Fourier transform transient absorption spectrometer for observation of multistep and multicolor photoreaction process

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Introduction] Intra- and intermolecular interaction processes, such as energy transfer and relaxation processes, play an important role in photochemical reactions, and knowledge of those processes is needed to understand the reaction path and the reaction mechanism. One of the methods to study the intra- and intermolecular interactions is two-dimensional (2D) spectroscopy, such as 2D NMR, 2D Raman/IR spectroscopy, 2D correlation spectroscopy, and 2D electronic spectroscopy. The 2D observation has several advantages: simplification of complex spectra consisting of many overlapping peaks, clarification of correlation between the observed spectral peaks, and establishment of unambiguous assignments based on correlation bands. Recently, we developed a Fourier transform 2D fluorescence excitation spectrometer (FT-2DFES) which is suitable for observing multicolor/multistep process because an intense white light covering whole visible wavelength region is adopted as an excitation light source. By using the system, we succeeded in separately observing the fluorescence excitation peaks from a mixed methanol solution of laser dyes (coumarin 480, rhodamine 6G, DCM, and LDS750). Furthermore, the energy transfer from rhodamine 6G to LDS750 was observed.

For further investigation of photoreaction process, the knowledge of transient species is very important. Then transient absorption spectroscopy is very useful to obtain the information about the transient species. In this study, we developed a Fourier transform 2D transient absorption spectrometer (FT-2DTAS) on the basis of the FT-2DFES system, and succeeded in observing two color multistep reaction process in photoisomerization of sudan red 7B (SR7B, also called oil violet).

System Setup] Figure 1 shows a schematic setup of FT-2DTAS system which is based on the FT-2DFES system. Pump light from a Xe lamp (Asahi Spectra Co., Ltd., Max-302, 100 W) was collimated and introduced into the tandem Fabry-Pérot interferometer (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 moved by a PZT stage (Piezosystem jena GmbH, NV40/1 CLE) around the spacing of FP-1. The reflectance of the mirrors in the interferometer 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. Transient absorption was monitored by an output light from an electric lamp (Maglite), and a spectrum of transmitted probe light at each mirror gap of FP-2 was observed with an array-type spectrometer (Ocean Photonics, USB4000). Based on the 2D interferogram (monitored wavelength vs spacing) acquired by the procedure described above, 2D transient absorption spectrum (monitored wavelength vs pump frequency) was obtained by Fourier transform of the intensity change of transmitted probe intensity as a function of the spacing at every wavelength (1 nm step in this study).

Results and Discussion] System evaluation was conducted by measuring the transient absorption spectra of SR7B whose structure is shown in Scheme 1. Two dimensional spectra of amplitude and phase on SR7B obtained by the FT-2DTAS system are shown in the figures 2(a) and (b), respectively. The horizontal axis is the monitored wavelength of probe light and the vertical axis is the excitation wavelength converted from the frequency obtained by
Fourier transform. Fluorescence signal was not included in the spectra, because no signal was detected without probe light. In the figure 2(a), five peaks are observed in the areas A to E surrounded by dashed lines. From the figure, the peaks in A and B are induced by excitation at approximately 540 nm light. Figure 2(b) clearly shows that the phase of peak in A is different from the phase of the peak in B by approximately π.

On the conventional transient absorption spectrum pumped by 532 nm laser light, the photobleaching and transient absorption peaks were observed at around 540 nm and 640 nm, respectively. From the results, the peaks in A and B can be assigned to the photobleaching due to the decrease of ground state population of trans form and the transient absorption due to the production of cis form of SR7B, respectively.

On the peaks in C and D, it is clear from the figure 2(b) that the phase of peak in C is the same as that in B and the phase of peak in D is the almost same as that in A. The results indicate that the peak in C is the decrease of transmitted light intensity, namely transient absorption, and peak in D is the increase of transmitted light intensity, namely photobleaching. Both peaks are induced by excitation at approximately 650 nm light.

From these results, the mechanism of the peak emergence is considered as described below. The peak in D is caused by the photo-isomerization from cis form to trans form by 650 nm light, and the population decrease of cis form induces the decrease of transient absorption corresponding to peak in B. Therefore the increase of transmitted light intensity, namely photobleaching, caused by 650 nm light is observed in area D. The peak in C is also caused by the photoisomerization from cis form to trans form by 650 nm light and the population increase of ground state of trans form. Then transient absorption due to the increase of trans form is observed in C. The peak in E can also be assigned to the transient absorption due to the increase of trans form caused by the photoisomerization passing through higher excited states of cis form by 400 nm light excitation. photoreaction pathways observed in this study is summarized in the figure 3. It should be noted that the signals observed in C to E are indistinguishable to the signals in A and B by the conventional method because they are buried in the strong signal in A or B. On the basis of the results, it is concluded that FT-2DTAS system is effective for observing multistep multicolor photoreaction process and suitable for the analysis of the photoreaction network such as shown in the figure 3.