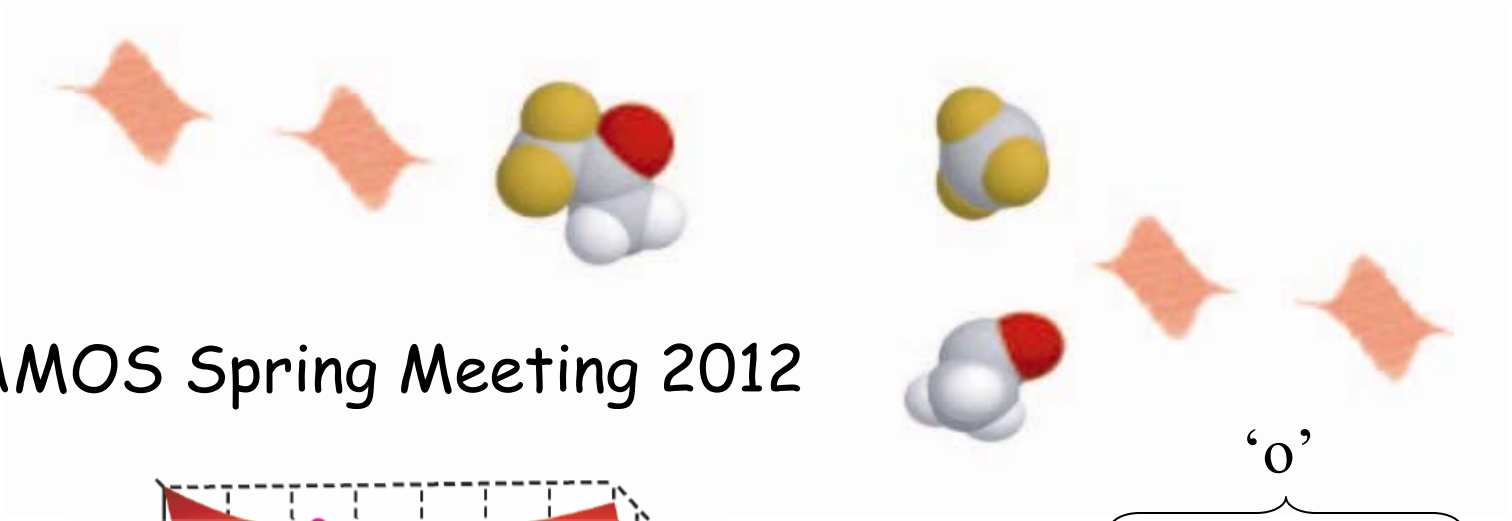
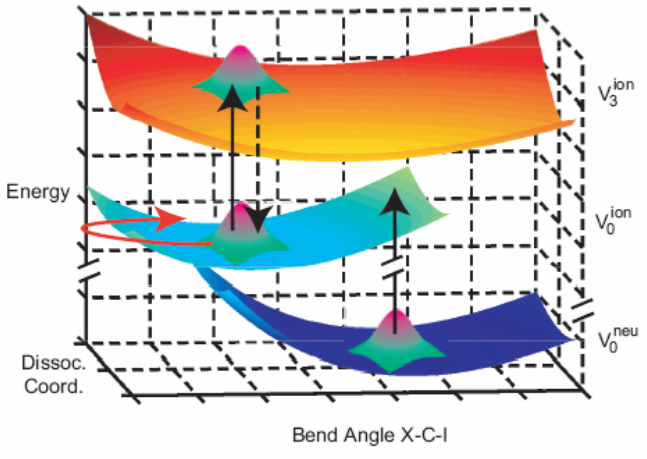
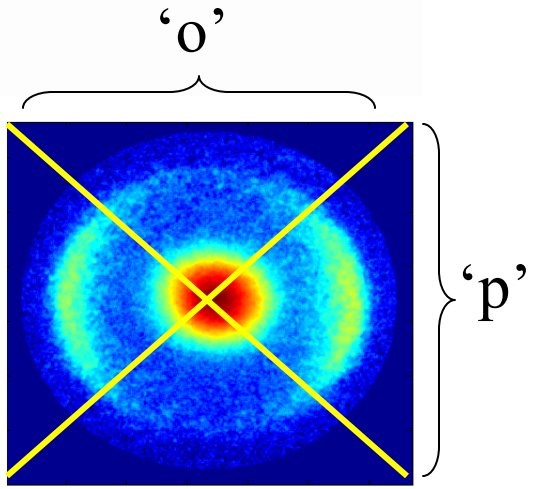
Strong Field Quantum Control



CAMOS Spring Meeting 2012





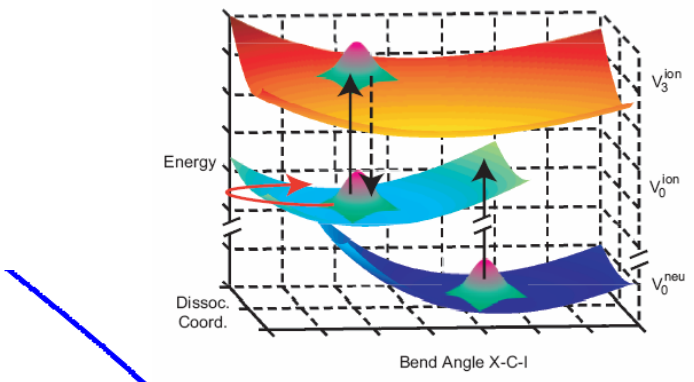
Motivation & Outline

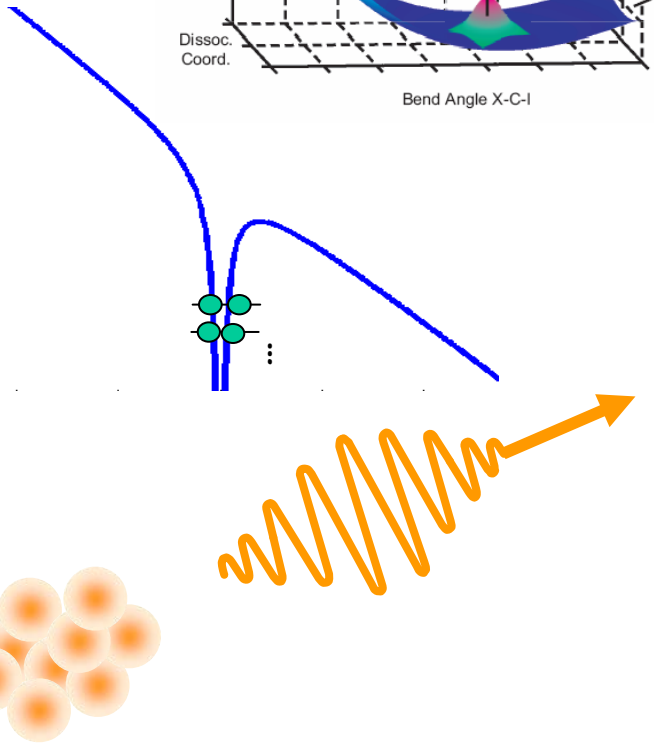
Motivation: Want to control molecular dynamics and develop control based spectroscopy

1. Controlling Molecular Dissociation
   - Closed loop control
   - Phase dependent dissociation

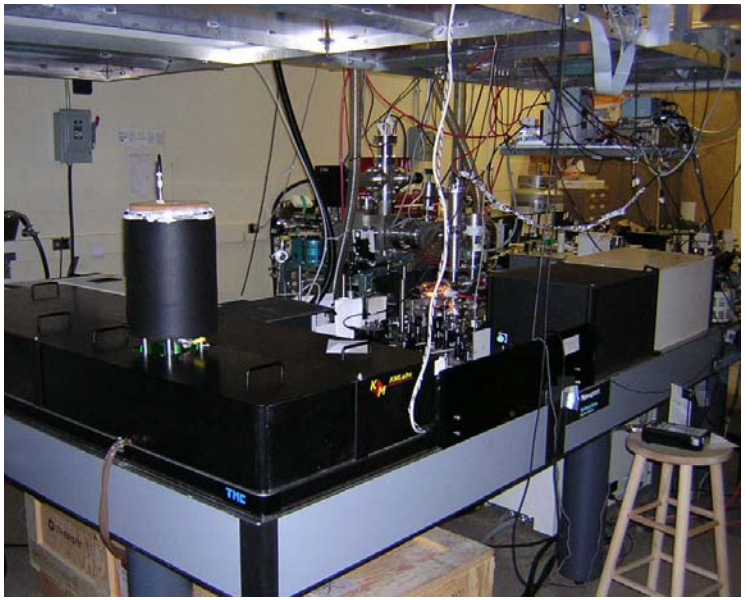
2. Controlling Molecular Ionization
   - Electronic hole wave packets
   - Pulse shape dependent ionization

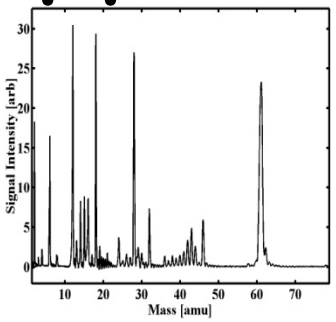
3. Control for Discrimination
   - Combine control & stimulated emission for 'perfect' discrimination
   - Quantum Control Spectroscopy





