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Two-dimensional subpicosecond time-resolved fluorescence anisotropy: Optical Kerr-gating with the excitation of alternating polarizations of light

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ABSTRACT

We have developed a subpicosecond time-resolved fluorescence anisotropy (TRFA) that newly implements a photoelastic modulator to alternate the polarizations of an excitation laser light. The setup facilitates virtually simultaneous detection of the parallel $I_{\parallel}$ and the perpendicular $I_{\perp}$ emission from a photoexcited molecule of interest by means of an ultra-short (optical Kerr-gating) shutter and a spectrograph coupled with a charge-coupled device. From a set of $I_{\parallel}(\lambda,t)$ and $I_{\perp}(\lambda,t)$ that comprise 2-D (two-dimensional) information on both a full range of spectra and subpicosecond time-resolved fluorescence decays, the 2-D TRFA, $R(\lambda,t)$, is directly given with better accuracy. To claim the merit of the technique we carried out a test for 2-D TRFA of Coumarin 153 in methanol.

1. Introduction

Time evolution of anisotropic properties can track dipole orientations or conformational changes in their photoexcited molecular systems, which is of extreme importance to examine its structure and excited-state dynamics [1]. Previously, we have set up the subpicosecond time-resolved fluorescence spectra (TRFS) using a spectrograph coupled with the optical Kerr-gating (OKG) [2]. In this paper, we take TRFS to the next level of the application that demonstrates the ability to probe time-resolved fluorescence anisotropy (TRFA). This setup, similar to the TRFS, but deals with detection of the time-resolved and the polarization-dependent emission by using a photoelastic modulator (PEM), which has been widely utilized in polarization spectroscopy [3–5] such as linear/circular dichroism, ellipsometry, and polarimetry.

Fluorescence anisotropy involves detection of the emission in a specific plane of polarization as $I_{\parallel}$ and $I_{\perp}$ that are those made parallel to and perpendicular to, respectively, the direction of the electric field of an excitation light. Under a particular configuration that both directions of the excitation light and of the detection of emission are collinear, such $I_{\parallel}$ or $I_{\perp}$ can be obtained when the polarization of the excitation light is parallel to or perpendicular to, respectively, the direction of the detection polarization. Since a PEM is capable of modulating an incident plane of the polarized light at a desired degree of retardation, the above scheme can be implemented by PEM that facilitates dynamic alternations of the polarization of an incident laser light. The following advantages are thus exploited. First, there is virtually no time lag between capturing both $I_{\parallel}(\lambda)$ and $I_{\perp}(\lambda)$, thus minimizing experimental inaccuracies, if any, due to optical misalignments, instability of laser system used, or sample degradation during the measurements. Second, since no physical movements of optical components are involved when switching between the parallel and perpendicular polarizations, it suffers less from optical misalignment than an ordinary measurement, where a detection polarizer (or a waveplate for an excitation laser) often needs to be rotated for the specific detection angle. Third, a set of $I_{\parallel}(\lambda,t)$ and $I_{\perp}(\lambda,t)$ obtained are free from corrections for a small magnitude difference of sensitivity. As is often the case in the ordinary setup, either of $I_{\parallel}(t)$ or $I_{\perp}(t)$ needs to be scaled in intensity by a pre-determined factor (g-factor) or by a tail-matching that both decay curves practically match at a later time region where depolarization is expected to occur.

In the basis of the aforementioned benefits, we present an efficient and reliable method to obtain the subpicosecond time-resolved fluorescence anisotropy, which is able to provide 2-D (two-dimensional) information on both a full range of spectra and subpicosecond time-resolved decays profile. We demonstrate its performance of both TRFS and TRFA by using a well-studied molecule of Coumarin 153.

2. Experimental setup and data analyses

2.1. Synchronization with PEM

PEM system (Hinds; FS50II head and PEM-90 driver) employed, however, cannot cooperate with an external trigger, because it

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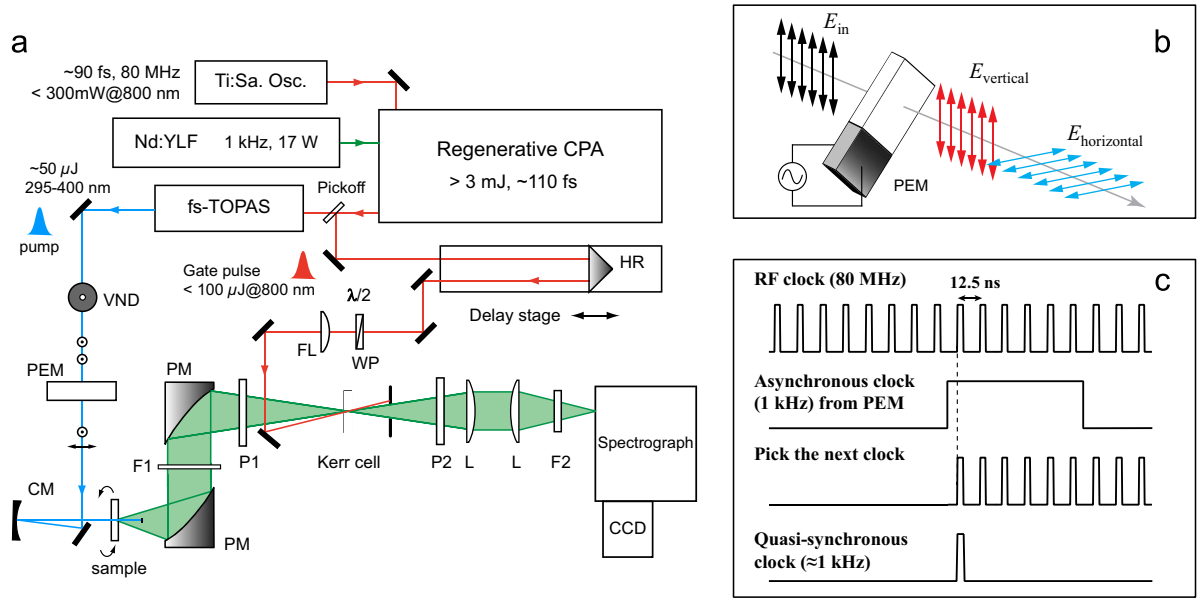

