Selective Control of Molecular Rotation

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KITP, Santa Barbara **May 2009**

Motivation for controlling molecular rotation, alignment/orientation

Control of chemical kinetics

Pulse shaping

Pulse compression

HHG control

Molecular imaging

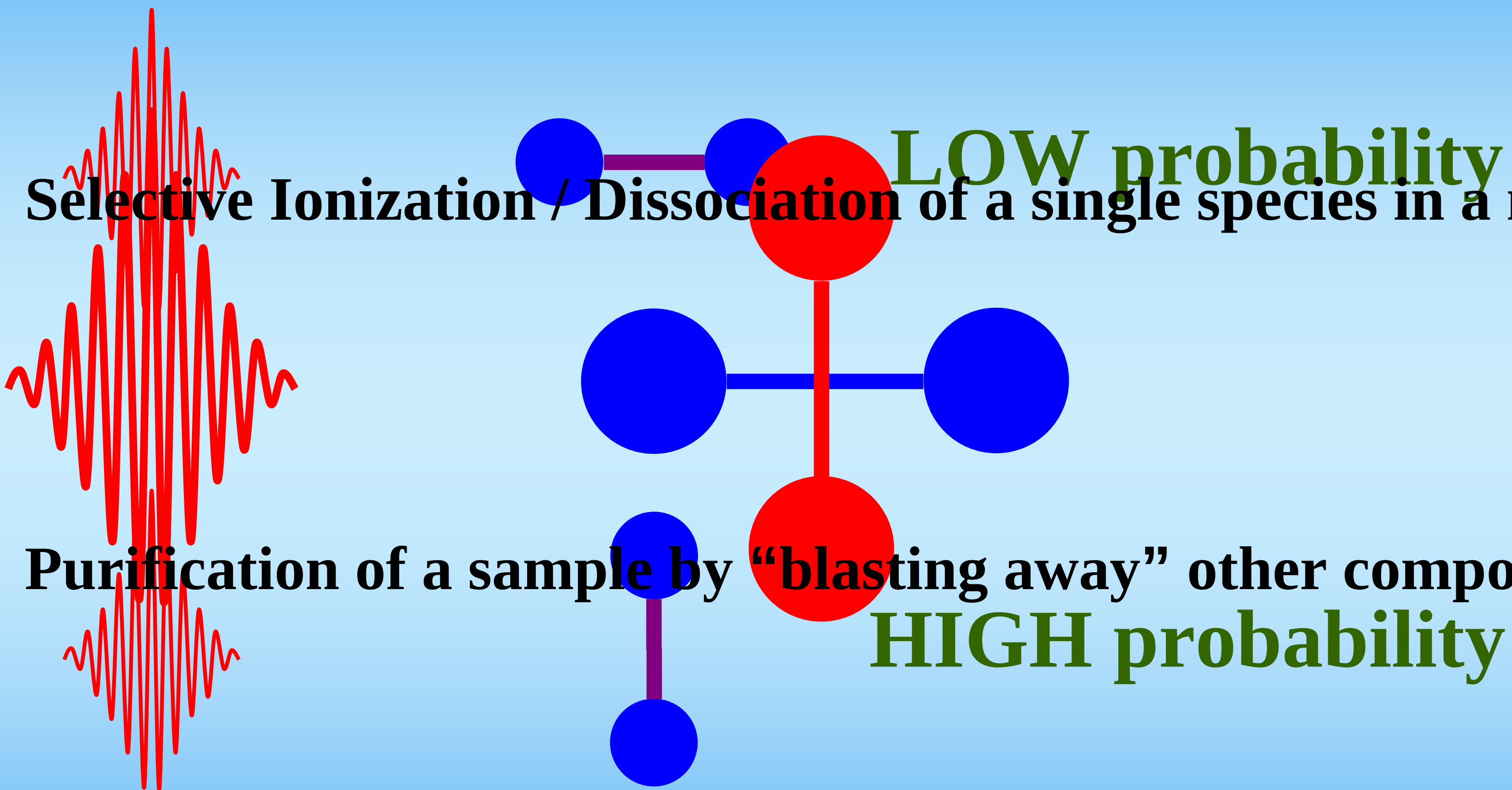
Quantum computation

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.



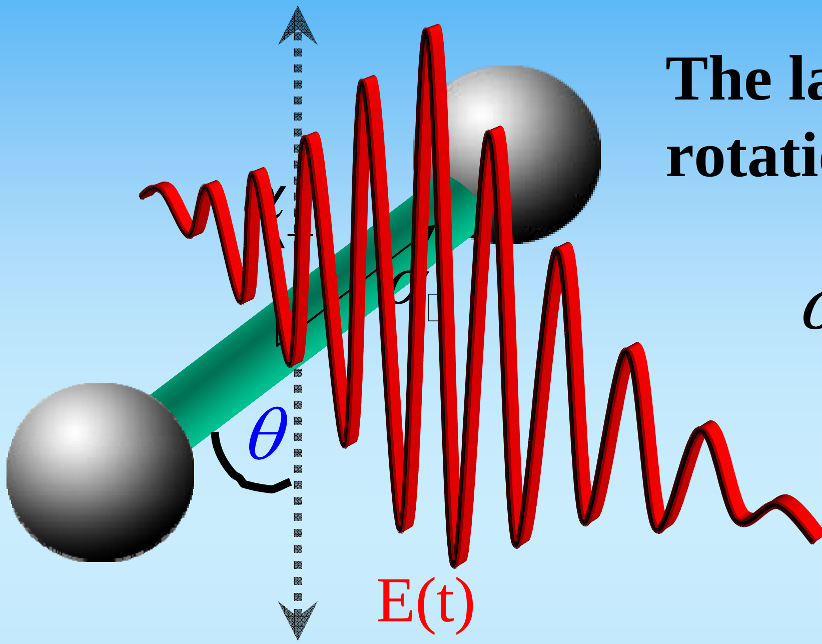
Outline

- 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**
- **Addressing close molecular species in a mixture**
  - **Selection of Isotopes**
  - **Selection of nuclear spin Isomers**
- **Unidirectional rotation**
- **Molecular alignment at liquid-air interfaces**
- **Summary**

Laser induced alignment



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

$$\alpha_{\parallel} \gg \alpha_{\perp}$$

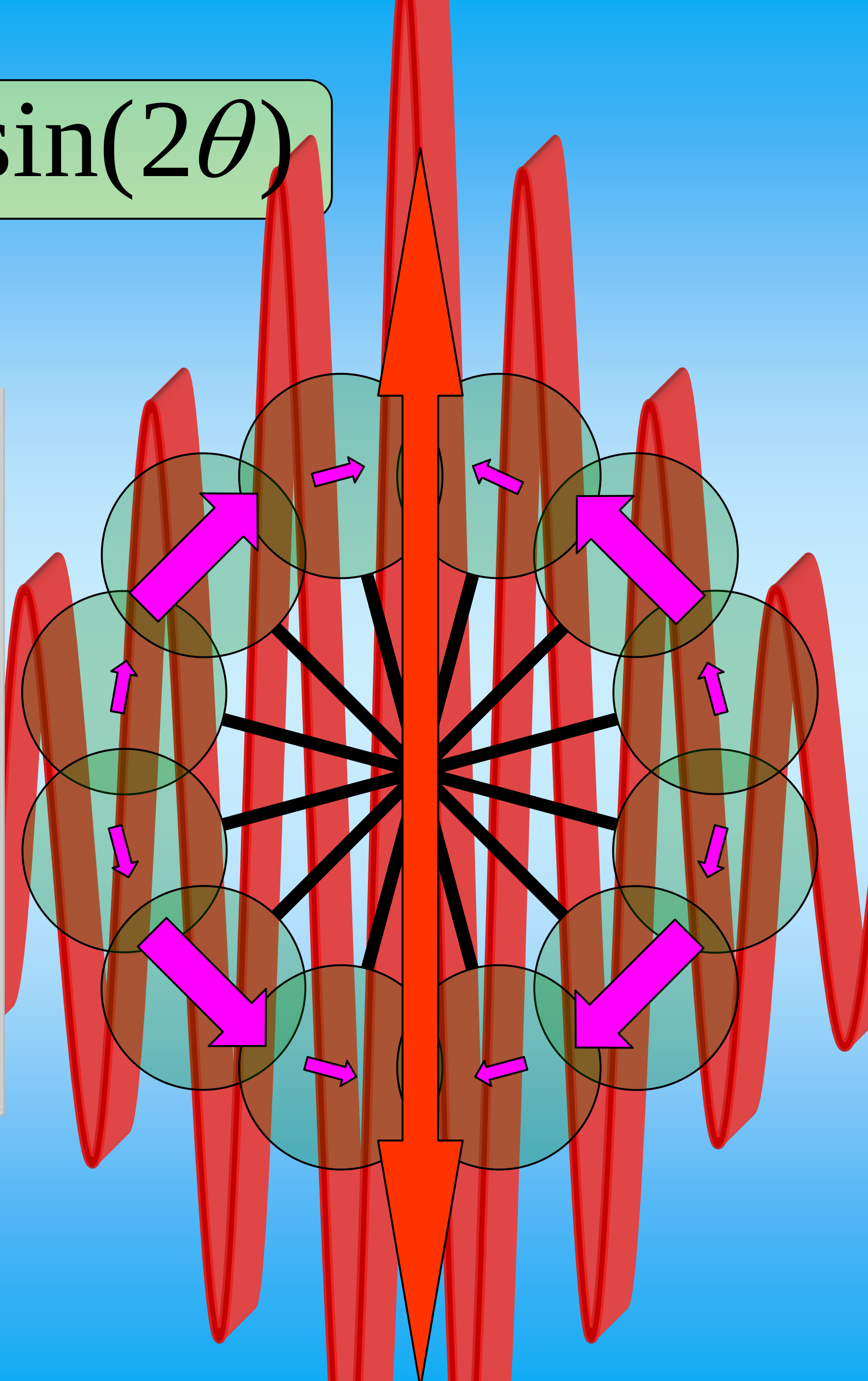
$$\hat{H} = \frac{\hat{L}^2}{2I} + V(\theta,t)$$

