

Field-free molecular orientation by a multicolor laser field

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We theoretically study the field-free molecular orientation by a multicolor laser field with a superposition of the fundamental wave and its harmonics. It is shown that the molecular orientation will be up to a maximum value pumped by the four-color laser field at the same laser intensity, and the molecular orientation direction and its degree can be controlled by varying the carrier-envelope phase of the four-color laser field. It is also indicated that the molecular orientation induced by a four-color laser field can be tremendously enhanced by applying another in-phase or out-phase four-color laser field at the beginning of the rotational wave-packet rephasing or the end of the rotational wave-packet dephasing.

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I. INTRODUCTION

Molecular alignment and orientation have attracted widespread interest because of their potential applications on chemical reaction dynamics [1–3], high-harmonic generation [4,5], and surface processing [6]. Compared with the molecular alignment, the molecular orientation with a “head-versus-tail” order will be faced with more challenges. So far, there are three primary techniques to obtain the molecular orientation. The first one is the use of a strong dc field, such as a hexapole field [7] or a brute force field [8], which is based on the effect of the permanent dipole interaction. However, the degree of the molecular orientation is relatively low, and the Stark effects induced by the strong dc field may influence the experimental outcome. The second one is to employ an intense laser field combined with a weak dc field [9–11], which is based on the combined effects of the permanent dipole interaction and the anisotropic polarizability interaction. The degree of the molecular orientation can be greatly improved, but the presence of the dc field may restrict its further application. The last one is to utilize an asymmetric laser field, such as two-color laser field [12–15] or half-cycle laser field [16–18], which is based on the combined effects of the anisotropic polarizability interaction and the anisotropic hyperpolarizability interaction. The molecular orientation can be achieved in both adiabatic and nonadiabatic regimes, and therefore it is desirable for further application of the oriented molecules.

The laser-induced molecular orientation is dominated by the asymmetric degree of the laser field, and therefore the main challenge is how to create as large an asymmetric laser field as possible. Two-color laser field has proven to be a powerful tool to realize and control the molecular orientation [12–15]. In this paper, we propose a multicolor laser field with a superposition of the fundamental wave and its harmonics to obtain the molecular orientation. It is shown that the molecular orientation will approach the maximum value by the four-color laser field under the same laser intensity, and the carrier-envelope phase of the four-color laser field can be used to manipulate the molecular orientation involving its direction and degree. It is also shown that the molecular orientation

induced by a four-color laser field can be tremendously enhanced when another in-phase or out-phase four-color laser field is applied at the beginning of the rotational wave-packet rephasing or the end of the rotational wave-packet dephasing.

II. THEORETICAL MODEL

We consider a linearly polarized multicolor laser field with a superposition of a fundamental wave and its harmonics, given by

$$E_N(t) = E_0 f(t) [\cos(\omega t + \Phi_1) + \cos(2\omega t + \Phi_2) + \dots + \cos(N\omega t + \Phi_N)], \quad (1)$$

where E_0 and Φ_N are, respectively, the field amplitude and carrier-envelope phase, $f(t)$ is the pulse envelope with the Gaussian shape of $f(t) = \exp[-2\ln 2 t^2 / \tau^2]$, and τ is the pulse duration. To expediently control the symmetry in the positive and negative electric field components of the multicolor laser field, we set $\Phi_1 = \Phi_2 = \dots = \Phi_N = \Phi_{\text{CEP}}$. It is easy to verify that the multicolor laser field is the maximum asymmetry for $\Phi_{\text{CEP}} = 0$ or π and complete symmetry for $\Phi_{\text{CEP}} = 0.5\pi$. When a polar molecule is subjected to the multicolor laser field, the time-dependent Schrödinger equation with the frame of a rigid-rotor description can be written as

