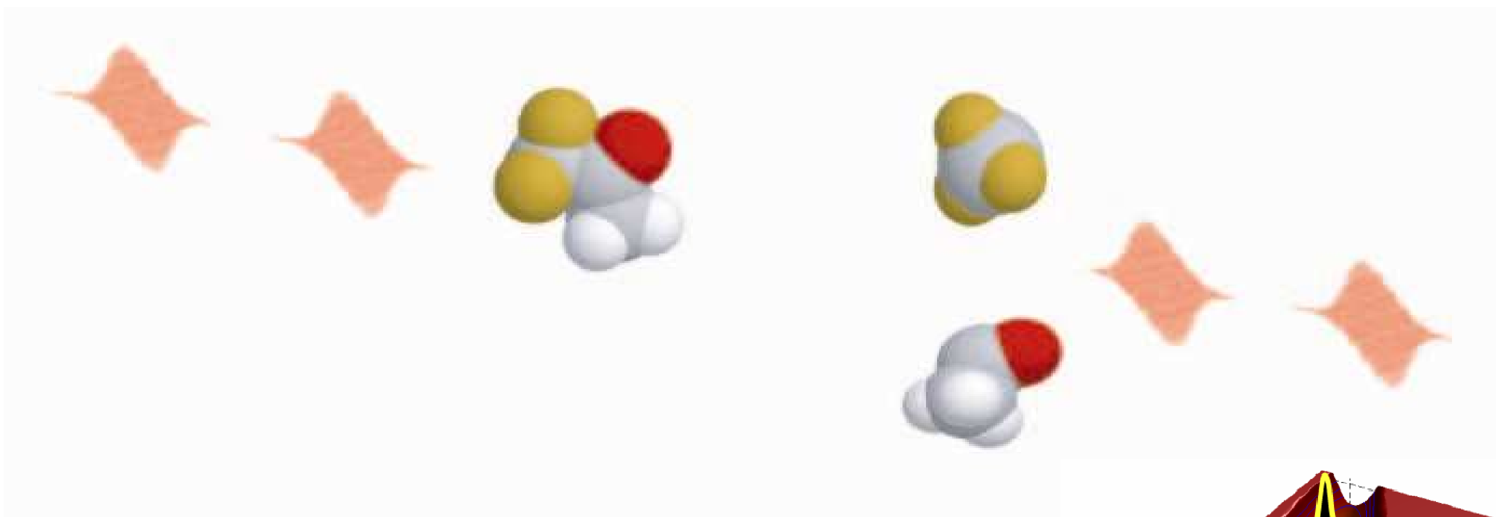
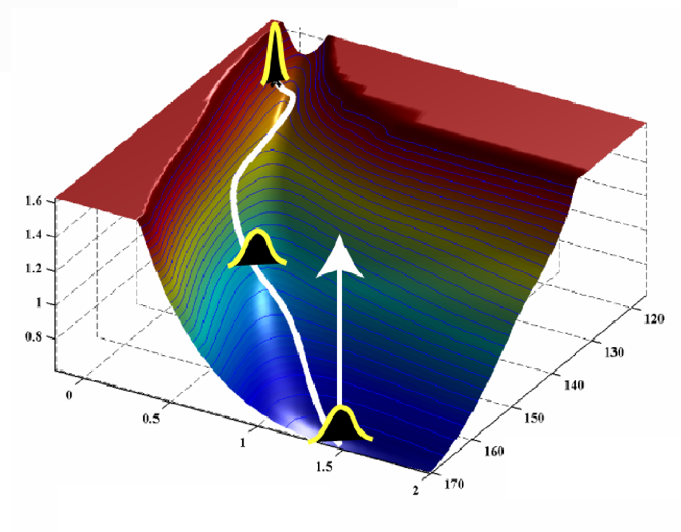
An Ultrafast Quantum Camera



University of Virginia

April 20th, 2007



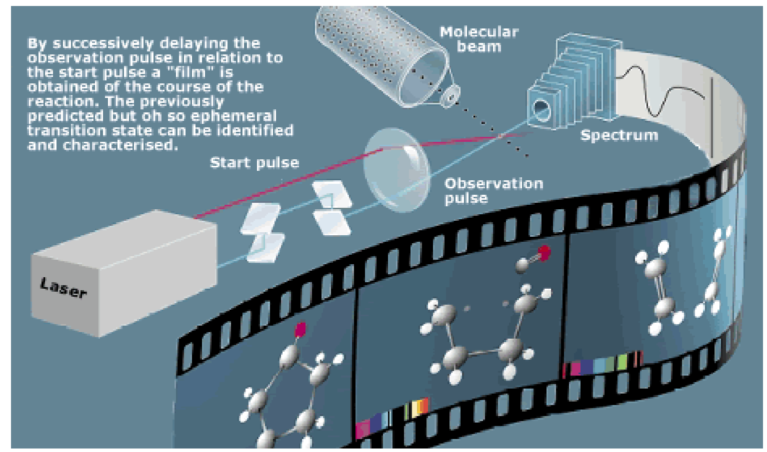
Motivation & Outline

Motivation: Making molecular movies in *real time*

- Need a fast camera (ultrafast laser)
- Need to control the action (shaped laser pulses)

Outline

1. The tools of the trade
   - Ultrafast lasers
   - Pulse shaping and learning algorithms



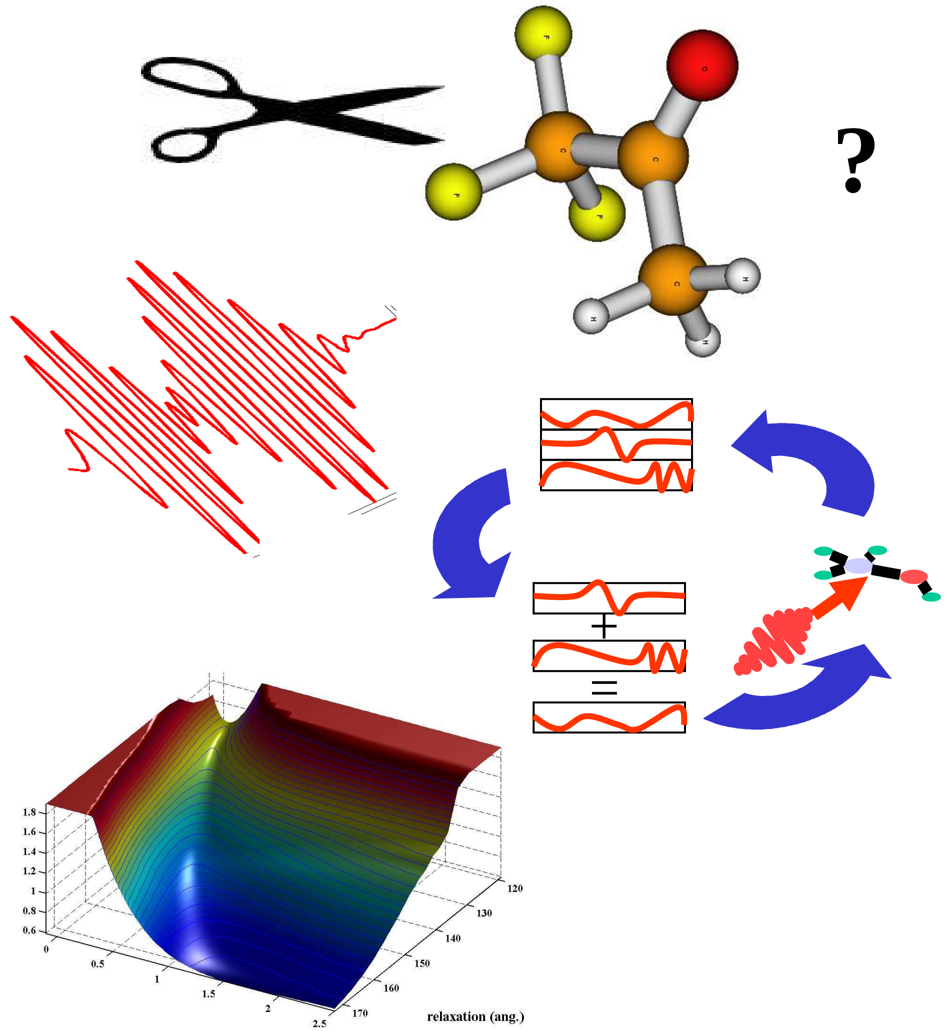
A. Zewail, 1999 Nobel Prize in chemistry

2. Demonstrating Control
   - Atomic population transfer & molecular fragmentation

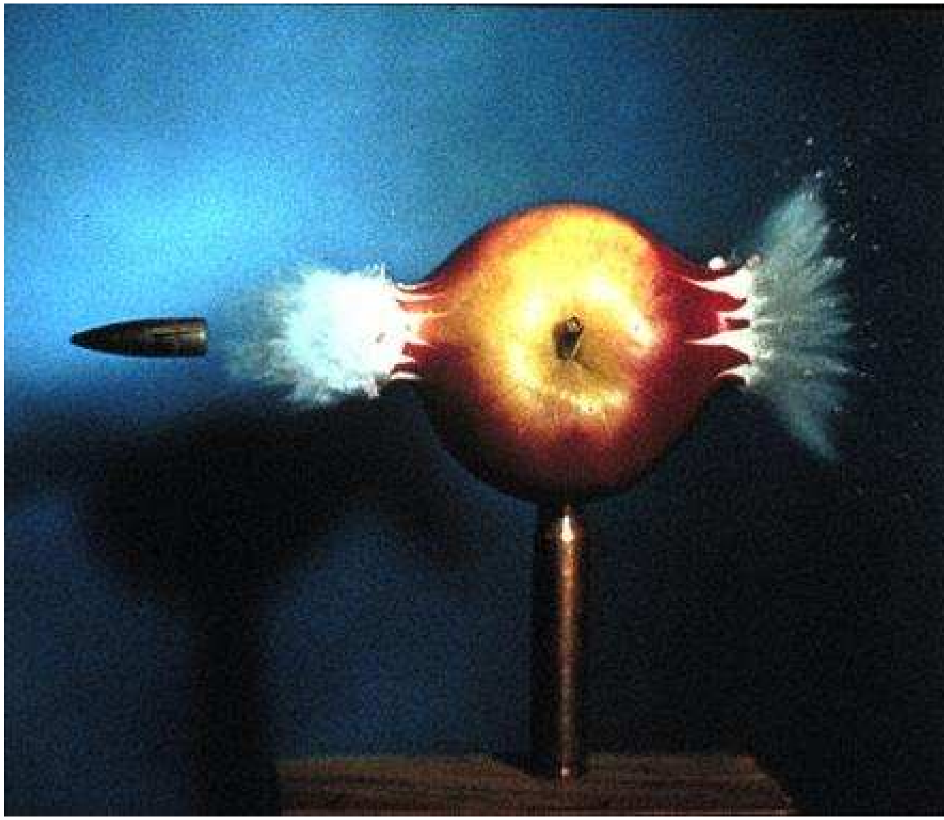
3. Understanding Control and Making Movies
   - Uncovering physical mechanisms underlying control
   - Seeking to measure molecular wavefunctions

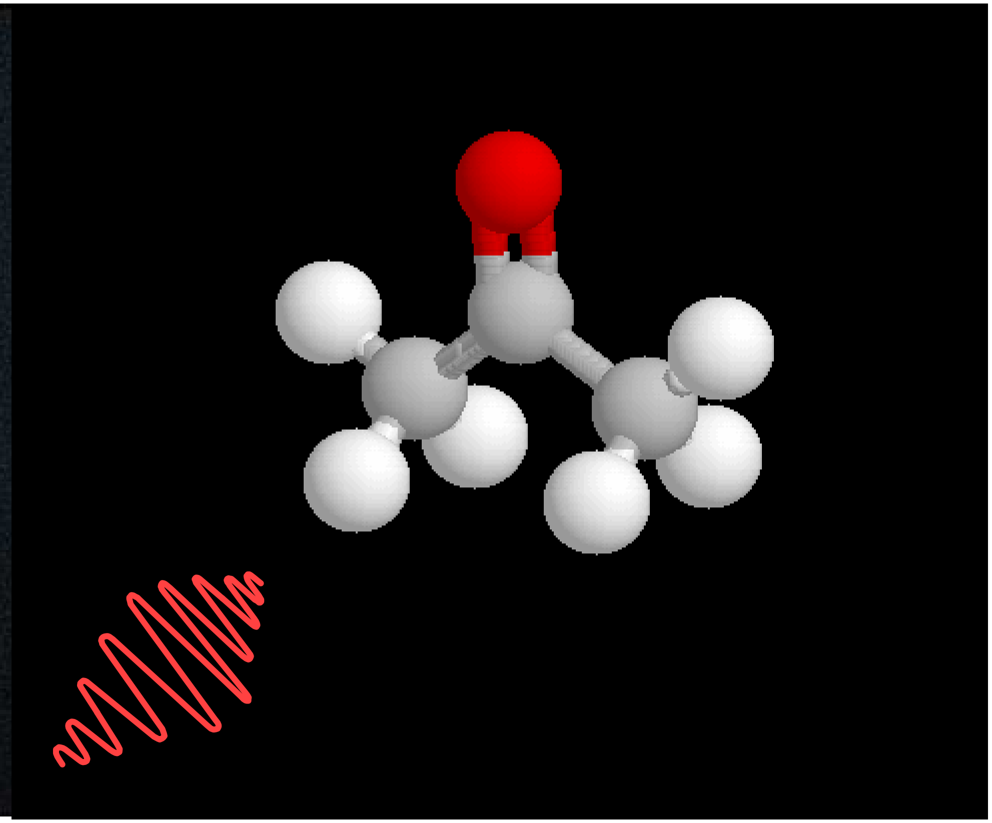
Making a Movie of Molecular Bond Breaking

- What if we don’t know how to break a given bond?
- Use feedback to figure out how!
- What tools do we need to do this?
- 3N-6 vibrational modes, 3 rotational modes - are all these needed to understand the dynamics?



Capturing Molecular Dynamics

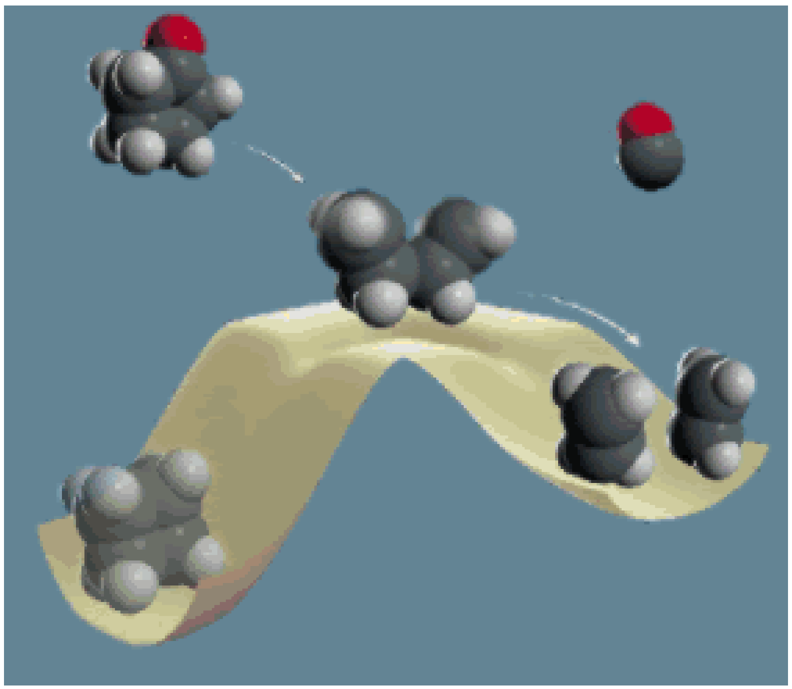


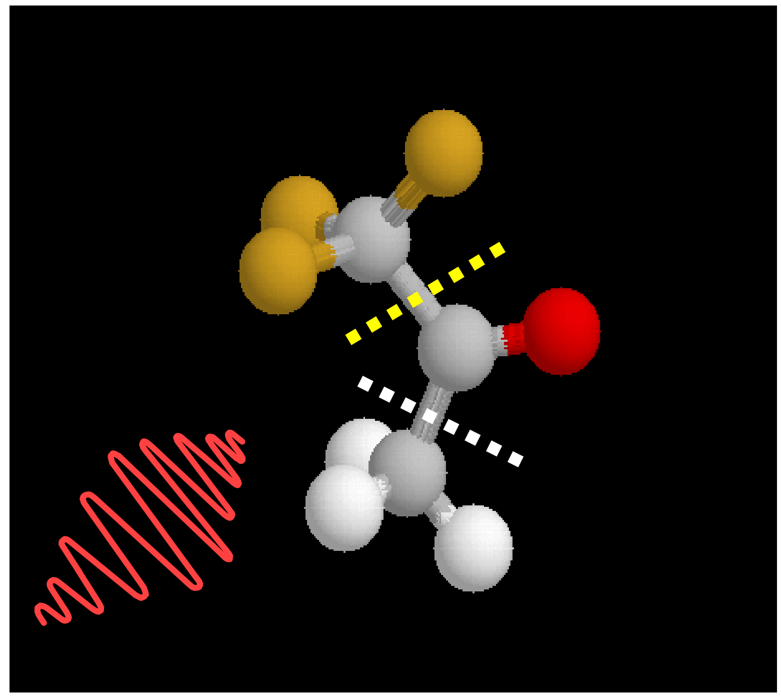


$\tau \approx 10^{-6} s$

$\tau \approx 10^{-14} s$

Controlling Molecular Dynamics

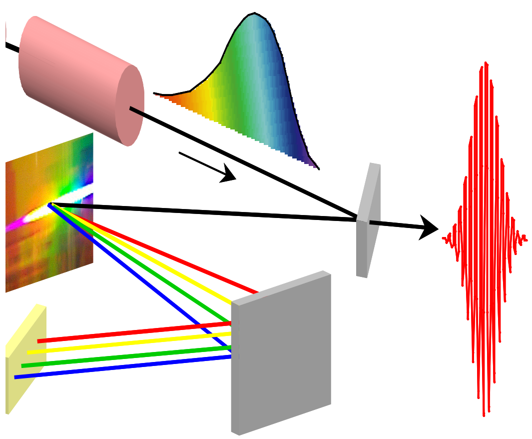




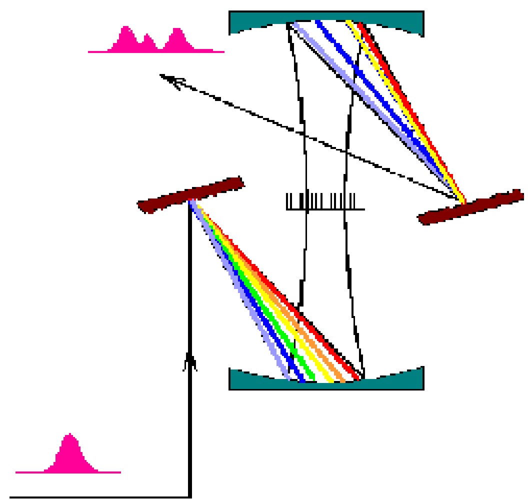
$E_{control} > E_{Hydrogen} (5*10^{11}\ V/m)$

