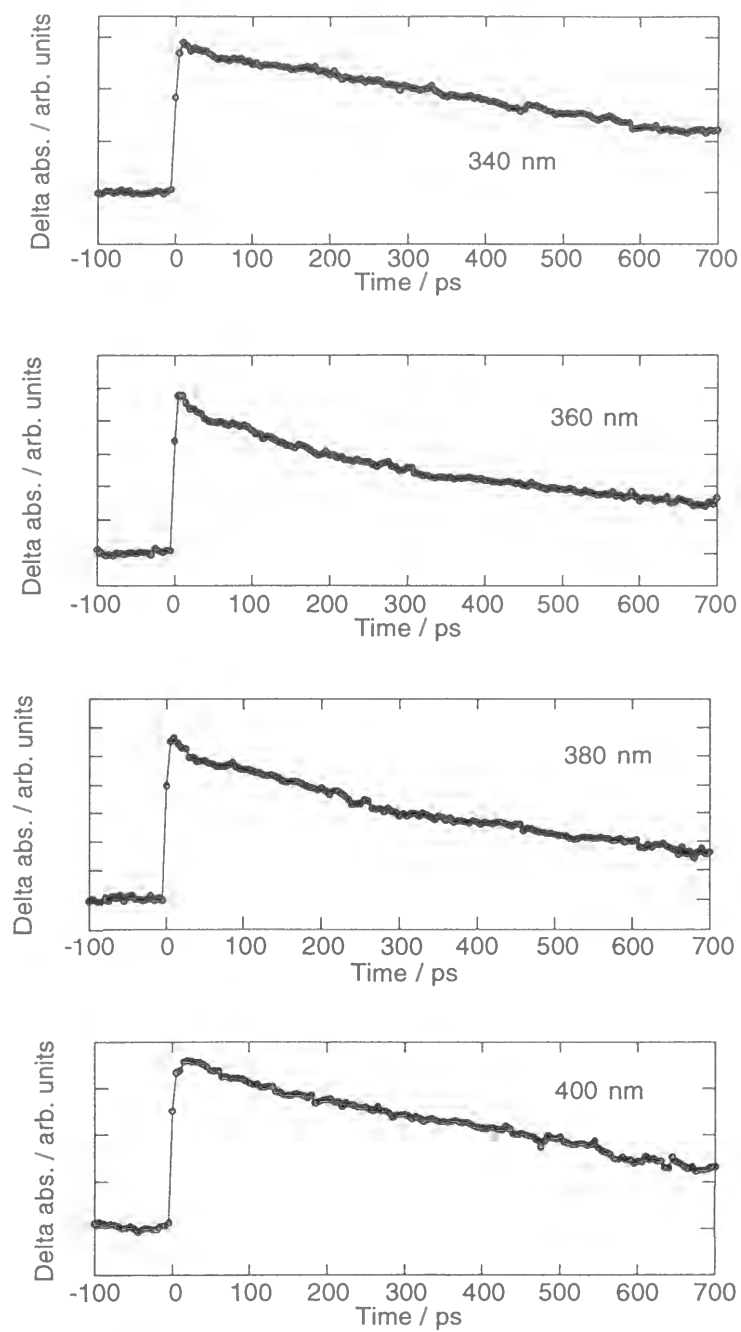


Figure 4-4. Transient absorption signals probed at four different wavelengths for all trans-1,3,5,7-octatetraene in acetonitrile in a 100 ps time scale.

4-3. Discussion

The feature of the observed dynamics is divided into three contributions. (1) a subpicosecond decay component at the longer wavelengths, (2) 10-15 ps decay component at all wavelength, (3) 600-800 ps decay component.

The lifetime of the S_1 state has been already determined to be 4 ns in alkane solvent by the picosecond time-resolved fluorescence spectroscopy [7]. The slow components of the observed signals in the present contain 600-800 ps decay time constants. We think that this decay component is attributed to the internal conversion to the ground state even though the time constant is much smaller than that observed in the previous studies in alkane solvents. In the case of trans-stilbene, the lifetime of the S_1 state is also strongly dependent on the solvent polarity and viscosity. For trans-stilbene, the isomerization around the C=C double bond from the trans to cis isomer is the origin of the nonradiative decay in the S_1 state. Based on this observation, it is considered that the observed difference is due to the solvent polarity which may reduce the barrier height of the deactivation process in the S_1 state.

The S_n - S_1 excited absorption spectrum of 1,3,5,7-octatetraene was measured by nanosecond time-resolved transient absorption spectroscopy [8]. The spectrum is broad, structureless and shows a peak at 330 nm with a long tail to the red region. The transient absorption signals at a longer time scale correspond to the S_n - S_1 excited state absorption. Therefore the transient absorption signals within a 50 ps time scale should give information about the internal conversion from the S_2 state to S_1 state and the vibrational relaxation in the S_1 state.

It is estimated that the lifetime of the S_2 state is around 400 fs in the gas phase from the linewidth of the absorption spectra [13,14]. From the integrated absorption intensity, the intrinsic radiative lifetime of the S_2 state was estimated to be 1.5 ns. This indicates S_2 - S_0 fluorescence quantum yield of less than 10^{-4} . The decay time constants of the fast components observed at the longer wavelengths are similar to the lifetime of the S_2 state in the gas phase. The oscillator strength of the S_n - S_1 transition is very small at the wavelength longer than 460 nm. This observation suggests that the transient absorption

components at the longer wavelengths originate from the other electronic excited state.

We consider that the subpicosecond decay components at the longer wavelengths reflect the internal conversion from the S_2 to S_1 state and the absorption bands are shifted to the blue side within this time scale. At a longer time scale, there are remaining absorption components. This nonzero transient absorption signal is assigned to the absorption from the S_1 state. The theoretical calculation supports our assignment [8]. It predicts that the allowed transitions from the 1^1B_u (S_2) state to 5^1A_g and 6^1A_g state are located at 549 and 425 nm, respectively. These wavelengths are longer than those which correspond to the allowed transition from 2^1A_g (S_1) state (350-360 nm). It should be noted that the absorbance of the fast components at the wavelengths longer than 480 nm has a smaller intensity than that at shorter wavelength. This reflects the difference of the oscillator strengths between S_n - S_2 and S_n - S_1 transition. The population in the S_1 state is created in a 500 fs time scale. However we cannot clearly observe the rise component of the transient absorption signals at the shorter probe wavelengths which comes from the population transfer through the S_2 - S_1 internal conversion. This may be due to the overlap of the excited state absorption between the S_n - S_2 and S_n - S_1 transitions.

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 was measured by the femtosecond transient absorption and fluorescence up-conversion spectroscopy [15,16]. This lifetime is around 200 fs in various solvents and is consistent with the fluorescence quantum yield. Furthermore the excited-state dynamics of diphenylpolyene compounds were also investigated by time-resolved absorption and fluorescence spectroscopy. Diphenylhexatriene (DPH) and diphenyloctatetraene (DPO) are the family whose dynamics have been investigated extensively [17-19]. The state ordering is the same as that of all-trans 1,3,5,7-octatetraene and the lifetime of the S_1 state is relatively long ($\sim$ ns). Transient absorption and fluorescence measurements of DPH showed that the initially formed 1B state relaxed to the equilibrium 1B/2A mixture within 10 ps [20]. Very recently, Yee et al. reported femtosecond transient absorption measurements of DPO and DPH in solution [21]. They found a subpicosecond decay

components at 720 and 780 nm, which was a red-edge of the S_n - S_1 transient absorption band and assigned to the internal conversion from the S_2 to S_1 state. These observations are quite similar to ours. The existence of the optically forbidden S_1 state is considered to be responsible for the initial ultrafast excited-state dynamics.

We consider that a 5-15 ps decay component is ascribed to the vibrational relaxation in the S_1 state. After the internal conversion to the S_1 state, the population in the vibrationally excited state is created, which is followed by the vibrational relaxation to the thermal equilibrium. Generally, the vibrational relaxation of large organic molecules in solution is known to occur in a 10-ps time scale [22]. In particular, the excited-state dynamics of trans-stilbene has extensively investigated by picosecond time-resolved resonance Raman spectroscopy [23,24]. It is clearly found that the vibrational relaxation in the S_1 state occurs in a 10 ps time scale.

In the case of the 1,3,5-hexatriene, the internal conversion to the ground state occurs in less than 1 ps, which is much faster than this component and we cannot observe the corresponding vibrational relaxation in the S_1 state [25,26]. The large difference of the lifetime between the S_2 and S_1 state allows us to separately detect the internal conversion from the S_2 to S_1 state and the vibrational relaxation in the S_1 state.

Finally we briefly mention the difference of the photophysical properties between 1,3,5-hexatriene and 1,3,5,7-octatetraene. Recent resonance Raman studies suggested that the internal conversion from the S_2 to S_1 state of 1,3,5-hexatriene occurred in about 20-40 fs, which was one order of magnitude smaller than that of 1,3,5,7-octatetraene [27,28]. This value is consistent with the estimated one from the linewidths of the absorption spectra under jet-cooled condition [13]. It was found that the linewidth of the spectrum became broader as decreasing the chain length. The origin band of jet-cooled all-trans-1,3,5,7-octatetraene has a full width at half-maximum intensity of 18 cm^{-1} . The corresponding lifetime is around 400 fs. The origin band of trans-1,3,5-hexatriene is about eight times broader, with a width of 155 cm^{-1} . The difference of the lifetime in the S_1 state between 1,3,5-hexatriene and 1,3,5,7-octatetraene may be due to a large difference of the barrier heights for the internal conversion to the S_0 state. From the

temperature dependence of the fluorescence decay rate, a barrier height for 1,3,5,7-octatetraene is ~ 17 kJ / mol [7]. Theoretical calculations suggest that the S_1 - S_0 radiationless decay channel is reached following the motion along a trans-cis isomerization path [29]. The predicted barrier of about 25 kJ / mol is consistent with the experimental values. On the other hand, the barrier height in the S_1 state for 1,3,5-hexatriene is less than 4 kJ / mol [30]. There exist two channels 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). Our previous spectroscopic observation and the other works give an activation energy of about 170 cm^{-1} (~ 2 kJ / mol), which is consistent with this theoretical prediction.

4-4 Conclusion.

We investigated the excited-state dynamics of 1,3,5,7-octatetraene in solution by femtosecond transient absorption spectroscopy. After the photoexcitation to the S_2 state, we observed the transient absorption in the very broad region (ultraviolet to visible region), whose dynamics depend on the probe wavelength. The subpicosecond decay component dominates at the wavelengths longer than 500 nm. The signals contain a 10 ps decay component at all wavelengths. Based on the results in the gas phase, we can consider that the subpicosecond decay components at the longer wavelengths reflect the internal conversion from the 1^1B_u to 2^1A_g state and the absorption bands are shifted to the blue side within this time scale. It should be noted that the absorbance at the wavelengths longer than 480 nm has a smaller intensity than that at shorter wavelength. This is due to the difference of the oscillator strengths between S_n - S_2 and S_n - S_1 transition. A 5-15 ps decay component observed in the transient absorption signal is ascribed to the vibrational relaxation in the S_1 state. The difference of the lifetime in the S_1 (2^1A_g) state between 1,3,5-hexatriene and 1,3,5,7-octatetraene may be due to a large difference of the barrier height in the deactivation process.

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Chapter 5

General Introduction

5-1. Propose of this study

Vibrational energy redistribution and relaxation play important roles common to all photoinduced processes of molecule [1,2]. By optical excitation, vibrational excess energy is produced locally inside a molecule. Dissipation of the excess energy strongly influences the pathway and the rate of the chemical reaction. This may cause a significant difference of the reactivity between the gas and solution phases. Solvent efficiently works as a heat bath. In the gas phase, these processes have been investigated extensively both in the electronic ground and excited states by various spectroscopic methods such as laser-induced fluorescence, high-resolution IR spectroscopy, and stimulated emission pumping [1]. Vibrational excitation to the selective modes has opened up the possibility for the preferential cleavage of a bond in a photodissociation or bimolecular reaction in some cases [2].

In contrast to this, there remain many unresolved problems in the vibrational relaxation process in solution [3-9]. This may come from the complexity of the interaction between the solute and surrounding solvents [10-12]. Furthermore, theoretical treatments of the chemical reaction dynamics sometimes assume that the vibrational relaxation in the electronic excited state completes much faster than the rate of the chemical reaction and the photoinduced reaction occurs from the vibrationally ground state. Recent ultrafast spectroscopic studies revealed that the reaction rate of some electron transfer or isomerization reactions was as fast as subpicosecond time scale, which was comparable to or faster than that of the vibrational energy redistribution [13]. The above assumption seems to be invalid for such a case. However there have been few studies to confirm this point. In this research, we excite a coumarin molecule to the S_n state by a third harmonic of the femtosecond Ti:Sapphire laser with an excess energy of 12000 cm^{-1} from the 0-0 transition of the S_1 state. We monitor the temporal evolutions of the fluorescence signals at several wavelengths in order to reveal the time scale of vibrational energy redistribution and relaxation process. We briefly discuss possible mechanisms of the ultrafast intramolecular energy redistribution after the short pulse excitation in solution.

5-2. Vibrational energy redistribution and relaxation processes in solution.

Information on the population lifetime of individual vibrational modes is necessary to gain an understanding the mechanism of the energy dissipation process. Before the development of the ultrafast laser techniques, one had to deduce the vibrational population lifetime from the spectral linewidth of the corresponding modes [5-7]. However, not only the vibrational population lifetime but also the vibrational dephasing come into the source of the broadening of the linewidth. Furthermore some other relaxation processes for the broadening sometimes have to be taken into account. On the frequency domain measurement, it is difficult to determine uniquely the lifetime of the population in a certain vibrational level.

With the advent of the ultrafast laser technology, particularly the generation of the intense ultrafast IR pulses, it has been possible to monitor directly the population dynamics of the individual states [3,4,14]. Until recently a considerable amount of experimental information has been accumulated on the relaxation of the vibrational energy in small molecules. In molecules with less than 10 atoms, it is relatively easy to obtain mode-specific information on the relaxation dynamics. It has been found that the experimentally observed lifetimes differ drastically from molecule to molecule and for different vibrations of the same molecules. Time constants are ranging from less than 1 ps to 240 ps. For N_2 molecule, the lifetime is quite long (an order of second). The depopulation rates depend critically on the individual vibrational frequency and the structure of the molecules [14].

Surrounding solvents sometimes affect the depopulation rate of the vibrational modes drastically. Recent studies of the ionic species of diatomic molecules in polar solvents revealed that the vibrational relaxation rate was much faster than that for the corresponding neutral species [15-20]. For example, Barbara and coworkers studied the dissociation and subsequent recombination, and vibrational relaxation dynamics of I_2^- in solution [15-17]. They found that the vibrational relaxation occurred in ~ 3 ps, which was much fast than that of I_2 in solution (50-200 ps). They suggested that the strong solute-solvent interaction such as long-range Coulombic interaction played an important role in

this fast vibrational relaxation. The situation is quite different for large molecules. It is well known that the density of the vibrational states per energy interval rises strongly with the number of atoms which makes up the polyatomic molecule. As a result of this high density, the excess energy is quickly redistributed over many vibrational manifold of the molecule [14]. In the following we briefly review the recent progress of the experimental results on the vibrational relaxation dynamics of large molecules. After describing the experimental results, we introduce the concept of the internal temperature and discuss the separability of the intra- and intermolecular processes.

5-3. What is IVR ? Definition and Background.

In this section, we briefly discuss the definition about the intramolecular vibrational energy distribution (IVR) because we sometimes use this term for different meanings and we do not have common language for describing this phenomena in between the gas and solution phases. In order to get intuitive insight for the IVR process, it is easy to think of molecules as a collection of balls and springs [1]. If one stretches the spring and suddenly releases it, balls are started to oscillate. As the time proceeds, the initial local oscillation would spread quickly and in an apparently complexed manner over the entire molecular framework. This is a simple description of IVR. From the quantum mechanical point of view, the photoexcitation produces arbitrary initial vibrational state which can be expressed by a superposition of the molecular eigenstates. This state evolves in time under the influence of the molecular Hamiltonian. During the evolution of the states, the vibrational energy is also distributed into the other states, which are not prepared by the initial excitation.

There are several misleading points that should be clarified with regard to the initially excited state and subsequent dynamics [1,2]. Many spectroscopic investigations of the IVR process are performed by continuous wave (cw) monochromatic laser or pulse laser. The cw laser excites the molecular eigenstates which are static in time and do not move at all. On the other hand, a short laser pulse can prepare a particular set of the initially localized excitations. It is referred to as a “zero-order bright state” (ZOBS). A ZOBS is not eigenstate and time-dependent. ZOBS and the time evolution of the initial state can be expressed by a superposition of the eigenstates. Therefore the initially prepared state moves in time and it appears as a quantum beat. If the initially prepared state is coupled with a relatively few dark state, the energy flow between the ZOBS and the other dark modes continues up to a sufficiently longer time than the lifetime of the electronic state. It is sometimes called “restricted IVR”. If a molecule is coupled with dense manifold of nearly equally coupled levels, the energy flow from the ZOBS to the other dark modes occurs irreversibly and is quickly dissipated over all the vibrationally manifolds (“Dissipative IVR”).

In solution phase, the low frequency solvent modes help to increase the density of the states which is coupled with the initially prepared state and the energy flow from the ZOBS to the other dark modes occurs unidirectionally. One could always consider that the IVR process causes the dissipation of the energy from an initially nonthermal energy distribution to a fully statistically thermalized state where all vibrational modes are populated according to a thermal Boltzmann factor and an vibrational temperature can be defined [14]. However this description is not apparent in the terms of the definition of the IVR. Hereafter, we use the term of “intramolecular energy redistribution” for expressing the energy redistribution process among the vibrational modes in solution in order to prevent the misunderstanding.

5-4. Studies on the vibrational relaxation dynamics of large molecules in solution.

Firstly, we describe the studies of the vibrational dynamics in the electronic ground states. Kaiser and coworkers have performed the extensive investigation on this subject [14,21,22]. They developed various methods for probing this process. For large molecules, the intramolecular energy redistribution in the electronic ground state affects the shape of the long-wavelength tail of the S_0 - S_1 transition. Changes of the absorption or fluorescence give direct information on the transient vibrational distribution. They investigated various molecules. For example, the transient absorption spectra of anthracene and tetracene after the excitation of the C-H stretching by a 5 ps infrared pulse were measured [14]. Figure 5-1 shows that the transient absorption spectra measured at 7 ps after the infrared excitation. It is clearly observed an increase of the absorption at lower energy region from 26000 to 25000 cm^{-1} in anthracene and 20500 to 19000 cm^{-1} in tetracene. This observation suggests a substantial transient increase in vibrational population as a result of the vibrational excitation and redistribution. They succeeded in reproducing the transient absorption spectra by assuming a Boltzmann distribution of a Franck-Condon active modes with the elevated temperature.

Excitation with higher energy should give higher internal temperature and more drastic changes of the absorption edge of the excited molecules. They used azulene for this purpose because azulene is known to undergo very fast internal conversion to the S_0 state after the photoexcitation to the S_1 state (< 2 ps) [21,22]. After the internal conversion, the population in the higher vibrational excited state is created in the electronic ground state. Figure 5-2 shows the results of the transient absorption spectra of azulene in CCl_4 . In this case, an excess energy of about 19000 cm^{-1} is put into a molecule after the internal conversion. After 10 ps, the log plot of the absorption spectrum at long wavelength-tail gives the straight line against the frequency. This is well simulated by the Boltzmann distribution with the temperature of 1200 K.

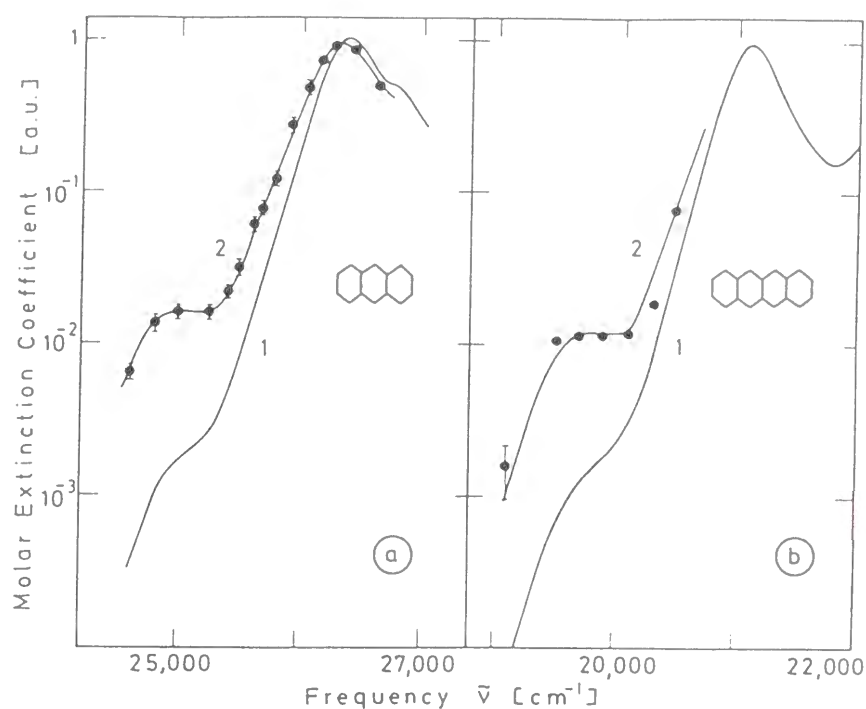


Figure 5-1. (a) Absorption spectra of anthracene in C_2Cl_4 . Curve 1 shows the spectrum at room temperature. Curve 2 shows the transient absorption spectrum of 7 ps after IR excitation. This is quoted from Ref. [14].

(b) Absorption spectra of tetracene in C_2Cl_4 . Curve 1 shows the spectrum at room temperature. Curve 2 shows the transient absorption spectrum of 3.5 ps after IR excitation. This is quoted from Ref. [14].

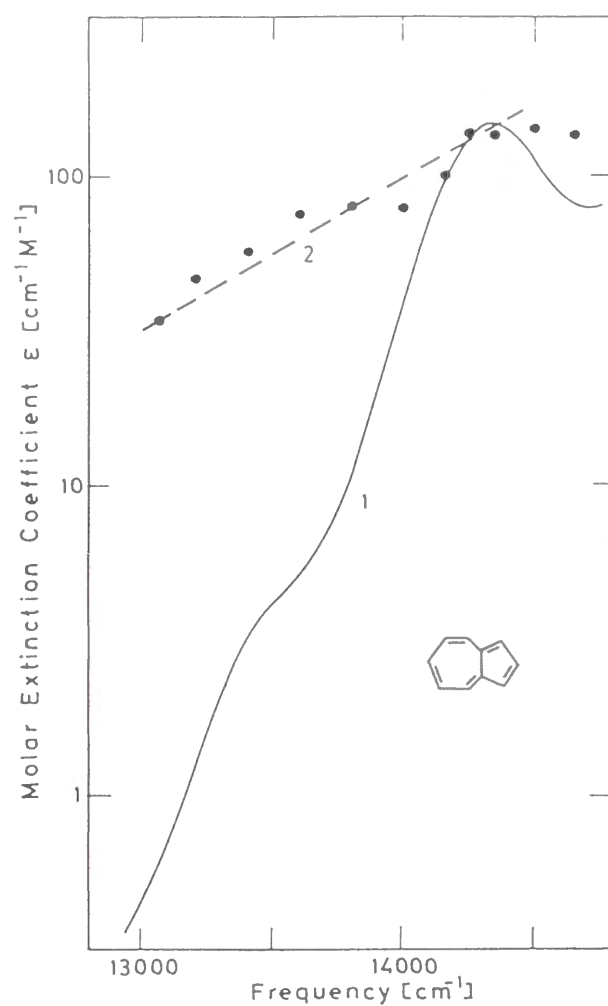


Figure 5-2. Low-energy tail of the absorption spectrum of azulene at 300 K (1, Solid line) and transient absorption spectrum measured at 10 ps after the excitation at the S_1 state (2, Closed circle). The broken line is calculated for a Boltzmann edge of 1200 K. This is quoted from Ref. [21].

Next we discuss the relaxation dynamics of large molecules in the electronic excited state. It has been revealed that the intramolecular energy redistribution in the lowest electronic excited state occurs ranging from <100 fs to 300 fs for several large dye molecules such as nile blue, cresyl violet, HITC, oxazine, and rhodamine compounds [23-31]. The subsequent cooling process of the vibrationally hot molecules in the electronic ground state proceeds on a time scale of 5 to 50 ps. In particular, Mokhtari et al. used the femtosecond up-conversion method to measure the excited-state dynamics of nile blue and oxazine 1 in solution after the photoexcitation to the S_1 state [23,24]. They found that the evolution of the fluorescence bandwidth contained fast (0.4-0.6 ps) and slow (4-6 ps) components. They attributed the fast one to the intramolecular energy redistribution process. Very recently Martini et al. investigated the relaxation dynamics of a cyanine dye, HITC in various solvents by transient bleach/stimulated emission experiment [28,29]. They used optical parametric generator and amplifier, which allows to tune the pump wavelength to different parts of the absorption band. They found that a stimulated emission signal rose with the time constants of 300 fs and 1.7-7.1 ps. The latter constants depend on the solvent. It is concluded that the former time constant represents the time scale of intramolecular energy redistribution process and the latter one is related to the vibrational cooling process in the S_1 state. Experiments with variable wavelengths show that the vibrational cooling is faster at higher energies in the S_1 state.

5-5. Studies on the vibrational relaxation dynamics of large molecules after the photoexcitation to the higher electronic excited state.

The fluorescence of organic molecules in the condensed phase or in the gas phase at a higher pressure always comes from the lowest electronic excited state even if it is excited to a higher electronic state. A molecule is quickly depopulated by the internal conversion to the S_1 state and this observation is frequently referred to as Kasha's rule. However, in the gas phase at low pressure, the fluorescence spectrum depends on the amount of the excess energy [32,33]. Lim and coworkers observed that broadening and red-shift of the fluorescence in naphthalene and anthracene upon excitation to the higher electronic state (Figure 5-3) [32]. Under collision free condition, the fluorescence is considered to come from the highly vibrational excited state since the vibrational relaxation is relatively slow. A question arises whether or not interaction with the surrounding medium or collision with other molecules, accelerated in the internal conversion and vibrational energy redistribution process.

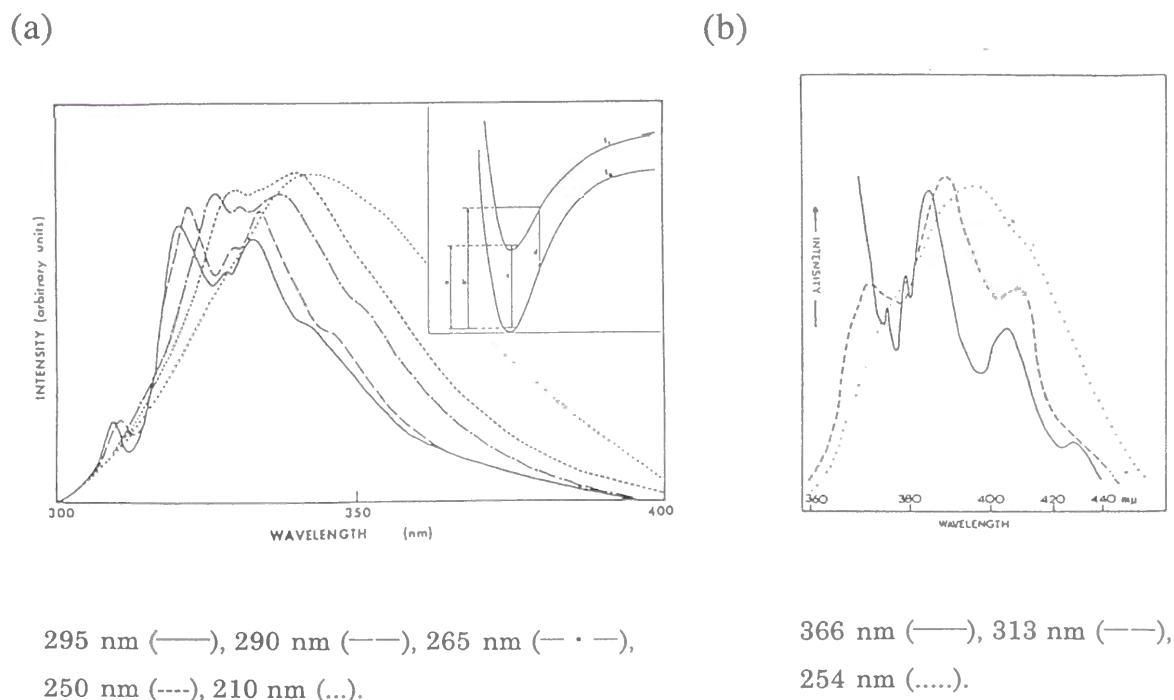


Figure 5-3. The excitation wavelength dependence on the emission spectra of naphthalene (a) and anthracene (b). This is quoted from Ref. [32,33].

Kaiser et al. investigated the relaxation of the highly lying S_n state in solution by femtosecond stimulated emission spectroscopy [30,31]. They obtained a 180 fs time constant for the intramolecular energy redistribution process of oxazine 1 and sulforhodamine B from the appearance of stimulated emission. They also found that the broadening of the emission band relaxed on a time scale of 10 ps which is caused by the intermolecular energy transfer to solvent. Very recently, vibronic dynamics of dye molecule IR 125 was investigated with 30 fs pump pulse and 20 fs probe pulse [26,27]. They observed the coherent vibrational motion in the emission signal around zero time delay. The buildup of the stimulated emission from the S_1 state occurs in a 1.2 ps. They discussed that the rate of the internal conversion and intramolecular energy redistribution depended on the energy-gap between the S_1 and S_2 state.

