Controlling the orientation of polar molecules in a rovibrationally selective manner with an infrared laser pulse and a delayed half-cycle pulse

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We propose a scenario used for controlling molecular orientation with an infrared laser pulse and a delayed half-cycle pulse, with LiH molecules as an example. The infrared laser pulse excites the molecules in a thermally initial state to a specific rovibrational state, and the half-cycle pulse orients the molecules by rotational excitation. Numerical calculation shows that an efficient field-free time-dependent orientation can be realized even at room temperatures. The feasibility has been analyzed for LiH molecules under present experimental conditions.

Controlling alignment and orientation of molecules with laser pulses has long been an important subject in control of molecular processes [1–4]. Recently, the molecular alignment and orientation attracted widespread attention in controls of photodissociation [5] and photoionization [6], quantum-information processing [7], molecular imaging [8], and attosecond science [9]. The alignment of a molecule means that its axis is parallel to a space-fixed direction, while the orientation implies that the axis of an aligned molecule should point to a particular direction. Molecular orientation is doubtless a more challenging issue than alignment especially from the experimental point of view.

Several approaches are theoretically proposed to control molecular orientation with laser pulses [10–12], based on optimal control method [13] or adiabatic theory [14–16]. The molecular orientation can also be realized by utilizing a combination of the laser field and an additional asymmetric interaction. Friedrich *et al.* pointed out that molecular orientation in a moderate electrostatic field can be greatly enhanced by applying an intense nonresonant laser field [17,18]. Sakai *et al.* on the basis of this approach investigated experimentally both one- and three-dimensional orientations in the adiabatic region [19,20]. Moreover, a striking approach was put forward to control the orientation of polar molecules with a half-cycle pulse (HCP) [21,22]. After the action of a HCP is over, a field-free time-dependent molecular orientation can be realized. The maximal value of the orientation parameter increases as a function of the field amplitude of the HCP until it reaches a saturation [23]. By superimposing a nonresonant laser pulse to a HCP, Daems *et al.* demonstrated that this saturation can be overcome [24].

However, most of the above-mentioned approaches are based on direct rotational excitation with a nonresonant laser pulse, and vibrational motion or excitation is not taken into account. By including the molecular vibration, it is possible to manipulate rovibrational wave-packet composition by an infrared (ir) laser pulse. Zou *et al.* studied the manipulation of orientation dynamics of CO molecules in a vibrationally selective manner using optimal control theory [25]. In the present work, we propose a scenario used for controlling the orientation of polar molecules with a resonant ir laser pulse and a time-delayed HCP. The basic idea is that the ir laser pulse excites molecules in a thermally initial state to a specific rovibrational state, whereas the HCP orients the molecules by rotational excitation. By choosing appropriate parameters of the ir laser pulse and the HCP, the time-dependent field-free orientation can be achieved.

We consider a polar diatomic molecule, initially in its electronic ground state, exposed to a resonant ir laser field and a time-delayed HCP field. The laser fields are linearly polarized, giving the selection rule $\Delta M = 0$. The molecular wave function $\Psi(t)$ can be obtained by solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\Psi(t) = [\hat{H}_0 + \hat{H}_I(t)]\Psi(t), \tag{1}$$

where the bare molecular Hamiltonian $\hat{H}_0$ can be expressed as

$$\hat{H}_0(R,\theta,\varphi) = -\frac{\hbar^2}{2mR^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{\hbar^2}{2mR^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$
$$-\frac{\hbar^2}{2mR^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \hat{V}(R), \tag{2}$$

where m is the reduced mass, R is the internuclear separation, θ is the angle between the molecular axis and the polarization direction of laser field, and φ is the azimuthal angle. $\hat{V}(R)$ denotes the internuclear potential. In our treatment, the ir laser pulse contains a resonant frequency of vibrational transition. Thus the first-order dipole interaction is dominant compared with the polarizability interaction [26]. The field-molecule coupling $\hat{H}_I$ is given by $\hat{H}_I(t) = -\mu(R)\epsilon(t)\cos\theta$, where $\mu(R)$ is the molecular dipole moment at R. The total laser pulse $\epsilon(t)$ is written as

$$\epsilon(t) = \sum_{k=\text{ir,HCP}} E_k f_k(t)\cos[\omega_k(t-\tau_k)], \tag{3}$$

with Gaussian temporal profile

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$$f_k(t) = \left(-\frac{4 \ln 2}{T_k^2}(t - \tau_k)^2 \right), \qquad (4)$$

where E_k, T_k, τ_k, and ω_k are the field amplitudes, full-widths at half-maximums (FWHMs), center times, and center frequencies of the pulses, respectively.