The 'Coherent' Control Toolbox

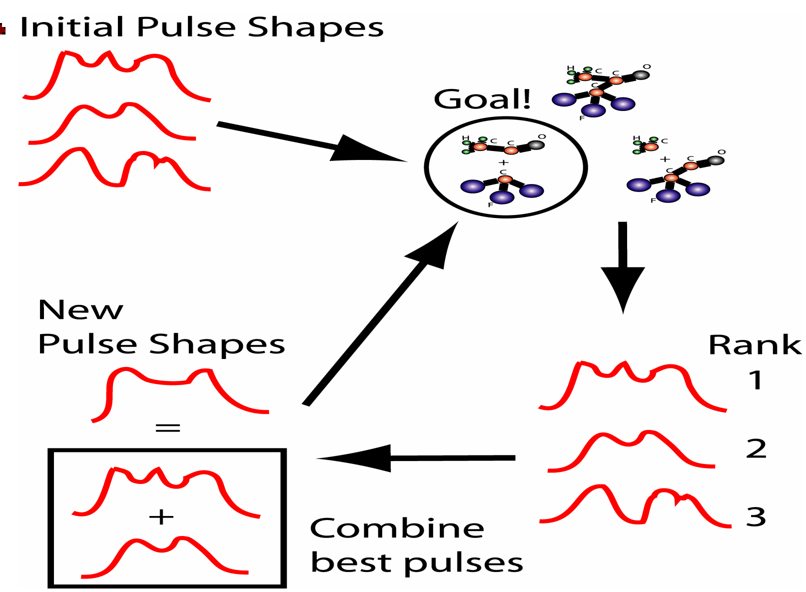
Amplified ultrafast lasers



Optical field control

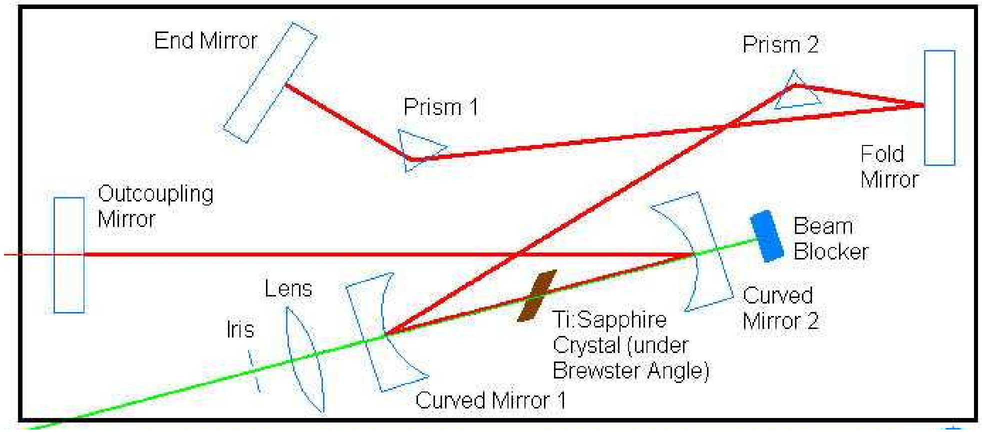


Feedback and
learning algorithms

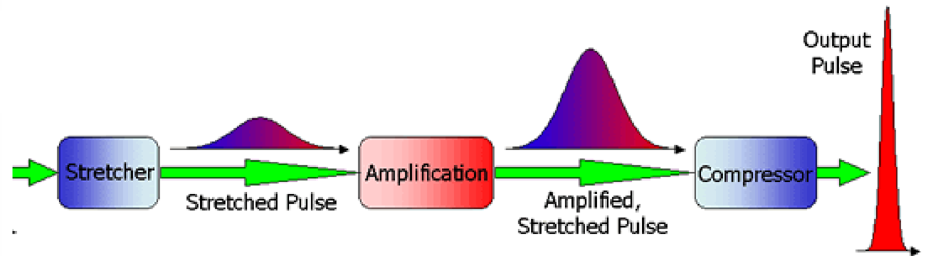


Amplified Ultrafast Lasers

Start with ‘modelocked’ ultrafast laser

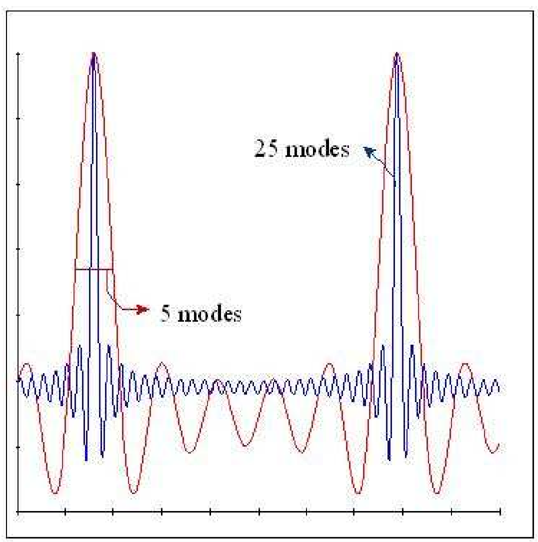


Stretch, amplify and compress



About 1 million modes lasing and locked in phase!

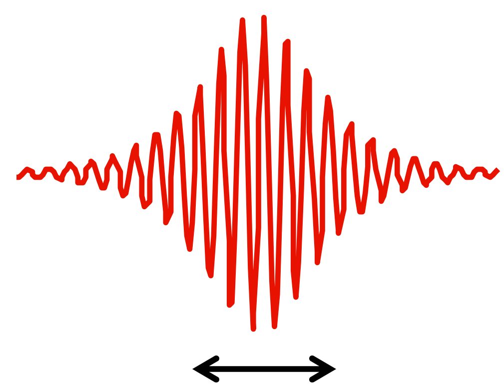
$E(t)=E_0(t)\cos(\omega t)$



$E_0(t)$

Time

Gain in amplifier of over 10^6



Output

$\tau = 3*10^{-14}$s

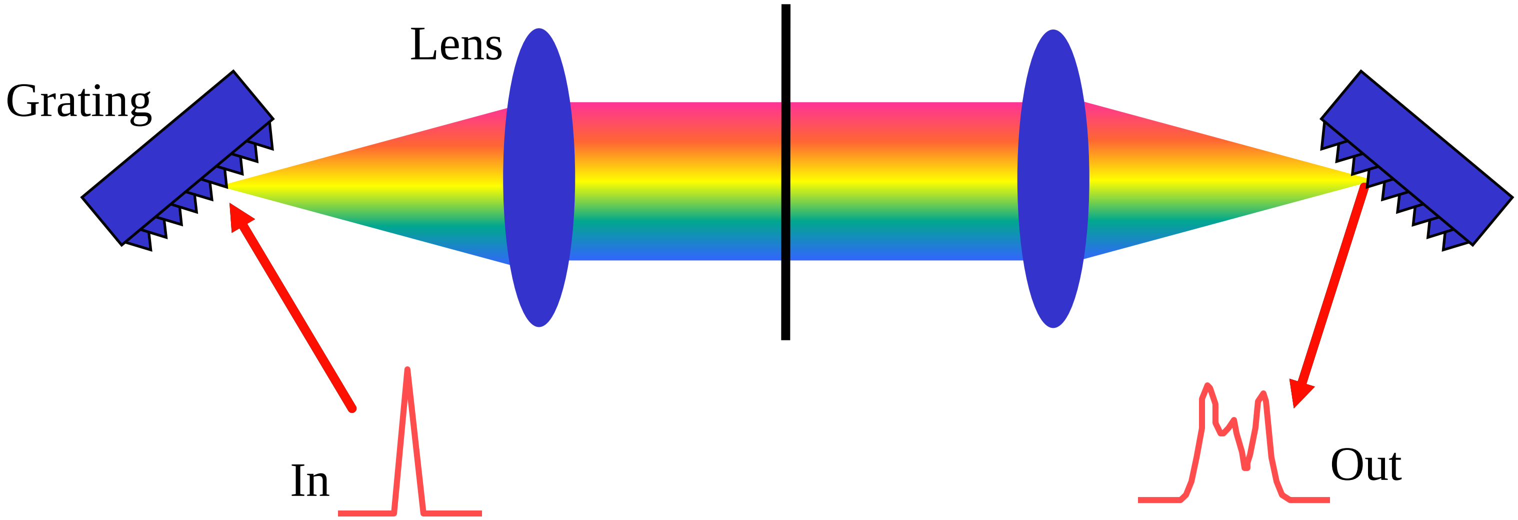
Energy = 10^{-3}J

τ

$I_{control}(10^{18}W/m^2) >> I_{sun}(6*10^7 W/m^2)$

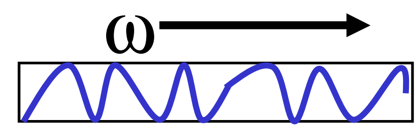
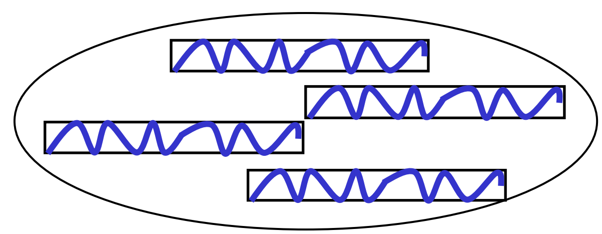
Ultrafast Optical Pulse Shaping

Programmable mask which shapes $E(\omega) = |E(\omega)|e^{i\phi(\omega)}$



Using a Genetic Learning Algorithm I

Based on biological model of natural selection

	In Nature	In Our Lab
Individuals:		E(t)  Shaped pulses E(t)
Genetic Code:		$\phi(\omega)$  Phase at each frequency
Population:		 Collection of pulse shapes

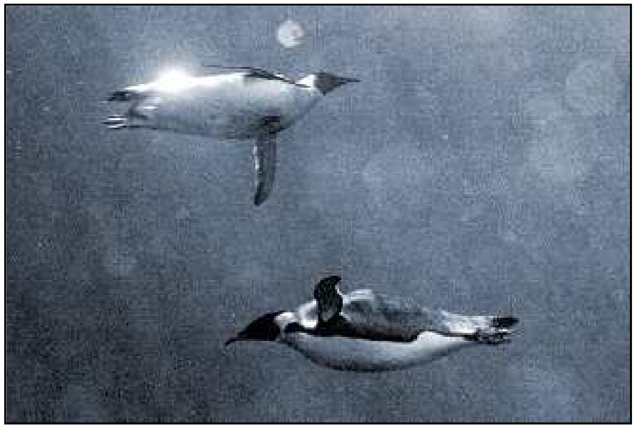
Using a Genetic Learning Algorithm II

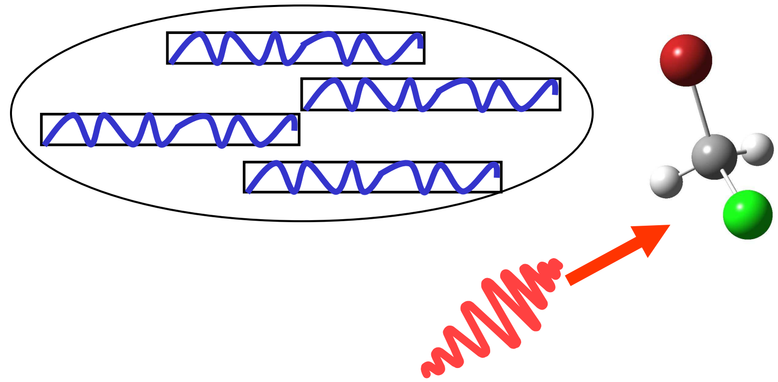
Based on biological model of natural selection

In Nature

In Our Lab

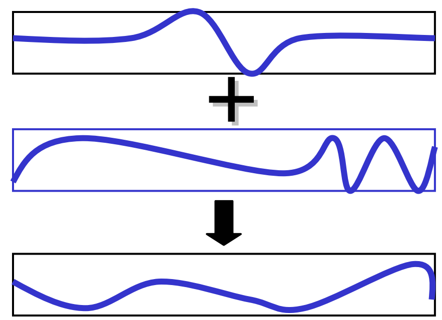
Survival of the Fittest:





Fitnesses = 1.95, 2.46, …

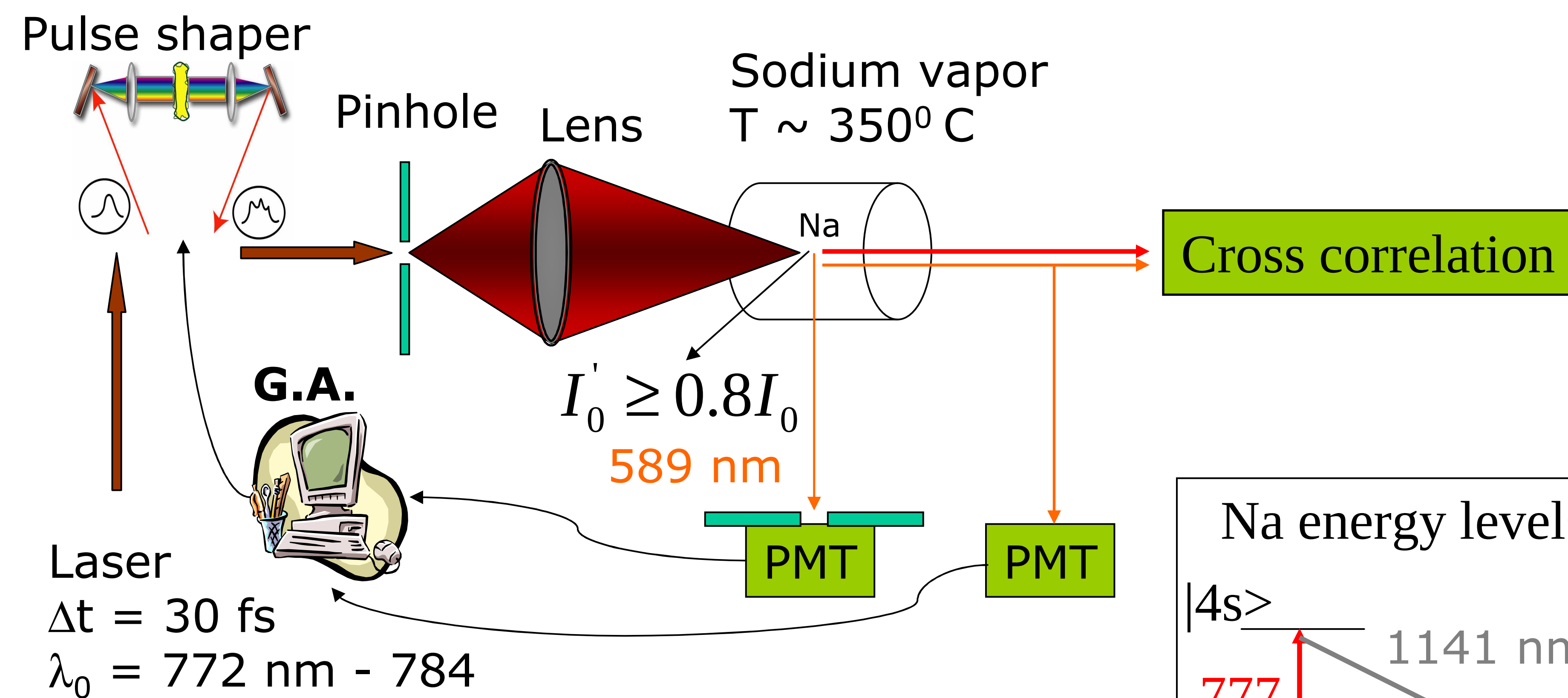
Reproduction:

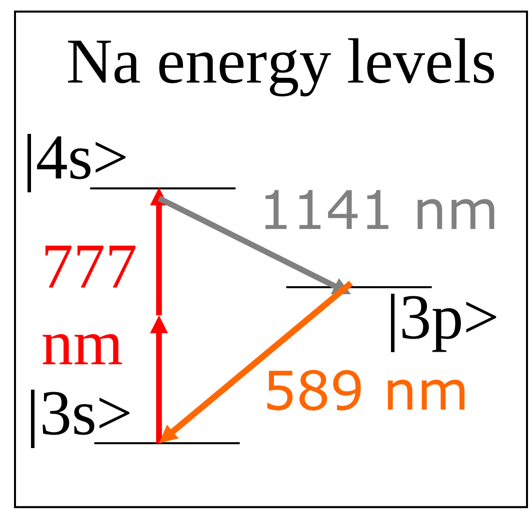


"Operators"

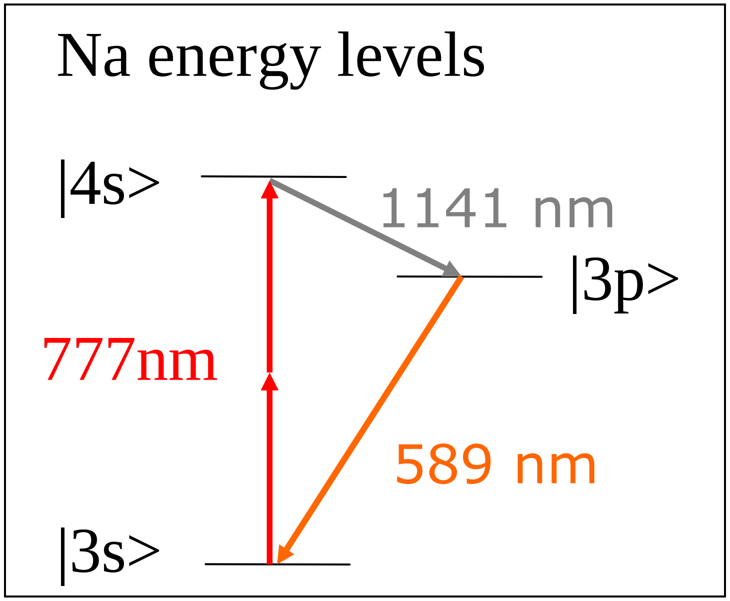
Crossover, Mutation, etc.

