# Ultrafast Laser Approaches to Quantum Entanglement and Control

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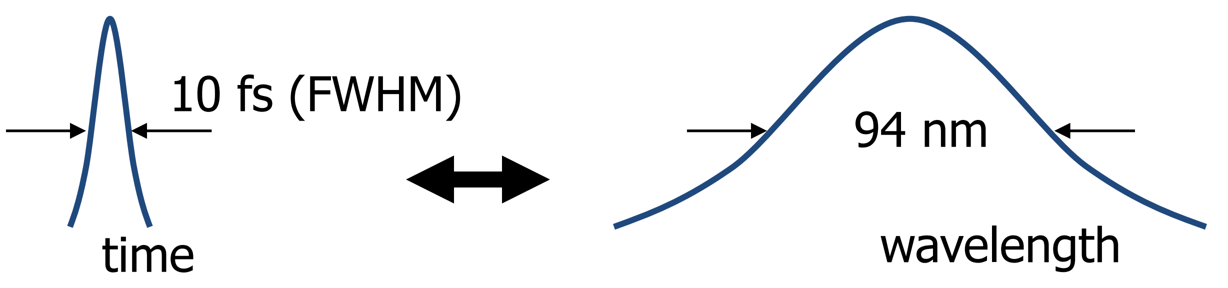
# An Ultrafast Laser Pulse

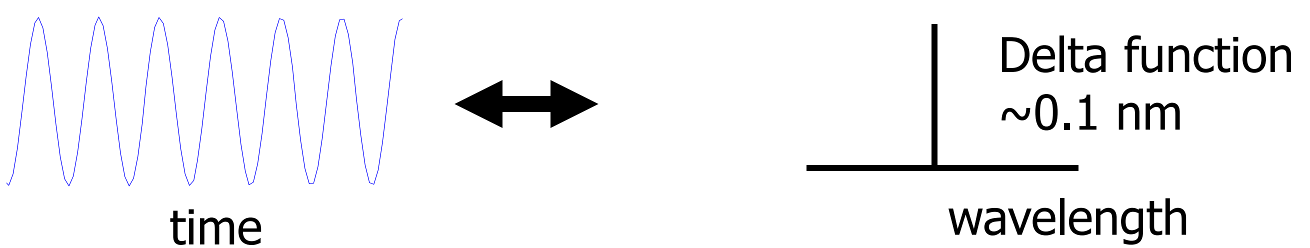
- Coherent superposition of many monochromatic light waves within a range of frequencies that is inversely proportional to the duration of the pulse

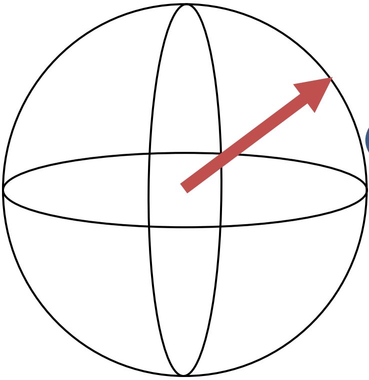
Short temporal duration of the ultrafast pulses results in a very broad spectrum quite unlike the notion of monochromatic wavelength property of CW lasers.

e.g.
Commercially
available
Ti:Sapphire
Laser at 800nm

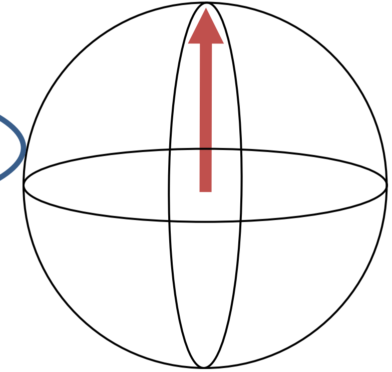



CW
Laser



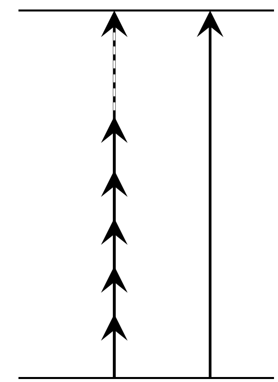


# Ideal Two-Level System



$$H^{FM} = \hbar \begin{pmatrix} \Delta + N\dot{\phi}(t) & \frac{\Omega_1}{2} \\ \frac{\Omega_1^*}{2} & 0 \end{pmatrix}$$

$$\Delta = \omega_R - N\omega$$

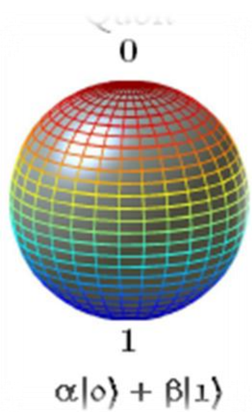



$$\vec{E}(t) = \mathcal{E}_0(t) e^{i\omega.t + i\phi(t)}$$

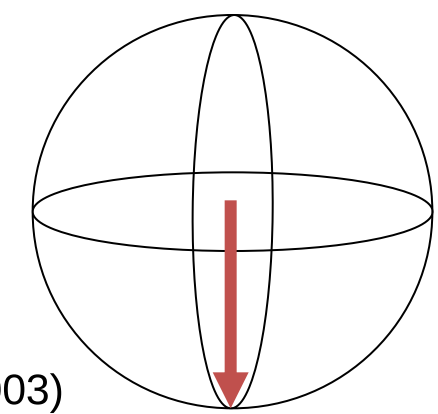
$$\Omega_1(t) = k(\mu_{eff}.\varepsilon(t))^N/\hbar$$

$$\mu_{eff}^N = \prod_n^N \mu_n$$

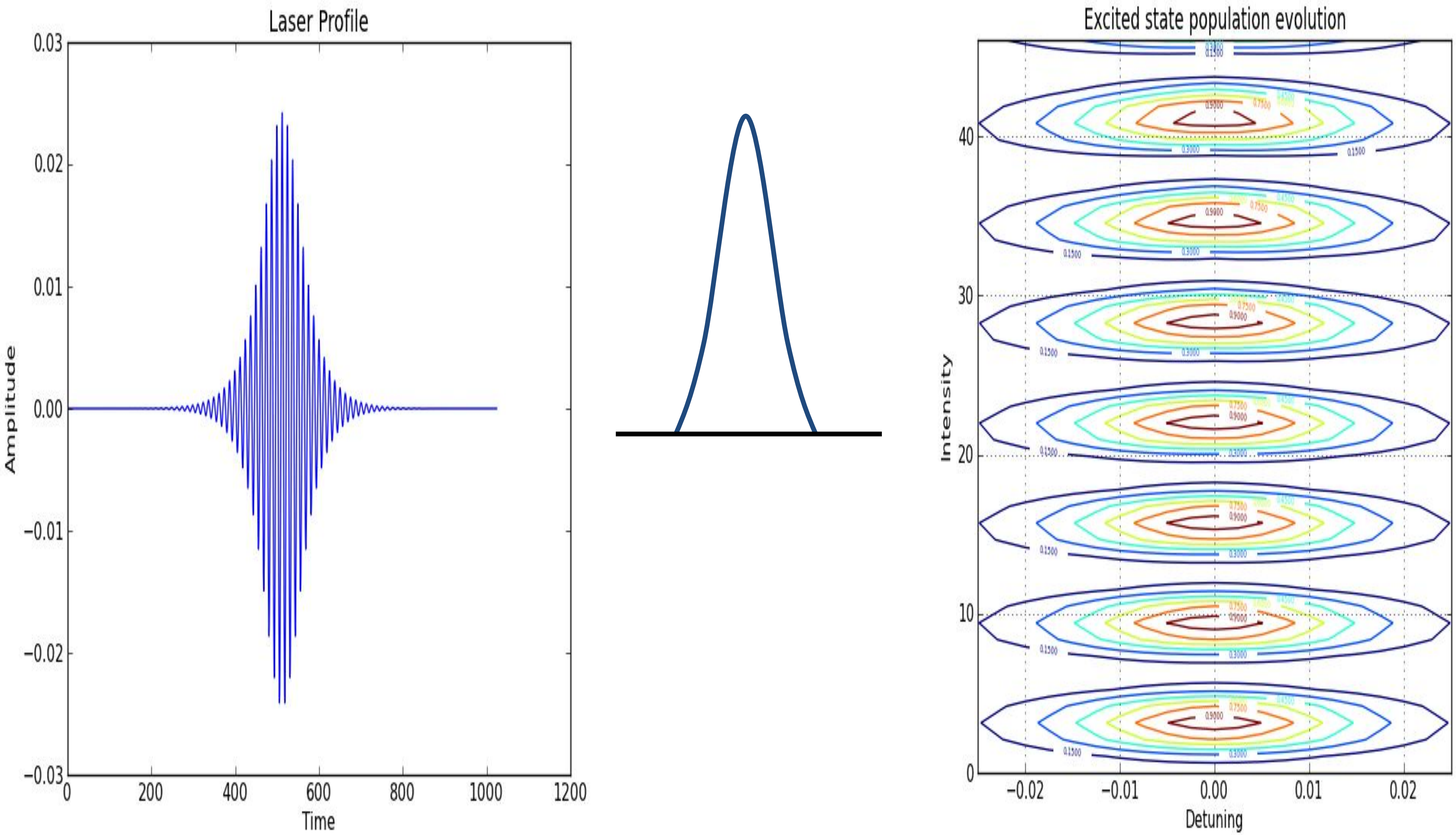
$$\omega_R = \omega_2 - \omega_1$$

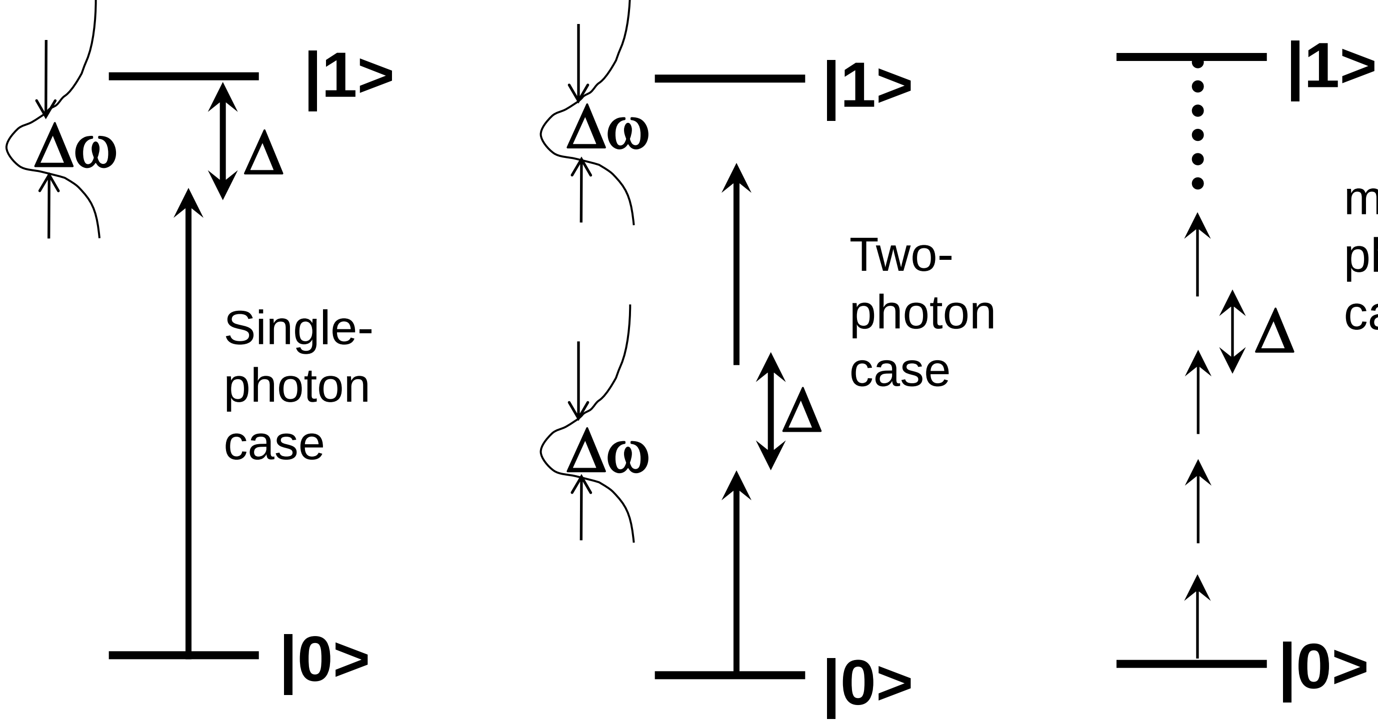



$$\frac{d\rho(t)}{dt} = \frac{i}{\hbar}[\rho(t), H^{FM}(t)]$$



Phys. Rep. **374**(6), 385-481 (2003)


Laser Profile
Amplitude
Time
0.03
0.02
0.01
0.00
−0.01
−0.02
−0.03
0
200
400
600
800
1000
1200
Excited state population evolution
Intensity
Detuning
0
10
20
30
40
−0.02
−0.01
0.00
0.01
0.02

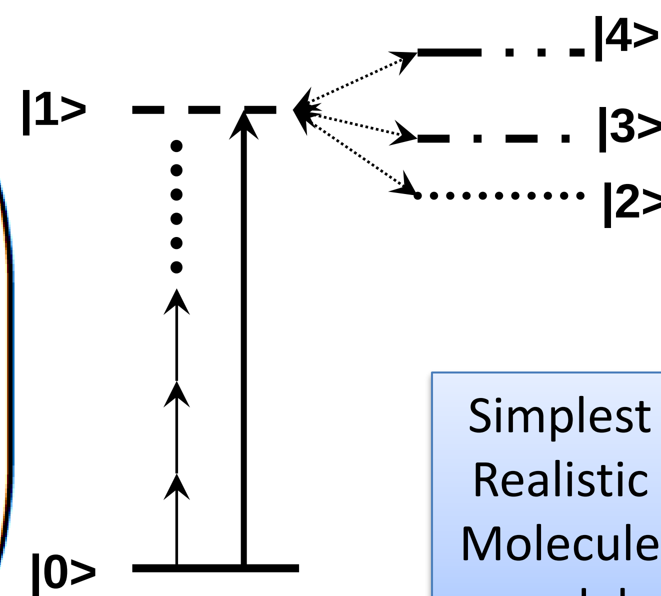



Ideal 2-Level model

$$\hbar \begin{pmatrix} \Delta + N\dot{\phi}(t) & \frac{\Omega_1}{2} \\ \frac{\Omega_1^*}{2} & 0 \end{pmatrix}$$

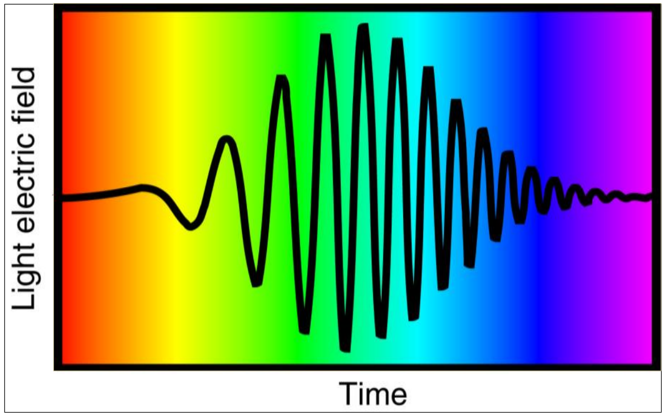
$$\hbar \begin{pmatrix} 0 & \Omega_1(t) & 0 & 0 & 0 & \cdots \\ \Omega_1(t) & \delta_1(t) & V_{12} & V_{12} & V_{12} & \cdots \\ 0 & V_{12} & \delta_2(t) & V_{12} & V_{12} & \cdots \\ 0 & V_{12} & V_{12} & \delta_3(t) & V_{12} & \cdots \\ 0 & V_{12} & V_{12} & V_{12} & \delta_4(t) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{pmatrix}$$

(columns: $|0\rangle$, $|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$, ...)




Simplest Realistic Molecule model

# Taylor Series Expansion of Instantaneous Phase of Electric Field




$$\vec{E}(t) = \mathcal{E}_0(t)e^{i\omega.t+i\phi(t)}$$

Phase

$$\phi(t) = b_0 + b_1 t + b_2 t^2 + b_3 t^3 + b_4 t^4 + b_5 t^5 + ....$$

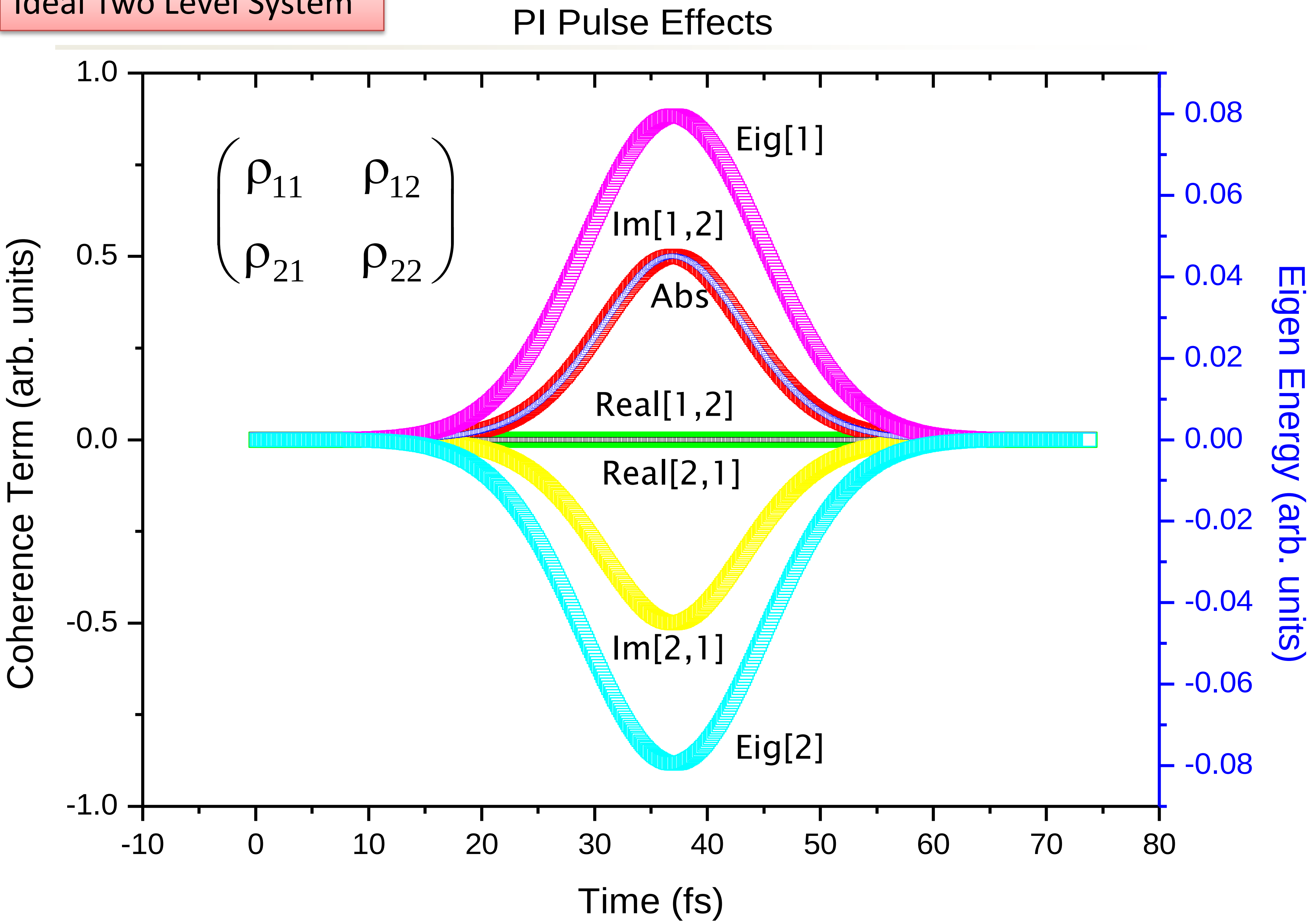
$$\dot{\phi}(t) = b_1 + 2b_2 t + 3b_3 t^2 + 4b_4 t^3 + 5b_5 t^4 + ....$$

