Ultimate field-free molecular alignment by combined adiabatic-impulsive field design

S. Guérin, A. Rouzée, and E. Hertz
Institut Carnot de Bourgogne, UMR 5209 CNRS,
Université de Bourgogne, BP 47870, 21078 Dijon, France

We show that a laser pulse designed as an adiabatic ramp followed by a kick allows one to reach a perfect postpulse molecular alignment, free of saturation. The mechanism is based on an optimized distribution of the energy between a weakly efficient but non saturating adiabatic ramp and an efficient but saturating impulsive field. Unprecedented degrees of alignment are predicted using state-of-the-art pulse shaping techniques and non-destructive field intensities. The scheme can be extended to reach high degrees of orientation of polar molecules using designed half-cycle pulses.

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Control of the angular distribution of molecules in space features major applications in physics and chemistry (see [1] for a review). In this quest, an important issue concerns the production of a high degree of field-free alignment induced by non-destructive fields, especially for non-cold molecules [2–4, 11]. It is well-known that an intense non-resonant impulsive laser field (i.e. of duration much shorter than the classical rotational motion of the molecule) leads to field-free alignment, appearing as periodic revivals. While the degree of alignment can be improved with an increasing field intensity, it is however limited by (i) destructive competing processes such as ionization and (ii) an intrinsic saturation as obtained in the model of the rigid rotor driven by a laser kick. Trains of kicks have been proposed to shift to higher values this intrinsic saturation of alignment [6] and also in the context of molecular orientation where the laser fields are replaced by Half-cycle pulses (HCP) [5]. However, such trains of pulses also show plateaus of saturation. In practice, intense and generally ionizing kicks will be required to reach a high degree of alignment, in particular for non-cold molecules. An alternative solution [5, 10] consists in truncating an adiabatic pulse to produce a so-called switched wavepacket exhibiting revivals of alignment. These revivals are free of saturation as can be intuitively understood from the structure of the field-induced double well potential that can be made as deep as desired. However, besides the complexity to produce such pulse shapes with sufficiently high intensities, this truncated adiabatic method suffers from its energetic inefficiency to reach a high degree of alignment.

In this paper, we show that designing a laser pulse combining both ingredients, i.e. made of a combination of an adiabatic ramp followed by a kick, allows one to overcome the intrinsic saturation in a robust way, and thus to reach unprecedented degrees of alignment for cold and moderately hot molecules, using non-destructive fields. This strategy generalizes an optimization procedure reported in Ref. [5] to maximize the alignment of the O2 molecule at a given pulse energy using pulse-shaping techniques.

The problem of optimization is considered as follows. For a given fluence of the kick (corresponding to the laser energy per surface unit), whose peak intensity and duration are limited respectively by the ionization of the molecule and by the conditions of the impulsive regime, we determine the minimum intensity and duration of the adiabatic ramp, maximizing the subsequent field-free alignment.

When a linear molecule is subjected to a non-resonant linearly polarized laser pulse, the effective dressed Hamiltonian reads [11]

\[ H = BJ^2 - \frac{1}{4} \mathcal{E}(t) \Delta \alpha \cos^2 \theta \]  

with \( B \) the molecular rotational constant, \( \Delta \alpha > 0 \) the anisotropic polarizability, \( \mathcal{E}(t) \) the laser field envelope, and \( \theta \) the angle between the laser polarization axis and the molecular axis. Coupling terms independent of \( \theta \) have been omitted since they do not affect the alignment, which is quantified through the observable \( \langle \cos^2 \theta \rangle \). The molecule is effectively subject to a double-well potential of the form \(-\cos^2 \theta\), with minima at \( \theta = 0 \) and \( \theta = \pi \) corresponding to the magnetic quantum number \( M = 0 \). The condition for adiabatic transport that allows one to connect the initial state, say the lowest one \( |J = 0 \rangle \), to the lowest pendular state \( |J = 0 \rangle \), is estimated with respect to the smallest detuning \( \Delta \) of the two-photon process between the rotational states: \( \tau_a \gg \hbar / 2 \Delta \), \( \tau_a \) characterizing the pulse duration. The adiabatic maximum alignment is given by [11]

\[ \max_{t} \langle \cos^2 \theta \rangle_t \sim 1 - 1/\sqrt{\gamma}, \quad \gamma = \mathcal{E}_a^2 \Delta / 4B \]  

