Control of Photoinitiated Reactions

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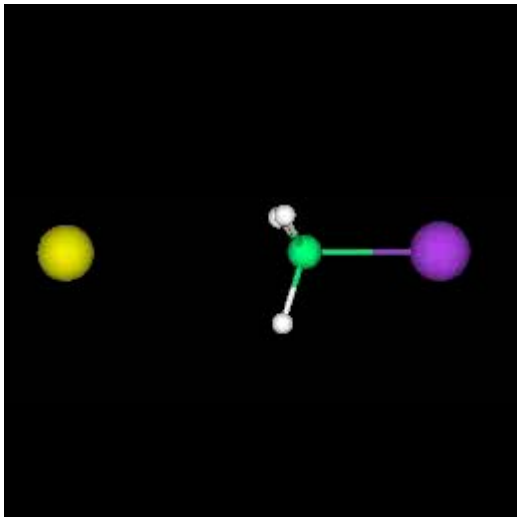
Much of photochemistry is like sailing – we have a little control but must go with the wind.

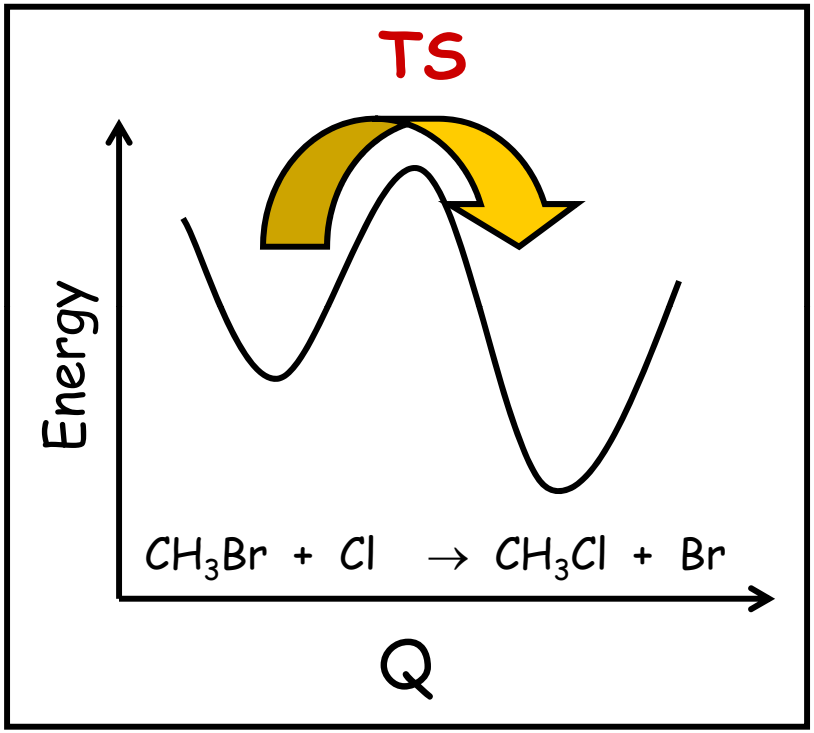
Can we harness the power to take us where we want to go?

Consider a simple chemical reaction.

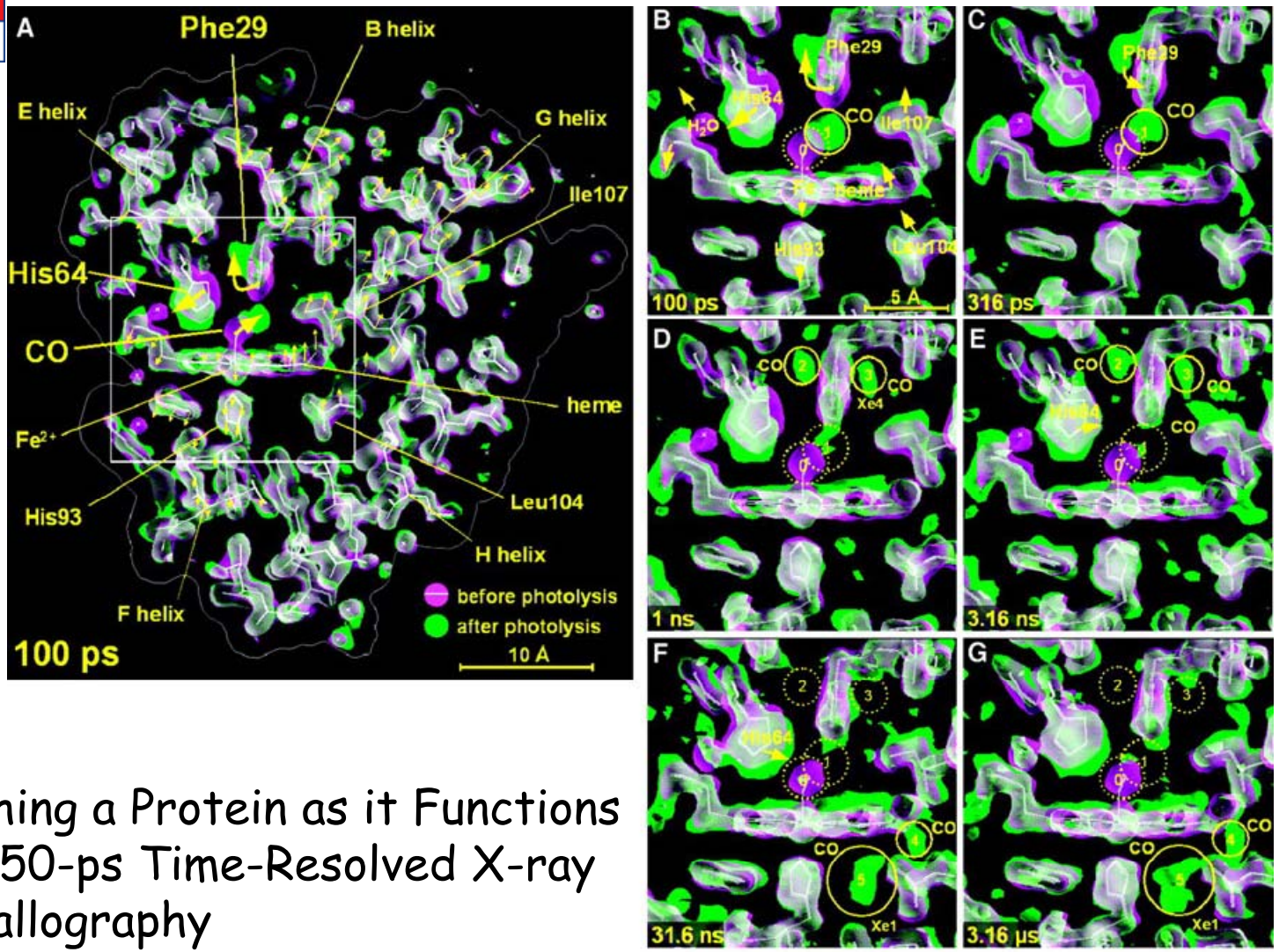
$$CH_3Br + Cl \rightarrow CH_3Cl + Br$$

Cl CH_3 Br





The intrinsic time scale for such dynamics begins at a few 10's of femtoseconds.



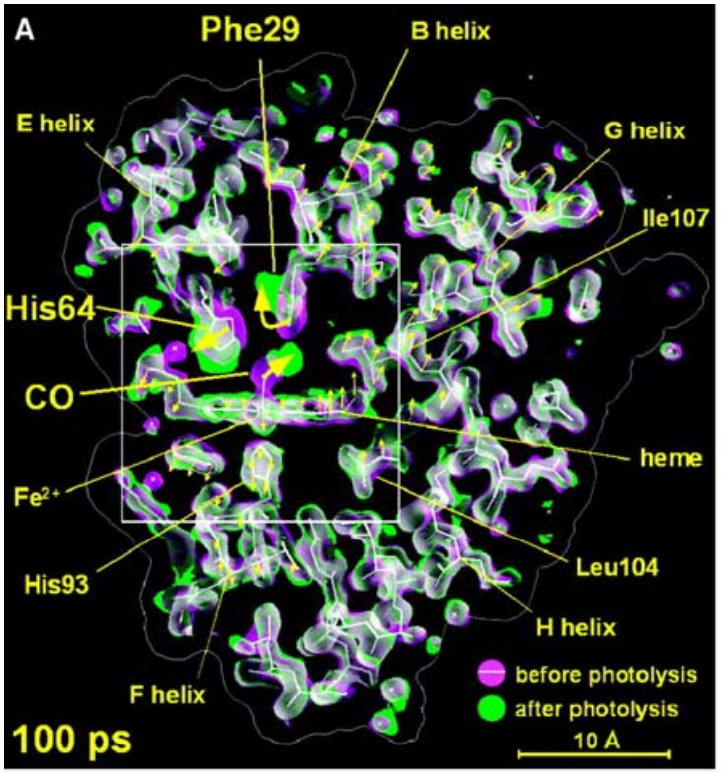
Watching a Protein as it Functions with 150-ps Time-Resolved X-ray Crystallography

F. Schotte, M. Lim, T. A. Jackson, A. V. Smirnov, J. Soman, J. S. Olson, G. N. Phillips, Jr., M. Wulff, and P. A. Anfinrud

Science 300: 1944-1947 (2003)