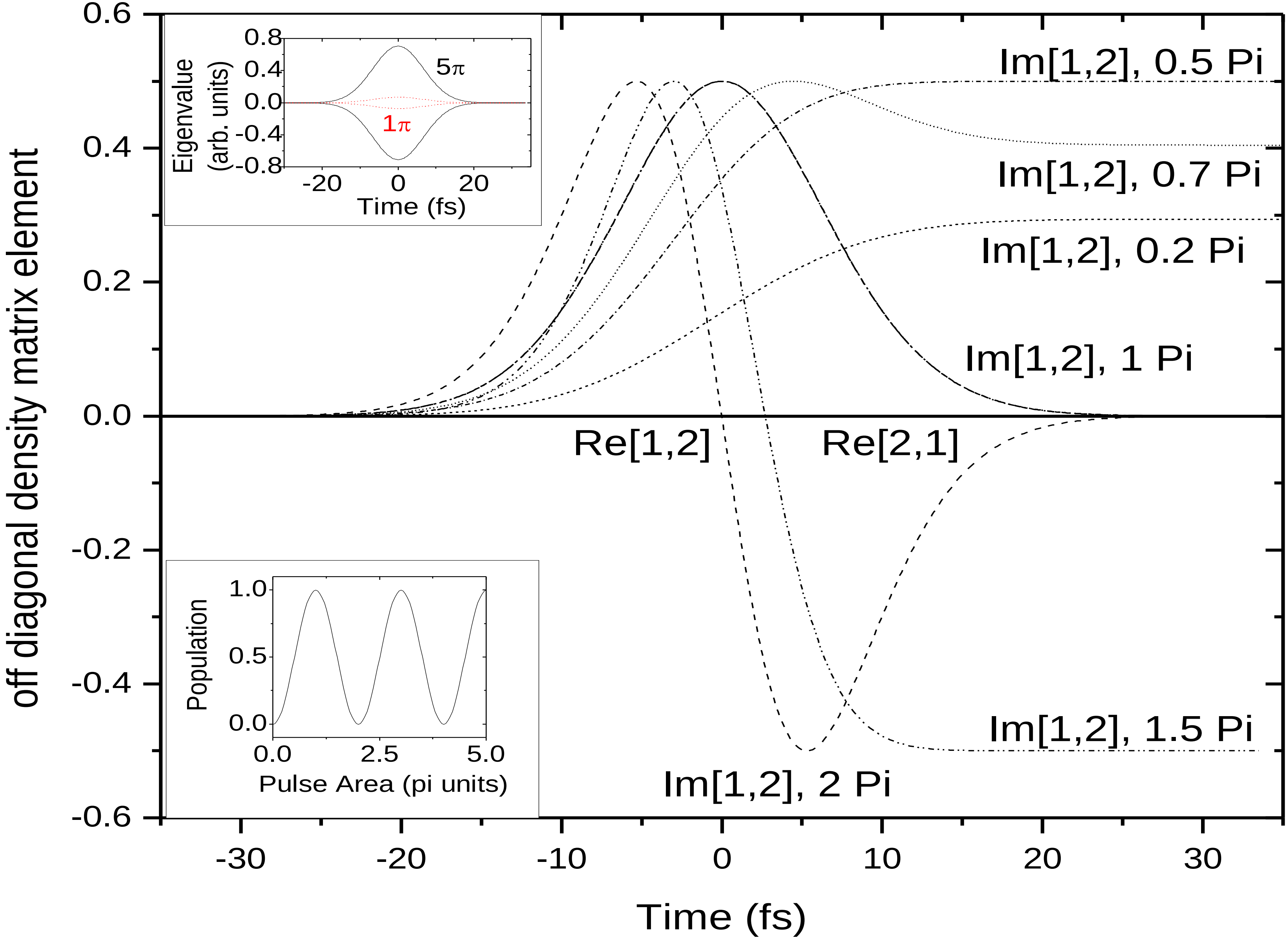
Frequency Sweep

Shaped Pulses

$$\frac{d\rho(t)}{dt} = \frac{i}{\hbar}[\rho(t), H^{FM}(t)]$$

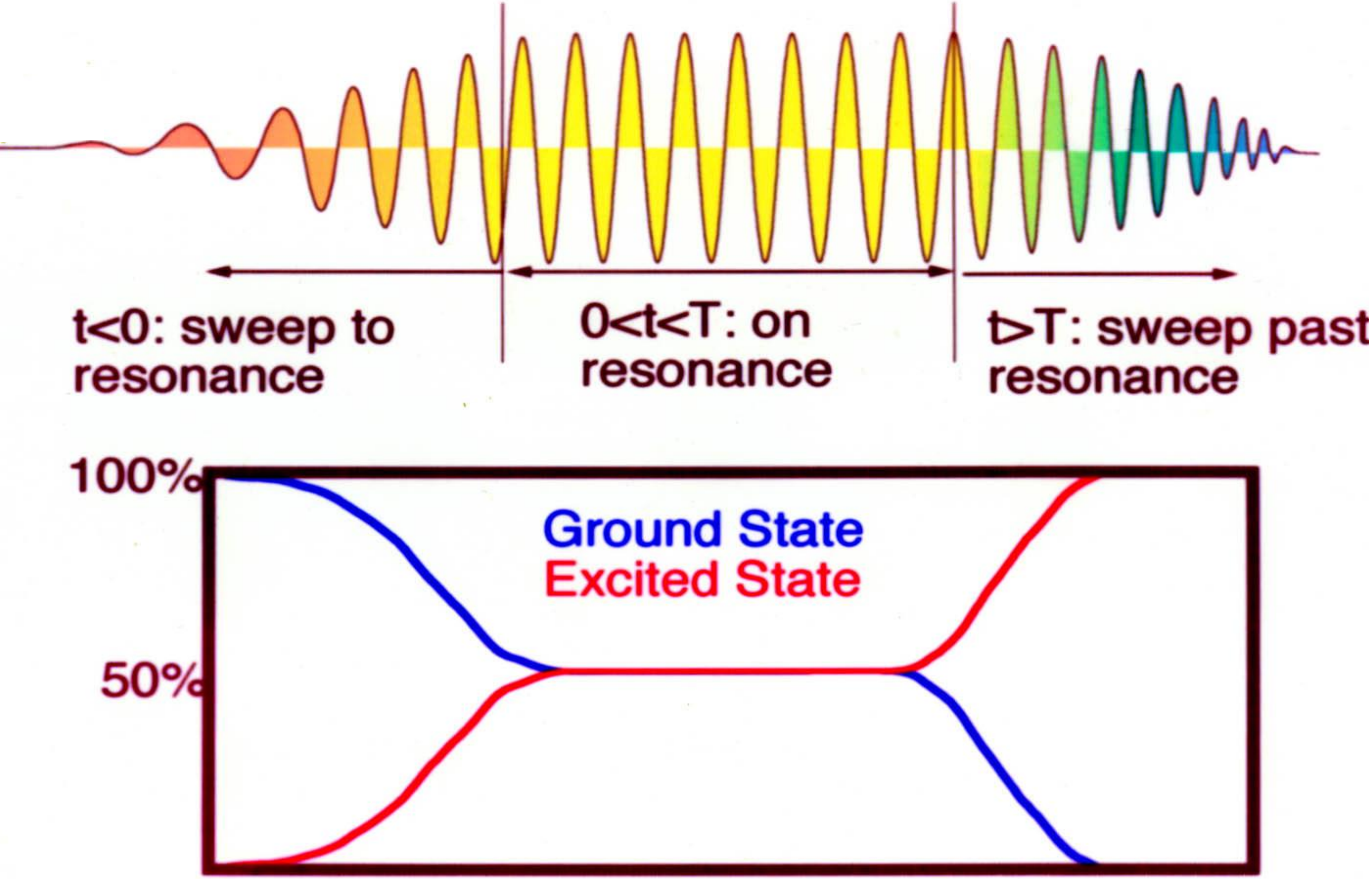
## Ideal Two Level System



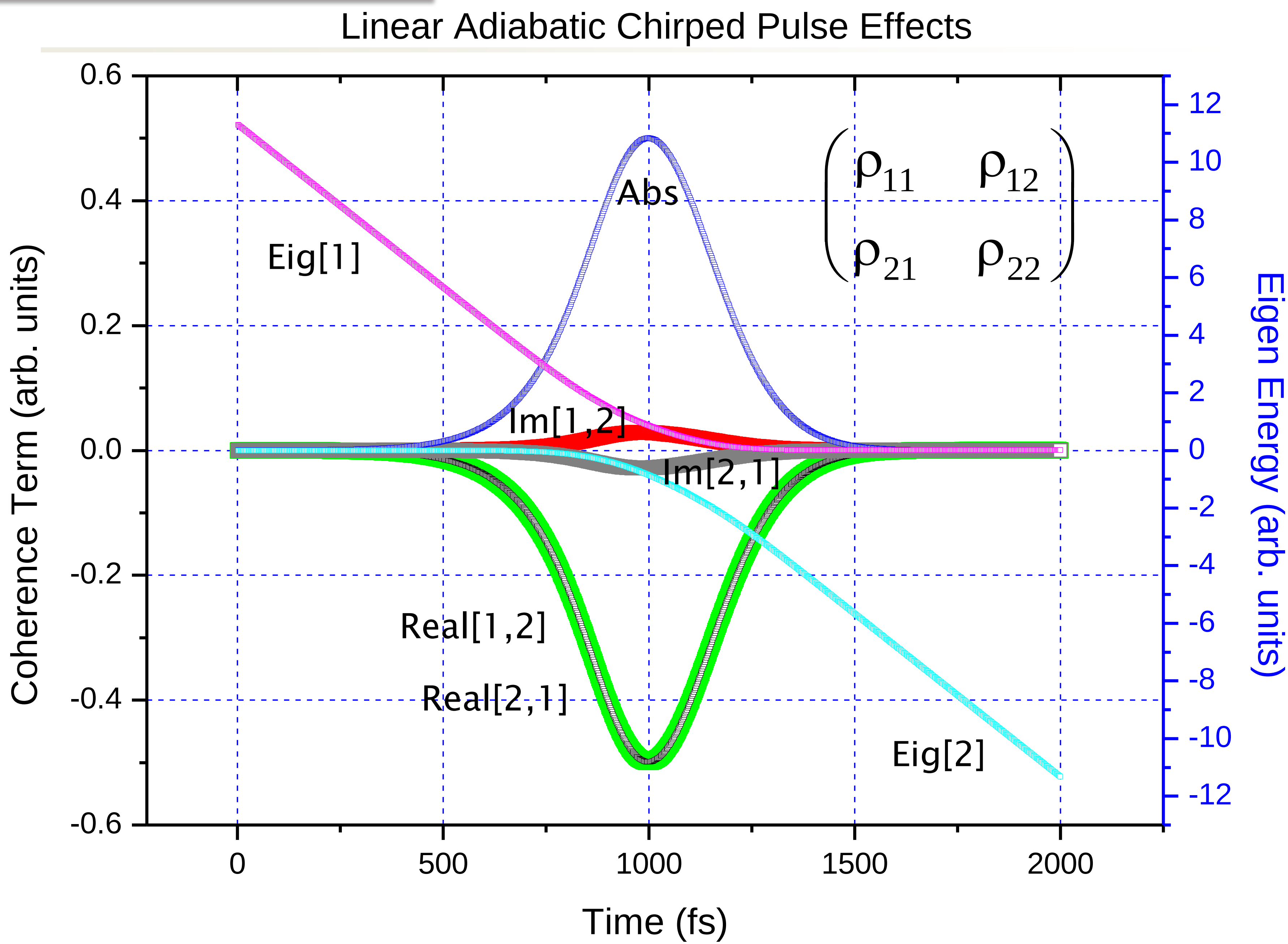


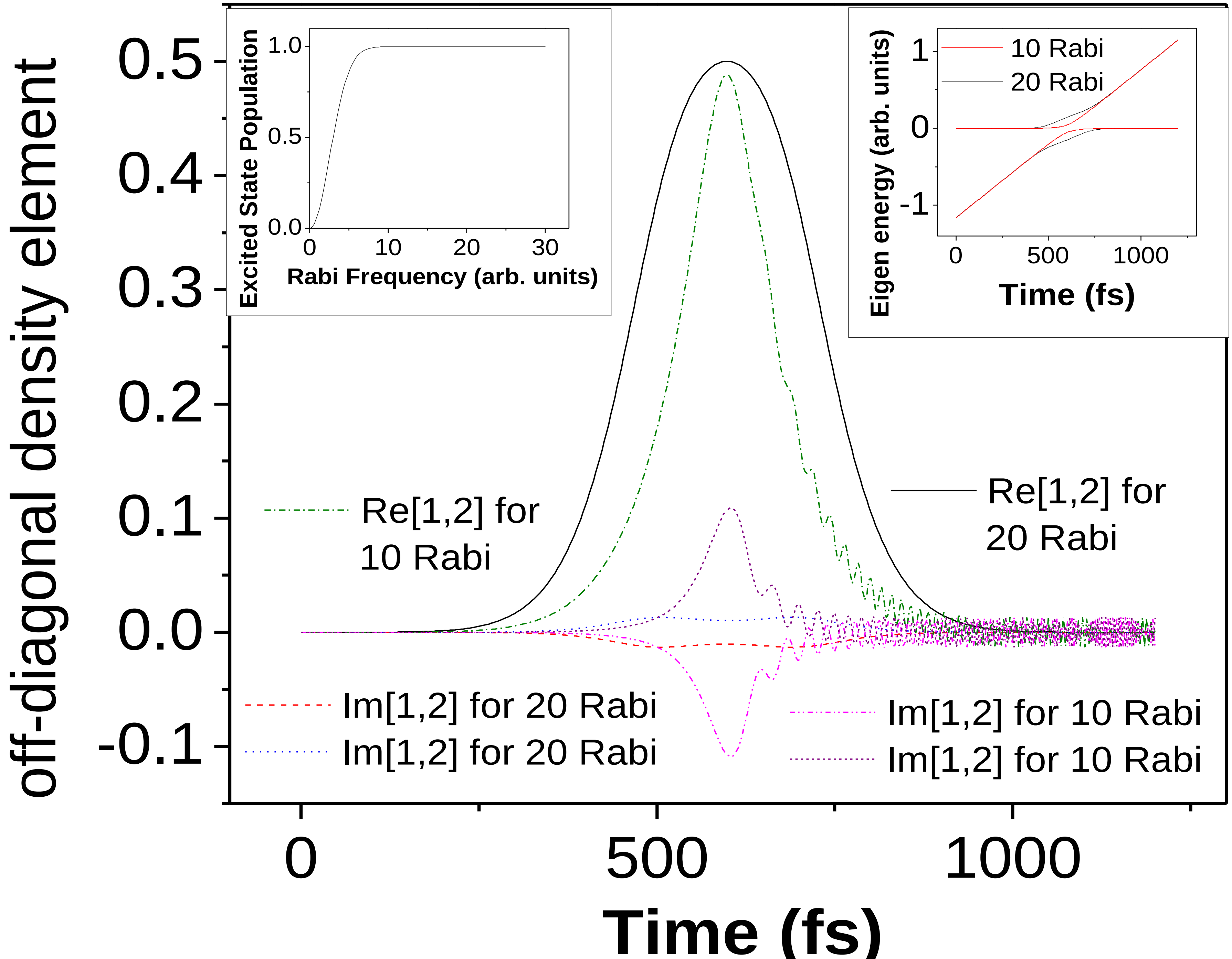
off diagonal density matrix element
Time (fs)
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-30
-20
-10
0
10
20
30
Im[1,2], 0.5 Pi
Im[1,2], 0.7 Pi
Im[1,2], 0.2 Pi
Im[1,2], 1 Pi
Re[1,2]
Re[2,1]
Im[1,2], 1.5 Pi
Im[1,2], 2 Pi
Eigenvalue (arb. units)
Time (fs)
5π
1π
Population
Pulse Area (pi units)

# Adiabatic passage in two-level system



## Ideal Two Level System (contd.)





off-diagonal density element
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
0
500
1000
Time (fs)
Re[1,2] for 10 Rabi
Re[1,2] for 20 Rabi
Im[1,2] for 20 Rabi
Im[1,2] for 20 Rabi
Im[1,2] for 10 Rabi
Im[1,2] for 10 Rabi
Excited State Population
1.0
0.5
0.0
0
10
20
30
Rabi Frequency (arb. units)
Eigen energy (arb. units)
1
0
-1
10 Rabi
20 Rabi
0
500
1000
Time (fs)

# Probing Coherence ⇒ Off-Diagonal Elements

All absorptions are associated with dispersion: from Spectroscopy

Kramer-Kronig relationship

⇒ All absorptions composed of Real part + Imaginary part

where Real part ⇒ Dispersive part

Imaginary part ⇒ Absorption

Rabi Flopping ⇒ Coupling through absorption

Adiabatic Process ⇒ Coupling through the Dispersive part—no absorption process

⇒ No population flopping

**Benefits of such study:**

- **Quantification of 2-level character in a multilevel system**
- **Off-diagonal density matrix elements switch from real to imaginary**
  - **Excitation process changes from being resonant to completely adiabatic**

J. Chem. Phys. 127, 124305 (2007)

# Challenges in using Molecules as Qubits

C O N T R O L

T E M P O R A L

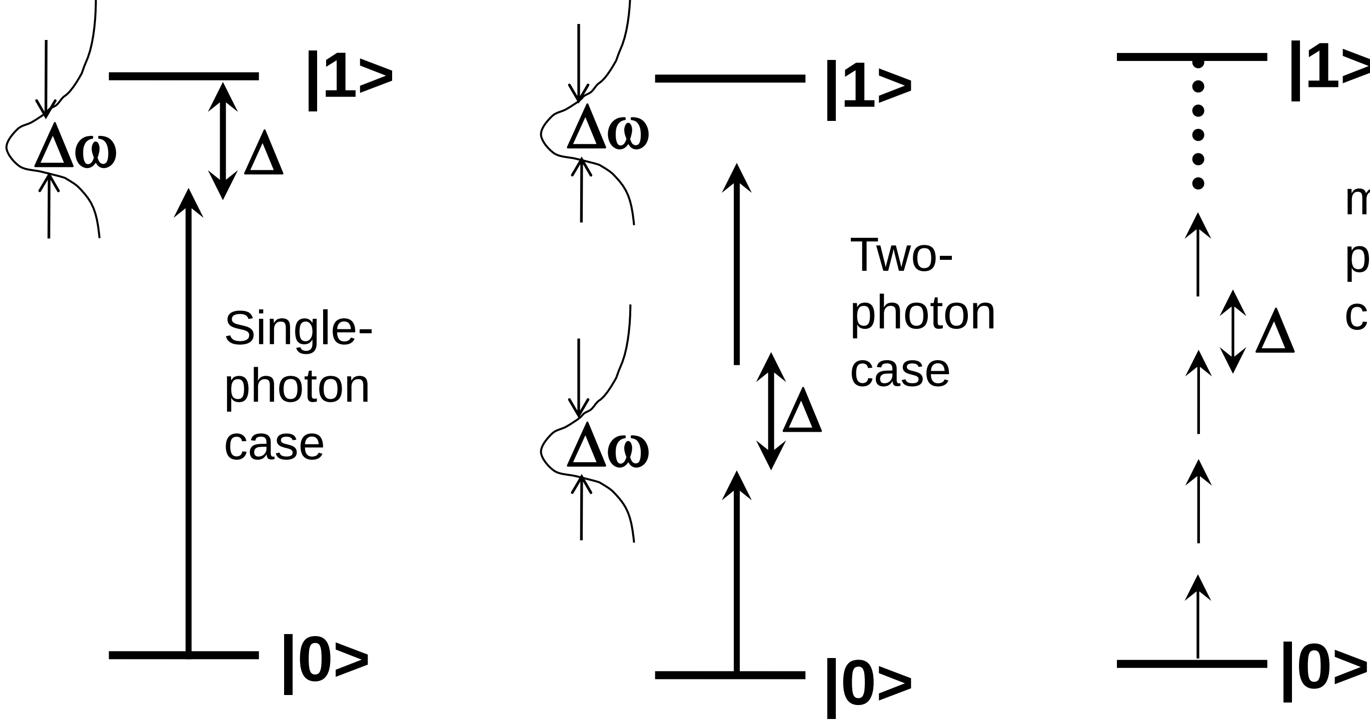
- Demonstrate "true 2-level" nature for molecules
  - All "real molecules" are always multilevel
- Increase Dephasing time of the "States" to be used as qubits

S P A T I A L

- Isolate or Control Molecules such that they can be made to interact under experimenter's discretion
  - Molecular Beams
  - Optical Tweezers

**Pulsed Optical Tweezers**

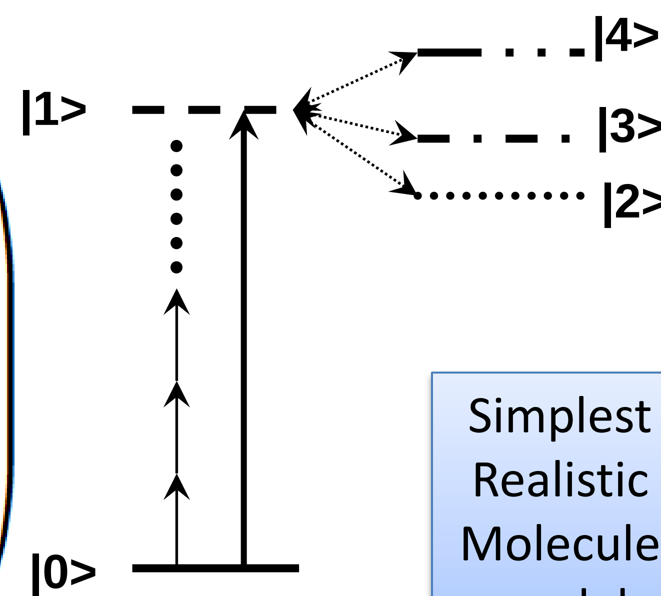
Ideal 2-Level model




$$\hbar\begin{pmatrix} \Delta + N\dot{\phi}(t)) & \frac{\Omega_1}{2} \\ \frac{\Omega_1^*}{2} & 0 \end{pmatrix}$$

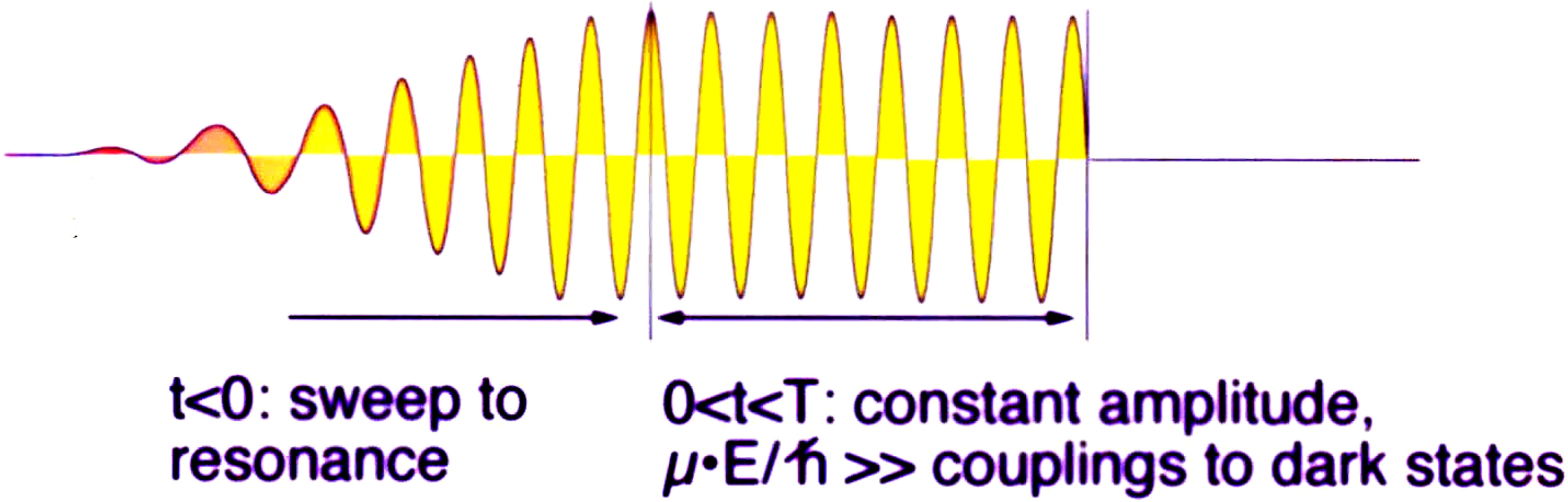
$$\begin{matrix} |0\rangle & |1\rangle & |2\rangle & |3\rangle & |4\rangle & \cdots \end{matrix}$$

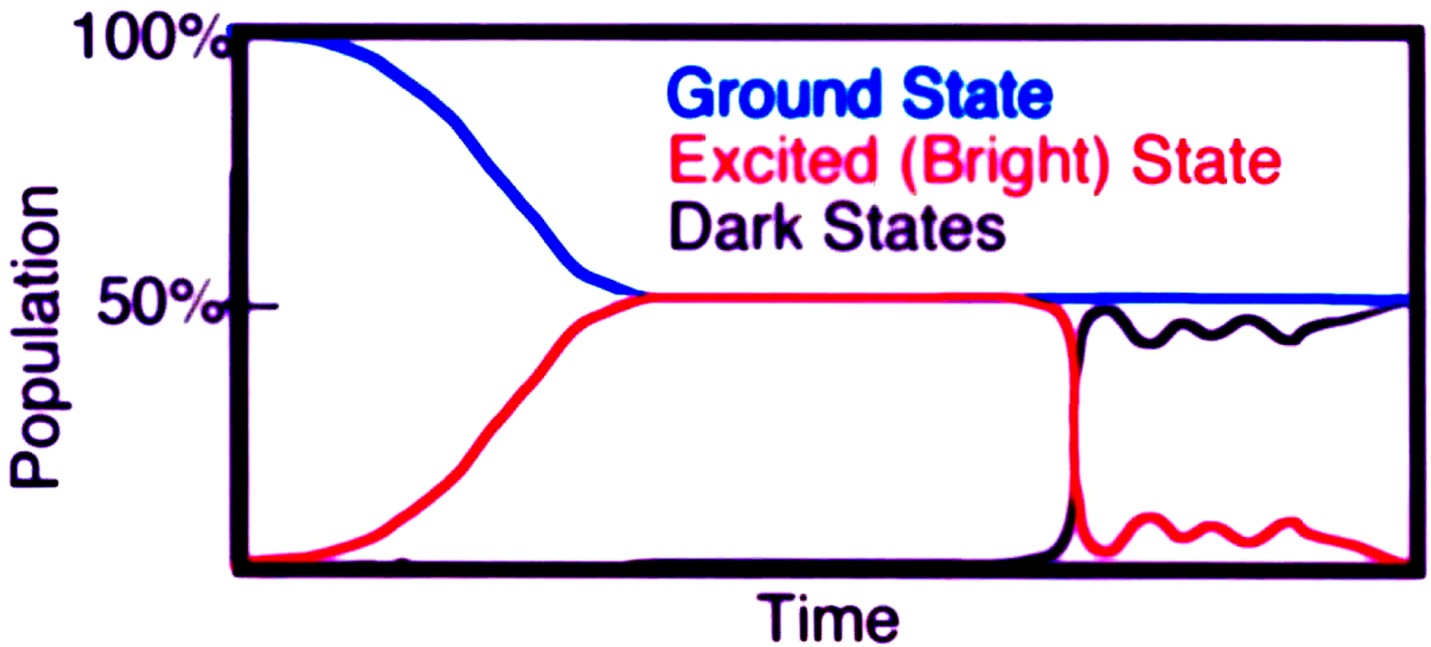
$$\hbar\begin{pmatrix} 0 & \Omega_1(t) & 0 & 0 & 0 & \cdots \\ \Omega_1(t) & \delta_1(t) & V_{12} & V_{12} & V_{12} & \cdots \\ 0 & V_{12} & \delta_2(t) & V_{12} & V_{12} & \cdots \\ 0 & V_{12} & V_{12} & \delta_3(t) & V_{12} & \cdots \\ 0 & V_{12} & V_{12} & V_{12} & \delta_4(t) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{pmatrix}$$




Simplest Realistic Molecule model

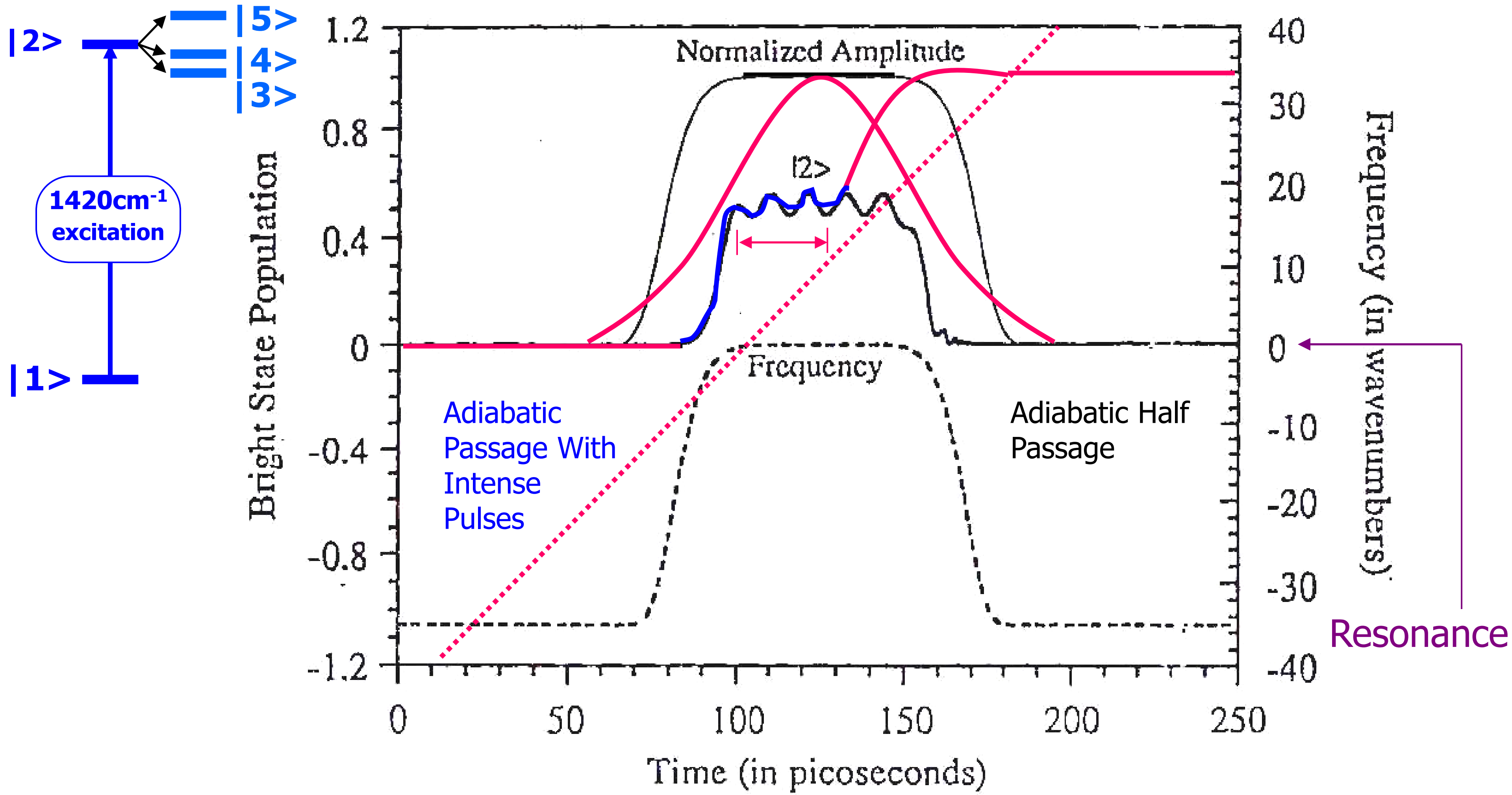
# Adiabatic half passage in coupled systems:



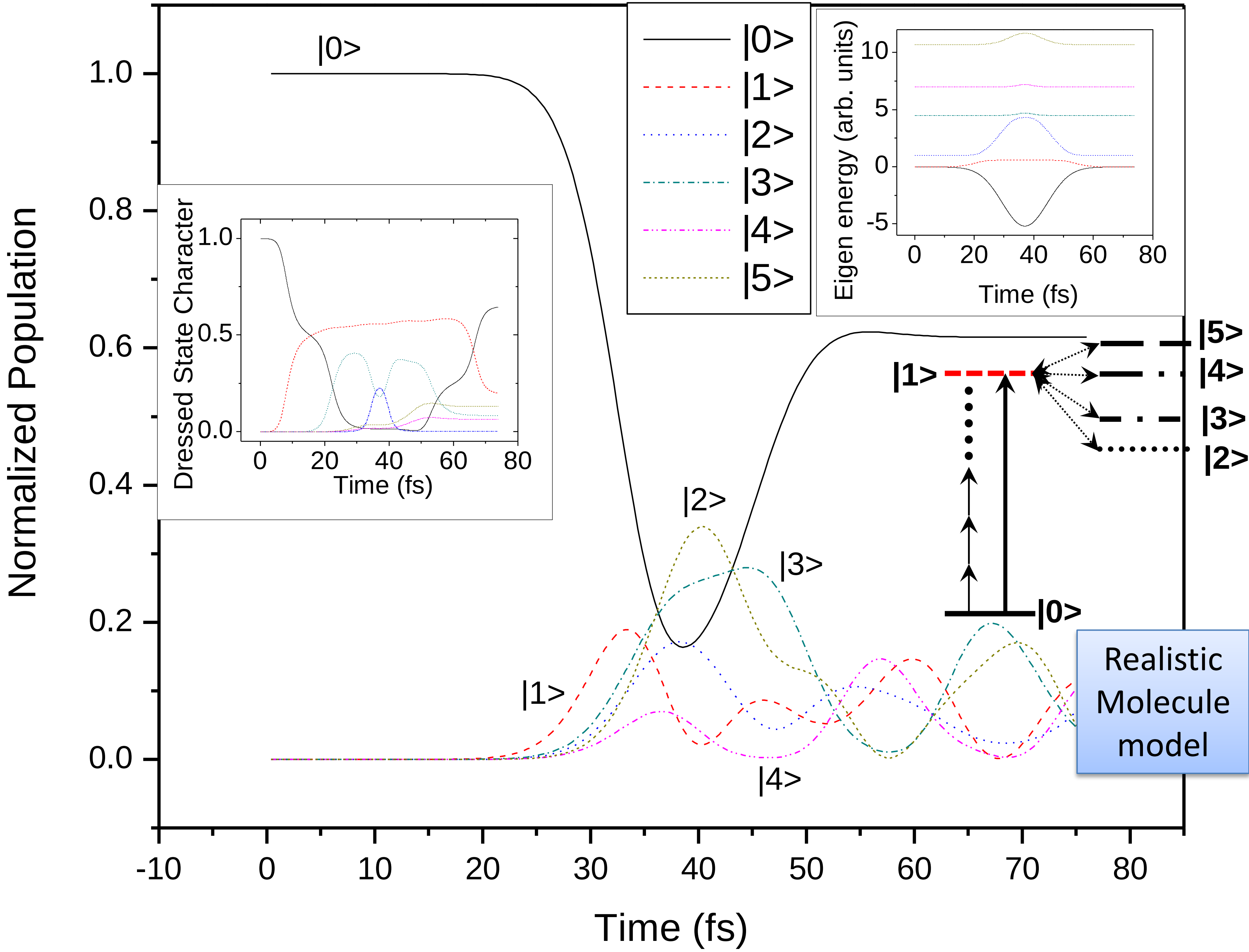



# Model Calculations with Shaped Pulses

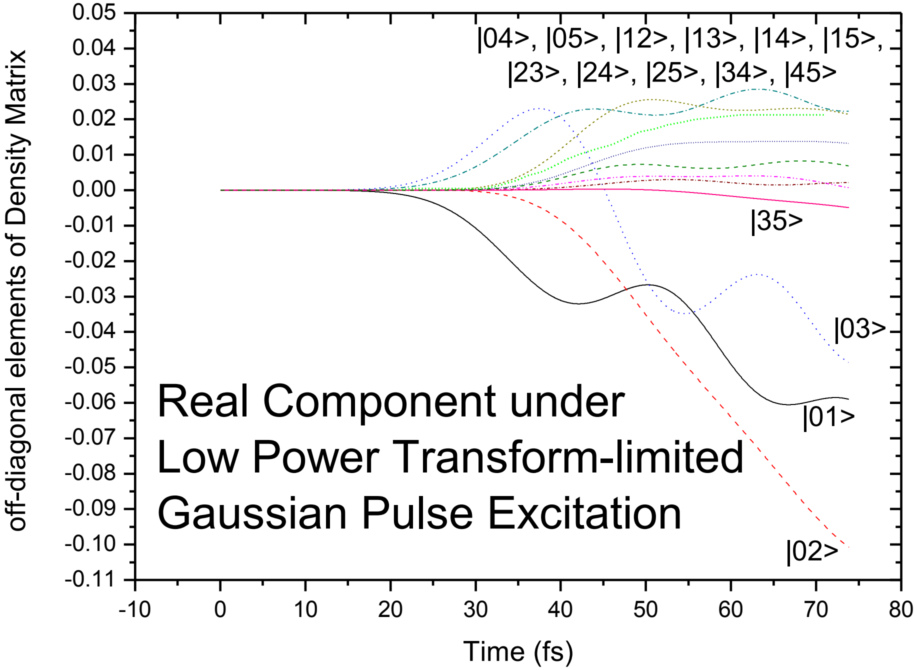
Anthracene

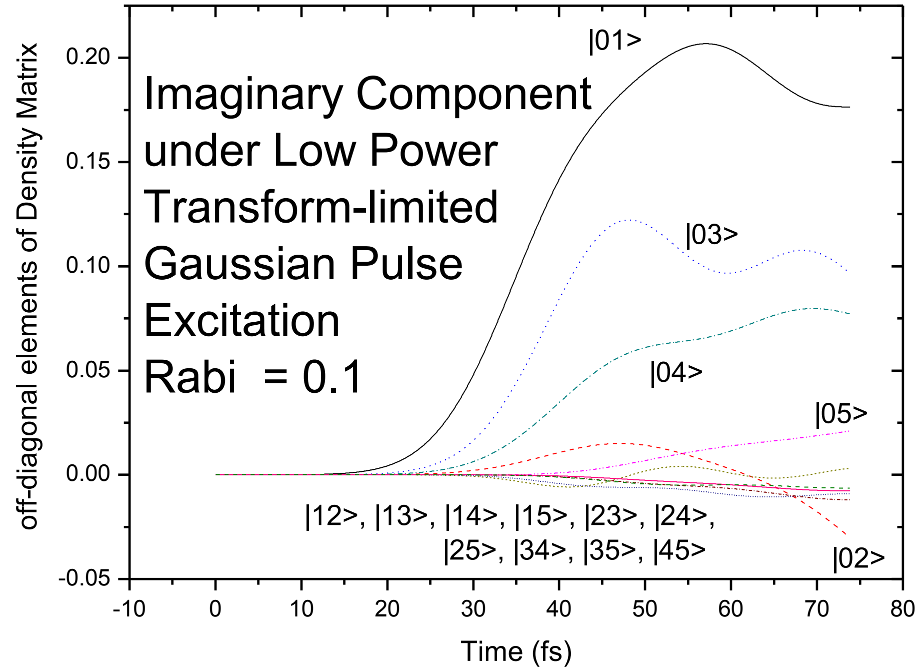



Phys. Rev. Lett. 88, 177901 (2002); J. Chem. Phys. 127, 124305 (2007)

