

Field-free molecular orientation at high temperature of $^1\Sigma$ and $^2\Pi$ molecules

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Abstract

We analyze the control of field-free molecular orientation at high temperature by a two-color laser bipulse strategy proposed in Phys. Rev. A **83**, 043410 (2011). A general study shows that there exist two types of linear molecules for which a different mechanism has to be used. For molecules with a large hyperpolarizability, a monochromatic laser pre-pulse is applied before the two-color laser pulse at a time close to the rotational period T_r , while for molecules with a small hyperpolarizability, the optimal delay is found close to $T_r/4$ or $3T_r/4$. We extend this analysis to the case of a $^2\Pi$ molecule such as NO where a similar control strategy can be derived. These control processes are found robust against temperature effects.

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I. INTRODUCTION

Laser control of quantum dynamics remains a field of growing interest with open questions coming both from the experimental and theoretical point of view [1–5]. Among other problems, one of the most challenging question is the production of field-free molecular orientation by laser pulses [6, 7]. On the theoretical side, different solutions have been proposed using optimal control theory [8, 9], adiabatic processes [10], train of half-cycle pulses (HCPs) [11–19], combination of HCP and laser pulses [20–22], two-color laser pulses [23–25], and so on [26–30]. In the sudden regime where the duration of the control field is short with respect to the rotational period, HCP appears to be a very efficient way to produce molecular orientation at least from a theoretical point of view. Indeed, since it is difficult with the present available technology to produce HCPs with a sufficient high intensity, the corresponding strategies are not so easy to transpose into the experimental domain. Only orientation by few cycles laser pulses in the THz regime has been experimentally implemented up to now [31]. From this perspective, a more promising approach in a near future seems to be the use of two-color laser pulses [32]. In the non-resonant situation, this approach has already been applied in adiabatic conditions [24], combined with a static electric field [33] or in the sudden regime [23, 25, 34]. It has been shown in Refs. [23, 35] that the maximum degree of orientation achievable by this latter strategy depends strongly not only on the hyperpolarizability but also on the polarizability. Moreover, the process has been found not robust against temperature effects for molecules with small hyperpolarizability terms such as CO and OCS molecules. Orientation by a two-color non-resonant process has been experimentally demonstrated in a molecular jet with carbon monoxide [36], but the maximum degree of orientation obtained at 60 K is relatively small (of the order of 0.06) despite using a strong laser intensity. In order to enhance the molecular orientation, a strategy consisting of a monochromatic non-resonant laser pulse at a delay of $T_r/4$ or $3T_r/4$ prior to the two-color pulse has been investigated [26]. This latter work has been carried out for only CO molecules at a specific temperature and thus the domain of validity of this strategy has not been explored. By performing a more general study, we show in this paper that this mechanism is only valid for molecules with a small hyperpolarizability (such as CO or OCS). In this case, a significant degree of orientation can be achieved even at room temperature. We show how this strategy has to be changed for molecules with a large hyperpolarizability. Finally, we

extend this orientation process by studying the case of a ${}^2\Pi$ ground state molecule such as NO where a similar control strategy can be derived.

This paper is organized as follows. In Sec. II, we present the model system and the problematics of the control of a linear molecule by a two-color laser pulse. The bipulse strategy is discussed in Sec. III for ${}^1\Sigma$ linear molecules. We extend this analysis to the case of ${}^2\Pi$ molecules in Sec. IV. Conclusions and prospective views are given in Sec. V.

II. THE MODEL SYSTEM

We consider the control of a linear molecule by non-resonant two-color linearly polarized laser fields of the form $\vec{\mathcal{E}}(t) = \vec{E}_\omega(t) \cos(\omega t) + \vec{E}_{2\omega}(t) \cos(2\omega t)$ where ω is the carrier wave frequency and $\vec{E}_\omega(t)$, $\vec{E}_{2\omega}(t)$ are the laser pulse envelopes of the ω and 2ω pulses, respectively [6, 7]. We assume that the relative phase between the two fields is fixed and equal to zero. In the case of a zero rotational temperature, the dynamics of the system is governed by the time-dependent Schrödinger equation $i\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)|\psi(t)\rangle$, where $H(t)$ is the Hamiltonian of the system. The units used throughout this paper are atomic units unless otherwise specified. Within the rigid rotor model and in a high-frequency approximation, the total Hamiltonian can be written as [24]:

$$\begin{aligned} H &= H_0 + H_{\text{int}} \\ &= BJ^2 - \frac{1}{4}(\Delta\alpha \cos^2\theta + \alpha_\perp)(E_\omega^2(t) + E_{2\omega}^2(t)) \\ &\quad - \frac{1}{8}[(\beta_\parallel - 3\beta_\perp) \cos^3\theta + 3\beta_\perp \cos\theta]E_\omega^2(t)E_{2\omega}(t), \end{aligned} \tag{1}$$

where B is the rotational constant and $\Delta\alpha = \alpha_\parallel - \alpha_\perp$ is the difference between the parallel and perpendicular components of the polarizability tensor. The polar angle θ is the angle between the internuclear axis and the direction of the field polarization. The terms β_\parallel and β_\perp correspond to the first-order hyperpolarizability components respectively parallel and perpendicular to the molecular axis. For numerical applications, we consider the parameters listed in Table I.

At a non zero temperature where different rotational states are initially populated, after the interaction with the field, each initial eigenstate $|J_0, M_0\rangle$ (the index 0 refers to the initial rotational level) of the unperturbed hamiltonian evolves into a large superposition of

TABLE I: Molecular parameters of different molecules used in the numerical computations and maximum value of $|\langle \cos \theta \rangle|$ for the two-color ($\omega, 2\omega$) and bi-pulse strategy. The optimal delay at the normalized temperature of 5 K/cm⁻¹ for each molecule is also listed. Numerical values of the polarizability and hyperpolarizability parameters are taken from refs [37–40]. The O and A parameters are expressed in atomic units.