Molecular Fragmentation & Ionization Apparatus





Detector

Delay

Interaction region

Laser

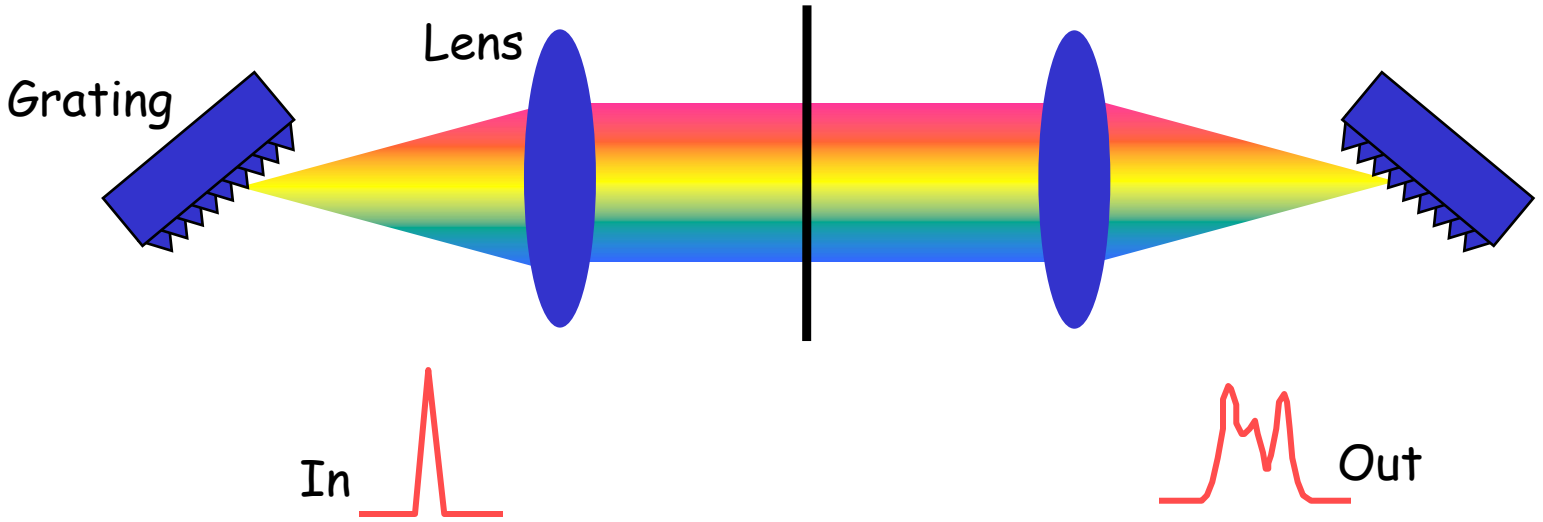
30 fs, 780 nm, 1kHz

Pulse Shaper

Computer w/ GA

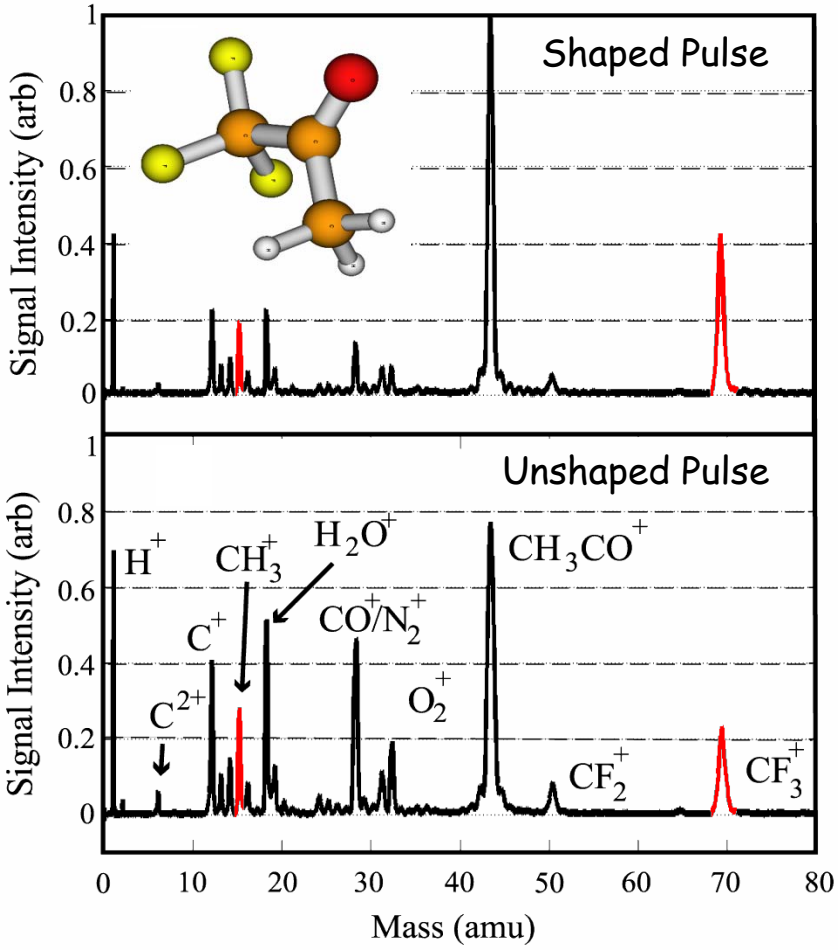
Ultrafast Optical Pulse Shaping

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

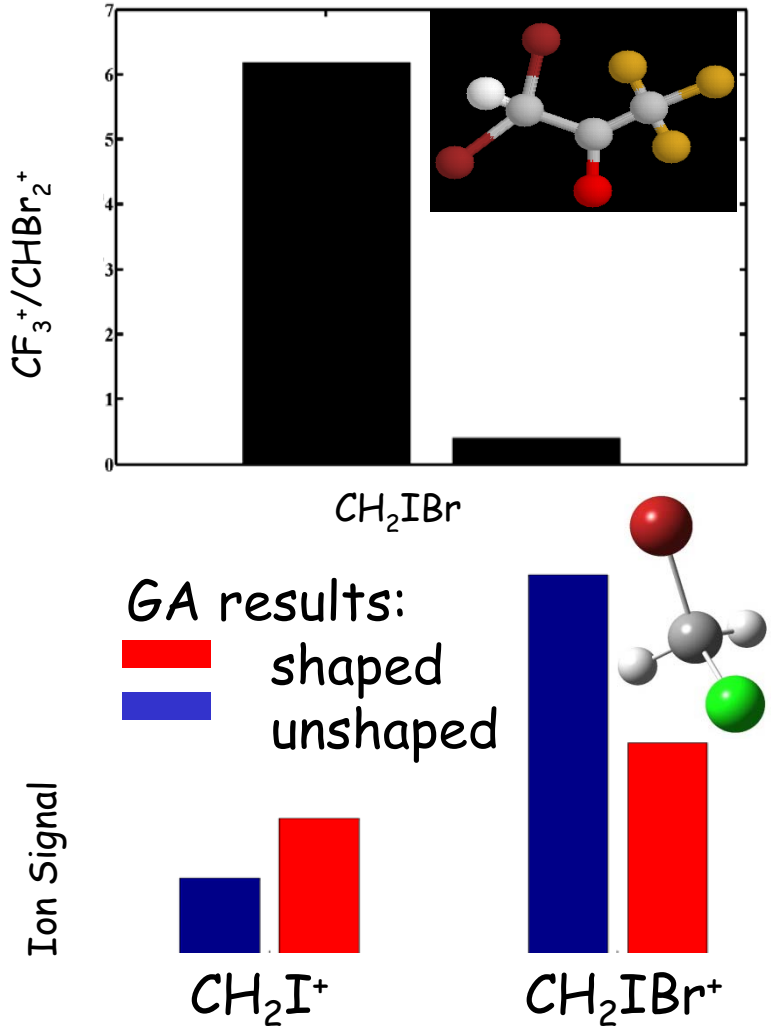


Closed Loop Molecular Control Results

CH_3COCF_3



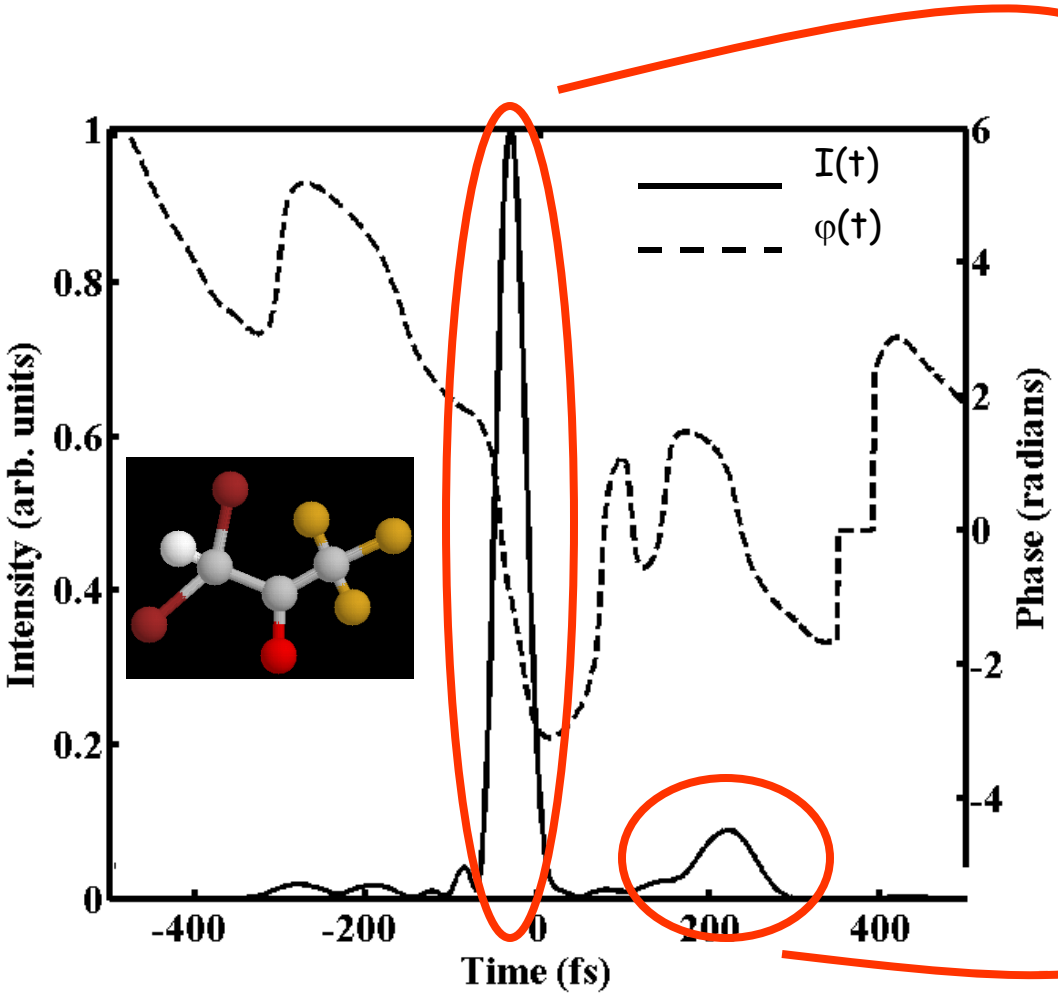
$CHBr_2COCF_3$



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

J. Chem. Phys. **127**, 131101 (2007)

Optimal Control Pulses

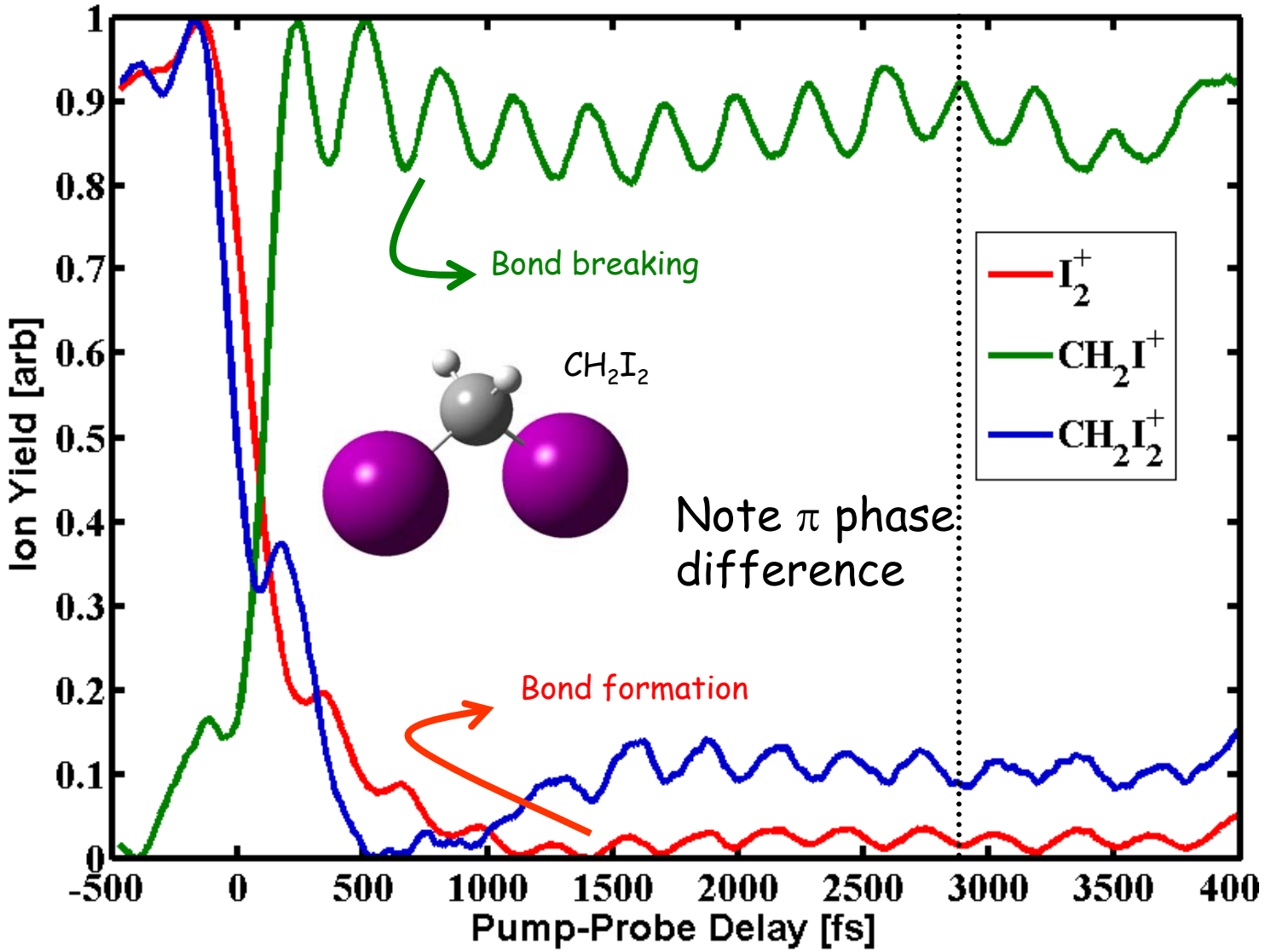


First sub-pulse 'pumps' (launches) wave packet

Second sub-pulse 'dumps' the wave packet

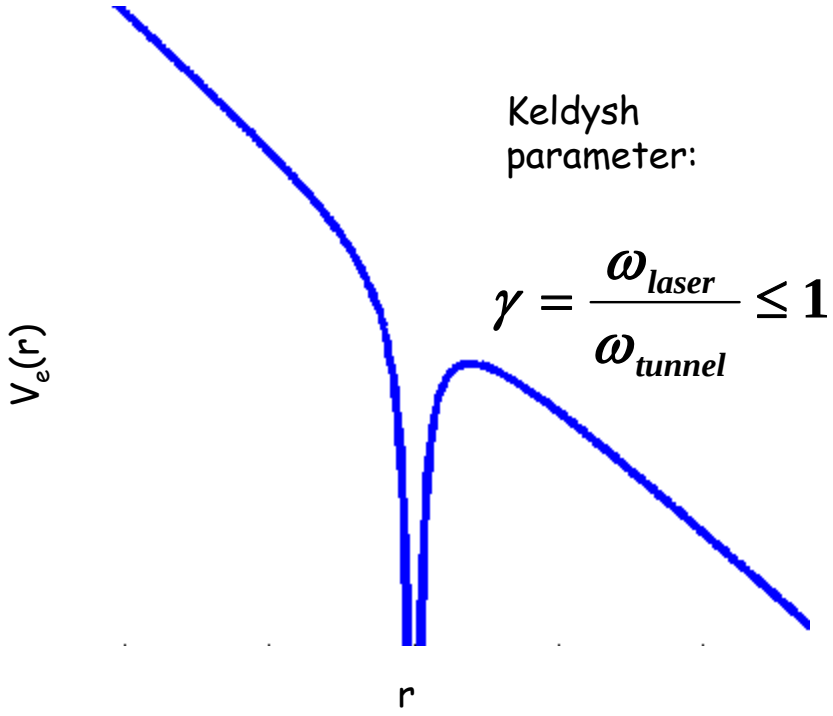
J. PhotoChem.& PhotoBio. A **180**, 277 (2006)

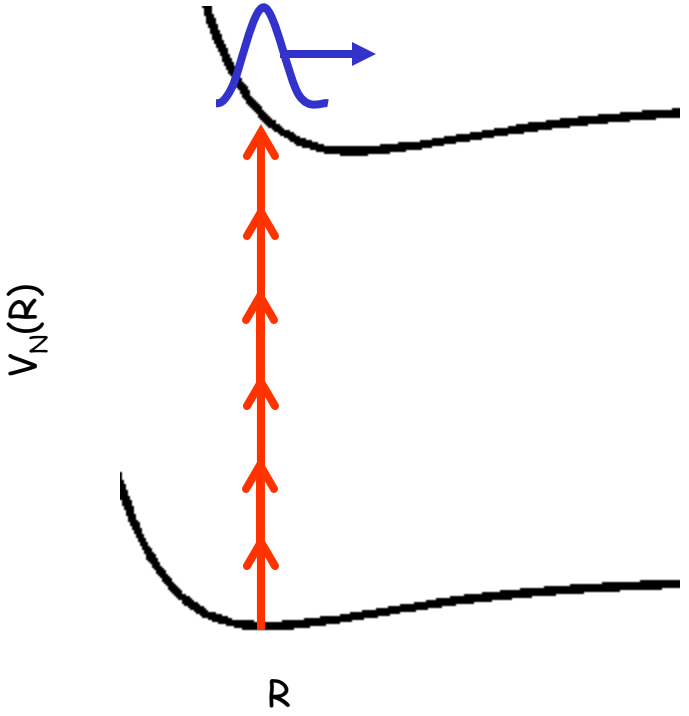
Pump-Probe Measurements: CH_2I_2



J. Chem. Phys. **127** 204305 (2007)

Strong Field Ionization (Pump)





Electron can tunnel out in a fraction of laser cycle – 'quasi static'

Ionic equilibrium doesn't overlap with neutral – launch wave packet

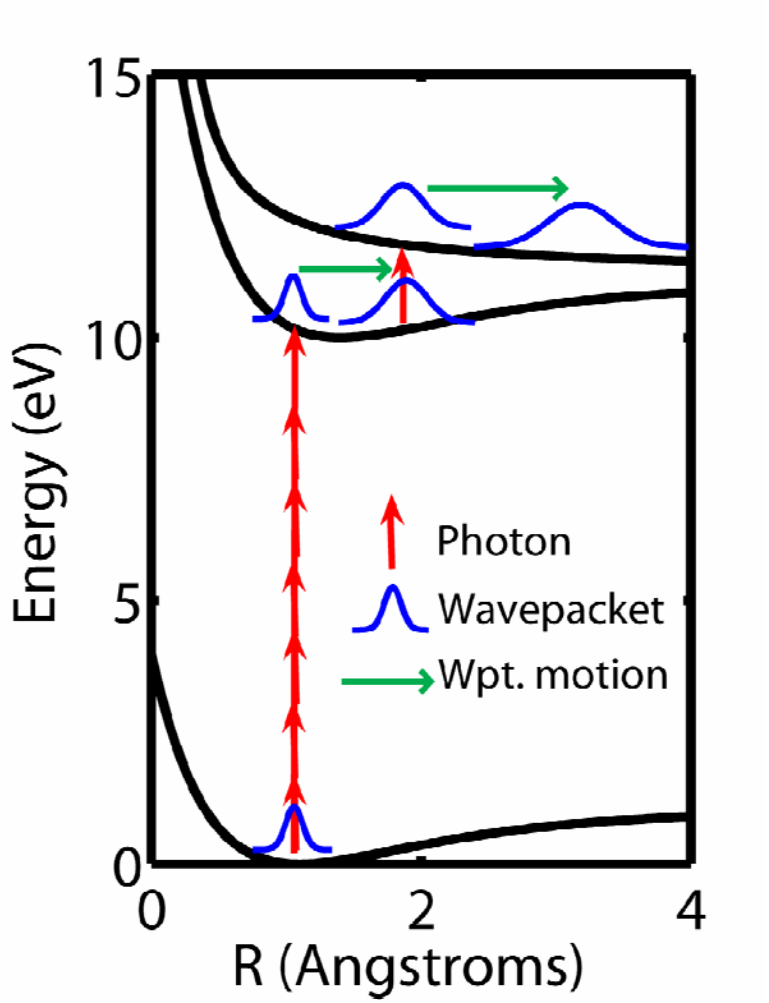
Resonant Dissociation (probe)

- Small molecules with many electrons can have 1-2 eV resonances in molecular ion

- Low excitation energy – 'moving hole around' in the ion

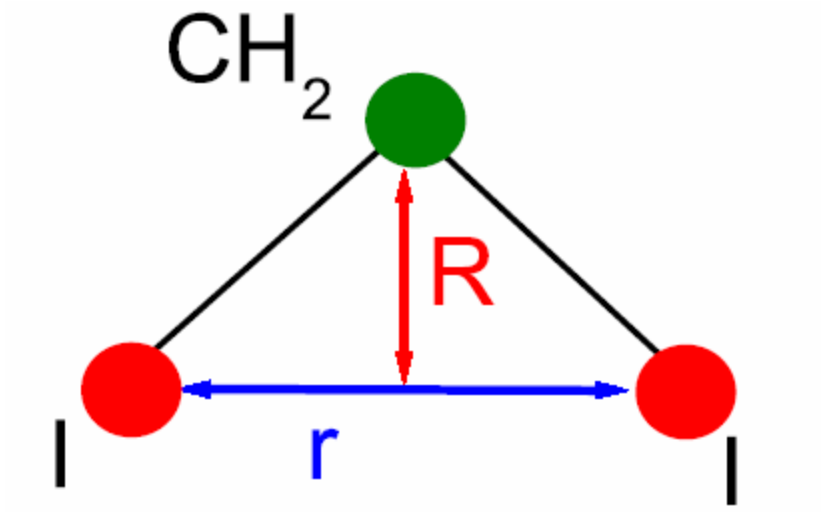
- Wave packet moves (and spreads)

- Can be transferred to dissociative excited state by probe pulse

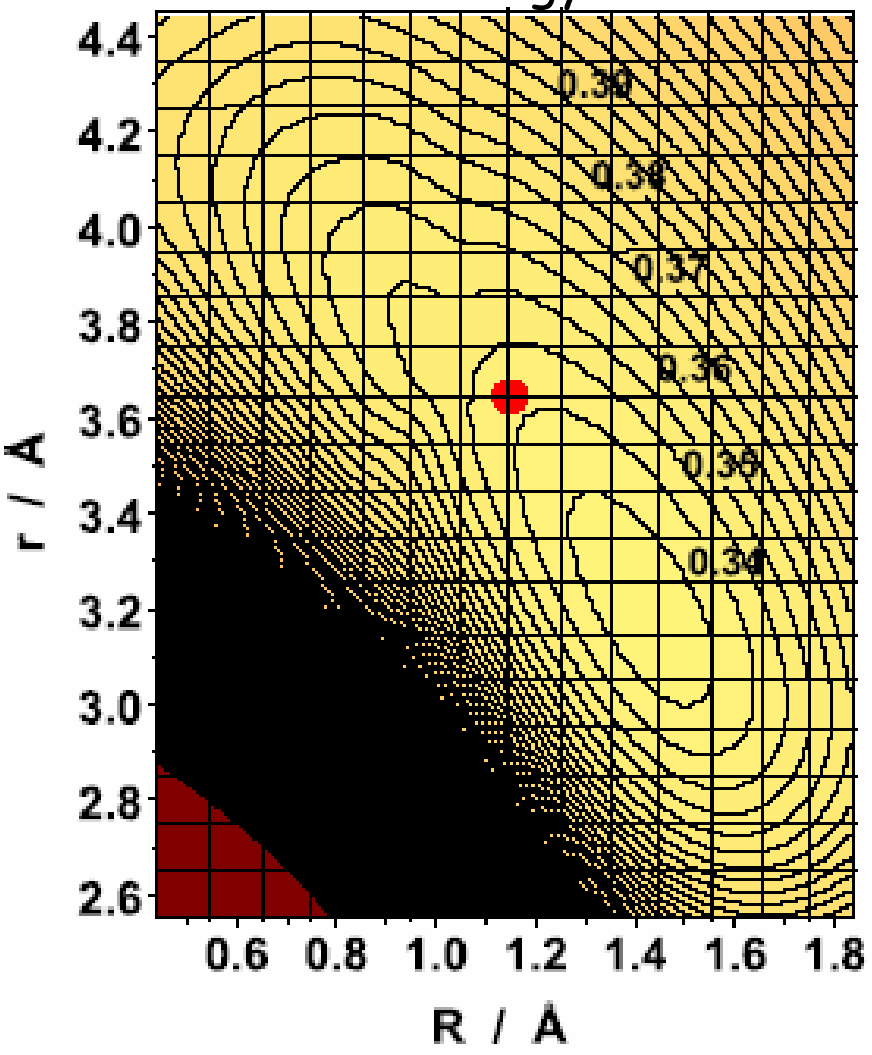


J. Chem. Phys. **127**, 131101 (2007)

Interpreting The Dynamics CH_2I_2

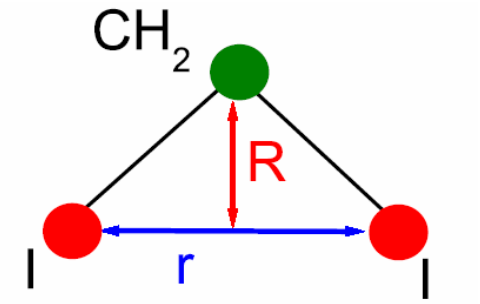


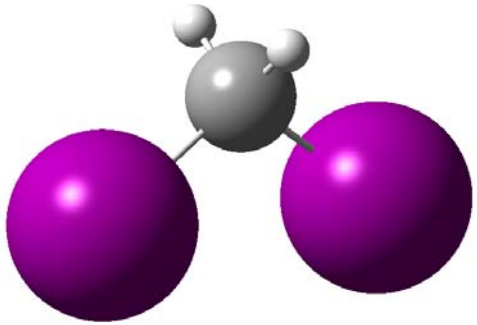
2D Bending, Stretching
Potential Energy Surface

