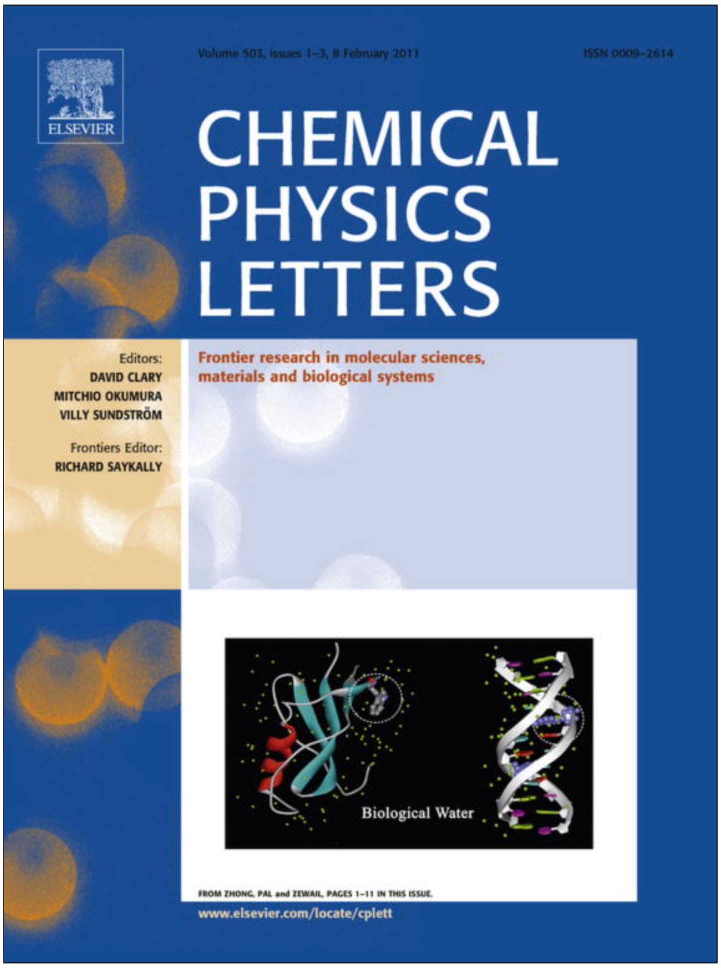

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Single-photon fluorescence enhancement in IR144 by phase-modulated femtosecond pulses

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ABSTRACT

In this Letter, we experimentally show that the single-photon fluorescence in IR144 solution can be enhanced by manipulating the laser spectral phase. We theoretically and experimentally validate that the single-photon fluorescence enhancement should be attributed to the non-resonant two-photon absorption from the state $S_1 \rightarrow S_2$. Finally, our proposed mechanism is further confirmed by repeating the SPF experiment in the low laser intensity, where the non-resonant two-photon absorption from the sate $S_1 \rightarrow S_2$ is eliminated.

1. Introduction

Coherent control has been a fascinating subject for its ability to control the dynamical process at various stages of a quantum system and drive it towards a desired final state or a specific outcome [1]. Especially, with the development of ultrafast pulse shaping technique, the coherent control strategy by pulse shaping method, involving the spectral phase modulation with the simple patterns of π-step [2,3], sinusoidal [4], cosinusoidal [4] and chirped function [4,5], or adaptive feedback control based on genetic algorithm or evolution algorithm [6–8], has been widely applied on various physical process [9], chemical reaction [10], and biological imaging [11,12].

Recently, single-photon fluorescence (SPF) enhancement has attracted great attention because of its potential applications on bioimaging, biophotonics and medicine by fluorescence spectroscopy, three-dimensional fluorescence imaging or photodynamic therapy [13–15]. Various experimental projects to enhance the SPF have been reported. Gerullo et al. and Bardeen et al. reported the SPF enhancement in LD690, LDS750 and IR125 fluorescent dyes using negatively chirped pulses [16,17], and the SPF enhancement was attributed to an intra-pulse pump-dump process. Recently, Goswami et al. demonstrated the SPF enhancement in IR125 fluorescent dyes by varying the laser polarization [18], but the physical control mechanism was unclear. In this work, we show that the SPF in IR144 can be enhanced by phase-shaped femtosecond pulses with a cosinusodial or chirped function. We theoretically and experimentally validate that the SPF enhancement is due to the non-resonant two-photon absorption from the state $S_1 \rightarrow S_2$.

