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Biologically inspired molecular machines driven by light. Optimal control of a unidirectional rotor

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Abstract. We investigate the extent to which unidirectional intramolecular torsional motion can be created in an oriented bicyclic model system driven solely by laser light. We apply the machinery of quantum control via specifically tailored laser pulses to induce such motion, eliminating the need for the thermally constrained steps conventionally used in molecular motor systems. Our approach does not rely on specific details of the potential surfaces to create a preferred direction. Rather, we use matter–field interaction and the tools of coherent optimal control to create a wave packet with nonzero angular momentum among unbound torsional states on an excited electronic surface. Analysis of the results of the control algorithm provides general insight into when and how optimal control theory can find solutions that could not be generated through simple intuitive schemes. We find that, under constrained polarization, the control algorithm reduces to a simple intuitive coherent control strategy wherein a first IR pulse creates a non-stationary wave packet on the ground surface and a subsequent UV pulse transfers it to the excited state. Allowing for polarization shaping, however, we find new control routes that go beyond the intuitive scheme.

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1. Introduction

The development of molecular machines has grown, during the past two decades, into an active and diverse subdiscipline of nanoscience. The understanding of natural molecular mechanical motions has inspired researchers in chemistry, physics and materials science to create synthetic systems with similar capabilities with the goal of assembling complex machines from molecular components. Artificial nanoscale devices have taken the form of molecular switches [1], propellers [2], muscles [3], gears [4], shuttles [5] and rotors [6], to name but a few of many imaginative examples (for a comprehensive monograph, see [7]).

Conventional molecular machines are driven incoherently, as an ensemble, for instance by changes in temperature [8], pH-value [9], redox potential [10] or light [11]–[13]. The more recent literature on current-driven dynamics in molecular-scale electronics [14]–[18], has illustrated the possibility of driving molecular machines individually, on a single device level, in the dry state. Here coherence is maintained (in the complete electronic + vibrational space) but the opportunities for control are limited, as the driving force is electronic. Together, the early research on incoherently driven, light-triggered molecular rotors [11]–[13] and the recent work on individually addressed, current-driven molecular machines in junctions [14]–[18] suggest the application of control theory to drive molecular motors with coherent light.

The latter field, the control of molecular systems with coherent light sources, has been extensively reviewed [19]–[28] and is well understood. Concepts and techniques of coherent control have been applied to problems as diverse as atomic physics and gas-phase molecular dynamics, solid-state physics and semiconductor device technology, solution chemistry and biology. Underlying the success of coherent control is the understanding that the coherence properties of laser light can be imprinted on the quantum state of the system through the light–matter interaction, along with the development of light sources that allow precise control over the spectral composition and phase properties of the electromagnetic field.

Among coherent control approaches, optimal control theory (OCT), wherein a systematic procedure is employed to determine the field properties that optimize a desired system observable, has been gaining increasing popularity. The success of this class of techniques owes to their rigorous theoretical understanding [24, 29, 30], the increasing power of computational
systems, and the advance of modern pulse shaping technologies [31]–[41]. The extent to which OCT can unravel control routes that could not be designed by simple intuitive schemes, however, has been a matter of controversy.

Here we apply OCT to develop a new form of molecular machines, one that marries the attractive features of conventional light-driven machines [42, 43] and individually triggered, current-driven machines [14]–[16], [18]. Specifically, we consider the problem of creating unidirectional intra-molecular rotation in a simple (but general) oriented model system, representing a class of biological molecules. A number of previous calculations have illustrated unidirectional torsion with short linear or circularly polarized pulses. Hoki et al [44, 45] show that linearly polarized pulses can be used to create unidirectional torsion in a chiral, randomly oriented system with an asymmetric ground state potential surface, via state ladder climbing, while circularly polarized pulses must be used to achieve the same effect in an oriented chiral molecule [44]. In these cases, the asymmetry of the potentials creates a preferred direction of motion. Yamaki et al [46] apply OCT to the same system to show that a single linearly polarized shaped pulse can make use of the asymmetries of both the ground and the excited state surfaces to drive unidirectional motion in either direction, and that the mechanism can be rationalized as a simple pump–dump process. An intuitive procedure based on a sequence of an IR and a UV unshaped pulses, with which wave packet localization on the ground surface is followed by projection onto the excited surface, was also shown to successfully achieve unidirectionality [47].

Our goal in the present work is three-fold. Firstly, we explore the possibility of using coherent control tools and concepts to drive sustained, unidirectional torsion in a symmetric system. Secondly, we ask to what extent OCT can devise control routes that go beyond intuitive schemes, rather than reduce to a simple pulse sequence that could have been guessed ahead of the optimization. Thirdly, and most interestingly, we illustrate the potential of polarization shaping as an efficient way of breaking symmetry and producing unidirectional motions.

As a simple but general model system we choose 1,1′-bicyclohexylidene (BCH). This simple olefin, shown in figure 1(a), is used as a 1D model of a class of much more complicated molecular rotors [6, 48, 49] (see figure 1(b)), that nonetheless shares their essential structural motives. Research in the field of conventional molecular machines has achieved intramolecular rotation in these systems through a series of steps consisting of a thermally induced inversion.
of helicity followed by a photochemically induced cis–trans-isomerization of the central C=C double bond. Our goal in the present contribution is to induce continuous unidirectional torsion in BCH coherently, solely through the interaction with a laser pulse. We are specifically interested in the case where the potential energy surfaces (PESs) and dipole moments along the torsional coordinate are totally symmetric. As in the experiments of [49, 50], our system is oriented and fixed onto a surface. Hence unidirectional motion induced in the molecular frame is not averaged out in the laboratory frame. We recognize the complexity of realistic molecules and hence begin our study with an ab initio calculation of the underlying PESs and dipole functions at a high level of the theory. Our calculations omit inter-nuclear vibrational motions and focus only on the torsional states of the ground and first excited state Hamiltonians.

In the following section, we first provide details of the electronic structure and spectroscopy of BCH and next outline our methods of time propagating the wavefunction and our control approaches. Section 3.1 examines the results of calculations performed with linear polarization alone. Finally, in section 3.2 we illustrate the potential of polarization optimization in this context. Our conclusions are summarized in the final section.