The Ultimate Goal

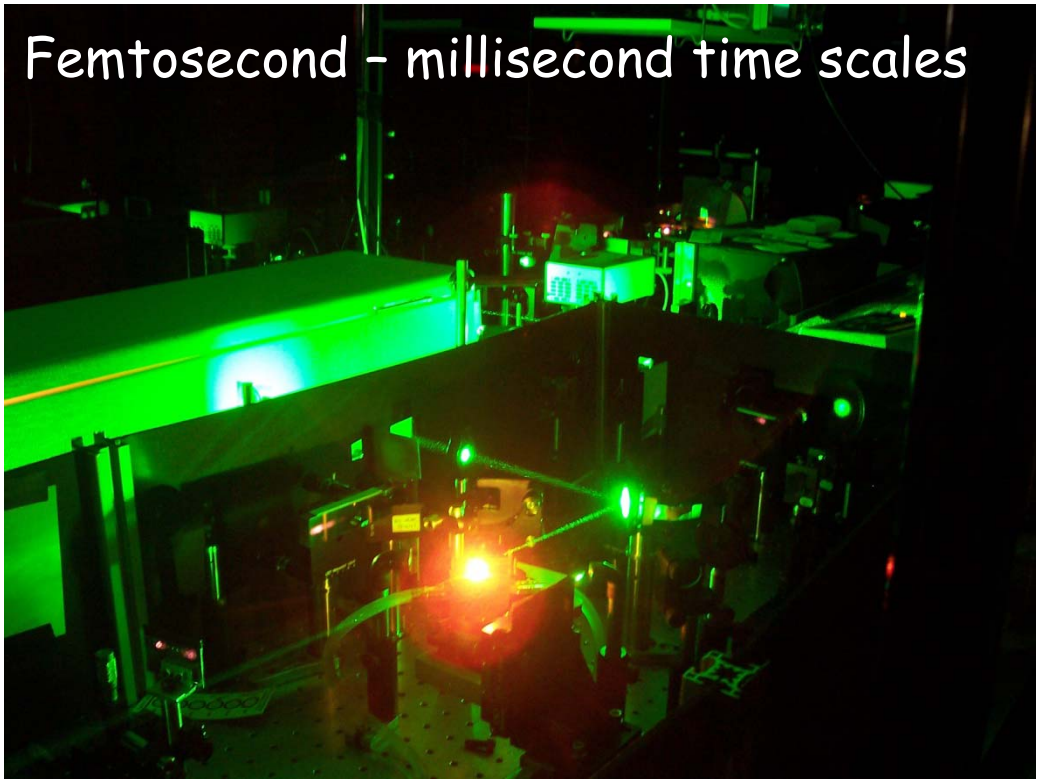
Watch a reaction as it occurs, watch a protein as it functions – with atomic level structural resolution and atomic level time resolution to monitor electronic configuration and nuclear postions during the course of the reaction.

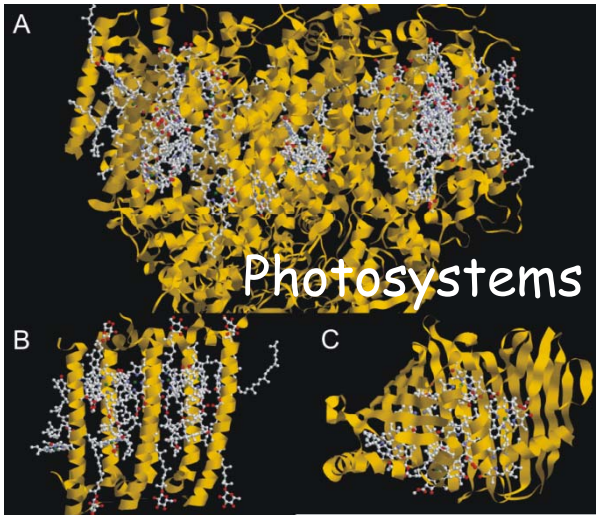


Can we observe as bonds deform, rupture and reform?

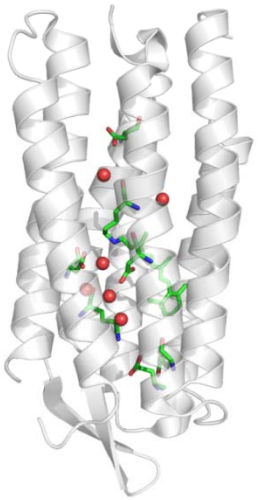
X-ray diffraction
X-ray spectroscopy
Electron diffraction
Electronic wave function imaging

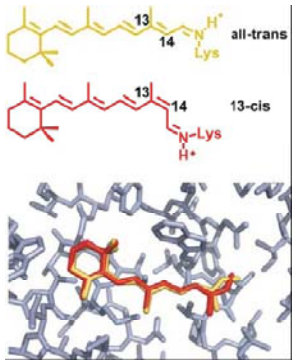
Light triggered reaction dynamics.





Retinal based proteins





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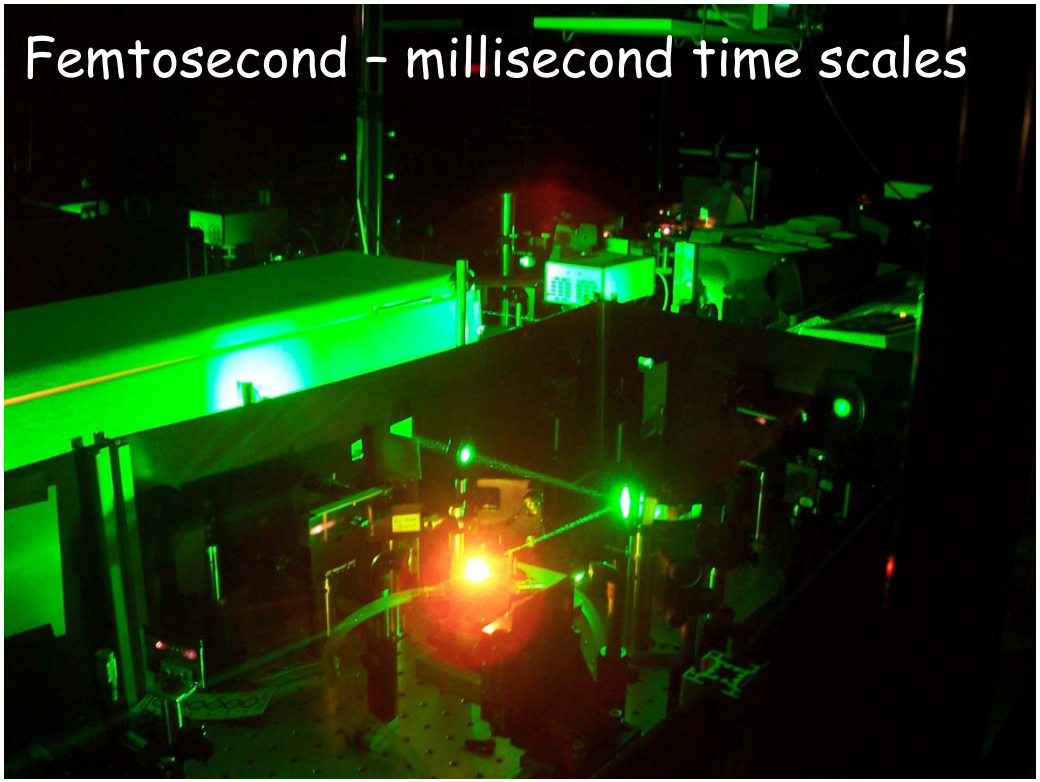
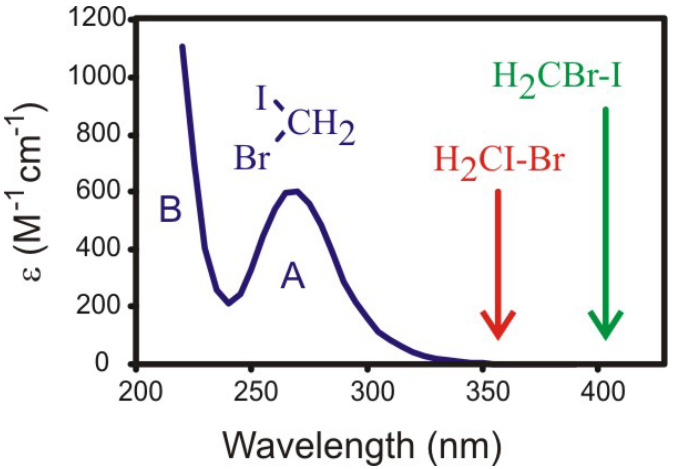
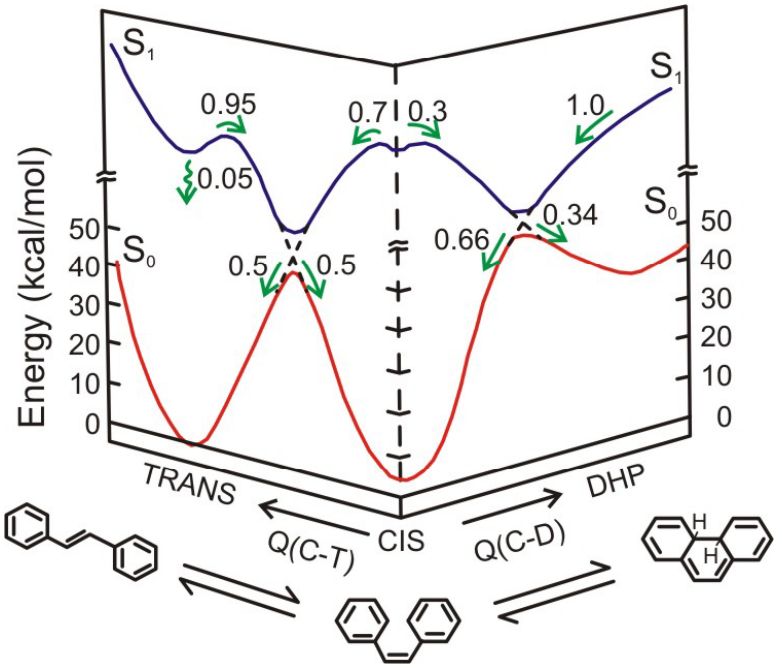
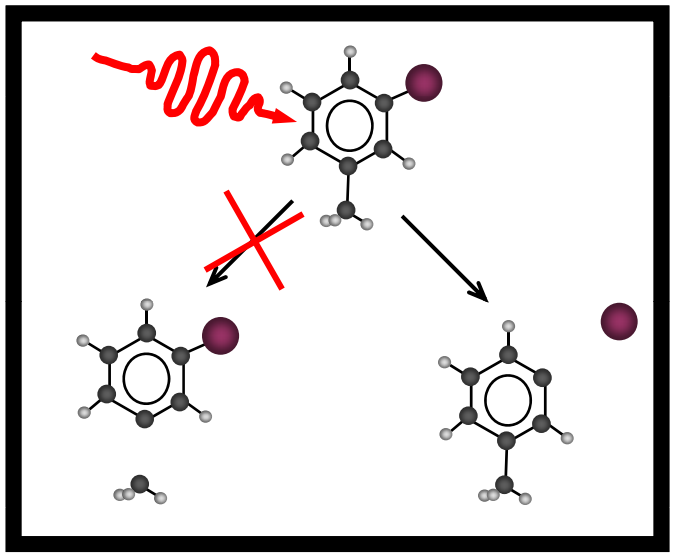


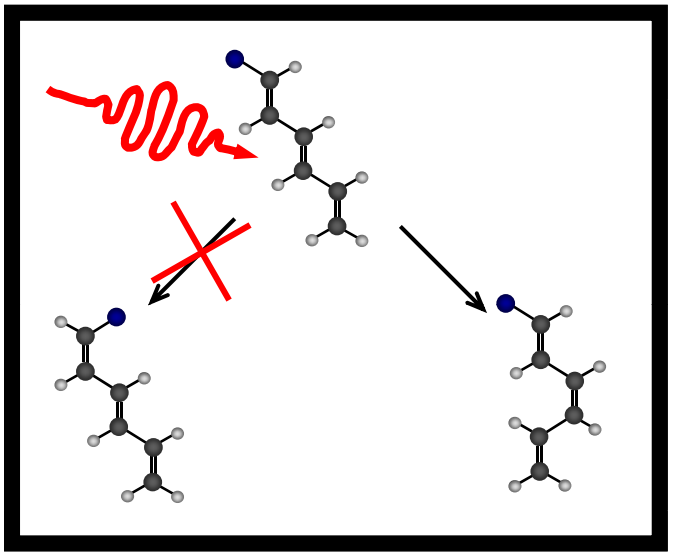




But – what beyond these?

