Field-free molecular orientation enhanced by two dual-color laser subpulses

Shian Zhang, Chenhui Lu, Tianqing Jia, Zugeng Wang, and Zhenrong Sun[a)]
State Key Laboratory of Precision Spectroscopy, and Department of Physics, East China Normal University, Shanghai 200062, People's Republic of China

In this paper, we theoretically show that the field-free molecular orientation created by a single dual-color laser pulse can be significantly enhanced by separating it into two time-delayed dual-color subpulses. It is indicated that the maximum enhancement of the molecular orientation created by two time-delayed dual-color subpulses can be achieved with their intensity ratio of about 1:2 and by simultaneously applying the second one at the beginning of the rotational wave packet rephasing or the end of the rotational wave packet dephasing induced by the first one. It is also shown that the enhancement or suppression of the molecular orientation can be coherently manipulated by varying the relative phase between the fundamental field and its second harmonic field of the second dual-color subpulse, and its enhancement is obtained around half rotational period. © *2011 American Institute of Physics*. [doi:10.1063/1.3610956]

Molecular orientation with a head-versus-tail order has attracted considerable attention due to its widespread applications in the molecular frame photoelectron angular distribution,[1,2] molecular imaging,[3] and attosecond science.[4] Several methods have been proposed to realize the molecular orientation with a strong dc field (i.e., hexapole field[5] and brute force field[6,7]), an asymmetric laser field (i.e., dual-color laser field[8–11] and half-cycle laser field[12–15]), or an intense laser field combined with a weak dc field,[16–18] and some suggestive techniques have been experimentally demonstrated.[17–22] Among the above-mentioned techniques, those based on the strong nonresonant linearly polarized laser field have been proven to be the most versatile method for the molecular orientation along the laser polarization direction, where the molecular orientation can be achieved in both nonadiabatic and adiabatic regimes. Especially, the nonadiabatic molecular orientation can be used to produce the field-free oriented molecules, and so it is desirable for further applications in various related fields.

It is very important for further applications of the oriented molecules that the maximal degree of the molecular orientation under the field-free condition can be achieved to the best of its abilities. Therefore, how to obtain high orientation degree is always researcher's attentive question. Generally, the essential requirement is the lowest rotational temperature of the molecules and the optimal laser intensity and pulse duration. Moreover, some sophisticated laser fields are usually proposed to further improve the molecular orientation, including of the laser pulse trains with the pulse separations being commensurate with the rotational period,[9] the slow turn-on and rapid turn-off laser pulse,[10] or the shaped

laser pulses by optimal control method.[23] In this paper, we propose a scheme to enhance the field-free molecular orientation by two dual-color laser subpulses instead of a single dual-color pulse, which was previously suggested to improve the laser-induced molecular alignment.[24–26] We show that the degree of the field-free molecular orientation can be significantly enhanced by separating a single dual-color laser pulse into two time-delayed dual-color subpulses, and the maximal molecular orientation can be obtained when the second one is applied at the beginning of the rotational wave packet rephasing or the end of the rotational wave packet dephasing induced by the first one with their intensity ratio of about 1:2. It is also indicated that the enhancement or suppression of the field-free molecular orientation can be manipulated by varying the relative phase between the fundamental field and its second harmonic field of the second dual-color subpulse. Furthermore, the physical control mechanism of the molecular orientation enhancement is discussed.

Our theoretical treatment of the molecular orientation is based on a rigid-rotor model as described in Ref. 8. We consider a dual-color laser field with a superposition of the fundamental field and its second harmonic field and given by

$$E(t) = E_0 \exp\left(-\frac{2\ln 2 t^2}{\tau^2}\right)[\cos(\omega t) + \cos(2\omega t + \Phi)],$$

(1)

where E_0 is the field amplitude, τ is the pulse duration, ω is the center frequency of the fundamental field, and Φ is the relative phase between the fundamental field and its second harmonic field, which determines the electric field structure of the dual-color laser pulse. It is easily verified that the dual-color laser field is maximally asymmetric for $\Phi = 0$ or π and completely symmetric for $\Phi = 0.5\pi$. When a linear molecule is exposed to the dual-color laser field $E(t)$, the time-dependent Schrödinger equation can be expressed based on a

