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Precise control of state-selective excitation in stimulated Raman scattering

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Multiphoton transitions can be manipulated by tailoring the ultrashort laser pulse. In this paper, we propose two schemes for achieving precise control of the selective excitation between two excited states in stimulated Raman-scattering process. We theoretically demonstrate that by properly designing the spectral phase distribution, the stimulated Raman transition probability for one excited state is kept at zero or a maximal value, while that for the other excited state can be continuously tuned over a wide range. Furthermore, the influence of the spectral bandwidth on the tunable range by the two schemes is discussed. We conclude that these schemes have significant application to the selective excitation of femtosecond coherent anti-Stokes Raman scattering.

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The selective excitation of a special state can improve the signal-to-noise ratio and the spectral resolution, and therefore it can be applied to the microscopic investigation of a complex molecular structure. However, for femtosecond pulse excitation, several states falling within the broad spectrum of the femtosecond pulse can be simultaneously excited, and it results in poor selectivity between the neighbor states. Fortunately, the quantum coherent control making use of the shaped femtosecond pulse provides a perfect method for realizing state-selective excitation [1–26]. The most successful application is the mode-selective excitation in femtosecond coherent anti-Stokes Raman scattering (CARS) [6–22]. Recently, state-selective excitation in the stimulated Raman-scattering process has attracted considerable interest [23–26]. In experimental studies, Weinacht *et al.* reported the selective excitation of the asymmetric C-O stretching mode (ν_1) and two quanta of the O-C-O bending mode (ν_2) in carbon dioxide gas (CO_2) by the adaptive pulse shaping based on the evolutionary algorithm (EA) [23]. Pearson *et al.* realized the selective excitation of symmetric and asymmetric C-H stretching modes in methanol solution (CH_3OH) by feedback optimization based on the genetic algorithm (GA) [24]. In theoretical work, Malinovskaya *et al.* proposed an analytical function for the shape of the intensity envelope of the pulse that allows for the selective excitation of a preselected vibrational mode with simultaneous suppression of an unfavorable one [25]. If the vibrational modes couple via an external field, the preselected mode excitation may be enhanced by coupling to the other Raman-active vibrational modes [26].

Quantum coherent control is dominated by the interference of different optical pathways connecting the initial and final states, and therefore the challenge for the state-selective excitation is how to induce the constructive or destructive interference between the different optical pathways by properly designing the spectral phase distribution. In previous studies, the state-selective excitation was usually performed by simultaneously manipulating the two states, and finally which state was suppressed or excited depended on their control efficiency. In this case, once one state was maximally suppressed or excited, the other state population was fixed. That is, the degree of control of state-selective excitation is invariable.

In this paper, we theoretically introduce two schemes for achieving a high degree of control of the selective excitation between two excited states in the stimulated Raman-scattering process. Here, one excited state is maximally populated or nonpopulated, while the other state population can be continuously tuned over a wide range.

Considering the interaction of the two laser fields, the pump field $E_p(t)$ and the Stokes field $E_s(t)$, with a three-level atomic system, as shown in Fig. 1. Here $|g\rangle$ and $|f_i\rangle$ $(i=1,2)$ are the ground and final excited states, respectively. $|g\rangle \rightarrow |f_i\rangle$ is coupled by the pump field $E_p(t)$ and Stokes field $E_s(t)$. The two excited stats $|f_1\rangle$ and $|f_2\rangle$ are uncoupled, and therefore the probability for the population transfer from one state to the other one via the external field is zero. Assuming that the two laser pulses are much shorter than the lifetime of the excited states and the population is initially in the ground state $|g\rangle$, the stimulated Raman transition amplitude of the two excited states $|f_i\rangle$ can be expressed by [27]

$$a_{f_i} \propto \int_0^{+\infty} E_p(\omega_p) E_s^*\left(\omega_p - \Omega_{R_i}\right) d\omega_p, \tag{1}$$

