Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics Letters 433 (2007) 416–421
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Selective excitation of CARS by adaptive pulse shaping based on genetic algorithm

Shian Zhang, Liang Zhang, Xiangyun Zhang, Litao Ding, Guoliang Chen, Zhenrong Sun *, Zugeng Wang

Key Laboratory of Optical and Magnetic Resonance Spectroscopy (Ministry of Education), East China Normal University, Shanghai 200062, PR China
Department of Physics, East China Normal University, Shanghai 200062, PR China
Department of Mathematics, East China Normal University, Shanghai 200062, PR China

Received 20 June 2006; in final form 12 November 2006
Available online 18 November 2006

Abstract

Selective excitation of coherent anti-Stokes Raman scattering (CARS) from the benzene solution is experimentally demonstrated by shaping femtosecond laser pulses based on genetic algorithm. Second harmonic generation frequency-resolved optical gating (SHG-FROG) technique is adopted to characterize the original and optimal laser pulses, and the mechanisms for the coherently selective excitation of coherent anti-Stokes Raman scattering (CARS) is discussed. The results show that two-pulse coherent anti-Stokes Raman scattering (CARS) has good signal-to-background ratio and high sensitivity, and it has attractive potential applications in the complicated molecular system, such as biomolecules and materials.

1. Introduction

Coherent anti-Stokes Raman scattering (CARS) has been used as the most common nonlinear spectroscopy. CARS is a four-wave mixing process, which involves a pump photon ω_p, a Stokes photon ω_s, a probe photon ω_{pr} (usually $\omega_p = \omega_{pr}$) and a signal photon ω_c ($\omega_c = \omega_p - \omega_s + \omega_{pr}$ or $\omega_c = 2\omega_p - \omega_s$) (as shown in the inset of Fig. 1). When the energy difference $\omega_p - \omega_s$ is equal to the vibrational level of the medium (Ω_R), CARS signal will be resonantly enhanced. So, CARS has evolved as a versatile alternative for spontaneous Raman scattering due to its decisive advantages of high collection efficiency, high spectral and spatial and temporal resolution, and insensitivity against fluorescence or luminescence background. However, femtosecond CARS technique has two major drawbacks: one is the existence of a strong non-resonant background from electronic nonlinear contributions, and another is low selectivity among neighboring energy levels due to the large bandwidth of the femtosecond pulses. While the former problem can be reduced using the complex polarization arrangement of three exciting beams [1,2], the latter can be solved only by coherent control [3–8].

Coherent control can manipulate the process dynamics at various stages under the effect of the coherent sources [9]. Broadband femtosecond laser pulses can simultaneously excite many excited states, and their manipulation will lead to the interesting results. Based on broadband femtosecond pulse shaping, coherent control can manipulate the light-matter interaction through different quantum interference pathways, and thus the desirable outcomes can be achieved [10–13]. As to the complicated quantum system, it is difficult to acquire the detail information of the quantum system, and the resulting laser field is often quite complicated and even impossible to be realized in the laboratory under the present technology. Recently, the successful emergence of a feedback-loop control technique develops an efficient method to optimize the light-matter interaction dynamics without any prior knowledge of the quantum system, and it has been successful applied into

* Corresponding author. Fax: +86 21 62604953.
E-mail address: zrsun@phy.ecnu.edu.cn (Z. Sun).

