# Coherent control of non-resonant two-photon transition in molecular system*

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In this paper, we study theoretically and experimentally the coherent control of non-resonant two-photon transition in a molecular system (Perylene dissolved in chloroform solution) by shaping the femtosecond pulses with simple phase patterns (cosinusoidal and $\pi$ phase step-function shape). The control efficiency of the two-photon transition probability is correlated with both the laser field and the molecular absorption bandwidth. Our results demonstrate that, the two-photon transition probability in a molecular system can be reduced but not completely eliminated by manipulating the laser field, and the control efficiency is minimal when the molecular absorption bandwidth is larger than twice the laser spectral bandwidth.

**Keywords:** two-photon transition, coherent control, pulse shaping
**PACC:** 3280Q, 4255B, 4265B

Quantum control strategy can steer a quantum system towards the desired target states or products by the light–matter interaction, and therefore has attracted considerable interest in various subjects. With the development of the ultrafast laser technique, now it is possible to shape such an ultrashort laser pulse into any arbitrary temporal shape by the spectral amplitude and/or phase modulation. Recently, the coherent control by shaping femtosecond pulse has been successfully applied in various nonlinear optical processes, such as one- and two-photon transition,[1] multiphoton ionisation,[2] photodissociation,[3] high harmonic generation,[4] coherent anti-Stokes Raman scattering spectroscopy,[5] atomic optics,[6] and so on.

Two-photon transition is a typical nonlinear optical process, where the two photons are simultaneously absorbed to excite a quantum system, as shown in Fig. 1(a). So far, the coherent control of two-photon transition has been widely investigated by manipulating the femtosecond pulse.[7−21] In an atomic system, the energy level structure is comparatively simple, so the pre-designed pulse can maximally meet the experimental requirement and the physical control mechanism is also easily described and understood. However, in a molecular system, it is difficult to design the optimal laser field due to its complicated energy level structure. The adaptive feedback control technique based on a certain learning algorithm can automatically optimise the laser field without any information about the molecular system, but the automatic optimisation is usually difficult to indentify the physical control mechanism that corresponds to the optimal laser field. Therefore, it is necessary to investigate the coherent control of two-photon transition in a molecular system with pre-designed pulse and to achieve the corresponding physical control mechanism; thus, more complicated control processes can be understood based on the theoretical evaluation. In this paper, we investigate experimentally and theoretically the coherent control of non-resonant two-photon transition in a molecular system with the simple spectral phase modulation pattern ($\pi$ phase step and cosinusoidal modulation). We demonstrate that the two-photon transition probability can be reduced but not completely eliminated by manipulating the laser field, and the control efficiency depends on the molecular absorption bandwidth, which is minimal when the molecular absorption bandwidth is larger than twice the laser spectral bandwidth.

Consider the non-resonant two-photon interaction

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of a weak ultrashort pulse $E(t)$ with a two-level molecular system, as shown in Fig. 1(a). Here, $S_0$ and $S_1$ represent the ground and excited states, respectively. The two-photon transition probability induced by the ultrashort pulse can be approximated by time-dependent perturbation theory as[8]

$$S_2 = \int_{-\infty}^{\infty} g(\omega_0) \left| \int_{-\infty}^{\infty} E^2(t) \exp(\mathrm{i}\,\omega_0 t)\,\mathrm{d}t \right|^2 \mathrm{d}\omega_0$$
$$= \int_{-\infty}^{\infty} g(\omega_0) \left| \int_{-\infty}^{\infty} E(\omega)\, E(\omega_0 - \omega)\,\mathrm{d}\omega \right|^2 \mathrm{d}\omega_0,$$

where $E(\omega) = A(\omega)\exp[\mathrm{i}\,\Phi(\omega)]$ is the Fourier transform of $E(t)$, $\omega_0$ is the transition frequency from the ground state to the excited state, and $g(\omega_0)$ is the molecular absorption line-shape function. As can be seen from the above equation, the control efficiency of the two-photon transition probability in a molecular system is correlated with two factors: the molecular absorption distribution $g(\omega_0)$ and the laser field $E(\omega)$. In this work, we investigate the influence of the molecular absorption bandwidth and the shaped laser field on the coherent control of the two-photon transition probability.

