1 Introduction

1.1 Importance of ultrafast phenomena research and its brief history

Photoreactions play important roles in photobiological and photochemical processes. In the former, visions of animals and photosynthesis in plants and algae are essential processes for human beings. In the latter, artificial photosynthesis is one of the hot topics for the realization of a sustainable society. The primary reaction mechanisms in these processes are essentially important to determine the efficiency of the whole process. The primary process could be elucidated by ultrafast spectroscopy using ultrashort laser pulses.

Generally, the public's attention has been attracted to the visual observation of fast processes such as horses galloping or crown-like structured water splashing on the surface induced by a stone falling. Such macroscopic motion can be captured by a fast camera. Further study of much smaller systems has been an attractive field of study for scientists to investigate material microscopic composition. All materials are composed of molecules or atoms forming gases, liquids, and solids. Motion in such systems is not only an extension from the macroscopic systems, such as translation and rotation, but also microscopic structural change. Most interesting and important structural changes of the microscopic systems are phase transitions in solid materials and chemical reactions of molecules.

Macroscopic phase transition proceeds in a mesoscopic scale starting from the deformation of the nuclei in a microscopic size. Hence, its initial process can proceed in an ultrafast time scale and is followed by the slower process, attaining the change in the mesoscopic or macroscopic size.

Chemical reactions are generally considered to take place not concertedly but randomly. Fast chemical reactions that cannot be identified by the eye and which have only ~10-ms resolution become observable by utilizing a strobe light with a short duration as demonstrated by Norrish and Porter.[1] The development of a discharge flash lamp by them was accelerated for the application in the battle actions at a night battle field, in which the time resolution of 10 ms was enough. After the war, Porter started to utilize the flash lamp for time-resolved measurement of molecular dynamics. The methodology is called a flash photolysis. The time-resolved spectral information could be obtained using the broad spectrum of the flash lamp. The time resolution of the flash photolysis was limited to a microsecond time range due to the duration of the discharge flash lamp at the time. For detection of the spectrum, a photographic dry plate was used. The limited time resolution is partly because of the time constant of the electric discharging circuit containing a high-capacitance condenser enabling the high current needed for the generation of an intense flash light. The duration is also limited by the disappearance time of the ions such as oxygen and nitrogen in the discharge plasma. To observe phenomena proceeding faster than the microsecond time scale, it is necessary to use new light sources, which can generate light pulses shorter than that of the flash lamp.

Laser based on light amplification by stimulated emission (SE) radiation[2] can be used to generate light with a much higher intensity for spectroscopy applications. The discovery of the Q-switched laser enabled the generation of a <10-ns giant pulse,[3] which enabled nanosecond time-resolved spectroscopy. After this, further improvement was realized by the discovery of the mode-locked method,[4] which enabled the generation of ultrashort picosecond-to-femtosecond laser pulses. Femtosecond laser pulses were applied for observation of the transition states of chemical reactions by Polanyi and Zewail.[5] Their pioneering work was followed by time-resolved studies of various chemical reactions, which has created a research field called femtochemistry. The method can also be used for photophysical and photobiological processes, such as vision[6] and photosynthesis.[7] The ultrafast dynamics provide key information for the study of photosensors,[8–10] optical memories,[11–13] and optical switches.[14–16]

1.2 Ti:sapphire laser

Ti:sapphire lasers (also known as $Ti:Al_2O_3$ lasers, titanium-sapphire lasers, or Ti:sapphs) are tunable lasers that emit red to near-infrared (NIR) light in the range from 650 to 1100 nm. These lasers are widely used in scientific research because of their tunability and their ability to generate ultrashort pulses. Lasers based on Ti:sapphire were first constructed in June 1982 by Moulton[17] at the MIT Lincoln Laboratory.

Titanium–sapphire refers to the lasing medium, a crystal of sapphire (Al_2O_3) that is doped with titanium ions Ti^{3+}. A Ti:sapphire laser is usually pumped with another laser with a oscillation wavelength of 514 to 532 nm, which is strongly absorbed by the titanium-doped material. Argon-ion lasers (514.5 nm) and frequency-doubled Nd:YAG, Nd:YLF, and $Nd:YVO_4$ lasers (527 to 532 nm) are used for the pumping. Ti:sapphire lasers operate most efficiently at wavelengths near 800 nm.

Mode-locked Ti:sapphire laser oscillators generate ultrashort pulses with a typical duration between a few ps and 10 fs (in special cases, even around 5 fs).[18–22]

In most cases, the pulse repetition frequency is around 70 to 90 MHz as determined by the length of the laser cavity. Ti:sapphire oscillators are normally pumped with a continuous-wave laser beam from an argon gas laser or frequency-doubled $Nd:YVO_4$ laser. Because of the inconvenience due to the requirement of water cooling of a long plasma tube containing argon gas and a buffer gas, the pump source has shifted to a solid-state $Nd:YVO_4$ laser. Typically, such an oscillator has an average output power of 0.4 to 2.5 W.

Application of the ultrashort pulse for time-resolved spectroscopy requires a broadband spectrum supporting the short pulse as mentioned above and a high enough power to enable a pump–probe measurement. The ultrashort pulse Ti:sapphire laser is commercially available in the spectral region of NIR

corresponding to the gain bandwidth of a Ti:sapphire crystal. However, for the study of dynamics in photoinduced excitations and/or chemical reactions, which involve species with a spectrum in the visible region, it is necessary to generate the ultrashort pulse with visible color. The visible laser pulse can be obtained from the NIR Ti:sapphire laser using an optical parametric amplifier (OPA). To obtain the visible laser pulse with an ultrashort duration, the visible spectrum should be broadened. This can be achieved by utilizing some amplifier with a special configuration called a noncollinear optical parametric amplifier (NOPA) to be described later in detail. Before the discussion of NOPA, nonlinear optics, which forms the basics of various principles in the generation and characterization of ultrashort pulses and in the measurement in time-resolved spectroscopy, is described in the following section.

2 Nonlinear Optical Processes and Nonlinear Susceptibilities

Under a high-intensity laser field irradiated to optical materials, nonlinear optical (NLO) processes start to be detectable above some intensity level of the incident field. This does not mean there is a threshold for the nonlinear process. Instead, this indicates that the signal due to the nonlinear process is increasing with incident power to reach the level of noise (contaminated in the signal) due to an optical source and/or some detector. In some NLO processes, there can be a threshold in such conditions that the nonlinear materials are located in an optical feedback system such as an optical cavity resonator. The resonator has some feedback and loss (including output), and the balance between them determines the threshold. In the case of lasers, the threshold level can be easily reached, especially by short-pulse lasers because short pulses can have a high-peak power with a moderate pulse energy below the thermal and/or optical damage induced by the accumulation of deposited energy in the material. Such damage processes include the following two types. One is the thermal damage effect induced by heat accumulation. The other involves the two- or multistep processes. In this case, the first step of photoexcitation creates an excited state, which can have intense absorption to be further excited into a higher excited-state, resulting in an irreversible photochemical reaction. Hereafter, we discuss the cases where such damaging processes are not involved except for mentioning them in some special cases.

Under the perturbative regime below the threshold level of the nonperturbative regime, nonlinear macroscopic polarization is the source generating the nonlinear processes. The polarization induced by N fields of E_k ($k = 1$ to N) is given by

$$P^{NL} = \varepsilon_0 \sum_{n=1}^{N} \chi^{(n)} \prod_{k=1}^{n} E_k. \tag{1}$$