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Controlling field-free molecular orientation with combined circularly and linearly polarized resonant pulses at low rotational temperatures

Fangping Chi [a,*], Yujun Yang [b], Fuming Guo [b]

[a] School of Physics and Optoelectronic Engineering, Ludong University, 186 Middle Hongqi Road, Zhifu District, Yantai 264025, China
[b] Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China

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ABSTRACT

We calculated the field-free orientation of linear molecules irradiated by combined circularly and linearly polarized resonant pulses at finite rotational temperatures. We show that operating with a series of circularly polarized pulses, aided by a linearly polarized pulse, all in resonance with molecular rotational transitions, one can prepare a rotational wave-packet populating mainly on a few lowest rotational eigenstates whose magnetic quantum numbers $M = 0$. Starting from this wave-packet and employing a particular series of linearly polarized pulses, the degree of orientation can be remarkably enhanced and well controlled.

1. Introduction

Control over the alignment and orientation of molecular sample with the aid of laser pulses has been an important issue and attracted considerable attention over the past two decades. Since molecules are anisotropic, the spatial orientation of molecular axes is important for a variety of angler resolved researches concerning chemical reaction dynamics [1], surface processing [2,3], and nanoscale design [4,5]. It also plays an important role in strong field processes such as high-order harmonic generation [6,7], nonsequential double ionization [8–10], impact single ionization [11–13], and attosecond laser pulse generation [14,15].

Field-free alignment can be achieved by sudden excitation of laser pulse much shorter than the rotational period of the molecule. Such pulse leaves the molecule an aligned wave-packet, i.e., a coherent superposition of rotational eigenstates $|J,M\rangle$, which undergoes periodical dephaseing and rephaseing in the subsequent temporal evolution. This results in periodical transient alignment at field-free conditions (see Ref. [16] for details). Comparing with alignment, field-free orientations another challenging goal since the interaction of the electric field with molecular permanent dipole moment is averaged to zero due to the rapid optical oscillations of the former. Up to now, several branches of methods have been proposed to realize field-free orientation. Typical examples include those based on the use of asymmetric terahertz half-cycle pulse (HCP) [17], train or hybrid of such pulses [18–21], and combined electrostatic field with nonresonant laser pulse [22–25]. Besides, it is proposed that picosecond two-color phase-locked laser pulses can provide orientation during or after the laser pulse through alternative one-photon or two-photon excitation [26]. Other two-color schemes involving the polarizability and hyperpolarizability interactions were also reported [27–30]. In addition to the combined field method, the two-color field method are more accessible from experimental point of view, comparing with the HCP based schemes, duo to the experimental difficulty in generating HCPs with sufficiently high intensity, and have been demonstrated by Ohmuraa and his coworker [31]. Recently, a technology progress has made it possible to generate intense ($\sim 1.55 \times 10^{13}$ W/cm^2) THz pulses with central frequencies ranging from 10 to 72 THz [32–34]. This has motivated the fruitful theoretical investigations of the possibility of orienting molecule with these pulses [35–39]. Since the time scale of the pulse's optical variation is very close to that of molecular rotation, the electric interaction with the molecular permanent dipole moment can no longer be cancelled out and orientation can take place under rather moderated pulse intensity.

All of the theoretical investigations show that the degree of field-free orientation or alignment is very sensitive to the rotational temperature of the molecular sample. And it declines more dramatically for heaver molecules due to a broader thermal distribution of their initial rotational wave functions. This is partially because large numbers of $M \neq 0$ components are involved in the aligned or orientated wave-packet (see what follows for details). However, since the generally employed linearly polarized pulses induce the $\Delta M = 0$ transitions only, other types of laser pulses must be considered to overcome the declination.

In this Letter, we calculated the orientation of molecules under the irradiation of $\hat{x} \sim \hat{y}$ circularly polarized pulses which can induce the $\Delta M = \pm 1$ transitions. Our results show that, using such pulses and assisted by a $\hat{z}$ polarized pulse, one can almost remove all of the $M \neq 0$ components in the oriented wave-packet. There-

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* Corresponding author. Fax: +86 535 669 7527.
E-mail address: fpchi9103@yahoo.com.cn (F. Chi).

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fore, the degree of field-free orientation is able to be improved by a large amount. And then, by using another particular series of $\hat{z}$ polarized pulses, the orientation degree can be completely controlled as well.