Fig. 1. (a) Schematic experimental setup for TRFA. Legends: CM—concave mirror; HR—hollow retroreflector; PM—parabolic mirror; WP—waveplate; VND—variable neutral density filter; F1/F2—spectral glass filter; P1/P2—thin grooved-polarizers configured at the crossed polarization to each other; PEM—photoelastic modulator; CCD—charge-coupled device detector. (b) PEM alternates the polarization vectors (E) of the linearly polarized incident light and creates the pulse-trains alternating with the vertical or horizontal polarization. (c) Quasi-synchronization scheme for femtosecond oscillator and PEM. See the text for details.

produces oscillating birefringence at a fixed frequency through a medium of quartz substrate [3]. Likewise, a commercially available ultrafast laser is a stand-alone system that has its own optical oscillator and governs an event in experiment. The presence of the two independent clocks, neither of which can be a master/slave to one another, creates an experimental difficulty in synchronization. To resolve this, we have carried a timing module (THALES Laser, DR85-A) that facilitates the asynchronous clocks to cooperate in what follows. First, synchronous triggers (1 kHz) were generated out of the PEM oscillation frequency (50 kHz) by using a home-made frequency divider, and then fed to the module along with an RF clock (80 MHz) from a femtosecond mode-locked laser. Synchronization with the RF clock occurs by delaying the start on the 'next timing' sequence [*cf.* Fig. 1(c)] to synthesize a 'quasi-synchronous' clock ($\approx$1 kHz), which triggers a pump laser to a regenerative chirp-pulsed amplification (CPA) [6] and also serves as the master clock. This quasi-synchronization scheme is practically feasible inasmuch as the effective time-window for a desired retardation of PEM lasts about a few microseconds, which is very much longer than the potential timing jitter of 12.5 ns at the most.

2.2. Optical Kerr-gate shutter

Fig. 1(a) presents a schematic diagram for the 2-D TRFA setup based on a femtosecond Ti:Sapphire ($\sim$110 fs) oscillator (Coherent, Vitesse) and a regenerative CPA (Quantronix, Titan). In an ultra-short optical shutter implemented by OKG [7], liquid benzene as a Kerr medium was filled in a static cell (1 mm thickness) and placed between two thin high-contrast polarizers (Moxtek; composed of two high-transmission ProFlux PPL05C polarizers combined with optical glue) in the cross-polarization configuration, where the polarization extinction is estimated to be $T_{\parallel}/T_{\perp} >$ 50 000. A small quantity of sample solution ($<$15 ml) was placed in a reservoir mounted onto a gear pump (Micropump), circulating through a flow cell (1 mm) where the UV laser beam, generated from an optical parametric amplifier (Light Conversion, TOPAS), was focused into the sample. Emission upon photoexcitation was imaged onto the Kerr cell via two 90° off-axis parabolic reflectors (Newport; ϕ=38 mm, effective focal lengths of 50 and 100 mm). The spot size in the Kerr cell was estimated to be $<$0.5 mm, assuring no significant aberration due to misalignments of the excitation beam and the two parabolic mirrors.

The gate beam (800 nm) was focused to the Kerr cell after traveling through a retroreflector on a delay stage, and its polarization was kept at 45° from the axes of the crossed polarizers throughout experiments. Typical input power of $<$80 μJ/pulse was used for the OKG. To avoid a breakdown of the cell, we have set a lens (150 mm focal length) at a distance of $\sim$130 mm from the cell to have a spot size of $\sim$0.6 mm, which is slightly larger spot size than the emission spot. The angle between the gate beam and the fluorescence was less than 10° as the gate beam traveling closely along the cone of the fluorescence beam [Fig. 1(a)].

In the Kerr-gate system, the overall throughput (efficiency) for linearly polarized input light as the open and closed shutters was estimated to be 50% and 0.5%, respectively, which we examined in Coumarin 153 at its fluorescence maximum wavelength (540 nm). As described in Ref. [7], the gating efficiency is totally dependent on the wavelength and on the fraction of the fluorescence being sampled by the ultra-short shutter. The shutter efficiency is prone to be deteriorated by imperfect overlapping of the gate pulse and the emission spot in the Kerr cell, and by the optical aberration of the imaging system and the depolarization inside the Kerr shutter. A minor leakage was constantly being subtracted as a baseline recorded at a negative time delay (*e.g.* −20 ps) with respect to the pump pulse. The temporal resolution of $\sim$0.6 ps (FWHM) was estimated from Raman scattering of a solvent by fitting with a Voigt model function. We found that the time-resolution is not influenced by the PEM.

2.3. Signal processes for TRFS and TRFA

The gated fluorescence was introduced to a polygraph spectrometer (Acton; Spectra Pro 2300i) attached to a CCD detector (Princeton; PIXIS 400B). At each delay time, the spectrum was composed of the sum of 40 cycles; one cycle collects the fluorescence upon 100 laser shots that correspond to an exposure time of 100 ms at the CCD detector. Between each cycle, the spectral data were transferred from the detector to a PC, cleaned up,