Control & Dynamics I
Inversion & Lasing in an atom (Na)

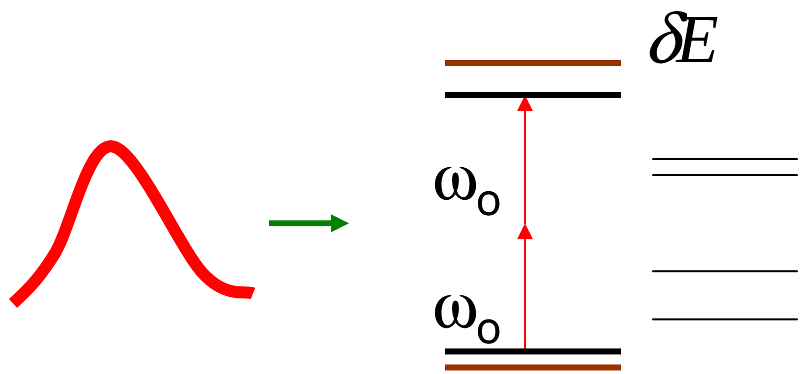




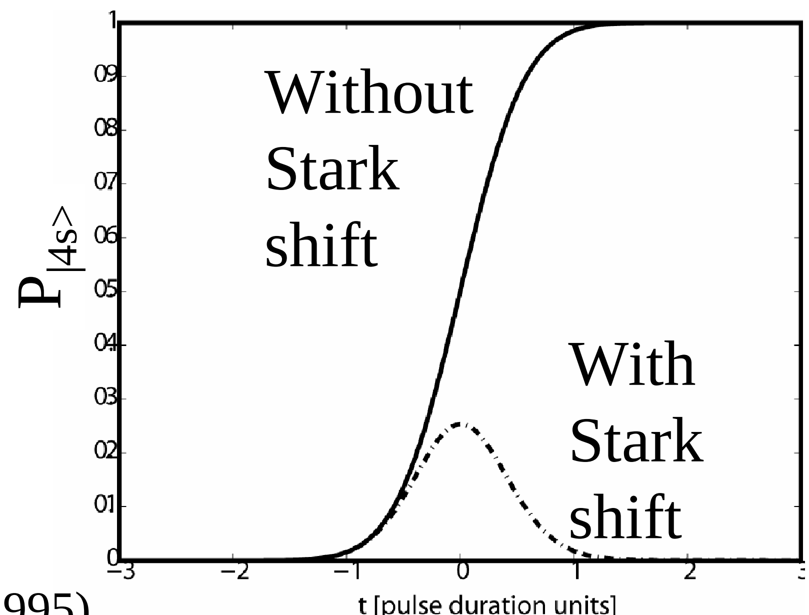
Strong Fields - Dynamic Resonance



Stark shift: $\delta E \propto \varepsilon(t)^2$

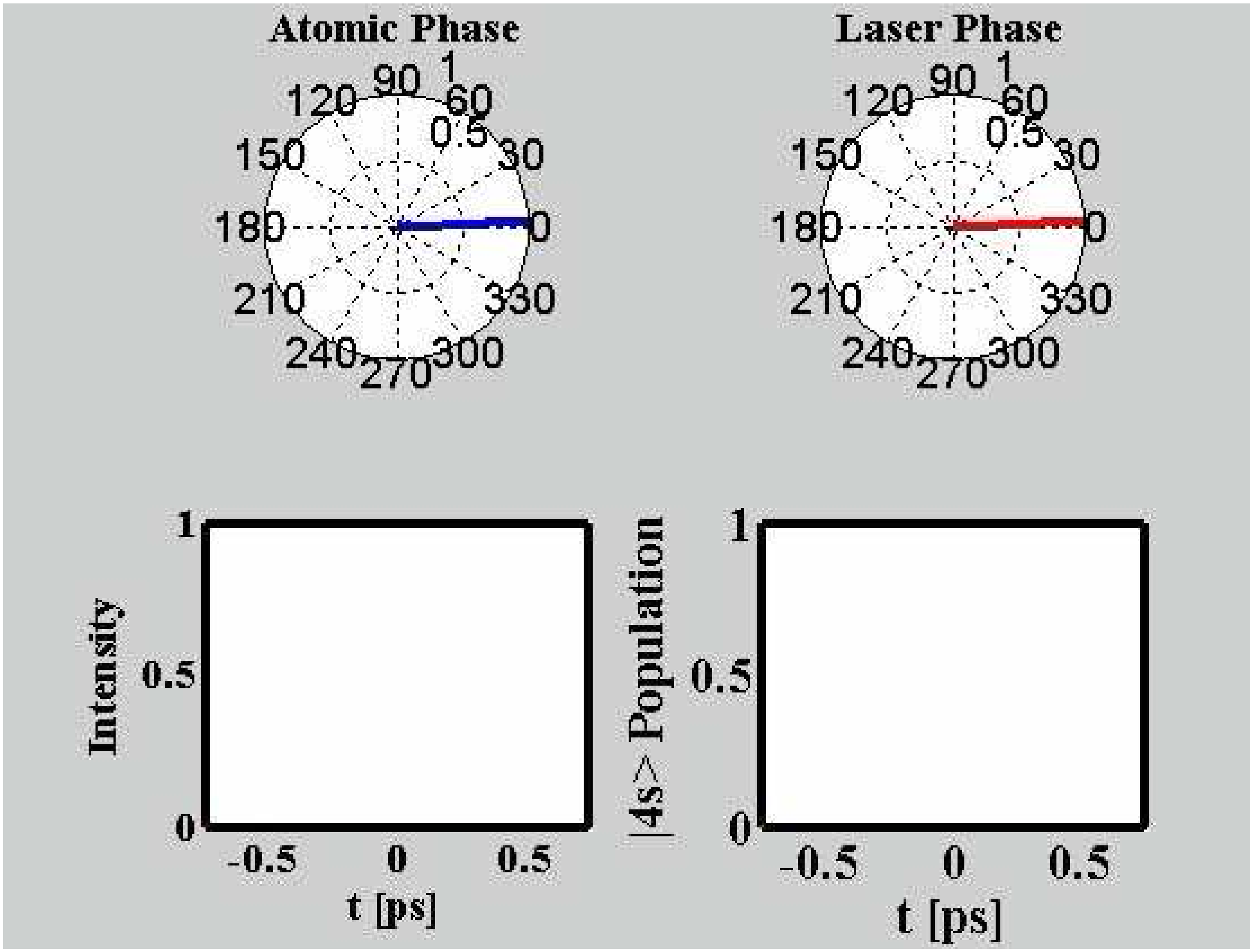


- Coupling strength and energy shifts are of the same order of magnitude -> low efficiency
- Absorption -> Emission



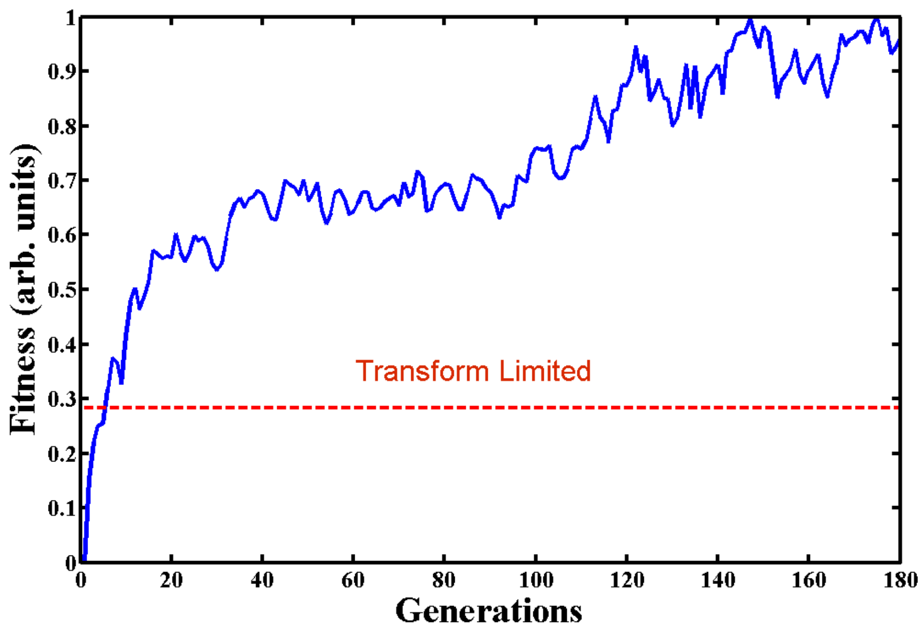
R. R. Jones *Phys. Rev. Lett.* ***74***, 1091 (1995)

Strong Fields – Dynamic Resonance

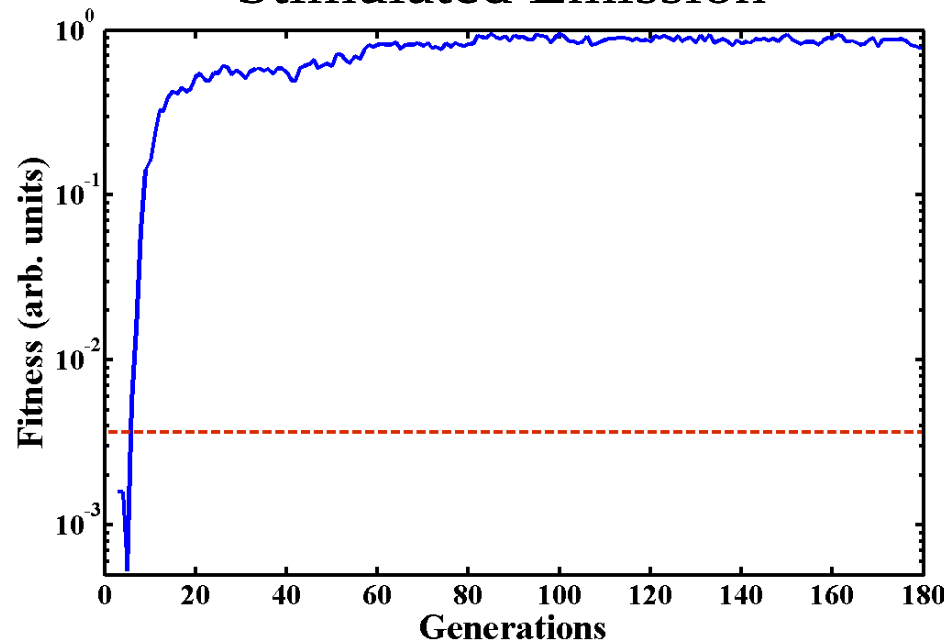


Using Feedback to get Inversion & Lasing in Na

Spontaneous Emission



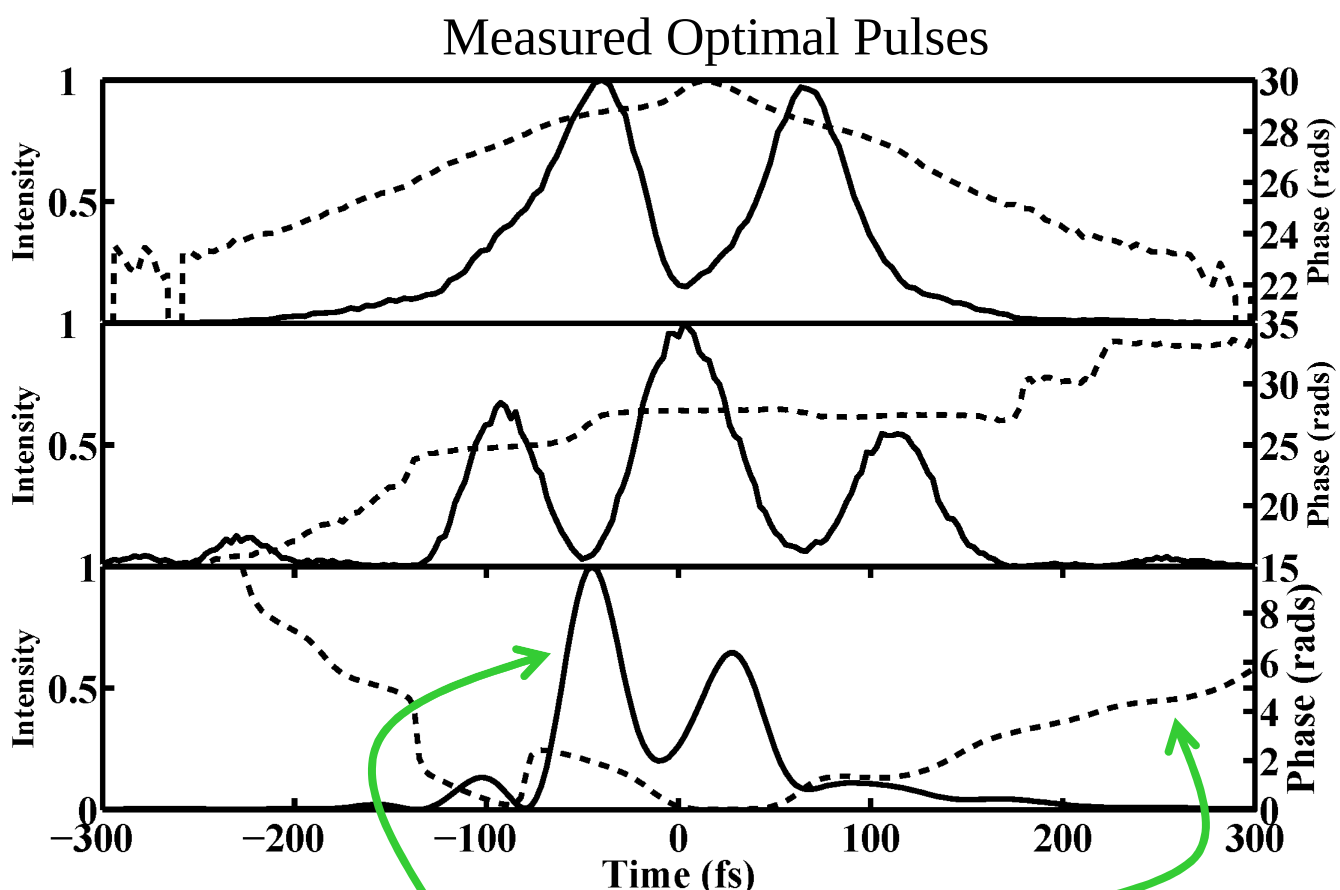
Stimulated Emission



Improvement over unshaped ~ 3

Improvement over unshaped ~ 10^3

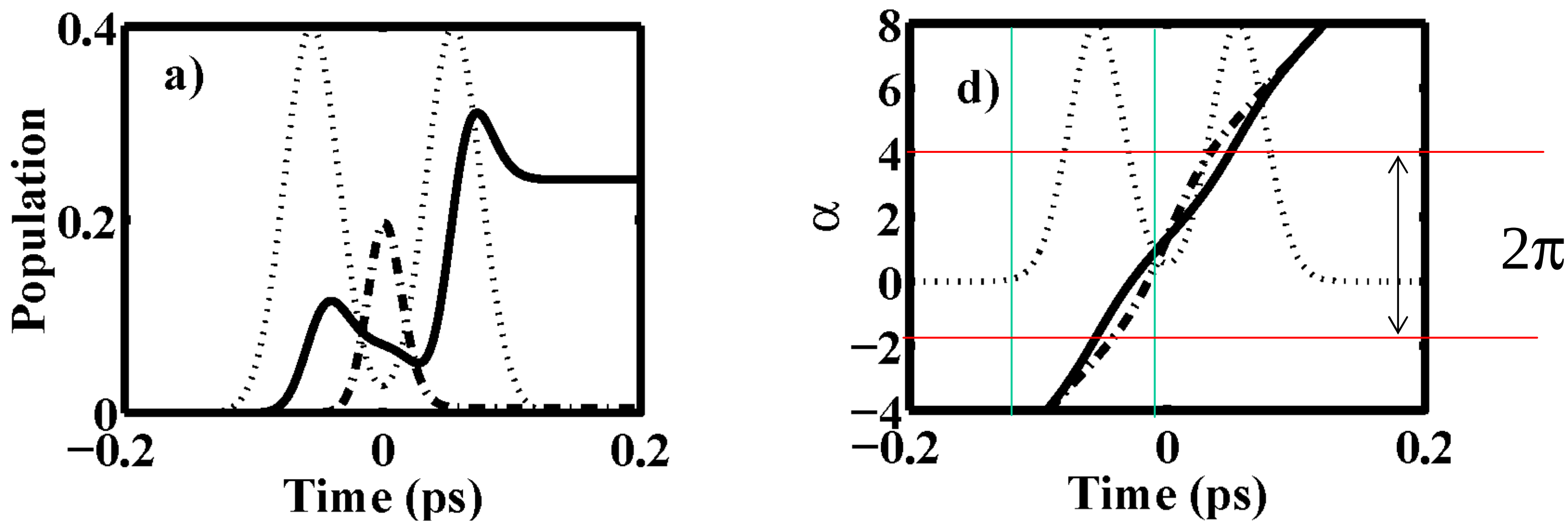
Understanding Single Atom Strong Field Dynamics



$$E(t) = A(t)\cos(\omega_0 t + \phi(t))$$

Phys. Rev. Lett. **96** 063603 (2006)

