Article

# Enhancing Intermediate State Absorption of Resonance-Mediated Multiphoton Absorption Process

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ABSTRACT: We theoretically and experimentally demonstrate the control of the intermediate state absorption in (1+2) resonance-mediated multiphoton absorption process by shaping the femosecond laser pulse. A theoretical model is proposed to investigate the intermediate state absorption of (1+2) resonance-mediated three-photon absorption process in the molecular system, and an analytical solution is obtained on the basis of time-dependent perturbation theory. Our theoretical results show that the intermediate state absorption can be enhanced by controlling the laser spectral phase due to final state absorption reduction, and this absorption enhancement efficiency increases with the increase of the laser intensity. These theoretical results are experimentally confirmed in IR144 dye by varying the laser spectral phase with a sinusoidal modulation function.
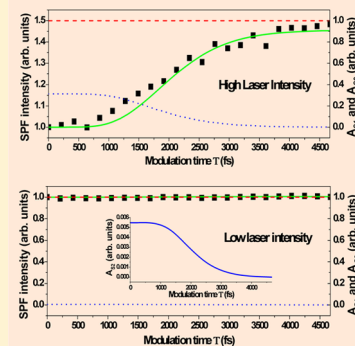
1. INTRODUCTION

Single-photon or multiphoton absorption (or fluorescence) in the molecular system has attracted widespread attention because of its potential applications on fluorescence correlation spectroscopy and fluorescence imaging spectroscopy and microscopy.[1,2] If the molecular absorption (or fluorescence) under the weak laser field can be effectively enhanced, its applications can be greatly extended. Recently, the coherent control strategy by making use of the femtosecond pulse shaping technique opens a new opportunity to manipulate the single-photon or multiphoton absorption (or fluorescence),[3−10] and several control schemes have been proposed to experimentally realize the single-photon or multiphoton absorption (or fluorescence) enhancement.[6−10] For example, Gerullo et al.[6] and Bardeen et al.[7] reported the single-photon fluorescence enhancement in LD690, LDS750, and IR125 dyes using a negatively chirped laser pulse. Lee et al.[8] realized the two-photon fluorescence enhancement in DCM dye by an optimal control based on evolutionary algorithm. Otake et al.[9] demonstrated the two-photon fluorescence enhancement in perylene dye by an adaptive feedback control with genetic algorithm. We achieved the two-photon fluorescence enhancement in Dichlorofluorecein dye by a phase-jump modulated laser pulse.[10]

In these previous studies,[3−10] the control of the final state absorption was primary considered. However, in actual experiments, the control of the target state was usually affected by its higher state. Recently, the intermediate state absorption control has attracted considerable interest. For example, Das et al.[11] reported the single-photon fluorescence enhancement of the (1+N) multiphoton absorption process in IR125 dye by the

laser polarization modulation. We demonstrated the single-photon fluorescence enhancement of the (1+2) resonance-mediated three-photon absorption process in IR125 and IR144 dyes by varying the laser polarization or spectral phase.[12,13] However, the single-photon fluorescence enhancement was just quantitatively explained by the higher excited state absorption.[11−13] To completely understand the physical control mechanism of the single-photon fluorescence enhancement, in this paper we establish a theoretical model to investigate the intermediate state absorption of the (1+2) resonance-mediated three-photon absorption process in the molecular system, and an analytical solution is obtained on the basis of time-dependent perturbation theory. We theoretically show that the intermediate state absorption can be enhanced by controlling the laser spectral phase due to final state absorption reduction, but the absorption enhancement depends on the laser intensity and the larger absorption enhancement is obtained for the higher laser intensity. We experimentally confirm these theoretical predictions in IR144 dye by a sinusoidal phase modulation.

