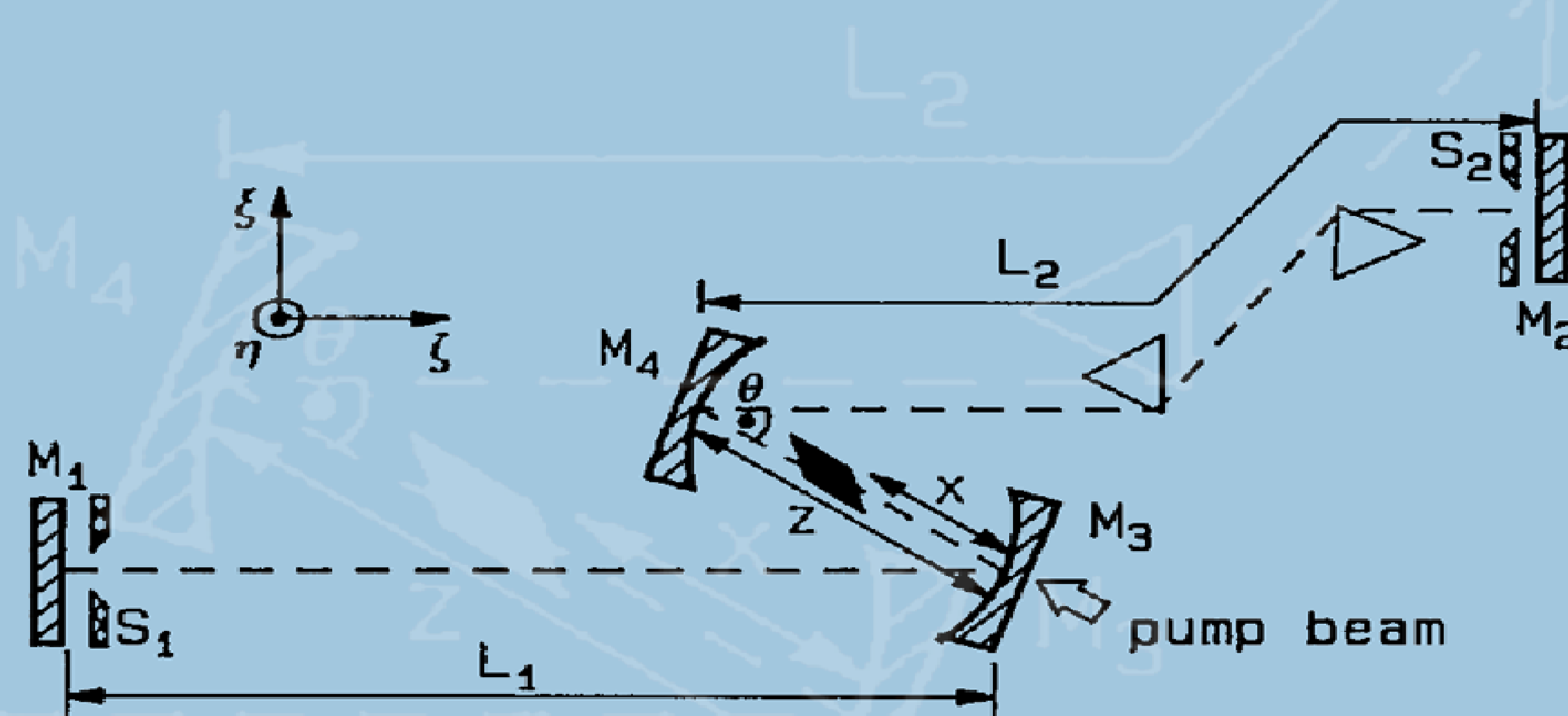
ULTRAFAST OPTICS



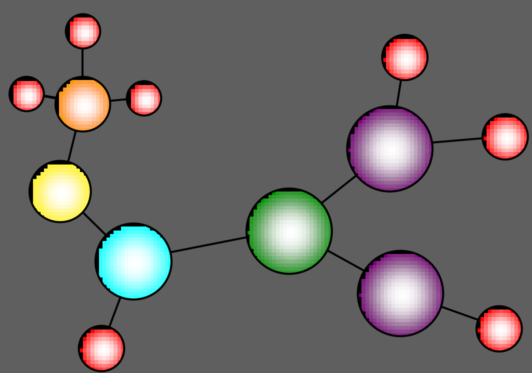
by PIOTR WASYLCZYK

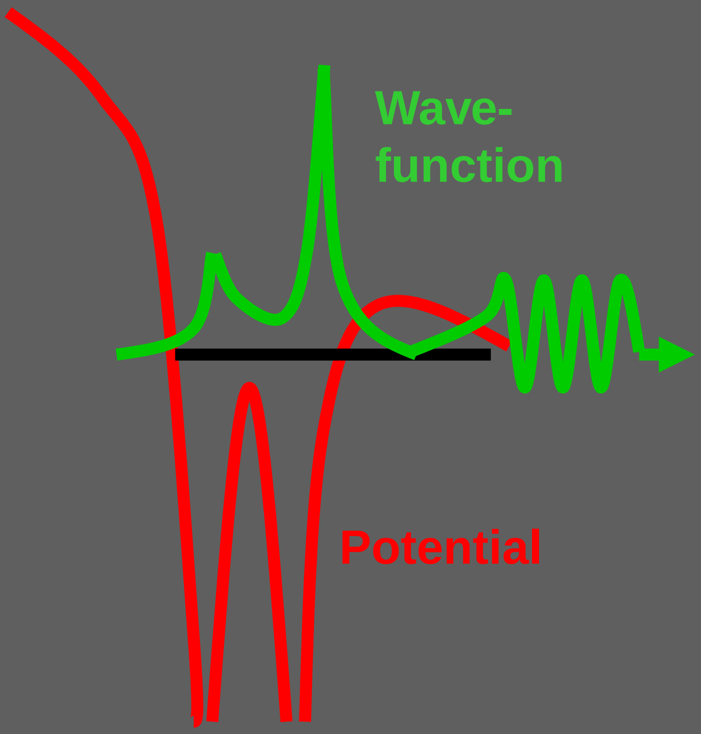
Coherent Control

Coherent Control attempts to control a chemical reaction with light, usually a cleverly shaped ultrashort laser pulse.