2. Model and methods

2.1. Model system. Spectroscopy and quantum chemistry

The nature of the electronically excited states of BCH has been the subject of discussion for several years, both experimentally [51]–[54] and theoretically [55]–[60]. Spectroscopically, one observes bands centered about 5.95 and 6.82 eV in the vapor phase [51], 5.95 and 6.32 eV in the crystalline phase [51] and 6.01 and 6.94 eV in n-pentane solution [52]. Whereas one strong absorption band may have been expected in the BCH UV-spectrum (corresponding to the π → π*-transition) [61], the appearance of two strong bands in the gas phase as well as in condensed phases is surprising. The π → π*-bands of the anti- and syn-isomers were numerically found identical [57]. Furthermore, the observation of two bands in the UV-spectrum of BCH crystal, where only the anti-isomer is present [51], rules out the possibility that the two π → π*-bands result from two different isomers that absorb at different energies. Whereas other possible valence excitation types have been proposed experimentally (σ → σ* [51] and π → (CH)₂π* [52]) and numerically (π → σ* [58]), the Rydberg nature of this band was illustrated only recently, first experimentally [54] and later numerically [59]. Its anomalous intensity was attributed to valence mixing [59] of the π → π*-state and the π, Rydberg manifold of states. A subsequent study provided a somewhat different explanation [60], based on calculation of both the π → π*-state and the first Rydberg (π → 3s_R) state within multiconfigurational complete active space self-consistent-field second-order perturbation theory in its multi-state version (MS-CASPT2). The main conclusion of [60] is that no valence mixing between the π → π*-state and the π → 3s_R-state occurs in the excited state wavefunctions. The π → π*-band origin is located beyond the vertical excitation energy of the Rydberg band. Thus, much of the apparent Rydberg intensity can be ascribed to the underlying, strongly absorbing valence-π → π*-band. Details can be found in [60].

In the present work we compute adiabatic PESs and transition and permanent dipole moments surfaces for the ground electronic state and the first excited electronic singlet state along the BCH torsional coordinate β, starting in the anti-BCH MP2/6-31G* equilibrium geometry (figures 2, 3), whereas the other coordinates are kept fixed at their equilibrium configurations. Our results are summarized in figure 4. The ground state potential (V₁) shows
minima at $\beta = 0$ (anti-conformation) and $\pi$ (syn-) with transition states at $\beta = \pi/2$ and $3\pi/4$. The first excited state ($V_2$) shows the opposite topology, with a barrier of about 25 kcal mol$^{-1}$ at $\beta = \pi$, while minima are observed for $\beta = \pi/2$ and $3\pi/4$. As determined in [60], at the anti-conformation using $C_{2h}$ symmetry conditions, $V_2$ has $\pi \rightarrow 3\pi_R$ character, while the $\pi \rightarrow \pi^*$ state is higher in energy ($V_3$). In calculations without symmetry considerations, both states mix and therefore the PESs for the $\pi \rightarrow 3\pi_R$ and $\pi \rightarrow \pi^*$ states show the same topological profile; accordingly, both states are bright. For simplicity, in this paper we have chosen the lowest-lying adiabatic state ($V_2$), assuming that the dynamical results would vary at most little if the $V_3$ state was chosen.

2.2. Eigenfunctions and eigenenergies

The torsional eigenfunctions and eigenenergies of BCH, \( \{ \Phi_\nu, E_\nu \} \), were computed by diagonalization of the field free torsional Hamiltonian

\[
\hat{H}(\beta) = \hat{T}(\beta) + \hat{V}(\beta) = \begin{pmatrix}
\frac{1}{2I_z} \frac{d^2}{d\beta^2} & 0 \\
0 & \frac{1}{2I_z} \frac{d^2}{d\beta^2}
\end{pmatrix} + \begin{pmatrix}
V_1(\beta) & 0 \\
0 & V_2(\beta)
\end{pmatrix},
\]

where \( \beta \) is the torsion angle, \( V_1 \) and \( V_2 \) are the \( S_0 \) and \( S_1 \) potential surfaces, respectively, \( I_z \) is the moment of inertia associated with the torsional motion,

\[
I_z = \sum_\alpha r_\alpha^2 m_\alpha,
\]

\[
r_\alpha = \sqrt{x_\alpha^2 + y_\alpha^2},
\]

and \( \alpha \) runs over the atoms (\( I_z = 1218.789.7374 \) a.u.). The eigenenergies and eigenfunctions were computed up to \( \{ E_i, \Phi_i \} \), \( i = 700 \) for the ground and excited states on a grid of 4096 points.

Several considerations regarding the symmetry of the system will prove useful. The torsion is symmetric with respect to \( \beta \rightarrow -\beta \) and \( \beta \rightarrow \pi - \beta \), but not with respect to \( \beta \rightarrow \pi/2 - \beta \). As a consequence, the minima in \( V_1 \) at \( \beta = 0 \) (anti-BCH) and \( \beta = \pi \) (syn-BCH) are not identical, the syn-conformation being about 87 cm\(^{-1}\) lower in energy than the anti-BCH. Due to their slightly different energies and curvatures, the ground state eigenfunctions \( \{ \Phi_\nu^1 \} \) are preferentially localized in one of the two minima. The excited state potential, \( V_2 \), by contrast, has a symmetric double-well structure and consequently the excited state eigenvalue spectrum is doubly degenerate.

Figures 5(a) and (b) show the energy eigenvalues \( \{ E_\nu^1 \} \) of the ground state Hamiltonian. Note that because the syn- and anti-BCH have different absolute energies, two of the eigenvalues of the syn-conformation are lower than the lowest anti eigenvalue (see figure 5(a)). In figure 5(b) the eigenvalues are sorted into syn and anti eigenvalues. Within each manifold, the linearity
in the vibrational index $\nu'$ indicates that the ground state eigenfunctions $\{\Phi_1^{\nu'}\}$ are essentially harmonic at low excitation.