Molecule	OCS	CO	LiH	NO
$B(\text{cm}^{-1})$	0.2029	1.931	7.513	1.6961
$\Delta\alpha$ (a.u.)	27.96	3.92	3.78	5.69
$\beta_{\parallel} + \beta_{\perp}$ (a.u.)	-106.7	32.6	864	15
—O—	1.23	-0.38	9.97	0.17
—A—	61.35	-8.60	8.29	12.48
$ \langle \cos \theta \rangle _{\max}(\omega - 2\omega)$	0.02	0.061	0.8	0.02
$ \langle \cos \theta \rangle _{\max}$ (bi-pulse)	0.3	0.26	0.82	0.11
Optimal delay (t/T_r)	0.25	0.27	1.04	0.25

rotational states $|J, M_0\rangle$. The corresponding wave function can thus be expressed as

$$|\psi_{J_0 M_0}(t)\rangle = \sum_{J=|M_0|}^{\infty} C_J^{J_0 M_0}(t) |J, M_0\rangle, \quad (2)$$

where $C_J^{J_0 M_0}$ are complex coefficients, which can be computed by solving the Schrödinger equation. A convenient way to quantify the degree of orientation consists of computing the expectation value $\langle \cos \theta \rangle$. For a non-zero temperature, this quantity can be written as

$$\langle \cos \theta \rangle = \sum_{J_0}^{\infty} p_{J_0} \sum_{M_0=-J_0}^{M_0=J_0} \langle \psi_{J_0 M_0}(t) | \cos \theta | \psi_{J_0 M_0}(t) \rangle, \quad (3)$$

$p_{J_0} = \frac{1}{\mathcal{Z}} g_{J_0} e^{-B(J_0(J_0+1)/k_B T)}$ being the weight given by the Boltzmann distribution, k_B the Boltzmann constant, and $\mathcal{Z} = \sum_{J_0=0}^{\infty} (2J_0 + 1) g_{J_0} e^{-B J_0(J_0+1)/k_B T}$ the partition function. The parameter g_{J_0} is the spin degeneracy which is equal to 1 for both the odd and even J_0 in the case of a heteronuclear diatomic molecule. In the next sections, we will need to separate the even and odd contributions of the rotational wave packet. We denote by $\langle \cos \theta \rangle_{\text{even}}$ and $\langle \cos \theta \rangle_{\text{odd}}$ these two contributions, i.e, the sum of Eq. (3) is carried out only over the even or odd values of J_0 respectively.

In a previous work [23], we have shown by using the sudden approximation that the efficiency of a two-color laser process depends mainly on two parameters, one parameter called A being related to the molecular polarizability, and the other, O , to the hyperpolarizability of the molecule. These two parameters are given by:

$$A = \frac{1}{4} \Delta\alpha \int_{-\infty}^{\infty} (E_{\omega}^2(t) + E_{2\omega}^2(t)) dt, \quad (4)$$

$$O = \frac{3}{32} (\beta_{\parallel} + \beta_{\perp}) \int_{-\infty}^{\infty} E_{\omega}^2(t) E_{2\omega}(t) dt. \quad (5)$$

Figure 1a shows the dependence of the maximum orientation as a function of these two parameters at a temperature of 0 K. We can notice the presence of two zones for which a significant orientation is obtained: an upper zone (I) requiring high O values and a flat zone (II) for moderate values of O . In these two regions, the maximum of orientation occurs at different times. In (I) the maximum of field-free orientation is reached for a time of the order of the true rotational period $T_r = \pi/B$ while in the zone (II) the maximum occurs at $T_r/2$. For a finite temperature, we remark that the flat zone (II) completely disappears as can be seen in Fig. 1b. This phenomenon can be explained as the destructive interferences between the orientation responses of the odd and even initial wave packets. We have displayed on Fig. 2 the evolution of the two expectation values $\langle \cos \theta \rangle_{\text{even (odd)}}$ as well as the total response $\langle \cos \theta \rangle$ for the CO molecule (Fig. 2a) and the LiH molecule (Fig. 2b). The simulations are carried out for a gaussian two-color laser pulse of full width at half maximum (FWHM) equal to 100 fs and a total peak intensity $I_{0,\omega} + I_{0,2\omega}$ of 70 TW/cm². The ratio between the peak intensities of the fundamental and harmonic $I_{0,\omega}/I_{0,2\omega}$ is taken to be 2 which is the optimal value previously found in [23]. We consider the same normalized temperature 5 K/cm⁻¹ for the two molecules in order to keep the same rotational distribution. As can be seen on Fig. 2a, the maximum orientation for the odd and even wave packets is reached at a time close to $T_r/2$ but the two responses are in phase opposition. This observation explains the dramatic decrease of the orientation with respect to the temperature for molecules with a moderate hyperpolarizability parameter [23]. While at zero temperature only the even wave packet exists, as soon as the first odd rotational level ($J_0 = 1$) becomes thermally populated, the two responses cancel themselves out at $T_r/2$ (this occurs at a temperature as low as 0.5 K for OCS) and only a small orientation response remains at the full rotational period. This behavior is not observed for molecules with a large hyperpolarizability (or belonging to the