2. Experimental setup

Our experimental arrangement is schematically shown in Figure 1. A mode-locked Ti:Sapphire regenerative amplifier (Spectra Physics, Spitfire) is used as the excitation source with the pulse width of about 50 fs, the centre wavelength of 800 nm and the repetition of 1 kHz. The output laser is sent into a 4F-configuration zero-dispersion pulse shaper, which is composed of a pair of diffraction gratings with 1200 lines/mm and a pair of concave mirrors with 200-mm focal length. A one-dimensional programmable liquid crystal spatial light modulator (CRI, SLM-128-D-VN) is placed at the Fourier plane of the pulse shaper, and used to manipulate the spectral amplitude and/or phase in the frequency domain. The shaped laser pulse is focused into a quartz cuvette containing the IR144 solution with a lens of 800-mm focal length. The diameter of beam waist at the focus is estimated to be 5.8×10^{-2} mm. The IR144 is dissolved in methanol with the concentration of 6×10^{-5} mol/L. The SPF signal is perpendicularly collected and measured by a spectrometer with a charge coupled device camera (Princeton Instrument, Acton-2300i).

3. Results and discussion

The shaped pulse with the cosinusoidal function has been proven a powerful tool to control various multiphoton absorption processes [19–21]. Here, we employ it to control the SPF in IR144. The inset of Figure 2a shows the normalized laser power spectrum and the spectral phase modulation applied on the laser spectrum with a cosinusodial function of $\phi(\omega) = \alpha \cos[\beta 2\pi(\omega - \omega_{\min})/(\omega_{\max} - \omega_{\min})]$, here $\omega_{\max}$ and $\omega_{\min}$ are the maximal and minimal frequency of the laser spectrum, and α and β represent the modulation amplitude and modulation period number. Figure 2a shows

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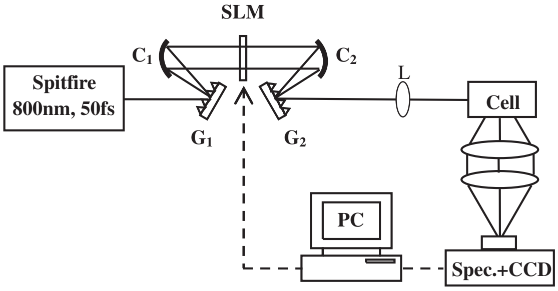

Figure 1. The experimental arrangement for controlling the single-photon fluorescence in IR144 solution by the spectral phase modulation, here a liquid crystal spatial light modulator (SLM) is placed at the Fourier plane of the pulse shaper and used to manipulate the spectral amplitude and/or phase in the frequency domain.