in the limits of low temperature \( T \), i.e. \( kT/B \ll 1 \), and of high field regime \( \gamma \gg 1 \). If we consider smooth pulses, such as Gaussian pulses of shape \( \mathcal{E}_a \sqrt{\Delta(t)} = \mathcal{E}_a e^{-2 \log 2 (t/\tau_a)^2} \) (with \( \mathcal{E}_a \) the peak amplitude of the field and \( \tau_a \) the full width at half maximum of the intensity), the adiabatic regime is already quite well achieved for \( \tau_a \sim T_{rot} \equiv \pi \hbar / B \). As a function of the fluence of a Gaussian ramp at its peak value \( F_a = \int_{-\infty}^{0} dt \Delta(t) \sim \mathcal{E}_a^2 \tau_a / 2 \sim 3 \mathcal{E}_a^2 \hbar / 2B \), we obtain

*Electronic address: sguerin@u-bourgogne.fr
This shows that the adiabatic alignment does not saturate but grows very slowly toward 1 as a function of the pulse fluence. For instance, we would obtain typically for the CO$_2$ molecule $\langle \cos^2 \theta \rangle_s \approx 0.987$ and $\langle \cos^2 \theta \rangle_a \approx 0.913$, at temperature and of width $\tau_a \approx 50$ ps. That corresponds to a pulse fluence above the saturation of the ionization.

On the other hand, the alignment in the impulsive regime, i.e. associated to the Hamiltonian in the impulsive approximation $H_{\text{imp}} = BJ^2 - 2\hbar \zeta \delta(t) \cos^2 \theta$, with $\delta(t)$ the Dirac distribution, is characterized by the dimensionless quantity

$$\zeta = F_k \Delta \alpha / 8 \hbar, \quad F_k = \xi_k^2 \int dt \Lambda(t) \quad (3)$$

with $F_k$ the fluence of the laser kick. For $T = 0$, the maximum alignment grows as a function of $\zeta$ as

$$\max_t \langle \cos^2 \theta \rangle_k \sim c_s - (c_s - 1/3) e^{-\zeta^{3/2}}, \quad (4)$$

until reaching the saturation at $c_s \equiv \langle \cos^2 \theta \rangle_k^{(\text{sat.})} \approx 0.92$. The efficiency of the kick is shown through the exponential growth of the alignment.

The mechanism we propose consists in combining a saturating but efficient laser kick with a non-saturating adiabatic ramp. The adiabatic ramp prepares a well-aligned state, which can be efficiently enhanced by the subsequent kick. The optimum compromise between the two fluences is more precisely established below. We first show the efficiency of alignment for the ideal conditions independent of the particular molecule (cold molecule, rigid rotor model, adiabatic regime for the ramp, and kick for the impulsive part of the pulse) and show how this efficiency survives when deviations from these conditions are considered.

The upper frame of Fig. 1 shows a typical signal $\langle \cos^2 \theta \rangle(t)$ (of period $T_{\text{rot}}$), calculated at $T = 0$, when the respective adiabatic and impulsive regimes are met (for an ideal model of a rigid rotor and with the impulsive approximation for the kick). The kick defines the origin of time $t = 0$. The predicted maximum degree of alignment $\max_t \langle \cos^2 \theta \rangle \approx 0.993$ is of unprecedented efficiency under non-destructive field intensities for most of the molecules. It is obtained right after the kick (or equivalently after one full period $T_{\text{rot}}$), precisely at a time $t_{\text{max}}$ which gets closer to 0 for higher intensities. In the conditions of the upper frame of Fig. 1, the maximum is located at $t_{\text{max}} \approx 0.0037 T_{\text{rot}}$. The signal exhibits a remarkably simple form of four revivals in a period with no noticeable oscillations in-between. This indicates a perfect rephasing of the wavepacket at the occurrence of the revivals. This strongly contrasts when kicks are applied without adiabatic ramp, as shown in the lower frame of Fig. 1.

