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# Selective excitation of femtosecond coherent anti-Stokes Raman scattering in the mixture by phase-modulated pump and probe pulses

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In this paper, we present a feasible method to realize and improve the selective excitation of femtosecond coherent anti-Stokes Raman scattering (CARS) in a mixture. We theoretically show that, by shaping both the pump and probe pulses with the  $\pi$  phase step, the CARS signal from one quantum system can be enhanced and simultaneously that from the other quantum system is effectively suppressed. Comparing with only shaping the probe pulse [D. Oron, N. Dudovich, D. Yelin, and Y. Silberberg, *Phys. Rev. Lett.*, **88**, 063004 (2002)], the selectivity of femtosecond CARS by shaping both pump and probe pulses can be greatly improved. Finally, we experimentally compare two shaping schemes by investigating the selective excitation of the femtosecond CARS in the mixture of dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and chloroform ( $\text{CHCl}_3$ ). © 2010 American Institute of Physics. [doi:10.1063/1.3298859]

Coherent anti-Stokes Raman scattering (CARS), a nonlinear four-wave-mixing process, is one of the most important nonlinear spectroscopic techniques.<sup>1–5</sup> Recently, femtosecond CARS technique has been widely utilized to investigate molecular constants,<sup>6</sup> collisional parameters,<sup>7</sup> local structure formation,<sup>8</sup> temperature,<sup>9,10</sup> and vibrational imaging.<sup>11,12</sup> However, due to the large bandwidth of the femtosecond pulse, femtosecond CARS suffers from two drawbacks: one is the strong nonresonant background and the other is the poor selectivity between neighboring Raman levels. The former is easy to be eliminated by polarization arrangement or coherent control method,<sup>13,14</sup> but the latter is only solved by coherent control method.<sup>14–19</sup>

With the progress of ultrafast laser technique, it has been possible to obtain such a laser pulse with the arbitrary temporal distribution by shaping the spectral phase and/or amplitude. Recently, the coherent control strategies by ultrafast pulse-shaping technique have been enormously successful in the selective excitation of special Raman mode. Silberberg *et al.*<sup>14</sup> demonstrated the selective excitation between neighboring Raman levels in pyridine by shaping both the pump and Stokes pulses with an approximate spectral phase function or only the probe pulse with the  $\pi$  phase step.<sup>15</sup> Materny *et al.*<sup>16,17</sup> reported the selective excitation in  $\beta$ -carotene and the mixture of benzene and chloroform by feedback optimization with a polynomial phase function. Bucksbaum *et al.*<sup>18</sup> showed the selective excitation in the methanol solution and the mixture of benzene and deuterated benzene by feedback optimization based on a genetic algorithm. Furthermore, our group successfully realized the selective excitation of one or more Raman levels in the benzene solution by the optimal feedback control technique.<sup>19</sup>

By the above-described control methods (open-loop or closed-loop scheme), the selective excitation of femtosecond CARS can be achieved. In this paper, we provide a new control project to realize the selective excitation of femtosecond CARS in a mixture. By shaping both the pump and probe pulses with the  $\pi$  spectral phase step, it is found that the CARS signal from one quantum system is enhanced and simultaneously that from the other quantum system can be effectively suppressed. Moreover, it is also shown that, comparing with shaping only the probe pulse, the selectivity of femtosecond CARS by shaping both the pump and probe pulses can be greatly improved. Finally, the theoretical expectation is experimentally validated in the mixture of dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and chloroform ( $\text{CHCl}_3$ ).

Figure 1(a) shows the schematic diagram of the energy level in the CARS process. The third-order nonlinear polarization, induced by the interaction of pump field  $E_p(t)$ , Stokes field  $E_s(t)$ , and probe field  $E_{pr}(t)$  with a quantum system including of the intermediate states  $|m\rangle$ ,  $|n\rangle$ ,  $|l\rangle$ , and the ground state  $|g\rangle$ , can be approximated by time-dependent perturbation theory as<sup>14,15,18</sup>

$$\begin{aligned}
 P^{(3)}(t) \propto & \frac{1}{\hbar^3} \sum_{mnl} \mu_{gl} \mu_{ln} \mu_{nm} \mu_{mg} \exp[-(i\omega_{lg} + \Gamma_{lg})t] \\
 & \times \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 E_p(t_3) E_s^*(t_2) E_{pr}(t_1) \\
 & \times \exp[(i\omega_{ln} + \Gamma_{ln})t_1] \exp[(-i\omega_{mn} + \Gamma_{mn})t_2] \\
 & \times \exp[(i\omega_{mg} + \Gamma_{mg})t_3],
 \end{aligned} \quad (1)$$

where  $\mu_{ij}(i, j = g, m, n, l)$  are the dipole moments and  $\omega_{ij} = 2\pi(E_i - E_j)/h$ . In frequency domain, the nonlinear polarization can be described by the nonresonant and resonant contributions, and given by