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

here, $H(t)$ is the total Hamiltonian of the molecule interacting with the electric field $E_N(t)$ in Eq. (1), and is expressed by

$$H(t) = B J_i(J_i + 1) - \mu E_N(t) \cos \theta - \frac{1}{2} [(\alpha_{\parallel} - \alpha_{\perp}) \cos^2 \theta + \alpha_{\perp}] E_N^2(t) - \frac{1}{6} [(\beta_{\parallel} - 3\beta_{\perp}) \cos^3 \theta + 3\beta_{\perp} \cos \theta] E_N^3(t), \quad (3)$$

where B is the molecular rotational constant, J_i is the angular momentum, μ is the molecular permanent dipole moment, θ is the angle between the molecular axis and the laser polarization, α_{\parallel} and α_{\perp} are the polarizabilities in the direction parallel and perpendicular to the molecular axis, and β_{\parallel} and β_{\perp} are hyperpolarizability components parallel and perpendicular to the molecular axis. The first term in Eq. (3) is the molecular rotational energy, and the second, third, and fourth

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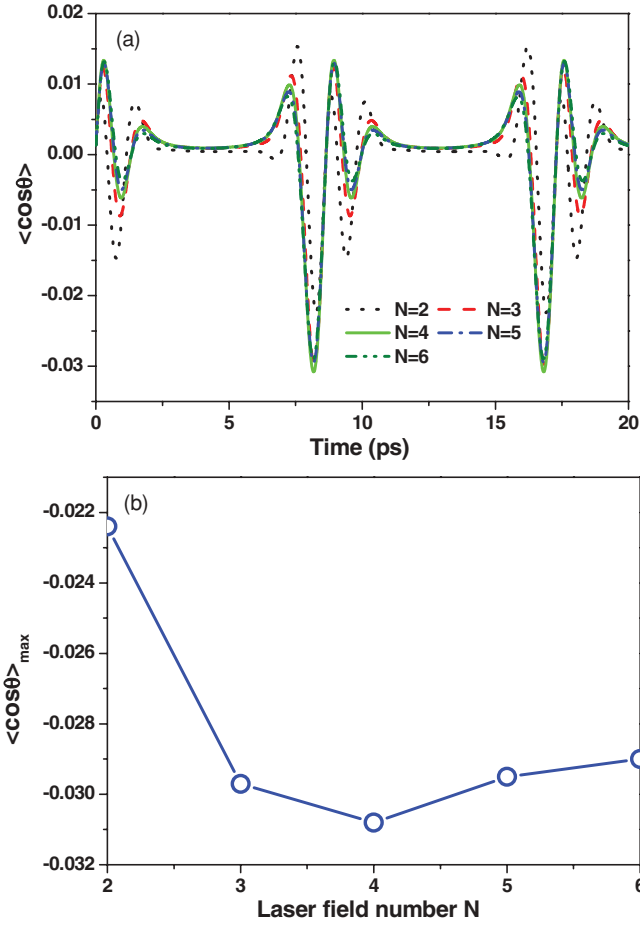


FIG. 1. (Color online) (a) The time evolution of the molecular orientation $\langle \cos \theta \rangle$ with the multicolor laser field number $N=2$ (the black dotted line), 3 (the red dashed line), 4 (the green solid line), 5 (the blue dash-dotted line), and 6 (the olive dash-dot-dotted line) under the same laser intensity of 1×10^{13} W/cm 2 . (b) The maximum degree of the molecular orientation $\langle \cos \theta \rangle_{\max}$ as the function of the multicolor laser field number N .

terms represent the interaction potentials with the permanent dipole moment, the polarizability, and the hyperpolarizability, respectively. Finally, the degree of the molecular orientation is given by the expectation value of $\langle \cos \theta \rangle$ and written as

$$\langle \cos \theta \rangle = \sum_{J_i} W_{J_i} \sum_{M_i=-J_i}^{J_i} \langle \Psi_{J_i M_i} | \cos \theta | \Psi_{J_i M_i} \rangle, \quad (4)$$

where W_{J_i} is the Boltzmann weight factor with $W_{J_i} = Q^{-1} g_{J_i} \exp[-BJ_i(J_i+1)/kT]$, and Q is the rotational partition function and g_{J_i} is the spin degeneracy factor.

