Manipulating the Torsion of Molecules by Strong Laser Pulses

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We demonstrate that strong laser pulses can induce torsional motion in a molecule consisting of a pair of phenyl rings. A nanosecond laser pulse spatially aligns the carbon-carbon bond axis, connecting the two phenyl rings, allowing a perpendicularly polarized, intense femtosecond pulse to initiate torsional motion accompanied by an overall rotation about the fixed axis. We monitor the induced motion by femtosecond time-resolved Coulomb explosion imaging. Our theoretical analysis accounts for and generalizes the experimental findings.

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A nonresonant laser field applies forces and torques on molecules due to the interaction between the induced dipole moment and the laser field itself. If the field is intense, but nonionizing, the forces and torques can be sufficient to effectively manipulate the external degrees of freedom of isolated gas phase molecules. In particular, the intensity gradient of a focused laser beam may deflect [1], focus [2], and slow [3] molecules through the dependence of the nonresonant polarizability interaction on the intensity. Likewise, the dependence of the induced dipole interaction on molecular orientation has proven highly useful for controlling the alignment and rotation of a variety of molecules [4,5]. Molecular manipulation by induced dipole forces extends beyond the external degrees of freedom and can also be applied to the internal degrees of freedom such as vibrational motion [6]. Notably, the electrical field from laser pulses can modify energy potential barriers such that photoinduced bond breakage of a small linear molecule is guided to yield a desired final product [7,8].

Here, we extend the use of the nonresonant polarizability interaction to achieve a transient modification of the torsional potential of the molecule 3,5-diflouro-3',5'-dibromo-biphenyl (DFDBrBPh), thereby inducing torsional motion of the two phenyl rings (Fig. 1). The results are accounted for by our theoretical analysis, and we point at two very diverse aspects of the current work: (i) The potential application of twisted molecules in molecular junctions, where they may serve as ultrafast (picosecond) molecular switches [9–12]; (ii) DFDBrBPh has two conformations that are mirror images of each other, the R_a and S_a enantiomers [13]. An extension of the present experiment will provide a unique temporally resolved study of the important chemical process deracemization [14–17], where one enantiomer is selectively converted into the other.

The experiment is carried out on isolated gas phase molecules at rotational temperatures of a few kelvin. Under these conditions each molecule is initially localized in the −39° or 39° conformation [Fig. 1(b)] and no thermally induced transitions between the two occur. The scheme to obtain torsional motion is based on the combination of two laser beams [Fig. 1(a)]. First, a 1064 nm, 9 ns (FWHM) linearly polarized laser pulse of peak intensity 7×10^{11} W/cm^2 fixes the carbon-carbon (C-C) axis between the two phenyl rings in the laboratory frame by adiabatic alignment [4,18]. This pulse is intense enough to keep the axis tightly confined, yet weak enough to modify the torsional potential only slightly. Next, an 800 nm laser pulse of intensity 5×10^{12} W/cm^2 and duration (FWHM) 700 fs, which we will refer to as the kick pulse, is applied with its polarization perpendicular to the aligned C-C bond axis. This polarization geometry ensures that the kick pulse primarily influences torsional motion while avoiding excitation of other normal modes. At time t_p with respect to the kick pulse, a linearly polarized,

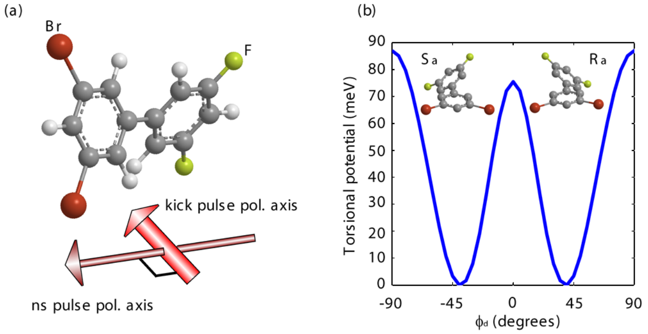

FIG. 1 (color online). (a) Model of DFDBrBPh and the laser geometry of the experiment. The molecule consists of a pair of phenyl rings. The substituted Br and F atoms are needed to identify the two rings in the experiment. (b) The torsional potential of DFDBrBPh [26]. The torsion is quantified by the dihedral angle, ϕ_d, between the two phenyl rings. The minima at dihedral angles of $\phi_d = \pm 39°$ result in the R_a and S_a enantiomers (see text).

