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Role of highest occupied molecular orbitals in molecular field-free alignment by a femtosecond pulse*

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This paper studies the molecular rotational excitation and field-free spatial alignment in a nonresonant intense laser field numerically and analytically by using the time-dependent Schrödinger equation. The broad rotational wave packets excited by the femtosecond pulse are defined in conjugate angle space, and their coefficients are obtained by solving a set of coupled linear equations. Both single molecule orientation angles and an ensemble of O_2 and CO molecule angular distributions are calculated in detail. The numerical results show that, for single molecule highest occupied molecular orbital (HOMO) symmetry σ tends to have a molecular orientation along the laser polarization direction and the permanent dipole moment diminishes the mean of the orientation angles; for an ensemble of molecules, angular distributions provide more complex and additional information at times where there are no revivals in the single molecule plot. In particular, at the revival peak instant, with the increase of temperature of the molecular ensemble, the anisotropic angular distributions with respect to the laser polarization direction of the $\pi_{\rm g}$ orbital gradually transform to the symmetrical distributions regarding the laser polarization vector and for two HOMO configurations angular distributions of all directions are confined within a smaller angle when the temperature of the molecular ensemble is higher.

Keywords: molecular field-free alignment, highest occupied molecular orbital, angular distribution, femtosecond pulse

PACC: 3310E

1. Introduction

Recent experiments have made it possible to have control over molecular rotational excitation and spatial alignment in intense linearly polarized and nonresonant laser fields. The ability to produce spatially aligned molecules has numerous potential applications ranging from laser-pulse shaping and high-harmonic generation to material deposition and chemical reaction dynamics.[1−3] The revival structures of strong-field-induced rotational wave packets under field-free conditions are well understood theoretically and experimentally.[4−7] Available experimental results show that the strongest degree of one-dimensional field-free alignment (nonadiabatic or impulsive alignment) obtained with a single pulse can be enhanced by using the two-pulse sequence in a parallel polarization geometry[8] and angular dependence of the ionization rate was observed with respect to the laser polarization direction.[9] In order to get more insight into molecular nonadiabatic alignment dynamics (pulse duration $\tau \ll T_{\rm rot}$ molecular rotational cycle), we analyse and calculate the highest occupied molecular orbital (HOMO) effects on molecular orientation property under field-free conditions after femtosecond pulse interaction.

2. Theory

We consider a linear molecule exposed to an intense nonresonant linearly polarized laser field (atomic units are used throughout the paper.)

$$\boldsymbol{E}(t) = \boldsymbol{\varepsilon} \cdot E_0 f(t) \cos(\omega t), \tag{1}$$

where $\boldsymbol{\varepsilon}$ is an unit vector along the polarization direction, E_0 is the amplitude of the laser field, $f(t)$ is the pulse envelope such as a Gaussian function $f(t) = \exp(-t^2/\sigma^2)$ characterized by a full-width at half maximum as the pulse duration $\tau \cong 5\sigma/3$ and ω is the laser frequency. It is rather accurate by using rigid-rotor models to describe the rotational dynamics of linear molecules in a laser field. The use of a linearly polarized laser implies the selection rule, $\Delta M = 0$, so

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M will remain constant. The Hamiltonian of the system subjected to an intense laser field is[10]

$$H(t) = B_{\rm e}\hat{\boldsymbol{J}}^2 - \frac{1}{2}E^2(t)[(\alpha_{||} - \alpha_{\perp})\cos^2\theta + \alpha_{\perp}] \times f^2(t) - \mu_0 E(t)\cos\theta f(t), \quad (2)$$

where $\hat{\boldsymbol{J}}^2$ is the angular momentum operator, $B_{\rm e}$ is the molecular rotational constant, θ is the angle which indicates the rotational direction of the rotor axis with respect to the polarization vector, μ_0 is the permanent dipole moment of the molecule, $\alpha_{||}$ and $\alpha_{\perp}$ are the components of the static polarizability, parallel and perpendicular to the molecular axis respectively. The time-dependent Schrödinger equation corresponding to the Hamiltonian of linear molecules can be cast in a dimensionless form

$$\frac{{\rm i}\hbar}{B_{\rm e}}\frac{\partial\psi(t)}{\partial t} = \frac{H(t)}{B_{\rm e}}\psi(t). \quad (3)$$

