PHYSICAL REVIEW A **81**, 053401 (2010)

Field-free molecular orientation control by two ultrashort dual-color laser pulses

Jian Wu and Heping Zeng[*]
State Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062, People's Republic of China

(Received 10 February 2010; published 4 May 2010)

We show that molecular orientation can be controlled by sequential three-photon Raman excitations with time-delayed dual-color ultrashort laser pulses. The field-free molecular orientation created by a dual-color ultrashort laser pulse can be significantly enhanced or completely suppressed when another in-phase or antiphase dual-color ultrashort laser pulse is applied at its full revival time. By applying the second dual-color ultrashort laser pulse at the half-revival time, the odd and even rotational wave packets for the impulsive molecular orientation can be promoted and depressed by changing its carrier-envelope phase.

DOI: 10.1103/PhysRevA.81.053401 PACS number(s): 33.80.−b, 33.15.Bh, 42.50.Wk, 37.10.Vz

Field-free control of the molecular alignment [1] can be achieved by ultrashort laser pulses through impulsive rotational Raman excitation, which has been extensively studied for molecular orbital reconstruction [2], high-order harmonic generation [3], and intense laser pulse propagation [4–6]. As compared with the molecular alignment, the molecular orientation [1] with distinguishable head versus tail orders is much more challenging and important for various applications such as chemical reaction control, molecular nanomaterial design, and so forth. Molecular orientation can be obtained by using dual-color laser pulses [7–9] or half-cycle terahertz pulses [10–13] of asymmetric optical potentials to change the molecular wave function parity. For a half-cycle terahertz pulse, the resulting orientation is determined by its interaction with the permanent dipole moment of the polar molecules [10–13]. However, for the laser pulse of fast oscillation frequency, the permanent dipole moment interaction is averaged out to be negligibly small over many oscillation cycles, and the observed orientation is primarily contributed by its interaction with the molecular hyperpolarizability. Owing to the rapid development of the ultrafast laser technology, the molecular orientation by intense laser pulse has attracted much attention for its table-top achievable and readily controllable. The molecular orientation can be further enhanced by using an intense laser pulse combined with a weak electrostatic field [14–17], a laser pulse of slow rising and rapid falling edges [18], or shaped ultrashort laser pulses [19,20]. Recently, by using nonresonant dual-color ultrashort laser pulses, all-optical field-free molecular orientation with periodic revivals was experimentally demonstrated [21], while the achievable molecular orientation degree was relatively low. On the other hand, coherent control of the field-free molecular orientation is highly desired for its practical applications.

In this article, we show that the field-free molecular orientation can be significantly enhanced or completely suppressed by sequential impulsive three-photon rotational Raman excitations with time-delayed ultrashort dual-color laser pulses. This molecular orientation control is very sensitive to the relative carrier-envelope phase (CEP) and time delay of the successive dual-color ultrashort laser pulses. The involved rotational wave packets for molecular orientation can be readily manipulated by changing the relative CEP and time delay of the dual-color laser pulses.

The orientation of molecules requires the change of the parity of the molecular rotational wave function. As schematically shown in Fig. 1(a), based on the three-photon Raman transitions [7], the dual-color ultrashort laser pulse can pump the population of the odd (or even) molecular rotational states to the even (or odd) ones, which breaks the parity of the molecular wave function and results in observable orientation of the molecules. This differs from the molecular alignment, where the coupling between the odd and even rotational states is not necessary. Our approach to control the field-free molecular orientation created by an ultrashort dual-color laser pulse, as schematically shown in Fig. 1(b), is to manipulate the involved rotational wave packets by using a second time-delayed dual-color ultrashort laser pulse. The two ultrashort dual-color laser pulses A and B, composed of the fundamental-wave (FW) and its second-harmonic (SH) fields, read as

