Torsional Control by Intense Pulses

S. Ramakrishna and Tamar Seideman*

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois. 60208-3113 USA
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We generalize the concepts of alignment and 3D alignment by moderately intense laser pulses to control both the overall rotations and the torsional motions of polyatomic molecules. Torsional control is applied to manipulate charge transfer events, hence introducing a potential route to light controlled molecular switches. Potential applications in areas such as molecular assembly, molecular spectroscopies, energy transfer, and molecule-based junctions are envisioned.

Molecular alignment by intense pulses has been the topic of rapidly growing activity during the past few years [1]. This activity owes both to the fascinating fundamental physics associated with rotational wave packet dynamics and to a variety of already demonstrated and projected applications in fields ranging from molecular spectroscopy and laser optics [2] through reaction dynamics and stereochemistry [3], to quantum storage and information processing [4]. In this approach, a moderately intense laser pulse aligns a molecular axis (axes) to the field polarization vector(s) through dipole or induced dipole interactions. Whereas a linearly polarized pulse induces 1D order, leaving the rotation about the field and molecular axes free, an elliptically polarized pulse aligns the three axes of the molecule to three axes defined in space [5]. Although most of the research in this area has focused on isolated molecules in the rotationally cooled molecular beam environment [1], recent work has illustrated the applicability of intense laser alignment to dissipative media, including dense gas cells [6], solutions [6,7], and matrices [8].

Here we extend the concepts of alignment and 3D alignment from a means of controlling solely the overall rotations of molecules with respect to the space-fixed axes, to a means of simultaneously controlling also their torsional motions. In particular, we illustrate numerically the application of circularly or elliptically polarized pulses to eliminate the torsional motions of polyatomic systems while hindering their overall rotations in space. The approach is applied to control of charge transfer reactions in solution with a view to making a new form of molecular switches. A variety of other potential applications of torsional control in polyatomic research are discussed.

As a simple example of an effect that we believe to be general, we consider torsional control and manipulation of a charge transfer event in donor-acceptor biphenyls [9,10]. We attempt, however, to present our results in as qualitative a manner as possible, so as to allow straightforward extension to other applications and other molecules that exhibit torsion. For simplicity we consider a circularly polarized alignment field, $\boldsymbol{\epsilon}(t) = \frac{1}{2}[\boldsymbol{\varepsilon}(t)e^{i\omega t} + \text{c.c.}]$, with $\boldsymbol{\varepsilon}(t) = 2^{-1/2}[\mp\varepsilon_x(t) \pm i\varepsilon_y(t)]$, but qualitatively similar dynamics are obtained with elliptically polarized fields.

Here ω is the laser frequency, $\varepsilon_\rho(t) = \hat{e}_\rho\varepsilon(t)$, $\rho = x, y, z$ are the space-fixed Cartesian axes, $\hat{e}_\rho$ is a unit vector along the ρ direction, and $\varepsilon(t)$ is the pulse envelope. In the far-off-resonance limit, the field-matter interaction reduces to the induced dipole Hamiltonian, $H_{\text{ind}} = -\frac{1}{4}\sum_{\rho,\rho'}\varepsilon_\rho\alpha_{\rho\rho'}\varepsilon_{\rho'}^*$, where $\alpha_{\rho,\rho'}$ are the Cartesian components of the polarizability tensor [1(a)]. In terms of the body-fixed Cartesian coordinates, $k = X, Y, Z$, the polarizability tensor takes the form, $\alpha_{\rho\rho'} = \sum_{kk'}\langle\rho|k\rangle\alpha_{kk'}\langle k'|\rho'\rangle$, where $\langle k|\rho\rangle$ are elements of the transformation matrix between the space- and body-fixed frames. We use the fact that, in the biphenyl derivatives considered, the field-matter interaction is strongly dominated by the two phenyl rings, to approximate the polarizability tensor by that of a bare biphenyl. Although this approximation is not numerically necessary, it lends the model generality and simplicity. The rigid rotor approximation, invoked in the vast majority of previous alignment studies, is not applicable here, because torsions are low frequency modes, comparable in time scale to the overall rotations. The high frequency vibrations, by contrast, can be approximated as rigid. The interaction Hamiltonian is thus of the form

