Field-free molecular orientation enhanced by tuning the intensity ratio of a three-color laser field*

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We theoretically study the field-free molecular orientation induced by a three-color laser field. The three-color laser field with a large asymmetric degree can effectively enhance the molecular orientation. In particular, when the intensity ratio of the three-color laser field is tuned to a proper value of $I_3 : I_2 : I_1 = 0.09 : 0.5 : 1$, the molecular orientation can be improved by $\sim 20\%$ compared with that of the two-color laser field at intensity ratio $I_2 : I_1 = 1 : 1$ for the same total laser intensity of 2×10^{13} W/cm^2. Moreover, we investigate the effect of the carrier-envelope phase (CEP) on the molecular orientation and use the asymmetric degree of the laser field to explain the result. We also show the influences of the laser intensity, rotational temperature, and pulse duration on the molecular orientation. These results are meaningful for the theoretical and experimental studies on the molecular orientation.

Keywords: molecular orientation, three-color laser field, carrier-envelope phase

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1. Introduction

Molecular orientation with a head-versus-tail order possesses extensive applications in physical and chemical fields such as attosecond science[1,2] and chemical reaction dynamics.[3] The common methods to obtain the molecular orientation are to use a strong dc field through the permanent dipole or to employ an intense laser field combined with a weak dc field based on the anisotropic polarizability and the permanent dipole.[4–8] However, the degree of molecular orientation created by the first method is relatively small, and the dc field may limit the further applications of these two methods. To achieve a large degree of molecular orientation without the presence of a dc field, a popular method is to use an asymmetric laser field such as a two-color laser field or a terahertz (THz) few-cycle laser field employing the combined influences of the anisotropic polarizability and hyperpolarizability.[9–15] The two-color laser field has proven to be a powerful approach to induce the molecular orientation. Kanai and Sakai employed a strong nonresonant two-color laser field to study the orientation of FCN molecules in an adiabatic regime.[16] In the nonadiabatic regime, the laser-induced molecular orientation can be used to produce oriented molecules under the field-free conditions, which is more desirable for some applications in related fields. Tehini and Sugny investigated the field-free orientation of LiH molecules induced by nonresonant and quasiresonant two-color laser pulses.[17] Moreover, Muramatsu *et al.* proposed an alternative and versatile approach to achieve completely field-free orientation of FCN molecules by an intense nonresonant two-color laser field with a slow turn on and rapid turn off.[18] Since a high asymmetric degree of the laser field can produce an effective improvement on the molecular orientation, Zhang *et al.* used a multicolor laser field with a large asymmetric degree to enhance the molecular orientation of CO molecules.[19] Usually, we can obtain the multicolor laser field from the harmonics or multiwave mixing processes through a crystal or glass.[20,21] Here, we employ the two beta barium borate (BBO) crystals to generate a three-color laser field with the superpositions of 800 nm, 400 nm, and 200 nm.

In this work, we numerically study the field-free orientation of CO molecules induced by a three-color laser field. The simulation results show that the molecular orientation can be further enhanced by tuning the intensity ratio of the three-color laser field to a proper value. We also particularly investigate how the carrier-envelope phase (CEP) of the three-color laser field manipulates the molecular orientation. In addition, we show the influences of the laser intensity, temperature, and pulse duration on the molecular orientation.

2. Numerical model

We use a linearly polarized three-color laser field. The combined laser field can be expressed as

$$E(t) = \sum_{n=1,2,4} E_n \exp[-(2\ln 2)t^2/\tau_n^2]\cos(n\omega_0 t + \Phi_n), \quad (1)$$

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where E_n is the field amplitude, τ_n is the pulse full width at half maximum (FWHM), ω_0 is the central frequency of the fundamental field, and Φ_n is the CEP of the three-color laser field, here we set $\Phi_1 = \Phi_2 = \Phi_4 = \Phi$. When a linear polar molecule interacting with the combined laser field $E(t)$, a quantum mechanical rigid rotor model can be used to describe the evolution of the molecular state. The time-dependent Schrödinger equation can be given as[22]