---

a)Author to whom correspondence should be addressed. Electronic mail: zrsun@phy.ecnu.edu.cn.

rigid-rotor model as

$$i\hbar \frac{\partial \Psi(\theta, t)}{\partial t} = [H_0 + V_\mu(\theta)E(t) + V_{pol}(\theta)E^2(t)$$
$$+ V_{hyp}(\theta)E^3(t)]\Psi(\theta, t) \quad (2)$$

with

$$H_0 = BJ(J+1), \qquad V_\mu(\theta) = -\mu\cos\theta,$$
$$V_{pol}(\theta) = -\frac{[(\alpha_\parallel - \alpha_\perp)\cos^2\theta + \alpha_\perp]}{2} \quad (3)$$
$$V_{hyp}(\theta) = -\frac{[(\beta_\parallel - 3\beta_\perp)\cos^3\theta + 3\beta_\perp]}{6},$$

where B is the rotational constant, J is the angular quantum number, μ is the permanent dipole moment, θ is the angle between the molecular axis and the laser polarization, $\alpha_\parallel$ and $\alpha_\perp$ are the polarizability components parallel and perpendicular to the molecular axis, and $\beta_\parallel$ and $\beta_\perp$ are hyperpolarizability components parallel and perpendicular to the molecular axis. Finally, the degree of the molecular orientation is given with the expectation value of $\cos\theta$ by considering the temperature-dependent Boltzmann distribution of initial rotational states, and written as

$$\langle\cos\theta\rangle = \sum_J \frac{g_J \exp[-BJ(J+1)/kT]}{Q}$$
$$\times \sum_{M=-J}^{J} \langle\Psi_{JM}|\cos\theta|\Psi_{JM}\rangle, \quad (4)$$

where Q is the rotational partition function, g_J is the spin degeneracy factor, and Ψ_{JM} is the rotational wavefunction of the time-evolving molecule that has started the laser interaction in a state characterized by the angular quantum number J and the magnetic quantum number M.

In our simulation, the time-dependent Schrödinger equation is numerically solved by a split-operator method.[27,28] We utilize the CO molecule as an example, and the molecular parameters are: $B = 1.93$ 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, $\beta_\perp = 4.994 \times 10^8$ Å^5.[9,29,30] The initial rotational temperature of the CO molecule is set to be 30 K. The centre frequencies of the fundamental field and its second harmonic field with the pulse width of 200 fs are 12 500 cm^{-1} and 25 000 cm^{-1}, corresponding to the centre wavelength of 800 nm and 400 nm, respectively. We assume that the polarizations of the fundamental field and its second harmonics are parallel and the intensity ratio of the two fields is 1:1.

Figure 1 depicts the time evolution of the molecular orientation $\langle\cos\theta\rangle$ at the rotational temperature of 30 K obtained for a single dual-color laser pulse with the laser intensity of 2×10^{13} W/cm^2, the pulse duration of 200 fs and $\Phi = 0$. The molecular orientation shows a non-adiabatic process, and it is enhanced after the laser pulse and recurs at full rotational periods $t = nT_{rot}$, where n is an integer number, and T_{rot} is the rotational period of the CO molecule with $T_{rot} = 1/(2BC) \approx 8.64$ ps. The field-free molecular orientation results from the interference contributions between the odd and even rotational wave packet, and therefore the instructive and destructive interferences lead to the observation of the positive and negative orientations, corresponding to the
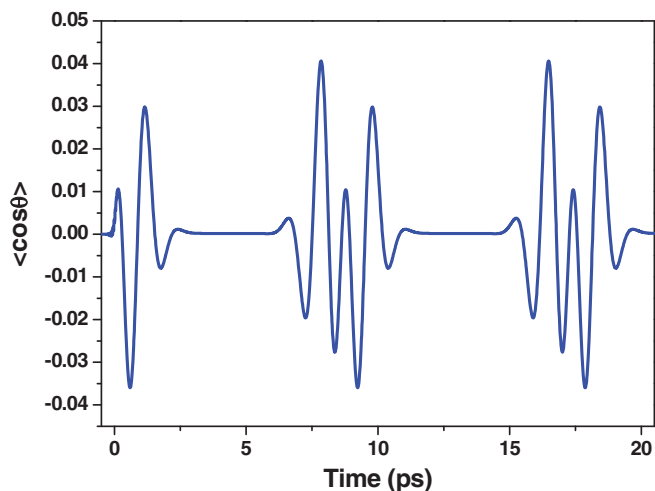

FIG. 1. Time evolution of the molecular orientation $\langle\cos\theta\rangle$ at the rotational temperature of 30 K by a single dual-color laser pulse with the laser intensity of 2×10^{13} W/cm^2 and the pulse duration of 200 fs.

positive and negative degrees. It can be seen in Fig. 1 that the maximum degrees of the positive and negative orientations are 0.041 and –0.036, respectively.