$$H_{\text{ind}} = -\sum_{j=1,2}\frac{1}{8}\varepsilon^2\Delta\alpha\sin^2\theta_j$$
$$+ \frac{1}{R^3}\left\{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - \frac{3(\boldsymbol{\mu}_1 \cdot \mathbf{R})(\boldsymbol{\mu}_2 \cdot \mathbf{R})}{R^2}\right\}, \quad (1)$$

where the first term is the sum of the interaction Hamiltonians of the two phenyl rings with the circularly polarized laser field, and the second accounts for the mutual interaction of the laser-induced dipoles in the two rings. In Eq. (1), $\Delta\alpha = \alpha_{ZZ} - \alpha_{XX} < 0$ is the polarizability anisotropy of an isolated phenyl ring, with the body-fixed Z axis defined as the normal to the ring, θ_j is the polar Euler angle between that axis and the space-fixed z axis (defined above by the light propagation direction), and $\mathbf{R}$ is the inter-ring vector, with magnitude R. Introducing the coordinate transformation $\beta_\pm = \theta_1 \pm \theta_2$ and invoking the small angle approximation, $\sin\theta_j \approx \theta_j$, applicable in the case of a strong interaction, we find that the induced dipole

interaction separates into 2 components. One involves the overall rotation of the molecule and gives rise to alignment with respect to the space-fixed axes. The second component is a harmonic function of the torsion angle $\beta_- \equiv \beta$,

$$V(\beta) = k\beta^2,$$

$$k = \frac{\varepsilon^2}{16}\left(-\Delta\alpha + \frac{\alpha_{XX}\Delta\alpha}{2R^3} - \frac{\Delta\alpha^2}{4R^3} + \frac{3\alpha_{XX}^2}{8R^3}\right),$$

(2)

where we note that the effective force constant k is positive. The physical picture contained in Eqs. (1) and (2) is simple and general. The laser field acts to force the two rings to a common plane, transforming the free (or essentially free— see below for the effect of a field-free torsional barrier) torsion into small amplitude, nearly harmonic librational motion about the planar configuration $\beta = 0$. We do not make the harmonic approximation in the calculations below but consider it a helpful limit for gaining qualitative insight.

The combined dynamics of the external rotations and the internal torsional motion subject to the interaction (1) are solved quantum mechanically by expansion in a basis of products of symmetric top eigenstates corresponding to the two rings. For the systems considered, the first term of Eq. (1) dominates and the second is neglected.

Figure 1 illustrates torsional alignment vs the dimensionless interaction parameter $\Omega_0 = 0.16(\Delta\alpha/B)I_0$, where $\Delta\alpha$ is given in Å^3, B is the rotational constant in Hz, and I_0 is the laser intensity in W cm^{-2}. In Table I we provide the parameter $\Delta\alpha/B$, which contains all the molecular information, for different systems of relevance. As an average measure of the effect, we employ the expectation value of $\cos^2\beta$ in the wave packet. The field effect is examined both for the case where there is no field-free torsional barrier and for cases where there is. Figure 1 clearly illustrates the potential of torsional alignment both as a control tool and as an analytical tool. The case shown as diamonds is
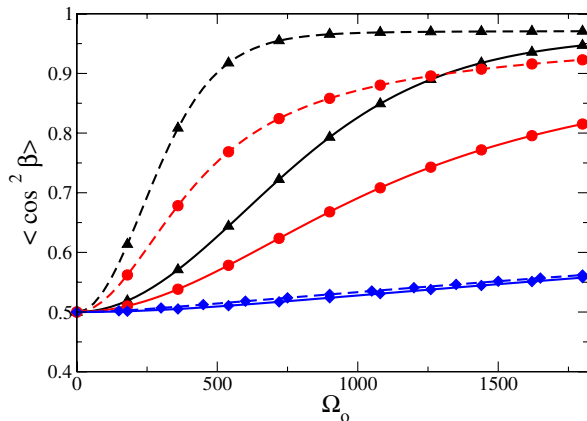