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

where $|\psi(\theta,t)\rangle$ is the wave function, θ is the angle between the molecular axis and the laser polarization direction, $H(t)$ is the total Hamiltonian and written as[16,23]

$$H(t) = H_0 + V_\mu(\theta)E(t) + V_{\rm pol}(\theta)E^2(t) + V_{\rm hyp}(\theta)E^3(t). \tag{3}$$

Here the field-free Hamiltonian H_0 is equivalent to $B_0\boldsymbol{J}^2$, B_0 is the rotational constant of the molecule, $\boldsymbol{J}^2$ is the squared angular momentum operator, and H_0 meets the relation $H_0|J,M\rangle = [B_0J(J+1) - D_0J^2(J+1)^2]|J,M\rangle = \varepsilon_J|J,M\rangle$, where $|J,M\rangle$ is the field-free rotational eigenstate with angular and magnetic quantum numbers J and M, and D_0 is the centrifugal distortion constant.[9,18,24] $V_\mu(\theta) = -\mu\cos\theta$ represents the interaction of the permanent dipole moment, μ is the molecular permanent dipole moment; $V_{\rm pol}(\theta) = -[(\alpha_{||} - \alpha_\perp)\cos^2\theta + \alpha_\perp]/2$ is the polarizability, $\alpha_{||}$ and $\alpha_\perp$ are the polarizabilities in the directions parallel and perpendicular to the molecular axis; and $V_{\rm pol}(\theta) = -[(\beta_{||} - 3\beta_\perp)\cos^3\theta + 3\beta_\perp\cos\theta]/6$ describes the hyperpolarizability, $\beta_{||}$ and $\beta_\perp$ are the hyperpolarizabilities in the directions parallel and perpendicular to the molecular axis. The degree of molecular orientation is characterized by the expectation of $\cos\theta$. Considering the thermal equilibrium of the molecular ensemble, the orientation is averaged over the Boltzmann distribution and expressed as

$$\langle\langle\cos\theta\rangle\rangle = \sum_J \frac{g_J\exp(-\varepsilon_J/kT)}{Q} \times \sum_{M=-J}^{J}\langle\psi_{J,M}|\cos\theta|\psi_{J,M}\rangle, \tag{4}$$

where g_J is the spin degeneracy factor, k is the Boltzmann constant, T is the molecular rotational temperature, Q is the rotational partition function, and $\psi_{J,M}$ is the rotational state with the initial state $|J,M\rangle$.

3. Results and analysis

In the simulation, the time-dependent Schrödinger equation is numerically solved through a split-operator method.[25,26] Here we consider the CO molecules as an example, and the molecular parameters used in this calculation are $B_0 = 1.931$ cm^{-1}, $D_0 = 6\times10^{-6}$ cm^{-1}, $\mu = 0.112$ D, $\alpha_{||} = 2.294$ Å^3, $\alpha_\perp = 1.77$ Å^3, $\beta_{||} = 2.748\times10^9$ Å^5, and $\beta_\perp = 4.994\times10^8$ Å^5.[27–29] The central wavelength of the fundamental field is 800 nm, the other two wavelengths are 400 nm and 200 nm, and the corresponding laser intensities can be expressed as I_1, I_2, and I_3. The initial pulse duration, CEP, and molecular rotational temperature are 200 fs, $\Phi = 0$, and 30 K, respectively.