$$\begin{aligned} E(t) &= E_A(t - T_d/2) + E_B(t + T_d/2) \\ &= E_{\mathrm{FW}_A}(t - T_d/2)\cos[\omega(t - T_d/2)] \\ &\quad + E_{\mathrm{SH}_A}(t - T_d/2)\cos[2\omega(t - T_d/2)] \\ &\quad + E_{\mathrm{FW}_B}(t + T_d/2)\cos[\omega(t + T_d/2)] \\ &\quad + E_{\mathrm{SH}_B}(t + T_d/2)\cos[2\omega(t + T_d/2) + \varphi_{\mathrm{CEP}}] \\ &= E_{\mathrm{FW}}(t,T_d) + E_{\mathrm{SH}}(t,T_d), \end{aligned} \tag{1}$$

where $E_{\mathrm{FW(SH)}_{A(B)}}(t) = (I_0)^{1/2}\exp[-(t/\tau_0)^2]$ is the pulse envelope, I_0 is the pulse peak intensity, $\tau_{\mathrm{FWHM}} = (2\ \ln\ 2)^{1/2}\tau_0$ is the pulse duration, ω and 2ω are the carrier frequencies of the FW and SH fields, and T_d is the time delay between pulses A and B. We use φ_{CEP} as the relative CEP of pulse B, which dominates the overall electric field of the dual-color pulse after an integral over the pulse duration. For $\varphi_{\mathrm{CEP}} = 0$ or π, the overall electric field of the dual-color pulse B is positive or negative, which is in-phase or antiphase with the dual-color pulse A, respectively. The transition probability of the three-photon Raman excitation shown in Fig. 1(a) is proportional to [22]

$$P_{J,J+1} \sim \left| \int_{-\infty}^{\infty} \varepsilon_{\mathrm{FW}}^2(\omega)\varepsilon_{\mathrm{SH}}^*(2\omega - \delta\omega_{\mathrm{J+1,J}})d\omega \right|^2, \tag{2}$$

where E_{FW} and E_{SH} are spectra of the FW and SH pulses in the frequency domain, $\delta\omega_{J+1,J} = E_{J+1} - E_J = 2(J+1)$

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[*] hpzeng@phy.ecnu.edu.cn

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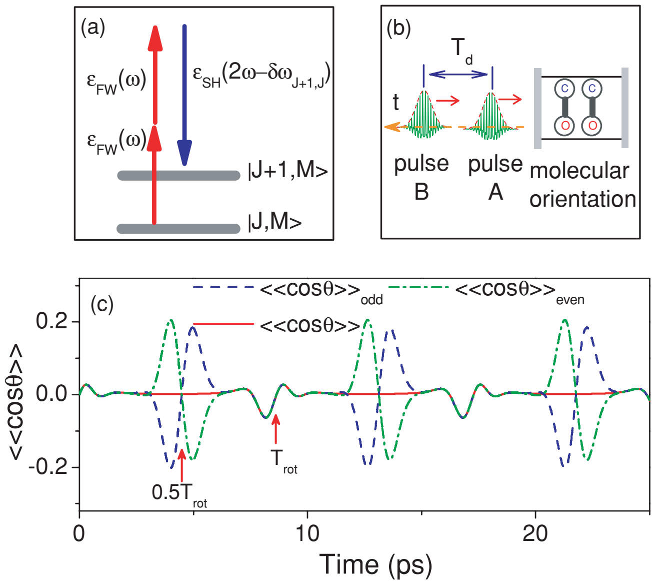

FIG. 1. (Color online) (a) The three-photon Raman transition by an ultrashort dual-color laser pulse. (b) The schematic illustration of the field-free molecular orientation control by two time-delayed ultrashort dual-color laser pulses. (c) The molecular orientation due to the periodical beats of the odd (dashed curve), even (dash-dotted curve), and both odd and even (solid curve) rotational wave packets.

