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Optimal feedback control of two-photon fluorescence in Coumarin 515 based on genetic algorithm

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Abstract

An optimal feedback control of two-photon fluorescence in the Coumarin 515 ethanol solution excited by shaping femtosecond laser pulses based on genetic algorithm is demonstrated experimentally. The two-photon fluorescence intensity can be enhanced by ~20%. Second harmonic generation frequency-resolved optical gating traces indicate that the optimal laser pulses are positive chirp, which are in favor of the effective population transfer of two-photon transitions. The dependence of the two-photon fluorescence signal on the laser pulse chirp is investigated to validate the theoretical model for the effective population transfer of two-photon transitions. The experimental results appear the potential applications in nonlinear spectroscopy and molecular physics.

1. Introduction

Recently, coherent control has attracted considerable interests for the ability to steer a quantum system towards a desired outcome through its interaction with light field and suppress other possible paths to undesirable outcomes [1–6]. The traditional approaches to quantum control explicitly require calculating the quantum dynamics and optimizing the light field with the exact knowledge of the molecular potential energy surfaces [7]. However, as to large molecules, it is difficult to acquire the detail information of the molecular system, and the resulting laser field is often quite complicated and even impossible to be realized in the laboratory under the present technology. Fortunately, a feedback-loop technique has been successfully developed to optimize efficiently the laser field without any prior knowledge of the atomic or molecular system [8–16]. Now, it has been widely applied on physical, chemical and biological processes, including adaptive pulse compression [8,9], manipulation of one or two-photon transitions in the atomic system [1,10], vibrational dynamics in the molecular system [11], molecular electronic population transfer [12], high harmonic generation [13], photodissociation channels [14], stimulated Raman scattering [15], coherent anti-Stokes Raman scattering [16] and the energy-flow pathways in light harvesting [17].

The key for feedback-loop control is the evolutionary algorithms [18,19]. Genetic algorithm (GA) [20] is one of the most important evolutionary algorithms, which is probabilistic search algorithms inspired by mechanisms of natural selection with some advantages. Its intelligence can organize the whole searching process with the information obtained in the evolution, and its parallelism has adequacy for large-scale evolution computation and capacity for searching several regions in the solution space

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at the same time. For the femtosecond laser pulses, two-photon transitions can be generated in all frequency components of the laser pulses as long as the sum of two-photon energies equals the energy difference between the ground and excited states. Meshulach and Silberberg [1] firstly achieved experimentally the coherent control of the two-photon transitions in cesium gas. Dayan and co-workers [6] demonstrate experimentally and theoretically coherent control of two-photon absorption with broadband down-convert light in rubidium gas. It is a challenge for quantum coherent control in the complicated molecular system because it is too complicated to exactly model. Brixner and co-workers [21] have successfully manipulated the ratio of two-photon fluorescence from two different molecules by the adaptive shaping pulse. In this Letter, we present an optimal feedback control of two-photon fluorescence in Coumarin 515 based on genetic algorithm, and the two-photon fluorescence can be enhanced by ~20%, and the dependence of two-photon fluorescence on the laser pulse chirp is further investigated to validate the theoretical model for the effective population of two-photon transitions.

2. Experiment

A Ti:sapphire mode-locked laser (Spitfire regenerative amplifier from Spectra-Physics Co.) is used as the excitation laser with the pulse duration of 50 fs, the repetition rate of 1 kHz and the center wavelength of 800 nm. The programmable 4-f pulse shaper is composed of a pair of diffraction gratings with 1200 lines/mm and a pair of spherical mirrors with a 150-mm focal length. A one-dimensional programmable liquid-crystal spatial light modulator array (SLM-256, CRI) is placed at the Fourier plane as an updatable filter for the spectral manipulation of the incident pulses. The shaped laser pulses are focused on the ethanol solution of Coumarin 515 with a lens of 20-mm focal length, and the laser intensity at the focus is estimated to be $\sim 3.1 \times 10^{16}$ W/cm^2. The two-photon fluorescence signal is detected by a photomultiplier and amplified by a lock-in. A computer is served for recording the data, evaluating the cost function, optimizing the spectral filter and updating SLM-256, and genetic algorithm is used as the optimal algorithm of feedback control. The original and optimal laser pulses are measured by second harmonic generation frequency-resolved optical gating (SHG–FROG) technique [22,23].