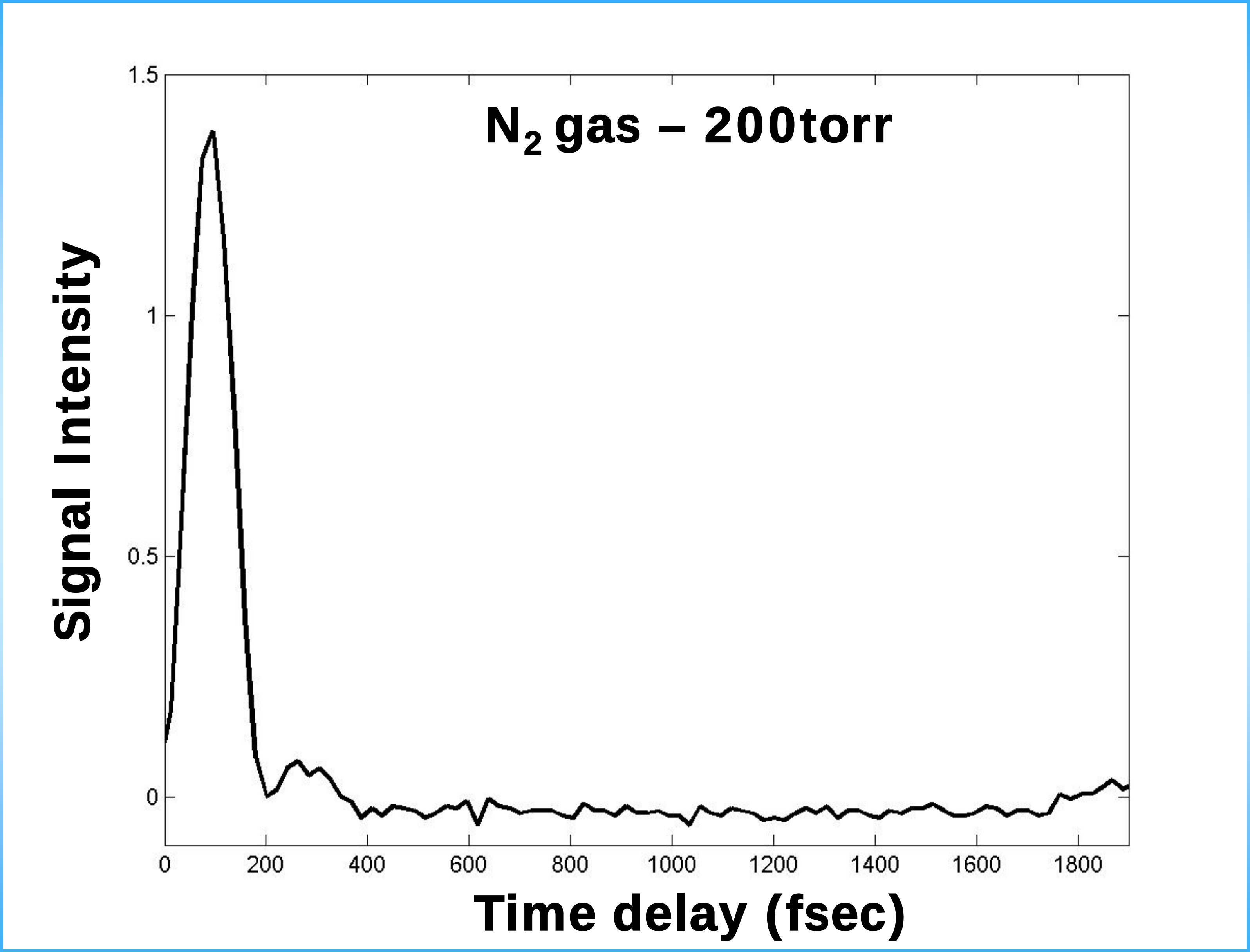
$$V(\theta,t) = -\frac{1}{4}E^2(t)\left[(\alpha_{\parallel} - \alpha_{\perp})\cos^2(\theta) + \alpha_{\perp}\right]$$

$$V(\theta,t) \propto -\Delta\alpha\cos^2(\theta)$$

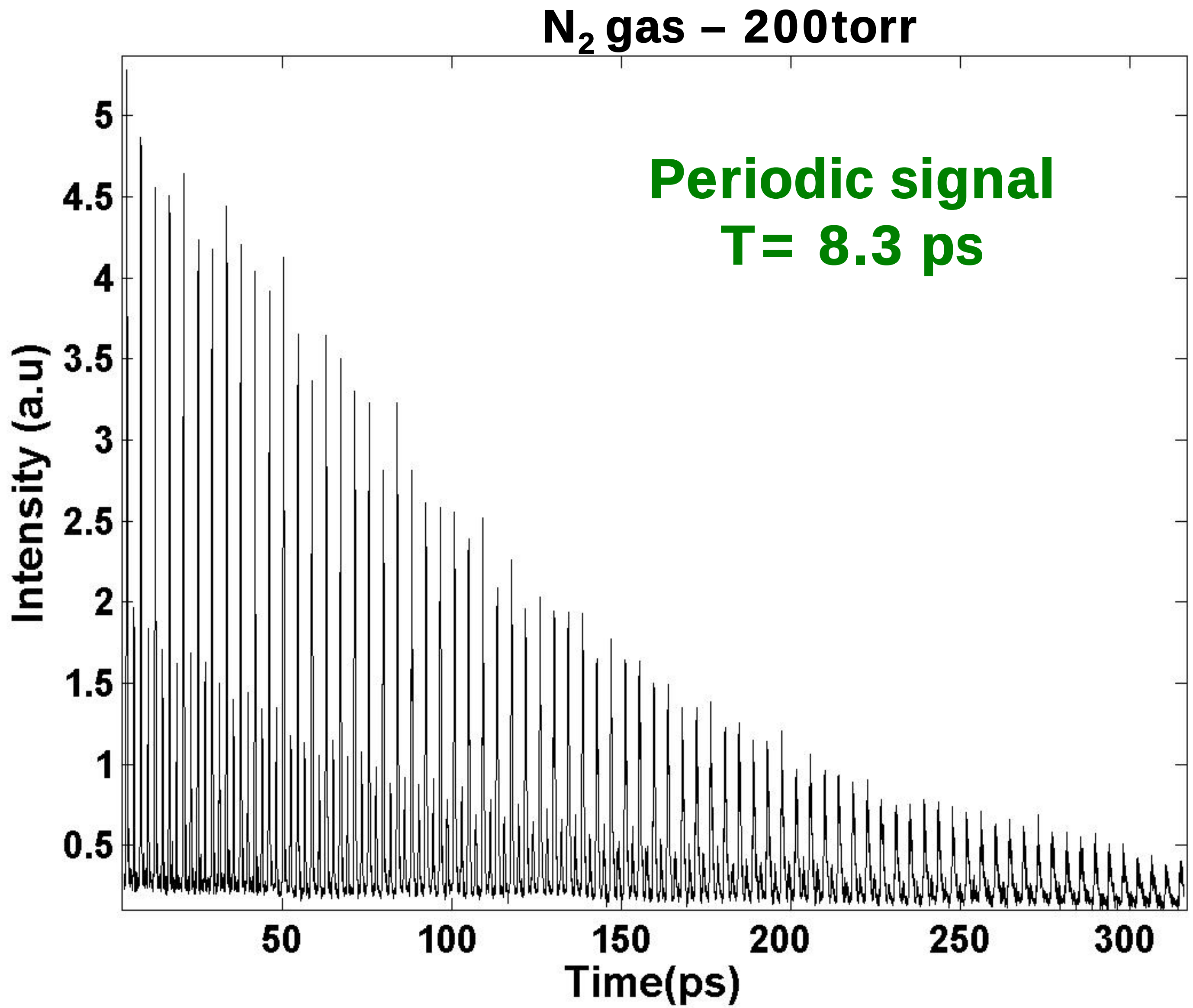
$$\tau(\theta) \propto -\frac{dV}{d\theta} \quad , \quad \omega(\theta) \propto -\sin(2\theta)$$

$$\omega(\theta) \propto -\sin(2\theta)$$





N2 gas – 200torr
Signal Intensity
Time delay (fsec)
1.5
1
0.5
0
0
200
400
600
800
1000
1200
1400
1600
1800



N2 gas – 200torr
Periodic signal
T= 8.3 ps
Intensity (a.u)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
50
100
150
200
250
300
Time(ps)

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Revivals of rotational wave packets

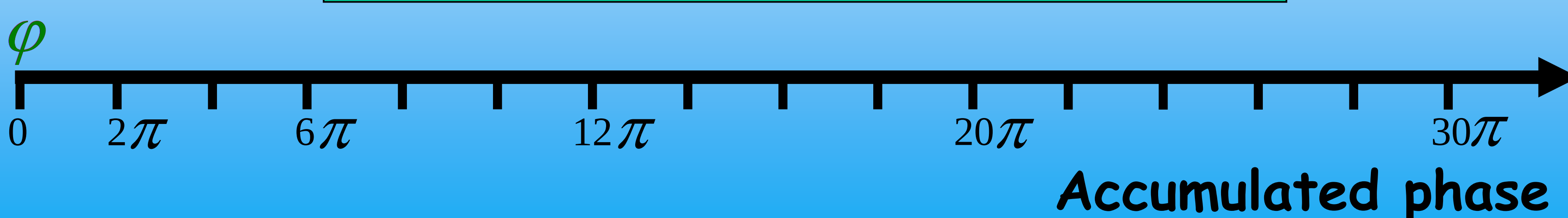
Rotational energy: $E_J = hBc\, J(J+1)$

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

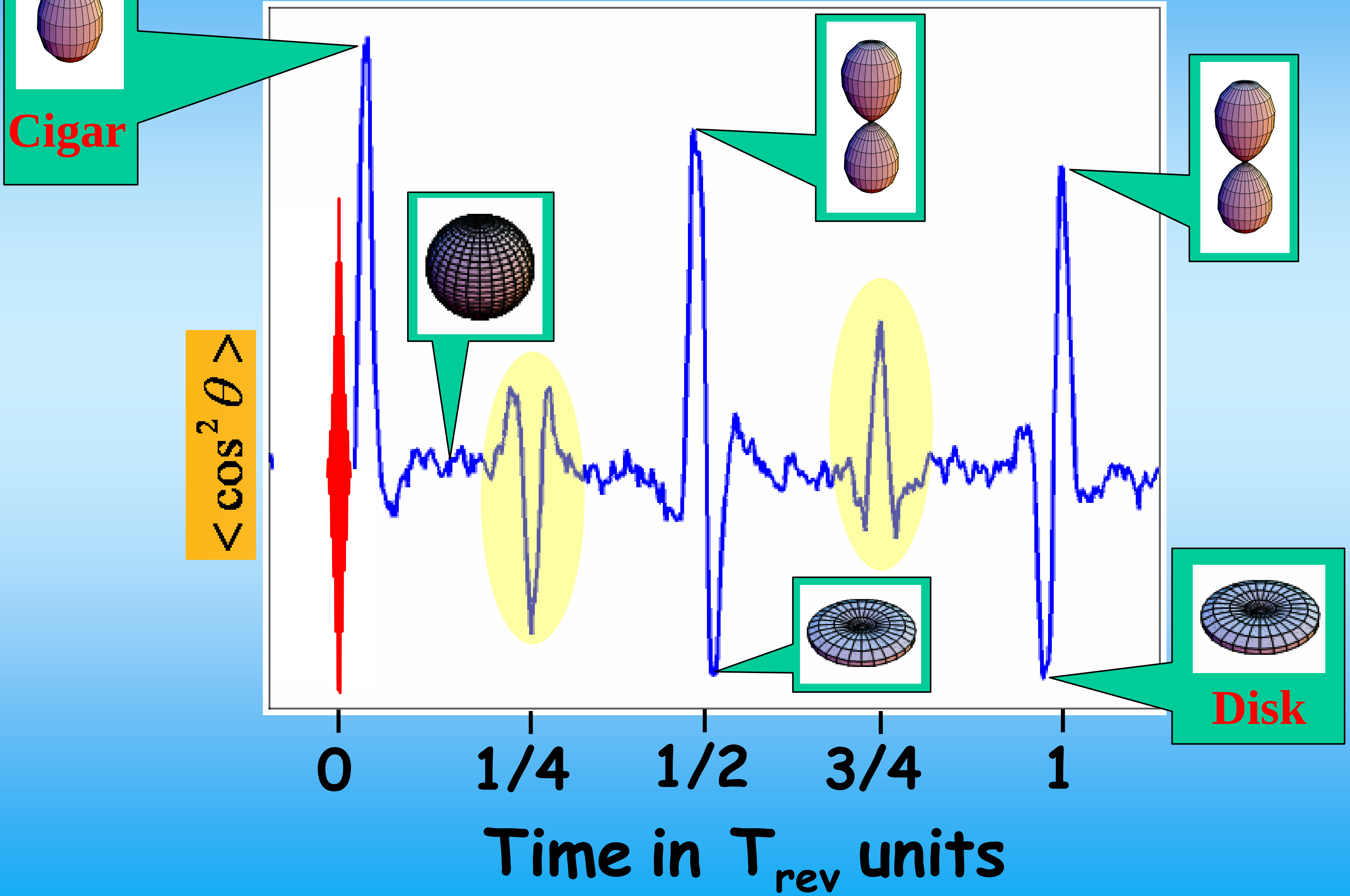
Quantum revival time: $$T_{rev} = \frac{1}{2Bc}$$

The wavefunction is periodic:

$\Psi(t + T_{rev}) = \Psi(t)$ **- full revival**



Alignment evolution through time
For N_2 , 100 fs pulse



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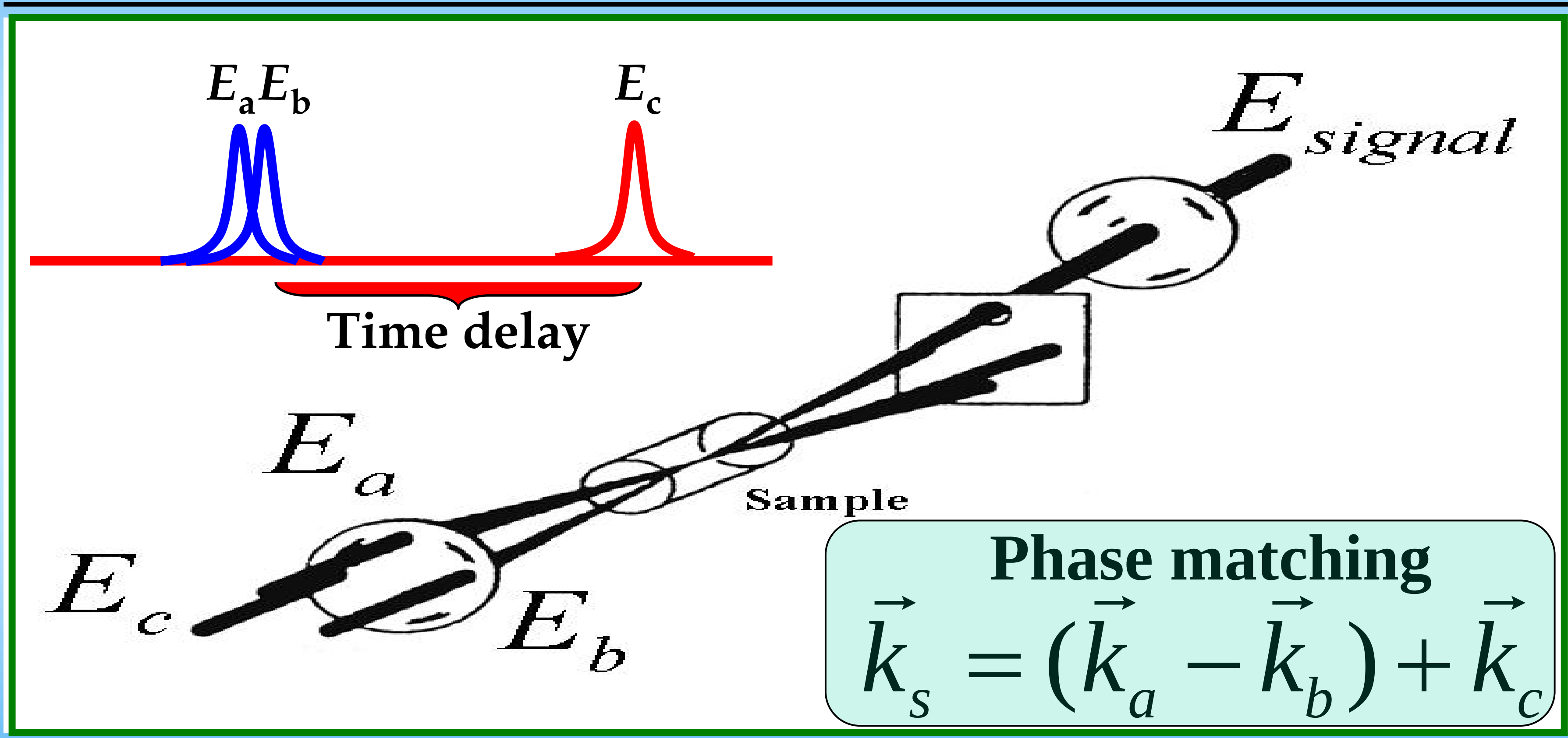
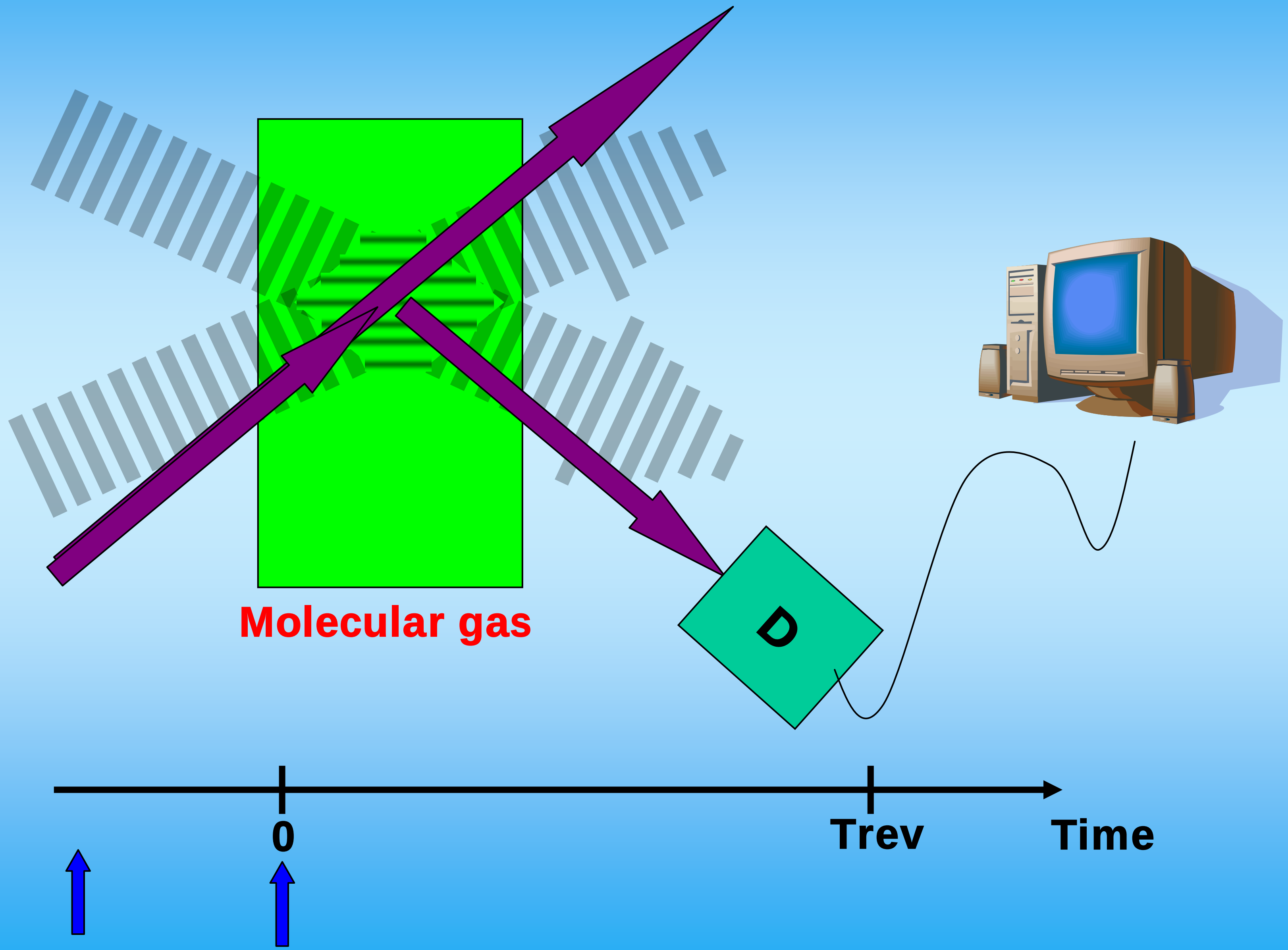
Experimental: time delayed degenerate four wave mixing

