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RESEARCH ARTICLE

Role of rotational state-selected for nonadiabatic alignment: OCS molecules in femtosecond laser fields

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Nonadiabatic alignment by intense nonresonant laser fields is a versatile technique to manipulate the spatial direction of molecules. By solving the time-dependent Schrödinger equation numerically the degree of alignment of the molecules initially in different rotational state are calculated and the results show that the degree of alignment strongly depends on the initial rotational state. Thus, the present study indicates that, for obtaining a high degree of alignment for molecules, appropriate selection of molecular rotational states is necessary.

Keywords nonadiabatic alignment, rotational state-selection, linear triatomic molecule

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1 Introduction

Laser manipulation of molecules for spatial orientation and alignment has attracted great attention both theoretically and experimentally. Molecular alignment plays a particularly important role in tunneling ionization [1, 2], tomographic reconstruction of molecular orbitals [3, 4], high harmonic generation [5, 6], and chemical reaction dynamics [7, 8]. Strong nonresonant laser field has been shown to give rise to molecular alignment along the laser polarization direction. If the laser pulse is long in comparison with the molecular rotational period the molecules are adiabatically aligned [9–11], and the alignment follows the laser temporal intensity profile and vanishes after the laser pulse. If laser pulse is short compared to the molecular rotational period the molecules are nonadiabatically aligned [12–14]. In this case the laser excites the molecules to a coherent superposition of eigenstates, i.e., forming a localized rotational wave packet, then the excited molecules are aligned periodically with a full revival time after the laser pulse. This is particularly valuable for some applications such as orbital tomographic reconstruction, steric reaction dynamics that require the aligned molecules under field-free conditions. In order to get a better alignment of molecules, several schemes have been proposed by means of optimizing either the laser field or the molecular assembly to be aligned. The former is achieved mainly by changing the laser temporal intensity profile, such as using a sequence of laser pulses [15–17] or shaping laser pulse [18–20]. The latter is done usually by employing rotational cold molecules or state-selected molecules. Experimentally, rotational cold molecules are produced by controlling supersonic expansion of molecular beam and state-selected molecules are produced by dipole deflector, quadrupole or hexapole state selector [21–24]. More interesting, recently Ghafur *et al.* [25, 26] first combined hexapole state-selection and femtosecond laser alignment for increasing alignment of NO, while for triatomic molecules Nielsen *et al.* [27] combined dipole deflection and femtosecond laser alignment to achieve a significant enhancement for the degree of OCS alignment. These studies indicate that state-selection is an effective way to enhance the degree of alignment and the molecules selected were confined to the ground rotational state. However, the dependence of the degree of alignment on molecular rotational states has not been discussed and the role of rotational population in coherent nonadibiatic molecular alignment is still not clear. In the present work we investigate the alignment of molecules in different rotational states and the role of rotational state selection for coherent rotational wavepacket formation theoretically. The comparison of the alignment of the state-selected molecules with that from thermal populated shows obviously the influence of the initial rotational state on the degree of alignment. Our results suggest the importance of appropriate selecting molecular rotational states in optimizing molecular alignment.

2 Theoretical methods

OCS is a linear triatomic molecule, with a doubly degenerate bending vibrational mode. If this vibrational mode is excited the molecule possesses angular momentum parallel to the molecular axis. Generally its rotational state is described by $|JlM\rangle$ as symmetry top with J, the total angular momentum quantum number, l, the projection of J on the molecular axis, and M, the projection of J on the laboratory-fixed axis. In a field-free condition the rotational energy and wave function of the molecules are

$$E_{Jl} = B_v[J(J+1) - l^2] - D_v[J(J+1) - l^2]^2 \tag{1}$$

$$|JlM\rangle = \left(\frac{2J+1}{4\pi}\right)^{\frac{1}{2}} D^{J^*}_{Ml}(\theta, \phi, 0) \tag{2}$$

