

## Laser-assisted molecular alignment in a strongly dissipative environment

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This paper shows that transient alignment of linear molecules in a dense collisional environment can result from the formation of trapped aligned “dark” states in a laser field constituting either a comb of resonant short pulses or a sinusoidally frequency-modulated wave with a continuous flux. Simulation of the laser-induced dynamics of CO molecules reveals that the latter approach is effective at room temperature and requires three orders of magnitude less laser intensity compared to known alignment techniques.

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Various molecular phenomena have been vastly enhanced with the advent of special laser tools by partial or complete ordering and/or spatial alignment of the molecules [1,2]. The ability to align (up to the quantum limit [3,4]) rotationally cold and noninteracting molecules in jets has opened up the opportunity for deep imaging of complex molecular structures (e.g., tomography of individual molecular orbitals [5]) and ultrafast dynamics [5,6]. There is a growing number of other proposed applications ranging from nanolithography to the development of ultrafast molecular switches and creation of quantum logic devices [1].

Obtaining transiently aligned molecules in dense dissipative media under high-temperature conditions is also an important objective. Recent experimental applications reside in nonlinear optics (e.g., for shaping, frequency tuning, compression, and other transformations of laser pulses [7,8], formation of transient optical gratings [9], and harmonic generation [10]), separation of nuclear and spin isomers [11], and rotational coherence spectroscopy [12]. This list is complemented by a number of promising proposals related to challenging problems in the control of chemical processes, x-ray generation [13], lasing in the terahertz range [14], and probing the dissipative characteristics of dense media [15]. The currently employed techniques for the low- and high-temperature molecular alignment share the same general principles and are based on the off-resonant action of strong laser fields. In the simplest case of linear molecules the alignment is caused by the additional field-induced term proportional to  $-\cos(\hat{\theta})^2$  in the molecular Hamiltonian, where  $\theta$  is the angle between the molecular axis  $\vec{\zeta}$  and the polarization direction  $\vec{z}$  of the laser field. Remarkable progress has been achieved in advancing such alignment techniques including their combination with other procedures [1]. Nevertheless, the effectiveness of all these techniques significantly degrades with increasing temperature. As a result, laser intensities of order 1–100 TW/cm<sup>2</sup> are employed to induce non-negligible deviations (typically of order  $\pm 0.01$ – $0.1$ ) in the degree of alignment  $\langle \cos(\hat{\theta})^2 \rangle$  from its isotropic value of 1/3 at room temperature. Propagation of such pulses through dense media is unavoidably accompanied by undesirable nonlinear side effects, such as ionization. Although the effects of the environment on alignment dynamics have not been extensively

studied [15–17], it is clear that they can only diminish the overall result.

In this work we propose a strategy for transient alignment of hot colliding linear molecules which is free of the above shortcomings. The strategy marries resonant coherent periodically varying laser radiation with incoherent decay processes for quantum state design. We will show that our method allows the peak laser intensity to be reduced by almost three orders of magnitude compared to conventional techniques.

To be specific, consider the case of linear heteronuclear molecules. We suppose that the molecular ground vibronic state  $|g\rangle$  has symmetry  $^1\Sigma$  and is coupled with some vibrationally (or vibronically) excited state  $|e\rangle$  of the same symmetry by the electric transition dipole moment  $\langle g|\hat{d}|e\rangle$  directed along the molecular axis  $\vec{\zeta}$ . Denote the molecular field-free rovibrational eigenstates and eigenenergies as  $|x_{J,M}\rangle$  and  $E_{x,J}$  ( $x = g, e$ ), where  $M$  is the quantum number associated with the  $z$  projection of molecular angular momentum  $J$ . For initial qualitative consideration we assume that the molecular rotational dynamics of both states is described by the rigid rotor approximation with equal rotational constants  $B_g = B_e = B$ .

Suppose that the sample of molecules is exposed to a laser field  $\vec{E}$  with polarization along the laboratory axis  $\vec{z}$  and carrier frequency tuned in resonance with the frequency  $\omega_0$  of the transition  $g \leftrightarrow e$ . The selection rules for the laser-induced dipole transitions are  $\Delta M = 0$  and  $\Delta J = \pm 1$ . The allowed transitions constitute several independent chains of coupled  $\Lambda$  systems (see Fig. 1).

