PAPER

Selective excitation and control of the molecular orientation by a phase shaped laser pulse

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We demonstrate that the selective excitation and further control of molecular orientation can be realized by a dual-color shaped laser pulse with V-style spectral phase modulation. Due to the instructive or destructive interference between the odd and even rotational wave-packet contributions, selective excitation of the molecular orientation is realized in the half rotational periods by the V-style phase modulated femtosecond laser pulse, and the positive and negative molecular orientations can be freely switched by varying the carrier-envelope phase of the shaped laser pulse. Moreover, by varying the modulation position of the V-style phase-shaped femtosecond laser pulse, the maximum degrees of the positive and negative molecular orientation in the half rotational periods can be continuously manipulated. Our scheme can provide a new method for the manipulation of the molecular orientation induced by the phase shaped laser pulse, and also has significant applications in the control of the molecular rotational wave-packet.

1. Introduction

An anisotropic quantum system, such as aligned molecules, has attracted both physicists' and chemists' interest because of its widespread applications in chemical reaction dynamics,[1–3] high-order harmonic generation,[4,5] ultrafast molecular imaging,[6] and attosecond science.[7] Comparing with the molecular alignment, which suffers from an averaging effect over the direction of the molecular axis, the molecular orientation with a "head-*versus*-tail" order is faced with greater challenges, but has more important applications in various related areas. So far, several different techniques have been utilized to realize the molecular orientation, such as the strong dc field (*i.e.*, the so called "brute force" method),[8] the weak dc field combined with an intense laser field,[9–11] or the asymmetric intense laser field.[12–17] However, the Stark effect induced by the strong dc electric field may influence the experimental results, and the presence of the dc field will also limit the further applications of the oriented molecules. Therefore, the field-free molecular orientation induced by a short asymmetric laser pulse has achieved more and more attentions, such as the dual-color or multi-color laser pulse,[12–15] or the half-cycle laser pulse.[16,17]

For those who dedicated on the research of the molecular alignment and orientation, an important issue is how to control the evolution of the molecular rotational wave-packet. With the advent of the ultrafast pulse shaping technique, the shaped laser pulse with the spectral phase modulation has shown to be one of the effective methods to manipulate the aligned or oriented molecules. Various phase modulation schemes, including the phase step modulation, the cubic phase modulation, and the closed feedback phase optimization, have been applied to the study of the molecular alignment or orientation control.[18–25] Recently, we demonstrated that, by the V-style spectral phase modulation, the degree and temporal structure of the molecular alignment can be effectively manipulated.[26] In this paper, we further show that the molecular orientation in half rotational periods can be selectively excited and further controlled by the V-style spectral phase modulation, and the selective excitation can be attributed to the instructive or destructive interference between the odd and even rotational wave-packet contributions. Furthermore, by varying the carrier-envelope phase of the shaped laser pulse, the positive and negative molecular orientations can be freely switched. Finally, we show that the degree of the molecular orientation in the half rotational periods can be continuously manipulated by scanning the modulation position of the V-style spectral phase modulation.

2. Theoretical model

We consider that a linear molecule is subjected to a linearly polarized dual-color laser pulse with the fundamental-wave (FW) and its second-harmonic (SH) fields, and the dual-color laser field can be written as

$$E(t) = E_{FW}(t)\cos(\omega_0 t) + E_{SH}(t)\cos(2\omega_0 t + \phi_{CEP}) \quad (1)$$

where $E_{FW(SH)}(t) = E_0 \exp((-2 \ln 2)t^2/\tau_0^2)$ is the pulse envelope with the Gaussian distribution, E_0 is the laser field amplitude,

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ω_0 is the laser central frequency, τ_0 is the pulse duration, and ϕ_{CEP} is the carrier-envelope phase (CEP) of the laser pulse. For $\phi_{CEP} = 0$ or π, the overall electric field of the dual-color pulse is totally reverse. Based on the rigid rotor model, the time-dependent Schrödinger equation of the interaction between the linear molecule and dual-color laser field can be approximated as

$$i\hbar \frac{\partial |\psi(\theta,t)\rangle}{\partial t} = H(t)|\psi(\theta,t)\rangle, \tag{2}$$

