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Two-dimensional observation of multicolor multistep photoreaction process by using white light excitation covering entire visible region

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ABSTRACT

Multicolor multistep photoisomerization process of azobenzene derivative in photostationary state was observed by newly developed Fourier transform two-dimensional (2D) spectroscopic technique. The photostationary state was generated by excitation using white light covering the entire visible region, and the photoreaction was monitored by measuring photoinduced bleaching and absorption signals detected by white light probe. The wavelength participating in excitation process for the observed signal was clarified by modulation frequency marked by passing the pump white light through a scanning tandem Fabry-Pérot interferometer, and the 2D amplitude and phase spectra were obtained by Fourier transform of the obtained 2D interferogram. By using the system, we succeeded in observing the multicolor multistep process in photoisomerization of Sudan red 7B [1-(4-[Phenylazo]phenylazo)-2-ethylaminonaphthalene, SR7B] that has two azo groups and shows several configurations. It was concluded from the analysis of obtained 2D amplitude and phase spectra that at least two reaction pathways of sequential photoisomerization reactions exist in the photostationary state of SR7B under the white light irradiation. The interpretation is supported by the results of quantum chemical calculations using density functional theory.

1. Introduction

In a photochemical reaction, photoexcitation plays a role of a trigger to start the reaction that proceeds through a combination of many inter- and intramolecular interaction processes, such as relaxation and energy transfer processes. Large number of studies have been carried out on the mechanism and dynamics about the photo-induced unimolecular reaction [1–7] by a monochromatic pump-probe measurements. However, under irradiation of intense laser light or white light such as solar light, multicolor multistep photoreaction pathways would also exist in parallel to the main reaction pathway initiated by one photon excitation [8–14], because the photoexcitation from the trigger state, intermediate state, and/or product state can be induced by the irradiated light. Thus, for understanding the intricate reaction path structure and reaction mechanism, a perspective about the reaction network is necessary under the white light irradiation of white light. However, by simple irradiation, it is difficult to clarify the relation between the wavelength and light induced event.

Recently, for observing the response of a photochemical system to the irradiation of white light, we have developed a Fourier transform two-dimensional (2D) fluorescence excitation spectrometer (FT-2DFES) [15] that utilizes intense white light covering the entire visible wavelength region as the excitation light source. In that system, a multiplex Fourier transform technique was adopted [16–20], which realizes an intense excitation and a high signal-to-noise ratio on a 2D spectrum. Furthermore, a tandem Fabry-Pérot interferometer (tandem FPI) was used for the modulation, and a high throughput of the excitation white light was achieved in order to modulate a transition with an absorption bandwidth larger than 100 THz, which is equivalent to 100 nm (FWHM) at around 550 nm. By using that system, we succeeded to separately observe the overlapping fluorescence excitation peaks of a mixed methanol solution of laser dyes (coumarin 480, rhodamine 6G, DCM, and LDS 750). Furthermore, the energy transfer from rhodamine 6G to LDS750 was observed [15].

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To investigate a photoreaction process in greater detail, knowledge of the transient species and the photoreaction pathways is vital. Photoexcitation by white light covering the entire visible region is very useful to induce the multicolor multistep process that can be monitored by several spectroscopic techniques, such as transient bleaching and transient absorption. Furthermore, for the optical control of reaction in future chemical research, it is necessary to consider not only the monochromatic process but also the multicolor multistep process, because the control process is intrinsically a sequential multicolor multistep process [14,21].

In the present study, we have developed a system to observe a multicolor multistep photoreaction process in the photostationary state generated by white light excitation covering the entire visible region, and called it the Fourier transform 2D photostationary state absorption spectrometer (FT-2DPsAS). The system was constructed by combining the FT-2DFES [15] system with probe white light, and was used to observe the multicolor multistep reaction process in the photoisomerization of Sudan red 7B [1-(4-[Phenylazo]phenylazo)-2-ethylaminonaphthalene] (abbreviated as SR7B, also called "oil violet") [22] that contains two azo groups and has several kinds of isomers as described later. In the 2D amplitude and phase spectra obtained by the system, several peaks attributed to transient absorption or bleaching were observed. By analysis of the spectra based on quantum chemical calculations using density functional theory, we conclude that, in the photostationary state of SR7B under the white light excitation, at least two reaction pathways of sequential photoisomerization reactions exist and the back photoreaction occurs from several kinds of photoisomers.

