## Coherent control of molecular rotational state populations by periodic phase-step modulation

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We theoretically demonstrate that the molecular rotational state populations through an impulsive nonresonant Raman process can be manipulated by shaping the femtosecond laser pulse with a periodic phase-step modulation. We show that, by precisely controlling these parameters characterizing the periodic phase-step modulation, both the odd and even rotational state populations can be completely suppressed or reconstructed as that induced by the transform-limited laser pulse, and the relative excitation between the odd and even rotational state populations can also be obtained. Furthermore, we show that the field-free molecular alignment can be manipulated due to the modulation of the odd and even rotational state populations.

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nonresonant Raman process can be approximated by the

Coherent control strategy has attracted widespread attention for its ability to steer a quantum system towards a target state or desirable outcome by the light-matter interaction [1-4]. The quantum coherent control is dominated by the interference of different optical pathways connecting the initial and final states, and so the main challenge is how to create the constructive or destructive interference among these different optical pathways. Recently, coherent control by means of shaping the femtosecond laser pulse has been successfully applied to manipulate various physical and chemical processes in atomic or molecular systems [5–11] such as nonresonant two-photon absorption [5,6], multiphoton ionization and dissociation [7,8], high-order harmonic generation [9], coherent anti-Stokes Raman scattering spectroscopy [10-13], and so on. These various schemes were realized by controlling the laser spectral phase and/or amplitude in the frequency domain based on either open- or closed-loop methods.

Recently, the manipulation of the molecular rotational state populations has attracted considerable interest because of its potential applications in molecular alignment and orientation [14–16]. In this paper, we show that the molecular rotational state populations through an impulsive nonresonant Raman process can be manipulated by shaping the femtosecond laser pulse with a periodic phase-step modulation. Our results show that the odd and even rotational state populations can both be completely suppressed or reconstructed as that by the transform-limited laser pulse, and the relative excitation between the odd and even rotational states can also be obtained. Finally, we show that the modulation of the molecular rotational state populations allows the control of the field-free molecular alignment.

As shown in Fig. 1(a), when a molecule is exposed to a weak laser field E(t), the transition probability from the molecular rotational states  $|J\rangle$  to  $|J + 2\rangle$  through an impulsive

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second-order perturbation theory as [6,15]  $P_{I-I+2} \propto \left| \int^{+\infty} E(\omega) E^*(\omega - \omega_I) d\omega \right|^2$ 

$$\sum_{J+2} \propto \left| \int_{-\infty}^{+\infty} E(\omega) E^*(\omega - \omega_J) d\omega \right|$$
$$\propto \left| \int_{-\infty}^{+\infty} A(\omega) A(\omega - \omega_J) \right|$$
$$\times \exp\{i [\Phi(\omega) - \Phi(\omega - \omega_J)] d\omega \right|^2, \quad (1)$$

where  $E(\omega) = A(\omega)\exp[i\Phi(\omega)]$  is the Fourier transform of E(t);  $A(\omega)$  and  $\Phi(\omega)$  are, respectively, the spectral amplitude and phase;  $\omega_J$  is the Raman frequencies with  $\omega_J = 2\pi (E_{J+2} - E_J)/h = 2\pi cB(4J+6) = (4J+6)\pi/T_{\text{rot}}$ ; *h* is Planck's constant, *c* is the speed of light in vacuum;  $E_J$  is the energy of the *J*th rotational state with  $E_J = hcBJ(J+1)$ ; *B* is the molecular rotational constant; *J* is the rotational quantum number; and  $T_{\text{rot}}$  is the rotational period of the molecule with  $T_{\text{rot}} = 1/(2Bc)$ . When an ensemble of molecules in thermal equilibrium is considered, the Raman transition probability  $P_{J-J+2}$  must be averaged over the Boltzmann distribution; thus the total Raman transition probability *P* in the molecular system can written as

$$P = \sum_{J} W_{J}^{2} P_{J-J+2}$$

$$\propto \sum_{J} W_{J}^{2} \left| \int_{-\infty}^{+\infty} A(\omega) A(\omega - \omega_{J}) \right|$$

$$\times \exp i [\Phi(\omega) - \Phi(\omega - \omega_{J})] d\omega \Big|^{2}, \qquad (2)$$

where  $W_J$  are Boltzmann weight factors with  $W_J = \exp[-BJ(J+1)/kT]/Q$ , Q is the rotational partition function, k is the Boltzmann constant, and T is the molecular rotational temperature.