where Ω_{R_i} is the transition frequency from the ground state $|g\rangle$ to the final excited states $|f_i\rangle$; and $E_p(\omega_p)$ and $E_s(\omega_s)$ are, respectively, the Fourier transform of $E_p(t)$ and $E_s(t)$ and given by

$$\begin{aligned} E_p(\omega_p) &= E_{p_0} \exp\left[-(\omega_p - \Omega_p)^2/\Delta_p^2\right] \exp[i\Phi_p(\omega_p)],\\ E_s(\omega_s) &= E_{s_0} \exp\left[-(\omega_s - \Omega_s)^2/\Delta_s^2\right] \exp[i\Phi_s(\omega_s)], \end{aligned} \tag{2}$$

where Ω_p and Ω_s are the center frequency of the pump and Stokes pulses, and Δ_p and Δ_s are the spectral bandwidth (full width at half maximum, FWHM) of the pump and Stokes pulses. For simplicity, we define two parameters as $\omega_n = \omega_p - \Omega_p$ and $\Omega_{d_i} = \Omega_p - \Omega_s - \Omega_{R_i}$ (i.e., the Raman detuning), thus the stimulated Raman transition amplitude can be simplified as

$$a_{f_i} \propto \int_{-\Omega_p}^{+\infty} E_{n_{0i}} \exp\left[-\left(\omega_n - \Omega_{n_i}\right)^2/\Delta_n^2\right] \times \exp\left[i\Phi_{n_i}(\omega_n)\right] d\omega_n, \tag{3}$$

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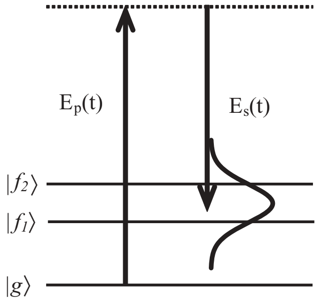

FIG. 1. Schematic diagram of the stimulated Raman scattering process. The excited states $|f_1\rangle$ and $|f_2\rangle$ are simultaneously excited by the pump field $E_p(t)$ and Stokes field $E_s(t)$.

with

$$E_{n_{0i}} = E_{p_0}E_{s_0}e^{-\frac{\Omega_{d_i}^2}{\Delta_p^2+\Delta_s^2}}, \quad \Omega_{n_i} = -\frac{\Delta_p^2}{\Delta_p^2+\Delta_s^2}\Omega_{d_i},$$
$$\Delta_n = \frac{\Delta_p\Delta_s}{\sqrt{\Delta_p^2+\Delta_s^2}}, \tag{4}$$
$$\Phi_{n_i}(\omega_n) = \Phi_p(\omega_n+\Omega_p) - \Phi_s(\omega_n+\Omega_p-\Omega_{R_i}).$$

We can then define a laser field as

$$E_{n_i}(\omega_n) = E_{n_{0i}}\exp\left[-(\omega_n-\Omega_{n_i})^2/\Delta_n^2\right]\exp\left[i\Phi_{n_i}(\omega_n)\right],$$

which indicates that this laser field is different for the two excited states, which depends on the resonant transition frequency Ω_{R_i} [see Eq. (4)]. Finally, the stimulated Raman transition probability of the two excited states $|f_i\rangle$ can be written as

$$P_{f_i} = |a_{f_i}|^2 \propto \left|\int_{-\Omega_p}^{+\infty} E_{n_i}(\omega_n)\,d\omega_n\right|^2. \tag{5}$$

