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Optimization of field-free molecular alignment by phase-shaped laser pulses

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We theoretically demonstrate the optimization of field-free molecular alignment by phase-shaped femtosecond laser pulses. The effect is assessed in O_2 at $T=60$ K under realistic conditions of intensity and pulse shaping. The spectral laser phase is sampled through 128 control parameters and a self-learning evolutionary algorithm combined with a nonperturbative regime calculation is used in order to design the specific phase that maximizes the degree of alignment. The postpulse molecular alignment appears significantly enhanced compared to a Fourier-transform-limited pulse of same energy. The analysis of the target state reveals that the solution is close to the optimal one.

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Laser-induced spatial manipulation of molecules has become a subject of growing interest in the last decade covering a range of applications in chemical reactions, surface processing, and ultrafast optics [1]. It is now well established that molecules with an anisotropic polarizability exposed to a strong laser pulse experience alignment. In the case of nonresonant short pulses (short with respect to the rotational period), periodic transient molecular alignment takes place after the end of the pulse [2–4] as a result of the subsequent dephasing and rephasing of the rotational wave packet formed in the vibronic ground state of the molecule. This so-called postpulse molecular alignment is particularly valuable for applications requiring a sample of aligned molecules under *field-free* conditions. In this view, a number of works have focused on the possibility of controlling the dynamics of postpulse alignment. By tailoring the laser pulse shapes, switching of alignment [5,6], control of the rephasing period [7], and control of the transient shapes [8] have been demonstrated. A specific elliptical polarization has been also exploited in order to establish an alternation of alignment along two perpendicular axes [9]. Since the degree of molecular alignment that can be reached with a single ultrashort laser pulse is known to be intrinsically limited, recent efforts have concentrated on the possibility of enhancing the total alignment. The maximization of alignment or orientation using a monotonically convergent algorithm has been recently investigated theoretically [10] but the outcome optimal field, found in the microwave part of the spectrum, is rather difficult to implement for practical applications. Experimentally, two alternative approaches have been tested. The first one, combining short and long pulses, has been successfully applied to enhance alignment of the iodobenzene molecule [11]. The second one, proposed by Leibscher *et al.* [12], relies on a sequence of several pulses. Such a multipulse strategy is based on optimal control theory in a space of parameters related to the relative peak intensities and delays between the pulses. The dimension of this space is for practical applications rather low due to the small number of pulses that can be reasonably used. It has been shown experimentally that a bipulse offers already a significant enhancement of the alignment in asymmetric top [13] and symmetric top [14] molecules. An alternative approach consists of designing the spectral phase of a single pulse with a large search space related to the available number of pixels controlling the phase. Recent attempts reported by different groups have revealed the complexity of this task [8,15]. This Rapid Communication aims at demonstrating the efficiency of such optimizations under realistic conditions of intensity, temperature, and pulse shaping in regard to the potentialities offered by the available pulse shapers. The optimal pulse shapes are synthesized iteratively using an evolutionary algorithm in a feedback loop. The investigation is conducted in O_2 because it is a molecule of fundamental interests in the field of molecular alignment and because its rotational constant leads to calculation times suitable with the time-consuming iterative procedure of a learning algorithm. We show theoretically that the field-free molecular alignment at a temperature of 60 K under constraint of constant energy is significantly enhanced by appropriately manipulating the spectral phase of a femtosecond laser pulse. The mechanism of control is analyzed and the solution reached by the algorithm after the optimization procedure is found to be very close to the target density matrix [16]. This approach appears superior to the bipulse strategy in terms of induced ionization since it requires a lower peak intensity. This property is related to the difference in the control mechanism of both approaches. The phase-shaping strategy adapts indeed predominantly the phase of the wave packet in contrast to the bipulse strategy that yields a broader wave packet.