Importantly, except for the nondegeneracy of  $J$  sublevels, these chains are identical to the diagrams of  $P$ -type transitions between magnetic sublevels of two molecular or atomic levels corresponding to  $J = J'$  (lower level) and  $J = J' - 1$  (higher level) induced by a continuous monochromatic resonant laser field which is elliptically polarized in the  $xy$  plane [see [18], Fig. 1(c)]. It was shown (see, e.g., [18,19]) in the latter case that there exists the unique stationary coherent “dark” state composed exclusively of the magnetic sublevels of the lower level which is not affected by laser radiation. As result, if such a system is subject to incoherent decay from the upper state to the lower one (e.g., through spontaneous radiative decay) then almost all the population will undergo coherent trapping in the dark state after the characteristic decay time.

The key concept underlying the proposed alignment scenario is to steer members of the molecular ensemble into the analogous trapped state providing desired asymmetry in

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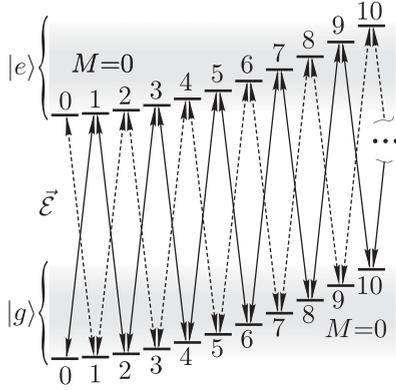


FIG. 1. Allowed dipole transitions between rotational sublevels with  $M = 0$  of the ground ( $|g\rangle$ ) and excited ( $|e\rangle$ ) states of a linear rigid molecule. The case with  $M > 0$  is identical except for the absence of levels with  $J < M$ . The numbers near each level indicate the quantum number  $J$ . Two distinct chains of coupled  $\Lambda$  systems are shown by the solid and dashed arrows.

the angular distribution of molecules. It must be stressed that this trapped state has to be nonstationary because of the nondegeneracy of the  $J$  sublevels. Therefore, the resulting molecular alignment will be transient. Ideally, the trapped state should be a pure state  $|\psi(t)\rangle = \sum_{j,m} a_{j,m}(t) |g_{j,m}\rangle$  which exactly satisfies the following two properties:

$$\forall t : (\hat{d}\vec{\mathcal{E}})|\psi\rangle = 0, \quad (1a)$$

$$\langle\psi(nT)|\cos(\hat{\theta})^2|\psi(nT)\rangle \rightarrow \max, \quad (1b)$$

where  $n$  is an integer and  $T = \frac{h}{2B_g}$  is the ground-state rotational revival time [1]. Conditions (1) guarantee the precise stability and purity conservation of the state  $|\psi(t)\rangle$  in the absence of decoherence in the rotational dynamics of the ground state  $|g\rangle$ . For further qualitative consideration we employ the multifrequency extension of the two-frequency model of Ref. [20]. Assume that the line broadening associated with any relaxation process is less than the splittings between  $J$  sublevels and that the laser field has the form

$$\vec{\mathcal{E}} = \vec{z}e^{i\omega_0 t} \sum_{j=0}^{J_{\max}} \sum_{q=-1/2}^{1/2} A_{j+2q,j} e^{i\omega_{j+2q,j} t} + \text{c.c.}, \quad (2a)$$

$$\forall m, j, j' : |A_{j,j'}\langle g_{j,m}|\hat{d}|e_{j',m}\rangle| \ll \hbar\omega_{j,j'}, \quad (2b)$$

where  $\omega_{j,j'} = \frac{1}{\hbar}(E_{e,j'} - E_{g,j}) - \omega_0$  and  $J_{\max}$  is the highest value of  $J$  among the non-negligibly populated  $J$  sublevels. Under the conditions (1) each transition shown in Fig. 1 will be driven by only one resonant frequency constituent of  $\vec{\mathcal{E}}$ . Hence, the laser-induced dynamics can be considered in the resonant approximation in which the effective Hamiltonian becomes time independent. Thus, the structure of  $|\psi(t)\rangle$  can be brought in line with the conditions (1) by the proper choice of amplitudes  $A_{j,j'}$ .