intense 800 nm, 25 fs (FWHM), 2×10^{14} W/cm^2 pulse appears and removes several electrons from the molecules, thereby triggering Coulomb explosion into ionic fragments. In particular, the Br^+ and F^+ fragment ions recoil in the planes defined by the two phenyl rings. By recording the velocities of both ion species with two-dimensional ion imaging [18], we thus determine the instantaneous orientation of each of the two phenyl rings at t_p. The time-resolved ion images are displayed in Fig. 2(a).

To establish that the ns pulse aligns the C-C axis, we have applied the probe pulse at $t_p = -0.87$ ps. This results in almost circularly symmetric ion images [Fig. 2(a)] and the small deviation from circular symmetry is explained by noting that the kick pulse has a finite value at -0.87 ps. The absence of ions in the innermost region, most clearly seen in the F^+ image, shows that the C-C bond is aligned perpendicular to the detector plane and that the distribution of the molecules around this axis is uniform. At $t_p = 0.47$ ps the deviation from circular symmetry is very clear and the ions start to localize around the polarization direction of the kick pulse. The F^+ ions remain radially confined away from the center, which shows that the kick pulse does not perturb the alignment of the C-C bond axis. Rather, it initiates an overall rotation of the molecule around this axis as is expected since the torque imparted by the kick pulse forces the second most polarizable axis (SMPA), perpendicular to the C-C axis and located 11° away from the Br-phenyl ring, to align along the kick pulse polarization on a time scale determined by the kick strength [19]. At $t_p = 1.47$ ps the Br^+ ions are localized around the polarization axis and the F^+ ion distribution exhibits a four-peaked structure. This behavior is compatible with alignment of the SMPA along the kick pulse polarization. In practice and consistent with theory [Fig. 3(a)], the SMPA alignment is not strong enough to resolve the two Br^+ signals located at ±11° with respect to the SMPA. It is, however, sharp enough to resolve the two pairs of F^+ ion signals due to the larger offset (28°) of the F-phenyl rings from the SMPA. The further localization of the Br^+ signal at 2.47 ps shows that the Br-phenyl planes have rotated into stronger alignment with the kick pulse polarization. Had the dihedral angle remained unchanged, the F^+ ion image should exhibit a distinct four-dot structure similar to the image at 1.47 ps but with a larger angular splitting. The four-dot structure at 2.47 ps is, however, significantly blurred compared to the case at 1.47 ps. Thus, we conclude that the kick pulse sets the molecule into rotation around the C-C axis and initiates torsional motion. At later times, the ion signals gradually broaden due to continued overall rotation around the C-C axis with dihedral dynamics imposed.

Further insight into the effect of the kick pulse is obtained by plotting the average angle between the F-phenyl rings and the kick pulse polarization as a function of t_p [Fig. 2(c)]. The increase from 22.5° at 1.47 ps to 26.5° at 3.8 ps shows that the F-phenyl rings gradually move away from the kick pulse polarization due to the overall rotation of the molecule around the C-C axis. The concurrent oscillations show that the overall rotation is accompanied by a periodically varying motion in ϕ_d. We estimate the period to be ~1 ps and the amplitude to ~0.6° for this oscillation.

We now present our physical model substantiating the experimental findings. In agreement with the observations, we assume that the C-C axis is perfectly aligned. Also, we neglect all normal modes, except the lowest one, corresponding to torsion. Within these approximations the task is reduced to describing the coupled rotations of the two phenyl rings. The experimental observables are the angles ϕ_{Br} and ϕ_{F} of the rings with respect to the kick pulse

