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Enhancing field-free molecular alignment by a polynomial phase modulation

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Abstract. A feasible scheme is proposed to enhance the molecular alignment by shaping the femtosecond laser pulse with a polynomial phase modulation that involves the second and third order dispersions. It is shown that the field-free molecular alignment can be obtained adiabatically during the interaction with the shaped femtosecond laser pulse, and can be reproduced at full rotational periods with the same degree as that at the peak of laser pulse when the shaped femtosecond laser pulse is gone off. It is also shown that the molecular alignment behavior by the shaped femtosecond laser pulse is same as that by the slow turn-on and rapid turn-off laser pulse in previous study, but the shaped femtosecond laser pulse can induce slightly higher alignment degree due to the different rising edge. In addition, it is indicated that our proposed scheme can be experimentally realized by using a programmable $4f$-configuration zero-dispersion pulse shaper combined with a one-dimensional liquid-crystal spatial light modulator.

1 Introduction

Molecular manipulation to achieve the spatially aligned molecules has attracted both physicists' and chemists' increasing interests in recent years due to its extensive applications on chemical reaction dynamics [1–3], high-harmonic generation [4,5], attosecond science [6,7] and molecular orbital imaging [8]. An intense nonresonant laser pulse has been demonstrated to be the most effective tool to create the molecular alignment based on the interaction between the induced molecular dipole moment and the laser field [9,10]. On the basis of the ratio of the laser pulse duration and the molecular rotational period, there are two alternative ways to induce the molecular alignment. One method is called as "adiabatic alignment", where the laser pulse duration is far longer than the molecular rotational period, i.e., the laser field can be considered as slow switching on and off, the molecular alignment proceeds adiabatically when the laser field is slowly turned on, and the molecular ensemble returns smoothly to the isotropic angular distribution when the laser pulse is slowly turned off. The other one is termed as "nonadiabatic alignment", referred to the reverse case that employs an intense laser pulse much shorter than the molecular rotational period, thus a freely evolved rotational wave packet is created, which will go through a periodic dephasing and rephrasing after the light-molecule interaction, and a field-free molecular alignment can be generated. Comparing with the adiabatic

alignment, the nonadiabatic alignment has an advantage that the aligned molecules can be further applied under the field-free conditions, but the degree of the molecular alignment in the nonadiabatic regime is lower than that in the adiabatic case under the same laser intensity.

In most cases, it is crucial to obtain the alignment degree as high as possible for the further applications of the laser-induced molecular alignment. In recent years, various schemes, such as the shaped femtosecond laser pulse with phase modulation [11–16], or the slow turn-on and rapid turn-off laser pulse [17], have been proposed to further enhance field-free molecular alignment. For example, Suzuki et al. [11] and Horn et al. [12] showed that the nonadiabatic molecular alignment can be enhanced by shaping femtosecond laser pulse with the adaptive feedback control based on an evolutionary algorithm. Rouzée et al. [13] and Ghafur et al. [14] realized the field-free molecular alignment enhancement by a shaped femtosecond laser pulse with a sigmoidal phase modulation. Zhang et al. [15,16] proposed that the field-free molecular alignment can be enhanced by the shaped femtosecond laser pulse with a cubic phase modulation or the square-shape laser pulse. Especially, Sakai et al. proposed a slow turn-on and rapid turn-off laser pulse to further enhance field-free molecular alignment [17–20], which combines the advantages of high alignment degree in adiabatic regime and field-free evolution in nonadiabatic regime. In this work, we present a scheme to enhance the molecular alignment by shaping the femtosecond laser pulse with a polynomial phase modulation that involves the second and third order dispersions. The shaped femtosecond laser pulse has the feature

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of slow turn-on and rapid turn-off shape, and therefore the induced molecular alignment has the characteristic of both the high degree in adiabatic regime and the field-free evolution in nonadiabatic regime. Comparing with the molecular alignment excited by the slow turn-on and rapid turn-off laser pulse in previous work, there is a slight enhancement by our proposed shaped femtosecond laser pulse due to the different rising edge. This phase-shaped femtosecond laser pulse provides another simple and feasible method to further enhance the molecular alignment.