Given that the basis states  $|g_{j,m}\rangle$  are expressed in terms of spherical harmonics, the decomposition coefficients  $a_{j,m}$  of the maximally aligned state follow the approximate relation  $a_{j+2,M} \simeq -a_{j,M}$  in the high- $j$  limit [21]. To satisfy Eq. (1a) for this state one can choose the real spectral amplitudes in the

decomposition (2a) such that

$$A_{j-1,j} \simeq -A_{j+1,j}, \quad (3a)$$

$$A_{j+1,j} = A_{j,j+1}. \quad (3b)$$

Physically, relation (3a) sets the optimal ratio between the amplitudes responsible for the pair of transitions constituting each  $\Lambda$  system in the chains shown in Fig. 1. Relation (3b) is dynamically redundant and merely constrains the slowly varying field amplitude to be real valued.

The resultant laser field has a simple form in the time domain as a comb of short (compared with the time scale of the associated classical rotations)  $\delta$ -function-like pulses applied at the time instants  $t = (n + \frac{1}{2})T$  ( $n = 0, \pm 1, \pm 2, \dots$ ). At first glance, it appears that we obtained a resonant counterpart of the well-known scenario of nonadiabatic alignment of non-interacting molecules via a series of “kick” pulses. However, the mechanism of alignment in our case is distinct and can be explained as follows (for details and illustrations see [28]). The molecules constituting the angularly squeezed aligned part of the orientational distribution at any revival instant  $t = nT$  appear delocalized (antialigned) in the plane orthogonal to the  $\vec{z}$  axis at the time  $\frac{1}{2}T$  after the alignment revival [1]. Therefore, the laser kick applied at  $t = (n + \frac{1}{2})T$  almost has no effect on these molecules and primarily excites the remaining portion of the molecules. According to the assumed conditions, the excited molecules undergo incoherent decay into the ground vibronic state and partly contribute to population growth of the dark state. As a result, we have population flow which continuously enhances transient molecular alignment. By and large, the nature of the laser field is qualitatively the same as in the method of orientation of molecules via their orientation-dependent selection [22], but now the population distribution is additionally managed by environment-driven decay.

The scenario above can be enhanced to avoid the concentration of laser energy into short intense spikes. To achieve this, notice that the alignment mechanism can be viewed as correlated management of the dynamics of the  $N$  individual  $\Lambda$  systems. In the above scenario all the  $\Lambda$  systems are accessed simultaneously and coherently, which results in strong laser field spikes with peak intensity proportional to  $N^2$ . However, one can avoid this by addressing the individual  $\Lambda$  systems in stages through sequential resonant excitations of the different rovibronic transitions.

A way to implement this idea was inspired by recent works in the field of frequency modulation spectroscopy of atomic coherent dark resonances [20,23,24]. Consider a governing field  $\vec{\mathcal{E}}$  of the form

$$\vec{\mathcal{E}}(t) = \vec{\mathcal{E}}_0 \cos[\omega_0 t + \delta\omega_0 t + \mu \sin(\Omega t)], \quad (4)$$

where  $\Omega = \frac{\pi}{T}$ ,  $\delta\omega_0 = -\Omega$ , and  $\vec{\mathcal{E}}_0$  is the time-independent amplitude. Its spectral decomposition reads

$$\vec{\mathcal{E}}(t) = \frac{\vec{\mathcal{E}}_0}{2} \sum_{n=-\infty}^{\infty} J_n(\mu) e^{i(\omega_0 + \delta\omega_0 + n\Omega)t} + \text{c.c.}, \quad (5)$$

where the expansion coefficients  $J_n(\mu)$  are Bessel functions of the first kind. Contrary to the kick scenario, approximately half of the spectral constituents (with even values of  $n$  and  $n = \pm 1$ ) are off-resonant with any transition and thus redundant. Each

pair of the remaining spectral constituents with  $n = \pm(2j + 1)$  ( $j = 1, 2, 3, \dots$ ) is resonant with the transitions within one of the individual  $\Lambda$  systems. Importantly, the analog of the key spectral relation (3a) is exactly satisfied for all values of  $j$  by virtue of relation  $J_n(\mu) = -J_{-n}(\mu)$ . However, the absolute amplitudes of the harmonics can significantly vary with  $n$  and even vanish, so the relations analogous to Eq. (3b) no longer hold. Due to the properties of Bessel functions, the strongest harmonics are associated with  $|n| \simeq \mu$ . Numerical analysis reveals that it is advantageous to tune the frequencies of these harmonics to cover the subset containing the most occupied rotational  $J$  sublevels, i.e., to choose  $\mu \simeq 2\sqrt{\frac{kT}{2B_g}}$  (here  $T$  is the gas temperature and  $k$  is the Boltzmann constant).

