



Controlling the orientation of polar molecules by half-cycle pulses

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Abstract

We study the quantum dynamics of a linear polar molecule subjected to electromagnetic pulses. For a sequence of half-cycle pulses we derive, from a simplified analytical model, conditions to induce a molecular orientation sustainable for hundreds of picoseconds. The predictions are confirmed by full numerical calculations for the molecule NaI. Analyzing the effect of finite temperatures we conclude that the process of maintaining the molecular orientation is robust to the thermal average.

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1. Introduction

Orienting molecules in a controlled manner is essential for a wide variety of applications. For instance, most chemical reactions depend on the relative orientations of the reactants [1,2]. Molecular orientation triggered by lasers is also important for laser-induced isomerization [3], molecular trapping [4], catalysis [5], high-order harmonic generation [6] and for nanoscale design by laser focusing of molecular beams [4].

There are various ways for inducing an orientation or an alignment of molecules by the aid

of static or time-dependent electromagnetic fields [6–12]. In particular, it has been shown recently that half-cycle pulses (HCPs) can induce molecular orientation or alignment without disturbing the electronic and vibrational modes [9,10,12]. Turning off the pulse the molecule remains oriented [9–11]. However, following previous schemes the achieved molecular orientation is then maintained for a few picoseconds only. In general, the molecule oscillates between the different rotational eigenstates and the time average (over a rotational period of the molecule) is zero [6–11].

In the present work we propose a scheme for maintaining the molecular orientation up to hundreds of picoseconds. This is accomplished by applying an appropriately designed train of ultra-short HCPs. The parameters of the pulse sequence are provided by a simplified analytical model that

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serves as a qualitative guide for full numerical calculations based on the exact solution of the time-dependent Schrödinger equation. We show furthermore that molecular orientation can be induced and maintained at finite temperatures.

2. Theory

We consider a diatomic molecule in the electronic ground state. The molecule which is assumed to have a relatively large permanent dipole moment and a large moment of inertia is subjected to a conveniently designed train of ultrashort HCPs. Present techniques deliver HCPs with a peak field of several hundreds of kV/cm and a duration in the subpicosecond regime [13]. Unipolar pulses as short as 0.1 fs and with intensities up to 10^{16} W/cm² may be available in the near future [14]. Furthermore, sampling and creating trains of ultrashort HCPs is already feasible [15,16]. For the purpose of the present study the HCPs have a duration of 1 ps (which is much shorter than the rotational period of the molecules under study) and peak amplitudes of up to 200 kV/cm (i.e., the pulses are too weak to damage the molecule). As shown in [9], HCPs with such characteristics induce no vibrational excitation. Under these circumstances the problem can be accurately described within the rigid-rotor and the impulsive approximations [8–10]. Specifically, the time-evolution of the molecule exposed to a train of linearly polarized HCPs is governed by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(\theta, \phi, t)}{\partial t} = \left[\frac{L^2}{2I} - \mu_0 V(t) \cos(\theta) \right] \Psi(\theta, \phi, t), \quad (1)$$

where $I = mR_0^2$ is the moment of inertia at the internuclear equilibrium distance R_0 and m is the reduced mass of the nuclei. L stands for the angular momentum operator, μ_0 is the permanent dipole moment, and θ (ϕ) specifies the polar (azimuthal) angle between the molecular axis and the applied field. The time-dependent shape $V(t)$ of the HCPs train is modelled, within the impulsive approximation, by series of N consecutive *kicks*, i.e.,

$$V(t) = \sum_{k=1}^N \Delta p_k \delta(t - t_k). \quad (2)$$

Here t_k is the time at which the k th pulse is applied and Δp_k is the area beneath the k th pulse. Physically, Δp_k is the momentum transferred by the k th pulse to the molecule.