2. THEORETICAL METHOD

Figure 1a shows the schematic diagram of the (1+2) resonance-mediated three-photon absorption process in the molecular system excited by the femtosecond laser pulse $E(t)$, where S_0, S_1, and S_2 are the ground state, intermediate state, and final
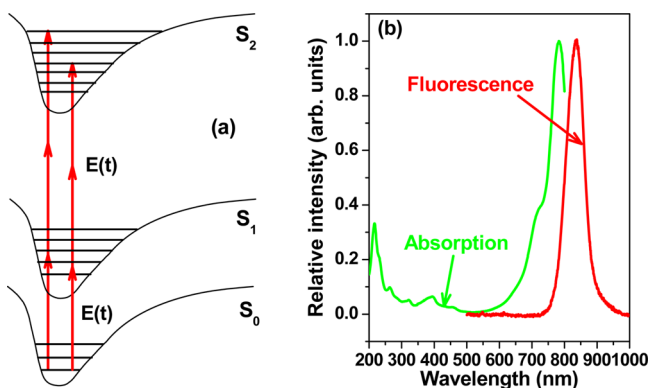
Figure 1. (a) Schematic diagram of the (1 + 2) resonance-mediated three-photon absorption process in the molecular system. (b) Absorption (green line) and fluorescence spectra (red line) of IR144 dye.

state, respectively. The transition from the S_0 to S_1 states is coupled by a single-photon absorption whereas the transition from the S_1 to S_2 states is coupled by a nonresonant two-photon absorption. Here, the $S_1 \rightarrow S_2$ state coupling originates from a manifold of intermediate V states that are far from resonance. In the present study, we consider the perturbative regime that the light−matter interaction can be well described by time-dependent perturbation theory. Thus, the S_1 state population P_{S1} of the (1+2) resonance-mediated three-photon absorption process can be given by

$$P_{S1} = A_{S1} - A_{S2} \tag{1}$$

where A_{S1} is the absorption in the S_1 state by the single-photon excitation process and A_{S2} is the absorption in the S_2 state by the (1+2) resonance-mediated three-photon excitation process, which is also corresponding to the absorption from the S_1 to S_2 states. In the molecular system with a broad absorption line, the multiphoton absorption is proportional to a sum of each individual transition. On the basis of the theoretical model of the atom system with narrow absorption line limit,[14,15] A_{S1} and A_{S2} can be written as

$$A_{S1} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} G(\omega_{S1}) | \int_{-\infty}^{+\infty} \mu_{S0 \rightarrow S1} E(t) \exp(i\omega_{S1}t) \, dt|^2$$

$$d\omega_{S1} \tag{2}$$

and

$$A_{S2} = \frac{1}{\hbar^6} \int_{-\infty}^{+\infty} G(\omega_{S2}) | \int_{-\infty}^{+\infty} G(\omega_{S1}) \sum_V \mu_{S0 \rightarrow S1} \mu_{S1 \rightarrow V} \mu_{V \rightarrow S2}$$

$$\times \int_{-\infty}^{+\infty} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} E(t_1) E(t_2) E(t_3) \exp[i(\omega_{S2} - \omega_V)t_1]$$

$$\times \exp[i(\omega_V - \omega_{S1})t_2] \exp(i\omega_{S1}t_3) \, dt_3 \, dt_2 \, dt_1 \, d\omega_{S1}|^2 \, d\omega_{S2} \tag{3}$$

where $\hbar$ is the Planck constant, $G(\omega_{S1})$ and $G(\omega_{S2})$ are the absorption line-shape functions in the S_1 and S_2 states, $\mu_{S0 \rightarrow S1}$, $\mu_{S1 \rightarrow V}$, and $\mu_{V \rightarrow S2}$ are the dipole matrix elements between a pair of states, and ω_{S1}, ω_V, and ω_{S2} are corresponding to the energy differences between the states S_0 and S_1, S_0, and V, and S_0 and S_2. By transforming eqs 2 and 3, we can further write A_{S1} and A_{S2} as

$$A_{S1} = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} G(\omega_{S1}) |\mu_{S0 \rightarrow S1} E_0 \tilde{E}(\omega_{S1})|^2 \, d\omega_{S1} \tag{4}$$

and

$$A_{S2} = \frac{\pi}{2\hbar^6} \int_{-\infty}^{+\infty} G(\omega_{S2}) | \int_{-\infty}^{+\infty} G(\omega_{S1}) \mu_{S0 \rightarrow S1} \mu_{S1 \rightarrow S2} E_0^3 \tilde{E}(\omega_{S1})$$

$$\times \int_{-\infty}^{+\infty} \tilde{E}(\omega) \tilde{E}(\omega_{S2} - \omega_{S1} - \omega) \, d\omega \, d\omega_{S1}|^2 \, d\omega_{S2} \tag{5}$$