Pursuing Selectivity:





- A substantial effort in physical chemistry has been directed toward harnessing light energy to perform selective chemistry.

- State-selection fails – fast energy redistribution randomizes the photon energy.

- Use pulses of light and coherent interactions

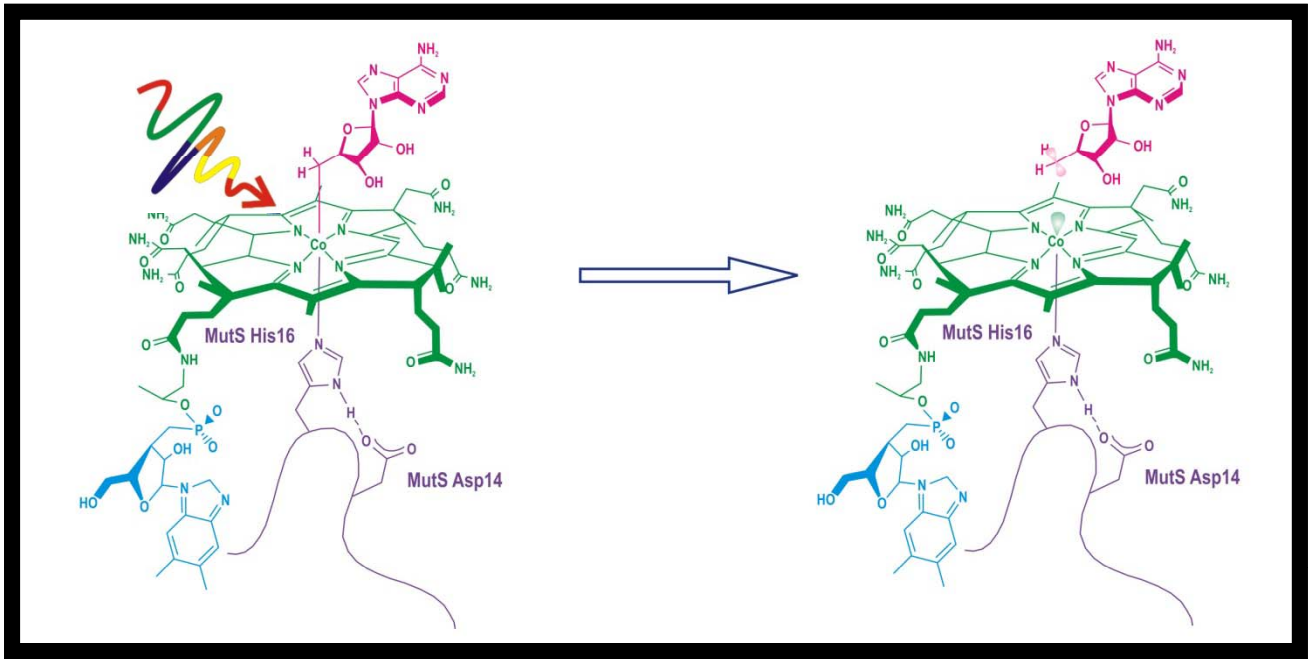
Coherent Control

1. Permit synchronization

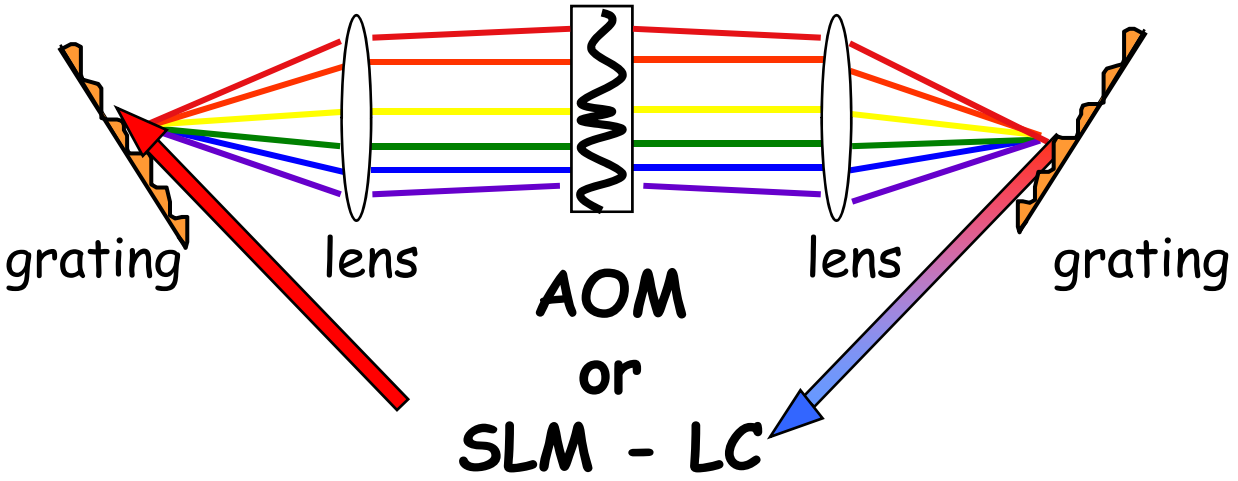
2. The direct participation of pulse shaping enables steering the chemical/biological pathway.

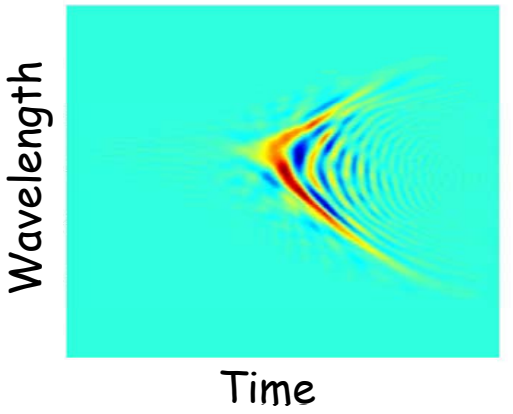
3. Ability to construct maps of reactive surfaces beyond simple 1-d model surfaces.

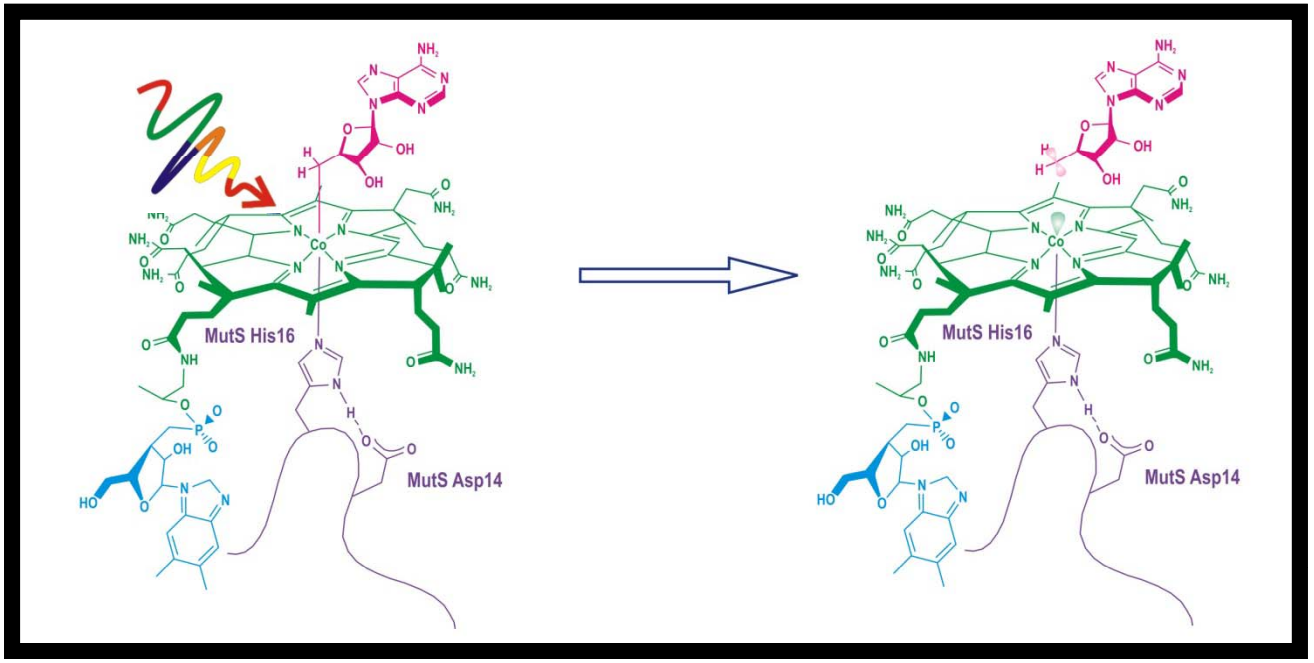
4. Access paths to control processes in completely new ways.



Photoexcitation of AdoCbl results in homolysis of the active Co-C bond.







