Cascaded Optical Kerr Gate for Fluorescence Measurement With High Signal-to-Noise Ratio

Zhenqiang Huang, Zhen Kang, Wenjiang Tan, Jinhai Si, and Xun Hou

***Abstract*— Traditional optical Kerr gates (OKG) often suffer from leakage fluorescence background when sampling and measuring fluorescence spectra due to the limited extinction of the polarizers used in optical Kerr gates. In this letter, we propose a cascaded optical Kerr gate (COKG) for measuring fluorescence spectroscopy with a high signal-to-noise ratio by suppressing this leakage fluorescence background. Our proposed COKG consists of an optical Kerr gate with a fast-switching time at the front stage and an optical Kerr gate with a high transmission at the back stage. The experimental results show that the signal-to-noise ratio for the COKG can be improved by about two orders of magnitude compared to the single OKG.**

***Index Terms*— Optical Kerr gate, leakage fluorescence, signal-to-noise ratio.**

I. Introduction

TIME-RESOLVED fluorescence spectroscopy is widely used to study the ultrafast dynamics processes of chemical and biological systems, which can give us fruitful information about excited state photoluminescence (PL) dynamics without interfering with other processes such as excited state absorption and ground state recovery. There are some common techniques for time-resolved fluorescence spectroscopy, such as time-correlated single-photon counting (TCSPC) [1], fluorescence upconversion [2] streak imaging [3], non-collinear optical parametric amplification [4], and optical Kerr gate (OKG) [5]. Among these techniques, the TCSPC and the streak camera have very high detection sensitivity and the time resolution of tens of picoseconds. For the ultrafast luminescence dynamics in the sub-picosecond time domain, only time-resolved measurement techniques using nonlinear optical effects can be applicable. Among them, the fluorescence up-conversion method is the most commonly used for ultrafast fluorescence measurement method in the sub-picosecond time domain. However, it is quite demanding in alignment and operation due to the phase matching. The noncollinear optical parametric amplifier method has the capability of broadband amplification and femtosecond time resolution. However, the strong superfluorescence background interferes with the detection of the amplified fluorescence signal. Comparing with the two nonlinear optical gates, OKG has no need of satisfaction of the phase-matching condition and high intensity of the probe light, which offers a simple way to gating wide spectral fluorescence with a femtosecond time resolution.

Previously, OKG method has been applied to study many ultrafast processes, for example, lasing dynamics [6], [7], solvation dynamics [8], vibrational relaxation [9], femtosecond filamentation process [10] and carrier diffusion process [11]. Improving the performance of the OKG is of great significance for the study of these ultrafast processes. Some Kerr media with faster response and greater nonlinear optical coefficients have been explored to achieve the high temporal resolution and signal transmittance of the OKG [12]. Besides, the signal-to-noise ratio of the system can also be improved by optimizing the arrangement of the OKG [5], [13]. However, traditional OKGs often suffer from leakage fluorescence background when sampling and measuring fluorescence spectra due to the limited extinction of the polarizers used in OKGs. The leaked fluorescence background greatly reduces the signal-to-noise ratio of measurement, especially when measuring the long-lived fluorescence with high time resolution. If the intensity of the leaked fluorescence signal is comparable to the intensity of the gated fluorescence signal from the OKG, the OKG cannot be used. Improving the signal-to-noise ratio of the OKG allows the measurement of long-lived fluorescence signals, thereby extending the range of fluorescence lifetimes that can be measured by the OKG method. Several studies have been addressed to this problem. For example, Arzhantsev et al. found that the limited surface flatness of the optical elements ($\lambda/10$ at 10 μm) of the OKG can still depolarise the polarisation state of the fluorescence, despite the use of two high quality Glan-Taylor polarizers (extinction ratio, $\sim 10^5$). This causes the extinction ratio of the OKG to deteriorate to 500:1. The leakage fluorescence increases significantly and the signal-to-noise ratio decreases due to the degradation of the OKG extinction ratio. In order to overcome this problem, some custom high flatness optical elements have been used. However, this method is dependent on the use of special custom optics, which have certain limitations in terms of universality [5]. Ryosuke Nakamura et al. developed a femtosecond spectral snapshot technique using a combination of an OKG and an electrically driven gate set in front of a charge-coupled device detector. This improvement suppressed the background signal to some extent, the time-resolved fluorescence spectra for laser dye solution with a several-nanoseconds lifetime were