where $\mu_{S1 \rightarrow S2}$ is the effective nonresonant two-photon coupling between the S_1 and S_2 states, E_0 is the peak spectral amplitude, and $\tilde{E}(\omega)$ is the normalized spectral field with $\tilde{E}(\omega) = E(\omega)/E_0$; here $E(\omega)$ is given by the Fourier transform of $E(t)$ with $E(\omega) = A(\omega) \exp[i\Phi(\omega)]$, and $A(\omega)$ and $\Phi(\omega)$ are the spectral amplitude and phase, respectively. Thus, the S_1 state population P_{S1} can be further simplified as

$$P_{S1} = \frac{E_0^2 \mu_{S0 \rightarrow S1}^2}{\hbar^2} \Big[\int_{-\infty}^{+\infty} G(\omega_{S1}) |\tilde{E}(\omega_{S1})|^2 \, d\omega_{S1}$$

$$- \frac{\pi E_0^4 \mu_{S1 \rightarrow S2}^2}{2\hbar^4} \int_{-\infty}^{+\infty} G(\omega_{S2}) | \int_{-\infty}^{+\infty} G(\omega_{S1}) \tilde{E}(\omega_{S1})$$

$$\times \int_{-\infty}^{+\infty} \tilde{E}(\omega) \tilde{E}(\omega_{S2} - \omega_{S1} - \omega) \, d\omega \, d\omega_{S1}|^2 \, d\omega_{S2} \Big] \tag{6}$$

It is easy to verify that the first term in eq 6 (i.e., A_{S1}) is independent of the laser spectral phase and therefore is uncontrollable, but the second term (i.e., A_{S2}) is at maximal value for the transform-limited laser pulse and can be effectively suppressed by varying the laser spectral phase. Because the three-photon absorption A_{S2} can be suppressed and the single-photon absorption A_{S1} is uncontrollable, the S_1 state population P_{S1} (i.e., intermediate state absorption) can increase by rationally designing the laser spectral phase. The single-photon absorption A_{S1} is proportional to the laser intensity (i.e., E_0^2) and the three-photon absorption A_{S2} is proportional to the cube of the laser intensity (i.e., E_0^6), and thus the laser intensity will affect the enhancement efficiency of the intermediate state absorption and the higher laser intensity will yield the larger enhancement efficiency.

3. EXPERIMENTAL RESULTS AND DISCUSSION

To verify the intermediate state absorption enhancement in the (1+2) resonance-mediated three-photon excitation process, we perform the experiment in IR144 dye, which was purchased from Exciton Company and used without further purification. In our experiment, IR144 dye is dissolved in methanol solution and its concentrations is 5×10^{-5} mol/L. The experimental arrangement is schematically shown in Figure 2. A Ti−sapphire mode-locked regenerative amplifier (Spectra-physics, Spitfire) is used as the excitation source with the pulse width of about 50 fs, the central wavelength of 800 nm and the repetition rate of 1 kHz. The output laser pulse is sent into a programmable 4f configuration zero-dispersion pulse shaper, which is composed of a pair of diffraction gratings with 1200 lines/mm, a pair of concave mirrors with focal length of 200 mm, and a one-dimension liquid-crystal spatial light modulator (SLM-S320d, JENOPTIK), and the SLM is placed at the Fourier plane and utilized to control the laser spectral phase in frequency domain. The phase-shaped femtosecond laser pulse is focused into a 10 mm quartz cuvette full of IR144 dye with a lens of 500 mm focal length. The fluorescence signal is perpendicularly collected and measured by a spectrometer with charge-coupled device (CCD).
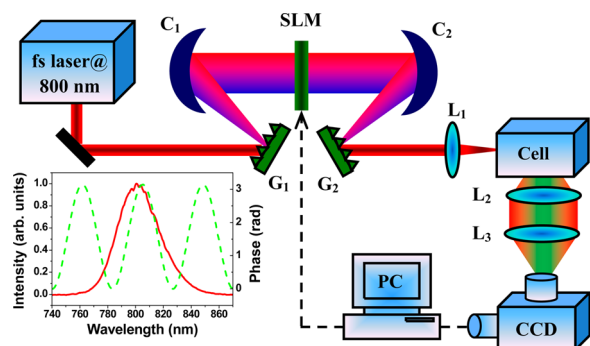
Figure 2. (a) Schematic diagram of the experimental arrangement. The output femtosecond laser pulse is shaped by a 4f-configuration pulse shaping system combined with a one-dimension liquid-crystal spatial light modulator (SLM-S320d, JENOPTIK). The inset shows the laser spectrum modulated by a sinusoidal phase modulation.