The complex electric field considered for the pulse inducing the molecular alignment is written as

$$E(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \varepsilon(\omega) e^{i\phi(\omega)} e^{-i\omega t} d\omega, \tag{1}$$

where $\phi(\omega)$ denotes the spectral phase and $\varepsilon(\omega)$ the spectral amplitude. $\varepsilon(\omega)$ is taken Gaussian with a full width at half maximum associated to a Fourier transform limited (FTL) pulse of 100 femtoseconds (fs). For concreteness, the spectral phase is controlled, like with the most common spatial light modulator [17], through 128 pixels equally distributed across the spectrum, i.e.,

$$\phi(\omega) = \sum_{n=-63}^{n=64} \Pi\left(\frac{\omega-\omega_n}{\Delta\omega}\right)\phi_n, \tag{2}$$

with $\Pi(x)=1$ for $|x|\leqslant 1/2$ and $\Pi(x)=0$ for $|x|>1/2$. ω_n, ϕ_n stand for the central pulsation and the applied phase of

the nth pixel while $\Delta\omega$ refers to the spectral sampling, i.e., the pulsation difference between two adjacent pixels ($\Delta\omega=0.8\times10^{12}$ rad/s here). The control is exercised in the present work by modifying the phase ϕ_n of the 128 pixels independently. These control parameters span over 2π and correspond to the genes of an individual for the evolutionary algorithm. Briefly, the algorithm starts with a population of 60 individuals randomly selected. The fitness of each individual is assessed by calculating the molecular alignment produced by the corresponding pulse shape as explained later on. At each new generation, the 10 fittest individuals (i.e., those achieving the largest alignment) are cloned and the algorithm generates from these "parents" 50 new individuals or "children" through both crossover and mutation. The mutation procedure is twofold. For half of the children, the phase of very few genes (about 1–2 %) is changed totally randomly while for the others, the phase of about 10% of the genes is modified by adding a random value within a range that is reduced along the optimization procedure. The algorithm produces thus a new population based on the success of the previous one and iteratively adapts the fitness of the population for the sought after effect. A large variety of pulse shapes can be synthesized with the present pulse-shaping technique. Nevertheless, the quality of the desired output wave form can be degraded by the pixelization of the spectral phase shaping. The main effect [18] is to introduce temporal replica with a period of $2\pi/\Delta\omega=7.8$ ps modulated by a $\mathrm{sinc}(\Delta\omega t/2)$ envelope corresponding to the Fourier transformation of the top hat pixel shape [defined by the Π function in Eq. (2)]. Experimentally, the temporal shaping is governed additionally by a Gaussian envelope due to the spatial beam profile in the phase mask. The product of the Gaussian and sinc terms is known as the "time window."

The molecular alignment is characterized by the quantity $\langle\cos^2\theta\rangle(t)$ where θ stands for the angle between the molecular axis and the field polarization. For a given spectral phase $\phi(\omega)$, the pulse intensity envelope is computed using Eq. (1). Considering a molecule initially in a state $|J_0,M_0\rangle$ (labeling the rotational and the magnetic quantum numbers), the wave function of the system after the interaction with the field is calculated by solving the time-dependent Schrödinger equation. The quantity $\langle\cos^2\theta\rangle_{|J_0,M_0\rangle}(t)$ is then evaluated and the averaging over the thermal distribution of rotational states is performed to provide $\langle\cos^2\theta\rangle(t)$ [3]. For O_2, only rotational states with odd J_0 values are populated. A set of $J=1-49$ in the vibronic ground state of the molecule has been used for the calculation since almost no excited electronic and vibrational states are thermally populated at the investigated temperature. Transient molecular alignment is expected to occur every $t=1/(8Bc)$ with a full revival period $T_r=1/(2Bc)$ where B is the rotational constant ($B=1.436$ cm^{-1} for O_2 giving $T_r=11.7$ ps). The revival shape depends on the laser excitation and the temperature T. In a first trial, the objective predetermined to the algorithm was the optimization of $\langle\cos^2\theta\rangle$ in O_2 for $T=60$ K at a fixed time delay $t=T_r$. By fixing the optimization time, we approach at best the most favorable experimental conditions in which the degree of alignment is evaluated at a particular delay by a probe pulse without having to scan the complete transient shape as faced

