Manipulating the torsion of molecules by strong laser pulses

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Outline

1. Laser induced alignment
2. Strategy to manipulate torsion
3. Results (proof-of-principle)
4. Perspectives
5. Summary and outlook
Laser induced alignment

A strong non-resonant laser pulse can align a gas of molecules.
Laser induced alignment

The non-resonant laser creates a broad superposition of (rotational) states in E through all the states in N:

\[ \Psi(t) = \sum_{E} c_{E}(t)\psi_{E}, \quad H_{0}\psi_{E} = \epsilon_{E}\psi_{E} \]

The coupling of states in E is well-described by an effective Hamiltonian:

\[ i\frac{\partial\Psi(t)}{\partial t} = H_{\text{eff}}\Psi(t) \]

\[ H_{\text{eff}} = H_{0} - \frac{1}{4} \sum_{ij} \alpha_{ij} F_{j}(t)F_{i}(t) \]
Increasing pulse duration

Laser induced alignment

REVIVALS

Short pulse (impulsive)

Long pulse (adiabatic)

Torres, de Nalda and Marangos PRA 72, 023420 (2005)
Scheme to manipulate the torsion
DFDBrBPh as a test molecule

Markers of ring (2) → F

Markers of ring (1)

Sₐ  "Mirror"  Rₐ

Torsion
Two pulse laser scheme for manipulation of torsion
Two pulse laser scheme for manipulation of torsion

1. Long ns pulse fixes the C-C axis.
Two pulse laser scheme for manipulation of torsion

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Two pulse laser scheme for manipulation of torsion

1. Long ns pulse fixes the C-C axis.
2. Short (fs) kick pulse induces change of $\phi_{\text{Br}}$ and $\phi_{\text{F}}$. 

![Diagram of a molecule with two pulses indicated: a long pulse fixes the C-C axis, and a short kick pulse induces a change in torsion angles $\phi_{\text{Br}}$ and $\phi_{\text{F}}$.]
Semi-classical model

\[ H = - \frac{1}{2I} \frac{\partial^2}{\partial \Phi^2} - \frac{1}{2I_{\text{rel}}} \frac{\partial^2}{\partial \phi_d^2} + V_{\text{tor}}(\phi_d) \]

\[ \phi_d = \phi_{\text{Br}} - \phi_F, \Phi = (1 - \eta)\phi_{\text{Br}} + \eta\phi_F \]

- Overall rotation on a ns time scale.
- Torsion on a ps time scale.
Semi-classical model

\[
H = -\frac{1}{2I} \frac{\partial^2}{\partial \Phi^2} - \frac{1}{2I_{rel}} \frac{\partial^2}{\partial \phi_d^2} + V_{tor}(\phi_d)
\]

\[
\phi_d = \phi_{Br} - \phi_F, \Phi = (1 - \eta)\phi_{Br} + \eta\phi_F
\]

- Overall rotation on a ns time scale.
- Torsion on a ps time scale.
- Treat slow dynamics classically and fast dynamics quantum mechanically.
Semi-classical model

\[
H = -\frac{1}{2I} \frac{\partial^2}{\partial \Phi^2} - \frac{1}{2I_{rel}} \frac{\partial^2}{\partial \phi_d^2} + V_{tor}(\phi_d) + V_{kick}(\Phi, \phi_d, t)
\]

\[
\phi_d = \phi_{Br} - \phi_F, \quad \Phi = (1 - \eta)\phi_{Br} + \eta \phi_F
\]
Semi-classical model

\[ H = -\frac{1}{2I} \frac{\partial^2}{\partial \Phi^2} - \frac{1}{2I_{rel}} \frac{\partial^2}{\partial \phi_d^2} + V_{\text{tor}}(\phi_d) + V_{\text{kick}}(\Phi, \phi_d, t) \]

\[ \phi_d = \phi_{Br} - \phi_F, \Phi = (1 - \eta)\phi_{Br} + \eta\phi_F \]

Quantum treatment of torsion:

\[ |\chi_\nu\rangle \rightarrow |\chi^\Phi_\nu(t)\rangle = \sum_{\nu'} c^\Phi_{\nu'}(t) e^{iE_{\nu'}(t-t_0)} |\chi_{\nu'}\rangle \]

\[ \dot{c}^\Phi_{\nu'} = -i \sum_\nu c^\Phi_{\nu}(t) e^{-i(E_{\nu} - E_{\nu'})(t-t_0)} \langle \chi_{\nu'} | V_{\text{kick}}(\Phi, t) | \chi_\nu \rangle \]
Semi-classical model

\[ H = -\frac{1}{2I} \frac{\partial^2}{\partial \Phi^2} - \frac{1}{2I_{rel}} \frac{\partial^2}{\partial \phi_d^2} + V_{\text{tor}}(\phi_d) + V_{\text{kick}}(\Phi, \phi_d, t) \]

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Quantum treatment of torsion:

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\[ \dot{c}_{\nu'}^{\Phi} = -i \sum_{\nu} c_{\nu}^{\Phi}(t) e^{-i(E_{\nu} - E_{\nu'})(t-t_0)} \langle \chi_{\nu'}|V_{\text{kick}}(\Phi, t)|\chi_\nu\rangle \]

Classical treatment of overall rotation:

\[ \Phi(t) = \Phi_0 - t \frac{1}{I} \left( \frac{\partial}{\partial \Phi} \int_{-\infty}^{\infty} dt' \langle V_{\text{kick}}(\Phi, t') \rangle \right) \bigg|_{\Phi=\Phi_0} \]
Results (proof-of-principle)
Do experiment and theory agree?