III. RESULTS AND DISCUSSION

In our simulation, the time-dependent Schrödinger equation is numerically solved by a split-operator method [19,20]. Here we employ the CO molecule as a model sample, and the molecular parameters used for the calculation are listed as follows: $B = 1.93$ cm $^{-1}$, $\mu = 0.112$ D, $\alpha_{\parallel} = 2.294$ Å 3 , $\alpha_{\perp} = 1.77$ Å 3 , $\beta_{\parallel} = 2.748 \times 10^9$ Å 5 , and $\beta_{\perp} = 4.994 \times 10^8$ Å 5 [14,21,22]. The center frequency ω of the fundamental-wave

field is $12\,500$ cm $^{-1}$, corresponding to the center wavelength of 800 nm, and its pulse duration τ is 200 fs. The initial rotational temperature is set to be 30 K.

Figure 1(a) shows the time evolution of the molecular orientation $\langle \cos \theta \rangle$ with the multicolor laser field number $N=2$ (the black dotted line), 3 (the red dashed line), 4 (the green solid line), 5 (the blue dash-dotted line) and 6 (the olive dash-dot-dotted line) under the same laser intensity of 1×10^{13} W/cm 2 , here $\Phi_{\text{CEP}} = 0$. As can be seen, the molecular orientation can be obtained in both positive and negative values after the laser field, corresponding to the positive and negative orientation, and repeatedly appears at the full rotational revival period of $t = nT_{\text{rot}}$ ($n = 1, 2, 3, \dots$), where T_{rot} is the rotational period of the CO molecule with $T_{\text{rot}} = 1/(2Bc) = 8.64$ ps. To illustrate the dependence of the molecular orientation degree on the multicolor laser number N , we present the maximum degree of the molecular orientation $\langle \cos \theta \rangle_{\max}$ as the function of the multicolor laser field number N , as shown in Fig. 1(b). With the increase of the laser field number N , the $\langle \cos \theta \rangle_{\max}$ first increases and then decreases, and it will approach the maximum value for the four-color laser field (i.e., $N=4$). Since the molecular orientation depends on