2 Theoretical method

We consider a linear molecular system that is subjected to a linearly polarized laser field with $E(t) = E_0 f(t) \cos(\omega_0 t)$, where E_0 is the laser field amplitude, ω_0 is the laser central frequency, and $f(t)$ is the temporal distribution of the pulse envelope with Gaussian shape $f(t) = \exp((-2\ln 2)t^2/\tau^2)$, here τ is the pulse duration. Based on the rigid rotor model, the time-dependent Schrödinger equation can be approximated as [21,22]

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

with

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

where B and μ are, respectively, the rotational constant and the permanent dipole moment of the molecule, J is the angular momentum, 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. The first term in equation (2) represents the molecular rotational energy, and the second and third terms describe the interaction potentials with the permanent dipole moment and the polarizability, respectively. The degree of the molecular alignment is characterized by the expectation value of $\cos^2\theta$ (i.e., $\langle\cos^2\theta\rangle$). Considering the thermal equilibrium of the molecular ensemble, $\langle\cos^2\theta\rangle$ is averaged over the Boltzmann distribution and written as:

$$\langle\cos^2\theta\rangle = \sum_J Q^{-1} g_J \exp\left[-BJ(J+1)/kT\right]$$
$$\times \sum_{M=-J}^{J} \langle\Psi_{JM} |\cos^2\theta| \Psi_{JM}\rangle, \quad (3)$$

where Q is the partition function, g_J is the spin degeneracy factor and Ψ_{JM} is the rotational wave function of the time-evolved molecules.

3 Results and discussion

In our theoretical simulation, the time-dependent Schrödinger equation in equation (1) is numerically solved
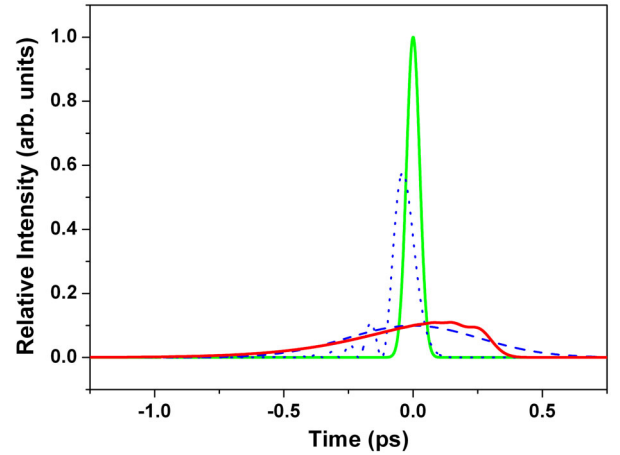

Fig. 1. The temporal intensity profile of the unshaped 60-fs laser pulse (green solid line) and the shaped laser pulse with a polynomial phase modulation $\Phi(\omega) = (1/2)\alpha_2(\omega - \omega_0)^2 + (1/6)\alpha_3(\omega - \omega_0)^3$ for $\alpha_2 = 13\,000$ fs^2 and $\alpha_3 = 260\,000$ fs^3 (red solid line), together with the shaped laser pulse with only the second order dispersion modulation for $\alpha_2 = 13\,000$ fs^2 (blue dashed line) and the third order dispersion modulation for $\alpha_3 = 260\,000$ fs^3 (blue dotted line).

by a split-operator method [23,24]. We use the CO molecule as the study example, and the molecular parameters are set as $B = 1.93$ cm^{-1}, $\mu = 0.112$ D, $\alpha_{||} = 2.294$ Å^3, $\alpha_\perp = 1.77$ Å^3 [25–27]. Thus, the rotational period of the CO molecule can be calculated as $T_{\rm rot} = 1/(2Bc) \approx 8.64$ ps, where c is the speed of the light in vacuum. The molecular rotational temperature is set to be 30 K. These parameters characterized the transform-limited laser pulse are set as follows, the laser central frequency is $\omega_0 = 12\,500$ cm^{-1} and the pulse duration (Full Width at Half Maximum) is $\tau = 60$ fs.