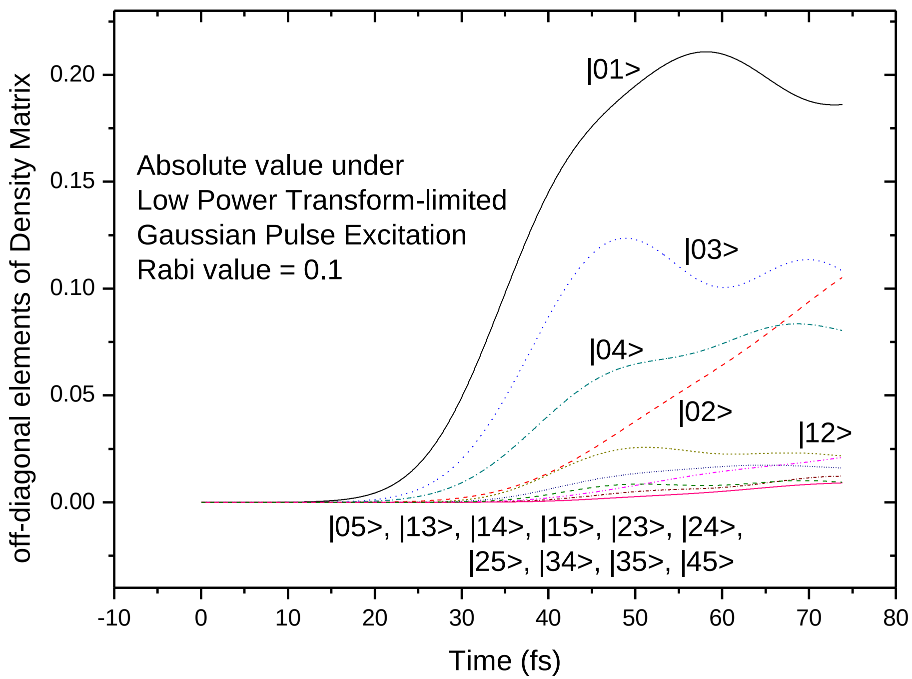


Normalized Population
Time (fs)
|0>
|1>
|2>
|3>
|4>
|5>
Dressed State Character
Time (fs)
Eigen energy (arb. units)
Time (fs)
Realistic Molecule model

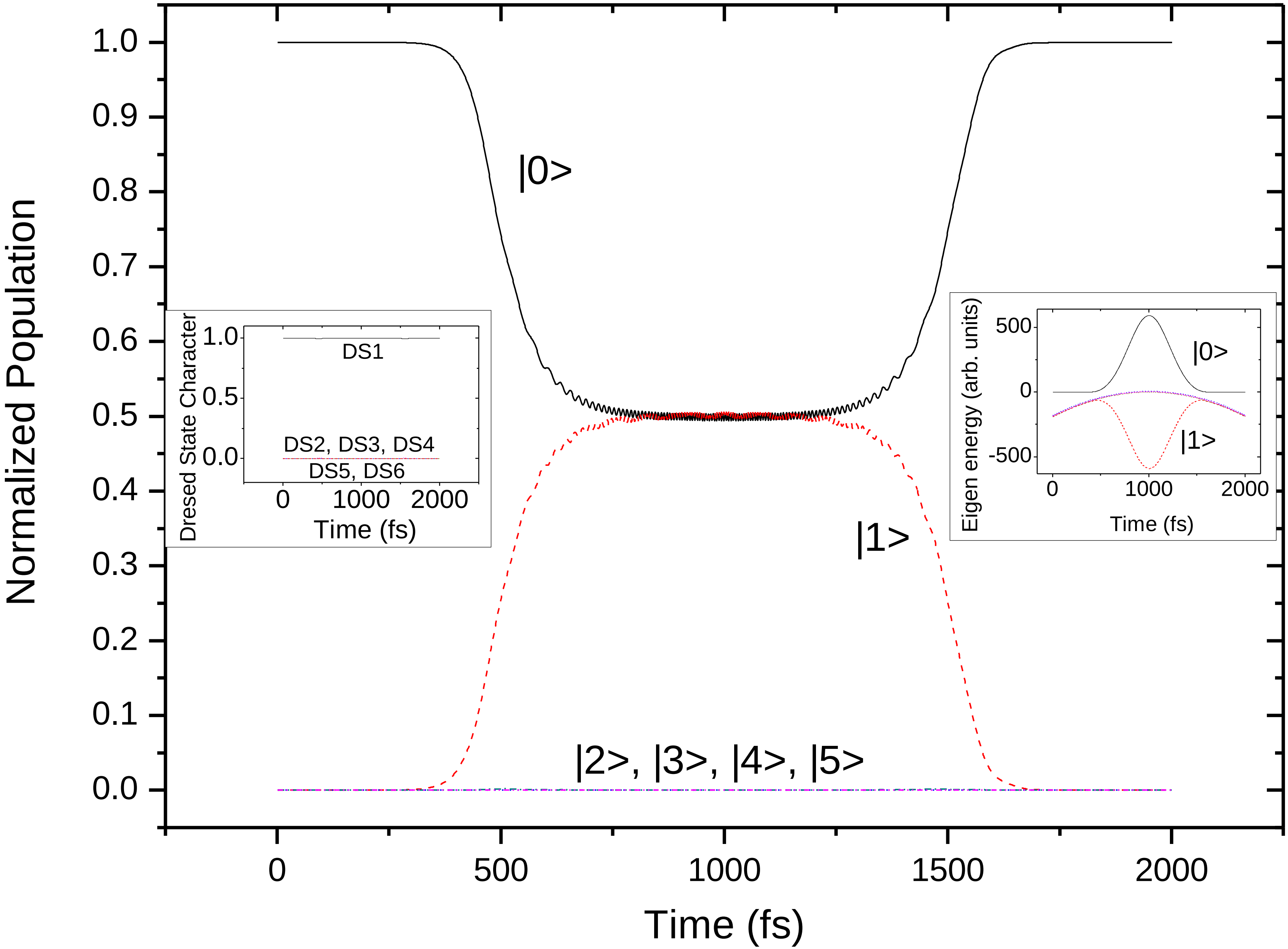


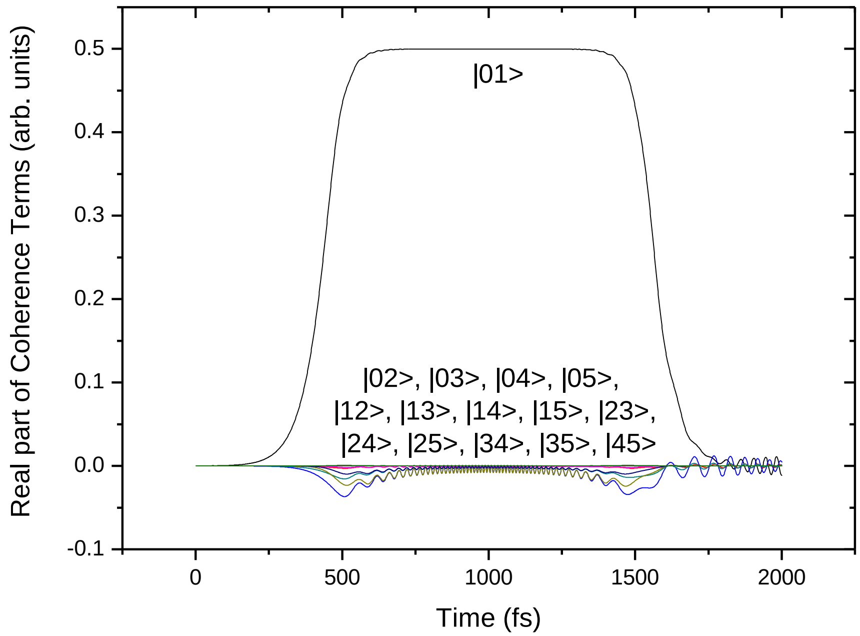



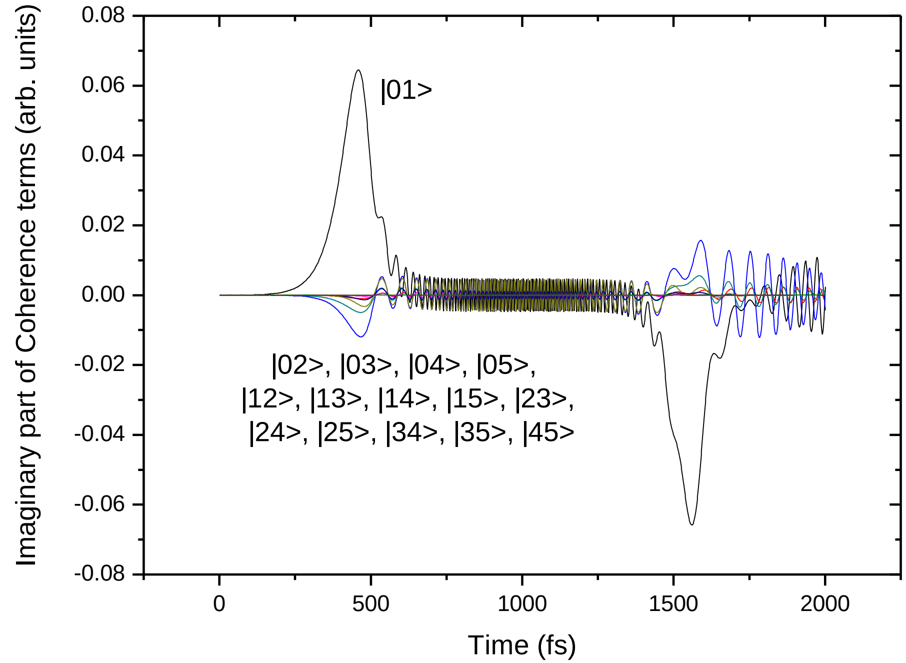

Both Real & Imaginary components are involved



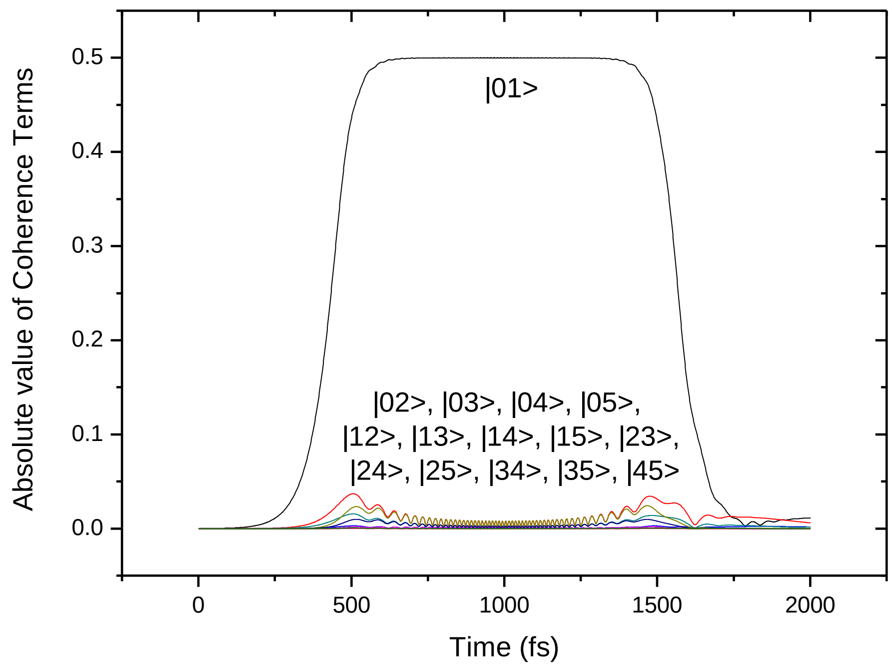
# Adiabatic Evaluation of the Multilevel System






The Real part is important

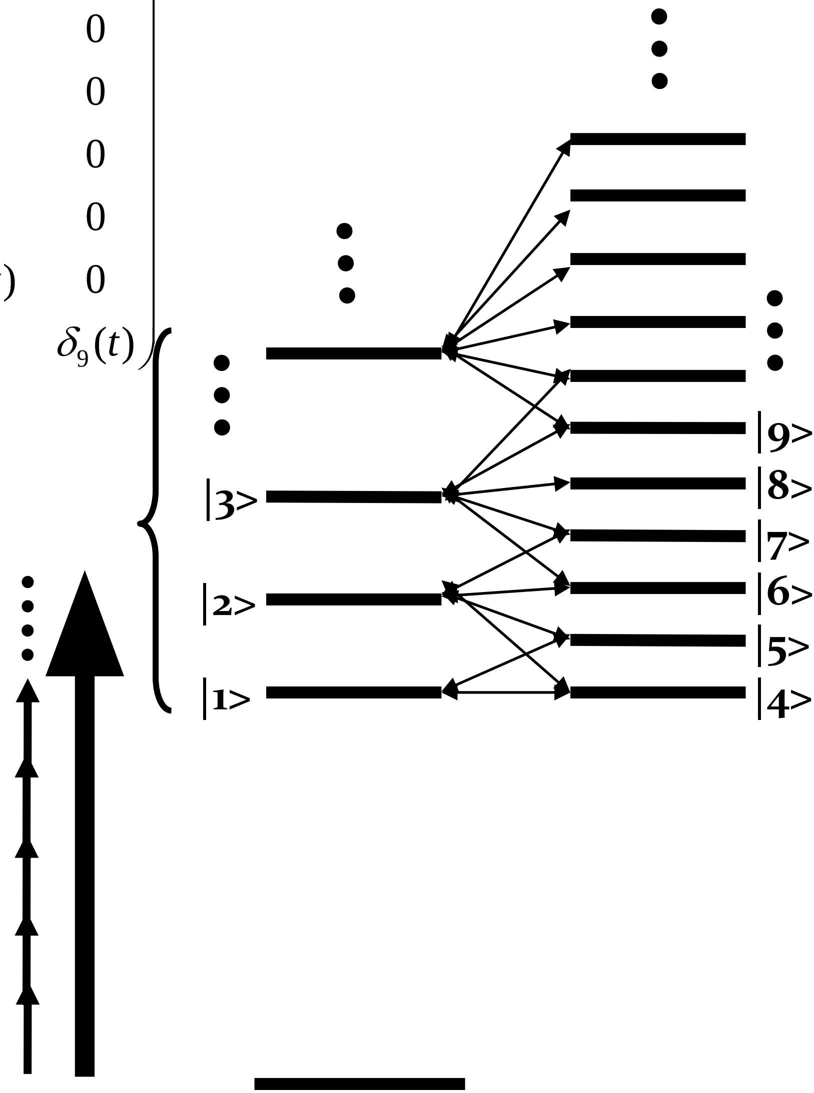


$$
\hbar
\begin{array}{cccccccccc}
|0\rangle & |1\rangle & |2\rangle & |3\rangle & |4\rangle & |5\rangle & |6\rangle & |7\rangle & |8\rangle & |9\rangle \\
\end{array}
$$

$$
\hbar\begin{pmatrix}
0 & \Omega_1(t) & \Omega_2(t) & \Omega_3(t) & 0 & 0 & 0 & 0 & 0 & 0 \\
\Omega_1^*(t) & \delta_1(t) & V_{12} & V_{13} & V_{14} & V_{15} & 0 & 0 & 0 & 0 \\
\Omega_2^*(t) & V_{12} & \delta_2(t) & V_{23} & V_{24} & V_{25} & V_{26} & V_{27} & 0 & 0 \\
\Omega_3^*(t) & V_{13} & V_{23} & \delta_3(t) & 0 & 0 & V_{36} & V_{37} & V_{38} & V_{39} \\
0 & V_{14} & V_{24} & 0 & \delta_4(t) & 0 & 0 & 0 & 0 & 0 \\
0 & V_{15} & V_{25} & 0 & 0 & \delta_5(t) & 0 & 0 & 0 & 0 \\
0 & 0 & V_{26} & V_{36} & 0 & 0 & \delta_6(t) & 0 & 0 & 0 \\
0 & 0 & V_{27} & V_{37} & 0 & 0 & 0 & \delta_7(t) & 0 & 0 \\
0 & 0 & 0 & V_{38} & 0 & 0 & 0 & 0 & \delta_8(t) & 0 \\
0 & 0 & 0 & V_{39} & 0 & 0 & 0 & 0 & 0 & \delta_9(t)
\end{pmatrix}
$$

**Can be further generalized...**

# Tier Model of Intramolecular Vibrational Relaxation

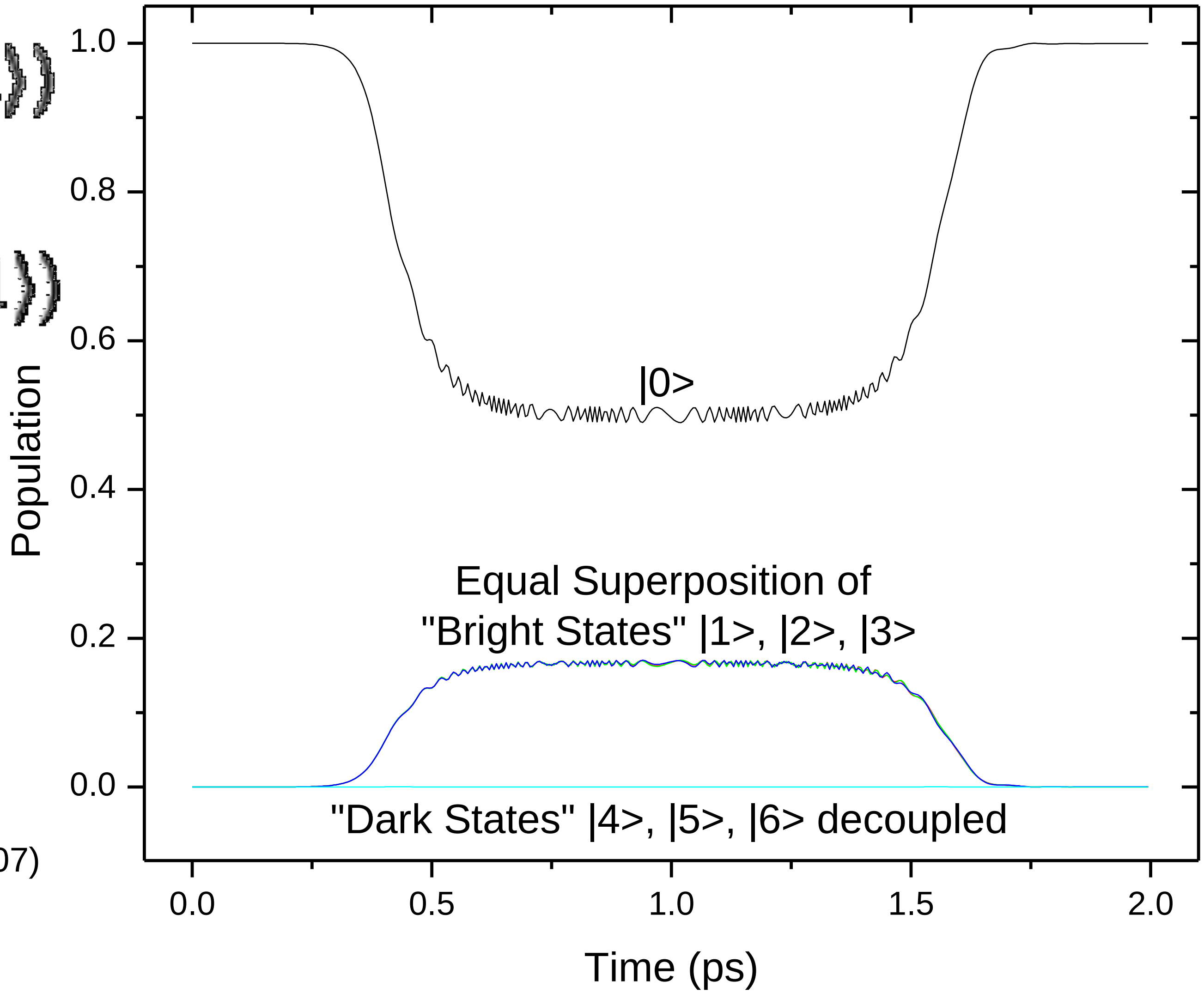


# Example of Simple Hadamard Gate in Molecules

Equal superposition between quantum states

$$|0\rangle \rightarrow \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$$

$$|1\rangle \rightarrow \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)$$




More than two states: "Qudits"

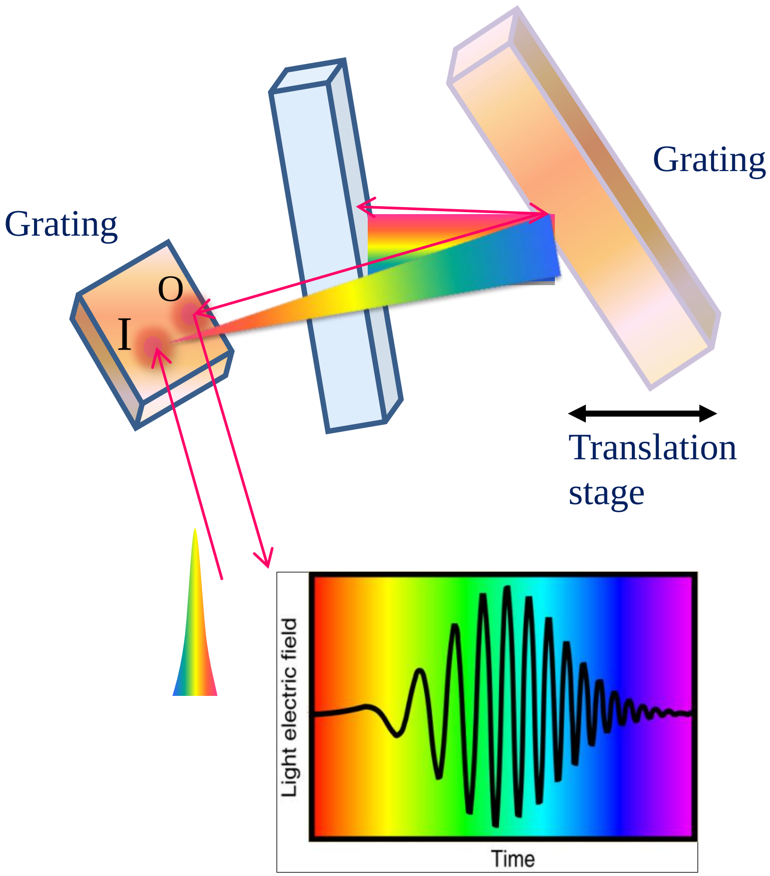
Int. J. Quant. Info. **5**, 179 -188 (2007)

# Control Knobs

- Spatial Modulation—to get individual molecular control in condensed phase
  - Gas Phase can use Molecular Beam Condition
- Laser Polarization
- Temporal Modulation
  - Simplest of all: Frequency Chirping

- Ask the Question:
  - How important are these parameters/knobs important in traditional Molecular Control?

# Frequency chirping




Chirped pulse

This pulse increases its frequency linearly in time (from red to blue). In analogy to bird sounds, this pulse is called a "chirped" pulse.