We separate a single dual-color laser pulse into two time-delayed dual-color laser subpulses and compare with the maximally attainable degree of the molecular orientation in these two cases. Figure 2 depicts the maximum degrees of the positive (red squares) and negative (blue circles) orientations $\langle\cos\theta\rangle_{max}$ by varying the time delay of the two dual-color laser subpulses, here their intensity ratio is $I_2/I_1 = 1:1$ with $I_1 = I_2 = 1 \times 10^{13}$ W/cm^2. The two olive dashed lines illustrate the maximum degrees of the positive and negative orientations created by a single dual-color laser pulse. The green line is the molecular orientation only created by the first dual-color laser subpulse, which show the state of the rotational wave packet when the second one is applied. The molecular orientation created by two dual-color laser subpulses is studied in a time delay with a full rotational period, and thus all
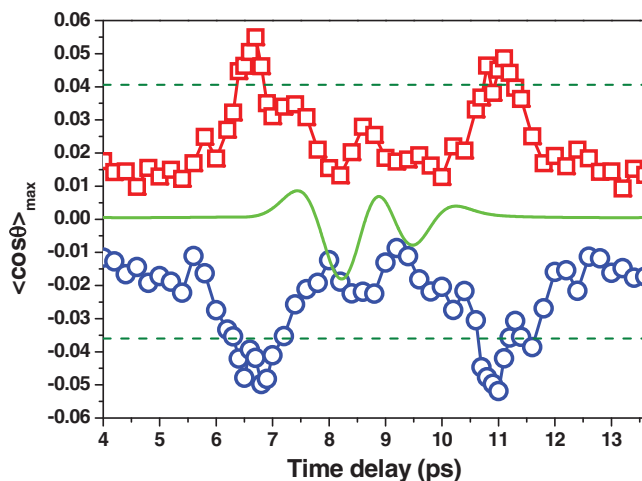

FIG. 2. Maximum degrees of the positive (red squares) and negative orientations (blue circles) $\langle\cos\theta\rangle_{max}$ by varying the time delay of two dual-color laser subpulses. Their intensity ratio is $I_2/I_1 = 1:1$ with $I_1 = I_2 = 1 \times 10^{13}$ W/cm^2.
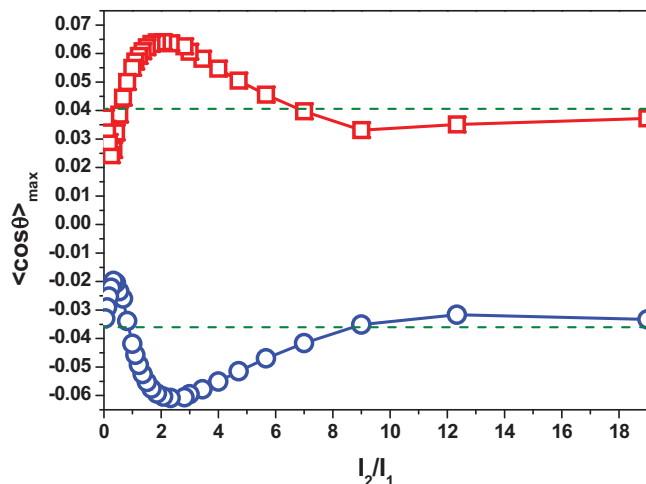
FIG. 3. Maximum degrees of the positive (red squares) and negative orientations (blue circles) $\langle\cos\theta\rangle_{max}$ created by two dual-color laser subpulses with the pulse separation of 6.82 ps as a function of the intensity ratio I_2/I_1 at a given total laser intensity of 2×10^{13} W/cm^2.