The shaped femtosecond laser pulse by modulating the spectral phase has shown to be one of the effective methods to manipulate or enhance the field-free molecular alignment [11–16]. Here, we present a new scheme to enhance the field-free molecular alignment by modulating the femtosecond laser pulse with a polynomial phase modulation $\Phi(\omega) = \Phi_2(\omega) + \Phi_3(\omega) = (1/2)\alpha_2(\omega - \omega_0)^2 + (1/6)\alpha_3(\omega - \omega_0)^3$, where $\Phi_2(\omega)$ and $\Phi_3(\omega)$ respectively represent the second and third order dispersion, and α_2 and α_3 are the modulation depth. Figure 1 shows the temporal intensity distribution of the unshaped femtosecond laser pulse (green solid line) and the shaped femtosecond laser pulse with the polynomial phase modulation (red solid line), together with the shaped femtosecond laser pulse with only the second order dispersion modulation (blue dashed line) and only the third order dispersion modulation (blue dotted line). One can see from Figure 1 that the second order dispersion modulation will stretch the unshaped femtosecond laser pulse duration and introduce a linear frequency sweep. The third order dispersion modulation will lead to an asymmetric pulse train formation that is characterized by an intense initial pulse preceded by a pulse sequence with decaying amplitudes.
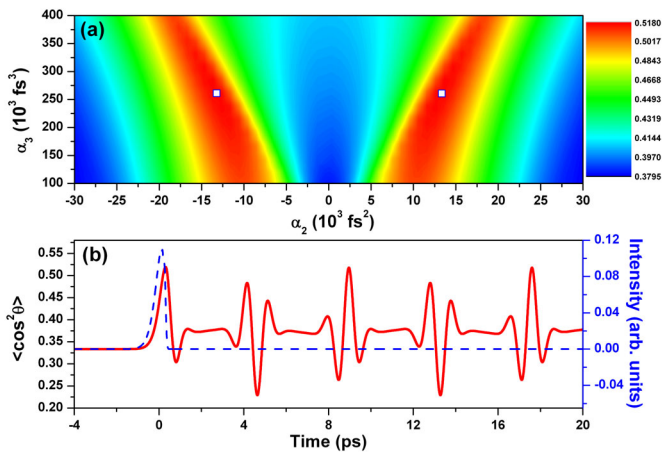
Fig. 2. (a) The dependence of the maximal degree of the molecular alignment induced by the shaped laser field on the phase modulation parameters α_2 and α_3, where the two white squares denote the maximum values of the maximal degree with $\alpha_2 = \pm 13\,000$ fs^2 and $\alpha_3 = 260\,000$ fs^3. (b) Time evolution of the molecular alignment (red solid line) induced by the shaped laser pulse (blue dashed line) with the polynomial phase modulation for $\alpha_2 = 13\,000$ fs^2 and $\alpha_3 = 260\,000$ fs^3. Here, the shaped laser intensity is $I = 1 \times 10^{13}$ W cm^2 and the molecular rotational temperature is $T = 30$ K.

Therefore, by combining the second and third order dispersion phase modulation, the shaped femtosecond laser pulse has the feature of slow turn-on and rapid turn-off shape, which is similar to the slow turn-on and rapid turn-off laser pulse in previous work [17–20]. In this work, we utilize the polynomial phase modulation to further enhance the field-free molecular alignment.