with the effective Hamiltonian

$$H(t) = BJ(J+1) - \mu_0 E(t)\cos\theta - \frac{1}{2}\left[(\alpha_\parallel - \alpha_\perp)\cos^2\theta + \alpha_\perp\right]E^2(t)$$
$$- \frac{1}{6}\left[(\beta_\parallel - 3\beta_\perp)\cos^3\theta + 3\beta_\perp\cos\theta\right]E^3(t), \tag{3}$$

where B and μ_0 are respectively the rotational constant and the permanent dipole moment of the molecule, J is the angular momentum, θ is the angle between the molecular axis and the direction of the dual-color laser field, $\alpha_\parallel$ and $\alpha_\perp$ are respectively the polarizability components parallel and perpendicular to the molecular axis, and $\beta_\parallel$ and $\beta_\perp$ are respectively the hyperpolarizability components parallel and perpendicular to the molecular axis. The degree of the molecular orientation is usually given by the expectation value of $\cos\theta$ (i.e., $\langle\cos\theta\rangle$). When the thermal equilibrium of the molecular ensemble is considered, the expectation value of $\cos\theta$ should be averaged over the Boltzmann distribution, and written as

$$\langle\cos\theta\rangle = \sum_J W_J \sum_{M=-J}^{J} \langle\Psi_{JM}|\cos\theta|\Psi_{JM}\rangle$$
$$= \sum_J \frac{g_J \exp[-BJ(J+1)/kT]}{Q} \sum_{M=-J}^{J} \langle\Psi_{JM}|\cos\theta|\Psi_{JM}\rangle \tag{4}$$

where g_J is the spin degeneracy factor, Q is the rotational partition function, k is the Boltzmann constant, and T is the molecular rotational temperature.

In our theoretical simulation, the time-dependent Schrödinger equation in eqn (2) is numerically solved by the split-operator method.[27,28] The CO molecule is used as the example, and the molecular parameters are set as $B = 1.93$ cm^{-1}, $\mu_0 = 0.112$ D, $\alpha_\parallel = 2.294$ Å^3, $\alpha_\perp = 1.77$ Å^3, $\beta_\parallel = 2.748 \times 10^9$ Å^5, $\beta_\perp = 4.994 \times 10^8$ Å^5.[29,30] Thus, the rotational period of the CO molecule can be calculated as $T_{rot} = 1/(2Bc) \approx 8.64$ ps, where c is the velocity of the light in vacuum. The central frequency of the fundamental wave field is $\omega_0 = 12\,500$ cm^{-1}, corresponding to the central wavelength of 800 nm. The pulse duration of the transform-limited laser pulse is $\tau_0 = 50$ fs, and all the peak intensities of the unshaped and shaped laser pulses are $I = 1 \times 10^{13}$ W cm^{-2}. The molecular rotational temperature is set to be $T = 30$ K.

3.   Results and discussion

We first show the time revolved molecular orientation induced by the transform-limited femtosecond dual-color laser pulse, as

depicted in Fig. 1, together with the odd (green dashed line) and even (blue dotted line) rotational wave-packet contributions. It can be seen that the odd and even rotational wave-packet contributions show the same evolution behavior around the full rotational periods, while exhibit the inverse evolution behavior around the half rotational periods. Since the molecular orientation results from the interference between the odd and even rotational wave-packet contributions, it will experience the destructive interference around the half rotational periods while instructive interference around the full rotational periods. Therefore, the result is that only the total contributions for the molecular orientation can be found around the full rotational periods. However, if the symmetrical contributions between the odd and even rotational wave-packets around the half rotational periods can be broken, it can be suggested that the selective excitation and further control of the molecular orientation can be realized.[31,32]