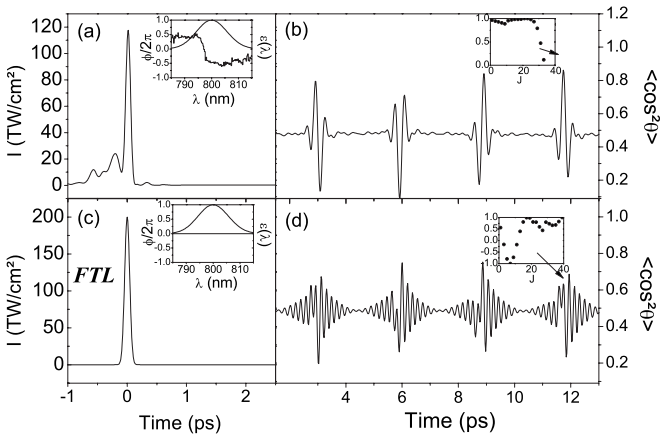

FIG. 1. (a) Optimized pulse shape, (c) FTL pulse. Spectral phases and amplitudes are shown in the insets. (b) and (d) $\langle\cos^2\theta\rangle(t)$ induced, respectively, by these two pulse shapes. The insets in (b) and (d) characterize the rephasing of the wave packet at $t=T_r$, i.e., $\cos(\omega_J T_r+\phi_J)$ vs J (see the text).

in Ref. [8]. The first full revival time is selected as the optimization target since it corresponds to the replica of the zero delay transient alignment where the pulse shaping is exercised. The intensity used for the FTL pulse of this run (i.e., considering $\phi_n=0\ \forall\ n$) is 200 TW/cm^2. Typically, the convergence of our algorithm for this purpose has been reached after about 60 generations. The spectral phase together with the pulse shape found out by the algorithm are depicted in Fig. 1(a) and the corresponding induced field-free molecular alignment in Fig. 1(b). The comparison with a FTL pulse is displayed in the bottom panels.

While the FTL pulse produces a maximum value of $\langle\cos^2\theta\rangle\approx0.75$, the phase-shaped pulse reaches a value significantly larger $\langle\cos^2\theta\rangle\approx0.86$ with a trace of alignment exhibiting revivals of larger duration. The algorithm succeeds therefore in designing a laser pulse with a better fitness for the issue of alignment by applying (see the inset) a rather simple spectral phase. Interesting insights can be gained into the effects exercised by the pulse shaping through an analysis in the spectral domain. As explained in Ref. [5], the quantity $\langle\cos^2\theta\rangle(t)$ can be developed in terms of Fourier components at Raman frequency ω_J [19], i.e., $\langle\cos^2\theta\rangle(t)=C_0+\Sigma_J a_J\cos(\omega_J t+\phi_J)$. The terms $a_J>0$ and ϕ_J correspond, respectively, to the amplitude and the phase of the Fourier components that are displayed in Fig. 2 for both FTL and shaped pulses of this investigation. One noticeable feature is the quasilinear phase ϕ_J as the outcome of the optimization. This peculiar result can be interpreted as follows. The alignment at the full revival $t=T_r$ is maximized when $\cos(\omega_J T_r+\phi_J)=1\ \forall\ J$ and thus for a phase $\phi_J=-\omega_J T_r+k2\pi=-2\pi cBT_r(4J+6)+k2\pi$, with k an integer, if the centrifugal distortion is neglected. It corresponds thus to a linear dependence of ϕ_J vs J with a negative slope. The latter is shown as a full curve in Fig. 2(b) and is fulfilled to a good approximation, for significant values of a_J (i.e., $J\lesssim25$), by the phase distribution ϕ_J resulting from the excitation with the optimized pulse shape. Based on this interpretation, all the Raman components ω_J should achieve a quite complete rephas-