2. System setup

Experimental system for FT-2DPsAS was developed on the basis of the system for FT-2DFES [15], and a schematic diagram is shown in Fig. 1. Pump light from a Xe lamp (Asahi Spectra Co., Ltd., Max-302, wavelength range: 350–800 nm, total power: 100 W) was collimated and introduced into the tandem FPI. In the tandem FPI, the mirror spacing of 1st stage FPI (FP-1) was fixed and that of 2nd stage FPI (FP-2) was scanned by a PZT stage (Piezosystem jena GmbH, NV40/1 CLE) around the spacing of FP-1. The reflectance of the mirrors in the interferometers was approximately 0.5 for the appropriate finesse and contrast of the interference fringe. Output beam from FP-2 was focused on the sample cell. Probe white light (MINI MAGLITE, 2AA, wavelength range: 380–800 nm) was also focused on the sample cell and the transmission spectrum of the probe was observed by an array-type spectrometer (Ocean Photonics, USB4000). A 2D interferogram including photostationary state signals, such as bleaching and absorption signals induced by white light excitation, was obtained by measuring the transmitted probe intensity as a function of both FP-2 spacing and monitored wavelength. Based on the 2D interferogram, a 2D spectrum (photostationary state signal intensity as a function of both pump and probe wavelengths) was obtained by Fourier transform of the 2D interferogram along the line of FP-2 spacing at every wavelength (1 nm step in this study).

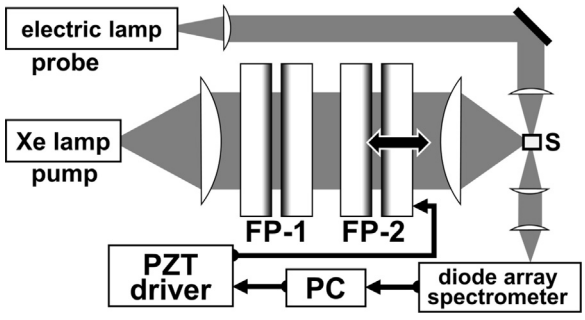

Fig. 1. Schematic setup of FT-2DPsAS. FP-1 and FP-2: Fabry-Pérot interferometer. Mirror gap of FP-2 is controlled by a PZT stage.

This system has two prominent features as previously reported [15] and described briefly as follows. One is that the tandem FPI realizes the modulation of transition with a large absorption bandwidth (>100 THz) of molecules in the condensed phase. The other is that the excitation by white light covering the entire visible region can carry out the simultaneous modulation of two or more transitions at different modulation frequencies. For the modulation of excitation light in the multiplex technique, the free spectral range (FSR) of the interferometer must be larger than 100 THz, because molecules in the condensed phase generally show absorption bandwidths larger than 100 THz, which is equivalent to 100 nm at around 550 nm. In order to modulate the pump light with a single FPI having FSR larger than 100 THz, the mirror spacing must be scanned in an unrealistic region narrower than 1 μm. The tandem FPI can modulate a transition with a large absorption bandwidth by using the beat between the two interferometers by scanning the spacing of FP-2 around that of FP-1. When the spacing of FP-2 is equal to that of FP-1, namely, the spacing difference ΔL is zero, both interferometers will show the same transmitted spectrum. Then, the transmitted spectrum from the tandem FPI will exhibit a strong fringe pattern over the entire visible region. By changing the spacing of FP-2, the fringe pattern is changed due to the change of the transmitted spectral feature of FP-2, and the intensity of each fringe peak shows an oscillation at the periodic spacing of FP-2 determined by half the wavelength corresponding to the fringe peak. Then, in the region of ΔL shorter than the visible wavelength, a large wavelength region is modulated at almost the same phase. As ΔL increases, the wavelength dependence of the modulation phase becomes remarkable. The above means that the modulation by the tandem FPI is characterized by ΔL and the tandem FPI can modulate the transition with a large absorption bandwidth.

For the measurements of the FT-2DPsA spectrum, a sample solution was added into a rectangular quartz cell whose inside dimensions were 2 mm by 10 mm. Pump white light from a Xe lamp was focused on the narrow side (2 mm width) of the cell after passing through the tandem FPI. Probe light from an electric lamp was focused on the wide side, and a spectrum of transmitted light was monitored with a diode-array monochromator. In the measurement of the 2D interferogram for 2D photostationary state absorption described below, the mirror spacing of FP-1 was kept at approximately 20 μm and that of FP-2 was moved from 18 μm to 22 μm in 10 nm steps. The required measurement time was shorter than ten minutes. All the experiments were carried out at room temperature.

3. Calculation details

Quantum chemical calculations were performed using Gaussian09 package [23]. As described below, SR7 B has several configurations as isomers, and the ground state energies of the isomers were optimized unrestrainedly by means of the DFT method. The 6–31G(d) basis set was used in the B3LYP calculations. All optimized structures were confirmed by vibrational frequency analysis in which only real frequency values were obtained for the *cis*- and *trans*-isomers. Calculations in acetone were performed by employing the self-consistent reaction field (SCRF) method based on the polarizable continuum model (PCM) [24,25]. Following this, TD-DFT calculations were carried out in acetone using B3LYP/6-31G(d), in order to determine the absorption peak wavelengths.