FIG. 1 (color online). Torsional alignment vs the interaction parameter Ω_0 at a temperature of $T = 30$ K (dashed curves) and $T = 77$ K (solid curves). The field-free torsional potential is $V_{\text{tor}}(\beta) = V_0[1 - \cos(4\beta - \pi)]$ (diamonds); $V_{\text{tor}}(\beta) = 0$ (circles); and $V_{\text{tor}}(\beta) = V_0[1 - \cos(4\beta)]$ (triangles) with a barrier $2V_0 = 62$ meV.

provided to quantify the range of applicability of this approach by illustrating the limit where torsional alignment is expected to be poor under conditions that do not cause undesired effects on the molecule or the solvent. Here the field-free barrier is large (62 meV), and located at $\beta = 0, \pi/2, \pi$, thus opposing the field-induced barrier. In realistic molecular systems the magnitude and location of the field-free torsional barrier vary over a large range. In porphyrin dimers (intensively studied for their role in photosynthesis), for instance, the torsional barrier is often less than 30 meV [11], whereas in donor-acceptor biphenyls it can be around 60 meV [9]. The field-induced potential is likewise molecule dependent and subject to control by synthetic techniques; see Table I. For the example of the porphyrin dimer of [11], for instance, the field-induced potential equals the field-free barrier at an intensity of ca. 7.6×10^{11} W cm^{-2}. The temperature effect illustrated in Fig. 1 is expected; both the hindrance of the field-induced and that of the field-free torsional barrier diminish as the temperature increases and higher energy torsional states are thermally populated.

Of the broad variety of potential applications of torsional alignment (*vide infra*) we explore here the control of charge transfer events [10]. In this problem laser alignment modifies the reaction dynamics via at least three correlated effects. Both the electronic coupling strength and the reorganization energy in the torsion mode are β-dependent. In bare biphenyl the former varies by ca. 2 orders of magnitude as β changes from 0 to $\pi/4$ [12]. The latter is significant in the absence of the field and vanishes in the strong laser interaction limit. Hence the average values of both parameters varies markedly with intensity. In addition, the frequency of librational motion is roughly linear in the field strength [Eq. (2)]. In photoinduced charge transfer processes, the alignment of the overall molecule to the polarization plane plays an additional role, since the excitation amplitude can be varied by changing the relative orientation of the excitation and alignment fields. As a result, the laser-controlled dynamics, and the extent to which alignment enhances the charge transfer event, vary with the nature of the charge transfer event, with properties of the solvent and with the temperature. Thus, while the qualitative effect proposed here is simple and general, its details are subtle and system dependent.

Three different scenarios can be envisioned in an attempt to disentangle the potential control mechanisms. In

TABLE I. Relevant molecular parameters for different monomers.

Monomer	$|\Delta\alpha|$ (Å^3)	B (MHz)
Benzene	5.82	5689.1
Naphthalene	11.41	1244.5
Anthracene	21.41	453.8
Tetracene	33.4	213.4
Porphyrin	60.0	763.0

charge transfer problems of the type studied in [13], torsional alignment modifies the charge transfer dynamics solely via its effect on the torsional reorganization energy. Here the donor group includes the biphenyl moiety, leading, as shown in [13], to ca 0.13 eV torsional reorganization energy. The consequent reduction of the (exoergic) transfer rate as compared to an analog where torsion is chemically eliminated is eightfold [13]. The dashed curves of Fig. 2 illustrate the electron transfer rate, k_{ET}, for different values of the interaction parameter Ω_0. Our results are obtained through solution of a Marcus theorylike formulation of nonadiabatic electron transfer that treats the high frequency and the torsional modes quantum mechanically while the solvent bath modes are accounted for classically,

$$
\begin{aligned}
k_{ET} = \frac{2\pi}{\hbar} \sum_{i,f} P_i |V_{if}|^2 (4\pi\lambda_s k_B T)^{-1/2} \sum_w \left(e^{-S} \frac{S^w}{w!} \right) \\
\times \exp\{-[\lambda_s + \Delta G + w\hbar\omega \\
- (E_i - E_f)]^2 / 4\pi\lambda_s k_B T\}.
\end{aligned}
\tag{3}
$$