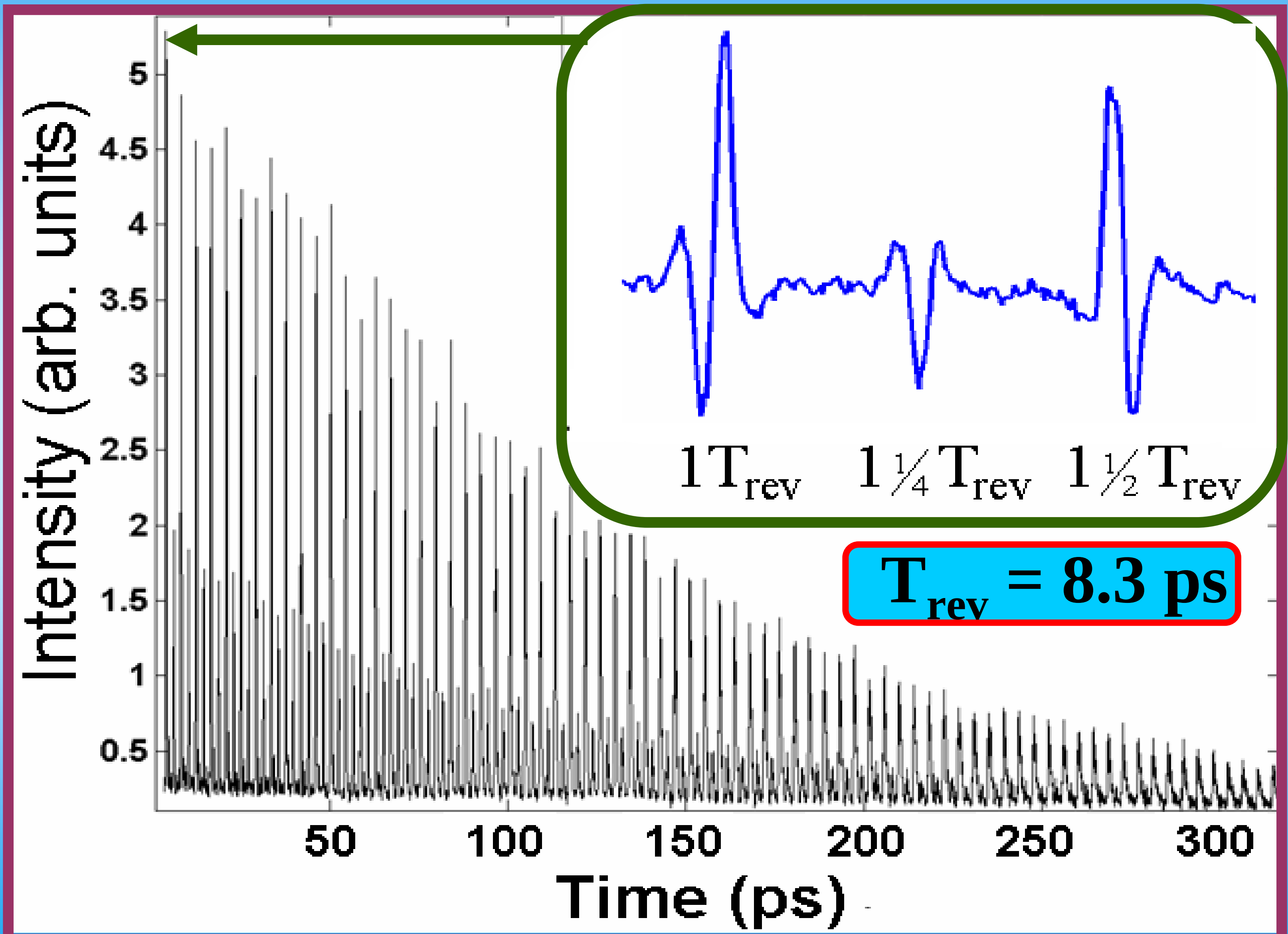


~ 70 femtosecond pulses ~ 0.1 mJ per pulse

Experimental: Transient Grating - TG



$^{14}N_2$ gas at room temperature



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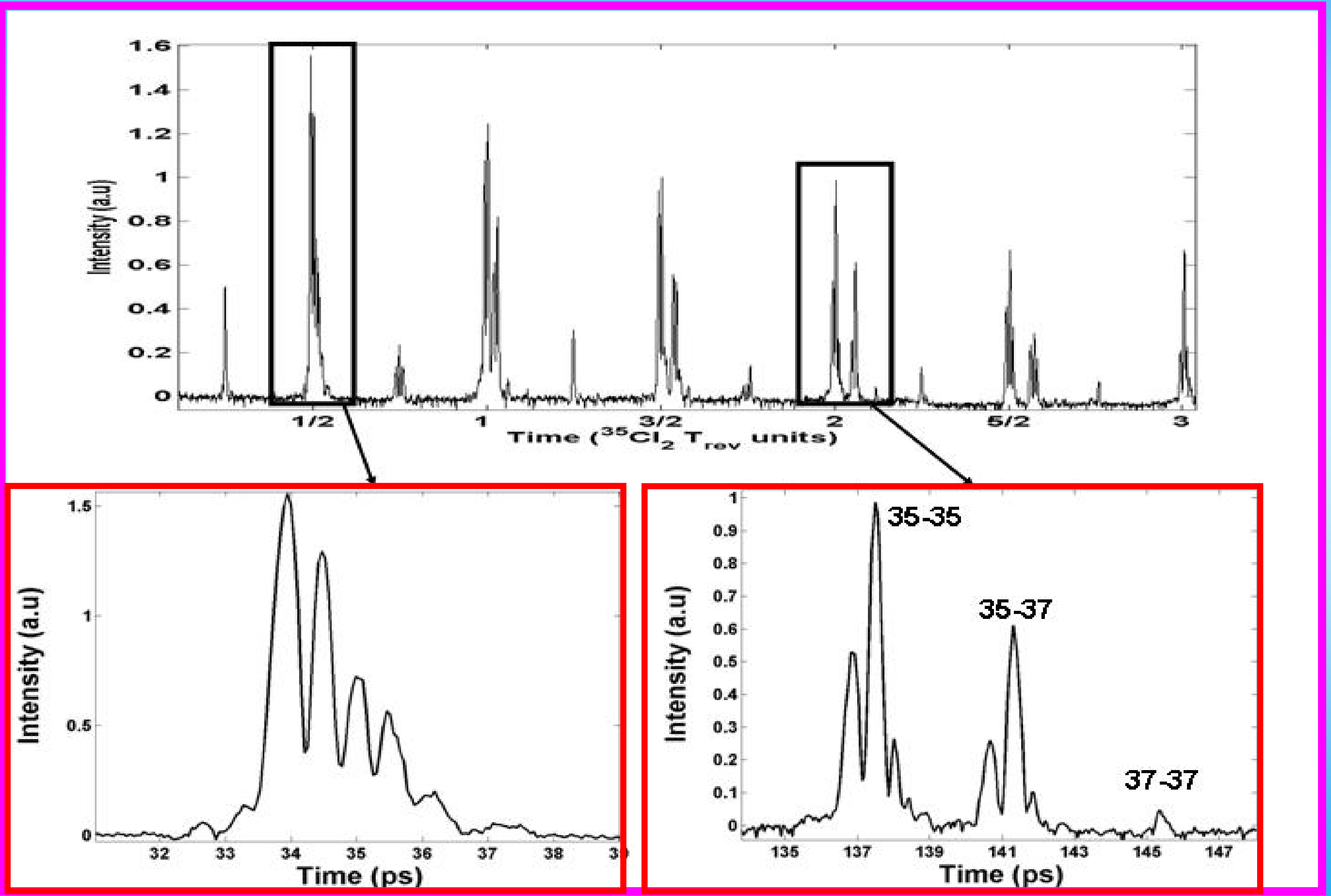
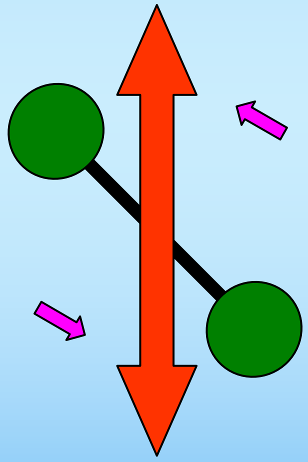
Alignment of Chlorine isotopologues

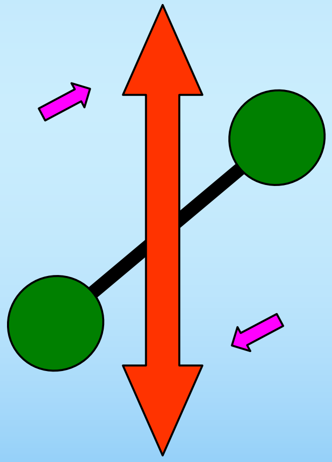


Controlling rotations with two pulses – classical picture

Applying another pulse just on time !

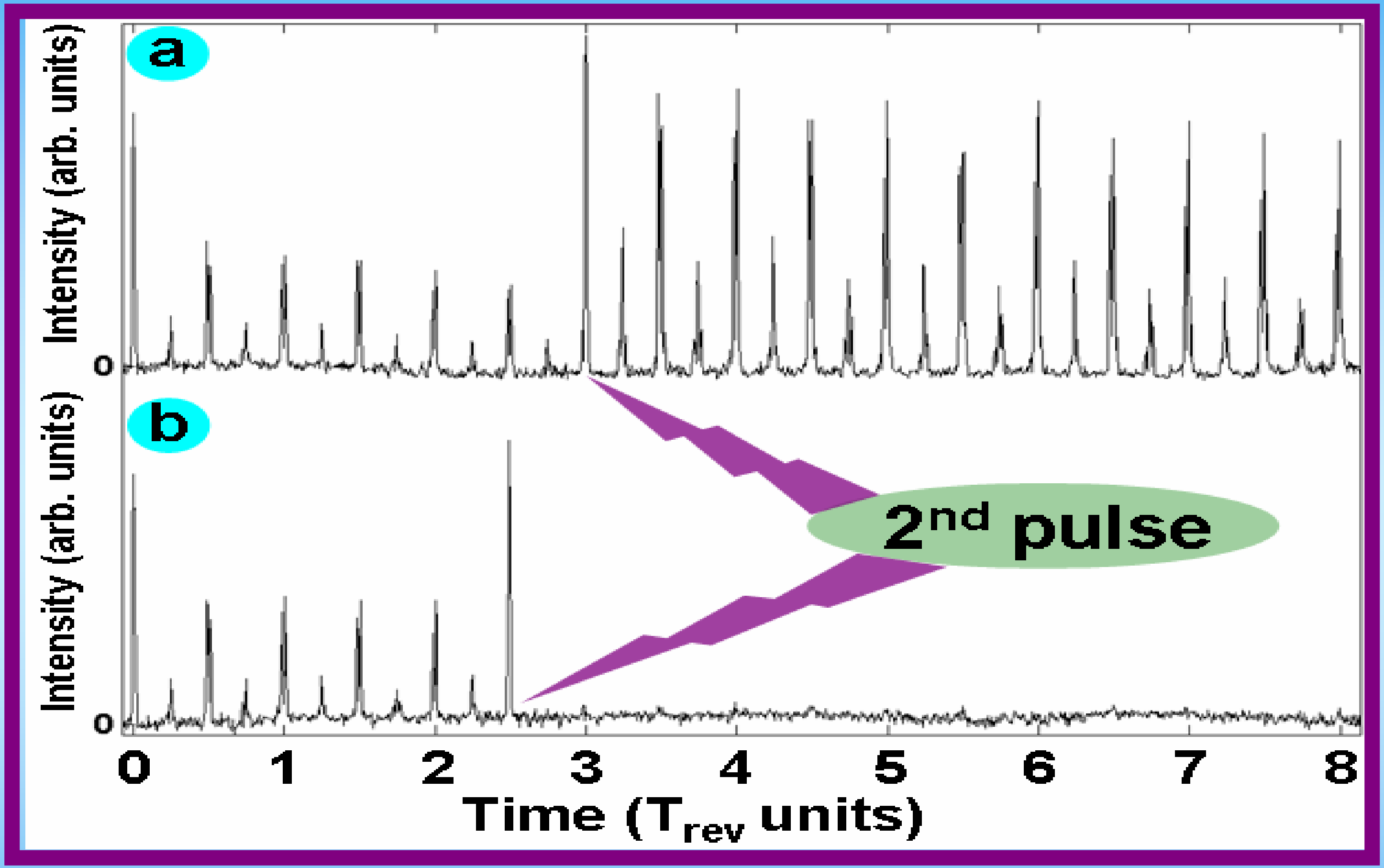


2nd pulse
At ½ T_{rev}



2nd pulse
At full T_{rev}

Rotational control in $^{14}N_2$

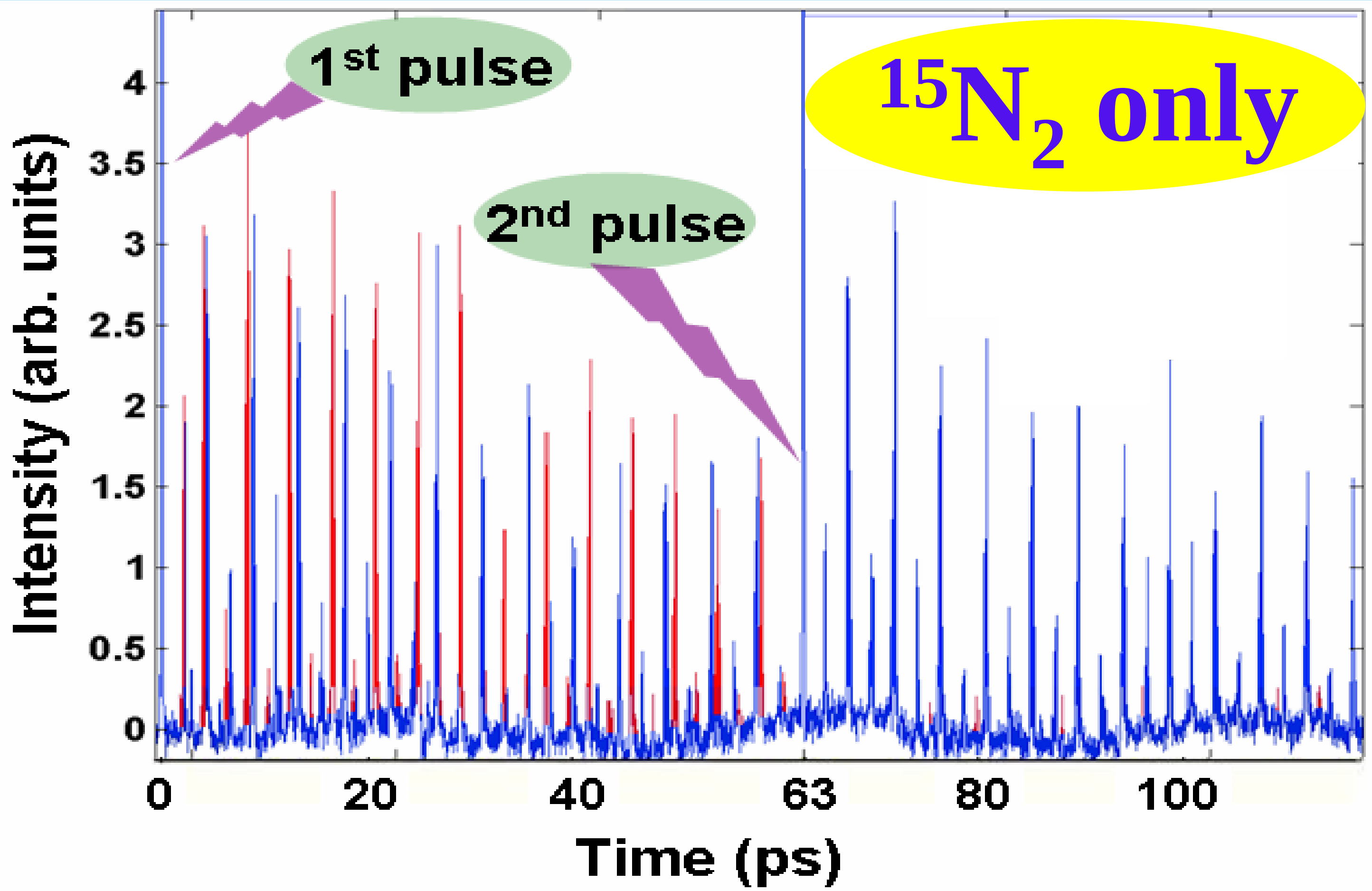


Fleischer, IA, Prior, Phys.Rev. A **74**, 041403(R) (2006)