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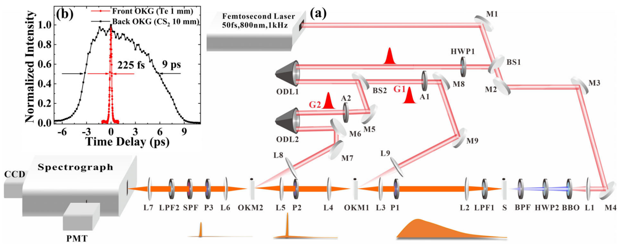

Fig. 1. (a) Experimental setup of the femtosecond cascaded optical Kerr gate for time-resolved fluorescence spectra measurement. M1- M9: mirrors; L1-L9: lenses; A1, A2: attenuator; BS1, BS2: beam splitter; P1, P2, P3: polarizers; LPF1, LPF2: long-pass filter (>425 nm); SPF: short-pass filter (<750 nm); BPF: band-pass filter (400 - 600 nm); ODL1, ODL2: optical delay line; OKM1, OKM2: optical Kerr medium; HWP1: 800 nm half-wave plate. HWP2: 400 nm half-wave plate. S: sample. (b) Instrument response function for the front OKG and the back OKG.

successfully measured. However, the use of detectors with an electrically driven gate increases the cost of the system. In addition, the opening time of the typical electrically driven gate is generally about 1 ns, so the leakage fluorescence within 1 ns cannot be well suppressed [14]. In addition, Wang et al. proposed a double-stage Kerr gate for ballistic imaging in turbid media [15]. The front and back stages of this double-stage optical Kerr gate both use identical optical Kerr gates that are opened sequentially with a certain delay time to achieve ultra-fast switching time. For the optical Kerr gated ballistic light imaging technology, the faster switching time can offer better filtering of the scattered photons and higher imaging contrast.

Inspired by this, we propose a cascaded optical Kerr gate (COKG) to suppress the leakage fluorescence background. Different from the setup proposed by Wang et al., in our experimental setup, the cascaded optical Kerr gate (COKG) was composed of a fast-switching front-stage OKG and a high-transmittance back-stage OKG. When this COKG was used for fluorescence measurements, the two series-connected optical Kerr gates were opened simultaneously. The leakage fluorescence from the front OKG was blocked by the back OKG. The intensity of the leakage fluorescence background from the COKG can be reduced by several orders of magnitude compared to that from a single optical Kerr gate (SOKG). A high signal-to-noise ratio for fluorescence measurements using the COKG has been demonstrated using coumarin 6 with nanosecond fluorescence lifetimes.

II. Experimental Details

Figure 1(a) shows the schematic diagram of the COKG. The light source is a femtosecond laser system with a wavelength of 800 nm and a pulse duration of 50 fs at a repetition rate of 1 kHz. The laser beam was split into two beams in a ratio of 2:8 by a BS1 beam splitter. The signal and gate beams were the transmitted (smaller) and reflected (larger) parts of the beam, respectively. For the gate beam, a half-wave plate (HWP1) was used to change the polarization of the gate pulse. The gate beam first passed through an optical delay line (ODL1, Newport, DL325) and was then split into two gate beams in a 5:5 ratio by a beam splitter BS2. The transmitted gate beam (G1) with a power of 20 mW was used to open the front OKG, which consists of a pair of crossed Glan-Taylor polarizers P1 and P2 (PGT5012, Union Optic, Inc., China) and an optical Kerr medium (OKM1) between them. The reflective gate beam (G2) with a power of 20 mW was used to open the back OKG after passing through the second optical delay line (ODL2). The back OKG consists of a pair of crossed Glan-Taylor polarizers P2 and P3 (PGT5012, Union Optic, Inc., China) and an optical Kerr medium (OKM2) between them. The role of the second delay line is to accurately compensate for the delay time of the second gate pulse. Finally, the probe pulse is gated by two OKGs in turn. The polarization directions of the polarizers P1, P2 and P3 are horizontal, vertical and horizontal, respectively.