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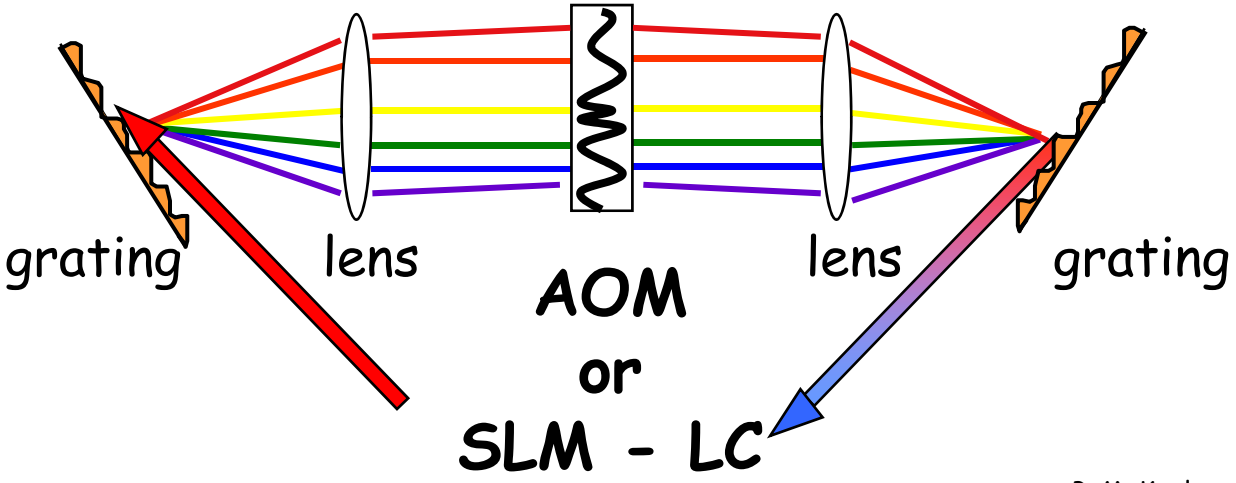
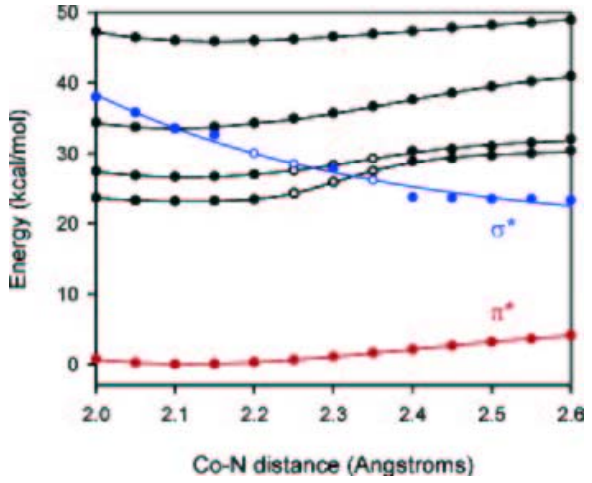


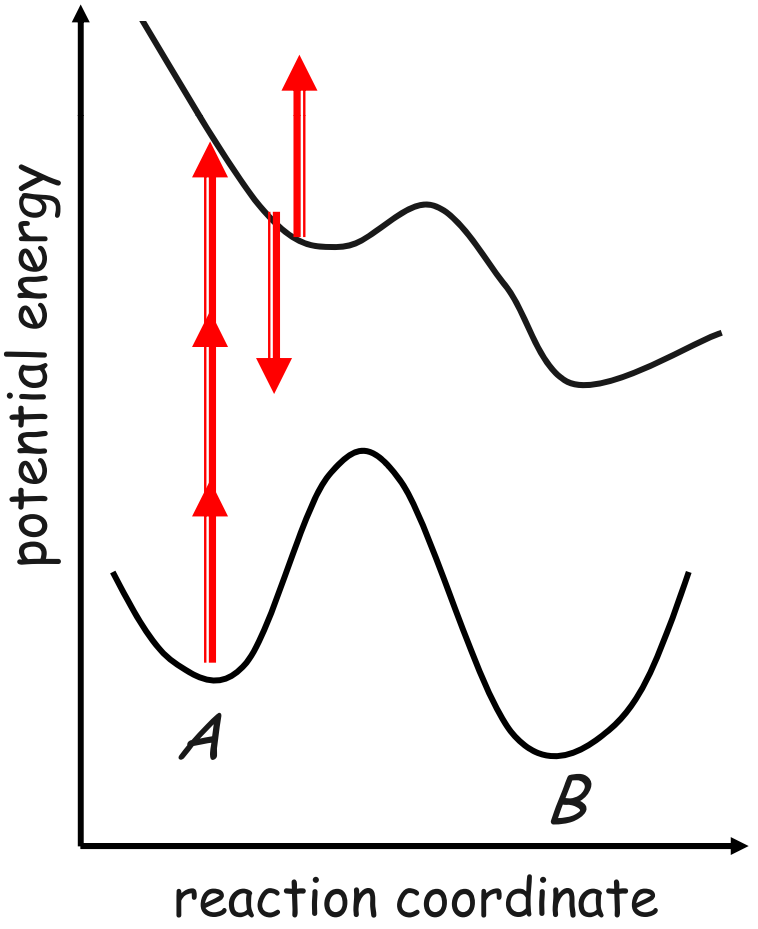


P. M. Kozlowski, J. Kuta, and W. Galezowski, 10.1021/jp066972w

Three classes of interaction capable of control:

1. Pump-Dump or Pump-Pump
2. Shaping of the one photon or multiphoton spectrum
3. Control of excited state wave packets directing reactivity.

Appropriately timed frequency components can "catch" population and dump to a product or a reactant state



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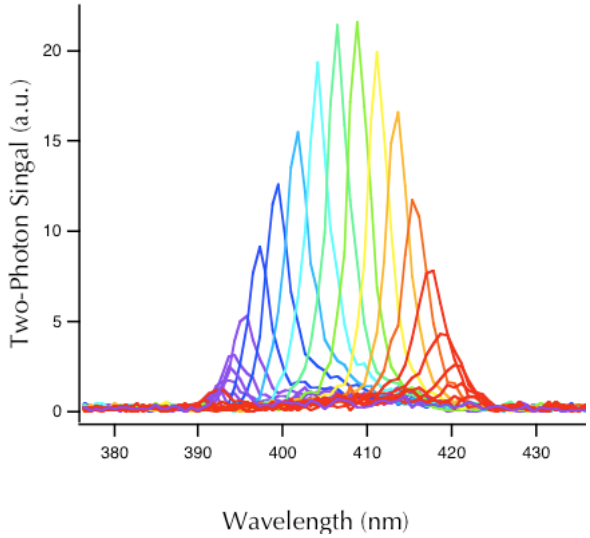
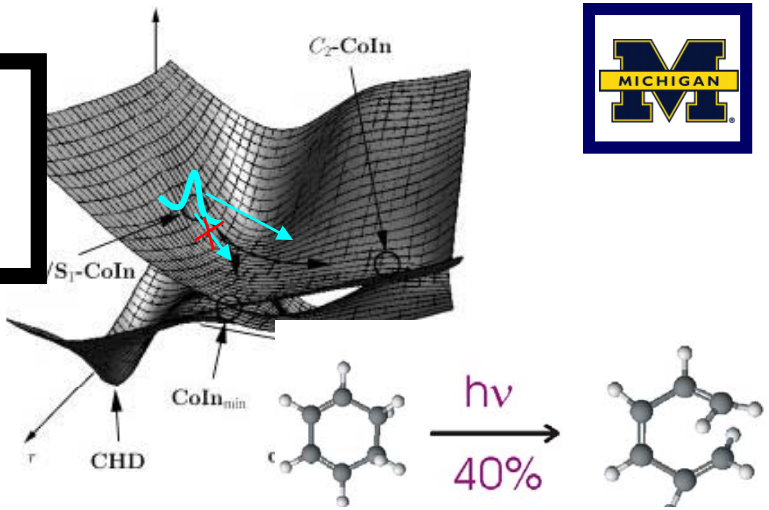
Second Harmonic Spectra of Phase-shaped excitation



Application of a sinusoidal phase leads to destructive interference of various frequency components tuning the 2ω spectrum

Three classes of interaction capable of control:



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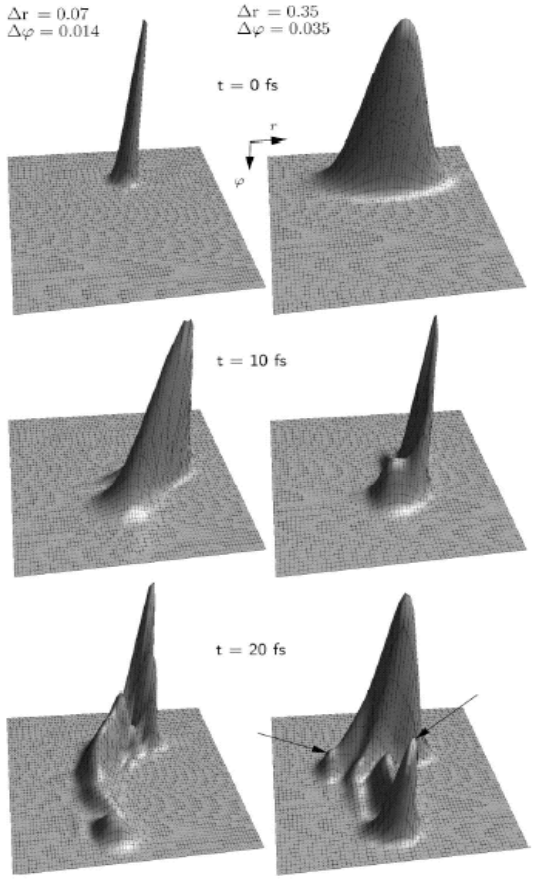
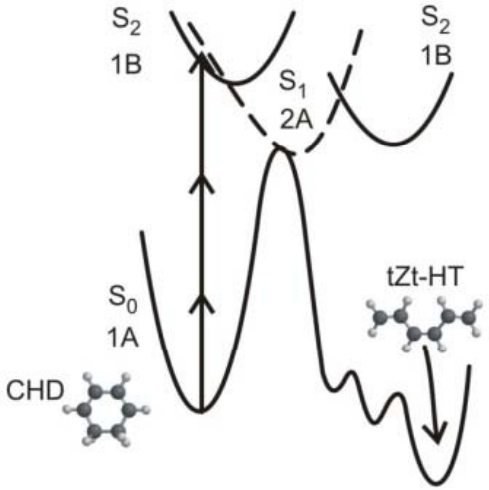