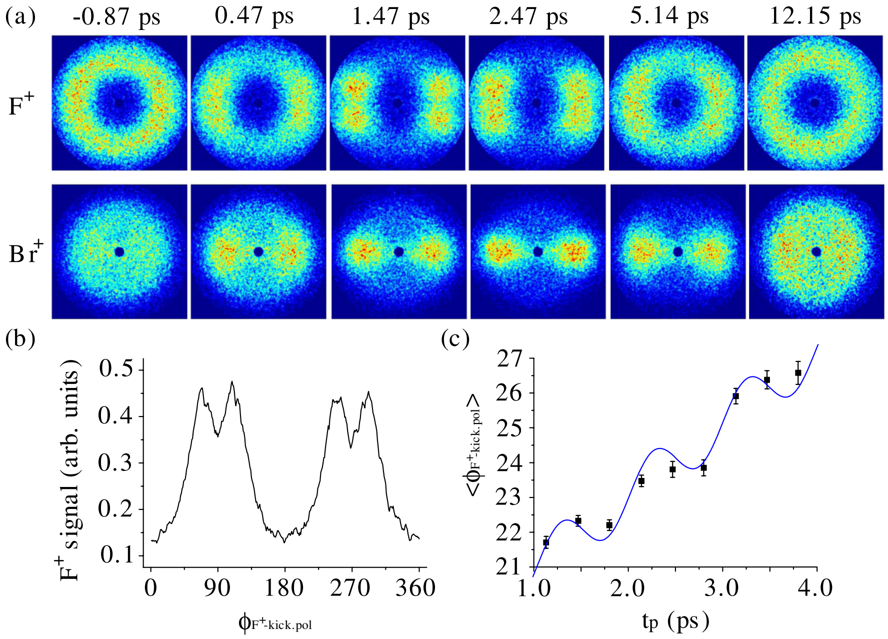

FIG. 2 (color online). (a) Ion images of F^+ and Br^+ fragments at probe times t_p. The ns pulse is polarized perpendicularly to the image (detector) plane and the 5×10^{12} W/cm^2, 700 fs (FWHM) kick pulse is polarized horizontally. (b) Angular distribution of the F^+ ions, at $t_p = 1.47$ ps, obtained by radially integrating the corresponding F^+ ion image. The splitting of the pairwise peaks is twice the average angle, $\langle \phi_{F^+\text{-kick.pol}} \rangle$, between the F^+ ion recoil and the kick pulse polarization. (c) $\langle \phi_{F^+\text{-kick.pol}} \rangle$ as a function of t_p, for times where a clear four-peak structure is visible in the angular distributions. The curve is a fit of the sum of a linear and a harmonic function to the experimental points (squares).

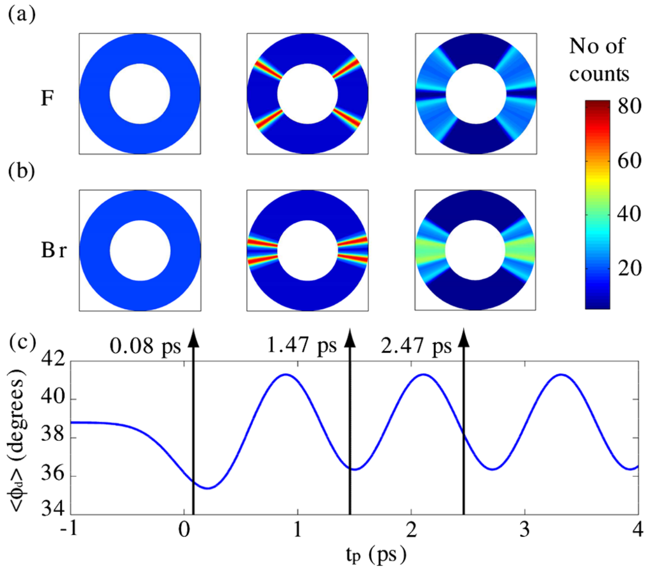

FIG. 3 (color online). Angular distributions of (a) F-phenyl and (b) Br-phenyl rings at $t_p = 0.08$, 1.47, and 2.47 ps. (c) Expectation value of the dihedral angle for a molecule starting out with the SMPA aligned along the kick pulse polarization. The kick pulse is as in Fig. 2.