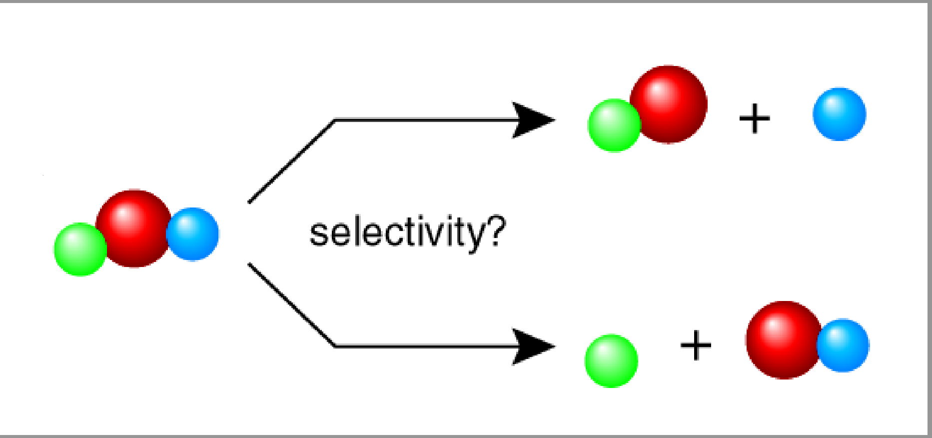
In most cases it combines:

1. shaped pulses,
2. iterative approach.





Coherent Control



Chemical reactions proceed in a manner determined by the molecular Hamiltonian.

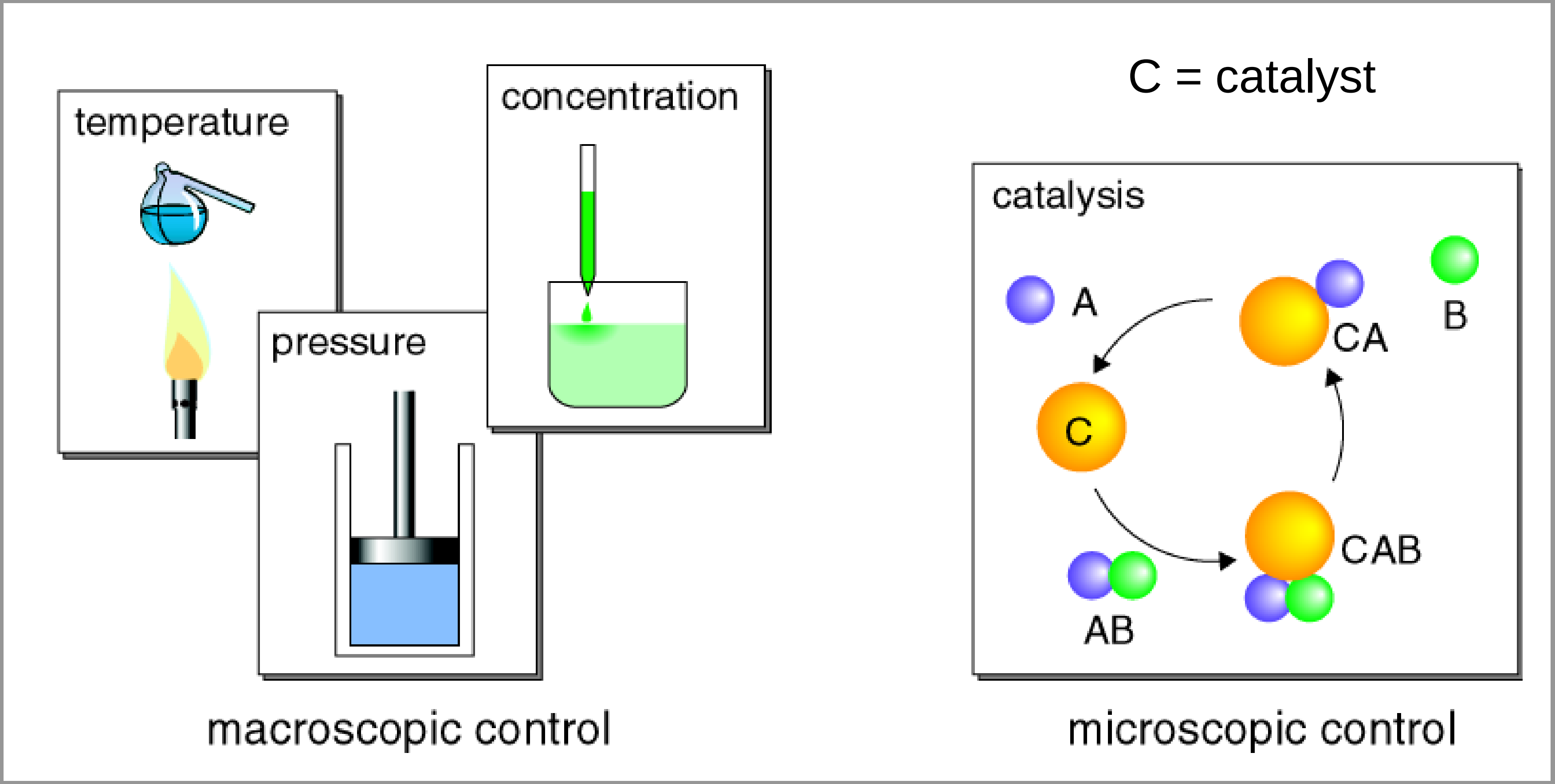
What if we'd like to change this and make different products?

Bring in a light frequency to excite a bond we'd like to break. But it's not so easy! There's a lot more to it.

A long-held dream of chemists. It's now coming true. Shaped ultrashort pulses are the key.