Selective alignment in isotopologues mixture

$^{14}N_2$ ~ 8.3ps $^{15}N_2$ ~ 8.9ps

7½ T_{rev} 7 T_{rev}



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$^{15}N_2$ - homonuclear molecule with atomic nuclear spin – $I = ½$

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

^{15}N atoms are Fermions

Anti-symmetric upon exchange

Ortho (Triplet)

Para (Singlet)

Symmetric Ψ_{spin}

Anti-Symmetric Ψ_{rot}

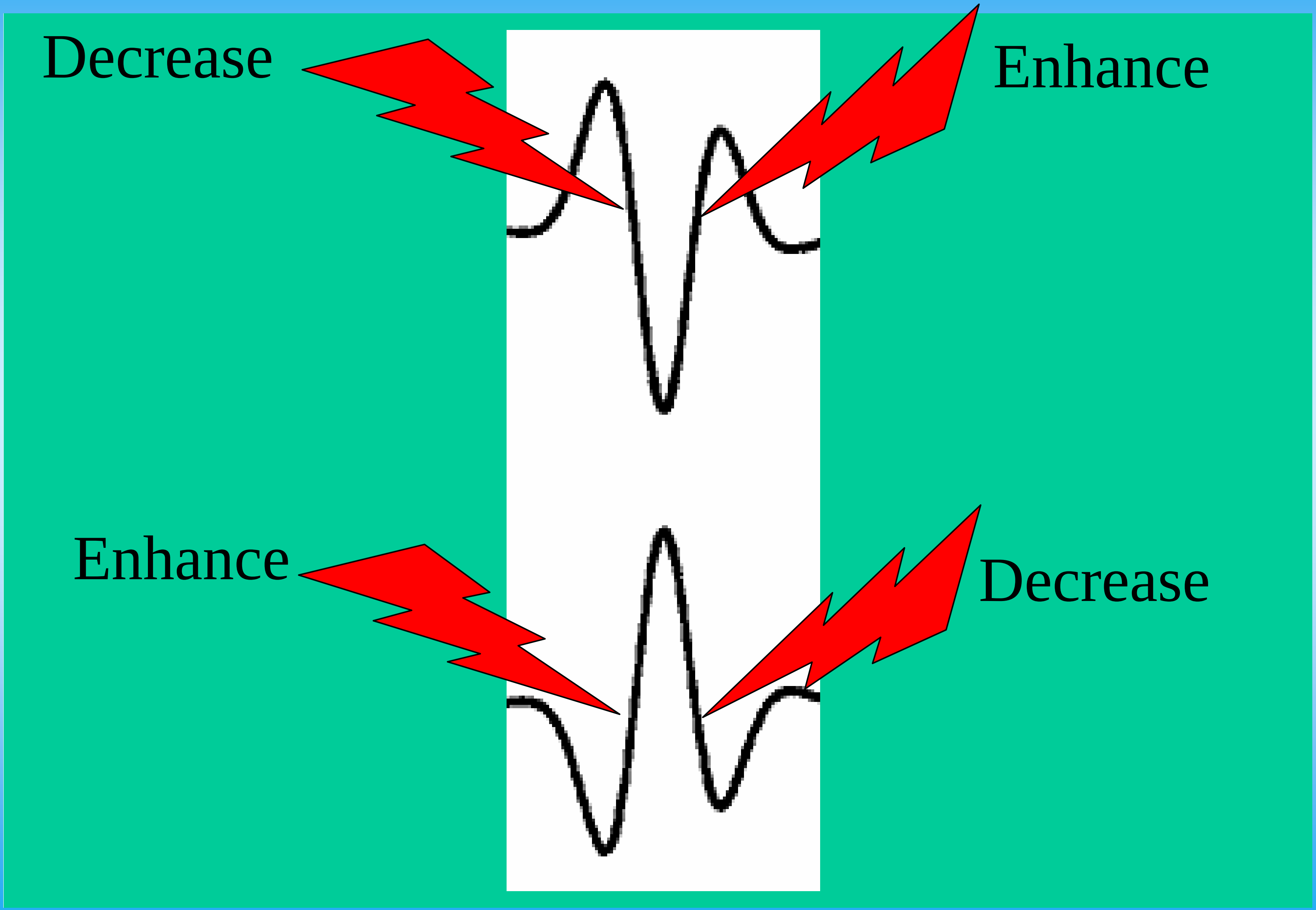
Odd J states

Anti-Symmetric Ψ_{spin}

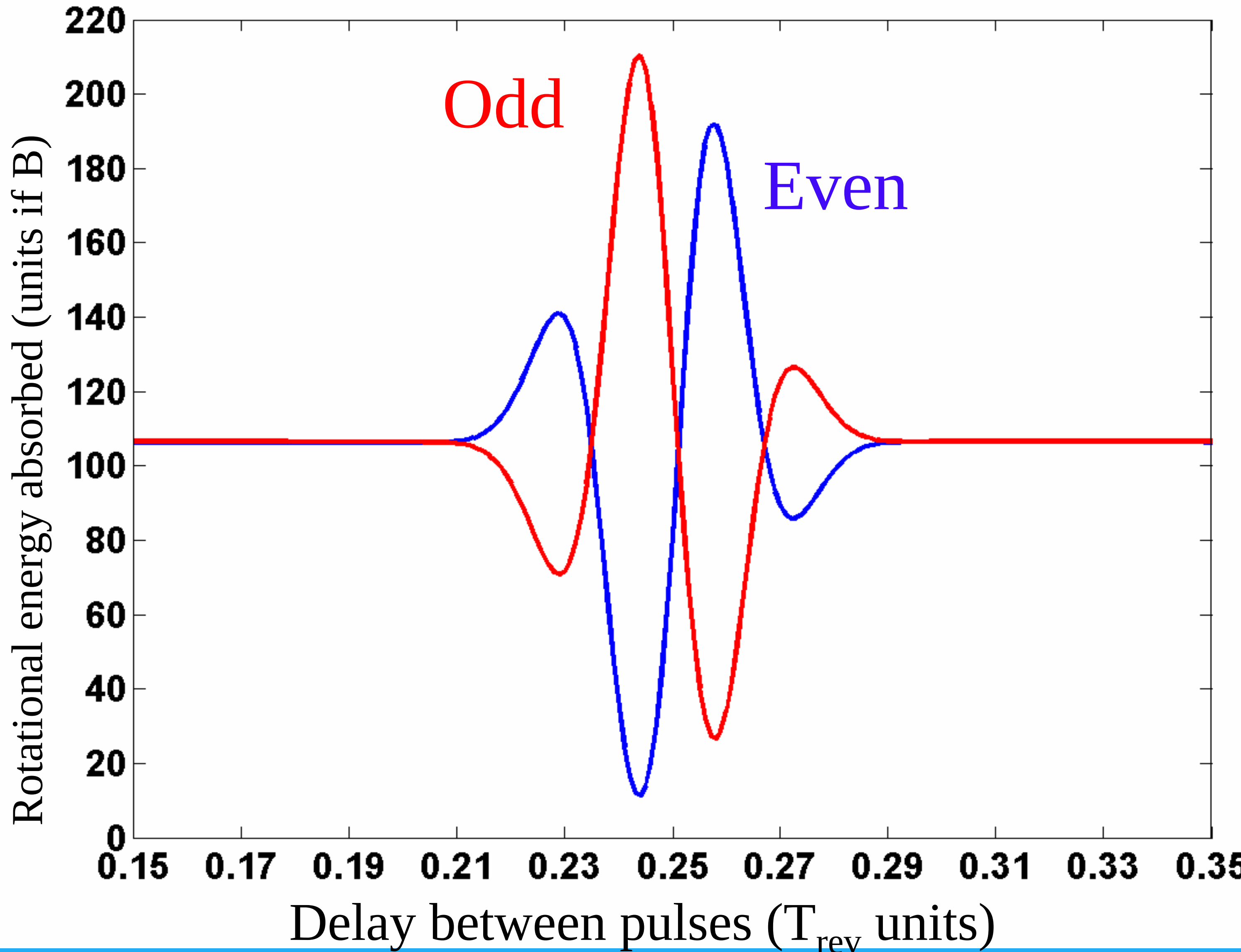
Symmetric Ψ_{rot}

Even J states

Calculated alignment factor for N_2 , 300 K

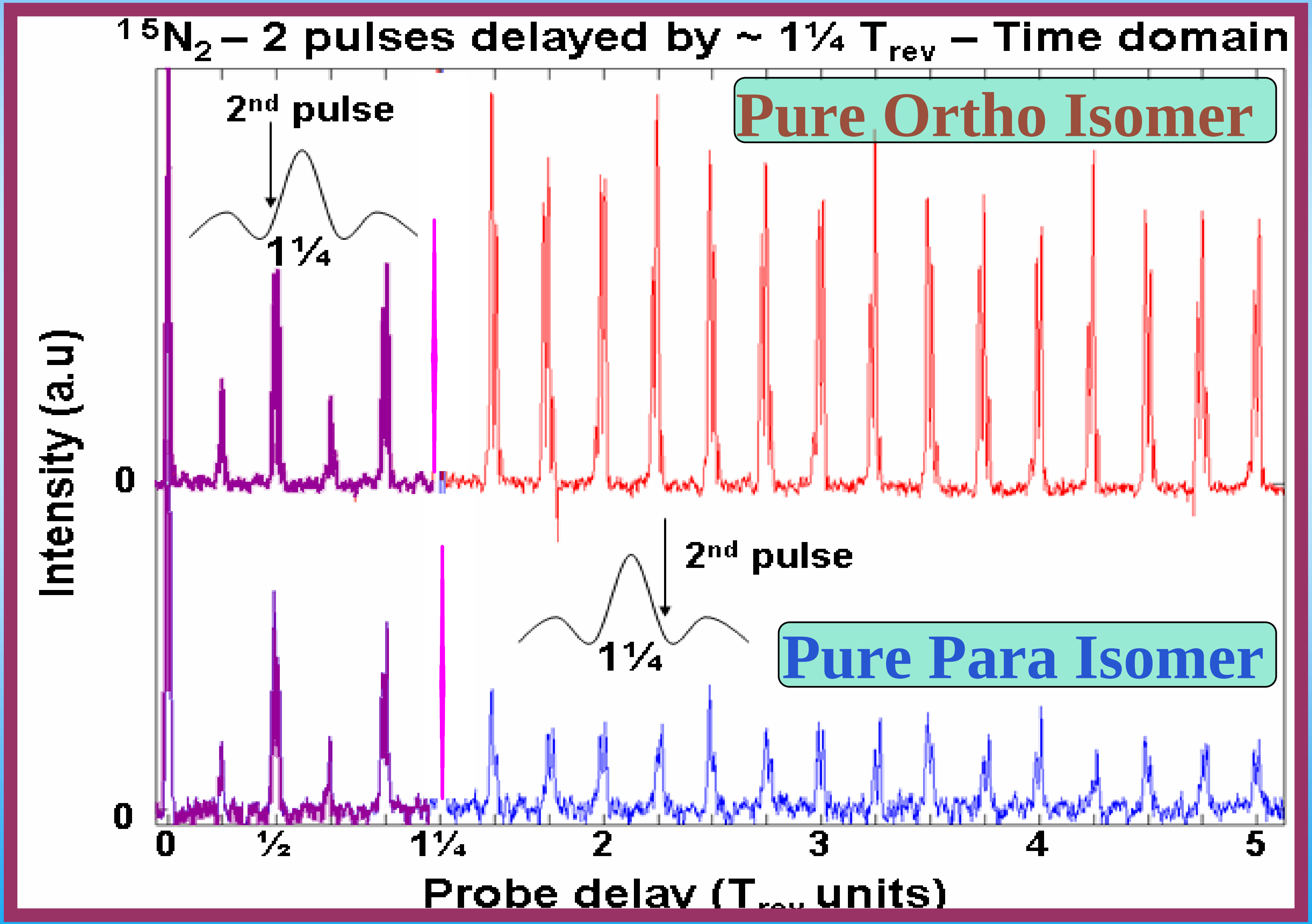


Energy absorbed by odd and even wavepackets

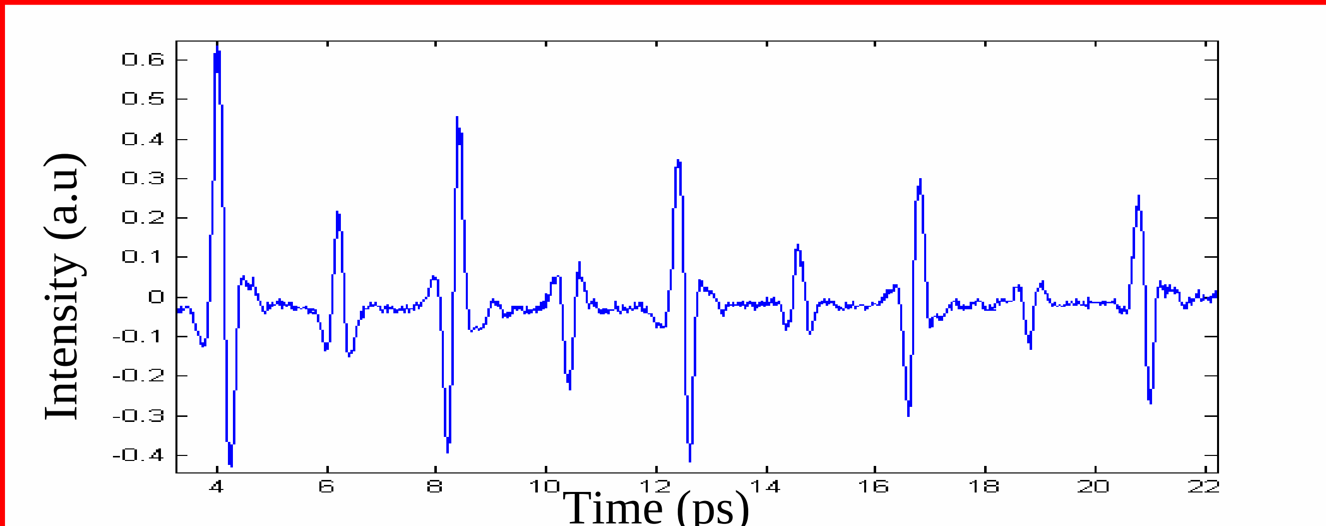


Spin isomer-selective alignment by two pulses

Fleischer, IA, Prior, Phys.Rev.Lett., **99**, 093002 (2007)