The phase of the laser pulse which is centered at $\omega_0$, can be expanded around $\omega_0$ to second order in $\omega$:

$$\varphi(\omega) \approx \varphi(\omega_0) + \frac{1}{1!}\frac{\partial\varphi}{\partial\omega}\bigg|_{\omega=\omega_0}(\omega-\omega_0) + \frac{1}{2!}\frac{\partial^2\varphi}{\partial\omega^2}\bigg|_{\omega=\omega_0}(\omega-\omega_0)^2$$

Linear chirp coefficient (chirp parameter in the frequency domain)

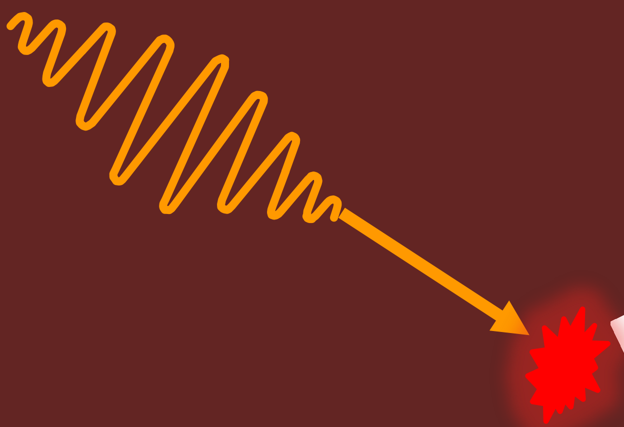
$$\beta = \frac{\partial^2\varphi}{\partial\omega^2}\bigg|_{\omega=\omega_0}$$

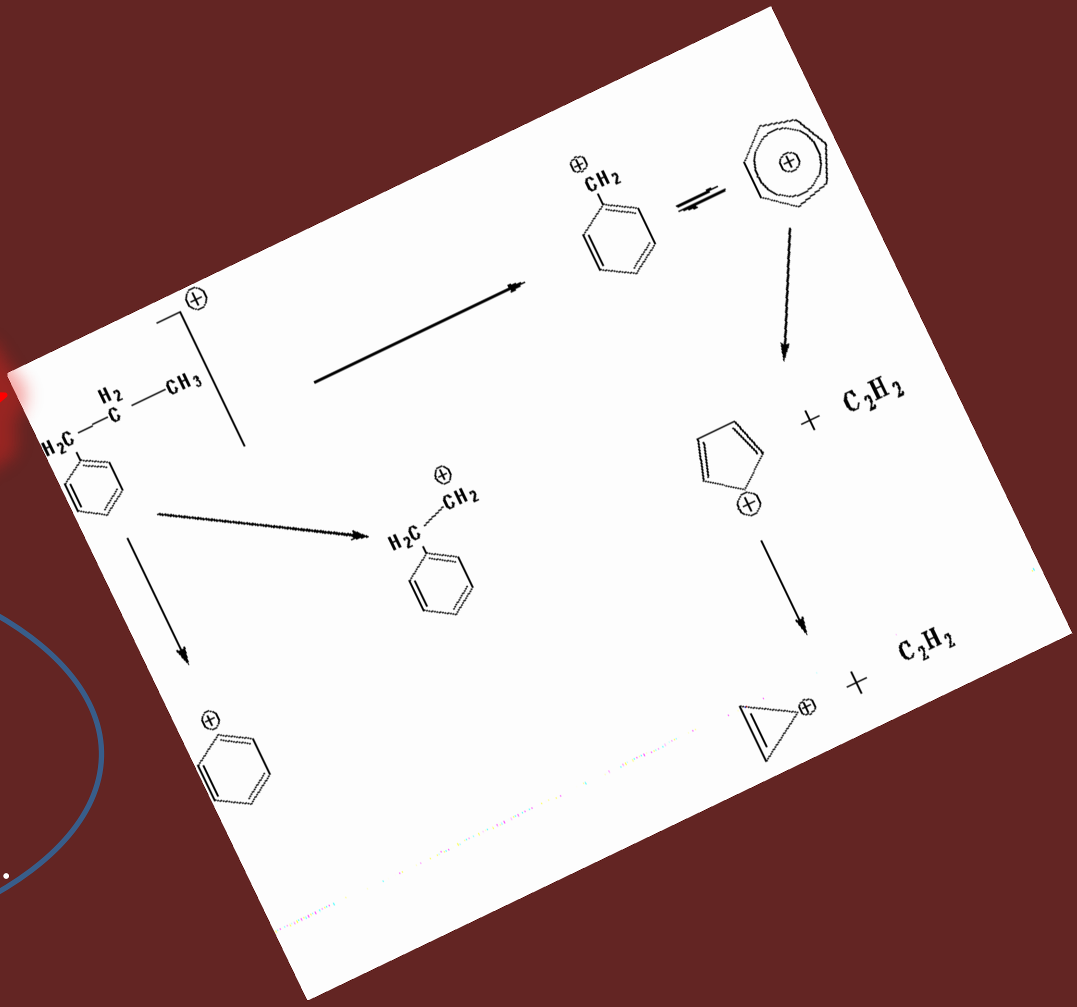
$\beta$ can be calculated as:

$$\tau^2 = \tau_0^{\,2} + \left[\frac{4\beta\ln 2}{\tau_0}\right]^2 ; \beta = \frac{\tau_0\sqrt{\tau^2 - \tau_0^2}}{4\ln 2}$$

Where $\tau$ is the pulse duration of the chirped laser pulse and $\tau_0$ is the chirp-free pulse duration of the transform limited pulse in FWHM.

# Photo-fragmentation: Gas Phase Coherent Control



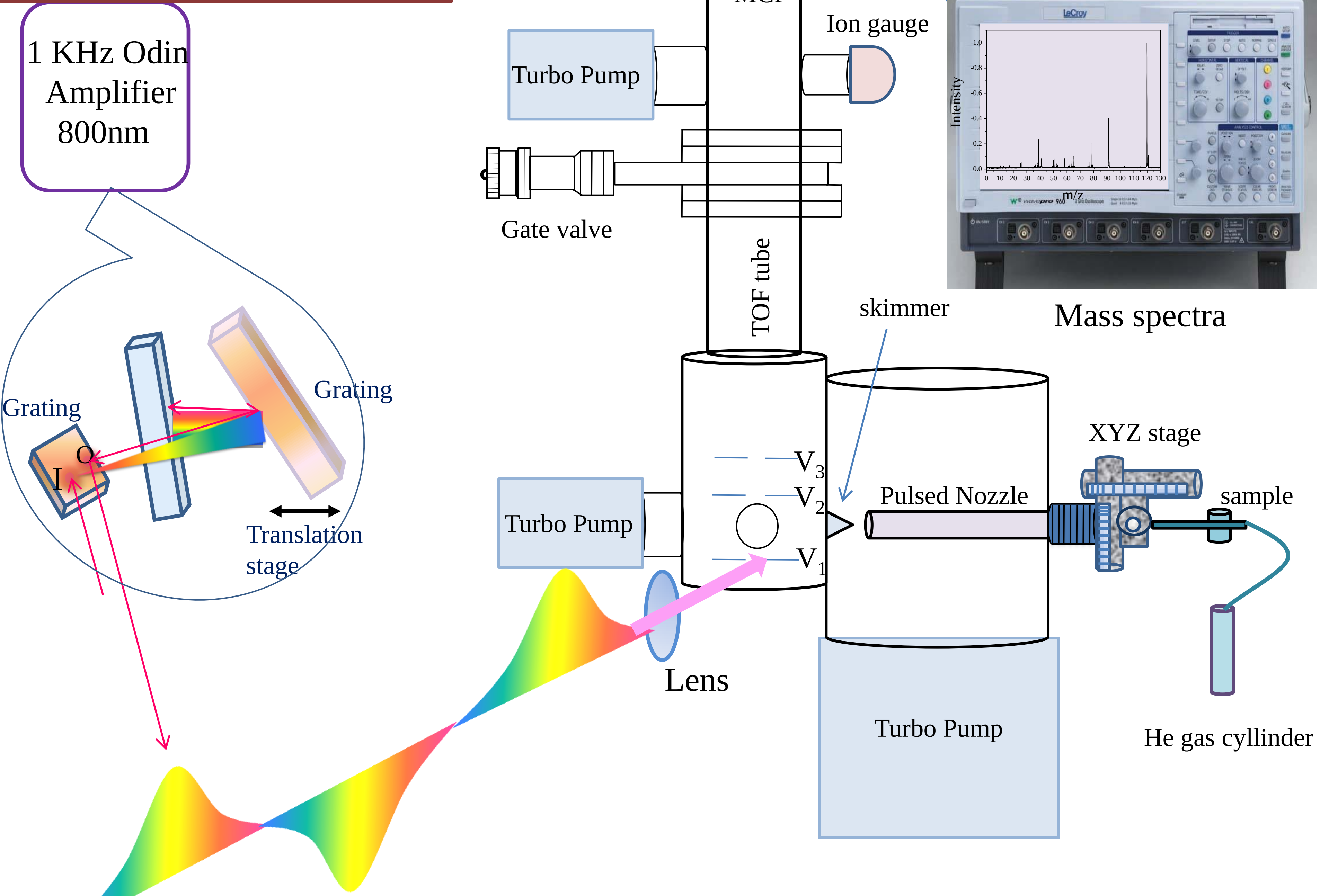



**Applications of coherent control**

- ✓ micro-electronic lithography
- ✓ fabrication of gene chips
- ✓ photodynamic therapy
- ✓Quantum information processing..

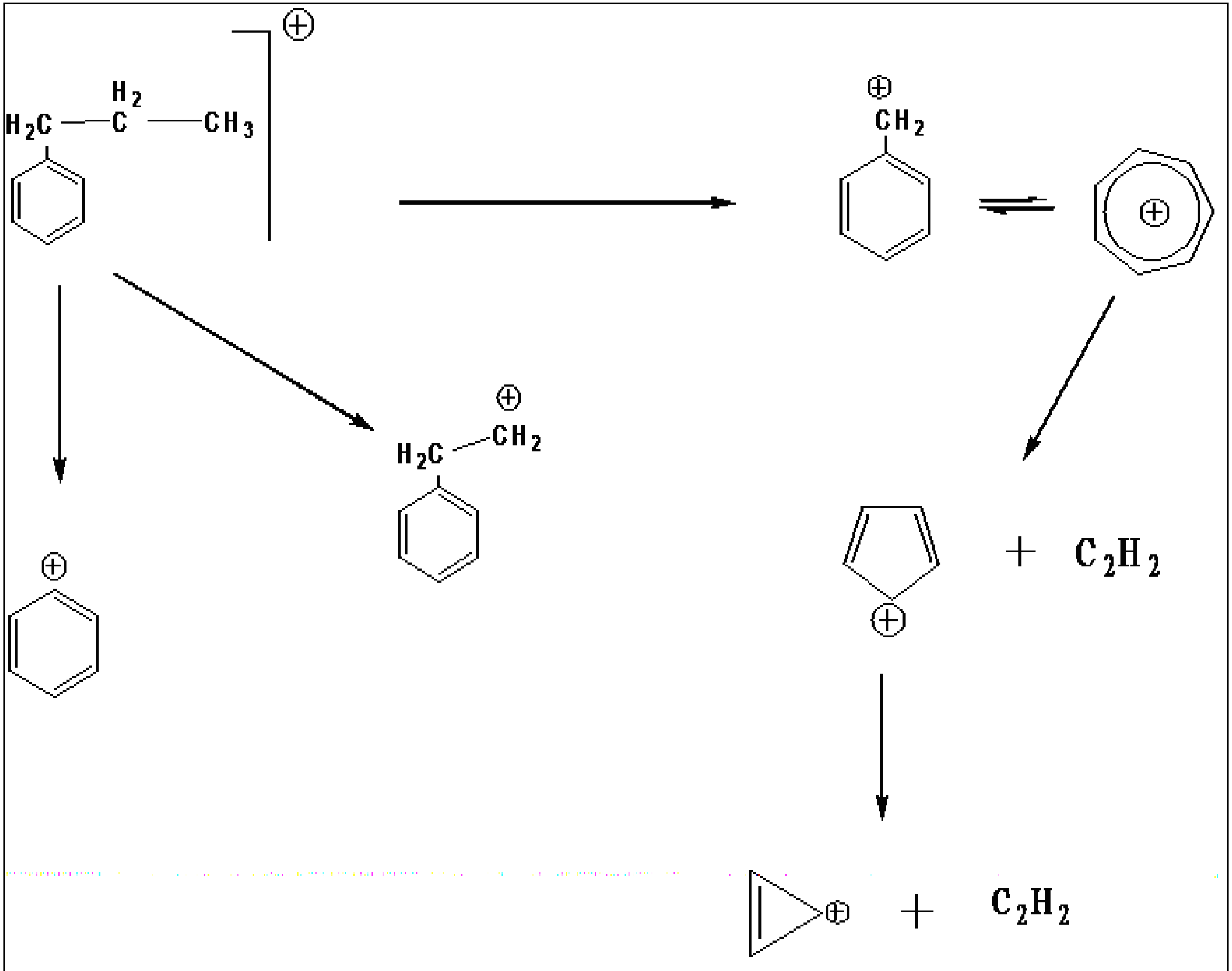
………..etc

# Molecular Beam Experiments…

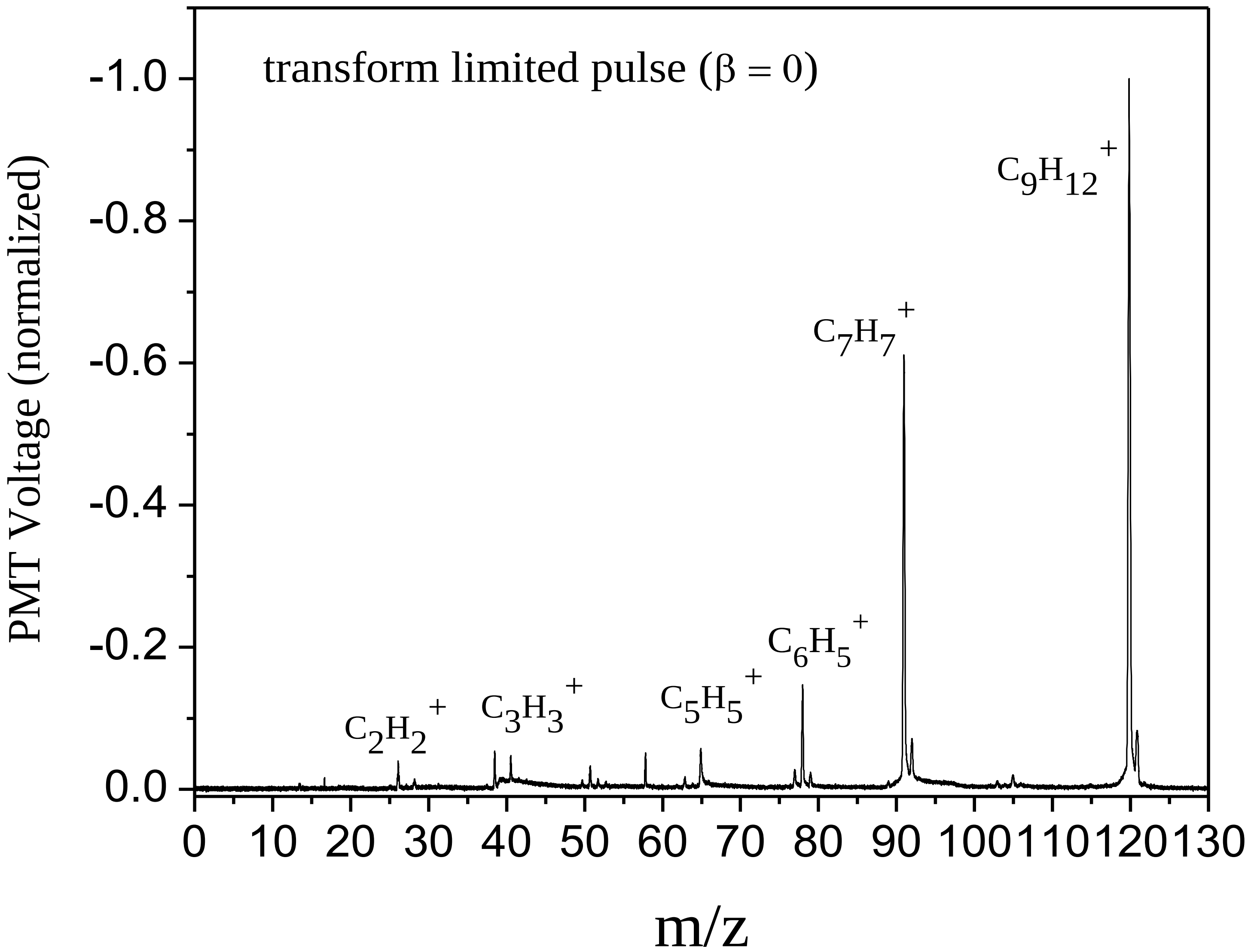


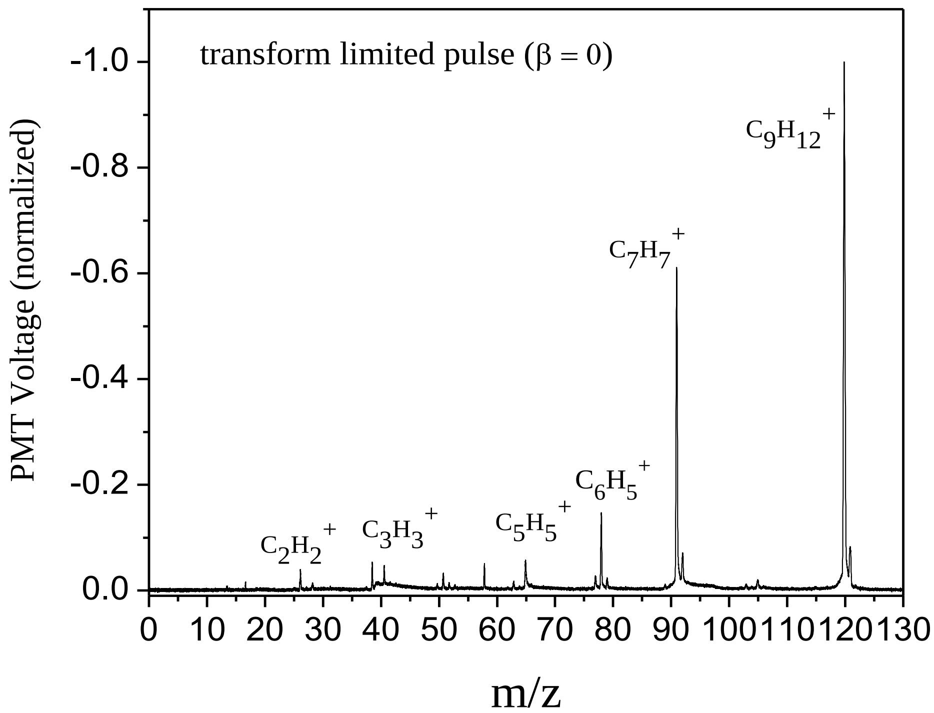

**Experimental set up for studying effect of femtosecond laser chirp**

# Possible Fragmentation Pathway for n-propyl-benzene

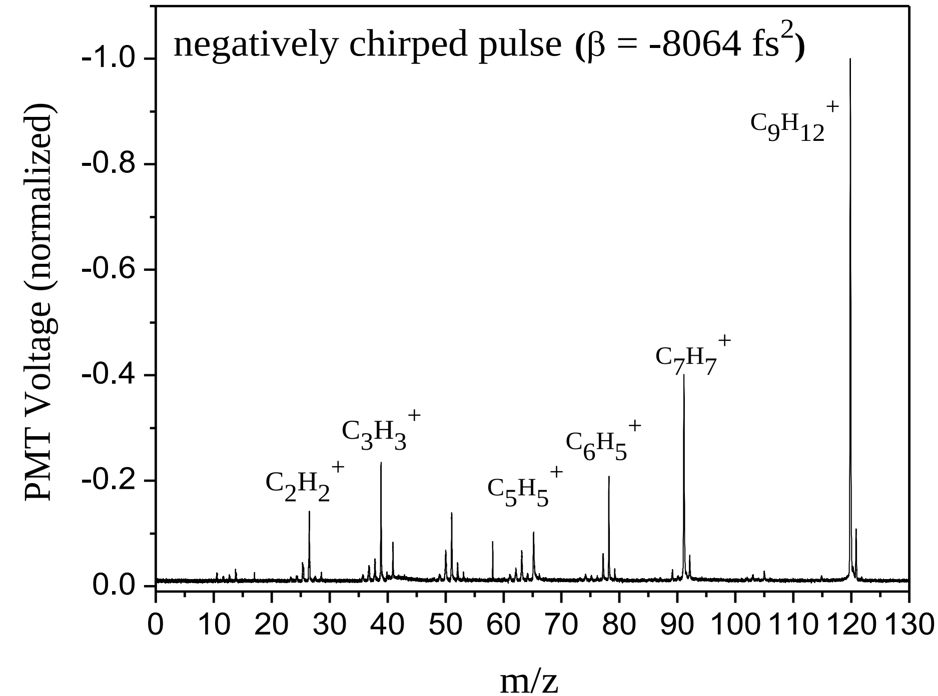


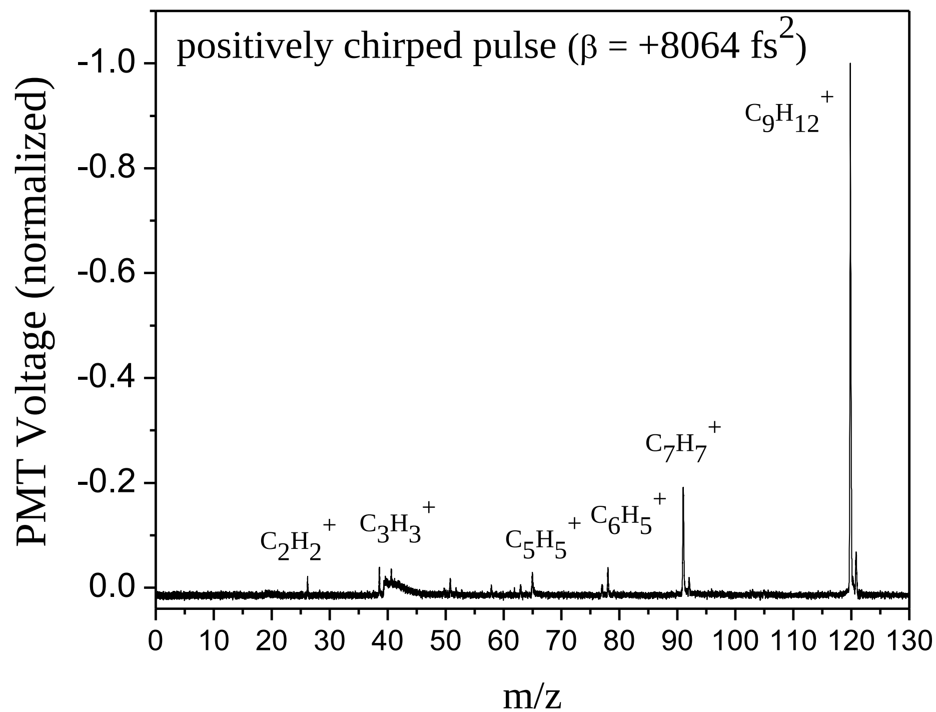
# Mass spectra of n-propyl benzene when the laser pulse is transform limited (β = 0)