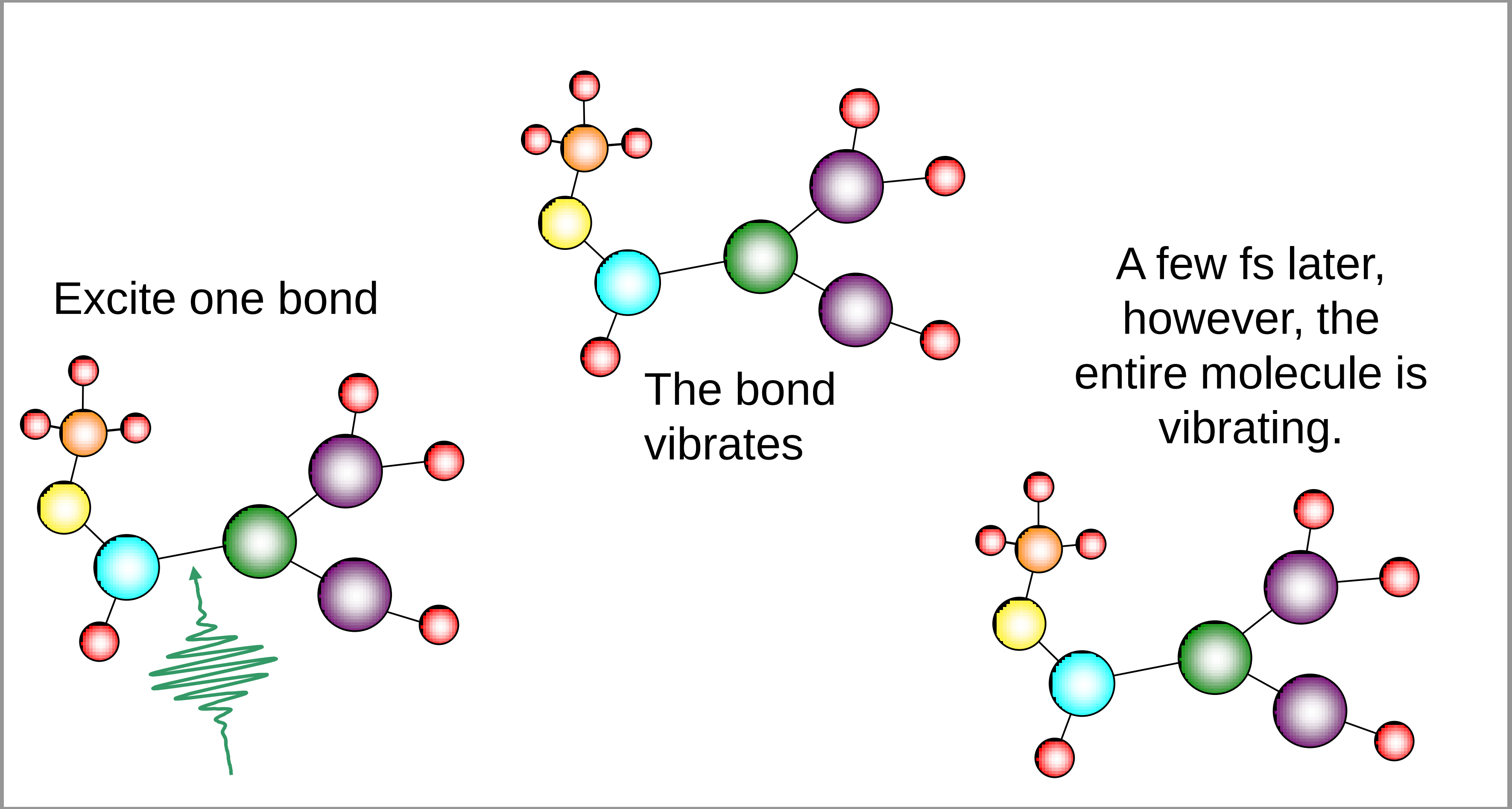
Some slides courtesy
Gustav Gerber, University of Wurzberg, Germany
Margaret Murnane and Henry Kapteyn, JILA
Robert Levis, Temple University

Conventional methods of chemical control



Much can be done, but not everything we'd like.

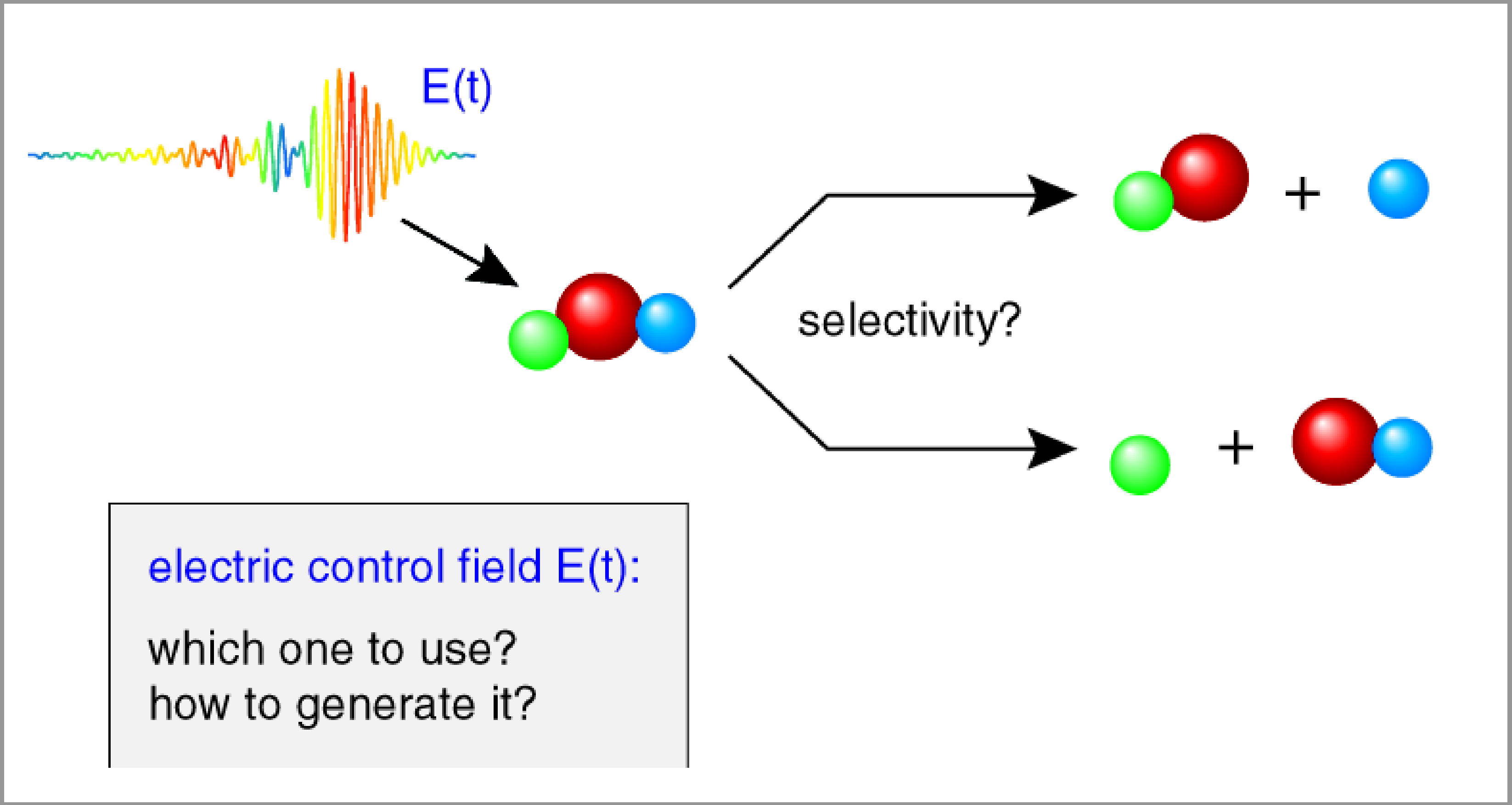
Intramolecular Vibrational Redistribution



Intramolecular Vibrational energy Redistribution (**IVR**) occurs on a few-fs time scale, so long pulses excite entire molecule, and the weakest bond breaks, no matter which bond was excited.