Understanding Single Atom Strong Field Dynamics



—— $P_{4s}(t), \alpha(t)$ shaped

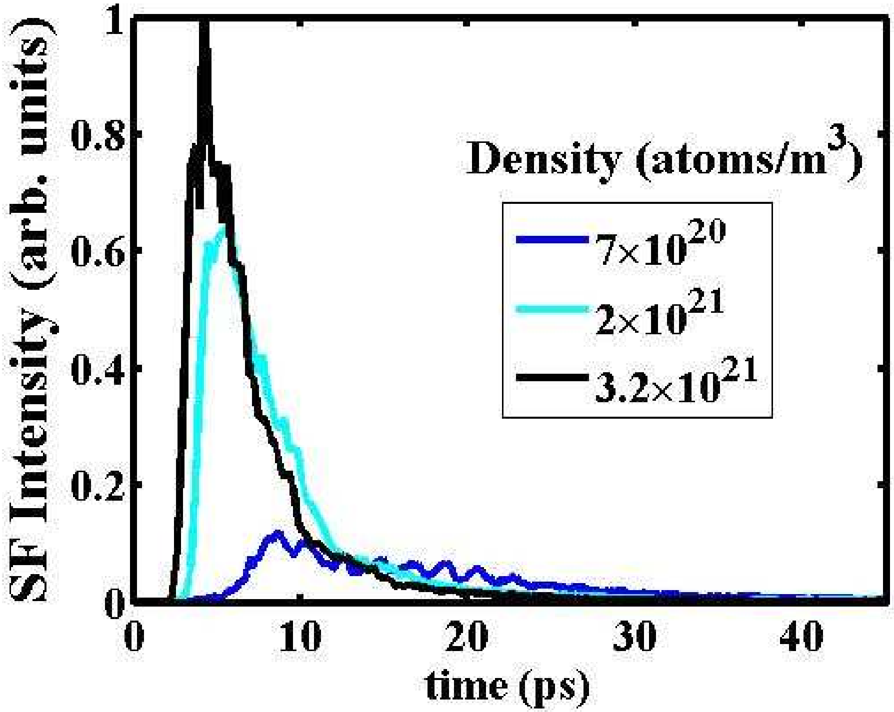
– · – $P_{4s}(t)$, $\alpha(t)$ unshaped

······ I(t) measured

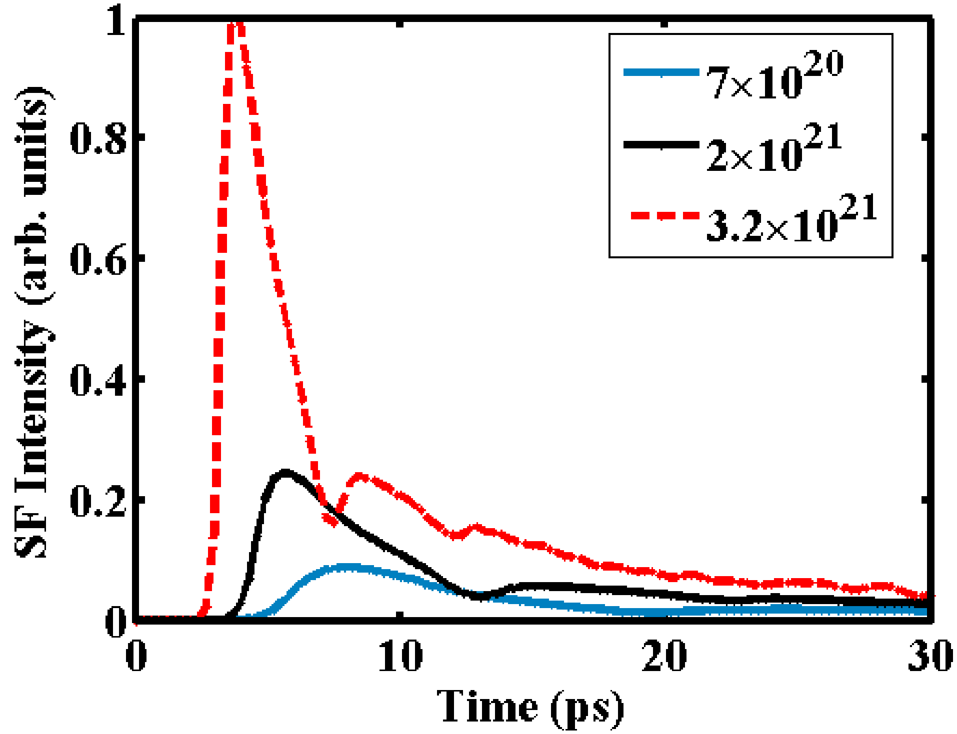
$\alpha(t)$ is the ‘atom-laser phase’

Phys. Rev. Lett. **96** 063603 (2006)

Measurement & Calculations of the Stimulated Emission



Experiment

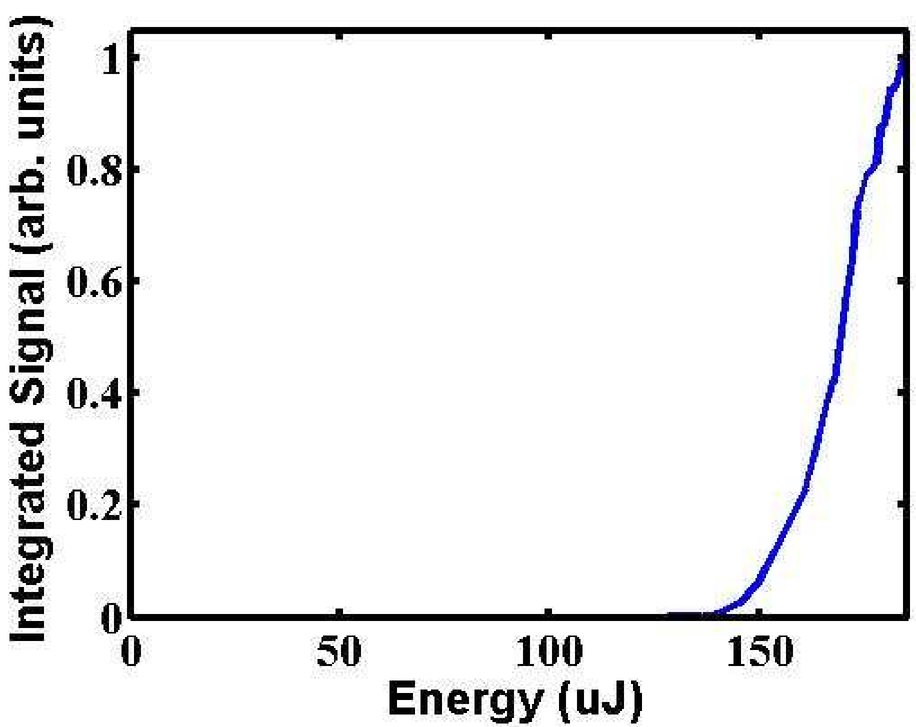


Theory

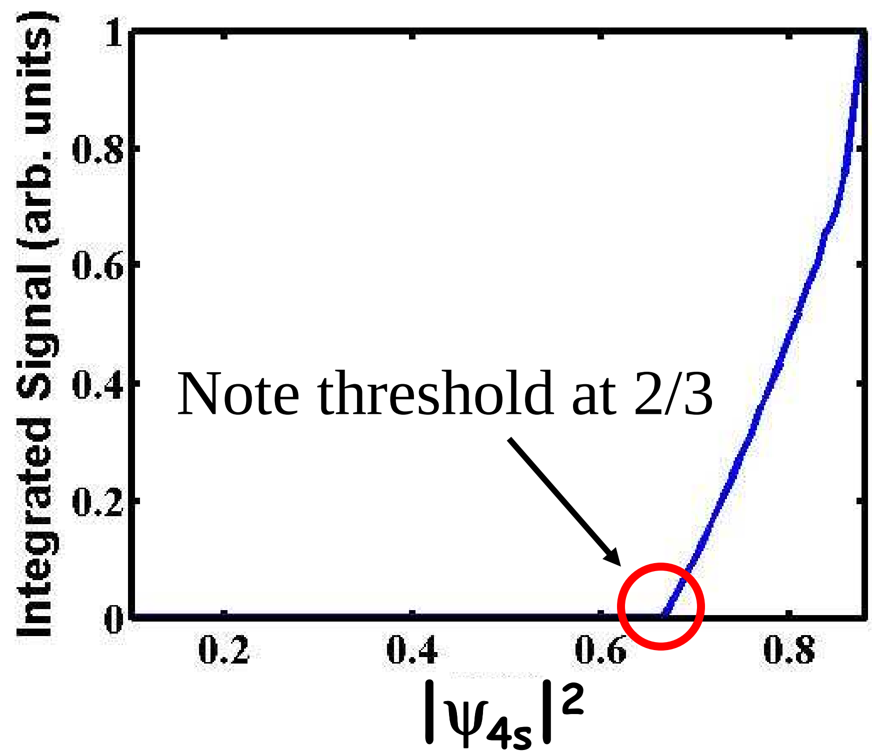
Physical Review A **74**, 051403(R) (2006)

Stimulated Emission vs $|\psi_{4s}|^2$

Experiment

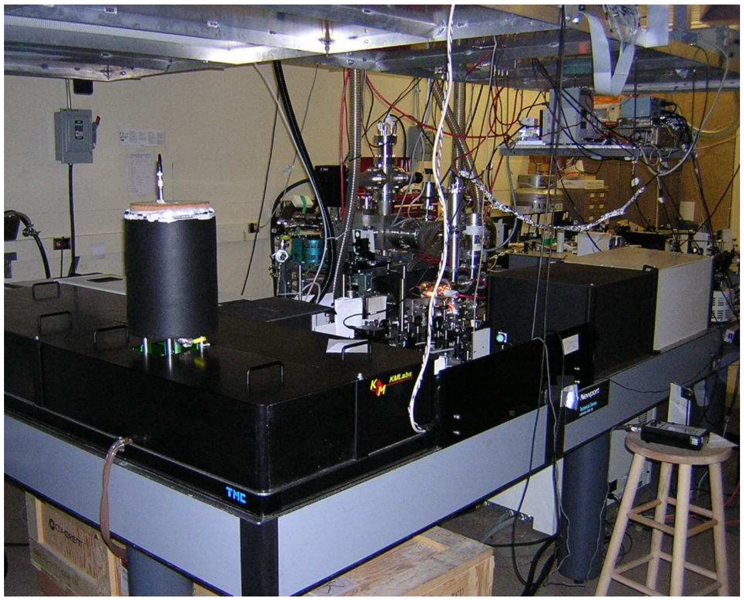


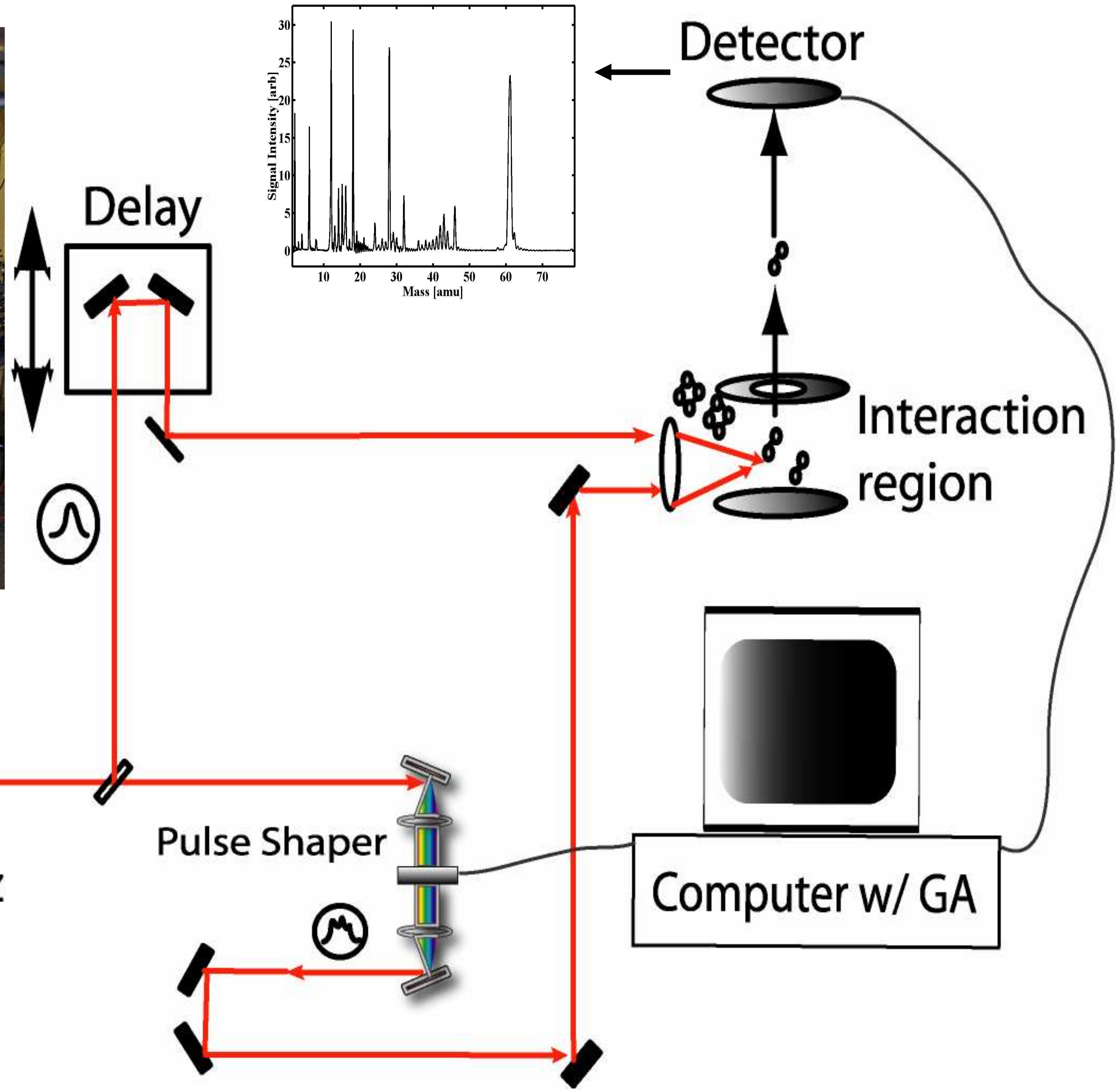
Theory



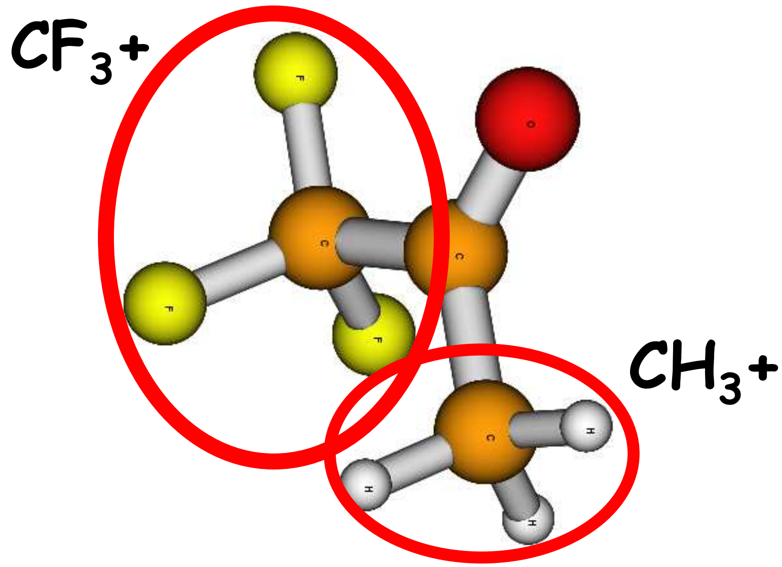
- ***Stimulated emission is superfluorescence – locking of atomic dipoles***
- ***Modest single atom gains lead to large stimulated gains***