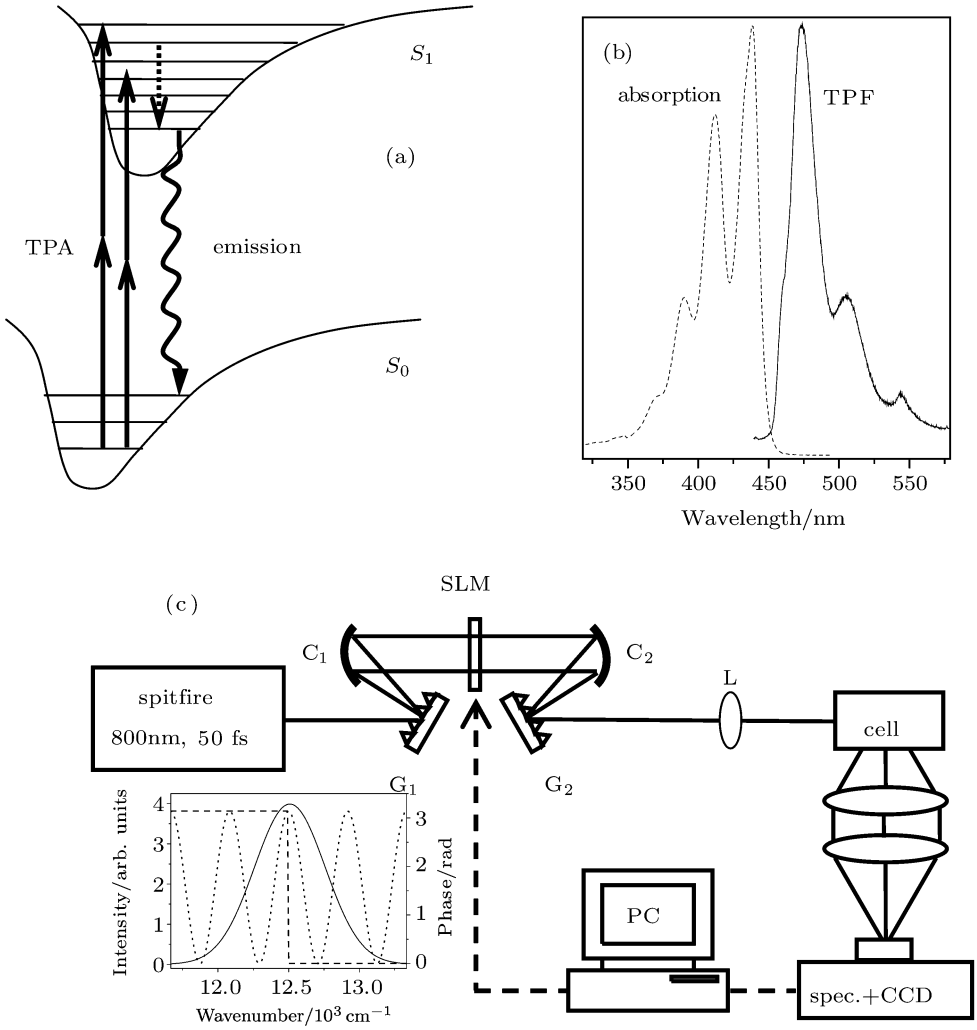


**Fig. 1.** (a) The schematic diagram of two-photon transition in a molecular system (TPA=two-photon absorption). (b) The absorption and fluorescence spectra of Perylene dissolved in chloroform solution. (c) Experimental setup for coherent phase control of non-resonant two-photon transition in the molecular system (SLM=spatial light modulator; PC=personal computer; CCD=charge-coupled device). Inset shows the spectral phase manipulation with $\pi$ step (dashed line) and cosinusoidal modulation (dotted line).

To demonstrate the coherent control of two-photon transition in the molecular system, we perform the experiment with Perylene dissolved in chloroform solution, and its absorption and emission spectra are shown in Fig. 1(b). The maximum of absorption band is at 438 nm with bandwidth [full width at half maximum (FWHM)]

of about 41 nm, and the maximum of emission band is at 473 nm with the bandwidth of about 24 nm. The experimental arrangement is schematically shown in Fig. 1(c). A Ti:sapphire regenerative amplifier (Spitfire, Spectra Physics) serves as the excitation source with the centre wavelength of 800 nm, spectral bandwidth of 32 nm, and the repetition rate of 1 kHz. The output femtosecond pulse is sent into a $4f$ 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 array (SLM-128-D-VN, CRI) is placed at the Fourier plane of the pulse shaper. The laser spectrum is spatially dispersed onto the liquid-crystal display (LCD), and thus the individual frequency component can be independently manipulated in amplitude and/or phase. The shaped laser pulse is focused into the quartz cell containing the dye Perylene solution with a lens of 60-mm focal length, and the two-photon fluorescence (TPF) is detected by a spectrometer with a charge coupled device camera (Acton, Princeton Instrument) to monitor the two-photon transition probability.