Quantum mechanically, field-free eigenstates of a molecule as a rigid rotor are labelled with the quantum numbers J and M and are represented in angular space as the spherical harmonics $Y_{JM}(\theta)$. We also assume that no vibrational levels are populated during the interaction. So the solutions of Eq.(3) can be expressed by the superposition of a series of field-free rotor spherical harmonics $Y_{JM}(\theta)$[11]

$$\psi(\Delta\omega) = \sum_{J'\geq|M|} F_{J'}(\Delta\omega)Y_{J'M}(\theta), \quad (4)$$

where $\Delta\omega(t) = \omega_{||}(t) - \omega_{\perp}(t)$, $\omega_{||}(t) = \alpha_{||}E^2(t)/(2B_{\rm e})$, and $\omega_{\perp}(t) = \alpha_{\perp}E^2(t)/(2B_{\rm e})$. The conversion factor is $\omega \approx 5\times10^{12}\alpha[{\rm cm}^3]I[{\rm W/cm}^2]/B[{\rm cm}^{-1}]$.[12] The time-dependent coefficients $F_J(\Delta\omega)$are complex in general and solely determine the solutions at given initial conditions. Introducing the state defined by Eq.(4) in the time-dependent Schrödinger equation, the equations for the evolution of the coefficients $F_J(\Delta\omega)$ are obtained as a set of coupled linear equations.

$$\frac{{\rm i}\hbar}{B_{\rm e}}\dot{F}_J(t) = [E_J/B_{\rm e} - f(t)^2\omega_{\perp}(t)]F_J(t) - f(t)^2\Delta\omega(t) \times\sum_{J'}F_{J'}(t)\langle JM|\cos^2\theta|J'M\rangle - \frac{1}{B_{\rm e}}\mu_0E(t)f(t) \times\sum_{J'}F_{J'}(t)\langle JM|\cos\theta|J'M\rangle, \quad (5)$$

where E_J are the eigenvalues of the field-free rotor which are given by $E_J = B_{\rm e}J(J+1)$ for a rigid rotor and the initial condition is prepared in a single rotational state $|J'M'\rangle$ with $F_{JM}(0) = \delta_{J,J'}(t)\delta_{M,M'}(t)$. In order to calculate $\langle JM|\cos\theta|J'M\rangle$ and $\langle JM|\cos^2\theta|J'M\rangle$, $\cos\theta$ and $\cos^2\theta$ can be expressed by spherical functions $\cos\theta = \sqrt{4\pi/3}Y_{10}$ and $\cos^2\theta = \sqrt{16\pi/45}Y_{20} + \sqrt{4\pi/9}Y_{00}$ respectively. Then using

$$\langle JM_1|Y_{lm}|J'M_2\rangle = (-1)^{M_1}{\rm i}^{l+J'-J}\begin{pmatrix} J & l & J' \\ -M_1 & m & M_2\end{pmatrix}\begin{pmatrix} J & l & J' \\ 0 & 0 & 0\end{pmatrix}\left[\frac{(2J+1)(2l+1)(2J'+1)}{4\pi}\right]^{\frac{1}{2}}, \quad (6)$$

where the explicit general form of $3j$-symbols $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3\end{pmatrix}$as shown in Ref.[13] (for linear molecules $\Delta J = J - J' = 0, \pm2$), we obtain the nonvanishing matrix elements. The molecular alignment after femtosecond pulse interaction is characterized by the time dependent expectation value of $\cos^2\theta$ for the single molecular orientation angle.

$$\langle\cos^2\theta\rangle = \langle\psi(t)|\cos^2\theta|\psi(t)\rangle = \sum_{J,J'\geq|M|}F_J^*(t)F_{J'}(t)\langle JM|\cos^2\theta|J'M\rangle. \quad (7)$$

For an ensemble of molecules (such as a molecular beam) the rotational alignment of molecules can be ascribed to the characteristic rotational temperature and initial temperature of the ensemble before the arrival of the laser pulse. Because the pulse duration is very short in comparison with the rotational reequilibration time of the ensemble, we introduce the time-dependent angular distributions of the molecular ensemble to describe the alignment dynamics as the thermal average of the squared modulus of the rota-

tional wave packets with a statistical weight given by the Boltzmann factor.

$$\rho(\theta,t)=\sum_{J}\exp[-J(J+1)/\gamma]/Q_{\rm r}\times\left|\sum_{J'}F_{J,J'}Y_{J'M}(\theta)\right|^2, \quad (8)$$

where $\gamma = kT/B_{\rm e}$ is the reduced rotational temperature and $Q_{\rm r} \cong T/(\delta\Theta_{\rm r})$is the rotational partition function, in which $\Theta_{\rm r}$ is the characteristic rotational temperature in the case of diatomic molecules ($\delta = 1$ for hetero-nuclear and $\delta = 2$ for homo-nuclear).