where B_v is the effective rotational constant, D_v is the centrifugal distortion constant, $D^J_{Ml}(\theta, \phi, 0)$ is the rotation matrix. If the molecule is in the ground bending vibrational state, $l = 0$. When the molecule is subjected to a linearly polarized laser field whose oscillation frequency is far from any molecular resonance, averaged over the pulse period, the interaction with the permanent dipole moment is zero, the interaction with the induced dipole moment is reduced to the polarizability interaction

$$\begin{aligned}\boldsymbol{H}_{eff}(t) &= -\frac{1}{4}\varepsilon^2(t)(\Delta\alpha\cos^2\theta + \alpha_\perp) \\ &= -\frac{1}{4}\varepsilon^2(t)\left[\frac{2\Delta\alpha}{3}D^2_{00}(\theta) + \frac{2\alpha_\perp + \alpha_{//}}{3}D^0_{00}(\theta)\right]\end{aligned} \tag{3}$$

where $\Delta\alpha = \alpha_{//} - \alpha_\perp$, $\alpha_{//}$ and $\alpha_\perp$ are components of polarizability parallel and perpendicular to the molecular axis respectively, $\varepsilon(t)$ is the temporal profile of the laser electric field, θ is the angle between the molecular axis and the polarization of laser. Terms that are independent of angle can be omitted in the process of calculation. As the interaction depends only on the polar angle θ, the quantum number M and l are conserved. In the process of laser-molecule interaction we represent the wave packet by expansion in a complete set of eigenstates

$$|\Psi(t)\rangle = \sum_J c_{JlM}(t)|JlM\rangle \tag{4}$$

and solve the time-dependent Schrödinger equation using Runge–Kutta method. Now the laser pulse leaves the system in a coherent superposition of states. After the interaction with the laser pulse, the wave packet evolves freely, that is

$$|\Psi(t)\rangle = \sum_J c_{JlM}(t)\mathrm{e}^{-\mathrm{i}E_{Jl}t/\hbar}|JlM\rangle \tag{5}$$

The degree of alignment is commonly quantified by the expectation value $\langle\cos^2\theta\rangle$,

$$\langle\cos^2\theta\rangle_{JlM}(t) = \langle\Psi(t)|\cos^2\theta|\Psi(t)\rangle \tag{6}$$

with J, l, M are the rotational quantum numbers of the initial rotational state. This result is based on the assumption that the molecules have been rotational state-selected. For a condition of thermal population, the degree of alignment of molecules should be written as

$$\langle\cos^2\theta\rangle_T(t) = \sum_J\sum_l P(J,l)\sum_M\langle\cos^2\theta\rangle_{JlM}(t) \tag{7}$$

with Boltzmann distribution $P(J, l)$.

3 Results and discussion

The nonadiabatic alignment of molecules is based on a “kick” interaction by short pulse laser, and thus it relies on the laser parameters such as pulse duration and intensity. For clearly showing the laser effect, we first calculate the dependence of the maximum degree of alignment on the laser intensity and pulse width as shown in Fig. 1, by selecting the molecules in the ground rotational state $|000\rangle$ and at the temperatures of 10 K. In Fig. 1(a) we fix the pulse duration at 90 fs as commonly used. The alignment of the state-selected molecules appears at about the intensity of 5×10^{11} W·cm^{-2}, while this value is higher for the thermally populated molecules in which the alignment appears at about 1×10^{12} W·cm^{-2}. In both cases, the alignment can be significantly enhanced as increasing the intensity and then goes into saturation and the only difference is that, for the state-selected molecules, the degree of alignment increase much faster. When the laser intensity is higher than 1×10^{13} W·cm^{-2}, the the strong ionization/dissociation process should take place. Therefore, wo choose the intensity of 1×10^{13} W·cm^{-2} for further calculation with different pulse widths. Figure 1(b) shows the dependence of maximum degree of alignment on pulse width at the laser intensity of 1×10^{13} W·cm^{-2}. On the whole the degree of alignment is low at short pulse width and is enhanced as the pulse width increasing. In fact, if the pulse is too short, the laser is not sufficient to excite an adequately broad range of J-states and the molecular alignment shrinks and eventually vanishes [14]. Under a certain temperature (saying 10 K for example), molecules are populated thermally in a number of states which are incoherent, and the alignment can also be destroyed. Thus, in the case of short pulse width, only a low degree of alignment can be achieved for thermally populated molecules. This incoherent destruction can be avoided for the state-selected molecules, and therefore it gives rise to a relative high degree of alignment in the whole region of laser pulse width.