We have compared the alignment with the one obtained with an ideal target state. The target state is defined as the state $|\psi_N\rangle$ that leads to the maximum alignment in the truncated Hilbert subspace spanned by the first $N$ rotational states. It corresponds to the eigenstate of $\cos^2 \theta$ in this subspace associated to the maximum eigenvalue. We obtain, in the conditions of the upper frame of Fig. 1, the projection on the target state $|\langle \psi_{N=13} | \phi(t_{\text{max}}) \rangle|^2 \approx 0.996$ at the time corresponding to the maximum of alignment, with $\phi(t)$ the state at time $t$. We determine the dimension $N$ of the target state taking the value that leads to the maximum projection $|\langle \psi_{N} | \phi \rangle(t_{\text{max}}) \rangle$. The alignment that would be obtained ideally with this target state $\langle \psi_{N=13} | \cos^2 \theta | \psi_{13} \rangle(t) \approx 0.993$. Lower frame: $\langle \cos^2 \theta \rangle(t)$ in the same condition as above but with $I_a = 0$.

FIG. 1: (Color online) Upper frame: Alignment determined through the observable $\langle \cos^2 \theta \rangle(t)$ (thick line) and $\langle \psi_{13} \cos^2 \theta | \psi_{13} \rangle(t)$ with the relevant target state $|\psi_{13}\rangle$ (thin line), calculated for $\zeta = 11$ (in the impulsive approximation), $\gamma = 142$ and temperature $T = 0$ as a function of the normalized time $t/T_{\text{rot}}$. This corresponds to non-ionizing intensities $I_k = 50$ TW/cm$^2$ (with $\tau_k = 100$ fs) and $I_a = 2.5$ TW/cm$^2$ for the CO$_2$ molecule ($T_{\text{rot}} \approx 42.8$ ps). The maximum alignment is $\max_t \langle \cos^2 \theta \rangle(t) \approx 0.993$. Lower frame: $\langle \cos^2 \theta \rangle(t)$ in the same condition as above but with $I_a = 0$.

Figure 2 displays a contour plot of the maximum post-pulse alignment (in a logarithmic scale) when the short and the adiabatic pulses are combined, as a function of the parameters $\zeta$ and $\gamma$ (and thus independently of the chosen molecule). The adiabatic pulse dramatically enhances the alignment at a given $\zeta$ and vice versa.
For a given $\zeta \gtrsim 3.8$ (which corresponds to the saturation value for $I_a = 0$), there is a value for $\gamma$ giving the best alignment. This optimum is shown by the straight line of equation $\gamma_{\text{opt}} \approx 7\zeta + 21$. On this optimum line, $\max_t(\cos^2 \theta)$ approaches exponentially 1 as $1 - ae^{-b\sqrt{\zeta + c\zeta}}$, with $a \approx 0.20$, $b \approx 1.2$, and $c \approx 0.053$. Larger values of $\gamma$ are shown to give a slightly smaller degree of alignment, that can be considered as practically constant (for not too large values of $\gamma$). One can improve the degree of alignment as much as desired by increasing $\zeta$ and $\gamma$ in the direction of the straight line. For a chosen $\zeta$, mainly responsible of the ionization, one has to take the intensity as low as possible by choosing the largest duration satisfying the impulsive regime.

Instead of a single kick, one can use a train of kicks centered at the rotational periods. The adiabatic ramp intensity has to be adapted in this case to $\gamma_{\text{opt}} = 7 \sum \zeta + 21$, i.e. to the sum of the $\zeta$'s of the kicks.

We have checked that this strategy can be extended for non-cold molecules. In this case, the contour plot of Fig. 2 has the same qualitative features. As expected, a similar degree of alignment requires higher $\zeta$ and $\gamma$ for higher temperatures. The line $\gamma_{\text{opt}}(\zeta)$ from where on the efficiency is optimal is of larger slope and larger ordinate at origin for larger temperatures. Even when the optimum cannot be reached in practice, we already obtain high degrees of alignment. For instance, for the normalized temperature $kT/B = 50$, with even $J$ considered in the thermal distribution (corresponding to $T \approx 30$ K for the CO$_2$ molecule), we obtain the unprecedent degree of alignment $\max_t(\cos^2 \theta) \approx 0.945$ for $\zeta = 22$ and $\gamma = 568$ in the impulsive regime (corresponding to non-destructive intensities $I_a \approx 10$ TW/cm$^2$ and $I_b \approx 50$ TW/cm$^2$ with $\tau_b = 200$ fs for the CO$_2$ molecule, see below the small correction to the degree of alignment when the impulsive approximation is not considered). Other initial thermal distributions lead to similar degrees of alignment, which implies that our strategy is applicable to a wide range of molecules and temperatures.