Figure 6 displays the corresponding eigenfunctions $\{\Phi_1^{\nu'}\}$. As seen in figure 5(b), both wells are essentially harmonic in the vicinity of the minima, with harmonic frequencies of $\omega_0^{\text{syn}} = 51.95 \text{ cm}^{-1}$ and $\omega_0^{\text{anti}} = 66.20 \text{ cm}^{-1}$, calculated as the average respective level spacing of the first ten eigenvalues. These frequencies are extremely low, as would be expected for a torsion of this type, where a very stable carbon–carbon double bond is being forced out of planarity, and a large mass ($\sim 1.2 \times 10^6 a_0^2 \text{me}^2$) is moved. Consequently, the density of vibrational states is large, about 261 eV$^{-1}$. As has been found previously [57], the syn-isomer is the more stable of the two isomers, even on the unrelaxed PES. Syn-BCH ($C_{2v}$) and anti-BCH ($C_{2h}$) were optimized at the MP2/6-31G* level using the Gaussian03 [62] quantum chemical software. At 0 K, the ZPE-corrected values give the relative stability of syn-BCH as 7.56 meV. Energies of the PES for the syn- and anti-minima, corrected with $\frac{1}{2}\omega_0^{\text{syn}}$ and $\frac{1}{2}\omega_0^{\text{anti}}$, respectively, yield a value of 11.2 meV. For comparison, the value computed in [57] (MP2/6-311G** on a HF/6-31G geometry) is 2.21 meV. Harmonic frequencies were also calculated at the MP2/6-31G* level of theory, yielding $\omega_0^{\text{syn}} = 73.48 \text{ cm}^{-1}$ and $\omega_0^{\text{anti}} = 71.22 \text{ cm}^{-1}$. The discrepancy between the harmonic frequencies ($\omega_0$) and the frequencies arising from diagonalizing the PES ($\omega$) is larger for the syn conformation ($\sim 20 \text{ cm}^{-1}$) than for the anti ($\sim 5 \text{ cm}^{-1}$) because the geometry of the PES is not relaxed for the syn isomer.

Approximately 350 eigenvalues lie on each side of the barrier. Given the near harmonicity of the well, transitions between these levels obey the $\Delta \nu = \pm 1$ selection rule to a good approximation. Assuming an average energy spacing of about 50 cm$^{-1}$ for all the states under the barrier, one can calculate the period $T_p$ of the associated radiation as

$$T_p = \frac{1}{\omega} = \frac{1}{\omega_c} = 667.281 \text{ fs}.$$

Thus, relatively long times would be needed to climb up the torsional ladder and hence transition from one isomer to the other through a ladder climbing mechanism is unlikely, requiring of order 350 transitions. Equation (4) illustrates also the small likelihood of thermal isomerization by twist of a carbon–carbon double bond.
The lowest ten eigenvalues \( \{ E^{\nu}_{v} \} \) of the excited state Hamiltonian are plotted in figure 7, where the doublet structure is readily observed. As discussed above, the frequency is small in comparison with the barrier height, hence tunneling does not take place at the level of excitation of figure 7, the tunneling splitting is negligible and the degeneracy is nearly rigorous. Because the two corresponding eigenvectors, \( \Phi^{\nu}_{1} \) and \( \Phi^{\nu}_{2} \), span a subspace of the Hamiltonian with essentially equal energies, any linear superposition of these functions is likewise an eigenfunction of \( H \) with the same eigenvalue \( E^{\nu}_{1} \approx E^{\nu}_{2} \). Several examples are shown in figure 8. Of particular interest are the superpositions \( \phi_{\pm} \) and \( \phi_{\mp} \) (figures 8(e)–(h)),

\[
\phi_{\pm} = \frac{1}{\sqrt{2}} (\Phi^{\nu}_{1} \mp \Phi^{\nu}_{2}),
\]

because they are localized at the geometry of the ground state transition state connecting the syn- and anti-isomers. Similar to the ground state counterparts, the energies behave quasi-harmonically in the vicinity of the minima, with a level spacing of \( \sim 50 \text{ cm}^{-1} \).
In section 3.1 we use a grid representation of the operators. In this method, the position space ($\beta \in [0, 2\pi]$) and the momentum space ($p \in [-p_{\text{max}}, +p_{\text{max}}]$) are discretized into $N_p$ grid points on reciprocal grids, with $\Delta x = 2\pi/N_p$ and $p_{\text{max}} = \pi/N_p \Delta x$. A fast Fourier transform (FFT) is used to switch between the two spaces. The Hamilton matrix (equation (1)) is then diagonalized, yielding the eigenenergies $\{E_\nu\}$ and eigenfunctions $\{\Phi_\nu(\beta)\}$ directly expressed in the position grid.

A complementary representation of the system, which will be useful below, is in terms of the eigenstates of the Hamiltonian operator (equation (1)). To construct these states, we begin by defining a primitive basis as the eigenstates of the kinetic portion of equation (1), the particle-on-a-ring states $(1/\sqrt{2\pi}) e^{in\theta}, \ n = 0, \pm 1, \pm 2, \ldots \pm n_{\text{max}}$ with eigenenergies $E_n = \hbar^2 n^2/2I$ and periodicity $2\pi$. With this primitive basis, the kinetic energy operator is diagonal, and the potential matrix elements are readily evaluated analytically by expanding the potentials as Fourier series

$$V(\beta) = \sum_{b=1}^{b_{\text{max}}} a_b \sin \frac{b\beta}{2}$$

and using the relation

$$\frac{a_b}{2\pi} \int_0^{2\pi} e^{in\beta} \sin(b\beta/2) e^{im\beta} d\beta = \frac{a_b \times 4b}{2\pi(-4m^2 - 8nm - 4n^2 + b^2)}, \quad b = \text{odd},$$

$$= 0, \quad b = \text{even}.$$  

Diagonalizing the total Hamiltonian in the particle-on-a-ring basis, we obtain the stationary states of the system as

$$\Phi_\nu(\beta) = \sum_{n=-n_{\text{max}}}^{n_{\text{max}}} c_n^\nu e^{in\beta}.$$  

The time evolving wave packet is expanded in terms of the stationary eigenstates as

$$\Phi_{\text{total}}(\beta, t) = \sum_{\nu=0}^{\nu_{\text{max}}} d_\nu(t) \Phi_\nu(\beta),$$

where $\nu_{\text{max}}$ is the total number of stationary states in the superposition. In the calculations of section 3.2, $\nu_{\text{max}} = 81$, of which eight are in the ground electronic state and the remaining 73 in the excited state. This basis size was chosen by including only the states with enough amplitude around $\pi$ to have a significant overlap ($\geq 10^{-4}$) with the initial state, as these are the only states that will participate in the system dynamics. Clearly, this method yields the same observables and energy eigenvalues as the grid representation outlined above, but each representation lends itself to a different description of the OCT targets, as discussed in section 3.2.

