

# Coherent enhancement in two-photon fluorescence in molecular system induced by phase-jump modulated pulse

Shian Zhang, Hui Zhang, Yan Yang, Tianqing Jia, Zugeng Wang, and Zhenrong Sun<sup>a)</sup>

*Department of Physics and State Key Laboratory of Precision Spectroscopy, East China Normal University, 200062 Shanghai, People's Republic of China*

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Coherent control of two-photon fluorescence (TPF) of 2',7'-dichlorofluorescein in methanol solution was experimentally investigated by shaping the femtosecond pulse with the phase jump. The experimental results indicated that the TPF intensity induced by the shaped femtosecond pulses with certain phase jump could be coherently enhanced. The physical mechanisms for TPF enhancement in the molecular system were explicitly discussed and analyzed, which could be attributed to the wave-packet constructive interference in the excited states. Finally, two phase-locked femtosecond pulses were used to explore the wave-packet constructive interference in the excited states of 2',7'-dichlorofluorescein, which validate experimentally the proposed mechanism. © 2010 American Institute of Physics. [doi:10.1063/1.3327843]

## I. INTRODUCTION

Quantum coherent control by shaping ultrashort laser pulses has attracted considerable attention for its ability to guide a quantum system to the target states or photoproducts with the light-matter interaction. As a typical nonlinear optical effect, the coherent control of the two-photon process has been widely investigated in theory and experiment.<sup>1-14</sup> Recently, the coherent enhancement in two-photon fluorescence (TPF) in the large molecular system by shaping the femtosecond laser pulses has attracted great interests.<sup>10-13</sup> Lee *et al.*<sup>10</sup> have reported the TPF enhancement in DCM in methanol solution by feedback control based on evolutionary algorithm. The spectral structure of the optimized pulse was found to have negative chirp, and it was proposed that the TPF enhancement was attributed to the wave-packet localization in the excited states. Wada and co-workers<sup>11-13</sup> have achieved the TPF enhancement in  $\alpha$ -perylene crystals and perylene in chloroform solution by feedback control based on genetic algorithm. It was found that the optimized pulses were the pulse trains with an alternately reversing pulse relation, and the TPF enhancement was attributed to the intramolecular dynamical processes.

The previous study has demonstrated that, for various pulse shapes, the physical control mechanism for the TPF enhancement in the molecular system may be different. In this paper, we experimentally investigated the coherent control of the TPF of 2',7'-dichlorofluorescein in methanol solution by shaping the femtosecond pulses with the spectral phase jump. It was found that the TPF intensity induced by the shaped femtosecond pulses with certain spectral phase jump could be obviously enhanced. The possible mechanisms for the TPF enhancement in the molecular system were put forward and explicitly discussed in the context, and

the wave-packet constructive interference in the excited states was considered as an essential contribution to the TPF enhancement in our experiment. Finally, phase-locked femtosecond pulses by the phase-locked loop technique were used to validate experimentally the proposed mechanism.

## II. EXPERIMENT

The experimental arrangement was schematically shown in Fig. 1(a). A mode-locked Ti: sapphire regenerative amplifier (Spitfire, Spectra-physics) was used as the excitation source with the pulse width of about 50 fs, the center wavelength of 800 nm, and the repetition rate of 1 kHz. The output pulses were shaped by a programmable 4f configuration zero-dispersion pulse shaper, which was composed of a pair of diffraction gratings with 1200 lines/mm and a pair of concave mirror with focal length of 200 mm. An one-dimensional liquid-crystal spatial light modulator (SLM) (256, CRI) was placed at the Fourier plane of the pulse shaper and used as the updatable filter for the spectral amplitude and phase modulation. The output shaped pulses was focused into a 10 mm sample cell full of the 2',7'-dichlorofluorescein solution with a lens of 600 mm focal length, and the laser intensity at the focus was estimated to be  $\sim 1.3 \times 10^{11}$  W/cm<sup>2</sup>. The TPF signal was detected by spectrometer with charge-coupled device, and a computer was used for recording the TPF signal and updating the SLM.