In their experiments, it is difficult to separate the rate of vibrational cooling from the internal conversion to the first electronic excited state. In general, a transient absorption spectrum consists of three contributions; absorption of the transient states, bleach of the ground state, and stimulated emission from the excited states. These different contributions often overlap with each other in the spectrum, which makes interpretation very complicated. In contrast, spontaneous emission measurement has an advantage in studying the excited state dynamics since only the excited state can be probed. We use the spontaneous emission measurement for probing the relaxation process in this research.

5-6. The concept of internal temperature.

As discussed in the previous section, the intramolecular energy redistribution is very fast and the molecule reaches in thermodynamic equilibrium very quickly. Therefore, the intramolecular energy redistribution causes the dissipation of the energy from an initially nonthermal energy distribution to the fully statistically thermalized state where all vibrational modes are populated according to a thermal Boltzmann factor and a mode-independent single temperature can be defined [14]. Kaiser and coworkers used this phenomenon for measuring the internal temperature of a molecule ("Molecular thermometer"). They calibrated it by using the temperature dependence of the static absorption spectra. One can use this thermometer to probe the detailed pathway of the energy flow from the solute to the solvent. A very rapid intramolecular redistribution within < 1 ps and an energy transfer to the solvent with a time constant of approximately 10 ps are found. The rate of these processes depends on the mode density of both solute and solvent and the excess energy. Kaiser et al. suggested that the intramolecular energy redistribution occurred much faster than intermolecular energy transfer process.

5-7. Vibrational cooling process.

The vibrational cooling processes have received considerable attention in many years. Recent various spectroscopic studies suggested that the vibrational cooling process in solution occurred in a 10 ps time scale [8,9,14]. The excess vibrational energy is transferred to vibrational energy of the other modes, rotational energy and translational energy. In polyatomic molecules, the energy transfer from one vibrational mode to a combination of the other modes is considered to be dominate mechanism among them. The detailed mechanism of the energy transfer process from the solute to the solvent has been investigated in a simple system [34-36]. For example, Harris and coworkers investigated the vibrational relaxation process of I_2 in Xe at various densities [36]. In this system, the vibrational to translational energy transfer is a unique pathway of the vibrational cooling process. They succeeded in reproducing the vibrational relaxation rates based on the extension of gas-phase isolated binary collision model. In this model, the rate is expressed by the product of the rate of collision by solvents in the state i and the probability for changing state i to state j in a collision. The energy transfer occurs via the collision by the solvents and the rate becomes faster in the solvent with higher density. This model has been applied to the polyatomic solutes such as azulene and cycloheptatriene from the gas to the compressed liquid phase [37-40]. It was shown that the description by an isolated binary collision model remained valid up to surprisingly high densities. When a certain density is passed, however, a further increase of the energy transfer rate slows down. They suggested that this was due to the reduction of the effective collision frequency through shielding of the solute by solvents.

Iwata and Hamaguchi investigated the vibrational relaxation process of trans-stilbene in solution by the picosecond time-resolved Raman spectroscopy [41,42]. They found that the vibrational relaxation rate shows a strong correlation with the thermal diffusivities of the bulk solvents. They proposed the following mechanism. The excess energy is shared with the solute and the nearest solvents at a very early stage of the dissipation process, and then the energy transfer follows into the bulk solvent. The latter process could be simulated by only considering the macroscopic diffusion of the heat.

Terazima and coworkers developed the transient grating and lens methods to monitor the translational temperature of the solvent after the photoexcitation of the solute to the electronic excited state. They have clearly shown that the refractive index change due to the temperature variation responses immediately after the heating without changing the density and this could be useful for detecting very fast temperature rise of the medium. They found that the thermalization process after the photoexcitation of Ni^{2+} and o-hydroxybenzophenone in aqueous solutions was very fast (less than 5 ps) [43,44].

5-8. Slow intramolecular energy redistribution process .

As discussed in the previous section, the intramolecular energy redistribution is observed to be much faster than the intermolecular energy transfer, i.e. both processes are well separated in time scale [14]. The results of some studies are not consistent with these general observations. For example, Sension et al. performed femtosecond transient absorption studies of cis-stilbene in solution [45,46]. In this reaction, vibrationally hot trans-stilbene is created within a few picosecond time scale after the photoisomerization of cis-stilbene. They monitored the time-resolved transient absorption spectra of photoproduct of trans-stilbene and simulated the transient spectra by assuming several Franck-Condon active modes. However, the transient spectrum at 6 ps could not be reproduced by assuming the Boltzmann distribution of the vibrational population at the elevated temperature. This means that the intramolecular energy redistribution is not completed at 6 ps and the spectrum shows the nonthermal population distribution in the electronic ground state. A comparison of the calculated and experimental absorption and emission spectra of cis-stilbene was performed by Todd et al. [47]. This study determined that it was not possible to simulate the absorption and the room temperature fluorescence spectra using the same potential surface if the vibrational relaxation was assumed to be completed. They suggested that the fluorescence at room temperature came from the vibrationally hot molecules where the vibrational relaxation of one or more of the modes is slower in a time scale of the isomerization reaction (~ a few ps). Similar behavior was observed in the proton transfer of TINUVIN [48].

Jean and coworkers measured the transient anti-Stokes Raman spectra of the electronic excited trans-stilbene in solution [49-51]. They found the nonequilibrium population in the $v=1$ level of the ethylenic band at 1570 cm^{-1} within their time resolution of 1 ps. The results show that the intramolecular energy redistribution is not completed on the time scale of vibrational energy transfer to the solvent. Furthermore recent studies of the time-resolved resonance Raman spectroscopy combined with the Raman excitation profile suggested that the intramolecular energy redistribution occurred in the picosecond range for trans-stilbene and bacteriorhodopsin [53-55].

So far several studies revealed that the intramolecular energy redistribution process was not necessarily ultrafast even in the case of large molecules. High density of the states may not cause the ultrafast intramolecular energy redistribution process as a unique reason .

5-9. Relationship between the solvation dynamics and the vibrational relaxation.

Maroncelli and coworkers examined how vibrational relaxation might contaminate the spectral dynamics of the transient fluorescence spectra for measuring the solvation dynamics [56]. They used cyclohexane as a solvent because not much contribution of the solvation dynamics is expected for this nonpolar solvent. They used a 366 nm pulse for excitation. With this excitation wavelength, on the order of 3500 cm^{-1} of excess vibrational energy is deposited into the molecule. Figure 5-4 shows the results of their experiment. At times comparable to the time required for this energy to relax from the Franck-Condon active modes, the emission spectrum should be very much different from the vibrationally relaxed (steady-state) spectrum. They also tried to simulate the emission spectra by assuming one high frequency mode and calculate the time evolution of the spectra based on the theoretical treatment of Loring et al. In the experimental spectra, they did not observe any evidence for the dramatic departures from the steady-state lineshape which is predicted by model calculation. They observed the narrowing ($\sim 300\text{ cm}^{-1}$) and a more subtle blue shift ($\sim 150\text{ cm}^{-1}$) of the spectrum that takes place on $\sim 10\text{ ps}$ time scale. It is suggested that this phenomena may be ascribed to the vibrational cooling in the excited electronic state. They concluded that these small changes should have little effect on the spectrum change that used to construct the spectral response function. The vibrational relaxation processes should not significantly interfere with the use of the dynamics Stokes shift to monitor the solvation dynamics in polar solvents.

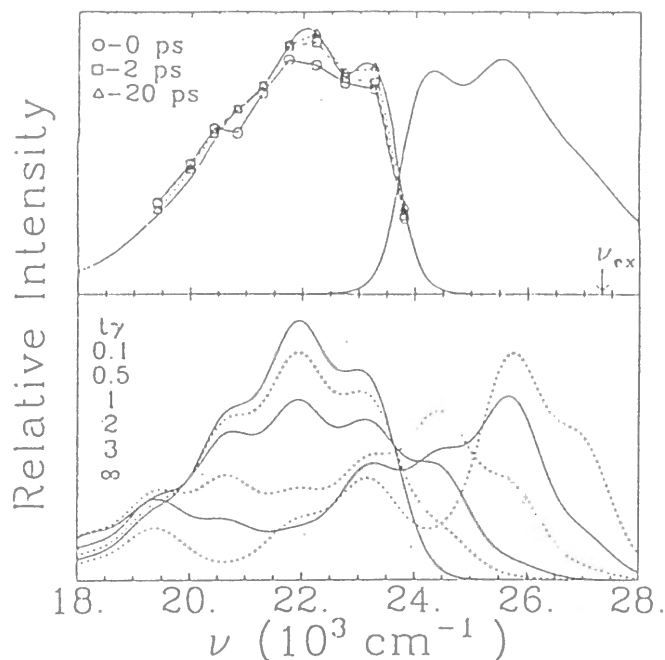


Figure 5-4. Time-resolved fluorescence spectra of coumarin 153 in cyclohexane. This is quoted from Ref. [56]. The top panel shows the observed time-resolved emission spectra as well as steady-state absorption and emission spectra. The bottom panel shows simulations of the time-resolved emission spectra predicted from a single harmonic oscillator description of the vibrational relaxation proposed by Loring and Mukamel. Detail of the calculation is explained in Ref. [57].

5-10. Summary

In this chapter, we briefly review the previous investigations on the intramolecular energy redistribution and intermolecular vibrational relaxation processes in solution. It is generally accepted that these two processes can be well separated. After the photoexcitation, excess energy is localized in the Franck-Condon active modes and then distributed in energy among the other vibrational modes within a molecule. This rapid redistribution of the excess energy creates a quasi-equilibrium of the vibrational population distribution which is well characterized by a single temperature. The energy dissipation from the solute to solvent occurs subsequently. However, the results of recent spectroscopic studies are not consistent with these general observations. They revealed that the intramolecular energy redistribution process was not necessarily ultrafast even in the case of large molecules. High density of the states may not cause the ultrafast intramolecular energy redistribution process as a unique reason. It will be needed mode-specific information for understanding the detailed mechanism of these processes even through the experimental difficulties always accompany. Our research aims at obtaining direct information about intramolecular energy redistribution process of dye molecules in solution with a large excess energy.

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Chapter 6

Experimental

6-1 Laser system.

The laser system for the present measurement is schematically shown in Figure 6-1. A Ti:sapphire laser system (Tsunami, Spectra-Physics) was operated at around 800 nm, with a repetition rate of 80 MHz and an average power of ~ 1.8 W pumped by a CW argon ion laser (Spectra Physics 2080). The pulse width was about 100 fs. The spectral width of the fundamental was constantly monitored by the spectral analyzer (Advantest). The pump beam passed through a periscope arrangement to rotate the plane of polarization by 90 degree. The output of the fundamental was divided into two parts. One of them (~ 1.2 W) was used for the third harmonic generation (267 nm, ~ 50 mW) in a tripler (Inrad Model 5-050). The output of the fundamental was frequency-doubled in a 1.5 mm LBO crystal. This second harmonic was mixed with the remaining fundamental in a 0.5 mm BBO crystal to produce the third harmonic. Inside the tripler, all optics were reflective for minimizing the effect of the group velocity dispersion. Maximum conversion efficiency of the tripler was around 10 %. The details of the tripler is described in the next section.

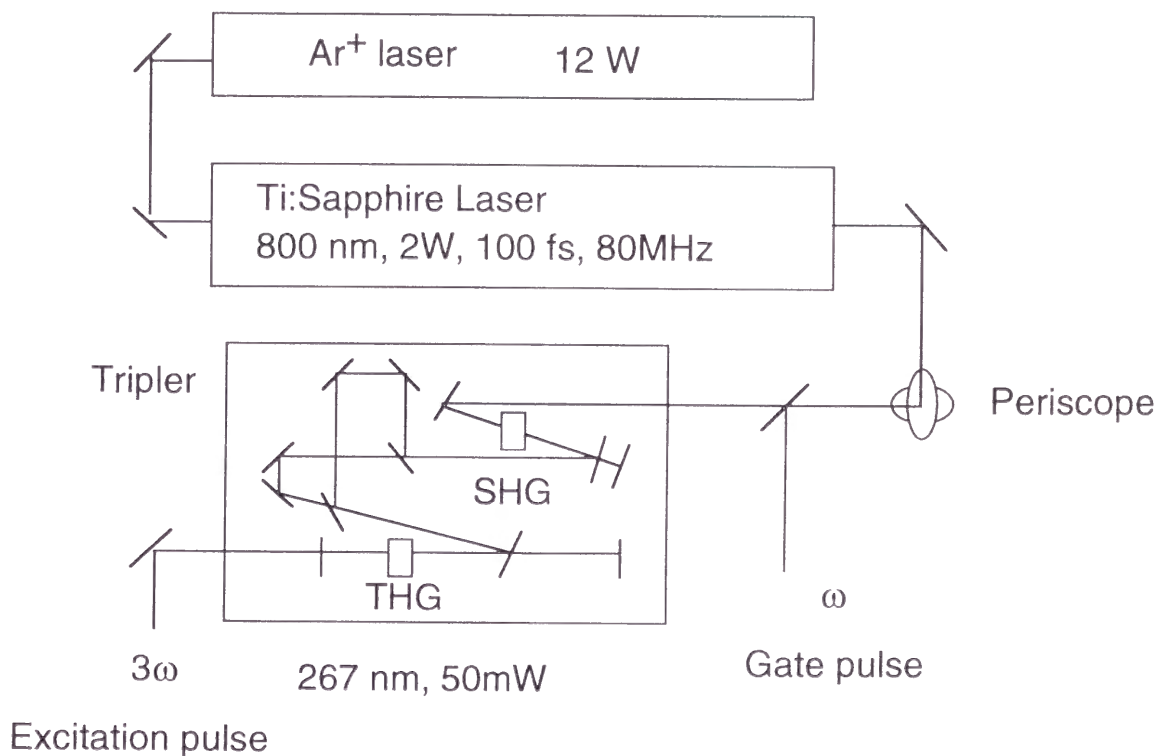


Figure 6-1. Schematic representation of the laser system.

6-2. Generation of the third harmonic of a Ti:Sapphire laser.

In order to get a sufficient power of the third harmonic of the Ti:Sapphire laser, we used a commercial harmonic generator (Inrad, tripler Model 5-050). The peak energy of the femtosecond pulse from a mode-locked Ti:Sapphire laser is very weak without amplification. Therefore it is important to focus the beam properly in front of the nonlinear crystal in order to achieve sufficient conversion efficiency. In this tripler, all focusing and recollimation are done with curved mirrors. The use of mirror avoids the problem of chromatic aberration and excess glass thickness found in lens-based approaches to frequency mixing. The schematic diagram of the tripler is shown in Figure 6-2. A horizontally polarized Ti:Sapphire laser beam is reflected by two mirrors (M1, M2) to adjust the beam height and polarization and focused onto the second harmonic generation (SHG) crystal (1.5 mm LBO crystal) by collimation mirror (M3) to produce blue light. The crystal is tilted to achieve the angle phase-matching and was translated in the focusing direction to the exact focal point of the fundamental beam. Both the SHG beam and the residual fundamental beam are recollimated by a dichroic mirror (M4). The resulting red and blue beams are divided into a reflected blue, second harmonic beam and a transmitted, red, fundamental beam by beam splitter (BS1). The fundamental undergoes two 90 degree reflections of a pair of mirrors (M7, M8) mounted on a translation stage. The reflected SHG undergoes a similar delay with the fundamental at another beamsplitter. The time delay between the SHG beam and the fundamental is adjusted by positioning the linear micrometer-translation stage. The polarization of the fundamental is rotated slightly by an optical element (PR1) to match the polarizations between the SHG and the fundamental. After both beams are recombined by a beam splitter (BS2), they traverse another optical element (PR2) that aligns both of the polarizations into the horizontal plane. The beams are focused onto the third harmonic generation (THG) crystal (0.5 mm BBO crystal) by a curved mirror (M9). The THG crystal is phase-matched through precise rotation of the crystal about the horizontal axis and is translated to the exact beam waist of the mixing beams. A recollimation optic (M10) transmits the fundamental and second

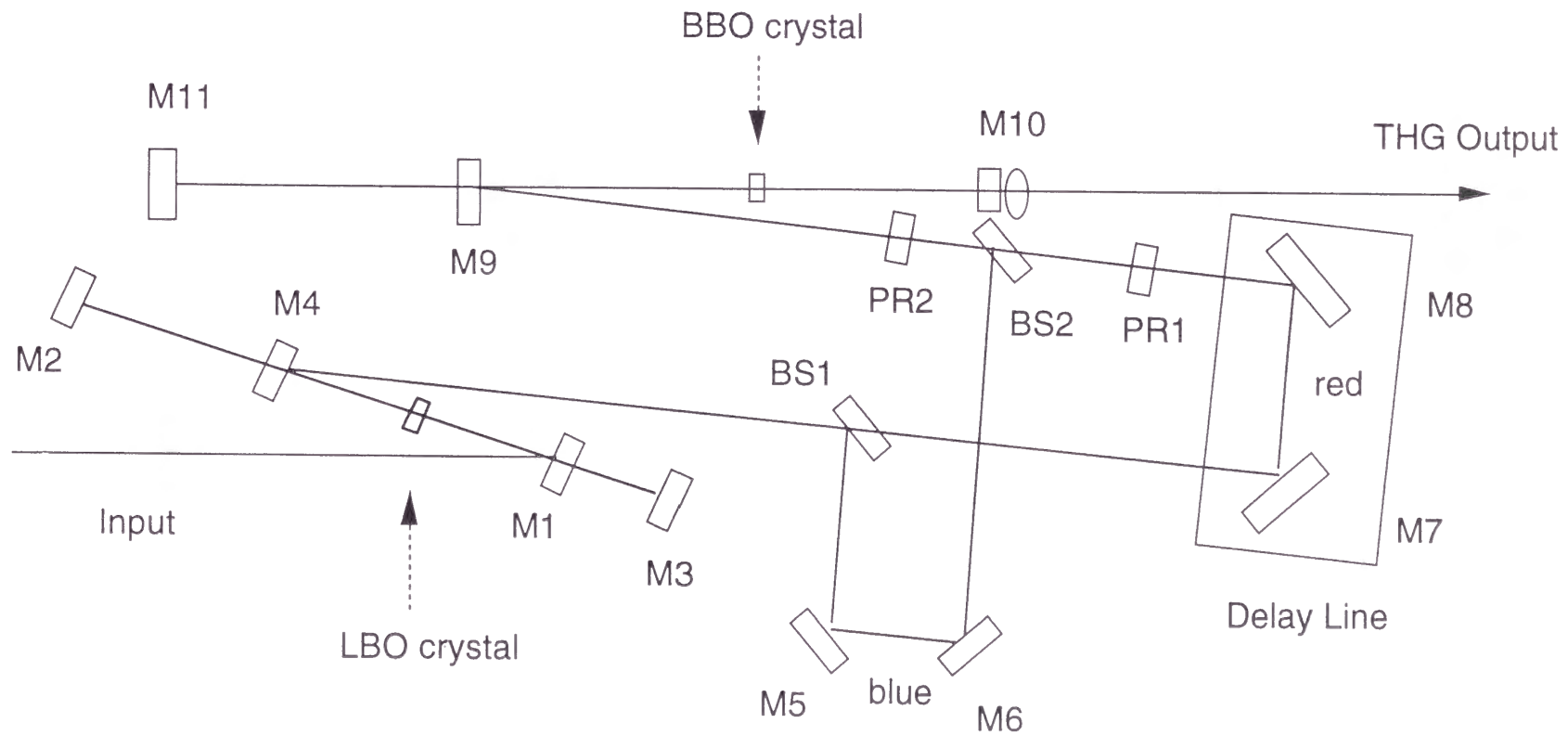


Figure 6-2. Optics configuration for the tripler. M, Mirror; BS, Beamsplitter, PR, Polarization rotator.

harmonic while reflecting a collimated THG beam toward the THG reflector (M11). The maximum conversion efficiency of this tripler is about 10 %.

6-3 Construction of fluorescence up-conversion spectrometer.

6-3-1 Principle.

Time-resolved fluorescence spectroscopy is a valuable method to obtain information on the excited-state dynamics in many chemical systems [1-5]. Two famous techniques are commonly used for the time-resolved measurements, i.e. time-correlated single photon counting (TCSPC) and the use of streak camera. The time-resolution of TCSPC is determined by the response of the electronic circuit and transit photoelectron-time spread in a photomultiplier tube [1]. The instrument response is around 20 ps. Streak camera technology has advanced greatly in the past several years. The time-resolved fluorescence spectrum can be measured at one time in principle because it can be achieved the spatial and temporal resolution simultaneously. One could easily measure the dynamics with the time resolution as fast as 1 ps by performing the proper deconvolution [6]. It requires, however, repetitive signal accumulation in order to improve the dynamic range.

To achieve the subpicosecond time resolution, it is necessary to use the fluorescence up-conversion technique. This method was first used in chemical research by Topp and coworkers in 1977, and has been extended by a number of researchers [7-9]. The fluorescence up-conversion involves the frequency mixing of incoherent fluorescence (resulting from exciting a sample with a short laser pulse) with another probe pulse in a nonlinear crystal. Time resolution is obtained by delaying the probe pulse relative to the excitation pulse by an optical delay line. The instrument response function is determined by the pulse width of both the excitation and probe pulses and the group velocity dispersion effect in the nonlinear crystal, which means that the time resolution is comparable to the temporal width of laser pulse.

The principle of the up-conversion measurement is shown schematically in Figure 6-3. The fluorescence emitted from the sample and a suitable delayed probe pulse is focused onto a nonlinear crystal. Sum frequency photons are generated only during the time that the probe pulse is present at the crystal. Therefore, frequency mixing works as a light gate and provides time resolution comparable to the laser pulse width. The temporal

profile of the fluorescence is obtained by varying the delay of the probe pulse at a nonlinear crystal. The efficiency of the up-conversion strongly depends on the phase-matching condition of the nonlinear crystal. Thus the spectrum at a certain time delay is obtained by varying the angle of the crystal.

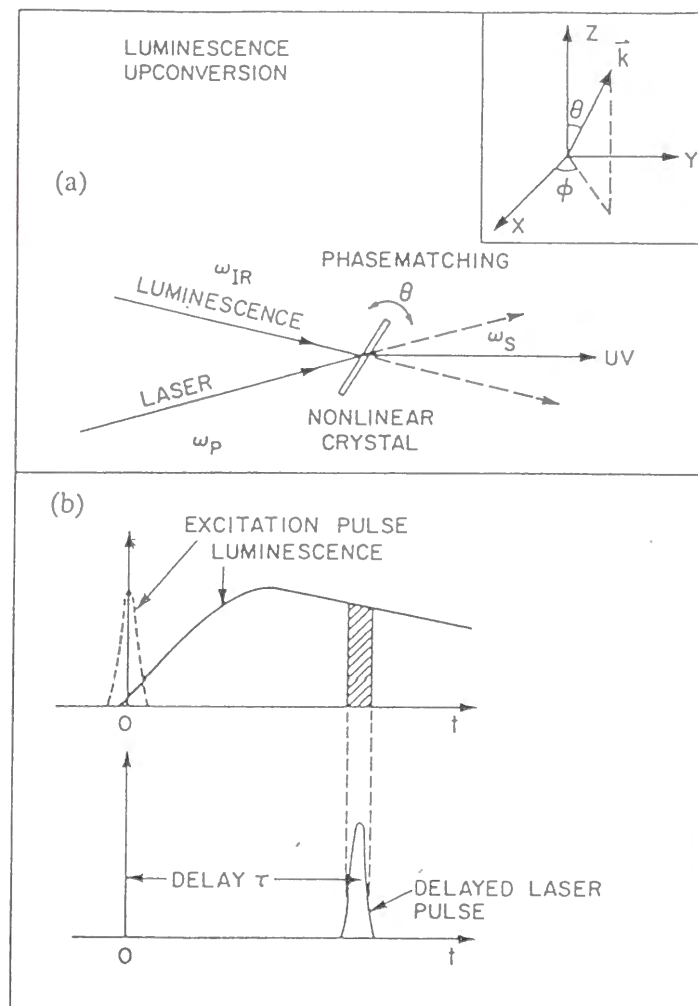


Figure 6-3. Schematic drawing of the principle for fluorescence up-conversion measurement. Sum frequency signal is generated in a nonlinear crystal (a) only during the time that a delayed laser pulse is present (b). This is a copy of Ref. [4].

6-3-2 Apparatus

Schematic configuration for the fluorescence up-conversion measurement is displayed in Figure 6-4. The third harmonic was used to excite the sample. The other part of the fundamental was used as a gating pulse. The excitation pulses were focused by a 50 mm focal length lens into a flowing sample cell. The cell consisted of the quartz plates with a spacer. The thickness of the sample cell was 1 mm. The sample solution was circulated by peristaltic pump to avoid degradation. Fluorescence was collected by a lens and focused with the gated pulse onto a 0.5 mm BBO (type-I) crystal. The focal lengths of the lens were 20 mm (for collecting the fluorescence) and 70 mm (focusing the fluorescence). The up-converted signal was spatially and spectrally isolated from the other light sources (fluorescence itself, gate pulse, and second harmonic of the gate pulse) by using an iris and the optical filter (UG-11, Schott). The signals were detected with a photomultiplier tube (R585S, Hamamatsu) connected to a photon counter (C5410, Hamamatsu) after passing through a monochromator (H-20, Jobin-Yvon). The spectral width of the monochromator was adjusted to ~ 8 nm. The signal was fed into a PC computer and averaged. This was also used for controlling a stepping motor for optical delay between the pump and probe pulses. All measurements were performed with the magic-angle polarization between the pump and probe beams by using a half-wave plate. The instrument response function was determined from the difference frequency generation between the third harmonic and the fundamental (*vide infra*). We also tried to use the elliptical mirror instead of the lens for collecting the fluorescence (Figure 6-5). The focal lengths of the mirror were 15 mm (for collecting the fluorescence) and 120 mm (focusing the fluorescence). The gated beam was focused with a 200 mm focal length lens. The elliptical mirror can be eliminated the spherical and chromatic aberrations and the group velocity dispersion effect [10,11]. In this case, the FWHM of the cross correlation was about 250 fs, which is slightly smaller than that by using the lens.

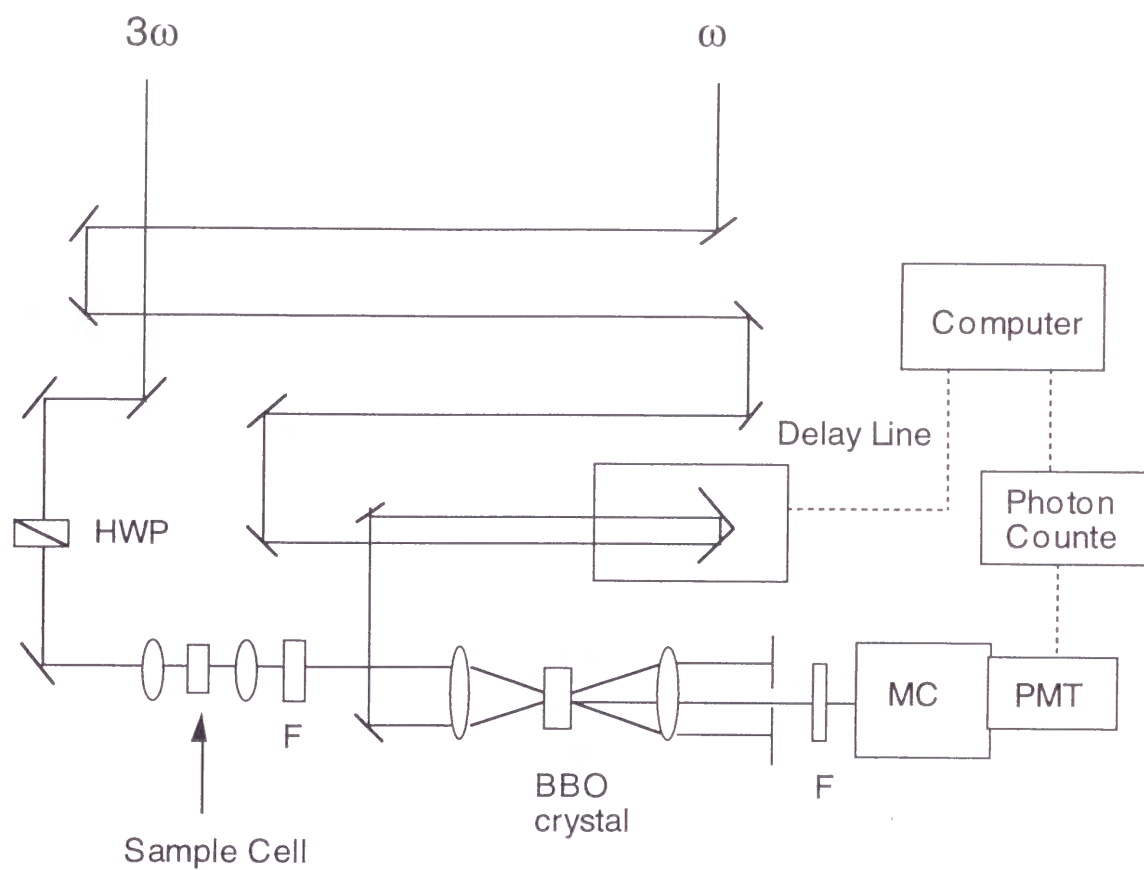


Figure 6-4. Experimental configuration for the fluorescence up-conversion measurement.

F, Cutfilter.; HWP, $\lambda/2$ waveplate.; MC, Monochromator.; PMT, Photomultiplier.

