

Mechanism of polarization-induced single-photon fluorescence enhancement

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The single-photon fluorescence (SPF) of IR125 can be enhanced when the laser polarization changes from linear through elliptical to circular [A. Nag and D. Goswami, *J. Chem. Phys.* **132**, 154508 (2010)]. In this paper, we further explain and discuss the physical control mechanism. Our theoretical and experimental results demonstrate that the SPF enhancement can be attributed to the nonresonant two-photon absorption of a higher excited state. We conclude that the SPF intensity involving the nonresonant multiphoton absorption of the higher excited state can be controlled by varying the laser polarization. © 2010 American Institute of Physics. [doi:10.1063/1.3515480]

I. INTRODUCTION

The essential goal of the quantum coherent control making use of the pulse shaping method is to steer a quantum system towards a desired outcome by inducing a constructive or destructive interference among different optical pathways.¹⁻³ Laser polarization shaping has proved to be a powerful tool in coherent control, and been widely employed to manipulate various nonlinear optical processes, involving photochemical reaction,^{4,5} multiphoton absorption,^{6,7} and coherent anti-Stokes Raman spectroscopy.^{8,9} Furthermore, the laser polarization shaping combining with the spectral phase and/or amplitude modulation was usually suggested to increase the control degree and efficiency.^{10,11}

The manipulation of single-photon absorption (SPA) or single-photon fluorescence (SPF) has attracted considerable interest because of its potential application on fluorescence imaging spectroscopy and microscopy¹² and fluorescence correlation spectroscopy.¹³ Previous studies demonstrated that the SPA or SPF in the fluorescent dye molecules (LD690, LDS750, and IR125) can be enhanced with the negatively chirped pulses,^{14,15} and the enhancement mechanism was attributed to an intrapulse pump-dump process. A very recent study by Goswami *et al.* showed that the SPF intensity in IR125 could be modulated by varying the laser polarization, it increased as the laser polarization changed from linear through elliptical to circular,⁷ but this physical control mechanism was unclear. In this paper, we expect to explain the physical control process of polarization-induced SPF enhancement. We theoretically and experimentally demonstrate that the SPF enhancement results from the nonresonant two-photon absorption (TPA) of a higher excited state. Finally, our proposed mechanism is further confirmed by performing the SPF experiment in Coumarin 480 without the nonresonant multiphoton absorption of the higher excited state.

II. EXPERIMENT

In our experiment, a Ti-sapphire mode-locked regenerative amplifier (Spectra-Physics, Spitfire) is used as the excitation source with the pulse width [full width at half maximum (FWHM)] of about 50 fs, the center wavelength of 800 nm, and the repetition rate of 1 kHz. An attenuator is used to vary the laser intensity, and a quarter wave plate ($\lambda/4$ wave plate) is employed to vary the laser polarization from linear through elliptical to circular and vice versa. The polarization-shaped laser pulse is focused into a 10-mm quartz cuvette containing fluorescent dye IR125 with a lens of 500-mm focal length. The IR125 is purchased from Exciton company and used without further purification, it is dissolved in methanol solution with the concentration of 5×10^{-5} mol/l. The SPF is perpendicularly collected and measured by a spectrometer with charge-coupled device (CCD) (PI, Acton 2300i). The grating in the spectrometer is 1200 lines/mm, and its blaze wavelength is 750 nm. In all measurements, we do not observe the photobleaching phenomenon and supercontinuum spectrum generation, and the SPF intensity is very stable within our measurement time. Figure 1 shows the normalized UV-visible absorption spectrum of the IR125 solution (red line) and its normalized SPF spectrum (green line). There are two distinct absorption bands around 783 and 216 nm, respectively. The maximum of the SPF spectrum corresponds to 824 nm with the bandwidth (FWHM) of about 43 nm.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the SPF intensity of IR125 as a function of the $\lambda/4$ wave plate rotation angle φ with the laser intensity of 1.2×10^{11} W/cm² (red squares), 1.2×10^{10} W/cm² (green circles), and 1.2×10^9 W/cm² (blue triangles). As can be seen, the SPF intensity appears periodical modulation and achieves maximum at $\varphi = \pi/4, 3\pi/4, 5\pi/4,$ and $7\pi/4$ (i.e., the circular polarization) and minimum at $\varphi = 0, \pi/2, \pi,$ and $3\pi/2$ (i.e., the linear polarization). That is to say, when the laser polarization changes from linear through elliptical to circular, the SPF intensity will increase. The experimental

