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Field-free molecular alignment control by phase-shaped femtosecond laser pulse

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In this paper, we theoretically show that the field-free molecular alignment can be controlled by shaping the femtosecond laser pulse with a periodic phase step modulation, involving the maximum degree and temporal structure of the molecular alignment. We show that the molecular alignment can be completely suppressed or reconstructed as that by the transform-limited laser pulse, the temporal structure of the alignment transient can be controlled with a desired shape, and the molecular alignment and antialignment for any temporal structure can be switched. Furthermore, we also show that both the degree and direction of the molecular alignment at a fix time delay can be continuously modulated. © *2011 American Institute of Physics*. [doi:10.1063/1.3666850]

I. INTRODUCTION

The spatial manipulation of the molecule has been one of the most important and intriguing subjects in physics, chemistry, and biology. Recently, the molecular alignment has attracted widespread interest for its potential applications such as high-order generation,[1,2] chemical reaction dynamics,[3,4] molecular frame photoelectron angular distribution,[5,6] surface processing,[7] and molecular orbital imaging.[8] A strong linearly polarized laser pulse was considered as the most effective method to realize the molecular alignment, where the molecule is aligned along the laser polarization direction.[9–12] The laser-induced molecular alignment can be obtained in non-adiabatic or adiabatic regimes that depend on the laser pulse duration.[13] In adiabatic process, i.e., the laser duration is much larger than the rotational period of the molecule, the molecular alignment is maximally obtained during the interaction with the laser pulse, and will disappear when the laser is off. In non-adiabatic process, i.e., the laser pulse is quickly turned on and off as compared to the molecular rotational period, the molecular alignment occurs after the laser pulse, and can be repeatedly constructed at the full of the molecular rotational periods. Comparing with the adiabatic alignment, the degree of the non-adiabatic alignment is lower, but it can obtain the aligned molecules under the free laser field, which is desired for further applications in various related fields. Usually, the degree of the molecular alignment is limited by the maximally applicable laser intensity before its saturation and ionization. Nowadays, various methods, such as the slow turn-on and rapid turn-off laser pulse,[14] the pulse trains with the time separation of the rotational period,[15–21] or the phase-shaped laser pulse,[22–28] have been proposed to further enhance the molecular alignment.

How to control the maximal degree and temporal structure of the field-free molecular alignment is always an attentive question for those who engage in the control of the molecular dynamical process. The shaped laser pulse with the spectral phase modulation has shown to be a versatile method to increase the maximal degree or change the time evolution of the field-free molecular alignment.[22–29] In this paper, we propose a pulse-shaping scheme to control both the maximal degree and temporal structure of the field-free molecular alignment. It is shown that the shaped laser pulse by a periodic phase step modulation can completely suppress the molecular alignment or reconstruct as that by the transform-limited laser pulse, control the temporal structure of the alignment transient with a desired shape, and switch the molecular alignment and antialignment for any temporal structure. It is also shown that the phase-shaped laser pulse can be utilized to continuously modulate both the degree and direction of the field-free molecular alignment at a fix time delay.

II. THEORY

We consider the case that a linear molecule is exposed to a linearly polarized laser field E(t) with the Gaussian profile $E(t) = A_0 \exp(-2\ln 2 t^2/\tau^2)\cos(\omega_0 t)$, where A_0 is the laser field amplitude, τ is the pulse duration, and ω_0 is the laser central frequency; thus, the time-dependent Schrödinger equation can be approximated based on a rigid-rotor model as[7,30]

$$i\hbar \frac{\partial|\Psi(\theta, t)\rangle}{\partial t} = [B\mathbf{J}^2 + V_\mu(\theta) + V_{pol}(\theta)]|\Psi(\theta, t)\rangle \quad (1)$$

with

$$V_\mu(\theta) = -\mu \cos\theta E(t),$$

$$V_\mu(\theta) = -\frac{1}{2}[(\alpha_{||} - \alpha_\perp)\cos^2\theta + \alpha_\perp]E^2(t), \quad (2)$$

