Field-free molecular alignment by shaping femtosecond laser pulse with cubic phase modulation

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We propose a scheme to enhance the field-free molecular alignment by shaping the femtosecond laser pulse with cubic phase modulation. We show that the molecular alignment can be obtained adiabatically during the shaped pulse and can be revived at the full rotational periods with the same degree as that at the peak of the shaped pulse. The behavior of the molecular alignment by the shaped pulse is the same as that by the slow turn-on and rapid turn-off laser pulse. Furthermore, we show that the shaped pulse with cubic phase modulation has a slight advantage in enhancing the field-free molecular alignment by comparing it with the slow turn-on and rapid turn-off laser pulse under the same laser intensity.

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Laser-induced molecular alignment has become an important and intriguing subject because of its widespread applications, such as chemical reaction dynamic [1,2], high-order harmonic generation [3,4], surface processing [5], and tomographic imaging of electronic orbitals [6]. Depending on the laser-pulse duration, the laser-induced molecular alignment can be achieved in both nonadiabatic and adiabatic regimes [7]. The nonadiabatic and adiabatic molecular alignment can complement each other according to the experimental requirement. For the nonadiabatic molecular alignment, there is the advantage that it can obtain the aligned molecules under the field-free conditions, which is desirable for further applications. For most applications, it is crucial to obtain as high a degree of field-free molecular alignment as possible. However, the degree of field-free molecular alignment is usually limited by the maximally applicable laser intensity due to its intrinsic saturation and ionization. Recently, several works have focused on various schemes to further enhance the field-free molecular alignment, such as the laser-pulse trains with the pulse separations being commensurate with the rotational period [8–14], the slow turn-on and rapid turn-off laser pulse [15], and the shaped laser pulse [16–19].

Previous studies demonstrated that the shaped laser pulse, by modulating the spectral phase, can provide an effective method to enhance the field-free molecular alignment [16–19], such as those in which Rouzée *et al*. [16] and Ghafur *et al*. [17] showed that the field-free molecular alignment can be enhanced by shaping the femtosecond laser pulse with a sigmoidal phase function; Renard *et al*. demonstrated that, at particular times, the field-free molecular alignment can be enhanced by modulating the spectral phase of the excitation pulse with periodic phase steps [18]; Sakai *et al*. realized the maximization of the field-free molecular alignment by shaping the femtosecond laser pulse with an adaptive feedback control based on a genetic algorithm and found that the molecular alignment was optimal by using a doubly peaked pulse with an appropriate interval [19]. In this paper, we present a scheme to enhance the field-free molecular alignment by modulating a femtosecond laser pulse with cubic phase modulation. Our results show that the shaped pulse is equivalent to the slow turn-on and rapid turn-off laser pulse when the laser-pulse duration is short enough using a few optical cycles, and the molecular alignment can be adiabatically achieved during the shaped pulse and can be revived at the full rotational periods with the same degree as that achieved at the peak of the shaped pulse. Furthermore, we also show that the degree of the field-free molecular alignment of the shaped pulse is slightly higher than that of the slow turn-on and rapid turn-off laser pulse under the same laser intensity.

When a linear molecule is subjected to the laser field $E(t)$ with the Gaussian shape $E(t) = E_0 \exp(-2\ln 2t^2/\tau^2)\cos(\omega_0 t)$, where E_0 is the field amplitude, τ is the pulse duration, and ω_0 is laser center frequency, the time-dependent Schrödinger equation can be expressed based on a rigid-rotor model as [7]

$$i\hbar \frac{\partial |\Psi(\theta,t)\rangle}{\partial t} = H(t)|\Psi(\theta,t)\rangle, \tag{1}$$

where $H(t)$ is the interaction Hamiltonian between the molecule and the laser field $E(t)$ and is written as

$$H(t) = BJ_i(J_i+1) - \mu E(t)\cos\theta - \tfrac{1}{2}[(\alpha_{||} - \alpha_\perp)\cos^2\theta + \alpha_\perp]E^2(t), \tag{2}$$