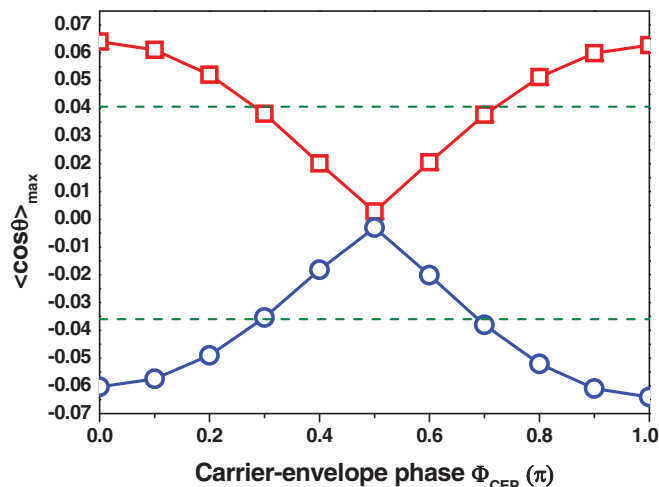
FIG. 4. Maximum degrees of the positive (red squares) and negative orientations (blue circles) $\langle\cos\theta\rangle_{max}$ by varying the relative phase Φ between the fundamental field and its second harmonic field of the second dual-color laser subpulse. Their pulse separation is 6.82 ps, and their intensity ratio is about $I_2/I_1 = 2:1$ with $I_1 = 0.65 \times 10^{13}$ W/cm^2 and $I_2 = 1.35 \times 10^{13}$ W/cm^2.

kinds of cases can be included. As can be seen, the molecular orientation created by two dual-color laser subpulses can be maximally enhanced at the time delay of 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. That is to say, by applying the second dual-color laser subpulse at the beginning of the rotational wave packet rephasing or the end of the rotational wave packet dephasing induced by the first one, the molecular orientation can be significantly enhanced and even exceeds that created by a single dual-color laser pulse with the intensity of two dual-color laser subpulses. Usually, the degree of the molecular orientation is limited by the maximally applicable laser intensity due to its intrinsic saturation and ionization, and so it is obvious that the limitation can be broken by separating it into two time-delayed dual-color laser subpulses.

As shown in Fig. 2, the molecular orientation created by a single dual-color laser pulse can be enhanced by separating it into two time-delayed dual-color laser subpulses with the same laser intensity. In order to achieve the optimal intensity ratio for the maximally attainable orientation degree, we study the molecular orientation by varying the intensity ratio of two dual-color laser subpulses while keeping a given total laser intensity. Figure 3 depicts the maximum degrees of the positive (red squares) and negative (blue circles) orientations $\langle\cos\theta\rangle_{max}$ created by two dual-color laser subpulses with the pulse separation of 6.82 ps as a function of the intensity ratio I_2/I_1 at a given total laser intensity of 2×10^{13} W/cm^2. It can be seen that the molecular orientation can be enhanced at their intensity ratio of $0.8 - 7$, and the optimal intensity ratio is about 2 with $I_1 = 0.65 \times 10^{13}$ W/cm^2 and $I_2 = 1.35 \times 10^{13}$ W/cm^2. Too large or small intensity ratio can result in a decrease of the orientation degree. The largest orientation degree is 0.064, which is enhanced by a factor of ~ 1.6. Therefore, it is important to select a suitable intensity ratio for achieving the maximum enhancement of the molecular orientation.