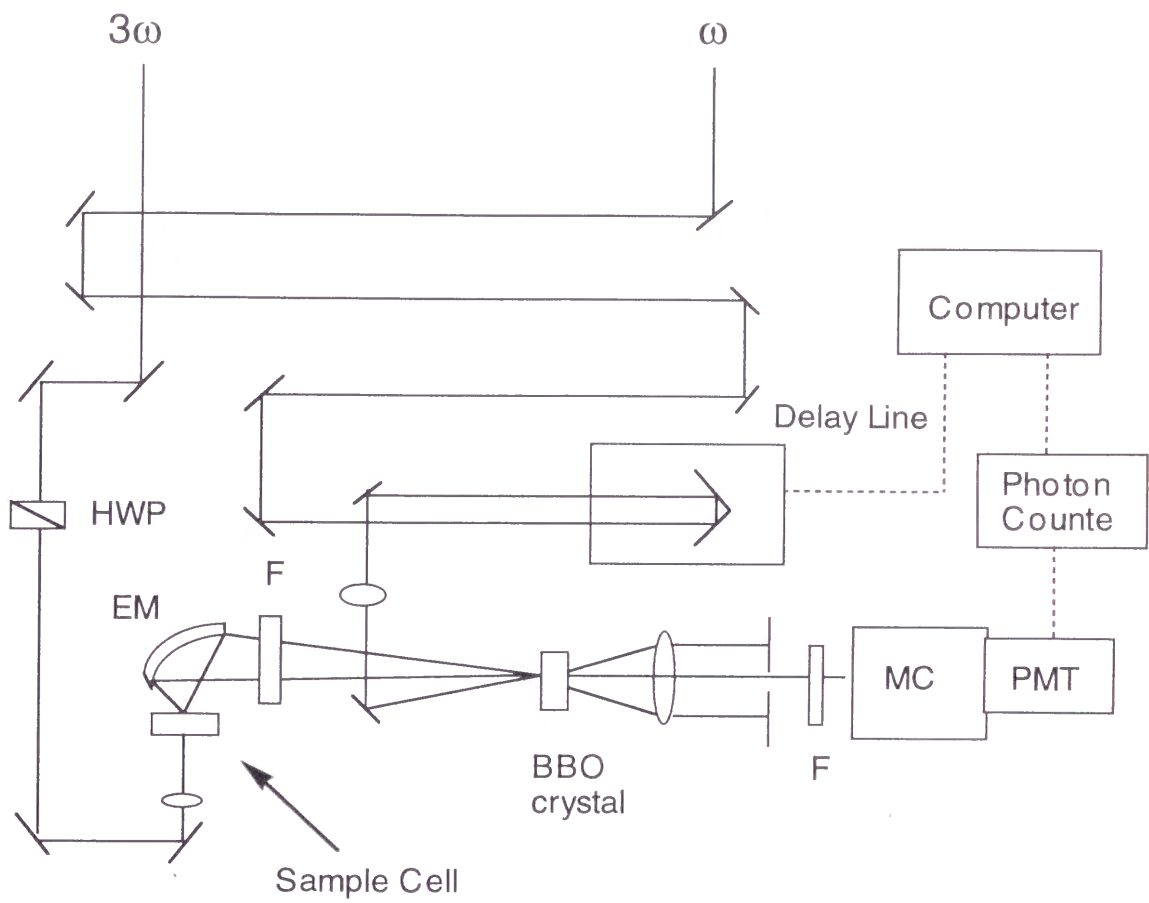


Figure 6-5. Experimental configuration for the fluorescence up-conversion measurement by using the elliptical mirror. EM, elliptical mirror.

6-3-3. Estimation of the instrument response function.

In the up-conversion experiment, the cross correlation between the excitation and gated pulses is used for estimating the instrument response function. If we use the second harmonic of a Ti:Sapphire laser as an excitation pulse, the sum frequency generation between the second harmonic and the fundamental can be used for this purpose. In this case, the signal of the sum frequency generation has much higher intensity than the up-conversion signal and the direction of the signal is almost same as that of the up-converted one. Therefore one can easily measure it by removing a cutoff filter which blocks the excitation pulses. Some problems might come from slight different divergence properties of the pump beams and the fluorescence signal between the sample and the up-conversion crystal. This means that we collect only a small cone of the forward scattering emission, while the angular spread of this emission is larger than that of the pump beam, and one would therefore expect these to be some temporal broadening relative to the cross correlation signal. Other possibilities also exist for empirically determining this function. One of the example is to use the spontaneous Raman scattering from the solvent. The up-converted signal between the solvent Raman scattering and the gated pulse is used for the instrument response function. Maroncelli and coworkers suggested that use of the solvent scattering leads to improvement in the fit of data [6].

In principle, the above method for measuring the instrument response function can be applied for the case of the third harmonic excitation. However the resulting signals are located in a deep UV region (~ 200 nm) so that we expect the temporal broadening due to a large group velocity dispersion effect in this wavelength region. In order to avoid this experimental problem, we used the difference frequency generation between the third harmonic and the fundamental. In this case, the direction of the resulting cross correlation signal is different from that of the up-conversion signal if we adopt the noncollinear geometry as shown in Figure 6-5. The result of the cross correlation signals observed at 400 nm is shown in Figure 6-6. The data were well fitted by a Gaussian function and the temporal width of the cross correlation was estimated to about 280 fs. This value is similar to that reported by Inrad. The temporal width is about three times longer than that

of the fundamental. It is mainly controlled by the group velocity dispersion of two nonlinear crystals. The temporal pulse width will be compressed by using a pair of prism and the nonlinear crystal with thinner thickness.

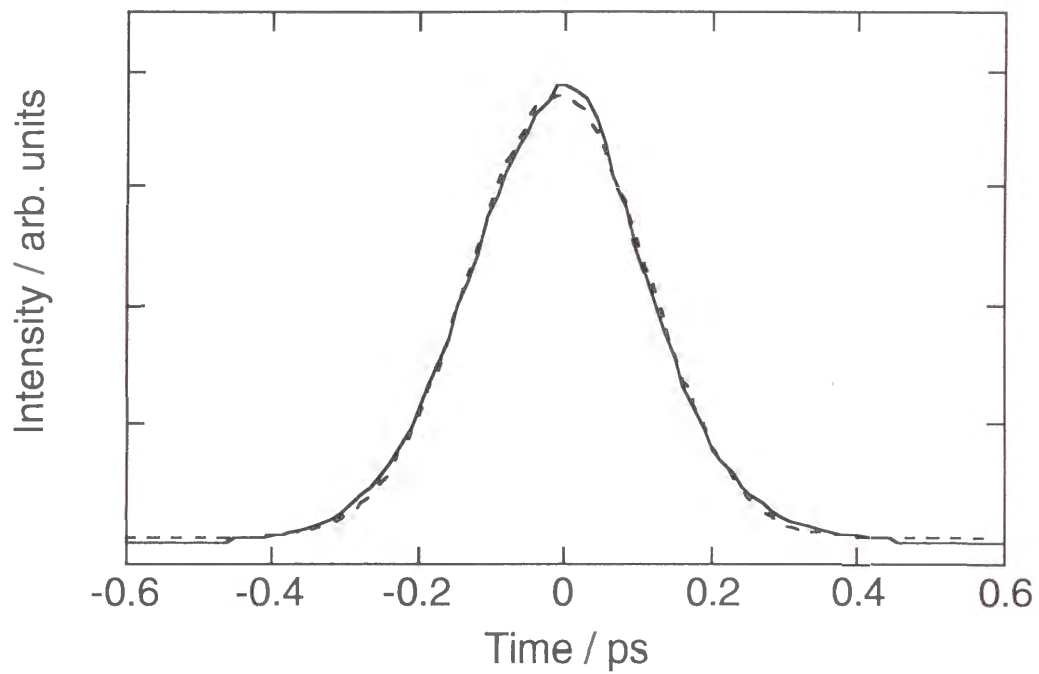


Figure 6-6. Cross correlation signal between the third harmonic and the fundamental (Solid line). The broken line shows the best fit to the data with a Gaussian function.

6-4. Steady-state absorption and fluorescence spectra

The steady state absorption and fluorescence spectra were recorded with a Hewlett Packard photodiode array absorption spectrometer (HP8453) and a SPEX fluorometer (Fluoromax). Both spectrometers were equipped with a temperature controlled cell holder whose temperature can be controlled in connection with a Neslab cooler. Temperature was varied between the melting and the boiling point of the solvents.

We took a special care of converting the fluorescence spectra from an energy scale to wavelength scale [12]. The usual fluorescence measurement, which is performed with a grating monochromator, determined a spectrum with the units $\text{photon s}^{-1} \text{area}^{-1} \text{nm}^{-1}$. Such a spectrum must be converted from a wavelength to an energy scale to compare it with our calculated spectra. This conversion involves both an abscissa and an ordinate change, i.e. the units of intensity are the same for the two scales. As a result the value of the intensity must be multiplied by $(\text{wavelength})^2/\text{constant}$ before the abscissa is changed. This conversion insures that the integrated area is conserved (i.e., the number of photons) and can alter both the width of the spectrum and the position of the peak. All measurements were performed at an ambient temperature (293 K).

6-5. Reagents

Laser grade coumarin 481 was purchased from Exciton and was used without further purification. Cyclohexane (spectrograde) was obtained from Wako Chemicals and also used without further purification. The sample solution was circulated through a quartz cell with a 1 mm optical path length. The concentration of the sample was adjusted to give an absorbance of about 0.5 at 267 nm.

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Chapter 7

Relaxation Processes from a Higher Electronic Excited State of Coumarin 481 in Cyclohexane

7-1. Steady-state absorption and fluorescence spectra.

Figure 7-1 shows the absorption and emission spectrum of C481 in cyclohexane. In nonpolar solvent, the Stokes shift is very small and the emission spectrum is close to a mirror image of the absorption spectrum. The strong absorption band, which is ascribed to the S_0 - S_1 transition, is located from 330 nm to 420 nm. At the wavelength shorter than 320 nm, a weak and featureless band is observed and the absorption intensity increases at the wavelength shorter than 270 nm. We excite C481 molecules at 267 nm, which corresponds to the red edge of the second absorption band. It is difficult to identify the character of this state because many electronic transitions are congested in this region. We refer this state to as the S_n state. The arrows indicate the monitoring wavelength of the fluorescence. The excitation of 267 nm pulse put an excess energy of about 12000 cm^{-1} from the 0-0 band of the emission spectrum.

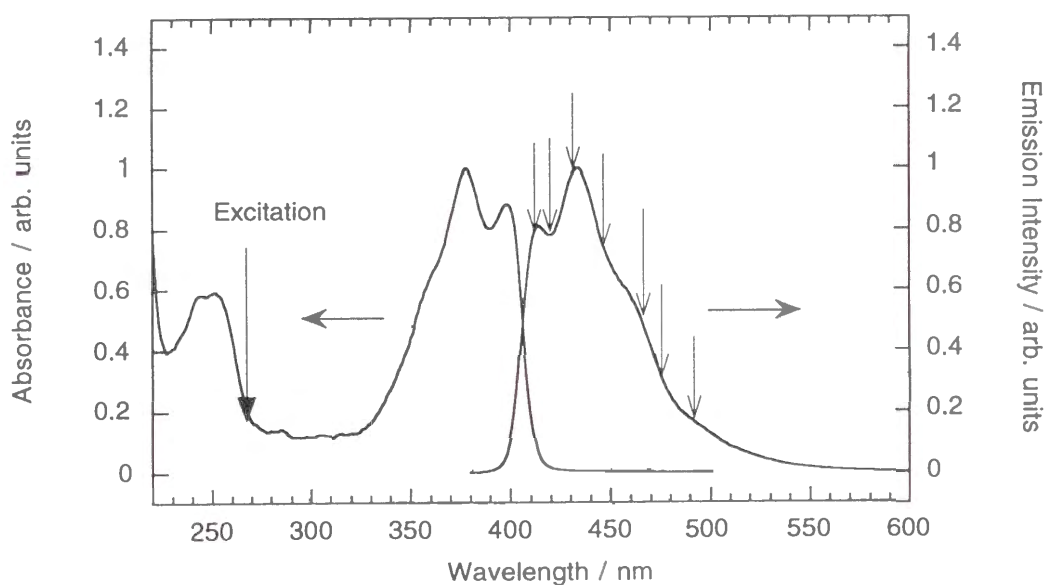


Figure 7-1. Static absorption and fluorescence spectra of coumarin 481 in cyclohexane. The excitation and monitoring wavelengths are indicated by the arrows.

7-2. The temporal profiles of the fluorescence signal within a few picosecond time scale.

The temporal profiles of the up-converted signals observed at a few wavelengths are displayed in Figure 7-2. A feature of dynamics is similar at each wavelength, i.e. an increase in emission intensity of sample with a subpicosecond time scale which is followed by a small change in a longer time scale (*vide infra*). Within the time scale of a few picoseconds, the data can be well fitted by a single exponential rise convoluted with the instrument response function. The results are summarized in Table 7-1. We obtained 200-300 fs time constants of the rising components in the signals. The instrument response function was measured by using the excitation pulse passing through the sample. Therefore we consider that the slow rising components do not come from the effect of the group velocity dispersion in the sample cell and solvent. We also found that the rising time constant in polar solvents such as methanol and acetonitrile is faster than that in cyclohexane. We can also conclude that the origin of the fast component is not due to the different divergence properties of the pump beam and fluorescence signal between sample and the up-conversion crystal. This means that we collect a small cone of the forward emission, the angular spread of this emission is larger than that of pump pulse, and one would therefore expect that there exists some temporal broadening relative to the instrument response function. The lower panel of Figure 7-2 shows the calculated curves by assuming several different time constants for the rising components. The time constants of the rising components are comparable to the temporal width of the instrument response function. As clearly shown in Figure 7-2, we can safely determine the time constant of larger than 100 fs. However, it is difficult to distinguish a small difference of the time constants.

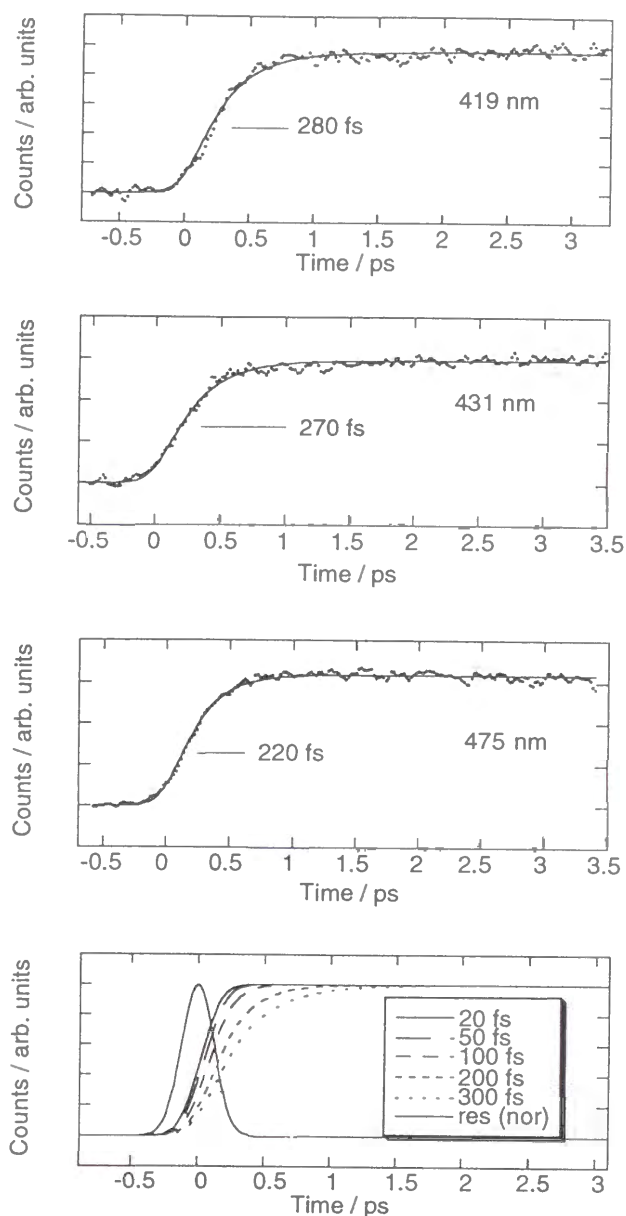


Figure 7-2. (Upper three curves) Fluorescence rises of coumarin 481 in cyclohexane excited at 267 nm and observed at 419, 431 and 475 nm. The solid line represents the best fits to the data by convoluting the instrument response function with a single exponential rise. (Lower) Calculated curve with a rise of several time constants convoluted by the instrument response function.

The observed fluorescence signals are considered to originate from the S_1 state based on the following reasons. The fluorescence band of S_0 - S_n transition is expected to be located at shorter wavelength where we observed. The contribution of this component is considered to be small. The oscillator strength of the absorption bands of the S_0 - S_n transition is much smaller than that of the S_0 - S_1 transition. The fluorescence intensity from the S_n state should be smaller than that from S_1 state. If the fluorescence from the S_n state were included in the observed signal, we would expect that there exist some rising and/or decay components within 1 ps. The accumulation of the population in the S_1 state causes the wavelength-dependent intensity change of the fluorescence at each wavelength. We could not find the corresponding components.

For large molecules, the density of the vibronic states is too high to excite a particular vibrational state by a femtosecond pulse because many vibronic levels are located within the bandwidth of the femtosecond pulse. However, only transitions with large Franck-Condon factors are strongly excited by the femtosecond pulse, i.e. the number of the states that involved in excitation are much smaller than that suggested by density of states [1]. In the general picture of the relaxation process, after the internal conversion from the S_n to S_1 state, an initially nonthermal energy distribution is created in the S_1 state according to the Franck-Condon principles within the framework of Born-Oppenheimer approximation. The intramolecular energy redistribution process causes the energy dissipation to a fully statistically thermalized state where all vibrational modes are populated according to a thermal Boltzmann factor and an vibrational temperature can be defined. The intermolecular energy transfer from the solute to solvent occurs successively [2,3].

From the results of the early-time dynamics, the time constants of the rising components do not depend on the wavelengths significantly. We cannot find any drastic rising and/or decaying components within a few ps time scale even with an excess energy of $> 12000 \text{ cm}^{-1}$. If the emission originates from the higher vibrational state, the shape of fluorescence spectrum is expected to be significantly distorted, which is different from that of the static fluorescence spectrum. We can consider that the observed dynamics

within a few picosecond time scale should depend on the wavelength. However, the observed spectrum is already intramolecularly relaxed one. We conclude that the observed dynamics is mainly controlled by the internal conversion from the S_n to S_1 state, i.e. the intramolecular energy redistribution completes within 100 fs after the photoexcitation to the S_n state and the subsequent internal conversion occurs with the time constant of 200-300 fs.

Previous studies of relaxation in excited electronic states of dye molecules show that intramolecular energy redistribution occurs in 200-500 fs [3-12]. In particular, Mokhtari et al. used the femtosecond up-conversion method to measure the excited-state dynamics of nile blue and oxazine 1 in solution after the photoexcitation to the S_1 state [4,5]. They found that the evolution of the fluorescence bandwidth contained fast (0.4-0.6 ps) and slow (4-6 ps) components. They attributed the fast one to the intramolecular energy redistribution process. In our system, we cannot find the corresponding components in the observed signals.

7-3. Spectral narrowing in a 10 ps time scale.

Figure 7-3 shows the time-resolved fluorescence spectrum in a 10 ps time scale. The reconstruction of the time-resolved spectra was performed according to the method by Maroncelli and Fleming [13]. The integrated intensity was calculated at each wavelength and scaled by using the value in intensity of the static fluorescence spectrum. The fluorescence spectrum becomes sharp as a function of time, i.e. the intensity increases near the peak of the spectrum and the intensity at the red-edge region decreases as the time goes on. The evolution of the spectrum is observed in a 10 ps time scale. Similar sharpening of the fluorescence spectra is observed in the other system. Maroncelli and coworkers performed similar experiments on the fluorescence dynamics of coumarin 153 in cyclohexane to check the possibility of the contamination of the vibration relaxation in the solvation dynamics [14]. They use a 366 nm pulse for excitation. With this excitation wavelength, on the order of 3500 cm^{-1} of excess vibrational energy is deposited into the molecule. They observed the narrowing ($\sim 300\text{ cm}^{-1}$) and a more subtle blue shift ($\sim 150\text{ cm}^{-1}$) of the spectrum that takes place on $\sim 10\text{ ps}$ time scale. It is suggested that this phenomena may be ascribed to the vibrational relaxation in the excited electronic state. They concluded that these small changes should had little effect on the spectral change that used to construct the spectral response function, and the vibrational relaxation processes should not significantly interfere with the use of the dynamics Stokes shift to monitor the solvation dynamics in polar solvents. Compared with this results, our observed change of spectral narrowing is observed more clearly than that by Maroncelli and coworkers. This may be due to the difference of the excess energy.

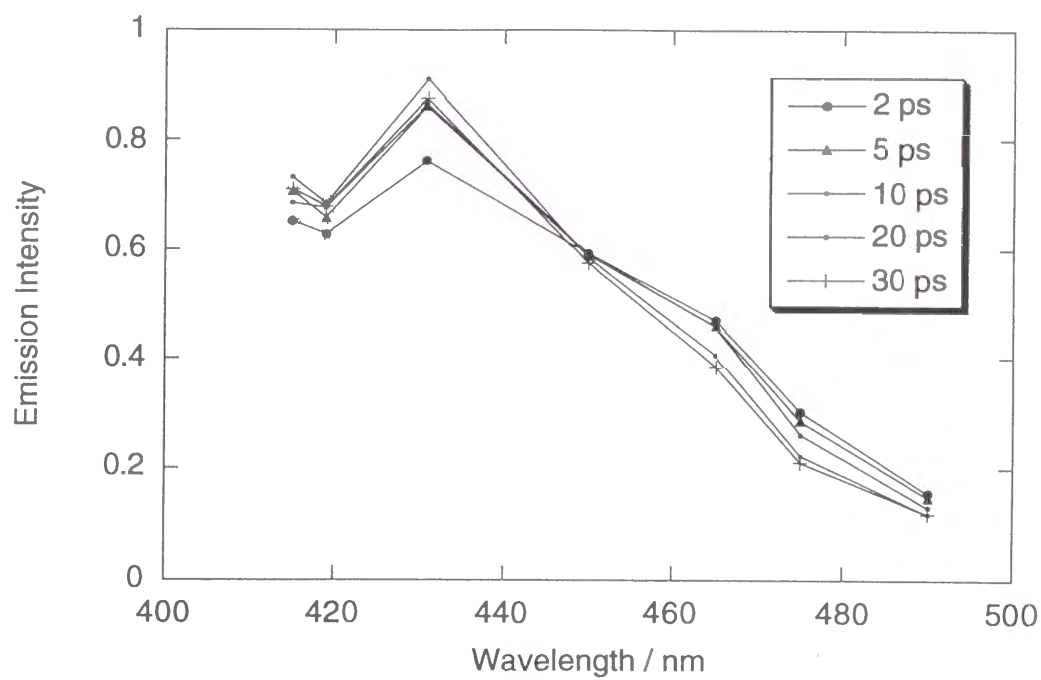


Figure 7-3. Time-resolved fluorescence spectrum in a 10 ps time scale.

Elsaesser and coworkers also found similar broadening of the emission spectra for sulforhodamine B in ethanol [12]. They estimated the transient internal temperature of 600 K based on the excess energy of 15000 cm^{-1} . They succeeded in reproducing the emission spectra by assuming two Franck-Condon active modes. It is suggested that the intramolecular energy redistribution can be well separated from the vibrational cooling process and the vibrationally hot molecules are well characterized by a transient internal temperature.

7-4 Temperature dependence of the steady-state fluorescence spectra

Figure 7-4 shows the temperature dependence of the steady-state fluorescence spectra. The fluorescence spectra are normalized with respect to its area. As the temperature increases, the spectra becomes broader, which is observed clearly at the wavelength shorter than 440 nm. The emission intensity below 400 nm increases at the higher temperature. On the other hand, the intensity decreases at the wavelength between 400 nm and 470 nm. At the wavelength longer than 470 nm, the intensity slightly becomes larger at the higher temperature. We also observed that the peaks of 0-0 and 0-1 bands shifted to the shorter wavelengths. These may be due to the anharmonicity of the potential surface in the electronic ground and/or excited state. The broadening of the emission spectra comes from the increase of the population distribution in the higher vibrational state.

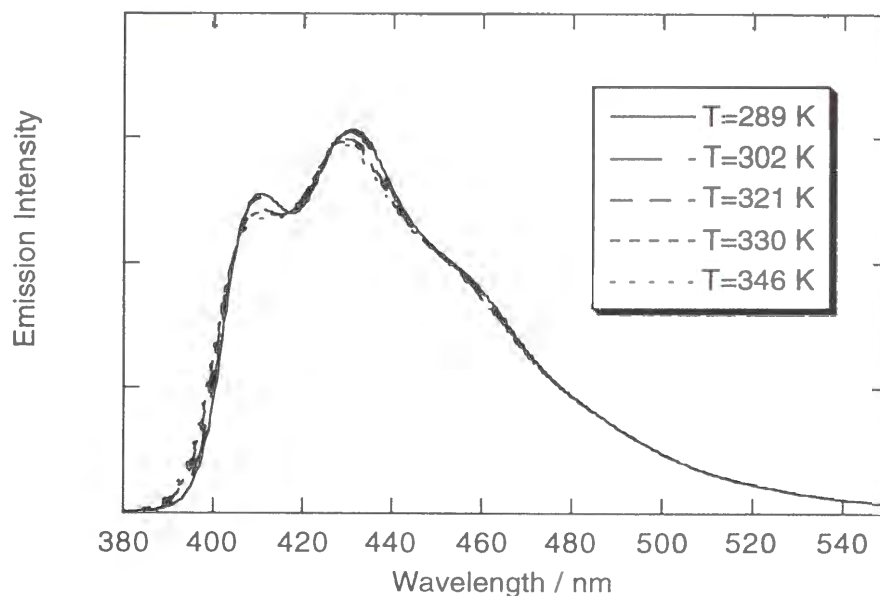


Figure 7-4. Temperature dependence of the steady-state fluorescence spectra

7-5. Mechanism of the ultrafast intramolecular energy redistribution process.

Hereafter we briefly consider possible the mechanisms of ultrafast intramolecular energy redistribution process in solution. As described in the introduction, it is considered that this process in solution occurs much faster than that in the gas phase under a low pressure or jet-cooled condition. In particular, the laser-induced fluorescence spectra for several coumarin compounds were measured [15]. The vibronic transition is well separated enough to observe a very sharp peaks and the linewidth does not depend on the excitation wavelength. This means that the intramolecular relaxation process without the surrounding solvent molecules is not fast. The surrounding solvent molecules play an important role in the ultrafast intramolecular process.

For large molecules such as coumarin compounds, density of the dark state is very high so that the energy flow from the one bright state to many dark states occurs irreversibly [1]. The decay rate of one Franck-Condon active mode is proportional to the density of the state. In solution, low frequency solvent modes, which sometimes refer to as instantaneous normal modes or phonons, increase the density of state by order of magnitude and it plays an important role in the dynamics of internal vibrational degrees of freedom. The anharmonic interaction terms induce the population flow from one vibrational modes into a combination of the other modes in which the energy between the initial and final states is matched. The low frequency solvent modes help to enhance this energy flow process. The solute-solvent interaction leads to energy flow from the solute to nearest solvent molecules in which the low frequency solvent motions can compensate for energy mismatch between the initial and final states of the energy transfer. This process occurs very efficiently (< 100 fs). Even in a small molecule such as deuterated ethanol, recent Raman echo study showed that the dephasing due to the intramolecular energy redistribution occurred as fast as 360 fs with the help of the coupling and the energy bath of the solvent that needs to make transitions [17].

7-6. Conclusion.

In summary we investigated the internal conversion and vibrational energy redistribution process of coumarin 481 in cyclohexane with a large excess energy by femtosecond UV fluorescence up-conversion method. We observed the 200-300 fs rising components at all wavelengths, however, we cannot find any drastic rising and/or decaying components within a few ps time scale even with an excess energy of $> 12000 \text{ cm}^{-1}$. We also observed a sharpening of the spectrum in a 10 ps time scale. This result suggests that the observed dynamics are mainly controlled by the internal conversion from S_n to S_1 state, i.e. the internal conversion occurs in a 200-300 fs time scale and the intramolecular energy redistribution takes place much faster than the former process, which does not affect the spectral evolution. The 10 ps components of the up-converted signals are attributed to the vibrational cooling process in the S_1 state. In order to gain information on the relaxation dynamics, we performed model calculation by assuming a few Franck-Condon modes. The detailed explanation for this simulation is presented in next chapter.

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Chapter 8

Model Calculation

8-1 Introduction

In this chapter, we perform the model calculation of the fluorescence spectra by assuming a few Franck-Condon active modes to gain information on the excited-state dynamics. Similar calculations were done by several groups and succeeded in reproducing the spectra of vibrationally excited states [1-6]. We also pay an attention to the difference of the emission spectra under the assumption that the initial state is either vibrationally unrelaxed or relaxed state. This comparison provides us information on the dynamics of the vibrational energy redistribution process. The main strategy is the same as that made in the Chapter 3. As shown in Figure 7-1, the absorption spectrum of C481 gives two clear maxima and one shoulder at higher frequencies which are interpreted as vibronic progressions of a few vibrational modes. A simplification is possible by making several assumptions [1,2].

