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# Orientation of molecules via laser-induced antialignment

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We show that field-free molecular orientation induced by a half-cycle pulse may be considerably enhanced by an additional laser pulse inducing molecular antialignment. Two qualitatively different enhancement mechanisms are identified, depending on the pulse order, and their effects are optimized with the help of quasiclassical as well as fully quantum models.

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The orientation and alignment of molecules have long been of interest in chemistry and physics. Alignment and antialignment conventionally refer to head-on versus broadside localization of the symmetry axis of a molecule, whereas orientation refers to control of the up and down directions of an aligned molecule. Modern applications of aligned and oriented molecules, such as high harmonic generation [1], laser pulse compression [2], nanolithography [3], control of photodissociation and photoionization processes [4], and quantum information processing [5], have motivated the development of all-optical techniques for aligning molecules under field-free conditions. A major advance has been the use of linearly polarized, ultrashort laser pulses to create a rotational wave packet by an impulsive Raman mechanism [6]. For short pulses, peak field-free alignment along the electric vector of the laser field is achieved after termination of the laser pulse, at a time that depends on the pulse strength. As the wave packet evolves, the molecule becomes antialigned at some later time. In an antialigned state, the polar angle between the electric field vector and the molecular axis is peaked at $\theta=\pi/2$, whereas the azimuthal angle is randomly distributed. The molecule also undergoes a series of field-free realignments [7] at integer multiples of the revival time, $\tau_{rev}=1/(2Bc)$, where $B=\hbar/(4\pi c I_m)$ is the rotational constant, $c$ is speed of light, and $I_m$ is the molecular moment of inertia. In addition, a number of fractional rotational revivals occur at rational fractions of $\tau_{rev}$ [8].

Orientation of molecules requires an asymmetric field that distinguishes between up and down, and a variety of methods have been proposed to break the field symmetry [9,10]. The most versatile proposal to orientation of dipolar molecules utilizes an asymmetric electromagnetic half-cycle pulse (HCP) [11,12] that induces field-free orientation after the end of the HCP. As was shown in Ref. [12], a single short HCP cannot provide perfect orientation, and its effect saturates with intensity. Because of the random initial direction of the molecular dipole, different molecules acquire different angular speeds after being kicked by a HCP. Molecules initially located at obtuse angles with respect to the HCP ($\pi/2 \leqslant \theta \leqslant \pi$) are too slow to catch up with molecules starting from acute angles ($0 \leqslant \theta \leqslant \pi/2$). Classical and quantum mechanical calculations presented in this paper show that the orientation factor does not exceed a maximum value of $\langle\cos(\theta)\rangle \approx 0.75$ after a single short HCP. This effect is similar to nonperfect focusing caused by spherical aberration in geometrical optics. It was shown theoretically [12–14] that the degree of field-free orientation and alignment could be enhanced by using trains of laser pulses. Moreover, strong alignment by a pair of pulses has been experimentally achieved [15,16] (for a recent review on field-free alignment, see Ref. [17]). Orienting molecules with multiple HCP's currently is a challenging experimental task because of the difficulty in making controlled pulse trains of sufficient strength.

In this paper, we propose a method of substantially increasing the degree of orientation by combining an asymmetric half-cycle pulse with a symmetric femtosecond laser pulse inducing *antialignment* in a molecular ensemble. Depending on the temporal order of pulses, we have identified two qualitatively different mechanisms for the orientation enhancement, which we term "orienting an antialigned state" and "correcting the rotational velocity aberration," respectively. In the former mechanism, a symmetric laser pulse pushes the molecular symmetry axis toward the plane perpendicular to the desired orientation direction and prepares the molecules in an antialigned state. When a delayed strong asymmetric HCP is applied to such an ensemble, all the molecules gain nearly the same rotational velocity. Because all the molecules depart from the antialigned state with close initial angles, they reach the orientation axis almost simultaneously at some later time. We show that such a pulse pair is capable of producing much greater orientation than is possible with a single, arbitrarily strong HCP. In the second mechanism, the antialigning pulse is applied shortly *after* the orienting HCP (or even simultaneously with it). Such a pulse decelerates the rotation of molecular dipoles having an acute angle with respect to the orientation direction and accelerates dipoles having obtuse angles. This effect compensates for the "spherical aberration" in the angular distribution of the rotational velocity and improves the overall orientation at some later time. We demonstrate that significantly enhanced orientation can be achieved by a proper choice of the delay between the pulses and of their relative intensities.