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where B, $\mathbf{J}^2$, and μ are, respectively, the rotational constant, the squared angular momentum operator, and the permanent dipole moment, θ is the angle between the molecular axis and the laser polarization direction, and $\alpha_\parallel$ and $\alpha_\perp$ are the polarizability components parallel and perpendicular to the molecular axis, respectively. The first term on the right side of Eq. (1) represents the molecular rotational energy, and the second and third terms are the interaction potentials with the permanent dipole moment and the polarizability, respectively. Finally, the molecular alignment is given by the expectation value of $\cos^2\theta$ (i.e., $\langle\cos^2\theta\rangle$). When an ensemble of molecules in thermal equilibrium is considered, the time-dependent molecular alignment $\langle\cos^2\theta\rangle$ is averaged over the Boltzmann distribution, and is written as

$$\langle\cos^2\theta\rangle = \sum_J W_J \sum_{M=-J}^{J} \langle\Psi_{JM}|\cos^2\theta|\Psi_{JM}\rangle, \tag{3}$$

where W_J are Boltzmann weight factors with $W_J = g_J \exp[-BJ(J+1)/kT]/Q$, Q is the rotational partition function, g_J is the spin degeneracy factor, k is the Boltzmann constant, and T is the molecular rotational temperature. It can be verified from Eq. (3) that $\langle\cos^2\theta\rangle$ is 1/3 for the isotropic molecules, and is 1 or 0 for all the molecules are aligned parallel or perpendicular to the laser polarization direction (i.e., the maximum alignment or antialignment).

III. RESULTS AND DISCUSSION

In our simulation, we use the CO molecule as example, and the molecular parameters are: B = 1.93 cm^{-1}, $\mu = 0.112$ D, $\alpha_\parallel = 2.294$ Å^3, and $\alpha_\perp = 1.77$ Å^3.[31,32] Thus, the rotational period of the CO molecule can be calculated as T$_{rot}$ = 1/(2Bc) $\approx$ 8.64 ps, where c is the speed of the light in the vacuum. The initial rotational temperature of the CO molecule is set to be 50 K. We assume that the laser central frequency ω_0 is 12 500 cm^{-1}, corresponding to the laser central wavelength of 800 nm, the laser intensity I is 1×10^{13} W/cm^2, and the pulse duration (full width at half maximum) τ is 200 fs.

The shaped femtosecond laser pulse with a periodic phase step modulation has been successfully employed to manipulate the molecular rotational wave packet.[29] Here, we utilize this phase-shaped laser pulse to control the maximum degree and temporal structure of the field-free molecular alignment. Figure 1(a) shows the laser spectrum modulated 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 α and β represent the modulation depth and modulation time, respectively. The shaped laser pulse in frequency domain is given by E$_s(\omega) = E(\omega) \times \exp[i \times \Phi(\omega)]$, where E$(\omega)$ is the Fourier transform of the unshaped laser pulse E(t), and therefore the shaped laser pulse in time domain E$_s$(t) is obtained by the inverse Fourier transform of E$_s(\omega)$.[33] Figure 1(b) shows the temporal intensity profile of the shaped laser pulse E$_s$(t) with the modulation depth $\alpha = \pi/2$ and the modulation time $\beta = 2153$ fs. One can see that the shaped laser pulse by the periodic phase step modulation is the multiple subpulse structure around the zero time delay. The modulation depth α is to
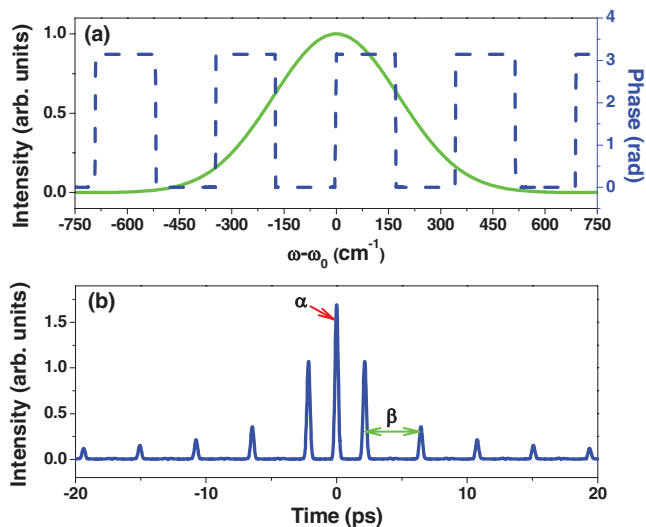