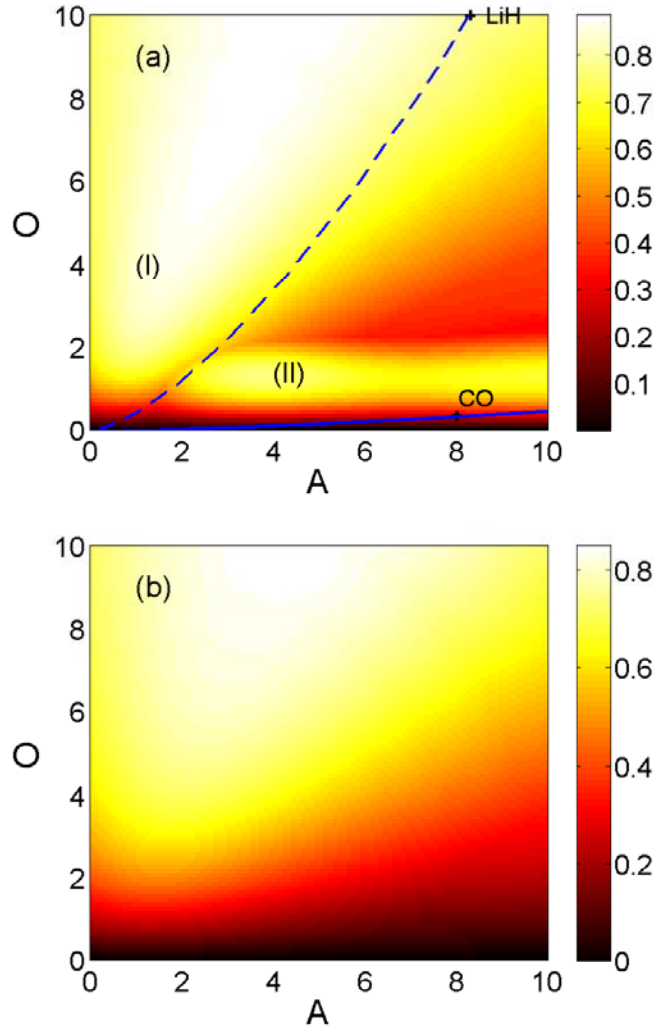


FIG. 1: (Color online) Maximum of $|\langle \cos \theta \rangle|$ at $T_{\text{norm}} = T/B = 0$ (a) and 5 K/cm^{-1} (b) as a function of the parameters A and O (in a.u.). The evolution of the coefficients O and A when the laser intensity is varied is also plotted for the LiH (dashed line) and CO (solid line) molecules. The crosses correspond to an intensity of 70 TW/cm^2 for the two-color laser pulse. The (I) and (II) labels refer to the two regions of high orientation (see the text).

zone (I) of Fig. 1). In this case, Fig. 2b shows that the maximum of $\langle \cos \theta \rangle_{\text{even (odd)}}$ at $T_r/2$ is almost negligible compared to the strong orientation reached at the full rotational period. A bipulse strategy will be introduced in the next section in order to enhance the maximum of orientation, but due to the different responses of Fig. 2, the optimization process will be different for these two types of molecules.

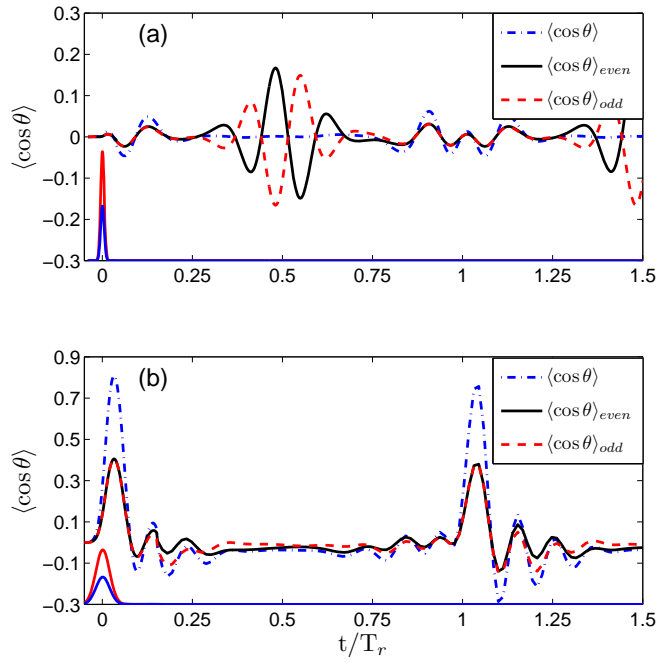


FIG. 2: (Color online) Evolution of $\langle \cos \theta \rangle$ (dotted lines), $\langle \cos \theta \rangle_{even}$ (solid lines) and $\langle \cos \theta \rangle_{odd}$ (dashed lines) for a 100 fs (FWHM) gaussian two-color laser pulse with a total peak intensity of 70 TW/cm^2 and a normalized temperature of 5 K/cm^{-1} . The panels (a) and (b) correspond respectively to the CO and LiH molecules. The temporal shape (arbitrary unit for height) of the two-color pulse is plotted at the bottom of each panel (in red or dark gray for the fundamental and in blue or black for the second harmonic).