In the case of a linearly polarized field the magnetic quantum number M_J , associated with the projection of the angular momentum along the polarization axis is conserved. Thus, the wave function describing the system can be approximated by a finite expansion using a basis of stationary eigenstates as follows:

$$|\Psi_M(t)\rangle = \sum_{J=0}^{J_{\max}} C_{J,M}(t) |J, M\rangle, \quad (3)$$

where M is the initial value of M_J . The angular momentum states $|J, M\rangle$ are represented by the spherical harmonics $Y_{J,M}(\theta, \phi)$. In Eq. (3) J_{\max} refers to the highest eigenstate that participates when the system evolves. Upon substituting Eq. (3) into Eq. (1) and after the time integration, we find the following stroboscopic map from $t = t_k$ to $t = t_{k+1}$:

$$\mathbf{C}_M^{(k+1)} = e^{i(\mu_0 \Delta p_k / \hbar) \mathbf{U}_M} e^{(-i/\hbar) \mathbf{E}_M (t_{k+1} - t_k)} \mathbf{C}_M^{(k)}, \quad (4)$$

where we have used $\mathbf{C}_M^{(n)} = \mathbf{C}_M(t_n)$ and the initial condition $\mathbf{C}_M^{(0)} = \mathbf{C}_M(t = 0)$. In Eq. (4) $\mathbf{C}_M(t)$ is the vector $\mathbf{C}_M(t) = (C_{0,M}(t), C_{1,M}(t), \dots, C_{J_{\max},M}(t))^T$, \mathbf{U}_M is a matrix whose components are given by $U_{JM,J'M} = \langle J, M | \cos \theta | J', M \rangle$, and $\mathbf{E}_M = \text{diag}(E_{0,M}, E_{1,M}, \dots, E_{J_{\max},M})$ [with $E_{J,M}$ being the eigenenergies]. The stroboscopic description of the evolution of the wave function given by Eq. (4) can be complemented with a continuous propagation between consecutive pulses (or *kicks*). Since between consecutive *kicks* the system propagates in a field-free fashion, one can describe the dynamics of the system in the time intervals $t_k \leq t < t_{k+1}$ through the relation

$$\mathbf{C}_M(t) = e^{(-i/\hbar) \mathbf{E}_M (t - t_k)} \mathbf{C}_M^{(k)}; \quad t_k \leq t < t_{k+1}. \quad (5)$$

The all-time description of the system is then obtained by alternating Eqs. (4) and (5). Once the wave function of the system has been computed, the degree of orientation of the molecule can be characterized by monitoring the expectation value

$$\langle \cos \theta \rangle_M(t) = \langle \Psi_M(t) | \cos \theta | \Psi_M(t) \rangle. \quad (6)$$

Complementary we inspect the time-dependent angular distribution of the probability density

$$P_M(\theta, t) = \int_0^{2\pi} |\Psi_M(\theta, \phi, t)|^2 d\phi. \quad (7)$$

Perfect orientation is achieved when $\langle \cos \theta \rangle_M(t) \in [-1, 1]$ acquires its extremal values.

The analysis above was made under the assumption that the unperturbed molecule resides initially in a specific eigenstate of the field-free system. For non-zero temperatures, however, one has to consider the thermal average of the orientation, which (for low temperatures) is given by

$$\langle \langle \cos \theta \rangle \rangle(t) = Z^{-1} \sum_{J=0}^{J_{\max}} P(J) \sum_{M_J=-J}^J \langle \cos \theta \rangle_{M_J}(t). \quad (8)$$

Here $P(J) = \exp[(-BJ(J+1)/k_B T)]$ is the Boltzmann distribution function associated with the rotational states, $Z = \sum_{J=0}^{J_{\max}} (2J+1)P(J)$ is the partition function, T is the temperature, k_B is the Boltzmann constant, and $B = \hbar^2/(2I)$ is the rotational constant of the molecule.