As can be seen in Eq. (2), the total Raman transition probability *P* is correlated with the laser spectral phase  $\Phi(\omega)$ , and therefore it can be controlled by shaping the laser spectral phase  $\Phi(\omega)$ . The shaped pulse with a periodic phase-step modulation has been proven to be a well-established tool in quantum coherent control because it is convenient to obtain

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FIG. 1. (Color online) (a) The schematic diagram of the impulsive nonresonant Raman process induced by the laser field E(t). (b) The periodic phase-step modulation applied on the laser spectrum.

the controllable multiple subpulse sequences, and therefore has been widely employed to manipulate various multiphoton absorption processes, such as the two-photon absorption [17] and the stimulated Raman scattering process [18]. In this paper, we employ the periodic phase-step modulation to control the molecular rotational state populations through an impulsive nonresonant Raman process. Figure 1(b) shows the modulated laser spectrum by the periodic phase-step modulation with the function of

$$\Phi(\omega) = \alpha/2 + 2\alpha/\pi \sum_{l=0}^{\infty} \sin[\beta(2l+1)(\omega-\omega_0)]/(2l+1),$$

where  $\alpha$  and  $\beta$  are, respectively, the modulation depth and modulation time, and  $\omega_0$  is the laser central frequency. In our simulation, we take the CO molecule as an example, and the molecular rotational constant  $B = 1.93 \text{ cm}^{-1}$  [19]; thus the rotational period of the CO molecule can be calculated as  $T_{\text{rot}} =$ 8.64 ps. In the calculation, 50 rotational states are considered, which can cover all the thermal and dynamic rotational levels distribution. We assume that the laser pulse has a Gaussian profile with the central frequency of 12 500 cm<sup>-1</sup>, corresponding to the laser central wavelength of 800 nm, and the spectral bandwidth [a full width at half maximum (FWHM)] of 300 cm<sup>-1</sup>.

Figure 2 shows the contour plot of the odd, even, and total Raman transition probabilities  $P_{\text{odd}}$  (upper panel),  $P_{\text{even}}$ 

(middle panel), and P (lower panel) as a function of the modulation depth  $\alpha$  and the modulation time  $\beta$  for the rotational temperature T = 300 K (a) and 30 K (b). Here,  $P_{odd}$  comprises only the odd rotational state contribution and  $P_{\text{even}}$  comprises only the even rotational state contribution. As can be seen, Pis strongly modulated by varying the modulation depth  $\alpha$  and the modulation time  $\beta$  [see Figs. 2(a-3) and 2(b-3)], which can be completely suppressed around  $\alpha = \pi$  and  $\beta = 2153$  fs,  $\alpha = \pi/2$  and  $\beta = 4317$  fs, and  $\alpha = 3\pi/2$  and  $\beta = 4317$  fs (labeled with dashed rectangles), and can also be reconstructed as that induced by the transform-limited laser pulse around  $\alpha = \pi$  and  $\beta = 4317$  fs (labeled with solid rectangles). Furthermore, one can seen that the relative excitation between  $P_{\text{odd}}$  and  $P_{\text{even}}$  can be obtained [see Figs. 2(a-1), 2(a-2), 2(b-1), and 2(b-2)].  $P_{odd}$  (or  $P_{even}$ ) is tremendously suppressed while  $P_{\text{even}}$  (or  $P_{\text{odd}}$ ) is almost unaffected around  $\alpha = \pi$  and  $\beta =$ 1088 fs,  $\alpha = \pi$  and  $\beta = 3241$  fs,  $\alpha = \pi/2$  and  $\beta = 2153$  fs, and  $\alpha = 3\pi/2$  and  $\beta = 2153$  fs (labeled with solid rectangles). Moreover, we can find that the manipulation of  $P_{odd}$ ,  $P_{even}$ , and P can be realized at both room (300 K) and low (30 K) rotational temperature. To further observe the manipulation of  $P_{\text{odd}}$ ,  $P_{\text{even}}$ , and P, we present  $P_{\text{odd}}$  (red dashed line),  $P_{\text{even}}$ (blue dotted line), and P (green solid line) as a function of the modulation time  $\beta$  with the modulation depth  $\alpha = \pi/2$  (upper panel) and  $\pi$  (lower panel) for the rotational temperature T = 300 K (a) and 30 K (b), as shown in Fig. 3. It is obvious that by precisely controlling the modulation depth  $\alpha$  and the modulation time  $\beta$ , both  $P_{odd}$  and  $P_{even}$  can be completely suppressed or reconstructed as that induced by the transformlimited laser pulse, and the relative excitation between  $P_{odd}$  and  $P_{\text{even}}$  can also be obtained. Consequently, we can conclude that the periodic phase-step modulation can provide an effective method to control the molecular rotational state populations.