3. Results and discussion

To demonstrate the optimal feedback control of two-photon fluorescence, we perform the experiment in the Coumarin 515 ethanol solution. Its molecular structure, absorption and fluorescence spectra are shown in Fig. 1, together with the schematic diagram of two-photon transitions. The maximum of the absorption band is near ~410 nm, and its FWHM is about 56 nm. Two-photon transitions can occur in all pairs of photons (ω_0-Ω, Ω), where ω_0 is the one-photon transition frequency, and both ω_0-Ω and Ω lie within the spectrum band of the excited femtosecond laser pulses. As shown in Fig. 2b, two-photon fluorescence can be observed from about 440 to 630 nm, and its corresponding peak is at about 482 nm.

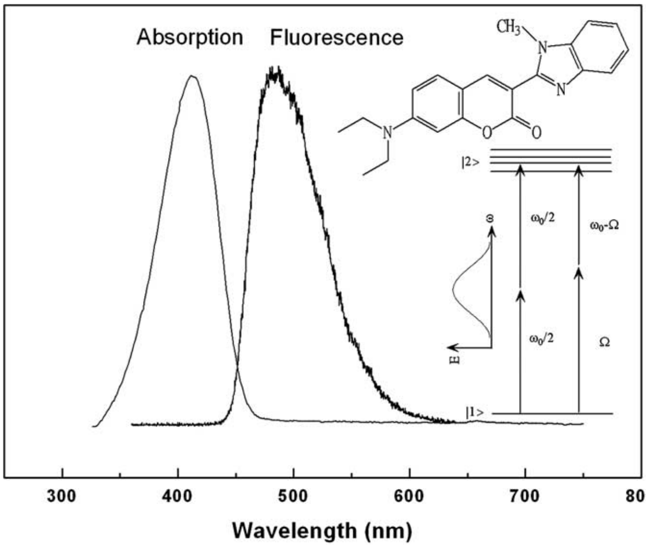

Fig. 1. The molecular structure, the absorption and fluorescence spectra of Coumarin 515, together with the schematic diagram of two-photon transition.

In the optimal feedback control experiment, genetic algorithm is used for global optimization of the spectral mask for the amplitude and phase of the laser pulses. Each of iteration in the genetic algorithm allows a change in all of the pixels of the spectral amplitude and phase mask and a decision whether the change is either accepted or rejected according to the calculated cost value. Firstly, the initial voltage values are generated randomly and applied to SLM-256 as the first generation, and their impacts on the two-photon fluorescence intensity are evaluated. Secondly, the fitness is calculated and the cost value is obtained, and then the voltage values of the new spectral mask for the second generation can be attained by genetic algorithm operation (select, crossover and mutate). Finally, the above-mentioned optimization procedure is repetitively performed till the cost value approaches convergence. Fig. 2a shows the dependence of the two-photon fluorescence intensity at 482 nm on the iteration number. Two-photon fluorescence signal achieves the optimal maximum after 31 generations, and the two-photon fluorescence spectra excited by the original (solid line) and optimal (dot line) pulses are presented in Fig. 2b. It is shown that two-photon fluorescence can be effectively enhanced by ~20%. In order to further explore its mechanisms, second harmonic generation frequency resolved optical gating (SHG-FROG) technique is used to measure the original and optimal laser pulses (as shown in Fig. 3). The SHG-FROG traces indicate that the original pulse is near transform-limited pulse with the slightly negative chirp, and the optimal pulse is