We consider a few vibrational modes with energies larger than kT . These active modes are treated in the harmonic approximation. Low frequency modes and modes with small Franck-Condon factors are lumped together. They cause a line broadening which is described by the line shape function. We use the time dependent wavepacket propagation scheme to calculate the vibrationally hot spectra of dye molecules. If we calculate the vibrationally unrelaxed spectra, we use frequency-domain calculation for convenience sake. Here we present the model calculation for supporting the experimental observations. However, this calculation only provides a qualitative picture for the behavior of the transient fluorescence spectra.

8-2 Calculation of the fluorescence spectrum

8-2-1 Frequency-domain approach

As it is well known, the emission intensity is given by summing the eigenstates among all the vibrational modes [7]. Within the framework of the Born-Oppenheimer approximation, the expression for the emission intensity is expressed by

$$I_F(\omega) \propto \omega^3 \times \sum_n P_n \sum_f |\langle n|f \rangle|^2 G(\omega_{nf} - \omega) \quad (1)$$

where $|n\rangle$ and $|f\rangle$ are nuclear wavefunctions of the excited and ground electronic states, respectively. ω_{nf} is their energy difference, P_n is the initial population of state $|n\rangle$, and $G(\omega)$ is the lineshape function. Eq. (1) is simply a sum of each vibrational modes for all possible n-f transitions, each weighted by its initial population and its vibrational overlap $|\langle n|f \rangle|^2$. In this calculation, we use the Gaussian lineshape function for simplicity.

$$G(\omega) = \frac{1}{\pi\Omega} \exp\left[-\frac{\omega^2}{\Omega^2}\right] \quad (2)$$

where the FWHM of the line profiles is equal to $2(\ln 2)^{1/2}\Omega$.

In the limit of no Duschinsky mixing, the multidimensional Franck-Condon integrals can be factored into the products of the each one dimensional factors. These one dimensional Franck-Condon factors have the following form [8].

$$\langle 0|0 \rangle = \left(\frac{2}{1+R}\right)^2 R^{\frac{1}{4}} \exp\left[-\frac{\Delta^2}{2(1+R)}\right] \quad (3)$$

$$\langle m|0 \rangle = \frac{\langle 0|0 \rangle}{(2^m m!)^{\frac{1}{2}}} \left(\frac{R-1}{R+1}\right)^{\frac{m}{2}} H_m \left[-\left(\frac{R}{R^2-1}\right)^{\frac{1}{2}} \Delta \right] \quad (4)$$

$$\langle 0|n \rangle = \frac{\langle 0|0 \rangle}{(2^n n!)^{\frac{1}{2}}} \left(\frac{1-R}{1+R}\right)^{\frac{n}{2}} H_n \left[-\left(\frac{1}{1-R^2}\right)^{\frac{1}{2}} \Delta \right] \quad (5)$$

$$\langle m|n\rangle = \langle 0|0\rangle^{-1} \sum_{k=0}^{\min(m,n)} \left(\frac{2R^{\frac{1}{2}}}{1+R} \right)^k \frac{(-1)^{n-k}}{k!} \times \left[\frac{m!n!}{(m-k)!(n-k)!} \right]^{\frac{1}{2}} \langle m-k|0\rangle \langle 0|n-k\rangle \quad (6)$$

where

$$R = \frac{\omega_n}{\omega_m} \quad (7)$$

$|n\rangle$ and $|m\rangle$ are vibrational wavefunctions of the electronic ground and excited states, respectively, ω_n and ω_m are the vibrational ground and excited states frequencies, H_m is the m th Hermite polynomial, and Δ is the displacement of the potential minima between the ground and excited states.

If the frequencies are the same in the vibrational ground and excited states, the Franck-Condon factors are expressed by the following recurrence relation.

$$\langle m|0\rangle = \langle 0|m\rangle = \exp\left(-\frac{s}{2}\right) \times s^{\frac{m}{2}} / \sqrt{m!} \quad (8)$$

$$\langle m|n\rangle = \langle 0|0\rangle^{-1} \sum_{k=0}^{\min(m,n)} \frac{(-1)^{n-k}}{k!} \times \left[\frac{m!n!}{(m-k)!(n-k)!} \right]^{\frac{1}{2}} \langle m-k|0\rangle \langle 0|n-k\rangle \quad (9)$$

where we define s as

$$s = \frac{1}{2} \Delta^2 \quad (10)$$

We sum all possible ground state vibrational combinations, stopping iteration of each mode when the absolute value of the Franck-Condon product drops below a certain small value. For calculating the vibrationally unrelaxed spectra, it is convenient to use this formula because we can easily replace any types of the population distribution in eq. (1).

8-2-2 Time-domain approach

For large molecules, the frequency domain approaches require the enormous number of levels that must be included in the sum over states. It sometimes becomes time-consuming. As described in the Chapter 3, the time domain approaches rely on Fourier transformation from the frequency to the time domain. It has several advantages for computational calculation [7,9]. Here we begin by transforming the vibronic expression for emission intensity into the time domain. We define the emission tensor as follows.

$$F_{nf} = \sum_f |\langle n|f \rangle|^2 G(\omega_{nf} - \omega) \quad (11)$$

By substituting eq. (2) into eq. (11), we obtain

$$\begin{aligned} F_{nf} &= \sum_f |\langle n|f \rangle|^2 \times \frac{1}{\pi\Delta} \exp\left[-\frac{(\omega_{eg}^0 + \omega_n - \omega_f - \omega)^2}{\Delta^2}\right] \\ &= \int_0^\infty dt \sum_f |\langle n|f \rangle \langle f|n \rangle| \times \exp\left[i(\omega_{eg}^0 + \omega_n - \omega_f - \omega)t - \frac{\Delta^2}{4}t^2\right] \end{aligned} \quad (12)$$

where $\omega_{nf} = \omega_{eg}^0 + \omega_n - \omega_f$. To derive the second equation, we use the following Fourier transformation.

$$\frac{1}{\pi\Delta} \exp\left(-\frac{\omega^2}{\Delta^2}\right) = \int_0^\infty dt \exp(i\omega t) \exp\left(-\frac{\Delta^2}{4}t^2\right) \quad (13)$$

Next, since

$$\langle f | \exp\left(-\frac{iHt}{\hbar}\right) = \langle f | \exp(-i\omega_f t) \quad (14)$$

where H is the excited state vibrational Hamiltonian, we can write eq. (12) as

$$F_{nf} = \int_0^\infty dt \sum_f \left| \langle n|f \rangle \langle f | \exp\left(-\frac{iHt}{\hbar}\right) | n \rangle \right| \times \exp\left[i(\omega_{eg}^0 + \omega_n - \omega)t - \frac{\Delta^2}{4}t^2\right] \quad (15)$$

If we consider the propagator $\exp(-iHt/\hbar)$ to operate on the right-hand side, then

$$\exp\left(-\frac{iHt}{\hbar}\right) | n \rangle = | n(t) \rangle \quad (16)$$

and we obtain the final result by using closure eq. (16) to remove the sum over f :

$$\sum_f |f \rangle \langle f| = 1 \quad (17)$$

$$F_{nf} = \int_0^\infty dt \langle n | n(t) \rangle \times \exp \left[i(\omega_{eg}^0 + \omega_n - \omega)t - \frac{\Delta^2}{4} t^2 \right] \quad (18)$$

Therefore, the emission intensity is rewritten by

$$I_F(\omega) \propto \omega^3 \times \sum_i P_i \int_{-\infty}^\infty dt \langle \chi_n | \chi_n(t) \rangle \exp[i(-\omega + \omega_{eg}^0 + \omega_n)t - g(t)] \quad (19)$$

where $g(t)$ is a Gaussian line shape function. The same results are obtained by using the Lorentzian line shape function for this transformation.

Assuming orthogonal harmonic potential surfaces, the time-dependent overlaps can be expressed for each vibrational mode as follows.

$$\langle i | i(t) \rangle = \prod_{k=1}^{3N-6} \langle i_k | i_k(t) \rangle \quad (19)$$

The method for calculating this overlap is the same as that used in Chapter 3 [11,12].

The physical meaning of the wavepacket propagation is schematically shown in Figure 8-1 [7,9,10]. The initial ground state wavepacket $|i(0)\rangle$ is brought into the excited state in the Franck-Condon region directly after the photoexcitation. It moves under the influence of the excited-state Hamiltonian H and the resulting wavepacket is not an eigenstate. The overlap of this moving wavepacket with $|i(0)\rangle$ then shows an oscillatory feature whose recurrence is determined by the vibrational frequency of the Franck-Condon active modes. The Fourier transformation of this overlap, which includes an appropriate exponential damping, gives vibronic structure of the absorption spectrum.

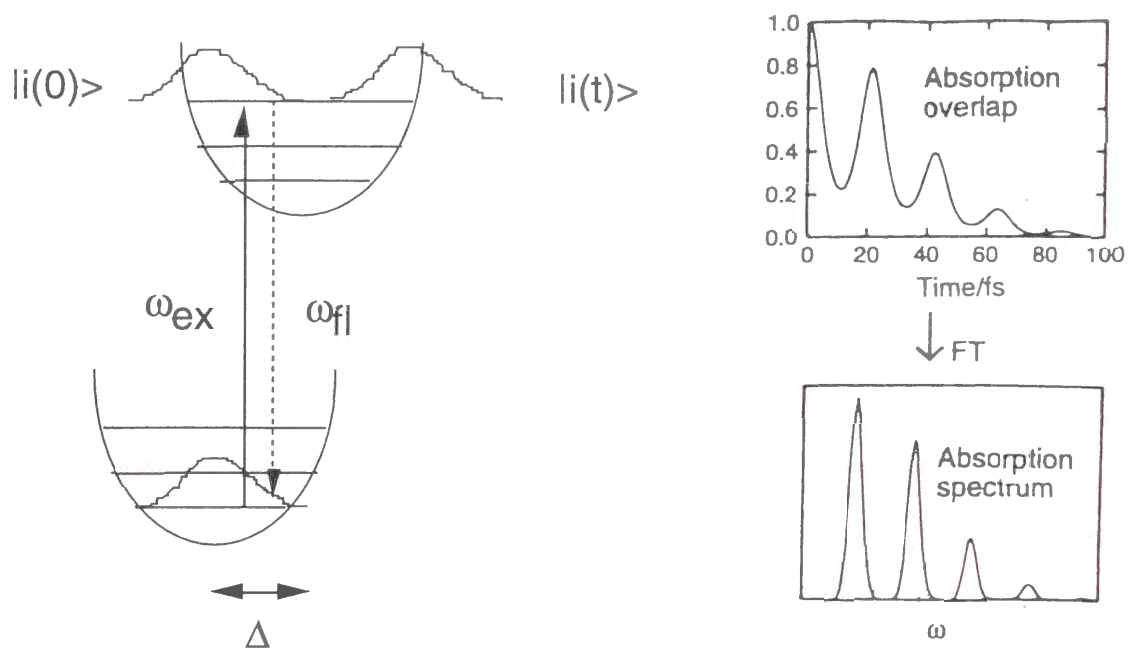


Figure 8-1. Schematic representation of the wavepacket propagation. The figure on the right hand is a copy of Ref. [10].

8-2-3. Comparison with the experimental results

For spectral calculation, we assume three Franck-Condon active modes, whose frequencies are the same as those observed in the LIF spectra of C481 under the jet-cooled condition. We treat the dimensionless displacement as a parameter. Figure 8-1 shows comparison of the calculated fluorescence spectra with the experimental one. Table 8-1 indicates the best-fit parameters used for this simulation. The consistency between them is relatively good, however we cannot well reproduce the behavior at the wavelength longer than 460 nm. In order to improve the quality of the simulation, we have to include the other vibrational modes and the anharmonicity of the potential surface in the ground and/or excited state. Resonance Raman measurement of C481 in solution helps us to obtain valuable information on the frequencies and displacements of the total Franck-Condon active modes in both ground and excited states.

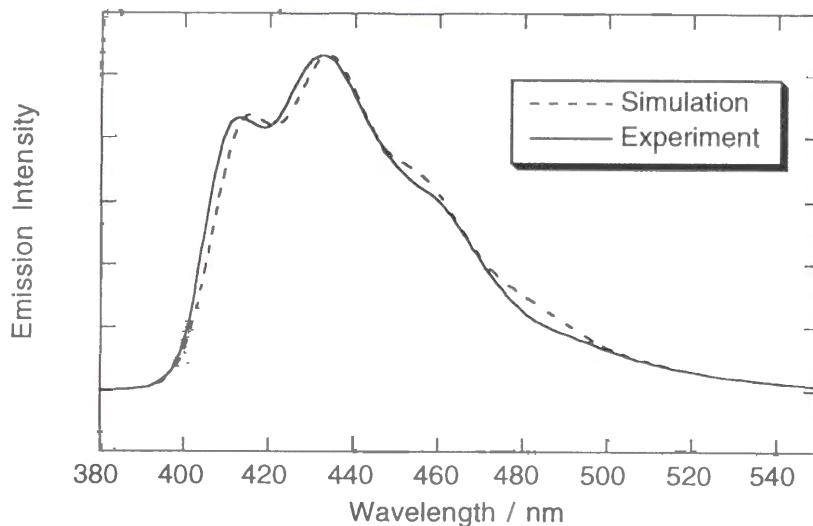


Figure 8-2. Comparison of the calculated fluorescence spectra with the experimental one.

Table 8-1. Best fit parameters of the simulated spectra.

ω / cm^{-1}	Δ
695	1.0
1169	1.5
1410	0.6

The other parameters are used as follows. $\omega_{00}=24200 \text{ cm}^{-1}$, $\Gamma=570.0 \text{ cm}^{-1}$, $T=293 \text{ K}$.

In the following two sections, two different model calculations for fluorescence spectra will be considered assuming two limiting cases: (i) ultrafast intramolecular energy redistribution process which creates the quasi-thermal equilibrium in the population distribution of the vibrational modes. (ii) slow intramolecular energy redistribution process which is comparable to or slower than our instrument response function. These calculations address the question whether the time-resolved fluorescence spectroscopy can distinguish the intramolecular energy redistribution and the intermolecular energy transfer processes.

8-2-4. Ultrafast intramolecular energy redistribution

In the first limiting case, the excess energy is assumed to be redistributed over all the vibrational manifolds in a very fast time scale (<100 fs) while intermolecular energy transfer is considerably slower. We assume that the excess energy of about 12000 cm^{-1} is statistically distributed over all the vibrational modes. We estimate an upper limit of the intramolecular vibrational temperature after the photoexcitation [13]. We have to know the vibrational frequencies of all modes for calculating the temperature. Here we adopted the approximation that the vibrational modes of coumarin 481 were located at equal intervals between 0 and 1600 cm^{-1} , except the C-H stretching (14 modes), which are assumed to have a single frequency of 3000 cm^{-1} [14-17]. The initial temperature was estimated to be about 640 K.

By using the parameters of the frequencies and displacements that are determined above, we simulate the vibrationally hot spectra of the fluorescence based on the Boltzmann population distribution at higher temperatures. Figure 8-2 displays the results of the simulation. By increasing the temperature, the spectra becomes broader. The tendency is similar to the temperature dependence of the fluorescence spectra. However, we cannot reproduce the peak shift of the fluorescence spectra because we do not include the anharmonicity of the potential energy surfaces. The anharmonicity may play an important role in the temperature dependence of the fluorescence spectra. Kaiser et al. estimated the transient temperature of the solute by measuring the red-edge of the absorption spectra after the photoexcitation to the particular vibrational mode or the electronic excited state. They suggested that the intramolecular energy redistribution for large molecules occurred faster than the vibrational cooling process and the transient temperature could be well characterized. This means that the spectrum can be simulated by using a few Franck-Condon active modes with a proper line shape function.

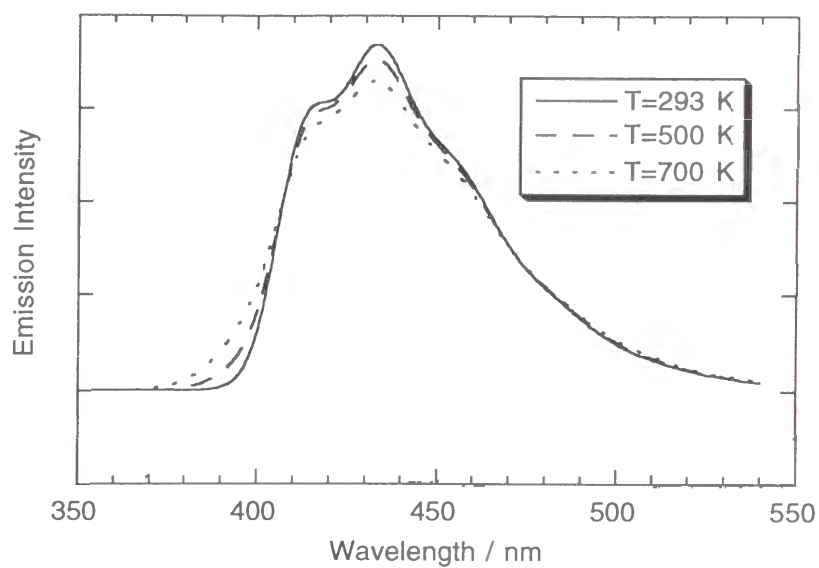


Figure 8-3. Temperature dependence of the fluorescence spectra simulated by the above model calculation.

8-2-5. Selective excitation of a few Franck-Condon active modes

It was shown in the previous section that in the case of the fully thermalized state, the fluorescence spectra become broader at higher internal temperature. This behavior is qualitatively similar to the experimentally observed fluorescence spectrum. On the other hand, assuming a selective, highly nonthermal distribution of the vibrational population, the fluorescence spectra are expected to be different in shape from that in the vibrationally relaxed state. In this calculation, we use the frequency domain expression for convenience. There is no prior information on the population distribution just after the internal conversion from the S_n to S_1 state. Only the limiting case will be discussed in the following. We simulated the fluorescence spectra from the lowest excited vibrational states of the Franck-Condon active modes.

Several time-resolved vibrational spectroscopic studies suggested that the vibrational population was mainly located in the $v=0$ and/or $v=1$ level within a few picosecond time scale even with a large excess energy. No one could observe the population at higher than the lowest vibrationally excited state. They only could observe the deviation from the thermal equilibrium in the lowest vibrationally excited state. Based on these observations, we tried to simulate the emission spectra from the population in the $v=1$ level as a limiting case. In this calculation we assumed that two Franck-Condon active modes were excited at the $v=1$ level or all three modes were excited at the $v=1$ level. In this case, the remaining excess energy is redistributed to the other dark modes.

Table 8-2 gives the parameter used for the simulation and the results are displayed in Figure 8-4. The shape of the spectra strongly depends on the distribution of the population in the vibrational modes. The peaks of the spectra in the case of po_1, po_3, po_4 are blue-shifted and the intensity at around 440 nm decreases significantly. On the other hand, the fluorescence spectrum in the case of po_2 has similar vibronic structures to that in the Boltzmann distribution of the vibrational population. However, the peak position of the spectrum is different from that in the Boltzmann distribution of the vibrational population. The calculated results show that the fluorescence spectra in the vibrationally unrelaxed state are different in shape from that in the vibrationally relaxed

state. However, we did not observe any evidence for dramatic difference from the steady-state fluorescence spectra within a few picoseconds. Direct comparison of this calculation with the experimental results is not possible since we do not know the exact population distributions of both a few Franck-Condon active modes and the other dark modes. Yet one important conclusion is drawn in this calculation. As seen from Figure 8-4, the shape of the fluorescence spectra is sensitive to the population distribution of the Franck-Condon active modes and the experimentally observed spectra are similar in shape to the static one. This means that the intramolecular energy redistribution is completed within our instrument response function and the observed spectra are intramolecularly relaxed ones. The initial vibrational population in the Franck-Condon active modes is quickly redistributed into the other dark modes and reaches the quasi-thermal equilibrium within the molecule. Therefore at least a strong deviation from a thermal energy distribution can be excluded for the observed fluorescence spectra. Since the intramolecular energy redistribution process is undoubtedly much more complicated than our model, this simulation should be taken as only suggestive of the real behavior.

Table 8-2. Quanta of excitation

data	ω_1	ω_2	ω_3
po_1	1	1	0
po_2	1	0	1
po_3	0	1	1
po_4	1	1	1

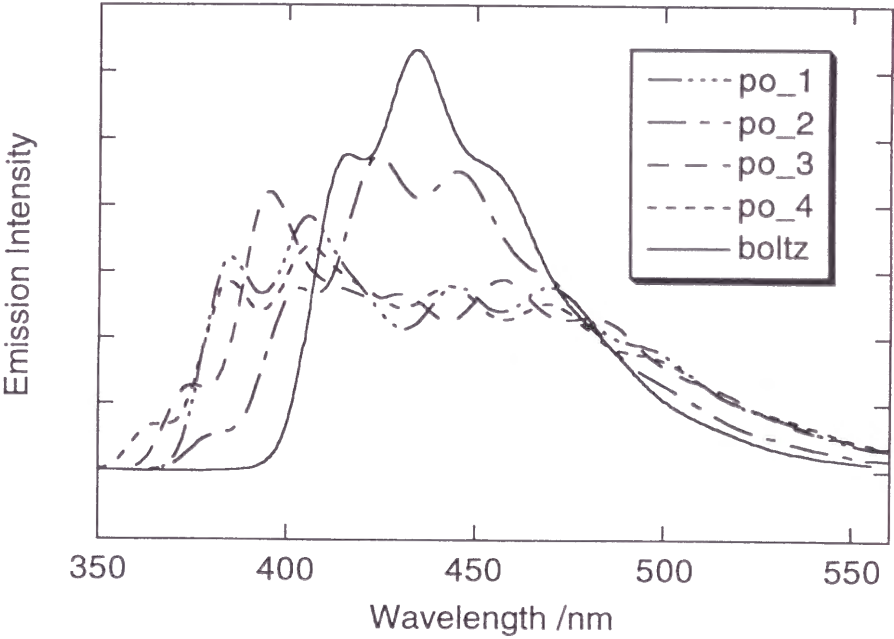


Figure 8-4. Calculation of the fluorescence spectra from the nonequilibrium vibrational states. po_1 ~ po_4 correspond to different vibrational excitations described in Table 8-2. The fluorescence spectrum at the Boltzmann distribution is shown in the solid line.

8-2-6. Vibrational cooling process

In this section, we discuss the mechanism of the vibrational cooling, i.e., energy dissipation processes in solution. There are several proposals in simulating the cooling rate of the vibrational excess energy. Firstly, several groups suggested that the energy dissipation kinetics was simulated by the isolated binary collision model as discussed in Chapter 6. In this model, the rate is expressed by the product of the rate of collision by solvents in the state i and the probability for changing the state i to the state j by a collision. The energy transfer occurs via the collision with the solvent molecules and the rate becomes faster in the solvent with higher density. This model has been applied to various molecules such as azulene and cycloheptatriene from the gas to the compressed liquid phase. It was revealed that this model was succeeded in reproducing the cooling kinetics in the low density region, however, a deviation was observed in high density region. This is due to the reduction of the effective collision frequency through shielding of the solute by solvents.

In the second proposal, Iwata et al. suggested that the cooling rate of the excess energy was directly correlated to the thermal diffusivity of the bulk solvent and the energy dissipation process was controlled by a macroscopic heat conduction [18]. They can reproduce the decay profiles of the anti-Stokes Raman spectra of trans-stilbene after the photoexcitation by using the thermal diffusion equation. In their treatment, they assumed that the excess energy was quickly distributed among the solute and the nearest solvents or solvents in the first shell within the instrument time resolution of 3 ps, and then the slow energy flow into bulk solvent occurs. The latter serve as rate determining process. In this model, the initial temperature should become lower than the estimated value of 640 K. We have to use the other method to estimate the initial temperature of the solute in this model so that we only discuss the time dependence of the internal temperature of the solute.

The temperature change in a media is controlled by the following diffusion equation.

$$\frac{\partial U}{\partial t} = D \nabla^2 U \quad (20)$$

where U is the temperature, D is the thermal diffusivity, and t is time. The thermal diffusivity is defined as

$$D = \frac{\lambda}{c\rho} \quad (21)$$

where λ is the thermal conductivity, c is the heat capacity, and ρ is the density. The solution of eq. (20) is given by

$$U(x, y, z, t) = \frac{1}{(4\pi Dt)^{3/2}} \iiint f(\xi, \eta, \zeta) \exp\left(-\left[(x-\xi)^2 + (y-\eta)^2 + (z-\zeta)^2\right]/4Dt\right) d\xi d\eta d\zeta \quad (22)$$

where $f(x, y, z)$ is the initial distribution of the heat. Eq. (22) shows that the entire time and space dependence of the temperature is determined if the initial heat distribution is known. Iwata et al. assumed that the excess energy was initially distributed uniformly inside the box [18].

$$\begin{aligned} f(x, y, z) &= U_b \quad (|x| \leq (a + r_0), |y| \leq (b + r_0), |z| \leq (c + r_0)) \\ &= 0 \quad (|x| > (a + r_0) \text{ or } |y| > (b + r_0) \text{ or } |z| > (c + r_0)) \end{aligned} \quad (23)$$

In this model, the size of the solute is expressed as a box of dimensions $2a \times 2b \times 2c$ and thickness of the nearest solvent layer is represented by r_0 . By substituting eq. (23) into eq. (22), we obtain the solution,

$$\begin{aligned} U(x, y, z, t) &= \frac{U_b}{8} \left\{ \text{erf}((a + r_0 - x)/(4Dt)^{1/2}) + \text{erf}((a + r_0 + x)/(4Dt)^{1/2}) \right\} \\ &+ \left\{ \text{erf}((b + r_0 - y)/(4Dt)^{1/2}) + \text{erf}((b + r_0 + y)/(4Dt)^{1/2}) \right\} \\ &+ \left\{ \text{erf}((c + r_0 - z)/(4Dt)^{1/2}) + \text{erf}((c + r_0 + z)/(4Dt)^{1/2}) \right\} \end{aligned} \quad (24)$$

Therefore, the temperature at the center of the solute molecule can be expressed by

$$U(x, y, z, t) = U_b \left\{ \text{erf}((a + r_0)/(4Dt)^{1/2}) \right\} \left\{ \text{erf}((b + r_0)/(4Dt)^{1/2}) \right\} \left\{ \text{erf}((c + r_0)/(4Dt)^{1/2}) \right\} \quad (25)$$

We calculated the volume of the C481 molecule by the group increment method and estimated to be 0.2339 nm^3 [19]. If we assume that box is a cube, the size is equal to 0.616 nm . In this calculation, r_0 is set to be 1.25 nm which is the same as that used in the case of trans-stilbene. The thermal diffusivity is calculated by using eq. (21) and

estimated to be $8.42 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ [20]. The calculated result of the temperature change is shown in Figure 8-5. We tentatively fit the calculated curve to a single exponential function to derive a characteristic time constant of the vibrational relaxation processes. We obtained the time constant of 10.9 ps for the vibrational cooling process.

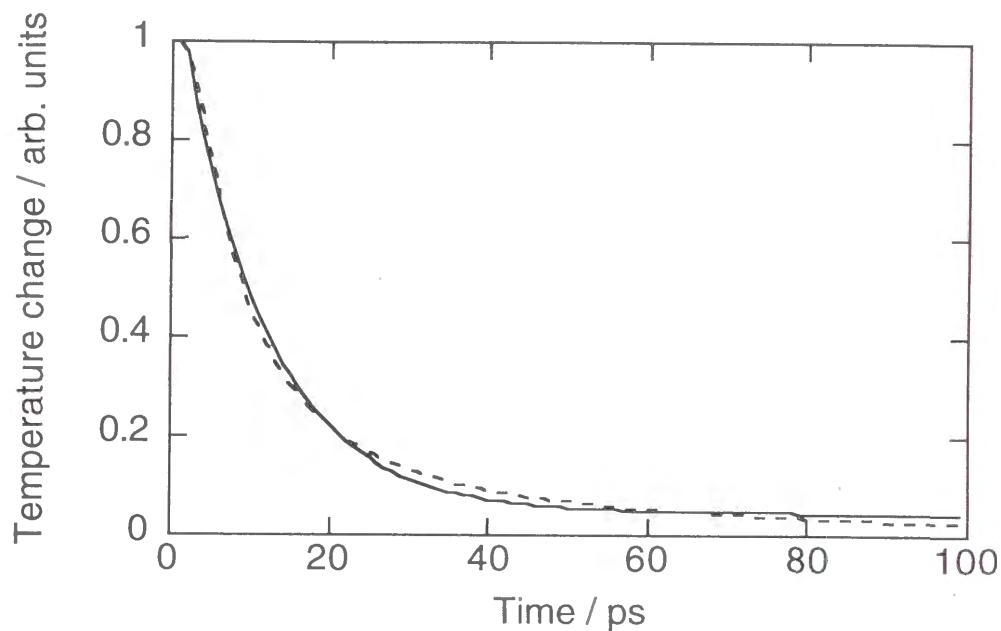


Figure 8-5. Time dependence of the temperature change of the solute. The calculated curves based on the box model (solid line) and best fit with the single exponential function (dashed line) are shown.

As discussed in Chapter 7, the fluorescence spectrum becomes sharp as a function of time, i.e. the intensity increases near the peak of the spectrum and the intensity at the red-edge region decreases as the time goes on. The decay or rise time constant of the fluorescence signals depends on the wavelength. The evolution of the spectrum is observed in a 10 ps time scale. The time scale of the spectral evolution is qualitatively similar to that of this simulation.

In this section, we have simulated the vibrational relaxation processes by using the simple macroscopic diffusion model. The 10 ps time components of the fluorescence signals are qualitatively explained as an energy transfer process from the solute to solvent, i.e., the vibrational cooling process in solution. In order to get further information about the initial heat distribution among the solute and nearest solvent shell, we need the other method to estimate the initial temperature of the solute within 1 ps. However, due to inconsistency between the static fluorescence spectrum and the calculated one, particularly at a longer wavelength, we did not attempt to fit the model function to the experimental data. It would be necessary to know the detailed information on a complete set of the frequencies and displacements of the Franck-Condon active modes.