Here, we utilize a V-style phase modulated dual-color laser pulse to realize the selective excitation and further control of the molecular orientation. The details of the V-style phase modulation has been described elsewhere.[26,33] Briefly, the shaped laser field by the V-style phase modulation in frequency domain $E_V(\omega)$ can be written as $E_V(\omega) = E(\omega) \times \exp[i\Phi(\omega)]$, where $E(\omega)$ is the Fourier transform of the transform-limited laser field $E(t)$, as shown in eqn (1), and $\Phi(\omega)$ is the V-style phase modulation function defined by $\Phi(\omega) = \tau|\omega - \omega_0 - \delta\omega|$, here τ and $\delta\omega$ represent the modulation depth and the modulation position, respectively. Thus, the shaped laser field in time domain $E_V(t)$ can be given by the reverse Fourier transform of $E_V(\omega)$. Fig. 2(a) presents the schematic diagram of the V-style spectral phase modulation in frequency domain, and the amplitude profile of the 50 fs transform-limited laser pulse in time domain is shown in Fig. 2(b), together with the corresponding shaped dual-color laser pulse with different modulation parameters (Fig. 2(c)–(e)). One can see from Fig. 2(c)–(e) that, two time-delayed sub-pulses with controllable relative intensity ratio can be formed by the
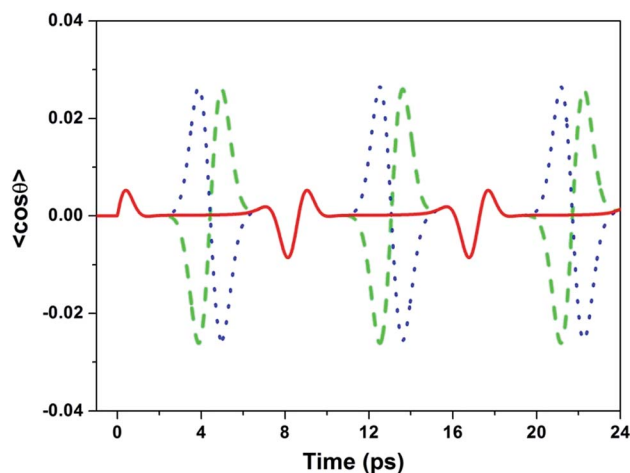

Fig. 1   Time revolved molecular orientation (red solid line) induced by a transform-limited femtosecond dual-color laser pulse, together with its odd (green dashed line) and even (blue dotted line) rotational wave-packet contributions.
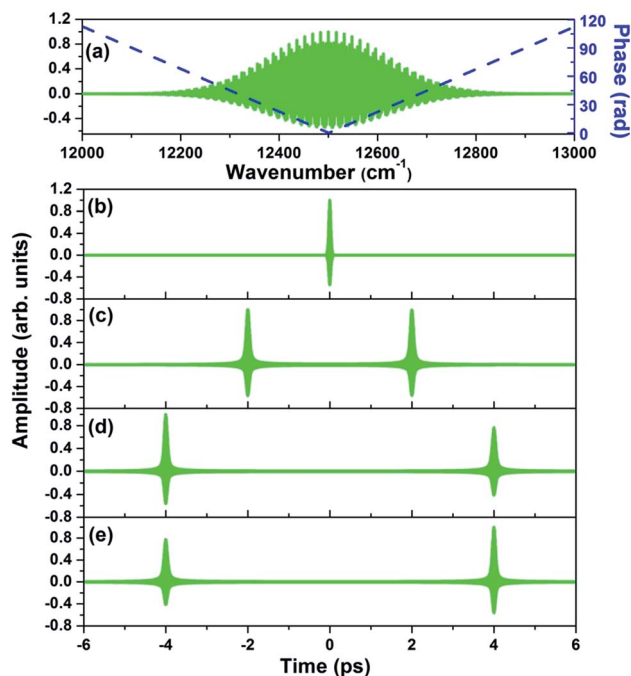
Fig. 2 (a) Schematic diagram of the 50 fs dual-color laser spectrum (green solid line) and the V-style spectral phase modulation $\Phi(\omega) = \tau|\omega - \omega_0 - \delta\omega|$ with $\tau = 2$ ps and $\delta\omega = 0$ cm^{-1} (blue dashed line). (b)–(e) The amplitude profile of the unshaped dual-color laser pulse (b) and the shaped laser pulse by the V-style spectral phase modulation with $\tau = 2$ ps and $\delta\omega = 0$ cm^{-1} (c), together with $\tau = 4$ ps and $\delta\omega = -20$ (d) and 20 cm^{-1} (e).