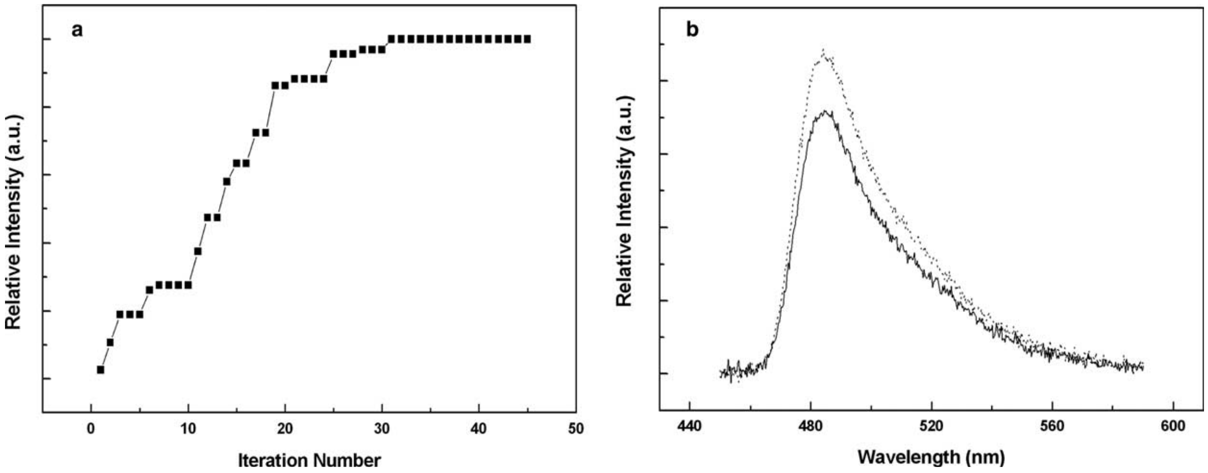

Fig. 2. (a) Optimal feedback signal as a function of the iteration number based on genetic algorithm. (b) The two-photon fluorescence spectra of Coumarin 515 excited by the original (solid line) and optimal (dot line) pulses.

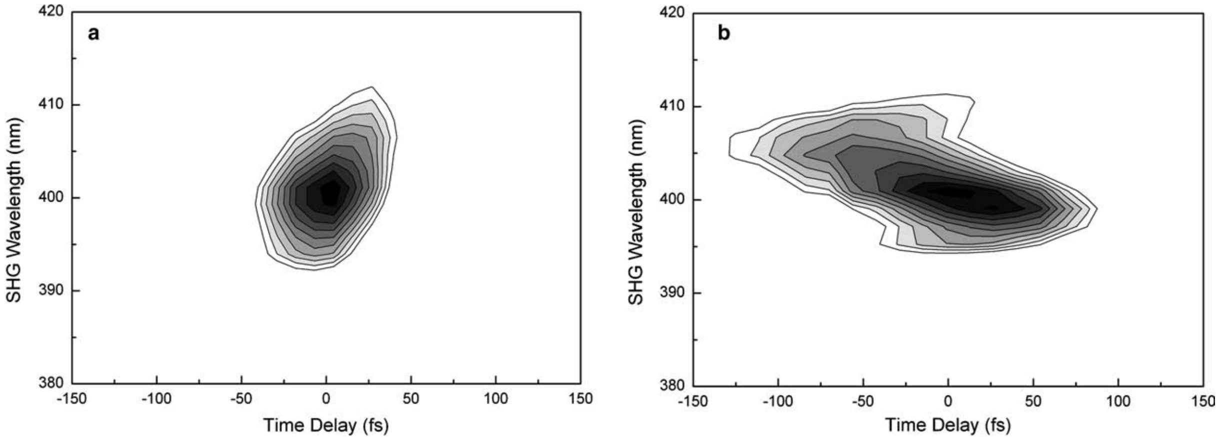

Fig. 3. Second-harmonic generation frequency resolved gating (SHG-FROG) traces for the original (a) and optimal (b) pulses.

positively chirped pulse. It means that the positively chirped pulse is in favor of the effective enhancement of two-photon fluorescence in the Coumarin 515 ethanol solution.

A theoretical model for the above-mentioned results is illustrated in Fig. 4, and the ground and excited states of Coumarin 515 are labeled S_0 and S_1, respectively. When a broadband femtosecond laser pulse interacts with the molecular system, the population in the ground states can be excited to higher ro-vibrational excited states by two-photon transitions, and the motion of the non-equilibrium population on higher ro-vibrational excited states results in a dynamic Stokes shift to lower ro-vibrational excited states. For a negatively chirped pulse, the ordering of the frequency components is from blue to red, the blue components firstly pump the population up to higher ro-vibrational excited state, which evolves for a brief period and shifts to lower ro-vibrational excited states, and then can be dumped back to the ground states by the delayed red components of laser pulses. The pump–evolve–dump process may result in the decrease of pure two-photon population and the suppression of two-photon florescence. However, a positively chirped pulse suppresses the above-mentioned pump–evolve–dump process, and it is in favor for the increase of pure two-photon population and the enhancement of two-photon fluorescence. Moreover, a transform-limited pulse should fall somewhere in between the positively and negatively chirped pulses. So, a positively chirped pulse can be in favor of the effective population transfer in the two-photon transitions and the effective enhancement in two-photon fluorescence of the Coumarin 515 ethanol solution.