3. Results and discussion

We calculate the time dependence of single molecular orientation exposed to a linearly polarized laser field for the case of a CO molecule $M = 0$ (molecular orbital symmetry σ; $T_{\rm rot} \equiv h/2B_{\rm e} = 8.636$ ps) and for the case of an O_2 molecule $M = 1$ (molecular orbital symmetry $\pi_{\rm g}$; $T_{\rm rot} = 11.537$ ps). CO and O_2 molecular parameters used in the calculation are shown in Table 1. The intensity of a laser with a wavelength of 800 nm is assumed to be below the ionization intensity ensuring that molecules are in a superposition of rotational eigenstates. Figure 1 shows the orientation angle of the O_2 molecular axis as a function of time and indicates that the O_2 molecule presents free-field alignment characteristics after one femtosecond laser pulse and in each alignment cycle there is a smallest angle (20.22° and 20.58° corresponding to the first and second revival peak respectively) which gradually augments and illustrates the attenuation of the free-field rotational alignment. It can be seen from Fig.2 that the smallest orientation angle of the CO molecular axis in each free-field rotational cycle is close to 0° and the mean of the alignment angle is smaller than that of O_2 due to the permanent dipole moment of the CO molecule. The highest occupied molecular orbitals (HOMOs) have an obvious effect on the minimum of the single molecular field-free rotational angle and symmetry σ tends to make molecules align along the laser polarization direction.

Table 1. CO and O_2 molecular parameters used in the calculations.[14−17]

	$\alpha_\perp$/Å^3	$\alpha_{\|\|}$/Å^3	$B_{\rm e}$/cm^{-1}	μ_0/D
CO (σ)	1.469	2.097	1.9313	2.51
O_2 ($\pi_{\rm g}$)	1.1	2.3	1.4456	

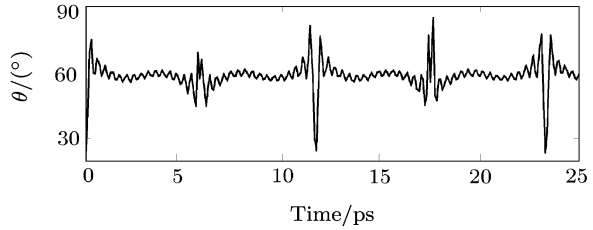


Fig.1. O_2 molecular free-field alignment by a femtosecond laser pulse with pulse duration 50 fs and $I = 5 \times 10^{12}$ W/cm^2 for all the figures following.

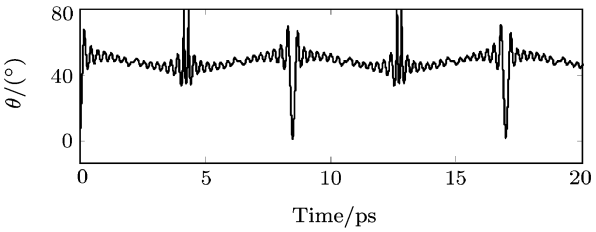


Fig.2. CO molecular free-field alignment by a femtosecond laser pulse.

The angular distributions of an ensemble of CO molecules around the revival peak of a free-field rotational cycle at 30 k and 5 k are shown in Fig.3. As seen from the three-dimensional picture the angular distribution formed after the short pulse interaction presents the expected maxima at the times of the revival peak (8.636 ps) around 0° orientation angle due to the HOMO symmetry σ of the CO molecule and coherent superposition of angular distribution with variant phase from each molecule. In particular, these distributions have shown a structured component at times where there are no revivals in the single molecule $\langle\cos^2\theta\rangle$ plot and when the temperature of the ensemble decreasing the angular distribution fluctuation becomes smooth.