$B_0 = 2(J+1)\pi/T_{\mathrm{rot}}$ is the Raman frequency, $E_J = J(J+1)B_0$ is the energy of the Jth rotational states, B_0 is the molecular rotational constant, and T_{rot} is the rotational period of the molecules. By considering the fast oscillation frequency of the laser fields as compared with the Raman frequency, the high-frequency terms in Eq. (2) were integrated to zero and the three-photon Raman transition probability then reduced to be

$$P_{J,J+1} \sim 1 + \cos(\delta\omega_{\mathrm{J+1,J}} T_d - \varphi_{\mathrm{CEP}}). \tag{3}$$

Therefore, by changing the relative time delay (T_d) and the CEP (φ_{CEP}) of the second dual-color laser pulse, we can control the involved three-photon Raman transition probability and consequently the field-free molecular orientation. Specifically, at the full revival time of the orientation with $T_d = T_{\mathrm{rot}}$, for all the rotational quantum numbers J, the Raman transition probability reaches its maximum value ($P_{J,J+1} = 2$) for $\varphi_{\mathrm{CEP}} = 0$ and becomes zero ($P_{J,J+1} = 0$) for $\varphi_{\mathrm{CEP}} = \pi$, which correspond to the enhancement and suppression of the created molecular orientation, respectively. Since the multiphoton transition probability of Eq. (2) is deduced for weak ultrashort laser pulses [22], its prediction on the molecular orientation control by Eq. (3) should be valid only for low field intensities. However, as we demonstrate in the following, it indeed works well even for field intensity of orders of 10^{13} W/cm^2, which is intense enough to noticeably orientate gaseous diatomic molecules.

To demonstrate the control of the field-free molecular orientation by using the dual-color laser pulses, we numerically solving the time-dependent Schrödinger equation [18] $i\hbar\partial|\psi\rangle/\partial t = H_{\mathrm{eff}}|\psi\rangle$ for the evolution of the rotational state $|\psi\rangle = \sum_{JM} C_{JM}|JM\rangle$, where $H_{\mathrm{eff}} = B_0 J(J+1) - 1/2\, \Delta\alpha E^2(t)\cos^2\theta - 1/6[(\beta_{//} - 3\beta_{\perp})\cos^3\theta + 3\beta_{\perp}\cos\theta]E^3(t)$ is the effective Hamiltonian, $\Delta\alpha$ is the polarizability difference between the components parallel and perpendicular to the molecular axis, $\beta_{//}$ and $\beta_{\perp}$ are the hyperpolarizability components parallel and perpendicular to the molecular axis, and θ is the angle between the molecular axis and the field polarization of the laser pulse. The first, second, and third terms in the effective Hamiltonian account for the molecular intrinsic Hamiltonian for the field-free evolution of the molecular rotational wave packets, the laser-induced molecular dipole for alignment, and the interaction between the molecular hyperpolarizability and the laser field for molecular orientation, respectively. We first calculated the terms $\langle\cos\theta\rangle_{J0M0} = \sum_{JM} C^{*}_{JM} C_{JM} \langle JM|\cos\theta|JM\rangle$ for each initial molecular rotational state $|\psi(t=0)\rangle_{J0M0} = |J_0 M_0\rangle$, then assembled them by considering the temperature-dependent Boltzmann distribution of the initial rotational states, and eventually obtained the observable molecular orientation $\langle\langle\cos\theta\rangle\rangle$ as a function of time [23]. We take molecular CO as an example, and the molecular parameters are [24] $B_0 = 1.93$ cm^{-1}, $\Delta\alpha = 0.524$ Å^3, $\beta_{//} = 2.748 \times 10^9$ Å^5, $\beta_{\perp} = 4.994 \times 10^8$ Å^5, $T_{\mathrm{rot}} = 8.642$ ps. The initial temperature is set to be 30 K. Here, the values of the polarizability (1 atomic unit $= 0.148$ Å^3) and hyperpolarizability (1 atomic unit $= 8.641 \times 10^7$ Å^5) are given in electrostatic units (esu). The laser pulse parameters are $\tau_{\mathrm{FWHM}} = 40.0$ fs and $I_0 = 3.5 \times 10^{13}$ W/cm^2 for each pulse, and the central wavelengths of the FW and SH fields are set to be 800 and 400 nm, respectively.