8-3. Conclusion

In this chapter, we perform the model calculation of the fluorescence spectra by assuming a few Franck-Condon active modes to gain information on the excited-state dynamics. The shape of the fluorescence spectra strongly depends on the distribution of the population in the vibrational modes. The fluorescence spectra in the vibrationally unrelaxed state are found to be different in shape from that in the vibrationally relaxed state. There is no experimental evidence for a distorted shape of the fluorescence spectra which would be indicative of a highly nonthermal energy redistribution. Therefore, a strong deviation from a thermal distribution of a few Franck-Condon active modes seems to be very unlikely in terms of the present model. This calculation supports our experimental conclusion, i.e., our observed fluorescence spectra indicate that the energy redistribution process completes within 100 fs. We should have observed the different fluorescence dynamics at different wavelengths within a few picoseconds if the intramolecular energy redistribution had occurred at much longer than 100 fs. However, a clear distinction between thermal and a moderate nonthermal energy distribution might be impossible at present stage. In other words, the concept of an intramolecular temperature works well as a rough approximation. We estimated the intramolecular vibrational temperature after the photoexcitation by making the assumption that the excess energy of about 12000 cm^{-1} is statistically distributed over all the vibrational modes. The initial temperature was estimated to be about 640 K. The assignment of the slow 10 ps components of the fluorescence signals to the vibrational relaxation process is supported by using a simple macroscopic diffusion equation.

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Chapter 9

Summary

Summary

Part I Photodynamics of Simple Linear Polyenes in Solution

We investigated the photoinduced dynamics of trans- and cis-1,3,5-hexatriene in cyclohexane and acetonitrile solutions by femtosecond transient absorption spectroscopy. After the internal conversion from the initially excited 1B (S_2) state to the 2A (S_1) state in tens of femtoseconds, the vibrational energy redistribution process in the 2A state and the internal conversion to the ground state occur in a subpicosecond time scale. 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.

The anisotropy change of the transient absorption signals at 400 nm for trans isomer clearly shows the different time dependence from that for cis isomer. The anisotropy decay provides us information about the change of direction in the dipole moment between transitions from the S_1 and S_2 state or the structural change in the S_1 state during the vibrational energy redistribution process. Even though we could not identify the origin of the anisotropy change exactly, we clearly observed the different initial values of the anisotropy and different time dependence between the trans and cis isomers. This means that 1,3,5-hexatriene has different potential minima and different intermediate geometries in the S_1 state for each isomer.

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 model calculation based on the time-dependent wave-packet propagation scheme supports this interpretation. We succeeded in reproducing the temporal behavior of the transient bleach recovery signals at three different wavelengths.

The different behavior 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, the conformational relaxation around the C-C single bond. For trans isomer, a significant amount of s-cis isomers is created and the bleach recovery in a subnanosecond time scale is attributed to the single bond relaxation. On the other hand, for cis isomer, the majority of the ground-state product is considered to be all-s-trans isomer so that there is only a minor contribution of s-cis isomer in the signal. Another explanation might be the conformational relaxation from s-cis to all-s-trans isomer which occurs faster than the vibrational relaxation process. All-s-trans isomer is formed predominantly within 20 ps.

We also investigated the excited-state dynamics of 1,3,5,7-octatetraene in solution by the femtosecond transient absorption spectroscopy. After the photoexcitation to the S_2 state, we observed the transient absorption in the very broad region from ultraviolet to visible, whose dynamics depends on the probe wavelength. The subpicosecond decay component dominates at the wavelengths longer than 500 nm. The signals contain a 10 ps decay component at all wavelengths. Based on the results in the gas phase, we consider that the subpicosecond decay components at the longer wavelengths reflect the internal conversion from the S_2 to S_1 state and the absorption bands are shifted to the blue side within this time scale. It should be noted that the absorbance at the wavelengths longer than 480 nm has a smaller intensity than that at the shorter wavelengths. This is due to the difference of the oscillator strengths between transitions from the S_1 and S_2 state. A 5-15 ps decay component observed in the transient absorption signal is ascribed to the vibrational relaxation in the S_1 state.

In this study, we investigated the photoinduced dynamics of 1,3,5-hexatriene and 1,3,5,7-octatetraene in solution by the femtosecond transient absorption spectroscopy. After the photoexcitation to the S_2 state, we observed the transient absorption in the very broad region (ultraviolet to visible region), whose dynamics depend on the probe wavelength. From the decay rate of the transient absorption signals, we can directly determine the time scale of the excited state dynamics such as the internal conversion and the vibrational relaxation. The rate of the internal conversion of both polyenes in solution is similar to that in the gas phase. We consider that the difference of the lifetime in the S_1

(2^1A_g) state between 1,3,5-hexatriene and 1,3,5,7-octatetraene is most probably due to a large difference of the barrier height in the deactivation process. From the bleach recovery of 1,3,5-hexatriene, we found that the vibrational relaxation in the ground state occurred in 10-20 ps and the conformational relaxation around the C-C single bond proceeded in 150-300 ps.

Part II Femtosecond Relaxation Processes from a Higher Excited Electronic State of a Dye Molecule in Solution

We studied the internal conversion and vibrational energy redistribution process of coumarin 481 in cyclohexane with a large excess energy by the femtosecond UV fluorescence up-conversion method. We observed the 200-300 fs rising components at all wavelengths. We also observed a sharpening of the spectrum in a 10 ps time scale. This result suggests that the observed dynamics are mainly controlled by the internal conversion from S_n to S_1 state, i.e. the internal conversion occurs in a 220-280 fs time scale and the intramolecular energy redistribution takes place much faster than the former process, which does not affect the spectral evolution. The 10 ps components of the up-converted signals are attributed to the vibrational cooling process in the S_1 state.

In order to gain further information on the relaxation dynamics, we performed model calculation of time-resolved fluorescence spectrum by assuming a few Franck-Condon modes. The shape of the fluorescence spectra strongly depends on the distribution of the population in the vibrational modes. The fluorescence spectra in the vibrationally unrelaxed state are found to be different in shape from that in the vibrationally relaxed state. However, the transient emission spectrum does not show any large deviation from that in the steady-state within 100 fs. This means that the vibrational population distribution reaches the quasi-thermal equilibrium in a very fast time scale. This calculation supports our experimental conclusion.

We estimated the intramolecular vibrational temperature after the photoexcitation by making the assumption that the excess energy of about 12000 cm^{-1} is statistically distributed over all 96 vibrational modes. The initial temperature was estimated to be

about 640 K. The assignment of the slow 10 ps components of the fluorescence signals to the vibrational relaxation process is supported by using a simple macroscopic diffusion equation. The concept of an intramolecular temperature works well as a rough approximation.

Acknowledgments

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Kaoru Ohta

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CHEMICAL PHYSICS LETTERS

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Ultrafast dynamics of photoexcited trans-1,3,5-hexatriene in
solution by femtosecond transient absorption spectroscopy

Kaoru Ohta ^{a,b}, Yukito Naitoh ^b, Kenichi Saitow ^c, Keisuke Tominaga ^{b,c},
Noboru Hirota ^a, Keitaro Yoshihara ^{b,c}

^a Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

^b Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

^c The Graduate University for Advanced Studies, Myodaiji, Okazaki 444, Japan

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Ultrafast
solution

Kaoru

Abstract

We have investigated the photoexcitation to the first excited singlet state and decay in less than 100 fs, indicating that the vibrational

1. Introduction

In the past two decades, much of the research has been devoted to the study of the photochemical dynamics of both experimental and theoretical studies. These molecular photofunctionalities substitute the retinal carotenoids in photosynthesis. Unlike its long-lived analogues, 1,3-butadiene, no fluorescence is observed even in low-temperature expansions [5]. The lifetimes of the isolated linear polyenes are attributed to energy transfer to

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Ultrafast dynamics of photoexcited trans-1,3,5-hexatriene in solution by femtosecond transient absorption spectroscopy

Kaoru Ohta^{a,b}, Yukito Naitoh^b, Kenichi Saitow^c, Keisuke Tominaga^{b,c},
Noboru Hirota^a, Keitaro Yoshihara^{b,c}

^a Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

^b Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

^c The Graduate University for Advanced Studies, Myodaiji, Okazaki 444, Japan

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Abstract

We have investigated the ultrafast dynamics of trans-1,3,5-hexatriene in cyclohexane and acetonitrile solutions following photoexcitation to the 1^1B_u state. The transient absorption in the visible region consists of an instantaneous rise (< 150 fs) and decay in less than 500 fs, whose time constant depends on the probe wavelength. The bleach recovery at 268 nm indicates that the vibrational relaxation in the ground state occurs in 15–20 ps, followed by a subnanosecond relaxation.

1. Introduction

In the past two decades, a great deal of effort has been devoted to studies of the photophysical and photochemical dynamics of small linear polyenes both experimentally and theoretically [1–4]. Biologically these molecules play important roles in the photofunctionality; substituted linear polyenes constitute the retinal proteins in visual pigments and the carotenoids in photosynthetic systems.

Unlike its longer chain and diphenyl-substituted analogues, 1,3-butadiene and 1,3,5-hexatriene exhibit no fluorescence and give broad absorption spectra even in low-temperature matrices and supersonic jet expansions [5]. These observations suggest that the lifetimes of the initially excited state, 1^1B_u , of small linear polyenes are extremely short and the immediate transfer to another dark electronic state follows.

The photodynamics of 1,3,5-hexatriene in the excited state is ascribed to the two electronic states – the ionic 1^1B_u and the covalent 2^1A_g states. The symmetry-forbidden $2^1A_g \rightarrow 1^1A_g$ transition is not easily detectable in absorption or fluorescence. Recent spectroscopic studies in the gas phase have revealed that the 2^1A_g state of cis-1,3,5-hexatriene is located about 5000 cm^{-1} below the 1^1B_u state [6–8]. On the other hand, the location of the corresponding 2^1A_g state in the trans isomer has not been determined precisely. The existence of this state is considered to be responsible for the excited state dynamics, i.e. internal conversion from the 1^1B_u to the 2^1A_g state occurs. The timescale of this internal conversion under the jet-cooled condition is found to be subpicosecond by a direct time-resolved study [9].

In the solution phase, resonance Raman spectroscopy has been used to investigate the excited-state

dynamics of trans- and cis-isomers by Ci et al. [10,11]. They found that the initial motion of the wave packet out of the Franck–Condon region took place on timescales of tens of femtoseconds. Since resonance Raman spectroscopy provides information only on the dynamics right after photoexcitation, a direct ultrafast time-resolved study is needed to understand the fate of photoexcited small linear polyenes in the condensed phase. We have studied the ultrafast dynamics of photoexcited trans-1,3,5-hexatriene in solution by femtosecond transient absorption spectroscopy.

2. Experimental

The details of the transient absorption measurement will be described elsewhere [12]. A regeneratively amplified Ti:sapphire laser system (NJA-4 and CPA-1, Clark-MXR) produced a 150 fs pulse around 800 nm, with a repetition rate of 960 Hz and a pulse energy of 700 $\mu\text{J}/\text{pulse}$. The output of the fundamental was frequency-doubled in the first BBO crystal. The second harmonic was divided into two parts. One of them was mixed with the remaining fundamental in the second BBO crystal to produce the third harmonic (268 nm, 30 $\mu\text{J}/\text{pulse}$) as the pump beam. The other was focused into deuterated water to generate the white light continuum, which was used as the probe beam. The absorption change was monitored by a photodiode through an interference filter (FWHM = 10 nm). All measurements were performed with the magic-angle polarization between the pump and probe beams. The instrumental response assumed with a Gaussian function was estimated to be 550 fs from the temporal rise of the excited state absorption or bleach recovery of Rhodamine 6G in ethanol. We also performed a one-color pump-probe experiment to measure the bleach recovery of the ground state, in which case the third harmonic of the fundamental was split into two halves and used for the pump and probe beams.

We purchased 1,3,5-hexatriene from Aldrich as a mixture of two isomers. Trans-1,3,5-hexatriene was prepared as described by Møller et al. [13]. The isomeric purity of the product was checked by gas chromatography and was found to be higher than 95%. Cyclohexane and acetonitrile (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. The concentration of the sample was 2.4×10^{-4} M, which gave an absorbance of about 1.0 at 268 nm. For the cyclohexane solution 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 and discussion

The static absorption spectra of trans-1,3,5-hexatriene in cyclohexane and acetonitrile are similar in shape and intensity, as reported [10]. The absorption peaks of the 0–0 bands are around 268 nm in both solvents.

Fig. 1 displays the transient absorption signals at three different probe wavelengths. The time profiles of the signals are fitted to a single- or bi-exponential function convoluted with the instrumental response function. Table 1 summarizes the results of the best fits of the transients. After photoexcitation, an instrument-limited rise (< 150 fs) can be seen at each probe wavelength. In cyclohexane, the observed signal at 400 nm decays with a time constant of about 400 fs. The decay of the transient absorption signal at 420 nm is faster than that at 400 nm. At both wavelengths, the signals contain small residual components on a longer timescale. At a probe wavelength longer than 450 nm the observed signals are symmetrical around zero delay and the temporal widths are similar to that of the instrumental response function. Thus, a faster decay is clearly observed at longer wavelengths. On the other hand, the transient absorptions at wavelengths shorter than 400 nm also show a feature similar to that observed at 400 nm. The observed absorption band is peaked around 400–450 nm and becomes weaker at both shorter and longer wavelengths. The transient absorption signals in acetonitrile are similar to those in cyclohexane, except that the slow decaying components have a greater intensity. These signals decay with time constants of 14 ps at 400 nm and 5 ps at

Table 1
Best-fit time constants
at different wavelengths

Solvent	λ (nm)
cyclohexane	400
	420
	450
	470
	500
acetonitrile	400
	420
	450
	470
	500

^a Relative amplitudes of the fast and slow components.

420 nm, as determined from the longer timescale.

Resonance Raman spectroscopy on the basis of its linear dependence on the excited state Franck–Condon displacement gives a timescale of about

Fig. 1. Transient absorption signals at 400, 420, and 450 nm. The instrumental response function is shown as a dashed line.

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Table 1
Best-fit time constants of transient absorption signals at five different wavelengths for trans-1,3,5-hexatriene in solutions

Solvent	λ (nm)	τ_1 (fs)	τ_2 (fs)
cyclohexane	400	440 ± 15 (0.97) ^a	– (0.03)
	420	220 ± 10 (0.98)	– (0.02)
	450	< 150	
	470	< 150	
	500	< 150	
acetonitrile	400	410 ± 15 (0.91)	13600 ± 2000 (0.09)
	420	250 ± 10 (0.94)	5200 ± 2000 (0.06)
	450	< 150	
	470	< 150	
	500	< 150	

^a Relative amplitude of each decay component is given in parentheses.

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These signals decay
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420 nm, as determined from the data measured on a longer timescale.

Resonance Raman spectroscopy revealed on the basis of its lineshape analysis that photoexcited trans-1,3,5-hexatriene leaves from the initially excited Franck–Condon region of the 1^1B_u state on a timescale of about 40 fs [10,11]. After depopulation

of the initially excited state, the internal conversion from the 1^1B_u to the 2^1A_g state is expected to occur. Hayden and Chandler studied femtosecond time-delayed photoionization of 1,3,5-hexatriene under supersonic jet conditions [9]. They concluded that the initially excited population decayed from the 1^1B_u state in less than 100 fs and internal conversion proceeded through an intermediate state with a decay time constant of about 250 fs [9]. Though their experiment was performed under jet conditions, we consider that the initially excited population in the 1^1B_u state decays on a similar timescale in solution because, on this timescale, the relaxation process is not much affected by collisions between the solute and solvent molecules. Furthermore, a similar behavior in the transient absorption signals was observed for β -carotene derivatives in the condensed phase [14]. Therefore, the instantaneous rise observed in the transient absorption means that we have probed the population on the way from the 1^1B_u to the 2^1A_g state.

By internal conversion, the population of the vibrationally excited 2^1A_g state is created immedi-

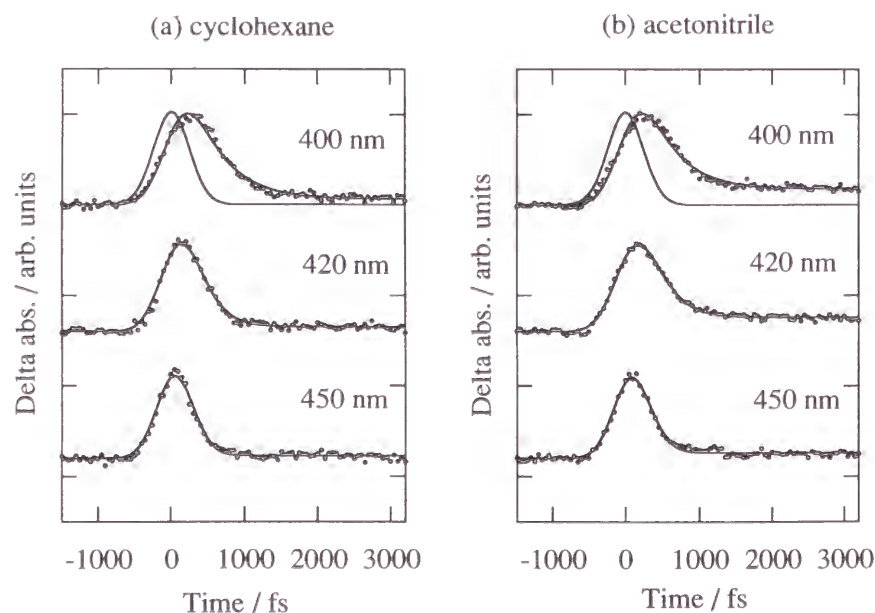


Fig. 1. Transient absorption signals probed at three different wavelengths for trans-1,3,5-hexatriene in (a) cyclohexane and (b) acetonitrile. The instrumental response function is shown in the top decay curve. The solid lines represent the best fits to the data by the convolution of the instrumental response function with a sum of two exponentials.

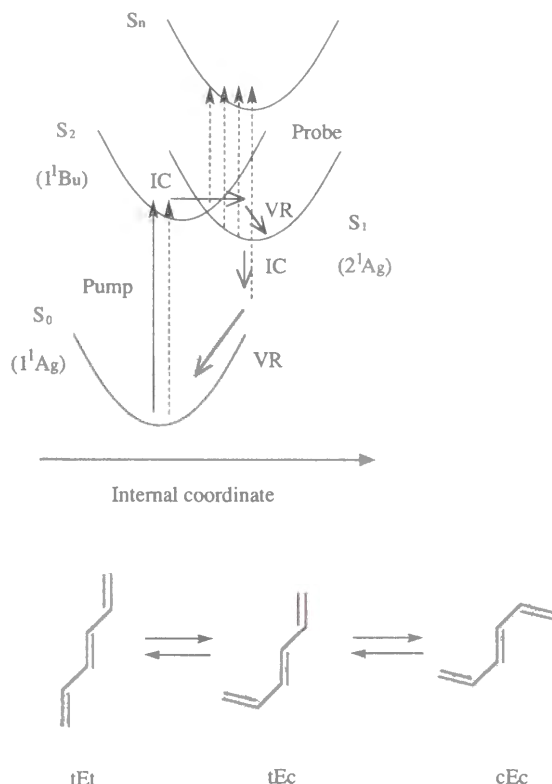


Fig. 2. The upper figure shows the photodynamics of trans-1,3,5-hexatriene following the photoexcitation to the 1^1B_u state. IC and VR denote internal conversion and vibrational relaxation, respectively. The solid and dashed arrows show the pump and probe beams, respectively. The lower figure represents the three different conformers of trans-1,3,5-hexatriene.

ately. The observed delayed responses can be attributed to the vibrational energy redistribution in the excited 2^1A_g manifold. The vibrationally hot state can be probed initially at longer wavelengths by the S_n-S_1 transition, as illustrated in Fig. 2. The redistribution process goes on and the population of the vibrationally relaxed 2^1A_g state should be produced on a subpicosecond timescale. At shorter wavelengths, we can probe this relaxed state. The difference in the decay rates may reflect the rates of the vibrational energy redistribution at different energy levels within the 2^1A_g potential. Our experiment shows that the population transfer to the bottom of the potential energy surface of the 2^1A_g state occurs in less than 500 fs. There may exist another process;

after the creation of the population in the vibrational hot 2^1A_g state, internal conversion to the S_0 state occurs directly without relaxation in the 2^1A_g state. In this case, the faster decay of the transient absorption observed at longer wavelengths corresponds to the effective decrease in the population in the S_1 state due to internal conversion to the S_0 state. Thus, the delta absorbance at wavelengths longer than 450 nm is expected to be greater than that at 400 nm. The intensity of the transient absorption is greater as the probe wavelength is shorter between 400 and 550 nm. Therefore, this process is not a major channel in the excited state dynamics.

The time-delayed photoelectron spectra show that the vibrational energy redistribution within the 2^1A_g state occurs on a timescale comparable to the lifetime of the 2^1A_g state (≈ 300 fs) under supersonic jet conditions [15]. From this finding, we consider that these processes in solutions are due mainly to the intrinsic nature of the excited state rather than the solvent-induced interaction. However, the observed ion signals in the supersonic jet expansion do not contain any slow components as observed in our transient absorption signals. The slow component of ours may be attributed to the vibrationally hot ground state because the highly vibrationally excited ground state cannot be monitored due to small Franck-Condon factors to the energetically accessible ion states. They also indicate that internal conversion from the 2^1A_g to the 1^1A_g state occurs immediately after the vibrational relaxation in the 2^1A_g state. In contrast to 1,3,5-hexatriene, longer polyenes such as 1,3,5,7-octatetraene and 1,8-diphenyl-1,3,5,7-octatetraene fluoresce strongly. The difference in the fluorescence quantum yield comes from a competition between the radiative decay of the excited state and internal conversion to the S_0 state. While longer polyenes have relatively long lifetimes in the S_1 state, in 1,3,5-hexatriene internal conversion to the S_0 state can occur predominantly.

Fig. 3 shows the one-color transient bleach recovery signals of trans-1,3,5-hexatriene in cyclohexane (a) and acetonitrile (b) at 268 nm. These signals can be fitted by a tri-exponential function; the results of the best fits are shown in Table 2. The transients show an instrument-limited appearance of a bleach followed by recovery which occurs on three timescales. The first two recovery times in these

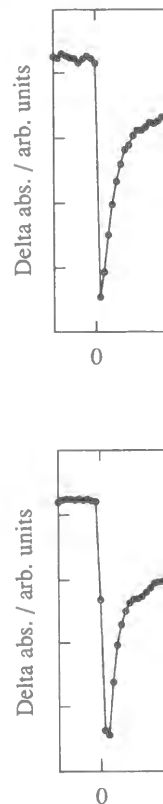


Fig. 3. Transient bleach recovery signals of trans-1,3,5-hexatriene in (a) cyclohexane and (b) acetonitrile. The solid line represents the best fit function. The insets show the experimental data points and the best fit function.

solvents are similar.

The first component of the recovery is attributed to the vibrational energy redistribution in the excited 2^1A_g state. When the population of the excited state relaxes to the bottom of the potential energy surface of the excited state (S_1), the recovery of the transient absorption at 268 nm, we can

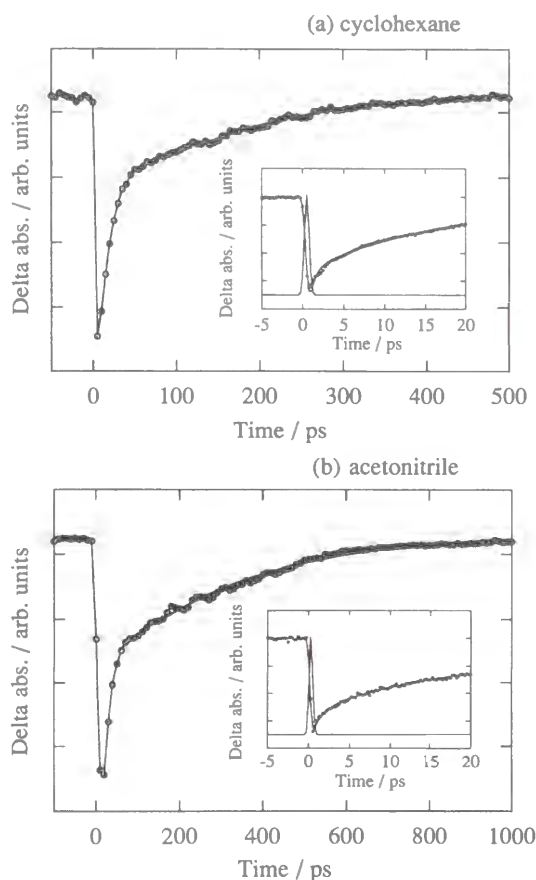


Fig. 3. Transient bleach signals on a subnanosecond timescale obtained by a one-color pump–probe experiment for trans-1,3,5-hexatriene in (a) cyclohexane and (b) acetonitrile. The solid line represents the best fit to the data with a single exponential function. The insets show that the transient bleach signals on early timescales and the instrumental response functions.

solvents are similar to each other, but the last slow components are different.

The first components of the transient bleach signals in cyclohexane and acetonitrile have recovery times of 0.8 and 1.2 ps, respectively. After photoexcitation, the population of the vibrationally relaxed 2^1A_g state is produced within 500 fs and then internal conversion from 2^1A_g to 1^1A_g takes place. When the population in the vibrational hot 1^1A_g state relaxes to some extent and the energy difference between the 1^1A_g state (S_0) and the highly excited state (S_n) matches the probe wavelength of 268 nm, we can probe the population in the vibra-

tionally hot 1^1A_g state as the fastest bleach recovery at 268 nm.

The second time constants of the bleach recovery of the transients in cyclohexane and acetonitrile are about 18 and 16 ps, respectively. Generally, the vibrational relaxation of large organic molecules in solution is known to occur in tens of picoseconds [16]. In related studies, picosecond time-resolved resonance Raman measurements have been performed to investigate the photochemical ring opening reaction of 1,3-cyclohexadiene in solutions [17–19]. After the photoexcitation of 1,3-cyclohexadiene, cis-1,3,5-hexatriene appears with a time constant of 6 ps and the vibrational relaxation of hot cis-1,3,5-hexatriene occurs with a 9 ps time constant. Based on these observations, we assign the second components to vibrational relaxation in the ground state. The difference in the time constants between the resonance Raman data and ours is probably due to that between the trans- and cis-isomers.

The transient bleach signal has a slow third component, 150–300 ps. The decay in acetonitrile is about twice as slow as that in cyclohexane. The ground state depletion fully recovers on this timescale. The quantum yield of the trans to cis photoisomerization of the C=C double bond in solution is low ($\phi_{\text{trans-cis}} = 0.016$) [2]. A vast majority of the excited trans-1,3,5-hexatriene molecules should finally return to the trans ground state. These results mean that it needs subnanoseconds to fully recover the original trans form. One possible origin of this slow component is the isomerization process about the C–C single bond and/or the C=C double bond in the ground state. This is supported by an ab initio calculation, which shows that the interaction between

Table 2

Best-fit time constants of transient bleach signals obtained by one-color pump–probe experiment for trans-1,3,5-hexatriene solutions

Solvent	τ_1 (ps) ^a	τ_2 (ps) ^a	τ_3 (ps) ^c
cyclohexane	0.8 ± 0.1 (0.38) ^b	18 ± 1 (0.62)	150 ± 10
acetonitrile	1.2 ± 0.1 (0.31)	16 ± 1 (0.69)	325 ± 15

^a τ_1 and τ_2 are the first and second components, respectively, of the bleach recovery signals observed on an early timescale.

^b Relative amplitude of each bleach recovery component, determined only from the results on an early timescale.

^c The third component of the bleach recovery signal observed on a slower timescale.

the 2^1A_g and 1^1A_g states is greater as the C–C single bond and the C=C double bond rotate from the all-trans configuration [20].

There exist three different C–C single-bond conformers (Fig. 2). Here, the trans and cis forms about the C–C single bond are denoted t and c, respectively, and those about the C=C double bond as E and Z, respectively. At room temperature, the tEt conformer certainly predominates over the two others. After photoexcitation, the system undergoes a full or partial rotation about the single bond in the S_2 , S_1 state and/or internal conversion to the S_0 state. The slow component may be due to the recovery process from a mixture of the tEc and cEc conformers to the tEt one in the ground state. In the low-temperature Ar matrices, the tEc and cEc conformers are produced under irradiation by Hg 253.7 nm light [21,22]. Furthermore, after photoexcitation of 1,3-cyclohexadiene, the timescale for the cZt to tZt isomerization of cis-1,3,5-hexatriene is longer than 200 ps [17,18]. In a recent study of the ring opening reaction of the dehydrocholesterol–previtamin D system, which are derivatives of 1,3-cyclohexadiene and cis-1,3,5-hexatriene, single-bond isomerization occurs in 125 ps in ethanol [23]. The timescale of the third component observed in our study matches these time constants of molecules having similar structures. As for the C=C double bond, a part of photoexcited trans-1,3,5-hexatriene may undergo partial rotation about the C=C bond from planarity. Accordingly, the third component is also considered to come from the rotation about the C=C bond from a non-planar geometry to the stable planar form because the trans isomer has a larger transition probability than the cis one [10,11]. In acetonitrile, the recovery takes twice as much time as that in cyclohexane. This may mean the energy stabilization of the distorted transients is greater in a polar solvent. Since transient absorptions in the visible region are similar in the two solvents, the contribution of this stabilization should be important for the dynamics in the ground state.