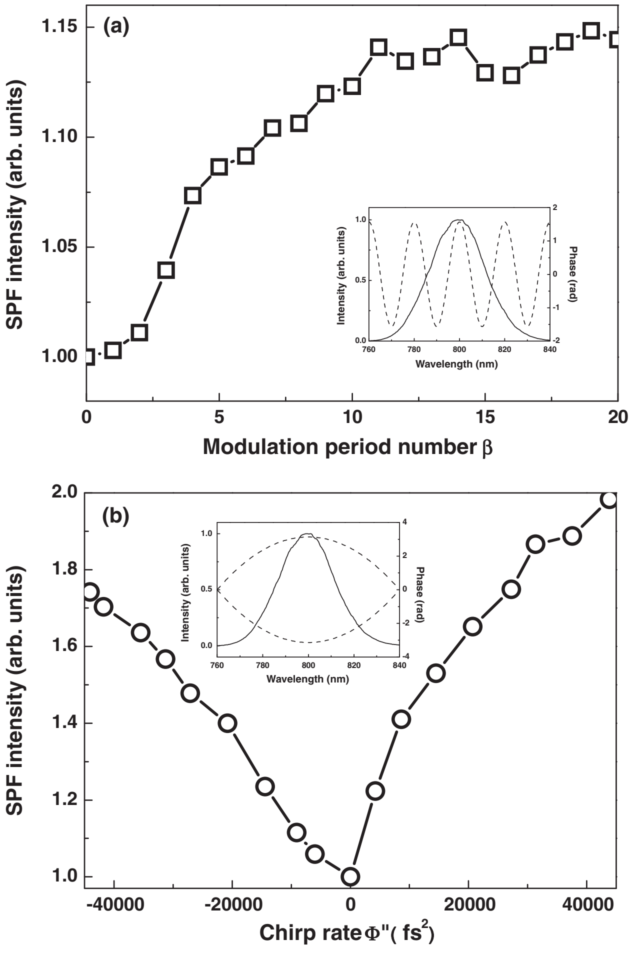

Figure 2. The normalized SPF intensity of IR144 in methanol as a function of modulation period number β with $\alpha = \pi/2$ for the cosinusodial phase modulation with the laser intensity of 1×10^{12} W/cm^2 (a) and the chirp rate ϕ'' for the chirp phase modulation with the laser intensity of 2.1×10^{12} W/cm^2 (b). Inset shows the schematic diagram of the cosinusoidal or chirp spectral phase modulation (dashed line) imposed on the laser spectrum (solid line).

the normalized SPF intensity of the IR144 solution as a function of the modulation period number β for $\alpha = \pi/2$ with the laser intensity of 1×10^{12} W/cm^2. The data are normalized by the SPF intensity induced by the transform-limited pulses. As can be seen, with the increase of the modulation period number β, the SPF intensity shows a fast increase following by a slow increase.

To further demonstrate that the SPF intensity of IR144 can be enhanced by the spectral phase modulation, we utilize a simpler phase modulation parameter with chirped function of $\phi(\omega) = \phi''(\omega - \omega_0)/2$, where ϕ'' is the linear chirp rate and ω_0 is the centre frequency of the laser spectrum, and the spectral phase modulation is shown in the inset of Figure 2b. Figure 2b shows the normalized SPF intensity of the IR144 solution as a function of the chirp rate ϕ'' with the laser intensity of 2.1×10^{12} W/cm^2. It can be seen that, with the increase of chirp rate ϕ'', the SPF intensity can be tremendously increased for both positive and negative chirp.

Since the single-photon absorption is a linear optical process, the laser spectral phase does not affect the single-photon transition probability, while it does in our experiment. To explore the physical control mechanism of the SPF enhancement, we measure the absorption spectrum of the IR144 solution, as shown in Figure 3a. It can be seen found that two distinct absorption bands around 218 and 741 nm are observed. Based on the laser wavelength and the absorption spectrum, the excitation process of IR144 in our experiment should be considered as a resonance-mediated (1 + 2) three-photon absorption, and the energy-level diagram is schematically plotted in Figure 3b. The population in the ground state S_0 is pumped to the intermediate excited state S_1 by single-photon transition, and then partial population is further excited to the final excited state S_2 by non-resonant two-photon transitions. We believe that the non-resonant two-photon absorption from the state $S_1 \rightarrow S_2$ results in the SPF enhancement of IR144.

To validate our proposed mechanism, we theoretically calculate the non-resonant two-photon transition probability P_2 from the state $S_1 \rightarrow S_2$. For the wideband absorption, i.e. the molecular absorption bandwidth is far larger than the laser spectral bandwidth, P_2 can be approximated as $P_2 \propto \int_{-\infty}^{+\infty} I^2(t)dt$ [22]. It indicates that P_2 depends on the temporal distribution of the laser intensity $I(t)$. It is easy to verify that, P_2 is maximal for the transform-limited pulse, and other intensity distributions can reduce P_2. Figure 4a and b show P_2 as a function of the modulation period number β for $\alpha = \pi/2$ and the chirp rate ϕ'', respectively. It can be seen that P_2 decreases with the increase of modulation period β or the chirp rate ϕ''. That is to say, comparing with the transform-limited pulses, P_2 will decrease by varying the spectral phase distribution.

According to the calculated results in Figure 4a and b, our experimental observation can be explained as follows. The single-photon transition probability from the state $S_0 \rightarrow S_1$ is uncontrollable by manipulating the spectral phase, while the non-resonant two-photon transition probability from the state $S_1 \rightarrow S_2$ can be manipulated. By shaping the spectral phase with the cosinusodial or chirped function, less population in the state S_1 is pumped to the state S_2, thus more population will reside in the state S_1, and therefore the SPF intensity from the state $S_1 \rightarrow S_0$ will increase.

Two-photon absorption is a nonlinear process, and so the laser intensity for two-photon absorption is much higher than that for sing-photon absorption. Thus the effect of two-photon absorption from the state $S_1 \rightarrow S_2$ on the population in the state S_1 can be eliminated by decreasing the laser intensity. So, we perform the experiment with the low laser intensity of 1×10^{10} W/cm^2, and the experimental results are presented in Figure 5. As can be seen, the SPF intensity keeps constant with the increase of the modulation period number β or chirp rate ϕ''. The experimental observation further confirms our proposed mechanism that the SPF intensity enhancement is due to the non-resonant two-photon absorption from the state $S_1 \rightarrow S_2$.