In practice we have to consider the short pulse with a finite duration and thus to quantify its effect on the degree of alignment with respect to the ideal impulsive approximation. In general, deviations from the impulsive regime at a given fluence reduce the degree of alignment. In the conditions of the upper frame of Fig. 1 (but not in the impulsive approximation), we have calculated the maximum degrees of alignment $\max_t(\cos^2 \theta) \approx 0.988$ and $\max_t(\cos^2 \theta) \approx 0.991$ for respectively $\tau_{\text{FWHM}} = 0.005 T_{\text{rot}}$ and $\tau_{\text{FWHM}} = 0.0025 T_{\text{rot}}$ (corresponding respectively to $\tau_{\text{FWHM}} = 200$ fs and $\tau_{\text{FWHM}} = 100$ fs for the CO$_2$ molecule). In these cases, the maximum degree of alignment is very close to $\max_t(\cos^2 \theta) \approx 0.993$ obtained in the impulsive regime. The degree of alignment will be more reduced with respect to the one obtained in the impulsive approximation for higher temperature, since the impulsive regime will be more difficult to be satisfied for initial conditions with higher $J$.

![FIG. 2: (Color online) Contour plot of $\log(1 - \max_t(\cos^2 \theta))$ as a function of $\zeta$ (in the impulsive approximation) and $\gamma$ for temperature $T = 0$. The straight line corresponds to the value of $\gamma$ that gives the maximum alignment for a given $\zeta$ (which exists only for $\zeta \gtrsim 3.8$).](image)

![FIG. 3: (Color online) Contour plot of $\log(1 - \max_t(\cos^2 \theta))$ as a function of the normalized duration of the ramp $\tau_a/T_{\text{rot}}$ and $\gamma$ for temperature $T = 0$ and $\zeta = 11$ (in the impulsive approximation). The straight dashed line corresponds to the adiabatic regime in the conditions of the optimum straight line of Fig. 2. The “x” and the “+”, located at $\tau_a \approx T_{\text{rot}}/4$ (for both) and respectively $\gamma = 142$, $\gamma = 297$, indicate examples of very high degrees of alignment (respectively $\max_t(\cos^2 \theta) \approx 0.994$ and $\max_t(\cos^2 \theta) \approx 0.995$) for a ramp of reduced duration with respect to an adiabatic ramp.](image)
In a next step, we study the deviations from the strict adiabatic limit for the ramp. Figure 3 shows that they lead to a an oscillating maximum of alignment from $\tau_a \sim T_{rot}/4$ up to the adiabatic regime. Specific ramp of intensities $\gamma$ and durations $\tau_a$ (as the ones indicated in Fig. 3) can thus be found to induce the same degree of alignment as in the completely adiabatic case (or even very slightly improving it). As will be shown, this will benefit its practical implementation. We have found that the duration of the ramp can be shortened, allowing the dynamics to be non-adiabatic with respect to the transition $J = 0/J = 2$, while approximately keeping adiabaticity with respect to the upper transitions. This strategy, that we will refer to as a combined partially-adiabatic impulsive strategy, allows one to reach a target state of higher dimension (thus of shorter duration) with respect to the strategy using a strict adiabatic ramp. We have indeed obtained $|\langle \psi_{N=16} | \phi(t_{\text{max}}) \rangle|^2 \approx 0.98$ and $|\langle \psi_{N=17} | \phi(t_{\text{max}}) \rangle|^2 \approx 0.99$ in the conditions marked in Fig. 3 respectively by “x” and “+”. This combined partially-adiabatic impulsive strategy is less robust with respect to the ramp shape, amplitude and duration as shown in Fig. 3. But, we have checked that it is quite robust with respect to the temperature, since it involves thermal initial conditions of preserved adiabaticity with $J > 2$. Figure 3 keeps indeed the same features when a moderate temperature is considered.

No better alignment has been found by varying other parameters (except of course the fluence of the short pulse, which is kept fixed).