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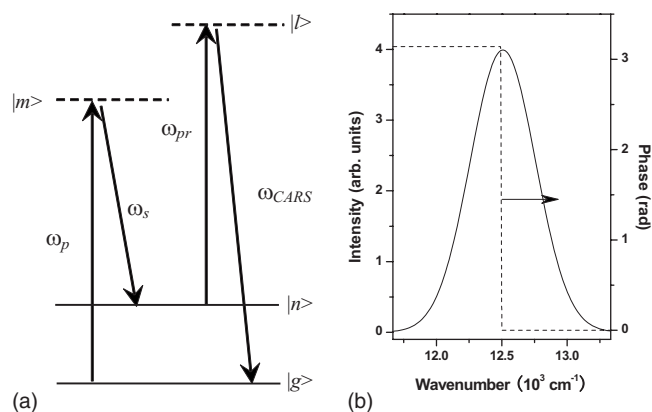


FIG. 1. (a) The energy level diagram of the CARS process. (b) The schematic diagram of the  $\pi$  spectral phase step applied on both the pump and probe spectra.

$$P_{nr}^{(3)}(\omega_{as}) \propto \int_0^{+\infty} d\Omega \int_0^{+\infty} E_p(\omega_p) E_{pr}(\omega_{as} - \Omega) E_s^*(\omega_p - \Omega) d\omega_p, \quad (2)$$

$$P_r^{(3)}(\omega_{as}) \propto \int_0^{+\infty} d\Omega \int_0^{+\infty} \frac{E_{pr}(\omega_{as} - \Omega) E_p(\omega_p)}{\Omega_R - \Omega + i\Gamma} E_s^*(\omega_p - \Omega) d\omega_p, \quad (3)$$

where  $E(\omega) = A(\omega) \exp[i\Phi(\omega)]$  is the Fourier transform of  $E(t)$ ,  $\Omega_R$  is the Raman resonant frequency, and  $\Gamma$  is the bandwidth of the Raman level. Since the nonlinear polarization is calculated separately by the nonresonant and resonant components, the CARS signal is the coherent summation of the two components. To simplify the CARS experimental arrangement, the pump and probe pulses usually share the same laser field (i.e., two-pulse CARS process). In this paper, we manipulate both the pump and probe pulses with the  $\pi$  phase step to realize the selective excitation of the two-pulse femtosecond CARS in a mixture and the spectral modulation is shown in Fig. 1(b).

Considering the two quantum systems A and B, their Raman resonant frequencies are 750 and 1250  $\text{cm}^{-1}$ , and both have the same level bandwidth of 10  $\text{cm}^{-1}$ . Assuming that  $\omega_p = 12\,500 \text{ cm}^{-1}$ ,  $\omega_s = 11\,500 \text{ cm}^{-1}$ ,  $\omega_{pr} = \omega_p = 12\,500 \text{ cm}^{-1}$ , and their spectral bandwidths [full width at half maximum (FWHM)] are all 500  $\text{cm}^{-1}$ . The frequency difference  $\omega_p - \omega_s = 1000 \text{ cm}^{-1}$  is set between the Raman resonant frequencies of the two quantum systems, and thus both the two quantum systems can be maximally excited. The CARS intensities from the two quantum systems as the function of the  $\pi$  phase step are calculated and shown in Fig. 2 (thick line). The results are normalized by the transform limited pulse excitation. The CARS signal from the quantum system A achieves the maximal enhancement at the  $\pi$  phase step position of 12 400  $\text{cm}^{-1}$  and the maximal suppression at the  $\pi$  phase step position of 12 600  $\text{cm}^{-1}$  (solid line). However, the CARS signal from the quantum system B approaches the maximal suppression at the  $\pi$  phase step position of 12 400  $\text{cm}^{-1}$  and the maximal enhancement at the  $\pi$  phase step position of 12 600  $\text{cm}^{-1}$  (dashed line). It can be seen that enhancing one CARS signal and simultaneously