In our experiment, the 2',7'-dichlorofluorescein dissolved in methanol solution with the concentration of  $1 \times 10^{-4}$  mol/l was used, and its UV-visible absorption and TPF spectra are shown in Fig. 1(b). The maximum of the absorption band is at 499 nm and its bandwidth [full width at half maximum (FWHM)] is about 31 nm. The maximum of the TPF signal corresponds to 526 nm and its bandwidth (FWHM) is about 54 nm. Figure 1(c) shows the schematic energy-level diagram of two-photon absorption (TPA) in the

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: zrsun@phy.ecnu.edu.cn.

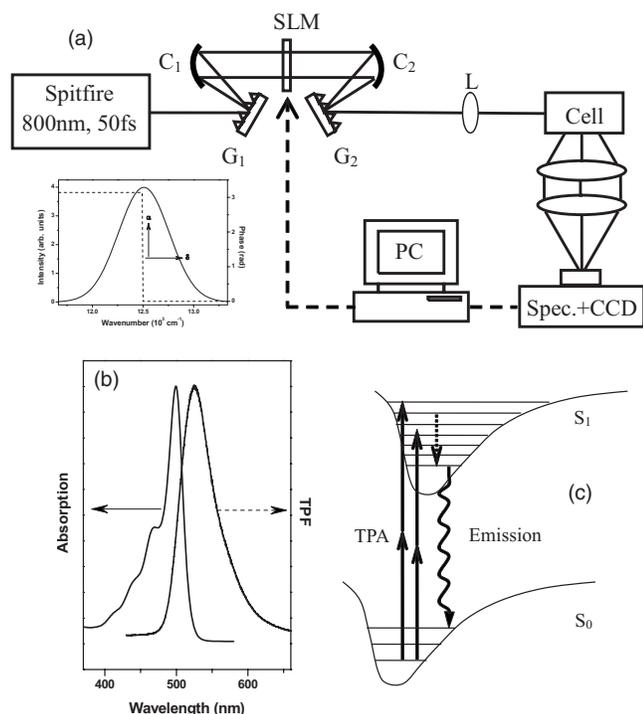


FIG. 1. (a) The Schematic diagram of the experimental arrangement. Inset shows the schematic diagram of the spectral phase jump (the modulation depth  $\alpha$  and phase step  $\delta$ ) applied on the femtosecond pulse spectrum. (b) The normalized absorption (dashed line) and TPF (solid line) spectra of 2',7'-dichlorofluorescein in methanol solution. (c) The schematic energy-level diagram of TPA in the two-level molecular system.

two-level molecular system. The TPA can occur for all pairs of the photons which satisfy the condition  $\omega_1 + \omega_2 = \omega_0$ , here  $\omega_0$  represents the absorption transition frequency, and both  $\omega_1$  and  $\omega_2$  are within the femtosecond pulse bandwidth.

### III. RESULTS AND DISCUSSION

In the experiment, we used the spectral phase jump (including of the modulation depth  $\alpha$  and phase step  $\delta$ ) to manipulate the TPF intensity of the 2',7'-dichlorofluorescein solution, and the spectral phase modulation is shown in the inset of Fig. 1(a). The phase jump modulation means that the spectral phase is set to zero for all frequencies smaller than the phase step position  $\delta$  and to the modulation depth  $\alpha$  for all frequencies larger than the phase step position  $\delta$ . The temporal electric field for the phase jump modulated pulses is a double subpulse structure, the intensity ratio between the two subpulses is controlled by the modulation depth  $\alpha$ , and their pulse interval depends on the phase step  $\delta$  (as shown in Fig. 2). The two subpulses have same intensity for  $\alpha = (2m + 1)\pi$  ( $m=0, 1, 2, \dots$ ), and their maximal pulse interval is achieved at the laser central frequency.