Hofmann and de Vivie-Riedle,
JCP 112, 5054 (2000)

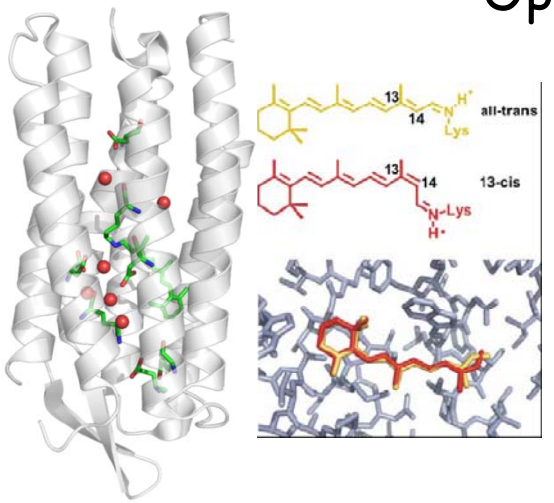
Optical Control

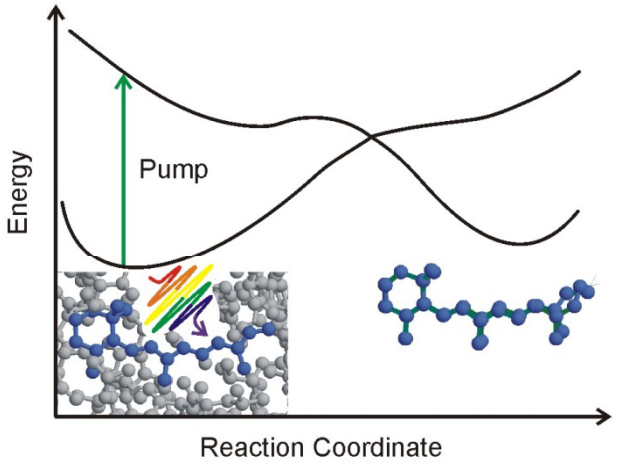


Cyclohexadiene – optimizing ring opening while suppressing solvent fragmentation

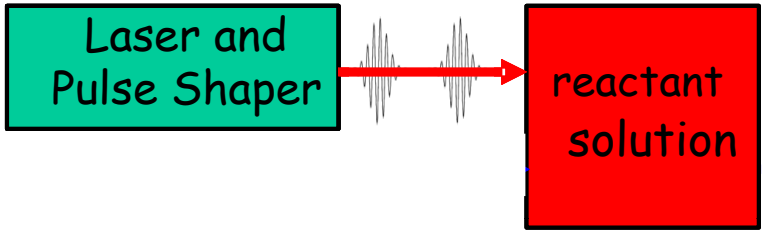
Bacteriorhodopsin

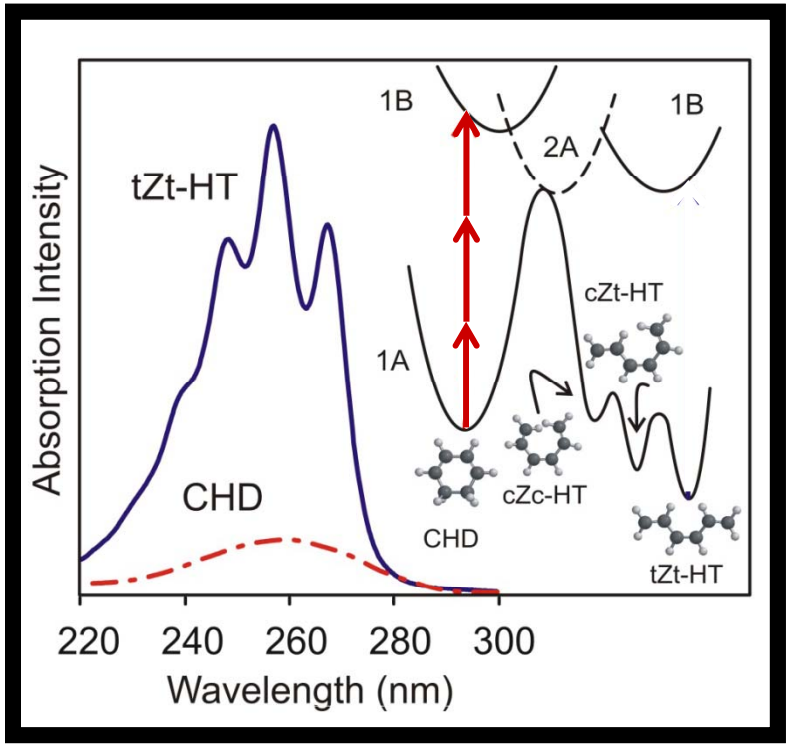
Optimizing 13-cis with multiphoton interactions

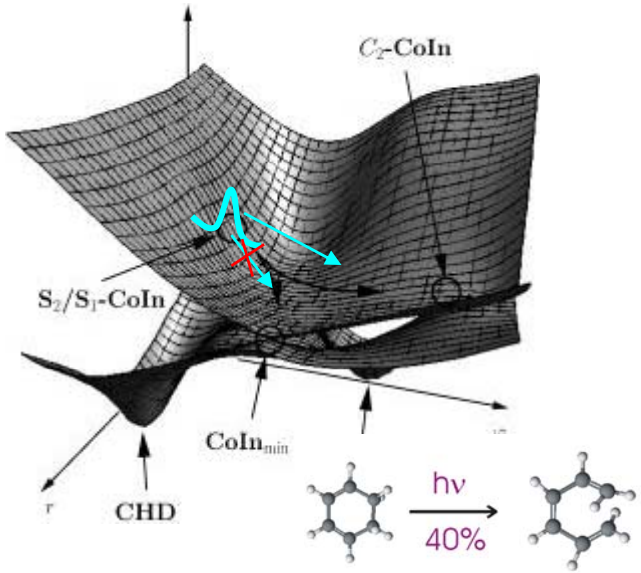




Control of a Chemical Transformation







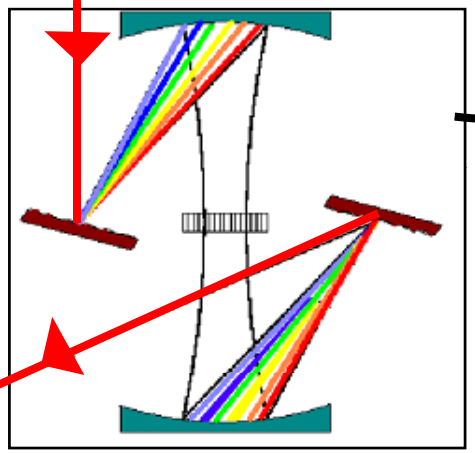
Hofmann and de Vivie-Riedle,
JCP 112, 5054 (2000)