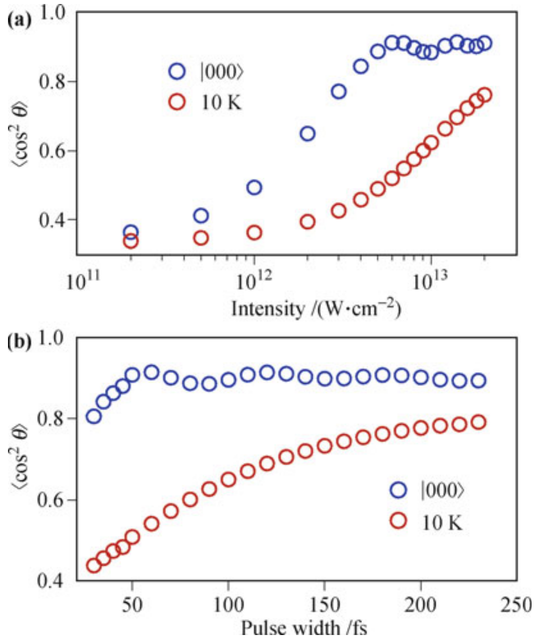

Fig. 1 Dependence of the maximum degree of alignment on the laser intensity with a 90 fs pulse width **(a)** and the pulse width with the laser intensity of 1×10^{13} W·cm^{-2} **(b)**.

In Fig. 2 we show the time evolution of alignment $\langle\cos^2\theta\rangle$ of the OCS. Ground rotational state $|000\rangle$ and two temperatures 10 K, 300 K are chosen to compare the alignment of molecules initially state-selected and thermal distribution. After the laser pulse action (turn-off at $t = 0$), the alignment occurs periodically with a full revival time of $\tau = 82.1$ ps. First, our results show that, for the molecules initially at 300 K and 10 K, the alignment is present around $\tau/2$ and τ, whereas for the molecules in $|000\rangle$, besides around $\tau/2$ and τ, the alignment is also attained around $\tau/4$ and $3\tau/4$. Second, for molecules with initially isotropic distribution (the averaged value of $\langle\cos^2\theta\rangle = 1/3$), the simulation shows that the molecules at 300 K are slightly aligned with a maximum degree of alignment of 0.39 through the interacted with the fs-laser pulse. The alignment can be increased to a maximum of 0.62 if the molecules are initially with the population of lower temperature at 10 K, and further enhanced and give a maximum of 0.89 if the molecules initially populated in one rotational state $|000\rangle$ state only. This enhancement is due to a noninterruption of the coherence for laser nonadibatical alignments from certain rotational state of molecules. It can be found in the figure, the noninterruption of the coherence also gives rise to a duration of alignment for the molecules in $|000\rangle$ state longer than that at 300 K or at 10 K. Therefore, the present results suggest that a unique initial rotational state population may be favor for increasing not only the degree of alignment but also the duration of alignment of molecules.

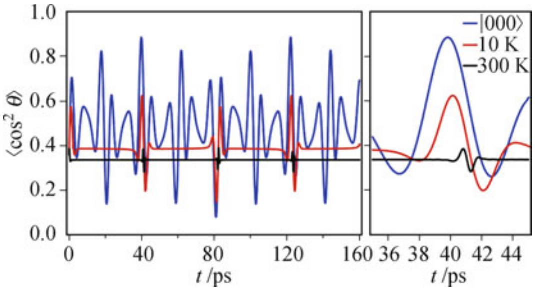

Fig. 2 Time evolution of alignment of OCS initially in different conditions. The right panel is the amplification of the time evolution in interval of 35–45 ps.