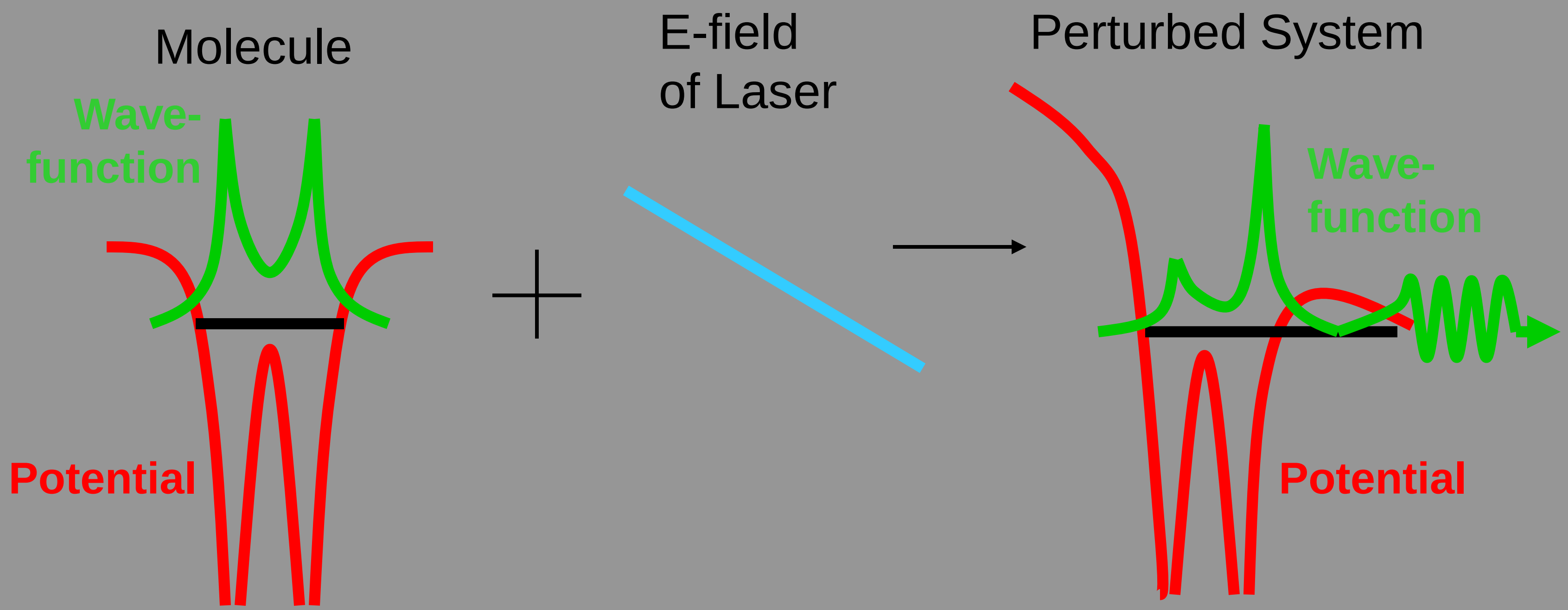
Coherent control: Using shaped ultrashort pulses to control the reaction

Can an ultrashort pulse cause a molecule to vibrate in such a way as to break the bond of our choice?



The physics of coherent control

The pulse electric field perturbs the molecule and potentially dissociates it.



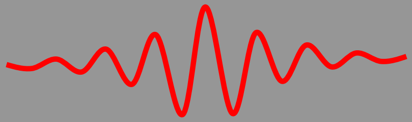
The trick is to compute the required pulse electric field.

Trying to do the theory for coherent control

First, we need to know the complete Hamiltonian for the molecule and radiation:

$$\boxed{H_{\text{system}} = H_{\text{molecule}} + H_{\text{radiation}} + H_{\text{interaction}}}$$