The Hamiltonian for a three-dimensional (3D) driven rigid rotator (linear molecule) interacting with a linearly polarized field is given by $H(\theta,t)=\hat{J}^2/(2I_m)+V(\theta,t)$, where $\hat{J}$ is the angular momentum operator and $V$ is the potential energy. For a symmetric laser pulse interacting with the induced polarization, the interaction term, averaged over the fast optical oscillations, is given by $V(\theta,t) = -(1/4)\varepsilon^2(t)[(\alpha_{\parallel}-\alpha_{\perp})\cos^2(\theta)+\alpha_{\perp}]$. Here, $\varepsilon(t)$ is the envelope of the laser field, and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the parallel and perpendicular components of the polarizability tensor, respectively. For an asymmetric HCP, the interaction with the dipole moment is given by $V(\theta,t)=-\mu\varepsilon(t)\cos(\theta)$, where $\mu$ is the permanent dipole moment and $\varepsilon(t)$ is the amplitude of the HCP. In the present paper we assume that the duration of the pulses is short enough, so that the excitation dynamics may be calculated in the impulsive limit. The impulse imparted to the rotator is characterized by dimensionless action or kick strength, $P$. For an asymmetric pulse, $P$ is given by $P_a=(\mu/\hbar)\int_{-\infty}^{\infty}\varepsilon(t)dt$, where the integration is performed over the unidirectional peak of the half-cycle pulse, and $P_s=(1/4\hbar)(\alpha_{\parallel}-\alpha_{\perp})\int_{-\infty}^{\infty}\varepsilon^2(t)dt$ for a symmetric pulse. Physically, the kick strength $P$ indicates to the maximal angular momentum (in units of $\hbar$) that the laser pulse is able to supply to a randomly oriented molecule.

We start with the mechanism of "orienting an antialigned state" and consider a rotator excited first with a symmetric pulse of strength $P_s$ at $t=0$ and then with an asymmetric pulse of strength $P_a$ at $t=t_1$. Henceforth the dimensionless time is measured in the units of $I_m/\hbar=\tau_{rev}/(2\pi)$. Considerable physical insight may be derived from the (semi)classical treatment of the problem, which is valid for $P_s,P_a \gg 1$. Classically, if the rotator is initially aligned at angle $\theta_0$, it will be found at the same angle just after the first kick but with angular velocity $-P_s\sin(2\theta_0)$, so that at some later time it will have an angle $\theta(t)=\theta_0-P_s t\sin(2\theta_0)$. When at time $t=t_1$ the orienting pulse of strength $P_a$ is applied, the velocity increment is $-P_a\sin\theta(t_1)$. The angle $\theta$ at time $t_2$ after the second pulse is

$$\theta(t_1+t_2)=\theta_0-P_s t_1\sin(2\theta_0) - t_2\{P_s\sin(2\theta_0)+P_a\sin[\theta_0-P_s t_1\sin(2\theta_0)]\}. \quad (1)$$

A similar expression may be derived for the inverse order of pulses, needed for the second mechanism of enhanced orientation. The orientation and alignment factors at $t=t_1+t_2$ are calculated by averaging $\cos^k\theta(t)$ over all values of $\theta_0$,

$$\langle\cos^k\theta(t)\rangle=\frac{1}{2}\int_0^{\pi}\cos^k\theta(t)\sin\theta_0 d\theta_0, \quad (2)$$

where $k=1$ and 2 for orientation and alignment, respectively.

The case of $P_s,P_a\sim 1$ requires a more general quantum-mechanical treatment. A quantum rotator initially in the ground state at $t=0$ acquires a phase factor produced by the first short symmetric pulse, $\psi(\theta,t=+0) = \exp[iP_s\cos^2\theta]Y_0^0(\theta)$. By expanding this expression as a sum of spherical harmonics, one presents the wave function at time $t$ as $\psi(\theta,t)=(1/\sqrt{4\pi})\Sigma_{J=0}^{\infty}c_J\exp[-iJ(2J+1)t]Y_{2J}^0(\theta)$. The coefficients $c_J$ are [13],