Figure 1(c) shows the simulated field-free molecular orientation of CO by a single dual-color ultrashort laser pulse (solid curve). The observed field-free molecular orientation is due to the periodical beats of the odd and even rotational wave packets, which cancel each other out, and no field-free molecular orientation results except for the full revival time where the in-phase and antiphase beats lead to the observed positive and negative orientation of the molecules, respectively. We then apply the dual-color pulse B at the full revival time of the molecular orientation to investigate its control dynamics. As expected, the molecular orientation created by pulse A was enhanced by a factor of 1.7 when an in-phase ($\varphi_{\mathrm{CEP}} = 0$) dual-color laser pulse B is applied at $T_d = T_{\mathrm{rot}}$, as shown in Fig. 2(a). It kicked the CO molecules to orientate in the same direction as the first pulse did and promoted the field-free orientation, since the molecular orientation changed from negative to positive at $T_d = T_{\mathrm{rot}}$. This is also consistent with the fact that the in-phase dual-color pulse B with $\varphi_{\mathrm{CEP}} = 0$ applied at $T_d = T_{\mathrm{rot}}$ increases the three-photon Raman transition probability $P_{J,J+1}$ [see Eq. (3)], which hence enhances the field-free molecular orientation.

However, as shown in Fig. 2(b) for $\varphi_{\mathrm{CEP}} = \pi$, the molecular orientation created by pulse A is completely suppressed after the excitation of pulse B. The antiphase pulse B stopped the orientation of the molecules with an antikick force at $T_d = T_{\mathrm{rot}}$. The molecular alignment was enhanced in the same degree for both the in-phase and antiphase dual-color laser pulse B when it was applied at $T_d = T_{\mathrm{rot}}$, which indicates the sensitivity of the molecular orientation on the CEP of the dual-color laser pulse. By applying the antiphase dual-color pulse B with $\varphi_{\mathrm{CEP}} = \pi$ at $T_d = T_{\mathrm{rot}}$, the three-photon Raman transition probability

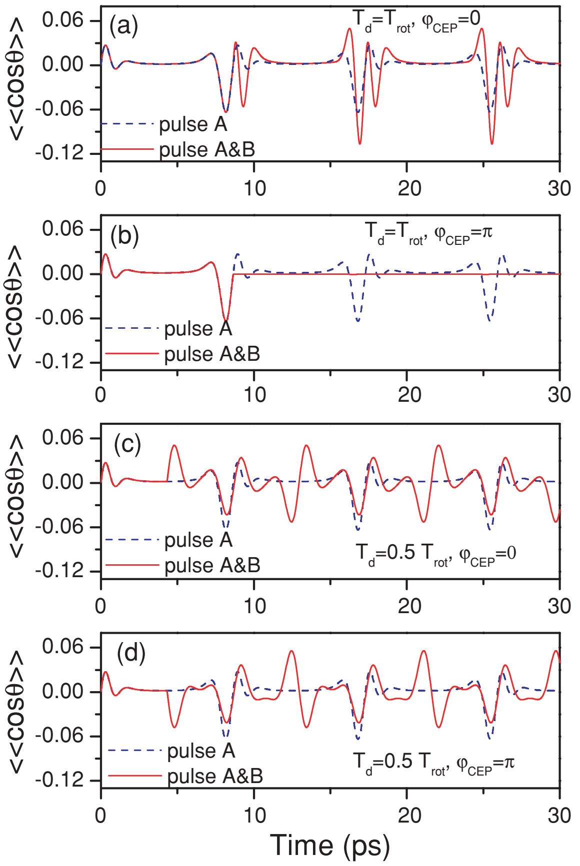

FIG. 2. (Color online) Molecular orientation $\langle\langle\cos\theta\rangle\rangle$ of CO molecules created by an ultrashort dual-color laser pulse A (dashed curves) and the manipulated molecular orientation (solid curves) when an additional dual-color ultrashort laser pulse B is applied at $T_d = T_{\mathrm{rot}}$ (a, b) and $T_d = 0.5\,T_{\mathrm{rot}}$ (c, d) with a CEP of $\varphi_{\mathrm{CEP}} = 0$ (a, c) and $\varphi_{\mathrm{CEP}} = \pi$ (b, d).