FIG. 1. (a) A periodic phase step modulation with the function of $\Phi(\omega) = \alpha/2 + 2\alpha/\pi \sum_{l=0}^{\infty} \sin[\beta(2l+1)(\omega-\omega_0)]/(2l+1)$ applied on the laser spectrum. (b) The temporal intensity profile of the shaped laser pulse with the modulation depth $\alpha = \pi/2$ and the modulation time $\beta = 2153$ fs.

control the relative amplitude between the central main-pulse and those side subpulses, and the central main-pulse vanishes and these side subpulses are maximal value when $\alpha = \pi$. The modulation time β is to change the subpulse separation, and the subpulse separation increases when β is increased.

Figure 2 shows the maximal degree of the field-free molecular alignment $\langle\cos^2\theta\rangle_{max}$ as the function of the modulation time β for the modulation depth $\alpha = \pi$, here the green dashed line is used to show the maximum degree of the molecular alignment induced by the unshaped laser pulse (i.e., the transform-limited laser pulse). As can be seen, the molecular alignment degree can be continuously modulated from 0.338 to 0.418, which illustrates that the molecular alignment can be completely suppressed or reconstructed as that by the transform-limited laser pulse. The minimum value (0.338) is obtained at $\beta = 2153$ fs, corresponding to the subpulse
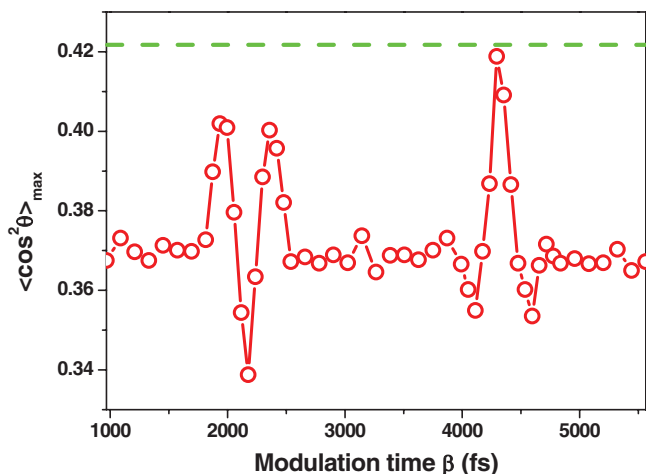

FIG. 2. The maximal degree of the field-free molecular alignment $\langle\cos^2\theta\rangle_{max}$ as the function of the modulation time β for the modulation depth $\alpha = \pi$. The green dashed line is used to show the maximum degree of the molecular alignment induced by the transform-limited laser pulse.

separation of 4.32 ps, which is equal to the half of the ro-
tational period (i.e., $T_{rot}/2$). The maximum value (0.418) is
obtained at $\beta = 4317$ fs, corresponding to the subpulse sepa-
ration of 8.64 ps, which is equal to the full of the rotational pe-
riod (i.e., T_{rot}). Consequently, we can conclude that the molec-
ular alignment is completely suppressed when the subpulse
separation is the half of the rotational period, and is recon-
structed as that by the transform-limited laser pulse when the
subpulse separation is the full of the rotational period. Usu-
ally, the degree of the molecular alignment is limited by the
maximally applicable laser intensity due to intrinsic satura-
tion and ionization. Our results indicate that the limitation
can be broken by shaping the laser pulse with this spectral
phase modulation. So, we believe that the shaped laser pulse
with the periodic phase step modulation can provide a feasible
method to further enhance the molecular alignment.