As a contrast, Fig.4 shows the angular distributions of an ensemble of O_2 molecules around the revival peak of a free-field rotational cycle at 30 k and 5 k. These distributions exhibit a more complex and complete difference from that of CO due to their HOMO symmetry $\pi_{\rm g}$. Although the maximal angular distribution comes up at the times of the revival peak (11.537 ps), the corresponding orientation angle is 23.175°, the angular distributions also provide more additional information at full revival times such as the anisotropic distribution with respect to polarization vector. Furthermore, with the decrease of temperature of the ensemble the angular distribution of O_2 molecules involves much variety, including several maxima around the revival peak at different orientation angles.

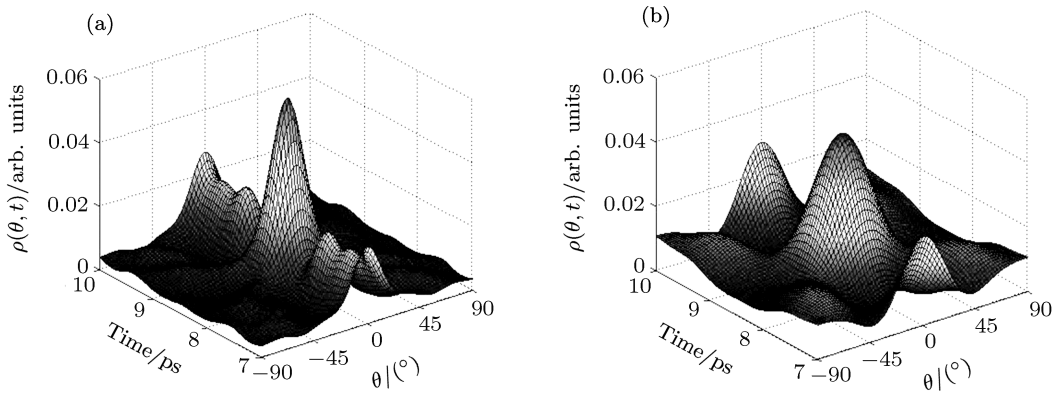


Fig.3. The angular distributions of an ensemble of CO molecules around the revival peak of a free-field rotational cycle at 30 k (a) and 5 k (b) aligned by a femtosecond laser pulse.

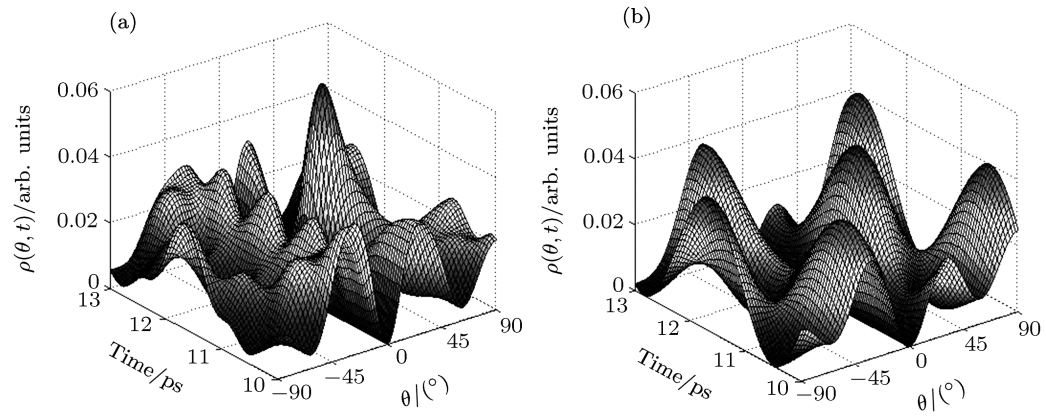


Fig.4. The angular distributions of an ensemble of O_2 molecules around the revival peak of a free-field rotational cycle at 30 k (a) and 5 k (b) aligned by a femtosecond laser pulse.