3. Calculation details

The expansion coefficients defining the wave function (Eq. (3)) are obtained from Eq. (5) between consecutive pulses and through the matching conditions in Eq. (4) at the times of applying the pulses. Once the wave function has been calculated, the quantities characterizing the molecular orientation are then computed from Eqs. (6)–(8). The highest relevant value J_{\max} of J is inferred when $\sum_{J=0}^{J_{\max}} \sum_{M_J=-J}^J |C_{J,M}|^2 \approx 1$ is achieved, which signifies that quantum states beyond J_{\max} are irrelevant.

As an example, we consider in this work NaI molecules. NaI is a polar molecule with a large moment of inertia (the rotational constant is $B \approx 0.12 \text{ cm}^{-1}$) and a permanent dipole $\mu_0 = 9.2 \text{ D}$. The large rotational period $\tau_{\text{rot}} = 138 \text{ ps}$ of NaI as compared to the applied pulse durations (1 ps) justifies the sudden approximation (Eq. (2)) used throughout the calculations. For the calculation of the pulse areas Δp_k we utilize sine-square HCPs (as

in [10]) with peak amplitudes up to 200 kV/cm and a duration of 1 ps. We use a maximum ratio of 1/10 between the pulse durations and the delay time of consecutive pulses [17].

4. Qualitative considerations

Applying an ultrashort HCP creates a wave packet formed by the different rotational eigenstates of the molecule. The molecule starts then to orientate in the direction of the applied field until it reaches its maximum orientation. Due to the large moment of inertia of the molecule, once the maximum orientation is reached, the molecule reverses its rotational motion and, after a process of alignment, it orientates in the opposite direction. This process is repeated periodically because, upon turning-off the pulse, the molecule evolves in a field-free fashion and a molecular orientation is only achieved at time intervals in the vicinity of the times at which the optimal orientation is reached. Hence, within the single pulse scheme, the molecular orientation is not stable and its average over a rotational period is zero. The situation changes, however, if a second HCP is applied when the molecule, after reaching its maximum orientation, starts to reverse its rotational motion. If the second pulse is sufficiently strong it induces a new reversal in the motion of the rotational wave packet and the molecule will return to its maximum orientation. If this procedure is iterated by applying an appropriately designed train of HCPs the molecule is expected to remain oriented, oscillating around its maximum orientation. This intuitive physical picture leads us to the following proposal. Applying, at first, auxiliary pulses induces an orientation which is maintained by a subsequent periodic train of HCPs.

The essential question is how to determine the appropriate parameters of the pulses. For this reason we analyze at first a simplified analytical model that is capable of producing analytical predictions of the laser parameters and then test these predictions by full-fledged numerical calculations. The analytical model consists of assuming that only the two lowest eigenstates participate in the evolution of the system. This two-level

approximation (TLSA) is certainly not appropriate for arbitrary pulse parameters. However, as shown below, it gives rough estimation in terms of simple analytical expressions for the pulse parameters that optimize the molecular orientation. Using the TLSA we introduce the Bloch vector \mathbf{B} with components $B_i = \mathbf{C}_M^i \sigma_i \mathbf{C}_M$, where σ_i represent the Pauli matrices ($i = x, y, z$). The evolution of the system is then described by alternating field-free and field-induced rotations of the real vector \mathbf{B} . From the geometrical interpretation of the Bloch vector \mathbf{B} one can find the pulse parameters of field-induced rotations that leave quasi-invariant the Bloch vector corresponding to the optimal molecular orientation. In the Bloch space the field-free evolution of the system between the pulses is given by rotating \mathbf{B} anticlockwise by an angle $\alpha = 2\pi t / \tau_{\text{rot}}$ round the z axis, while the action of each pulse amounts to rotating anticlockwise by an angle $\beta = 2\mu_0 \Delta p_k / \sqrt{3}\hbar$ round the x axis. The molecule in its initial ground state is represented by the vector $(0,0,1)$ [note that this vector is invariant under rotations round the z axis, i.e., it is a stationary state]. The maximum orientation of the molecule within the TLSA ($\langle \cos \theta \rangle = 1/\sqrt{3}$) corresponds to the Bloch vector $(1,0,0)$. The first pulse applied at $t = t_1$ induces a rotation of \mathbf{B} around the x axis. If the angle β of the pulse-induced rotation is $\beta = (2n + (1/2))\pi$ ($n \in \mathbb{Z}$), then after the pulse the vector \mathbf{B} will be given by $(0,-1,0)$. After the