V-style phase modulation, where the modulation depth τ determines the time separation Δt of the two sub-pulses with $\Delta t = 2\tau$, and the modulation position $\delta\omega$ determines the relative intensity ratio between the two sub-pulses. Therefore, the shaped laser pulse with the V-style spectral phase modulation is similar to the simplest extension of a single pulse to a train of two pulses with controllable relative intensity ratio.[34–36]

By employing the shaped laser pulse formed by the V-style spectral phase modulation, we can realize the selective excitation and control of the rotational wave-packet in the molecular orientation. Fig. 3 shows the time revolved molecular orientation (red solid lines) induced by the V-style spectral phase shaped femtosecond laser pulse for carrier-envelope phase $\phi_{CEP} = 0$ (a) and π (b), together with the odd (green dashed lines) and even (blue dotted lines) rotational wave-packet contributions. Here, the modulation depth is set as $\tau = 2.16$ ps, corresponding to the time separation of the two sub-pulses $\Delta t = 2\tau = 4.32$ ps, and the modulation position is $\delta\omega = 0$ cm^{-1}. This indicates that two sub-pulses with equal intensity and the time separation of half rotational period of the molecule can be formed by the V-style spectral phase modulation. One can see from Fig. 3 that, due to the precise excitation of the second sub-pulse at the position of the half rotational period, the symmetrical contributions of the odd and even rotational wave-packets are broken, and selective excitation of the molecular orientation at these positions is realized. Furthermore, by observing Fig. 3(a) and (b), one can see that this selective excitation of the positive
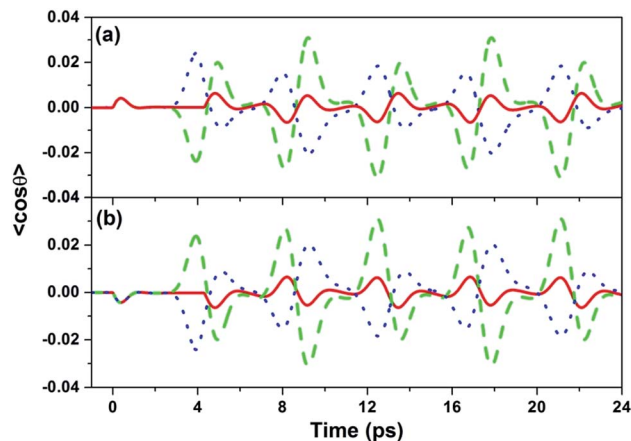

Fig. 3 Time revolved molecular orientation (red solid lines) induced by the V-style spectral phase shaped femtosecond laser pulse with the modulation depth $\tau = 2.16$ ps and the modulation position $\delta\omega = 0$ cm^{-1} for carrier-envelope phase $\phi_{CEP} = 0$ (a) and π (b), together with their odd (green dashed lines) and even (blue dotted lines) rotational wave-packet contributions.

and negative molecular orientation can be freely switched by simply changing the carrier-envelope phase ϕ_{CEP} from 0 to π.

In order to explore the physical origin why the selective excitation of the molecular orientation in the half rotational periods can take place by the V-style spectral phase modulation, we further investigate the population in each rotational state, which can be obtained by the Fourier transform of the molecular orientation signal, and the results are presented in Fig. 4. As can be seen, both the odd and even rotational states are populated under the excitation of the transform-limited laser pulse (red squares). However, only the odd rotational states are populated under the case of the V-style phase modulation for both the carrier-envelope phase $\phi_{CEP} = 0$ (green circles) and π (blue triangles). This can be illustrated by considering both the pattern of the field amplitude and the contributions of the
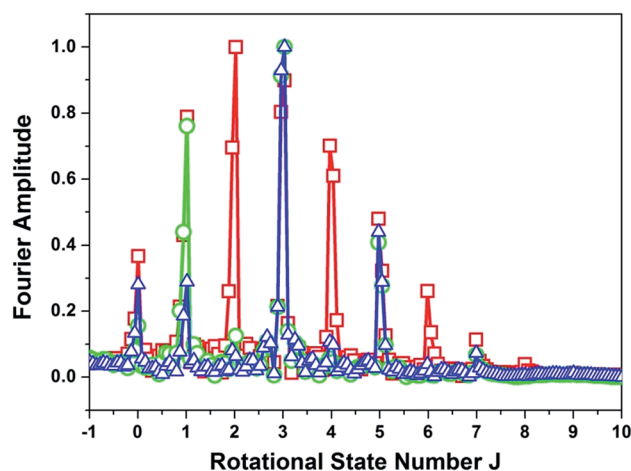

Fig. 4 Fourier transform of the molecular orientation signal induced by the transform-limited laser pulse (red squares) and the V-style spectral phase shaped femtosecond laser pulse with $\tau = 2.16$ ps and $\delta\omega = 0$ cm^{-1} for $\phi_{CEP} = 0$ (green circles) and π (blue triangles).