Figure 3(a) shows the TPF intensity of the 2',7'-dichlorofluorescein solution as the function of the modulation depth  $\alpha$  for  $\delta = 12\,500\text{ cm}^{-1}$ . As can be seen, the TPF intensity is periodically modulated and enhanced around  $\alpha = (2m + 1.5)\pi$  ( $m=0, 1, 2, \dots$ ). The TPF spectra induced by the transform limited pulses (solid line) and the shaped pulses with  $\alpha = 1.5\pi$  and  $\delta = 12\,500\text{ cm}^{-1}$  (dashed line) are shown in Fig. 3(b). It can be found that, comparing with the

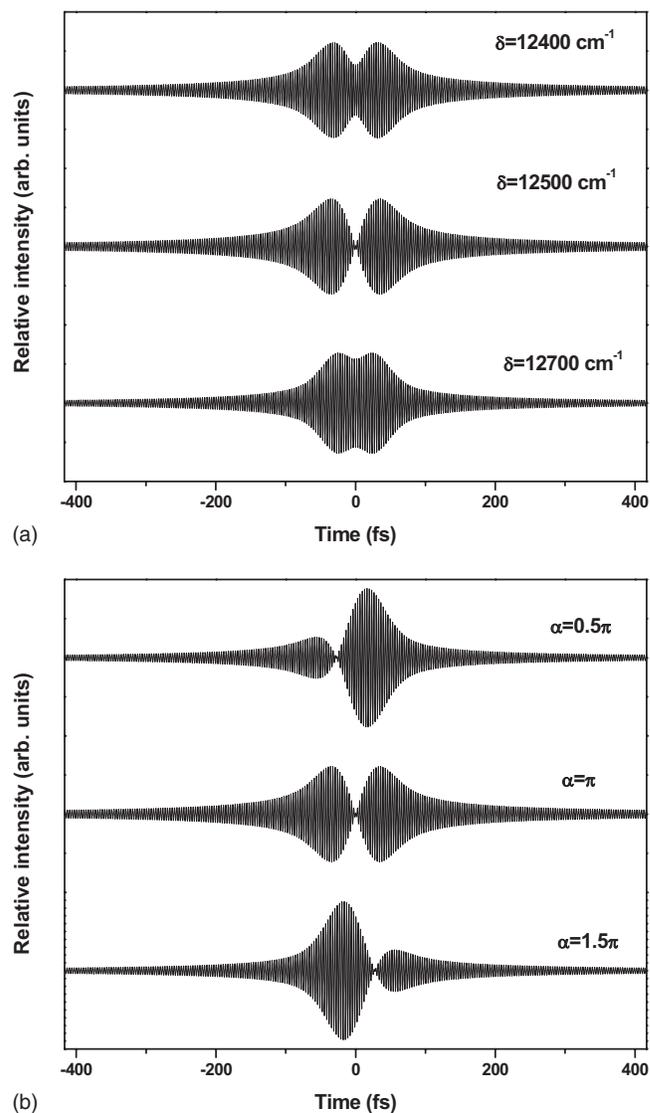


FIG. 2. The temporal laser field obtained by inverse Fourier transform of the shaped spectrum for  $\alpha = \pi$  with  $\delta = 12\,400$ ,  $12\,500$ , and  $12\,700\text{ cm}^{-1}$  (a), and  $\delta = 12\,500\text{ cm}^{-1}$  with  $\alpha = 0.5\pi$ ,  $\pi$ , and  $1.5\pi$  (b).

transform limited pulses, the TPF intensity induced by the shaped pulses can be enhanced by about 16%. It should be noted that the transform limited pulses should achieve maximal excitation efficiency for the nonresonant two-photon excitation process.<sup>2</sup> However, our experimental observation implies that the molecular event driven by the coherent interaction with the shaped pulses should play a crucial role for the TPF enhancement.