As can be seen from Eq. (5), the pump field $E_p(\omega_p)$ and Stokes field $E_s(\omega_s)$ in the stimulated Raman process can be simplified as the laser field $E_{n_i}(\omega_n)$. All photons in this laser field contribute to the stimulated Raman transition probability P_{f_i}. It is easy to verify that the P_{f_i} is maximal for $\Phi_{n_i}(\omega_n) = 0$. Two cases can occur, one is the transform-limited (TL) pump and Stokes pulses, i.e., $\Phi_p(\omega_n+\Omega_p) = \Phi_s(\omega_n+\Omega_p-\Omega_{R_i}) = 0$ for any ω_n, the other is the shaped pump and Stokes pulses with the phase relation of $\Phi_p(\omega_n+\Omega_p) = \Phi_s(\omega_n+\Omega_p-\Omega_{R_i})$ for any ω_n. Other phase distribution, i.e., $\Phi_{n_i}(\omega_n) \neq 0$, can reduce or even completely eliminate the P_{f_i}. A simple method to completely eliminate the P_{f_i} is to apply a phase function $\Phi_{n_i}(\Omega_{n_i}+\Omega) = \pi + \Phi_{n_i}(\Omega_{n_i}-\Omega)$ for any Ω that inverts the sign of $E_{n_i}(\Omega_{n_i}+\Omega)$ and $E_{n_i}(\Omega_{n_i}-\Omega)$, and thus all photons destructively interfere [see Eq. (5)]. If only the pump pulse (or Stokes pulse) is modulated, the spectral phase function can be written as $\Phi_p(\Omega_{n_i}+\Omega_p+\Omega) = \pi + \Phi_p(\Omega_{n_i}+\Omega_p-\Omega)$ [or $\Phi_s(\Omega_{n_i}+\Omega_p-\Omega_{R_i}+\Omega) = \pi + \Phi_s(\Omega_{n_i}+\Omega_p-\Omega_{R_i}-\Omega)$].

Based on the above discussion and analysis, it can be seen that the complete elimination of the stimulated Raman transition probability or the reconstruction as that TL excitation is correlated with the resonant transition frequency Ω_{R_i}, and therefore this provides a feasible method to realize the selective excitation of the two excited states by properly designing the spectral phase distribution. In what follows, we will demonstrate that the population for one state is kept at zero or maximal value, but the other state population can be continuously tuned over a wide range. In our simulation, CH_3OH is used as the model system; it has two closely vibrational modes with large Stokes shift and cross section, the symmetric C-H stretching mode (2832 cm^{-1}) and the asymmetric C-H stretching mode (2948 cm^{-1}), and the separation between the two Raman modes is 116 cm^{-1}. We assume that the center frequencies of the pump and Stokes laser pulses Ω_p and Ω_s are 15 390 and 12 500 cm^{-1} and their spectral bandwidths Δ_p and Δ_s are 600 cm^{-1}. The frequency difference of the pump and Stokes pulses is set between the two Raman shifts (i.e., $\Omega_p - \Omega_s = 2890\ cm^{-1}$), and therefore both the two Raman modes can be maximally excited. Thus, the Raman detuning of the two Raman modes Ω_{d_1} and Ω_{d_2} can be calculated as 58 and $-58\ cm^{-1}$, and the center frequencies of the laser fields Ω_{n_1} and Ω_{n_2} are -29 and 29 cm^{-1}.

We first demonstrate that the stimulated Raman transition probability for one excited state is kept at a maximal value, while that for the other one can be continuously manipulated.