where B, J_i, and μ are the rotational constant, the angular momentum, and the permanent dipole moment, θ is the angle between the molecular axis and the laser polarization direction, and $\alpha_{||}$ and $\alpha_\perp$ are the polarizability components parallel and perpendicular to the molecular axis, respectively. In Eq. (2), the first term is the molecular rotational energy, and the second and third terms represent the interaction potentials with the permanent dipole moment and the polarizability, respectively. Finally, the degree of the molecular alignment is given with the expectation value of $\cos^2\theta$ by considering the temperature-dependent Boltzmann distribution and is given by

$$\langle \cos^2\theta \rangle = \sum_{J_i} W_{J_i} \sum_{M_i=-J_i}^{J_i} \left\langle \Psi_{J_i M_i} \middle| \cos^2\theta \middle| \Psi_{J_i M_i} \right\rangle, \tag{3}$$

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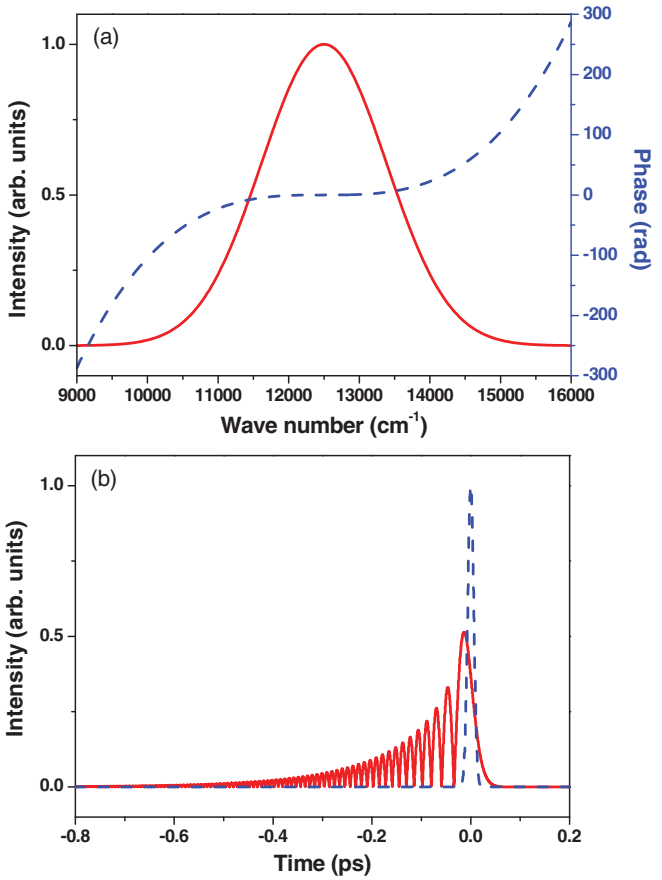

FIG. 1. (Color online) (a) The schematic of the 10-fs laser spectrum (red solid line) and the cubic phase modulation $\Phi(\omega) = \alpha(\omega - \omega_0)^3$ with $\alpha = 1000$ fs^3 (blue dashed line). (b) The temporal intensity profile of the unshaped laser pulse (blue dashed line) and the shaped laser pulse by the cubic phase modulation with $\alpha = 1000$ fs^3 (red solid line).

where W_{J_i} are Boltzmann weight factors with $W_{J_i} = g_{J_i} \exp[-BJ_i(J_i+1)/kT]/.Q$, Q is the rotational partition function, and g_{J_i} is the spin degeneracy factor. In our simulation, the time-dependent Schrödinger equation (1) is numerically solved by the pseudospectral time-dependent method [20], and its propagation is performed in the rotational energy basis by the second-order split-operator method [21,22].

The shaped laser pulse, by modulating the spectral phase, has been successfully employed to enhance the field-free molecular alignment [16–19]. Here, we enhance the field-free molecular alignment by modulating the femtosecond laser pulse with cubic phase modulation $\Phi(\omega) = \alpha(\omega - \omega_0)^3$, where α is the modulation depth. The spectral phase modulation is shown in Fig. 1(a), and the temporal intensity profile of the shaped pulse is presented in Fig. 1(b), together with the unshaped pulse (blue dashed line). It can be seen that the cubic phase modulation leads to the formation of a pulse train. With an increase in the negative time delay, the subpulse intensity decreases. Comparing with the unshaped pulse, the subpulse duration in the shaped pulse is slightly broadened, especially the last few subpulses. When the modulation depth α is increased, the subpulse number increases, but the subpulse intensity decreases. If the unshaped pulse duration is short enough using a few optical cycles, the subpulse separation in the shaped pulse will be very small. When the linear molecule is exposed to the shaped pulse, the effect of the subpulse separation on the molecular alignment can be neglected, thus, the shaped pulse can be considered as the slow turn-on and rapid turn-off laser pulse [15], and so the behavior of the molecular alignment will be the same as that induced by the slow turn-on and rapid turn-off laser pulse.

