



Photoisomerization dynamics study on *cis*-azobenzene derivative using ultraviolet-to-visible tunable femtosecond pulses

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ABSTRACT

We performed the transient absorption measurement and the first rate equation (RE) analysis for *cis* isomer of 4-carboxy-2',6'-dimethylazobenzene to clarify the quantitative difference between the photoisomerization process and the thermal relaxation process from the S_1^c excited state. The RE analysis enabled us to determine the *cis*-to-*trans* photoisomerization rate per each pump pulse to be 3% under the condition of the 430 nm, 150 fs pump pulse with energy of 200 nJ. Moreover, the signal due to the yielded *trans* molecules appearing in the transient absorption was assigned from the following observed result: the transient absorbance change at the 380 nm probe mostly decreased within 300 fs after the 430 nm pulse pumping and then slowly decreased to zero, while the absorbance change at the 350 nm probe had a *positive constant component* in the over one picosecond time region. The RE analysis showed that this constant component is due to the yielded *trans* molecules, and its positive value is due to the fact that the absorption cross-section of the S_0^t -to- S_2^t transition in their *trans* molecules is larger than that of the S_0^c -to- S_2^c transition in the original *cis* molecules.

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1. Introduction

Azobenzene and its derivatives are typical molecules showing photoisomerization. Those molecules have been attracting much attention not only from the viewpoint of photochemistry but also for their high potential in biological applications. Recently, photoresponsive DNA tethering azobenzene molecules has been discussed [1]. Moreover, it has been reported that 4-carboxy-2',6'-dimethylazobenzene (AzD) is a molecule that thermal isomerization almost never occurs in and hence is an efficient photo-regulator for DNA hybridization [2]. On the other hand, the photoisomerization mechanism following S_2 -state excitation of *trans*-azobenzene without substitution has been investigated [3]. In addition, the femtosecond photoisomerization of *cis*-azobenzene without substitution has been examined [4]. Moreover, the ground-state kinetics on thermal isomerization of azobenzene and 4-dimethylamino-4'-nitroazobenzene has been studied [5]. In those investigations the main focus has been on the inversion

processes and the rotation processes in the photoisomerization mechanisms, but the assignment and time-dependent behaviors of the signal due to the isomer to be yielded in the ultrafast dynamics on the basis of the quantitative analysis have not been discussed clearly. Also, ultrafast photoisomerization processes of AzD useful as an efficient photo-regulator have been unknown up to now.

We are very interested in the coherent control of DNA hybridization processes based on the quantum control of its AzD photoisomerization. In this paper, we clarify the photo-excited state dynamics of *cis*-AzD in ethanol to distinguish the thermal relaxation processes and the photoisomerization processes for the first time, by transient absorption measurements using UV-to-visible tunable femtosecond pulses and the first quantitative rate equation analysis which describes the time-dependent populations in related electronic states considering the feature of absorption spectral structures. The signal due to the *trans* molecules yielded from the photoexcited *cis* molecules is assigned. Moreover, a determination method of the photoisomerization rate per pump pulse is proposed and its rate is obtained. In addition, the kinetic rate constants and absorption cross-sections between different electronic excited states and between excited and ground states are investigated.

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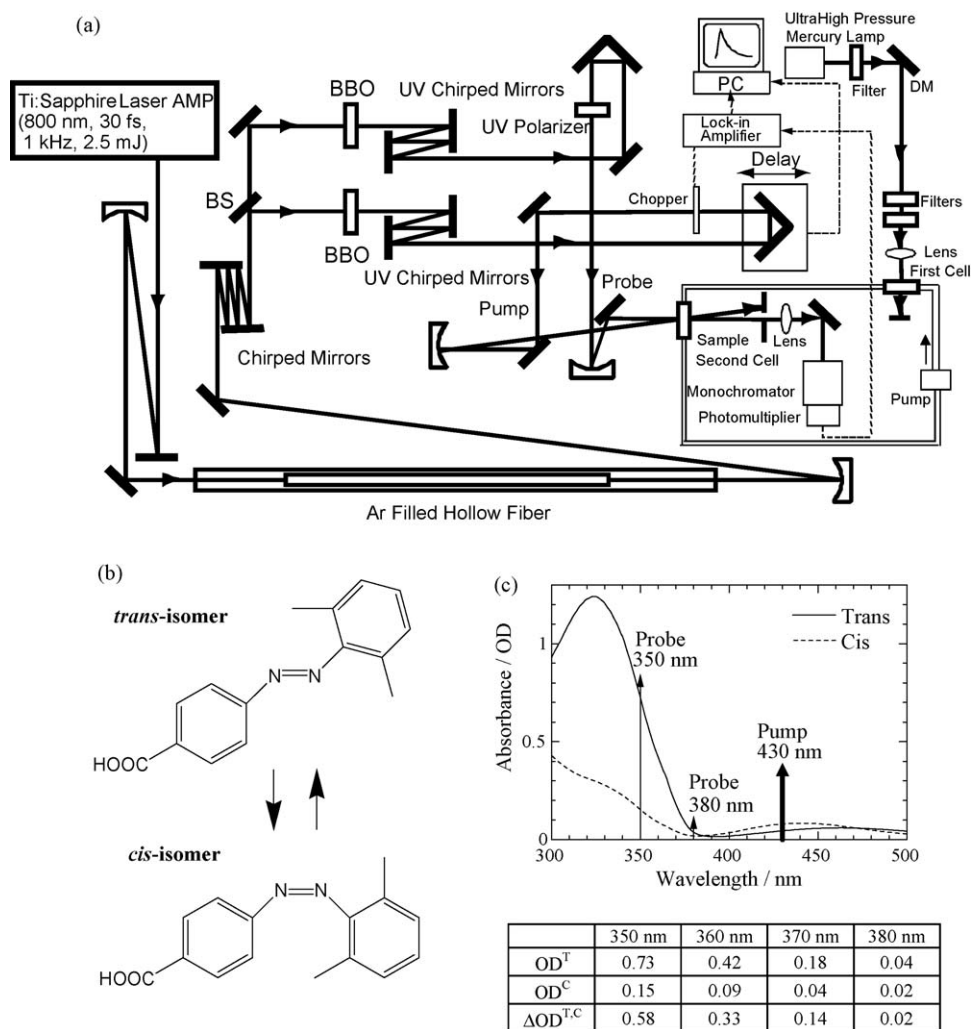