The signal beam was frequency doubled in a 1 mm BBO crystal to produce the excitation pulse at 400 nm. The excitation pulse with a power of 7 mW was used to excite sample solutions contained in a 2-mm quartz cuvette. Coumarin 6 in ethyl alcohol with a concentration of 10^{-3} M/L was used as the sample. A 400 nm half-wave plate was used to rotate the polarization of the excitation pulse at the magic angle (54.7°) with respect to the first polarizer of the OKG. The collected fluorescence was then passed through the front OKG and the back OKG. To obtain maximum transmission efficiency, the polarization of the gate beam was rotated by $\pi/4$ with respect to the polarizer P1 by HWP1. The gated fluorescence was focused and transferred to the entrance slit of the spectrograph (Princeton Instruments, SpectraPro - MS3504i) through the lens L7 (focal length, f7=150 mm). The gated fluorescence spectra were recorded with a TE-cooled (-60 °C) CCD camera (Andor, DU970P-UVB). Single wavelength detection with high sensitivity was achieved using a photomultiplier (PMT) (Hamamatsu, H10682-210) behind the exit slit of the spectrograph.

For the COKG, the temporal resolution depends on the shorter switching time of the two cascade OKGs. The signal transmittance of the COKG depends on the product of the signal transmittance of the two cascade OKGs. In our experiment, the front OKG is used to gate fluorescence with high temporal resolution. The back OKG is used to gate the fluorescence passing through the front OKG with a high signal transmittance. According to the needs, yttrium aluminum garnet (YAG) and other materials with fast switching time, relatively high signal transmittance and wide range of transmittance spectra can be used as the OKM in the front OKG. Here, a piece of tellurate glass (Te) with a thickness of 1 mm was used as OKM1 to provide a faster switching time and adequate signal transmittance. A 400 nm excitation pulse was used as a probe to measure the instrument response function (IRF). Fig. 1(b) shows the measured IRF for the front OKG and the back OKG. Each data point was obtained by averaging 16 pulses. The measurement interval for every two data points is 0.5 s. The switching time and signal transmittance of the front OKG were measured to be approximately 225 fs and 13%, respectively. To achieve the highest possible signal transmittance for the back OKG, a commonly used carbon disulfide (CS_2) filled in a 10 mm quartz cuvette with high optical nonlinearity was used as OKM2. The switching time and signal transmittance of the back OKG were measured to be 70% and 9 ps, respectively.

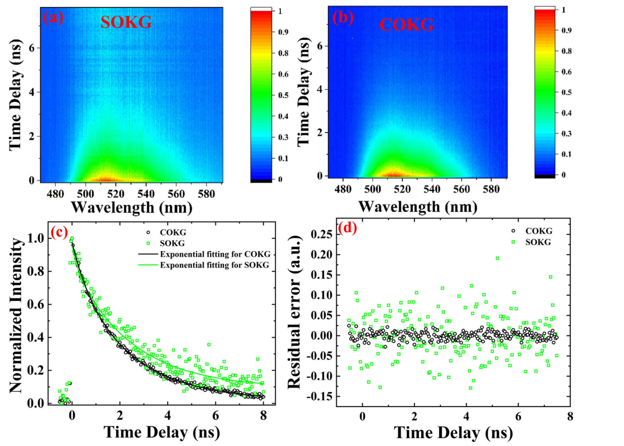

Fig. 2. (a) Time-resolved fluorescence spectra using the SOKG, (b) Time-resolved fluorescence spectra using the COKG for 10-mm OKM2, (c) Time-resolved fluorescence signal at the peak wavelength of 515 nm for the COKG and the SOKG methods, (d) Corresponding residual errors for both methods.

The angle between the direction of propagation of the gate pulse and the signal pulse in two OKGs is 60° and 10° respectively. The beam angle of 60° between the probe beam and the gate beam was used to suppress the broadening of the switching time caused by their group velocity dispersion in the OKM1.