The relative phase Φ between the fundamental field and its second harmonic field of the dual-color laser pulse is an important parameter to manipulate the molecular orientation involving its degree and direction.[9,20] Similarly, we also employ the relative phase Φ to manipulate the molecular orientation created by two time-delayed dual-color laser subpulses. Figure 4 depicts the maximum degrees of the positive (red squares) and negative (blue circles) orientations $\langle\cos\theta\rangle_{max}$ by varying the relative phase Φ between the fundamental field and its second harmonic field of the second dual-color laser subpulse. Here, the pulse separation of two dual-color laser subpulses is 6.82 ps, and their intensity ratio is about $I_2/I_1 = 2:1$ with $I_1 = 0.65 \times 10^{13}$ W/cm^2 and $I_2 = 1.35 \times 10^{13}$ W/cm^2. It can be seen that the molecular orientation achieves the maximum enhancement at $\Phi = 0$ and π, which are in and out-phase with the first dual-color laser subpulse, respectively. Obviously, both the in and out-phase two dual-color laser subpulses can realize the molecular orientation enhancement. Moreover, it is interesting that the molecular orientation is almost completely suppressed at $\Phi = 0.5\pi$. In this case, the second dual-color laser subpulse is completely symmetric in the magnitude of the positive and negative electric field components. In other words, the symmetric laser field cannot induce the molecular orientation but can suppress the molecular orientation induced by other asymmetric laser pulse. The same result can also be obtained with the pulse separation of 11.02 ps. These observations reflect the fact that the rotational wave packet induced by a dual-color laser pulse can be enhanced or suppressed by applying another one at the beginning of the rotational wave packet rephasing or the end of the rotational wave packet dephasing and varying the relative phase Φ between the fundamental field and its second harmonic field.

To demonstrate the physical control mechanism of the molecular orientation enhancement by separating a single dual-color laser pulse into two time-delayed dual-color laser subpulses, we further observe the time evolution of the molecular rotational wave packet. Figure 5 depicts the time
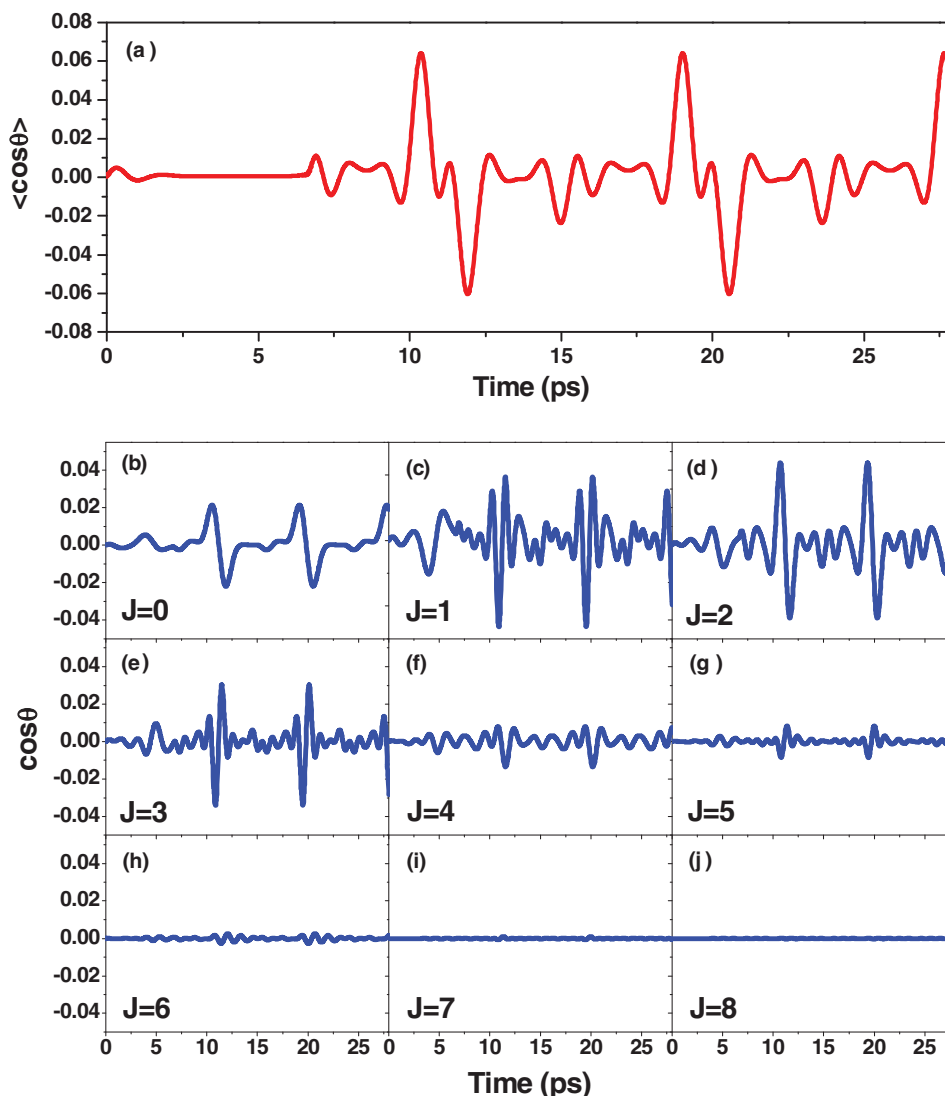
FIG. 5. Time evolution of the molecular orientation $\langle\cos\theta\rangle$ created by two dual-color laser subpulses (a), together with the contribution of each rotational state $J = 0$ (b), 1 (c), 2 (d), 3 (e), 4 (f), 5 (g), 6 (h), 7 (i) and 8 (j). Their pulse separation is 6.82 ps, and their intensities are $I_1 = 0.65 \times 10^{13}$ W/cm^2 and $I_2 = 1.35 \times 10^{13}$ W/cm^2.