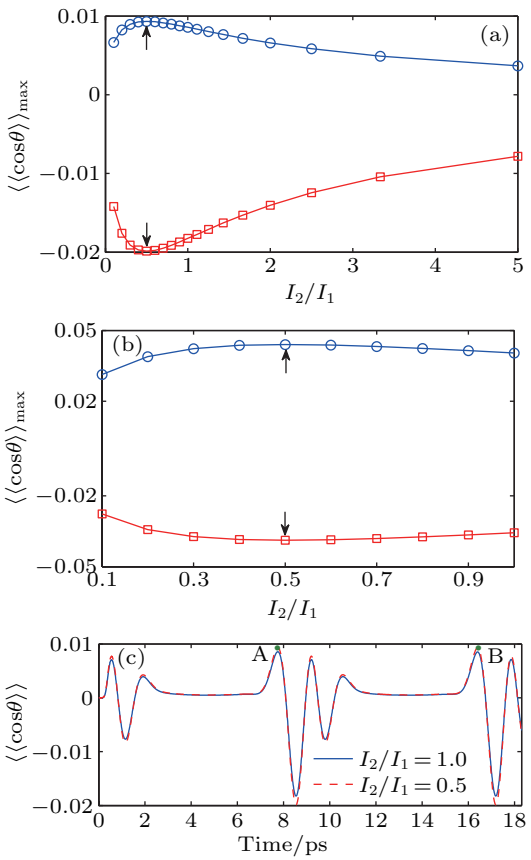


Fig. 1. (color online) The maximum degree of the positive (blue circle lines) and negative (red square lines) orientation with respect to the laser intensity ratio I_2/I_1 for different total laser intensities of (a) 2×10^{13} W/cm^2 and (b) 4×10^{13} W/cm^2. (c) The time evolution of molecular orientation with different intensity ratios of 1.0 (blue solid lines) and 0.5 (red dotted lines) at the same total laser intensity of 2×10^{13} W/cm^2. Black arrows represent the optimal orientation.

Figures 1(a) and 1(b) show the maximum degree of the positive (blue circle curves) and negative (red square curves) orientation with respect to the laser intensity ratio I_2/I_1 created by the two-color laser field with different total laser intensities of 2×10^{13} W/cm^2 and 4×10^{13} W/cm^2, respectively. We can observe that the maximum degree of molecular orientation appears with the maximum value when the intensity ratio is tuned to 0.5 (marked in black arrows). As shown in Fig. 1(c), we plot the time evolution of molecular orientation with different intensity ratios of 1.0 (blue solid curves) and 0.5 (red dotted curves) in Fig. 1(a). The period between green dots A and B is about 8.64 ps, which agrees well with the rotational

period of CO molecules $T_{\rm rot} = 1/(2B_0c) \approx 8.64$ ps, where c is the speed of light in a vacuum. For a given total laser intensity, by adjusting the intensity ratio of the two-color laser field to a proper value 0.5, the molecular orientation is enhanced by $\sim 9\%$ compared with that at intensity ratio 1.0.

In order to obtain the optimal intensity ratio of the three-color laser field, we scan the ratio I_3/I_1 while keeping I_2/I_1 as a constant 0.5 for the total laser intensity 2×10^{13} W/cm^2, as shown in Fig. 2(a). The black arrows show that the optimal ratio between I_3 and I_1 is 0.09. Figures 2(b) and 2(c) show the envelopes of two-color and three-color laser fields for the same total laser intensity, respectively; they induce the molecular orientation that is presented in Fig. 2(d). Seen from the envelope in Figs. 2(b) and 2(c), the three-color field shows a higher asymmetric degree than the two-color field. Therefore, in Fig. 2(d), the molecular orientation plotted in green solid curves is further improved by $\sim 11\%$ compared with that in red dotted curves.

Figures 3(a) and 3(b) show the maximum degree of molecular orientation induced by a three-color laser field with the intensity ratio of $I_3 : I_2 : I_1 = 0.09 : 0.5 : 1.0$ by scanning the total laser intensity at 30 K for panel (a) and molecular rotational temperature at 1×10^{14} W/cm^2 for panel (b). As can be seen, the maximum degree of molecular orientation is enhanced with the increase of the total laser intensity or with the decrease of the rotational temperature. In Fig. 3(c), in comparison with the initial laser intensity 2×10^{13} W/cm^2 (green solid curves), the increased intensity 1×10^{14} W/cm^2 (yellow dotted curves) produces an obvious enhancement on the molecular orientation and that presents a considerable oscillation; then by decreasing the rotational temperature from 30 K to 10 K (black dash-dotted curves), the molecular orientation is further enhanced since cooling improves the purity of the molecular coherent state.