0009-2614/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2006.11.060

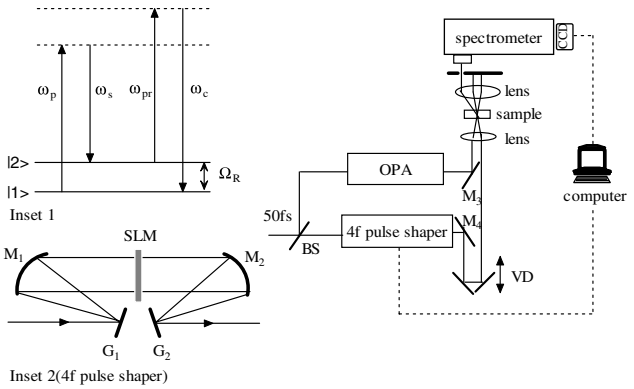

Fig. 1. The schematic diagram for experimental set-up (BS, beam-splitter; VD, variable delay line); Inset 1 is the schematic diagram for the CARS process; Inset 2 is the schematic diagram of 4 f pulse shaper composed of two grating (G_1 and G_2), spatial light modulator (SLM) and two con-focal concave mirrors (M_1 and M_2).

pulse compression [14,15], two photon transitions [16], high harmonic generation [17], chemical dissociation [18], stimulated Raman scattering [3]. The key for the feedback-loop technique is the evolutionary algorithm [19,20]. Genetic algorithm (GA) is one of the most important evolutionary algorithms, which is a probabilistic search algorithm inspired by the mechanisms of natural selection with many advantages. The derivatives of the objective functions and their related information are not necessary in the whole optimization process. 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 at the same time.

Recently, femtosecond pulse shaping has been widely applied to investigate the coherent Raman processes. The broadband femtosecond laser pulses can be in favor for obtaining a broadband Raman spectrum. The selective excitation of one or more Raman-active modes in methanol liquid has been demonstrated by an evolutionary learning procedure based on genetic algorithm [3]. A narrow-band coherent anti-Stokes Raman spectrum with a width of less than 15 cm^{-1} has been obtained by tailoring the probe pulse phase [7], and the nonresonant background is reduced to a minimum by shaping the excitation pulses [8]. As well known, there are three major drawbacks for single-pulse coherently controlled CARS [3,21]. The limited bandwidth can not overlap rather large Raman shift, the difficulty on the phase matching condition results in low CARS efficiency, and the weak CARS signal is difficult to be detected from rather strong excited femtosecond pulses and the existence of strong non-resonant background from electronic nonlinear contributions. However, two-pulse coherently controlled CARS can be used to overcome the above-mentioned drawbacks. The pump–Stokes laser pulses can be tuned to overlap large Raman shift, and the spatial phase matching condition can be easily achieved to increase the CARS efficiency, and the CARS signal can be spatially separated from the strong excited femtosecond pulses, and the strong non-resonant background from electronic nonlinear contributions can be reduced. So, the CARS signal-to-background ratio will be largely improved. In this Letter, we experimentally demonstrate that coherent anti-Stokes Raman scattering can be selectively excited by shaping femtosecond pump laser pulses. By optimal feedback control based on genetic algorithm, some molecular Raman vibrational modes of benzene can be selectively excited and the other modes can be suppressed, and second harmonic generation frequency-resolved optical gating (SHG-FROG) traces are used to characterize the original and optimal pulse, and then its mechanisms are discussed and analyzed.

2. Experiment

The experimental setup for adaptive pulse shaping is schematically shown in Fig. 1. A Ti:sapphire mode-locked laser (Spectra-Physics Spitfire amplifier) is used as the excitation source with the pulse duration of 50 fs, the repetition rate of 1 KHz, and the center wavelength of 800 nm. Approximately 0.5 mJ laser pulse is used to pump an optical parametric amplifier (OPA) (Spectra-Physics, OPA-800C) to generate the Stokes pulse with the bandwidth of about 750 cm^{-1}. The other part sends into the programmable 4 f pulse shaper, which 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), independent control of the phase and amplitude for each pixels, is placed at the Fourier plane of the shaper as an updatable filter for the spectral manipulation of the pump pulses. The frequency difference of the pump and Stokes beams is carefully adjusted to the Raman shift of the benzene solution. The shaped pump pulses and the Stokes pulses are attenuated into 2–3 μJ and focused by a lens into the 1 mm benzene sample with a small angle, and the CARS signal is generated and detected by the spectrometer/CCD. A computer is served for recording the feedback CARS signal, evaluating the cost function, optimizing the spectral mask and updating the SLM. The CARS signal from the benzene solution is optimal feedback controlled based on genetic algorithm, and coherently selective excitation of CARS from the different benzene Raman modes can be successfully achieved. Second harmonic generation frequency-resolved optical gating (SHG-FROG) technique [22,23] is used to characterize the original and optimal pump pulses, and the SHG-FROG traces provide the necessary frequency and temporal information to reconstruct the spectral amplitude and phase of the pump pulses.