III. Results and Discussion

Firstly, we measured the time-resolved fluorescence spectra of coumarin 6 using the SOKG and the COKG methods, respectively. For the COKG, the group velocity dispersion will broaden the time slice fluorescence gated by the front OKG. As a result, some spectral components may not be gated by the back OKG. Thus, a CS_2 filled in a 10 mm quartz cuvette was used here as the OKM2 to ensure the high transmission of the back OKG and to avoid the simultaneous loss of these spectral components. Because the spectral components of the fluorescence and the gate pulse have different group velocities as they propagate through the OKM2, the gate pulse can catch up with the fluorescence pulse as it passes through the OKM2. A thicker OKM2 corresponds to an increase in the switching time of the back OKG [13]. The ODL2 was used to adjust the relative delay time of the back and front gate beams so that the back OKG can just gate the fluorescence signal passing through the front OKG. The results are shown in Figs. 2(a) and 2(b). It can be seen that the gated transient spectra for both methods have the same peak wavelength of 515 nm and a similar fluorescence lifetime of approximately 2 ns, which is consistent with the previous work [16]. In addition, the transient fluorescence signal using the COKG has a higher signal-to-noise ratio than that using the SOKG.

To clearly observe the different signal-to-noise ratio for the COKG and the SOKG methods, the time-resolved fluorescence signal at the peak wavelength of 515 nm was measured as described above. From Fig. 2(c), it can be seen that the experimental data for the SOKG show more significant fluctuations than those for the COKG. As the gated fluorescence signal gradually fades, the fluctuations become more pronounced with increasing delay time. The average lifetimes for both OKGs were obtained by exponential fitting of the results to be 2.3 ns and 2.4 ns respectively. The average lifetimes are in agreement with previous work [16]. However, the degree of agreement between the fitted curves and the experimental data is significantly different. The residual errors for both OKGs have been calculated and are shown in Fig. 2(d). It can be seen that the range of residual errors for the SOKG is significantly larger than that of the COKG from Fig. 2(d). We also calculated the residual sum of squares for both methods in order to quantitatively assess the degree of dispersion of the residuals. The residual sums of squares for the SOKG and the COKG were 0.595 and 0.019 respectively. The residual sum of squares for the SOKG is approximately 31 times higher than that of the COKG.

Furthermore, the noise intensities were measured to analyse the influence of noise from different sources on the results. The noise intensities were measured 10 times repeatedly under each condition in the negative time delay. Firstly, the dark current noise from the detector was measured by closing the input to the monochromator. The intensity of the dark current noise was measured to be approximately 50. In the absence of fluorescence signal for the COKG, the total intensity of the pump stray light and the dark current noise was then measured to be also about 50. The result indicates that the pump leakage noise can be negligible for both OKGs in our experiment. In addition, in the absence of pump light, the total intensity of the leakage fluorescence and the dark current noise of the SOKG and the COKG were measured separately. The average noise intensity of leakage fluorescence for the SOKG and the COKG was calculated to be about 5350 and 50, respectively, by subtracting the dark current intensity from the total noise intensity. This indicates that the main noise of the SOKG is the leakage fluorescence. However, the noise intensity of the leaked fluorescence for the COKG is about one percent of that of the SOKG, which is just comparable to the noise intensity of the dark current in the experiment. This is because the COKG has much less leakage fluorescence noise due to the two sets of perpendicular polarizers. Besides, the theoretical extinction ratio of the COKG is about 10^5 of that of the SOKG. However, we found that the introduction of the back OKG did not reduce the intensity of the leakage fluorescence noise for the COKG to 10^{-5} of that for the SOKG. We speculate that the fluorescence may have been partially depolarized by the lens and the quartz cuvette containing CS_2 between the two polarizers in the back OKG, resulting in a decrease in the extinction ratio of the OKG. If these effects are eliminated, a further improvement in the signal-to-noise ratio can be expected.