Figure 1b shows the absorption (green solid line) and fluorescence spectra (red solid line) of IR144 dye. There are two distinct broadband absorption peaks around the wavelength of 216 and 785 nm, which are corresponding to the S_1 and S_2 states. The fluorescence peak position is at 837 nm, corresponding to single-photon fluorescence (SPF), which results from the S_1 to S_0 state transition. In our experiment, we utilize a sinusoidal phase modulation to control the single-photon fluorescence of IR144 dye, and the spectral phase modulation is shown in the inset of Figure 2. The sinusoidal phase modulation can be defined by the function of $\Phi(\omega) = A \sin[T(\omega-\omega_0)]$, where ω_0 is the laser central frequency and A and T represent the modulation amplitude and modulation time, respectively. The sinusoidal phase modulation in frequency domain leads to a sequence of subpulses in time domain,[16−18] and the modulation amplitude A and the modulation time T are used to control the number and temporal separation of these subpulses, respectively.

We first demonstrate the single-photon fluorescence intensity control of IR144 dye by varying the laser intensity, and the experimental measurement and the theoretical calculation from eq 6 are presented in Figure 3, together with the single-photon absorption in the S_1 state A_{S1} (red dashed line) and the three-photon absorption in the S_2 state A_{S2} (blue dashed line). With the increase of the laser intensity, the single-
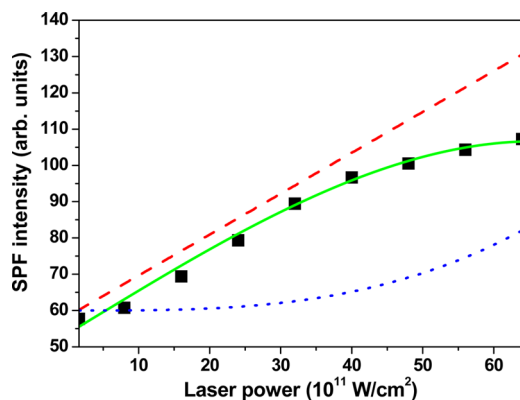

Figure 3. Experimental (black squares) and theoretical (green solid line) single-photon fluorescence intensity by varying the laser intensity. The single-photon absorption A_{S1} (red dashed line) and the three-photon absorption A_{S2} (blue dotted line) are also presented.

photon absorption A_{S1} is proportional to the laser intensity and therefore is a monotonous increase, whereas the three-photon absorption A_{S2} is proportional to the cube of the laser intensity and therefore is a slow and then fast increase, and thus the S_1 state population P_{S1} or single-photon fluorescence intensity shows a fast and then slow increase. Obviously, these theoretical results are in good agreement with our experimental measurement.

Figure 4 shows the normalized experimental (black squares) and theoretical (green solid line) single-photon fluorescence
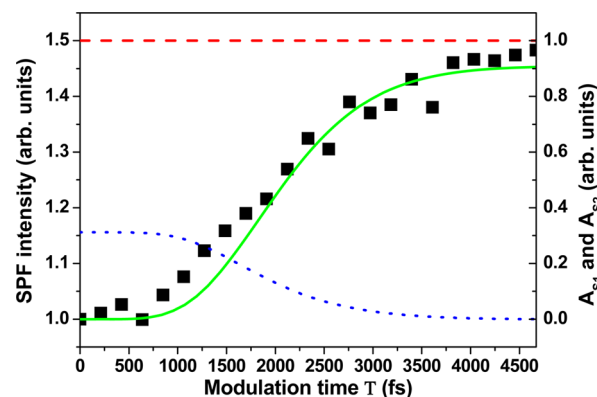