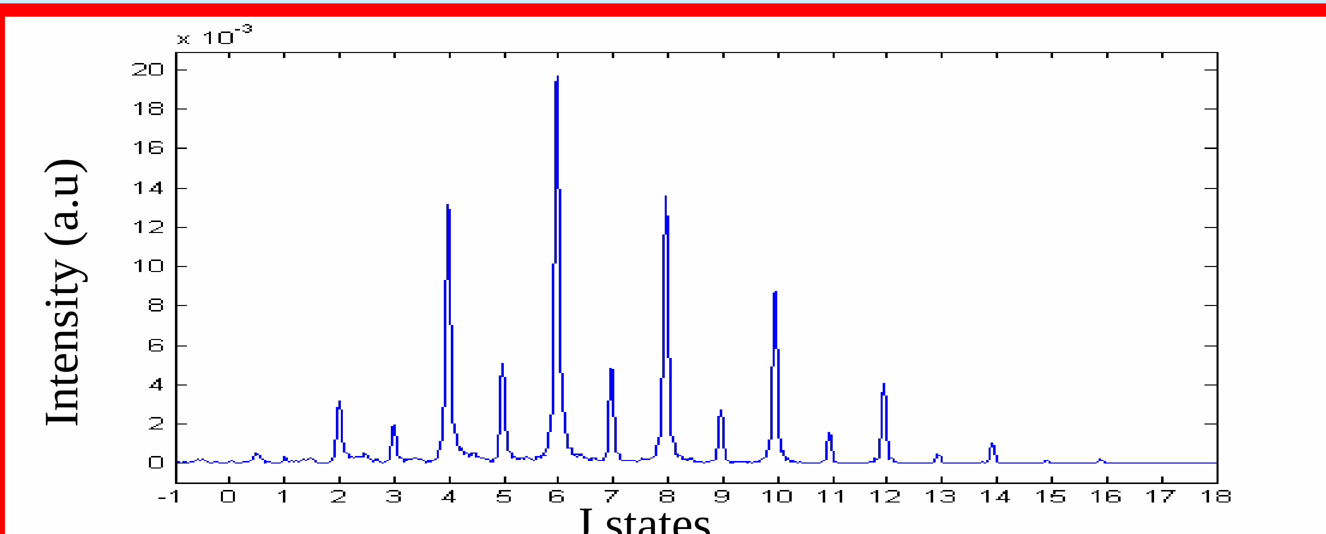


Frequency analysis

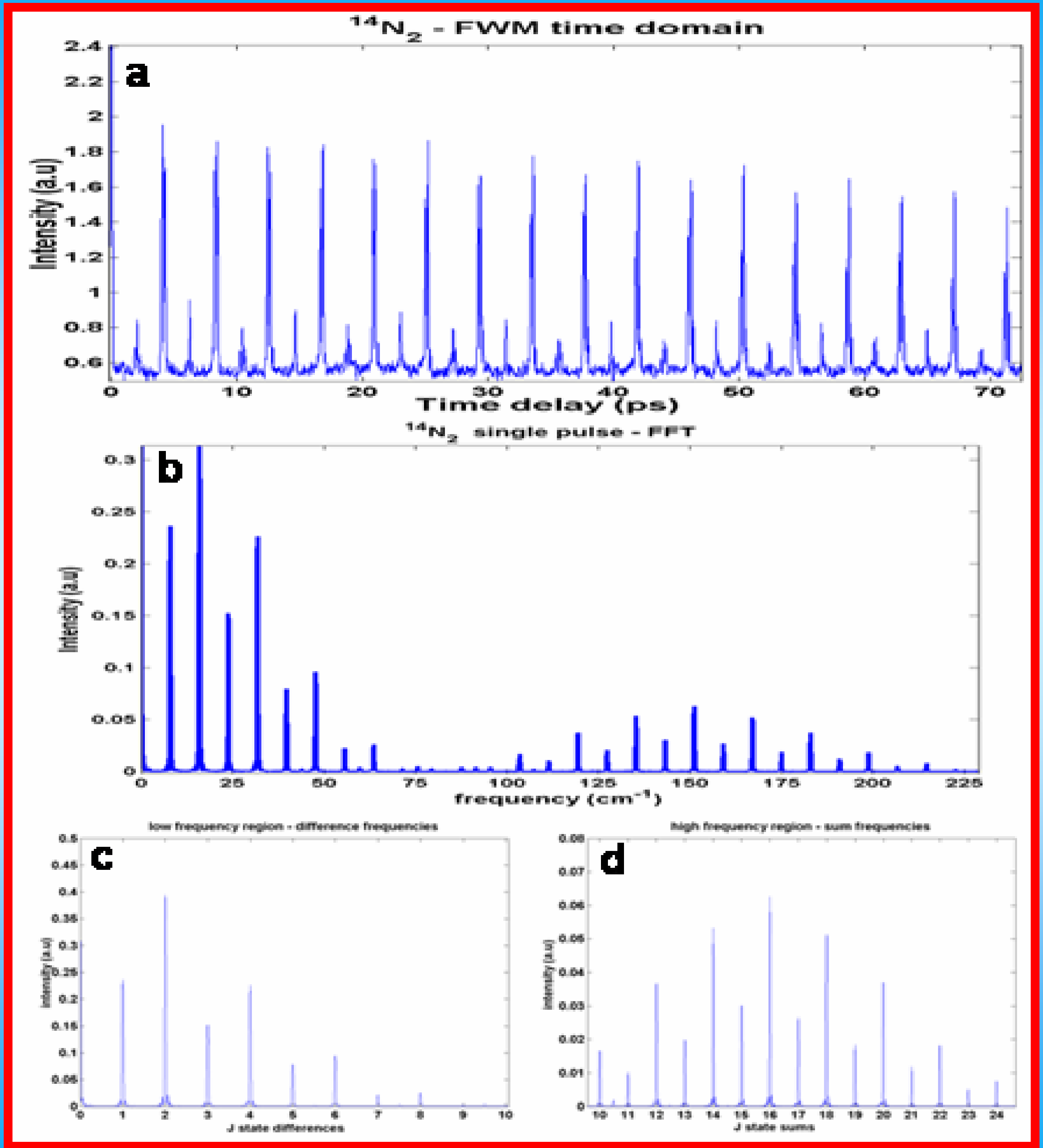


$$Signal \propto \delta n$$

$$\delta n \propto \left\langle \cos^2 \theta \right\rangle$$



Participating rotational state population

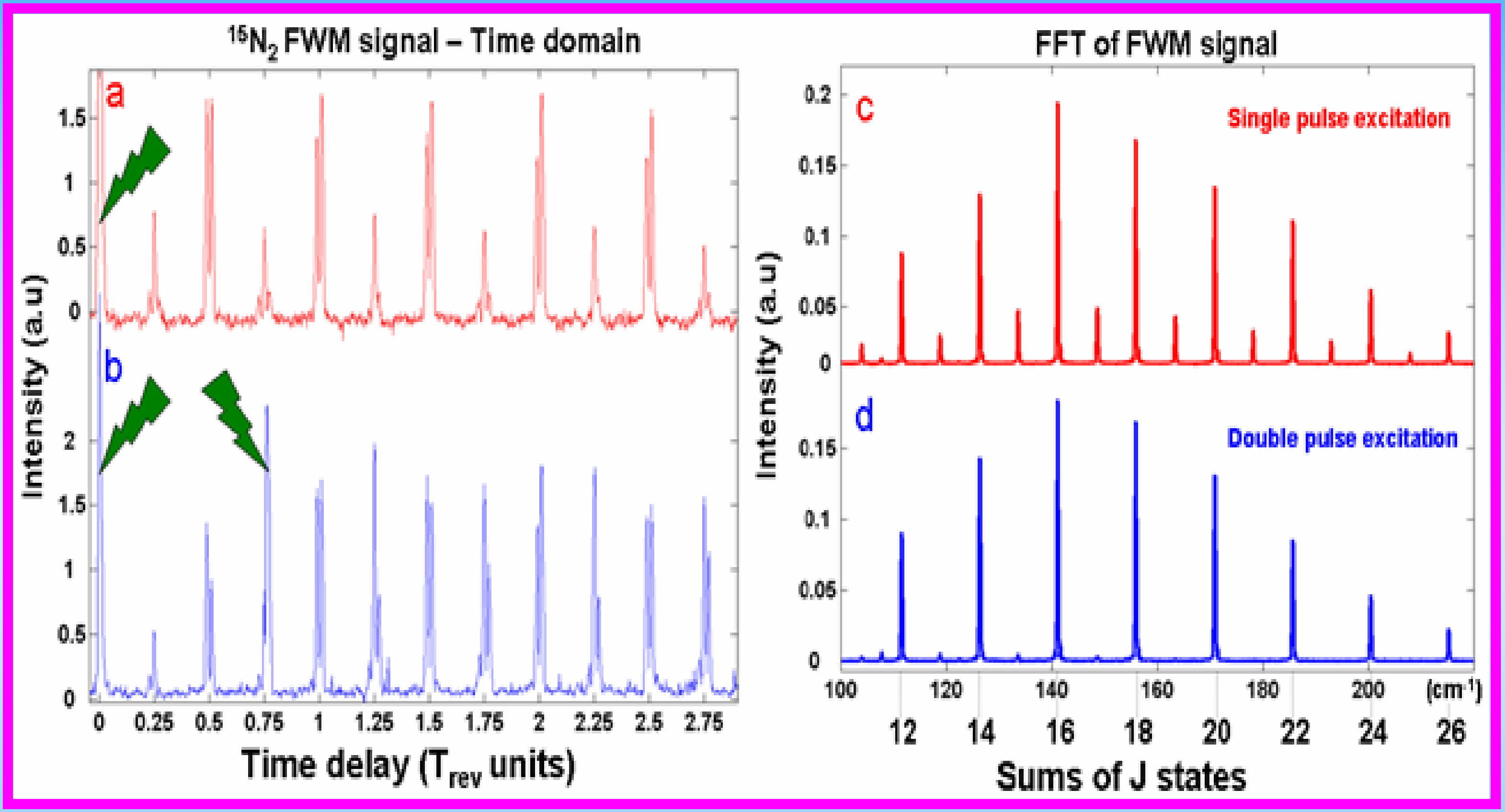


$$Signal \propto (\delta n)^2$$

$$\propto \left\langle \cos^2 \theta \right\rangle^2$$

Binary
SUMS
and
DIFFERENCES
of the J states

Single pulse vs. double pulse



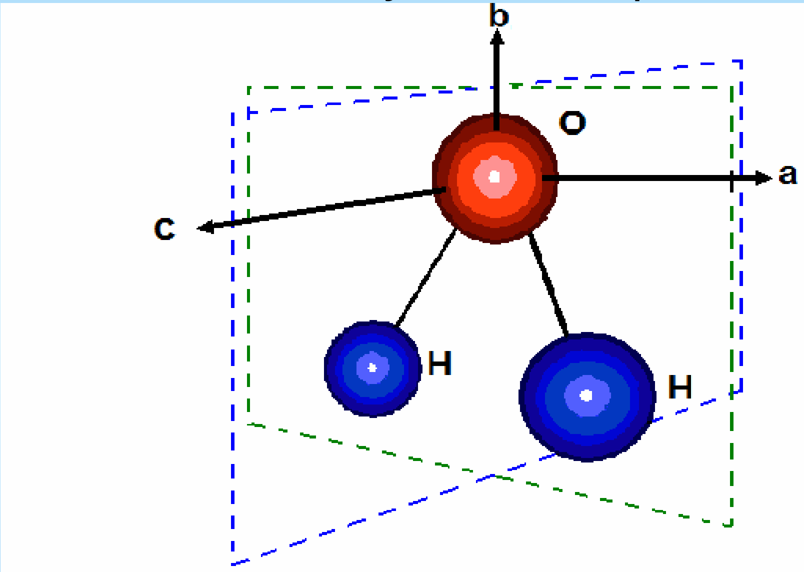
Odd Sum ⟷ Odd J + Even J

Even Sum ⟷ Odd J + Odd J , Even J + Even J

Laser Alighment of Ortho/Para Water Molecules