Control and Dynamics II - Molecules

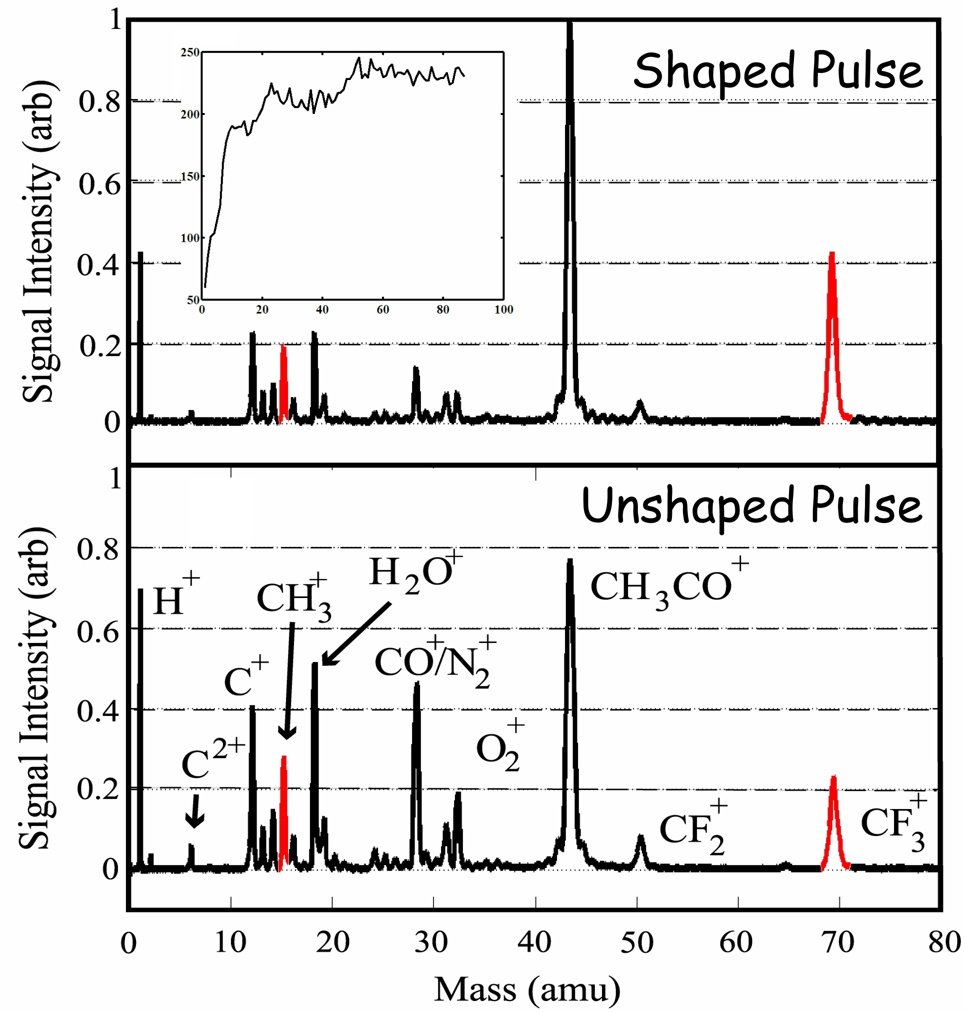




Control in Trifluoroacetone (CH_3COCF_3)



Control goal = CF_3^+/CH_3^+

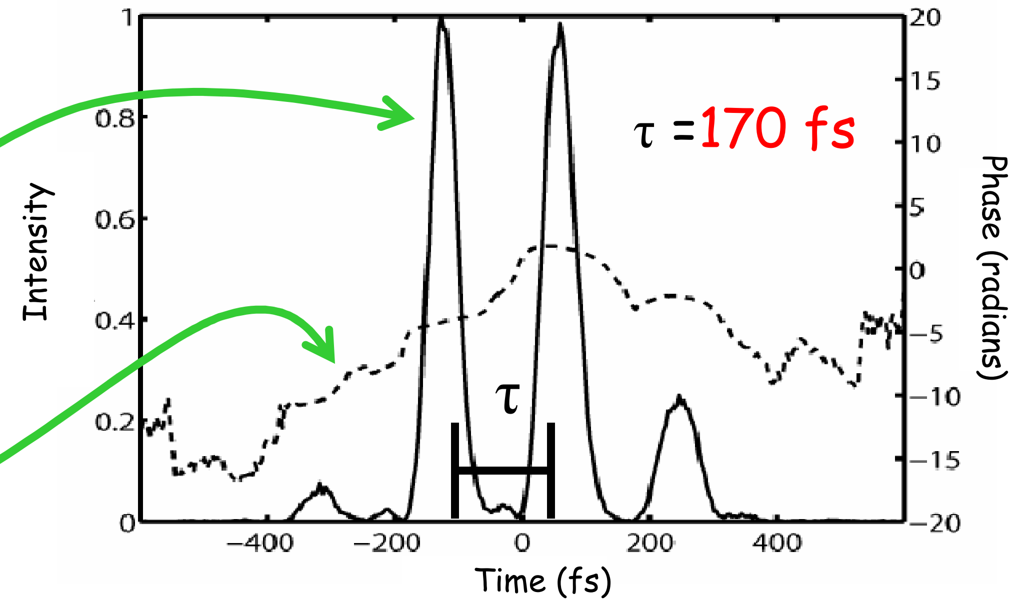


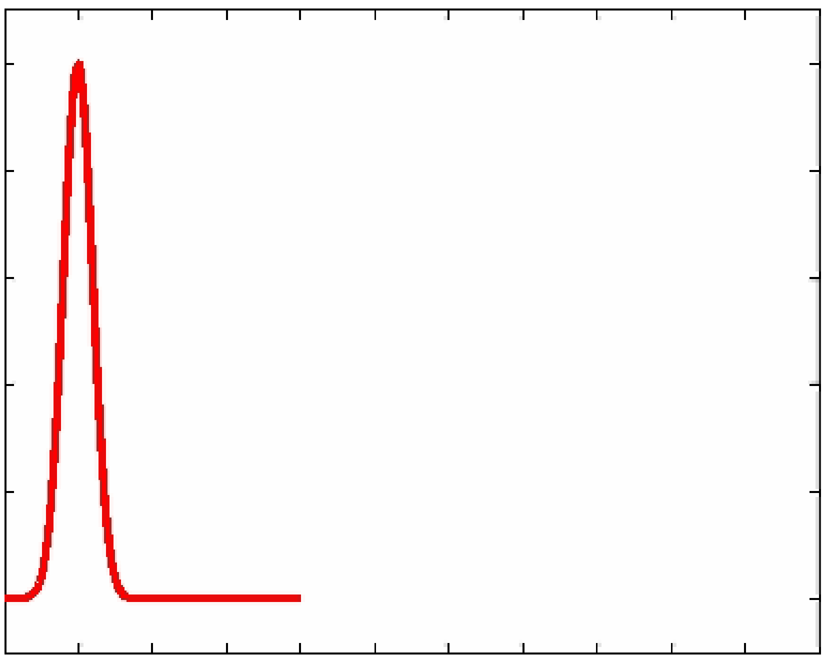
R. J. Levis, G. M. Menkir, and H. Rabitz, Science **292**, 709 (2001).

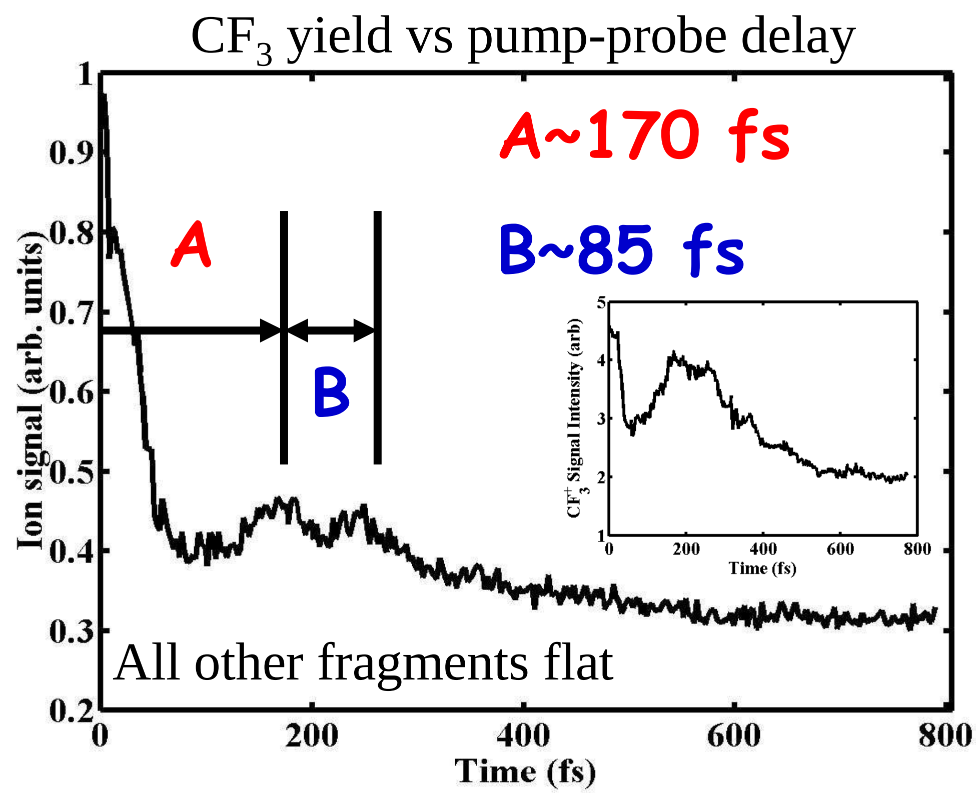
D. Cardoza, M. Baertschy, T. Weinacht, J. Chem Phys. **123**, 074315 (2005).

Optimal solution & Pump-Probe Measurement

$$E(t) = A(t)\cos(\omega_0 t + \phi(t))$$

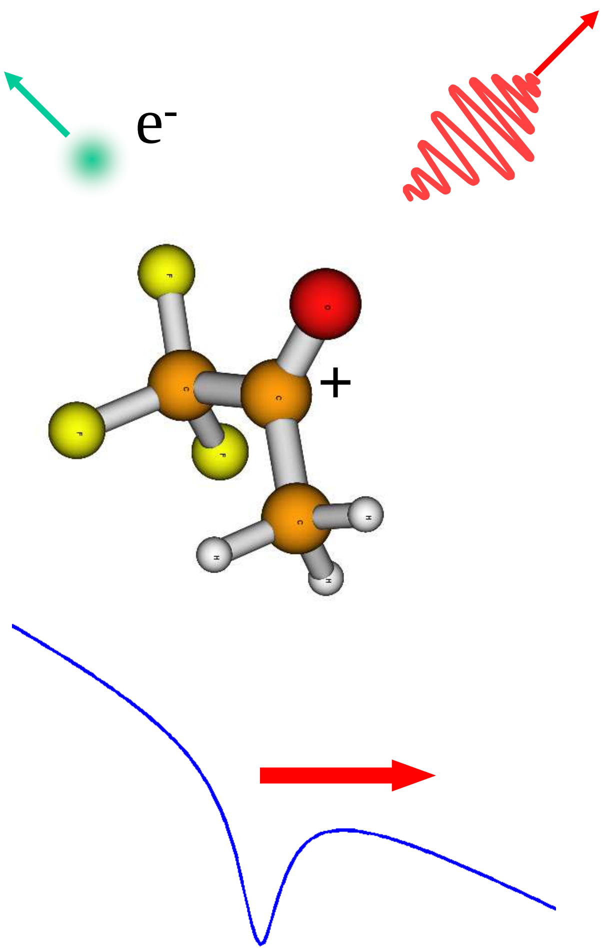


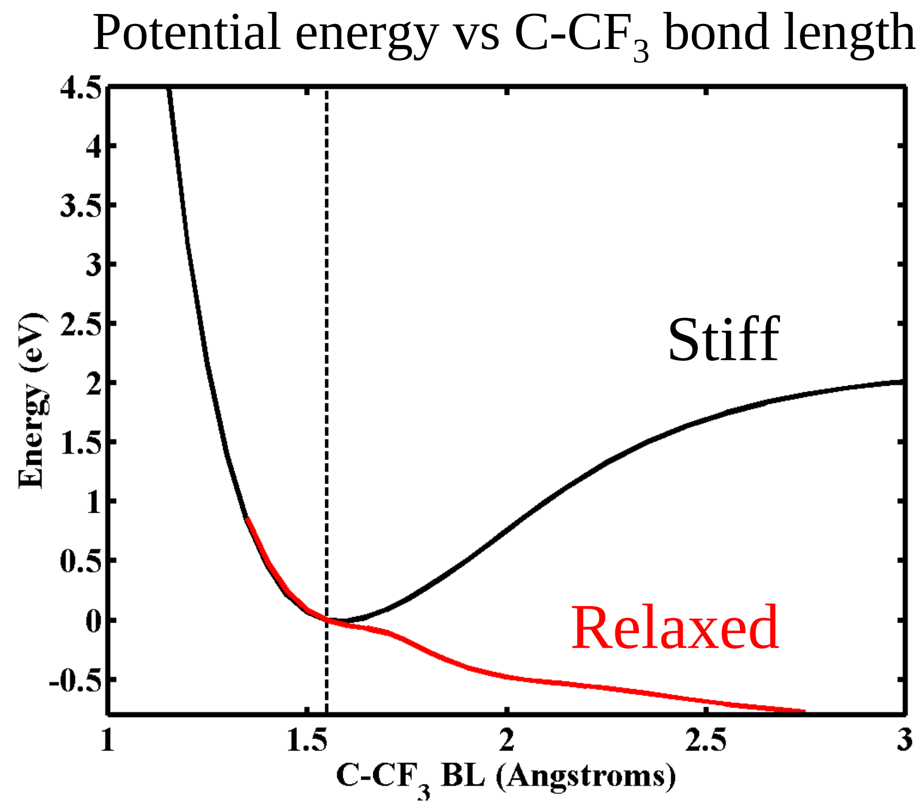




Laser cooperates with
Molecular dynamics

How Can We Describe the Dynamics?