√ Fixed C-C axis and uniform distr. of rings prior to kick.

Exp.:  
-0.87 ps  
1.47 ps  
2.47 ps

Theory:  
F⁺  
Br⁺  
F  
Br
Do experiment and theory agree?

√ Fixed C-C axis and uniform distr. of rings prior to kick.

Exp.:
- F^+
- Br^+
- F
- Br

Theory:

-0.87 ps
1.47 ps
2.47 ps

kick pulse pol., 5x10^{12} W/cm^2, FWHM=700 fs

Long pulse pol. axis
Do experiment and theory agree?

√ Fixed C-C axis and uniform distr. of rings prior to kick.

Exp.:  
-0.87 ps  
1.47 ps  
2.47 ps  

Theory:  
F⁺  
Br⁺  
F  
Br
Do experiment and theory agree?

√ Fixed C-C axis and uniform distr. of rings prior to kick.

Exp.: F^+  Br^+  F  Br

Theory:  -0.87 ps  1.47 ps  2.47 ps
Do experiment and theory agree?

√ Fixed C-C axis and uniform distr. of rings prior to kick.

Exp.:

Theory:

-0.87 ps
1.47 ps
2.47 ps

F⁺
Br⁺
F
Br
Do experiment and theory agree?

√ Fixed C-C axis and uniform distr. of rings prior to kick.

Exp.:
-0.87 ps
1.47 ps
2.47 ps

Theory:

F^+

F

Br^+

Br
Do experiment and theory agree?

√ Fixed C-C axis and uniform distr. of rings prior to kick.

√ Maximal confinement of F-ring around 1.47 ps.

Exp.: -0.87 ps  1.47 ps  2.47 ps

F⁺

Br⁺

F

Br

Theory:
Do experiment and theory agree?

√ Fixed C-C axis and uniform distr. of rings prior to kick.

√ Maximal confinement of F-ring around 1.47 ps.

Conclusion: Experiment and theory agree!
Do we induce torsion?

The Br-rings and F-rings do not align maximally at the same time.

The dihedral angle is not fixed at $\pm 39^\circ$.

Exp.:
- $F^+$
- $Br^+$

Kick pulse pol.
Do we induce torsion?

The Br-rings and F-rings do not align maximally at the same time.

The dihedral angle is not fixed at $\pm 39^\circ$.

So there must be torsion...
Do we induce torsion?

Drift of $F^+$ motion due to rotation, but recurrent dips every $\sim 1$ ps.
Do we induce torsion?

Drift of F\(^+\) motion due to rotation, but recurrent dips every \(\sim 1\) ps.

Explained by theory: Periodic torsional motion.

Predicted torsional motion for \(\parallel\)-geometry.

Kick pulse pol.
Do we induce torsion?

Drift of F⁺ motion due to rotation, but recurrent dips every ~ 1 ps.

Explained by theory:
Periodic torsional motion.

⟨φ⟩ (degrees)

Drift of F-ring

Experiments:
||-geometry can be realized using an elliptically pol. ns pulse.

1.47 ps 2.47 ps
Perspectives
Use in molecular junctions

- Axially chiral molecules can act as a switch in a molecular junction:
  - Flow of charge
  - || Rings: Charge passes.
  - \( \perp \) Rings: Charge cannot pass.

- Torsional control \( \Rightarrow \) Ultrafast charge modulations.
Time-resolved studies of processes involving torsion

- Time-resolved study of the conversion between enantiomers.
- De-racemization: Selective conversion from a racemate (1:1 mixture of $S_a$ and $R_a$) to a pure compound (e.g., $S_a$'s only).
Prerequisites for de-racemization

1. Overcome the torsional barrier

- Pre-alignment of rings and higher kick laser intensity.

2. Selectivity

- Alignment of C-C axis insufficient.
Prerequisites for de-racemization

1. Overcome the torsional barrier

- √ Pre-alignment of rings and higher fs laser intensity.

2. Selectivity

- √ Ensured by orientation.

Kick pulse pol.
Example of de-racemization with initial racemate of "DFDBrBPh" exposed to an elliptically polarized ns pulse and a kick pulse of intensity $1.2 \times 10^{13}$ W/cm$^2$ and FWHM=1 ps:

99% of $R_a$ is converted into $S_a$.

13% of $S_a$ is converted into $R_a$. 
Summary

• We have extended the use of non-resonant strong laser fields to the manipulation of the torsion of molecules.

• Experimental and theoretical proof-of-principle results.

• Perspectives include molecular switches and time-resolved study of de-racemization.

Outlook

• More and better experiments (pre-alignment of rings with elliptically pol. ns pulse, increased kick strength, orientation).

• Use a pure quantum model and do quantum optimal control theory.

• The use of axially chiral molecules as molecular switches.
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