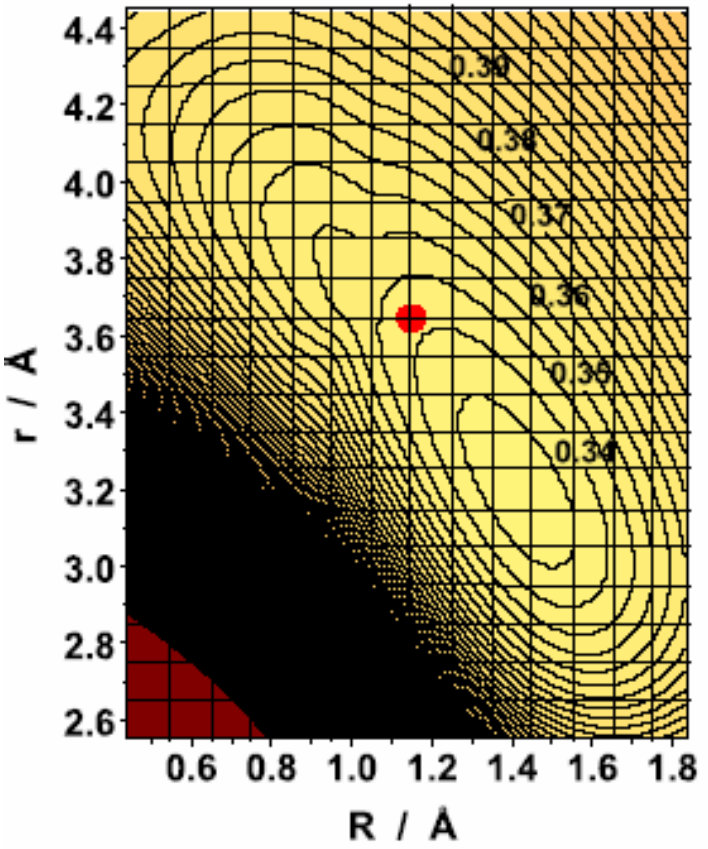


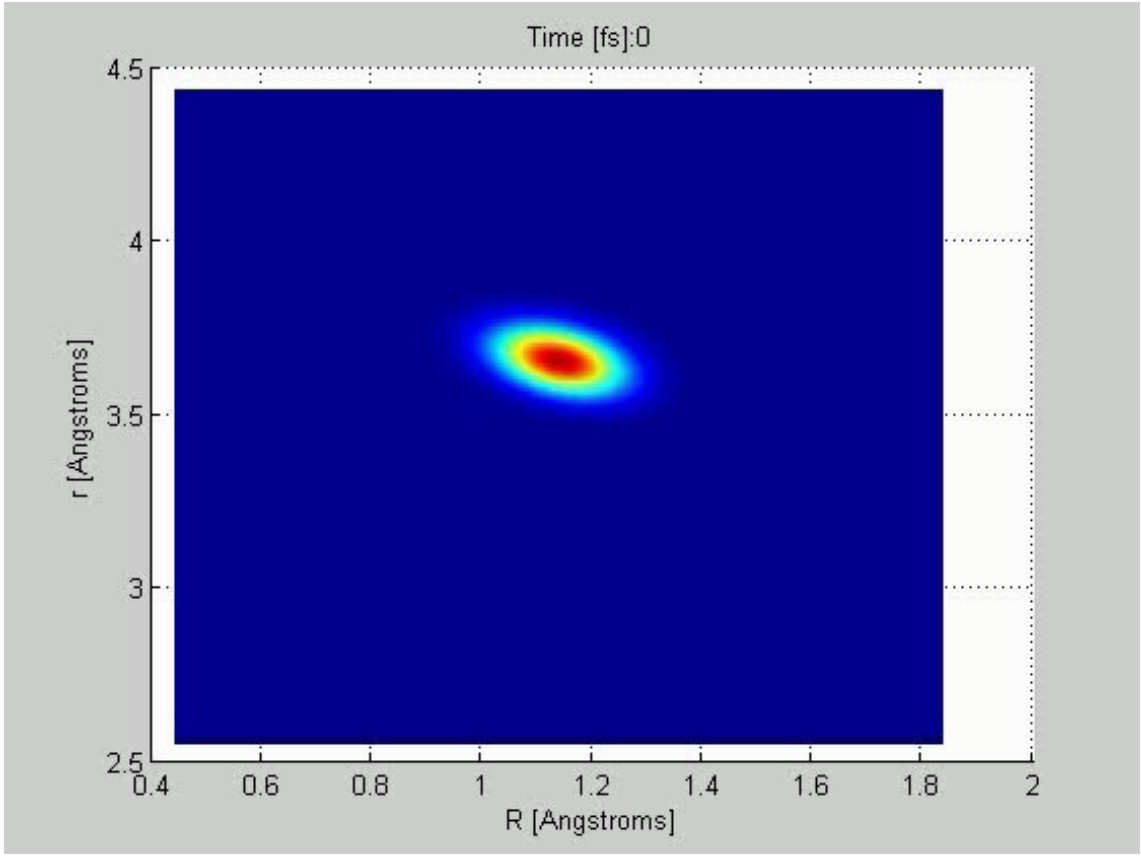
PES calculated by Tamás Rozgonyi,
Hungarian Academy of Sciences

Wave Packet Dynamics

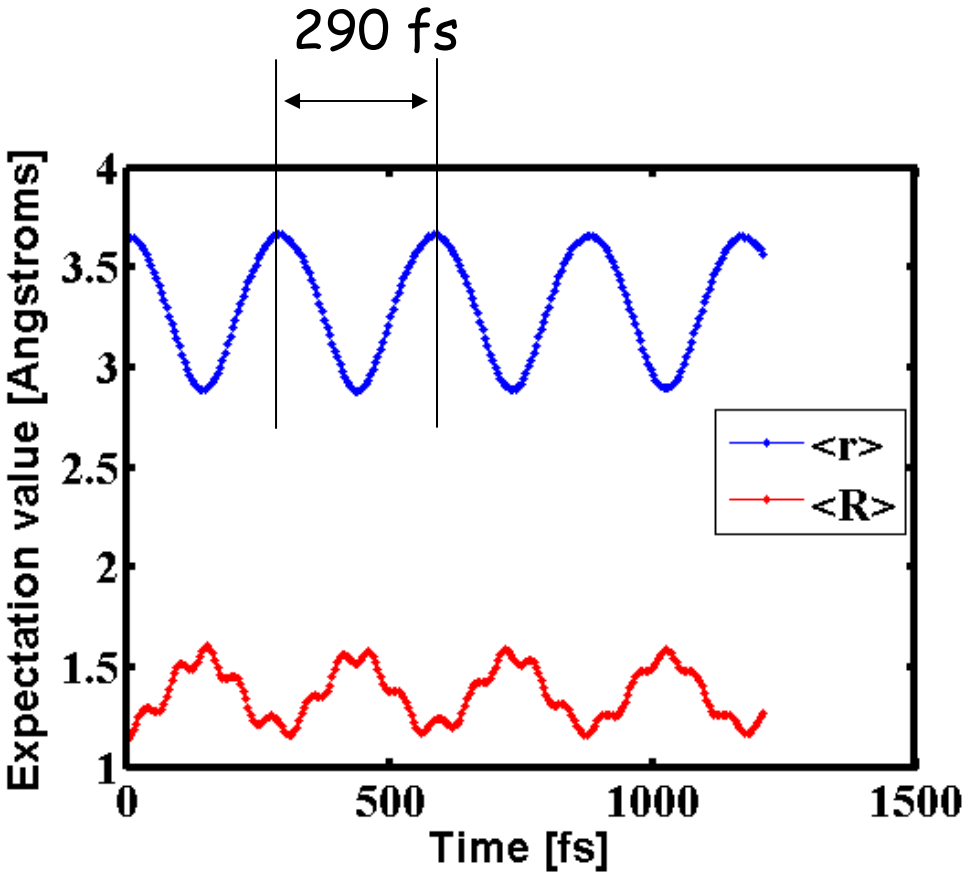




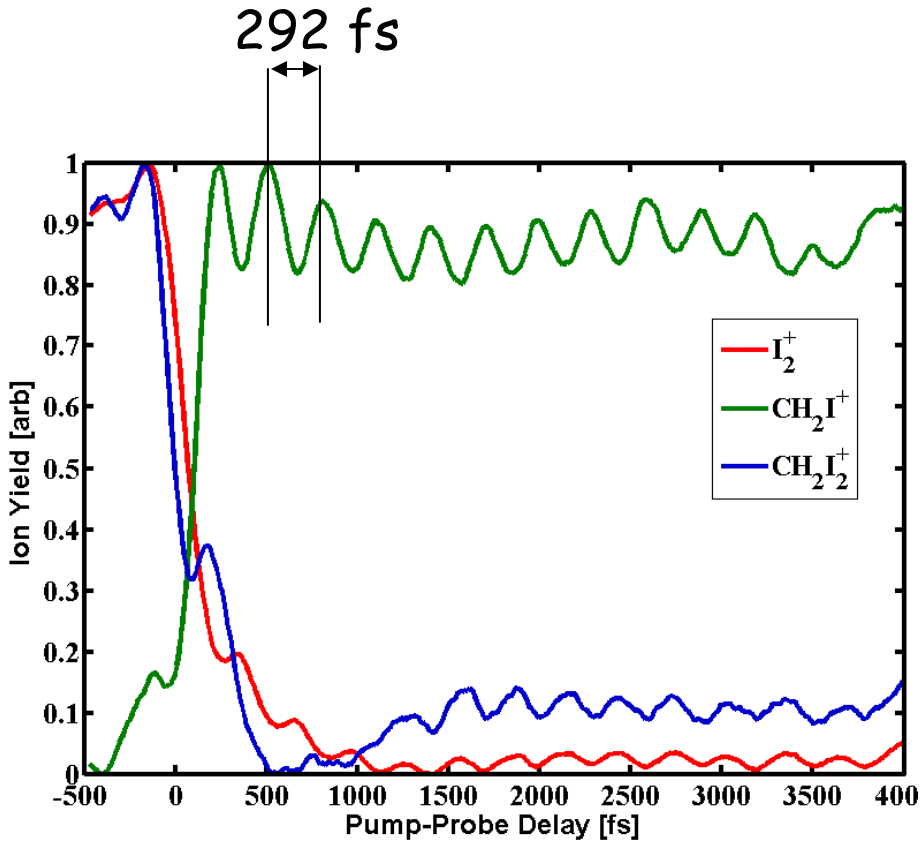




Comparing Experiment with Calculated Dynamics

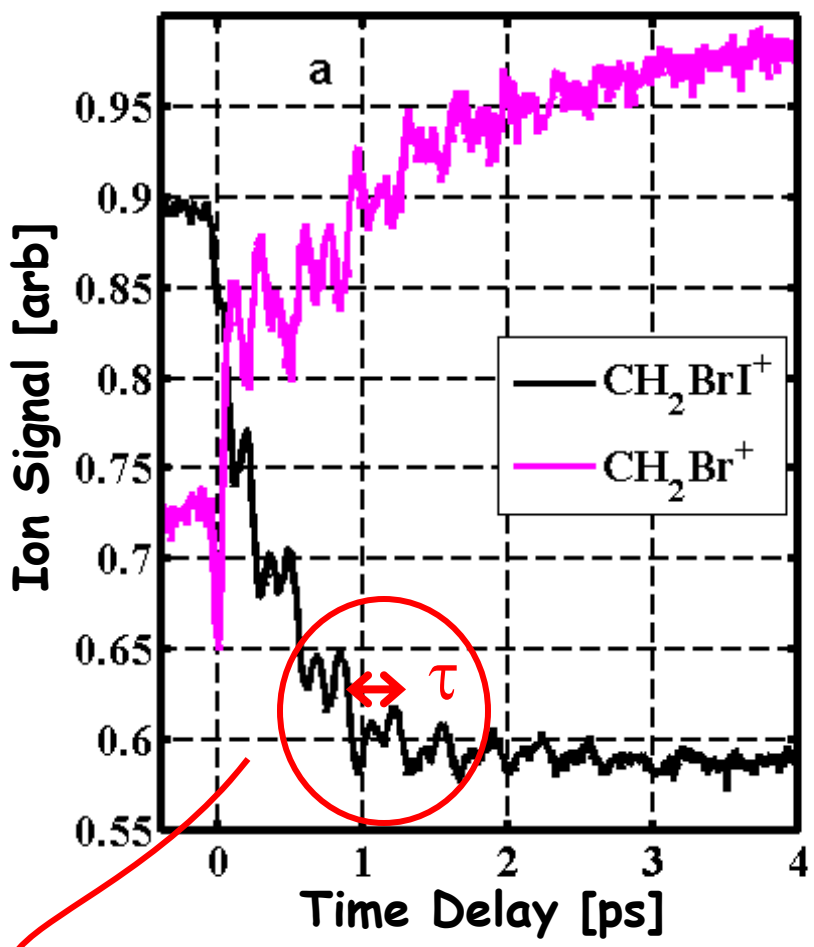


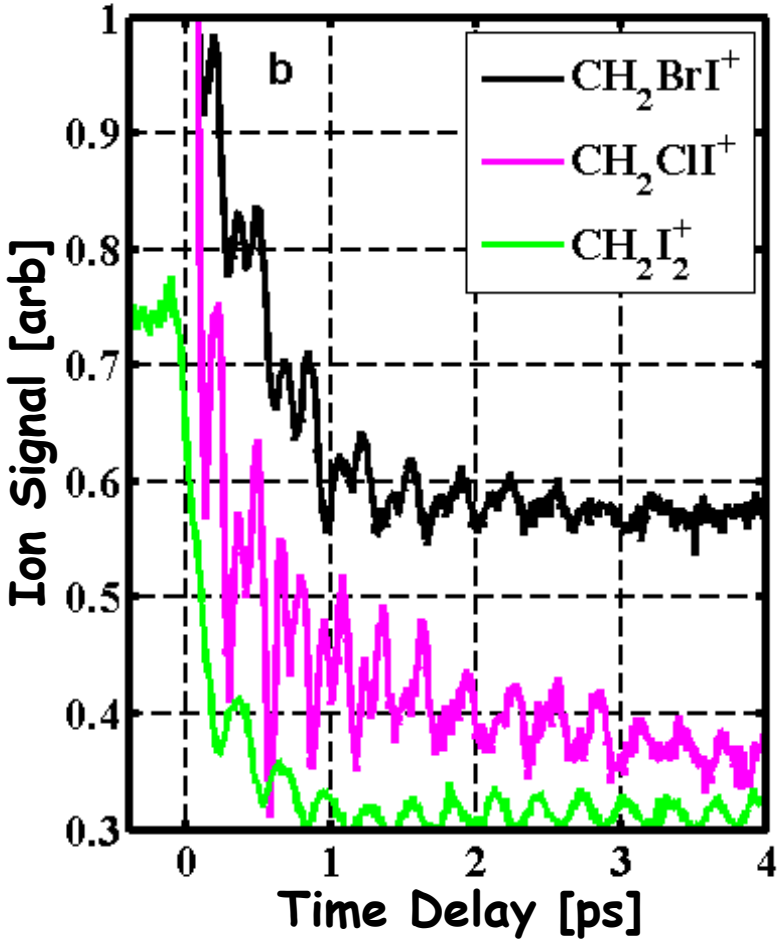
Wave packet calculations



Pump-probe measurements

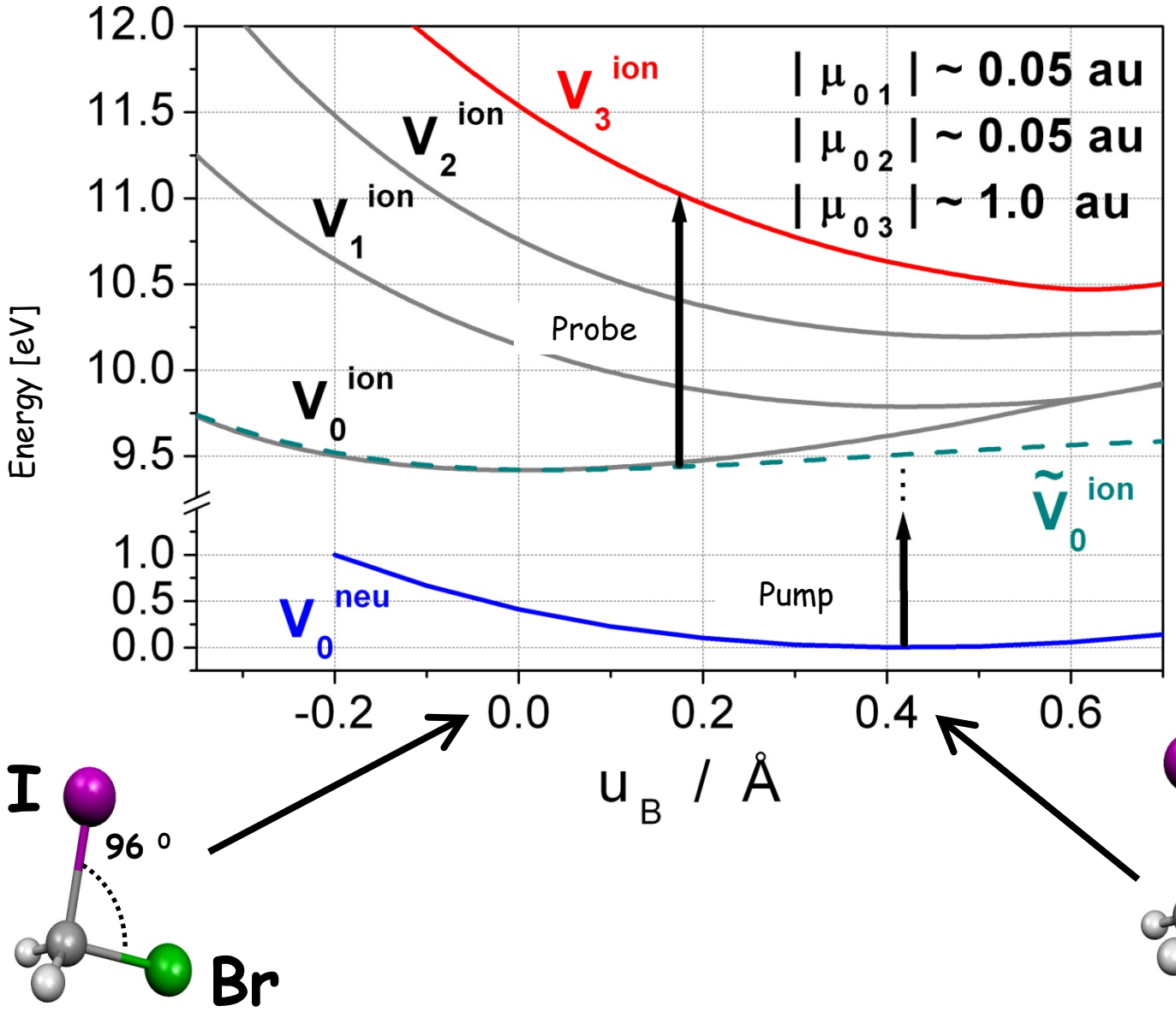
What Happens if we Break the Symmetry of the Molecule?: CH_2IBr





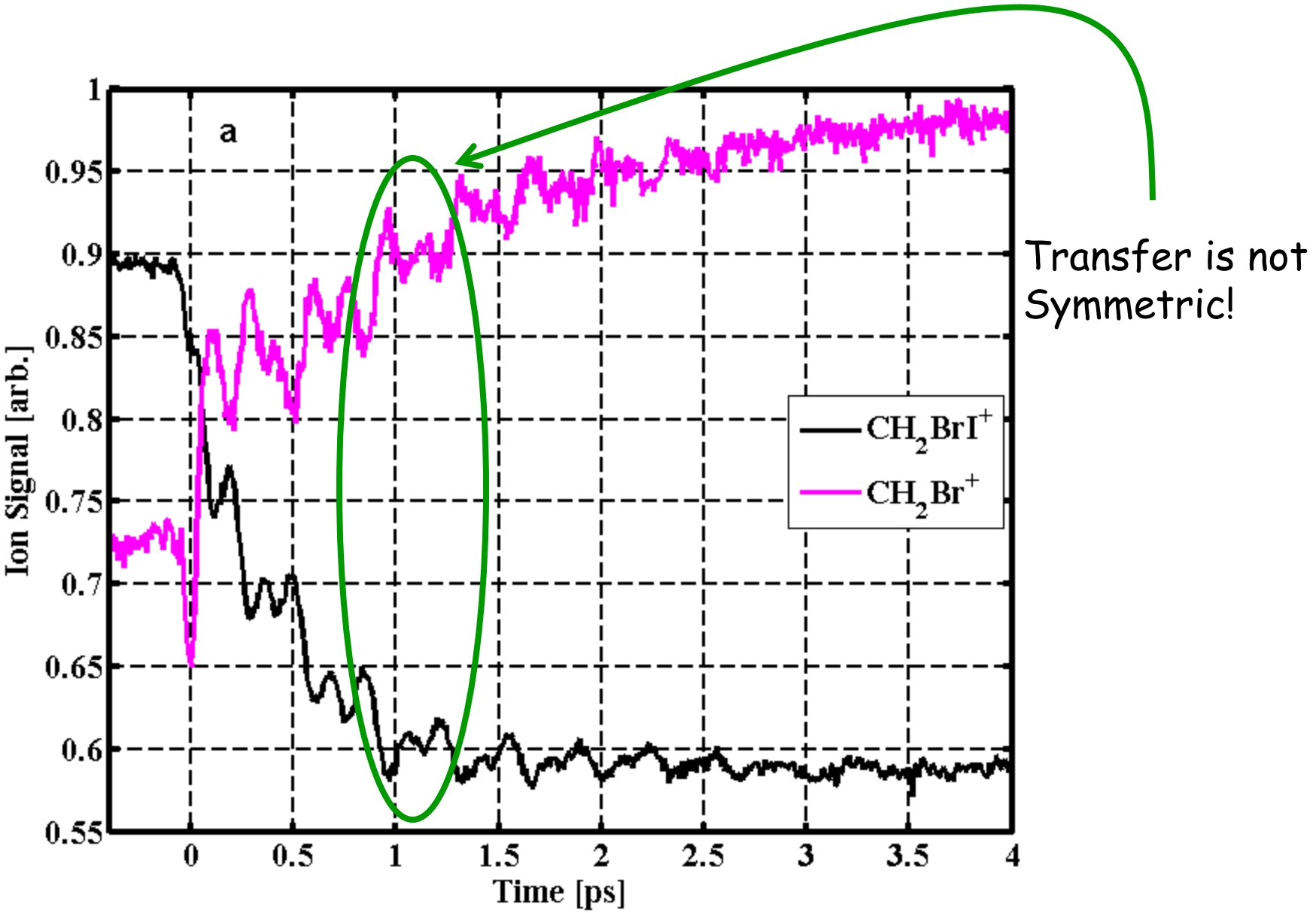
Note two (unequal) oscillations per vibrational period!

