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Selective excitation and suppression of coherent anti-Stokes Raman scattering by shaping femtosecond pulses*

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Femtosecond coherent anti-Stokes Raman scattering (CARS) suffers from poor selectivity between neighbouring Raman levels due to the large bandwidth of the femtosecond pulses. This paper provides a new method to realize the selective excitation and suppression of femtosecond CARS by manipulating both the probe and pump (or Stokes) spectra. These theoretical results indicate that the CARS signals between neighbouring Raman levels are differentiated from their indistinguishable femtosecond CARS spectra by tailoring the probe spectrum, and then their selective excitation and suppression can be realized by supplementally manipulating the pump (or Stokes) spectrum with the π spectral phase step.

Keywords: coherent anti-Stokes Raman scattering (CARS), selective excitation, selective suppression, pulse shaping

PACC: 3280K, 4265B

Coherent anti-Stokes Raman scattering (CARS), a nonlinear four-wave-mixing process, is one of the most important nonlinear spectroscopic techniques.[1−7] It can be generated at the frequency $\omega_{\rm as} = \omega_{\rm p} + \omega_{\rm pr} - \omega_{\rm s}$, when three beams, a pump beam with frequency $\omega_{\rm p}$, a Stokes beam with frequency $\omega_{\rm s}$ and a probe beam with frequency $\omega_{\rm pr}$, interact in the nonlinear medium (as shown in Fig. 1(a)). For simplicity, the pump and probe pulses usually share the same source. When the energy difference $\omega_{\rm p} - \omega_{\rm s}$ is tuned coincidently into the vibration level, a resonant CARS signal can be achieved and provides information about the molecular vibration motion. Picosecond CARS have been successfully used to investigate chemical and biological samples.[8,9] However, due to the broad spectral bandwidth of the femtosecond laser pulses, this results in the existence of two drawbacks for the femtosecond CARS: strong non-resonant background and poor selectivity between neighbouring energy levels. The former can be eliminated by the polarization arrangement or coherent control method[10,11] but the latter is only solved by the coherent control method.[11−16]

A promising method for the mode-selective excitation of femtosecond CARS is coherent control by the femtosecond pulse shaping technique, where the spectral phase and/or amplitude of the femtosecond pulses are shaped to manipulate the light-matter interaction based on quantum interference and finally achieve the desired outcomes. With the development of the femtosecond laser technique, it becomes possible to obtain laser pulses with arbitrary temporal and spectral distributions. In a simple quantum system, pre-designed pulses can be favourable for the experimental requirements. However, for complex cases, the feedback control based on a learning algorithm is an efficient method to optimize the laser field and achieve the desired results. So far, coherent control based on shaping the femtosecond pulses has been widely applied to realize the selective excitation of femtosecond CARS processes.[11−16] For example, Silberberg *et al.* demonstrated the selective excitation of the two Raman levels in pyridine by simultaneously shaping the pump and Stokes pulses with an approximate spectral phase function.[11,12] Bucksbaum *et al.* achieved selective excitation in a methanol solution and a mixture

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of benzene and deuterated benzene based on a genetic algorithm.[13] Materny *et al.* presented selective excitation in β-carotene and a mixture of benzene and chloroform based on an evolutionary algorithm.[14,15] Our group realized the selective excitation of one or more Raman levels in benzene by the optimal feedback control technique.[16]

The selective excitation of femtosecond CARS is easy to realize for CARS signals with rather large and distinguishable Raman level space by phase modulation or close-loop optimization. However, if the neighbouring Raman levels are too close to be distinguished from their femtosecond CARS spectra, it is tremendously difficult to perform their selective excitation or suppression. An important question, which is still open, is how to differentiate the CARS signals between neighbouring Raman levels from their indistinguishable CARS spectra and realize their selective excitation and suppression. In this paper, we present a new method to realize the selective excitation and suppression in femtosecond CARS. Our research shows that the selective excitation and suppression between neighbouring Raman levels can be realized by manipulating both the probe and pump (or Stokes) spectra, even if their CARS spectra are indistinguishable.