2.3. Time-dependent nuclear dynamics

The time-dependent nuclear dynamics evolve the following time-dependent Schrödinger equation:

$$\frac{i}{\hbar} \frac{\partial}{\partial t} \begin{pmatrix} \Psi^1(\beta, t) \\ \Psi^2(\beta, t) \end{pmatrix} = \hat{H}(\beta, t) \begin{pmatrix} \Psi^1(\beta, t) \\ \Psi^2(\beta, t) \end{pmatrix},$$

where $|\Psi^1(\beta, t)|^2$ and $|\Psi^2(\beta, t)|^2$ represent the adiabatic populations on the ground and excited state surfaces, respectively. Assuming that the two states are not non-radiatively coupled, the complete Hamiltonian is

$$\hat{H}(\beta, t) = \begin{pmatrix} \frac{1}{2I} \frac{d^2}{d\beta^2} & 0 \\ 0 & \frac{1}{2I} \frac{d^2}{d\beta^2} \end{pmatrix} + \begin{pmatrix} V_1(\beta) & 0 \\ 0 & V_2(\beta) \end{pmatrix} - \begin{pmatrix} \mu_{11}(\beta) \cdot \vec{e}(t) \\ \mu_{12}(\beta) \cdot \vec{e}(t) \end{pmatrix} \begin{pmatrix} \mu_{12}(\beta) \cdot \vec{e}(t) \\ \mu_{22}(\beta) \cdot \vec{e}(t) \end{pmatrix},$$  

(12)

where $\vec{e}(t)$ is the electromagnetic field.

In section 3.1, equation (11) is integrated in time using the split operator method [63, 64], within which the time evolution operator is approximated as

$$e^{-i\hat{H} \Delta t} \approx e^{-i(\hat{T}/2) \Delta t} \cdot e^{-i\hat{V} \Delta t} \cdot e^{-i(\hat{T}/2) \Delta t},$$  

(13)

$\hat{V}$ being the complete potential operator (including the field–matter interaction). Attractive features of the method are its simplicity and the scaling of the error as the third order in the time step $\Delta t$. As above, the kinetic terms of the time evolution operator are evaluated by using the FFT to switch between position and momentum spaces.

In section 3.2, the state space-based wave packet of equation (10) is propagated via the fourth-order complex Runge–Kutta algorithm. The method has a local truncation error which is fourth order in $\Delta t$, and lends itself well to optimal control calculations with a target operator in state space. This can be important for calculations like those of section 3.2, as the level of convergence of the algorithm is much more strongly dependant on the precision of the integration than a simple time propagation.

2.4. Optimization of the laser pulse

Having developed potential energy and dipole moment curves in section 2.1 and explored the spectroscopic and dynamical properties in sections 2.2 and 2.3, respectively, we proceed in this subsection to introduce a unidirectional rotor based on BCH. To that end we apply OCT [65] to determine the pulse shape that will set BCH into sustained unidirectional torsion. Within this approach [65], the functional to be maximized is

$$J_0 = |\langle \Psi_i(T) | \phi_i(T) \rangle|^2 - \alpha_0(t) \int_0^T [\epsilon(t)]^2 \, dt - 2 \text{Re}[\langle \Psi_i(T) | \phi_i(T) \rangle]$$

$$\times \int_0^T \langle \Psi_i(t) | \frac{\partial}{\partial t} + i\hat{H}(t) | \phi_i(t) \rangle \, dt],$$  

(14)

where $\Psi_i(t)$ is the time-evolving wavefunction, $\Psi_i(0) = \psi_i(0)$ is the initial wavefunction, $\phi_i(T)$ is the target state at final time $T$ and $\alpha_0(t)$ is a parameter weighting the intensity. Requiring that $\delta J_0 = 0$ and exploiting the time invariance relation,

$$\langle \Psi_i(T) | \phi_i(T) \rangle = \langle \Psi_i(t) | \Psi_i(t) \rangle,$$  

(15)

4 Equivalently, $\hat{H}$ in the exponent can be split in the order $\hat{V}/2, \hat{T}$ and $\hat{V}/2$. 

one obtains a pair of differential equations for the time evolution of \( \Psi_1(t) \) and \( \Psi_1^f(t) \), which we solve iteratively, using the algorithm of [65]. We omit details of the method, as these are extensively discussed elsewhere in this issue, and note the specific parameters used in section 3.

3. Results

In this section we examine the possibility of inducing unidirectional torsion in the class of biological molecules represented here by their common BCH moiety using OCT. We ask also when and to what extent the results of OCT can be intuitively anticipated, that is, reduce to a simple, readily understood scheme. We begin, in section 3.1, by restricting the control algorithm to linear polarization. In section 3.2 we show that a more flexible approach, where the polarization is shaped, provides substantially more extensive control. The initial state for all propagations is the lowest torsional state of the ground Hamiltonian,

\[
\Psi(t = 0) = \left( \Phi_1^1 \right).
\]  

(16)

3.1. Linear polarization

In order to achieve unidirectional rotation on the excited state surface, the excited state wave packet needs to have torsional momentum of only one sign, positive or negative. Thus, a simple formulation of a target wavefunction for the OCT algorithm is obtained by fitting a Gaussian function to \( \Phi_1^1 \), and displacing it in momentum space to be centered about a momentum \( p_d \neq 0 \),

\[
\Phi_i(T) = \left( \frac{2}{\pi a^2} \right)^{1/4} \exp \left[ i \beta p_d - \left( \frac{\beta - \beta_0}{a} \right)^2 \right]
\]  

(17)

with

\[
\Psi_i(T) = \left( 0 \quad \Phi_i(T) \right).
\]  

(18)

Here we take the target wave packet center to be \( \beta_0 = \pi \) and its width to be 0.09 rad.