Potential Energy Curves for CH_2IBr^+

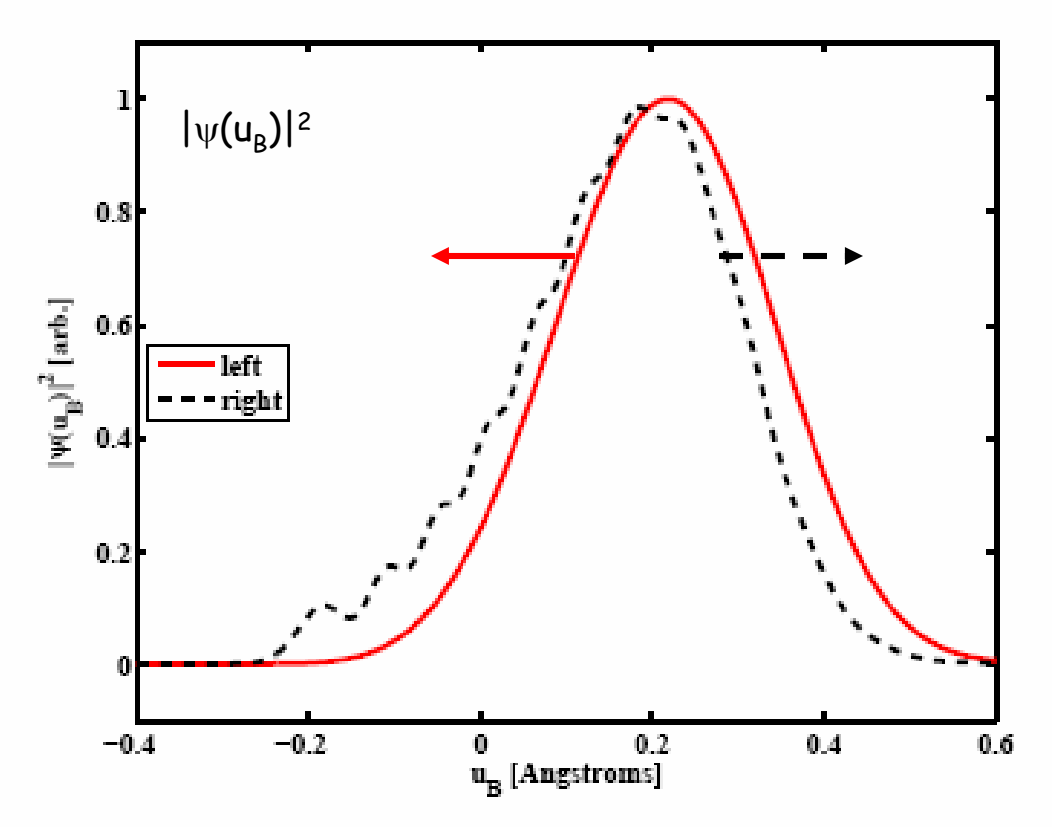


V_3^{ion} is dissociative

Displacement along other coordinates is very small


a
Ion Signal [arb.]
Time [ps]
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0
0.5
1
1.5
2
2.5
3
3.5
4
CH2BrI+
CH2Br+
Transfer is not
Symmetric!

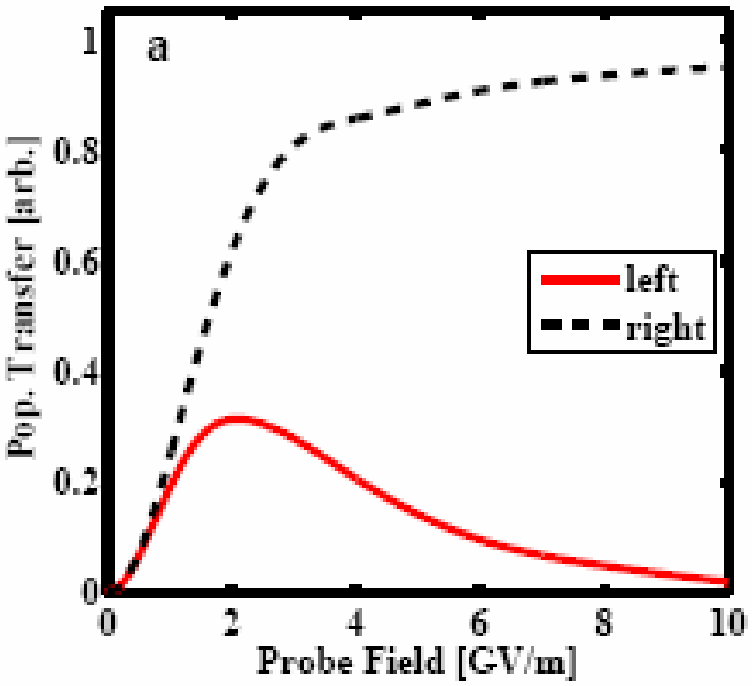
Does Dissociation Depend on Phase or Amplitude?



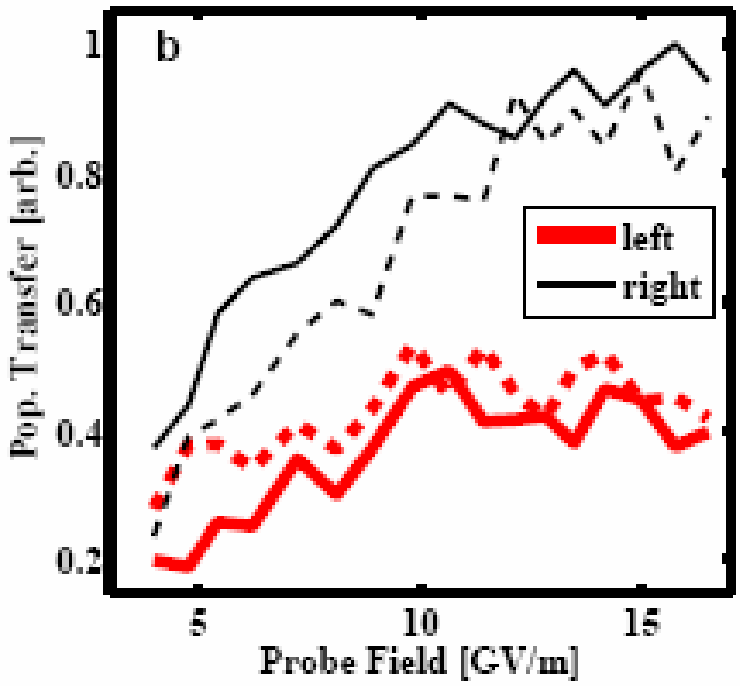
Left and right going wave packets have the same amplitude

Intensity Dependence

Calculation

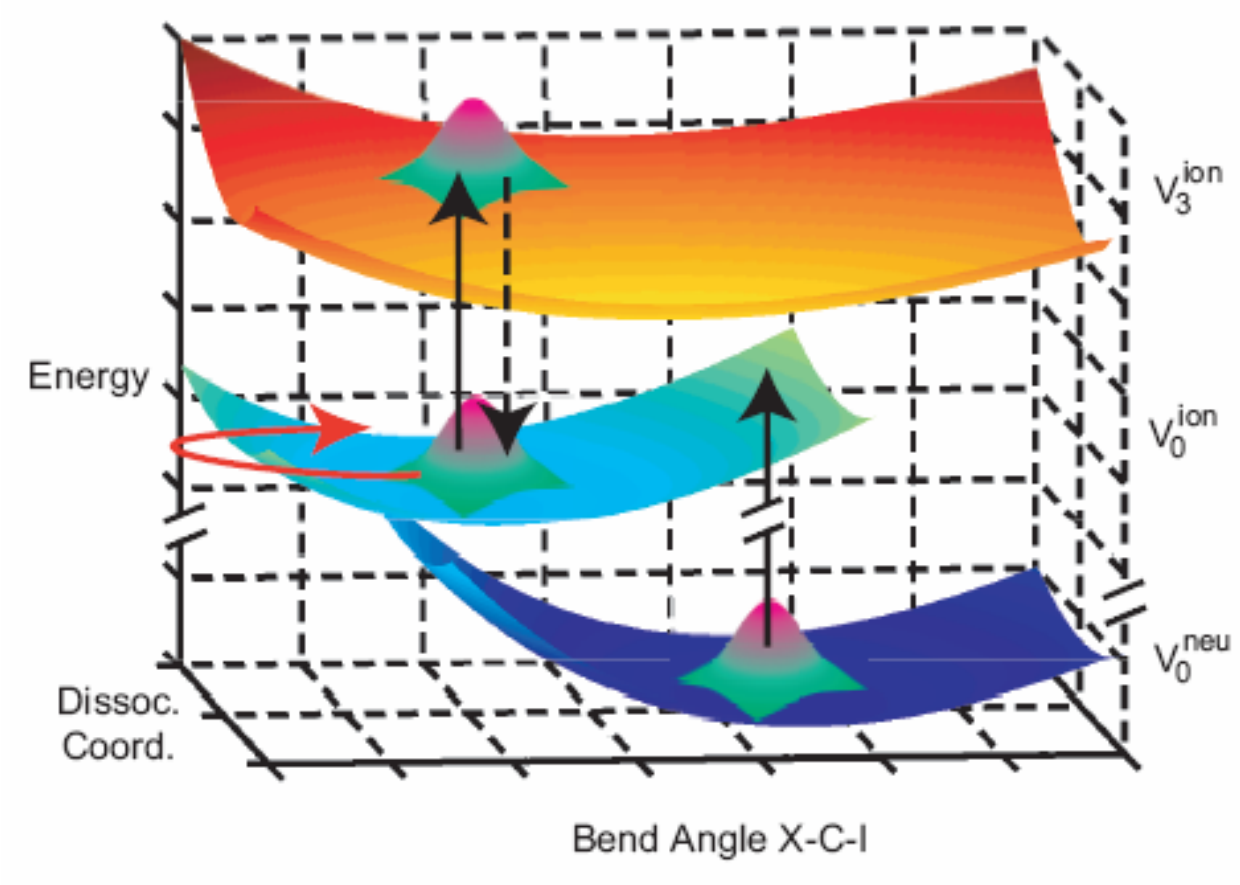


Experiment



- Molecule is transparent for left going wave packet in large fields!
- Accounting for intensity volume averaging leads to excellent agreement between experiment and theory

Picturing the Dynamics



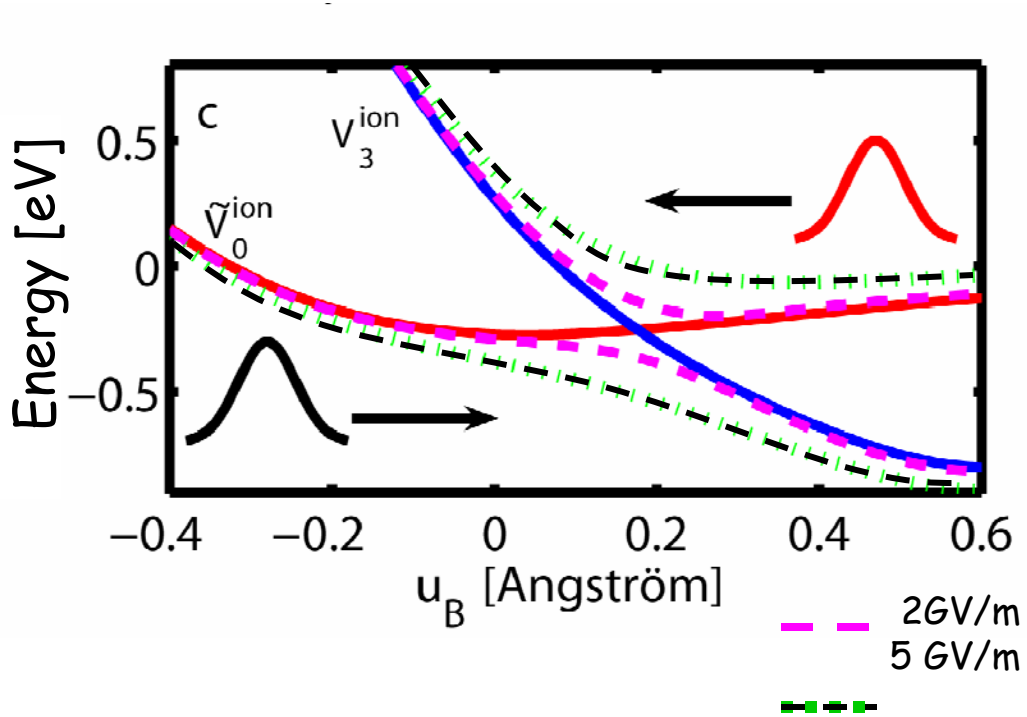
Physical Review A 79 043407 (2009)

Understanding the Dynamics: 'Dressed States'

Diagonalize:

$$\begin{bmatrix} V_3^{ion}(R) - h\nu_{probe} & \frac{\mu_{03}E_{probe}}{\hbar} \\ \frac{\mu_{03}E_{probe}}{\hbar} & V_0^{ion}(R) \end{bmatrix}$$

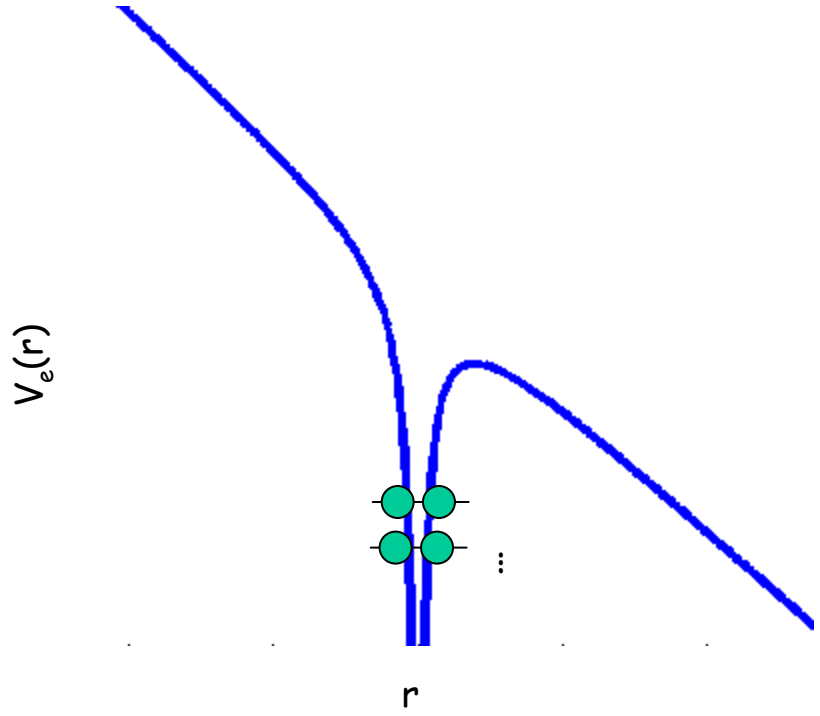
Laser molecule interaction



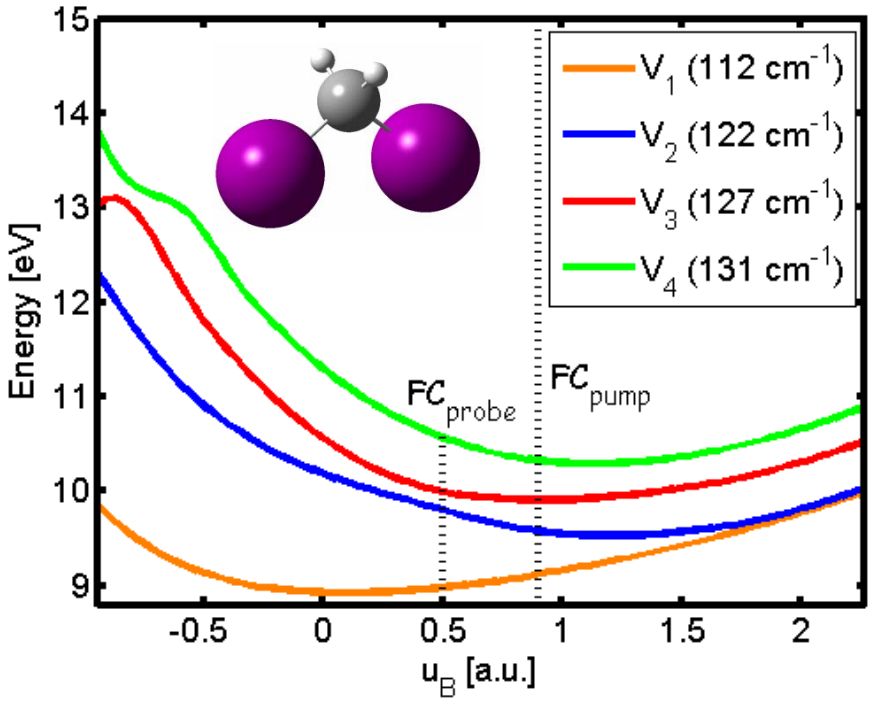
Dissociation depends on:

- Strong laser field 'dressing' the potentials
- Spatially varying *phase* of the wave function

Revisiting Molecular Ionization (CH_2I_2)

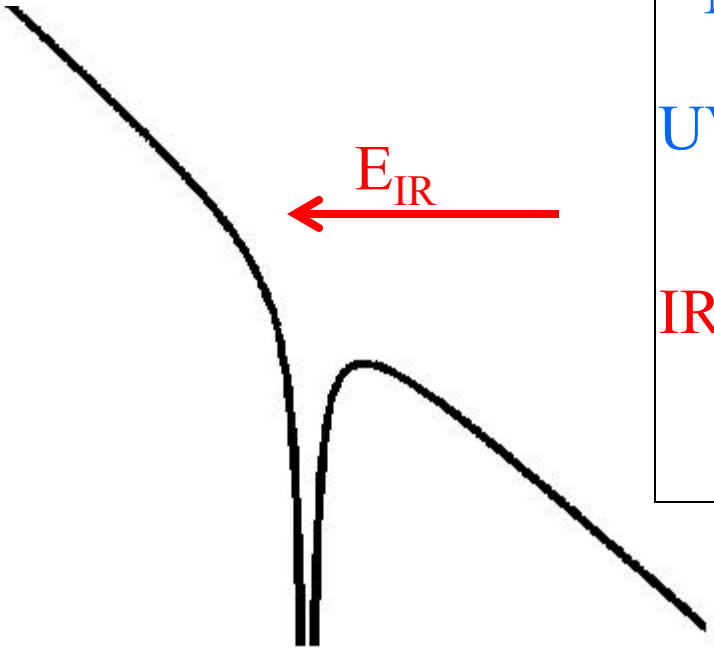


Molecule with many electrons…
Lots of electrons to choose from



Multiple low lying electronic states
with comparable tunneling rates

Comparing Weak and Strong Field Ionization

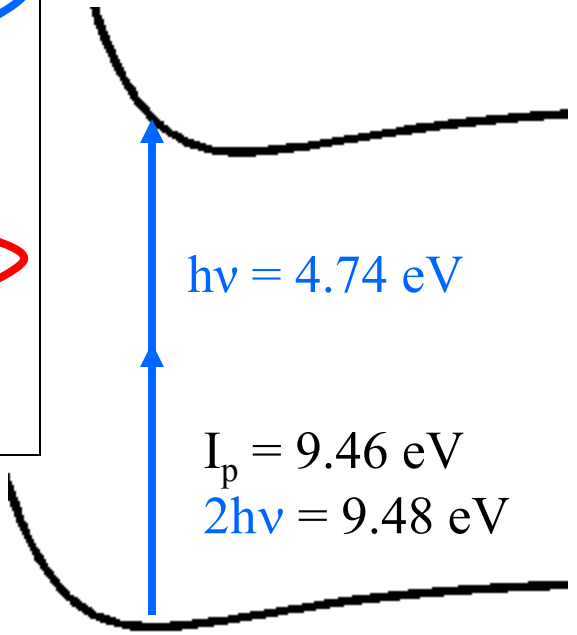


'Multiphoton'

UV $\gamma = \frac{\omega_{laser}}{\omega_{tunnel}} \sim 10$

IR $\gamma = \frac{\omega_{laser}}{\omega_{tunnel}} \sim 1$

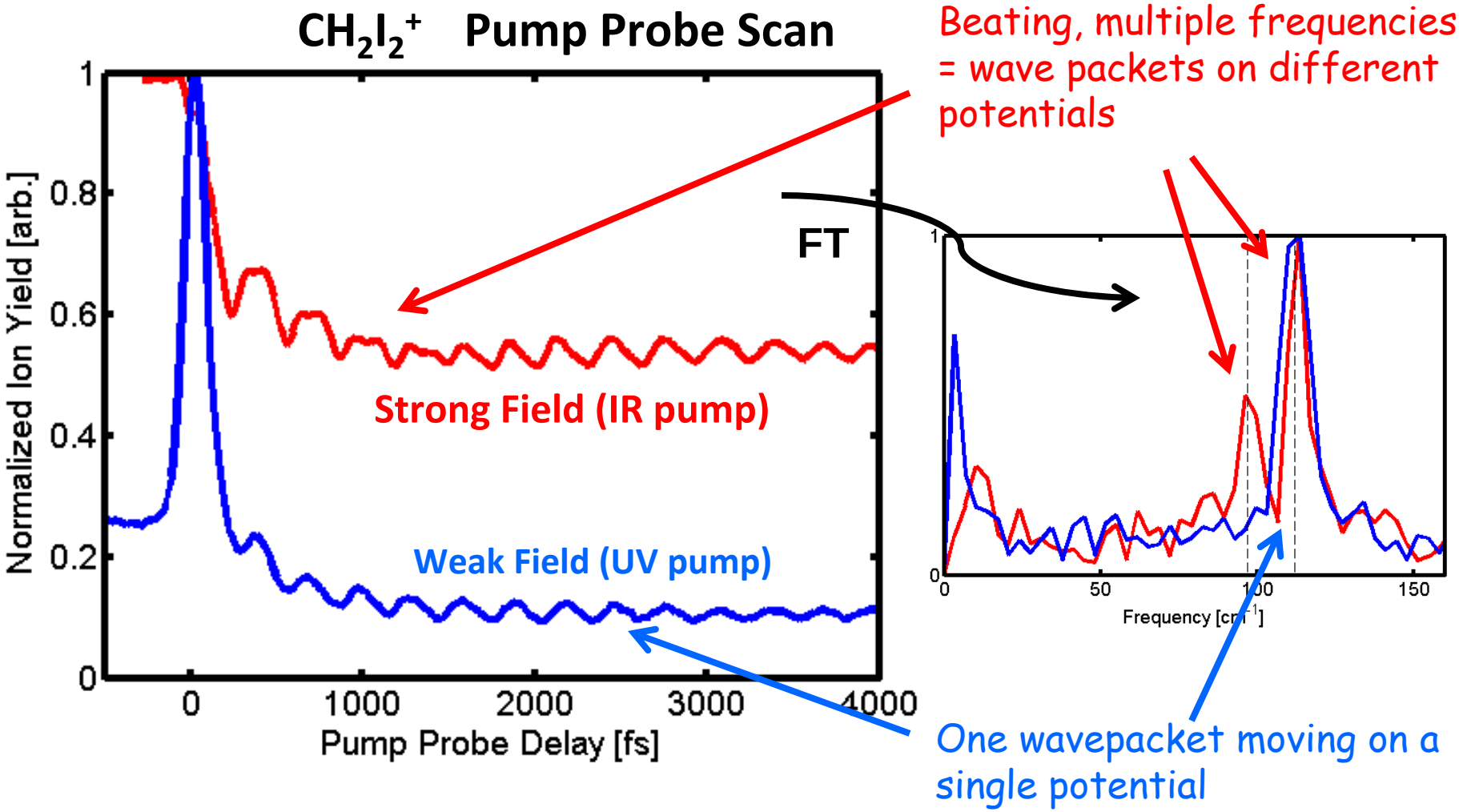
Tunnel + Multiphoton



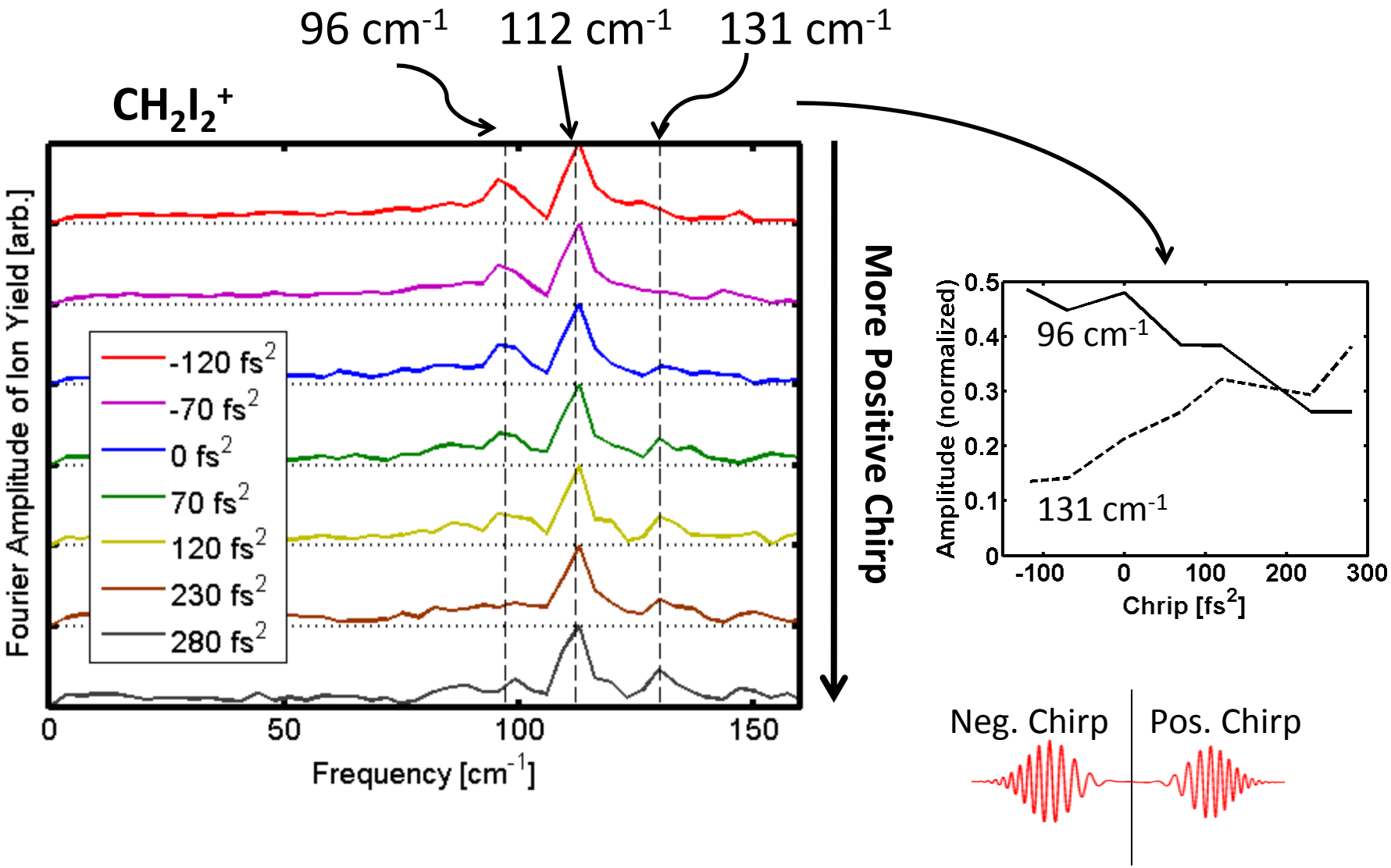
Strong Field IR Ionization (Tunneling)

Weak Field UV Ionization ('Multiphoton')

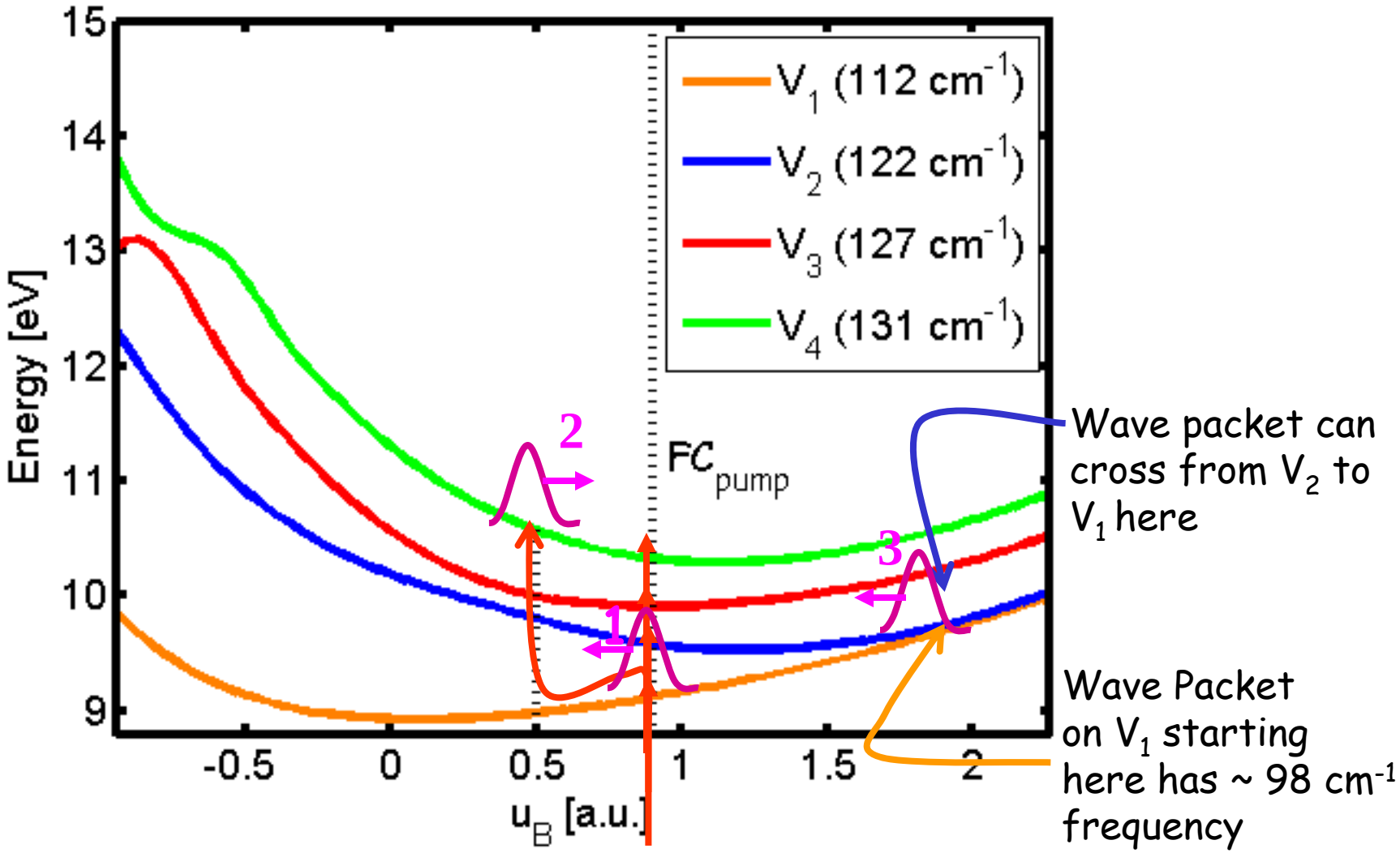
Strong vs Weak Field Ionization



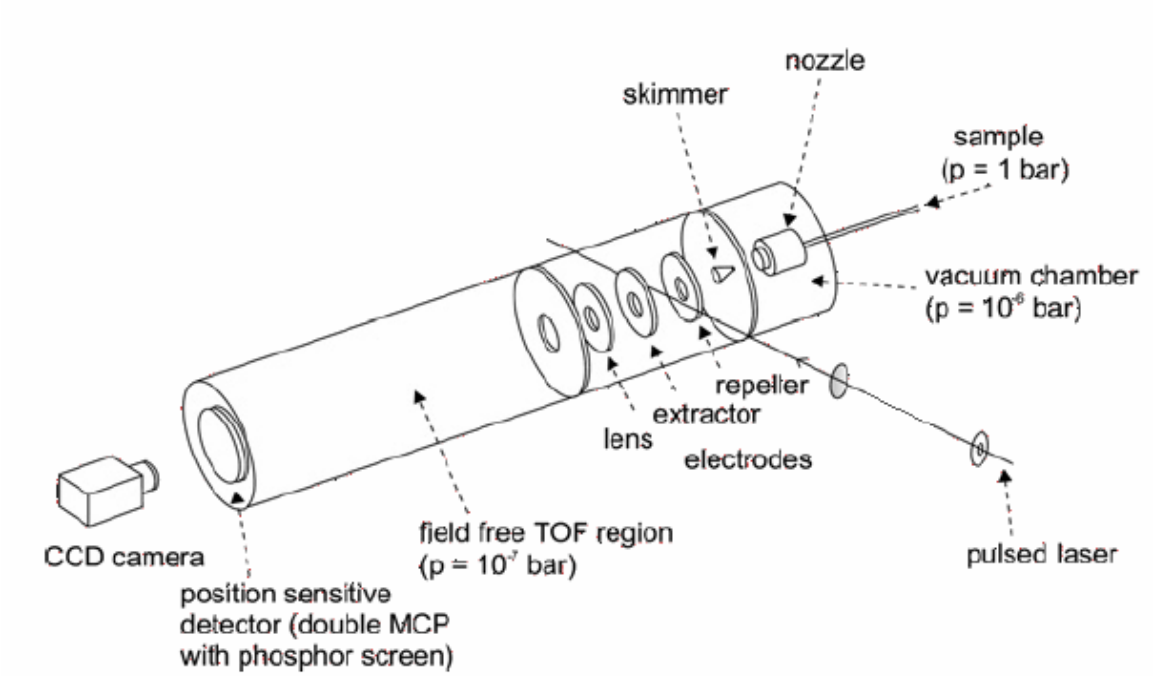
Multiple Electronic States Controlled by Chirp