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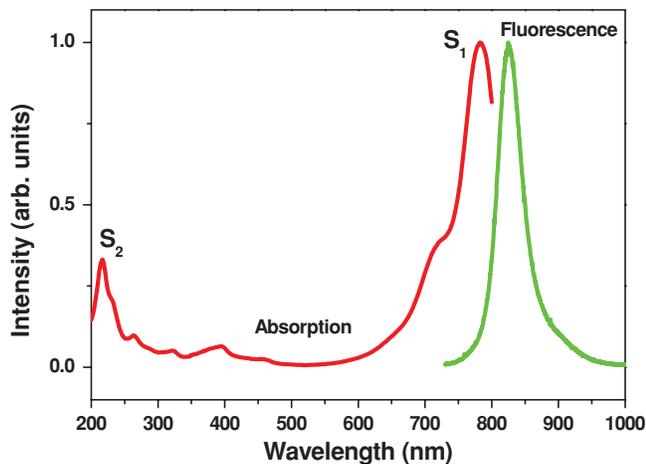


FIG. 1. Normalized UV-visible absorption spectrum of the IR125 in methanol solution (red line) and its normalized SPF spectrum induced by the 800-nm laser pulses (green line).

observation is good consistent with the previous study by Goswami *et al.*⁷ Furthermore, it can be found that, with the decrease of the laser intensity, the polarization-induced control efficiency decreases.

According to the laser wavelength and the absorption spectrum of the IR125 solution (see Fig. 1), the excitation process in our experiment should be described as resonance-mediated (1+2) three-photon absorption, and the energy-level diagram is schematically plotted in Fig. 3, here S_0 , S_1 , and S_2 represent the ground state, intermediate excited state, and final excited state, respectively. The population in S_0 is excited to S_1 by SPA, and then partial population is further pumped to S_2 by nonresonant TPA. We reasonably believe that the nonresonant TPA of the higher excited state S_2 results in the SPF enhancement in IR125.

Next, we theoretically discuss the influence of the nonresonant multiphoton absorption of S_2 on the population of S_1 by varying the laser polarization. We consider the

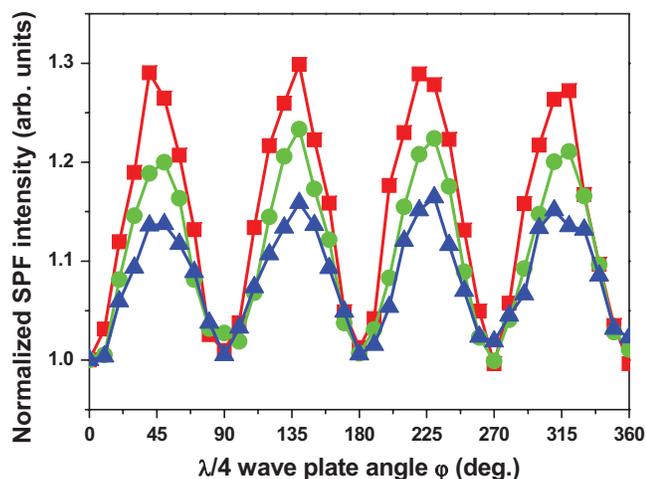


FIG. 2. Normalized SPF intensity of IR125 as a function of the $\lambda/4$ wave plate rotation angle φ with the laser intensity of 1.2×10^{11} W/cm² (red squares), 1.2×10^{10} W/cm² (green circles), and 1.2×10^9 W/cm² (blue triangles). The SPF intensity increases as the laser polarization changes from linear through elliptical to circular.

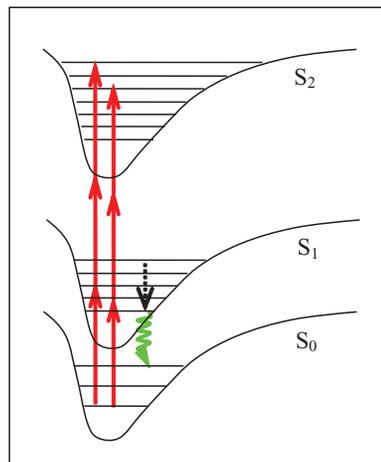


FIG. 3. The schematic energy-level diagram of resonance-mediated (1+2) three-photon absorption process.