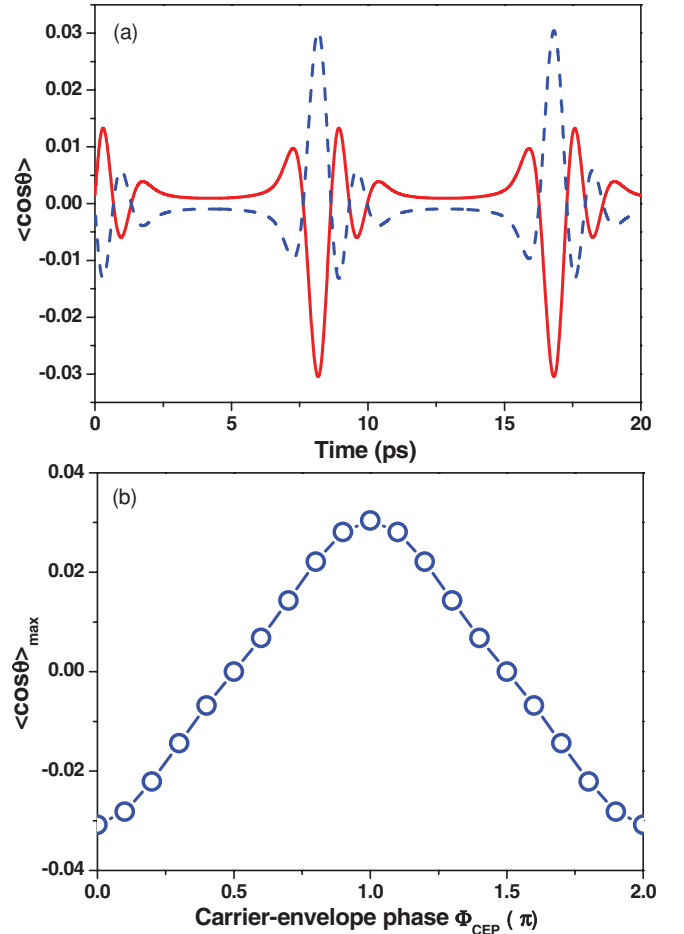


FIG. 2. (Color online) (a) The time evolution of molecular orientation $\langle \cos \theta \rangle$ by the four-color laser field with the carrier-envelope phase $\Phi_{\text{CEP}} = 0$ (the red solid line) and π (the blue dashed line). (b) The maximum degree of the molecular orientation $\langle \cos \theta \rangle_{\max}$ as the function of the carrier-envelope phase Φ_{CEP} .

the asymmetric degree of the optical field, the result indicates that the four-color laser field achieved the largest asymmetry. Compared with the previous result induced by the two-color laser field, the $\langle \cos \theta \rangle_{\max}$ induced by the four-color laser field can be enhanced by a factor of ~ 1.4 .

The carrier-envelope phase Φ_{CEP} determines the electric field structure of the laser pulses, and therefore is usually employed to control the molecular orientation [13,14]. Next we investigate the Φ_{CEP} dependence of the four-color laser field on the molecular orientation. Figure 2(a) shows the time evolution of the molecular orientation $\langle \cos \theta \rangle$ for $\Phi_{\text{CEP}} = 0$ (the red solid line) and π (the blue dashed line). It can be seen that the orientation direction for $\Phi_{\text{CEP}} = 0$ is always opposite that for $\Phi_{\text{CEP}} = \pi$. That is to say, the orientation direction can be expediently switched on or off at any revival time by manipulating Φ_{CEP} . Figure 2(b) shows the maximum degree of the molecular orientation $\langle \cos \theta \rangle_{\max}$ as the function of Φ_{CEP} . With the increase of Φ_{CEP} , the $\langle \cos \theta \rangle_{\max}$ can be continuously modulated from the negative (or positive) to positive (or negative) value. It is indicated that the orientation degree can also be effectively controlled by manipulating Φ_{CEP} . Therefore, it can be concluded that the carrier-envelope

phase modulation can provide an effective tool to control the molecular orientation involving its degree and direction.

The maximum degree of the molecular alignment and orientation is limited by the laser intensity and pulse duration before its intrinsic saturation and photoionization [15,23], but this limitation can be broken by utilizing two phase-locked time-delayed laser fields [14,24]. We also utilize two phase-locked four-color laser fields to further enhance the molecular orientation, here the two laser fields have the same polarization direction, center frequency, pulse duration, and laser intensity. If the carrier-envelope phase difference $\Phi_{\text{CEP}2} - \Phi_{\text{CEP}1}$ between two four-color laser fields is 0 or π , they are called as the in- or out-phase four-color laser fields, respectively. Figure 3(a) shows the maximum degree of the positive (the red squares) and negative (the blue circles) orientation $\langle \cos \theta \rangle_{\max}$ by applying two in-phase time-delayed four-color laser fields, here $\Phi_{\text{CEP}1} = \Phi_{\text{CEP}2} = 0$. The green dashed line is the molecular orientation only induced by a four-color laser field, which is used to show the state of the rotational wave packet when another in- or out-phase