evolution of the molecular orientation $\langle\cos\theta\rangle$ created by two dual-color laser subpulses (a), together with the contribution of each rotational state $J = 0$ (b), 1 (c), 2 (d), 3 (e), 4 (f), 5 (g), 6 (h), 7 (i), and 8 (j). Here, their pulse separation is 6.82 ps, and their intensities are $I_1 = 0.65 \times 10^{13}$ W/cm^2 and $I_2 = 1.35 \times 10^{13}$ W/cm^2. As can be seen, the revival structure of the rotational wave packet created by the first dual-color laser subpulse is strongly modulated by the second one (see Figs. 5(b)–5(j)). Consequently, the molecular orientation for total rotational wave packet contribution is achieved around half rotational period and even far exceeds than that obtained around full rotational period (see Fig. 5(a)). That is to say, the enhancement of the molecular orientation is obtained around half rotational period but not full rotational period. Figure 6 depicts the maximum degrees of the positive (red squares) and negative (blue circles) orientations $\langle\cos\theta\rangle_{max}$ created by two dual-color laser subpulses as a function of the rotational temperature. As expected, the degree of the molecular orientation increases with the decrease of the

rotational temperature, which is the same as that created by a single one.

In conclusion, we have demonstrated that by separating one dual-color laser pulse into two time-delayed dual-color laser subpulses, the molecular orientation can be significantly enhanced. The maximum enhancement of the molecular orientation is obtained when the second dual-color laser subpulse is applied at the beginning of the rotational wave packet rephasing or the end of the rotational wave packet dephasing induced by the first one with their intensity ratio of 1:2. It was also shown that the relative phase between the fundamental field and its second harmonic field of the second dual-color laser subpulse can be utilized to control the enhancement or suppression of the molecular orientation. Additionally, the physical control mechanism of the molecular orientation enhancement can be elucidated by the time evolution of the molecular rotational wave packet created by two dual-color laser subpulses. May be, the molecular orientation created by a single dual-color laser pulse can be further enhanced
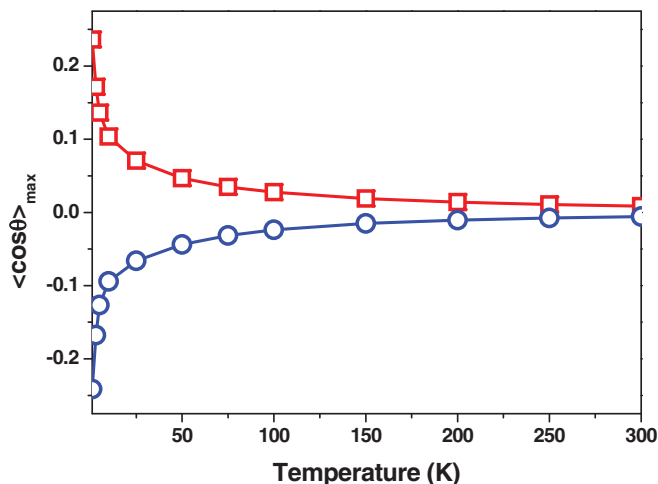
FIG. 6. Maximum degrees of the positive (red squares) and negative orientations (blue circles) $\langle\cos\theta\rangle_{max}$ created by two dual-color laser subpulses as a function of the rotational temperature. Their pulse separation is 6.82 ps, and their intensities are $I_1 = 0.65 \times 10^{13}$ W/cm^2 and $I_2 = 1.35 \times 10^{13}$ W/cm^2.

by separating it into more dual-color laser subpulses, which needs further exploration.