Generally, two possible mechanisms for the TPF enhancement in the molecular system can be summarized. One is the increase in two-photon excitation efficiency, such as the higher-order nonlinear optical effect in the strong field and the intramolecular vibrational process.<sup>11–13</sup> The other is the wave-packet dynamical process in the excited states, such as wave-packet localization and wave-packet constructive interference.<sup>15–18</sup>

To demonstrate the TPF enhancement is not attributed to the high pulse intensity effect. The laser intensity dependence of the TPF intensity was measured. The log-log plot of the TPF intensity versus the laser intensity for the shaped

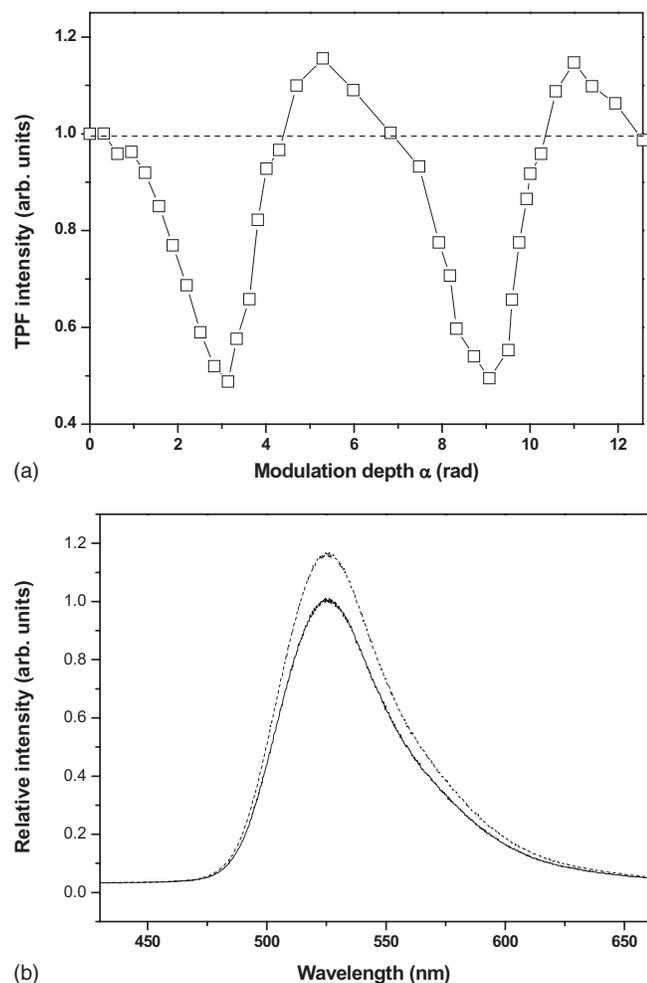


FIG. 3. (a) The TPF intensity as the function of the modulation depth  $\alpha$  for  $\delta = 12500 \text{ cm}^{-1}$ . (b) The TPF spectra of 2',7'-dichlorofluorescein in methanol solution excited by the transform limited pulses (solid line) and the shaped pulses with  $\alpha = 1.5\pi$  and  $\delta = 12500 \text{ cm}^{-1}$  (dashed line).

pulses with  $\alpha = 1.5\pi$  and  $\delta = 12500 \text{ cm}^{-1}$  is shown in Fig. 4, here the solid line is the result of the linear fitting and its slope is about 2.0. So, it should be attributed to the two-photon process, and the higher order nonlinear optical effect