3. Results and discussion

When the pump and Stokes pulses are overlapped temporally and spatially (here, the pump pulses are also used as the probe pulses), the CARS signals can be observed

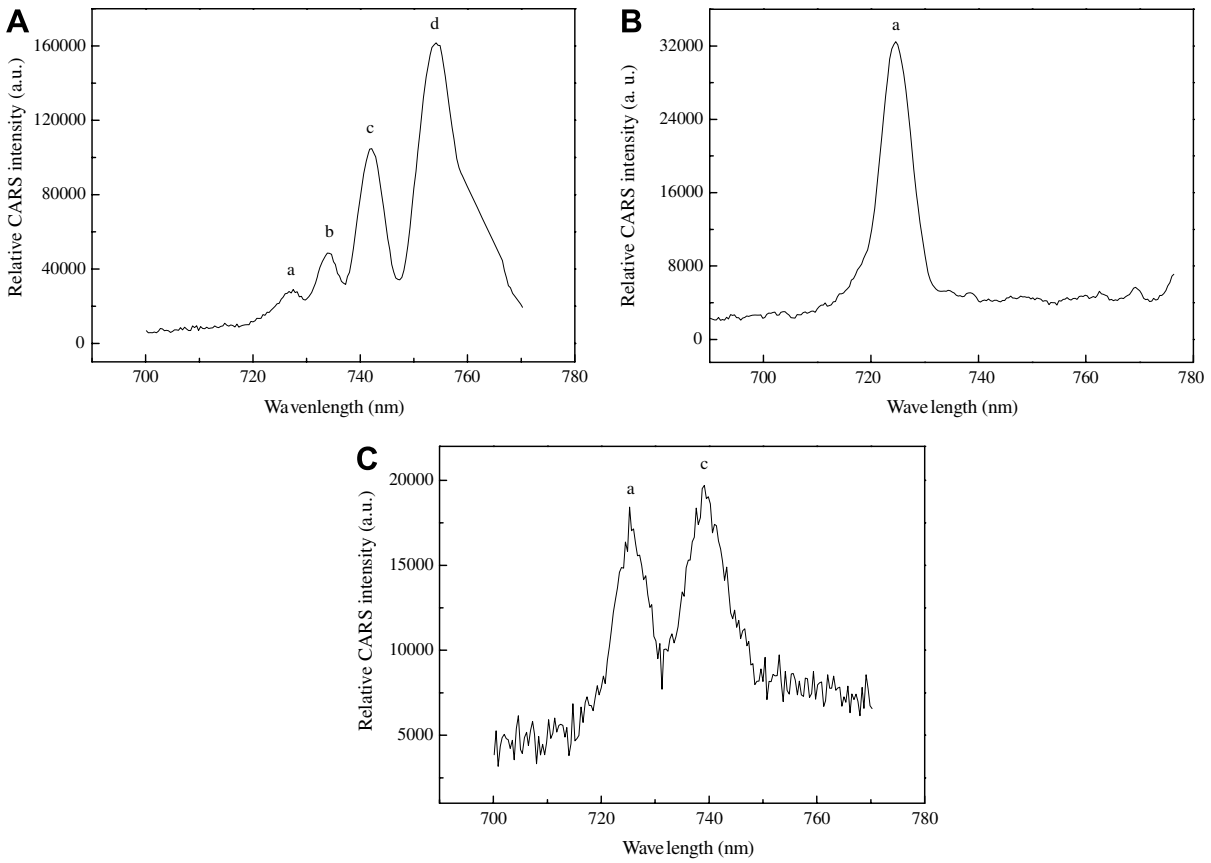

Fig. 2. CARS signals from the benzene solution excited by the original pulse (A) and the optimal pulses for the selective excitation of the Raman modes at 726 nm (B) and both the Raman modes at 726 nm and 742 nm (C), respectively.