As discussed in [65], if the initial and target states are orthogonal to each other, there is a trivial, solution for the optimal field, namely \( \vec{e}(t) = 0 \). From equation (18) it is evident that \( \langle \Psi_i(t) | \Psi_i(t) \rangle = 0 \) at all times for the first iteration. Thus, for \( \vec{e}(t) = 0 \) subsequent iterations will not generate nonzero overlap. To circumvent this problem, we use a very weak nonzero initial field. The initial frequency does not necessarily have to be resonant with \( \Delta V_{2-1} = V_2(\pi) - V_1(\pi) = 0.228 E_h \), since it only needs to transfer some population from the ground to the excited state, producing a nonzero overlap that will generate a nonzero \( \vec{e}(t) \) solution in the course of the OCT iteration. The seeding pulse is taken to be of the form

\[
|\vec{e}(t)| = \epsilon_0 \sin(\omega_0 t),
\]  

(19)

where \( \omega_0 = 0.250 E_h \), and \( \epsilon_0 = 10^{-6} \) a.u., resulting in a population transfer of less than \( 10^{-6} \). Two different scenarios were simulated, a pure electronic transition and a vibronic transition.
3.1.1. Pure electronic transition. The length of the sought optimal pulse was set to 500 fs and the field was taken to be polarized along the X-axis. The target momentum was taken to be $p_d = 30.0 \hbar$, centered about $\beta = \pi$. No penalty function $\alpha_0$ or envelope was added to the field. The dotted curve in figure 9 shows the overlap of the target state $\Phi_f(T)$ and the function $\Psi^k_i(t)$ at iteration $k$ versus the iteration number, and tests the convergence behavior of the algorithm. The algorithm converges to an overlap of $\sim 65\%$ within ten iterations. The dotted curves in figures 10(a) and (b) show, respectively, the obtained field in the time domain, and the field-driven population transfer from the ground to the excited state. At the end of the pulse, almost the entire wave packet (> 99\%) is in the excited state. The Fourier transform of the pulse (not shown) illustrates how the pulse evolves from its initial value of 0.25$E_h$. As could have been expected, the frequency has shifted towards a central value resonant with the UV transition at $\beta = \pi$, with $\Delta V_{2-1} \sim 0.228E_h$. The spectrogram of the pulse shows no significant frequency chirp. The $\sim 65\%$ overlap of $\Psi_i$ and $\phi_i$ at the final time $T$ does not suffice for $\Psi_i$ to have the desired expectation value of the torsional momentum; only negligible torsional momentum is created in the excited state at the end of the 500 fs long pulse. This observation can be ascribed to the fact that the only nonzero transition dipole moment, $\vec{\mu}_{12}$ is symmetric about $\beta = \pi$. We show below that much better control is obtained when the permanent dipole moments are taken into account, and the pulse length is increased, to allow for more flexible dynamics.

3.1.2. Vibrational and electronic transition. We proceed by setting the pulse length to two picoseconds and including the nonzero components of the permanent dipole vector, $\vec{\mu}_{11}$ in equation (12). As in the previous simulation, a seed pulse with $\omega_0 = 0.250E_h$ and $\epsilon_0 = 10^{-6}$ a.u. is used as a trial pulse amplitude to couple the two electronic states. The target wavefunction is the same as above (see equation (17)). The solid curve in figure 9 illustrates the overlap element $\langle \phi_i(T) | \Psi^k_i(T) \rangle$ versus $k$, and serves to study the convergence properties of the algorithm. Convergence is reached after about 12 iterations, at which point the overlap element reaches $\sim 71.4\%$. The X- and Y-components of the optimized field are displayed in figure 10 (the field components

Figure 9. Convergence behavior of the OCT-algorithm, observed through the overlap of the target state $\Phi_f(T)$ and the wave packet at the $k$th iteration, $\Psi^k_i(t)$. The dotted curve corresponds to a constrained optimization, where only electronic transitions are included. The solid curve corresponds to an optimization where both electronic and vibrational transitions are involved.
Figure 10. (a) Optimal electric field. The dotted curve corresponds to a constrained optimization, where only electronic transitions are included (only the pulse envelope is shown). The solid and dashed curves give the $X$- and $Y$-components of the field resulting from an optimization where both electronic and vibrational transitions are involved. (b) Population transfer from the ground to the excited electronic state. The dotted and solid curves distinguish the two types of optimization as in part (a).

Figure 11. Fourier transform (FT) of the pulse shown in figure 10(a). (a) FT of the $X$-component, with the inset displaying the intensities of the very low frequencies. (b) FT of the $Y$-component.
Figure 12. Spectrograms of (a) $\epsilon_X(t)$ and (b) $\epsilon_Y(t)$ of figure 10. The former spectrogram has been divided into two different frequency regimes, so as to distinguish the low- and high-frequency components (cf figure 10(a)). For the low-frequency regime, a gating function of 1 ps FWHM was used to resolve the two low IR-frequencies. For the high-frequency regime, a shorter gating function (FWHM = 50 fs) was set, providing good resolution in the frequency and time domains. The left ordinate shows the frequency in $Eh$ and the right ordinate in cm$^{-1}$.

differ since they interact with differently structured dipole moment components (recall figure 4)). The Fourier transform again reveals one group of frequencies centered about $\Delta N_{2-1} = 0.228 Eh$. Interestingly, however, the OCT-algorithm has made use also of IR-transitions, as can be seen by the intensity peaks at very low frequencies in figure 11. With the pulse of figures 10(a) and (b), the expectation value of $\langle \Psi_i(T) | \hat{p}_z | \Psi_i(T) \rangle$ is 5.80 $\hbar$ after the 2 ps pulse, showing significant torsional momentum transfer to the excited state. The spectrograms of the $X$- and $Y$-components of the field are displayed in figure 12. The time/energy resolution of the spectrogram depends on the duration of the gating function. Since a Gaussian function has been used, this period is defined by its full-width at half-maximum (FWHM). Short gating functions resolve the pulse in time while smearing out the frequency information and vice versa.