Experimental Setup

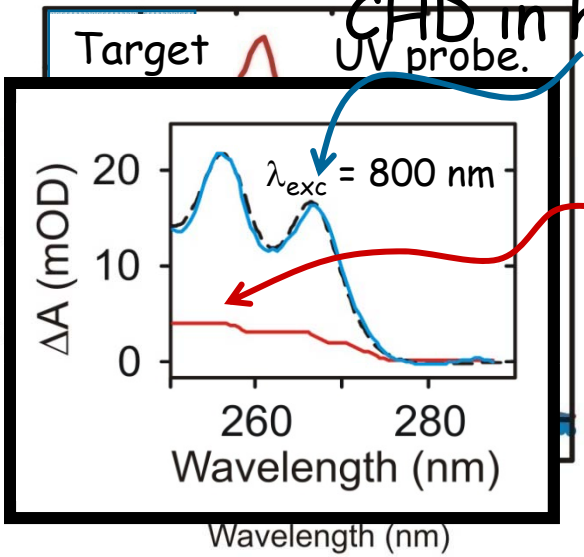
800 nm, 24 nm bandwidth, 50 fs, 1 kHz

Amplified Laser System

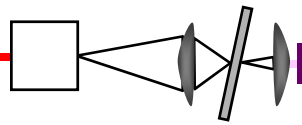
Pulse shaper

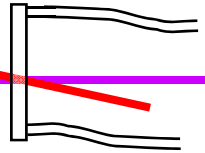


CHD in hexane rammed in < 1ms



hexane





Frequency Doubled Continuum

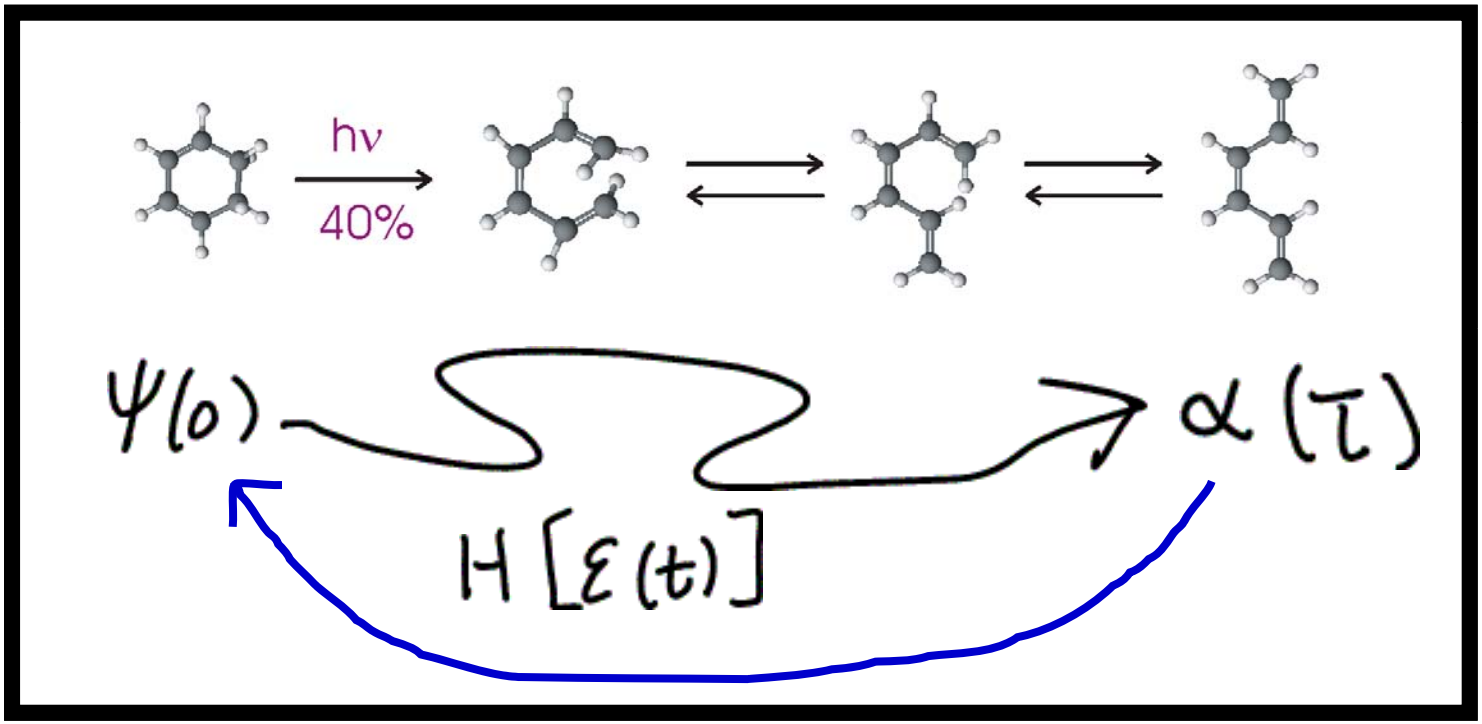
Sample cell

Spectrometer

ca. 1-12 ns Delay

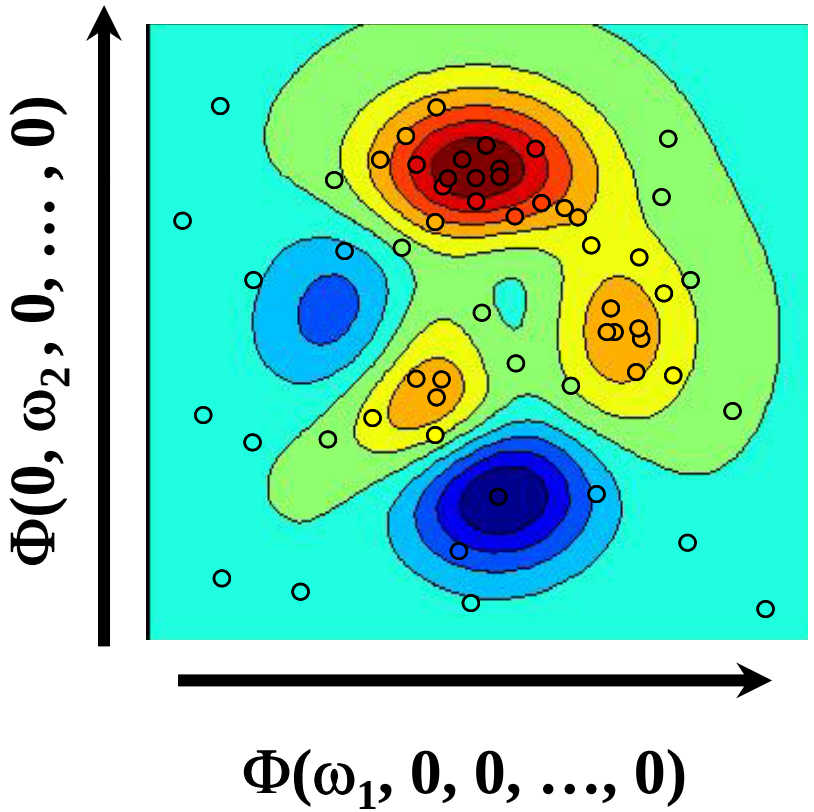
What pulses will take a system to a desired target state – at a target time?

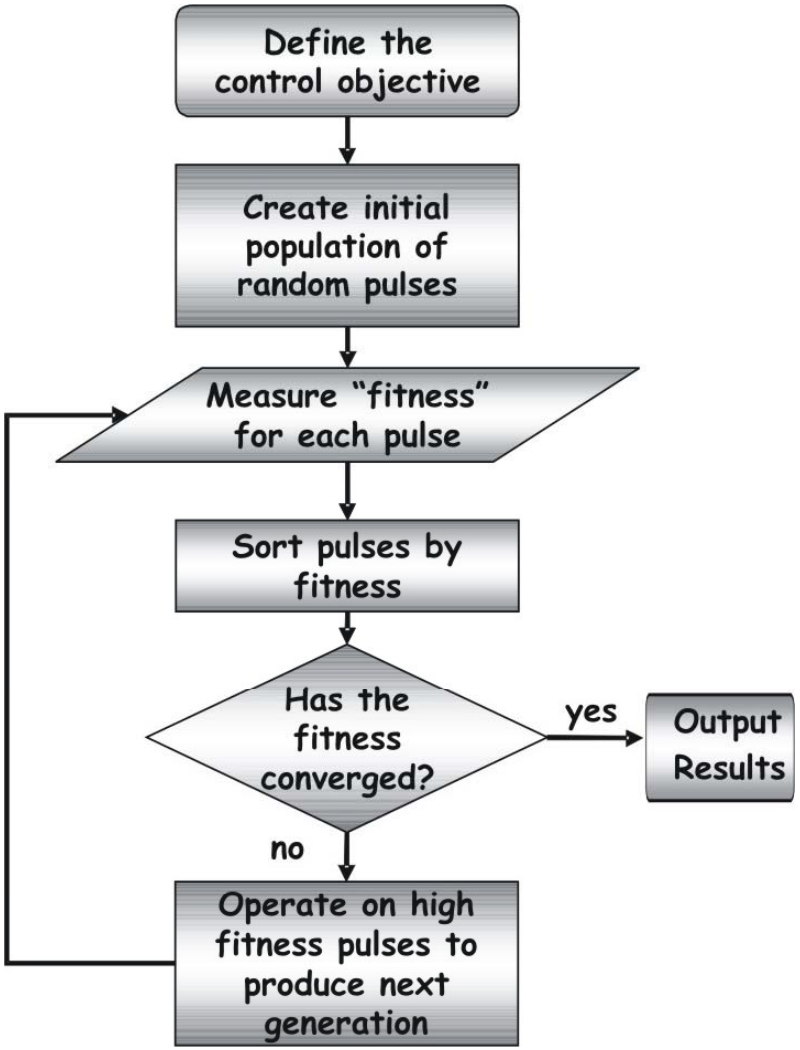
Systematic search of parameter space – given an intuitive expectation of mechanism



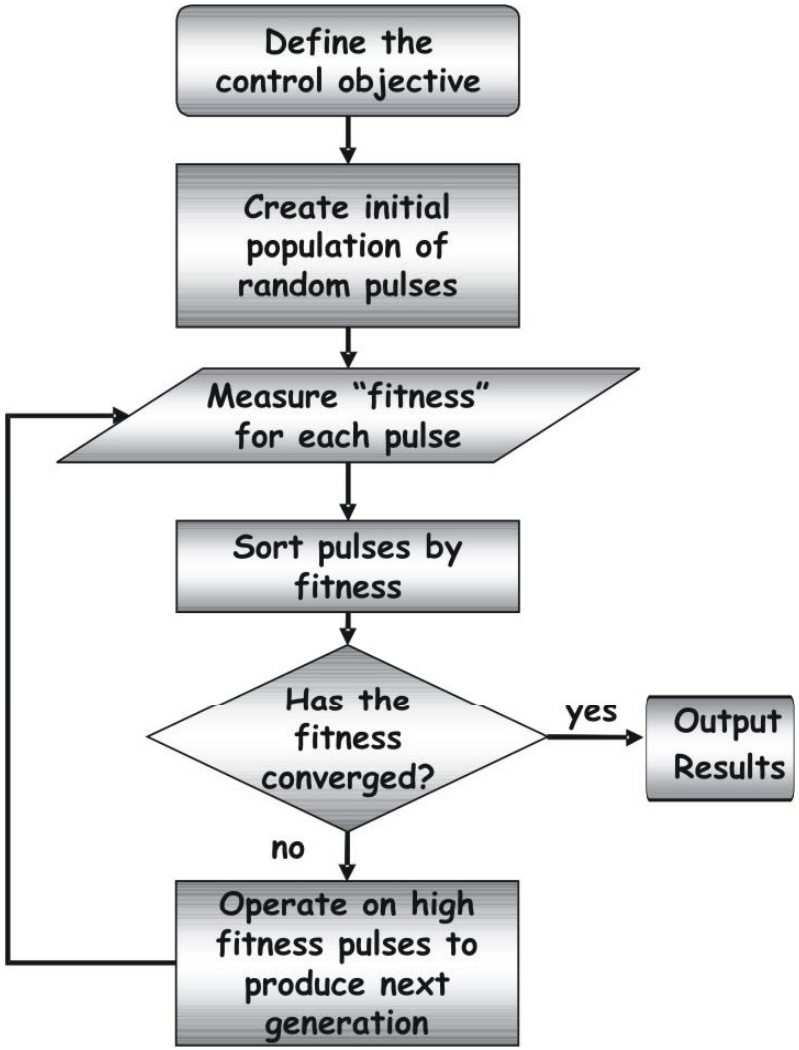
Empirical approach: learn through trial and feedback, in calculations or in experiments

Closed-loop feedback & adaptive search algorithm





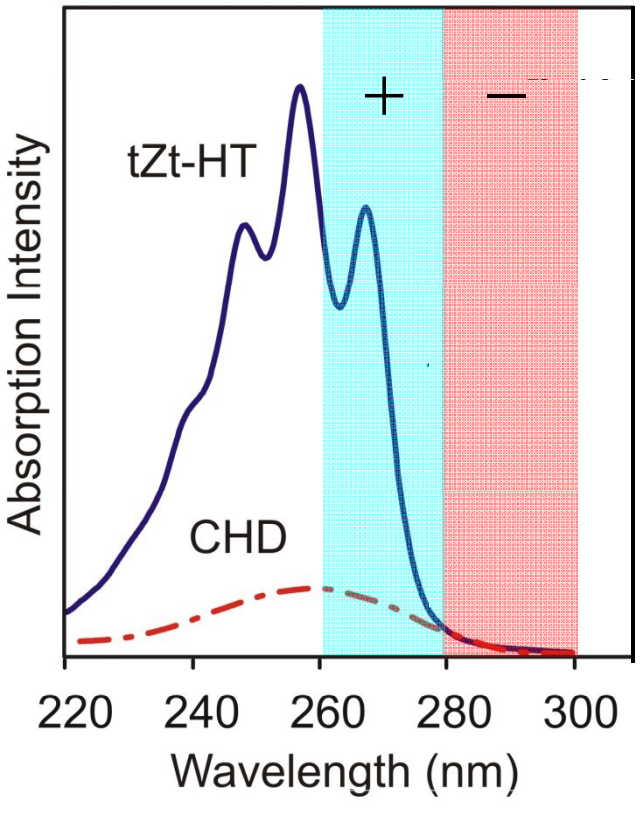
Fitness functions:



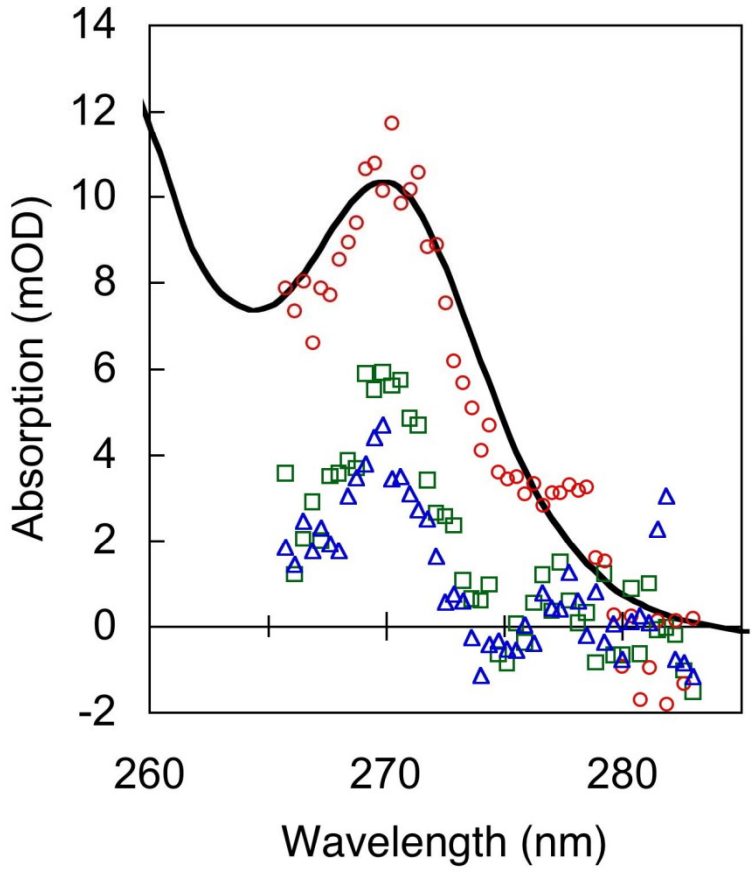
$$J(E) = \int_{260}^{280} \Delta A(\lambda, E) d\lambda$$

$$J(E) - C(E)$$

$$= \int_{260}^{280} \Delta A(\lambda, E) d\lambda - \int_{280}^{300} \Delta A(\lambda, E) d\lambda$$



Probe at 12 ns, subtract background:



Goal 1 increases HT formation (>100%)

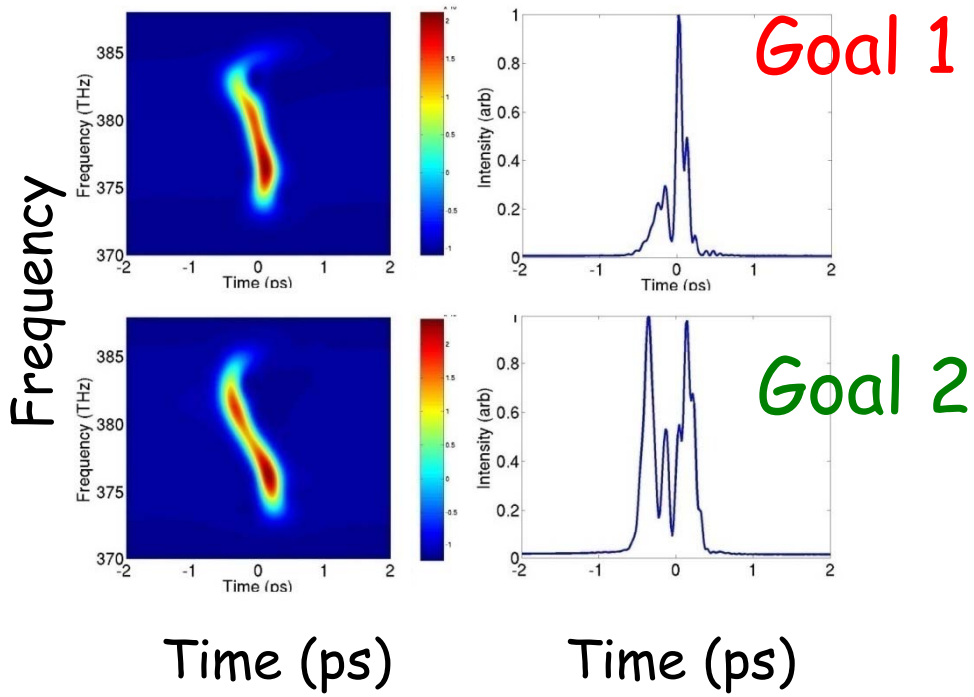
Goal 2 increases slightly - (background suppressed)

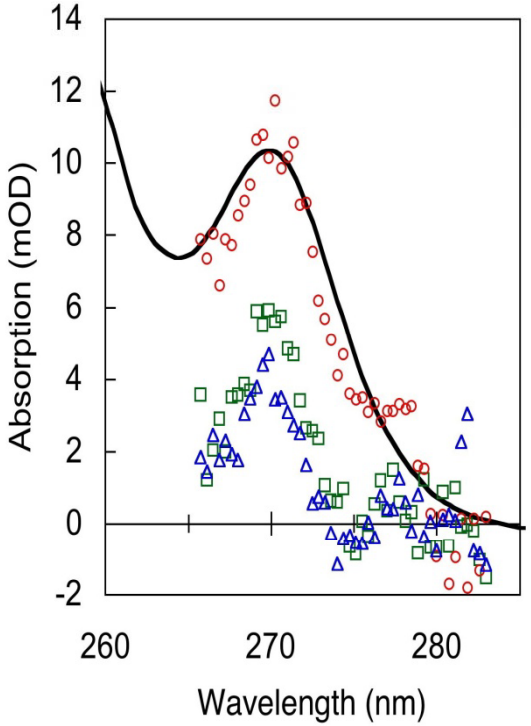
Transform Limit

Sample Optimal Pulses

CHD in Hexane

Husimi





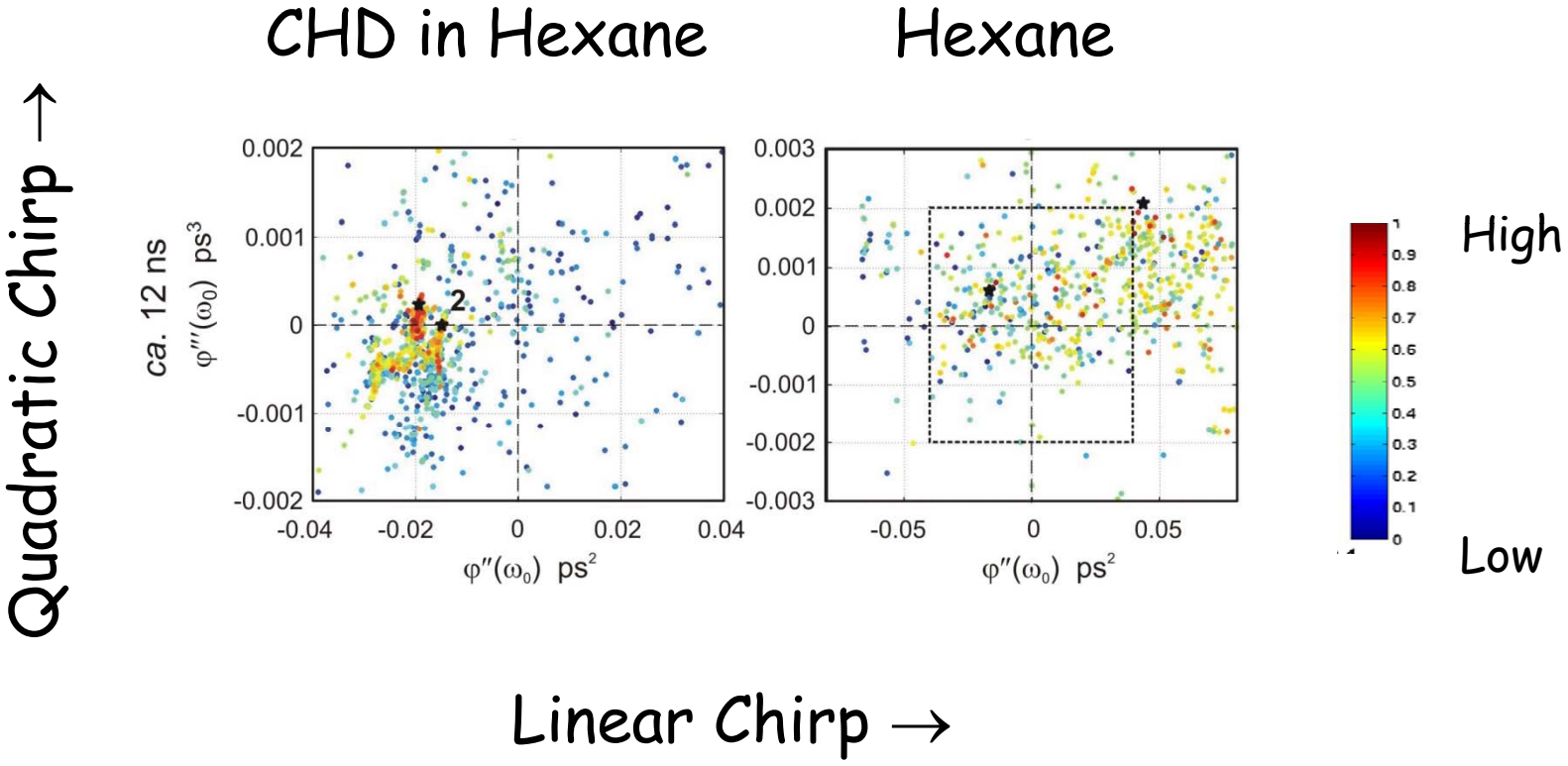
Fit the phase of each pulse to a polynomial:

Linear chirp coefficient

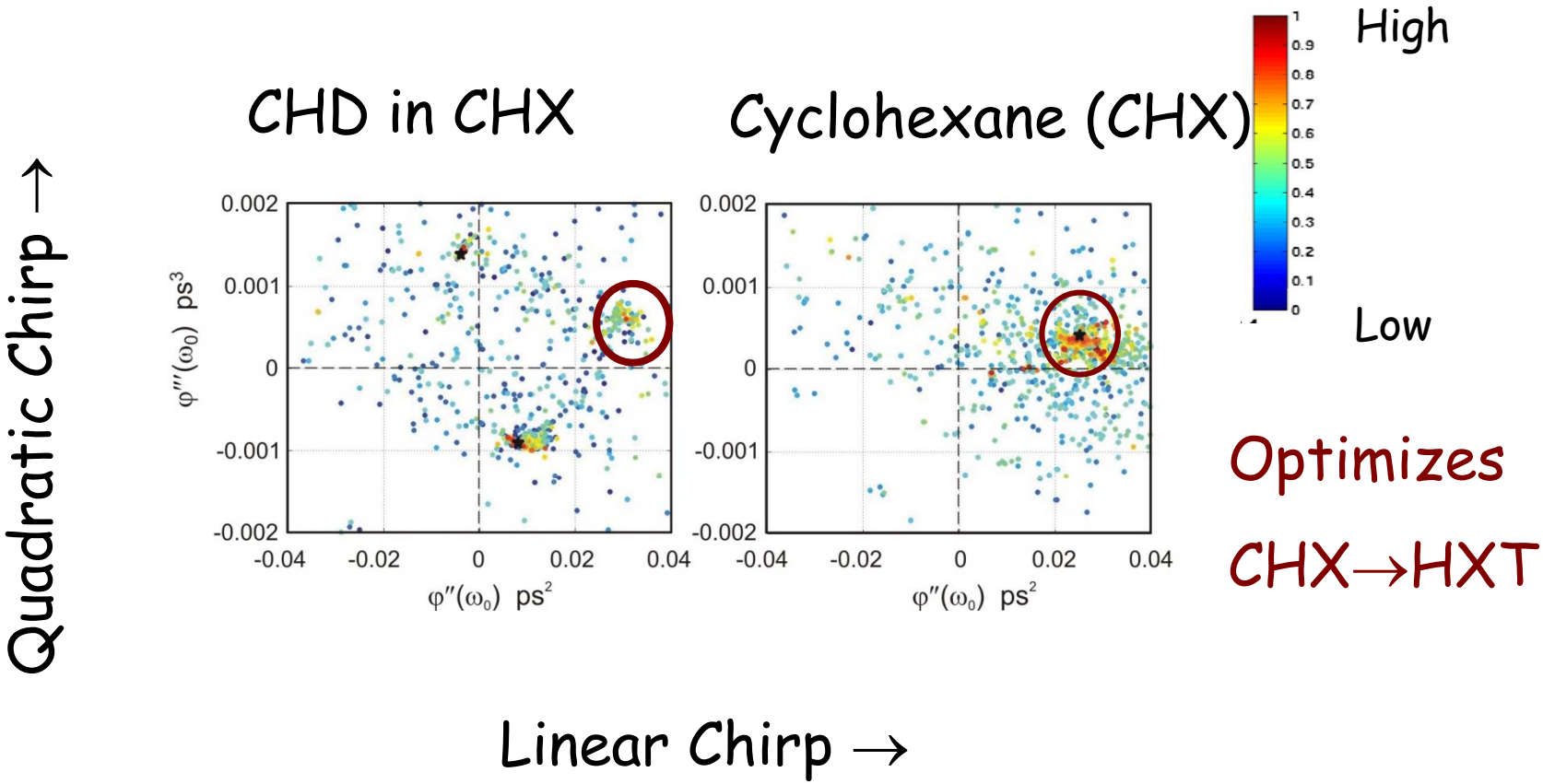
$$\phi(\omega) \approx \phi(\omega_o) + \phi(\omega_o)'(\omega - \omega_o) + \frac{\phi(\omega_o)''}{2!}(\omega - \omega_o)^2 + \frac{\phi(\omega_o)'''}{3!}(\omega - \omega_o)^3 + \ldots$$

Quadratic chirp coefficient

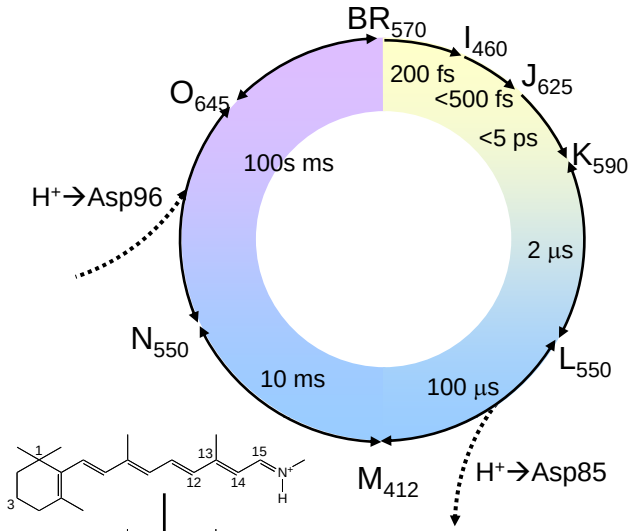
Fitness map projected onto ϕ'' and ϕ'''

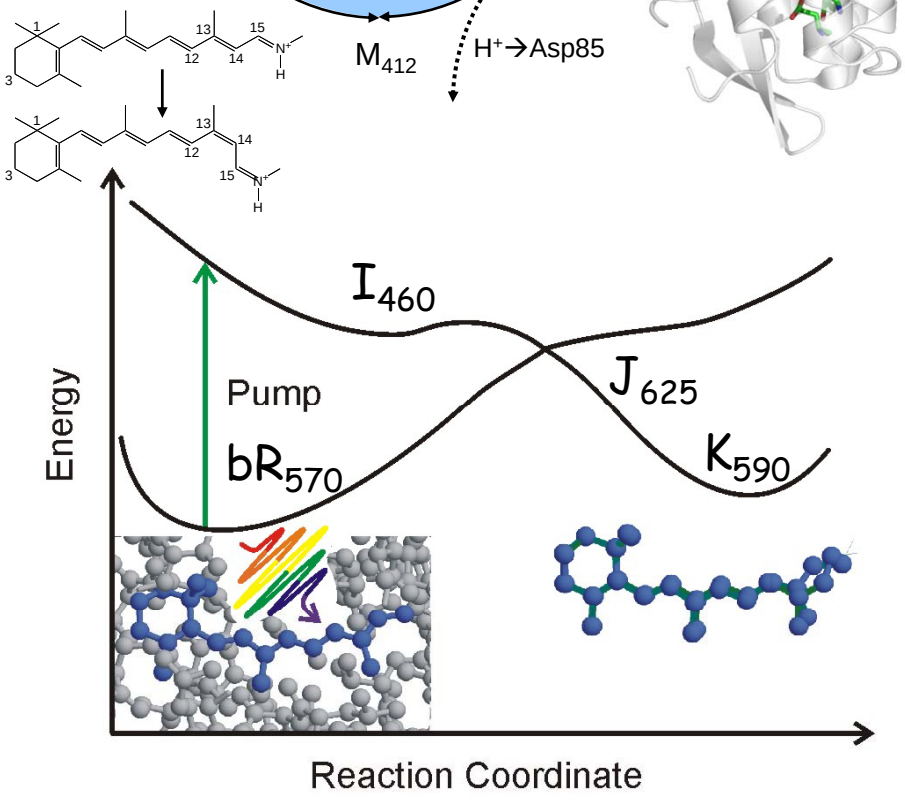


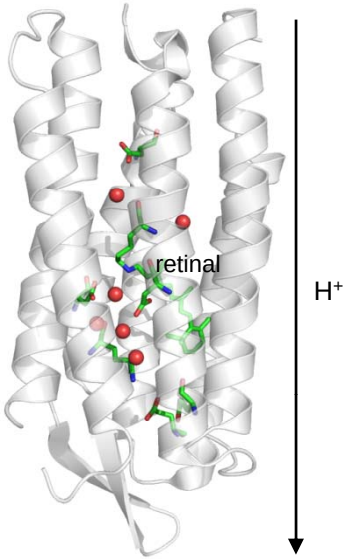
Fitness map projected onto ϕ'' and ϕ'''

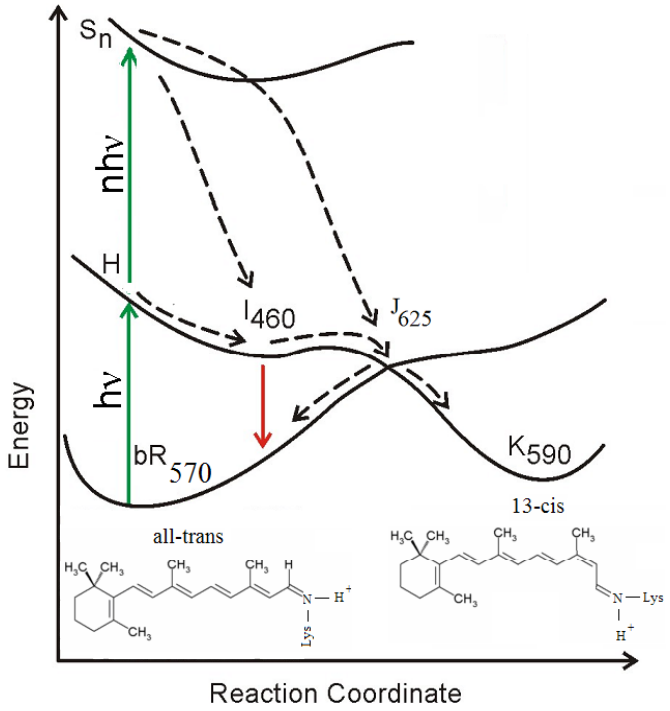


Bacteriorhodopsin Isomerization









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