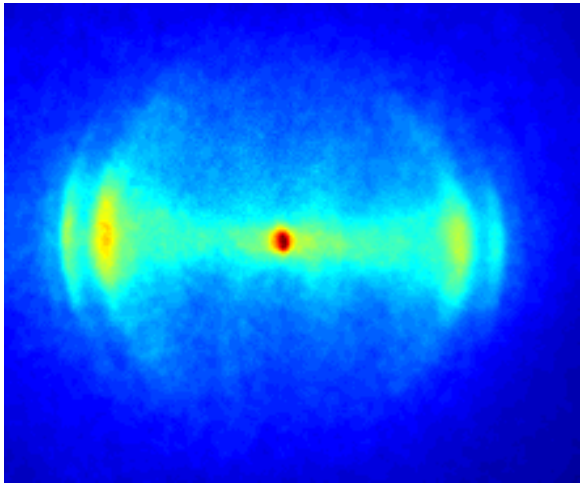


Different Frequencies Correspond to Different Ionic States Excited by Pump

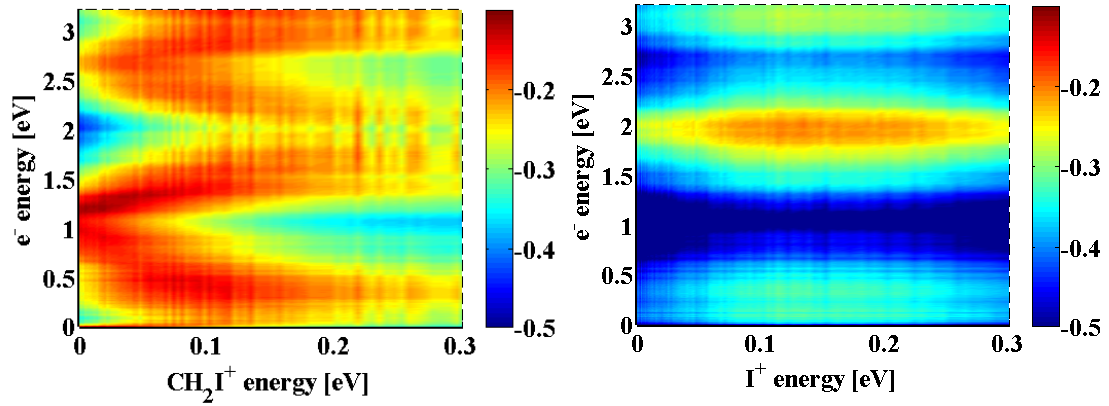


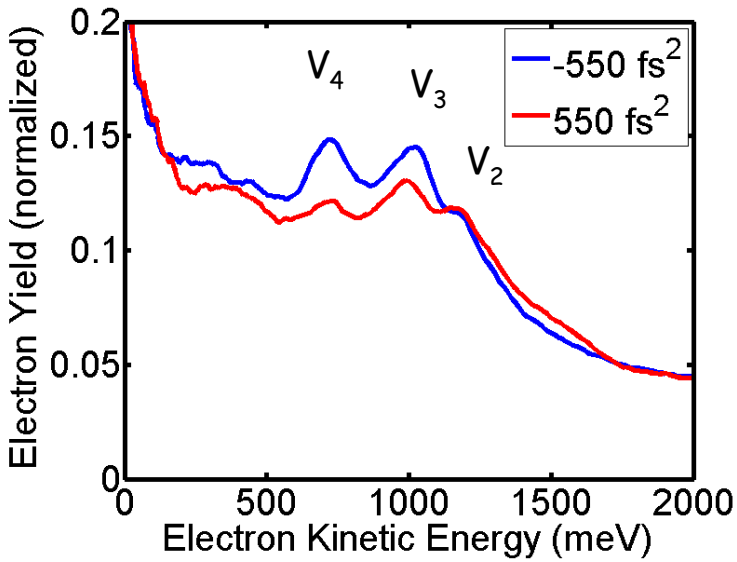
Control over Ionization Viewed with Velocity Map Imaging



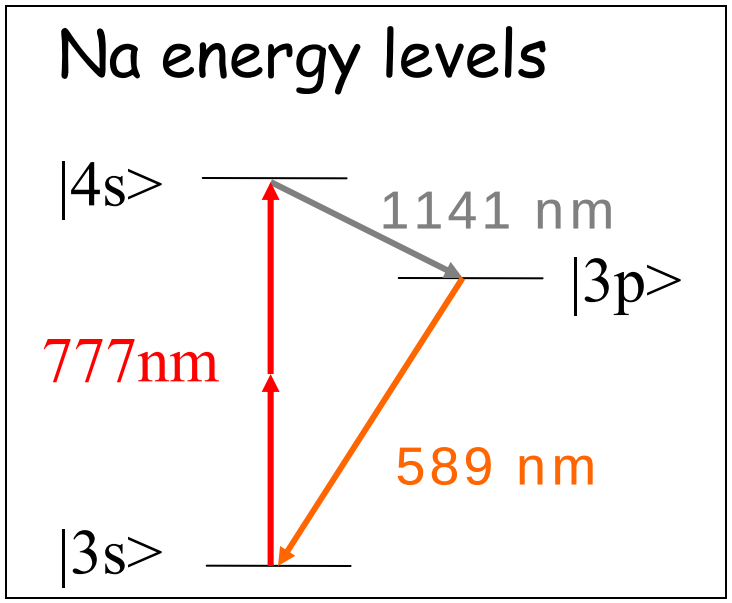


Variations in yield with pulse shape – correlation spectroscopy

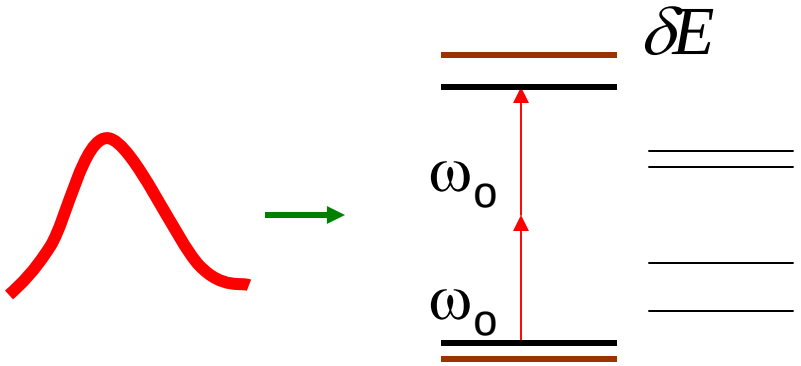




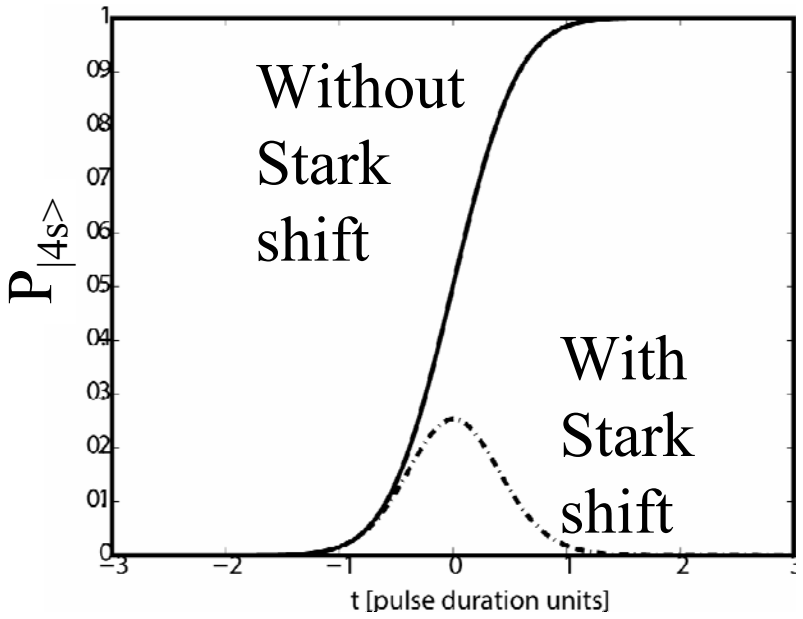
Strong Fields - Dynamic Resonance



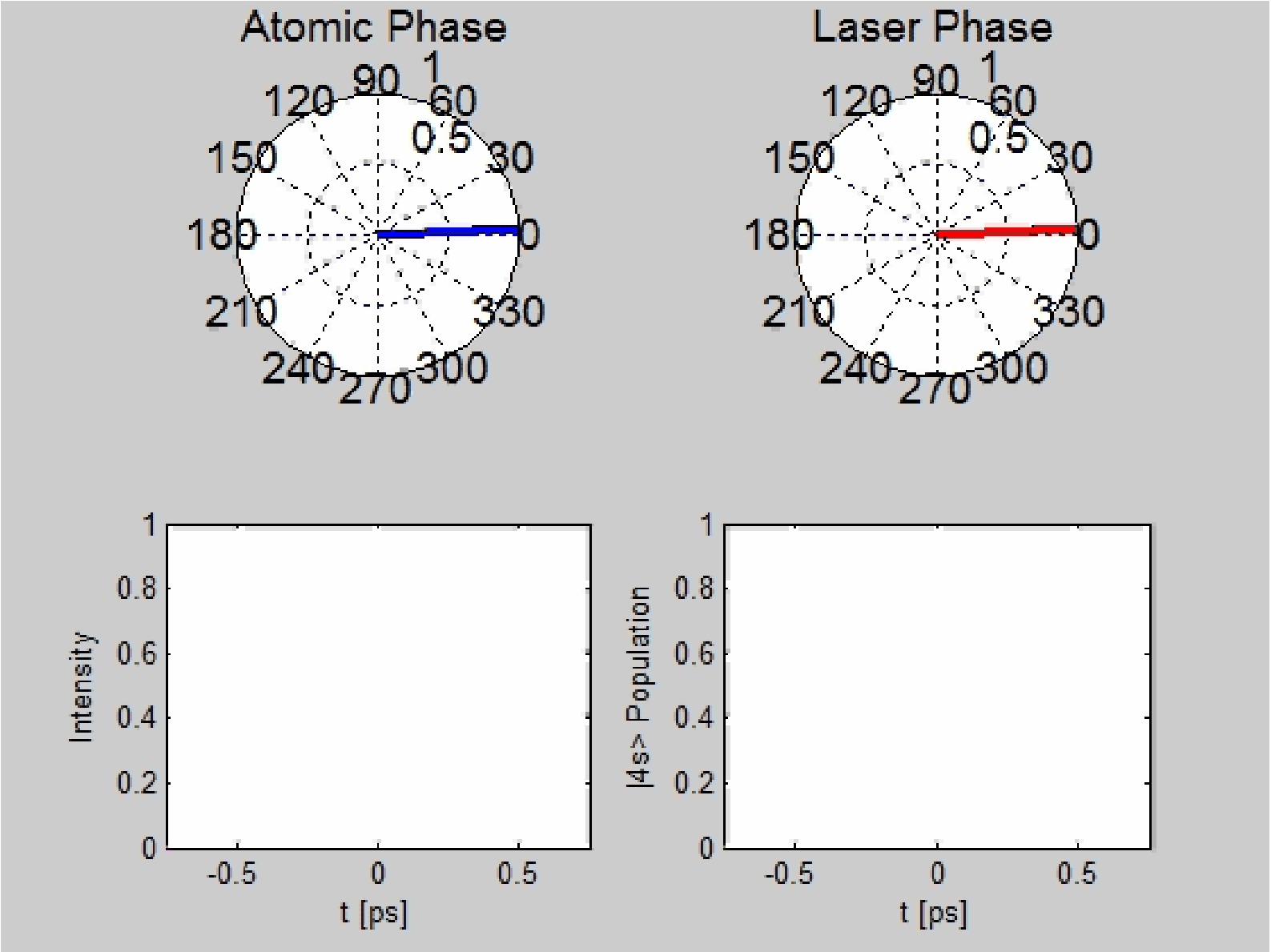
Stark shift: $\delta E \propto \varepsilon(t)^2$



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

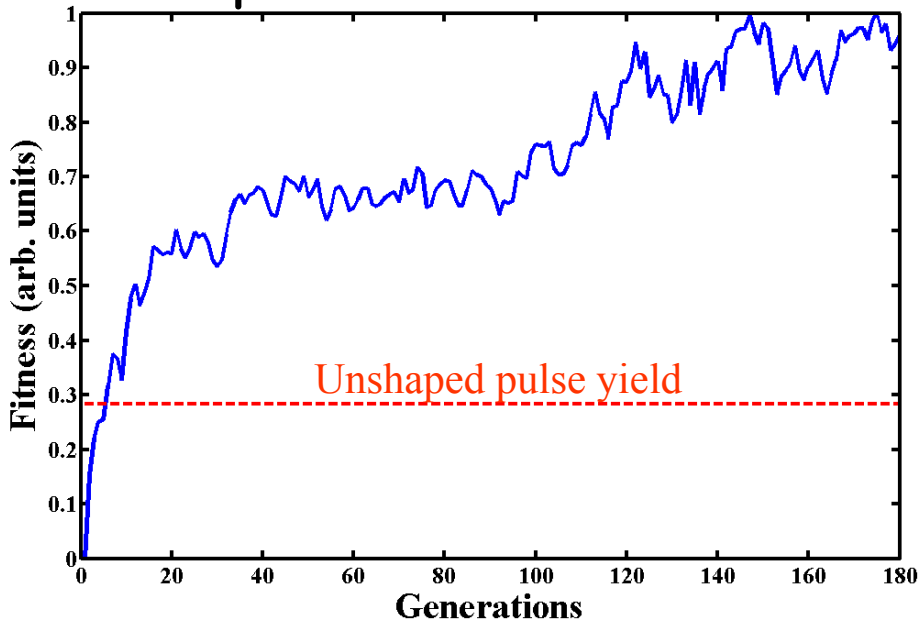


Strong Fields – Dynamic Resonance



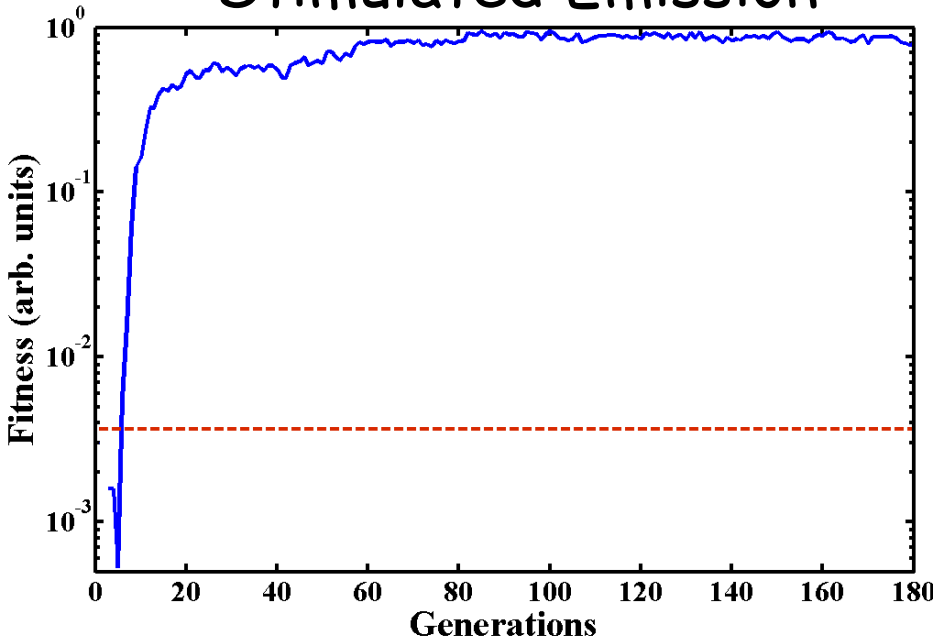
Spontaneous vs Stimulated Emission - Na

Spontaneous Emission



Improvement over unshaped ~ 3

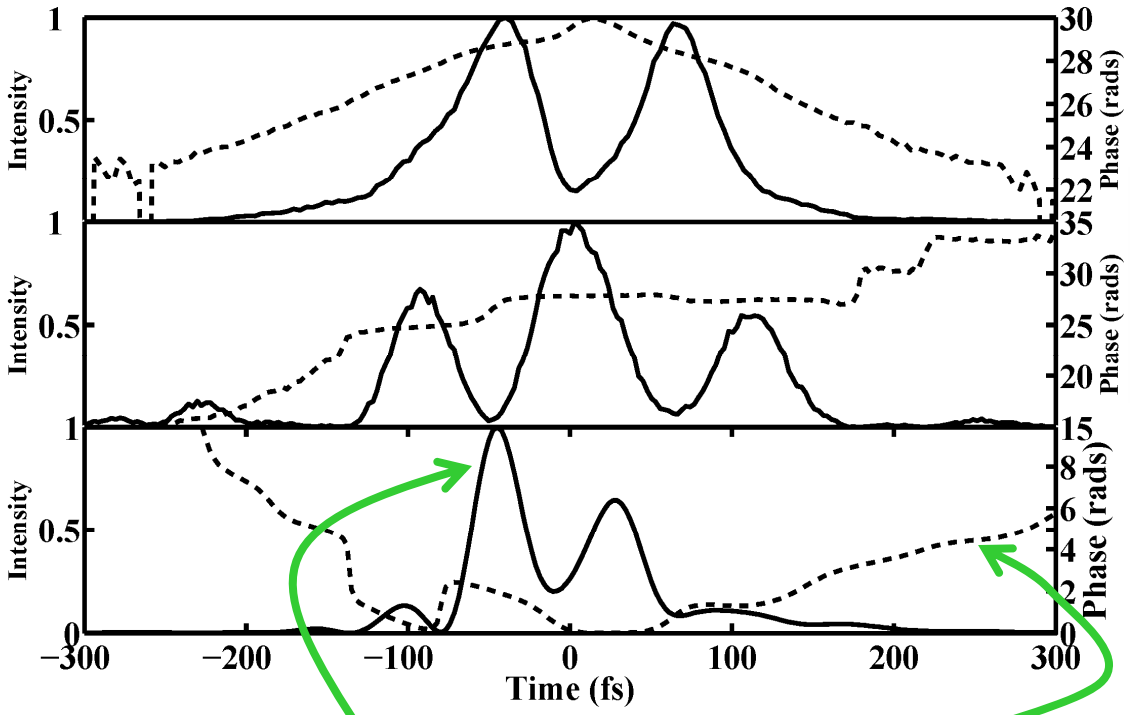
Stimulated Emission



Improvement over unshaped ~ 10^3

Understanding Single Atom Strong Field Dynamics

Measured Optimal Pulses



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

Put these measured pulses into the Schrödinger equation with H given by:

$$\hat{\mathbf{H}}'' = \begin{pmatrix} 0 & \chi(t)e^{i\alpha(t)} \\ \chi(t)e^{-i\alpha(t)} & 0 \end{pmatrix}$$

$\alpha(t)$ is 'atom-field phase',
$\chi(t)$ is two-photon coupling

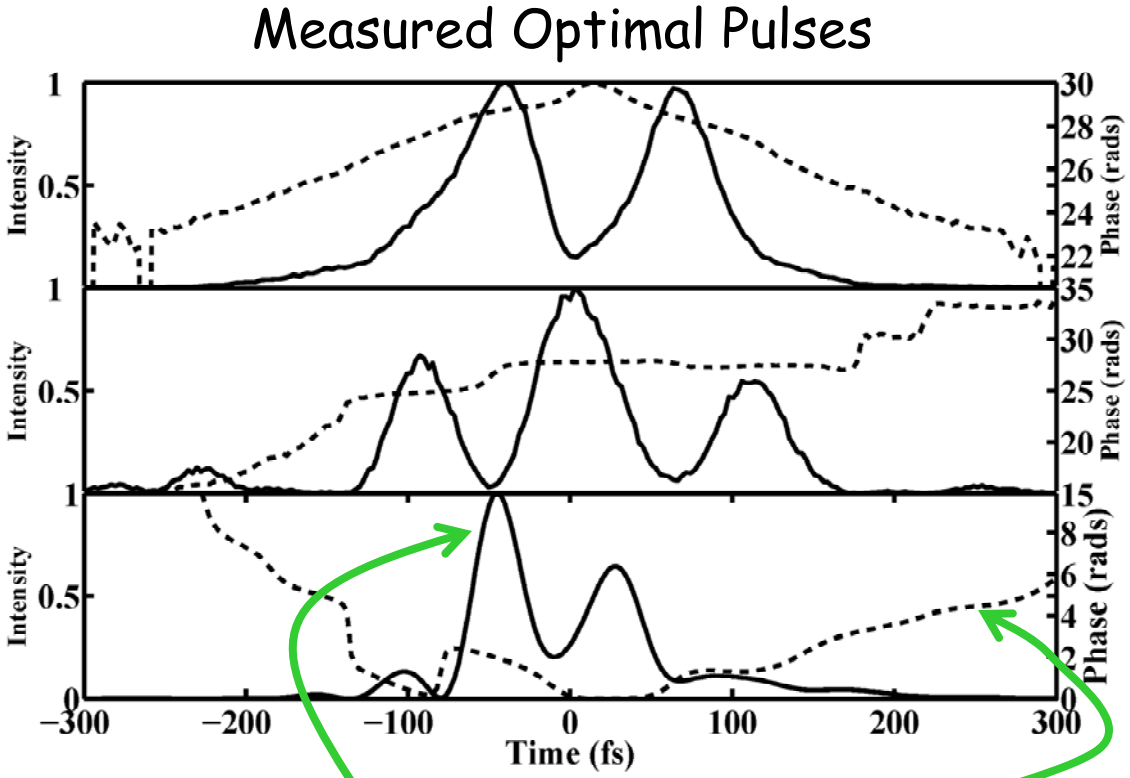
$$\alpha(t) = \int_{-\infty}^{t} \delta_{\omega}^{(s)}(t')dt' - \Delta t + \varphi(t)$$