Fig. 1. (a) Experimental setup for femtosecond transient absorption measurements of *cis*-4-carboxy-2',6'-dimethylazobenzene. (b) Molecular structure of *trans*- and *cis*-4-carboxy-2',6'-dimethylazobenzene. (c) Steady-state absorption spectra of *trans*- and *cis*-4-carboxy-2',6'-dimethylazobenzenes in ethanol. Pumping (430 nm) and probing (350 and 380 nm) wavelengths were also shown.

2. Experimental

The experimental setup for transient absorption measurements is shown in Fig. 1(a). The molecular structures of *trans*- and *cis*-AzDs are shown in Fig. 1(b). Fig. 1(c) shows the measured steady-state absorption spectra of their molecules in ethanol. The *cis*-AzD dissolved in ethanol at the concentration of 3.0×10^{-2} mol/l at room temperature was used for transient absorption measurements. Before the pump-probe experiment, the *cis*-AzD sample was prepared according to the following procedure. The solution was pumped through two different cells in a closed cycle system. The first 100 μm cell was used for the establishment of a photostationary *cis*-form by exposing the cell to a CW incoherent light (330–375 nm light) for 3 h. A 500 W ultra-high pressure mercury lamp with a IR cut filter, a dichroic mirror, a colored glass filter and a long pass filter was employed to prepare the *cis*-form. The second cell with an optical pathlength of 1.0 mm was used for the femtosecond experiments.

The highly time-resolved absorption measurements were carried out using a femtosecond Ti:sapphire laser amplifier system operating at a central wavelength of 800 nm. The system provided optical pulses with a duration of 30 fs (full-width at half-maximum: FWHM) and pulse energy of 2.5 mJ at a 1 kHz repetition rate. The pump (430 nm) and the probe pulses (350 and 380 nm) were generated by the setup shown in Fig. 1(a). The setup consisted

of an Ar-gas filled hollow fiber (a 300 μm innerdiameter, a 45 cm length) for a spectral broadening, visible chirped mirrors for a chirp compensation, a broadband beam splitter (the reflection-to-transmission ratio of 2-to-1), two BBO crystals (a 500 μm thickness, type I) for independent frequency doublings, and ultraviolet (UV) chirped mirrors for a UV chirp compensation. The beam diameter (110 μm) of the pump pulse at the sample was larger than that (50 μm) of the probe pulse. The flow rate of the AzD solution in the second cell was high enough to exchange the excited volume between successive excitations. To keep the concentration of the *cis*-forms always 100% as an initial state during the measurement, the AzD solution was irradiated in the first cell by the ultra-high pressure mercury lamp with suitable filters. The probe pulse after passing through the sample was detected by a photomultiplier attached to a monochromator as a filter to avoid the scattering noise of the pump pulse. A lock-in-amplifier was used to get a good signal-to-noise ratio for the transient absorption change (a chopping frequency of the pump pulse: 460 Hz). The time zero and the instrumental response function were determined by the third-order cross-correlation measurement using only the solvent before and after each experiment [4]. FWHMs of the pump and the probe pulses were estimated to the order of 150 fs and hence the FWHM of the instrumental response function was about 150 fs. All the transient absorption data shown here were measured at the magic angle of

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