The nonlinear polarization, induced by the interaction of the pump laser field $E_{\mathrm{p}}(t)$, the Stokes laser field $E_{\mathrm{s}}(t)$ and the probe laser field $E_{\mathrm{pr}}(t)$ with a quantum system including the intermediate states $|m\rangle$, $|n\rangle$, $|k\rangle$ and the ground state $|g\rangle$, can be approximated by the third-order time-dependent perturbation theory[11,12,15]

$$\begin{aligned} P^{(3)}(t) \propto & -\frac{1}{\hbar^3}\sum_{mnk}\mu_{gk}\mu_{kn}\mu_{nm}\mu_{mg}\exp\left[-\left(\mathrm{i}\,\omega_{kg}+\varGamma_{kg}\right)t\right] \\ & \times\int_{-\infty}^{t}\mathrm{d}t_1\int_{-\infty}^{t_1}\mathrm{d}t_2\int_{-\infty}^{t_2}\mathrm{d}t_3 E_p\left(t_3\right)E_s^*\left(t_2\right)E_{\mathrm{pr}}\left(t_1\right) \\ & \times\exp\left[\left(\mathrm{i}\,\omega_{kn}+\varGamma_{kn}\right)t_1\right]\exp\left[\left(-\mathrm{i}\,\omega_{mn}+\varGamma_{mn}\right)t_2\right]\exp\left[\left(\mathrm{i}\,\omega_{mg}+\varGamma_{mg}\right)t_3\right], \end{aligned} \tag{1}$$

where μ_{ij} are the dipole moments and $\omega_{ij}=2\pi(E_i-E_j)/h$. In the frequency domain, the nonlinear polarization can be described by the nonresonant and resonant contributions; the former, the nonresonant contribution, is attributed to the instantaneous electronic responses, and the latter, the resonant contribution, reflects the energy level information of the quantum system. For the Raman transition by the intermediate level $|i\rangle$, the nonlinear polarization can be written as

$$P^{(3)}\left(\omega_{\mathrm{as}}\right)=P_{\mathrm{r}}^{(3)}\left(\omega_{\mathrm{as}}\right)+P_{\mathrm{nr}}^{(3)}\left(\omega_{\mathrm{as}}\right) \tag{2}$$

with

$$\begin{aligned} P_{\mathrm{r}}^{(3)}\left(\omega_{\mathrm{as}}\right) & \propto\int_0^{+\infty}\frac{E_{\mathrm{pr}}\left(\omega_{\mathrm{as}}-\varOmega\right)}{\varOmega_{\mathrm{R}}-\varOmega+\mathrm{i}\varGamma}\mathrm{d}\varOmega\int_0^{+\infty}E_{\mathrm{p}}\left(\omega_{\mathrm{p}}\right)E_{\mathrm{s}}^*\left(\omega_{\mathrm{p}}-\varOmega\right)\mathrm{d}\omega_{\mathrm{p}}, \\ P_{\mathrm{nr}}^{(3)}\left(\omega_{\mathrm{as}}\right) & \propto\int_0^{+\infty}E_{\mathrm{pr}}\left(\omega_{\mathrm{as}}-\varOmega\right)\mathrm{d}\varOmega\int_0^{+\infty}E_{\mathrm{p}}\left(\omega_{\mathrm{p}}\right)E_{\mathrm{s}}^*\left(\omega_{\mathrm{p}}-\varOmega\right)\mathrm{d}\omega_{\mathrm{p}}, \end{aligned}$$

where $E(\omega)=A(\omega)\exp[\mathrm{i}\,\varPhi(\omega)]$ is the Fourier transform of $E(t)$, $\varOmega_{\mathrm{R}}$ is the Raman resonant frequency, and $\varGamma$ is the bandwidth of the Raman level. The $P_{\mathrm{r}}^{(3)}$ and $P_{\mathrm{nr}}^{(3)}$ represent the resonant and nonresonant nonlinear polarization, respectively. Equation (2) shows that the CARS signal is the result of the coherent superposition of the resonant and nonresonant contributions.