2. Theory and numerical details

We limit our consideration to a linear molecule in its ${}^1\Sigma$ electronic and ground vibrational state. For non-${}^1\Sigma$ state molecules, the angular momentum due to electric motion can couple to that due to rotation and a different approach should be employed (see Refs. [28,40] for details). Since the amplitude of the external field employed here is moderate, we omit the polarizability and hyperpolarizability terms in the interaction Hamiltonian and model the molecule as a rigid rotor. The Hamiltonian can then be defined as

$$\begin{aligned} H(t) &= BJ^2 - \vec{E}(t) \cdot \vec{\mu}_0 \\ &= BJ^2 - [E_x(t)\mu_0 \sin\theta\cos\phi + E_y(t)\mu_0 \sin\theta\sin\phi + E_z(t)\mu_0\cos\theta] \end{aligned} \tag{1}$$

where B and $\vec{\mu}_0$ are, respectively, the rotational constant and permanent dipole moment of the molecule. $\vec{E}(t)$ represents the external field with three components $\vec{E}_x(t)$, $\vec{E}_y(t)$ and $\vec{E}_x(t)$. θ and φ are spherical angles relating $\vec{\mu}_0$ to the space fixed x, y, z-axis system.

We expand the wave function of the molecule in the unperturbed molecular rotational eigenstates, i.e., the spherical harmonics $|J, M\rangle = Y_{J,M}(\theta, \phi)$

$$\psi(t) = \sum_{J,M} c_{J,M}(t)|J, M\rangle \exp(-i\varepsilon_J t/\hbar) \tag{2}$$

The expansion coefficients are represented by $c_{J,M}(t)$, and ε_J denotes the eigenenergy corresponding to the $|J, M\rangle$ state.

Taking $\hbar/B$ as the unit of time, B the unit of energy, and substituting Eqs. (1) and (2) into the time dependent Schrödinger equation, we get a series of first-order differential equations:

$$\begin{aligned} \frac{dc_{JM}(t)}{dt} = i\{ & c_{J-1,M-1}\langle J, M|\omega_x \sin\theta\cos\phi + \omega_y \sin\theta\sin\phi|J-1, M-1\rangle \\ & \times \exp[i2Jt] + c_{J-1,M+1}\langle J, M|\omega_x \sin\theta\cos\phi \\ & + \omega_y \sin\theta\sin\phi|J-1, M+1\rangle \exp[i2Jt] \\ & + c_{J+1,M-1}\langle J, M|\omega_x \sin\theta\cos\phi + \omega_y \sin\theta\sin\phi|J+1, M-1\rangle \\ & \times \exp[-i2(J+1)t] + c_{J+1,M+1}\langle J, M|\omega_x \sin\theta\cos\phi \\ & + \omega_y \sin\theta\sin\phi|J+1, M+1\rangle \exp[-i2(J+1)t] \\ & + c_{J-1,M}\langle J, M|\omega_z \cos\theta|J-1, M\rangle \exp[i2Jt] \\ & + c_{J+1,M}\langle J, M|\omega_z \cos\theta|J+1, M\rangle \exp[-i2(J+1)t]\} \end{aligned} \tag{3}$$

Here, $\omega_\eta(t) = E_\eta(t)\mu_0/B$, $(\eta = x, y, z)$ are the dimensionless interaction parameters. The dipole matrix elements in Eq. (3) are

$$\begin{aligned} \langle J, M|\sin\theta\cos\phi|J-1, M-1\rangle &= -i\langle J, M|\sin\theta\sin\phi|J-1, M-1\rangle \\ &= -\frac{1}{2}\sqrt{\frac{(J+M-1)(J+M)}{(2J-1)(2J+1)}} \end{aligned} \tag{4-a}$$

$$\begin{aligned} \langle J, M|\sin\theta\cos\phi|J-1, M+1\rangle &= i\langle J, M|\sin\theta\sin\phi|J-1, M+1\rangle \\ &= \frac{1}{2}\sqrt{\frac{(J-M-1)(J-M)}{(2J-1)(2J+1)}} \end{aligned} \tag{4-b}$$

$$\langle J, M|\cos\theta|J-1, M\rangle = \sqrt{\frac{(J+M)(J-M)}{(2J-1)(2J+1)}} \tag{4-c}$$

The matrix elements for $J \to J + 1$ transitions can be found by setting $J = J + 1$ in Eqs. (4-a)–(4-c).