interaction of a polarized laser field $\vec{E}(t)$ with a nonchiral isotropic molecular system, the N -photon transition probability can be approximated as¹⁶

$$P_N \propto \int_{-\infty}^{+\infty} G(\omega_a) \left| \int_{-\infty}^{+\infty} \vec{E}(t) \exp(i\omega_a t) dt \right|^2 d\omega_a, \quad (1)$$

where ω_a is the single-photon transition frequency from S_1 to S_2 , $G(\omega_a)$ represents the line-shape function correlated with the molecular absorption. Considering a laser field with linear polarization $\vec{E}(t) = A(t) \cos(\omega t) \vec{e}_x$ propagating in a quarter wave plate ($\lambda/4$ wave plate), the output laser field can be written as

$$\begin{aligned} \vec{E}_{\lambda/4}(t) = & A(t) \cos(\varphi) \cos(\omega t) \vec{e}_x \\ & + A(t) \sin(\varphi) \cos(\omega t + \pi/2) \vec{e}_y, \end{aligned} \quad (2)$$

here φ is the angle between the input laser polarization and the $\lambda/4$ wave plate optical axis. The output laser is linear polarization for $\varphi = 0, \pi/2, \pi$, and $3\pi/2$, circular polarization for $\varphi = \pi/4, 3\pi/4, 5\pi/4$, and $7\pi/4$, and elliptical polarization for other rotation angle φ . Thus, the N -photon transition probability can be expressed by

$$\begin{aligned} P_N \propto & \int_{-\infty}^{+\infty} G(\omega_a) \left| \int_{-\infty}^{+\infty} \{ [A(t) \cos(\varphi) \cos(\omega t)]^N \right. \\ & \left. + [A(t) \sin(\varphi) \cos(\omega t + \pi/2)]^N \} \exp(i\omega_a t) dt \right|^2 d\omega_a \\ \propto & [\cos^{2N}(\varphi) + \sin^{2N}(\varphi)] \int_{-\infty}^{+\infty} G(\omega_a) \\ & \times \left| \int_{-\infty}^{+\infty} \vec{E}(t) \exp(i\omega_a t) dt \right|^2 d\omega_a. \end{aligned} \quad (3)$$

If the molecular absorption is a wide line limit, the N -photon transition probability can be further simplified as

$$P_N \propto [\cos^{2N}(\varphi) + \sin^{2N}(\varphi)] \int_{-\infty}^{+\infty} I^N(t) dt. \quad (4)$$

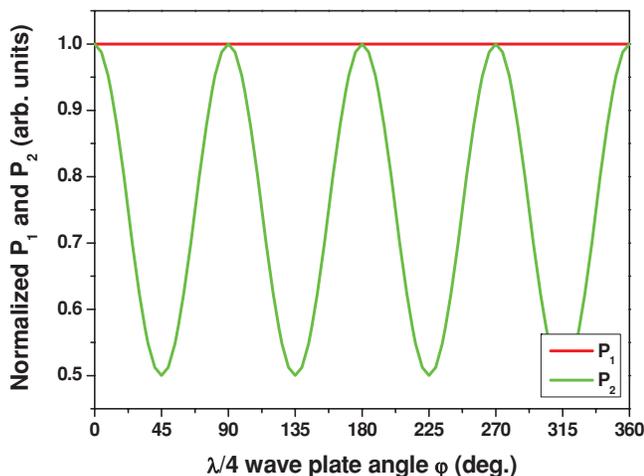


FIG. 4. Normalized single-photon transition probability P_1 (red line) and two-photon transition probability P_2 (green line) as a function of the $\lambda/4$ wave plate rotation angle φ . When the laser polarization changes from linear through elliptical to circular, the P_1 keeps constant while the P_2 decreases.

We calculate the single-photon transition probability P_1 and two-photon transition probability P_2 as a function of the $\lambda/4$ wave plate rotation angle φ , and the calculated results are presented in Fig. 4. As can be seen, when the laser polarization changes from linear through elliptical to circular, the P_1 (red line) keeps constant while the P_2 (green line) decreases. It is obvious that the laser polarization does not change the single-photon absorption, but it does tremendously affect the nonresonant multiphoton absorption. Therefore, above experimental observations can be intuitively understood as follows. The P_1 from S_0 to S_1 is equal for linear and circular polarization, while the P_2 from S_1 to S_2 for linear polarization is much larger than that for circular polarization. Thus, comparing with the linear polarization, more population will reside in S_1 for circular polarization, and therefore the SPF intensity increases as the laser polarization changes from linear through elliptical to circular. Furthermore, since the

