Selective Control of Molecular Rotation

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Motivation for controlling molecular rotation, alignment/orientation

Control of chemical kinetics
Pulse shaping
Pulse compression
HHG control
Molecular imaging
Quantum computation
etc ...
Control of Laser induced Ionization/Dissociation

Selective Ionization / Dissociation of a single species in a mixture.

Purification of a sample by “blasting away” other components.

LOW probability

HIGH probability
Outline

• Molecular alignment by femtosecond pulses
• Rotational revivals
• Experimental setup (as seen by a theorist)
  • Addressing close molecular species in a mixture
    – Selection of Isotopes
    – Selection of nuclear spin Isomers
• Unidirectional rotation
• Summary
Outline

• Molecular alignment by femtosecond pulses
  • Rotational revivals
  • Experimental observations
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• Molecular alignment at liquid-air interfaces
• Summary
Laser induced alignment

The laser field couples to the molecular rotation via the anisotropic polarizability

$$\alpha_{\perp}$$

$$\hat{H} = \frac{\hat{L}^2}{2I} + V(\theta, t)$$

$$V(\theta, t) \propto \left[ \frac{1}{4} \hat{H}^2 (\alpha_{\Delta} \alpha_{\perp} \cos^2(\theta)) + \alpha_{\perp} \right]$$

$$\tau(\theta) \propto -\frac{dV}{d\theta}$$

$$\omega(\theta) \propto -\sin(2\theta)$$
\[ \omega(\theta) \propto -\sin(2\theta) \]
Periodic signal
\[ T = 8.3 \text{ ps} \]
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Rotational energy: \( E_J = \hbar B c J(J+1) \)

Rotational wave packet: \( \Psi(t) = \sum_{J,m} c_J^m Y_J^m e^{-i\pi J(J+1)t/T_{\text{rev}}} \)

Quantum revival time: \( T_{\text{rev}} = \frac{1}{2Bc} \)

The wavefunction is periodic:
\[ \Psi(t + T_{\text{rev}}) = \Psi(t) \quad \text{- full revival} \]
Alignment evolution through time

For \( N_2 \), 100 fs pulse
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Experimental: time delayed degenerate four wave mixing

\[ E_a E_b = E_c \]

Phase matching

\[ \vec{k}_s = (\vec{k}_a - \vec{k}_b) + \vec{k}_c \]

\~ 70 femtosecond pulses \~ 0.1 mJ per pulse
Experimental: Transient Grating - TG

Molecular gas
$^{14}\text{N}_2$ gas at room temperature

$T_{\text{rev}} = 8.3\ \text{ps}$
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Alignment of Chlorine isotopologues

\[ \text{Trev (Cl}_2) \approx 70 \text{ ps} \]

- Cl\(^{35}\) - 7.5%
- Cl\(^{37}\) - 2.5%
- Cl\(^{35}\) - Cl\(^{35}\) - 9/16
- Cl\(^{37}\) - Cl\(^{37}\) - 1/16
- Cl\(^{35}\) - Cl\(^{37}\) - 6/16
Controlling rotations with two pulses – classical picture

Applying another pulse just on time!

$2^{nd}$ pulse
At $\frac{1}{2} T_{rev}$

$2^{nd}$ pulse
At full $T_{rev}$
Rotational control in $^{14}\text{N}_2$ 

Selective alignment in isotopologues mixture

$^{14}$N$_2$ $\sim$ 8.3ps  
$^{15}$N$_2$ $\sim$ 8.9ps

$7\frac{1}{2}$ $T_{rev}$  
7 $T_{rev}$

$^{15}$N$_2$ only

[Graph showing time vs. intensity with two pulses and labels for first and second pulse, and $^{15}$N$_2$ only highlighted]
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$^{15}\text{N}_2$ - homonuclear molecule with atomic nuclear spin – $I = \frac{1}{2}$

$$\Psi = \Psi_{\text{elec}} \Psi_{\text{vib}} \Psi_{\text{rot}} \Psi_{\text{spin}}$$

$^{15}\text{N}$ atoms are Fermions

Anti-symmetric upon exchange

Ortho (Triplet)  
Symmetric $\Psi_{\text{spin}}$  
Anti-Symmetric $\Psi_{\text{rot}}$  
Odd J states

Para (Singlet)  
Anti-Symmetric $\Psi_{\text{spin}}$  
Symmetric $\Psi_{\text{rot}}$  
Even J states
Calculated alignment factor for $N_2$, 300 K

- Decrease
- Enhance
- Enhance
- Decrease
Energy absorbed by odd and even wavepackets
Spin isomer-selective alignment by two pulses

Frequency analysis

\[ \text{Signal} \propto \delta n \]
\[ \delta n \propto \left\langle \cos^2 \theta \right\rangle \]

Participating rotational state population
Signal $\propto (\delta n)^2$
$\propto \langle \cos^2 \theta \rangle^2$

Binary SUMS and DIFFERENCES of the J states
Single pulse vs. double pulse

Odd Sum  ↔  Odd J + Even J
Even Sum  ↔  Odd J + Odd J, Even J + Even J
Laser Alignment of Ortho/Para Water Molecules


Rotational Hamiltonian (rigid rotor model)

\[ \hat{H} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c} \]

\((a,b,c)\) are the molecule principal axes

C\(_{2v}\) symmetry, irreducible representations:

\(A_1, A_2, B_1, B_2\).
Spin-Dependent Alignment

Calculated time dependent alignment factor after an excitation by a short linearly polarized 20 fs laser pulse of $10^{13} W / cm^2$ maximal intensity, at 20K.

Simultaneous alignment and antialignment of two different spin isomers can be achieved.
Spin-Selective Alignment by Two Pulses

After application of an additional pulse (of the same intensity and duration) at $t=1.9$ ps

As a result, only the Para molecules experience transient alignment!
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Field Free Unidirectional Rotation

\[ L_y = 0 \]
\[ L_z = 0 \]
\[ (-L_y) = 0 \]
\[ L_x = 0 \]
Controlling the sense of rotation

Optical Centrifuge for Molecules

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Controlling the sense of rotation

\( \langle L_Y \rangle \neq 0 \)
Angular momentum as a function of 2nd pulse polarization

Max \( \langle L_y \rangle \) @ \( \pm 45^0 \)
Field free unidirectional rotation

Finite temperature simulations by:
• Spectral decomposition
• Direct FDTD
• Classical ensemble dynamics

NJP, submitted (2009)
Anisotropic time averaged angular distribution

Control of:
- Collisional cross section
- Diffusion processes
- Surface scattering
- Deflection by external inhomogeneous fields

Yet to be demonstrated experimentally!
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Summary

Selective addressing of close molecular species:
- Molecular isotopes
- Spin Isomers

- Not based on specific molecular resonances.
- Conducted at room temperature.
- Can be applied to all symmetric linear molecules.

Double pulse scheme - selective ionization (dissociation).

Unidirectional rotation – anisotropic diffusion.
  directional surface scattering.
  interesting optical features.

- Should be implemented to molecules larger than diatomics
- May be useful for detection and identification in mixtures
The End

Thank you