In Eq. (3) the summation over the initial i, and final f states refers to torsional quantum modes, P_i represents the (Boltzmann) probability of occupancy of the initial torsional state at temperature T, ΔG is the free energy change, and the w-summation pertains to the vibrational states of the product. The reorganization of the solvent modes is given by λ_s whereas that of the quantum vibrational mode is given by $S\hbar\omega$. The quantum treatment of the torsional mode allows for the energies of the initial (E_i) and final (E_f) torsional states to explicitly appear in the expression
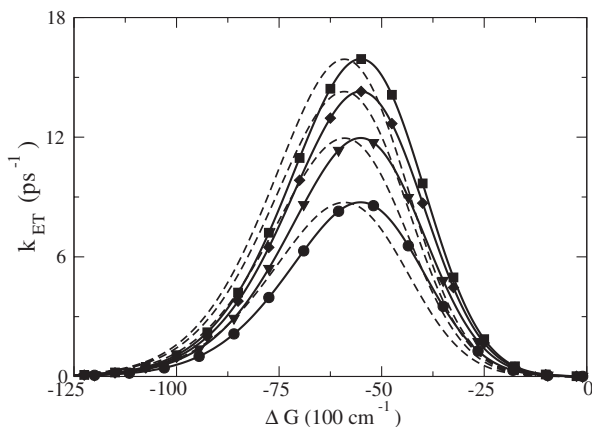

FIG. 2.   Dashed curves: rate vs free energy change ΔG for an electron transfer reaction where the donor group includes a biphenyl group and the initial and final states are displaced in equilibrium in the torsional mode, see, e.g., [13]. Alignment controls the charge transfer through its effect on the reorganization energy. Solid curves: transfer rate for a reaction where the donor and acceptor groups are attached to the two rings of a biphenyl and the initial and final states have the same torsional equilibrium configuration. Alignment controls the charge transfer by confining the system to the configuration where the electronic coupling strength is maximum. The interaction strength is $\Omega_0 = 0$ (circles), 600 (triangles), 900 (diamonds), and 1200 (squares) and the temperature is 77 K.

for the driving force of the reaction. Finally, the electronic coupling term, $|V_{if}|^2 = |\langle\psi_i(\beta)|V_{el}(\beta)|\psi_f(\beta)\rangle|^2$, is the square of the matrix element between the initial and final torsional wave functions ($\psi_{i(f)}$), where $V_{el}(\beta)$ is the electronic coupling across the system [12]. Since the matrix element between the torsional wave functions is treated without invoking the Condon approximation, this term does not factor into the conventional product of a pure electronic part and a contribution that involves the torsional reorganization energy. We note in Fig. 2 the shift of the parabolic Marcus-type curve by an energy comparable to the effective reorganization energy. As noted below, larger shifts may be expected in photoinduced processes when the equilibrium displacement is upon excitation. Such shifts provide conditions under which the field can turn the reaction on or off.

Similarly, one can envision situations where the effect of reorganization is minor and the dependence of the electronic coupling on the charge transfer outcome dominates. An example of this situation is a 2-state electron transfer reaction where the donor and acceptor groups are attached to the two moieties undergoing mutual torsion but there is no torsional equilibrium displacement between the initial and final states. Here, the field controls the reaction outcome only via its effect on the electronic coupling in Eq. (3), i.e., by confining the system to the planar configuration. The solid curves of Fig. 2 illustrate the computed rate vs the free energy and the interaction strength in such a situation. The field does not displace the curves with respect to one another, since the reorganization energy vanishes, but it enhances the transfer rate.