at 726 nm, 733 nm, 742 nm and 754 nm (as shown in Fig. 2A). According to Ref. [24], the corresponding CARS assignments are presented in Table 1. As shown in Fig. 2A and Table 1, the observed peaks at the wavelength of 726 nm, 733 nm, 742 nm and 754 nm can be attributed to symmetric and anti-symmetric C–H parallel bending vibration modes, anti-symmetric C–C parallel bending vibration and symmetric C–C stretching vibration modes, respectively.

For the optimal feedback control, genetic algorithm is used to selectively excite CARS from the benzene solution. Firstly, the initial voltage values are generated randomly and loaded on the pixels of SLM-256 as the first generation, and their impacts on the CARS intensity from the different Raman modes of the benzene molecule are evaluated, respectively. Secondly, the fitness for the CARS intensity contrast ratio of the different benzene Raman modes is calculated, and the corresponding cost value is obtained. Genetic algorithm allows a change in all of the pixels of the spectral mask and a decision whether the change is either accepted or rejected according to the calculated cost value. The voltage values of the new spectral mask for second generation can be attained by genetic algorithm operation (select, crossover and mutate). Their impacts on different benzene Raman modes are determined and evaluated. So, the above-mentioned optimization procedure is repetitively performed till the cost value approaches convergence and the CARS intensity contrast ratio of the different benzene Raman modes approaches to the optimal maximum. As shown in Fig. 2B,C, the shaped pulses can be optimized to selectively excite CARS from the benzene solution at 726 nm and both of 726 nm

Table 1
The corresponding CARS assignments

Peak	Wavelength (nm)	Assignments
a	726	$\nu_{17}^{H\|\|}(e_{2g})$ (corresponding to the Raman shift of 1178 cm^{-1}): the symmetric C–H parallel bending vibration
b	733	$\nu_{14}^{H\|\|}(e_{1u})$ (corresponding to the Raman shift of 1030 cm^{-1}): the anti-symmetric C–H parallel bending vibration
c	742	$\nu_2^{CC}(a_{1g}) + \nu_{18}^{C\|\|}(e_{2g}) - \nu_{18}^{C\|\|}(e_{2g})$ (corresponding to the Raman shift of 999 cm^{-1}), where $\nu_{18}^{C\|\|}(e_{2g})$: the anti-symmetric C–C–C parallel bending vibration
d	754	$\nu_2^{CC}(a_{1g})$ (corresponding to the Raman shift of 991.6 cm^{-1}): the symmetric C–C stretching vibration