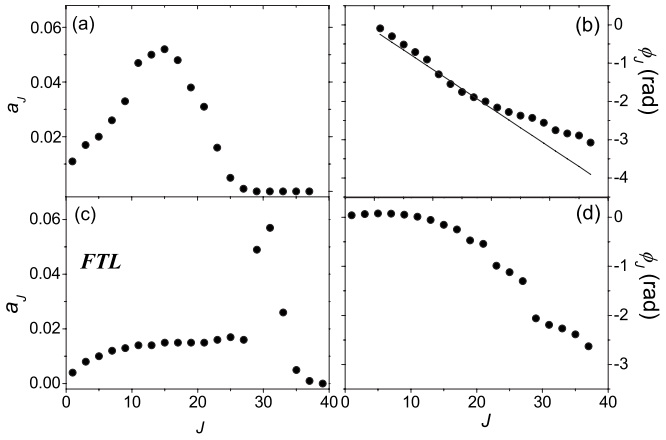

FIG. 2. (a) Amplitude a_J and (b) phase ϕ_J vs J of the Fourier components at Raman frequency of $\langle\cos^2\theta\rangle(t)$ for the optimized pulse shape. (c) and (d) are the same as (a) and (b) for the FTL pulse. The full curve in panel (b) refers to the criteria of complete rephasing of the rotational wave packet (see the text).