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The Photochemical Dynamics of Trans-1,3,5-Hexatriene in Solution Investigated by the Ultrafast Transient Absorption Spectroscopy

K. Ohta^{a,b}, Y. Naitoh^b, K. Tominaga^b, N. Hirota^a, and K. Yoshihara^b

^a Department of Chemistry, Kyoto University, Kyoto 606, Japan

^b Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Abstract The excited-state dynamics of trans-1,3,5-hexatriene in solution were investigated by ultrafast transient absorption spectroscopy. The transient absorption in the visible region consists of the instantaneous rise (<150 fs) and decays in less than 500 fs, whose time constant depends on the probe wavelength. The bleach recovery at 268 nm indicates that the vibrational relaxation in the ground state occurs in 15-20 ps followed by a subnanosecond relaxation.

1,3,5-Hexatriene is one of the simplest linear polyenes whose derivatives, such as retinal and carotenoids, play important roles in the vision and light harvesting systems. In the excited-state dynamics, however, there still remain unresolved processes giving rise to a complete lack of fluorescence and the broad absorption spectra even under jet-cooled conditions. In order to directly reveal the excited-state dynamics in solution, we have performed the ultrafast transient absorption measurement of trans-1,3,5-hexatriene in cyclohexane and acetonitrile solutions.

Our experimental apparatus was based on a regeneratively amplified Ti:sapphire laser which produced a 150 fs pulse at around 800 nm. The third harmonic light was used as the pump pulse which excited trans-1,3,5-hexatriene to the 1^1B_u state (S_2). The transient absorption and bleach recovery were probed by using a white light continuum and third harmonic light, respectively.

Figure 1(a) shows the transient absorption signals probed at three different wavelengths in cyclohexane. They consist of an instrument-limited rise (<150 fs) and subpicosecond decay at each probe wavelength. The observed signal at 400 nm decays with a time constant of about 400 fs. At longer wavelengths the decay of the signal gradually becomes faster and reaches the instrument response function at probe wavelengths longer than 450 nm. The third slow decaying component appears clearly at shorter wavelengths. The transient absorption signals in acetonitrile are similar to those in cyclohexane.

Compared with the previous studies on this molecule [1,2], it is considered that the photoexcitation to the 1^1B_u state is followed by the internal conversion to the 2^1A_g state (S_1) which occurs within 100 fs. The dependence on the probe wavelength is attributed to the dynamics in the 2^1A_g state. The population of the vibrationally excited 2^1A_g state is created immediately after the internal conversion and probed initially at longer wavelengths by the S_n - S_1 transition. The vibrational energy redistribution process goes on and the population of the vibrationally relaxed 2^1A_g state should be produced in a subpicosecond time scale. At shorter wavelengths, we can probe this relaxed state. The difference in the decay rates may

reflect the rates of the vibrational energy redistribution at different energy levels in the 2^1A_g manifold. Our experimental results show that the population transfer to the bottom of the potential energy surface of the 2^1A_g state occurs in less than 500 fs. The femtosecond time-resolved photoionization studies under jet-cooled conditions showed that the excited-state dynamics takes place in a similar time scale [1]. From this finding, we consider that the excited-state dynamics in the solution phase is mainly controlled by the intrinsic nature of this molecule rather than the solvent-assisted interaction.

Figure 1(b) shows the one-color transient bleach recovery signals at 268 nm. The transient exhibits an instrument-limited appearance of a bleach followed by the recovery which occurs in three time scales. The first two recovery times in both solvents are similar to each other, which are around 1 ps and 15-20 ps. The third component gives different time constants; 150 ps in cyclohexane and 325 ps in acetonitrile. The ground-state depletion fully recovers in this time scale.

The first recovery of transient bleach signal shows that it takes 1 ps to observe the population of the vibrationally excited 1^1A_g state (S_0) at 268 nm. We assign the second component to the vibrational relaxation time in the 1^1A_g state in comparison with the related system [3].

The quantum yield of the trans to cis isomerization of the C=C double bond in solution is so low that most of the excited molecules should finally return to the ground state of trans form. The slow third component indicates the existence of additional relaxation process. One possible origin is a conformational change around the C-C single bond. After photoexcitation, s-cis isomer is produced in the excited state or in the vibrationally excited ground state and returns back to the original s-trans one in a subnanosecond time scale since all s-trans isomer certainly predominates at room temperature.

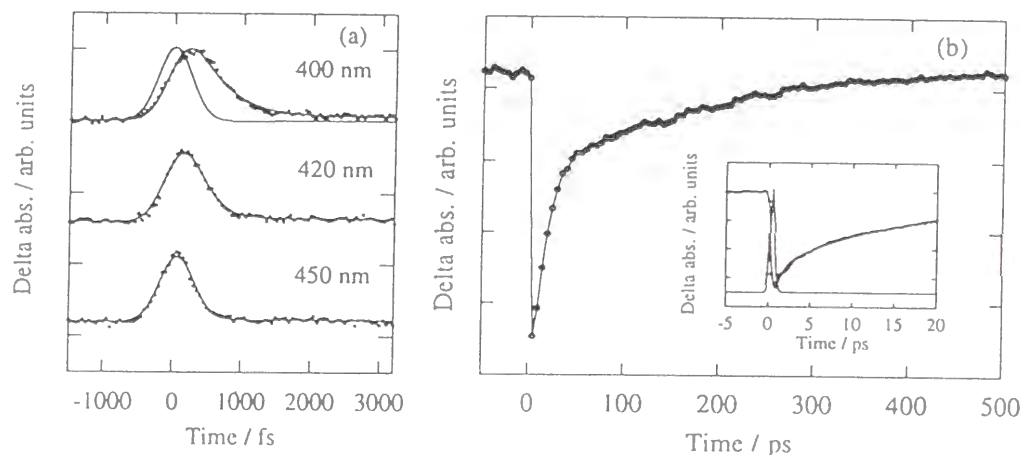


Fig. 1. Transient absorption signals probed at three different wavelengths (a) and transient bleach signal (b) in cyclohexane. The inset of Fig. 1(b) shows the transient bleach signal in an early time scale and the instrument response function.

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Femtosecond transient absorption studies of *trans*- and *cis*-1,3,5-hexatriene in solution

Kaoru Ohta ^{a,b}, Yukito Naitoh ^b, Keisuke Tominaga ^b, Noboru Hirota ^a, Keitaro Yoshihara ^{b*#}

^a *Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606, Japan*

^b *Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

Abstract

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 S₂ to S₁ state occurs within 100 fs and the lifetime of the S₁ 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 S₁ 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 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.

Corresponding author. Present address: Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa 923-12, Japan

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 ~ 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, 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 isomer, 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 1B state, whereas the vertical transition to the 2A state might overlap or even be located at higher energy than that to 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}

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 occurred 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 wavepacket 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

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 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 1kHz centered at around 800 nm. The pulse energy was around 900 μ J/pulse. The fundamental pulse was doubled by a 1mm 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 $\mu\text{J}/\text{pulse}$. The other beam was focused into H_2O or D_2O flow cell to generate the white light continuum which lay between 300 nm 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 analog 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 chromatography, 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 assure 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 nm to 280 nm. The maximum molar extinction coefficient in cyclohexane is $\epsilon_{\text{max}}=51740 \text{ M}^{-1}\text{cm}^{-1}$ for the *trans* isomer²¹ and $41000 \text{ M}^{-1}\text{cm}^{-1}$ for the *cis* isomer²². 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 results at five probe wavelengths ranging from 360 nm 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 ($< 150 \text{ fs}$) 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 nm to 500 nm. These absorption signals possess an instantaneous rise and subpicosecond decay component which are rather similar to those for *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 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 *trans* isomer is similar to that for *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 nm and 257 nm and the minimum between these peaks, 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 ps and 150 ps. However, the transient at 262 nm recovers faster than that at 268 nm and reaches the baseline at around 20 ps, and 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 ps 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 constants 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 longer recovery with the time constant of 320 ps. At 259 nm, the behavior is similar to that between 268 nm 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 *cis* isomer in the first 20 ps are similar to those of *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 show 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.

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.

Based on the lineshape analysis of the resonance Raman spectroscopy, the initial motion of the wavepacket 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 coworkers estimated the time constant for the internal conversion to the 2A state to be 40 fs in the isolated molecule condition based on the linewidth 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.

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 fs 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 $<155.7\text{cm}^{-1}$.¹⁶ Fuss and coworkers have studied the excess energy dependence of 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 1.4ps^{-1} . The temperature dependence on the lifetime of the 2A state in the gas phase gave an activation energy of about 170cm^{-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 C=C double bond is very small, the branching to the product of this isomerization is considered to be small.

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 1A and 2A state.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 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 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 Based on 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 coworkers 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 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 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 azulene³³,

stilbene³⁴ and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole³⁵, 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 nm 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 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 ($\phi_{\text{trans-cis}}=0.016$, $\phi_{\text{cis-trans}}=0.034$).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

Furukawa and coworkers 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 them to *s-cis* isomers based on the *ab-initio* MO 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 experiment. 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 C-C single bond to a stable all s-trans form follows in a slower time scale.

In general, the absorption cross section of s-cis isomers is smaller than that of 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 *cis* isomer, $cZc < tZc < tZt$ and, for *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.

In order 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 about a factor of 2.5 by changing temperature from 286 K to 326 K. The rate constant depends on the solvent viscosity and temperature and is frequently expressed by the following Arrhenius-type equation:

$$k = \frac{A}{\eta^a} \exp\left(-\frac{\Delta E}{k_b T}\right) \quad (1)$$

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 ($0 \leq a \leq 1$). 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 photochemical ring opening reaction of 1,3-cyclohexadiene suggests 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 excess energy enough 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 a sufficient amplitude 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 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 s-cis isomers 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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Figure captions

Figure 1. Schematic diagram of the apparatus for transient absorption measurement.

HS, Harmonic separator; PD, Photodiode; IF, Interference filter; $\lambda/2$, $\lambda/2$ waveplate.

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 represent the best fits to the data by the convolution of the instrument response function with a sum of the two exponentials.

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

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.

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).

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.

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.

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.

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.

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.

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

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)
acetonitrile	550	350 ± 50 (0.94)	---- (0.06)
	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.

Table 3. Best Fit Time Constants of Transient Bleach Recovery Signals Obtained by One-Color Pump-Probe Method.

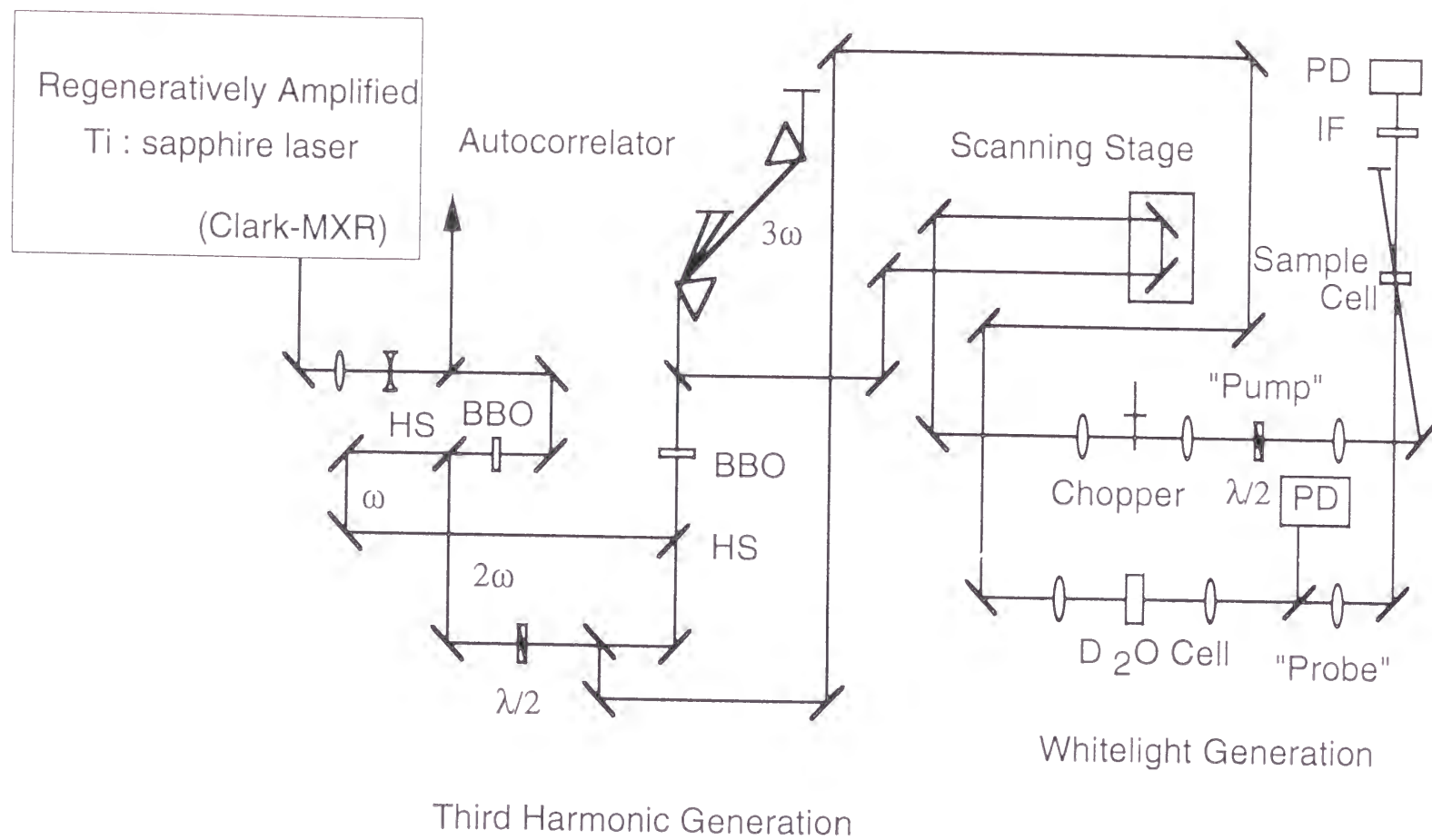
Solute / Solvent	λ / nm	τ_1 / ps ^a	τ_2 / ps ^a	τ_3 / ps ^c
trans-HT	268	$0.8 \pm 0.1(0.38)^b$	18 ± 1 (0.62)	150 ± 10
/ cyclohexane	262	*	*	180 ± 20
	259	0.6 ± 0.2 (0.09)	13 ± 1 (0.91)	184 ± 10
trans-HT	268	$1.2 \pm 0.1(0.31)$	16 ± 1 (0.69)	325 ± 15
/ acetonitrile	262	*	*	325 ± 35
	259	*	*	305 ± 30
cis-HT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

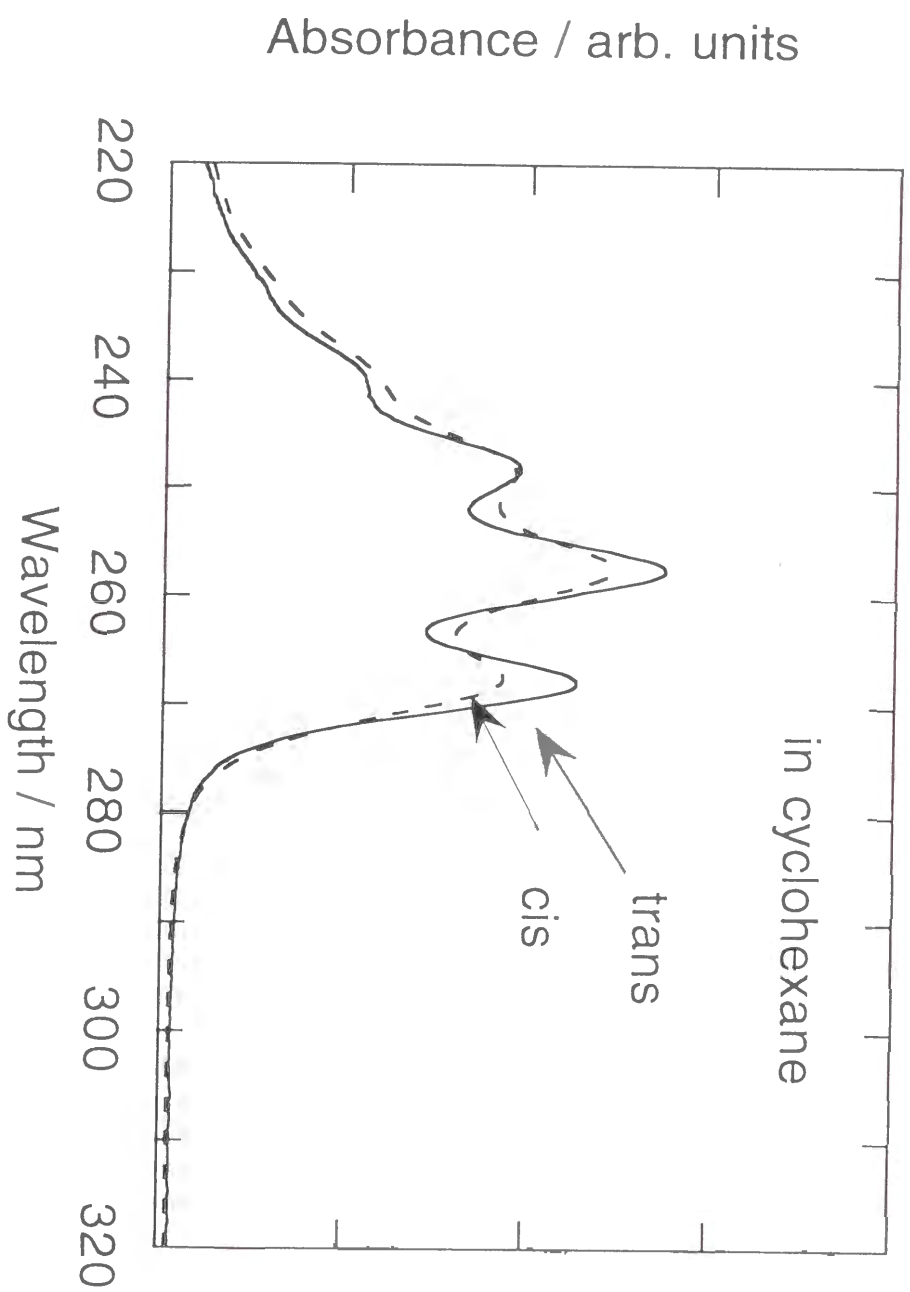
^a τ_1 and τ_2 are the first and second components, respectively, of the bleach recovery signals observed on an early time scale.

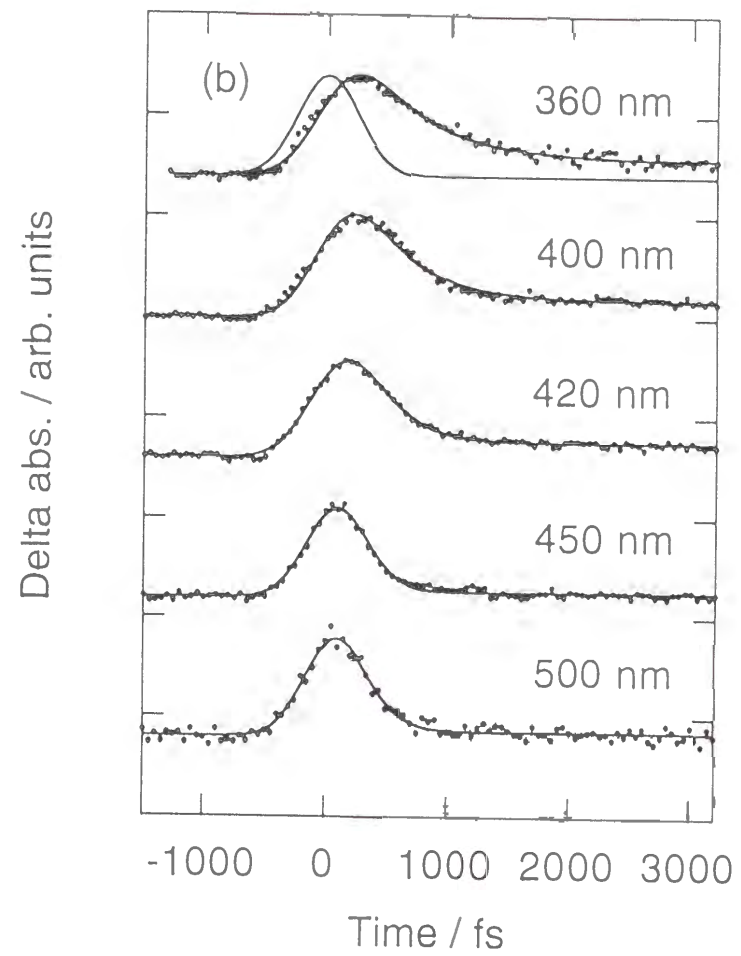
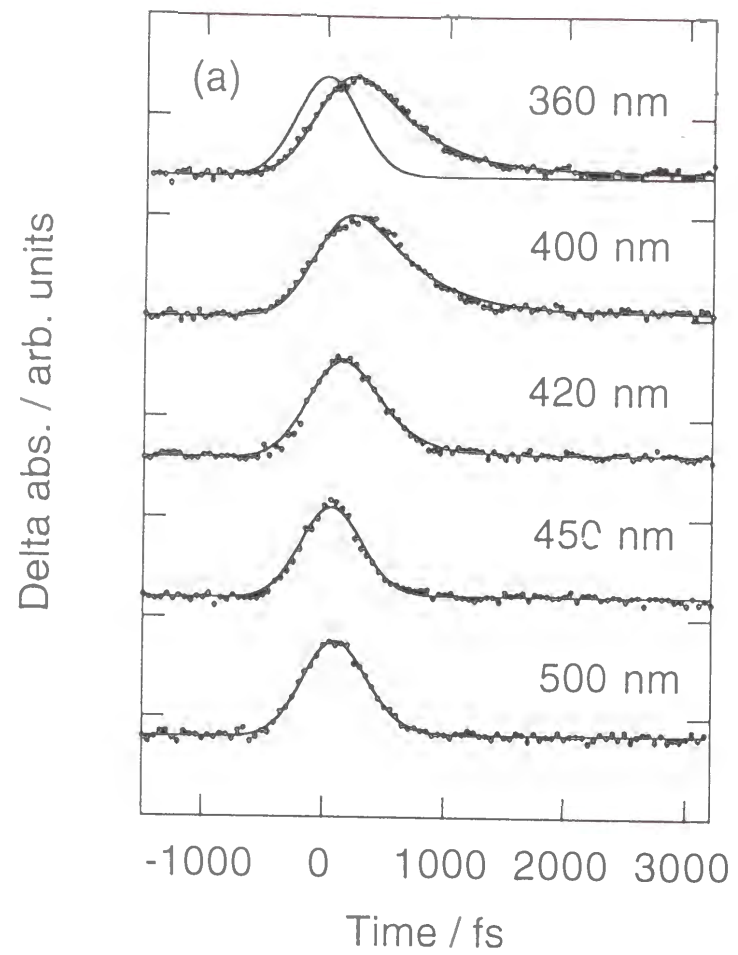
^b Relative amplitude of each bleach recovery component, determined only from the results on an early time scale.

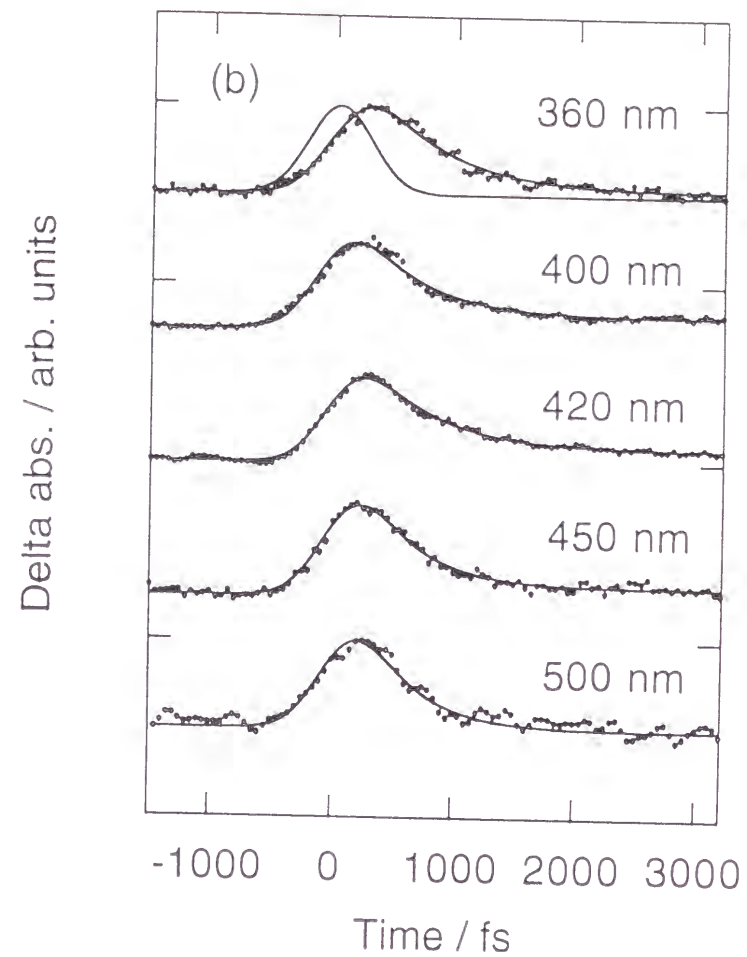
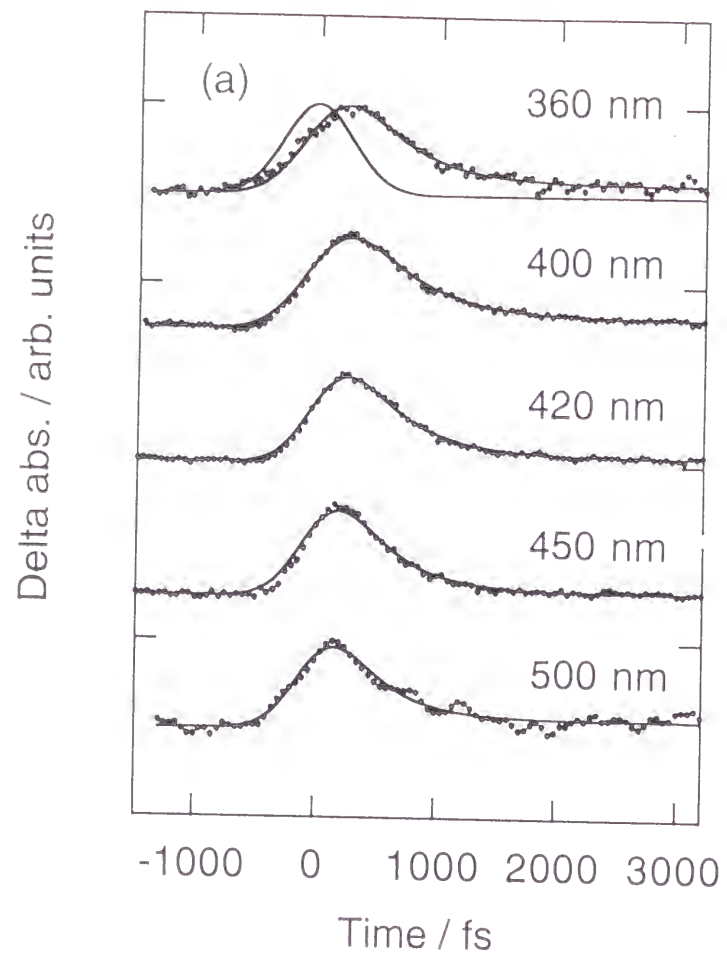
^c The third component of the bleach recovery signal observed on a slower time scale.