Practical generation of such pulses could be done directly by applying a short pulse right afterward a truncated adiabatic pulse. Such truncated adiabatic pulses, as produced in Ref. [10], remain however of quite low intensity with the current technology. An alternative implementation that can be achieved with state-of-the-art technology consists in spectrally shaping the phase and the amplitude of a femtosecond laser pulse. Optimization based on spectral phase shaping has been already shown to enhance the degree of alignment of the O$_2$ and N$_2$ molecules [5, 12]. The main feature resulting from this optimization procedure is roughly a sigmoidal phase shape that corresponds approximately in the time domain to a ramp followed by a kick. Making the ramp adiabatic or partially adiabatic, as prescribed above, for a wide range of molecules will require in general to shape both spectral phase and amplitude of an intense femtosecond laser pulse. We emphasize that a partially adiabatic ramp, of duration shorter than for the adiabatic ramp, is of practical interest in such a shaping technique, since it will be easier to produce from a femtosecond laser. Figure 4 describes such a shaping to implement the partially adiabatic ramp followed by the kick in the conditions of the point marked by “x” in Fig. 3 for the CO$_2$ molecule. We have chosen here a Gaussian ramp (of full width at half maximum $\tau_a = 10$ ps and peak intensity $I_a = 2.5$ TW/cm$^2$) and a short pulse (of full width at half maximum $\tau_k = 200$ fs and peak intensity $I_k = 25$ TW/cm$^2$) arriving at the maximum of the Gaussian ramp. Figure 4 shows the corresponding spectral amplitude and phase, respectively denoted $A(\omega)$ and $\phi(\omega)$, and defined through the complex field $E_0(t) = A(t)e^{i\phi(t)}$. Here $\phi(t)$ is the instantaneous phase, which can be averaged since the corresponding instantaneous frequency $d\phi/dt$ is high with respect to the rotational frequency. These spectral parameters can be generated for instance from a Gaussian Fourier transform limited pulse (i.e. corresponding to $\phi(\omega) = 0$), centered at 800 nm with a full width at half maximum of 200 fs, shaped in phase and amplitude using a spatial light modulators with 640 pixels [13, 14]. The field generated taking into account the pixelization of the device is displayed in the lower frame of Fig. 4. We estimate that the initial energy required is about 5 mJ and that the pulse should be focalized on 20 $\mu$m. With this field, we obtain the expected value $\langle \Delta \theta^2 \rangle = 0.992$ in the CO$_2$ molecule at $T = 0$ with the complete model (i.e. without considering the impulsive approximation and taking into account the centrifugal distortion). A rough estimation of the ionization probability, using the techniques described in Ref. [13], gives in this case $P_{\text{ion}} \lesssim 10^{-4}$. We obtain with the complete model $\langle \cos^2 \theta \rangle \approx 0.915$ for the CO$_2$ molecule at $T = 30$ K using $I_a = 10$ TW/cm$^2$ and $I_k = 50$ TW/cm$^2$. 

![FIG. 4: Tailored spectral amplitude $A$ (upper frame, full line) and phase $\phi$ (middle frame) from an initial 200 fs Fourier transform limited pulse (upper frame, dashed line) to generate the required field amplitude (lower frame) with $I_k = 25$ TW/cm$^2$, $\tau_k = 200$ fs ($\zeta \approx 11$), $I_a = 2.5$ TW/cm$^2$ ($\gamma \approx 142$) and $\tau_a = 10$ ps ($\tau_a \approx T_{rot}/4$).](image-url)
corresponding to $P_{\text{ion}} \lesssim 5 \times 10^{-3}$.

In conclusion, we have presented a strategy combining an adiabatic ramp with an impulsive laser field yielding unprecedented efficiency for the degree of alignment using non-destructive fields. This strategy can be extended to orient polar molecules. We can use an adiabatic ramp of an electric field followed by a Half cycle pulse (HCP). The ramp can be in practice generated for instance by using the tail of the subsequent HCP itself, or better, by stretching another HCP. We obtain $\max_t \langle \cos \theta \rangle \approx 0.95$ at $T = 0$ with a HCP of peak amplitude 140 kV/cm and of full width at half maximum $\tau_k = 1$ ps, and a ramp of amplitude 2 kV/cm and duration $\tau_a = 18$ ps for the KCl molecule ($T_{\text{rot}} = 128$ ps). The implementation of this strategy with hybrid pulses (i.e. combining a laser and an electric field [16]) would allow the enhancement of the orientation. Such a strategy can also be applied to enhance 1-dimensional and 3-dimensional alignment (using shaped elliptical pulses for instance) of asymmetric tops.

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