ing at $t=T_r$. The latter is confirmed by the inset of Fig. 1(b) displaying the value $\cos(\omega_J T_r+\phi_J)$ vs J. The comparison with the FTL pulse [Fig. 1(d)] is remarkable. While for the FTL pulse the different components exhibit significant dephasing, the algorithm succeeds in designing pulse shape that plays on the relative timing between them to lead in a quasiperfect synchronization at $t=T_r$. The inspection of the amplitudes a_J [Figs. 2(a) and 2(c)] provides further indications as well. A comparison between the FTL and the shaped pulse reveals that the latter tends to promote the excitation of the lower J levels. We argue that the algorithm guides the excitation towards this solution because the low J levels are intrinsically easier to rephase due to their lower energy. One longstanding question in the field of control by feedback-optimized-shaped pulses concerns the occurrence of the "optimal solution." To address this question, we have followed the procedure described in Ref. [16], where a target density matrix has been defined. It has been shown that the target density matrix provides the optimum alignment that can be reached for a given reduced Hilbert space (defined by the states significantly populated during the interaction). We have analyzed the wave packet resulting from the optimization at $t=T_r$ and the outcome is the achievement of 86% of the target density matrix with a degree of alignment around 97% of the latter. In view of the limitation of the search space, this is a compelling result. It should be noted furthermore that the maximum peak intensity of the tailored pulse [Fig. 1(a)] has been reduced to about 115 TW/cm^2 due to the energy-constant pulse shaping. This aspect is crucial in regard to ionization. A rough estimation of the ionization probability following the model of Ref. [20] yields a value $P_{\text{ion}}\approx 0.36$ for the shaped pulse drastically reduced compared to the FTL pulse for which the ionization is almost saturated ($P_{\text{ion}}\approx 0.99$). These values are of great importance for an experimental demonstration and the high ionization induced by the FTL pulse is expected to strengthen the enhancement of alignment observed in Fig. 1 for the shaped pulse compared with the FTL pulse. A set of runs performed in similar conditions has confirmed the general features of the present optimization reflecting its robustness. Other different FTL peak intensities from 50 to 300 TW/cm^2 have been investigated as well. In particular, for a peak intensity of 50 TW/cm^2 the algorithm has converged towards the FTL pulse shape and did not succeed in enhancing the alignment. Our investigation confirms thus the general idea that the optimization likely occurs for intensities where the alignment by a FTL pulse is saturated. At $T=60$ K the saturation of the alignment occurs around 100 TW/cm^2 vs 200 TW/cm^2 for $T=300$ K. While the optimization at room temperature (attempted in Ref. [8]) is in principle possible, the experimental observation would nevertheless require larger intensity giving rise to important ionization. For $T=60$ K, the algorithm did optimize the alignment for all intensities $I\geqslant 100$ TW/cm^2. Corresponding optimized pulse shapes all exhibit similar features, i.e., a long leading edge with several subpeaks prior to a major pulse centered at $t=0$ [Fig. 1(a)]. Although some changes particularly in the leading edge make each pulse specific with respect to the peak intensity, the result is found to be rather robust to the spatial averaging. The recurrent temporal structures observed in the optimized pulse shapes should shed light on the control mechanism. The analysis of the dynamical alignment reveals that the long tail induces a prealignment that reaches its maximum around $t=0$ where the field presents its maximum intensity. The underlying mechanism thus exhibits analogy with the multipulse strategy proposed in Ref. [12] and reported experimentally [13,14] using a sequence of two pulses. We have compared the possibilities offered by both approaches. The alignment with a bipulse in the conditions of temperature and energy of this work is found numerically maximized for a sequence of pulses of intensities $I=40-160$ TW/cm^2 time delayed by about 3050 fs. The maximum alignment ($\langle\cos^2\theta\rangle\approx 0.86$) is similar to the one obtained with the optimized phase-shaped laser pulse. Although the global alignment is comparable, the control exercised by the bipulse strategy is nevertheless different and less attractive as shown below. The optimized pulse shape leads to a wave packet with precisely adapted phase, while the bipulse favors the creation of a broader wave packet in the J space at the cost of lower rephasing quality. Since the fitness (i.e., the maximum value of $\langle\cos^2\theta\rangle$) reached by both methods is the same, it cannot be excluded *a priori* that the algorithm could recover the bipulse solution. We argue that the constraints of the present pulse shaping are unfavorable to a bipulse strategy. When using a realistic description of the pixel shape, the pulse shaping with large extent (out to 3 ps) is indeed limited by the time window and inherent replica whereas tailoring located near zero time exhibits a better fidelity. For these reasons, the algorithm has converged towards an alternative pulse shape that is better suited with the 128 pixels control. Although the resulting maximum alignment is similar, the present phase shaping features a crucial benefit. In order to reach the same degree of alignment, the bipulse approach requires a large peak intensity, i.e., 160 TW/cm^2 vs 115 TW/cm^2 for the optimized pulse, leading to a high ionization probability ($P_{\text{ion}}\approx 0.85$). This clearly makes the phase-shaping technique superior. The multipulse strategy should imply more than two pulses to reduce the ionization

and appears then more complicated to implement experimentally.

To conclude, we have investigated the optimization of postpulse molecular alignment in O_2 by means of phase-shaped fs laser pulses. The alignment at $T=60$ K is shown significantly enhanced using a specific laser pulse shape designed by an evolutionary algorithm. While a bipulse strategy is expected to produce similar global alignment, the solution found out by the present approach appears superior in terms of peak intensity and induced ionization. Further works at $T=100$ K as well as in other molecules (N_2 and CO_2) have corroborated these results. Based on these findings, the phase-shaping of fs laser pulses by self-learning algorithms turns out to be a valuable alternative approach to the multipulse strategy. Optimally shaped laser pulses feature promising applications in the frame of alignment. As suggested in Ref. [21], the postpulse molecular alignment can be exploited in order to achieve isotopic separation. The basic idea is to provide at a specific time two molecular isotopes with drastically different angular distributions (i.e., one aligned with the other one delocalized). Using the present optimization procedure, we have been able to improve significantly this favorable configuration. This potentiality will be investigated in a future publication.

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