Finally, to make sure that the SPF enhancement in IR144 results from the non-resonant two-photon absorption from the state $S_1 \rightarrow S_2$, the effect of the state $S_2 \rightarrow S_1$ internal conversion must be considered. If the lifetime of the state S_1 is larger than that of the state $S_2 \rightarrow S_1$ internal conversion, the population depletion from the state $S_1 \rightarrow S_2$ will not affect the population in the state S_1. To exclude the possibility, we measure the time-resolved SPF

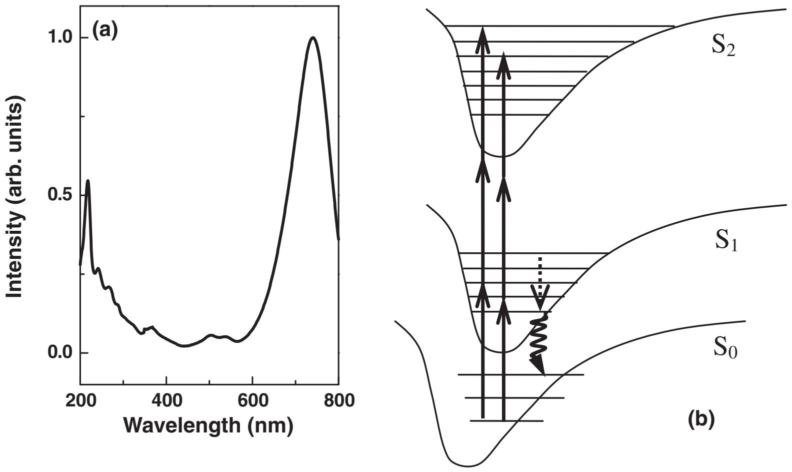

Figure 3. (a) The normalized absorption spectrum of IR144 in methanol solution, there are two distinct absorption bands around 741 and 218 nm. (b) The schematic diagram of resonance-mediated (1 + 2) three-photon absorption process.

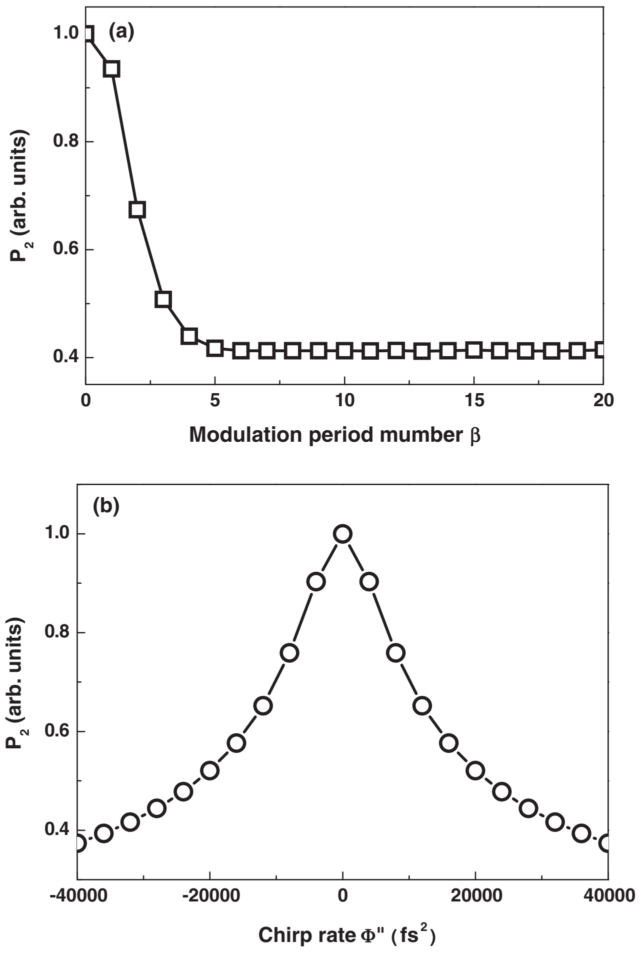

Figure 4. The calculated two-photon transition probability P_2 as a function of the modulation period number β with $\alpha = \pi/2$ for the cosinusodial phase modulation (a) and the chirp rate ϕ'' for the chirp phase modulation (b).