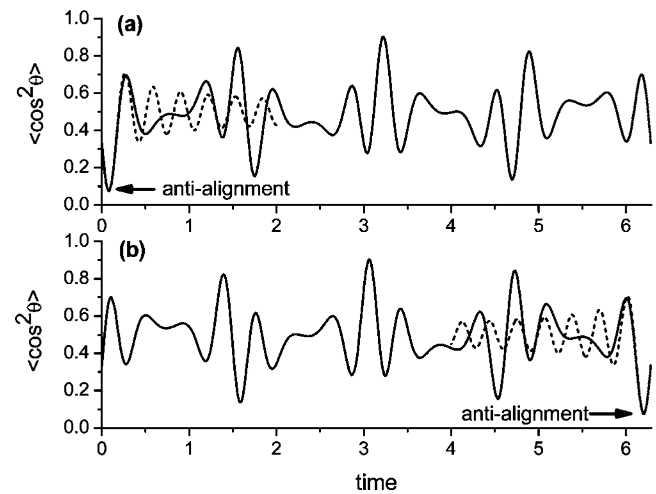


FIG. 1. Alignment factor vs time after excitation by a laser pulse with (a) $P_s=-10$ and (b) $P_s=10$. Solid curves present quantum results. Dashed curves are calculated classically (a) for positive time and (b) for negative time (shifted by $\tau_{rev}$). Strong antialignment is seen in both cases.

$$c_J=\sqrt{\pi(4J+1)}(iP_s)^J\frac{\Gamma(J+1/2)}{\Gamma(2J+3/2)}\,{}_1F_1(J+1/2,2J+3/2,iP_s), \quad (3)$$

where ${}_1F_1$ is the confluent hypergeometric function. At time $t=t_1$ the rotator is kicked by the orienting pulse, acquiring another phase factor, $\psi(\theta,t_1+0)=\exp[iP_a\cos\theta]\psi(\theta,t_1-0)$. We use the well-known expression $\exp(iP_a\cos\theta) =\Sigma_{j=0}^{\infty}i^j\sqrt{4\pi(2j+1)}j_j(P_a)Y_j^0(\theta)$, where $j_j(P_a)$ is a spherical Bessel function, and again expand the wave function in a series of spherical harmonics, $\psi(\theta,t_1+0)=\Sigma_{l=0}^{\infty}d_l Y_l^0(\theta)$, where

$$d_l=\frac{1}{\sqrt{4\pi}}\sum_{l'=0}^{\infty}\sum_{j=0}^{\infty}i^j\sqrt{(2j+1)}j_j(P_a)c_{l'}\exp[-il'(2l'+1)\tau] \times\sqrt{(2j+1)(4l'+1)(2l+1)}\frac{C(j,2l',l|0,0,0)^2}{2l+1}.$$

Here $C(j,2l',l|0,0,0)$ is a Clebsch-Gordan coefficient. This new wave function is allowed to propagate freely until $t=t_1+t_2$, at which point the orientation and alignment factors are calculated by $\langle\cos^k\theta\rangle=\langle\psi(\theta,t)|\cos^k\theta|\psi(\theta,t)\rangle$, $k=1,2$.

Our analysis shows that strong transient antialignment may be achieved via two related methods. The first one is of a (quasi)classical nature. It operates on a short time scale ($t\ll\tau_{rev}$) and requires *negative* values of the kick strength $P_s$. Pulses with negative $P_s$ produce antialignment by pushing molecules into the equatorial plane ($\theta=\pi/2$). Figure 1(a) shows the expectation value of $\langle\cos^2\theta\rangle$ calculated both classically and quantum mechanically for a pulse with $P_s=-10$. Both treatments predict a deep minimum, $\langle\cos^2\theta\rangle_{\min}=0.077$, shortly after the pulse at $t_m\approx 0.8/|P_s|$. The *negative* kick strength is typical of a circularly polarized light pulse propagating in the direction of the desired orien-

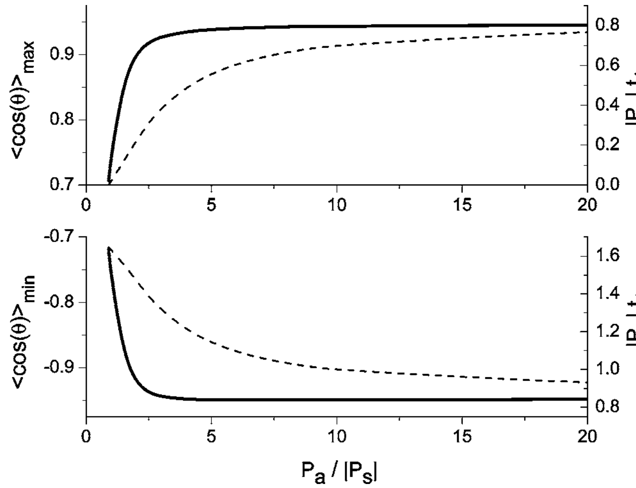


FIG. 2. Classically optimized orientation factor (solid curves) and delay between pulses (dashed curves). The laser pulse is fired before the half-cycle pulse.