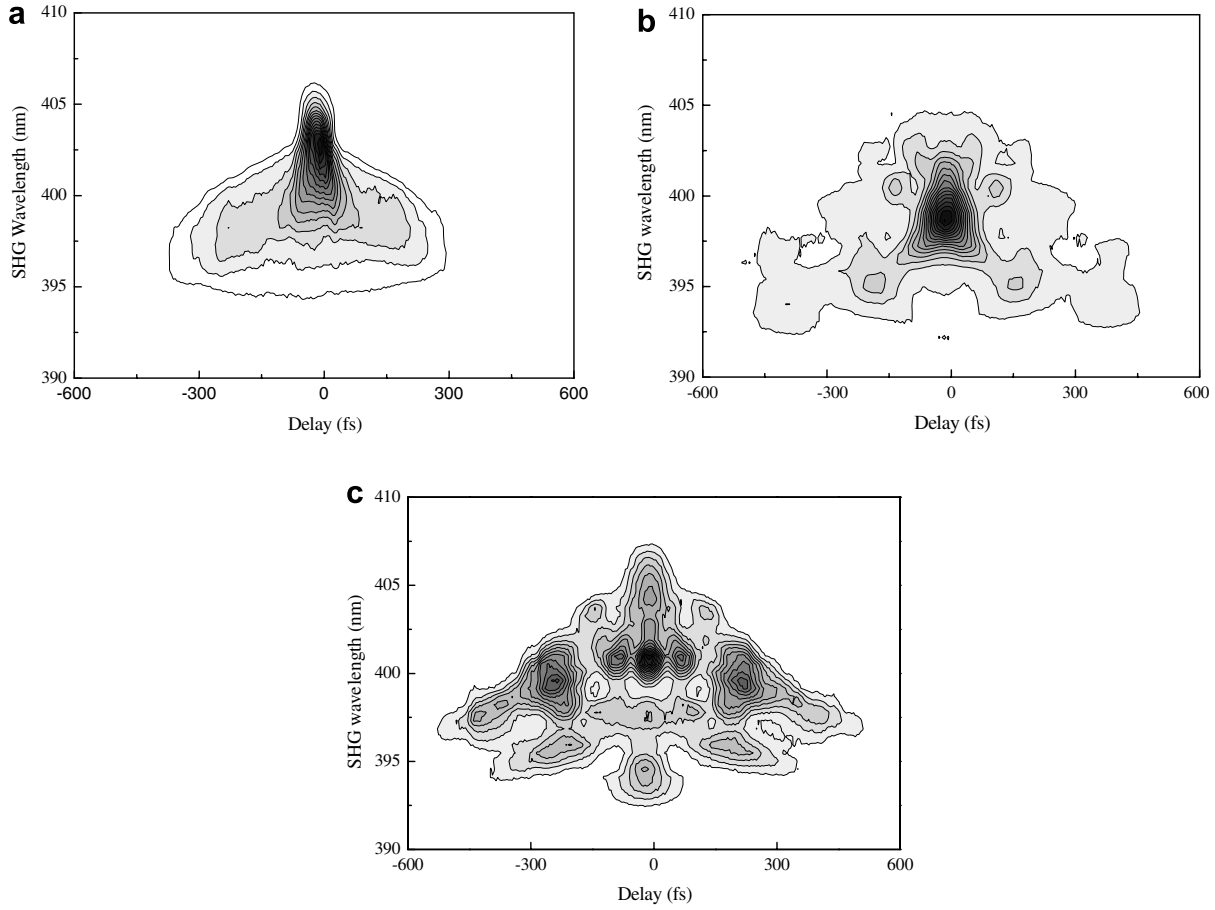

Fig. 3. Second harmonic generation frequency resolved gating (SHG-FROG) traces for the original (a) and optimal pump pulses for the CARS at 726 nm (b), and both of 726 nm and 742 nm (c), respectively.

and 742 nm, respectively. As shown in Fig. 2B, the CARS at 726 nm is selectively excited and enhanced by optimizing the shaped pump pulses, and the CARS signals at 733 nm, 742 nm and 754 nm are almost suppressed. As shown in Fig. 2C, the CARS signals at 733 nm and 754 nm are efficiently suppressed by the optimal pump pulses, and the CARS signals at 726 nm and 742 nm are selectively excited, and thus their intensity decreases observably.

In order to explore the experimental mechanisms, second harmonic generation frequency resolved optical gating (SHG-FROG) technique is used to characterize the original and optimal pump laser pulses. As shown in Fig. 3, the SHG-FROG traces indicate that the optimal pump pulses are strongly modulated. For further analyzing the optimal laser pulses, their phase and amplitude are calculated from the SHG-FROG traces. As shown in Fig. 4, their phase and amplitude are deeply modulated, and the modulated pulse trains can selectively excite desired coherent anti-Stokes Raman scattering with the suppression of the undesired Raman scattering.