For simplicity, the pump and probe pulses usually share the same laser field (i.e. two-pulse CARS). In this case, the pump and probe pulses cannot be separately controlled. In our simulation, we discuss the case that the pump and probe pulses come from two laser fields. Considering the quantum system including three Raman levels at resonant frequencies 500 cm^{-1}, 1000 cm^{-1} and 1500 cm^{-1}, all these levels have the same bandwidth of 10 cm^{-1}, as shown in Fig. 1(a). Assume that $\omega_{\mathrm{p}}=12500$ cm^{-1}, $\omega_{\mathrm{s}}=11500$ cm^{-1}, $\omega_{\mathrm{pr}}=\omega_{\mathrm{p}}=12500$ cm^{-1}, and their bandwidths are all 500 cm^{-1}. Due to the broadband pump, Stokes and probe laser pulses, the three vibrational levels can be simultaneously excited. The ability to differentiate the CARS signals between neighbouring Raman levels from their indistinguishable femtosecond CARS spectra is demonstrated by tailoring the probe spectrum to generate a narrow-band probe pulse, and this has been successfully applied.[17,18] As shown in Fig. 1(b), the frequency components of the probe pulse in the window are preserved and those out of the window are cut off; this is similar to a slit. Figure 2 shows the CARS spectra of this quantum system for a transform-limited probe pulse and a shaped probe pulse with a spectral width of 50 cm^{-1} centred at a frequency of 12500 cm^{-1}. Only a single broadband CARS peak is observed for the transform-limited probe pulse (as shown in Fig. 2(a)). However, three distinct CARS peaks A, B and C are observed at the frequency of 13000 cm^{-1}, 13500 cm^{-1} and 14000 cm^{-1} for the shaped probe laser pulse (as shown in Fig. 2(b)) respectively. The frequency differences between three CARS peaks and the central frequency of the shaped probe pulse are equal to the resonant frequencies of the three Raman levels, respectively, and therefore the three Raman peaks are attributed to the three Raman levels.

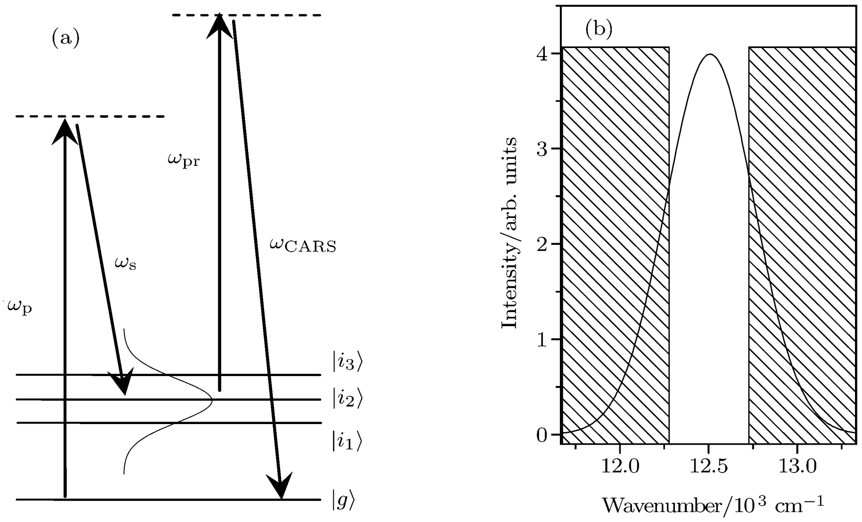

Fig. 1. (a) Energy level diagram for the CARS process, where three Raman levels are simultaneously excited by the broadband pump, Stokes and probe laser pulses. (b) Schematic diagram of the amplitude modulation applied on the probe laser pulse spectrum, where the frequency components in the window are preserved and those out of the window are cut off.