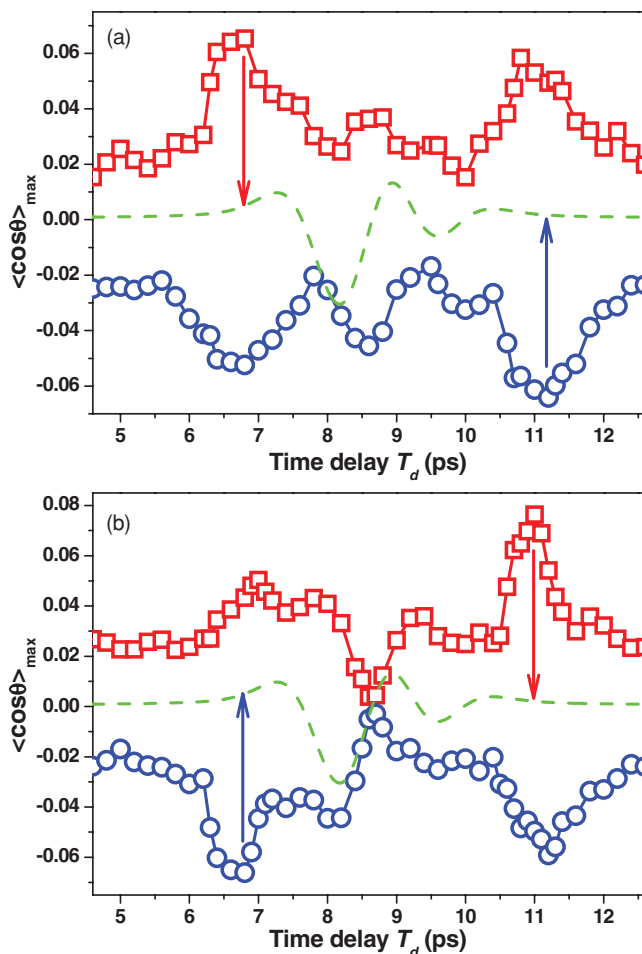


FIG. 3. (Color online) (a) The maximum degree of the positive (the red squares) and negative (the blue circles) orientation $\langle \cos \theta \rangle_{\max}$ by applying two (a) in-phase and (b) out-phase time-delayed four-color laser fields. The green dashed line is the molecular orientation only induced by a four-color laser field.

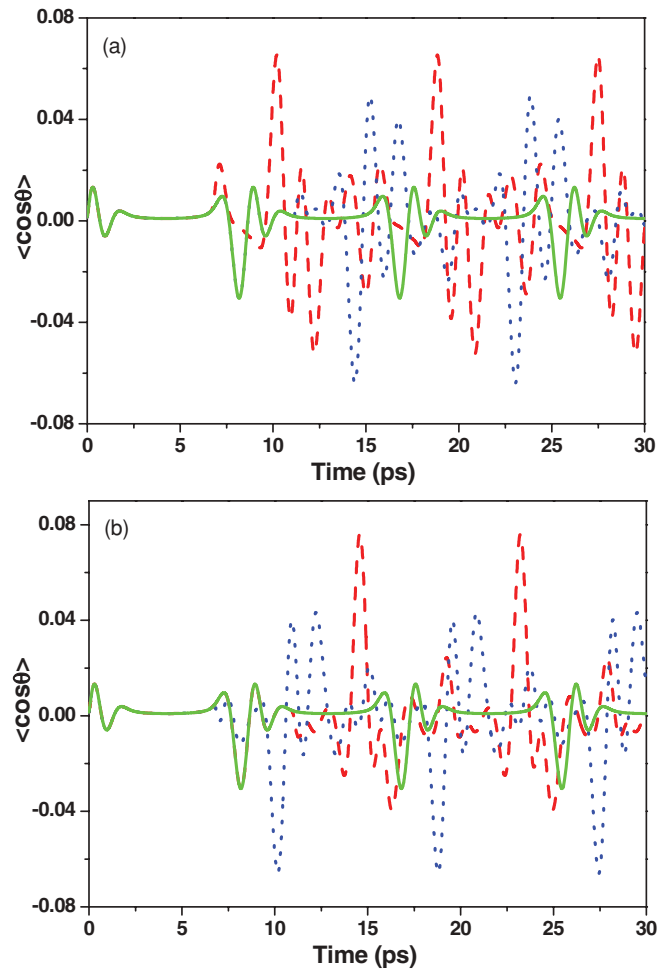


FIG. 4. (Color online) The time evolution of the maximum positive (the red dashed line) and negative (the blue dotted line) orientation $\langle \cos \theta \rangle$ by applying two (a) in-phase and (b) out-phase time-delayed four-color laser fields, together with the molecular orientation only induced by a four-color laser field (the green solid line).