Differential Stark shift

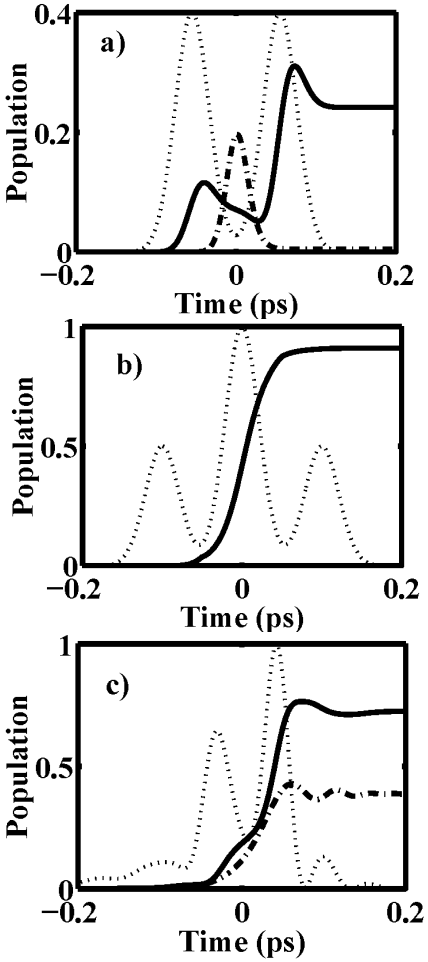
Detuning

Laser Phase

Understanding Single Atom Strong Field Dynamics



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



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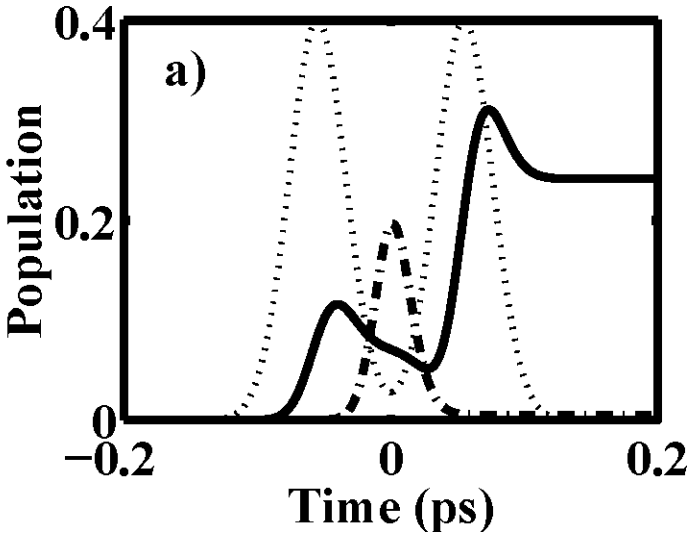
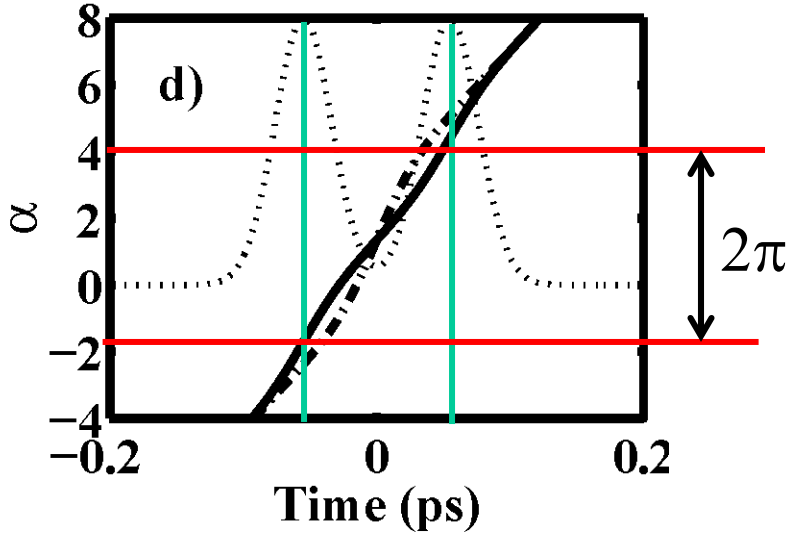




—— $P_{4s}(t)$,$\alpha(t)$ shaped

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

····· I(t) measured

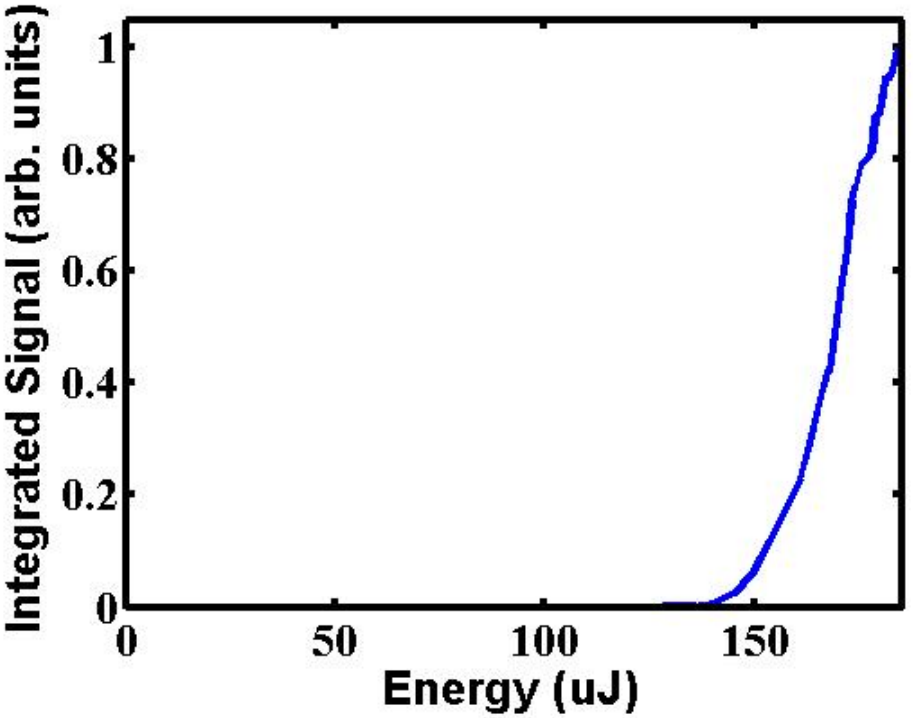
$\alpha(t)$ is the 'atom-field phase'

$$P_{4s} \propto \left| \int_{-\infty}^{\infty} \chi(t) \exp[i\alpha(t)] dt \right|$$

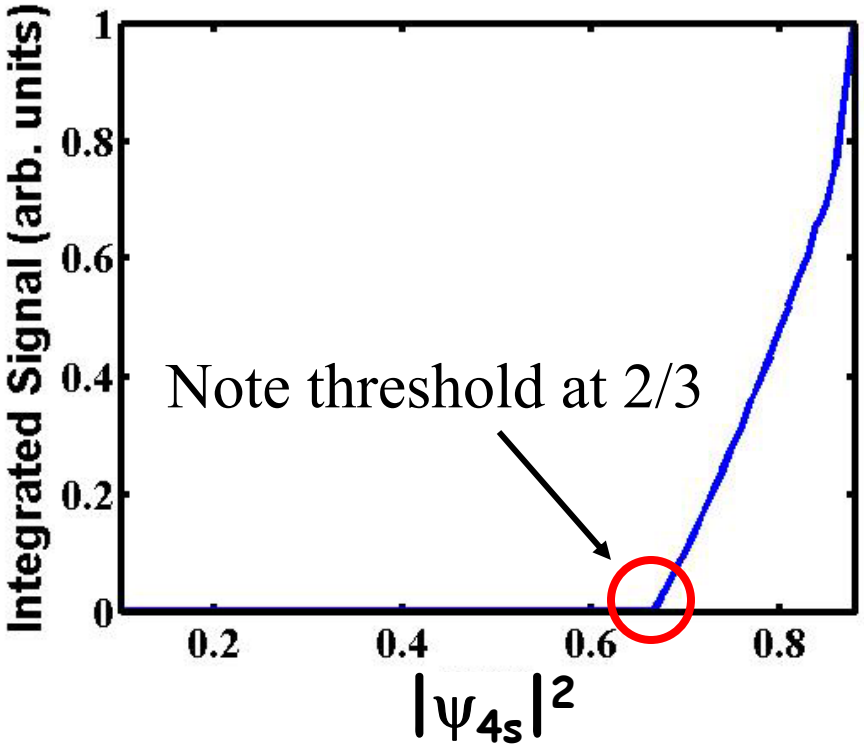
Phys. Rev. Lett. **96** 063603 (2006)

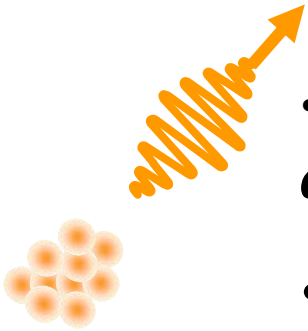
Stimulated Emission very sensitive to excited state population

Experiment



Theory





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

Control based Discrimination

Photoselective adaptive femtosecond quantum control in the liquid phase

T. Brixner, N. H. Damrauer, P. Niklaus & G. Gerber

Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent light sources can be used to manipulate the outcome of light–matter interactions by exploiting interference phenomena

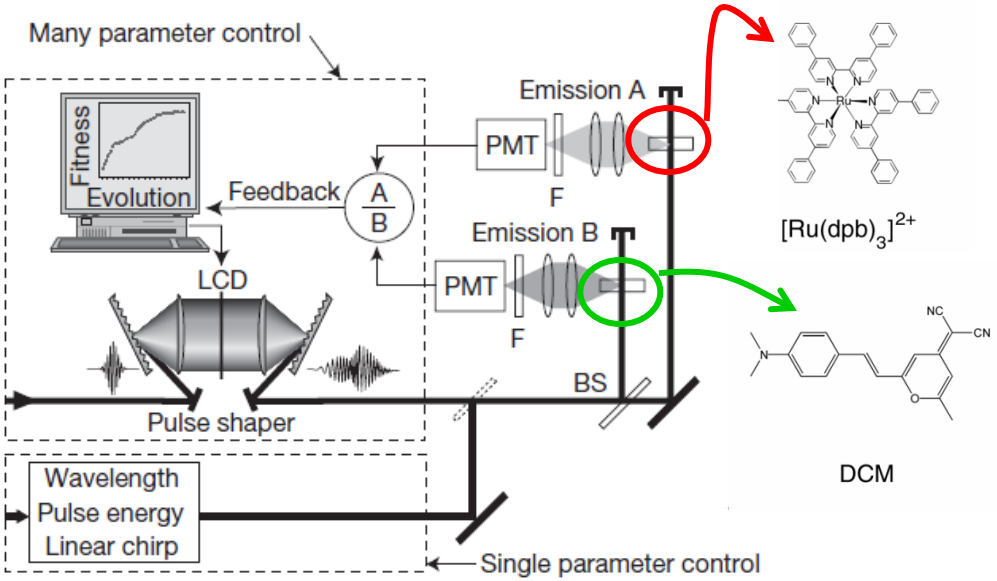
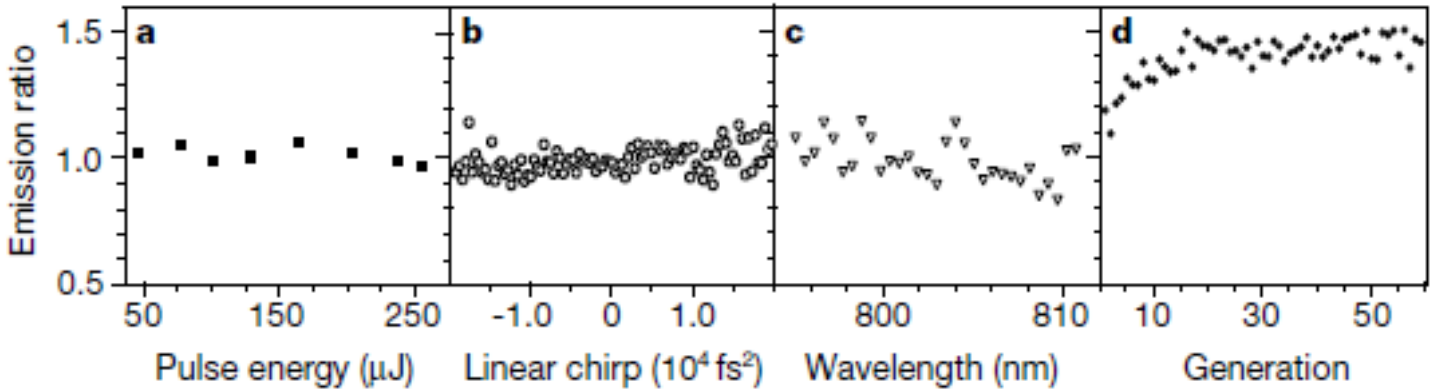


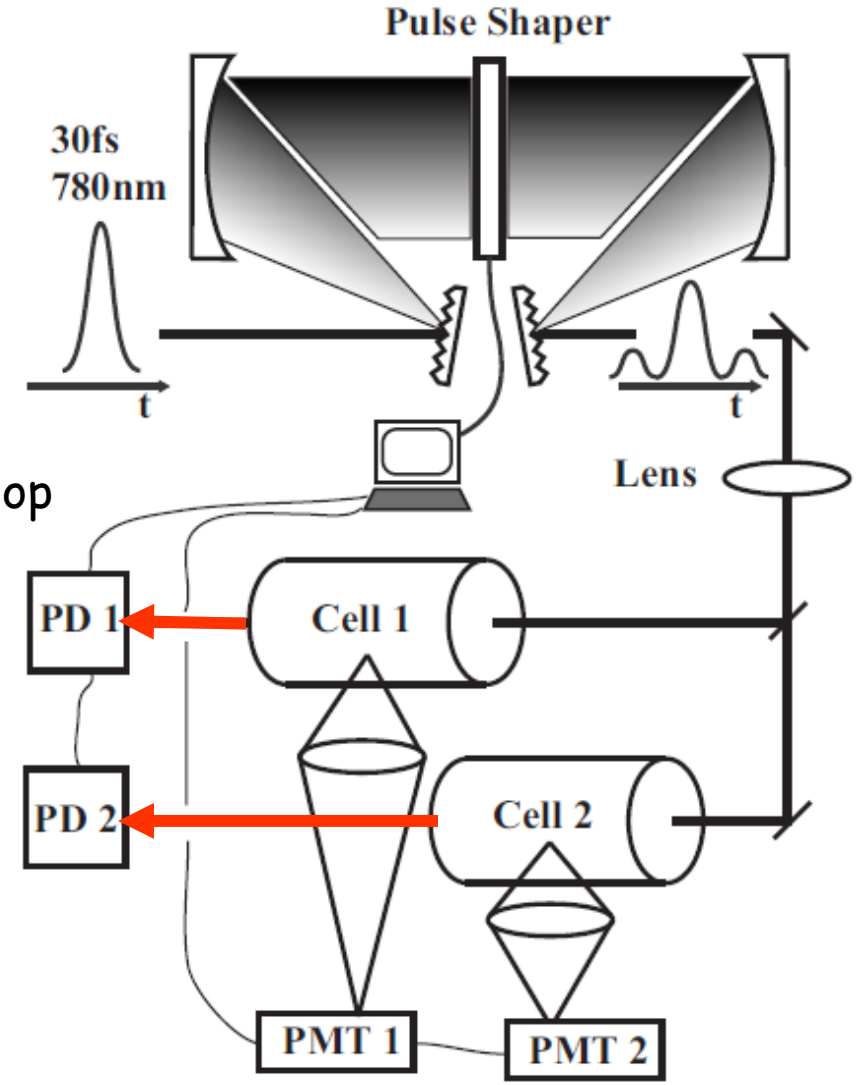
Figure 1 Experimental set-up. Our femtosecond laser system delivers 80-fs, 1-mJ pulses

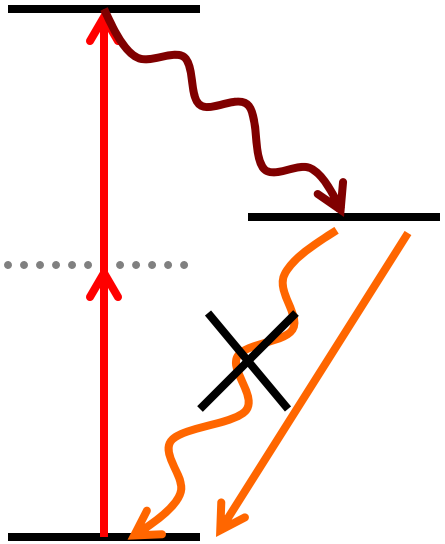


T. Brixner *et al* Nature 414, 57 (2001)

Consider the Same Experiment, but now with Stimulated Emission…

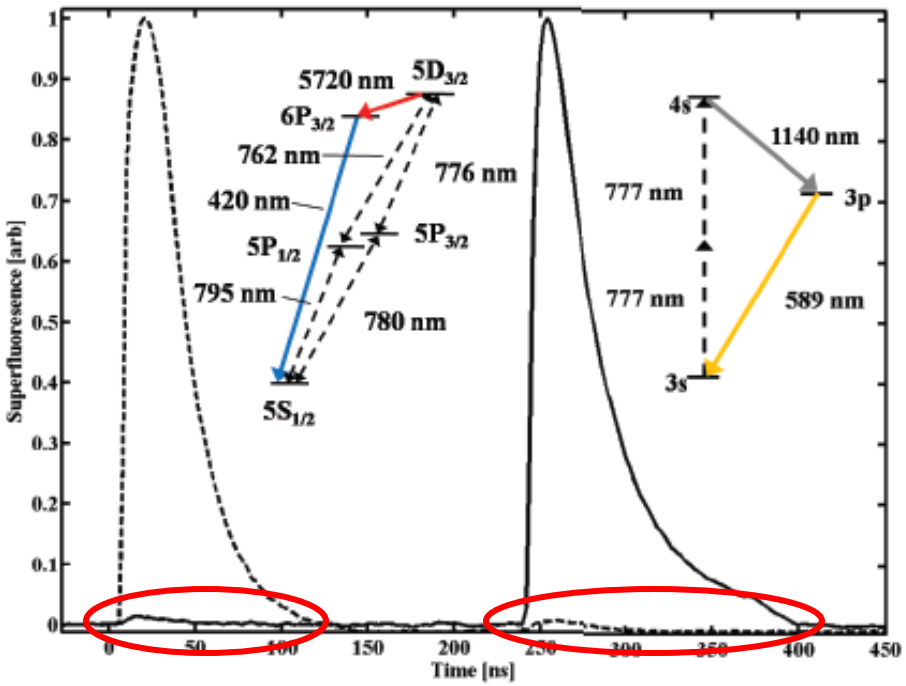
Combine closed loop learning control with stimulated emission