$H_{\text{radiation}}$ known



$H_{\text{interaction}}$

weak field: known $\langle \psi_f | \mu \cdot E | \psi_i \rangle$

strong field: unknown

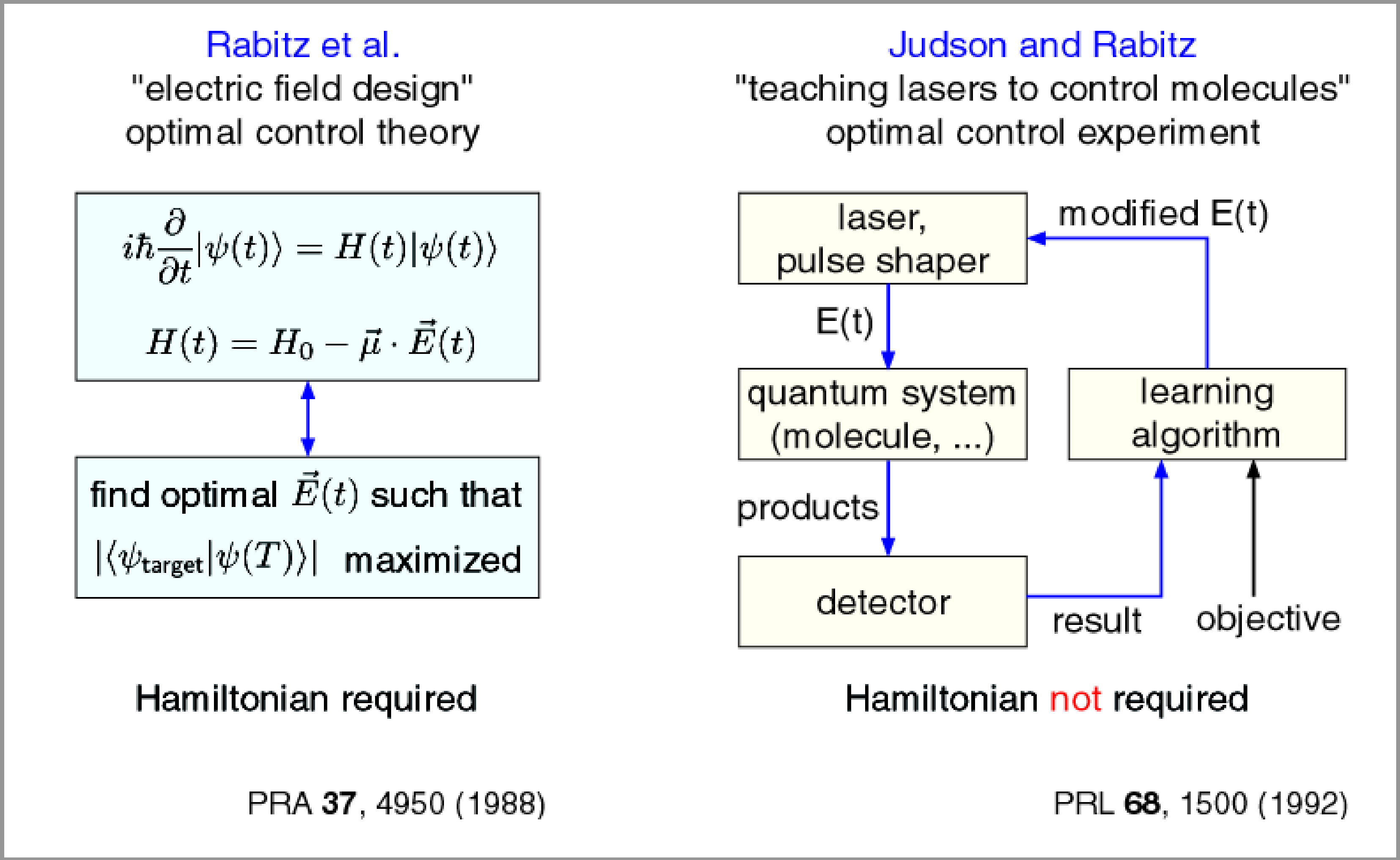
H_{molecule}

small molecules: approximate

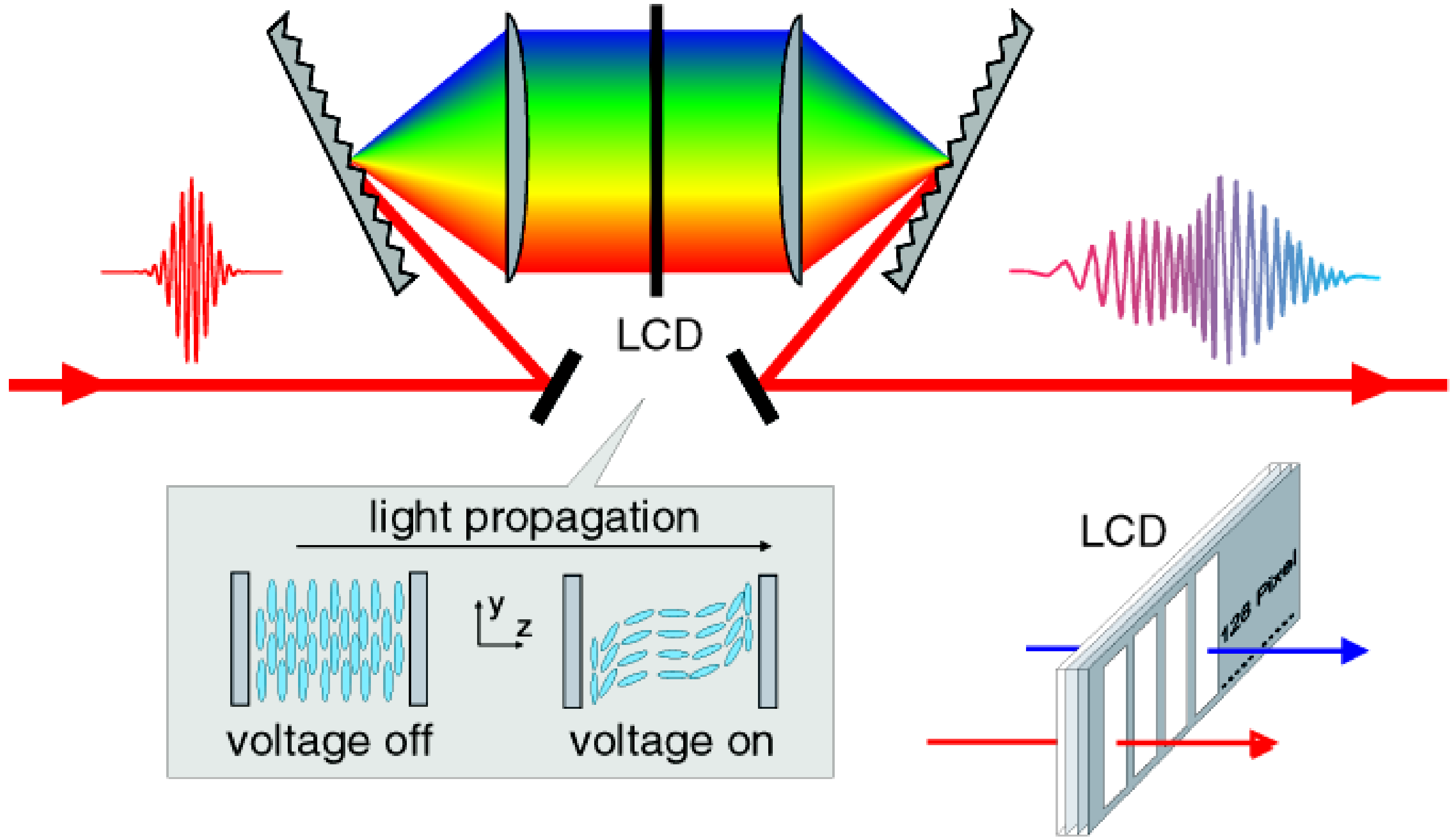
large molecules: unknown

It’s hopeless to solve the problem for all but the simplest molecules.

We could try to solve the problem theoretically, but it's easier to just do it iteratively in the lab.