To demonstrate the control of the molecular alignment
induced by the phase-shaped laser pulse, we further observe
the temporal structure of the molecular alignment. Figure 3
shows the time-dependent molecular alignment $\langle\cos^2\theta\rangle$ with
the modulation depth $\alpha = \pi$ for the modulation time β of
(a) 568, (b) 1137, (c) 1596, and (d) 2044 fs (red solid lines),
together with (a) 3749, (b) 3180, (c) 2721, and (d) 2273 fs
(blue dashed lines). As can be seen, the temporal structure of
the molecular alignment at the half or full of the rotational
periods becomes more complex and greatly depends on β
(i.e., the subpulse separation). We can obtain the shape with
one alignment (or antialignment) and two antialignments (or
alignments) (see Fig. 3(d)), or the shape with two alignments
and two antialignments (see Figs. 3(a) and 3(c)). Obviously,
the temporal structure of the molecular alignment can be con-
trolled with a desired shape by the periodic phase step mod-
ulation. For the transform-limited laser pulse excitation, the
odd and even rotational states evolve out of phase around the
quarter rotational period, and so no molecular alignment oc-
curs at these time delays due to the destructive interference
between the odd and even rotational state contributions, but it
is obvious that the evolution behavior can be changed by the
phase-shaped laser pulse and the molecular alignment around
quarter rotational period is obtained (see Fig. 3(b)).

By comparing the solid and dashed lines in Fig. 3, one
can see that the molecular alignment and antialignment can
be switched for any temporal structure by rationally design-
ing the modulation time β. That is to say, for the molecular
behavior with a specific β_1, such as the molecular alignment
(or antialignment), we always can find another corresponding
β_2 that induces an opposite behavior at any time delay, such
as the molecular antialignment (or alignment). Since β only
affects the sulbpulse separation in the shaped laser pulse, we
consider the relation between β_1 and β_2 from the subpulse
separation. Our calculations indicate that the two subpulse
separations Δt_1 and Δt_2 satisfy the relation $\Delta t_2 = T_{rot}-\Delta t_1$,
here Δt_1 and Δt_2 are the subpulse separations for β_1 and β_2,
respectively. In other words, Δt_1 and Δt_2 are symmetric with
the half of the rotational period (i.e., $T_{rot}/2$).

As shown in Fig. 3, the subpulse separation of the shaped
laser pulse will affect the temporal structure of the molec-
ular alignment, and so the maximum degree of the molec-
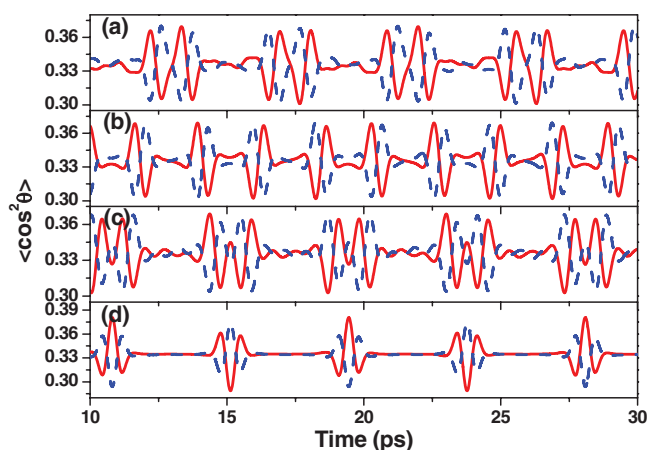ular alignment in Fig. 2 is achieved at different time delays.

FIG. 3. The time-dependent molecular alignment $\langle\cos^2\theta\rangle$ with the modu-
lation depth $\alpha = \pi$ for the modulation time β of (a) 568 fs, (b) 1137 fs,
(c) 1596 fs, and (d) 2044 fs (red solid lines), together with (a) 3749 fs,
(b) 3180 fs, (c) 2721 fs, and (d) 2273 fs (blue dashed lines).