odd and the even rotational wave-packets. For $\phi_{CEP} = 0$, the pattern of the field amplitude is shown in Fig. 2(c). The odd and even rotational wave-packet contributions by the first sub-pulse of the V-style phase modulation, which is the same as that shown in Fig. 1, are then excited by the second sub-pulse at the position of the half rotational periods. Considering the slope of the curves of the odd (*i.e.*, positive) and even (*i.e.*, negative) rotational wave-packet contributions,[37] the instructive interference for the odd rotational wave-packet contributions while the destructive interference for the even rotational wave-packet contributions will occur due to the excitation of the second sub-pulse. Therefore, the result is that only the odd rotational states are populated. Similarly, for $\phi_{CEP} = \pi$, both the field pattern of the two sub-pulses shown in Fig. 2(c) and the contributions of the odd and even rotational wave-packets presented in Fig. 1 are totally reverse, and therefore the same result can be obtained, *i.e.*, only the odd rotational states are populated.

Finally, we demonstrate the maximum degrees of the positive (red squares) and negative (blue circles) molecular orientation in the half rotational periods by varying the modulation position $\delta\omega$ with the modulation depth $\tau = 2.16$ ps, and the result is shown in Fig. 5. One can see that the degree of the molecular orientation at the half rotational periods can be continuously controlled by varying the modulation position. For $\delta\omega = 0$ cm^{-1}, corresponding to a shaped laser pulse with two sub-pulses of equal intensity, the maximal value of the degree of the molecular orientation is observed. With the increase of the absolute value of the modulation position $\delta\omega$, the maximal degree of the molecular orientation decreases and gradually approaches to zero, which means that the selective excitation of the molecular orientation will disappear. The reason is that the larger absolute value of the modulation position $\delta\omega$ will progressively diminish one of the two shaped sub-pulses, and it is back to the case of the excitation with single laser pulse. Therefore, the selective excitation of the molecular orientation can not only be switched by varying the
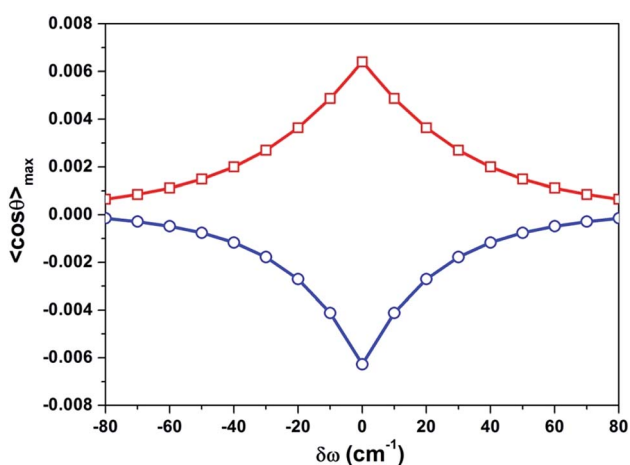
carrier-envelope phase ϕ_{CEP} but also be continuously controlled by scanning the modulation position $\delta\omega$.

It should be pointed out that, although the selective excitation of the molecular orientation in this work is obtained at the relatively lower molecular rotational temperature $T = 30$ K, the effect is still applicable for higher temperatures (*e.g.*, room temperature), except for a much lower degree of the molecular orientation. In fact, it is a common method to obtain the higher (or lower) degree of the molecular orientation by reducing (or increasing) the molecular rotational temperature.

4. Conclusions

In summary, we have shown that the selective excitation of the molecular orientation is realized and further controlled by a shaped laser pulse with the V-style spectral phase modulation. By precisely control the modulation depth, the selective excitation of the molecular orientation at half rotational periods is obtained. The positive and negative molecular orientations can be freely switched by changing the carrier-envelope phase, and the degree can also be continuously manipulated by scanning the modulation position. The physical origin of the selective excitation by the V-style phase modulation can be well illustrated by considering the instructive and destructive interferences between the odd and even rotational wave-packet contributions. We believe that these results provide a valuable method to manipulate the molecular orientation degree and direction, and are also expected to be significant for the applications in various related areas.

Acknowledgements

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Fig. 5 The maximum degrees of the positive (red squares) and negative (blue circles) molecular orientation in the half rotational period by varying the modulation position $\delta\omega$ with the modulation depth $\tau = 2.16$ ps.

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