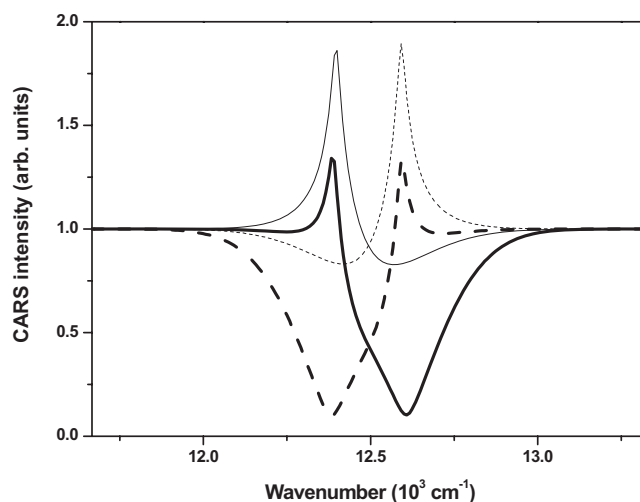


FIG. 2. The CARS intensities from the quantum system A (solid line) and the quantum system B (dashed line) as the function of the  $\pi$  phase step applied on both the pump and probe spectra (thick line) and only probe spectrum (thin line).

suppressing the other one can be achieved by shaping both the pump and probe pulses with the  $\pi$  spectral phase step, and so it provides a feasible experimental project to realize the selective excitation in their mixture.

In the previous study, the selective excitation of femtosecond CARS can also be realized by shaping only the probe pulse with the  $\pi$  phase step.<sup>15</sup> In order to reveal the advantage by shaping both the pump and probe pulses, we also calculate the CARS intensities from the two quantum systems as the function of the  $\pi$  phase step applied on the probe pulse, and the simulated results are presented in Fig. 2 (thin line). Their CARS intensities can also be enhanced or suppressed in certain phase step position, which is similar to that obtained by shaping both the pump and probe pulses. However, it can be found that, comparing with shaping only the probe pulse, the CARS intensity by shaping both the pump and probe pulses can be more suppressed. For the mode-selective excitation, it is crucial that one Raman mode is enhanced and, simultaneously, the other one is maximally suppressed. It can be concluded that, by shaping both the pump and probe pulses, the selectivity of femtosecond CARS can be greatly improved.

To experimentally validate above theoretical expectation, we perform the experiment in dibromomethane ( $\text{CH}_2\text{Br}_2$ ), chloroform ( $\text{CHCl}_3$ ), and their mixture ( $\text{CH}_2\text{Br}_2 + \text{CHCl}_3$ ). The Raman shift in  $\text{CH}_2\text{Br}_2$  is 1388  $\text{cm}^{-1}$ , corresponding to the C–H vibration mode, and the Raman shift in  $\text{CHCl}_3$  is 1518  $\text{cm}^{-1}$ , corresponding to the C–Cl vibration mode. In the experiment, a Ti-sapphire mode-locked regenerative amplifier (Spectra-physics, Spitfire) is used as the excitation source with the pulse width (FWHM) of about 50 fs, the center wavelength of 800 nm, and the repetition rate of 1 kHz. The output laser pulse is split into three beams. One is used to pump an optical parametric amplifier to generate the Stokes pulse. One is shaped by a 4f-configuration zero-dispersion pulse shaper as the pump and probe pulses or only the probe pulse. The pulse shaper is composed of a pair of diffraction gratings 1200 lines/mm and a pair of concave