Since the quantum number M is conserved, the wave function can be expanded as [21]

$$\Psi_M(R, \theta, \varphi, t) = \sum_{J'} \chi_{J'}(R, t) Y_{J',M}(\theta, \varphi). \qquad (5)$$

The initial state is an eigenfunction of $\hat{H}_0$, $\Psi_M(R, \theta, \varphi, 0) = \chi_{\nu,J}(R) Y_{J,M}(\theta, \varphi)$, where $\chi_{\nu,J}(R)$ is a vibrational eigenfunction corresponding to the rovibrational quantum numbers (ν, J). Substituting Eq. (5) into Eq. (1), one can calculate the time-dependent wave function of the rovibrational state for the given initial condition. The details of this numerical calculation can be found in our previous papers [27–29].

We first consider a case in which the initial state of a cold molecule at rotational temperature $T=0$ K is $|\nu=0, J=0, M=0\rangle$. The calculations are based on the potential $V(R)$ and the molecular dipole moment $\mu(R)$ in the $X\,^1\Sigma^+$ state of LiH with rotational constant $B_e=7.5$ cm^{-1} and harmonic vibrational frequency $\omega_e=1404.02$ cm^{-1} [30]. The major feature of the HCP is a large asymmetry in the magnitude of the positive and negative peak values of the electric field because it is not a complete optical period. Such a HCP has been generated experimentally [31]. It is difficult to describe accurately the realistic HCP of Ref. [31] using a simple expression. In the present work, for simplicity, as done by Machholm *et al.* [21], we model a HCP using the envelope function in Eq. (3) with the peak frequency of 1 THz ($\hbar\omega_{HCP}=36$ cm^{-1}) and the temporal width of 450 fs ($T_{HCP}=279$ fs). This treatment can describe the main features of the HCP, and has been successfully applied by Machholm *et al.* [21]. The center frequency of the ir laser pulse is fixed at the transition frequency, 1368 cm^{-1}, of $|\nu=1, J=1\rangle \leftarrow |\nu=0, J=0\rangle$. Figures 1(a) and 1(b) depict the electric fields of the ir laser pulse and the HCP used in the calculation, respectively. The FWHM T_{ir} is 1500 fs which corresponds to the frequency width (bandwidth) of 10 cm^{-1}. The peak intensity of the ir laser pulse is chosen to be $I_{ir}=3.0\times10^{10}$ W/cm^2 which corresponds to the peak field strength amplitude of 4.75×10^8 V/m, and the peak field strength of the HCP is $E_{HCP}=2.0\times10^7$ V/m. The center times τ_{ir} and τ_{HCP} are 0 and 2000 fs, respectively. Figure 1(c) displays the time-dependent molecular orientation described by the expectation value $\langle\cos\theta\rangle_{\mathbf{n}}(t)=\langle\Psi_M(R,\theta,\varphi,t)|\cos\theta|\Psi_M(R,\theta,\varphi,t)\rangle$, where $\mathbf{n}=(\nu,J,M)$ denotes the dependence on the initial state. From Fig. 1(c), we can see that the orientation is generated after the action of the HCP is over. Under the impulse of the HCP, the orientation parameter reaches its peak value 0.596 and then oscillates with time at the molecular rotational period, which implies that field-free time-dependent orientation is realized. The field-free molecular orientation dynamics can also be seen from Fig. 2 which shows the evolutions of $|\Psi_{M=0}(R,\theta,t)|^2$ at four different moments in polar coordinates. The initially spatial symmetry is broken
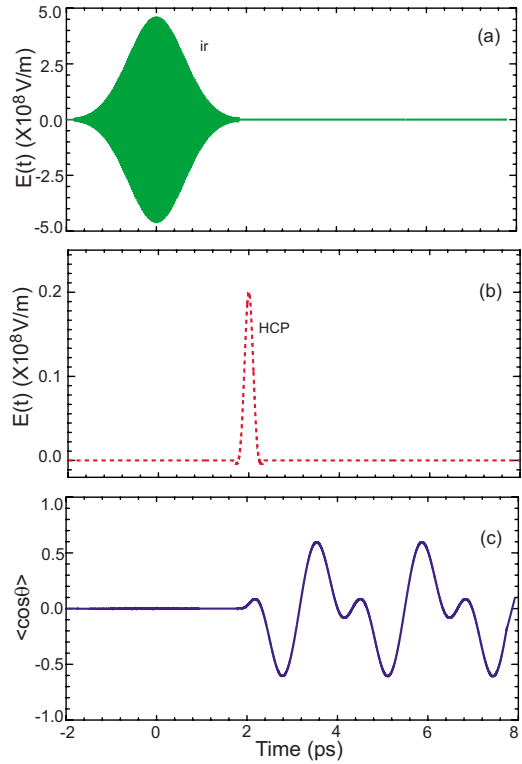