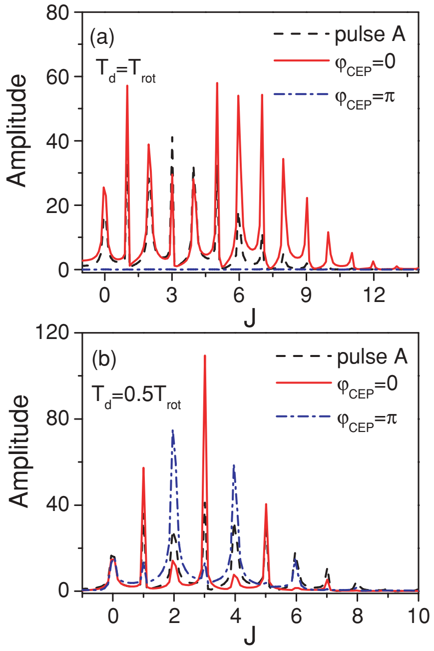

FIG. 3. (Color online) Fourier transform of the orientation signal excited by the pulse A (dashed curves) and both the pulses A and B with $\varphi_{\mathrm{CEP}} = 0$ (solid curves) and $\varphi_{\mathrm{CEP}} = \pi$ (dash-dotted curves) when the pulse B is applied at (a) $T_d = T_{\mathrm{rot}}$ and (b) $T_d = 0.5\,T_{\mathrm{rot}}$, respectively.

$P_{J,J+1}$ becomes zero [see Eq. (3)], which completely depletes the population transition from the odd (or even) to the even (or odd) rotational states. It is actually the cause of the suppressed molecular orientation and is consistent with the fact that orientation requires a strong coupling between the odd and even rotational states so that the parity of the wave function is broken. This kind of molecular orientation control with modified odd and even rotational wave packets and parity can be achieved with dual-color laser pulses through three-photon Raman excitations as schematically shown in Fig. 1(b), rather than one-color laser pulses which influence the molecular alignment [25–27] only but not orientation. The molecular alignment could be enhanced for both in-phase and antiphase dual-color pulses since it is not sensitive to the CEP phases of the applied second pulses. Significantly different from the molecular alignment, the molecular orientation enhancement is observed only for the in-phase pulses, while complete suppression results for antiphase pulses. Figure 3(a) shows the Fourier transform of the orientation signals when the dual-color laser pulse B is applied at $T_d = T_{\mathrm{rot}}$. For $\varphi_{\mathrm{CEP}} = 0$ (or π), the in-phase (or antiphase) kick of the pulse B promoted (or stopped) the created field-free molecular orientation with enhanced (or suppressed) rotational wave packets. Although the second laser pulse is applied at the full revival time of the molecular orientation, the results are almost the same as it is applied at the same time of the first pulse. Usually, the degree of the molecular alignment or orientation is limited by the applicable laser field intensity before its saturation and ionization. Sequential laser pulses with proper time delays can indeed break this limit and have been successfully applied for molecular alignment enhancement [25–27].

The dependence of the maximum molecular orientation degree on the CEP of the dual-color pulse B is shown in Fig. 4(a) for $T_d = T_{\mathrm{rot}}$. The molecular orientation changed by closely following the simplified three-photon Raman transition probability of Eq. (3) as a function of φ_{CEP}, which reached its maximum value with enhanced molecular orientation for $\varphi_{\mathrm{CEP}} = 0$ or 2π and became zero with completely suppressed molecular orientation for $\varphi_{\mathrm{CEP}} = \pi$. We also scanned the time delay of the dual-color laser pulse B around $T_d = T_{\mathrm{rot}}$ to investigate the molecular orientation dynamics, and the results are shown in Figs. 4(b) and 4(c) for $\varphi_{\mathrm{CEP}} = 0$ and π, respectively. For the in-phase pulse B with $\varphi_{\mathrm{CEP}} = 0$, the molecular orientation degree shows a maximum value at $T_d = T_{\mathrm{rot}}$ and decreases gradually as its time delay is detuned from T_{rot}. For the antiphase pulse B with $\varphi_{\mathrm{CEP}} = \pi$, the molecule orientations changed from negative to positive and crossed zero at $T_d = T_{\mathrm{rot}}$ for the depleted coupling between the odd and even rotational wave packets.