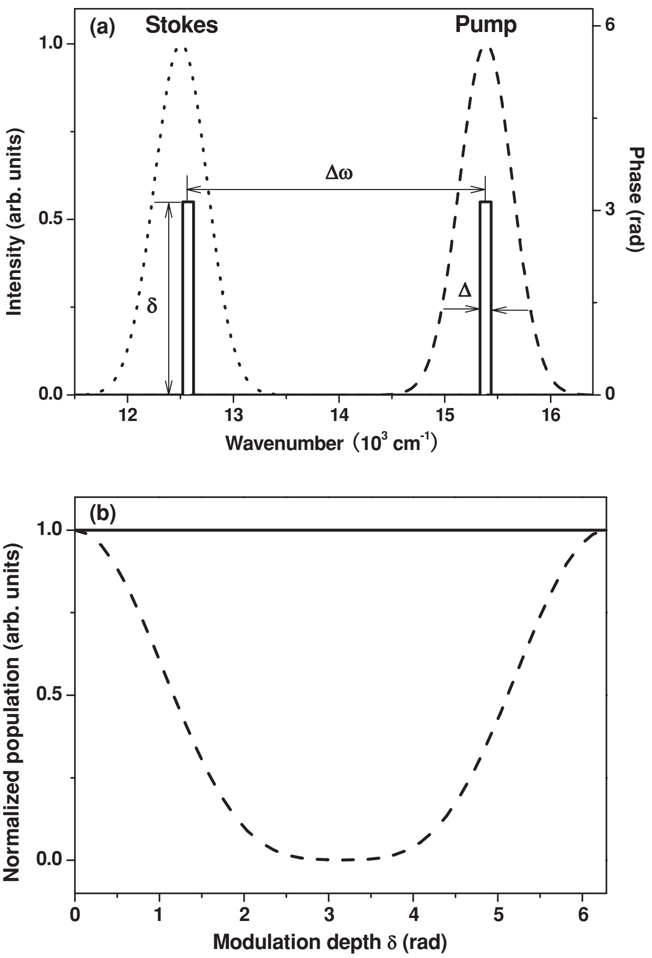

FIG. 2. (a) Schematic diagram of the rectangular step phase functions $\Phi_{p/s}(\omega) = \delta\,\mathrm{rect}[(\omega-\omega_0^{p/s}/\Delta]$ applied on the pump and Stokes spectra, here $\Delta\omega = 2832\ cm^{-1}$ and $\Delta = 116\ cm^{-1}$. (b) P_{f_1} (solid line) and P_{f_2} (dashed line) as the function of the modulation depth δ. The P_{f_2} can be continuously tuned from zero to the maximal value, while the P_{f_1} is kept at the maximal value.