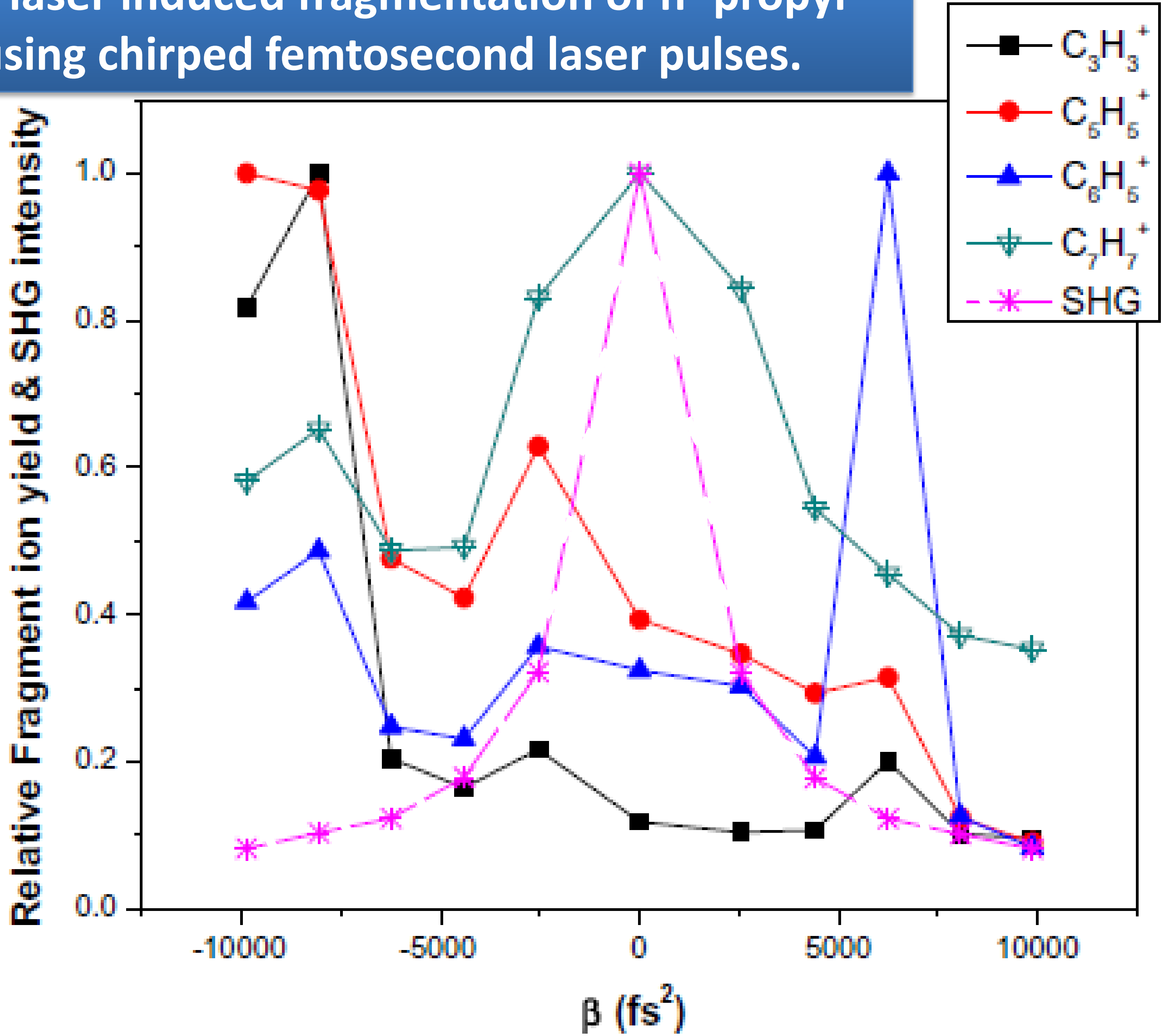



# Mass spectra of n-propyl benzene



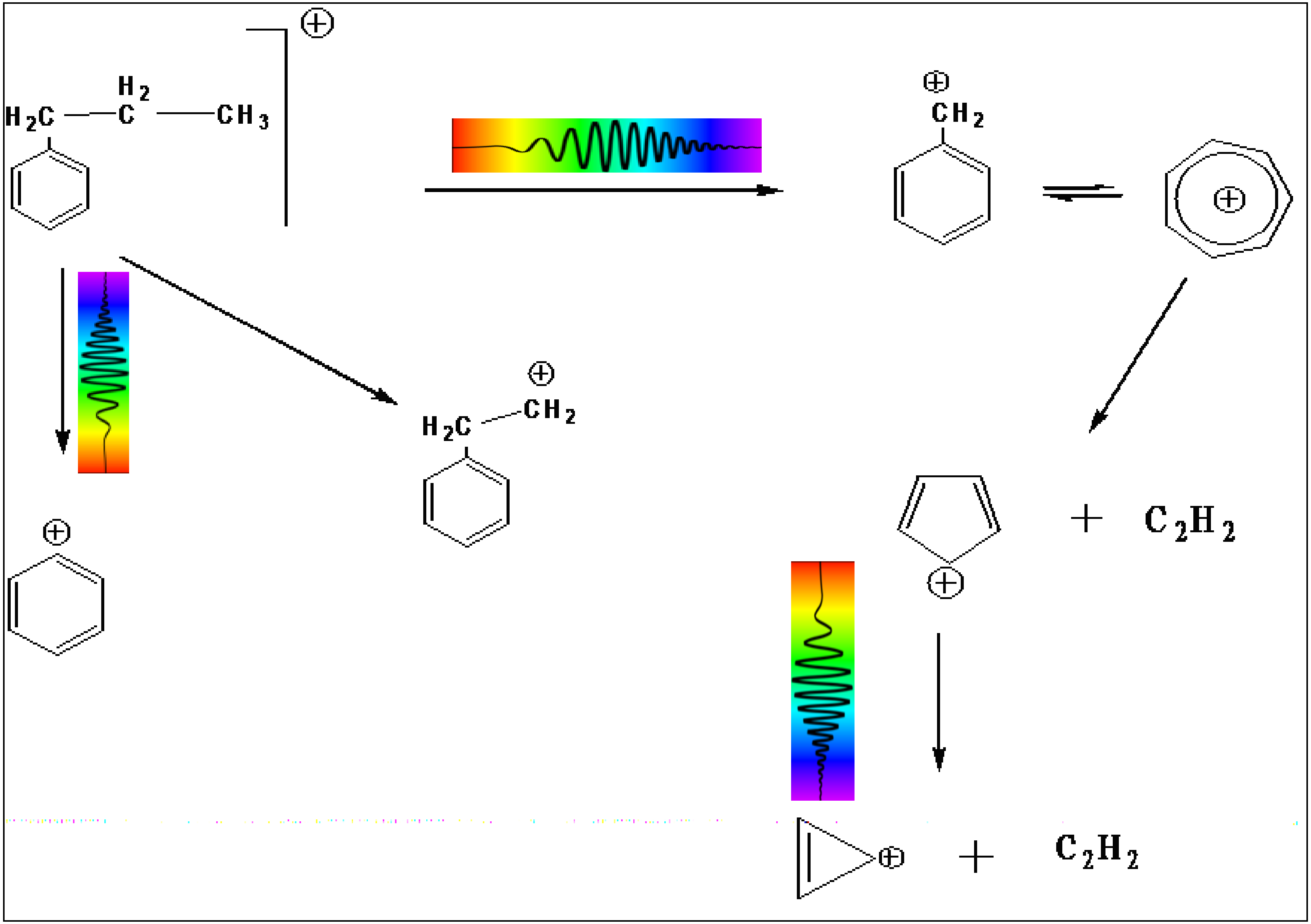



# Control of laser induced fragmentation of n- propyl benzene using chirped femtosecond laser pulses.

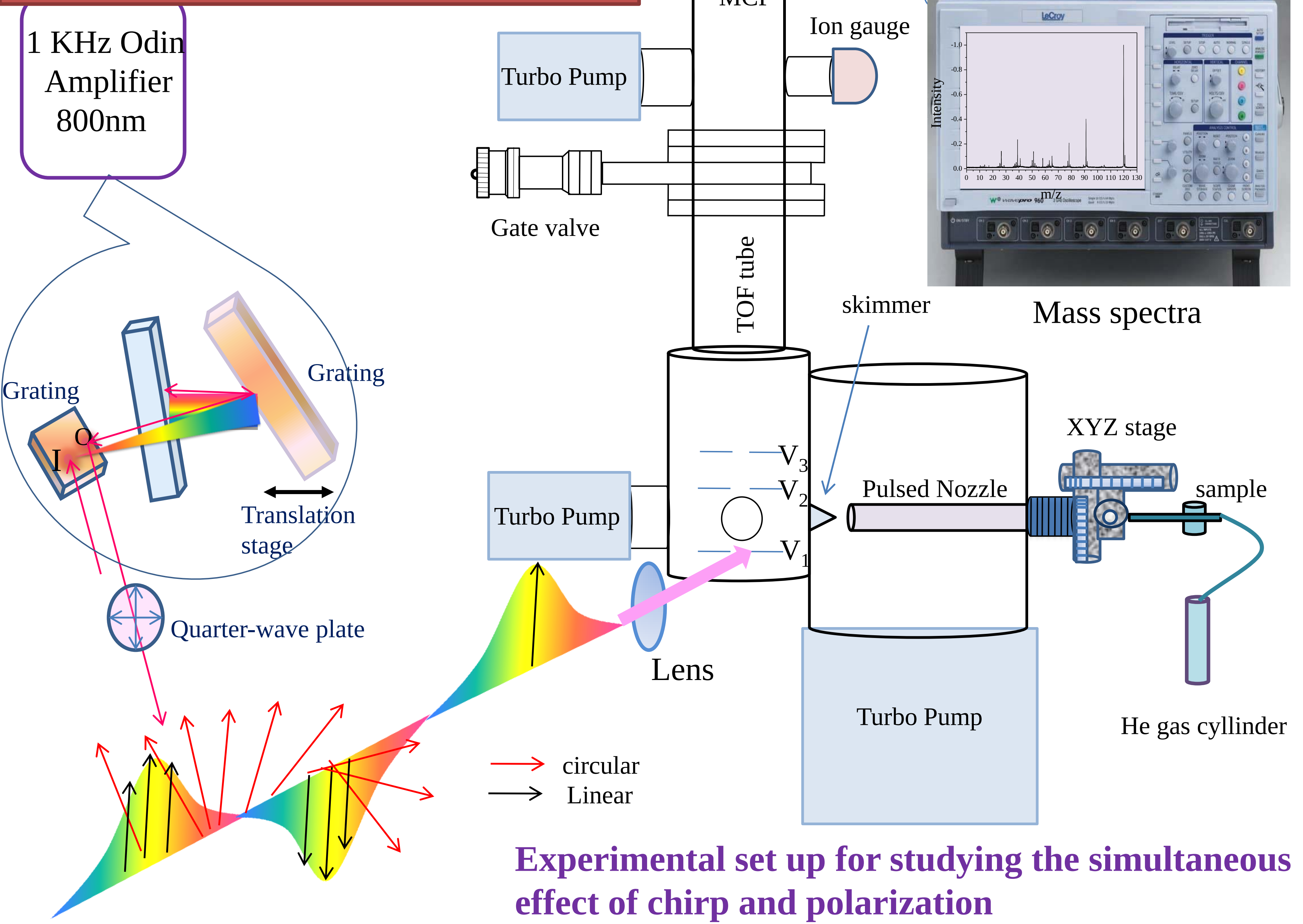



T. Goswami, S. K. Karthick Kumar, A. Dutta, D. Goswami *Chem. Phys.* 380 (2009) 47

# Fragmentation pathway as a result of Chirping

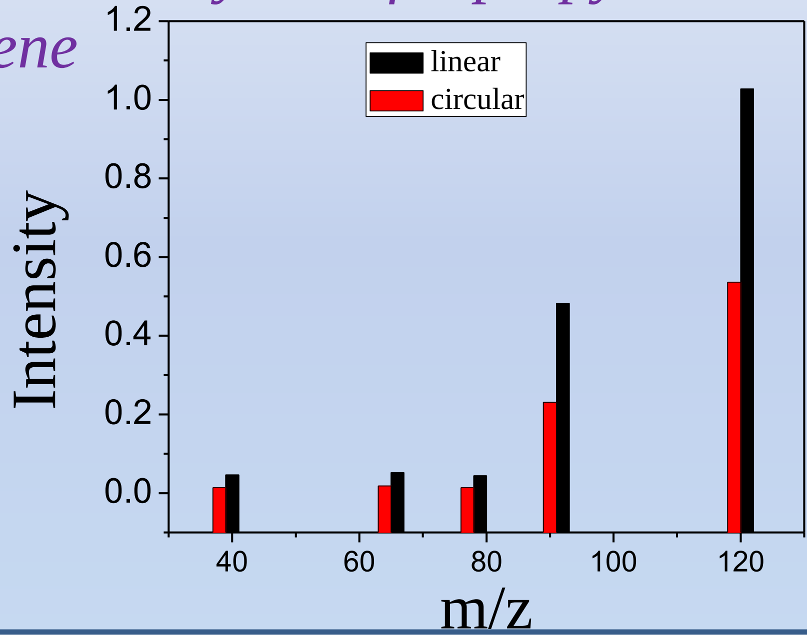


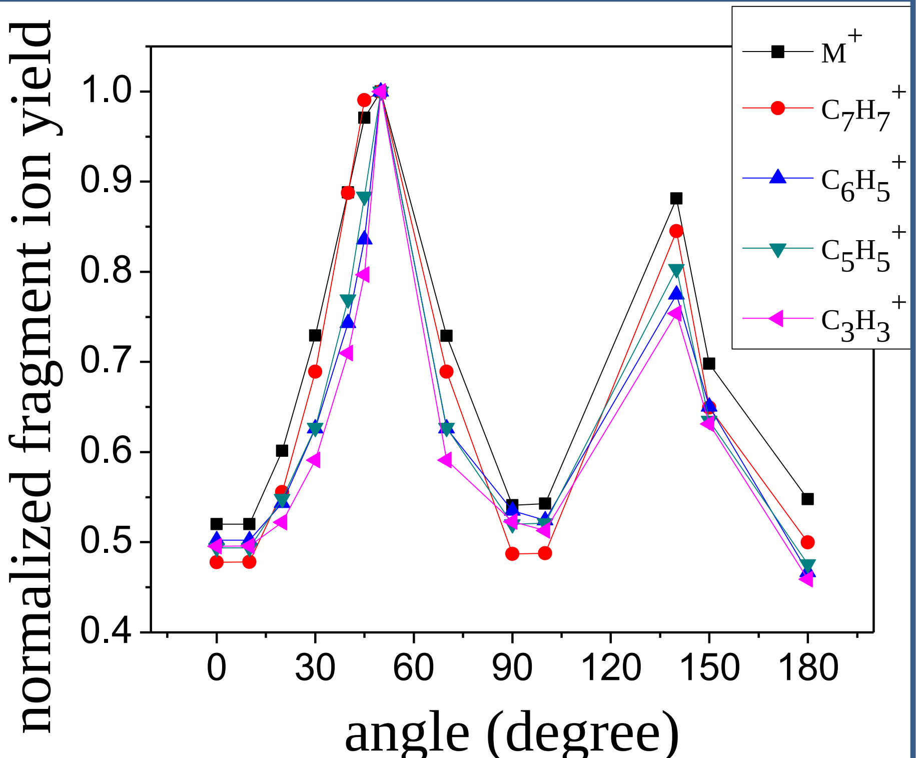
# Lets add the Effect of Laser Polarization now…




**Experimental set up for studying the simultaneous effect of chirp and polarization**

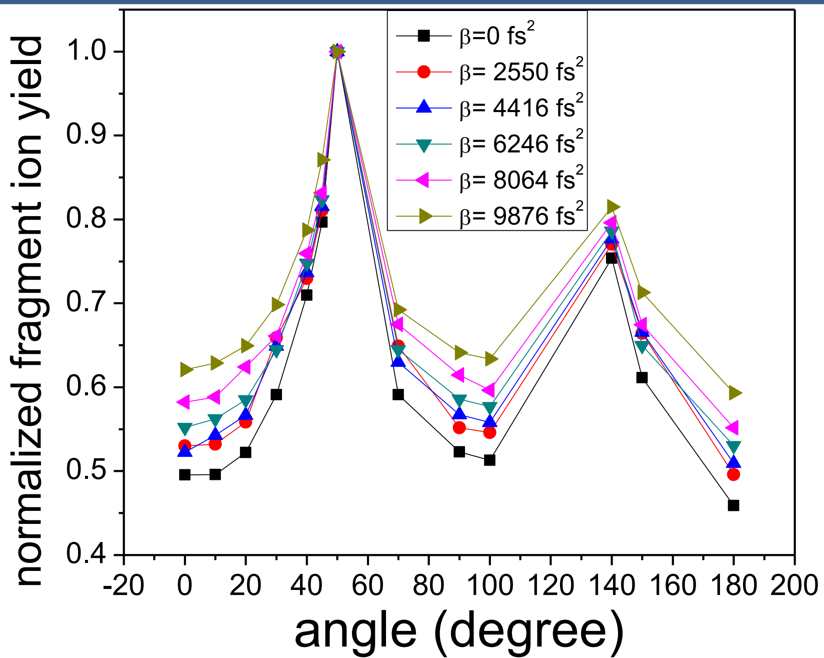
*Polarization dependence of different fragment ion yield of n-propyl benzene*




*Variation of different fragment ion yields with polarization angle*

Both Chirp & Polarization

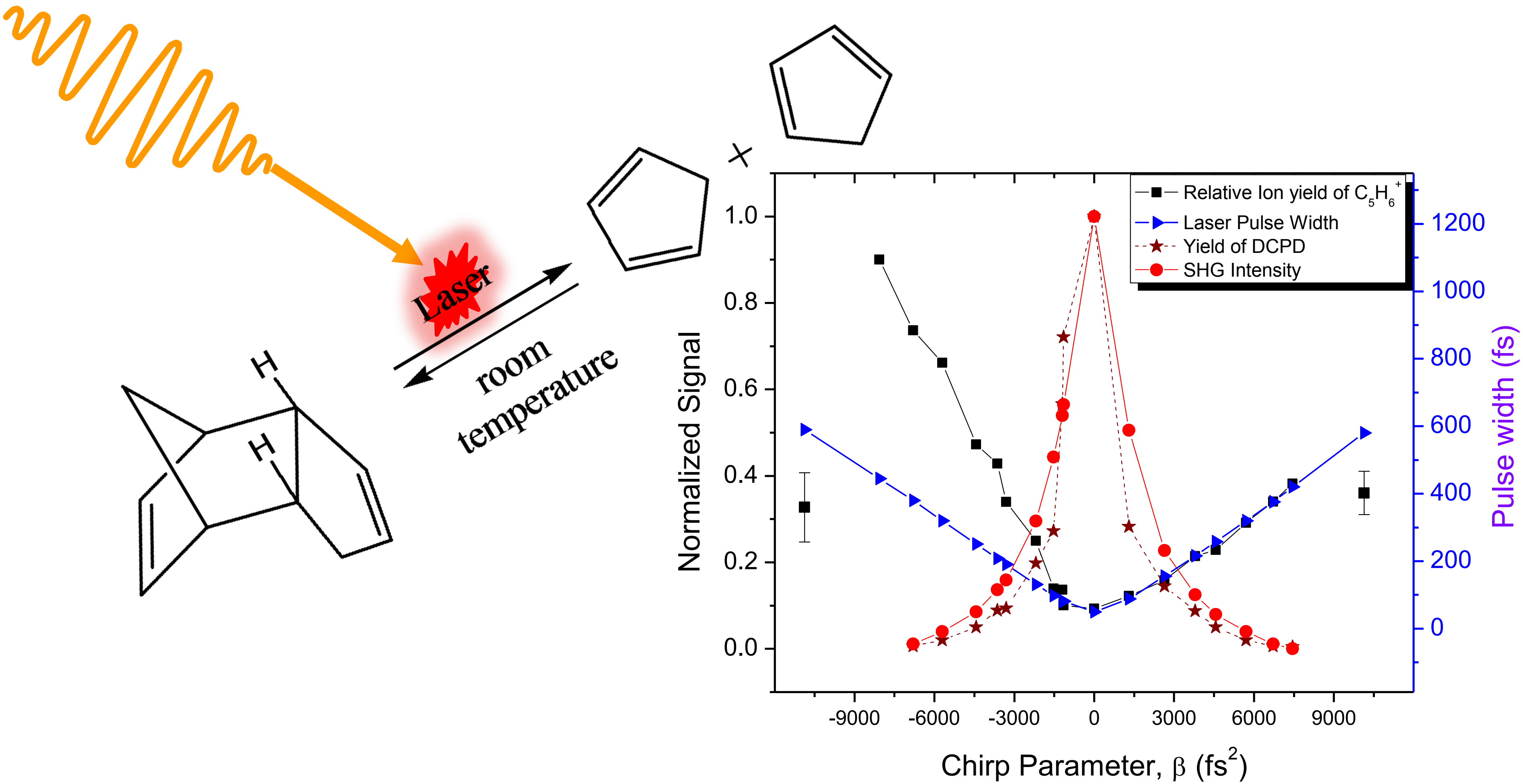



*The two important control parameter chirp and polarization are 'mutually exclusive' in nature*

# Multi-parameter Control with Laser Polarization & Pulse Chirp

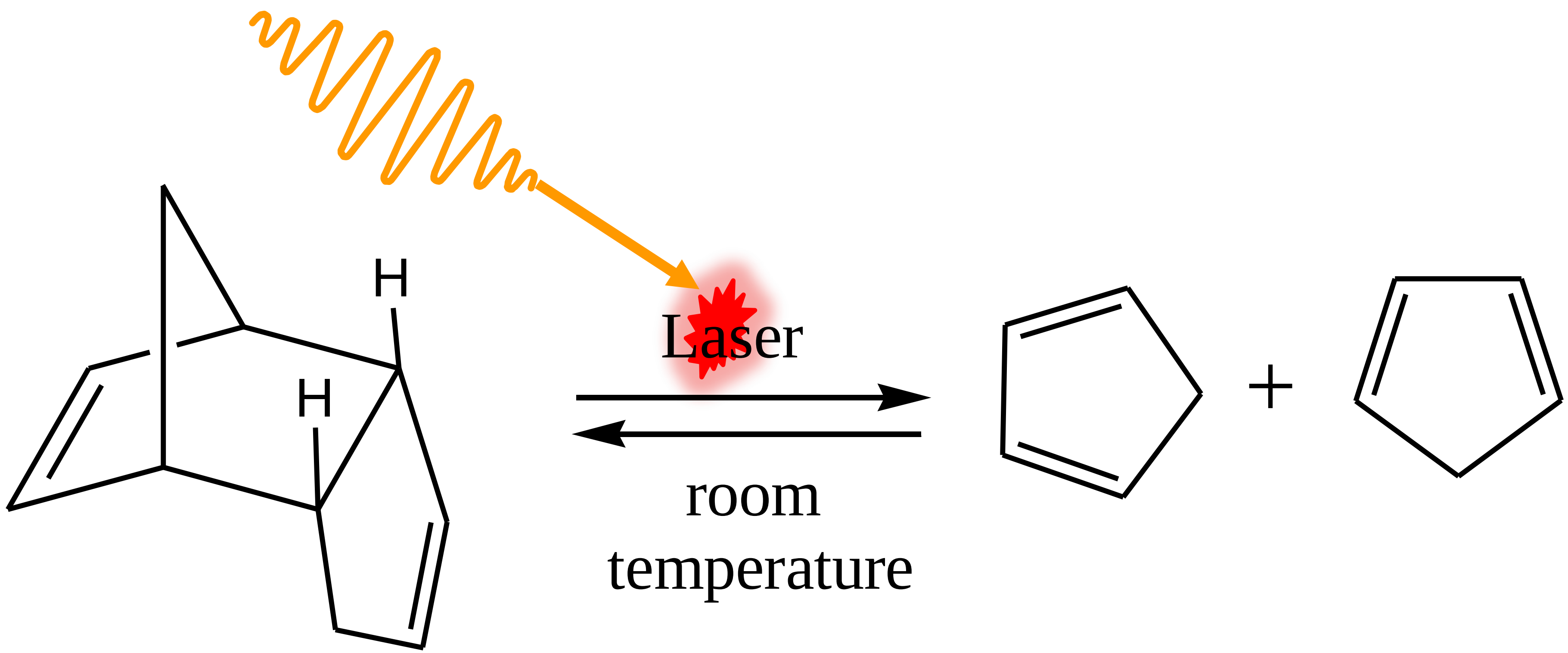
- Chirp affects the ratio of the individual fragment ion pattern
- Polarization affects the overall fragment ion pattern but not their relative yield
- Laser Polarization & Laser Pulse Chirp are thus

**Mutually exclusive Control "Knobs"**

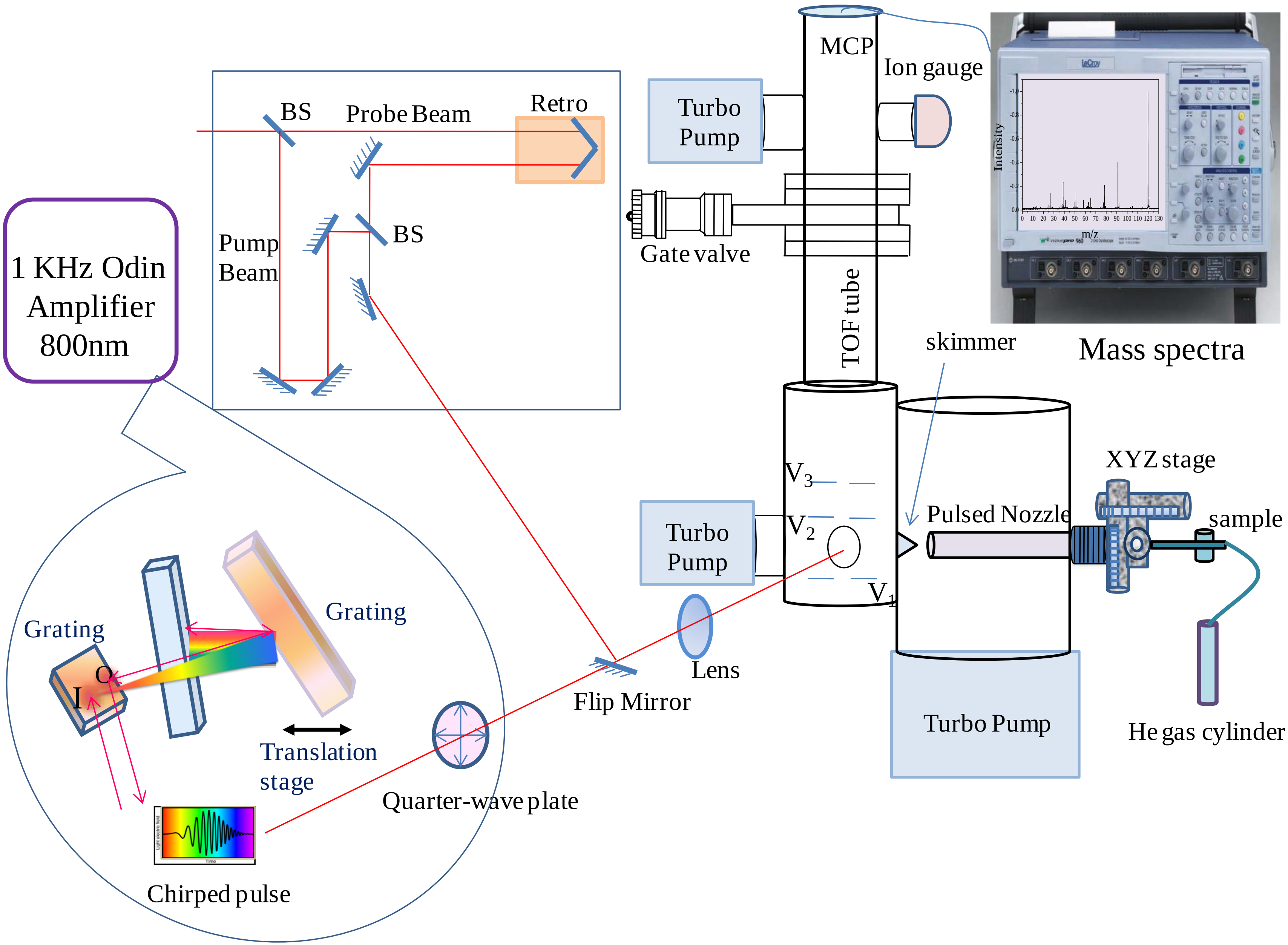


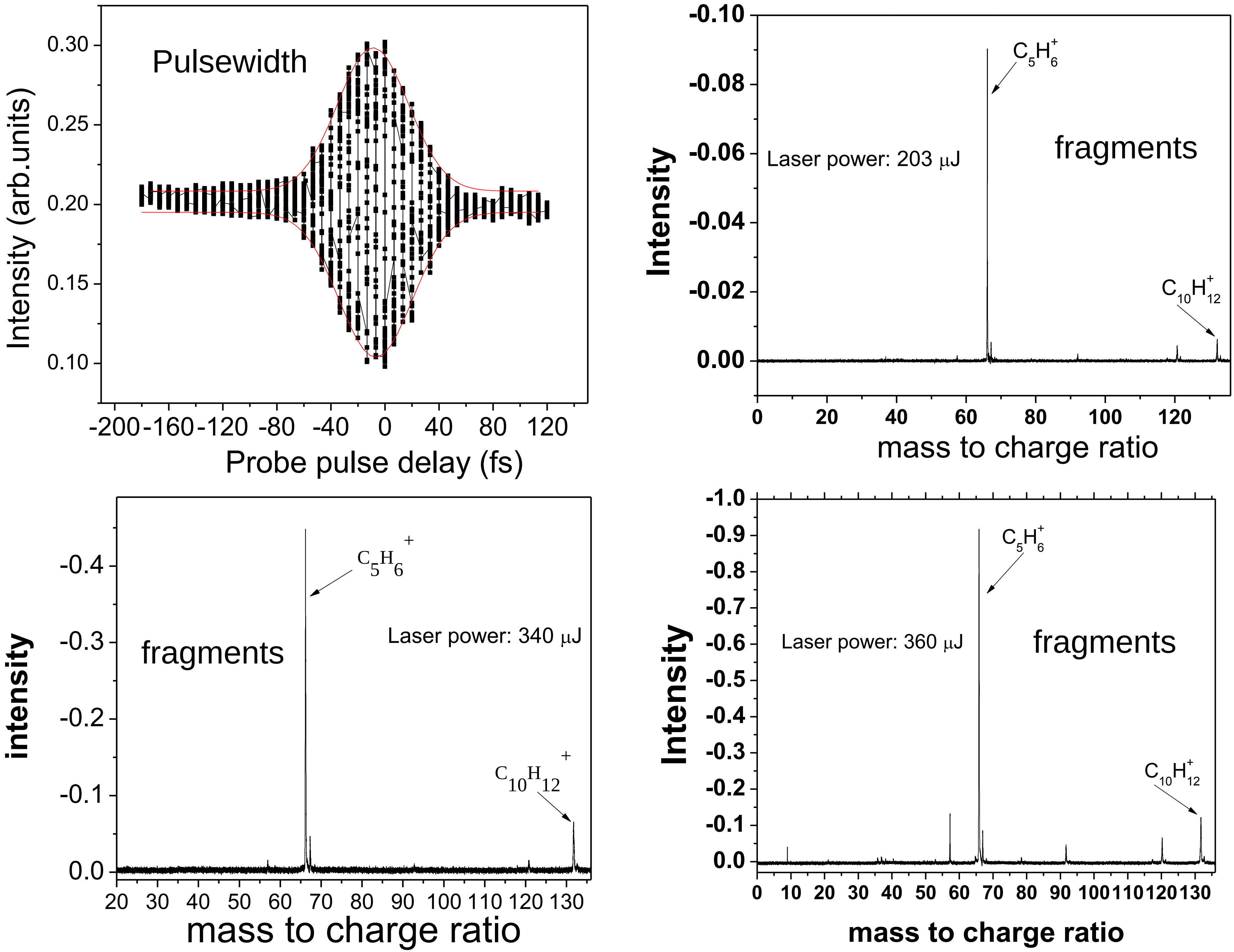

**Controlling Chemical Dynamics**

# Dimerization reaction of cyclopentadiene

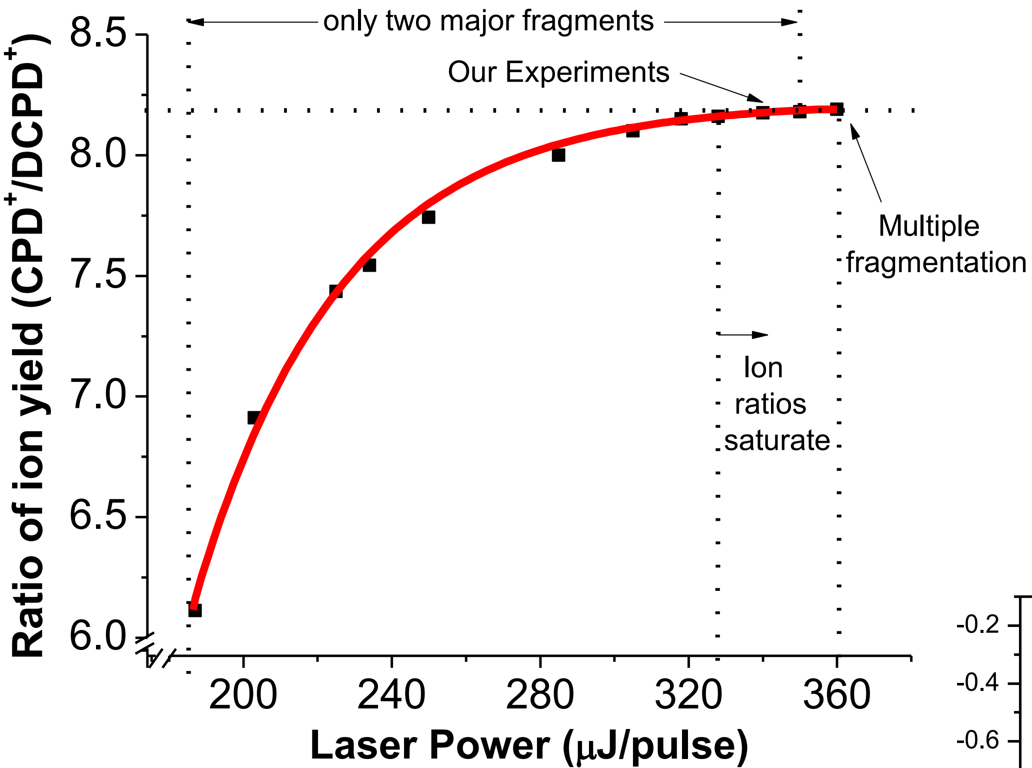


# Schematic Experimental setup



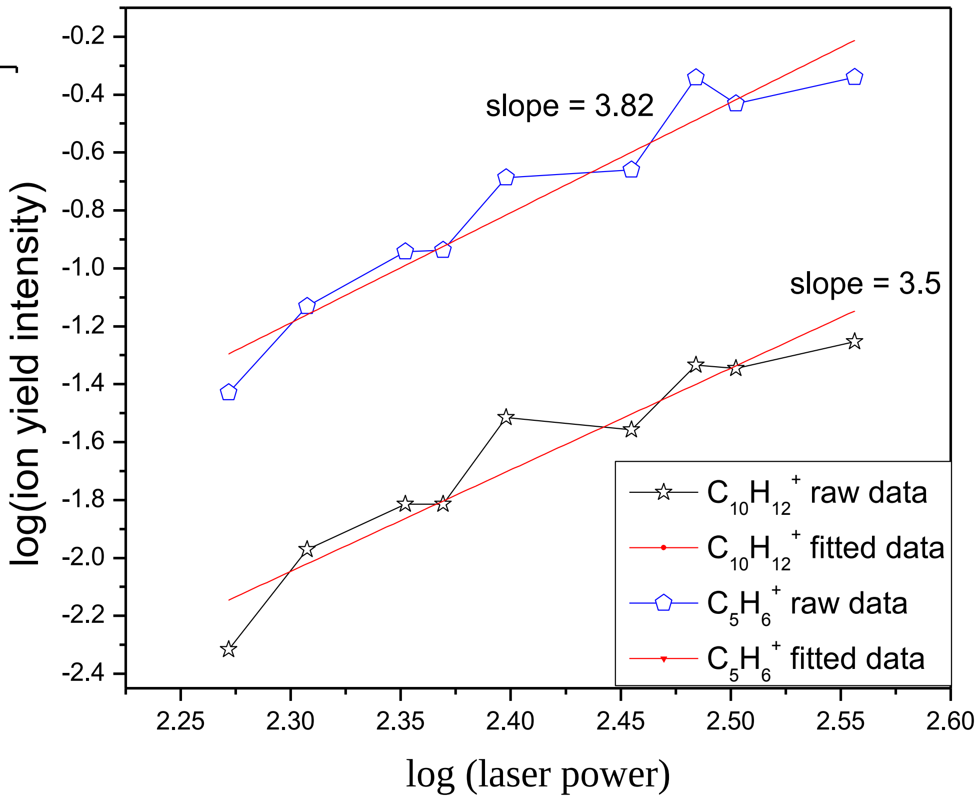


Pulsewidth
Intensity (arb.units)
0.30
0.25
0.20
0.15
0.10
-200 -160 -120 -80 -40 0 40 80 120
Probe pulse delay (fs)
-0.10
-0.08
-0.06
-0.04
-0.02
0.00
Intensity
Laser power: 203 μJ
fragments
$C_5H_6^+$
$C_{10}H_{12}^+$
0 20 40 60 80 100 120
mass to charge ratio
-0.4
-0.3
-0.2
-0.1
0.0
intensity
fragments
Laser power: 340 μJ
$C_5H_6^+$
$C_{10}H_{12}^+$
20 30 40 50 60 70 80 90 100 110 120 130
mass to charge ratio
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
Intensity
Laser power: 360 μJ
fragments
$C_5H_6^+$
$C_{10}H_{12}^+$
0 10 20 30 40 50 60 70 80 90 100 110 120 130
mass to charge ratio