FIG. 1. (Color online) (a) The time-dependent electric fields of an ir laser pulse. (b) The electric fields of a HCP. (c) The orientation parameter $\langle\cos\theta\rangle(t)$ for LiH molecules at initially rotational temperature $T=0$ K. The laser parameters are chosen to be as follows: $I_{ir}=3.0\times10^{10}$ W/cm^2 corresponding to $E_{ir}=4.75\times10^8$ V/m, $E_{HCP}=2.0\times10^7$ V/m, $T_{ir}=1500$ fs, $T_{HCP}=279$ fs, $\tau_{ir}=0$, and $\tau_{HCP}=2000$ fs.

and the wave packet is localized in a narrow region. We have also performed the calculation by changing the sign of E_{HCP} but keeping the other parameters unchanged (the calculated result is not shown here). It is found that the direction of the field-free orientation can be controlled by changing the sign of the E_{HCP}.
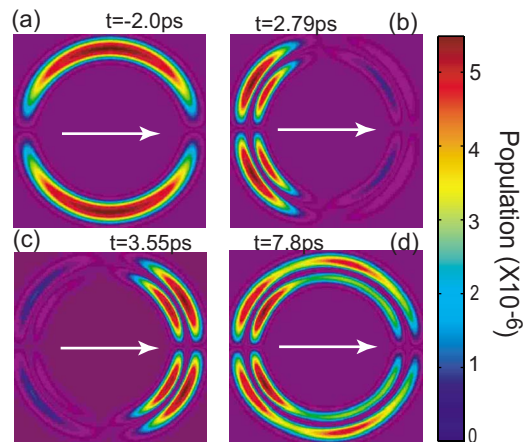
The time evolutions of the rovibrational populations