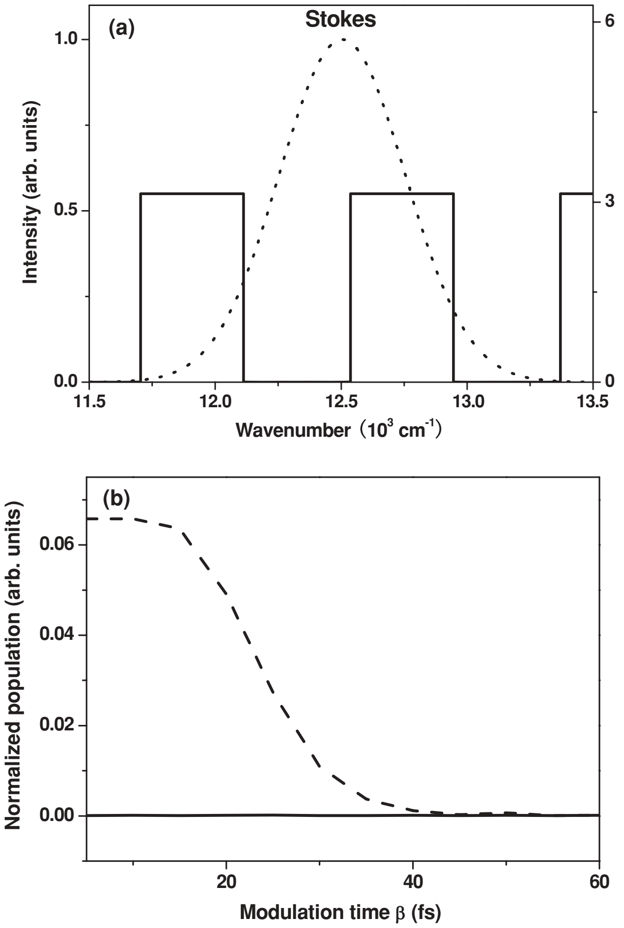

FIG. 3. (a) Schematic diagram of the square phase modulation function $\Phi_s(\omega) = \frac{\alpha}{2} + \frac{2\alpha}{\pi}\sum_{l=0}^{\infty}\frac{\sin[\beta(2l+1)(\omega-\omega^s_{\mathrm{ref}})]}{2l+1}$ applied on the Stokes spectrum; $\omega^s_{\mathrm{ref}} = 12\,529$ cm^{-1} and $\alpha = \pi$. (b) P_{f_1} (solid line) and P_{f_2} (dashed line) as the function of the modulation time β. P_{f_2} can be continuously tuned from 6.6% of the TL excitation to zero, while P_{f_1} is kept constant on its zero level.

We modulate the phase of both the pump and Stokes pulses with the rectangular step phase function $\Phi_{p/s}(\omega) = \delta\,\mathrm{rect}[(\omega - \omega_0^{p/s})/\Delta]$, here δ is the modulation depth and Δ is the phase step width. The spectral modulation is shown in Fig. 2(a). To keep the excited state $|f_1\rangle$ with the maximal population, we set $\Delta\omega = 2832$ cm^{-1} ($\Delta\omega = \omega_0^p - \omega_0^s = \Omega_{R_1}$). So, varying the modulation depth δ does not affect the transition probability of the excited state $|f_1\rangle$. Figure 2(b) shows the stimulated Raman transition probabilities P_{f_1} and P_{f_2} as the function of the modulation depth δ for $\Delta = 116$ cm^{-1}. As can be seen, manipulating the modulation depth δ does not change P_{f_1} but does enormously affect P_{f_2}, which can be continuously tuned from zero to the maximal value. The maximal P_{f_2} corresponds to both the shaped pump and Stokes pulses recovering to the TL pulses. The zero P_{f_2} should result from the destructive interference among different optical pathways in stimulated Raman-scattering process.

Similarly, it also can be realized that the stimulated Raman transition probability for one excited state is kept at zero, while that for the other excited state is independently controlled. We apply a square phase modulation function $\Phi_s(\omega) = \frac{\alpha}{2} + \frac{2\alpha}{\pi}\sum_{l=0}^{\infty}\frac{\sin[\beta(2l+1)(\omega-\omega^s_{\mathrm{ref}})]}{2l+1}$ on the Stokes spectrum, here α and β represent the modulation amplitude and the modulation time, respectively. The simple spectral modulation is schematically plotted in Fig. 3(a). We set $\omega^s_{\mathrm{ref}} = 12\,529$ cm^{-1} ($\omega^s_{\mathrm{ref}} = \Omega_{n_1} + \Omega_p - \Omega_{R_1}$) and $\alpha = \pi$, and thus the excited state $|f_1\rangle$ is kept nonpopulated by varying the modulation time β when all photons in the laser field for the excited state $|f_1\rangle$ transition satisfy the phase relation of $\Phi_{n_1}(\Omega_{n_1} + \Omega) = \pi + \Phi_{n_1}(\Omega_{n_1} - \Omega)$ for any Ω. Figure 3(b) shows the stimulated Raman transition probabilities P_{f_1} and P_{f_2} as the function of the modulation time β. We note a zero value in P_{f_1} but a strong variation in P_{f_2}. With the increase of the modulation time β, P_{f_2} can be continuously tuned from 6.6% of the maximal value to zero. The zero P_{f_2} indicates that all photons in the laser field for the excited state $|f_2\rangle$ transition have also the phase relation of $\Phi_{n_2}(\Omega_{n_2} + \Omega) = \pi + \Phi_{n_2}(\Omega_{n_2} - \Omega)$ for any Ω.