It is foreseeable that as the time resolution improves, the fluorescence lifetime increases and the fluorescence intensity decreases, the signal-to-noise ratio of the SOKG may decrease further. This is because the ratio of the intensity of the gated fluorescence to the intensity of the leakage fluorescence during the switching time will continue to decrease significantly. As a result, the signal-to-noise ratio of the SOKG will decrease significantly. Therefore, the advantages of the weak leakage fluorescence of the COKG will be more significant in the above cases. To further verify the technical advantages of the high signal-to-noise ratio of the COKG, we schematically

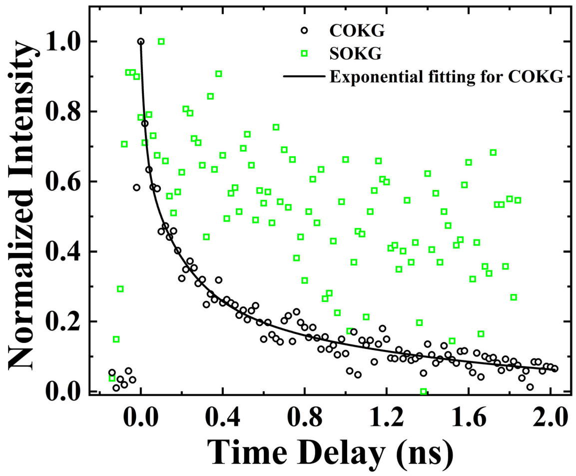

Fig. 3. Time-resolved micro-region fluorescence signal at the peak wavelength of 520 nm of coumarin 153.

measured the time-resolved micro-region fluorescence signal at the peak wavelength of 520 nm of coumarin 153 using the SOKG and the COKG methods, respectively. The 400 nm frequency doubled laser pulse focused through a 40x objective was used as the excitation beam. Due to the low intensity of the microfluorescence, the CS_2 with a thickness of 5 mm was used as the front OKM and the CS_2 with a thickness of 10 mm was used as the back OKM. The results are shown in Figure 3. It can be seen that the fluorescence signal for the SOKG can hardly provide valuable dynamic information due to the deteriorated signal-to-noise ratio. However, the fluorescence signal for the COKG can still be measured with a good signal-to-noise ratio. The lifetimes were obtained by exponential fitting to be approximately 1.2 ns, which was in agreement with previous macroscopic measurements [17]. It should be noted that the use of more optics elements in COKG reduces the overall signal transmittance of the system, resulting in a further weakening of the gated signal intensity, which may cause the gated signal intensity to be below the detection sensitivity of the detector and undetectable. Therefore, the COKG places higher demands on the sensitivity of the detector. In addition, the use of transmissive optics in the optical path inevitably introduces temporal dispersion. In order to obtain accurate spectral dynamics, it is necessary to measure and correct for this temporal dispersion, and this should be investigated further. Recently, we have carried out the research work on lasing dynamics and micro-region fluorescence using this technology.

IV. Conclusion

We have demonstrated a COKG method for measuring fluorescence spectroscopy with a high signal-to-noise ratio by suppressing the leakage fluorescence background. In our experiment, to achieve high time resolution and signal transmission, a 1-mm tellurate glass plate and a commonly used CS_2 with high optical nonlinearity were used as Kerr media for the front and back OKGs. The multi-wavelength time-resolved fluorescence spectra of coumarin 6 were measured using the SOKG and COKG methods, respectively. The results show that the transient fluorescence signal using the COKG has a higher signal-to-noise ratio than that using the SOKG. And the experimental data for the SOKG show more significant fluctuations than those for the COKG. Furthermore, the residual sum of squares of the curve fitting for the SOKG is approximately 31 times higher than that for the COKG. The intensity of the leakage fluorescence noise for the COKG is only one percent less than that for the SOKG. Our results indicate that the COKG is suitable for long-lived fluorescence with a high signal-to-noise ratio. For the long-lived fluorescence measurement, especially micro-region fluorescence, the SOKG may not be suitable because the intensity of the gated fluorescence signal is comparable to the intensity of the leaked fluorescence signal. While COKG can play its unique technical advantages of high signal-to-noise ratio.

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