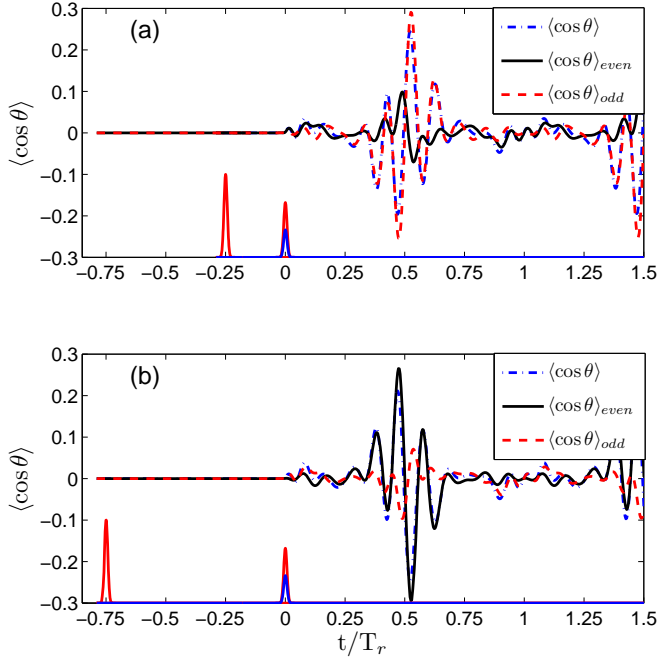


FIG. 3: (Color online) Evolution of $\langle \cos \theta \rangle$ (dotted lines), $\langle \cos \theta \rangle_{\text{even}}$ (solid lines) and $\langle \cos \theta \rangle_{\text{odd}}$ (dashed lines) for the CO molecule produced by a two-color laser pulse (with the same characteristics as in Fig. 2) combined with a single color pre-pulse with a delay of $T_r/4$ (a) and $3T_r/4$ (b). The temporal shape (arbitrary unit for height) of the different pulses is plotted at the bottom of each panel (in red or dark gray for the fundamental and in blue or dark for the harmonic).

III. BIPULSE STRATEGY FOR Σ -STATE MOLECULE

In this section, we analyze the strategy consisting of a monochromatic laser pre-pulse at a specific delay prior to the two-color pulse. We will first study the case of molecules with a small hyperpolarizability (or type II). For such molecules, the optimal delay for the pre-pulse is found to be close to $T_r/4$ or $3T_r/4$. These specific delays induce a selective excitation of the odd or even initial wave packets as was already demonstrated for molecular alignment [41, 42] or in the case of the combination of a HCP and a monochromatic pre-pulse [43]. As illustrated on Fig. 3, the odd and even orientation responses are enhanced and suppressed (resp. suppressed and enhanced) when the delay is of $T_r/4$ (resp. $3T_r/4$).

This strategy leads to a significant enhancement of orientation and the maximum of

$|\langle \cos \theta \rangle|$ obtained at a time close to $T_r/2$ is four times larger than the maximum reached at T_r in the case of a single two-color pulse. It is worth mentioning that the transient orientation obtained at $T_r/2$ depends directly on the intensity of the pre-pulse, while the maximum orientation at T_r remains unchanged by the application of the pre-pulse. Note also that at a temperature of 10 K, the optimal delay is not exactly equal to $T_r/4$ for the CO molecule but is slightly inferior to this value ($0.27 \times T_r$). The delay approaches the exact value of $T_r/4$ with increasing rotational temperature.

Using this technique, one can also produce a macroscopic orientation at very high temperature as shown in Fig. 4 where the case of the CO molecule was considered. The degree of orientation of the order of 0.1 reached at this temperature is comparable and even higher than the one observed with the ODS technique [44] that was proposed to orient molecules at high temperature. This approach seems also more promising experimentally since it does not require any specific frequency for the laser pulses as in the ODS method. We have also

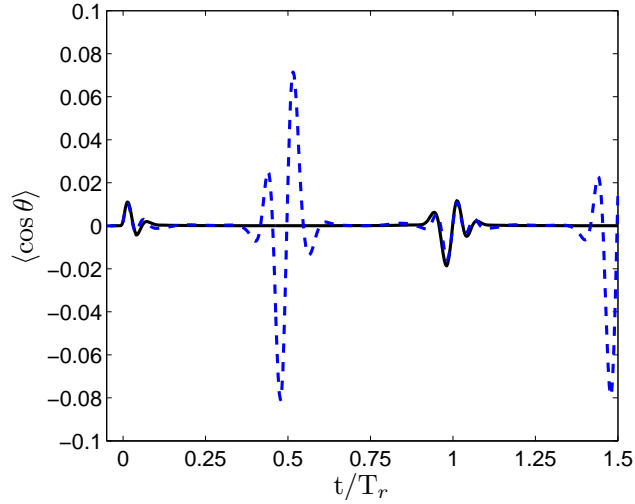


FIG. 4: Evolution of $\langle \cos \theta \rangle$ for the CO molecule at 300 K in the case of a single two-color laser pulse (solid line) and of a bipulse (dashed line) strategy. A gaussian two-color pulse of 100 fs FWHM and a total peak intensity of 70 TW/cm^2 has been used. The delay for the bipulse process has been fixed to $T_r/4$.

studied the behavior of the molecular orientation when the intensity of the laser pulses is varied. In these numerical simulations made at a temperature of 10 K, we have used the same peak intensity for the pre-pulse and the two-color laser pulse. For these conditions,

while the maximum of $|\langle \cos \theta \rangle|$ for a single two-color pulse increases very slowly with the intensity to reach a value of 0.1 at 200 TW/cm^2 , in the case of the bipulse strategy the saturation is almost achieved for a peak intensity of 80 TW/cm^2 , which yields a maximum value of 0.3. A more general analysis (which can be applied to any molecule) is made in Fig. 5 where the maximum of $|\langle \cos \theta \rangle|$ for the bipulse strategy is displayed as a function of the O and A parameters. The A parameter for the pre-pulse is assumed to be equal to the one of the two-color pulse. We observe on this figure that the zone (II) corresponding to moderate values of the O parameter which disappears at a non-zero temperature for a single two-color pulse (see Fig. 1b) is revealed by the bipulse strategy. This remark shows the interest of this approach for molecules of type (II).