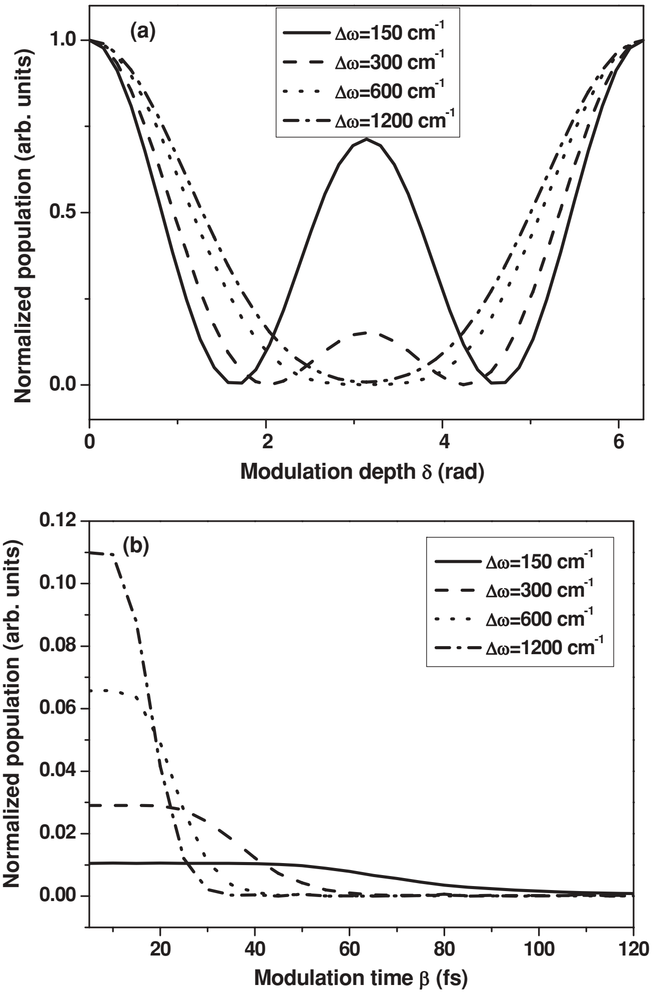

FIG. 4. P_{f_2} as the function of (a) modulation depth δ and (b) modulation time β with the Stokes spectral bandwidth of 150 (solid line), 300 (dashed line), 600 (dotted line), and 1200 (dash dotted line) cm^{-1}. Broadening the spectral bandwidth does not affect the tunable range by the modulation depth δ, but it can expand the tunable range by the modulation time β.

By rational pulse design, the stimulated Raman transition probability for one excited state can be continuously tuned over a wide range, while that for the other one is kept at maximal value or zero, as demonstrated above. Next we investigate the influence of the laser spectral bandwidth on the tunable range by the two shaping schemes. Figures 4(a) and 4(b) show the stimulated Raman transition probability P_{f_2} as a function of, respectively, the modulation depth δ and the modulation time β with the Stokes spectral bandwidths of 150 (solid line), 300 (dashed line), 600 (dotted line), and 1200 (dash dotted line) cm^{-1}. As can be seen, increasing the spectral bandwidth does not affect the tunable range by the modulation depth δ [see Fig. 4(a)], but it can increase the tunable range by the modulation time β [Fig. 4(b)]. By varying the pump spectral bandwidth, similar results can also be obtained.

In summary, we have theoretically demonstrated two schemes for achieving precise control of the selective excitation between two excited states in stimulated Raman process. By shaping the phase of both the pump and Stokes pulses with rectangular step phase functions, the stimulated Raman transition probability for one excited state can be tuned from maximal value to zero, while that for the other excited state is kept at a maximal value, and the tunable range is independent of the laser spectral bandwidth. By applying a square phase modulation function to the Stokes spectrum, the stimulated Raman transition probability for one excited state can be tuned independently over a wide range while that for the other excited state is kept at zero, but the tunable range depends on the laser spectral bandwidth and increases with the broadening of the spectral bandwidth. If multiple excited states are involved, the schemes can be employed iteratively once the excited states are identified. We believe that the schemes can be applied to the coherent anti-Stokes Raman-scattering process.

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