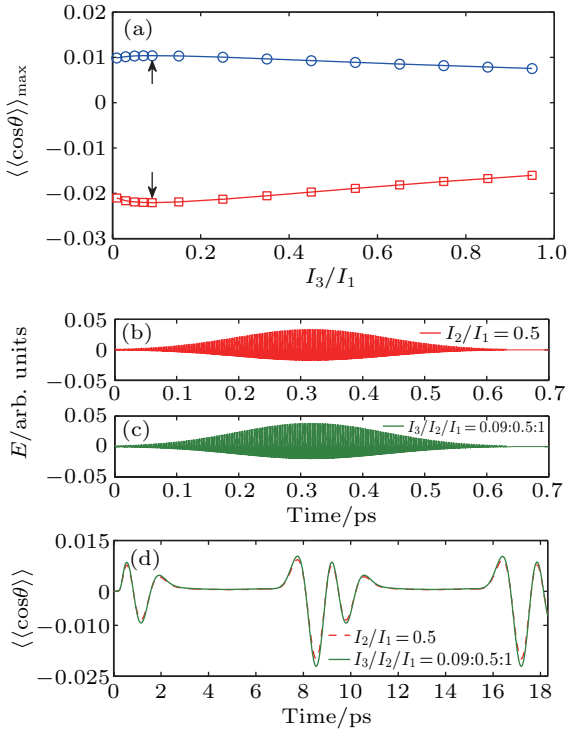


Fig. 2. (color online) (a) The maximum degree of the positive (blue circles lines) and negative (red squares lines) orientation with respect to the laser intensity ratio I_3/I_1 for a given total intensity of 2×10^{13} W/cm^2 with intensity ratio $I_2/I_1 = 0.5$. The field envelopes of (b) two-color and (c) three-color laser fields for the same total laser intensity of 2×10^{13} W/cm^2. (d) The time evolution of molecular orientation created by the two-color laser field (red dotted lines) and for the three-color laser field (green solid lines). Black arrows are the optimal orientation.

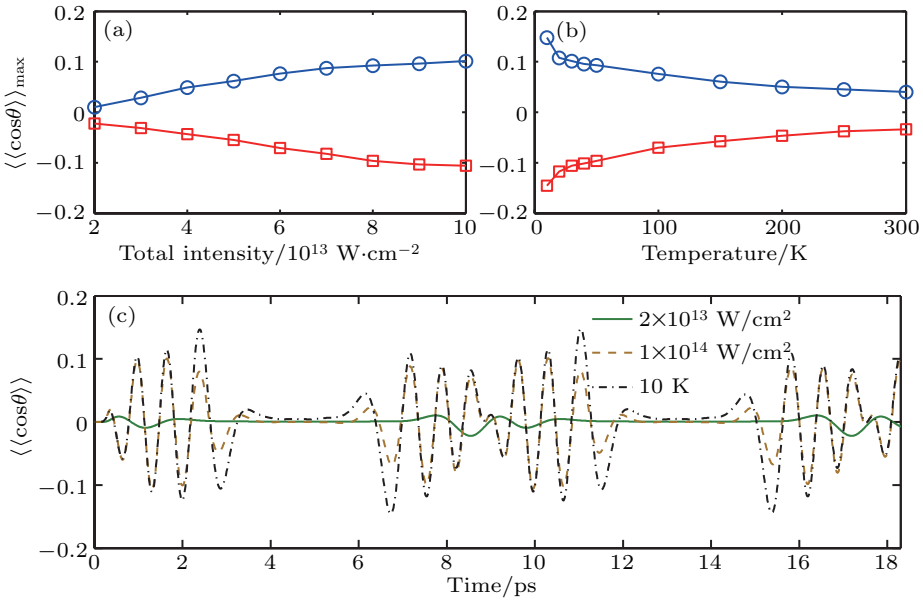


Fig. 3. (color online) The maximum degree of the positive (blue circles lines) and negative (red squares lines) orientation with (a) increasing total laser intensity at temperature of 30 K and (b) increasing temperature at the total intensity of 1×10^{14} W/cm^2. (c) The time evolution of molecular orientation; green solid and yellow dotted lines are for the total intensities of 2×10^{13} W/cm^2 and 1×10^{14} W/cm^2 at temperature 30 K, respectively; black dash-dotted lines are for the temperature 10 K at intensity 1×10^{14} W/cm^2.