Next, optimizing rotational state-selected is necessary for increasing molecular alignment as initial condition is important for further coherent motion of the rotational wavepacket. Therefore, one should consider to explore the degree of alignment for the molecules in different rotational states. Figure 3 shows the time evolution of alignment for the molecules initially in specific rotational state, where $|JlM\rangle$ has been used to denote $|J-lM\rangle$ and $|Jl-M\rangle$ as they have the same alignment dynamics. The results for four typical rotational states $|100\rangle$, $|111\rangle$, $|211\rangle$ and $|808\rangle$ respectively are presented here. It can be seen that the time evolution of alignment depends on the initial rotational state. The revival structures for all four states are in phase at $\tau/2$ and τ, whereas at $\tau/4$ and $3\tau/4$ the revival structures are out of phase. It is known that the alignment in thermal condition is a weighted average over the populated rotational states. At $\tau/2$ and τ the signals add constructively, whereas at τ and $3\tau/4$ the signals add destructively which wipes the alignment out, as shown in Fig. 2. With increasing rotational temperature the molecular assembly consists of

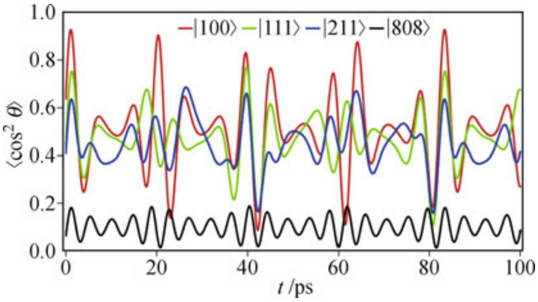

Fig. 3 Time evolution of alignment of OCS initially in different rotational states selected.

Table 1 The maximum degree of alignment $\langle\cos^2\theta\rangle$ for OCS molecules in different initial states $|JlM\rangle$. The last column gives the averaged value over different M substates.

J \ $\lvert M\rvert$	0	1	2	3	4	5	6	7	8	
					l=0					
0	0.89									0.89
1	0.93	0.83								0.86
2	0.81	0.91	0.69							0.80
3	0.82	0.76	0.86	0.54						0.73
4	0.77	0.79	0.70	0.78	0.43					0.69
5	0.78	0.68	0.73	0.65	0.68	0.34				0.63
6	0.66	0.67	0.65	0.66	0.60	0.59	0.27			0.58
7	0.74	0.64	0.63	0.62	0.61	0.56	0.52	0.23		0.56
8	0.74	0.69	0.63	0.61	0.59	0.56	0.51	0.45	0.19	0.54
					l=1					
1	0.84	0.77								0.79
2	0.91	0.69	0.83							0.79
3	0.77	0.78	0.78	0.54						0.71
4	0.80	0.79	0.72	0.72	0.59					0.72
5	0.68	0.75	0.68	0.66	0.58	0.38				0.62
6	0.69	0.69	0.65	0.63	0.63	0.64	0.38			0.61
7	0.65	0.71	0.64	0.64	0.60	0.56	0.49	0.27		0.56
8	0.68	0.71	0.62	0.67	0.62	0.59	0.55	0.51	0.25	0.57

more higher rotational states which may low the degree of alignment. Thus, a well-cooling condition is useful to avoid the thermal average wiping out in final degree of alignment for a molecular assembly.

Moreover, the maximum degree of alignment is sensitive to the initial state. In Table 1 we summarize the maximum degree of alignment for various rotational state $|JlM\rangle$ from J=0 to 8. The highest degree of alignment achieved theoretically is for the case of the molecules initially in $|100\rangle$ which give rise to $\langle\cos^2\theta\rangle = 0.93$, whereas for large rotational quantum numbers $J = |M|$ the degree of alignment generally is low, for example, the molecules initially in $|808\rangle$ give rise to $\langle\cos^2\theta\rangle = 0.19$. As state selection accompany with the partial alignment effect usually, i.e., this pre-alignment effect contributes in different ways to the further laser nonadibiatic alignment. The last column of Table 1 summarize the maximum degree of alignment corresponding to the different rotational level (different J and l since the energy is degenerated for different M value with the J and l). A trend of the degree of alignment decreasing with increasing rotational energy (or the total rotational quantum number J) is obvious for the projection quantum number l to the molecular axis both with the values of 0 and 1. For the higher rotational level with more energy-degenerated states, the degree of alignment are significant decreased due to the comparatively lower degree of alignment in these single states and the weighted average effect. All these results indicate a quite large dependence of the time evolution and the maximum degree of molecular alignment on their initial rotational states.