Although figure 12 involves a tradeoff, it illustrates clearly that the low-frequency (IR) components peak strongly at early times, whereas the high-frequency (UV) components are nearly equally distributed over the pulse duration. Thus, the control algorithm reveals that (within the constraint of linear polarization) the best combination of fields to achieve unidirectional torsion consists of a short IR followed by a narrow band UV subpulse. The IR pulse populates a ground torsional wave packet, which the UV subpulse projects onto the
excited surface at an opportune instant, when the torsional wave packet has reached the turning point and the ground–excited overlap is optimized.

Furthermore, it is seen that the IR pulse duration is under \( \sim 800 \) fs. Considering that the IR frequencies are in the range of 40–200 cm\(^{-1}\), application of equation (4) shows that the pulse includes very few optical cycles, just one in the case of the lowest frequency (for 40 cm\(^{-1}\) \( T_p \sim 834 \) fs) and four in the highest. The optimal control algorithm thus confirms the usefulness of the IR + UV strategy, applied in the previous research to similar problems [47], [66]–[69]. In the next subsection, we ask to what extent and how could the pulse parameters be set intuitively, bypassing the optimization, to yield the same level of control. In section 3.2 we investigate the extent to which unconstrained (polarization shaping) OCT can generate new solutions, that significantly surpass those of intuitive schemes.

3.1.3. IR + UV strategy. The goal of the IR + UV strategy is to create torsional momentum in the ground state and then transfer it with an ultrashort (short with respect to torsional motions) pulse to the excited state. We use the same parameters as in the OCT calculations discussed in the previous subsection but with the target state on the electronic ground state,

\[
\Psi_f(T) = \left( \Phi_f(T) \quad 0 \right),
\]

where \( \Phi_f(T) \) is a Gaussian wavefunction (equation (17)) having 30.0 \( \hbar \) of initial torsional momentum, centered about \( \beta = \pi \). The field is linearly polarized and hence only the \( \vec{\mu}_{11} \) component of the dipole contributes to the field–matter interaction. In this case, the overlap \( \Psi_i(t) | \Psi_f(t) \) is not necessarily zero, because both functions belong to the same Hamiltonian, thus no seeding pulse is needed to start the algorithm. A period of 2 ps is simulated and no envelope function or weighting function is used. Inspecting the convergence behavior of the overlap, analogous to the discussion of the previous subsection, we find that the algorithm is able to increase the overlap up to \( \sim 87\% \), with the final wavefunction having a momentum expectation value of 18.00 \( \hbar \). The optimized field is a sinusoidal function, with a central feature of about 52.0 cm\(^{-1}\), as determined through Fourier transform of the final field. This result has been expected: the underlying mechanism is torsional ladder climbing, and in order to excite the \( \text{syn} \)-isomer, the pulse needs to be resonant with the level spacing around \( \beta = \pi \). These results confirm the conclusion of the previous subsection that, under the conditions of the constraint optimization considered, the best method to achieve sustained unidirectional torsion in BCH is the IR + UV strategy.

It remains to discover, however, how sensitive the results are to the parameters of an analytically constructed pulse. We thus proceed to examine the results of a pulse of the form

\[
\vec{\epsilon}(t) = E_{\text{IR}}(t) \cdot \vec{\epsilon}_Y + E_{\text{UV}}(t) \cdot \vec{\epsilon}_X.
\]

where

\[
E_j(t) = E_j^0 \cdot \sin (\omega_j t) \cdot s_j(t), \quad j = \text{IR, UV},
\]

and \( s_j(t) \) is an envelope function of duration \( t_p \). The parameters of the two pulses are chosen to satisfy the following conditions:

1. The IR frequency is resonant with the transitions in the \( \text{syn} \) configuration of the ground state, so that ladder climbing is facile (cf figure 5(b)), slope of the solid curve).
2. The IR-pulse duration allows only a few half-cycles.
3. $E^0_{\text{IR}}$ allows sufficient torsional momentum to be gained in the electronic ground state. In order to maintain comparable fluence while decreasing the pulse duration with respect to that of the OCT algorithm, we are required to increase the field amplitude.

4. The UV frequency is resonant with $\Delta V_{2-1}$ in the vicinity of $\beta = 0$.

5. The UV-pulse duration is chosen such that the expectation value of the torsional momentum $p^1_z(t)$ during the electronic transition remains close to its maximum $p^1_{z\text{max}} \sim 19.5\hbar$.

6. $E^0_{\text{UV}}$ is chosen so that population transfer is $>95\%$.

We find that these conditions are satisfied with the IR-laser parameters set to: $\omega_{\text{IR}} = 51.0 \text{ cm}^{-1} = 0.232 \times 10^{-3}E_h$, $E^0_{\text{IR}} = 4.0 \text{ GV m}^{-1}$, $t^\text{IR}_p = 1485 \text{ fs}$,

$$s_{\text{IR}}(t) = \begin{cases} \sin \left( \frac{\pi t}{t^\text{IR}_p} \right), & 0 \leq t \leq t^\text{IR}_p, \\ 0, & t > t^\text{IR}_p \end{cases}$$

and the UV-laser parameters to: $\omega_{\text{UV}} = 50000 \text{ cm}^{-1} = 0.228E_h$, $E^0_{\text{UV}} = 2.5 \text{ GV m}^{-1}$, $t^\text{UV}_p = 80 \text{ fs}$

$$s_{\text{UV}}(t) = \begin{cases} \sin \left( \frac{\pi t}{t^\text{UV}_p} \right), & 1675.0 \leq t \leq 1675.0 + t^\text{UV}_p, \\ 0, & t > 1675.0 + t^\text{UV}_p \end{cases}$$

Although we show below that the IR+UV pulse sequence induces the desired motion, the sensitivity to the precise detail of the pulse suggests the advantage of OCT.