The CEP determines the electric field structure, and then the changed laser field produces an effect on the molecular orientation. Figure 4(a) shows the maximum degree of molecular orientation with respect to CEP ranging from 0 to 2π by using a three-color laser field with the total laser intensity of 1×10^{14} W/cm^2 and temperature of 10 K at intensity ratio $I_3 : I_2 : I_1 = 0.09 : 0.5 : 1.0$. The corresponding field envelope, the time evolution of molecular orientation, and the asymmetric degree of laser field are presented in Figs. 4(b)–4(i), 4(j)–4(k), and 4(l), respectively. When the CEP of the laser field meets the relation $\Phi = p\pi$ ($p = 0, 1, 2, \ldots$), the maximum degree of molecular orientation presents the largest value; while for $\Phi = q\pi/2$ ($q = 1, 3, 5, \ldots$), it shows the smallest value, as shown in Fig. 4(a). We use the asymmetric degree of the laser field to explain this result, which can be defied as

$$\delta = (E_{\max+} - |E_{\max-}|)/(E_{\max+} + |E_{\max-}|), \tag{5}$$

where $E_{\max+}$ and $E_{\max-}$ are the maximum values of the positive and negative laser fields, respectively. Viewed from Fig. 4(l), the laser field has the maximum asymmetry for $\Phi = 0$, π, 2π and the complete symmetry for $\Phi = 0.5\pi$, 1.5π.

It should be noted that the oscillations of the laser field between Figs. 4(b)–4(e) and Figs. 4(f)–4(i) exhibit a symmetric relation at zero axis when the CEP difference is π, resulting in the same asymmetric degree but opposite. Therefore, we can see that the time evolution of molecular orientation also shows the reserve behavior (see the blue solid and green dash-dotted curves in Figs. 4(j) and 4(k)). Moreover, in Figs. 4(e) and 4(g), the laser field presents a difference at $\Phi = 0.75\pi$, 1.25π, but they show the same molecular orientation due to the equal asymmetric degree in Fig. 4(k). In addition, from Figs. 4(b)–4(i), and 4(l), we can observe that the periods of the laser field oscillation and molecular orientation induced by CEP are 2π.

Figures 5(a)–5(c) show the maximum degree of molecular orientation by individually scanning the pulse duration of these three laser fields, respectively. The black arrows indicate that the optimal pulse duration is 200 fs for the central wavelength 800 nm or 400 nm, and 100 fs for the central wavelength 200 nm.