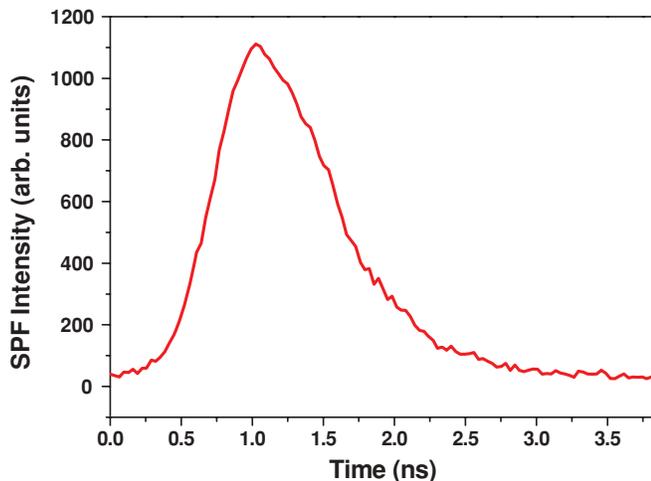


FIG. 5. The time-resolved SPF intensity of the IR125 solution measured with TCSPC technique.

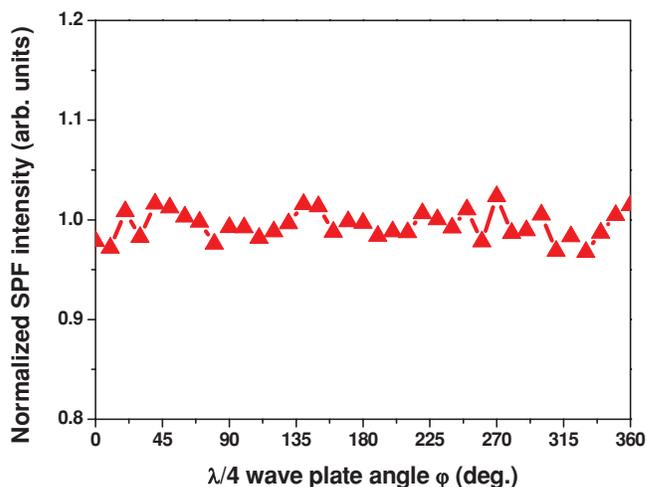


FIG. 6. Normalized SPF intensity of Coumarin 480 as a function of the $\lambda/4$ wave plate rotation angle φ . The SPF intensity keeps constant when the laser polarization changes from linear through elliptical to circular.

SPA and nonresonant TPA are, respectively, proportional to $P_1 \propto \int_{-\infty}^{\infty} I(t) dt$ and $P_2 \propto \int_{-\infty}^{\infty} I^2(t) dt$, decreasing the laser intensity will reduce the polarization-induced control efficiency, as shown in Fig. 2.

To ensure that the SPF enhancement in IR125 is due to the population depletion of $S_1 \rightarrow S_2$ by nonresonant TPA, we should consider the $S_2 \rightarrow S_1$ internal conversion, if the lifetime of the $S_2 \rightarrow S_1$ internal conversion is shorter than that of S_1 , this population depletion will not affect the $S_1 \rightarrow S_0$ fluorescence. To exclude the possibility, we measure the time-resolved SPF intensity using time-correlated single-photon counting (TCSPC) technique,¹⁷ and the experimental result is shown in Fig. 5. As can be seen, the SPF intensity in the decay is monotonous decrease. The experimental observation indicates that the $S_2 \rightarrow S_1$ internal conversion does not occur in our measurement, and its effect on the $S_1 \rightarrow S_0$ fluorescence can be excluded.

In order to further confirm our proposed mechanism, we perform the SPF experiment in Coumarin 480 without the nonresonant multiphoton absorption of the higher excited state. The Coumarin 480 is also dissolved in methanol solution with the concentration of 5×10^{-5} mol/l, and its absorption maximum corresponds to 390 nm, so we use the second-harmonic generation pulse at 400 nm generated by a 1-mm thickness type-I BBO nonlinear crystal as the excitation source. Figure 6 shows the SPF intensity of Coumarin 480 as a function of the $\lambda/4$ wave plate rotation angle φ . It can be seen that there is no difference in the SPF intensity between linear and circular polarization. The experimental result is in agreement with above theoretical expectation (see Fig. 4).

IV. CONCLUSION

In conclusion, we have theoretically and experimentally investigated the physical control mechanism of the SPF enhancement in IR125 as the laser polarization changed from linear through elliptical to circular, and the nonresonant two-photon absorption of a higher excited state was considered

as the essential contribution. Finally, we performed the SPF experiment in Courmarin 480 without the nonresonant multiphoton absorption of the higher excited state, and the SPF intensity kept constant, which further confirmed our proposed mechanism. We hope that these results will have potential application on fluorescence imaging and fluorescence correlation spectroscopy.

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