Figure 13 summarizes the results obtained with the analytical pulse sequence of equation (21) (section 3.1.3). The laser pulse is depicted in panel (a). Panel (b) shows the oscillations in the expectation values of the torsional momenta $p_z(t)$ for the electronic ground and excited states. While for the former $p^1_z(t)$ oscillates around zero (solid curve), in the latter, once the UV-laser has triggered the electronic transition, $p^2_z(t)$ maintains a positive value (dashed curve), undergoing acceleration and deceleration depending on the slope of $V_2$ at the center of the wave packet. Panel (c) shows the evolution of the expectation value of the torsion angle, $\beta(t)$, in the ground (solid) and excited (dashed) states. A full rotation cannot be depicted in this representation, because $\beta$ spans the $0 \rightarrow 2\pi$ range. A complementary view of the same dynamics in thus provided in panel (d), which shows the probability density $|\Psi(t, \beta)|^2$ versus time and position.

An alternative way of describing the same driven torsional dynamics is in terms of the torsional eigenstates, as calculated in the previous section,

$$C^1_\nu(t) = \langle \Psi^1(t, \beta)|\Phi^1_\nu(\beta) \rangle$$

for the ground and

$$C^2_\nu(t) = \langle \Psi^2(t, \beta)|\Phi^2_\nu(\beta) \rangle$$

for the excited state, where the $\beta$-dependence has been integrated out. The square absolute value of these coefficients after turn off of the pulse is shown in figure 14. Whereas the ground state is dominated by the lowest few torsional components, the excited state torsional wave packet is centered about $\nu = 485$ and is broad, involving $\sim 20$ significantly populated states. Clear dominance of the odd components reflects our breaking of the symmetry of the two torsion senses. The need to determine the pulse parameters to high accuracy, however, limits the applicability of the method.
3.2. Polarization shaping

In this section we relax the constraint of linear polarization imposed in section 3.1 and allow the control algorithm to vary with time the polarization of the field to explore the potential advantage of polarization shaping. We remark that polarization shaping has been demonstrated in several experiments [41], [70]–[75].

To gain complementary insight into the controlled torsional dynamics, we perform the calculations in basis set space, rather than in grid space (see section 2.3). A target operator that

Figure 13. IR + UV strategy. (a) The laser pulse applied. (b) The expectation values of the torsional momentum in the ground and excited states. (c) The expectation values of the torsional angle in the ground and excited states. (d) The squared absolute value of $|\Psi(t, \beta)|^2$. After the UV pulse $>95\%$ of $|\Psi(t, \beta)|^2$ is in the excited state. Several cycles of the unidirectional rotation are shown, as the probability density exits and re-enters the periodic boundaries in the direction $2\pi \rightarrow 0$ at times $t \sim 2$ ps and $t \sim 3.1$ ps.

Figure 14. Squared modulus of the projection of $\Psi(t, \beta)$ onto its torsional components in the ground (a) and excited (b) states.
Figure 15. Polarization shaping. (a) The squared modulus of $\Phi(\beta, t)$. (b) The expectation value of the angular momentum. The polarization-shaped pulse is 100 fs long.

embodies the dynamics that we seek to control is a projector onto states with positive angular momentum,

$$\hat{O}_{\text{target}} = \sum_{n>0}^{n_{\text{max}}} |e^{in}\rangle \langle e^{in}|.$$  \hspace{1cm} (27)

In these calculations, we have used a penalty function amplitude of $\alpha_o = 50$ and a penalty function shape of the form described in [76]. This restricts the field strength and ensures that the field grows from zero at a finite rate and approaches zero smoothly toward the target time. Using this method, we are able to restrict ourselves to very short timescales (10–100 fs) while significantly improving our control over the torsional dynamics as compared to the linear polarization approach.

Figure 15 displays the results. Panel (a) may be compared with figure 13(d) for the IR + UV scheme of section 3.1.3. The probability density exhibits unidirectional motion beginning immediately after the short pulse and persisting for several cycles before (coherent) dephasing begins to spread the wave packet. Noteworthy is the difference in the extent of reflection from interaction with the barriers in figures 15 and 13(d). At the point where the wave packet first
Figure 16. Results of polarization shaping with all dipole/field interactions included. (a) Ground (---) and excited (solid) state population along with the portion of the excited state population above the central barrier at 0.22809 Hartrees (solid curve with superimposed circles). (b) Ground (---) and excited (solid) state angular momentum during and immediately after the pulse. (c) $X$- (left ordinate) and $Y$- (right ordinate) field components. Note the scale difference indicating that the $Y$-component of the field is much more intense.

encounters the excited state torsional barrier at the $0/2\pi$ juncture (see figure 4(a)), a faint line can be seen moving in the direction counter to the bulk of the wave packet, which continues rotating onward to emerge from the $\beta = 0$ side of the coordinate system. This represents portions of the total wave packet that are reflected from the barrier. This happens most noticeably for wave packets that have a great deal of population at energies not too far above the peak value of the torsional barrier. In figure 15(a), however, such reflection is not observed, since in the polarization-shaped case the center of the wave packet lies energetically above the highest bound state, as seen in figure 17 and discussed below.

Within the IR + UV scheme, the ground state angular momentum must be built up before it can be transferred to the excited state. Within the optimized polarization scheme, the creation of the phase relations necessary for unidirectional rotation and the population of the excited state are done simultaneously. Panel (b) displays the excited state angular momentum after the pulse, where it is seen that unidirectional rotation begins immediately after the pulse turnoff. The magnitude of this angular momentum once the wave packet accelerates down the slope of the potential approaches $250\hbar$, and maintains a large positive value, persisting picoseconds.

Although population transfer occurs steadily through the interaction time with the pulse, it is not until the last 10 fs that the excited state angular momentum begins to change appreciably (figure 16(b)). Thus, the phase information necessary for unidirectionality builds up gradually in the course of population transitions, but is only triggered in the final sharp sub-pulse near 100 fs. The differences between the dynamics induced by the IR + UV scheme and those induced by the polarization-shaped pulse are twofold. Firstly, the polarization-shaped pulse is able to increase the $Y$-component of the field at the expense of the $X$-component, thus offsetting the large
Figure 17. The correspondence between the transition strengths \( \langle \Phi_1^\dagger | \mu_{12}^r | \Phi_2^r \rangle \) (a) and the populations of torsional states in the excited electronic state after the pulse (b), (c). Panel (b) corresponds to the IR + UV scheme and panel (c) to the polarization shaping approach. The shift of the center of the wave packet towards higher energy states is clearly seen. The state numbers here refer to the most highly populated subset of the 73 total excited states. In this representation, state number 46 marks the highest bound state.