Using T to denote the rotational temperature of the molecule, the initial state of the molecular can be decided by the Boltzmann distribution:

$$c_{J,M} = \left[p^{-1}\exp\left(-\frac{BJ(J+1)}{k_B T}\right)\right]^{1/2}, \quad p = \sum_J (2J+1)\exp\left[-\frac{BJ(J+1)}{k_B T}\right] \tag{5}$$

where k_B is the Boltzmann constant. With these initial conditions, Eqs. (3) can be solved numerically with forth-order Runge-Kutta method.

We use the expectation value

$$\begin{aligned} \langle\cos\theta\rangle(t) = \langle\psi(t)|\cos\theta|\psi(t)\rangle = 2\sum_{J,M}|c_{J,M}| \cdot |c_{J+1,M}| \cdot \langle J+1, M|\cos\theta|J, M\rangle \\ \cdot \cos[2(J+1)t + \arg(c_{J,M}) - \arg(c_{J+1,M})] \end{aligned} \tag{6}$$

to describe the degree of orientation. We can see in Eq. (6) that the degree of orientation are affected by three kinds of factors: the population parameters $|c_{J,M}|$, which remains constant under field-free conditions; $\cos[2(J+1)t + \arg(c_{J,M}) - \arg(c_{J+1,M})]$, which we call the phase difference factors and varying their values between ±1 with time; and the matrix elements $\langle J+1, M|\cos\theta|J, M\rangle$, which are definite values described by Eq. (4-c). Here, we would like to concentrate on the last kind of factors, i.e., $\langle J+1, M|\cos\theta|J, M\rangle$s. It is clear from Eq. (4-c) that for the same J, the larger the M, the smaller the $\langle J+1, M|\cos\theta|J, M\rangle$ value. Hence lower orientation degree is obtained when more $M \neq 0$ components are involved in the wave packet. Quantum mechanically, it is because of the inherent angular distribution of the eigenstates of the free rotors, i.e., the $|J, M = 0\rangle$ state has been originally squeezed with respect to the $\hat{z}$ direction except for the $|J = 0, M = 0\rangle$ case, while the $|J, M \neq 0\rangle$ states are less squeezed, and get even more confined to $\hat{x} \sim \hat{y}$ plane for larger M s. As a result, these components will contribute to the oriented wave packet more negatively comparing to the $M = 0$ ones. On the other hand, for $T \neq 0$ K cases, large numbers of $M \neq 0$ components will be involved in the initial wave packet due to the thermal distribution. If the molecule is irrigated by the $\hat{z}$ polarized pulses, M will be a good quantum number and its value will remain unchanged throughout the orientation process. Thus, the orientation degree will decline comparing with the $T = 0$ K case, in which the molecule initially populates completely on the ground rotational state. This is especially evident for heavier molecules with small rotational constants.

In order to eliminate the $M \neq 0$ components, we refer to employ a combination of $\hat{x} + i\hat{y}$ and $\hat{x} - i\hat{y}$ polarized pulses, which are responsible for $\Delta J = \pm 1$, $\Delta M = +1$ and $\Delta M = -1$ transitions, respectively. Our calculation shows that, when the initial phases of the pulses are chosen to be $\frac{\pi}{2}$ or $-\frac{\pi}{2}$, assisted by a particular $\hat{z}$ polarized resonant pulse, one can in general remove all of the $M \neq 0$ components from the oriented wave-packet. Thus the degree of orientation could be remarkably improved by succeeding pulses. We then apply another train of specially designed $\hat{z}$ polarized pulses, and the degree of orientation is well controlled.

For the convenience of description, we write the external field $\vec{E}(t)$ as follows:

$$\begin{aligned} \vec{E}(t) = E_0\sum_{J=1}^{J_{\max}} g_J(t)\left[\cos\left(\omega_J t - \frac{\pi}{2}\right)\hat{x} + \sin\left(\omega_J t - \frac{\pi}{2}\right)\hat{y}\right] \\ + E_0\sum_{J=1}^{J_{\max}} f_J(t)\left[\cos\left(\omega_J t + \frac{\pi}{2}\right)\hat{x} - \sin\left(\omega_J t + \frac{\pi}{2}\right)\hat{y}\right] \\ + E_0[h'(t)\sin(\omega_2 t) + \sum_{J=1}^{J_{\max}} h_J(t)\sin(\omega_J t + \pi)]\hat{z} \end{aligned} \tag{7}$$

where $g_J(t)$ and $f_J(t)$ are time envelopes of the $\hat{x} + i\hat{y}$ and $\hat{x} - i\hat{y}$ circularly polarized pulses, respectively. $h'(t)$ and $h_J(t)$ are time envelopes