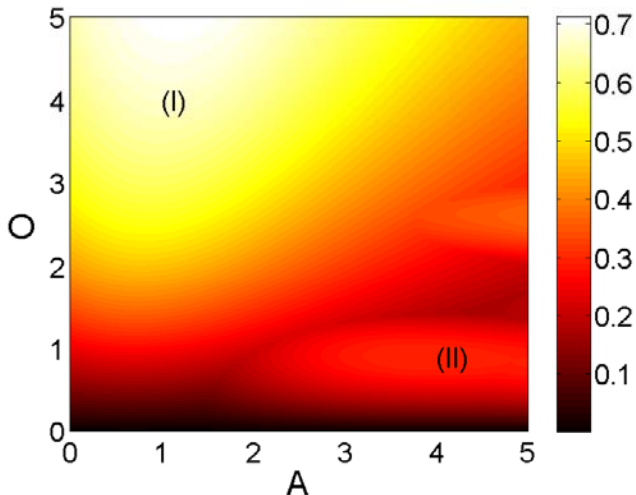


FIG. 5: Maximum orientation $|\langle \cos \theta \rangle|$ as a function of the two parameters O and A (in a.u.) for a monochromatic pre-pulse with a delay of $T_r/4$ with respect to the two-color pulse (see the text). The normalized temperature is fixed to 5 K/cm^{-1} .

For molecules with a large hyperpolarizability such as LiH, this strategy is not valid. For these molecules the transient orientation response at $T_r/2$ is absent. A mechanism based on a selective excitation of the two wave packets is thus unnecessary. In the same conditions as for the CO molecule, numerical simulations reveal that the optimal delay for the pre-pulse is located approximatively at the rotational period (see Table I). The improvement due to the bipulse process for the LiH molecule is however small since the degree of orientation obtained with a single two-color pulse is already significant (of the order of 0.8).

IV. THE CASE OF A Π - STATE MOLECULE

In this section, we extend this strategy to the case of a molecule in a ${}^2\Pi$ ground electronic state. To simplify the discussion, we first consider specifically the NO molecule, a general analysis will be presented at the end of this section. A very efficient approach using a hexapole selection with a static field and a sudden monochromatic pulse has been proposed for orienting the NO molecule at very low temperature [45]. Unfortunately, this method is not valid at higher temperature or even at 0 K when no hexapole selection is made. Due to the small NO hyperpolarizability, the degree of orientation achieved with a two-color laser pulse is very small and a bipulse strategy can be used to enhance the orientation response.

A. The model system

A ${}^2\Pi$ molecule has non-zero orbital and spin momenta \vec{L} and \vec{S} , the quantum numbers corresponding to the signed projections of these two quantities over the internuclear axis are denoted by Λ and Σ . For the NO molecule, we get $\Lambda = \pm 1$ and $\Sigma = \pm 1/2$. The total angular momentum can be written as $\vec{J} = \vec{R} + \vec{L} + \vec{S}$ where \vec{R} is its nuclear rotational part. We introduce the quantum number Ω associated to the projection of the total electronic angular momentum, which satisfies $\Omega = \Lambda + \Sigma$, and $\bar{\Omega}$ the absolute value of Ω . The two possible values for $\bar{\Omega}$ are 1/2 and 3/2. The field-free Hamiltonian of such a molecule includes the spin-orbit interaction characterized by the parameter A_0 ($A_0 = 123.13 \text{ cm}^{-1}$ for NO), and is given by:

$$\begin{aligned} H_0 &= H_{\text{rot}} + H_{\text{SO}} \\ &= B_0(\vec{J} - \vec{L} - \vec{S})^2 + A_0\vec{L} \cdot \vec{S} \\ &\simeq B_0(\vec{J} - \vec{L} - \vec{S})^2 + A_0L_ZS_Z \end{aligned}$$

where B_0 is the rotational constant. The eigenvectors and eigenvalues of H_0 can be derived explicitly [46]. The eigenvalues $\lambda^{(1,2)}$ can be written as

$$\begin{aligned} \lambda^{(1)} &= B_0[(J - 1/2)(J + 3/2) - X_J/2] \\ \lambda^{(2)} &= B_0[(J - 1/2)(J + 3/2) + X_J/2], \end{aligned}$$

where $X_J = \sqrt{4(J + \frac{1}{2})^2 + Y(Y - 4)}$, $Y = A_0/B_0$. Note that the quantum numbers J and M are half integers in the case of a $^2\Pi$ molecule. The corresponding eigenvectors of the unperturbed Hamiltonian are given by

$$\begin{aligned} |\Psi_{JM\varepsilon}^{(1)}\rangle &= a_J |J\bar{\Omega} = 1/2M\varepsilon\rangle + b_J |J\bar{\Omega} = 3/2M\varepsilon\rangle \\ |\Psi_{JM\varepsilon}^{(2)}\rangle &= -b_J |J\bar{\Omega} = 1/2M\varepsilon\rangle + a_J |J\bar{\Omega} = 3/2M\varepsilon\rangle \end{aligned}$$

where the kets $|J\bar{\Omega}M\varepsilon\rangle$ are defined by

$$|J\bar{\Omega}M\varepsilon\rangle = |J\Omega M\rangle + (-1)^\varepsilon |J - \Omega M\rangle \quad (6)$$