In order to demonstrate the above-mentioned hypothesis, we investigate the dependence of the two-photon fluorescence intensity on the laser pulse chirps (as shown in Fig. 5). Note that varying the pulse chirps does not change the pulse energy and the power spectrum. For the two-photon transitions in the broad absorption band of molecular system, on the one hand, the positive chirp is in favor of the effective population transfer in two-photon transitions, whereas pump–evolve–dump process for the negative chirp goes against two-photon population. On the other hand, two-photon transition probability greatly depends on the intensity of laser pulses [4], namely, the

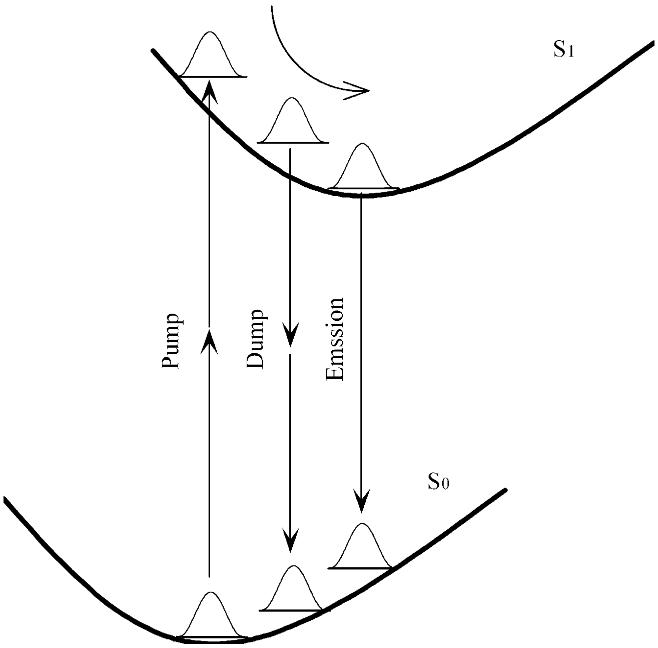

Fig. 4. Schematic diagram for the wave packet dynamics excited by a femtosecond laser pulse.

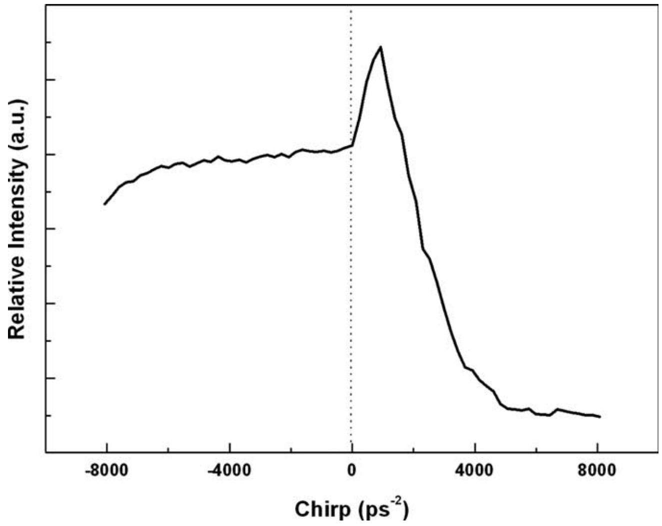

Fig. 5. Two-photon fluorescence intensity as a function of the pulse chirps in the Courmain 515 ethanol solution.

two-photon transition probability is proportional to $S \propto \int_{-\infty}^{\infty} I^2(t)\,\mathrm{d}t$. For a given pulse energy and power spectrum, with the laser pulse chirp increasing, the laser pulses are broadened, and thus $\int_{-\infty}^{\infty} I^2(t)\,\mathrm{d}t$ decreases. For the positive chirp, the two-photon fluorescence intensity lies on the balance between the advantage of the positive chirp and the disadvantage of the pulse broadening to the two-photon transitions. Consequently, with the increase of the positive chirp, the two-photon fluorescence signal exhibits a slow increase followed by a fast decrease. Furthermore, with the negative chirp increasing, the two-photon fluorescence intensity should show fast decrease for the disadvantage of the pulse broadening and pump–evolve–dump process. However, it does not, which may arise from the compensation of the negative laser pulse chirp for the positive dispersion of the solution. Accordingly, two-photon fluorescence intensity shows the asymmetric dependence on the laser pulse chirp (as shown in Fig. 5).

4. Conclusions

In summary, we have shown the optimal feedback control of the two-photon transition in a molecular system (Coumarin 515) based on genetic algorithms, and the two-photon fluorescence intensity can be enhanced by ~20%. Second harmonic generation frequency-resolved optical gating (SHG-FROG) trances indicate that the optimal pulse is a positively chirped pulse. The dependence of the two-photon fluorescence intensity on the laser pulse chirp indicates that a positively chirped pulse can be in favor of the effective population transfer of two-photon transitions and the effective enhancement of two-photon fluorescence. The experimental results appear the potential applications in nonlinear spectroscopy and molecular physics.

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