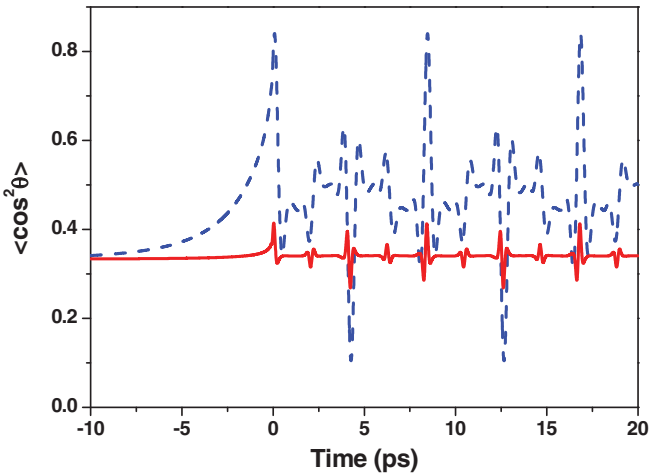

FIG. 2. (Color online) Time-dependent molecular alignment $\langle\cos^2\theta\rangle$ induced by the shaped pulse with $\alpha = 50\ 000$ fs^3 for the rotational temperatures $T = 300$ K (red solid line) and 10 K (blue dashed line). Here, the laser intensity of the unshaped pulse is 1.4×10^{15} W/cm^2, and, thus, the laser intensity of the shaped pulse is 3.2×10^{13} W/cm^2.

To confirm our above prediction, we calculate the time evolution of the molecular alignment $\langle\cos^2\theta\rangle$ induced by the shaped pulse. In our simulation, we use the N_2 molecule as an example, and the molecular parameters are $B = 1.989$ cm^{-1}, $\alpha_{||} = 2.38$, and $\alpha_{\perp} = 1.45$ Å^3 [7]. The laser-center frequency ω_0 is 12 500 cm^{-1}, corresponding to the laser-center wavelength of 800 nm, and its pulse duration τ (the full width at half maximum) is 10 fs. Figure 2 shows the time-dependent molecular alignment $\langle\cos^2\theta\rangle$ by the shaped pulse with $\alpha = 50\ 000$ fs^3 for the rotational temperatures $T = 300$ K (red solid line) and 10 K (blue dashed line), here, the laser intensity of the unshaped pulse is 1.4×10^{15} W/cm^2, and, thus, the laser intensity of the shaped pulse is 3.2×10^{13} W/cm^2. As expected, the molecular alignment is adiabatically achieved during the shaped pulse and is revived at the full rotational periods with the same degree as that achieved at the peak of the shaped pulse (i.e., the last subpulse). It can be found that the behavior of the molecular alignment is the same as that by the slow turn-on and rapid turn-off laser pulse [15]. Usually, the degree of the molecular alignment is limited by the maximally applicable laser intensity due to its intrinsic saturation and ionization, but it is obvious that the limitation can be broken by separating it into several subpulses with the cubic phase modulation. So, we believe that the present scheme can provide an effective method to further enhance the field-free molecular alignment.