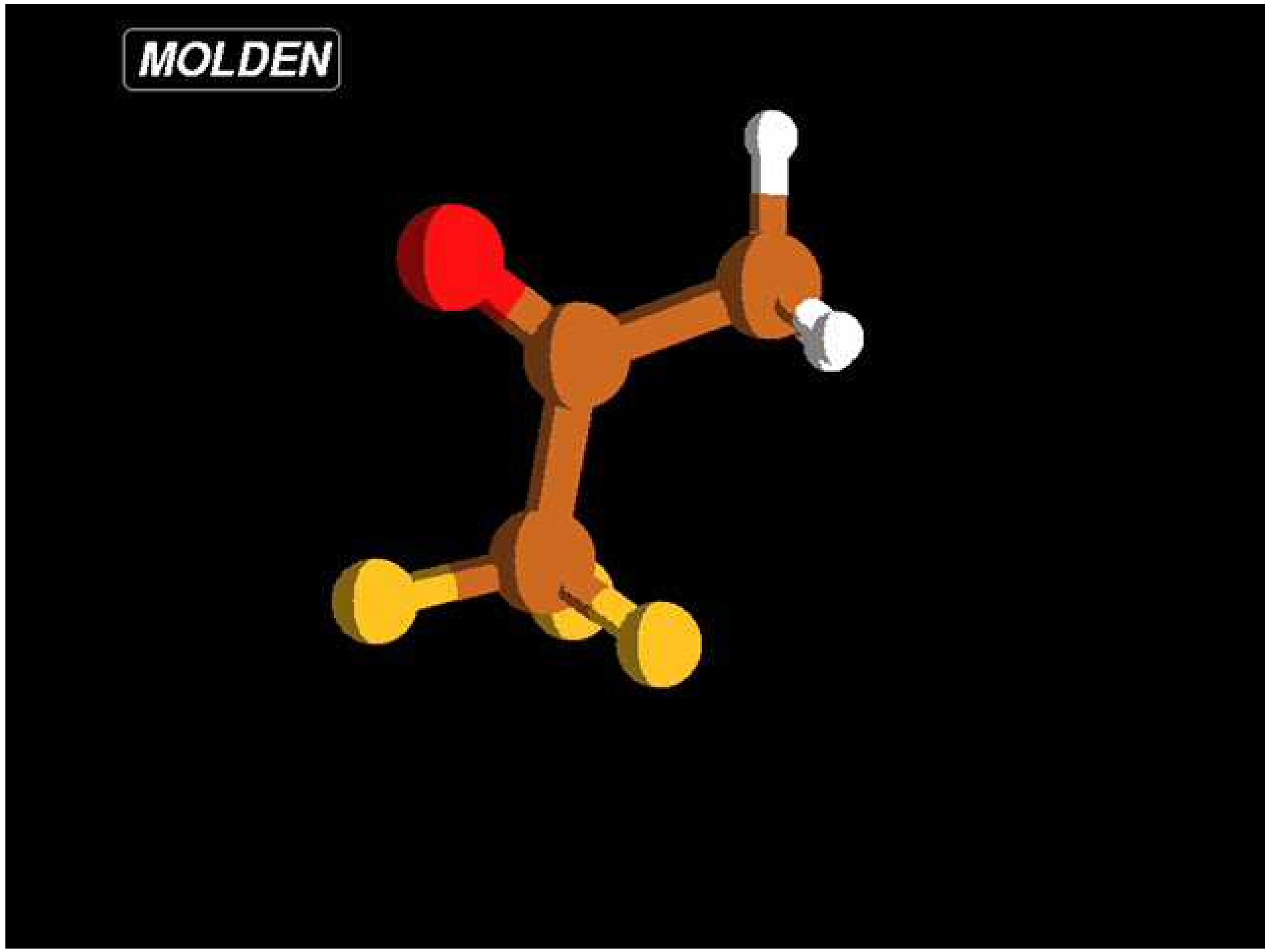
First Ionization, then dissociation

Molecular Relaxation

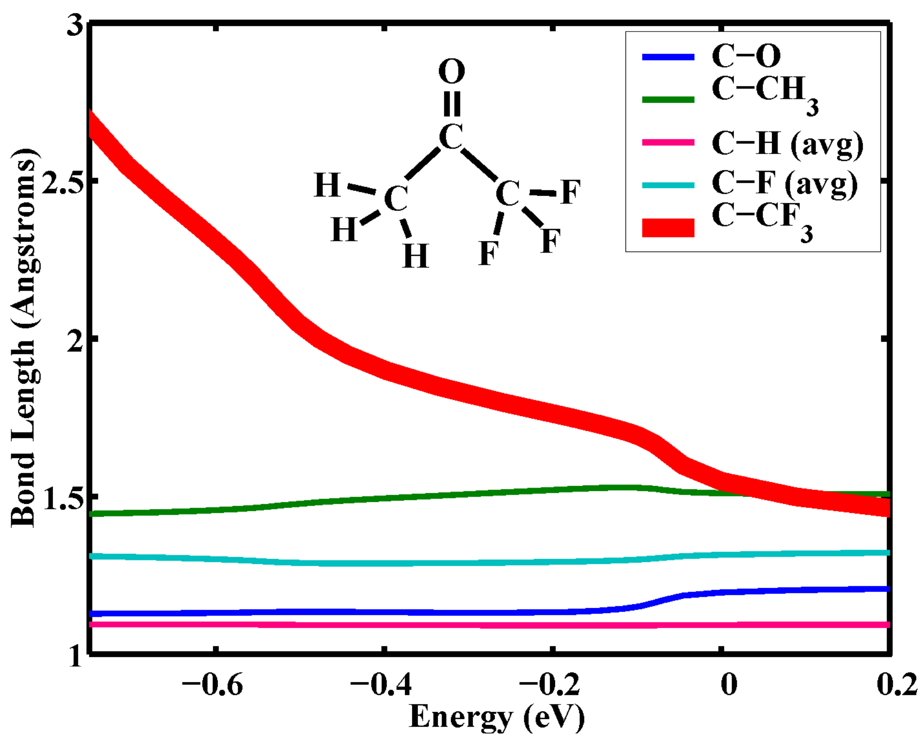
$CH_3COCF_3^+$

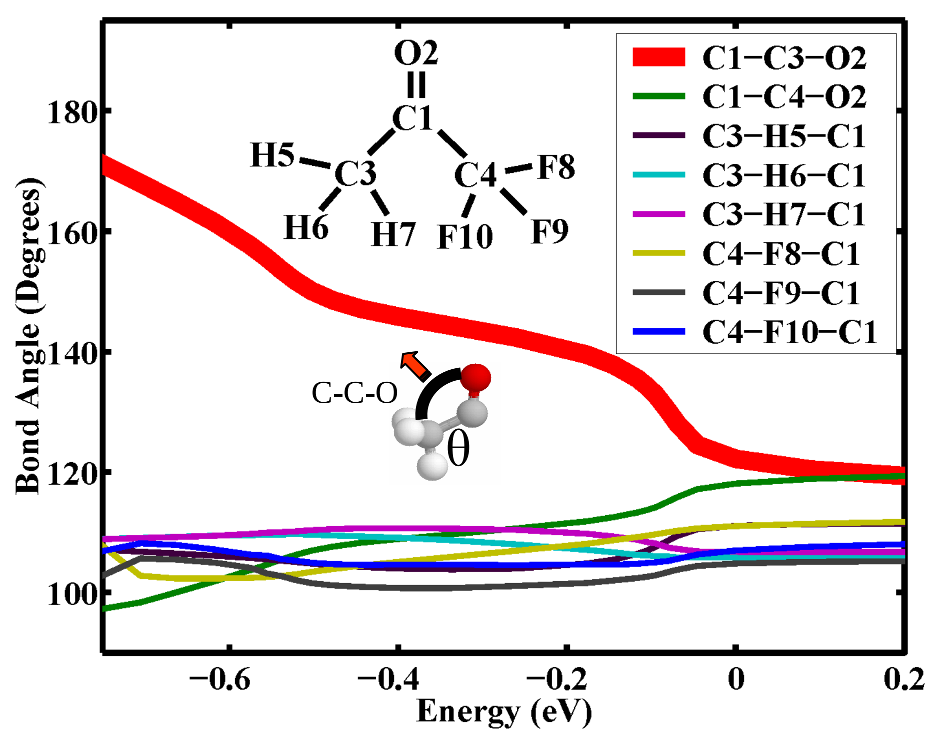
↓

$CF_3 + CH_3CO^+$

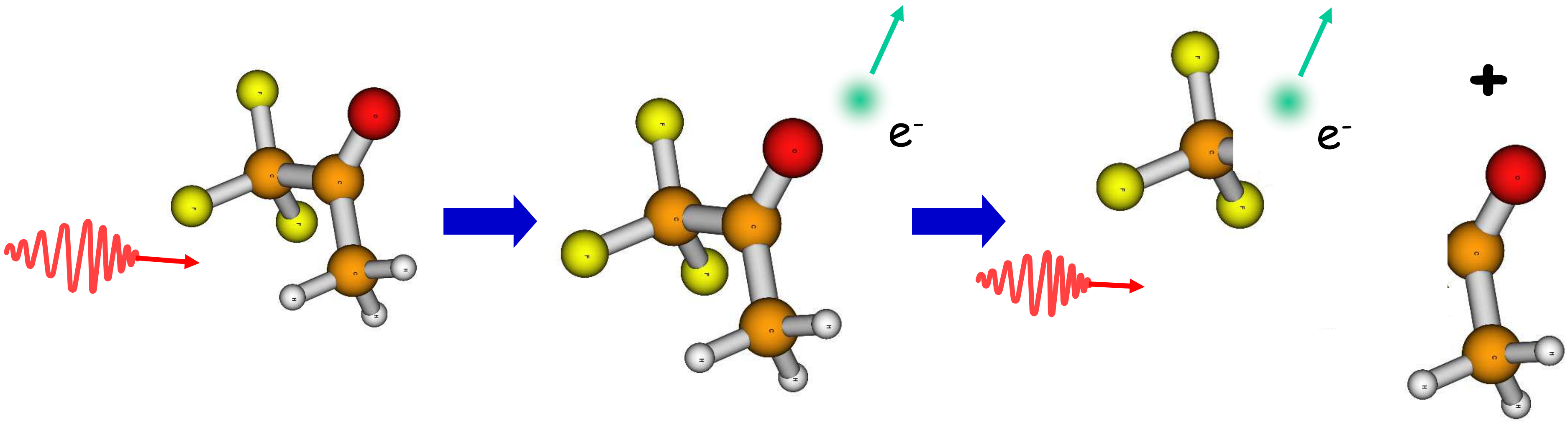


Molecular Relaxation II





Enhanced Molecular Ionization

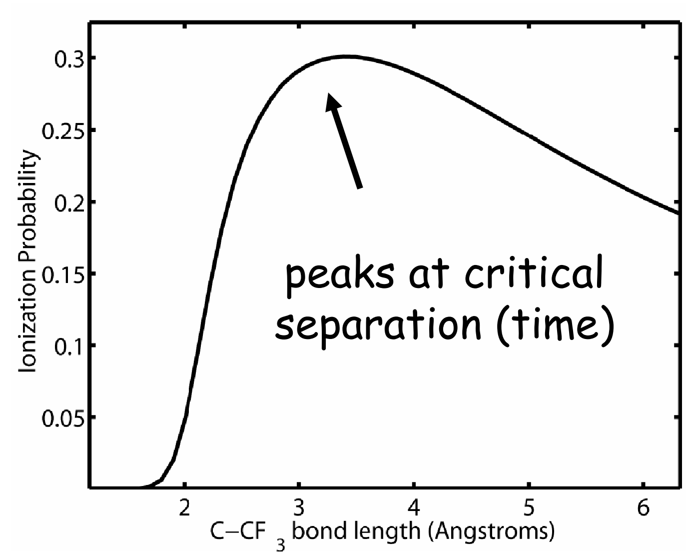


nhν + TFA ⟶ TFA^+ ⟶ nhν + CF_3 + CH_3CO^+

⟶ CF_3^+ + CH_3CO^+

<u>"Diatomic" EI calculation</u>

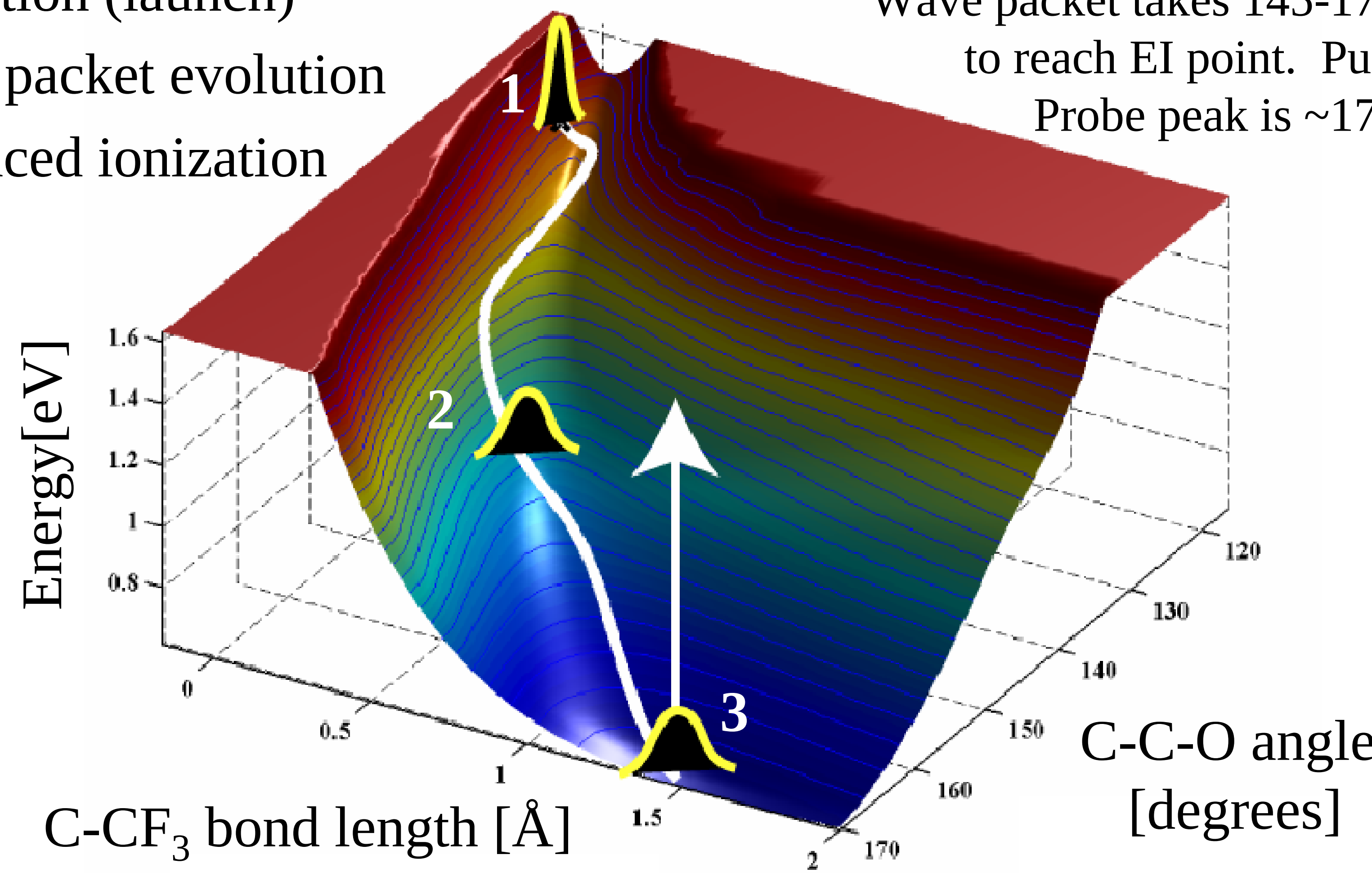
- Ionization probability increases at $R_{critical}$
- Treat CH_3CO^+ and CF_3 as atomic-like



Control Model

1. Ionization (launch)
2. Wave packet evolution
3. Enhanced ionization

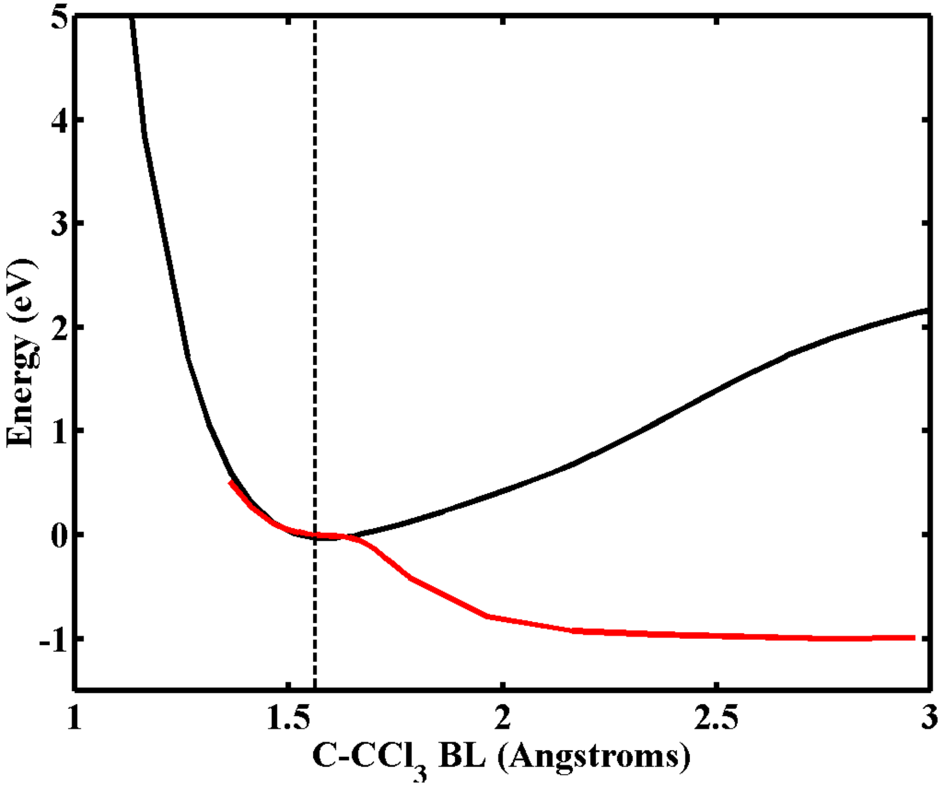
Wave packet takes 145-175 fs to reach EI point. Pump-Probe peak is ~170 fs



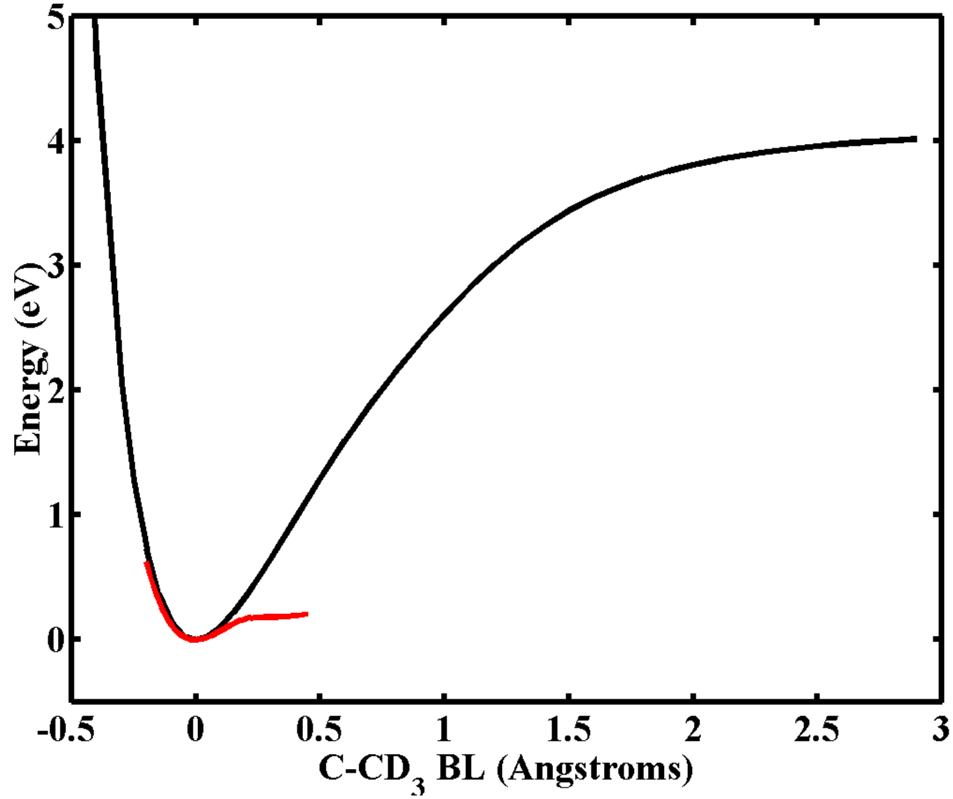
J. Chem. Phys. **123** 074315 (2005)

Predictions for 'Family Members'