Up to now, we used two simplifications which need consideration for real, dense, high-temperature molecular ensembles. First, molecular rotational dynamics does not exactly match the rigid rotor model, so one has to take into account both the differences between the rotational constants  $B_g$  and  $B_e$  as well as the nonrigidity corrections (e.g.,  $D_g$ ,  $D_e$ , etc.). As a result, the resonant interaction regime can be simultaneously accessed only for some selected subset of  $\Lambda$  systems involving only  $J$  sublevels with  $J_- \leq J \leq J_+$ . It was numerically determined that the best choice of such a subset matches the condition  $\mu \simeq 2\sqrt{\frac{kT}{2B_g}}$ . Second, a collisional, rather than a radiative, relaxation mechanism is expected to be dominant. In this work, we express the evolution of the density matrix  $\rho$ , describing the state of the molecules, in terms of a model of random collisions [17,25] which allows the handling of dissipative effects having similar vibrational and rotational decay rates (such conditions may be implemented in the laboratory by carefully choosing the buffer gas):

$$i\hbar \frac{d\rho(t)}{dt} = [(\hat{H}_0 - \hat{\alpha}\vec{\epsilon}), \rho] + i\hbar \frac{\rho_0 - \rho}{\tau}. \quad (6)$$

Here  $\hat{H}_0$  is the molecular Hamiltonian,  $\tau$  is the relaxation time, and  $\rho_0$  is the thermodynamic equilibrium state in the absence of the laser field.

As an example, consider the alignment of CO molecules in a hot dense gaseous environment ( $T = 288$  K,  $\tau = 1.33 \times 10^{-9}$  s) driven by a laser field tuned in resonance with the  $0 \rightarrow 1$  vibrational transition ( $B_g = 1.92285$  cm $^{-1}$ ,  $B_e = 1.90535$  cm $^{-1}$ ,  $D_g \simeq D_e = 6.1216 \times 10^{-6}$  cm $^{-1}$ ,  $\omega_0 = 2143.21$  cm $^{-1}$  [26],  $|\langle g|\hat{d}|e\rangle| \simeq 0.17$  D [27]). For numerical simulations we chose the following parameters: laser field intensity  $I = I_0$ ,  $\mu = 14.75$ , and  $\delta\omega_0 = -1.5\Omega$ , where  $I_0 = 2.34 \times 10^8$  W/cm $^2$  is taken as a reference intensity. The chosen values of  $\mu$  and  $\delta\omega_0$  are adjusted to afford high control efficacy in the maximally populated part of the rotational distribution ( $J_- \simeq 4$ ,  $J_+ \simeq 8$ ). We also neglected the effect of spontaneous emission since the related decay times are about six orders longer than  $\tau$ .

The temporal evolution of the laser-induced alignment in the quasistationary periodic regime [i.e., when the interaction time of the laser field (4) is sufficiently longer than  $\tau$ ] was calculated via numerical solution of Eq. (6) with the periodic boundary condition  $\rho(t) = \rho(t + \frac{2\pi}{\Omega})$ . The results are shown in Fig. 2(a). The temporal dependence of the degree of alignment has the form of rapid beat-like oscillations. The minimal and