By increasing the modulation depth α, the subpulse number in the shaped pulse increases, thus, the interaction time

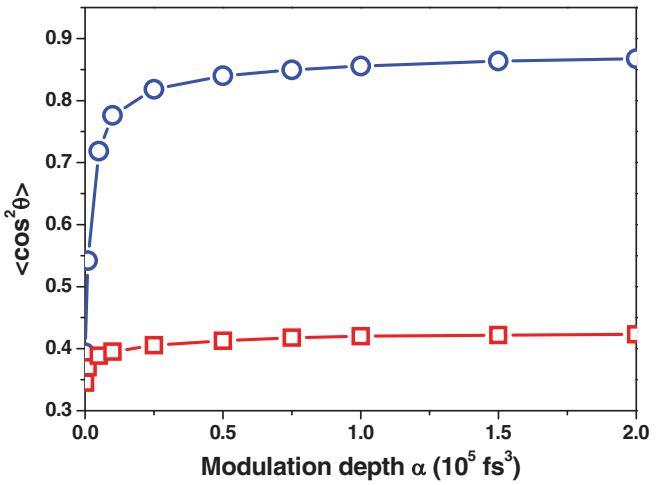

FIG. 3. (Color online) The degree of molecular alignment $\langle \cos^2\theta \rangle$ at the full rotational periods as a function of modulation depth α for the rotational temperatures $T = 300$ K (red squares) and 10 K (blue circles). Here, the laser intensity of the shaped pulse is kept at 3.2×10^{13} W/cm^2.

between the shaped pulse and the molecule will lengthen, which is similar to that by increasing the rising time of the slow turn-on and rapid turn-off laser pulse. Next, we study the effect of the modulation depth α on the field-free molecular alignment. However, increasing the modulation depth α will also lead to a decrease in the subpulse intensity. To ensure that the molecular alignment is effected by the subpulse number but not its intensity, we fix the laser intensity of the shaped pulse (i.e., the last subpulse), which can be realized by varying the laser intensity of the unshaped pulse. Figure 3 shows the degree of molecular alignment at the full rotational periods as a function of the modulation depth α for the rotational temperatures $T = 300$ K (red squares) and 10 K (blue circles); here, the laser intensity of the shaped pulse is fixed at 3.2×10^{13} W/cm^2. One can see that the degree of the field-free molecular alignment increases and then remains constant with the increase in modulation depth α, which indicates that the molecular alignment changes from nonadiabatic to adiabatic processes. Comparing with the unshaped pulse (i.e., $\alpha = 0$), the molecular alignment induced by the shaped pulse can be enhanced significantly under the same laser intensity. Obviously, this observation is the same as that by increasing the rising time of the slow turn-on and rapid turn-off laser pulse [15].

Since the behavior of the molecular alignment by the shaped pulse is the same as that by the slow turn-on and rapid turn-off laser pulse, we compare the maximally attainable degree of the field-free molecular alignment with the two schemes under the same laser intensity. Figure 4(a) shows the temporal intensity profile of the slow turn-on and rapid turn-off laser pulse. As compared with the shaped pulse with cubic phase modulation [see Fig. 1(b)], it can be seen that the rising process of the laser intensity (or subpulse intensity) is slightly different, the laser intensity of the slow turn-on and rapid turn-off laser pulse rises with Gaussian shape, while the subpulse intensity in the shaped pulse increases with approximate Lorentz shape. Figure 4(b) shows the time-dependent molecular alignment