In the CARS process, CARS signal depends on the population transfer from the ground states to the excited states [25], which is influenced by the amplitude and phase of the femtosecond pulses participating in and the delay between the pump and Stokes beams. For the femtosecond pulses, both the pump and Stokes laser pulses have broad bandwidth, and therefore can overlap several vibrational modes at 991.6 cm^{-1}, 999 cm^{-1}, 1030 cm^{-1} and 1178 cm^{-1} in the benzene solution. The CARS signals can be generated by the coupling of the pump and Stokes pulses with the Raman energy levels, and so the amplitude and phase of the pump and Stokes pulses and their pulse delay are the dependent factors. For our experiments, CARS process is degenerated for $\omega_p = \omega_{pr}$, and so the CARS process can be simplified into Λ type three-level quantum system. So, a multiple Λ type three-level quantum system, including of a ground states and four excited states and the virtual states (as shown in Fig. 5), can be used to interpret the selective excitation of the CARS signals from the benzene solution, and so the CARS signals depend on the coherent Raman population transfer from the ground states to the excited states.

For the femtosecond pulses, the broad bandwidth can overlap several Raman vibrational modes of the benzene molecule and the CARS signals can be excited by the original pump and Stokes pulses. For the adaptive coherent control, the amplitude and phase of the pump pulses can be adaptively optimized by manipulating spatial light