ACKNOWLEDGMENTS

[1] J. L. Hansen, L. Holmegaard, L. Kalhøj, S. L. Kragh, and H. Stapelfeldt, Phys. Rev. A **83**, 023406 (2011).
[2] D. Dimitrovski, M. Abu-samha, and L. B. Madsen, Phys. Rev. A **83**, 023405 (2011).
[3] M. Lein, J. Phys. B **40**, R135 (2007).
[4] P. Lan, P. Lu, W. Cao, Y. Li, and X. Wang, Phys. Rev. A **76**, 021801(R) (2007).
[5] D. H. Parker and R. B. Bernstein, Annu. Rev. Phys. Chem. **40**, 561 (1989).
[6] H. J. Loesch and J. Remscheid, J. Chem. Phys. **93**, 4779 (1990).
[7] B. Friedrich and D. R. Herschbach, Nature (London) **353**, 412 (1991).
[8] T. Kanai and H. Sakai, J. Chem. Phys. **115**, 5492 (2001).
[9] J. Wu and H. Zeng, Phys. Rev. A **81**, 053401 (2010).
[10] M. Muramatsu, M. Hita, S. Minemoto, and H. Sakai, Phys. Rev. A **79**, 011403(R) (2009).
[11] M. J. J. Vrakking and S. Stolte, Chem. Phys. Lett. **271**, 209 (1997).
[12] C. M. Dion, A. Keller, and O. Atabek, Eur. Phys. J. D **14**, 249 (2001).
[13] M. Machholm and N. E. Henriksen, Phys. Rev. Lett. **87**, 193001 (2001).
[14] A. Matos-Abiague and J. Berakdar, Phys. Rev. A **68**, 063411 (2003).
[15] C. -C. Shu, K. -J. Yuan, W. -H. Hu, J. Yang, and S. -L. Cong, Phys. Rev. A **78**, 055401 (2008).
[16] B. Friedrich and D. Herschbach, J. Chem. Phys. **111**, 6157 (1999).
[17] U. Buck and M. Farnik, Int. Rev. Phys. Chem. **25**, 583 (2006).
[18] A. Goban, S. Minemoto, and H. Sakai, Phys. Rev. Lett. **101**, 013001 (2008).
[19] L. Holmegaard, J. H. Nielsen, I. Nevo, H. Stapelfeldt, F. Filsinger, J. Küpper and G. Meijer, Phys. Rev. Lett. **102**, 023001 (2009).
[20] S. De, I. Znakovskaya, D. Ray, F. Anis, Nora G. Johnson, I. A. Bocharova, M. Magrakvelidze, B. D. Esry, C. L. Cocke, I. V. Litvinyuk, and M. F. Kling, Phys. Rev. Lett. **103**, 153002 (2009).
[21] O. Ghafur, A. Rouzée, A. Gijsbertsen, W. K. Siu, S. Stolte, and M. J. J. Varkking, Nat. Phys. **5**, 289 (2009).
[22] K. Oda, M. Hita, S. Minemoto, and H. Sakai, Phys. Rev. Lett. **104**, 213901 (2010).
[23] J. Salomom, C. M. Dion, and G. Turinici, J. Chem. Phys. **123**, 144310 (2005).
[24] M. Leibscher, I. Sh. Averbukh, and H. Rabitz, Phys. Rev. Lett. **90**, 213001 (2003).
[25] C. Z. Bisgaard, M. D. Poulsen, E. Péronne, S. S. Viftrup, and H. Stapelfeldt, Phys. Rev. Lett. **92**, 173004 (2004).
[26] C. Z. Bisgaard, S. S. Viftrup, and H. Stapelfeldt, Phys. Rev. A **73**, 053410 (2006).
[27] M. D. Feit, J. A. Fleck, Jr., and A. Steiger, J. Comput. Phys. **47**, 412 (1982).
[28] A. D. Bandrauk and H. Shen, J. Chem. Phys. **99**, 1185 (1993).
[29] K. A. Peterson and T. H. Dunning, Jr., J. Mol. Struct.: THEOCHEM **400**, 93 (1997).
[30] M. Pecul, Chem. Phys. Lett. **404**, 217 (2005).