with $\varepsilon = 0, 1$ and $\langle\theta, \phi|J\Omega M\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D_{M,\Omega}^{J*}(\theta, \phi)$ the Wigner rotation matrix. The coefficients a_J , and b_J can be expressed as $a_J = \sqrt{\frac{X_J+Y-2}{2X_J}}$ and $b_J = \sqrt{\frac{X_J-Y+2}{2X_J}}$ [46]. For low values of J , we have $a_J \approx 1$ and $b_J \approx 0$ and the eigenfunctions $|\Psi_{JM\varepsilon}^{(1)}\rangle$ and $|\Psi_{JM\varepsilon}^{(2)}\rangle$ of H_0 can be identified to the wave functions $|J\frac{1}{2}M\varepsilon\rangle$ and $|J\frac{3}{2}M\varepsilon\rangle$ respectively. This situation corresponds to the Hund (a) case. For very high J values, we get the Hund (b) case for which $a_J = b_J \approx 1/\sqrt{2}$. Numerical simulations show that the Hund (a) case is always verified for the NO molecule up to very high peak intensities (150 TW/cm²) and temperature (300 K). In the following, we will treat the orientation problem within this approximation, i.e, we will not consider the $|\Psi_{JM\varepsilon}^{(1,2)}\rangle$ functions but the $|J\bar{\Omega}M\varepsilon\rangle$ ones.

The interaction Hamiltonian is similar to the $^1\Sigma$ case but the matrix elements of the $\cos\theta$ and $\cos^2\theta$ operators are different. For the $\cos\theta$ operator, the matrix elements in the $|J\bar{\Omega}M\varepsilon\rangle$ basis read

$$\begin{aligned} \langle J'\bar{\Omega}M\varepsilon' | \cos\theta | J\bar{\Omega}M\varepsilon \rangle &= \\ Q_{JM} \delta_{J',J} \delta_{\varepsilon',\varepsilon\pm 1} + \left(P_{JM} \delta_{J',J+1} + P_{J-1M} \delta_{J',J-1} \right) \delta_{\varepsilon',\varepsilon} \end{aligned} \quad (7)$$

where the P_{JM} and Q_{JM} coefficients are functions of J and M . The quantum numbers M and $\bar{\Omega}$ are conserved during this transition. The $\cos\theta$ matrix contains non-diagonal elements in J ($\Delta J \pm 1$) for a transition conserving ε and diagonal elements in J ($\Delta J = 0$) for a transition coupling two different values of ε ($\varepsilon = 0, 1$) [47]. The matrix elements Q_{JM} have significant values only for small values of J ($Q_{1/2,1/2} = 1/3$). For higher rotational states, these coefficients decrease quickly towards 0. The non-diagonal elements P_{JM} are comparable to the matrix elements of a $^1\Sigma$ type molecule and tend to 1/2 for high values of

J . The matrix elements of the $\cos^2 \theta$ operator are given by

$$\begin{aligned} \langle J' \bar{\Omega} M \varepsilon' | \cos^2 \theta | J \bar{\Omega} M \varepsilon \rangle = \\ \left(S_{JM} \delta_{J', J+2} + S_{J-2M} \delta_{J', J-2} + R_{JM} \delta_{J', J} \right) \delta_{\varepsilon, \varepsilon'} \\ + \left(T_{JM} \delta_{J', J+1} + T_{J-1M} \delta_{J', J-1} \right) \delta_{\varepsilon', \varepsilon \pm 1} \end{aligned}$$

where S_{JM} , R_{JM} , T_{JM} are functions of J and M . The $\cos^2 \theta$ matrix induces transitions with the selection rules $\Delta J = 0, \pm 2$ if the quantum number ε is conserved and transitions $\Delta J = \pm 1$ for a transition between two different ε levels. The coefficients T_{JM} responsible for the transition $\Delta J = \pm 1$ have non-negligible values only for the transition between the two first rotational levels ($J = 1/2$ and $J = 3/2$).

B. Bipulse strategy for the NO molecule

We first consider the case of the NO molecule at zero temperature interacting with a single two-color pulse. In this case, only the level $J = 1/2$, $\bar{\Omega} = 1/2$ is populated but this level corresponds to four degenerate states associated with the two magnetic numbers ($M_0 = \pm 1/2$) and the parity $\varepsilon = 0, 1$. In order to simplify the discussion, we only analyze the time evolution of the $|J = \frac{1}{2}, \bar{\Omega} = \frac{1}{2}, M_0 = \frac{1}{2}, \varepsilon = 0\rangle$ initial state. For a two-color excitation, the behavior of $\langle \cos \theta \rangle$ will be similar for the four degenerate equally populated initial states. After interaction with the laser field, the initial wave function evolves into a large superposition of rotational levels which can be decomposed into two wave functions according to their parities $\varepsilon = 0$ and $\varepsilon = 1$, which also accounts for the Λ -type doubling:

$$|\Psi(t)\rangle = |\Psi_{\varepsilon=0}(t)\rangle + |\Psi_{\varepsilon=1}(t)\rangle \quad (8)$$

where

$$|\Psi_{\varepsilon}(t)\rangle = \sum_{J=1/2}^{\infty} C_J(t) |J \frac{1}{2} \frac{1}{2} \varepsilon\rangle, \quad (9)$$

the C_J parameters being complex coefficients given by the solutions of the Schrödinger equation. The population in the $\varepsilon = 1$ state is essentially brought by the $\Delta J = \pm 1$ transition from the level $J = 1/2$, $\varepsilon = 0$ to the level $J = 3/2$, $\varepsilon = 1$ due to the interaction term T_{JM} of $\cos^2 \theta$. Each wave function $|\Psi_{\varepsilon}\rangle$ evolves then independently undergoing $\Delta J = 0, \pm 2$ (due

to the term S_{JM} of $\cos^2 \theta$) and $\Delta J = \pm 1$ (due to the term P_{JM} of $\cos \theta$) transitions to form a broad superposition of rotational states. The quantity $\langle \cos \theta \rangle(t)$ can then be written as:

$$\langle \cos \theta \rangle = \sum_{\varepsilon=0}^1 \sum_{\varepsilon'=0}^1 \langle \cos \theta \rangle_{\varepsilon, \varepsilon'} \quad (10)$$

where $\langle \cos \theta \rangle_{\varepsilon, \varepsilon'} = \langle \Psi_{\varepsilon} | \cos \theta | \Psi_{\varepsilon'} \rangle$. The quantities $\langle \cos \theta \rangle_{\varepsilon, \varepsilon'}$ with $\varepsilon \neq \varepsilon'$ average approximately to zero since the interaction terms Q_{JM} of $\cos \theta$ coupling the two ε levels are negligible for high values of J .