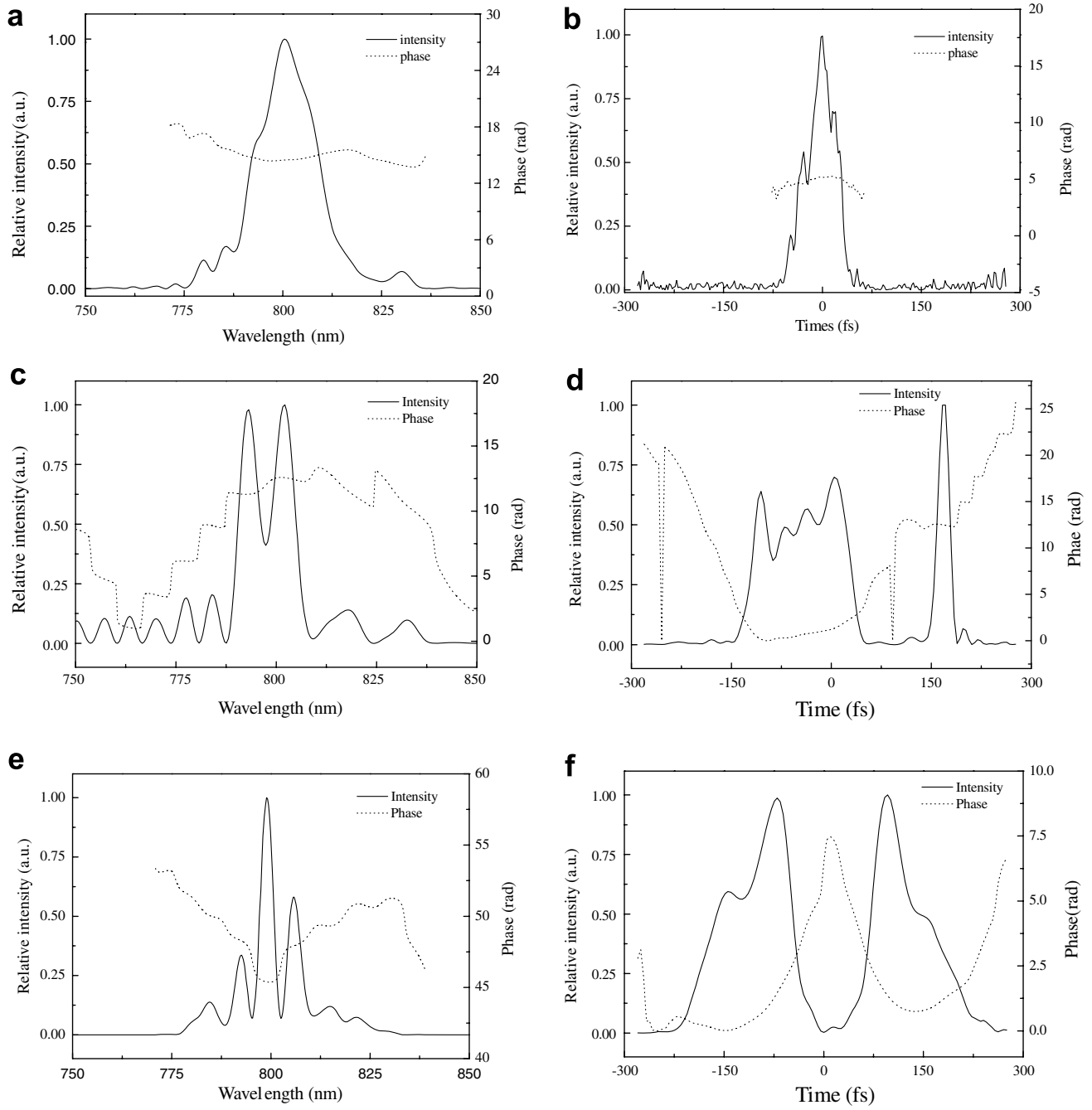

Fig. 4. The amplitude and phase for the original (a,b) and optimal pump pulses for the selective excitation of the CARS at 726 nm (c,d), and both of 726 nm and 742 nm (e,f), respectively.

modulator (SLM) based on genetic algorithm. The optimized pump pulses can be achieved for the selective population transfer in the desired excited states and the coherent suppression of the population transfer in the undesired excited states. So, the corresponding desired CARS can be selectively generated by the optimized pump pulses, and the corresponding undesired CARS can be coherently suppressed. Furthermore, coherent anti-Stokes Raman scattering (CARS) is a resonant four-wave mixing process, and so CARS signal can also be affected by the modulated pump and Stokes pulses through the third or fifth-order nonlinear polarization. However, their physical processes are too complicate to be easy to discern here, and the challenging task remains to determine which features in these complicated pulse shapes are necessary for mode-selective excitation.

4. Conclusion

In conclusion, the selective excitation of CARS from the benzene solution is achieved by shaping femtosecond laser pulses based on genetic algorithm. The CARS signals

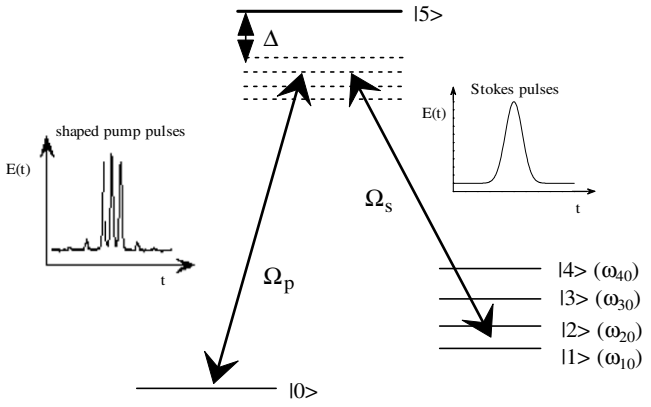

Fig. 5. Schematic picture of multiple Λ type three-level quantum system.

from the benzene solution at 726 nm and both of 726 and 742 nm can be selectively excited. Second harmonic generation frequency-resolved optical gating (SHG-FROG) traces indicate that the optimal pump pulse is strongly modulated into the pulse trains and their amplitude and phase are manipulated by spatial light modulator (SLM). The experimental results show two-pulse coherent anti-Stokes Raman scattering has good signal-to-background ratio and high sensitivity, and it has attractive potential applications in the complicated molecular system, such as biomolecules and materials.