Perhaps the most interesting situation is that where the transfer is between the moieties undergoing torsion and the initial and final states exhibit an equilibrium displacement. In particular, in photoinduced reactions, where a substantial equilibrium displacement is found between the ground and initially excited state, torsional alignment of the ground state is expected to provide an efficient control tool. An interesting example, which has been studied experimentally in considerable detail, is the donor-acceptor compound dimethylamino-cyanobiphenyl [9]. In the ground state it exhibits a shallow double well potential in the torsional mode with 39° equilibrium, whereas the relevant excited states are planar [9]. We defer details of this system and our method of addressing it, so as to focus here on the general torsional control problem. It is noted only that our results illustrate the anticipated enhancement of the electron transfer rate through laser alignment of the torsion while exhibiting sensitivity of the enhancement to details of the system, the solvent, and the reaction mechanism. They thus suggest not only the potential of torsional control for the application of molecules to make electronic and photonic devices, but, perhaps more interestingly, its potential as a method of understanding electron transfer processes in solvated molecules.

While in the context of enhancing ET reactions minimization of the torsion ($\beta \to 0$) is desired, it is interesting to

extend the approach to force β to a general value. One potential route to that end is *meta* or *ortho* substitution in one of the rings with a group that provides a significant dipole moment. The application of a static electric field in the plane perpendicular to the major axis of the elliptically polarized laser field could thus allow fixing the torsion angle at a desired value.

The range of potential applications of torsional control combined with 3D alignment is intriguing. One inviting opportunity is field-guided molecular assembly, where we envision applying a laser field to guide the assembly of molecules into surface-supported mono- or multilayers with uniform alignment and torsion angles. Here, we are inspired by the rich literature on devices such as field-effect transistors, where much effort has been devoted to fabricating molecular layers with these properties by chemical substitutions [14]. The importance of alignment and torsional control in such systems has been often stressed in the literature and arises from the effect of these properties on the electric, magnetic, and optical properties of the construct. The application of chemical methods to that end, however, lacks generality and is difficult; ideally one would choose (or design) the molecules according to their functionality, rather than based on their alignment properties. Whereas the qualitative physics we envision is the same as in the familiar alignment of isolated small molecules, the details differ, since lower degrees of alignment would suffice to achieve the goal and since, for typical polarizabilities, lower intensities are expected to provide a given degree of alignment.

A second area where we expect this approach to have an impact is the rapidly expanding field of molecular junctions [15]. Here, a general method of producing uniform alignment and torsion angles of the molecular components would assist the optimization of the conductance properties of the junction, whereas field control over torsion and conformation could provide a potential approach to switches and rectifiers.

The significance of a handle over the torsional motions of polyatomic molecules, however, goes beyond potential applications in device technology. No less interesting is the potential of torsional control for understanding the mechanism of reactions that are too complex to address numerically. We note here that substantial effort has been devoted to the development of methods of hindering the torsional modes for the purpose of unraveling reaction mechanisms [9]. Most often chemical means are applied to that end. It is evident, however, that chemical substitution inevitably modifies other aspects of the dynamics [9]. The results of [16] illustrate that torsion plays a major role in a variety of spectrosopies, including core level photoelectron and photoluminescence spectrosopies. Laser torsional control may find applications both in the interpretation of such spectra and in their use to probe molecular potentials. The results of [17] further illustrate the potential of torsional control as a tool for the interpretation of spectroscopy and its conversion into structural and dynamical information, e.g.,

regarding torsion-mediated intermode energy flow. Another class of systems where torsional control is expected to provide long sought insights are *para*-substituted oligophenyls, blue laser dyes whose planarity is known to be strongly temperature dependent [18]. Finally, we note the potential of torsional control in elucidating and manipulating excitation transfer pathways [19].

In summary, we extended the concepts of molecular alignment and 3D alignment by moderately intense laser pulses to control simultaneously the overall rotations and the torsional motions of polyatomic molecules. The method was applied to enhance charge transfer events in donor-acceptor systems. Several of the potential applications of the combination of 3D alignment with torsional control in fundamental and applied research were sketched.

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*t-seideman@northwestern.edu

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