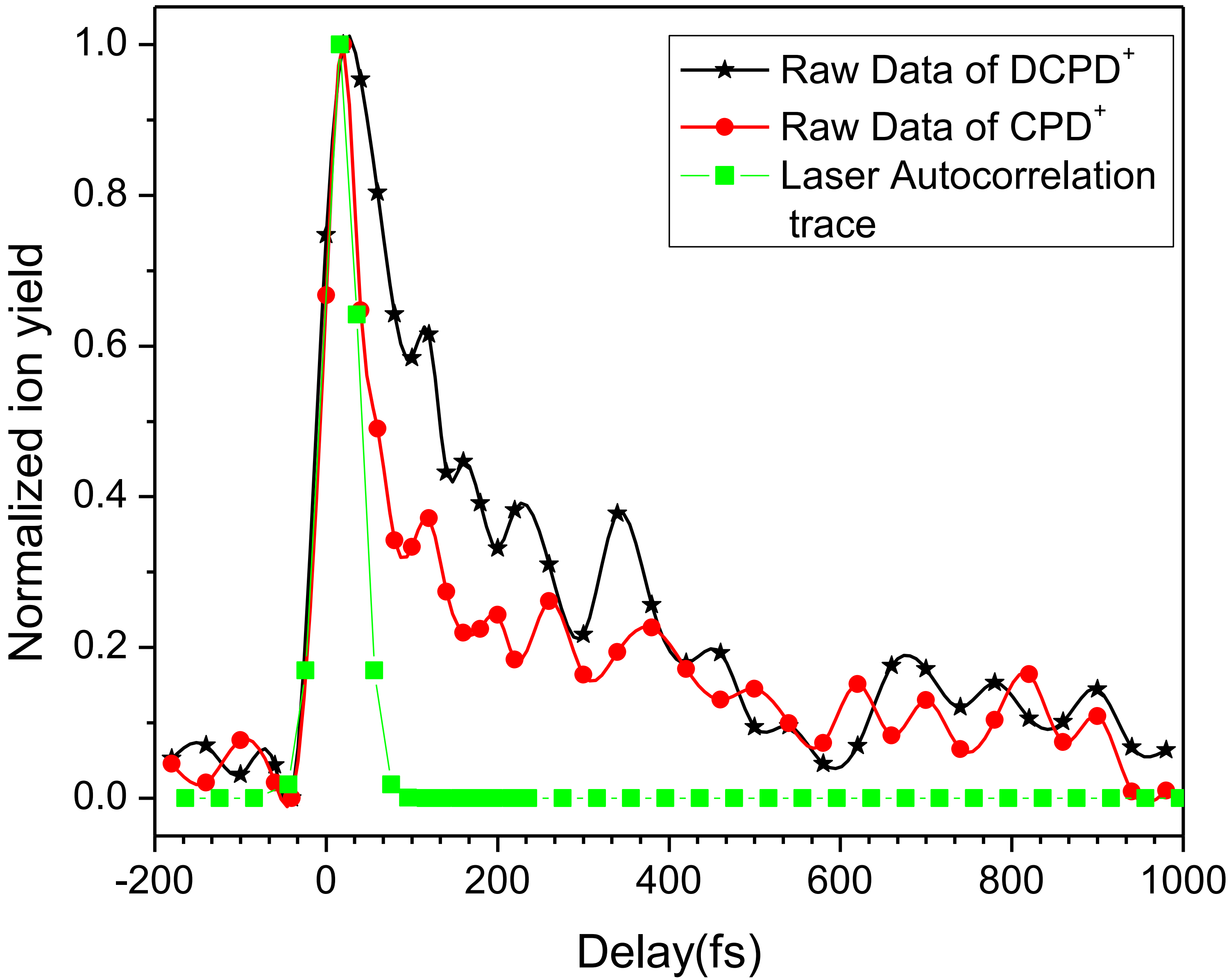



# Laser intensity dependence of the parent ion as well as cyclopentadiene yield

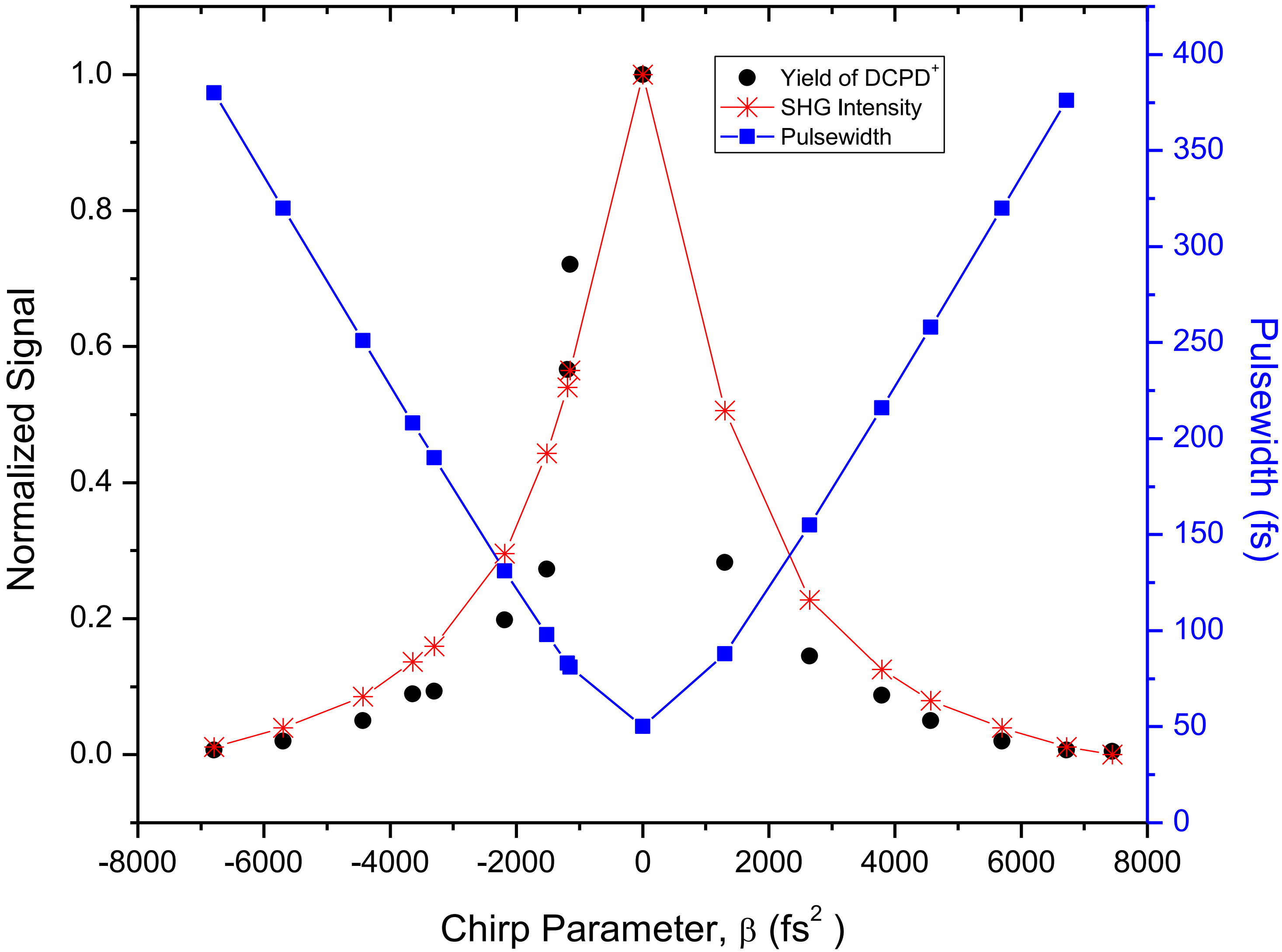
Laser intensity dependence of the ratio of the cyclopentadiene yield to the parent dicyclopentadiene ion



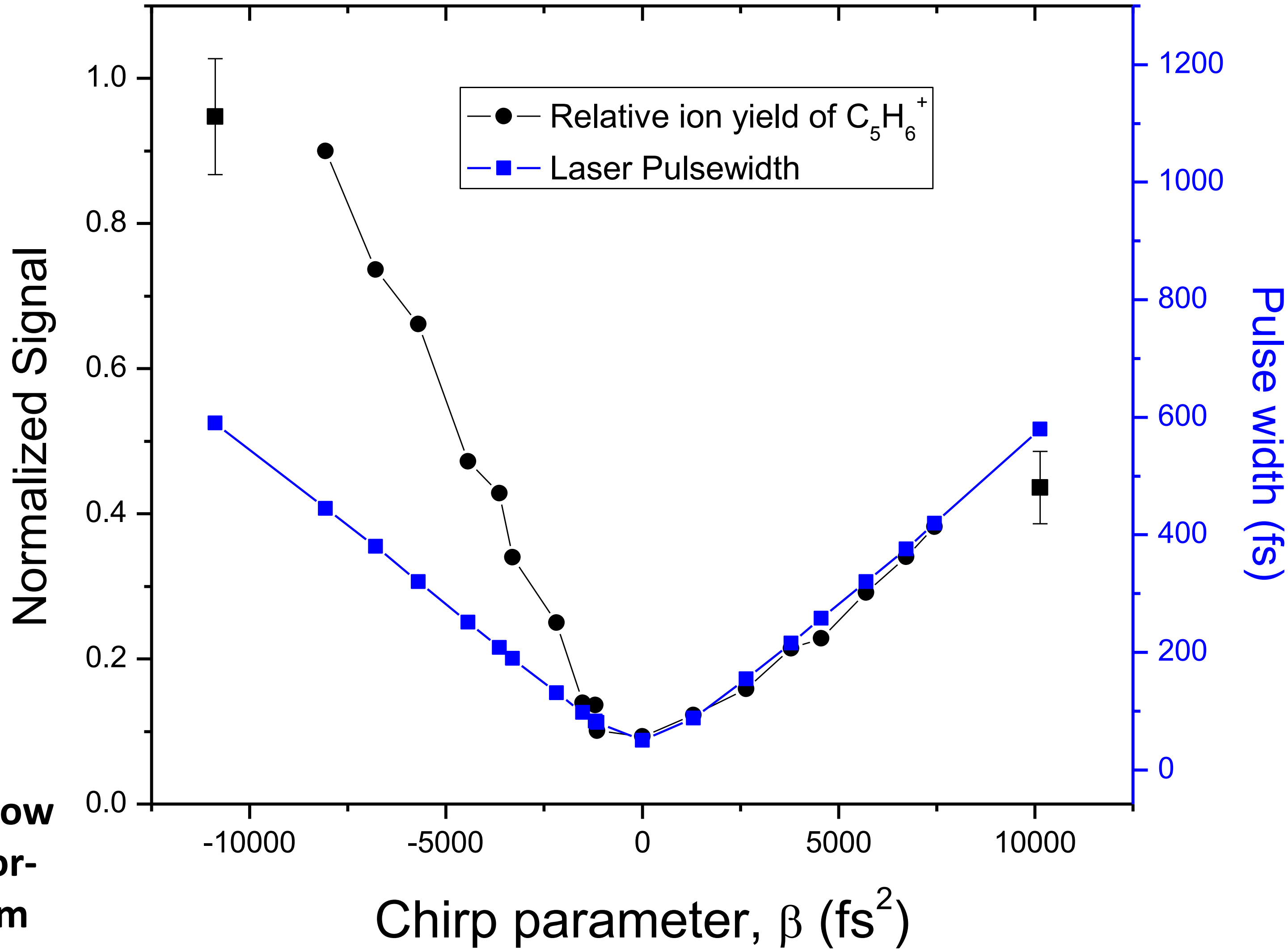
# Degenerate pump-probe transient spectra at 800 nm



# Chirp effect on parent ion yield compared to integrated SHG intensity and pulse width



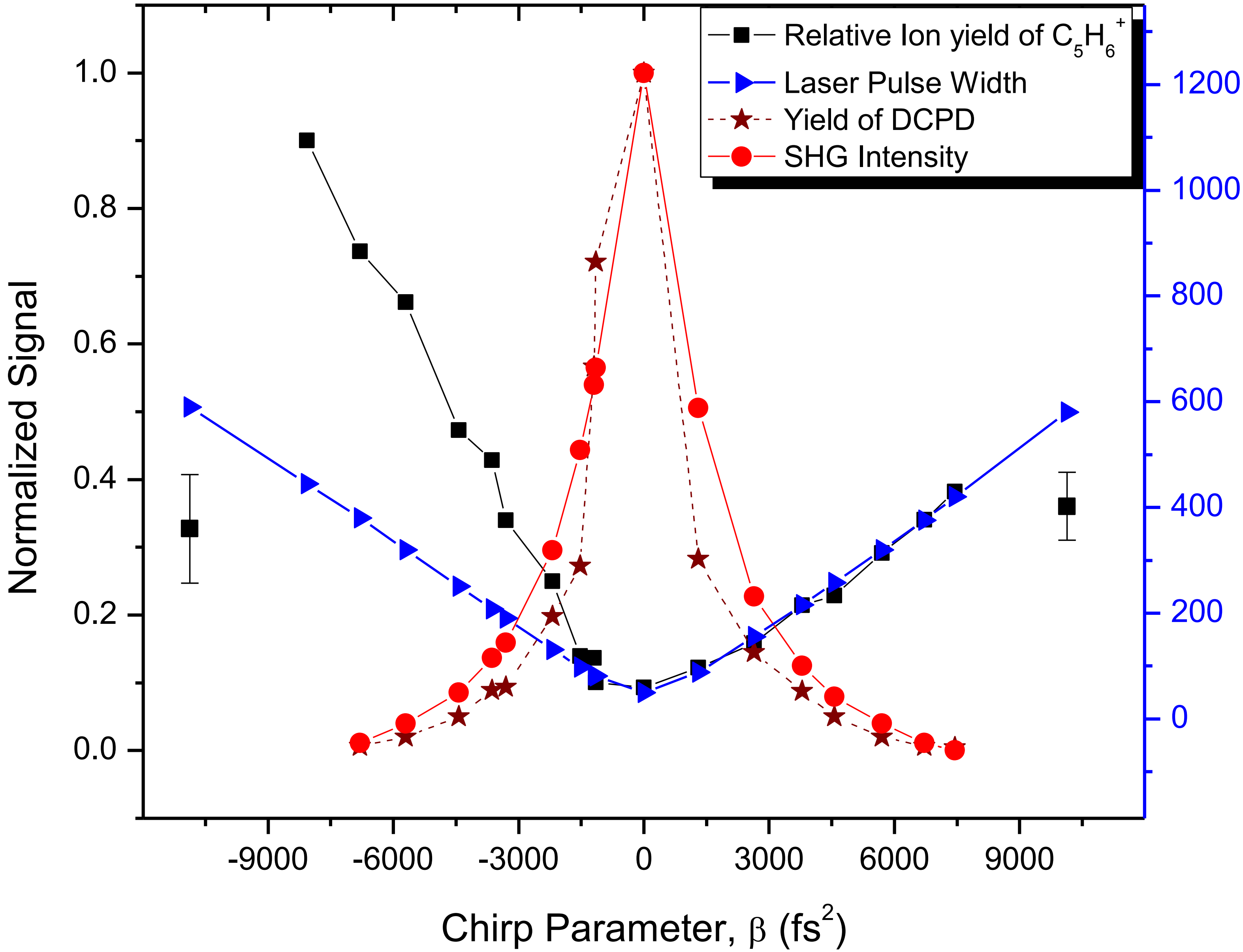
# Effect of chirp on the relative yield of $C_5H_6^+$ in comparison to pulse width




**At very large chirps, the effect of pulse width in reducing the intensity of the pulse width overwhelms the chirp effect.**

**Data at large chirps also have maximum error-bars, so we show these data with error-bars as the maximum possible cases.**

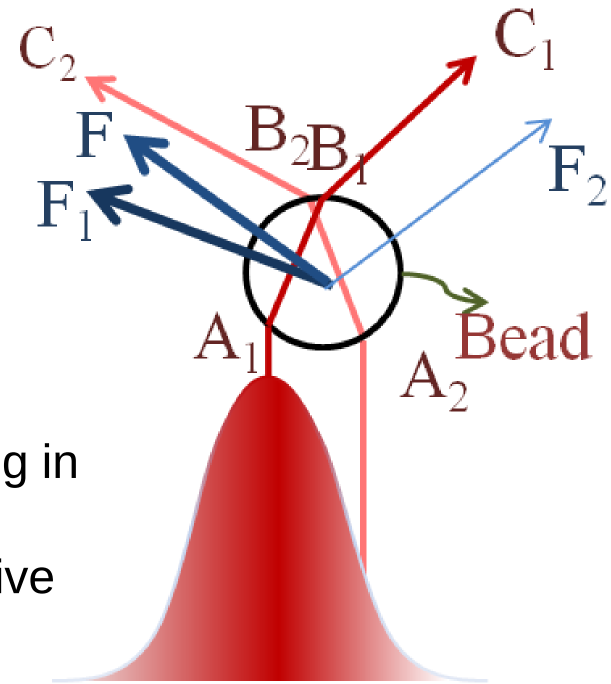
# Summary on Femtosecond Chirp Pulse Control



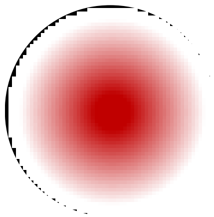
# Conclusions

- Spatial Control with Pulsed Laser opens up possibility of Spatiotemporal control
  – Polarization can also play an important role in spatial control
    - Control Knobs are: Spatial Modulation; Temporal repetition (exploring temporal shaping) and polarization
- Traditional Molecular Control
  – Control Knobs explored:
    - Frequency chirp
    - Laser Polarization
  – Control of Dimerization verses its breakdown

# Spatial Control: Basics of optical trapping

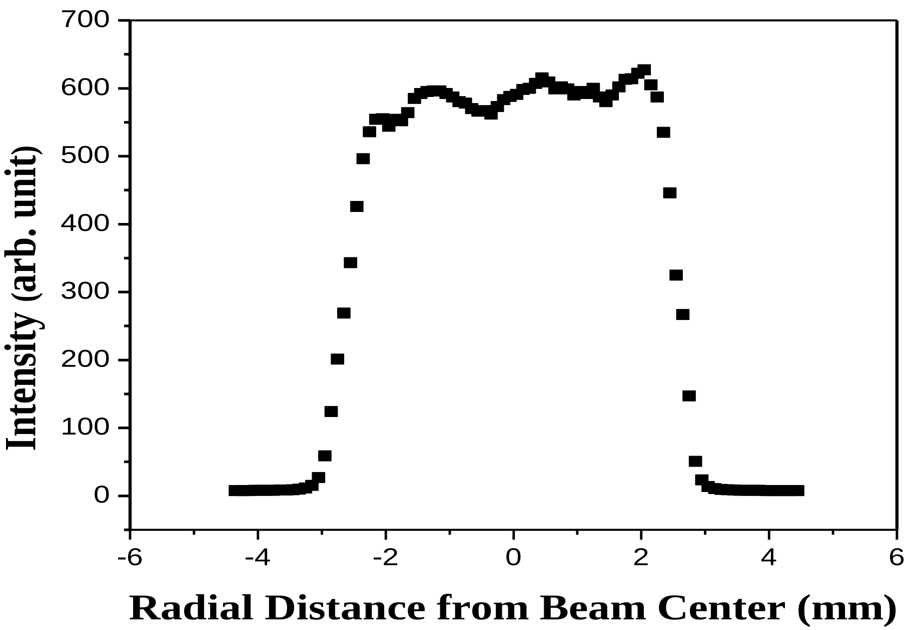



Beam bending in higher refractive index micron size beads



Para-axial Gaussian Mode:
$E=E_0 \exp(-2r^2/w^2)$

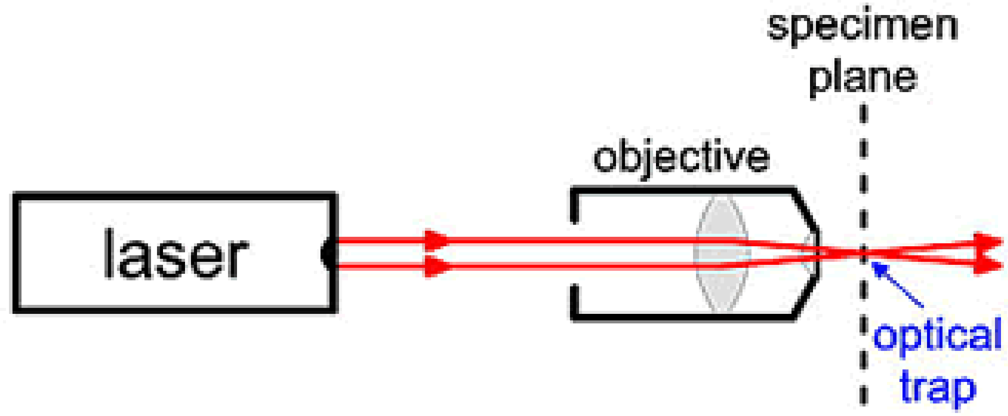
Radiation pressure from photon flux



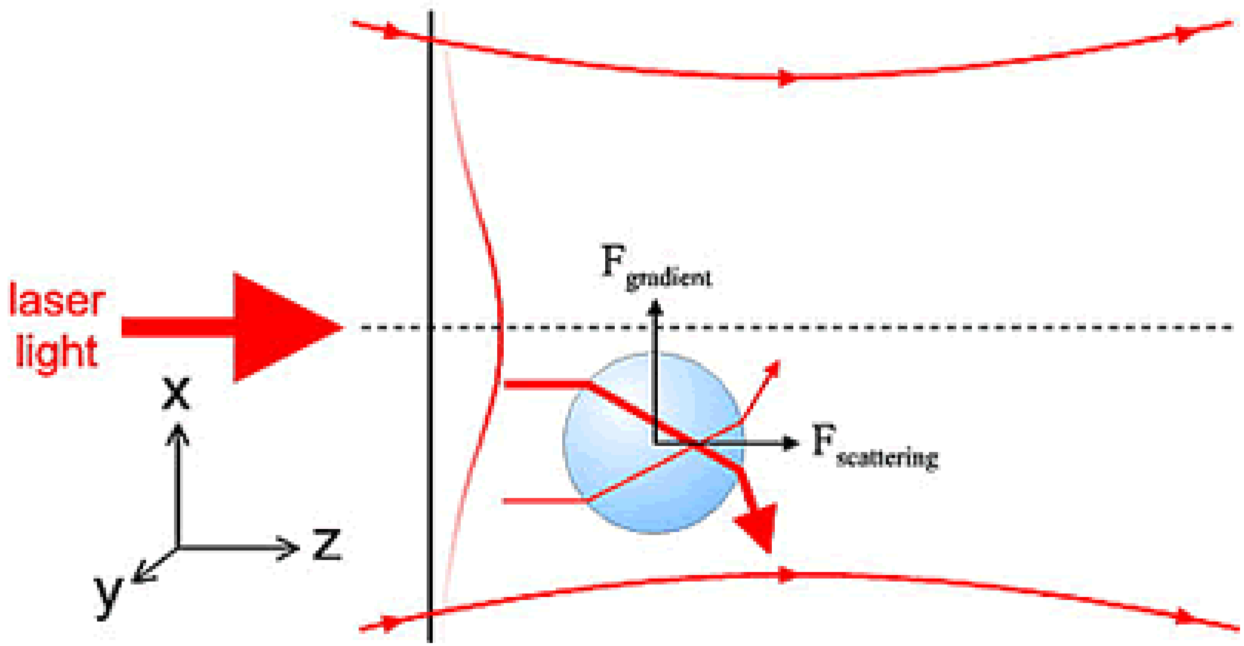

Flat-top Gaussian Mode

❖No trapping was observed as $\nabla E^2 \cong 0$

- ❖ For single beam optical trap, paraxial Gaussian beam is essential spatially
- ❖ Temporally, however, laser can be either cw or pulsed




**Optical tweezers use light to manipulate microscopic objects. The radiation pressure from a focused laser beam is able to trap small particles. In biological systems, optical tweezers are used to apply pN-range forces and measure nm range displacements in objects ranging in size from 10 nm to ~100 mm.**