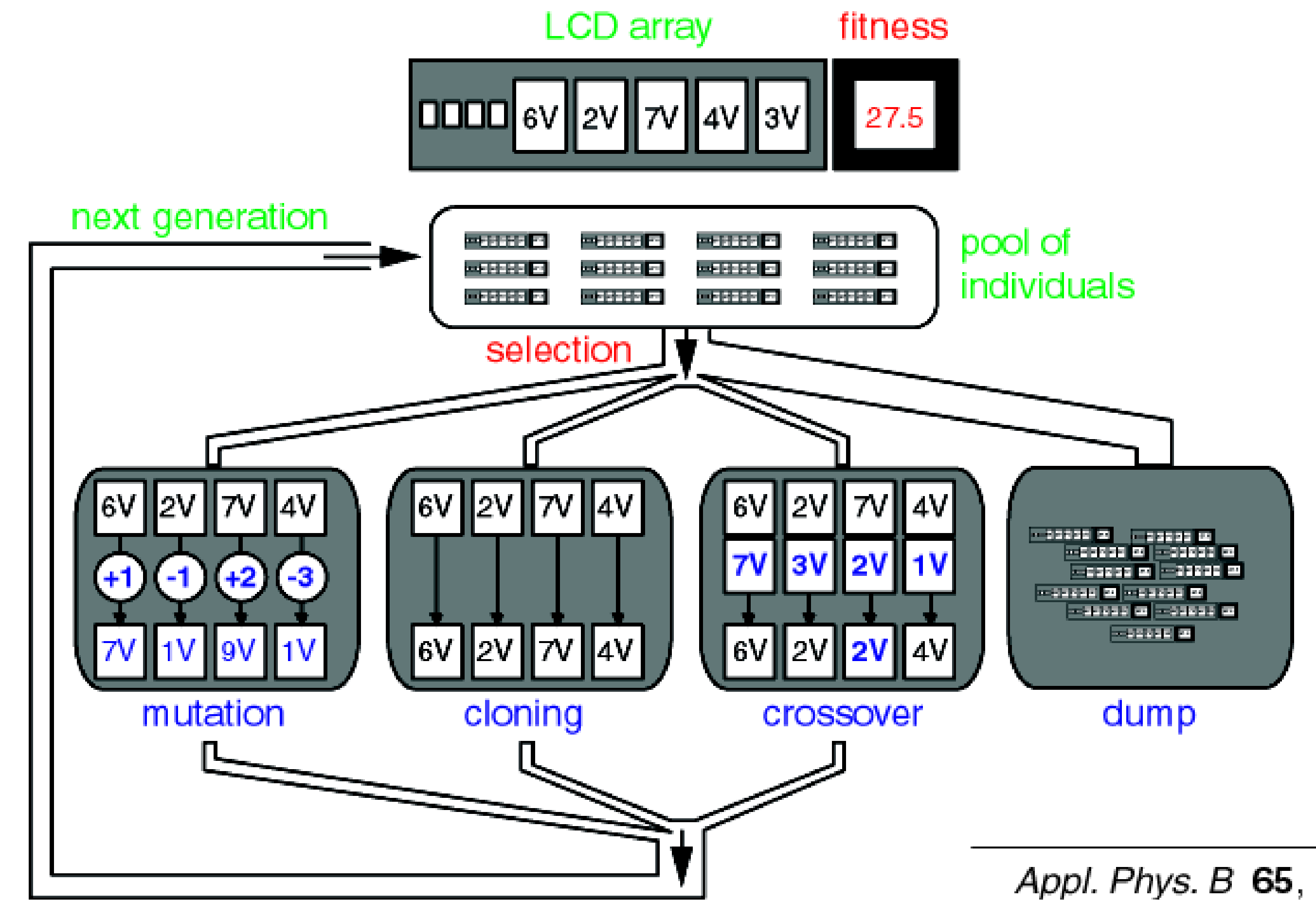
Pulse-shaping is important for coherent control.



Appl. Phys. B **68**, 281 (1999)
A. M. Weiner: *Rev. Sci. Instrum.* **71**, 1929 (2000)

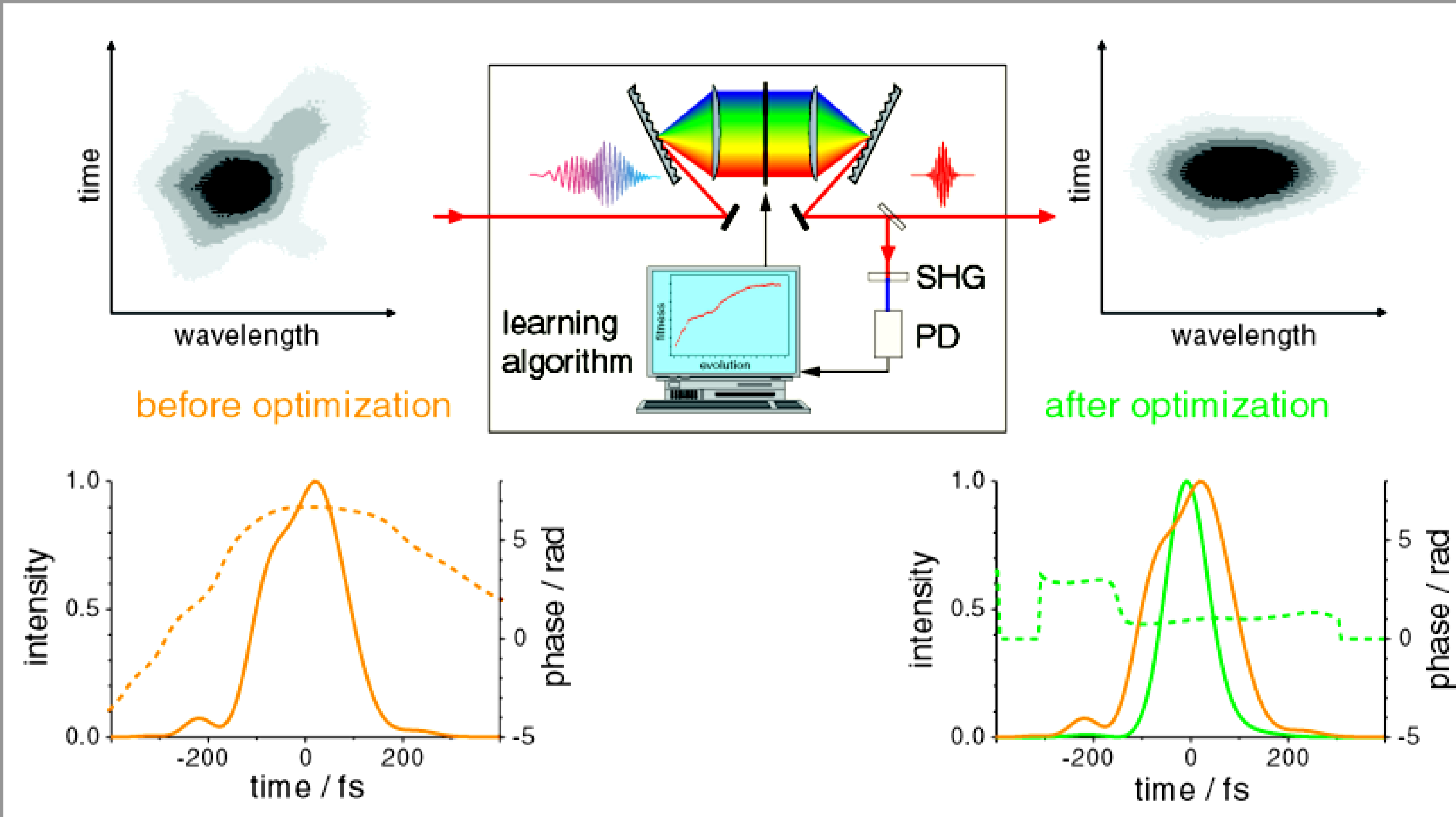
Genetic algorithm for coherent control

This algorithm was developed for computer optimization, but, for coherent control, it can be implemented as part of an experiment.