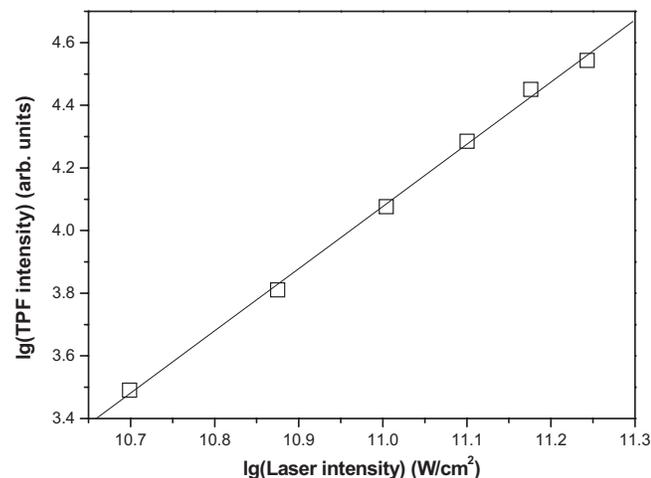


FIG. 4. The log-log plot of the TPF intensity of 2',7'-dichlorofluorescein in methanol solution vs the laser intensity of the shaped pulse with  $\alpha = 1.5\pi$  and  $\delta = 12500 \text{ cm}^{-1}$ .

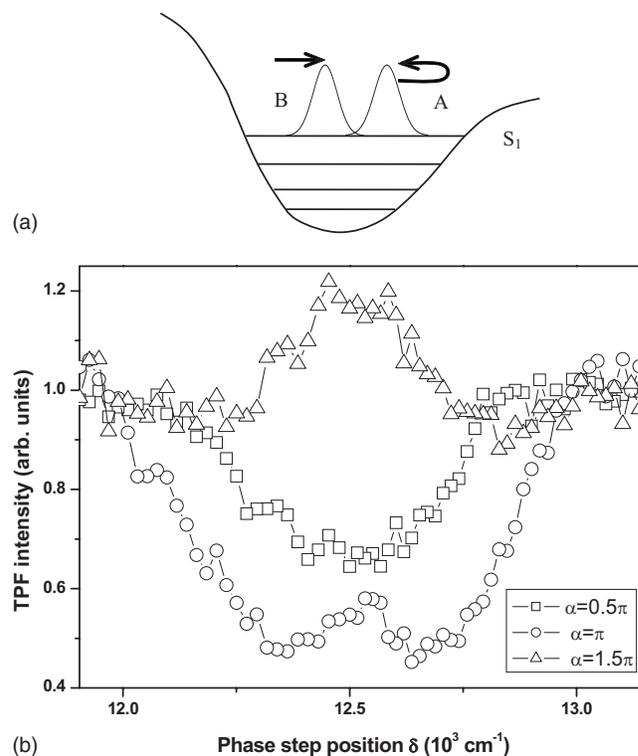


FIG. 5. (a) The theoretical model for the wave-packet dynamical process induced by the shaped pulses with two subpulses. (b) The TPF intensity of 2',7'-dichlorofluorescein in methanol solution as the function of the phase step  $\delta$  for  $\alpha = 0.5\pi$  (squares),  $\pi$  (circles), and  $1.5\pi$  (triangles), respectively.

can be excluded in our measured laser intensity region ( $\sim 1.3 \times 10^{11} \text{ W/cm}^2$ ). In previous report about the TPF enhancement in  $\alpha$ -perylene crystal and perylene in chloroform solution induced by the shaped femtosecond pulse sequences,<sup>11-13</sup> the physical control mechanism was attributed to the intramolecular vibrational process with an increase in the two-photon excitation efficiency. However, our experimental observation cannot be explained by the above-mentioned mechanism, and the TPF enhancement should be attributed to the wave-packet dynamical process in the excited states. A negative chirp results in the wave-packet localization and a positive chirp can cause the wave-packet delocalization.<sup>15</sup> So, it can be deduced that the TPF enhancement in our experiment is not due to the wave-packet localization because of the shaped pulse without the negative chirp. Since the shaped pulses are double subpulse structure, the TPF enhancement may result from the constructive interference of the wave packets in the excited states prepared by the two subpulses.