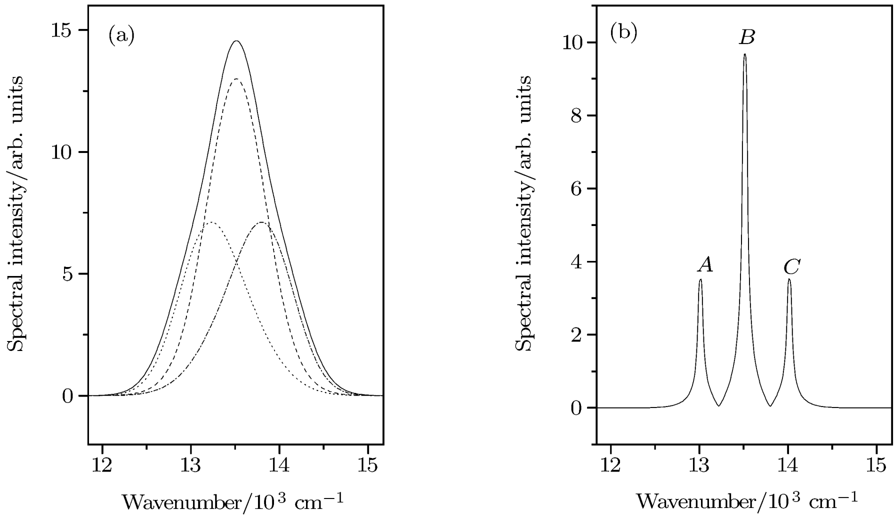

Fig. 2. CARS spectra for the transform-limited probe pulse (a) and the shaped probe pulse with the spectral width 50 cm^{-1} centred at the frequency of 12500 cm^{-1} (b).

Since the CARS signals between neighbouring Raman levels can be differentiated by tailoring the probe spectrum, their selective excitation and suppression are possible to be realized by supplementally manipulating the pump spectrum with a π phase step. In our simulation, the π phase step from low to high frequency (from high to low frequency) means that the spectral phase is set to π for all frequencies smaller (larger) than a reference frequency ω_π and to zero for all frequencies larger (smaller) than ω_π, as shown in Fig. 3(a). Figure

3(b) shows the intensities of the three CARS signals as a function of the π phase step applied on the pump spectrum from low to high frequency. As can be seen, the three CARS signals have a minimal value for the π phase step position at the frequency of 12250 cm^{-1} (solid line), 12500 cm^{-1} (dashed line) and 12750 cm^{-1} (dotted line), respectively. Thus the CARS signals can be selectively suppressed by the π spectral phase step applied on the pump spectrum, and the calculated results are shown in Fig. 4. This indicates that the CARS signals A, B and C are suppressed at the π phase step position of 12250 cm^{-1}, 12500 cm^{-1} and 12750 cm^{-1}, respectively.

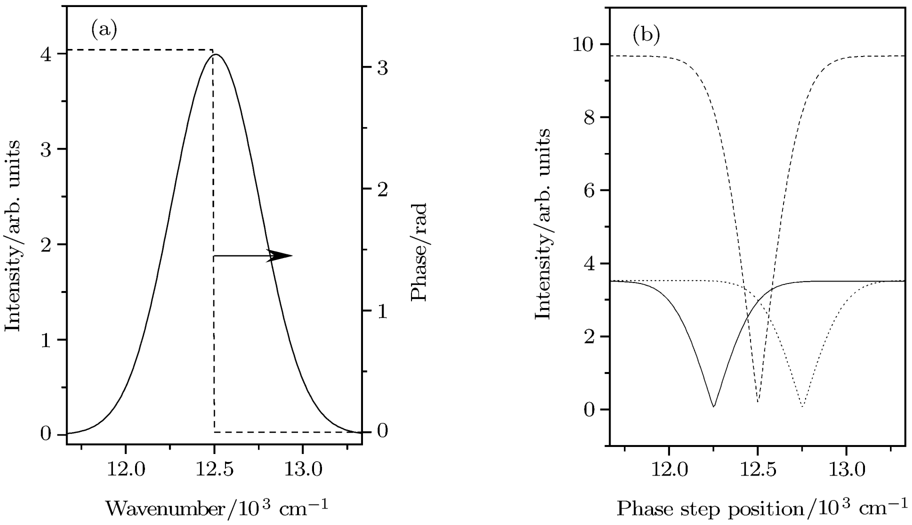

Fig. 3. (a) Schematic diagram of the π spectral phase step from low to high frequency applied on the pump spectrum, (b) the intensities of CARS signals A (solid line), B (dashed line) and C (dotted line) as a function of the π spectral phase step position.