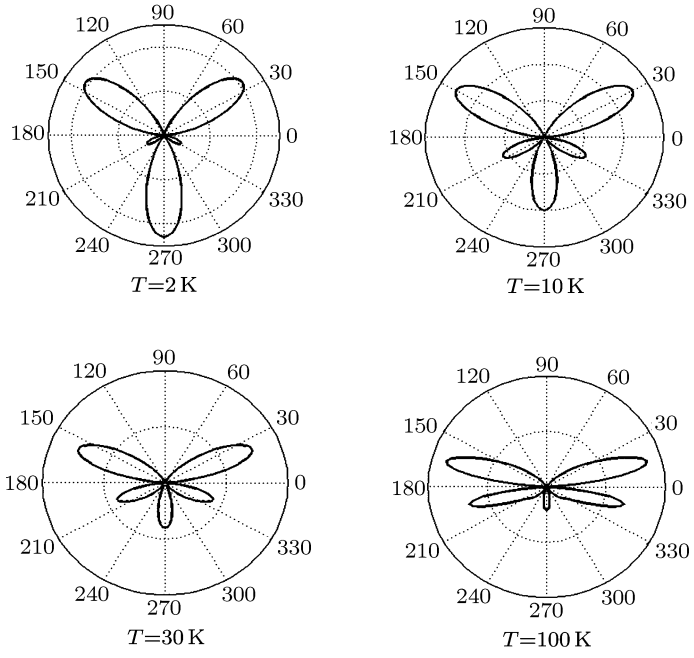


Fig.5. Snapshots of the angular distribution of an ensemble of O_2 molecules at the revival peak instant with different temperatures following a femtosecond laser pulse interaction.

Figures 5 and 6 show that at the revival peak instant the angular distributions of HOMO symmetry π_g and σ vary with the temperature of a molecular ensemble. As can be seen from Fig.5, the anisotropic angular distribution around 90° in the backward direction gradually decreases with the increase of temperature and the symmetrical distributions regarding laser polarization direction appear simultaneously, in particular the distributions of all directions tend to parallel the polarization vector when the temperature is higher. For σ symmetry as shown in Fig.6, the angular distributions are all directions at lower temperatures with prominent distribution along the laser vector; with the increase of temperature the angular distributions are confined within 30°. Two angular distributions of HOMO symmetry π_g and σ similarly tend to parallel the laser vector with the increase of temperature at the revival peak instant.

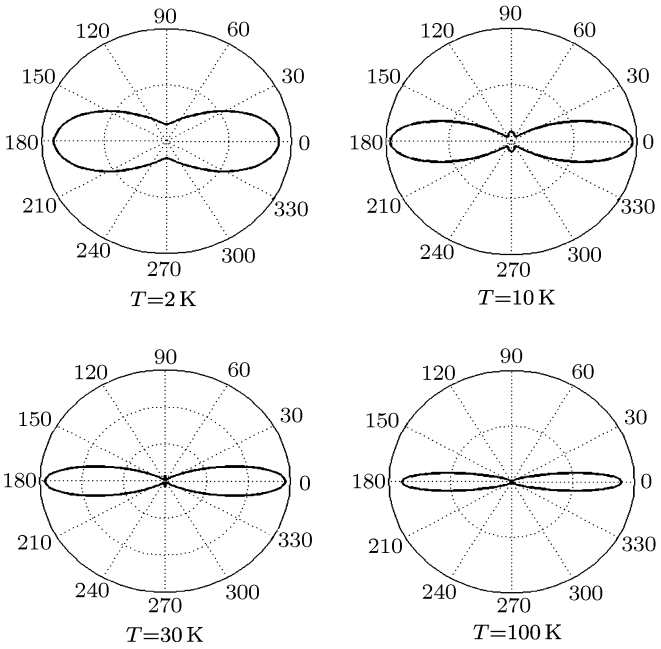


Fig.6. Snapshots of the angular distribution of an ensemble of CO molecules at the revival peak instant with different temperatures following a femtosecond laser pulse interaction.

4. Conclusion

In summary, the calculated results of the orientation angles of a molecule and angular distributions of a molecular ensemble after a femtosecond pulse interaction show that HOMO space configuration has a prominent effect on angular distributions of the molecular ensemble and the smallest orientation angle of a single molecule. The permanent dipole moment and molecular rotational constant influence the mean of the alignment angles and revival cycles respectively in the field-free alignment process. The angular distributions of an ensemble of molecules provide more complex and additional information at times where there are no revivals in the single molecule plot. Furthermore, for HOMO symmetry π_g at the revival peak instant, with the increase of temperature of the ensemble the dissymmetrical angular distributions regarding laser polarization direction gradually transform to symmetrical distributions and for two HOMO configurations angular distributions of all directions tend to parallel the laser polarization vector with the increase of temperature of the molecular ensemble. These results help us to better understand the importance of HOMO symmetry in molecular field-free alignment.

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