Figure 4. Normalized experimental (black squares) and theoretical (green solid line) single-photon fluorescence intensity as the function of the modulation time T for the modulation amplitude $A = \pi$ with the laser intensity of 4.8×10^{12} W/cm^2, together with the single-photon absorption A_{S1} (red dashed line) and the three-photon absorption A_{S2} (blue dotted line).

intensity as the function of the modulation time T for the modulation amplitude $A = \pi$ with the laser intensity of 4.8×10^{12} W/cm^2, and the single-photon absorption in the S_1 state A_{S1} (red dashed line) and the three-photon absorption in the S_2 state A_{S2} (blue dotted line) are also presented. All experimental data are normalized by the transform-limited laser pulse excitation, and hereafter the same method is utilized. As can be seen, by increasing the modulation time T, the single-photon absorption A_{S1} is constant, and the three-photon absorption A_{S2} can be effectively suppressed, and therefore the S_1 state population P_{S1} or single-photon fluorescence intensity can greatly increase. This experimental observation is consistent with above theoretical prediction.

To demonstrate the effect of the laser intensity on the intermediate state absorption enhancement, we present the normalized experimental (black squares) and theoretical (green solid line) single-photon fluorescence intensity as the function of the modulation time T for the modulation amplitude $A = \pi$ with the laser intensity of 4.8×10^{11} W/cm^2, and also the single-photon absorption in the S_1 state A_{S1} (red dashed line) and the three-photon absorption in the S_2 state A_{S2} (blue dotted line) are given together, as shown in Figure 5. One can see that the S_1 state population P_{S1} or single-photon fluorescence intensity almost cannot increase and therefore its enhancement efficiency is tremendously reduced. Inset shows the enlarged diagram of the three-photon absorption in the S_2 state A_{S2}. It can be seen that the three-photon absorption A_{S2} can also be effectively suppressed, which is the same as that in Figure 4 with the higher laser intensity of 4.8×10^{12} W/cm^2, whereas the three-photon absorption A_{S2} is far smaller than the single-photon absorption A_{S1}, which leads to the enhancement
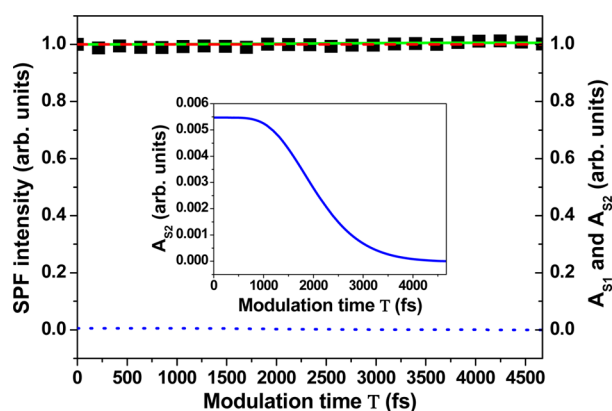
Figure 5. Normalized experimental (black squares) and theoretical (green solid line) single-photon fluorescence intensity as a function of the modulation time T for the modulation amplitude $A = \pi$ with the laser intensity 4.8×10^{11} W/cm^2, together with the single-photon absorption A_{S1} (red dashed line) and the three-photon absorption A_{S2} (blue dotted line). The inset shows the enlarged diagram of the three-photon absorption A_{S2}.

efficiency reduction of the S1 state population P_{S1} or single-photon fluorescence intensity.

4. CONCLUSIONS

In conclusion, we have presented a theoretical model to investigate the intermediate state absorption of the (1+2) resonance-mediated three-photon absorption process in the molecular system and obtained an analytical solution based on time-dependent perturbation theory. Our theoretical results showed that, by controlling the laser spectral phase, the intermediate state absorption can be enhanced due to the final state absorption reduction, but the laser intensity will affect the absorption enhancement and the higher laser intensity can yield the larger absorption enhancement. We experimentally validated the intermediate absorption enhancement in IR144 dye by a sinusoidal phase modulation and the effect of the laser intensity on the absorption enhancement. Our theoretical and experimental results can be further extended to understand and control the intermediate absorption enhancement of various resonance-mediated multiphoton absorption processes, and have significant applications on molecular fluorescence spectroscopy and imaging.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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