Figure 5(a) shows the theoretical model for the wave-packet dynamical process in the excited states induced by the shaped pulses with two subpulses. The two sub pulses successively prepare two wave packets (A and B) in the excited states by nonresonant TPA. If two subpulses are phase-locked and their pulse interval is the integral multiples of the vibrational period of the excited states, the two wave packets will constructively interfere.<sup>17,18</sup> When the two wave packets have the same amplitude in the interaction region, their constructive interference can be maximally achieved. To experimentally observe the wave-packet constructive interference

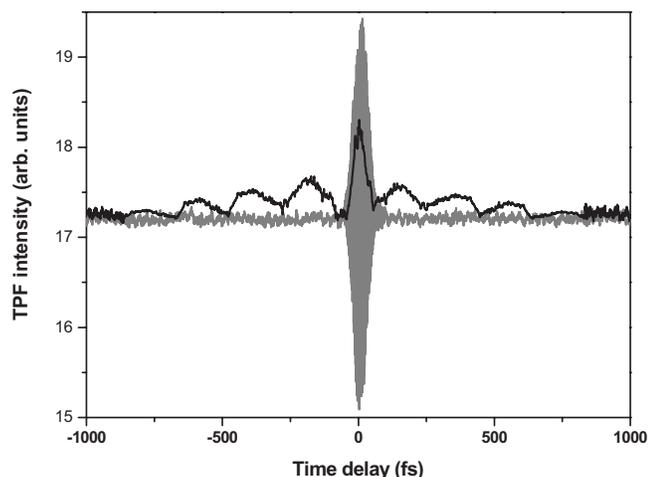


FIG. 6. The TPF intensity dependence of 2',7'-dichlorofluorescein in methanol solution on the pulse interval for two not-phase-locked pulses (gray line) and two phase-locked pulses (black line).

in the excited states, the TPF intensity as the function of the phase step position  $\delta$  was measured. Figure 5(b) shows the experimental results for  $\alpha=0.5\pi$  (squares),  $\pi$  (circles), and  $1.5\pi$  (triangles), respectively. It is indicated that no coherent peak at  $\delta=12\,500\text{ cm}^{-1}$  is observed for  $\alpha=0.5\pi$ , a weak coherent peak is observed for  $\alpha=\pi$ , and an intense coherent peak is obtained for  $\alpha=1.5\pi$ , which is larger than that excited by the transform limited pulses.

The wave-packet amplitude is proportional to the pulse intensity, and the wave packet can be greatly weakened during the evolution process in the excited states. For  $\alpha=0.5\pi$ , the first wave packet is much weaker than the second one in the interaction region, the constructive interference is very weak, so no coherent peak at  $\delta=12\,500\text{ cm}^{-1}$  is observed [the squares in Fig. 5(b)]. However, for  $\alpha=1.5\pi$ , the first wave packet can be weakened to comparatively same amplitude with the second wave packet after the evolution process, the maximal constructive interference will occur, and consequently an intense coherent peak at  $\delta=12\,500\text{ cm}^{-1}$  can be achieved [the triangles in Fig. 5(b)].

In order to further validate the above-proposed mechanism, time-resolved two-photon fluorescence spectra of 2',7'-dichlorofluorescein in methanol solution have been measured by phase-locked femtosecond pulse pairs generated by the phase-locked loop technique. The experimental arrangement was explicitly described in Ref. 17, and the experimental results are shown in Fig. 6. The black line is for two phase-locked pulses with zero relative phase, and the gray line is for two not-phase-locked pulses. For the phase-locked pulses, the two-photon fluorescence intensity is observed to be periodically recurring features. It indicates the constructive interference between two-photon wave packets in the molecular excited states, and its interval is about 830

fs. So, it is further proved that the TPF enhancement in our experiment should be attributed to the constructive interference between the wave packets in the excited states excited by two-photon process.

#### IV. CONCLUSIONS

In summary, we have successfully achieved the coherent enhancement in the TPF of 2',7'-dichlorofluorescein in methanol solution induced by the shaped pulses with the spectral phase jump, and the TPF intensity can be maximally enhanced by about 16%. The theoretical and experimental results indicate that the constructive interference of two wave packets in excited states induced by the shaped pulses results in the TPF enhancement in our experiment.

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