tation, in which case the interaction is proportional to $P_s \sin^2\theta = P_s - P_s\cos^2\theta$. The second method of achieving antialignment uses laser pulses with *positive* $P_s$, which cause a substantial alignment on a short (classical) time scale *after* the kick [see Fig. 1(b)]. However, if it were possible to invert the dynamics and travel back in time, one would observe strong antialignment *before* the kick. Remarkably, the effect of quantum revivals [8] provides such an option. Indeed, $\psi(\theta, t_{rev}-\tau) = \psi(\theta, -\tau)$, and, for strong enough pulses, quantum dynamics just before one full revival cycle is equivalent to classical dynamics analytically continued to *negative times*. As a result, considerable antialignment is observed in this time domain [see Fig. 1(b)].

Figure 2 shows the results of direct numerical maximization of the orientation factor $|\langle\cos(\theta)\rangle(P_s, P_a, t_1, t_2)|$ using the classical model [Eqs. (1) and (2)] with an antialigning prepulse ($P_s<0$). When optimized, the model was formally extended to negative times to cover effects in the full revival time domain. At zero initial temperature, the optimal solution depends only on $P_a/P_s$ and the products $P_s t_1$ and $P_a t_2$. Figure 2 displays the highest postpulse orientation factor $\langle\cos\theta\rangle$ (solid line) and the optimal delay between pulses (dashed line) as a function of $P_a/|P_s|$. There are two optimal solutions of almost the same efficiency. The first one provides maximal orientation in the direction of the HCP shortly after the pulse (upper panel in Fig. 2). The second one (lower panel in Fig. 2) delivers enhanced orientation in the *opposite* direction in the full revival domain. In both cases, an impressive value of $|\langle\cos\theta\rangle_{max}| \approx 0.95$ is achieved (as compared to the limit of $\langle\cos\theta\rangle_{max} \approx 0.75$ for a single HCP). As seen from Figure 2, to attain such an efficiency, the HCP should be applied close to the moment of the best antialignment $t_m \approx 0.8/|P_s|$, as was discussed in the introduction. It is easy to show that the same degree of orientation may be achieved by combining a HCP with an *aligning* laser pulse ($P_s>0$). The apparent symmetry relations,

$$\langle\cos(\theta)\rangle(P_s, P_a, -t_1, -t_2) = \langle\cos(\theta)\rangle(-P_s, -P_a, t_1, t_2),$$

$$\langle\cos(\theta)\rangle(P_s, -P_a, t_1, t_2) = -\langle\cos(\theta)\rangle(P_s, P_a, t_1, t_2), \quad (4)$$

reduce this problem to the already studied case of the antialigning pulse.

We used the same approach to analyze the second mechanism of enhanced orientation mentioned in the introduction. In the simplest, nonoptimized version, the orienting and antialigning pulses are applied simultaneously ($t_1=0$). Direct numerical maximization of the expression in Eq. (2) shows that $\langle\cos(\theta)\rangle_{max}=0.89$ when $P_a/|P_s| \approx 2.34$ and $|P_s| t_2 \approx 0.78$. When the hybrid pulse is composed of an orienting component and an aligning one ($P_s>0$), the symmetry relations (4) predict the same orientation, but in the opposite direction ($\langle\cos(\theta)\rangle = -0.89$) just before one full revival cycle ($P_s t_2 \approx -0.78$). This effect was reported in a recent paper

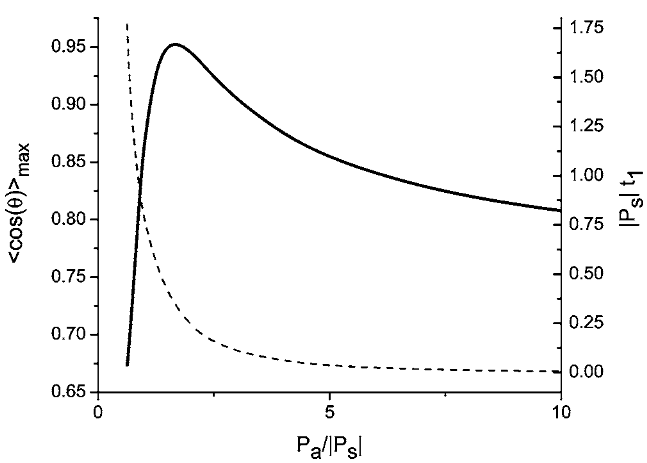


FIG. 3. Classically optimized orientation factor (solid curve) and delay between pulses (dashed curve). The laser pulse is fired after the half-cycle pulse.