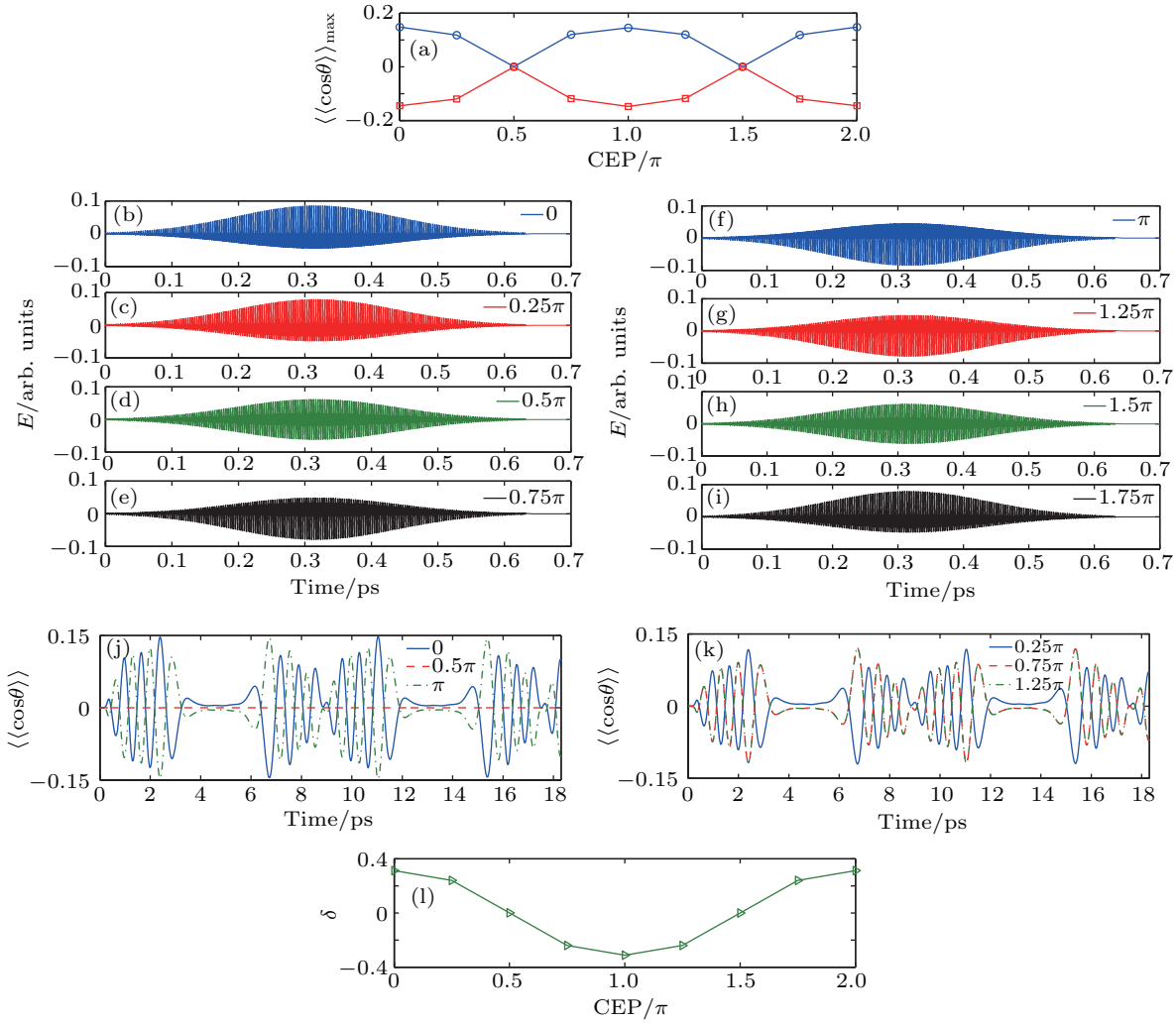


Fig. 4. (color online) (a) The maximum degree of the positive (blue circles lines) and negative (red squares lines) orientation for different CEP with total laser intensity of 1×10^{14} W/cm^2 and temperature of 10 K. (b)–(i) The field envelope with various CEP from 0 to 1.75π. The time evolution of molecular orientation; blue solid, red dotted, and green dash-dotted lines correspond to 0, 0.5π, π for (j) and 0.25π, 0.75π, 1.25π for (k). (l) The corresponding asymmetric degree of the three-color laser field with different CEP.

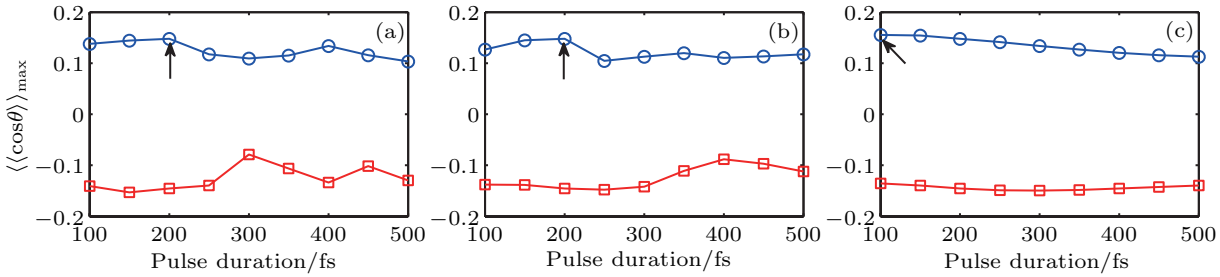


Fig. 5. (color online) The maximum degree of the positive (blue circles lines) and negative (red squares lines) orientation by individually scanning the pulse duration of the first (a), second (b), or third (c) laser field, respectively. Black arrows correspond to the optimal orientation.

4. Conclusion

We have theoretically investigated the field-free orientation of CO molecules created by a three-color laser field. For the same total laser intensity of 2×10^{13} W/cm^2, tuning the intensity ratio of the two-color laser field to a proper value 0.5, we found that the molecular orientation can be enhanced by $\sim 9\%$ compared with that at the intensity ratio 1.0. By employing a three-color laser field with intensity ratio $I_3 : I_2 : I_1 = 0.09 : 0.5 : 1.0$, it can be further improved by $\sim 11\%$. It was also shown that the CEP can manipulate the molecular orientation, and we used the asymmetric degree of laser field to explain this result. Moreover, when the CEP difference is π, the oscillations of the laser field exhibit a symmetric relation at zero axis, which results in the equal asymmetry but opposite; and the periods of the laser field oscillation and molecular orientation created by CEP are 2π. Finally, we also studied the effects of the laser intensity, rotational temperature, and pulse duration on the molecular orientation. The simulation showed that the optimal pulse duration is 200 fs for the central wavelength 800 nm or 400 nm, and 100 fs for the central wavelength 200 nm. We believe these results can provide an experimental basis and some potential applications on the molecular orientation.