polarization axis. In the theoretical treatment it is, however, convenient to refer to the dihedral angle $\phi_d = \phi_{\mathrm{Br}} - \phi_{\mathrm{F}}$ and the overall rotation around the C-C axis described by the weighted azimuthal angle $\Phi = (1 - \eta)\phi_{\mathrm{Br}} + \eta\phi_{\mathrm{F}}$, with η given in terms of the moments of inertia, $\eta = I_{\mathrm{F}}/(I_{\mathrm{Br}} + I_{\mathrm{F}})$. This change of coordinates separates the dynamics of the molecule into two rotations of different time scales. The first, ϕ_d, is an internal rotation corresponding to torsional motion. The time scale of torsion is ps, as can be inferred from the torsional potential. The second rotation, Φ, is an overall rotation with a period of ns, as follows from the total moment of inertia $I = I_{\mathrm{Br}} + I_{\mathrm{F}}$. This separation motivates the introduction of a semiclassical model, where ϕ_d is treated fully quantum mechanically, while Φ is treated classically. Briefly, due to the kick pulse the field-free torsional state of energy E_ν evolves as (we apply atomic units, $m_e = e = a_0 = \hbar = 1$) $|\chi_\nu\rangle \rightarrow |\chi_\nu^\Phi(t)\rangle = \sum_{\nu'} c_{\nu'}^\Phi(t) e^{-iE_{\nu'}(t-t_0)}|\chi_{\nu'}\rangle$, with t_0 a time prior to the kick pulse. The time-dependent coefficients satisfy the differential equations $\dot{c}_{\nu'}^\Phi(t) = -i\sum_\nu c_\nu^\Phi(t) e^{-i(E_\nu - E_{\nu'})(t-t_0)}\langle\chi_{\nu'}|V_{\mathrm{kick}}(\Phi, t)|\chi_\nu\rangle$, with the kick pulse polarization interaction

$$\begin{aligned} V_{\mathrm{kick}}(\Phi, \phi_d, t) = -\tfrac{1}{4}F_0^2(t)[&\alpha_{xx}(\phi_d)\cos^2(\Phi + \eta\phi_d) \\ &+ \alpha_{yy}(\phi_d)\sin^2(\Phi + \eta\phi_d) - 2\alpha_{xy}(\phi_d) \\ &\times \cos(\Phi + \eta\phi_d)\sin(\Phi + \eta\phi_d)]. \end{aligned} \tag{1}$$

Here α_{ij}'s are dynamic polarizability tensor components obtained by our quantum chemistry calculations and F_0 is the kick pulse field envelope. The effect of the kick pulse on the overall rotation amounts to an angular momentum kick and consequently

$$\Phi(t) = \Phi_0 - t\frac{1}{I}\left(\frac{\partial}{\partial\Phi}\int_{-\infty}^{\infty} dt'\langle V_{\mathrm{kick}}(\Phi, t')\rangle\right)\Bigg|_{\Phi=\Phi_0}, \tag{2}$$

where $\langle\rangle$ denotes averaging over the ensemble of torsional states.

Figure 3 shows the results of a calculation with laser parameters identical to the experimental values and an initial rotational temperature of 0 K. Prior to the kick pulse, the angular distributions of the Br- and F-phenyl rings [left panels, Figs. 3(a) and 3(b)] are isotropic as in the experiment. Maximum alignment of the SMPA occurs at 1.3 ps and the confinement of the F-phenyl rings at a large angle with respect to the kick pulse polarization [cf., middle panel, Fig. 3(a)] explains the distinct four-dot structure observed at $t_p = 1.47$ ps [Fig. 2(a)] in the experimental F^+ ion image. Also, at $t_p = 1.47$ ps the confinement of the Br-phenyl rings at a small angle with respect to the kick pulse polarization predicts a much less distinct, if any, four-dot structure in good agreement with the Br^+ ion image. At $t_p = 2.47$ ps the angular localization of the F-phenyl rings has broadened [right panel, Fig. 3(a)] and a blurred four-dot structure is seen, consistent with the experimental result at $t_p = 2.47$ ps. The distribution of the Br-phenyl rings is also broadened [right panel, Fig. 3(b)], but remains localized around the kick pulse polarization fully consistent with the Br^+ ion distribution, recorded at 2.47 ps.

The theoretical value $\langle\phi_d\rangle$ exhibits oscillations [Fig. 3(c)] with a period of ~1.2 ps and amplitude of ~2.45°. The period agrees well with the experimental value (~1 ps), and smaller modulation in $\langle\phi_d\rangle$ is expected in the experiment (~0.6°) since here the SMPA is not prealigned. The behavior is ascribed to a wave packet of vibrational modes in the torsional double well potential [Fig. 1(b)] for a molecule starting out with the SMPA aligned. The qualitative agreement of Figs. 2(b) and 3(c) verifies the interpretation of the kick pulse inducing time-dependent torsional motion.