Acknowledgements

This research was supported by National Natural Science Foundation of China (No. 10234030 and 10574046), National Key Project for Basic Research of China (No. 1999075204), Program for New Century Excellent Talents in University (NCET-04-0420), the Doctoral Program of High Education (20050269011), Phosphor Program sponsored by Shanghai Science and Technology Committee (No. 06QH14003) and Twilight Project sponsored by Shanghai Education Committee (No. 03SG23).

References

[1] Y. Saito, N. Hayazawa, H. Kataura, T. Murakami, K. Tsukagoshi, Y. Inouye, S. Kawata, Chem. Phys. Lett. 410 (2005) 136.
[2] Y. Zhang, C. Gan, K. Lu, C. Li, X. Hou, Opt. Commun. 205 (2002) 163.
[3] T.C. Weinacht, J.L. White, P.H. Bucksbaum, J. Phys. Chem. A 103 (1999) 10166.
[4] B.J. Pearson, J.L. White, T.C. Weinacht, P.H. Bucksbaum, Phys. Rev. A. 63 (2001) 063412.
[5] T.C. Weinacht et al., Chem. Phys. Lett. 344 (2001) 333.
[6] N. Dudovich, D. Oron, Y. Silberberg, Phys. Rev. Lett. 88 (2002) 123004.
[7] D. Oron, N. Dudovich, D. Yelin, Y. Silberberg, Phys. Rev. Lett. 88 (2002) 063004.
[8] D. Oron, N. Dudovich, D. Yelin, Y. Silberberg, Phys. Rev. A. 65 (2002) 043408.
[9] D. Goswami, Phys. Rep. 374 (2003) 385.
[10] L.C. Zhu, V. Kleiman, X.N. Li, S. Lu, K. Trentelman, R.J. Gordon, Science 270 (1995) 77.
[11] A. Shnitman, I. Sofer, I. Golub, A. Yogev, M. Shapiro, Z. Chen, P. Brumer, Phys. Rev. Lett. 76 (1996) 2886.
[12] D. Meshulach, D. Yelin, Y. Silberberg, Opt. Commun. 138 (1997) 345.
[13] D.S. Yee, K.J. Yee, S.C. Hohng, D.S. Kim, Phys. Rev. Lett. 84 (2000) 3474.
[14] D. Yelin, D. Mashulach, Y. Silberberg, Opt. Lett. 22 (1997) 1793.
[15] T. Brixner, A. Oehrlein, M. Strehle, G. Gerber, Appl. Phys. B 70 (2000) S119.
[16] D. Meshulach, Y. Silberberg, Nature 396 (1998) 239.
[17] R. Barteels et al., Nature 406 (2000) 164.
[18] A. Assion et al., Science 282 (1998) 919.
[19] D. Zeidler, S. Frey, K.L. Kompa, M. Motzkus, Phys. Rev. A 64 (2001) 023420.
[20] B.J. Pearson, J.L. White, T.C. Weinacht, P.H. Bucksbaum, Phys. Rev. A 63 (2001) 063412.
[21] N. Dudovich, D. Oron, Y. Silberberg, Nature 418 (2002) 512.
[22] K.W. Delong, R. Trebino, J. Hunter, W.E. White, J. Opt. Soc. Am. B 11 (1994) 2026.
[23] R. Trebino, K.W. DeLong, D.N. Fittinghoff, J.N. Sweetser, M.A. Krumbügel, B.A. Richman, Rev. Sci. Instrum. 68 (1997) 3277.
[24] G. Herzberg, Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand Reinhold, New York, 1945.
[25] S.A. Malinovskaya, P.H. Bucksbaum, P.R. Berman, Phys. Rev. A 69 (2004) 013801.