The previous study demonstrated that, by the cosinusoidal spectral phase modulation, the two-photon transition probability in an atomic system can be completely eliminated in certain spectral phase modulation.[7] Here, we also conduct this experiment in Perylene solution by introducing the cosinusoidal spectral phase modulation $\Theta(\Omega) = \alpha\cos(\beta\Omega + \phi)$, where $\alpha$, $\beta$ and $\phi$ represent the modulation depth, the modulation period and the initial phase position, respectively. The simple phase manipulation is presented in the inset of Fig. 1(c) (dotted line). Figure 2 shows the experimental (squares) and calculated (solid line) results of the TPF intensity as a function of the modulation depth $\alpha$. The trace in Fig. 2 is normalised by the transform limited pulse excitation. As can be seen from Fig. 2, with the increase of modulation depth $\alpha$, the TPF intensity shows a slow decay accompanied with an oscillation. The oscillation period is consistent with that obtained in the atomic system, but the TPF is not completely eliminated at certain modulation depth. It can be found that, by manipulating the laser spectral phase, the TPF intensity shows the same evolution in both molecular and atomic system, but the TPF in the molecular system cannot be completely eliminated. We believe that the difference is due to the broad absorption line in the molecular system. When the laser spectral phase is modulated, part of photons in the excitation pulse can always satisfy the condition of two-photon transition because of the abundant energy levels in the molecular system.

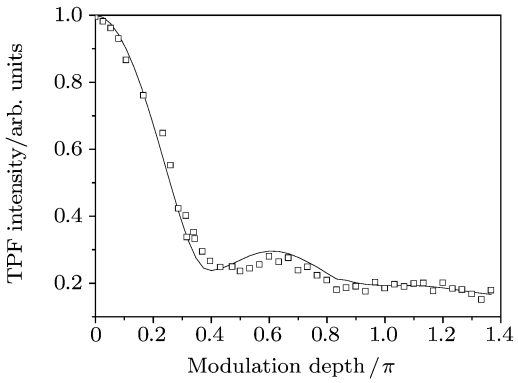


**Fig. 2.** Experimental (square) and calculated (solid line) TPF intensity of Perylene solution as a function of the modulation depth $\alpha$ for the cosinusoidal phase modulation.

Since the control efficiency of two-photon transition probability is correlated with the bandwidth of molecular absorption spectrum, we investigate the influence of the absorption spectrum bandwidth on the coherent control of two-photon transition. In an atomic system with very narrow absorption bandwidth (the narrow band limit), it was demonstrated that, when the excitation pulse is modulated with the $\pi$ spectral phase step, the two-photon transition probability can be eliminated in certain spectral phase modulation, but this coherent feature will vanish in the molecular system with very broad absorption spectrum (the broad band limit).[8] Similarly, we measure the TPF intensity of Perylene solution as a function of the $\pi$ phase step position, and the spectral phase modulation is shown in the inset of Fig. 1(c) (dashed line). In our experiment, the molecular absorption spectrum bandwidth (41 nm) and the laser spectral bandwidth (32 nm) are comparable. The experimental result is shown in Fig. 3, together with the theoretical calculation. The trace is also normalised by the transform limited pulse excitation. It can be seen that, the coherent feature still exists, but the control efficiency is

greatly reduced. Actually, the coherent feature is correlated with both the molecular absorption spectrum bandwidth and the laser spectral bandwidth.

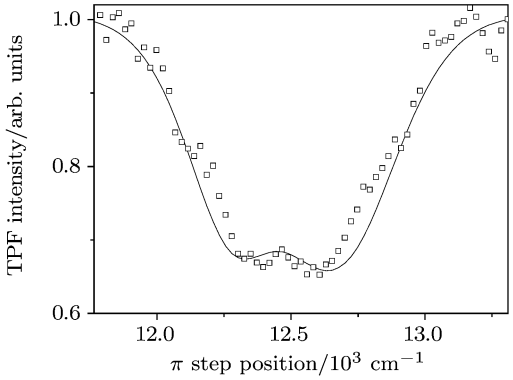


**Fig. 3.** Experimental (square) and calculated (solid line) TPF intensity of Perylene solution as a function of the $\pi$ phase step position.

We found theoretically that if the molecular absorption spectrum bandwidth is more than twice the laser spectral bandwidth, the coherent feature will disappear and the control efficiency will be minimal.[21]

In summary, we have demonstrated the coherent control of two-photon transition in a molecular system by tailoring the femtosecond pulse. Our results showed that the control efficiency of two-photon transition probability is correlated with the laser field and molecular absorption bandwidth. The two-photon transition probability can be reduced but cannot be eliminated by manipulating the laser field, and the control efficiency is minimal when the molecular absorption bandwidth is larger than twice the laser spectral bandwidth. We can conclude that the two-photon transition probability in the molecular system can be effectively controlled, and the control efficiency depends on the ratio of molecular absorption bandwidth and laser spectral bandwidth.

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