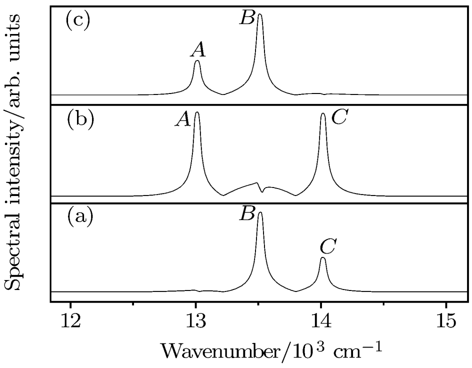

Fig. 4. CARS spectra for the selective suppression of Raman signals A (a), B (b) and C (c) with the π spectral phase step applied on the pump spectrum.

Similarly, special Raman mode can also be selectively excited by simultaneously scanning the pump spectrum with the π spectral phase step from low to high frequency and from high to low frequency (as shown in Fig. 5). The calculated results are shown in Fig. 6; only CARS signal A is excited for the π phase step from low to high frequency at 12458 cm^{-1} and from high to low frequency at 12783 cm^{-1} (Fig. 6(a)), only CARS signal B is excited for the π phase step from low to high frequency at 12266 cm^{-1} and from high to low frequency at 12733 cm^{-1} (Fig. 6(b)), and only CARS signal C is excited for the π phase step from low to high frequency at 12233 cm^{-1} and from high to low frequency at 12525 cm^{-1} (Fig. 6(c)). By the way, by manipulating both the probe and Stokes pulses with the same methods, selective excitation and suppression of the femtosecond CARS can also be re-

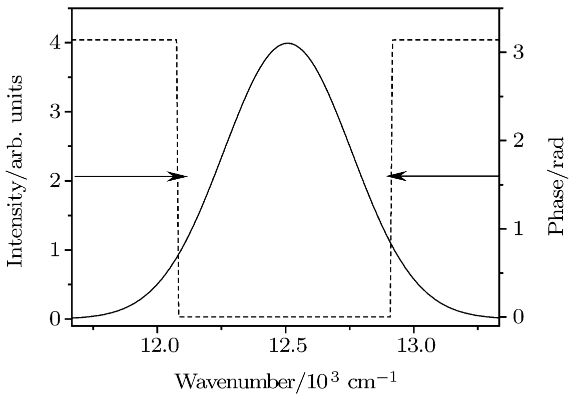

Fig. 5. Schematic diagram of the π spectral phase step from low to high frequency and high to low frequency applied simultaneously on the pump spectrum.

alized, and the same results are achieved.

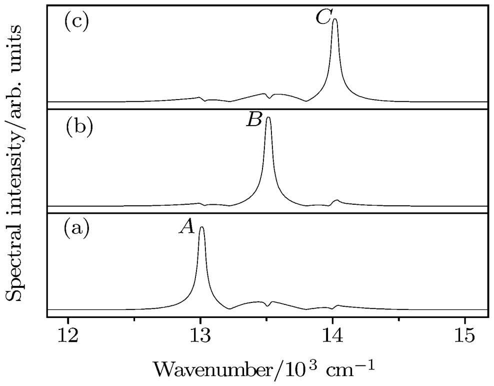

Fig. 6. CARS spectra for the selective excitation of Raman signals A (a), B (b) and C (c) with the π spectral phase step applied on the pump spectrum.

In the CARS process, the CARS signal depends on the population transferring from ground state $|g\rangle$ and intermediate states $|i_1\rangle$, $|i_2\rangle$ and $|i_3\rangle$. In our simulation, since the CARS signal can be selectively excited or suppressed by manipulating the pump (or Stokes) spectrum with the π spectral phase step, it means that the three intermediate states can be selectively populated by the shaped pump (or Stokes) pulse. The use of the state population to explain the selective excitation in simulated Raman scattering has been theoretically demonstrated by Berman *et al.*[19]

In summary, we have theoretically shown that, by tailoring the probe spectrum, the CARS signals between neighbouring Raman levels are differentiated from their indistinguishable CARS spectra, and then their selective excitation and suppression can be achieved with the π spectral phase step applied on the pump (or Stokes) spectrum. Our theoretical results provide a feasible method to realize the selective excitation and suppression between neighbouring Raman levels in indistinguishable femtosecond CARS spectra, and may have potential applications in mode-selective excitation and suppression in the nonlinear optical process.

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