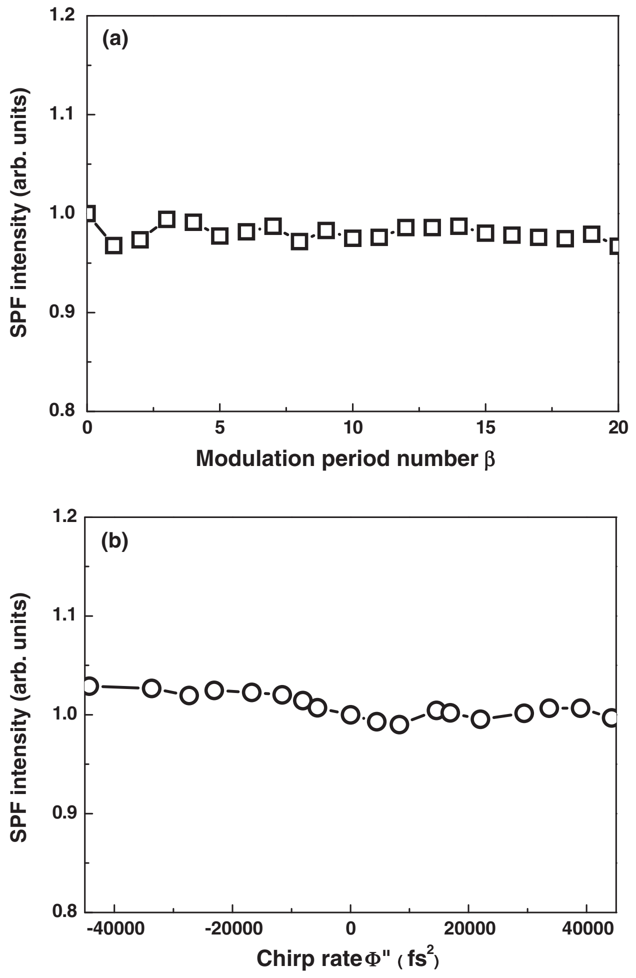

Figure 5. The normalized SPF intensity of IR144 in methanol as a function of the modulation period number β with $\alpha = \pi/2$ for the cosinusodial phase modulation (a) and the chirp rate ϕ'' for the chirp phase modulation (b) with the laser intensity of 1×10^{10} W/cm^2.

intensity using time-correlated single photon counting (TCSPC) technique [23], as shown in Figure 6. As can be seen, the SPF intensity in the decay shows monotonous decrease, this observation indicates that the state $S_2 \rightarrow S_1$ internal conversion does not occur in our measurement.

4. Conclusion

In conclusion, we have experimentally demonstrated that the SPF intensity in IR144 can be enhanced by shaping laser spectral

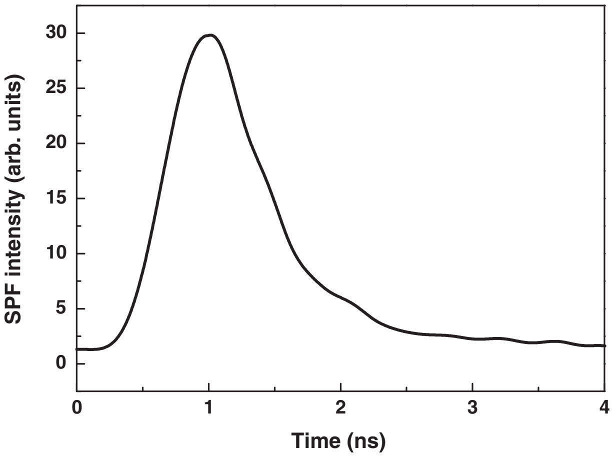

Figure 6. The time-resolved SPF intensity of IR144 in methanol solution measured using time-correlated single photon counting (TCSPC) technique.

phase with a cosinusodial or chirped function. The excitation process was described as resonance-mediated (1 + 2) three-photon absorption, and the SPF enhancement was attributed to the non-resonant two-photon absorption from the state $S_1 \rightarrow S_2$. Finally, the proposed mechanism was further confirmed by performing the SPF experiment with the low laser intensity, where the effect of the two-photon absorption from the state $S_1 \rightarrow S_2$ was eliminated. We believe that these results have potential application on the control of the single-photon fluorescence in resonance-mediated (1 + *N*) multiphoton absorption processes.

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