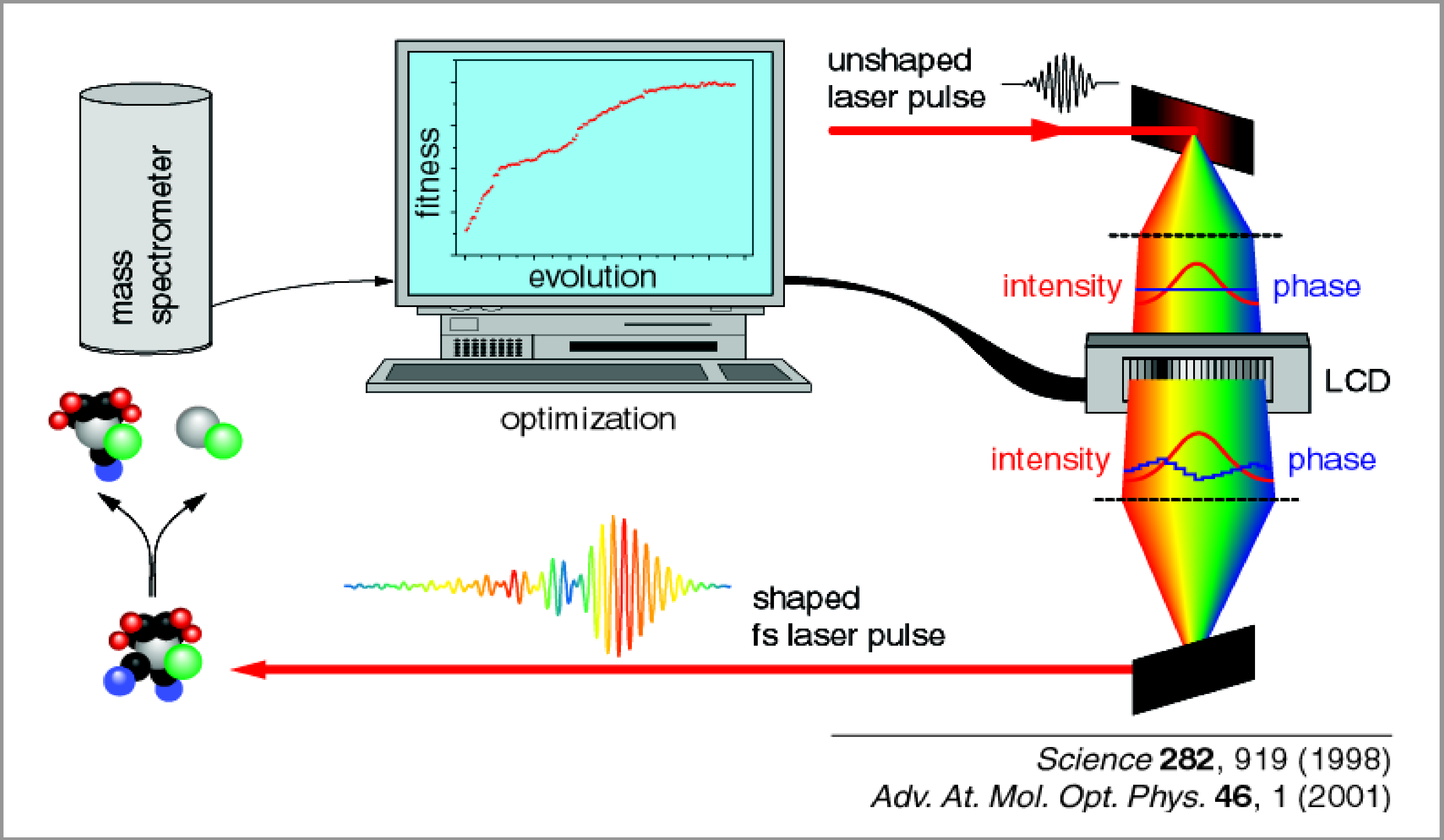
Appl. Phys. B **65**, 779 (1997)

A genetic algorithm can minimize the pulse length.



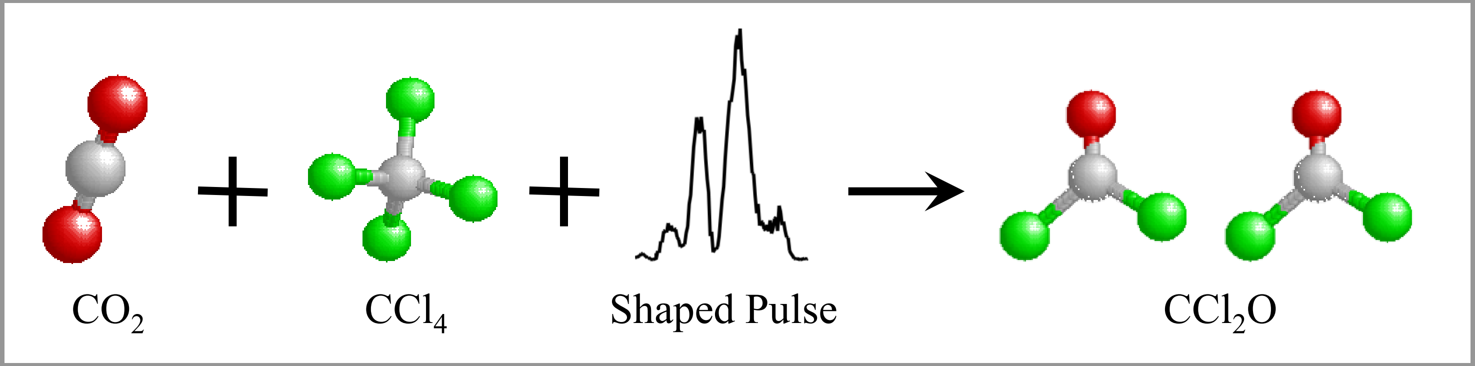
Appl. Phys. B **68**, 281 (1999)

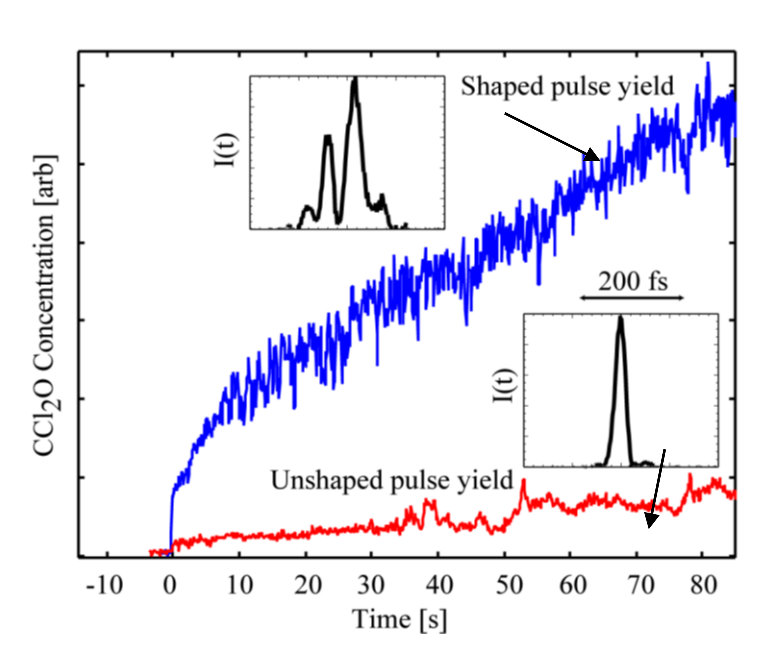
Using a learning algorithm to perform coherent control