In order to analyze the physical control process of the manipulation of  $P_{odd}$ ,  $P_{even}$ , and P by the periodic phase-step modulation, we present the temporal intensity profile of the shaped laser pulse with (a) the modulation time  $\beta = 2153$  fs for the modulation depth  $\alpha = \pi/4$  (red solid line),  $\pi/2$  (blue dashed line), and  $\pi$  (green dotted line) and (b) the modulation depth  $\alpha = \pi$  for the modulation time  $\beta = 1088$  fs (red solid line), 2153 fs (blue dashed line), 3241 fs (green dotted line), and 4317 fs (purple dash-dotted line), as shown in Fig. 4. One can see that the shaped pulse for the periodic phase-step modulation is the multiple subpulse structure. The modulation depth  $\alpha$  is to control the relative amplitude between the central subpulse and these side subpulses, and the central subpulse vanishes and these side subpulses are maximal value when  $\alpha = \pi$ . The modulation time  $\beta$  is to control the subpulse separation, and the subpulse separation increases with the increase of the modulation time  $\beta$ . As can be seen from Fig. 4(b), when the modulation time  $\beta$  is 1088, 2153, 3241, and 4317 fs, the subpulse separation is 2.16, 4.32, 6.48 and 8.64 ps, respectively, which are equal to a quarter, half, three quarters, and full molecular rotational period (i.e.,  $T_{rot}/4$ ,  $T_{rot}/2$ ,  $3T_{rot}/4$ , and  $T_{\rm rot}$ ). That is to say, the relative excitation between  $P_{\rm odd}$ and  $P_{\text{even}}$  can be obtained when the subpulse separation is around one quarter or three-quarters of the molecular rotational period (i.e.,  $T_{\rm rot}/4$  or  $3T_{\rm rot}/4$ ), and both  $P_{\rm odd}$  and  $P_{\rm even}$  can be completely suppressed or reconstructed as that induced by the transform-limited laser pulse when the subpulse separation



FIG. 2. (Color online) The contour plot of the odd, even, and total Raman transition probabilities  $P_{odd}$  (upper panel),  $P_{even}$  (middle panel), and P (lower panel) as a function of the modulation depth  $\alpha$  and the modulation time  $\beta$  for the rotational temperature T = 300 K (a) and 30 K (b).



FIG. 3. (Color online) The odd, even, and total Raman transition probabilities  $P_{odd}$  (red dashed line),  $P_{even}$  (blue dotted line), and P (green solid line) as a function of the modulation time  $\beta$  with the modulation depth  $\alpha = \pi/2$  (upper panel) and  $\pi$  (lower panel) for the rotational temperature T = 300 K (a) and 30 K (b).