E. Gershnabel, IA, Phys. Rev. A 78, 063416 (2008)

Asymmetric top



C_{2v} symmetry, irreducible representations: A_1, A_2, B_1, B_2.

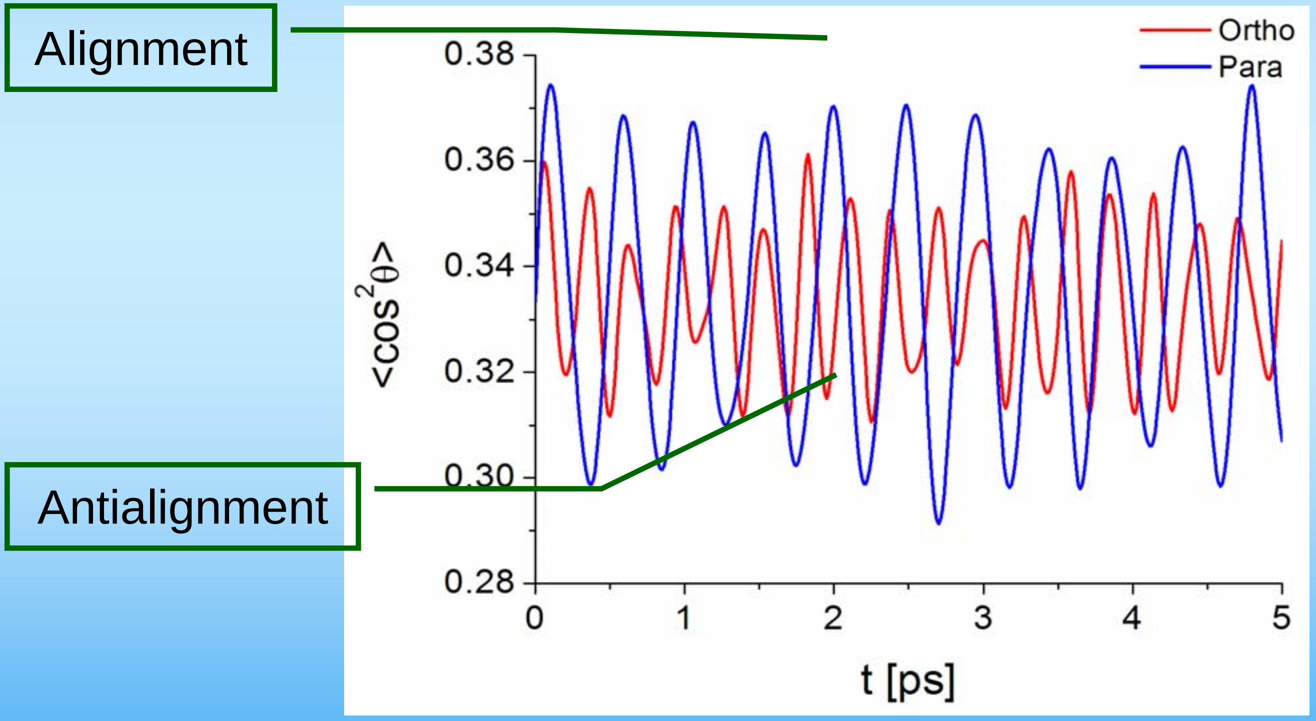
Rotational Hamiltonian
(ridid rotor model)

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

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

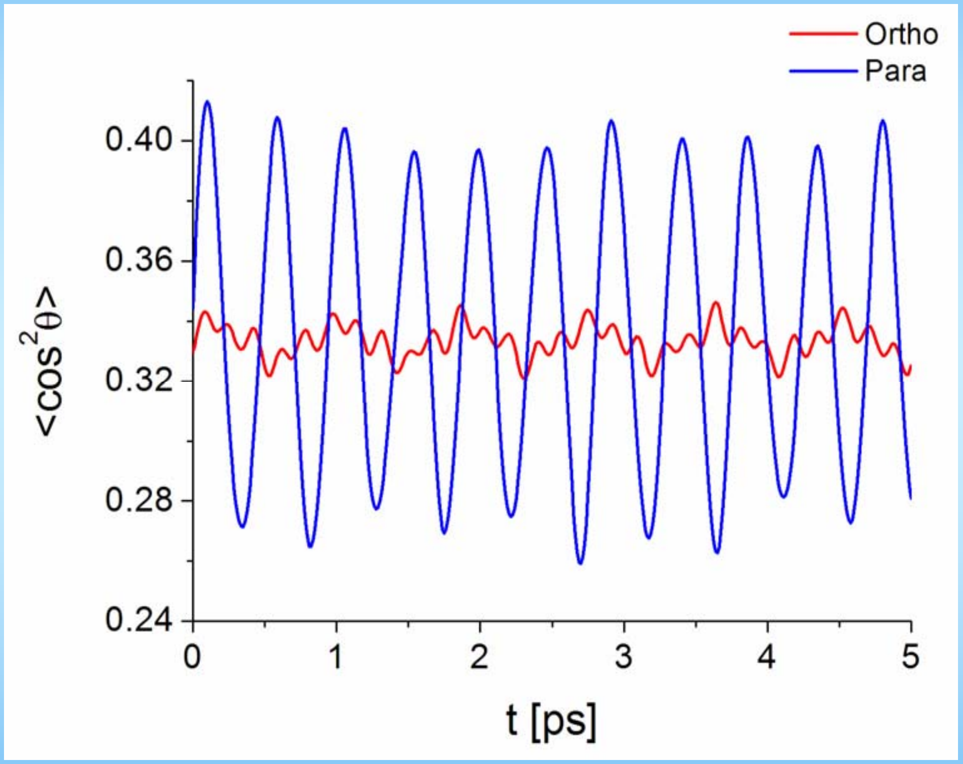
Spin-Dependent Alignment

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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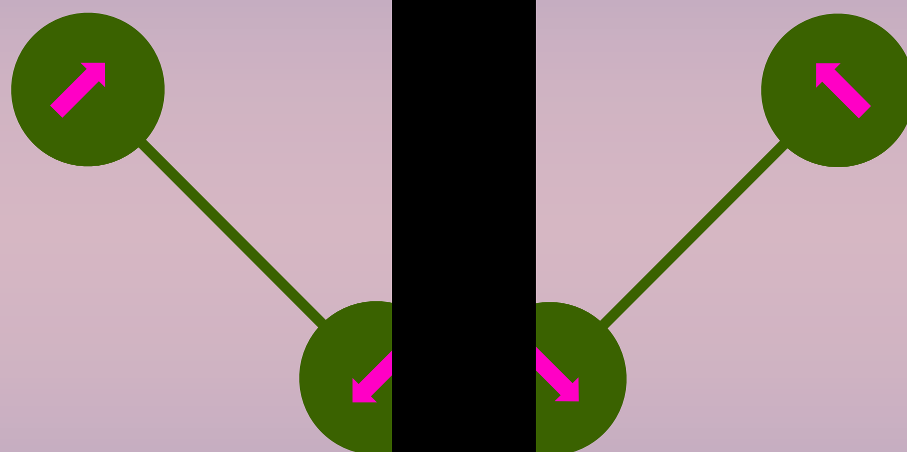
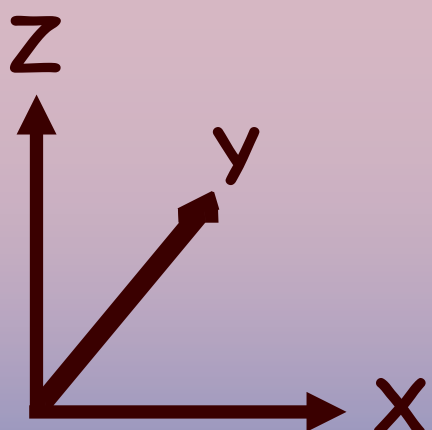
Field Free Unidi[redacted]tional Rotation