CH_3COCCl_3

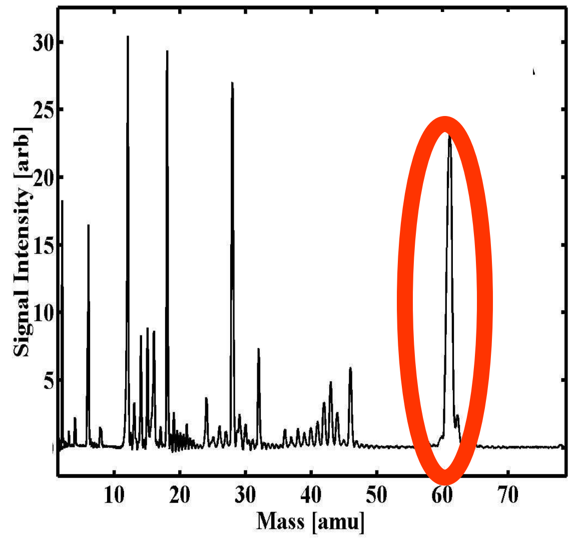


CH_3COCD_3

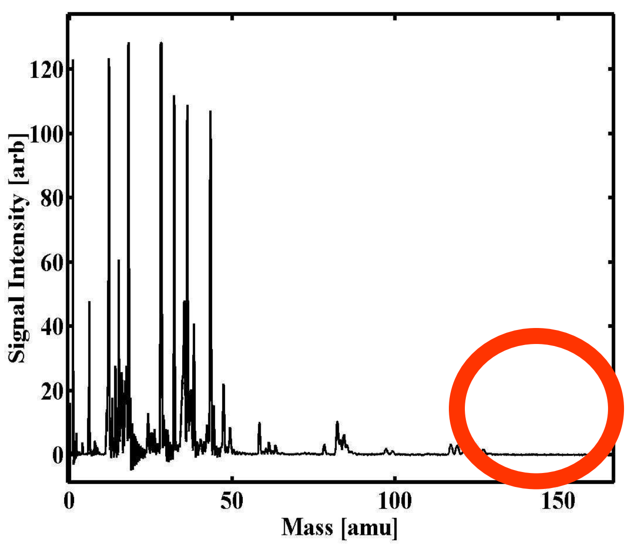


Fragmentation of Family Members

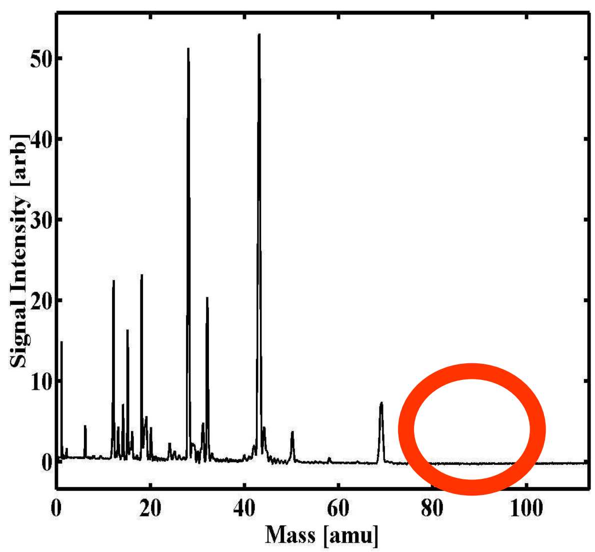
CH_3COCD_3



CH_3COCCl_3

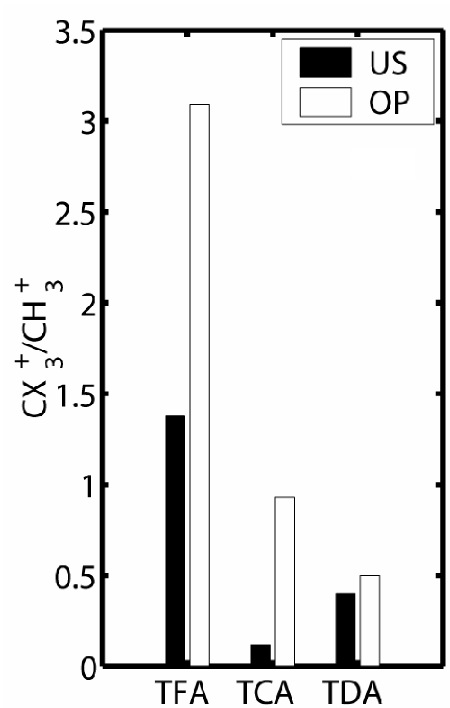


CH_3COCF_3

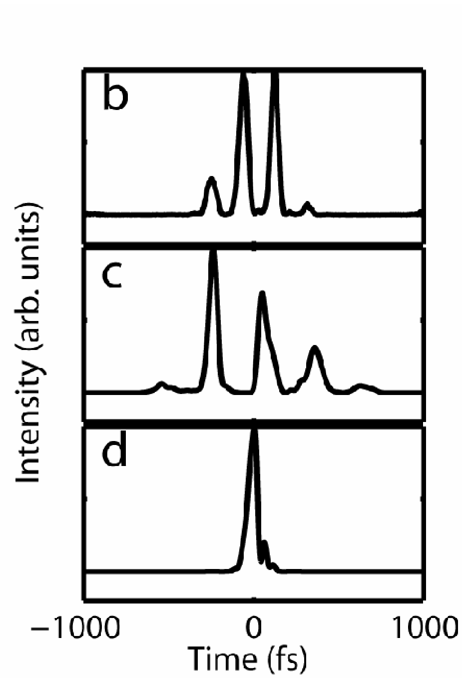


Results for CH_3COCCl_3 and CH_3COCD_3

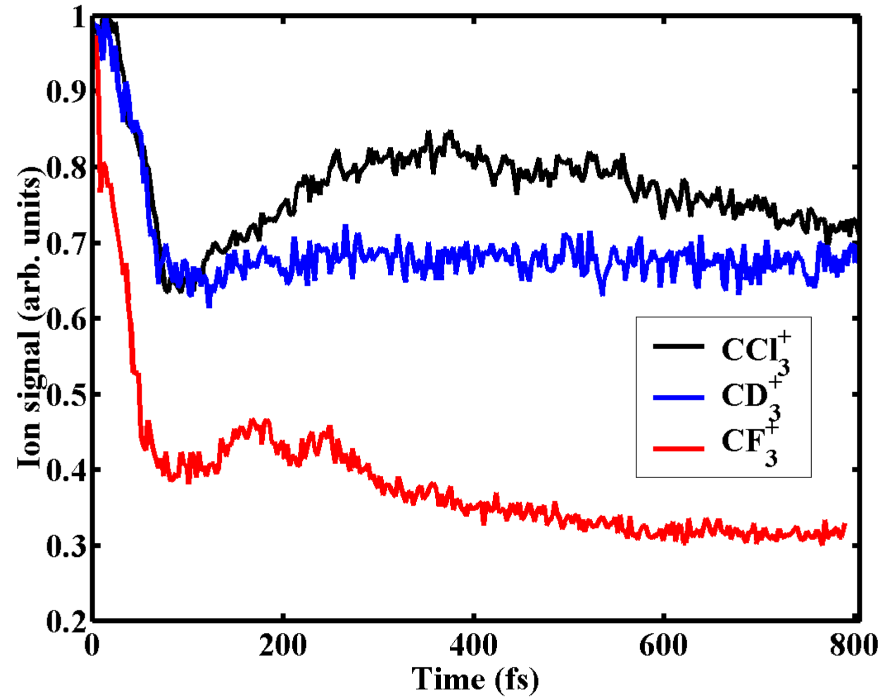
Control



Pulse Shape

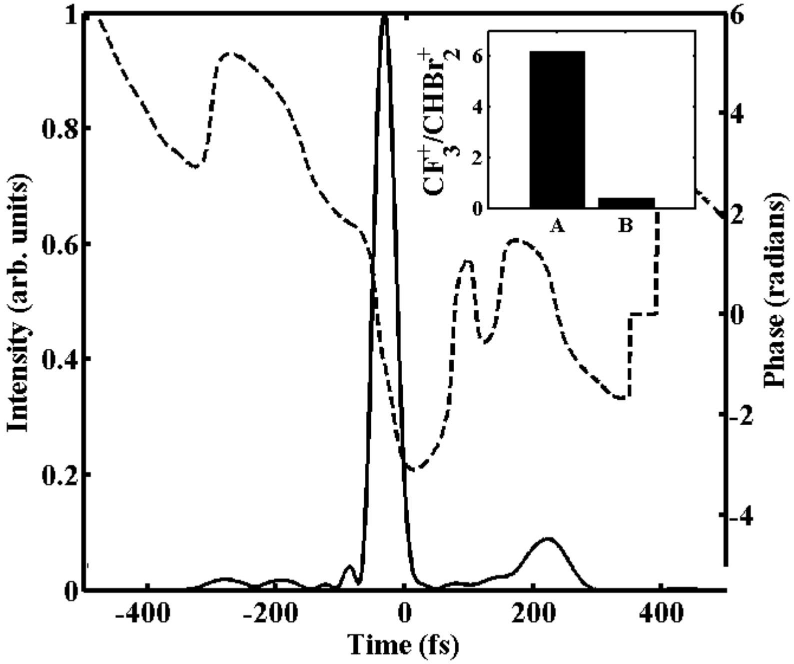


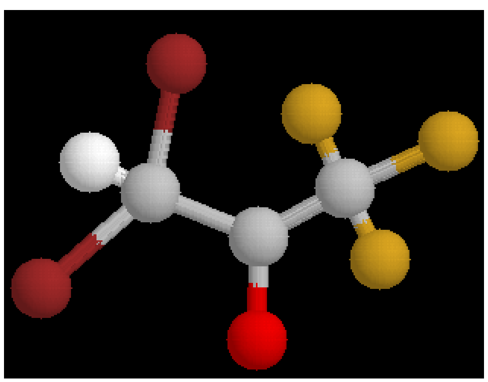
Pump-probe



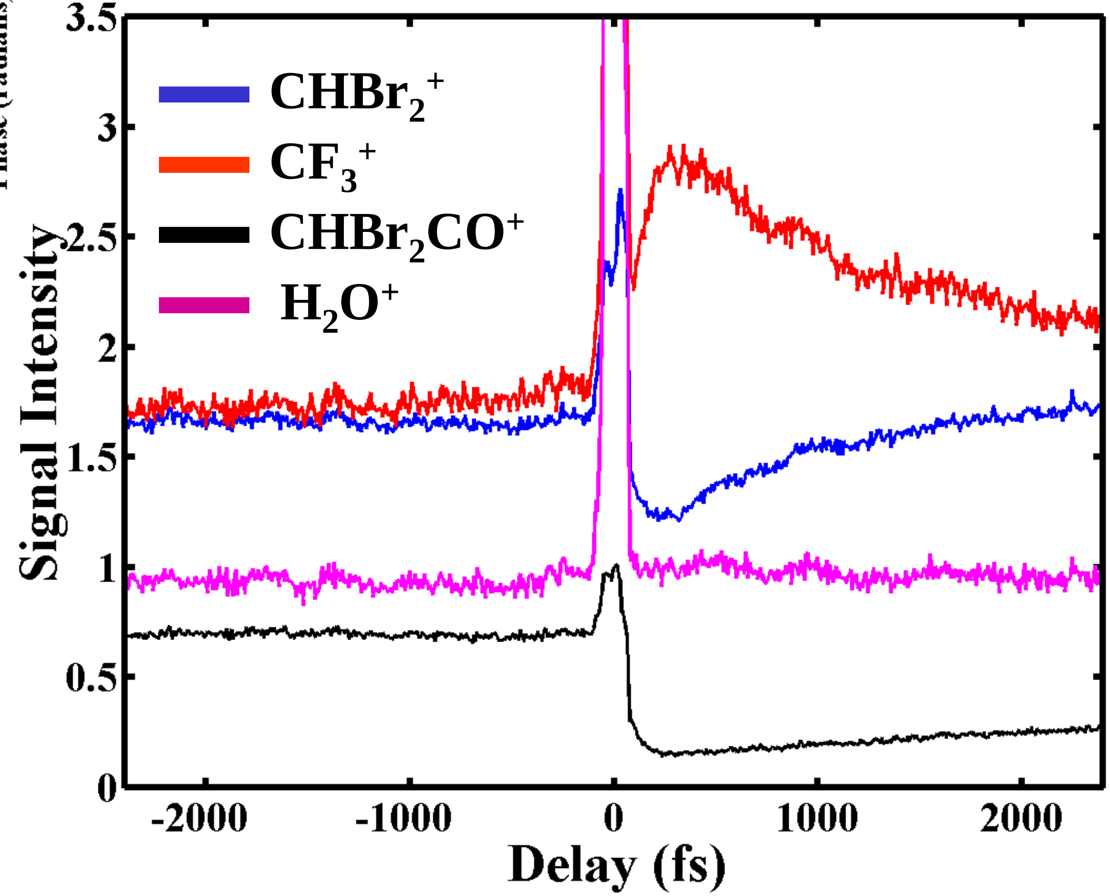
Chemical Physics Letters **411**, 311 (2005)

Similar But Different – Charge Transfer





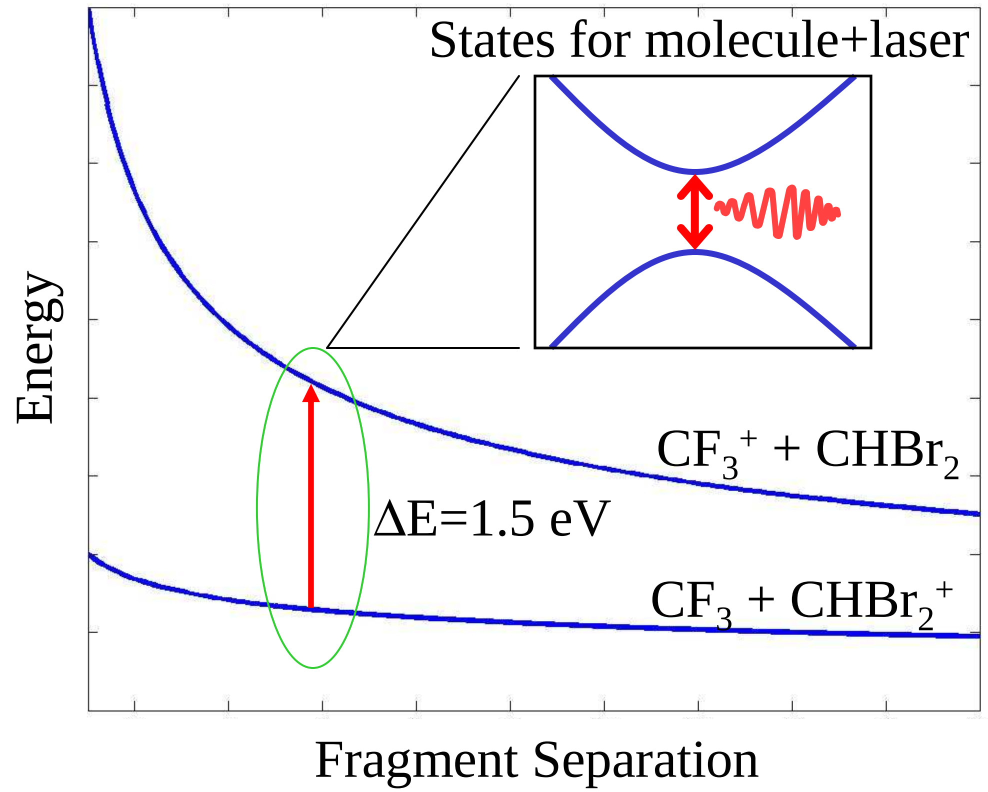
Pump Probe for $CHBr_2COCF_3$

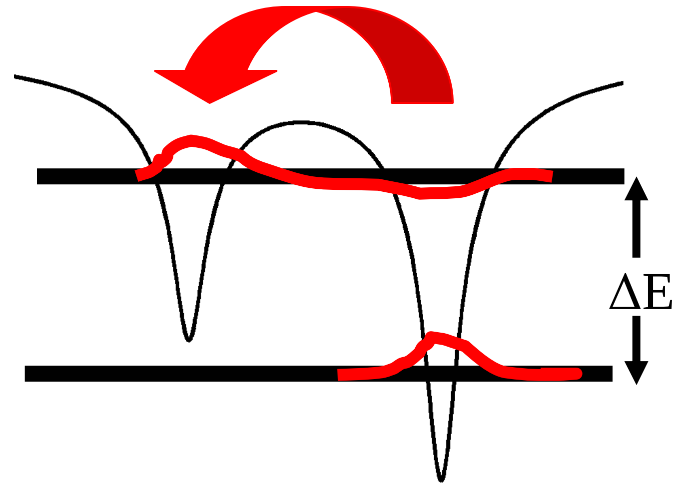


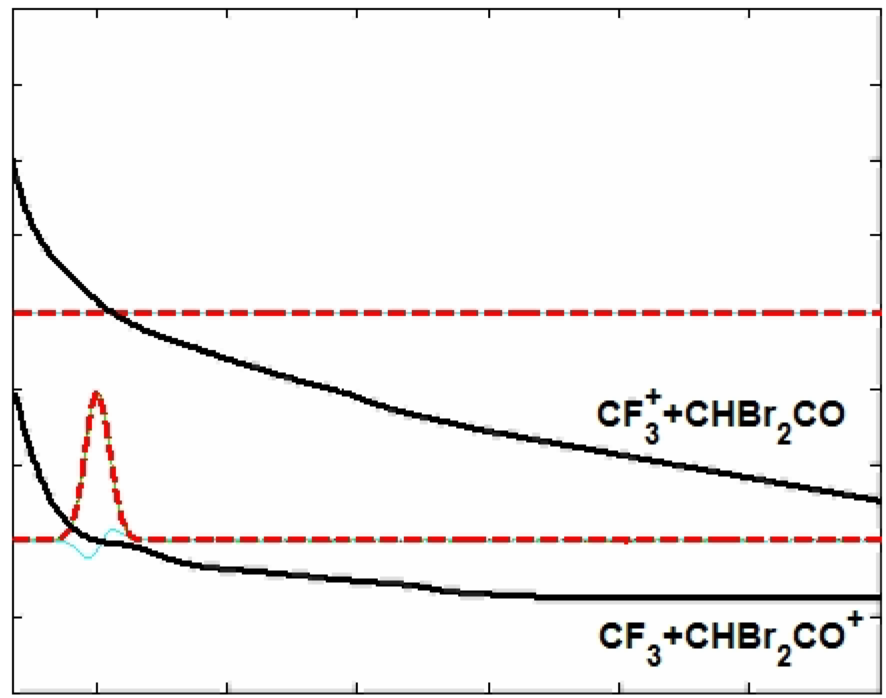
J. of Photochemistry & Photobiology A 180, 277 (2006)