The difference between the \( X \) - and \( Y \)-components of the dipole function (see figure 4) that hinders unidirectional rotation. Secondly, the optimal pulse produces a higher energy torsional wave packet, dominated by states whose energy is above the central torsional barrier (figures 16(a) and 17). This wave packet decoheres more slowly than the one due to the IR + UV scheme as it suffers less from collisions.

Within the IR + UV scheme, there is an anticipated close correspondence between the populations in the excited state levels after the pulse sequence and the strengths of their transitions from the ground torsional state. Inevitably, the strength of transitions into bound states is well above that for transitions into states above the barrier, and hence the excited state wave packet contains \( \sim 26\% \) of bound states. The short shaped pulse, by contrast, is able to concentrate the pulse fluence in a short time and thus offset the trend determined by the transition strengths and place \( \sim 90\% \) of the excited state population in torsional states above the 0.22809 \( E_h \) barrier.

Examination of the control fields involved in the polarization shaping approach shows that in some respects similar mechanisms apply in this case as in the IR + UV scheme. Figure 18 shows the Fourier transforms of the \( X \)- and \( Y \)-components of the field, illustrating that the frequency spectrum of the \( Y \)-component (red) is reminiscent of that shown in figure 11 for the linearly polarized field. While both the \( X \)- and \( Y \)-field components contain frequencies corresponding to ground-to-ground, excited-to-excited and ground-to-excited transitions, the
Figure 18. Frequency domain representation of the $X$- (black) and $Y$- (red) components of the field, where the $X$-component is referred to the right ordinate and the $Y$-component to the left ordinate. The $X$-component is considerably weaker and much broader in frequency space.

$Y$-component of the polarization-shaped pulse is not nearly as broad in frequency space as the $X$-component. Both the high- and the low-frequency components of the $Y$ field component are active throughout the pulse, leading to greater resolution in the frequency domain relative to the $X$ field component, which is much more concentrated in time and hence broader in frequency domain. Further, one observes a large difference between the peak intensity of the most represented frequency in the $Y$ field component (normalized to 1 for ease of comparison) and that of the $X$-component (only 0.03). As noted above, this is due to the large difference in strengths of the $X$- and $Y$-components of the transition dipole in figure 4(c). The relevant parameter is the interaction strength $\epsilon_X(t)\langle \Phi_1^a|\mu|\Phi_2^a \rangle$, which requires a much lower field strength to be comparable to $\epsilon_Y(t)\langle \Phi_1^a|\mu|\Phi_2^a \rangle$.

Complementary insights are provided by the temporal evolution of the fields, provided in figure 16(c). Here we find that the $Y$-component of the field is shaped in both the low-frequency (overall envelop) and high-frequency (fine structure) regimes and that its amplitude is high throughout. The $X$-component, by contrast, has a very small (although nonzero) amplitude at all but the very early and very late portions of the interaction time, leading to a broadening in the frequency domain representation. As will be seen below, this does not reduce to a simple two pulse control field, as the small oscillations in the $X$-component of the field lead to definite polarization when taken in concert with the $Y$-component of the field. Population transfer from the ground to the excited electronic state continues steadily during the pulse, but with low amplitude oscillations that indicate the creation of coherences. This interpretation is further supported by the results of calculations with only one of the field components. When only $\epsilon_X(t)$ is applied and $\epsilon_Y(t)$ is set to zero, only $\sim30\%$ of the population is transferred to the excited state. When only $\epsilon_Y(t)$ is applied, $\sim60\%$ of the population is in the excited state, the results of section 3.1.1 are reproduced, but with no unidirectionality to the excited state wave packet. The wave packet splits into two counter-propagating wave packets, leaving the net angular momentum zero.

Lastly, it is instructive to examine the evolution of the total electric field over time. Here we clearly see the use of multiple elliptical polarizations spanning tens of femtoseconds along with more exotic forms where the polarization changes rapidly with time. By plotting the changes

in the $X$ and $Y$ control fields simultaneously, we can follow the establishment and change of particular pulse polarizations (figure 19). At early times, $t \sim 0$–40 fs, the pulse is elliptically polarized (panels (a)–(d)) with a slight change of the orientation around 40 fs (panel (d)). An entirely different behavior, however, is found in the later portions of the pulse, $t \sim 50$–90 fs (panels (e)–(i)), where the polarization direction varies rapidly. Finally, the pulse ends with a slowly varying elliptical polarization that decreases in amplitude as the pulse smoothly decays to zero (panel (j)). Figure 19 thus clarifies the manner in which the polarization-shaped pulse breaks the rotational symmetry of the system and optimally induces unidirectional torsion.

4. Conclusion

In the preceding sections we explored the extent to which coherent light–matter interactions alone could drive unidirectional rotation in a symmetric system. We addressed also the more general question if and when can optimal control strategies provide solutions that could not be attained by intuitive approaches. Time-dependent approaches based on momentum space and state space formulations were used in the application of complimentary coherent control techniques, and useful information about wave packet shaping in multiple regimes was unraveled. As an experimentally relevant model system we used the BCH molecule, a simple olefin that serves as a prototype of a class of more complicated molecular rotors that share its essential structural motives. Our conclusions, however, are largely general.

Under constrained polarization conditions, we find that the optimal control algorithm reduces to a simple two-pulse sequence, where a first IR pulse excites a wave packet of torsional states and a subsequent UV pulse, timed to an instance where the system is localized at the ground state turning point, projects it onto an excited PES. The structure of the excited surface gives rise to unidirectional motion along the torsional coordinate. We found, however, that with the restriction to linear polarization removed, significantly better solutions are unraveled. In particular, an interesting polarization shaping approach is introduced, where elliptically polarized light breaks the symmetry between the two senses of torsion.
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