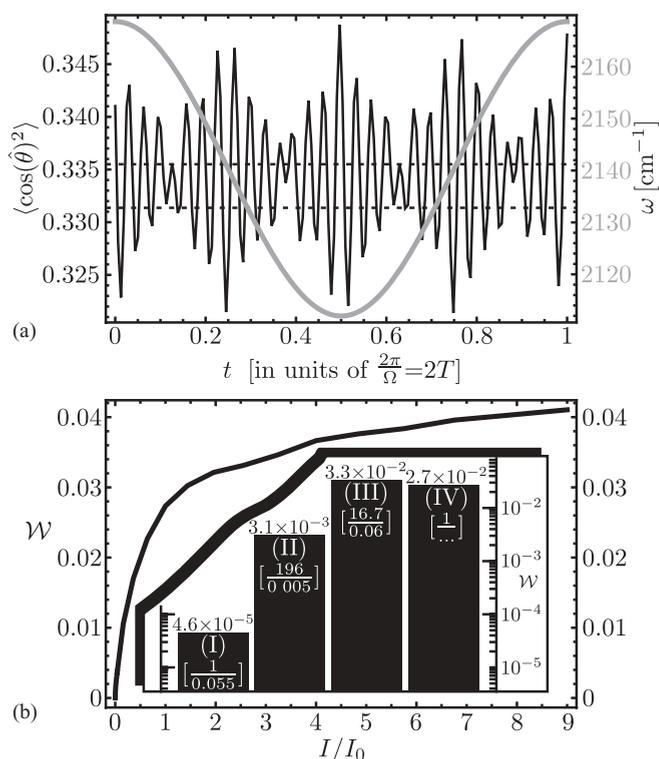


FIG. 2. (a) Degree of alignment  $\langle \cos(\hat{\theta})^2 \rangle$  of CO molecules (thin black curve, left scale) induced by a frequency-modulated laser field and the corresponding local field frequency (thick gray curve, right scale) as functions of time (one period is shown). The extremal alignment degrees afforded by a monochromatic field of the same fluence are indicated by dashed lines. (b) Dependence of the amplitude  $\mathcal{W}$  of variation of the alignment degree vs the radiation intensity. Inset: Comparison of the alignment performance attainable with different scenarios (see text). The numerator (denominator) values in squared brackets denote the peak kick intensity (duration) in units of  $I_0$  and  $T$ , respectively.

maximal values of  $\langle \cos(\theta)^2 \rangle$  are, respectively, achieved at  $t = (n + \frac{1}{2})T$  and  $t = nT$ , in agreement with the conclusions of the qualitative analysis. One can also see that the alignment effect induced by the frequency-modulated field is almost eight times stronger than the action of a monochromatic field of the same fluence.

Figure 2(b) provides complementary information about the dependence of the attainable amplitude  $\mathcal{W} = \langle \cos(\hat{\theta})^2 \rangle_{\max} - \langle \cos(\hat{\theta})^2 \rangle_{\min}$  of variations of the degree of alignment with respect to laser intensity  $I$ . We find that  $\mathcal{W} \sim \sqrt{I}$  at  $I < I_0$ , and this behavior is specific for the resonant alignment mechanism (in conventional methods based on off-resonant laser fields one has  $\mathcal{W} \sim I$  at low intensities). At  $I > I_0$  the temporal profile of  $\langle \cos(\hat{\theta})^2 \rangle$  weakly depends on  $I$ . This alignment saturation effect results from violation of the inequalities (2b). It may be beneficially used in applications for achieving the position-independent molecular aligning across the laser spot.

In the inset of Fig. 2(b) we compare the proposed frequency modulation approach [bar (IV)] with other methods employing periodic combs of short resonant laser kicks defined by Eqs. (2) and (3) [bar (III)] as well as “traditional” off-resonant laser

kicks [bars (I) and (II)] which have either the peak [case (I)] or the averaged intensity [cases (II) and (III)] equal to  $I_0$  [28]. In the simulations the temporal intensity profiles of the pulses were taken as rectangular, whereas the duration of the kicks in all cases and the carrier frequency in case (III) were optimized to attain maximal values of  $\mathcal{W}$ . We find that the frequency-modulation approach is one to three orders of magnitude more efficient than conventional techniques (I) and (II), depending on whether the averaged or peak intensity is limited (for further details, see [28]). We also found that the minimal peak intensity required with nonresonant techniques to attain the same degree of alignment, as in Fig. 2(a), is  $\sim 1.4 \times 10^{11}$  W/cm<sup>2</sup>, which is  $\sim 600$  times higher than  $I_0$ . These findings provide a promising outlook for the proposed method in applications to molecular optics, since most nonlinear destructive effects strongly depend on the peak field intensity. It is worth stressing, however, that the traditional strategies substantially outperform our technique in the

strong field limit because of the saturation effects mentioned above.

As a concluding remark, the necessary techniques for both phase modulation and generating the combs of the short pulses are under active investigation (see, e.g., [29–32]) and becoming commercially available. Similar laser phase-modulation-based methods were already successfully applied in experiments for the spectroscopy of atomic dark resonances [23,24]. Our results together with these experimental advances can be viewed within the general framework of enhancing the performance of various dynamical systems under periodic operation which is widely exploited, for example, to manage chemical and biochemical reactors [33]. The prerequisite analysis of the underlying general principles of periodic coherent control of open quantum systems will be the subject of forthcoming work.

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