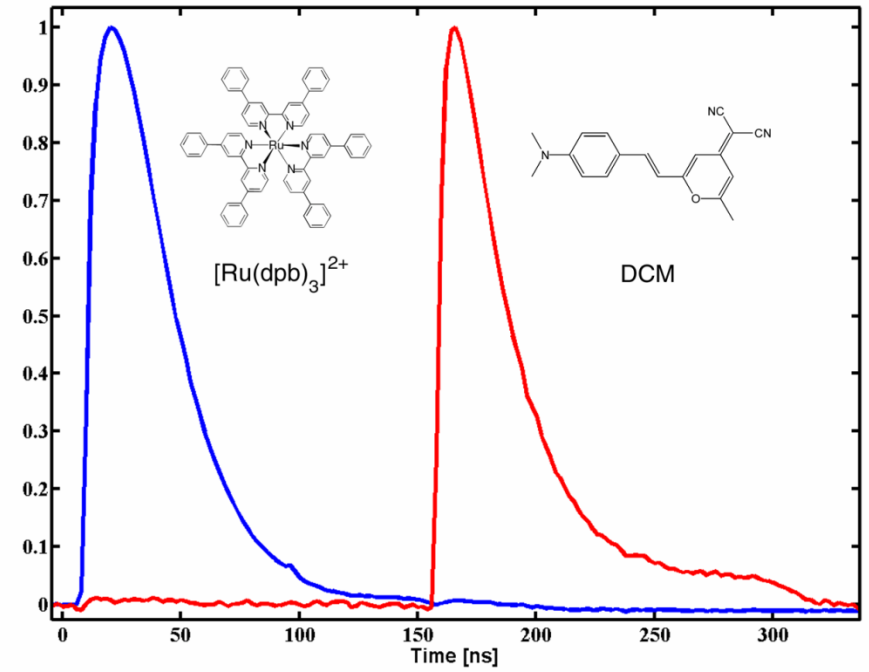




…to Achieve 'Perfect' Discrimination

Rb Na $[Ru(dpb)_3]^{2+}$ DCM



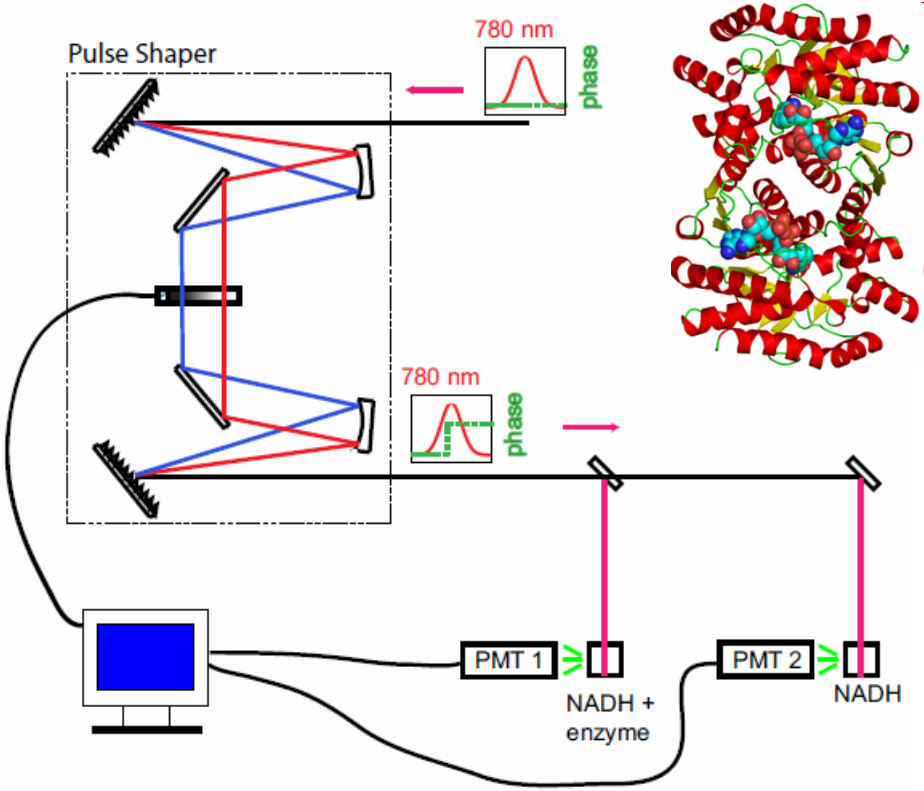


Control ratios >10^4 (earlier work demonstrated ~2)

Stimulated emission microscopy:
Min *et al* Nature **461**, 1105 (2009)

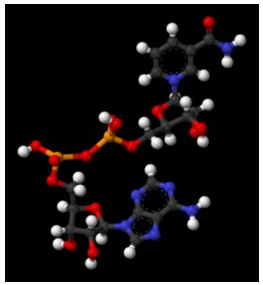
S. D. Clow *et al* New J of Phys (2010)

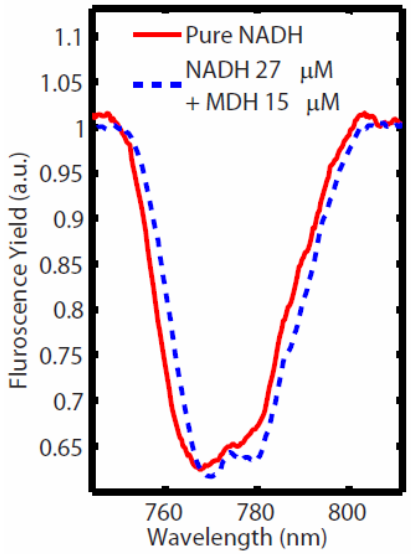
Control based Discrimination for measuring Enzyme Binding

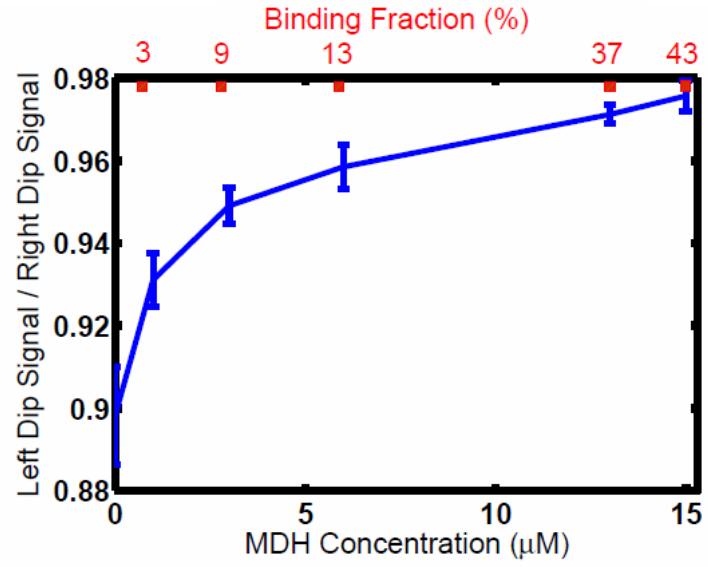


MDH

NADH

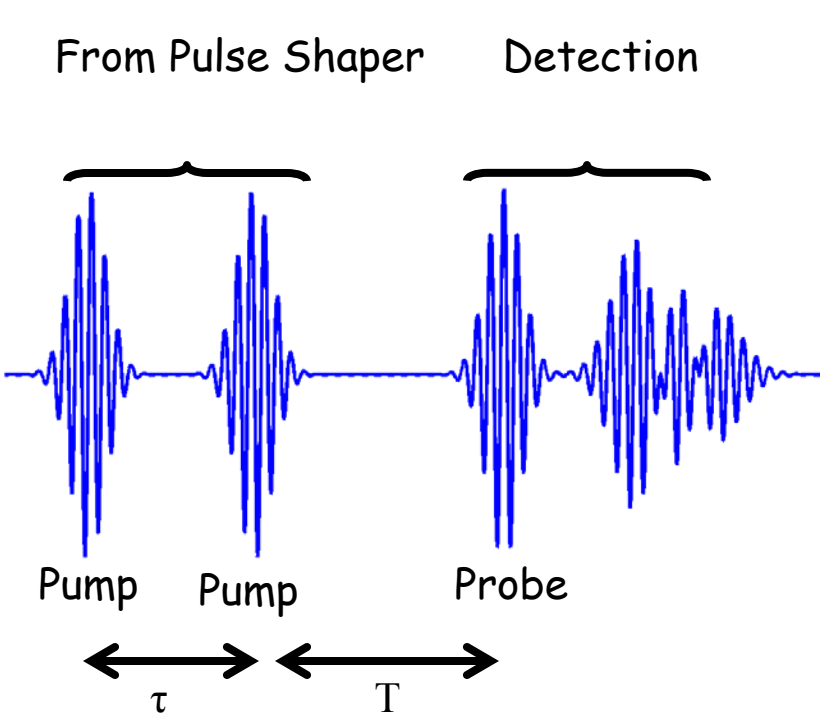


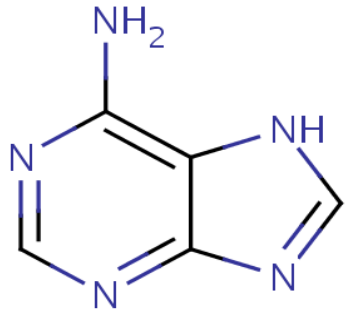




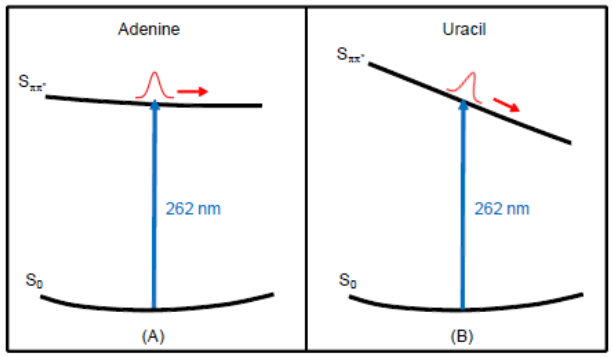
NADH: nicotinamide adenine dinucleotide
MDH: mitochondrial malate dehydrogenase

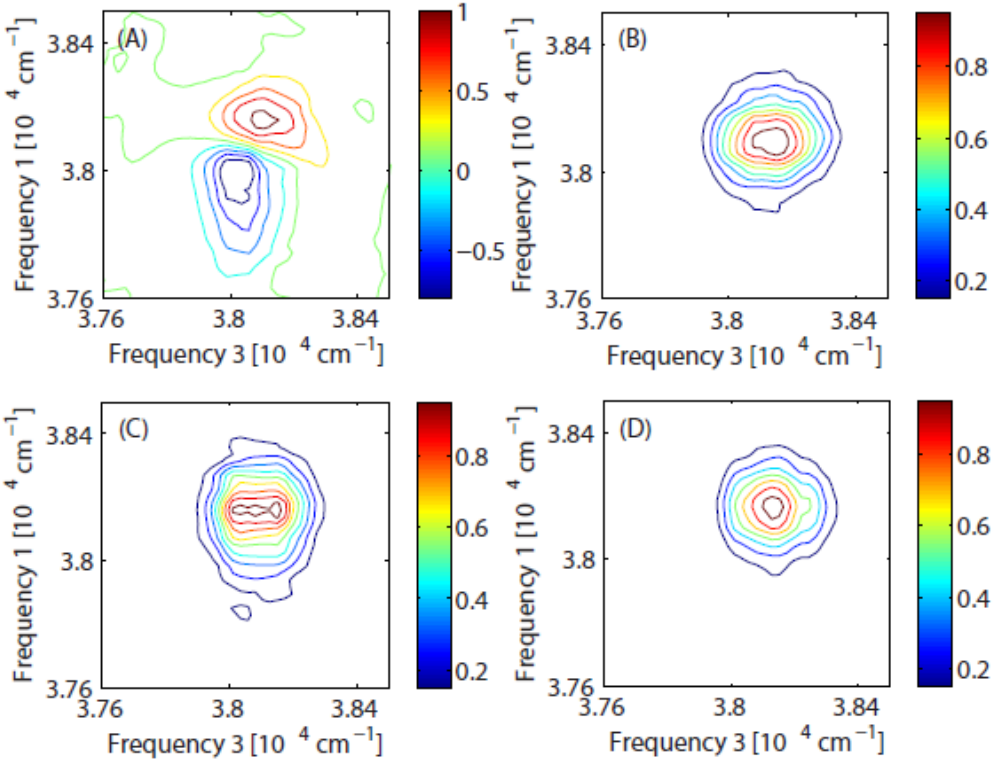
Other Implementations of Quantum Control/Pulse Shape Spectroscopy





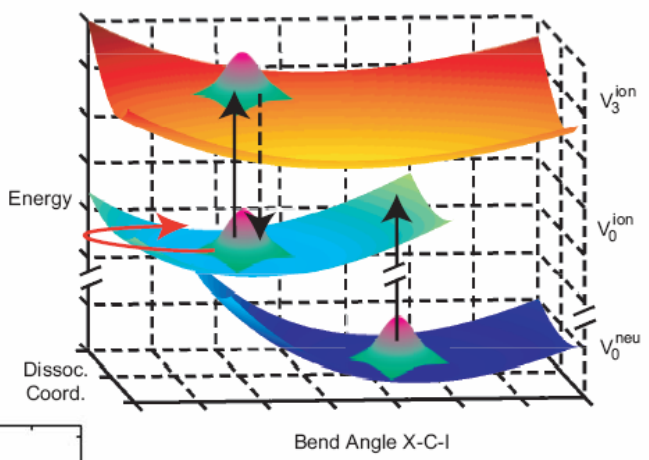
Adenine

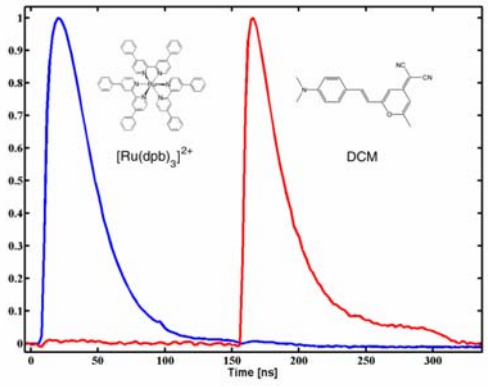


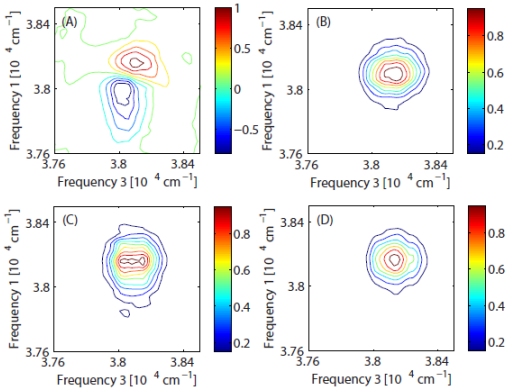


Conclusions & Future Work

- Shaped laser pulses can be used to control dissociation and ionization
- Control + stimulated emission can lead to 'perfect' control
- Quantum Control Spectroscopy has many applications







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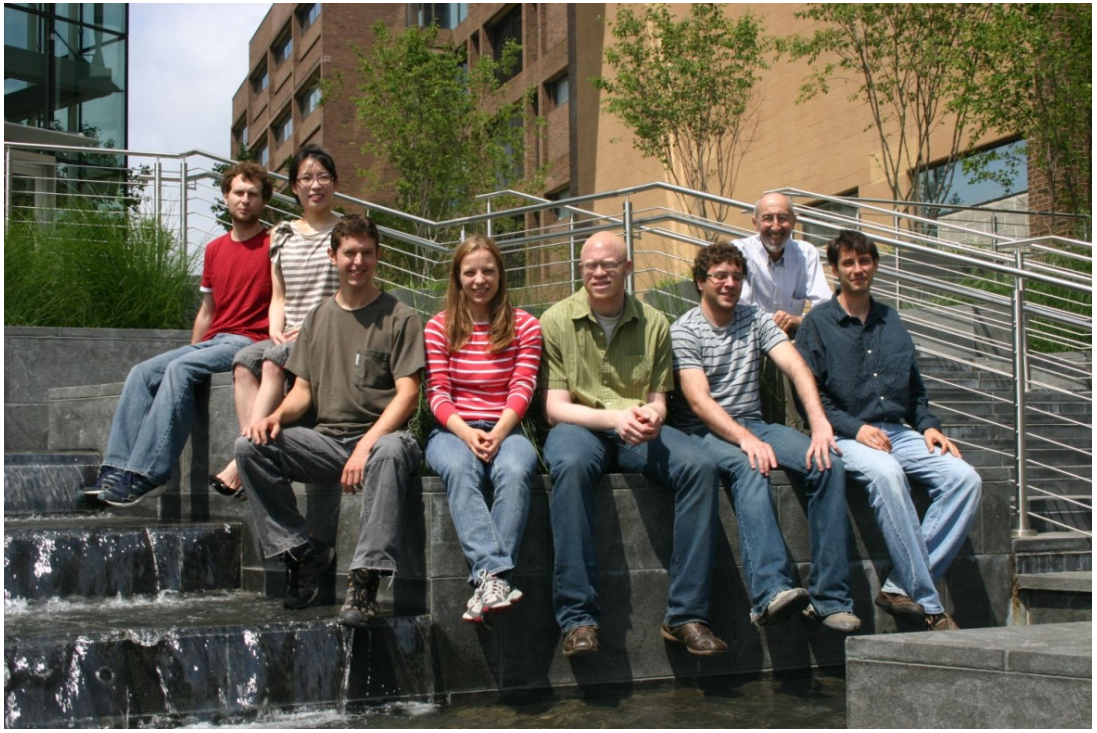

http://ultrafast.physics.sunysb.edu