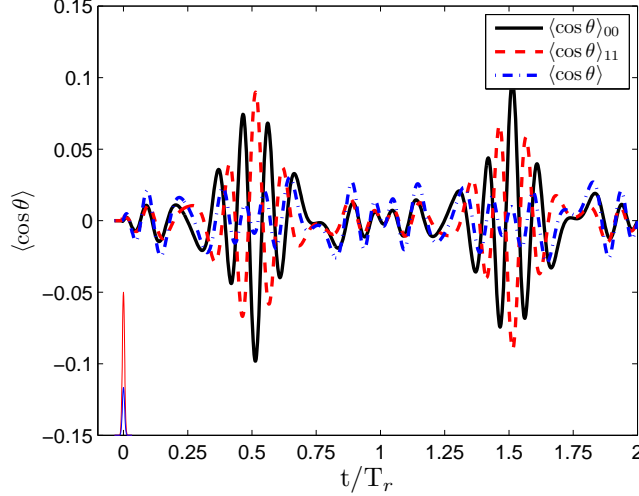


FIG. 6: (Color online) Evolution of $\langle \cos \theta \rangle$ (dotted line), $\langle \cos \theta \rangle_{00}$ (dashed line) and $\langle \cos \theta \rangle_{11}$ (solid line) for the NO molecule excited by a two-color gaussian pulse with a 100 fs FWHM and a total peak intensity of 70 TW/cm².

Figure 6 displays the temporal evolution of $\langle \cos \theta \rangle_{\varepsilon, \varepsilon'}(t)$. We observe that the two components $\langle \cos \theta \rangle_{00}(t)$ and $\langle \cos \theta \rangle_{11}(t)$ interfere destructively at time $T_r/2$ and constructively at T_r . The maximum orientation of both the two responses obtained at $T_r/2$ is at least four times larger than the value achieved at T_r . Starting from this analysis, a parallelism can be done with the case of $^1\Sigma$ molecule, the odd and even responses being replaced by the $\varepsilon = 0, 1$ ones. In order to enhance the molecular orientation, it is thus natural to explore the efficiency of the bipulse strategy in this case. Systematic numerical simulations show that the optimal delay for the pre-pulse is of the order of $T_r/4$ or $3T_r/4$ as can be seen in Fig. 7a or 7b, respectively. The expectation value of $\langle \cos \theta \rangle$ reaches a maximum of 0.13 for the delay $T_r/4$ while the degree of orientation is approximately equal to 0.02 for a two-color pulse

in the same conditions. This optimal delay does not exactly correspond to the extinction of

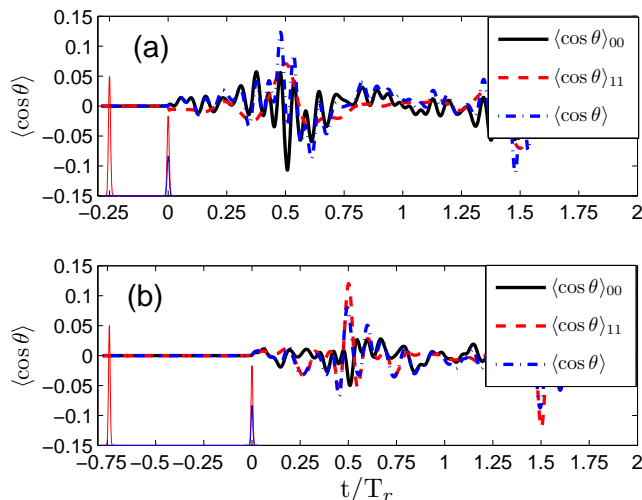


FIG. 7: (Color online) Evolution of $\langle \cos \theta \rangle$, $\langle \cos \theta \rangle_{00}$, $\langle \cos \theta \rangle_{11}$ for a bipulse strategy with a delay of $T_r/4$ (panel (a)) and a delay of $3T_r/4$ (panel (b)).

one of the two orientation responses $\langle \cos \theta \rangle_{00}$ or $\langle \cos \theta \rangle_{11}$ but to a change of these responses to maximize the orientation at a certain time close to $T_r/2$. Note that this strategy is also valid at higher temperature. For example, at a temperature of 9 K ($T_{\text{norm}} \sim 5 \text{ K/cm}^{-1}$), we get a maximum of 0.11, while at a temperature of 50 K ($T_{\text{norm}} \sim 30 \text{ K/cm}^{-1}$) a maximum value of 0.08 is reached. Note that these values are enhanced by 5.5 times at 9 K and 8 times at 50 K with respect to the degrees of orientation produced by a single two-color pulse which are respectively of 0.02 and 0.01 in the same conditions. A general analysis of the control scheme with a delay of $T_r/4$ between the pre-pulse and the two-color laser field is presented in Fig. 8. This figure, which is an extension of Fig. 1b and 5 to $^2\Pi$ molecules, clearly shows that the two regions of high orientation are preserved. On contrary, only the region (I) exists when the pre-pulse is not used as can be checked in Fig. 8a. The position of the two zones (I) and (II) in the (O,A)- diagram of Fig. 5 and 8b and the efficiency of the control process are similar in the $^1\Sigma$ and $^2\Pi$ molecules cases. Note that a third zone of high orientation for $O \simeq 2.5$ and $A \simeq 14$ also appears for $^2\Pi$ molecules.