Since the shaped femtosecond laser pulse by this polynomial phase modulation is similar to the slow turn-on and rapid turn-off laser pulse, which can be used to further enhance the molecular alignment, we seek for the optimal pulse shape by varying the two modulation depths α_2 and α_3. Figure 2a shows the dependence of the maximal degree of the molecular alignment on the phase modulation depths α_2 and α_3, here the laser intensities of the shaped femtosecond laser pulse are kept at $I = 1 \times 10^{13}$ W cm^2. As can be seen, the maximal degree of the molecular alignment will be greatly affected by the phase modulation depths α_2 and α_3, which is maximally obtained with $\alpha_2 = \pm 13\,000$ fs^2 and $\alpha_3 = 260\,000$ fs^3, here two open squares are used to show the optimal value. The positive and negative values of modulation depth α_2 show the same effect on the maximal degree, which indicates that the sign of linear frequency-sweep by the second order dispersion does not affect the molecular alignment. Figure 2b presents the time evolution of the molecular alignment (red solid line) induced by the shaped femtosecond laser pulse (blue dashed line) with the polynomial phase modulation for the optimal modulation depths, i.e., $\alpha_2 = 13\,000$ fs^2 and $\alpha_3 = 260\,000$ fs^3. One can see from Figure 2b that the molecular alignment can be achieved adiabatically during the shaped femtosecond laser pulse, which implies that the rising time
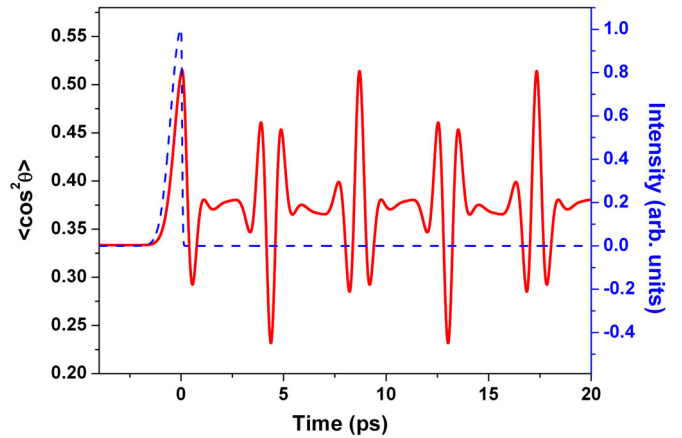

Fig. 3. Time evolution of the molecular alignment (red solid line) induced by the slow turn-on and rapid turn-off laser pulse (blue dashed line) with the rising time of 1.2 ps and the falling time of 100 fs under the laser intensity $I = 1 \times 10^{13}$ W cm^2 and the molecular rotational temperature $T = 30$ K.

of the shaped femtosecond laser pulse is long enough to ensure the interaction between the linear molecule and the laser field to be adiabatic. Furthermore, the molecular alignment can be reproduced at full rotational periods with the same degree as that at the peak of laser pulse, that is to say, a field-free molecular alignment can be obtained after the interaction with the shaped femtosecond laser pulse. The maximal degree of the molecular alignment at the full rotational period is about 0.52, and such a value is far higher than that produced by the transform-limited laser pulse (i.e., 0.37 by calculation) under the same laser intensity. Therefore, we believe that our scheme can provide another effective method to further enhance the field-free molecular alignment.

As can be seen from Figure 2b, the evolutionary behavior of the molecular alignment by the shaped femtosecond laser pulse is almost the same as that induced by the slow turn-on and rapid turn-off laser pulse in previous work [17–20]. Next we demonstrate the field-free molecular alignment excited by the slow turn-on and rapid turn-off laser pulse, and compare the maximally attainable degree of the molecular alignment by the two schemes under the same laser intensity. Figure 3 shows the time evolution of the molecular alignment (red solid line) induced by the slow turn-on and rapid turn-off laser pulse (blue dashed line) with the rising time of 1.2 ps and the falling time of 100 fs under the same laser intensity $I = 1 \times 10^{13}$ W cm^2 and the molecular rotational temperature $T = 30$ K. Here, in order to ensure the generation of the adiabatic process, the rising time of the slow turn-on and rapid turn-off laser pulse is set to be 1.2 ps, which is a little longer than the shaped femtosecond laser pulse. One can see that the maximal degree of the molecular alignment at the full rotational period is about 0.514, which is slightly smaller than that by the shaped femtosecond laser pulse ($\sim$0.52) shown in Figure 2b. This difference can be attributed to the different rising edges of the two laser pulses, where the rising edge of the shaped femtosecond laser pulse is
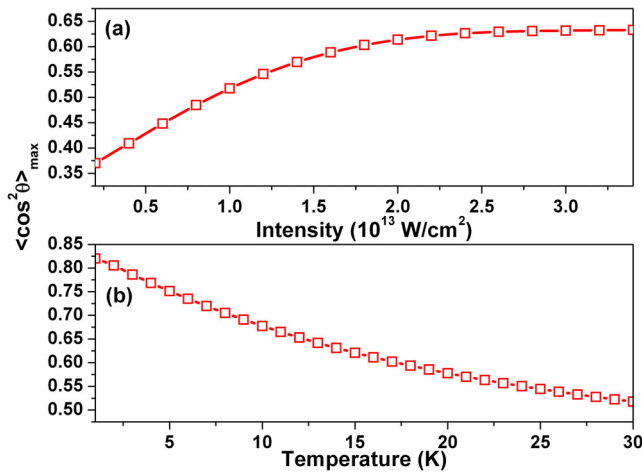
Fig. 4. The dependence of the maximal degree of the molecular alignment induced by the shaped field on the laser intensity with the molecular rotational temperature $T = 30$ K (a) and on the molecular rotational temperature with the laser intensity $I = 1 \times 10^{13}$ W cm^2 (b).