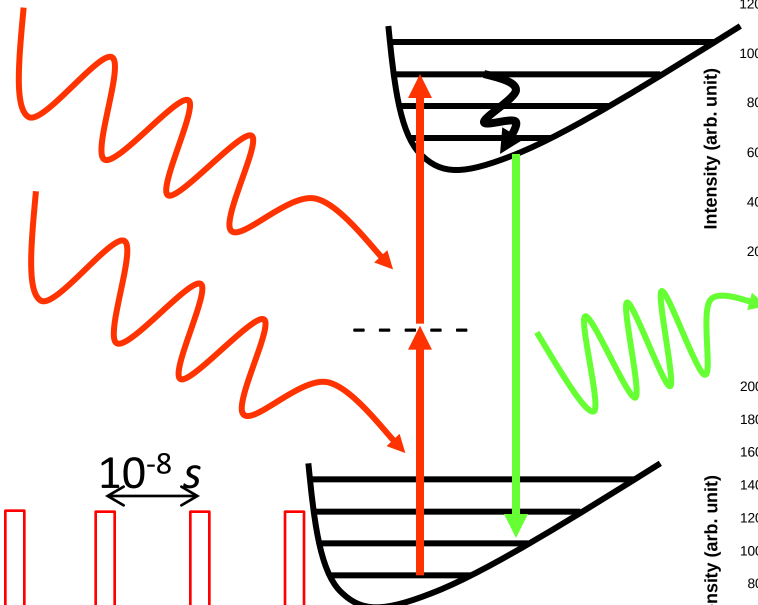
# Advantages offered by a femtosecond pulsed laser

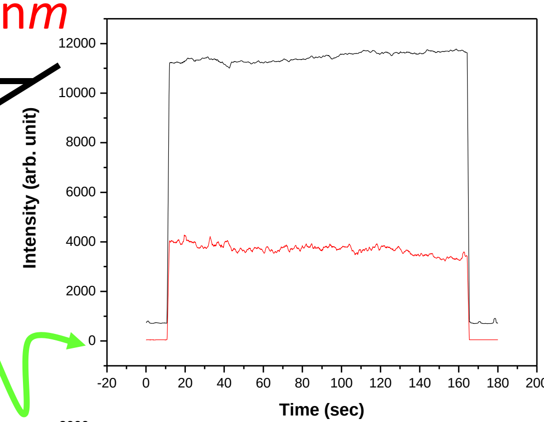
- ■ simultaneous detection of two-photon fluorescence and back-scattered light
- ■ bright-field video imaging ■ continuous-wave/mode-locked laser operation

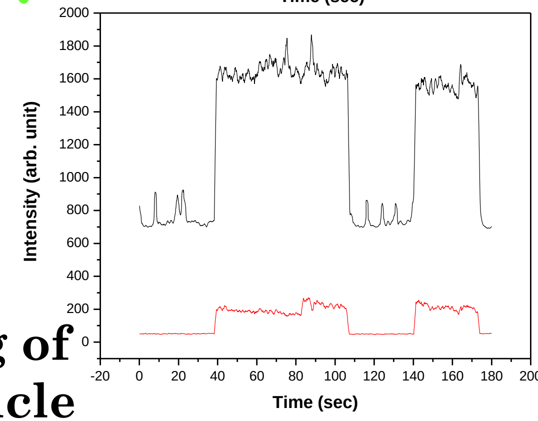
➢ molecular fluorescence (two-photon fluorescence) at ~800 *nm*

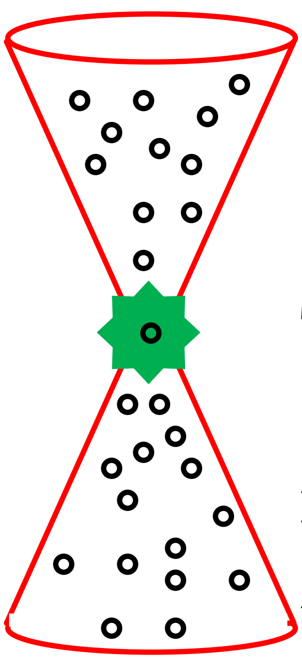
➢ ~$10^5$ times force exerted on the particle: possibility of trapping smaller & smaller particles (λ >> d)

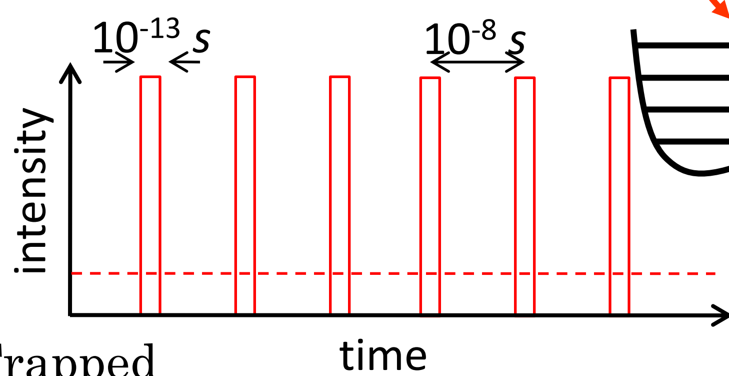
➢ intrinsic 3D fluorescence: direct observation of trapping





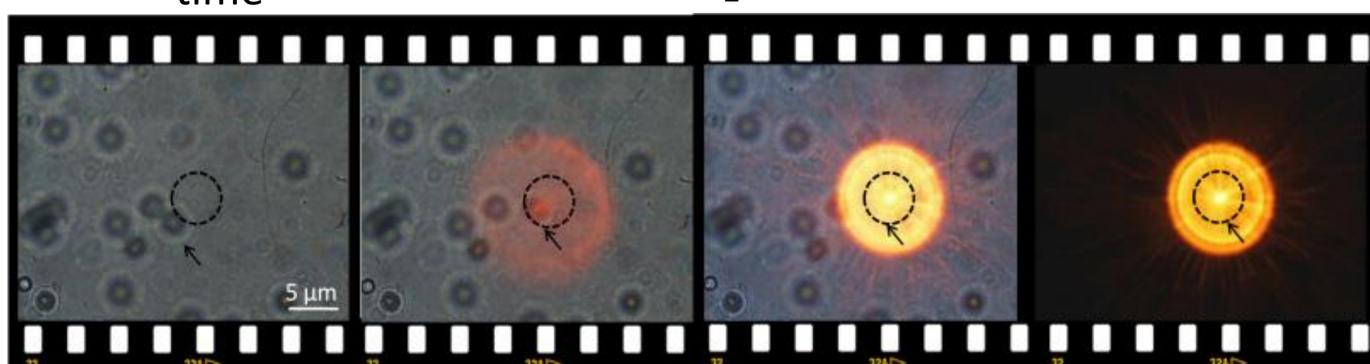






**Trapping of Mie particle**

Trapped 4 and 1 micron particles stably with fs 800nm

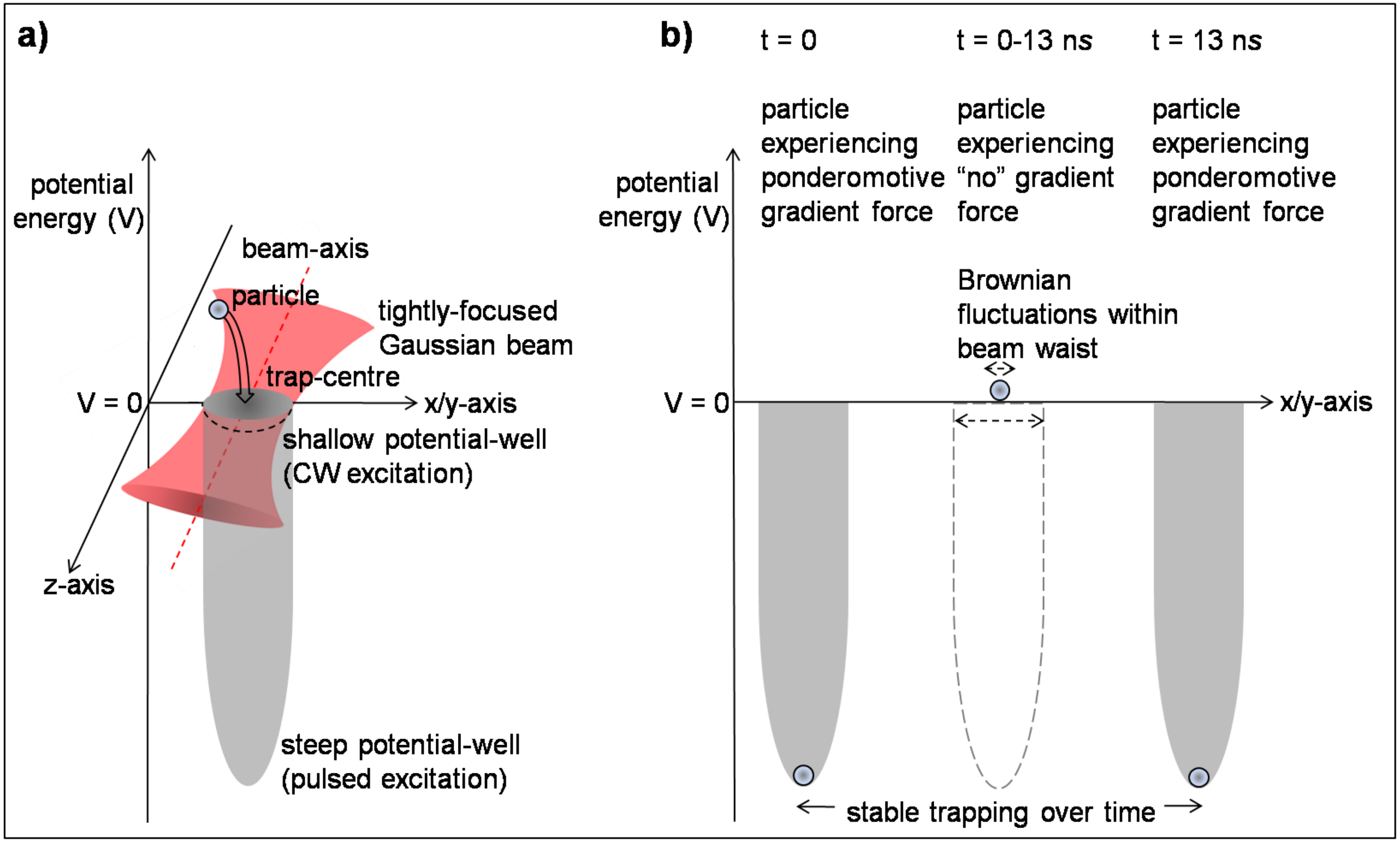


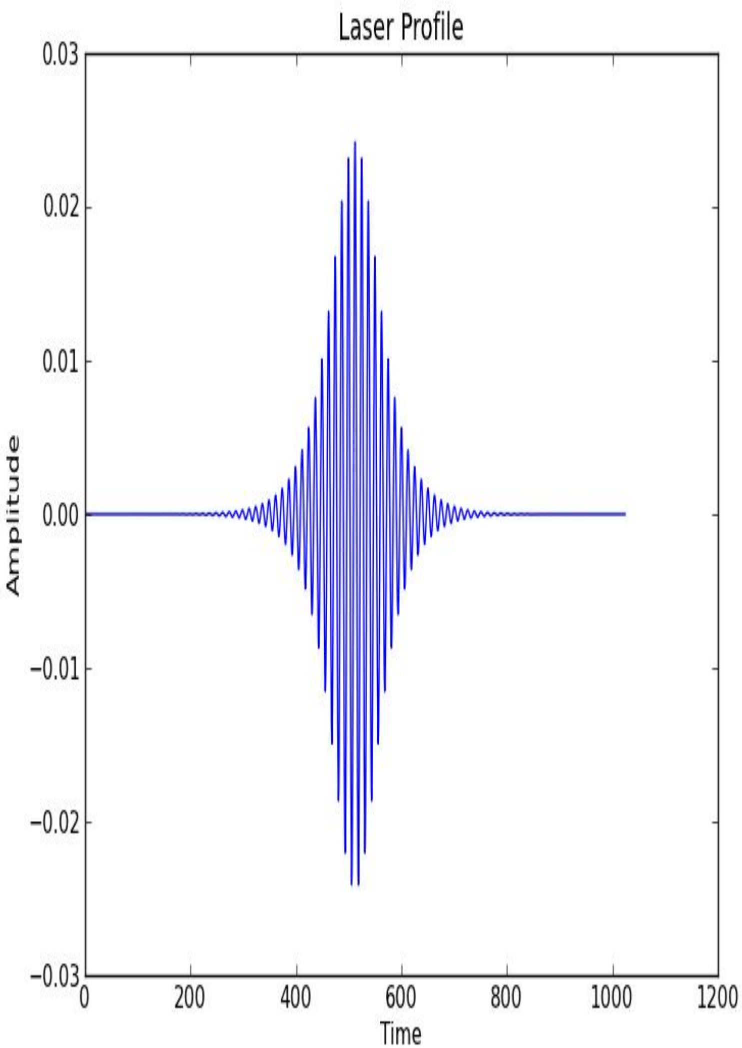
# Spatial Trapping: Optical trapping—towards trapping of single macromolecules

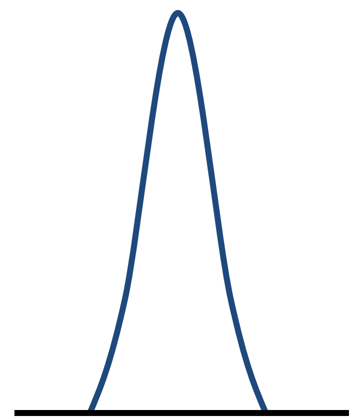
➢A. K. De, D. Roy, A. Dutta, D. Goswami, *Appl. Opt.*, **48**, G33 (2009)

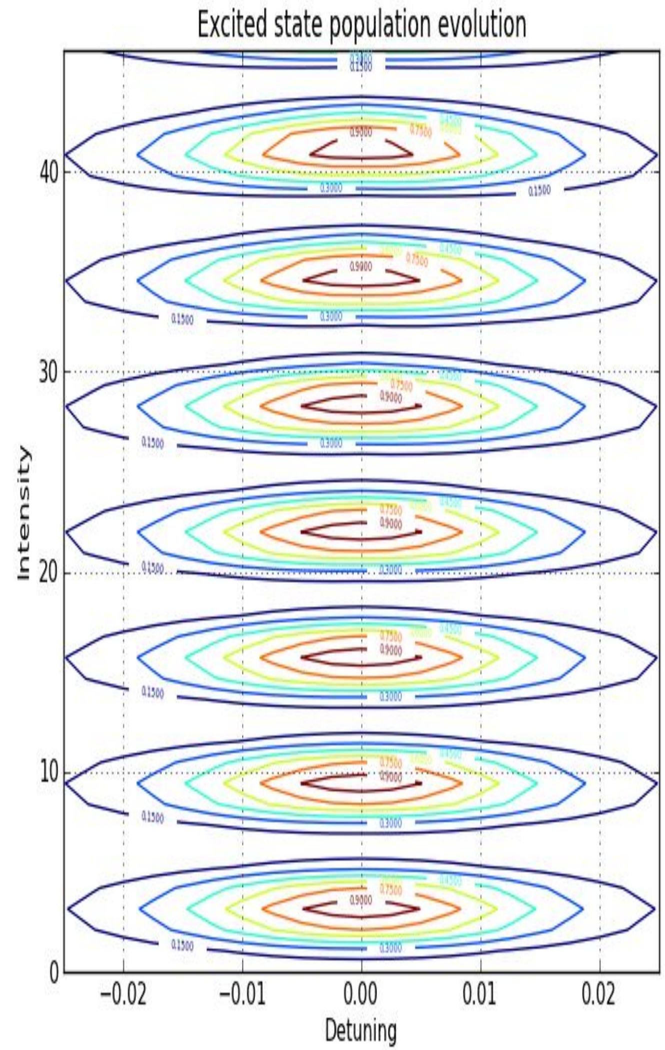
## Trapping of Rayleigh (λ»d) particles

- force depends on polarizability: e.g., latex nano-particles are hard to trap
- high peak power of an ultra-short pulse but '**Repetition Rate is Critical**'
- requires high repetition rate of the pulses




Laser Profile
Amplitude
Time
0.03
0.02
0.01
0.00
−0.01
−0.02
−0.03
0
200
400
600
800
1000
1200

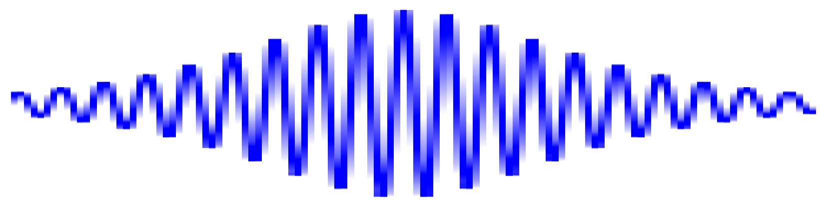



Excited state population evolution
Intensity
Detuning
0
10
20
30
40
−0.02
−0.01
0.00
0.01
0.02

# When we go to few cycle pulses, we need to evolve some further issues…

## Definitions of parameters and formalization of analysis

Few cycle limit?

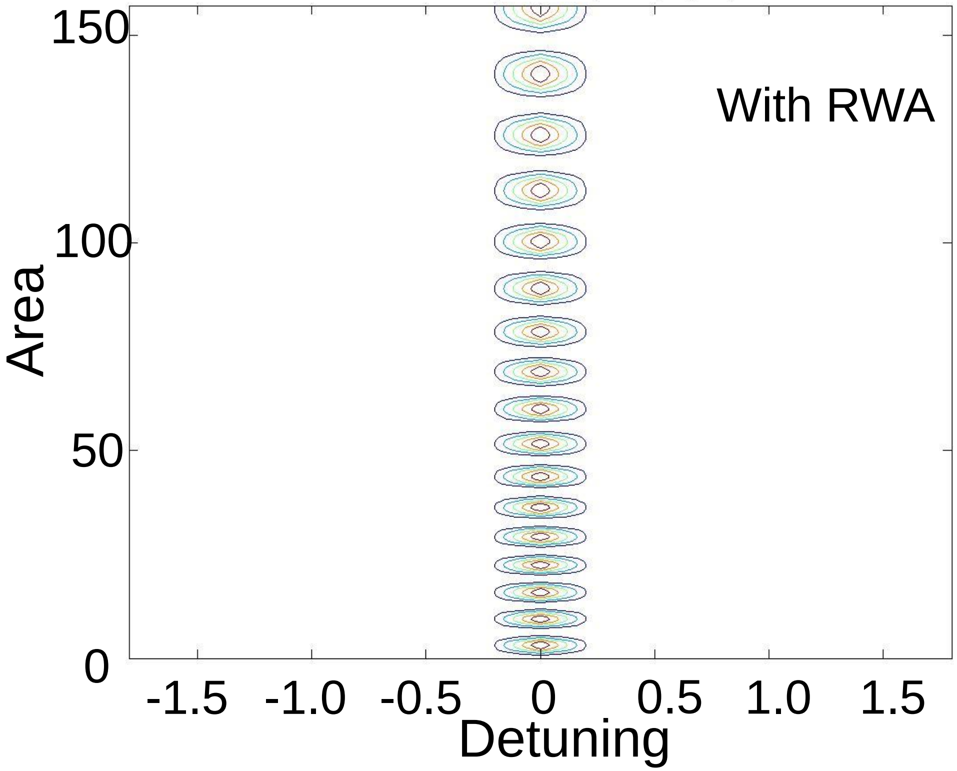


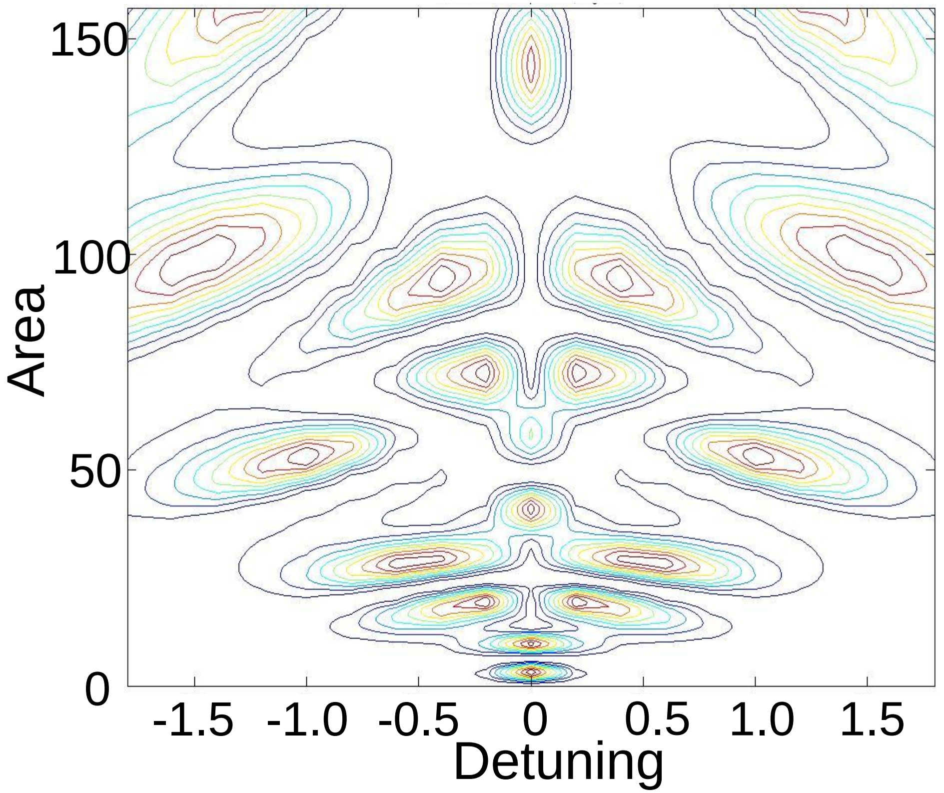
- $n$: number of cycles
- $E_0(t)$: the envelope profile (gaussian, $\cos^2$, sech,...)
- $\chi(n, E_0(t))$: the area of corresponding to the last peak in the inversion profile before the cycling effect/nonlinear effects come into the picture.

**Definition (Starting of the cycling/nonlinear effect)**

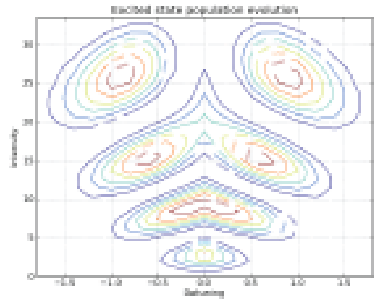
If we consider the 0 detuning cross-section of the inversion profile, the peaks should appear at every odd multiple of $\pi$. We take that area to be the beginning of the cycling effect, after which the distance between two consecutive peaks become deviate from $2\pi$.

# Secant Hyperbolic Pulse
# 6-cycles limit

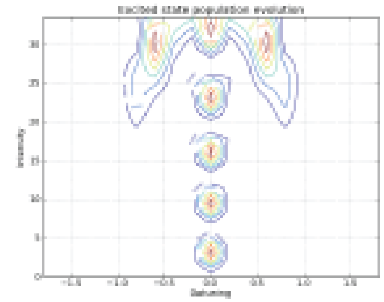


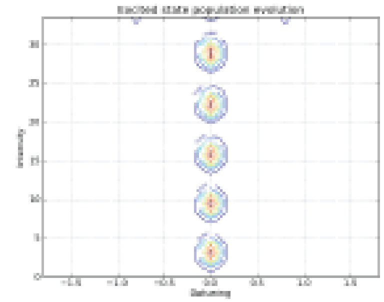
# Typical Example: cosine squared



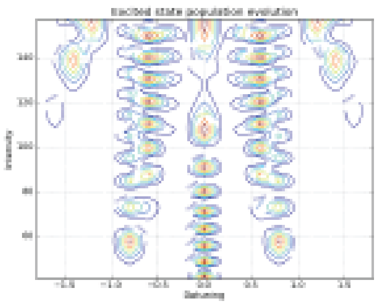
(a) n=1;$\chi = \pi$



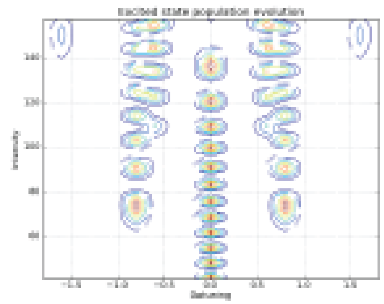
(b) n=6;$\chi = 5\pi$



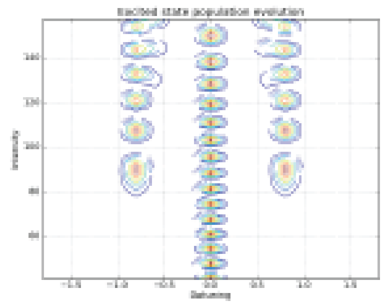
(c) n=11;$\chi = 9\pi$



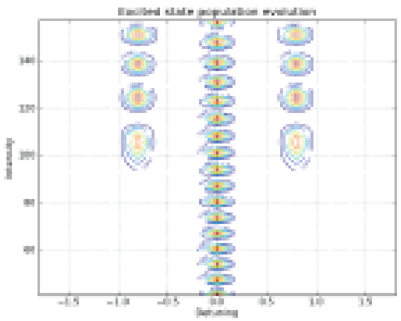
(d) n=16;$\chi = 13\pi$



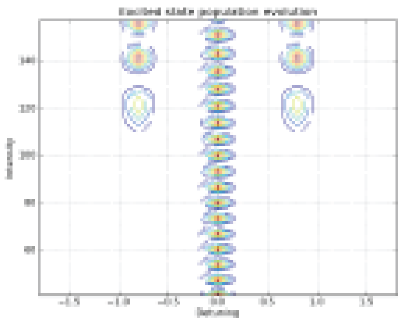
(e) n=21;$\chi = 17\pi$



(f) n=26;$\chi = 21\pi$



(g) n=31;$\chi = 27\pi$



(h) n=36;$\chi = 31\pi$

# $\chi(n, cos^2)$ vs n

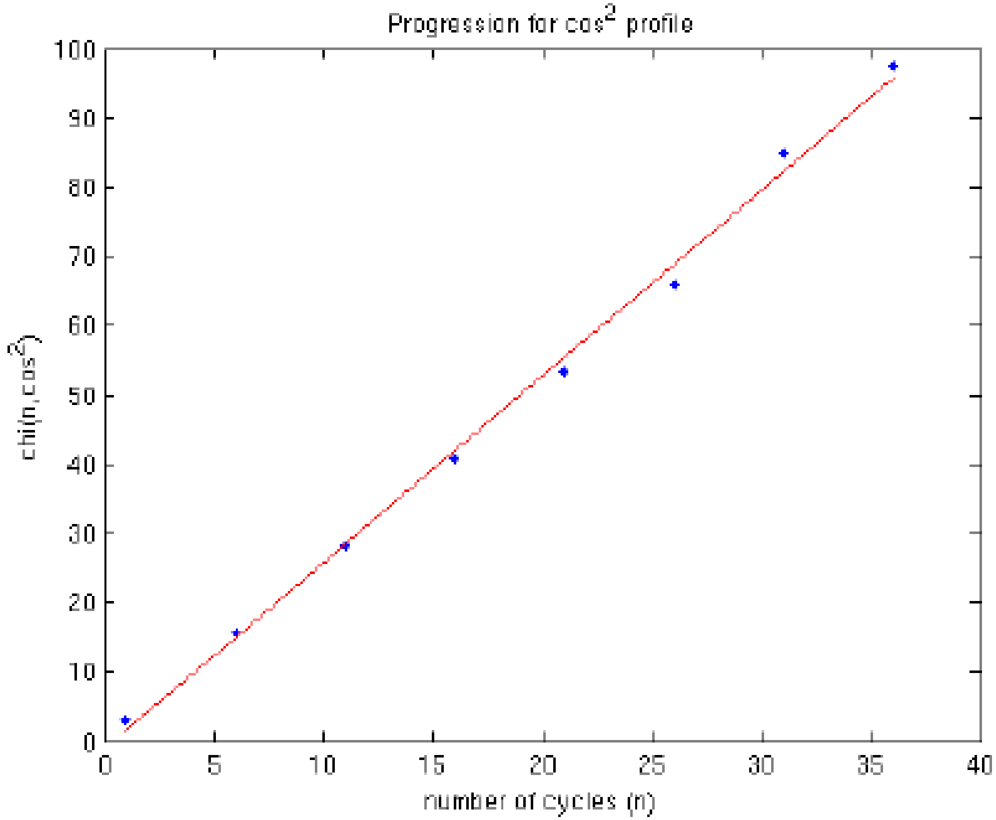
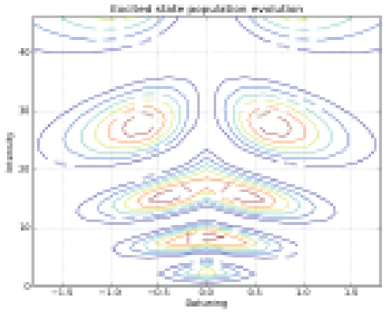
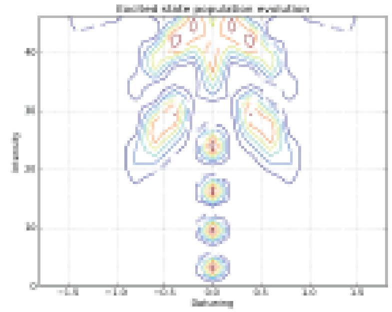