Now we point at some possible future applications of induced torsional motion. For one thing, DFDBrBPh represents a class of molecules, where the conductivity can be controlled by manipulating the torsion. Such a molecule used as a molecular junction between two conductors, thus offers an attractive alternative to mechanical break junctions [20]. In particular, the fact that the dihedral angle with the present laser pulse-based method can be altered on a ps time scale opens intriguing possibilities for studying ultrafast modulation and switching of electrical charge flow.

Another new application within reach is a time-resolved study of deracemization [14–17], where one enantiomer is steered into its mirror form. To this end, we break the inversion symmetry with respect to the C-C bond axis by orienting each molecule rather than just aligning in order to discriminate between the two enantiomeric forms. Theory [21] and experiment [22] show that orientation can be

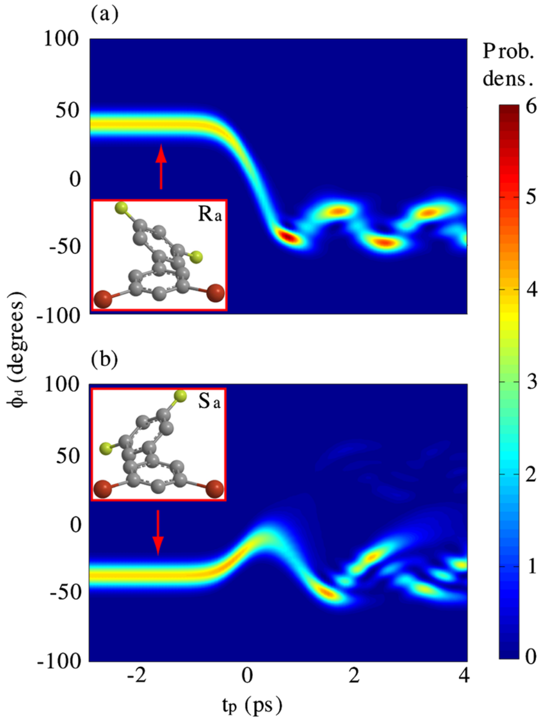

FIG. 4 (color online). Time evolution of the dihedral angle for a molecule starting out as (a) an R_a or (b) an S_a enantiomer. Initially, the molecule is 3D oriented with the Br-phenyl end pointing out of the paper and the SMPA aligned at an angle of 13° with respect to the kick pulse polarization. The kick pulse triggering the torsional motion has a peak intensity of 1.2×10^{13} W/cm^2 and duration (FWHM) of 1.0 ps. The torsional barrier is reduced by 1/4 rather than increasing the kick strength further. Such modification of the torsional potential may be accomplished by replacing DFDBrBPh with, e.g., halogen substituted biphenylacetylene.

added to 3D alignment by combining the ns alignment pulse with a static electric field. Next, to reduce the role of overall rotation, the SMPA can be aligned prior to the kick pulse by employing an elliptically rather than a linearly polarized ns pulse [4,12]. Finally, the interaction strength between the molecule and the kick pulse needs to be increased either through higher intensity, a longer kick pulse, or by trains of synchronized kick pulses [23–25]. Assuming initial orientation and confinement of the SMPA, we have calculated the ϕ_d dynamics for both conformations of a molecule closely related to DFDBrBPh. The results are shown in Fig. 4, and clearly, the present method would allow for a time-resolved study of the transition from one enantiomer and into the other. A quantitative analysis of the efficiency of the process shows that after the pulse 99% of the molecules starting out as R_a changed into S_a enantiomers, whereas only 13% of the S_a enantiomers changed into R_a. The inverse process causing an excess of R_a enantiomers, is simply achieved by inverting the orientation of the molecules.

In conclusion, we have performed fs time-resolved studies of torsional motion by a combination of aligning, kick, and ionizing pulses, and we supported the observations by an accompanying theory. We believe that the present work opens new directions of cross-disciplinary research firmly anchored in strong-field physics as exemplified by ultrafast switching in molecular junctions and fs time-resolved studies of deracemization.

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