subsequent field-free motion of the molecule during a time delay $t_2 - t_1 = (\tau_{\text{rot}}/4) + \gamma$ ($\gamma \ll \tau_{\text{rot}}/4$), the Bloch vector evolves to the position 1 in Fig. 1a, i.e., to a well oriented state. Once the vector \mathbf{B} reaches the position 1 at $t = t_2$, a second pulse with parameters such that $\beta = (2n + 1)\pi$ is applied rotating the Bloch vector round the x axis to position 2 in Fig. 1a. Then the system is left to evolve in a field-free fashion until it returns to the position 1 [see Fig. 1a] at $t = t_3 = t_2 + 2\gamma$. If this procedure is iterated the Bloch vector will remain oscillating between positions 1 and 2, maintaining the orientation of the molecule. This considerations lead us to the following procedure for inducing and maintaining the orientation of a molecule residing initially in its rotational ground state: one applies, at first, an auxiliary pulse with a peak amplitude that provides the kick $\Delta p_1 = \sqrt{3}\hbar\pi/4\mu_0$. After a subsequent time delay $t_2 - t_1 = (\tau_{\text{rot}}/4) + \gamma$ ($\gamma \ll \tau_{\text{rot}}/4$), a periodic train of HCPs is applied with a period $\tau_p \approx 2\gamma$ and with each pulse having twice the area of the auxiliary pulse.

5. Results

As evident from Fig. 1b, the TLSA (solid line) can not reproduce quantitatively the full dynamics of the system (dashed line), but qualitatively it is

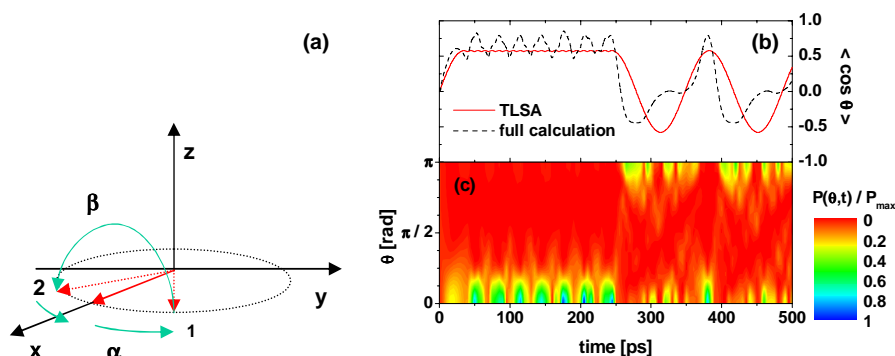


Fig. 1. (a) Geometrical interpretation of the orientation scheme (see text for details). (b) Time dependence of the orientation quantity $\langle \cos \theta \rangle$ for a pulse width of 1 ps and for the pulse parameters as derived from the TLSA (for optimal orientation) [$t_1 = 0$, $t_2 = 39.5$ ps, $t_k = t_2 + (k - 2)\tau_p$, $\tau_p = 10$ ps, $F_1 = 93.5$ kV/cm, and $F_k = 187$ kV/cm ($k \geq 2$)]. Solid (dashed) curve is the result of the TLSA (full numerical calculations). (c) Numerically exact angular distribution of the probability density $P(\theta, t)$ normalized to its maximum value P_{max} as a function of time and θ obtained with the same pulse parameters as in (b).