We finally point out that for molecules in a $^2\Pi$ state with large hyperpolarizability values, the optimal delay for the pre-pulse will be close to T_r as for the LiH molecule. The data available in the literature on this point are very limited. As a consequence, we have not been able to test this prediction on a real molecule.

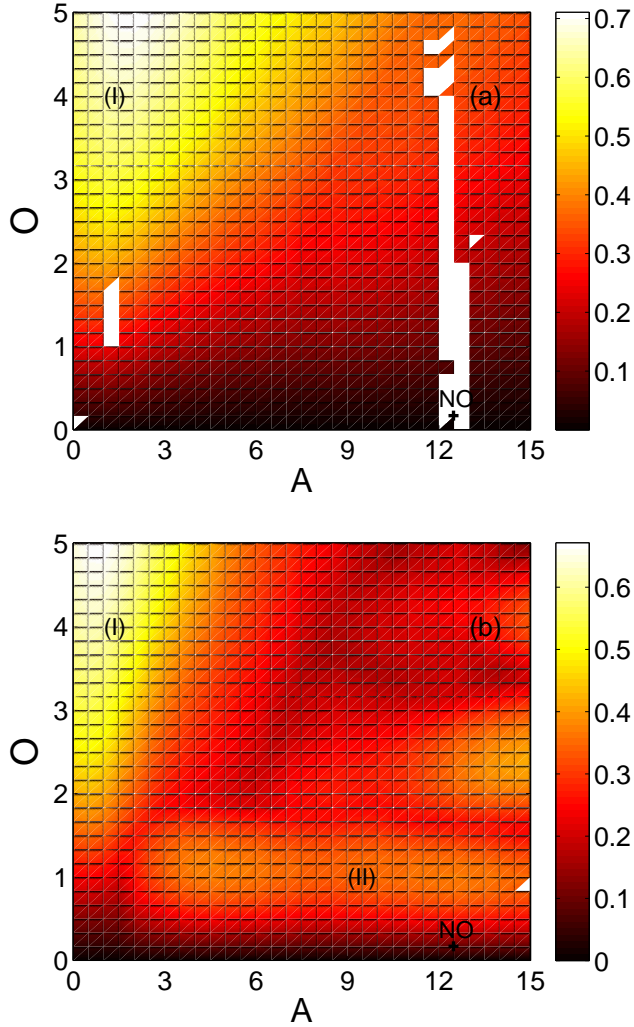


FIG. 8: (Color online) Same as Fig. 1b and 5 but for $^2\Pi$ molecules. A pre-pulse has been used in the computations of panel (b) and not of panel (a). The labels (I) and (II) indicate the position of the two regions of high orientation. The normalized temperature is fixed to 5 K/cm^{-1} .

V. CONCLUSION

In this paper, we have analyzed and extended the bipulse strategy proposed in [26] in order to produce molecular orientation at high temperature in $^1\Sigma$ and $^2\Pi$ molecules. Two different control strategies can be designed according to the molecules considered, and in particular the value of the corresponding hyperpolarizability term. These mechanisms are particularly simple and robust and only differ by the delay to use between the pre-pulse and the two-color laser field. More precisely, for molecules with a large hyperpolarizability

with respect to the polarizability component, the pre-pulse has to be applied one rotational period before the two-color laser pulse, while in the case of a small hyperpolarizability term, the optimal delay between the two pulses is close to $T_r/4$ or $3T_r/4$. Numerical tests have demonstrated the efficiency of the proposed procedure for both $^1\Sigma$ and $^2\Pi$. For instance, we obtain an unexpected orientation of 0.1 at room temperature for the benchmark CO molecule. In addition, a basic feature of the method under consideration is that it allows a thorough interpretation of the laser induced molecular orientation through the dynamics of the even and odd rotational wave functions. This understanding, which is a fundamental ingredient of the robustness of our control strategy, has huge significance in view of experimental applications. From a theoretical point of view, an open problem is the extension of this control strategy to symmetric and asymmetric top molecules. In particular, an interesting question would be to generalize the mechanism to such molecules using even and odd rotational wave packets. In the case of symmetric tops, note that the state of the system not only depends on the quantum numbers J and M , but also on K , the projection of the angular momentum onto the symmetry axis of the molecule.

Until now, the production of field-free molecular orientation has been only envisaged at low temperatures as the proposed control schemes predict almost no post-pulse orientation at high temperatures. This requires constraining experimental setups including supersonic jet or hexapole focusing. On the contrary, our proposed method in this paper is efficient even at room temperature which uses standard laser pulses with an intensity of the order of 50 TW/cm^2 and a duration of 100 fs. Note that the efficiency of this approach is only limited by the maximum field intensity that can be used to prevent the ionization of the molecule. As shown by the large zones of high molecule orientation in Figs. 1, 5, and 8, we have also checked the robustness with respect to the intensity and the duration of the laser field and found it to be remarkably good, as long as the time delay between the pulses is well controlled. This delay is the only crucial parameter of our control scheme which is not a limitation in terms of experimental applications nowadays [48, 49].

In conclusion, we emphasize that the efficiency of this approach especially at high temperature and its robustness with respect to experimental parameters seem to be a promising step towards the practical implementation of this method and the experimental production

of molecular orientation even at room temperature.

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