Figure: $\chi(n, cos^2) = 2.693n - 1.122$

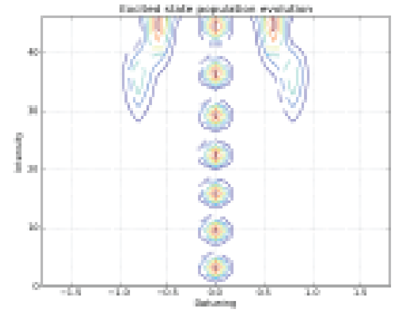
# Gaussian



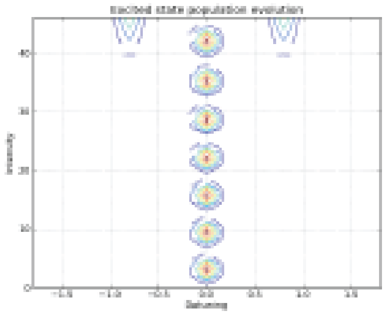
(a) n=1;$\chi = \pi$



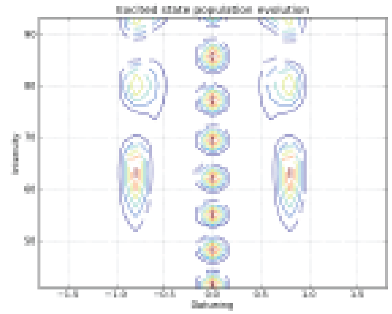
(b) n=6;$\chi = 3\pi$



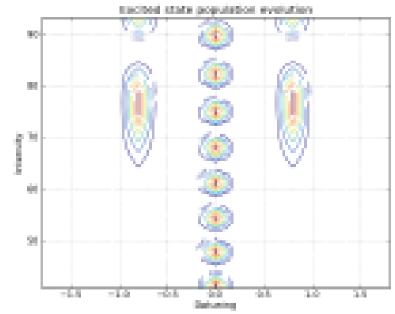
(c) n=11;$\chi = 5\pi$



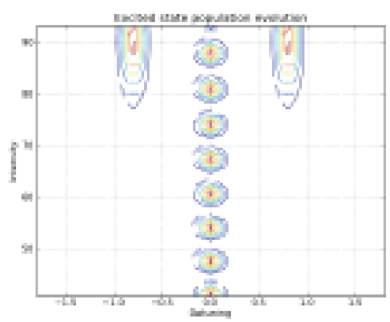
(d) n=16;$\chi = 7\pi$



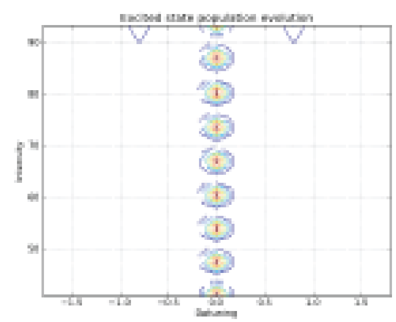
(e) n=21;$\chi = 9\pi$



(f) n=26;$\chi = 11\pi$



(g) n=31;$\chi = 13\pi$



(h) n=36;$\chi = 15\pi$

# $\chi(n, gaussian)$ vs n

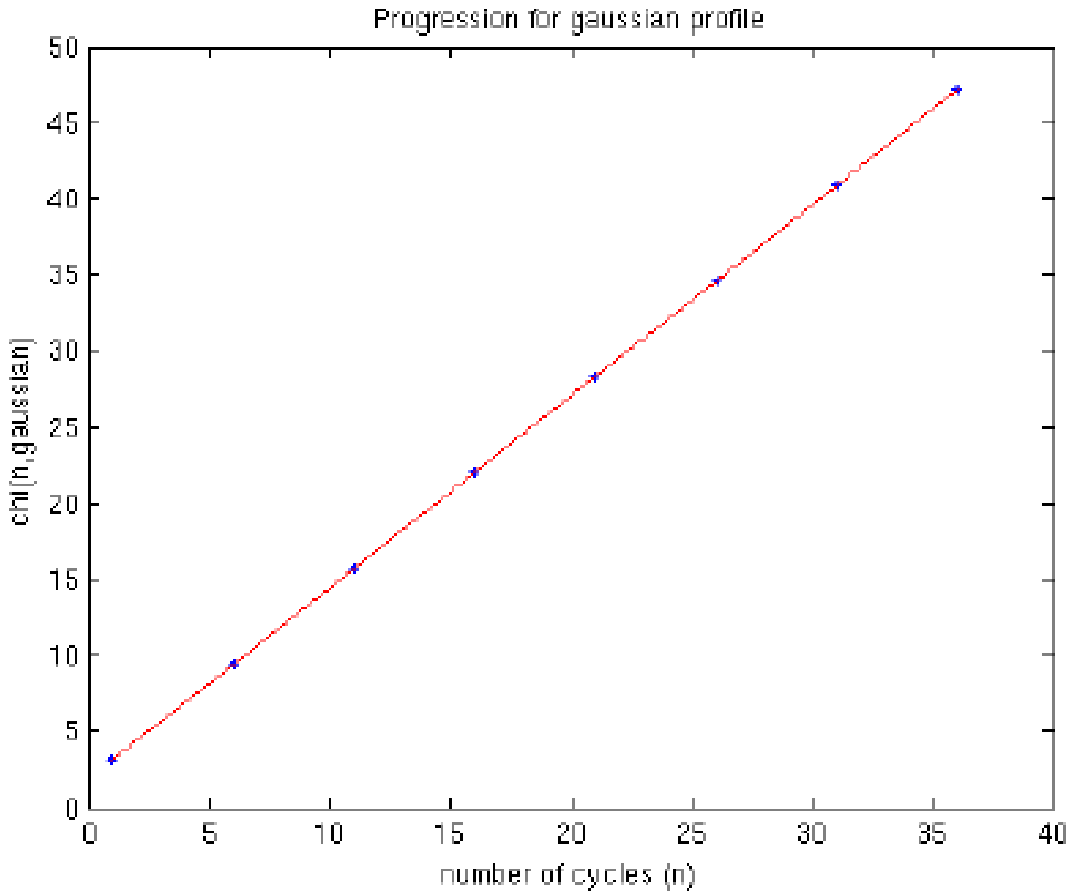
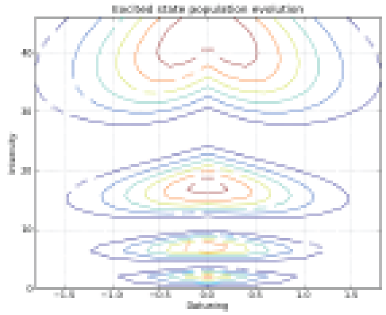
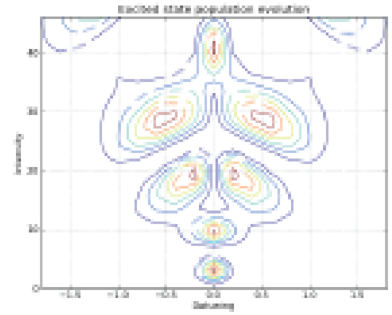



Figure: $\chi(n, gaussian) = 1.257n + 1.885$

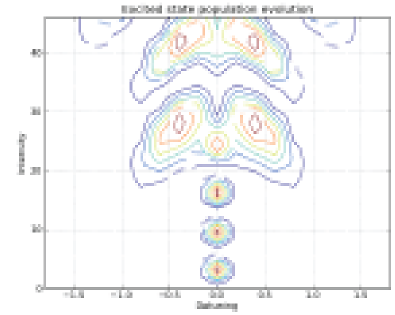
# Hyperbolic Secant



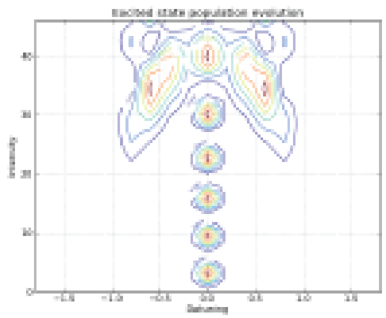
(a) n=1; $\chi = \pi$



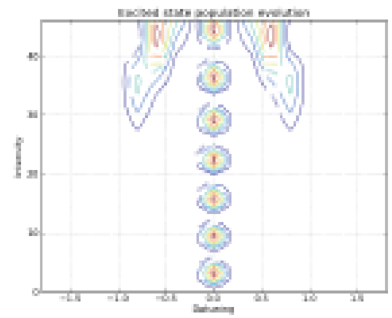
(b) n=6; $\chi = \pi$



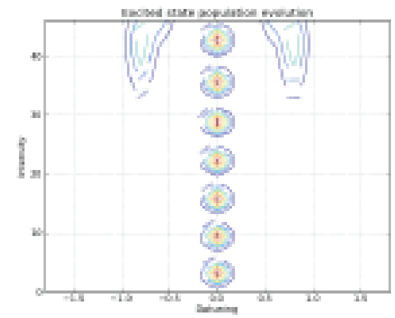
(c) n=11; $\chi = 3\pi$



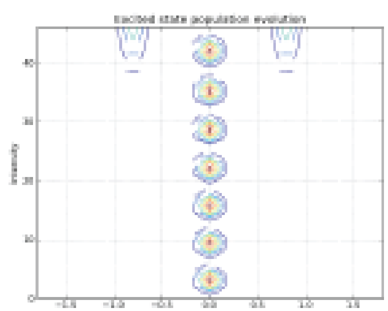
(d) n=16; $\chi = 5\pi$



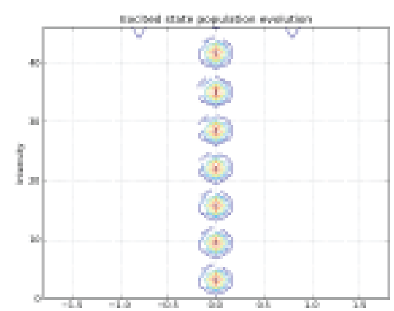
(e) n=21; $\chi = 7\pi$



(f) n=26; $\chi = 9\pi$



(g) n=31; $\chi = 11\pi$



(h) n=36; $\chi = 13\pi$

# $\chi(n, sech)$ vs n

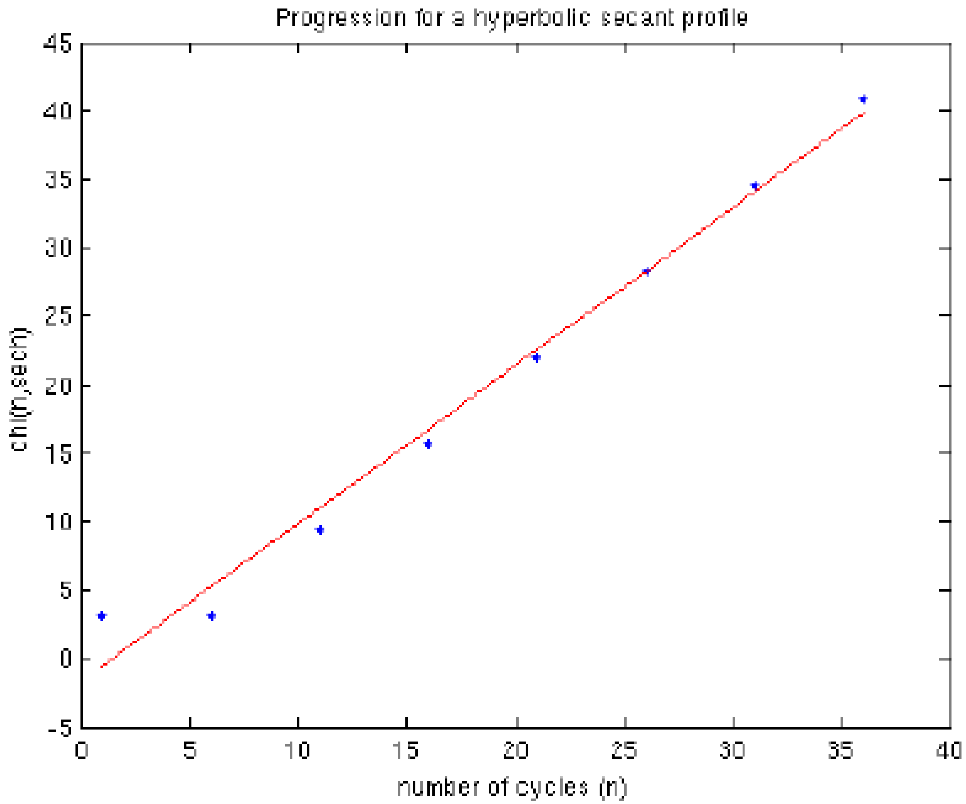
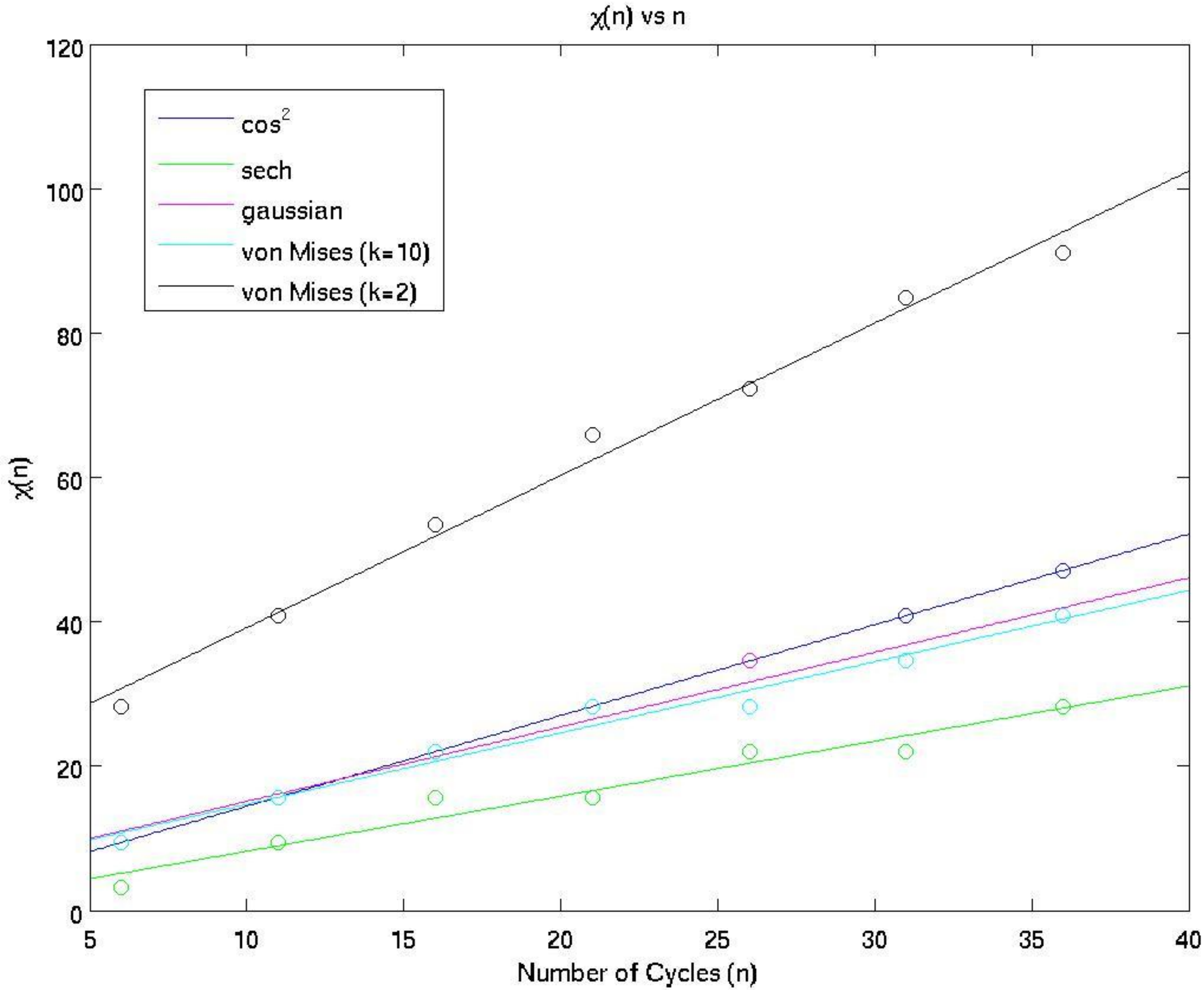



Figure: $\chi(n, sech) = 1.152n - 1.676$

# Best Fit for the various envelop profiles



# Comparison

The following is a comparative table of the equations of $\chi$ w.r.t. n for the various cases.

| Profile | $\chi(n)$ | $\frac{\partial \chi}{\partial n}$ |
|---|---|---|
| $cos^2$ | 1.2566n+1.8850 | 1.2566 |
| sech | 0.7630n+0.5834 | 0.7630 |
| gaussian | 1.0322n+4.8021 | 1.0322 |
| von Mises (k=10) | 0.9874n+4.8470 | 0.9874 |
| von Mises (k=2) | 2.1094n+18.0866 | 2.1094 |

Table: Fit parameters for given profiles

- **χ(n) characterizes the critical limit of area, after which the cycling effect dominates the envelop profile effect, for few-cycle pulses.**
- **This measure <u>is dependent</u> on the envelop profile under question.**

# Present Status

- Many cycle envelop pulses:
  - Area under pulse important
- Interestingly,
  - Envelop Effect still persists even in the few cycle limit results

- Measure of nonlinearity has to be consistent over both the domains…

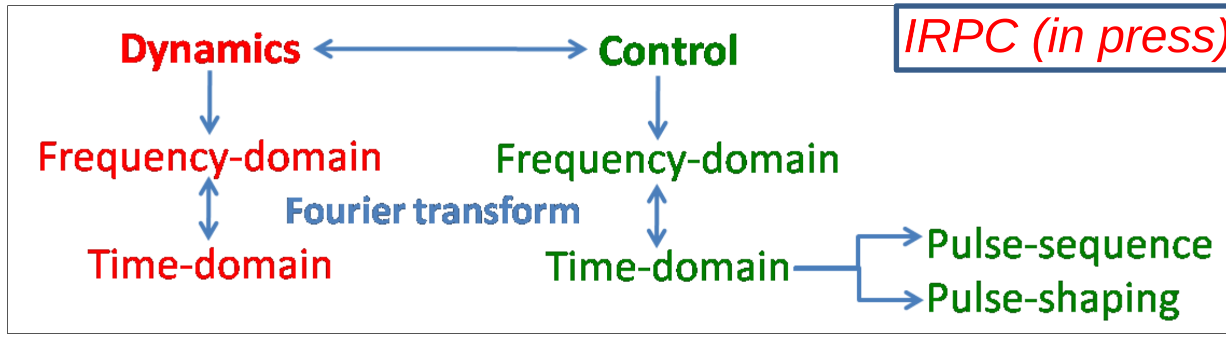
# Other impacts

## *Coherent control of 2-photon fluorescence Microscopy*

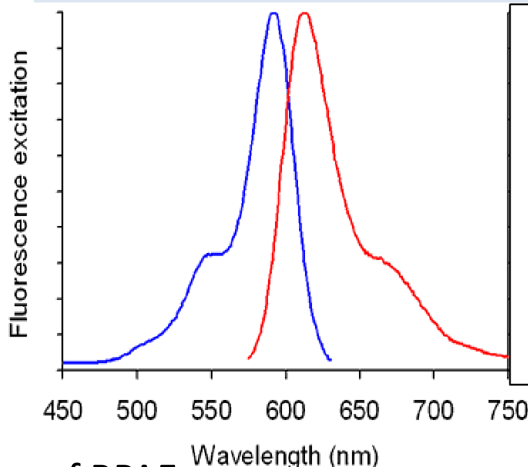
- the goal is to control two-photon fluorescence with applications in imaging by controlling laser light

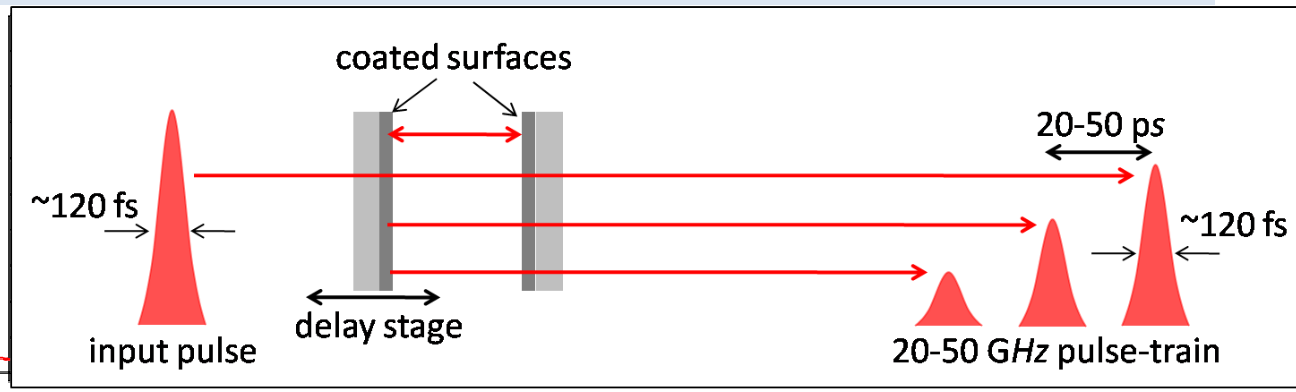
JBO Letters

*IRPC (in press)*



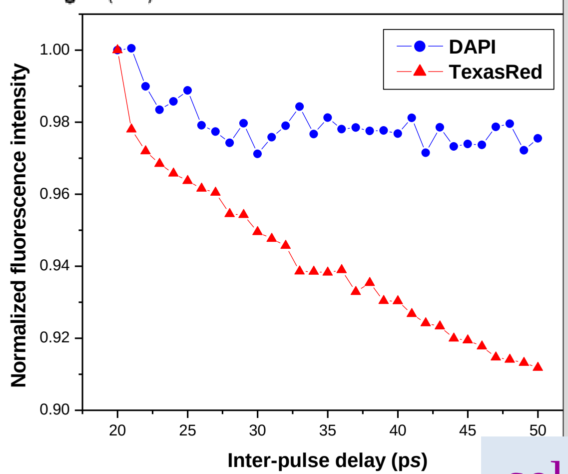

## Ultrafast pulse-pair control in fluorescence laser-scanning microscopy

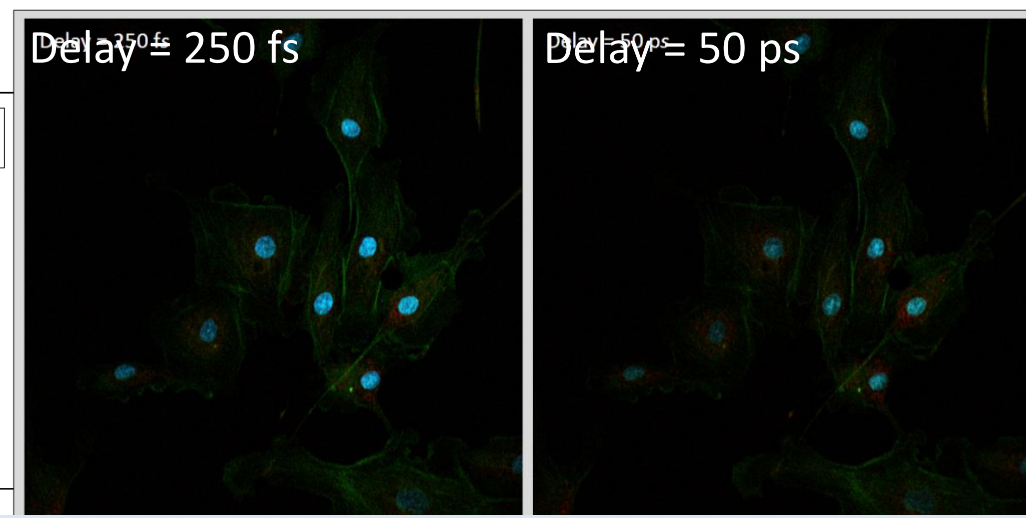


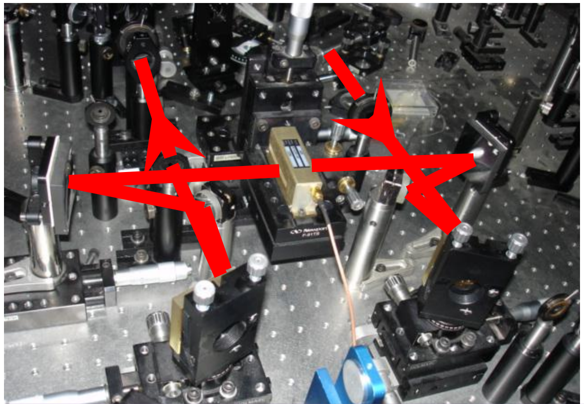

Images of BPAE cells at 2 different delays between pulse pairs

- Major change only in the blue fluorescence but almost no change in red or green fluorescence



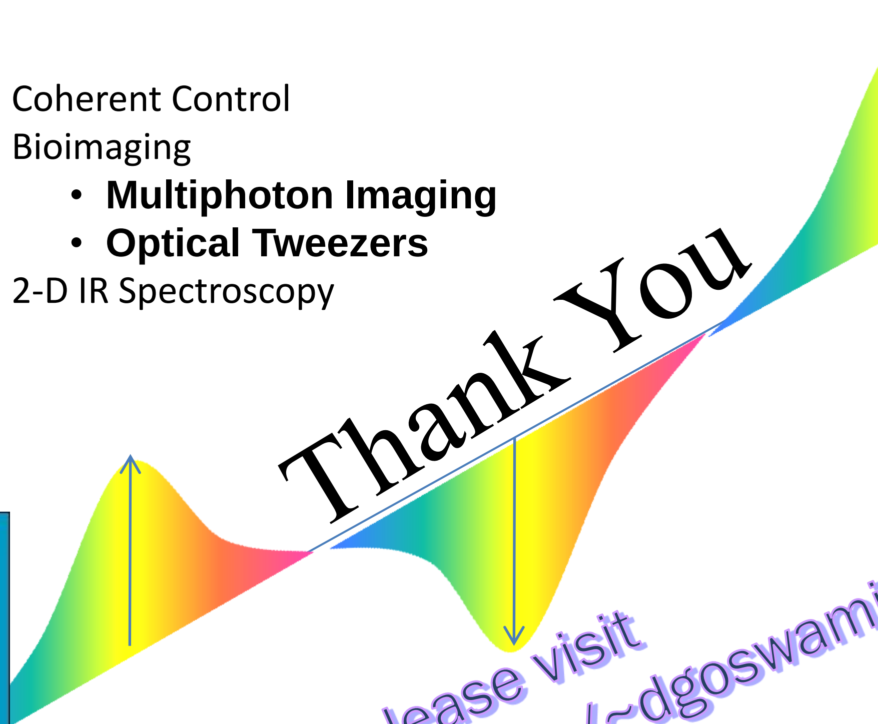

selective fluorescence suppression from TexasRed



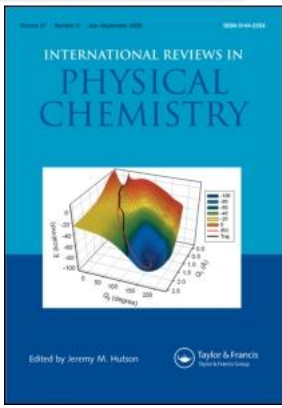
**Femtosecond Pulse Shaper**

- Coherent Control
- Bioimaging
    - **Multiphoton Imaging**
    - **Optical Tweezers**
- 2-D IR Spectroscopy

# Thank You



Measurement of Nonlinearities

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