not the Gaussian shape, as can be seen from the red solid line in Figure 1.

The laser intensity and molecular rotational temperature are two important parameters to affect the molecular alignment, and next we discuss the dependence of the degree of the molecular alignment on the laser intensity and the molecular rotational temperature. Figure 4 shows the maximal degree of the molecular alignment $\langle \cos^2 \theta \rangle_{\max}$ as the function of the shaped laser intensity with the molecular rotational temperature $T = 30$ K (a) and that of the molecular rotational temperature with the shaped laser intensity $I = 1 \times 10^{13}$ W cm^2 (b). One can see from Figure 4a that, with the increase of the shaped laser intensity, the maximal degree of the molecular alignment increases and then saturates at about $I = 3 \times 10^{13}$ W cm^2, corresponding to the intensity of the transform-limited laser pulse $I = 2.8 \times 10^{14}$ W cm^2. Generally, the degree of the molecular alignment induced by the maximally applicable laser intensity is limited by its intrinsic saturation and ionization. Our results suggest that the limitation can be broken due to the laser intensity decrease by this femtosecond pulse shaping method. On the other hand, it can be seen from Figure 4b that the maximal degree of the molecular alignment can be considerably increased when the molecular rotational temperature is decreased, and so it is a common method to obtain the higher degree of the molecular alignment by reducing the molecular rotational temperature.

Finally, we analyze the feasibility and advantages of our proposed scheme in the real experiment. In our designed scheme, the crucial question for experimental realization is how to get the shaped femtosecond laser pulse with the polynomial phase modulation that involves the second and third order dispersions. With the advent of the ultrafast pulse shaping technique, the programmable $4f$-configuration zero-dispersion pulse shaper combined with a one-dimensional liquid-crystal spatial light modulator has shown to be a well-established arrangement to shape the femtosecond laser pulse [28,29]. Based on the idea of Fourier transformation between time and frequency domains, such a shaped femtosecond laser pulse with almost arbitrary temporal distribution in the time domain can be obtained by modulating the laser spectral phase/amplitude in the frequency domain. Thus, by applying this polynomial phase modulation on the liquid-crystal modulator of the femtosecond pulse shaping system, the shaped femtosecond laser pulse in our proposed scheme can be easily obtained, and here the second- and third-order dispersions can be independently controlled. So far, both the phase modulations of second and third order dispersions have been successfully applied to control the multi-photon absorption and material processing in the experiment [30,31]. In our previous scheme by the third-order dispersion [15], the unshaped laser pulse duration should be very short and the modulation depth needs to be very large, and therefore these rigorous requirements will bring some difficulties for experimental realization. However, here our present scheme by combining the second- and third-order dispersions can overcome the two defects.

4 Conclusions

In summary, we have presented a strategy to further enhance the molecular alignment by employing the shaped femtosecond laser pulse with a polynomial phase modulation that involves the second and third order dispersions. Our results showed that the molecular alignment can be achieved under the free laser field, and the field-free molecular alignment can be adiabatically obtained during interaction with the shaped pulse and reproduced at full rotational periods with the same degree as that at the peak of laser pulse. This strategy combines the advantages of both the adiabatic and nonadiabatic molecular alignment, and therefore can obtain the field-free alignment with the higher degree. By the well-established ultrafast pulse shaping technique, our proposed scheme can be easily realized in the experiment, and can also be further applied to the relative study of the field-free molecular alignment.

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