useful to locate the appropriate parameter space for inducing and maintaining molecular orientation. E.g., using the predictions of the TLSA, we deduce from Fig. 1b, that the application of an appropriate train of pulses leads to a long-time stabilization of the molecular orientation. It is also notable from Fig. 1b that the inclusion of higher levels (as done in the full calculation) can increase the molecular orientation. For an overall understanding we show in Fig. 1c the angular and time-resolved probability density $P(\theta, t)$ normalized to its maximum value P_{\max} . Before switching on the first pulse ($t < 0$), the angular distribution is isotropic (i.e., there is no orientation). Upon applying the first and the second pulses the angular distribution of $P(\theta, t)$ is well localized around $\theta = 0$; for $\theta > \pi/4$ there is hardly a probability density. This situation of strong orientation is maintained until $\tau_f \approx 250$ ps, when the train of HCPs is turned off. The subsequent evolution of the system occurs in a field-free manner with the rotational period of the molecule, passing from post-pulses alignment features in which the probability density is well packed simultaneously around $\theta = 0$ and $\theta = \pi$ [cf. Fig. 1c], and reaching again a strong orientation at $t \approx \tau_f + \tau_{\text{rot}}$. We remark that within the proposed scheme the orientation can be sustained as long as the duration of the applied train of pulses, one can therefore control the time the molecular orientation lasts by appropriately designing the sequence of HCPs.

It is worth noting that the molecular orientation displayed in Figs. 1b and c can be considered rather strong and stable if compared to previous schemes (e.g., [7–11]). On the other hand, as clear from Fig. 1b, the full numerical results indicate the possibility of achieving even stronger orientation when the complete spectrum is included in the treatment.

In general, the strength of the alignment or the orientation decreases drastically with increasing temperatures [8,9,11]. The results of the full numerical calculations are shown in Fig. 2 for $T = 2$ and 10 K. The parameters for pulses provided by the TLSA [see the caption of Fig. 1b] were used with the exception of the time delay between the first kick and the train of pulses that we have changed to the value $t_2 = 10$ ps, since with in-

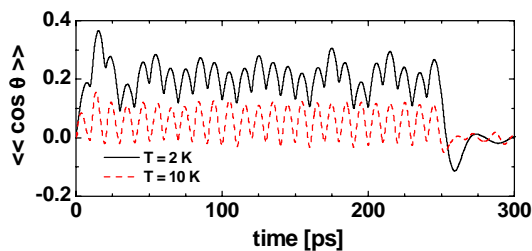


Fig. 2. Thermally averaged orientation ($\langle\langle\cos\theta\rangle\rangle$) as a function of time for $T = 2$ K (solid line) and $T = 10$ K (dashed line). HCPs were applied at times $t_l = (l - 1)\tau_p$ ($\tau_p = 10$ ps, $l \geq 1$) with same pulse strengths as in Fig. 1b.

creasing the temperature the molecule reaches its maximum orientation faster. Results depicted in Fig. 2 show that, within our scheme, molecular orientation can be achieved and maintained even at finite but low temperatures. Since the TLSA provides a useful qualitative picture of the system only at $T \approx 0$ K, the pulse parameters predicted by this model are not expected to be the optimal ones at yet higher temperatures. In this case, to find the optimal HCP pulse parameters for inducing significant molecular orientation we are developing a full numerical optimization procedure. Nevertheless, as the destruction of the molecular interaction at high temperatures is mainly due to the inclusion of a large number of states with different magnetic quantum numbers in the thermal average, one can expect that to achieve strong and sustainable molecular orientation at room temperature a train of elliptically polarized HCPs will be in principle required since linearly polarized pulses are unable to drive the azimuthal motion of the molecular axis.

6. Conclusions

An appropriately designed train of HCPs can induce a molecular orientation that can be sustained and stabilized for a long-time period. The pulse parameters for this process are derivable from a simplified analytical model. It is further shown that the molecular orientation is robust to thermal average.

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