References

[1] Lan P, Lu P, Cao W, Li Y and Wang X 2007 *Phys. Rev. A* **76** 051801(R)
[2] Kraus P M, Baykusheva D and Wörner H J 2014 *J. Phys. B* **47** 124030
[3] Bisgaard C Z, Clarkin O J, Wu G, Lee A M D, Geßner O, Hayden C C and Stolow A 2009 *Science* **323** 1464
[4] Kasai T, Fukawa T, Matsunami T, Che D C, Ohashi K, Fukunishi Y, Ohoyama H and Kuwata K 1993 *Rev. Sci. Instrum.* **64** 1150
[5] Li H, Franks K J, Hanson R J and Kong W 1998 *J. Phys. Chem. A* **102** 8084
[6] Sakai H, Minemoto S, Nanjo H, Tanji H and Suzuki T 2003 *Phys. Rev. Lett.* **90** 083001
[7] Goban A, Minemoto S and Sakai H 2008 *Phys. Rev. Lett.* **101** 013001
[8] Sugawara S, Goban A, Minemoto S and Sakai H 2008 *Phys. Rev. A* **77** 031403(R)
[9] De S, Znakovskaya I, Ray D, Anis F, Johnson N G, Bocharova I A, Magrakvelidze M, Esry B D, Cocke C L, Litvinyuk I V and Kling M F 2009 *Phys. Rev. Lett.* **103** 153002
[10] Wu J and Zeng H P 2010 *Phys. Rev. A* **81** 053401
[11] Machholm M and Henriksen N E 2001 *Phys. Rev. Lett.* **87** 193001
[12] Shu C C, Yuan K J, Hu W H and Cong S L 2010 *J. Chem. Phys.* **132** 244311
[13] Kitano K, Ishii N and Itatani J 2011 *Phys. Rev. A* **84** 053408
[14] Fleischer S, Zhou Y, Field R W and Nelson K A 2011 *Phys. Rev. Lett.* **107** 163603
[15] Si J H and Hirao K 2007 *Appl. Phys. Lett.* **91** 091105
[16] Kanai T and Sakai H 2001 *J. Chem. Phys.* **115** 5492
[17] Tehini R and Sugny D 2008 *Phys. Rev. A* **77** 023407
[18] Muramatsu M, Hita M, Minemoto S and Sakai H 2009 *Phys. Rev. A* **79** 011403(R)
[19] Zhang S, Shi J, Zhang H, Jia T, Wang Z and Sun Z 2011 *Phys. Rev. A* **83** 023416
[20] Liu H, Yao J and Puri A 1994 *Opt. Commun.* **109** 139
[21] Zhang H, Liu H, Si J H, Yi W H, Chen F and Hou X 2011 *Opt. Express* **19** 12039
[22] Ortigoso J, Rodriguez M, Gupta M and Friedrich B 1999 *J. Chem. Phys.* **110** 3870
[23] Zhang S, Lu C, Jia T, Wang Z and Sun Z 2011 *Phys. Rev. A* **83** 043410
[24] Huang Z, Wang D, Leng Y and Dai Y 2015 *Phys. Rev. A* **91** 043809
[25] Feit M D, Fleck J J A and Steiger A 1982 *J. Comput. Phys.* **47** 412
[26] Bandrauk A D and Shen H 1993 *J. Chem. Phys.* **99** 1185
[27] Peterson K A and Dunning T H 1997 *J. Mol. Struct. Theochem.* **400** 93
[28] Pecul M 2005 *Chem. Phys. Lett.* **404** 217
[29] Lapert M, Tehini R, Turinici G and Sugny D 2009 *Phys. Rev. A* **79** 063411