FIG. 2. (Color online) The images of $|\Psi_{M=0}(R,\theta,t)|^2$ plotted at four different moments in polar coordinates. The arrows indicate the direction of the laser polarization vector.
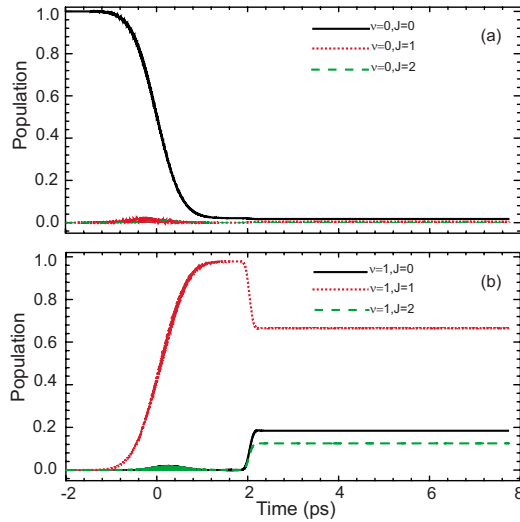
FIG. 3. (Color online) Time evolutions of rovibrational state populations. (a) $\nu=0$ and (b) $\nu=1$. The laser parameters are the same as those in Fig. 1.
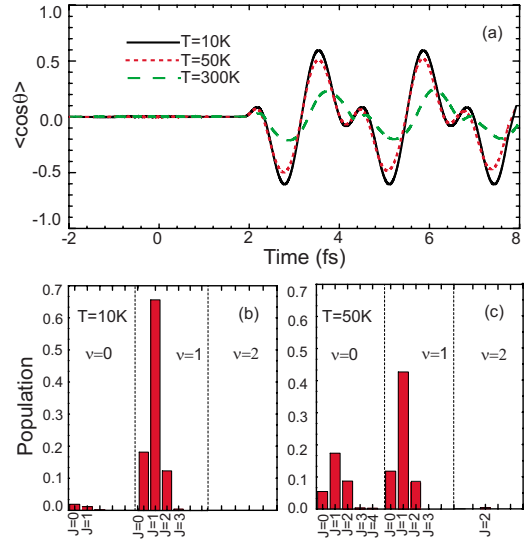

FIG. 4. (Color online) (a) The time evolutions of thermally averaged orientations $\langle\cos\theta\rangle_T(t)$ at different initially rotational temperatures. (b) Rovibrational population of oriented LiH molecules at $T=10$ K after the action of the HCP is over. (c) Same as (b) but at $T=50$ K.

$P_{\nu'',J''}(t)$ are presented in Fig. 3 by projecting the wave function $\Psi_M(R,\theta,\varphi,t)$ on an eigenfunction $\chi_{\nu'',J''}(R)Y_{J'',M}(\theta,\varphi)$ [32]. According to the selection rule for the rovibrational transitions $|\nu\pm1,J\pm1\rangle\leftarrow|\nu,J\rangle$ excited by one-photon, the lowest rovibrational state $|\nu=0, J=0\rangle$ can be coupled with the states of even ν and even J or the states of odd ν and odd J. Since the ir laser pulse used in this work possesses the narrower frequency width and lower intensity, the transition caused by it is mainly $|\nu=1,J=1\rangle\leftarrow|\nu=0,J=0\rangle$. Almost all the population (about 98%) is transferred from the initially rovibrational state to the $|\nu=1, J=1\rangle$ state. About 1.7% of the population still remains in the initial ground state, while the population of other states is negligibly small. After the HCP is turned on, the rotational state composition of the excited wave packet is determined by the electric dipole selection rule $\Delta J=\pm1$ and the intensity of the HCP. At the studied intensity, only the rotational states of $J\leqslant2$ are populated on the $\nu=1$ vibrational level, as shown in Fig. 3(b). We can conclude that a complete control of orientation can be achieved by bringing the molecule into the $\nu=1$ vibrational state.

The above results are obtained using the ground rovibrational state as the initial state. In an experiment, a molecular beam produced by supersonic expansion will be rotationally cold, but with a finite rotational temperature, typically $T<10$ K [10]. Considering the effect of temperature is equivalent to statistically averaging over the solutions of the Schrödinger equation for all possible initially rotational states $|J,M\rangle$ weighed by a Boltzmann factor [13,21,24]. Figure 4(a) shows the evolutions of thermally averaged orientations $\langle\cos\theta\rangle_T(t)$ at different rotational temperatures. At a lower temperature, $T=10$ K, only initially rotational states of $J\leqslant2$ make a significant contribution to the molecular orientation [21]. From Fig. 4(a), we can see that the effect of temperature on the orientation is very small, and the orientation parameter with a peak value of 0.595 can be obtained at $T=10$ K. At a higher temperature, $T=50$ K, all initially rotational states of $J\leqslant6$ are included. The peak value of the