FIG. 4. (Color online) The temporal intensity profile of the shaped laser pulse with (a) the modulation time  $\beta = 2153$  fs for the modulation depth  $\alpha = \pi/4$  (red solid line),  $\pi/2$  (blue dashed line), and  $\pi$  (green dotted line) and (b) the modulation depth  $\alpha = \pi$  for the modulation time  $\beta = 1076$  fs (red solid line), 2153 fs (blue dashed line), 3241 fs (green dotted line), and 4317 fs (purple dash-dotted line).

is a half or full molecular rotational period (i.e.,  $T_{\rm rot}/2$  or  $T_{\rm rot}$ ).

When a laser pulse is applied to a molecule, a coherent rotational wave packet is created from the contribution of the populated rotational states by the laser-molecule interaction. The production of the coherent rotational wave packet induced by the laser field leads to the macroscopic molecular alignment along the laser polarization direction. As shown in Fig. 2, since the impulsive Raman transition probability (i.e., rotational state populations) can be manipulated by the periodic phase-step modulation, we can control the coherent rotational wave packet and consequently the field-free molecular alignment. To demonstrate the control of the field-free molecular alignment due to the modulation of the molecular rotational state populations, we numerically calculated the time-dependent molecular alignment  $\langle \cos^2 \theta \rangle$  based on a rigid-rotor model as described in Ref. [20], where  $\theta$  is the angle between the molecular axis and the laser polarization direction.

Figure 5 shows the time-dependent molecular alignment  $\langle \cos^2 \theta \rangle$  (green solid line) by the shaped laser pulse with the modulation depth  $\alpha = \pi$  for the modulation time  $\beta = 1028$  fs (a), 1137 fs (b), 2153 fs (c), and 4317 fs (d), together with the odd (red dashed line) and even (blue dotted line) rotational state contributions and the temporal intensity profile of the shaped laser pulse (purple dash-dotted line). Here, the intensity of the unshaped laser pulse is  $1 \times 10^{13}$  W/cm<sup>2</sup>, and the molecular rotational temperature is 300 K. When  $\beta = 1028$  fs (or 1137 fs), corresponding to the subpulse separation of 2.06 ps (or 2.28 ps),  $\langle \cos^2 \theta \rangle_{odd}$  is unaffected (or suppressed) while  $\langle \cos^2 \theta \rangle_{even}$  is suppressed (or unaffected). When  $\beta = 2153$  fs, corresponding to the subpulse separation of 4.32 ps (i.e.,  $T_{rot}/2$ ), both  $\langle \cos^2 \theta \rangle_{odd}$  and  $\langle \cos^2 \theta \rangle_{even}$  are suppressed



FIG. 5. (Color online) Time-dependent molecular alignment  $\langle \cos^2 \theta \rangle$  (green solid line) by the shaped laser pulse with the modulation depth  $\alpha = \pi$  for the modulation time  $\beta = 1028$  fs (a), 1137 fs (b), 2153 fs (c), and 4317 fs (d), together with the odd (red dashed line) and even (blue dotted line) rotational state contributions and the temporal intensity profile of the shaped laser pulse (purple dash-dotted line).

and therefore  $\langle \cos^2 \theta \rangle$ . When  $\beta = 4317$  fs, corresponding to the subpulse separation of 8.64 ps (i.e.,  $T_{\rm rot}$ ), both  $\langle \cos^2 \theta \rangle_{\rm odd}$  and  $\langle \cos^2 \theta \rangle_{\rm even}$  are reconstructed as that induced by the transform-limited laser pulse, and  $\langle \cos^2 \theta \rangle$  recovers to the maximal value. Obviously, these observations are consistent with our above predictions.

In summary, we have presented a scheme to manipulate the molecular rotational state populations through an impulsive nonresonant Raman process using the periodic phase-step modulation. The shaped pulse is the pulse train, and the subpulse separation is continuously controllable. We showed that the relative excitation between the odd and even rotational state populations can be obtained when the subpulse separation is around one quarter or three quarters of the rotational period, and the total rotational state populations can be completely suppressed or reconstructed as that by the transform-limited laser pulse when the subpulse separation is a half or full rotational period. We also showed that the field-free molecular

rotational period. We also showed that the field-free molecular alignment can be controlled due to the modulation of the rotational state populations. We believe that these results are expected to be significant for the control of the molecular dynamics and related applications in various fields.

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