time-delayed four-color laser field is applied. As can be seen, both the positive and negative orientations can be tremendously enhanced around the time delay of $T_d = 6.82$ and 11.02 ps, corresponding to the beginning of the rotational wave-packet rephasing and the end of the rotational wave-packet dephasing, respectively. The maximum enhancement of the positive orientation is up to 0.065 at the beginning of the rotational wave-packet rephasing (the red arrow), and that of the negative orientation is up to -0.064 at the end of the rotational wave-packet dephasing (the blue arrow). This phenomenon is different from the previous results where the maximum enhancement of the molecular alignment is obtained at the full rotational revival period [24]. Actually, the molecular orientation can be enhanced at the full rotational revival period (i.e., $T_d = 8.64$ ps), but it is not the optimal time delay.

Similarly, the significant enhancement of the molecular orientation can also be obtained by applying two out-phase time-delayed four-color laser fields, as shown in Fig. 3(b), here $\Phi_{\text{CEP1}} = 0$ and $\Phi_{\text{CEP2}} = \pi$. However, the maximum enhancement of the positive orientation is up to 0.076 at the end of the rotational wave-packet dephasing (the red arrow), and that of the negative orientation is up to -0.066 at the beginning of the rotational wave-packet rephasing (the blue arrow). This observation will be reversed by applying two in-phase time-delayed four-color laser fields [see Fig. 3(a)]. Compared with the two in-phase time-delayed four-color laser fields, it can be found that applying two out-phase time-delayed four-color laser fields has more advantages for enhancing the molecular orientation. Furthermore, it is noted that the molecular orientation is completely suppressed at the time delay of $T_d = 8.64$ ps (i.e., the full rotational revival period T_{rot}), which indicates that the molecular orientation induced by a laser field can be counteracted by applying another out-phase laser field at $T_d = T_{\text{rot}}$.

To demonstrate the dynamics of the enhanced molecular orientation induced by two phase-locked time-delayed four-color laser fields, we further observe the revival structure of the molecular orientation. Figure 4 shows the time evolution of the maximum positive (the red dashed line) and negative (the blue dotted line) orientation $\langle \cos \theta \rangle$ by applying two (a) in-phase and (b) out-phase time-delayed four-color laser

fields, together with the molecular orientation only induced by a four-color laser field (the green solid line). As can be seen, the revival shape of the molecular orientation induced by two four-color laser fields becomes more complicated, and it depends on the time delay and carrier-envelope phase of the second four-color laser field, but its revival period remains unchanged. Moreover, the molecular orientation can be obtained in the whole range of the full revival period. Since the molecular orientation is the result of the interference between the odd and even rotational wave packets, these observations indicate that the second four-color laser field can tremendously change the time evolution of the odd and even rotational wave packets created by the first four-color laser field, while it does not affect their revival period.

IV. CONCLUSION

In summary, we have theoretically investigated the molecular orientation by a multicolor laser field with a superposition of the fundamental wave and its harmonics. The main results are included as follows: (1) the molecular orientation is up to the maximum value by the four-color laser field at the same laser intensity, (2) the carrier-envelope phase of the four-color laser field can be employed to control the molecular orientation involving its degree and direction, and (3) the degree of the molecular orientation induced by a four-color laser field can be tremendously enhanced by applying another in-phase or out-phase four-color laser field at the beginning of the rotational wave-packet rephasing or the end of the wave-packet dephasing. So we believe that the theoretical results can provide an experimental basis and great potential applications on the molecular orientation and alignment.

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