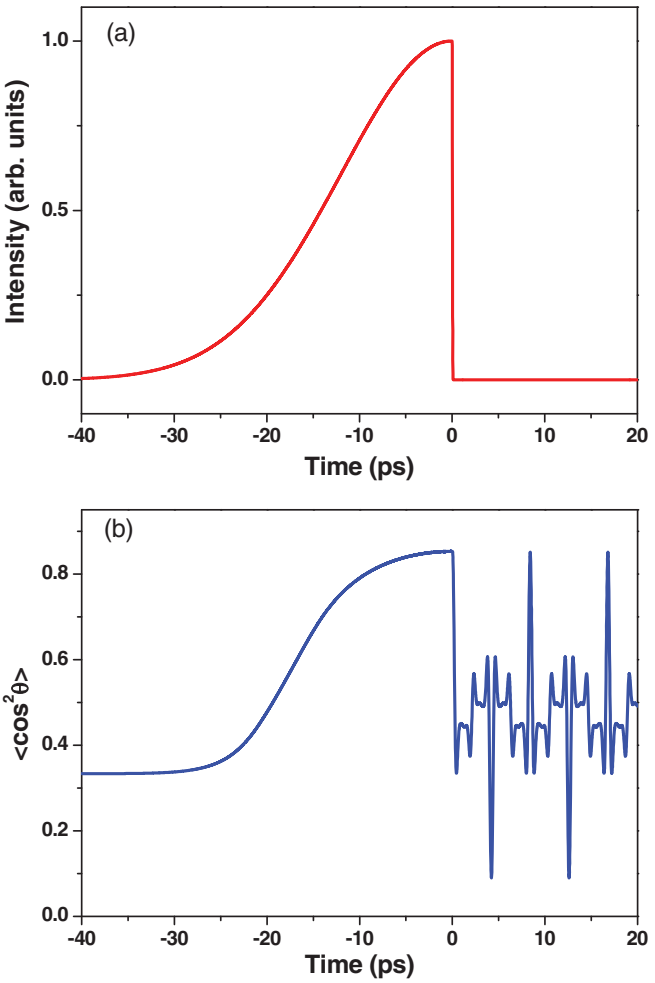

FIG. 4. (Color online) (a) The temporal intensity profile of the slow turn-on and rapid turn-off laser pulse with the rising time of 30 ps and the falling time of 50 fs. (b) Time-dependent molecular alignment $\langle \cos^2\theta \rangle$ induced by the slow turn-on and rapid turn-off laser pulse with the laser intensity of 3.2×10^{13} W/cm^2 for the rotational temperature $T = 10$ K.

$\langle \cos^2\theta \rangle$ induced by the slow turn-on and rapid turn-off laser pulse with the rising time of 30 ps and the falling time of 50 fs for the rotational temperature $T = 10$ K, corresponding to the adiabatic process. Here, the laser intensity is also set to 3.2×10^{13} W/cm^2, which is equal to the laser intensity of the shaped pulse in Fig. 3. One can see that the degree of the molecular alignment at the full rotational periods is 0.85, which is slightly smaller than that by the shaped pulse ($\sim$0.87) as shown in Fig. 3. That is to say, comparing with the slow turn-on and rapid turn-off laser pulse, the shaped pulse has a slight advantage in enhancing the field-free molecular alignment. This result illustrates that the shape of the rising edge of the laser pulse will affect the degree of the molecular alignment in the adiabatic process, and, therefore, it can provide a feasible parameter to further optimize the field-free molecular alignment.

Finally, we analyze the feasibility of our present scheme in an experiment. Two important issues for our scheme must be addressed, one is the generation of the femtosecond laser pulse with a few optical cycles and the other is the femtosecond laser pulse shaping. Now, a 5-fs laser pulse can be obtained directly

from a Ti:sapphire laser [23], which can completely meet the requirement of our scheme. With the progress of the ultrashort pulse-shaping technique, the spectral phase modulation, with an almost arbitrary shape, can be realized by a programmable 4*f*-configuration zero-dispersion pulse shaper combined with a one-dimensional liquid-crystal spatial light modulator [24]. The falling time of the laser pulse is a crucial parameter in the laser-induced molecular alignment, which decides whether the degree of the molecular alignment at the full rotational periods can be achieved maximally. By shaping the ultrashort femtosecond laser pulse with cubic phase modulation, such as a 5-fs laser pulse, the falling time of the last subpulse in the shaped pulse can ensure that the field-free molecular alignment is maximal in any laser intensity and rotational temperature.

To summarize, we have presented a scheme to enhance the field-free molecular alignment by shaping the femtosecond laser pulse with cubic phase modulation. The shaped pulse is a pulse train, and the subpulse intensity decreases with the increase in the negative time delay. If the laser pulse is short enough using a few optical cycles, the shaped pulse can be considered as the slow turn-on and rapid turn-off laser pulse. We showed that the molecular alignment can be achieved adiabatically during the shaped pulse and can be revived at the full rotational periods with the same degree as that achieved at the peak of the shaped pulse. We also showed that the field-free molecular alignment of the shaped pulse can be improved slightly by comparing with the slow turn-on and rapid turn-off laser pulse under the same laser intensity. Our present scheme can also be applied to the molecular orientation. By superimposing the shaped pulse and its second harmonic, i.e., dual-color laser pulse, the field-free molecular orientation can be enhanced significantly.

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