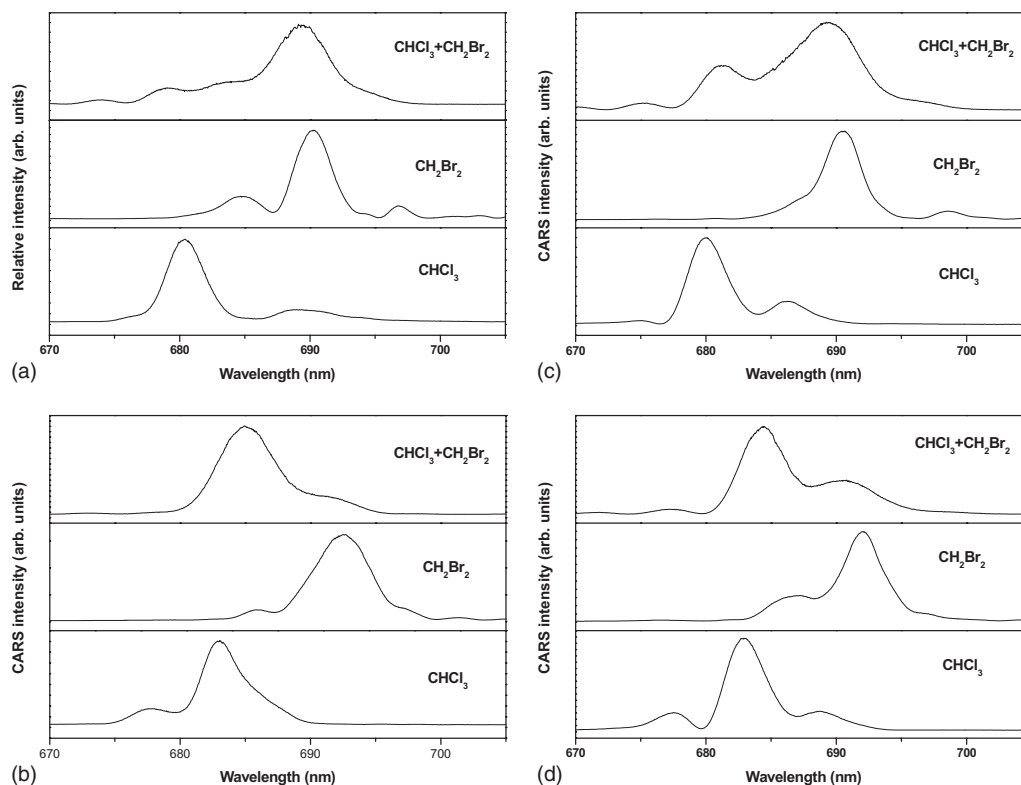


FIG. 3. The CARS spectra from dibromomethane ( $\text{CH}_2\text{Br}_2$ ), chloroform ( $\text{CHCl}_3$ ) and their mixture ( $\text{CH}_2\text{Br}_2 + \text{CHCl}_3$ ) by shaping both the pump and probe pulses with the  $\pi$  phase step position of 792 nm (a) and 809 nm (b) and shaping only the probe pulse with the  $\pi$  phase step position of 792 nm (c) and 809 nm (d).

mirrors with the focal length of 200 mm. A one-dimensional programmable liquid-crystal spatial light modulator array (SLM-256, CRI) is placed at the Fourier plane of the pulse shaper and used as the updatable filter for the spectral phase and/or amplitude modulation. The frequency difference of the pump and Stokes pulses is set between the Raman shifts in  $\text{CH}_2\text{Br}_2$  and  $\text{CHCl}_3$ . In order to achieve the approximate CARS intensities of the  $\text{CH}_2\text{Br}_2$  and  $\text{CHCl}_3$  in their mixture, the  $\text{CH}_2\text{Br}_2$  and  $\text{CHCl}_3$  are mixed by the volume ratio 1:1.6. The CARS spectra of  $\text{CH}_2\text{Br}_2$ ,  $\text{CHCl}_3$ , and their mixture  $\text{CH}_2\text{Br}_2 + \text{CHCl}_3$  are recorded by a spectrometer with a charge coupled device.

In the experiment, the CARS spectra of  $\text{CH}_2\text{Br}_2$  and  $\text{CHCl}_3$  in their mixture are not clearly distinguishable, and so, which molecular system being selectively excited is determined by comparing the CARS intensity from the individual molecular system and their mixture. Figure 3 shows the CARS spectra from  $\text{CH}_2\text{Br}_2$ ,  $\text{CHCl}_3$ , and their mixture  $\text{CH}_2\text{Br}_2 + \text{CHCl}_3$  by shaping both the pump and probe pulses (a, b) and only the probe pulse (c, d). It can be seen that both the two shaping schemes can realize the selective excitation of femtosecond CARS. As shown in Figs. 3(a) and 3(c), when the  $\pi$  phase step position is set at 792 nm, the  $\text{CHCl}_3$  in the mixture is selectively excited and the  $\text{CH}_2\text{Br}_2$  is suppressed. As shown in Figs. 3(b) and 3(d), when the  $\pi$  phase step position is tuned to 809 nm, the  $\text{CH}_2\text{Br}_2$  in the mixture is selectively excited and the  $\text{CHCl}_3$  is suppressed. However, comparing with the two shaping schemes, it can be found that the CARS intensity by shaping both the pump and probe pulses can be more suppressed than by only shaping the

probe pulse, and so the selectivity of femtosecond CARS by shaping both the pump and probe pulses can be obviously improved.

In summary, we have theoretically demonstrated that, by shaping both the pump and probe pulses with the  $\pi$  spectral phase step, enhancing the CARS signal of one quantum system and simultaneously suppressing the other one can be achieved, and so it provides a feasible method to realize the selective excitation of femtosecond CARS in their mixture. Comparing with shaping only the probe pulse, it was found that shaping both the pump and probe pulses can greatly improve the selectivity of femtosecond CARS. Finally, the theoretical expectation was experimentally validated in the mixture of dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and chloroform ( $\text{CHCl}_3$ ). The presented results appear the promising application on mode-selective excitation and microscopic investigation in complex molecular structure.

## ACKNOWLEDGMENTS

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