Dynamic Resonance

Dynamic Resonance during Dissociation

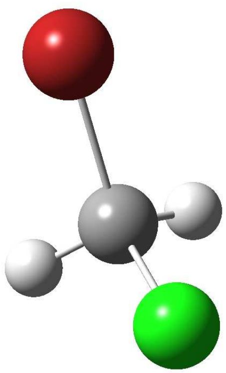




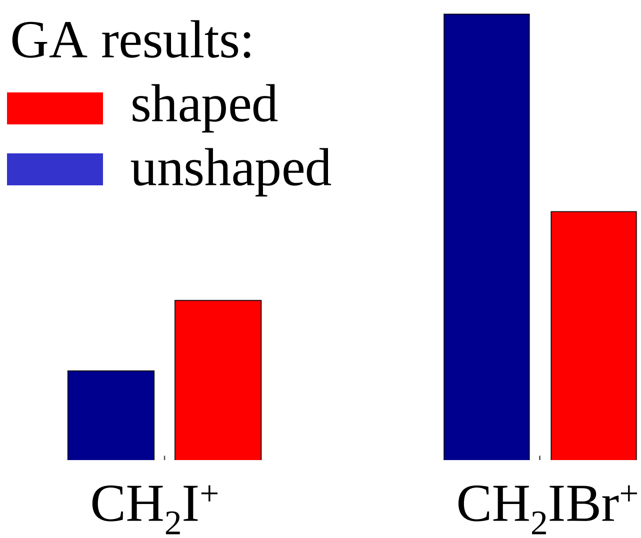


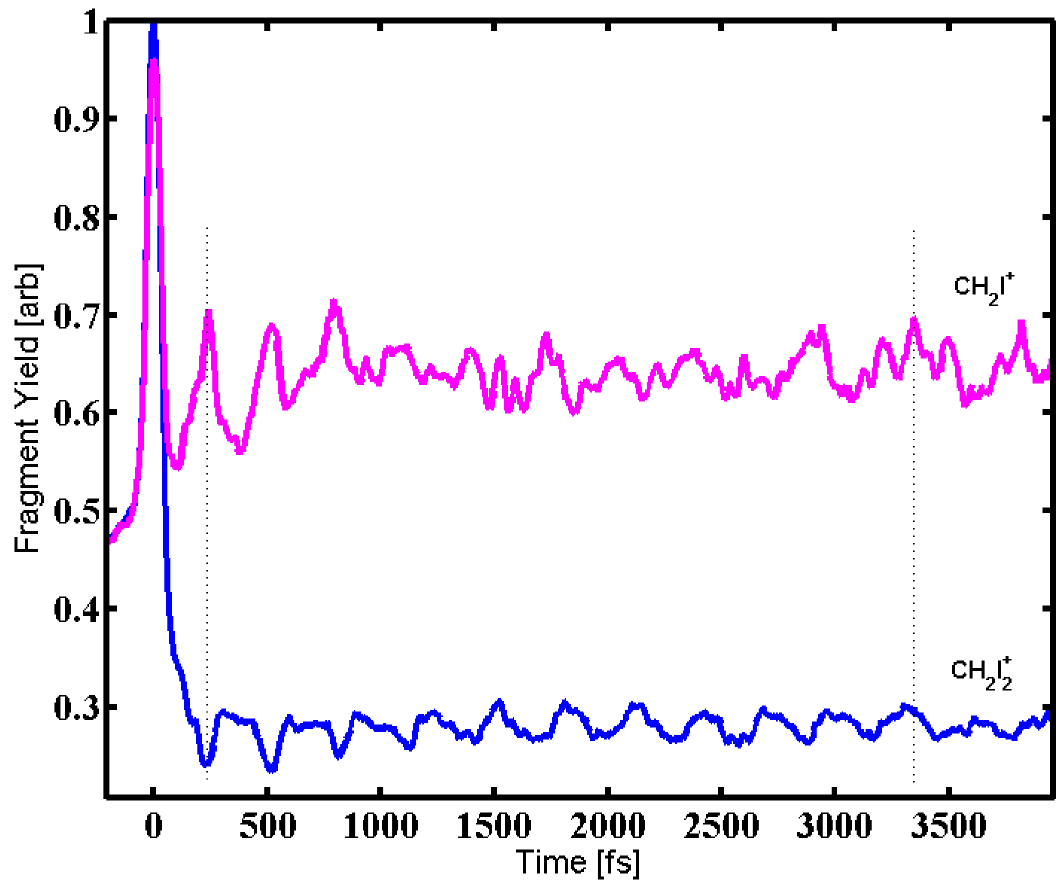
Similar to case of Na
- but here dynamics are
driven by nuclear motion

Oscillations & Bond Breaking

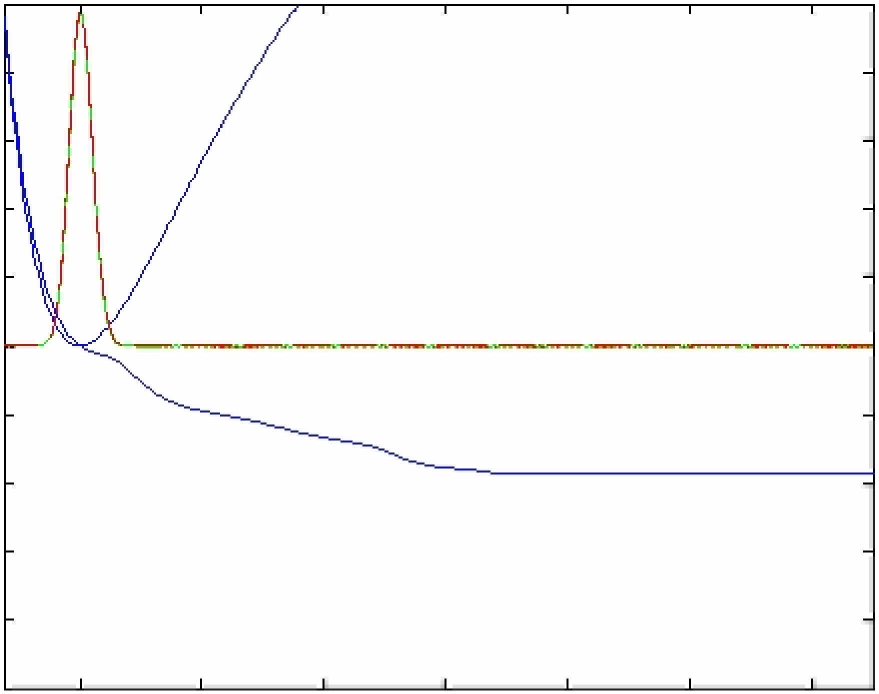


CH_2XY,
X,Y =
F, Cl, Br, I





Can We Measure ψ(t)?



$$\psi(t) = |\psi(t)| e^{-i\phi(t)}$$

$$\psi(t+\tau) = |\psi(t+\tau)| e^{-i\phi(t+\tau)}$$

$$\psi_{tot} = \psi(t) + \psi(t+\tau)$$

$$\psi_{tot}^{*}\psi_{tot} = |\psi(t)|^2 + |\psi(t+\tau)|^2 + 2|\psi(t)||\psi(t+\tau)|\cos[\phi(t) - \phi(t+\tau)]$$

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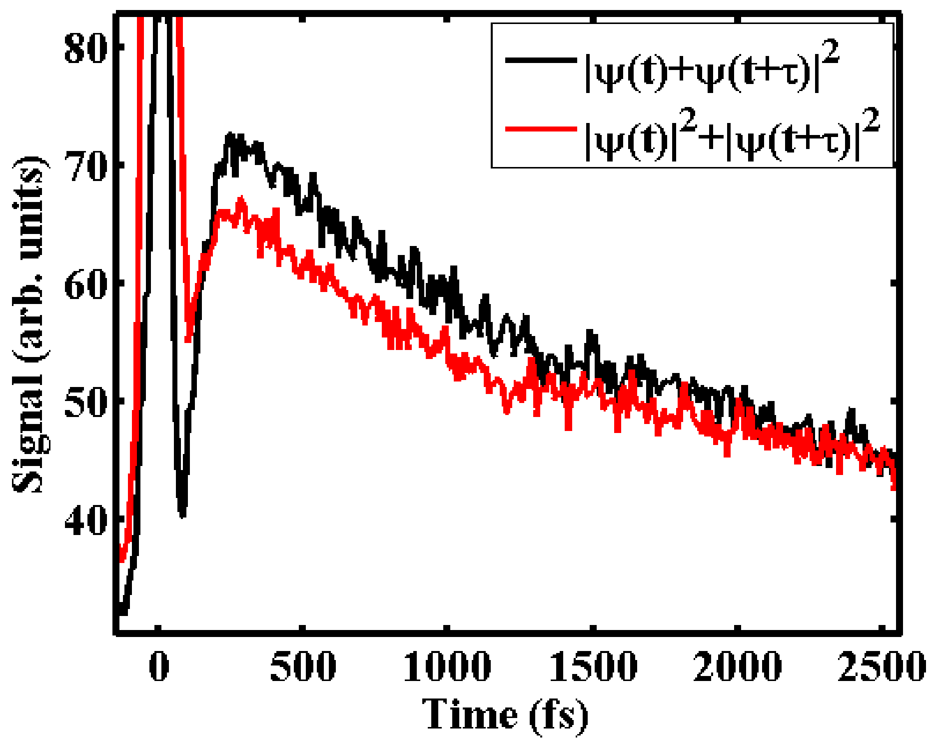
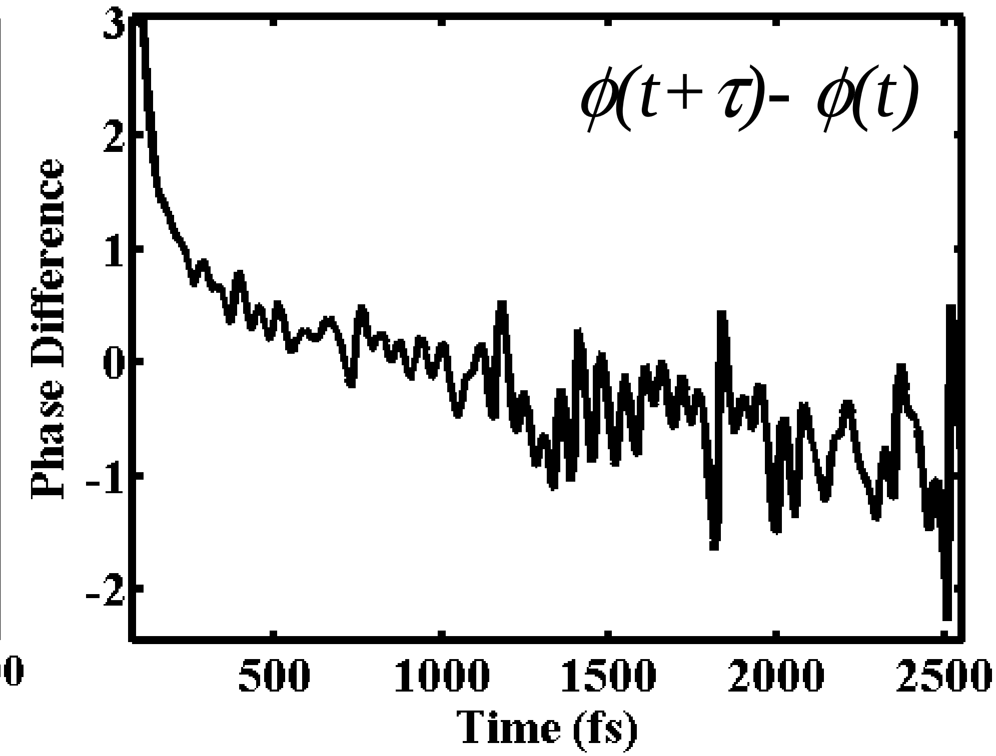
Measurement gives amplitude – Interference gives phase

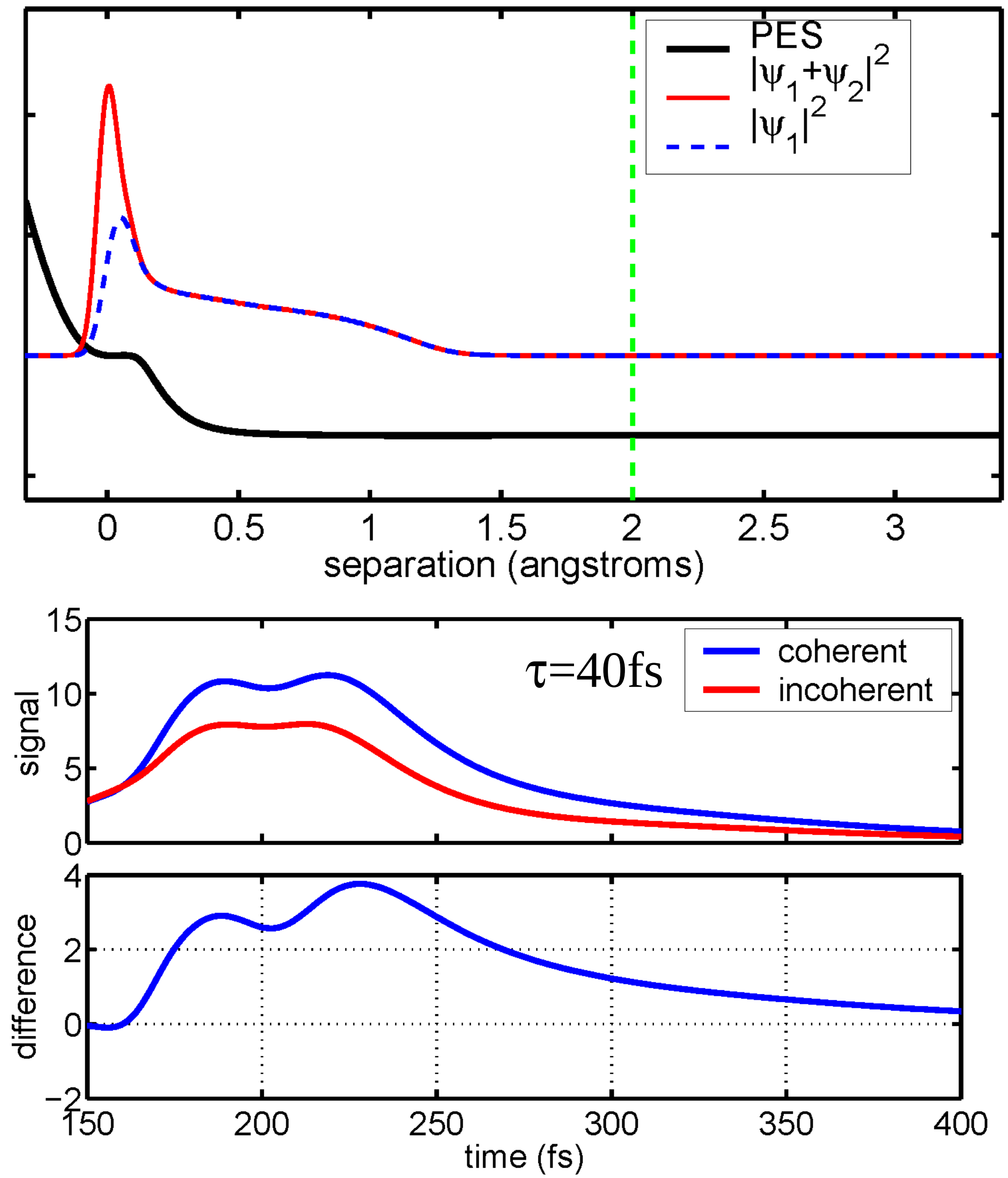
Preliminary Measurements





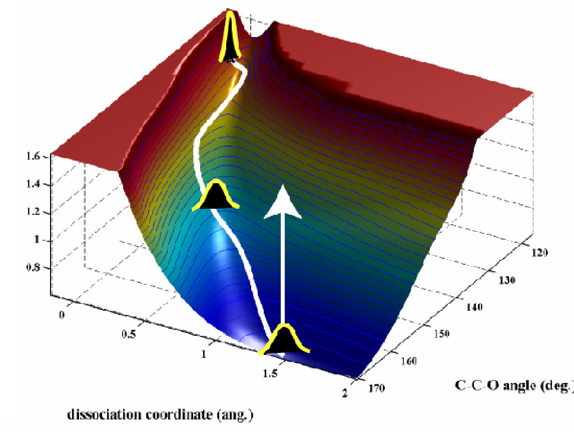
30 fs Pump-pump delay

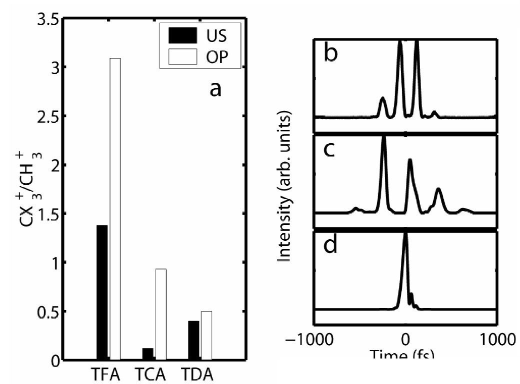
Wave Packet Simulations

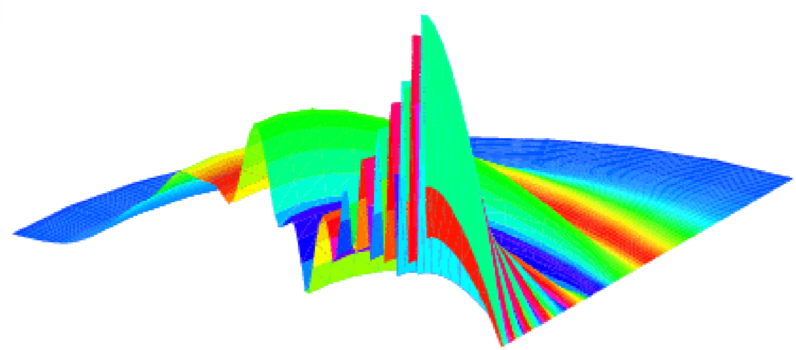


Conclusions & Future Directions

- Can *discover* and *understand* optimal pulse shapes for fragmentation
- See systematic behavior - ‘photonic reagents’
- En route to making molecular movies – measuring ψ(t)







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