As shown in Fig. 1(c), at the half revival time of $T_{\mathrm{rot}}/2$, the field-free molecular orientation changes from negative (or positive) to positive (or negative) for the odd (or even) rotational wave packets. By applying the dual-color laser pulse

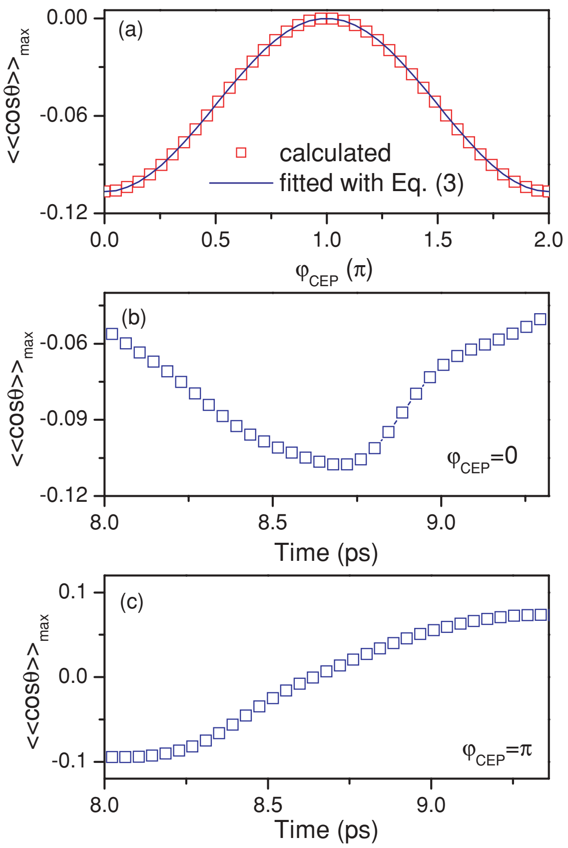

FIG. 4. (Color online) Dependences of the maximum degree of the field-free molecular orientation on the CEP (a) and time delay (b, c) of the ultrashort dual-color laser pulse B. The time delay is $T_d = T_{\rm rot}$ for (a), and the CEP is $\varphi_{\rm CEP} = 0$ and $\varphi_{\rm CEP} = \pi$ for (b) and (c), respectively.

B at $T_d = T_{\rm rot}/2$, we then can selectively promote or depress the odd or even rotational wave packet, which will dominate the succeeding dynamics of the field-free molecular orientation.

For $\varphi_{\rm CEP} = 0$, the in-phase pulse B applied at $T_d = T_{\rm rot}/2$ will promote the odd rotational wave packets and depress the even rotational wave packets, resulting in an additional revival structure of the field-free molecular orientation at $(n + 1/2)T_{\rm rot}$ $(n = 0, 1, 2 \ldots)$ as shown in Fig. 2(c). The additional molecular orientation revivals at $(n + 1/2)T_{\rm rot}$ reversed in the direction when the CEP of the pulse B was changed to $\varphi_{\rm CEP} = \pi$, as shown in Fig. 2(d), due to the fact that the even rotational wave packets are promoted and the odd ones are depressed by the antiphase dual-color pulse B. The selective promotion and depression of the odd and even rotational wave packets are also clearly shown in Fig. 3(b) for the Fourier transform of the molecular orientation signals, where the populations of the odd or even rotational states are increased as compared with the decreased even or odd ones when the CEP of pulse B is tuned to be $\varphi_{\rm CEP} = 0$ and π, respectively.

In summary, we have shown that the field-free molecular orientation created by a first ultrashort dual-color laser pulse can be controlled by using a second dual-color laser pulse, which could be enhanced, suppressed, or manipulated by changing the relative time delay or CEP of the second dual-color laser pulse. The experimental performance of this molecular orientation control is ensured by the achievable energetic femtosecond laser pulse with millijoules of pulse energy and precise phase control with attosecond resolution [21,28]. This is expected to be significant for field-free molecular orientation by ultrashort laser pulses and related applications in various fields.

ACKNOWLEDGMENTS

This work was partly funded by the National Natural Science Fund (10525416 and 10804032), the National Key Project for Basic Research (2006CB806005), and Projects from Shanghai Science and Technology Commission (08ZR1407100 and 09QA1402000).

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