

# FEMTOSECOND TRANSIENT ABSORPTION STUDIES OF SIMPLE POLYENES IN SOLUTION

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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.

*Keywords:* 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-

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state dynamics in solution, we have performed the ultrafast transient absorption measurement of *trans*- and *cis*- HT in cyclohexane and acetonitrile solutions [1, 2].

## 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

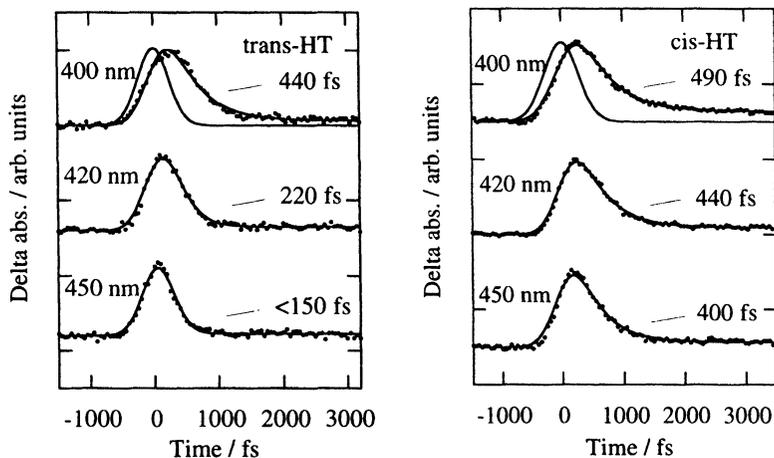


FIGURE 1 Transient absorption signals probed at three different wavelengths in cyclohexane. The instrument response function is shown in the top decay curve.

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 [3, 4]. 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.

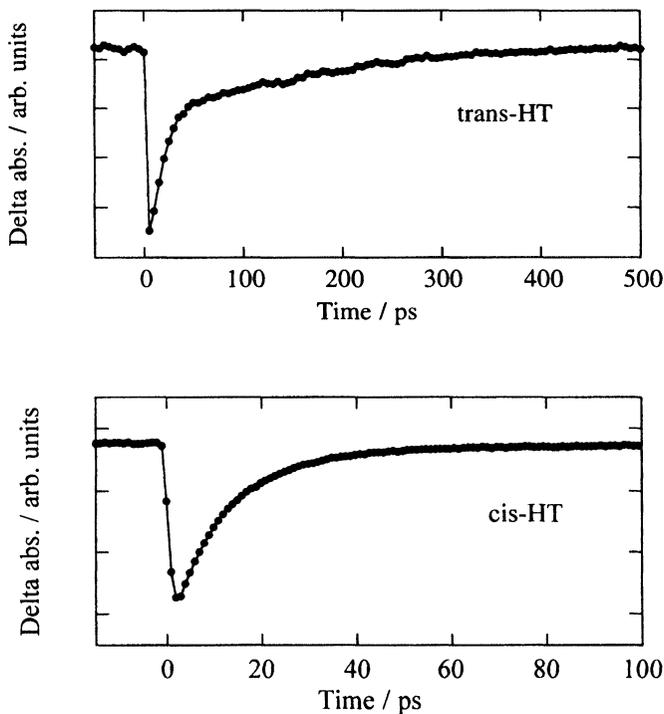


FIGURE 2 Transient bleach recovery signals at 268 nm in cyclohexane.

The temporal profile of *trans*-HT in the first 20 ps is similar to that 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 [5].

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.

## References

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