L_y [redacted] $(-L_y) = 0$

$L_z = 0$ $L_x = 0$

Controlling the sense of rotation

VOLUME 82, NUMBER 17 PHYSICAL REVIEW LETTERS 26 APRIL 1999

Optical Centrifuge for Molecules

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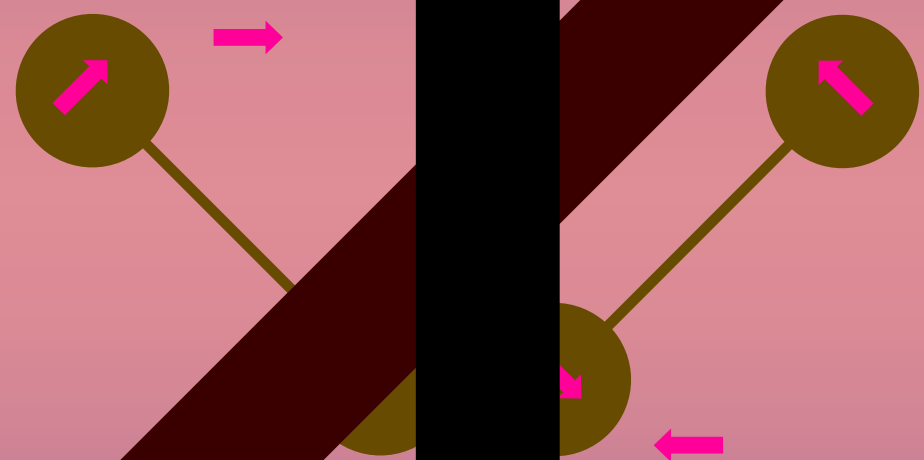
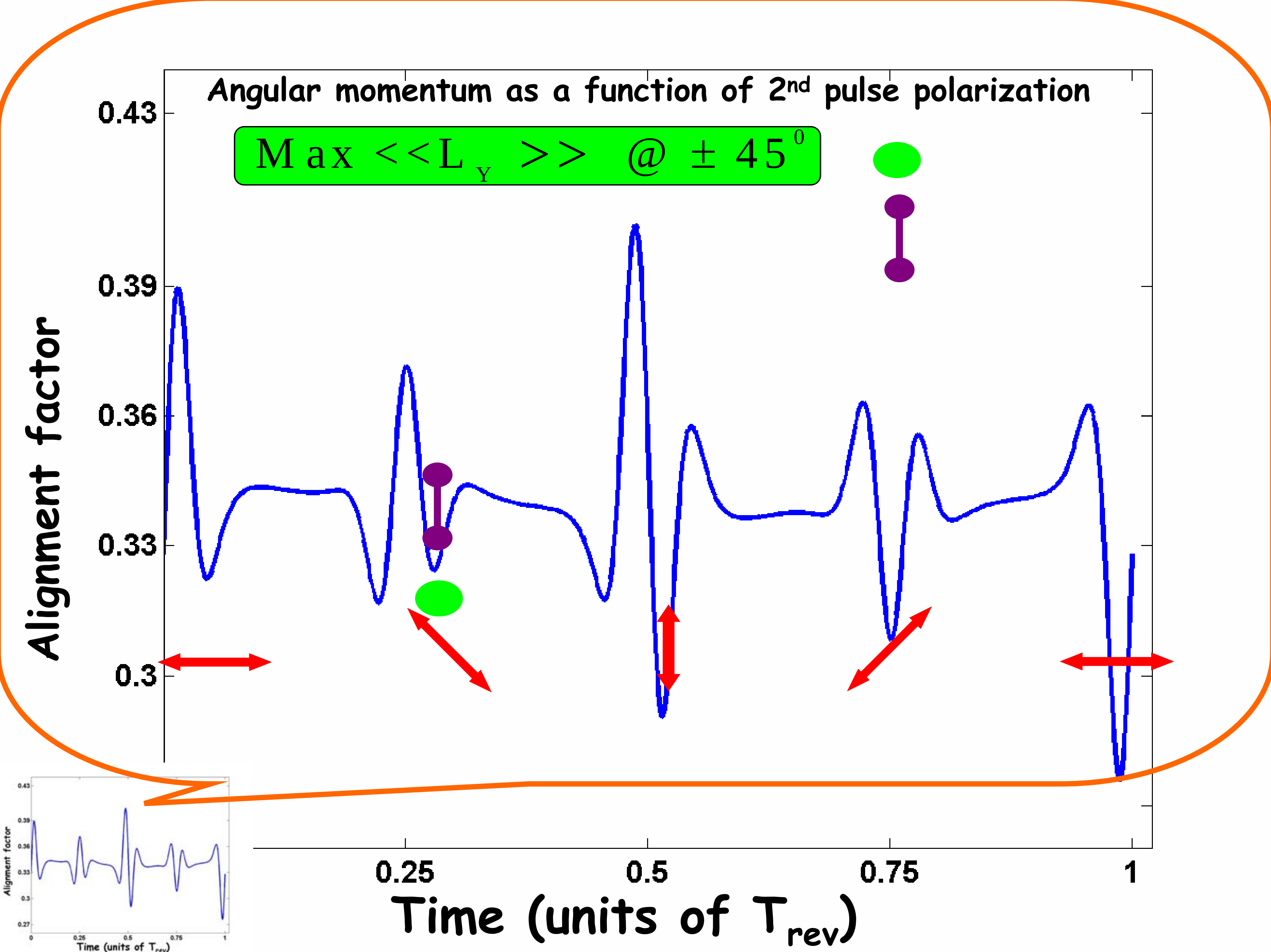
[2]*Ottawa-Carleton Chemistry Institute, Carleton University, Ottawa, Ontario, Canada K1S 5B6*

Controlling the [redacted]se of rot



$$\langle\langle L_Y \rangle \text{[redacted]} \neq 0$$

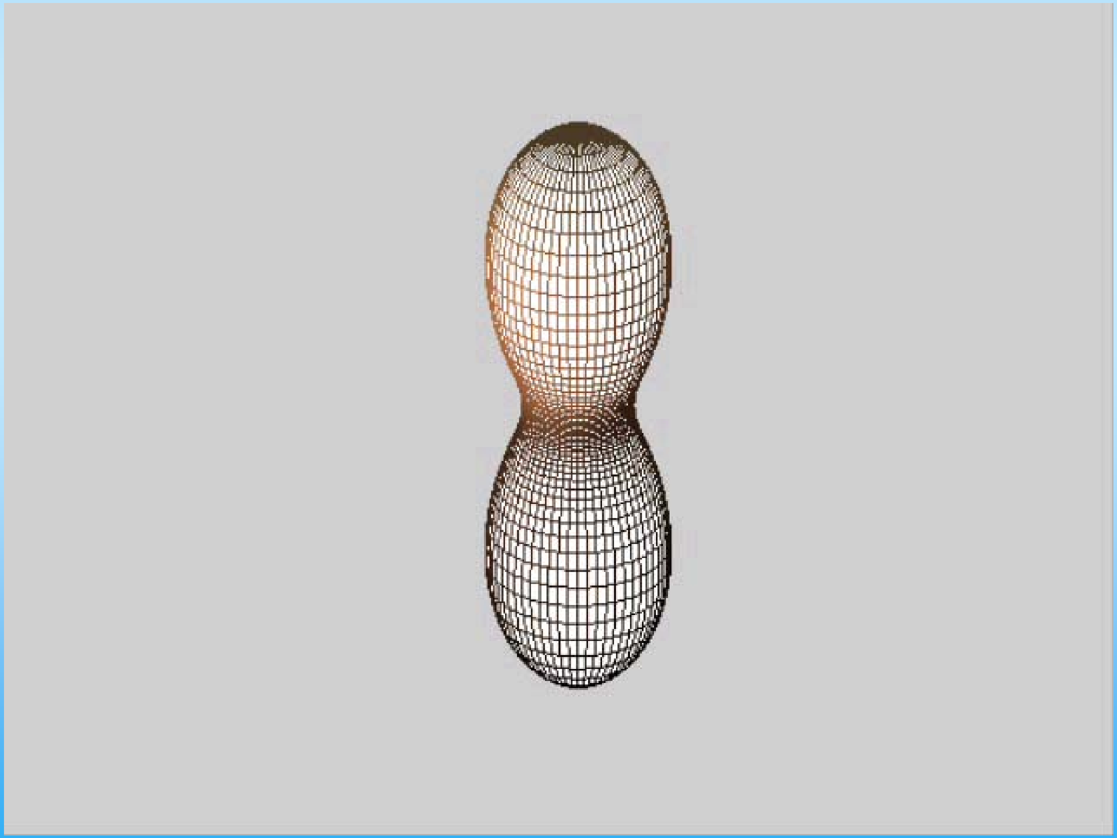


Angular momentum as a function of 2nd pulse polarization
Max <<L Y >> @ ± 45 0
Alignment factor
0.43
0.39
0.36
0.33
0.3
0.25
0.5
0.75
1
Time (units of T rev)

Field free unidirectional rotation

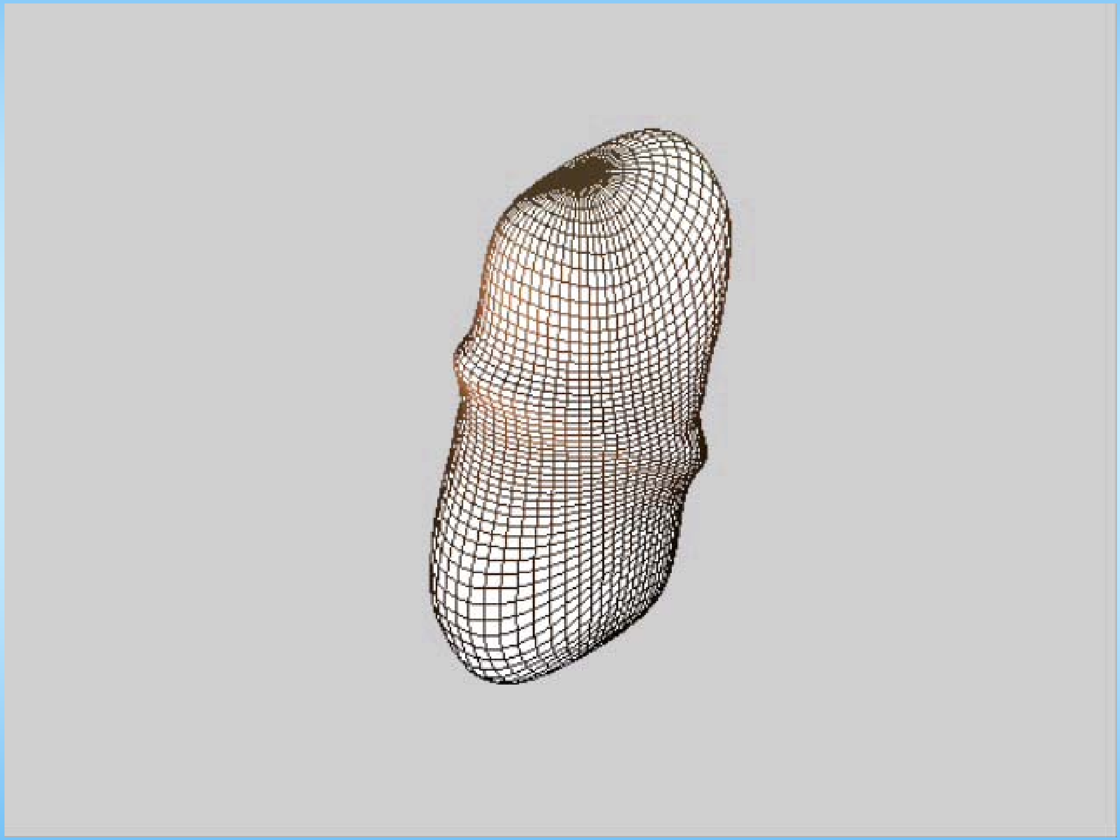
Finite temperature simulations by:

- 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