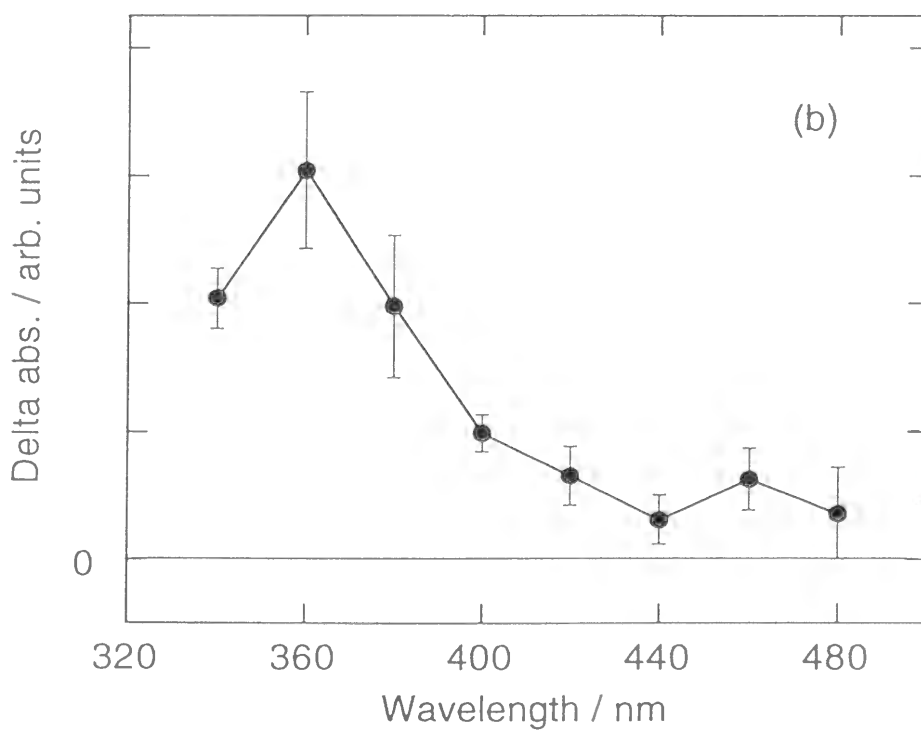
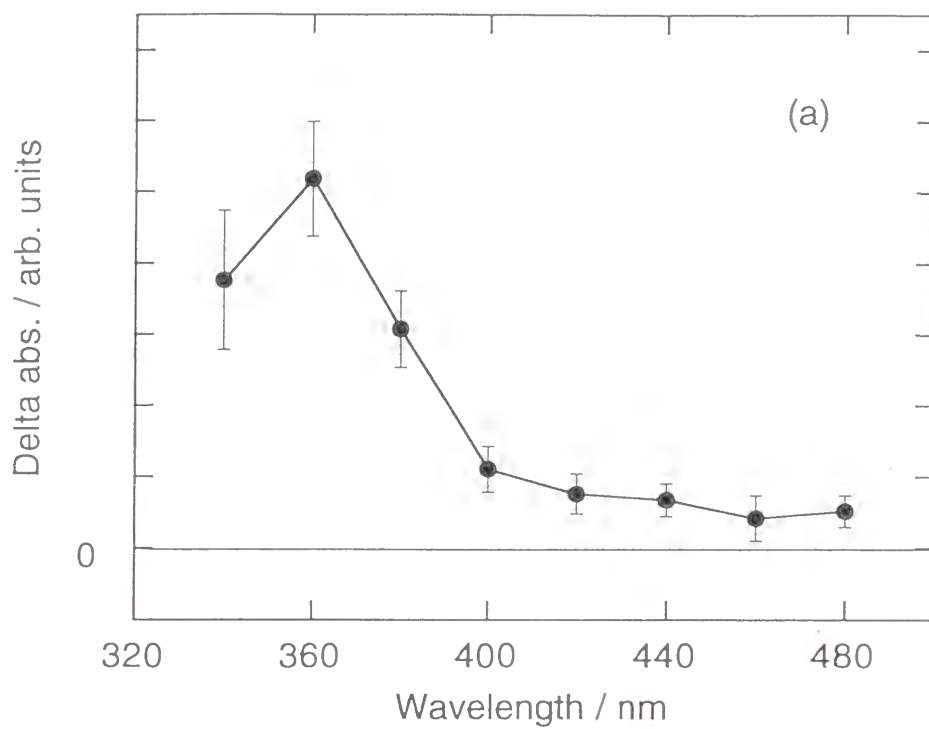
Asterisl indicates the data which can not be fitted well by a sum of exponential functions.

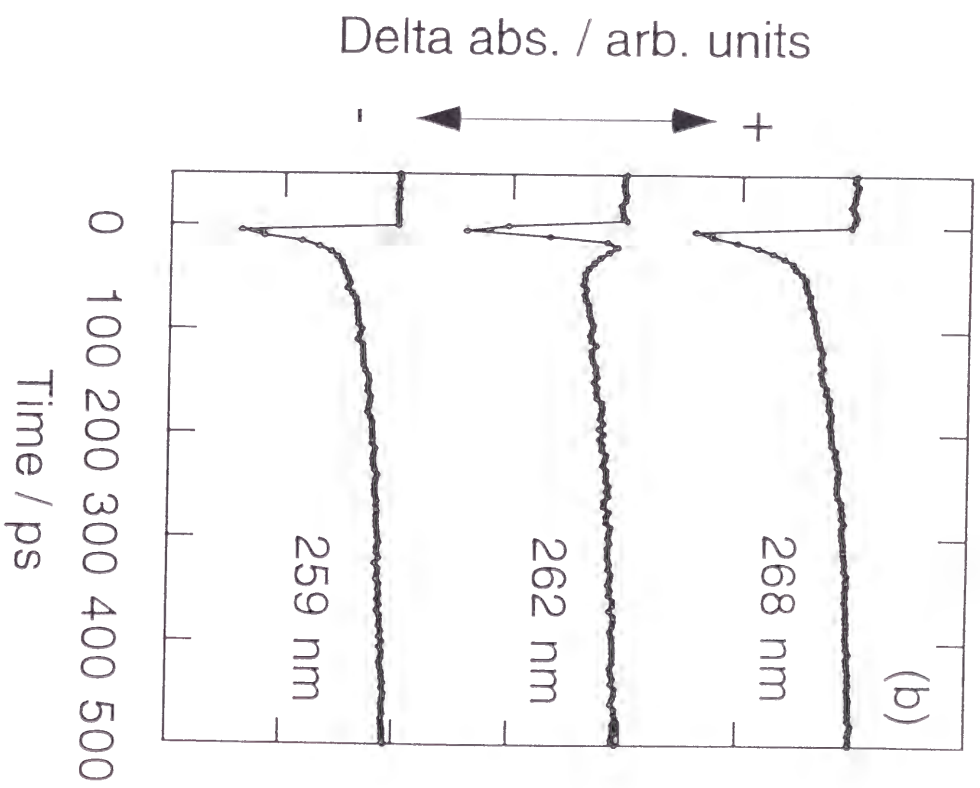
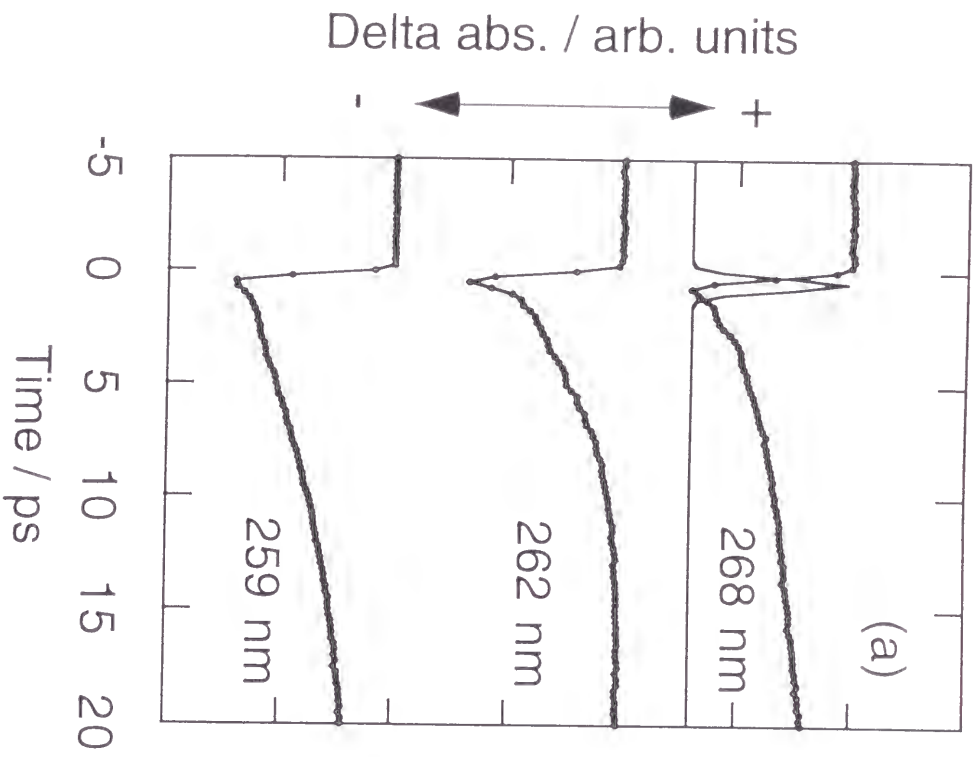


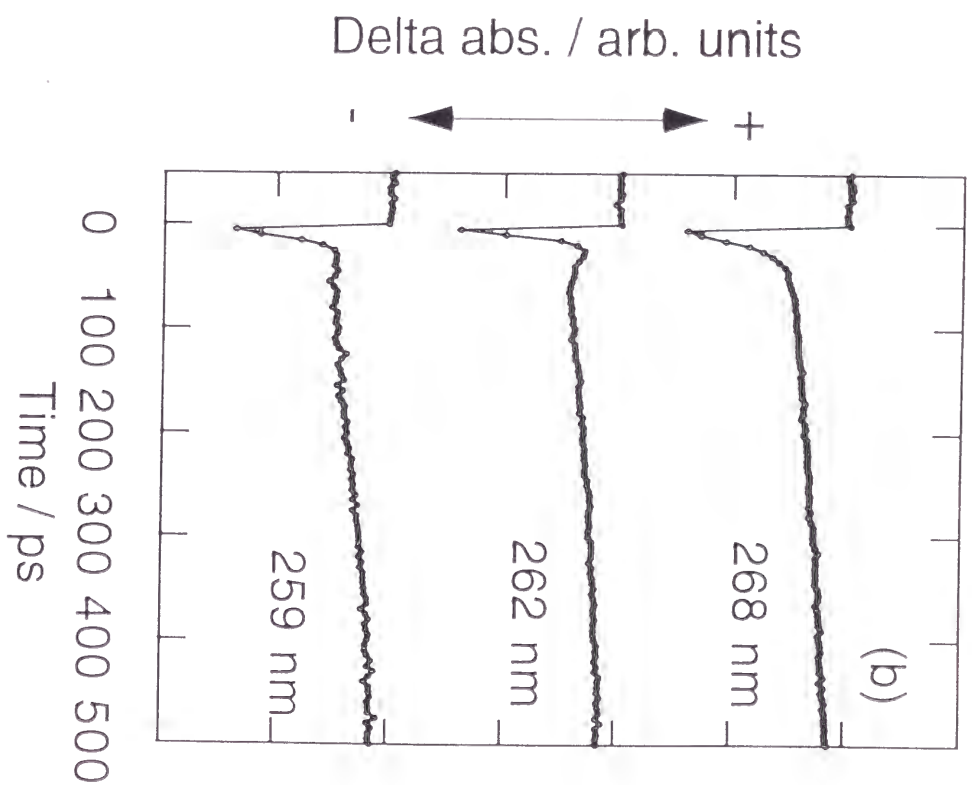
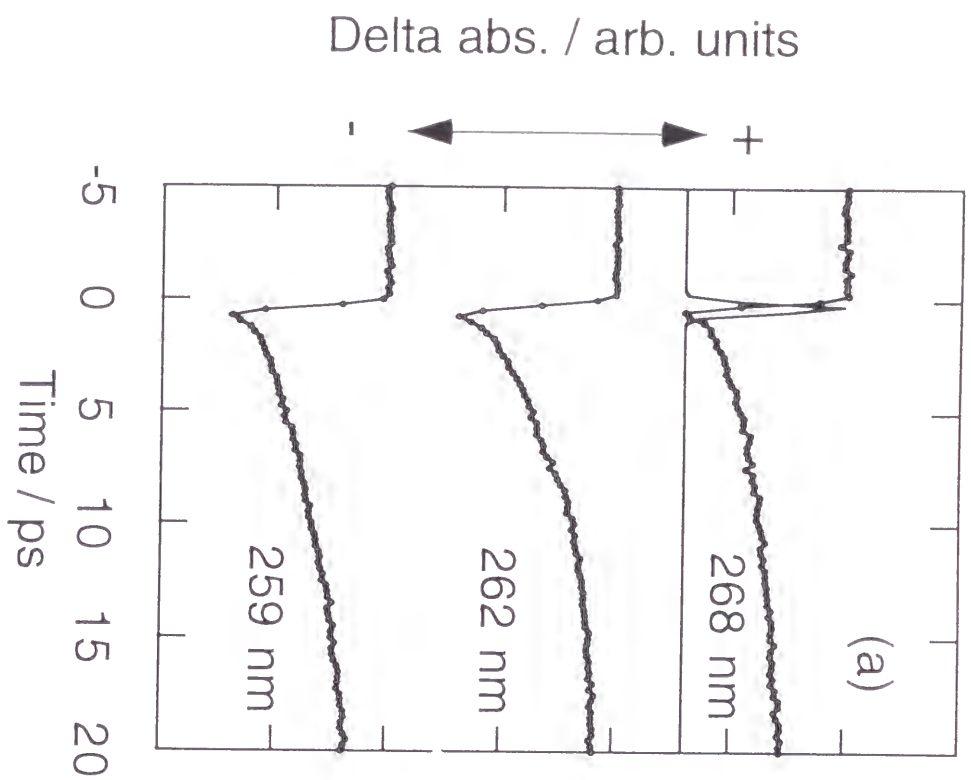


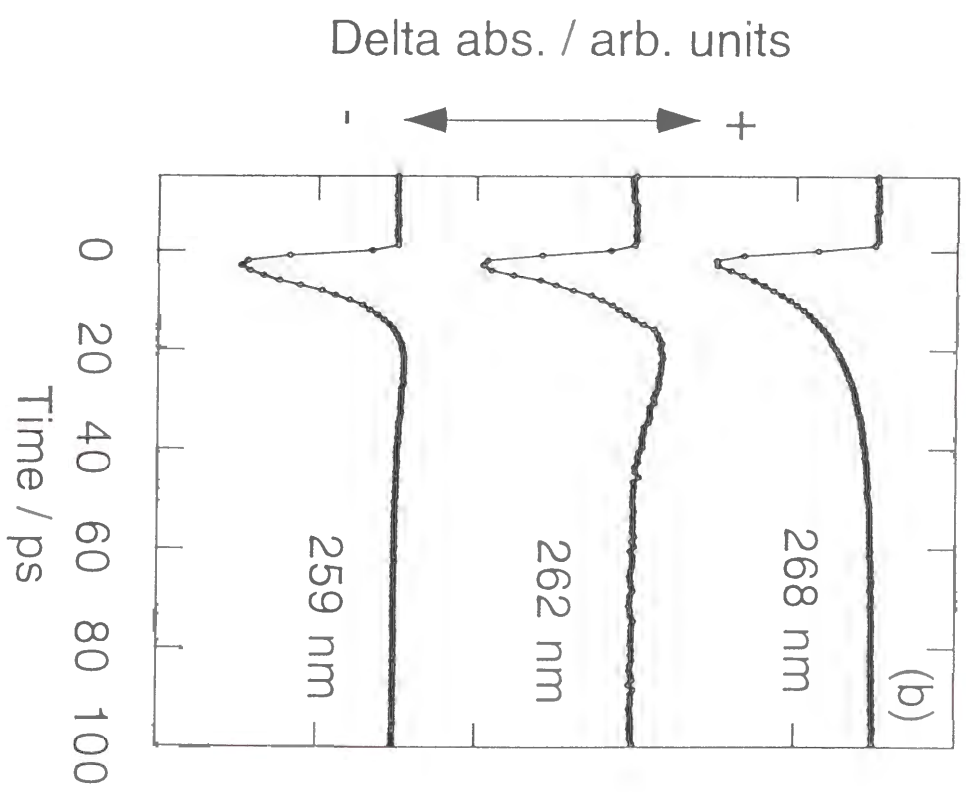
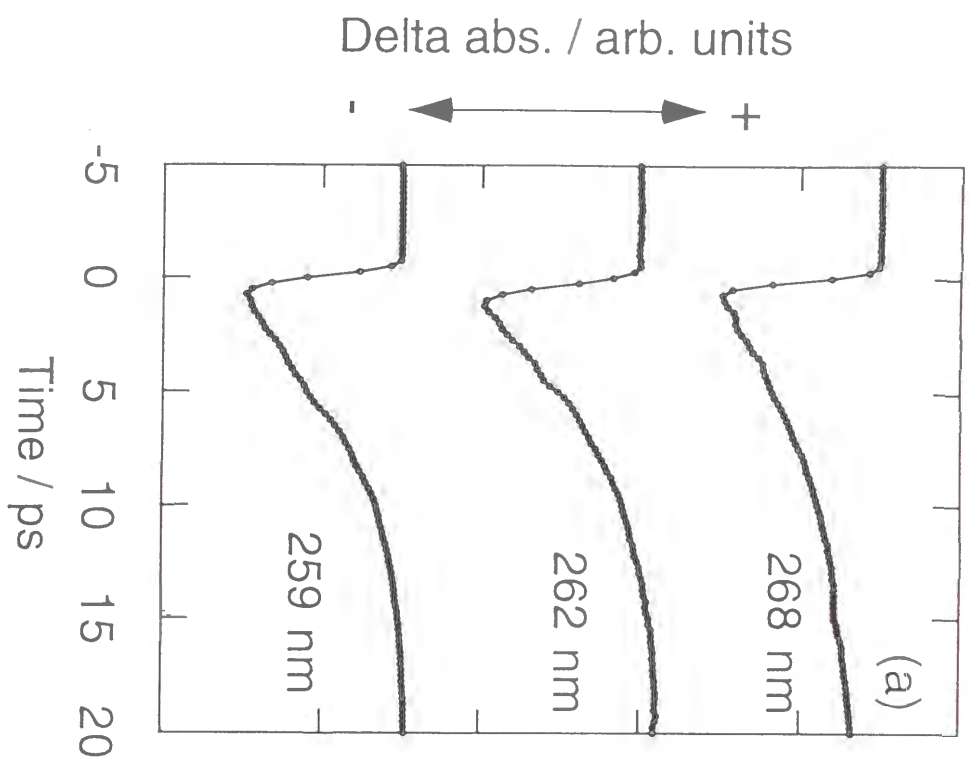


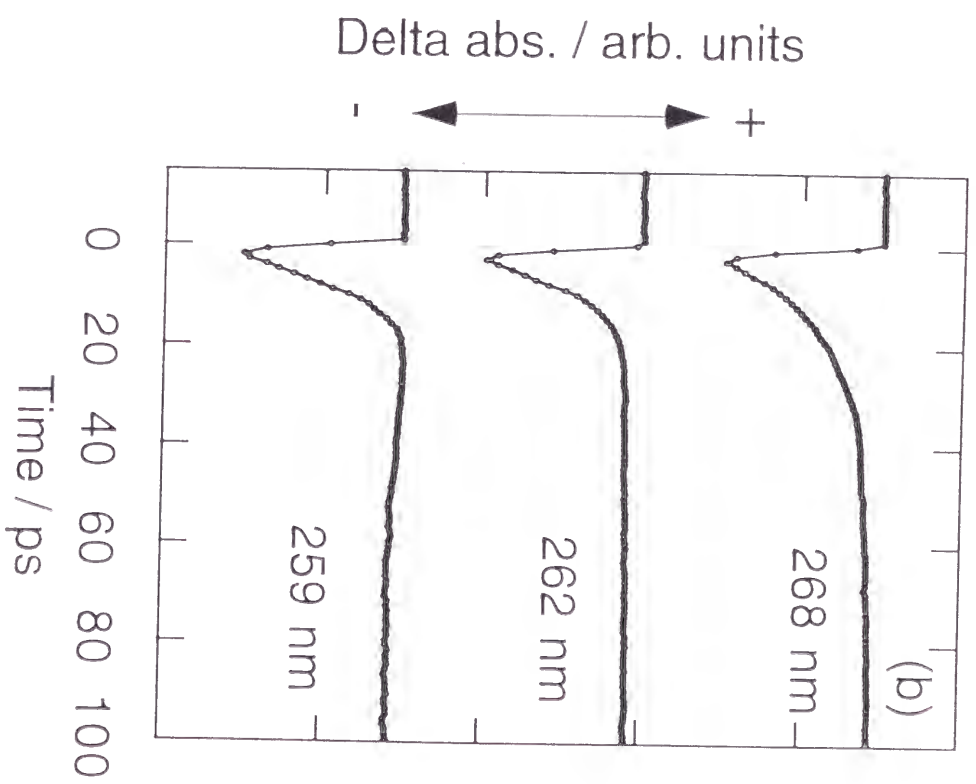
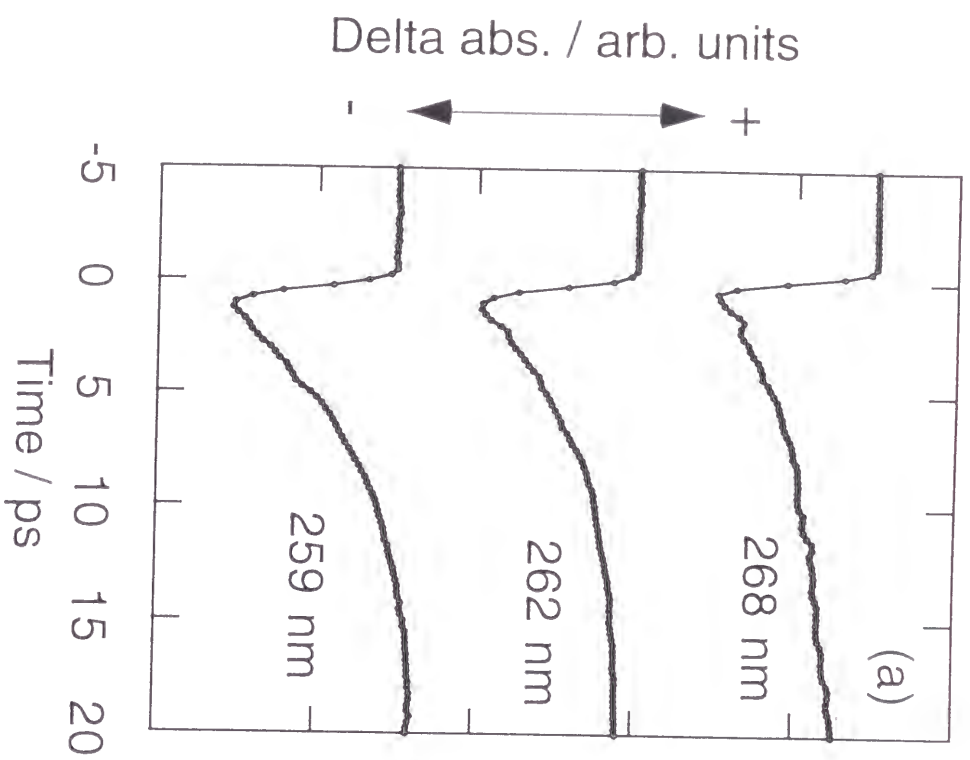


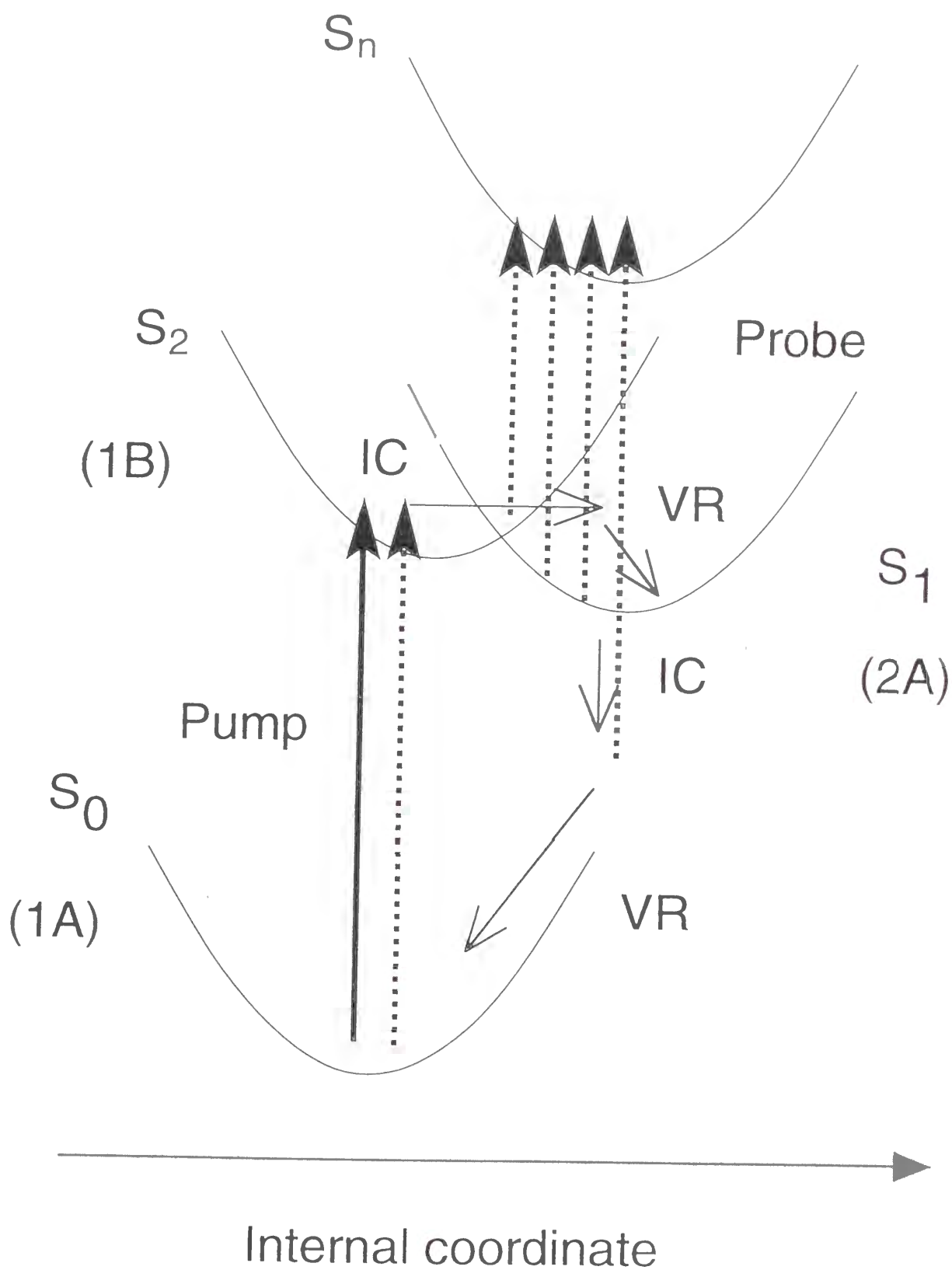


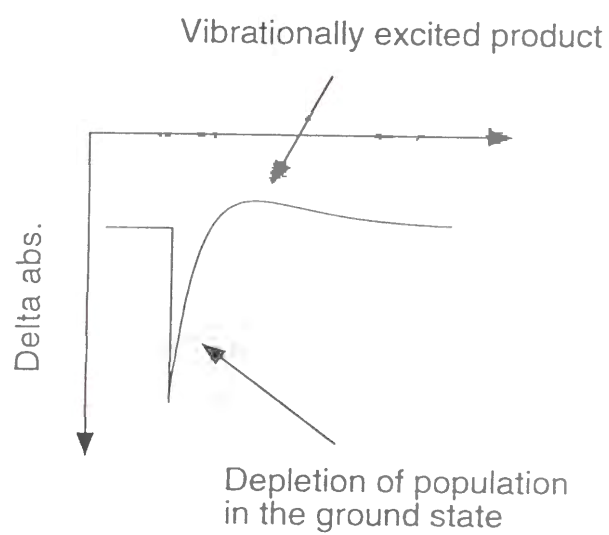
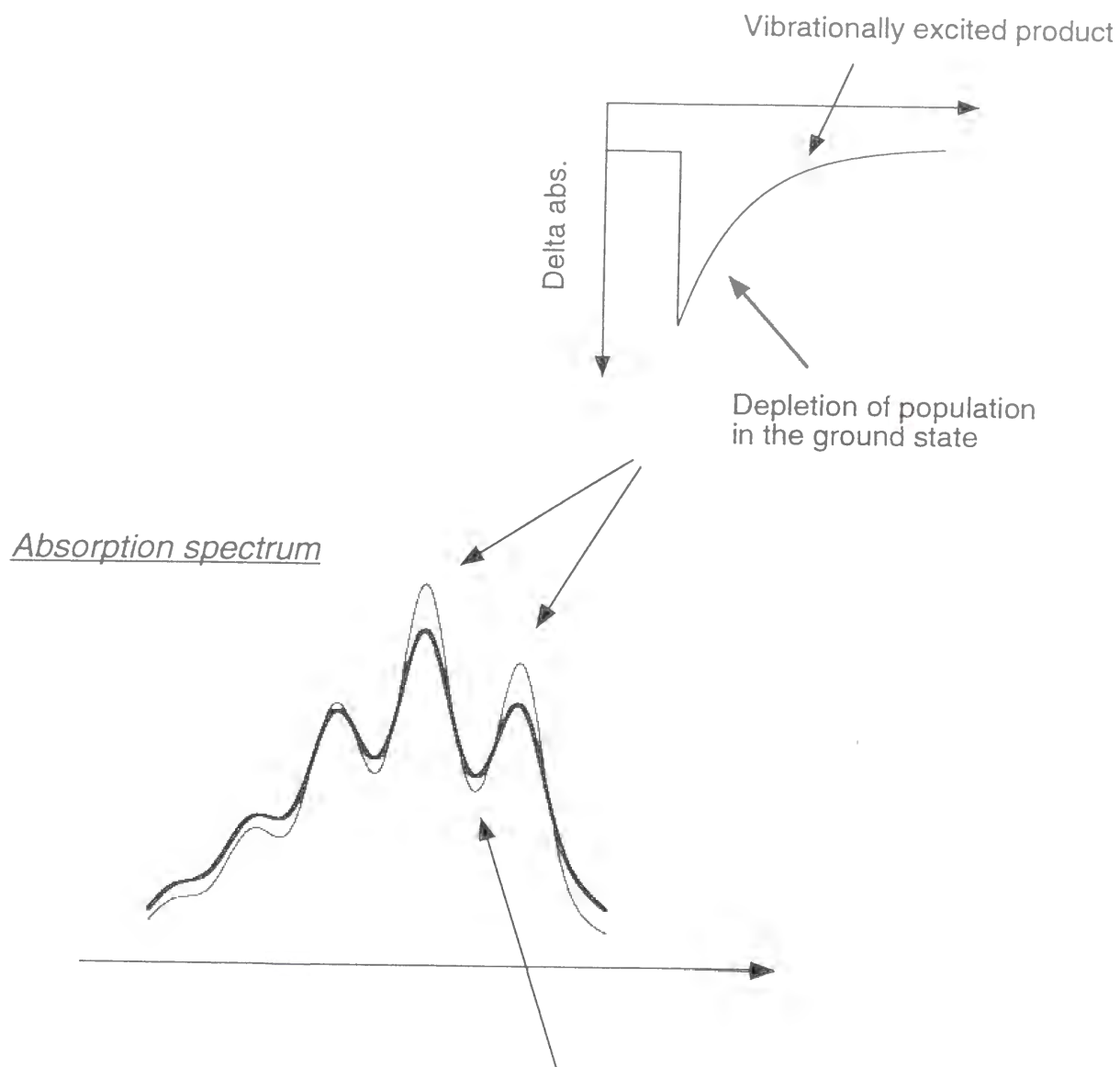