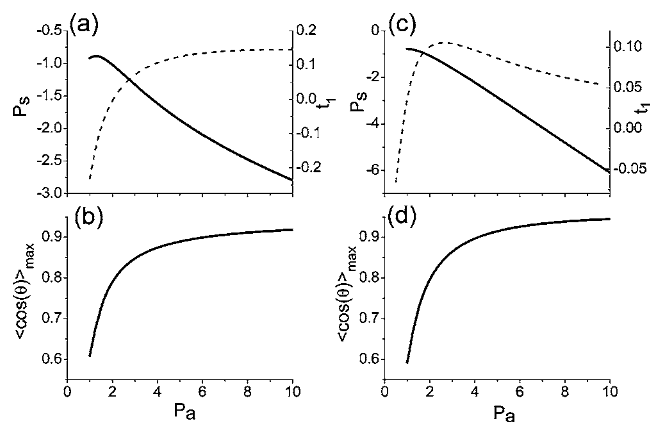


FIG. 4. Quantum-mechanical optimized results. Left column, (a) and (b), corresponds to the laser pulse fired before the HCP; right column, (c) and (d), corresponds to the reversed order of pulses. Upper panels (a) and (c) display the optimal strength of the antialigning pulse (solid lines) and delay between pulses (dashed lines) as a function of the HCP strength. Lower panels (b) and (d) present the highest value of the postpulse orientation factor vs the strength of the HCP. Negative delay times correspond to the second pulse applied *before* one full revival (as explained in the text).

[18] as a result of direct numerical simulation of the quantum rotational dynamics of molecules excited by a single hybrid pulse. Our (quasi)classical analysis reveals a more efficient optimal solution when the HCP precedes the antialigning laser pulse (see Fig. 3). The maximal orientation $\langle\cos(\theta)\rangle_{\max}\approx 0.96$ is reached at $P_a/|P_s|\approx 1.6$ and the optimal delay is $t_1\approx 0.36/|P_s|$.

We performed also a fully quantum-mechanical analysis of the problem using the above-described methodology. Figure 4 demonstrates the optimized values of the antialigning pulse strength, $|P_s|$, the delay between pulses, $t_1$, and the maximal orientation factor, $\langle\cos\theta\rangle_{\max}$, as a function of $P_a$. Very good agreement between quantum and (quasi)classical results is observed even for moderate antialigning and orienting pulses, $P_s, P_a \sim 3$. Remarkably, significantly enhanced orientation may be achieved with field strength available currently in the laboratory. Considering a KCl molecule in the ground state (revival time $t_{rev}\approx 128$ ps, dipole moment $\mu\approx 10.3$ D, polarization anisotropy $(\alpha_{\parallel}-\alpha_{\perp})\approx 3.1$ A$^3$ (data taken from Ref. [19]), one expects $P_a\sim 10$ for a HCP with the amplitude of 85 kV/cm and duration of about 2 ps ($1/e$ half width). According to Fig. 4, the orientation factor $\langle\cos(\theta)\rangle_{\max}\approx 0.95$ may be observed if the HCP is followed by a delayed antialigning pulse of 2 ps duration and $2.8\times 10^{11}$ W/cm$^2$ peak intensity. Our analysis is easily generalized to the finite temperature by thermal averaging over various initial rotational states. It shows that the hybrid scheme with delayed pulses produces robust orientation enhancement even at thermal conditions. Thus, the same single HCP provides $\langle\cos(\theta)\rangle_{\max}\approx 0.59$ for KCl molecules at 5 K. However, the orientation factor increases up to $\langle\cos(\theta)\rangle_{\max}\approx 0.69$ if a 2 ps laser pulse having $2.3\times 10^{11}$ W/cm$^2$ peak intensity precedes the HCP and prepares the ensemble in the antialigned state.

The transparent physics behind the interplay between antialignment, orientation, and revivals provides a solid basis for the future design of more sophisticated and efficient solutions. Enhanced antialignment and better correction of the "spherical aberrations" of a single HCP may be performed by trains of symmetric laser pulses, similar to forced multipulse alignment techniques [12–16]. A hybrid pair of delayed pulses may be followed by a series of well-timed symmetric laser pulses designed to preserve the achieved orientation over an extended time period [20,21].

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