Next, we will show that the maximum degree of the molec-
ular alignment can occur at a fix time delay and can be contin-
uously modulated by precisely controlling the two modulated
parameters α and β. Figure 4(a) shows the degree of the field-
free molecular alignment $\langle\cos^2\theta\rangle$ at the time delay of 17.49 ps
(corresponding to the full rotational period T_{rot}) as the func-
tion of the modulation depth α for the modulation time β
= 4317 fs. One can see that, with the increase of α, the molec-
ular alignment degree can be continuously modulated from
0.423 to 0.261. That is to say, both the degree and direction of
molecular alignment can be continuously controlled by vary-
ing α. The maximum alignment (i.e., $\langle\cos^2\theta\rangle = 0.423$) is ob-
tained at $\alpha = 0$ or 2π, corresponding to the transform-limited
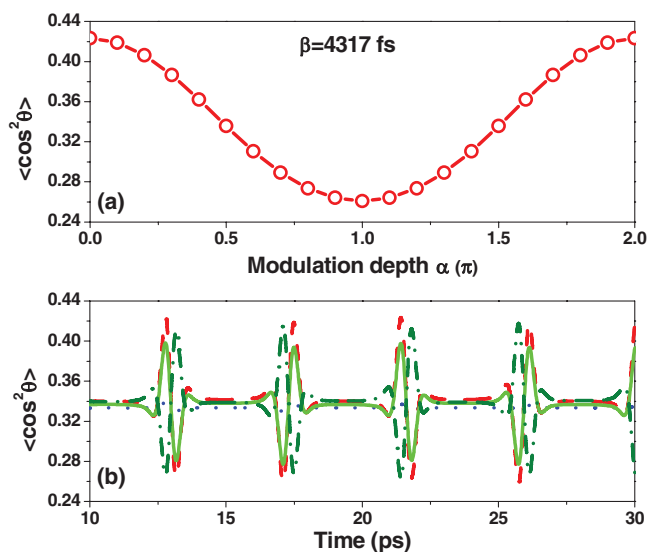laser pulse, and the maximum antialignment (i.e., $\langle\cos^2\theta\rangle$

FIG. 4. (a) The degree of the field-free molecular alignment $\langle\cos^2\theta\rangle$ at the
time delay of 17.49 ps (i.e., the full rotational period T_{rot}) as the func-
tion of the modulation depth α for the modulation time $\beta = 4317$ fs.
(b) The time-dependent molecular alignment $\langle\cos^2\theta\rangle$ with the modulation
time $\beta = 4317$ fs for the modulation depth $\alpha = 0$ (red dashed line), 0.25π
(green solid line), 0.5π (blue dotted line), and π (olive dash-dotted line).

$= 0.261$) is obtained at $\alpha = \pi$, corresponding to the subpulse separation with the full rotational period T_{rot}. Figure 4(b) shows the time-dependent molecular alignment $\langle \cos^2\theta \rangle$ with the modulation time $\beta = 4317$ fs for the modulation depth $\alpha = 0$ (red dashed line), 0.25π (green solid line), 0.5π (blue dotted line), and π (olive dashed-dotted line). One can see that α only changes the degree and direction of the molecular alignment but not affects its temporal structure.

IV. CONCLUSIONS

In summary, we have theoretically demonstrated that the maximum degree and temporal structure of the field-free molecular alignment can be controlled by shaping the femtosecond laser pulse with a periodic phase step modulation. Our results showed that the molecular alignment can be completely suppressed when the subpulse separation of the shaped laser pulse is half of the rotational period, and can be reconstructed as that by the transform-limited laser pulse when the subpulse separation is the full of the rotational period; the temporal structure of the molecular alignment depends on the subpulse separation of the shaped laser pulse, which can be controlled with a desired shape; and the molecular alignment and antialignment for any temporal structure can be switched by precisely selecting the subpulse separation. Finally, we showed that both the degree and direction of the molecular alignment at a fix time delay can be continuously modulated by rationally designing the modulated parameters characterizing the periodic phase step modulation. Our present scheme can also be applied to the field-free molecular orientation. By simultaneously shaping the fundamental laser pulse and its second harmonic with the periodic phase step modulation, the maximum degree and temporal structure of the molecular orientation can be controlled.

ACKNOWLEDGMENTS

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