orientation parameter is decreased, but the molecular orientation is comparatively robust towards thermal averaging. Even at room temperature, $T=300$ K, all initially rotational states of $J\leqslant14$ make a significant contribution, the orientation parameter can still reach a larger value, 0.231. Figures 4(b) and 4(c) show the rovibrational populations at rotational temperatures $T=10$ and 50 K, respectively, after the action of the HCP is over. At the higher temperature, $T=50$ K, although the control of orientation is lowered, about 74% of the total population is distributed in the $\nu=1$ vibrational state. At the lower temperature, $T=10$ K, exhilaratingly, about 97% population is transferred to the $\nu=1$ vibrational state, and the maximal population in the $J=1$ rotational state exceeds 65%. The efficiency of population transfer at $T=50$ K is lower than that at $T\leqslant10$ K, but it can be enhanced by adjusting the amplitudes of E_{ir} and E_{HCP}.

For the purpose of comparison, we have performed the calculations just with the HCP without the ir pulse, which corresponds to the approach proposed by Machholm and Henriksen [21]. The time evolutions of thermally averaged orientation parameters $\langle\cos\theta\rangle_T(t)$ at different initially rotational temperatures for $\nu=1$ and $\tau_{\text{HCP}}=0$ are shown in Fig. 5. After the impulse of the HCP, the field-free orientation of molecules is achieved, with full revivals. However, the amplitudes of $\langle\cos\theta\rangle_T(t)$ in Fig. 5 are smaller than those in Fig. 4(a). At the higher temperature, $T=50$ K, the peak value of orientation is decreased to 0.228, while it is 0.509 in Fig. 4(a). Especially when the initial state of the molecules is a thermodynamically equilibrium state at $T=300$ K, the peak value of the orientation parameter in Fig. 5 is four times smaller than that in Fig. 4(a). The oscillations of the orientation parameters with time is wiped out due to the less efficient orientation for the higher initial J states. In addition, the initial condition for a single vibration state of $\nu=1$ would be harsh in a molecular beam experiment. Thus our scenario
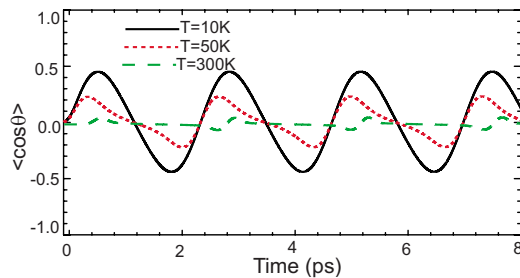
FIG. 5. (Color online) The time evolutions of thermally averaged orientations $\langle \cos \theta \rangle_T(t)$ induced merely by the HCP at $T=10$, 50, and 300 K, where $\nu=1$ and $\tau_{\mathrm{HCP}}=0$.

has some advantage over the single pulse approach especially at higher temperatures.

In principle, our scenario can also be applied to other polar diatomic molecules, but this depends on molecular properties such as moment of inertia and dipole moment [21]. For a molecule with a larger rotational inertia, its rovibrational energy levels are dense, and hence its excitation and orientation are not easily controlled by the ir laser pulse and the HCP. A smaller dipole moment requires the stronger ir laser intensity to achieve an efficient excitation transition

between two vibrational states of a molecule. Finally, we examine the feasibility of this scenario. At the lower temperature, $T \leq 10$ K, the simple ir laser pulse employed in the present work is enough to achieve the population transfer with a high-fidelity. Experimentally, it has been possible to generate extremely short HCP with a peak field of up to 1.5×10^7 V/m [31]. A standard molecular beam technique can provide the molecular samples with lower initially rotational temperatures ($T \leq 10$ K).

In conclusion, we have investigated how to achieve the field-free orientation in a rovibrationally selective manner using a resonant ir laser pulse and a delayed HCP, with LiH molecules as the example. The ir laser pulse with narrow frequency width creates a single rovibrational state in the electronic ground state, and the HCP orients the molecules by rotational excitation. An efficient field-free time-dependent orientation can be realized even at room temperatures. The possibility analysis of this scenario indicates that an experimental realization should be feasible.

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