The alignment mechanism can be obtained by exploring the rotational transition process during the laser-molecule interaction. Figure 4 shows the Fourier transform spectra of the time evolution of alignment that the molecules initially populate in the state of $|100\rangle$, $|111\rangle$ and $|808\rangle$, respectively, as discussed above. The beat frequencies in the figures correspond to the rotational transition frequencies $\nu_{J,J'} = (E_{J'} - E_J)/h$, and a rotational wave packet can be formed via sequential transitions,

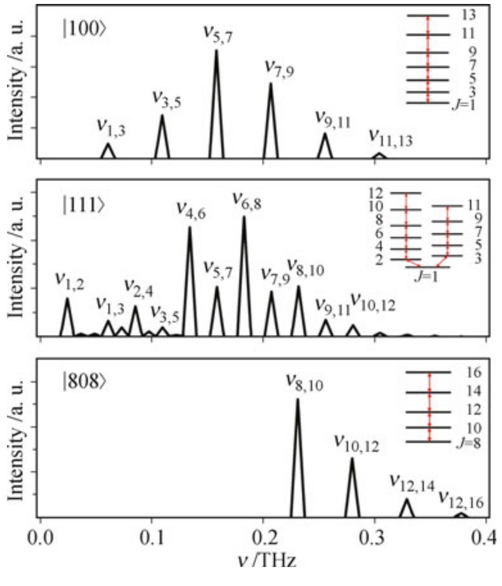

Fig. 4 Fourier transform of the time evolution of alignment for OCS molecules initially in the rotational state $|100\rangle$, $|111\rangle$, and $|808\rangle$.

following the selection rules for transitions. From the Fourier transform spectra we can obtain the excitation pathways in the nonadiabatic interaction of fs-laser with molecules. In the case of $|100\rangle$, the transition frequencies are $\nu_{J,J+2} = B_v(4J+6)$ restricted by the selection rule of $|\Delta J| = 2$, the state population is transferred via $J = 1 \to 3 \to 5 \to 7 \to 9 \to 11 \to 13$. It is same for the case of $|808\rangle$, $|\Delta J| = 2$ transition are permitted and the state population is transferred via $J = 8 \to 10 \to 12 \to 14$. However, in the case of $|111\rangle$, the transitions process follow the selection rule of $|\Delta J| = 2$ and $|\Delta J| = 1$. With increasing values of J, the system favor a $|\Delta J| = 2$ excitation, as illustrated by Meijer *et al.* [28], therefore we believe that the wave packet is produced mostly via two predominant excitation pathways: $J = 1 \to 2 \to 4 \to 6 \to 8 \to 10 \to 12$, and $J = 1 \to 3 \to 5 \to 7 \to 9 \to 11 \to 13$.

4 Conclusion

In this present work we studied the initial rotational state dependence of the degree of alignment for OCS molecules. From the numerical simulations, the degree of alignment is shown to be sensitive to the initial rotational state. High degree of alignment can be obtained for only a few rotational states. In our calculation, the molecules initially in the pure rotational state $|100\rangle$ give rise to higher degree of alignment than initially in the other states including the ground state $|000\rangle$. The maximum degree of alignment is $\langle\cos^2\theta\rangle = 0.93$. Comparing with the molecules of thermal population, the molecules appropriately state-selected exihibit obvious higher degree and longer duration of alignment. We propose that high degree of alignment can be obtained experimentally by the appropriate selection of initial rotational state.

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