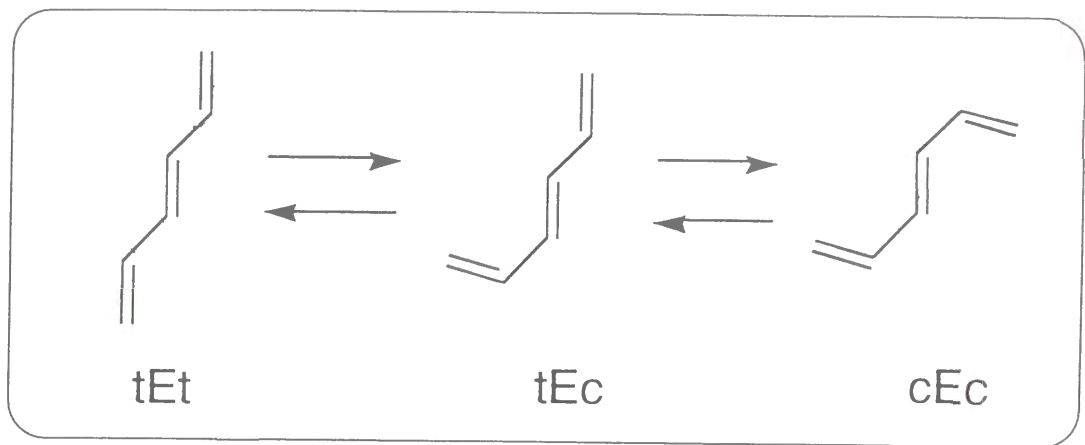




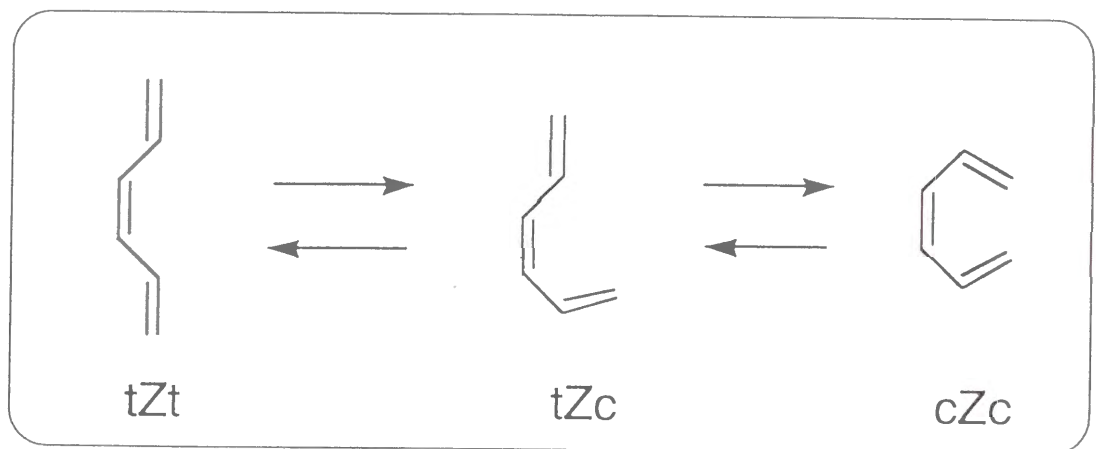




trans-HT



cis-HT



FEMTOSECOND TRANSIENT ABSORPTION STUDIES OF
SIMPLE POLYENES IN SOLUTION

KAORU OHTA^{1,2}, YUKITO NAITOH², KEISUKE TOMINAGA²,
NOBORU HIROTA¹, KEITARO YOSHIHARA²

¹ Department of Chemistry, Kyoto University, Kyoto 606, Japan

² Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

We have conducted femtosecond transient absorption experiments on the excited-state dynamics of trans- and cis-hexatriene (HT) in solution. The transient absorption in the visible region decays with the time constant of about 500 fs, indicating that the internal conversion (IC) to the ground state occurs quite efficiently. The bleach recovery signal contains several time constants. The vibrational relaxation in the ground state occurs in 10-20 ps and the slow relaxation process, which may be due to the conformational change around C-C single bond, proceeds in a subnanosecond time scale.

KEY WORDS: transient absorption, hexatriene, excited-state dynamics, vibrational relaxation

1. INTRODUCTION

The photochemistry of small linear polyenes has stimulated a great deal of interest over the past two decades as a simple model for more complex systems such as retinals and carotenoids. However, the excited-state properties of HT have not been well understood because of a complete lack of fluorescence and broad absorption spectra even under a jet-cooled condition. In order to directly reveal the excited-state dynamics in solution, we have performed the ultrafast transient absorption measurement of trans- and cis-HT in cyclohexane and acetonitrile solutions.¹

2. EXPERIMENTAL

Both isomers of HT were pumped by the third harmonic of a regeneratively amplified Ti:Sapphire laser which produced a 120 fs pulse at around 800 nm. The transient absorption and bleach recovery were probed by using a white light continuum and third harmonic, respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows the transient absorption signals in cyclohexane probed at three different wavelengths. They consist of an instrument-limited rise (<150 fs) and subpicosecond decay at each probe wavelength. For trans-HT, the signal observed at 400

nm decays with a time constant of about 400 fs. At longer wavelengths the decay of the signal gradually becomes faster and approaches the instrument response function at probe wavelengths longer than 450 nm. On the other hand, the temporal profiles of cis-HT do not depend on the probe wavelength significantly. The transient absorption signals in acetonitrile are similar to those in cyclohexane.

It is considered that the photoexcitation to the S_2 state is followed by the IC to the S_1 state which occurs within 100 fs.^{2,3} The probe wavelength dependent decay of the transient absorption is ascribed to the vibrational energy redistribution (VER) in the S_1 state and the IC to the S_0 state. The difference observed in trans- and cis-HT may depend on which contribution is larger in the two competitive processes.

Figure 2 shows the one-color transient bleach recovery signals at 268 nm. The transient exhibits an instrument-limited appearance of a bleach followed by the recovery which occurs in several time scales. The temporal profiles of trans-HT in the first 20 ps are similar to those of cis-HT. However, in a longer time scale, these signals are quite different to each other. While, in trans-HT, it takes 150-300 ps to fully recover the bleach, cis-HT needs almost no more than 100 ps.

The transient bleach signal within the first 20 ps shows that it takes about 1 ps to observe the population of the vibrationally excited S_0 state at 268 nm and the subsequent vibrational relaxation in the S_0 state occurs in 10-20 ps.⁴

The low quantum yield of trans-cis photoisomerization of the C=C double bond in solution means that recovery process to the original form dominates in the signal. One plausible origin of the 100-ps component is a conformational change around the C-C single bond. After photoexcitation, s-cis isomer is produced in the excited state or in the subsequent vibrationally excited ground state. The thermal redistribution among different s-cis isomers occurs in a subnanosecond time scale. The different behavior between trans- and cis-HT may reflect different product distribution and dynamics among s-cis isomers.

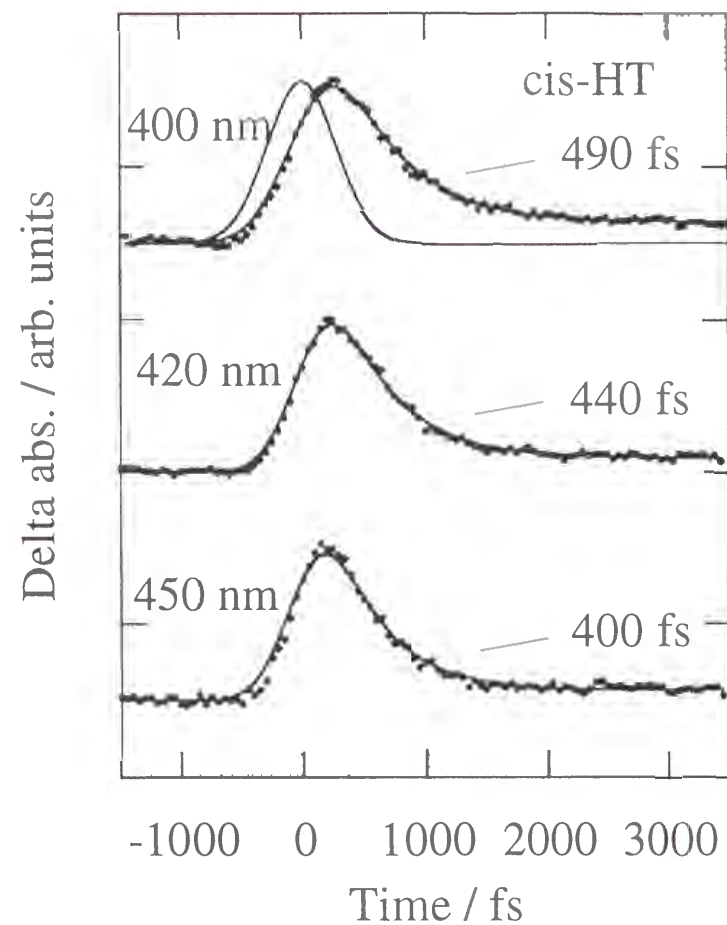
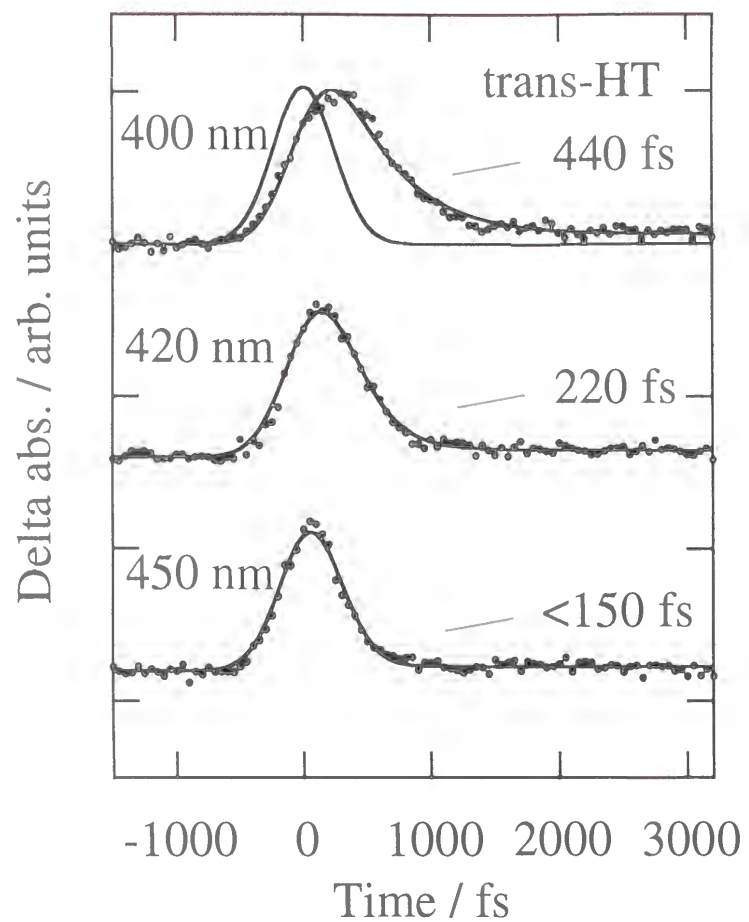
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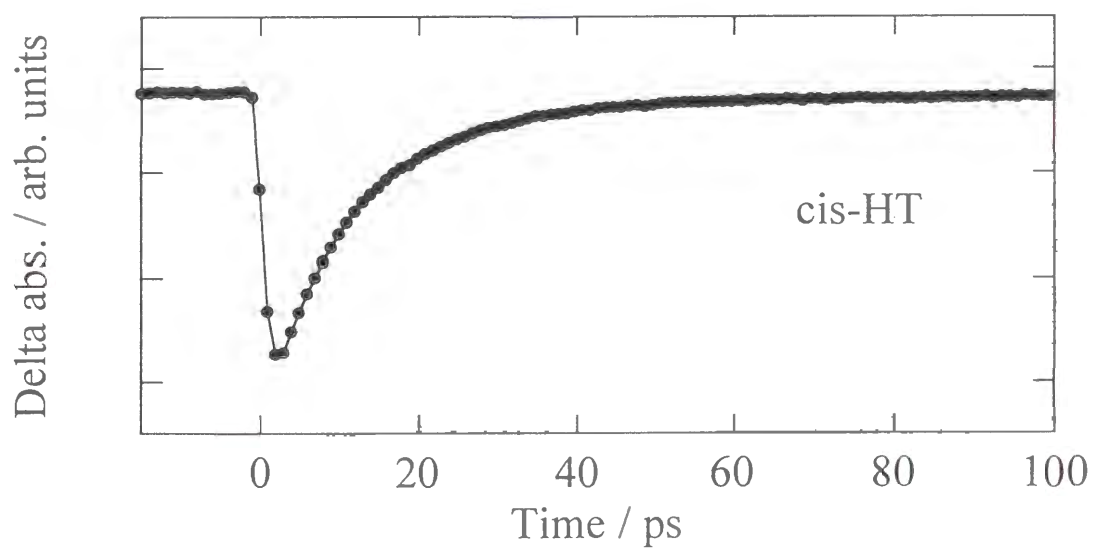
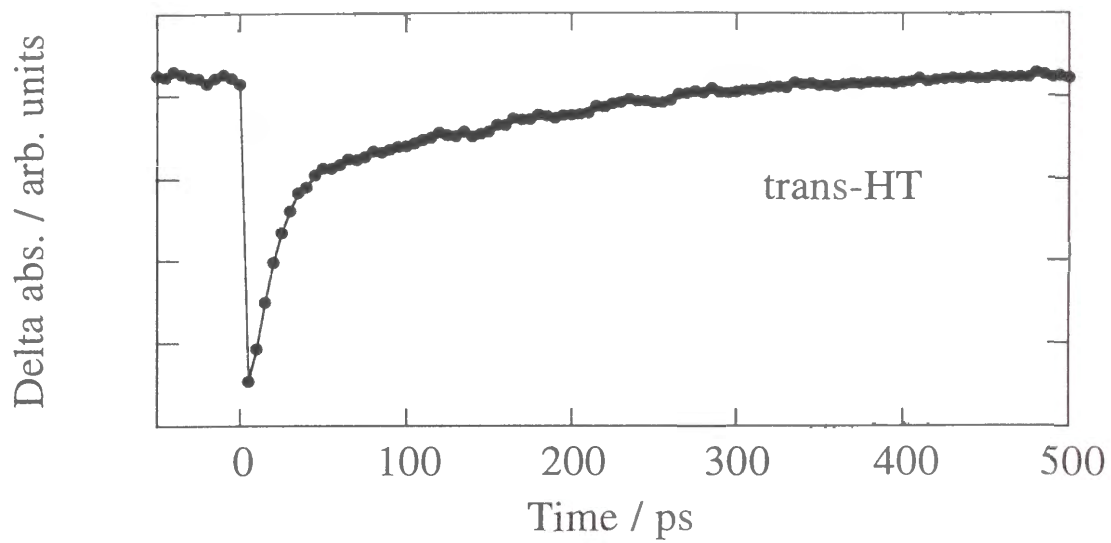
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FIGURE CAPTIONS

Figure 1. Transient absorption signals probed at three different wavelengths in cyclohexane. The instrument response function is shown in the top decay curve.

Figure 2 Transient bleach recovery signals at 268 nm in cyclohexane.





Femtosecond relaxation processes from a higher excited electronic state of a dye molecule in solution

Tai Jong Kang ^{a#1}, Kaoru Ohta ^{a,b}, Keisuke Tominaga ^{a*} and Keitaro Yoshihara ^{a#2}

^a *Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

^b *Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606, Japan*

Abstract

We have investigated the internal conversion and intramolecular energy redistribution process of coumarin 481 in cyclohexane after the photoexcitation by a third harmonic of the Ti:Sapphire laser (267 nm). The fluorescence signals rise with time constants of 220-280 fs at all the wavelengths, and we do not find any drastic change of the spectral shape within a few picosecond time scale. These results suggest that the observed dynamics are mainly due to the internal conversion from the S_n to S_1 state, the intramolecular energy redistribution takes place much faster than the former process.

#1 Permanent address: Department of Chemistry, Taegu University, Kyoungsan, 712-714, Korea

#2 Present address: Japan Advanced Institute of Science and Technology, Tatsunokuchi, Ishikawa, 923-12, Japan

1. Introduction

Understanding of the relaxation of the excited vibronic states in solution is a fundamental problem in photochemistry [1,2]. In solution phase, chemical processes such as solvation dynamics [3,4] and electron transfer [5] have been recently investigated by means of ultrafast laser techniques. In these processes, the fate of the excess energy in the excited state is a key issue since it strongly influences the pathway and the rate of the chemical reactions.

In the past decade, a wide variety of experimental techniques have been applied to observe the relaxation processes of the excited vibronic states in a real time [6-15]. Several groups studied the intramolecular energy redistribution after the photoexcitation to highly-lying S_n states. Kaiser et al. obtained a 180 fs time constant for the energy redistribution process in the S_1 state of oxazine 1 and sulforhodamine B from the appearance of the stimulated emission [14,15].

The fluorescence of the organic molecules in the condensed phase or in the gas phase at high pressures mostly comes from the lowest electronic excited state even if it is excited to a higher electronic state (Kasha's rule). However, in the gas phase at low pressures, the fluorescence spectrum depends on the amount of the excess energy. Upon excitation to the higher electronic state, the spectrum becomes broader and slightly red-shifted for naphthalene and anthracene [16,17]. Increasing attention has been focused on the roles of the surrounding solvents to the internal conversion and intramolecular energy redistribution process.

In this Letter, we present the results on the relaxation dynamics from a higher electronic (S_n) state of coumarin 481 (C481) in cyclohexane by the femtosecond UV fluorescence up-conversion method. In general, a transient absorption spectrum consists of three contributions; absorption of the transient states, bleach of the ground state, and stimulated emission from the excited states. These different contributions often overlap with each other in the spectrum, which makes interpretation very complicated. In contrast, spontaneous emission measurement has an advantage in studying the excited state

dynamics since only the excited state can be probed. In this experiment, we excite C481 to the S_n state by a third harmonic of the femtosecond Ti:Sapphire laser with an excess energy of 12000 cm^{-1} from the 0-0 transition of the S_1 state and monitor the temporal evolutions of the fluorescence signals at several wavelengths. We briefly discuss possible mechanisms of the ultrafast intramolecular energy redistribution after the short pulse excitation in solution.

2. Experimental

The details of the experimental setup will be described elsewhere [18]. Briefly, a Ti:sapphire laser system (Tsunami, Spectra-Physics) produced a 100 fs pulse at around 800 nm, with a repetition rate of 80 MHz and an average power of $\sim 1.8\text{ W}$. The output of the fundamental was divided into two parts. One of them ($\sim 1.2\text{ W}$) was frequency tripled by an Inrad Tripler (Model 5-050). The femtosecond UV pulse of the third harmonic ($\sim 50\text{ mW}$) was used to excite the coumarin molecules to highly-lying singlet states and the ultrafast fluorescence dynamics was followed by an up-conversion technique. The fluorescence up-conversion was done in a type I phase-matched BBO crystal (thickness 0.5 mm). The cross-correlation between the pump and gate pulses was measured by the difference frequency generation, which was used as the instrument response function. The cross-correlation trace was well represented by a Gaussian function with FWHM of 280 fs. The polarization direction of the pump with respect to the gate pulse was adjusted to the magic angle with a half-wave plate. The concentration of the coumarin solution was adjusted to give the absorbance of approximately 0.2-0.3 at the excitation wavelength. The sample solution was circulated through a quartz cell with a 1 mm optical path length. The absorption spectrum of a coumarin solution was checked after the measurements to ensure that no photodegradation had occurred.

Coumarin 481 and cyclohexane (spectrograde) were purchased from Lambda Physik and Wako Chemicals, respectively, and used without further purification. The steady-state absorption and fluorescence spectra were recorded with a Hewlett Packard photodiode array absorption spectrometer (HP8453) and a SPEX fluorometer

(Fluoromax), respectively. All measurements were performed at an ambient temperature (293 K).

3. Results and Discussion

Figure 1 shows the absorption and emission spectra of C481 in cyclohexane. In a nonpolar solvent, the Stokes shift is very small and the emission spectrum is close to a mirror image of the absorption spectrum. A strong absorption band is located from 420 nm to 330 nm. At the wavelength shorter than 320 nm, a weak and featureless band is observed and the absorption intensity increases at wavelengths shorter than 270 nm. We excite C481 molecules at 267 nm, which corresponds to the red edge of the second strong absorption band. It is difficult to assign the character of this state because a couple of electronic transitions may overlap in this region. We refer to this state as the S_n state. The arrows indicate the wavelengths for monitoring the fluorescence.

The temporal profiles of the fluorescence signals observed at several wavelengths are displayed in Figure 2. All the signals show a rise within a subpicosecond time scale. However, in a 10-ps time scale, the signals have either a rising or decaying component depending on the wavelength. We obtained 220-280 fs time constants for the fast rising components by convoluting the signal with the instrument response function. We conclude that these rise components are due to intrinsic dynamics in the excited state and not due to the experimental artifact from the following observations. The group velocity dispersion in the sample cell or solvent is not responsible for the rise components since in the measurement of the instrument response function the excitation pulse was passed through the sample. We also found that the rising time constant is dependent on a sample, and in polar solvents such as methanol and acetonitrile it is smaller than that in cyclohexane [18].

The bottom panel of Figure 1 shows the calculated signals by assuming several different time constants for the rising component. The time constants of the rising component are comparable to the temporal width of the instrument response function. As

clearly shown in Figure 1, we can safely determine the time constant larger than 100 fs. The time constant of the rise varies with the monitoring wavelength; 220 fs at the blue edge of the emission spectrum and 280 fs at the red edge. In this Letter we will not discuss this small variation and consider that the dynamics of the rise is independent of the wavelength. Further experiment will be needed to clarify this small difference.

After the optical excitation to the highly excited electronic states by the femtosecond pulse, several subsequent processes could occur. (1) Electronic dephasing between the excited state and ground state, which normally occurs faster than 60 fs [19,20]. (2) By the optical excitation, many vibronic bands which are accessible by a broad spectrum of the excitation pulse are coherently excited, and dephasing time of these vibrational bands is equal to the pulse duration [21,22]. (3) Intramolecular energy redistribution among the vibrational modes such as from the Franck-Condon active modes to the non-Franck Condon active modes. (4) Internal conversion from the highly excited electronic state to lower electronic states. (5) Vibrational cooling due to energy flow into the solvent. These processes may occur with different time scales, or some of them may proceed simultaneously. In the following we discuss the observed spectral evolution in light of the processes mentioned above.

The observed fluorescence signals are considered to originate from the S_1 state based on the following reasons. The oscillator strength of the S_n - S_1 transition is much smaller than that of the S_1 - S_0 transition. The fluorescence intensity from the S_n state should be smaller than that from the S_1 state. If the fluorescence from the S_n state were included in the observed signal, we would observe some decay components which correspond to the disappearance of the population in the S_n state. The contribution of this component is considered to be negligibly small.

From the results of the initial spectral evolution, the time constants of the rising components do not depend on the wavelength significantly. A large deviation from the static fluorescence spectrum is not observed in the transient spectrum within a few picosecond time scale even the molecule has an excess energy of 12000 cm^{-1} from the 0-0 transition in the S_1 state. Therefore, the present result clearly shows that the vibrational

population is not localized in several particular modes at the longer than 100 fs. If the vibrational population is localized, it is expected that the shape of fluorescence spectrum is significantly distorted, which is different from that of the static fluorescence spectrum. We are currently performing a model calculation of the transient emission spectrum by considering several vibrational modes.

We consider that the observed dynamics are mainly due to the internal conversion from the S_n to S_1 state; i.e. after the photoexcitation to the Franck-Condon active modes in the S_n state, intramolecular energy distribution is completed in the S_n state within 100 fs, and subsequent internal conversion to the S_1 state occurs with the time constant of 220 - 280 fs. Since the excess energy of 12000 cm^{-1} from the S_1 0-0 transition may be distributed among 96 vibrational modes (number of atoms is 34), the transient emission spectrum does not show a large deviation from that in the steady-state within 100 fs even if the molecule possesses the large excess energy.

Hereafter we briefly discuss the mechanism of the ultrafast intramolecular energy redistribution process in solution. So far there have been several studies on the internal energy redistribution process after the short pulse excitation in solution. In particular, Mokhtari et al. used the femtosecond up-conversion method to measure the excited state dynamics of nile blue and oxazine 1 in solution after the photoexcitation to the S_1 state [7,8]. They found that the evolution of the fluorescence bandwidth contains fast (0.4-0.6 ps) and slow (4-6 ps) components. They attributed the subpicosecond component to the intramolecular energy redistribution process. Martini and Hartland investigated the vibrational relaxation process of a cyanine dye, HITC, in various solvents [12,13]. A stimulated emission signal is found to rise with the time constants of 300 fs and 1.7-7.1 ps. The latter constants depend on the solvent. It is concluded that the former time constant represents the time scale of intramolecular energy redistribution process and the latter one is related to the vibrational cooling in the S_1 state.

As described in the introduction, an energy redistribution process in solution occurs much faster than that in the gas phase under a low pressure or jet-cooled condition. The energy transfer from the Franck-Condon active modes to the non-Franck-Condon

active modes is accelerated by the presence of the surrounding solvent molecules in solution. For large molecules such as coumarins, density of the dark state is so high that the energy flow from the one bright state to many dark states occurs irreversibly [23]. The population transfer from one Franck-Condon active mode to the other modes is dependent on the density of the state and anharmonic interactions between one Franck-Condon active mode and the other modes. In solution, low frequency solvent modes, which are sometimes referred to as phonon modes, increase the density of state by an order of magnitude and they play an important role in the dynamics of internal vibrational degrees of freedom. The anharmonic interaction terms induce the population flow from one vibrational mode into the combination of the other modes in which the energy between the initial and final states is matched. The low frequency solvent modes help to enhance this energy redistribution process. This process occurs very efficiently (< 100 fs). Even in a small molecule such as deuterated ethanol, recent Raman echo study showed that the dephasing due to the intramolecular energy redistribution occurs as fast as 360 fs with the help of the coupling between the solute and the energy bath of the solvent [24].

Figure 3 shows the time-resolved fluorescence spectrum in a 10 ps time scale which is reconstructed by using the static fluorescence spectrum [25]. The fluorescence spectrum becomes sharper as a function of time, i.e. the intensity increases near the peak of the spectrum and the intensity at the red edge region decreases as the time proceeds. The time scale of the spectral evolution is about 10 ps. This phenomenon is ascribed to the vibrational cooling in the excited electronic state. After the internal energy redistribution completes in the S_1 state, the excess energy is deposited into the solvent, and the solvent is locally heated around the solute. This heat is eventually dissipated into the bulk solvent, which takes place in a 10 ps time scale.

A similar narrowing of the fluorescence spectra is observed in other systems. Maroncelli and coworkers performed similar experiments on the fluorescence dynamics of coumarin 153 in cyclohexane to investigate a possible contribution of vibrational relaxation in the spectral evolution [26]. They used a 366 nm pulse for excitation. With this excitation wavelength, an excess vibrational energy of ca. 3500 cm^{-1} is deposited into

the molecule. They observed the narrowing ($\sim 300 \text{ cm}^{-1}$) and a subtle blue shift ($\sim 150 \text{ cm}^{-1}$) of the spectrum that takes places on $\sim 10 \text{ ps}$. Compared with their results, the narrowing is more clearly seen in our case. This may be due to the difference of the amount of excess energy.

A cooling of the local structure was found to occur at the same time scale in other systems. Iwata and Hamaguchi investigated the vibrational relaxation process of trans-stilbene in solution by the picosecond time-resolved Raman spectroscopy [27]. They showed that the peak position of the C=C stretching band is useful as an indicator of the internal temperature of the solute. It was found that the energy flow into the bulk solvent occurs with the time constant of 11 ps in n-hexane. Elsaesser and coworkers estimated the transient internal temperature of 600 K in the system of sulforhodamine B in ethanol after depositing an excess energy of 15000 cm^{-1} [15]. They reproduced the emission spectra of the vibrationally hot molecules by assuming two Franck-Condon active modes and a transient internal temperature. The calculation of the transient emission spectra as well as the temperature dependence of the static emission spectra will be reported elsewhere [18].

Acknowledgment

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Figure Captions

Figure 1. Static absorption and fluorescence spectra of coumarin 481 in cyclohexane. The excitation and monitored wavelengths are indicated by the arrows. Inset: molecular structure of coumarin 481.

Figure 2. (Upper traces) Fluorescence rises of coumarin 481 in cyclohexane excited at 267 nm and observed at 419, 431 and 475 nm. The solid line represents the best fits to the data by convoluting the instrument response function with a single exponential rise.

(Bottom trace) Calculated curve with a rise of several time constants convoluted by the instrument response function.

Figure 3. Time-resolved fluorescence spectrum in a 10-ps time scale.