Coherent control of a simple gas phase reaction

Reaction under study

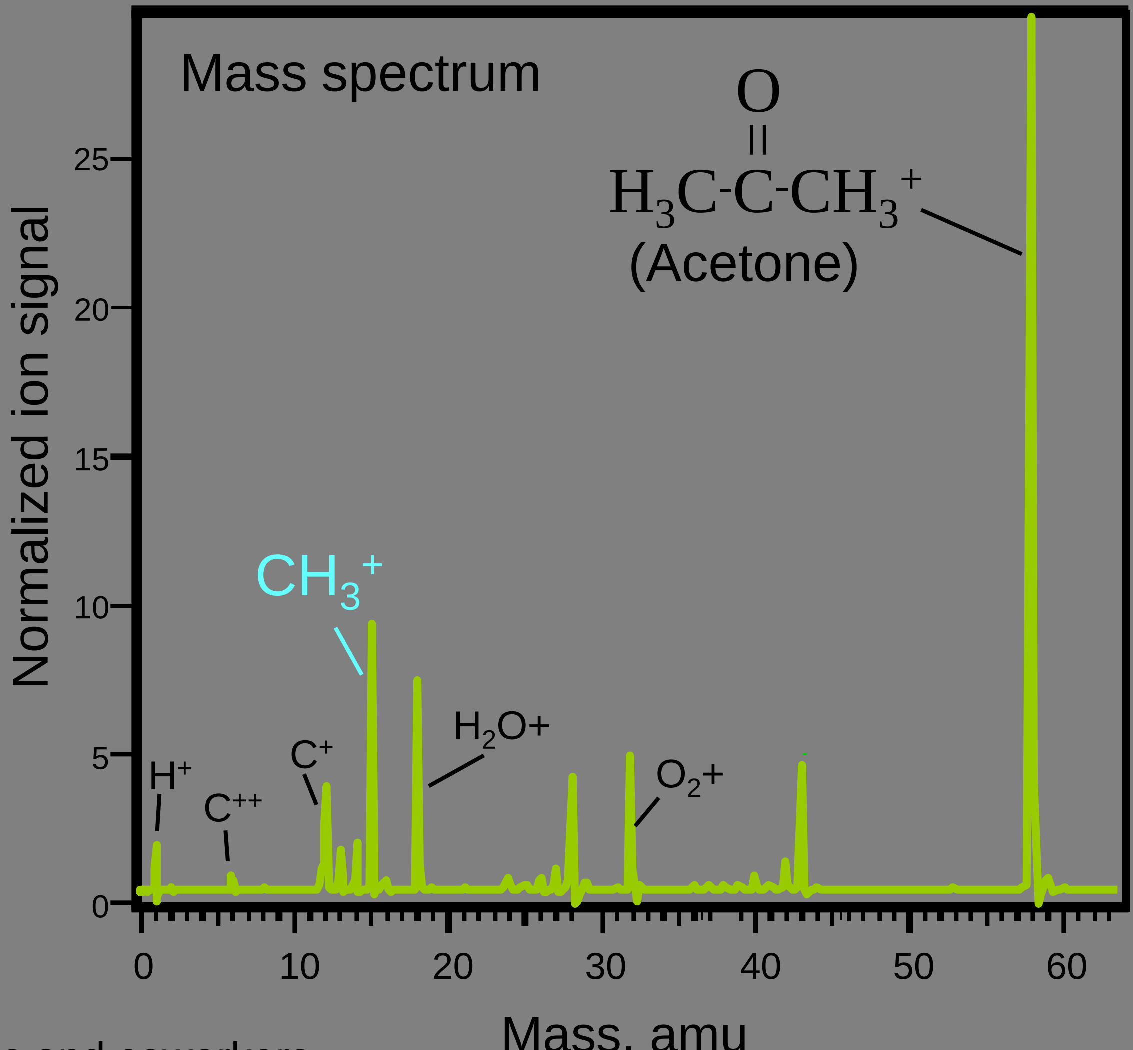


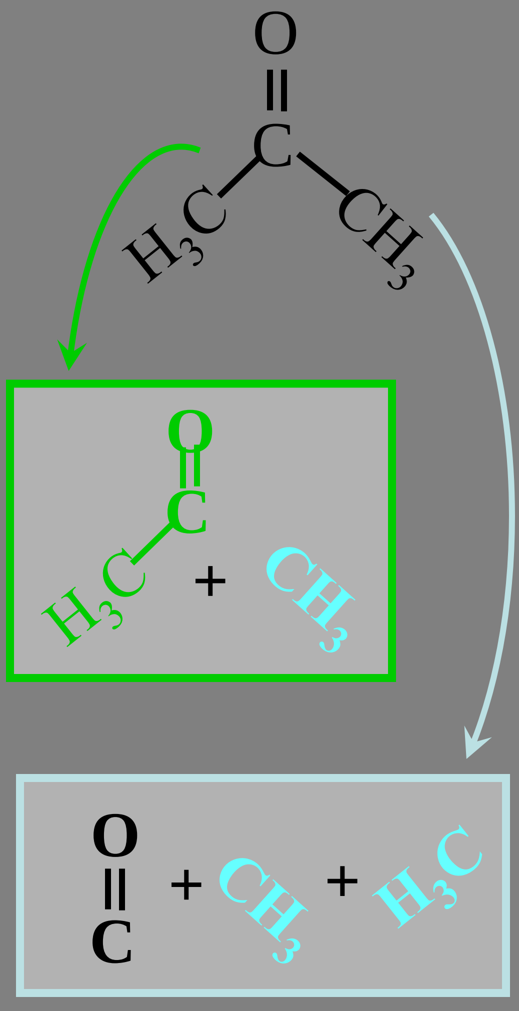


Murnane and Kapteyn, University of Colorado

Coherent control with acetone (gas phase)

Acetone can be broken into various pieces. A laser pulse could help.

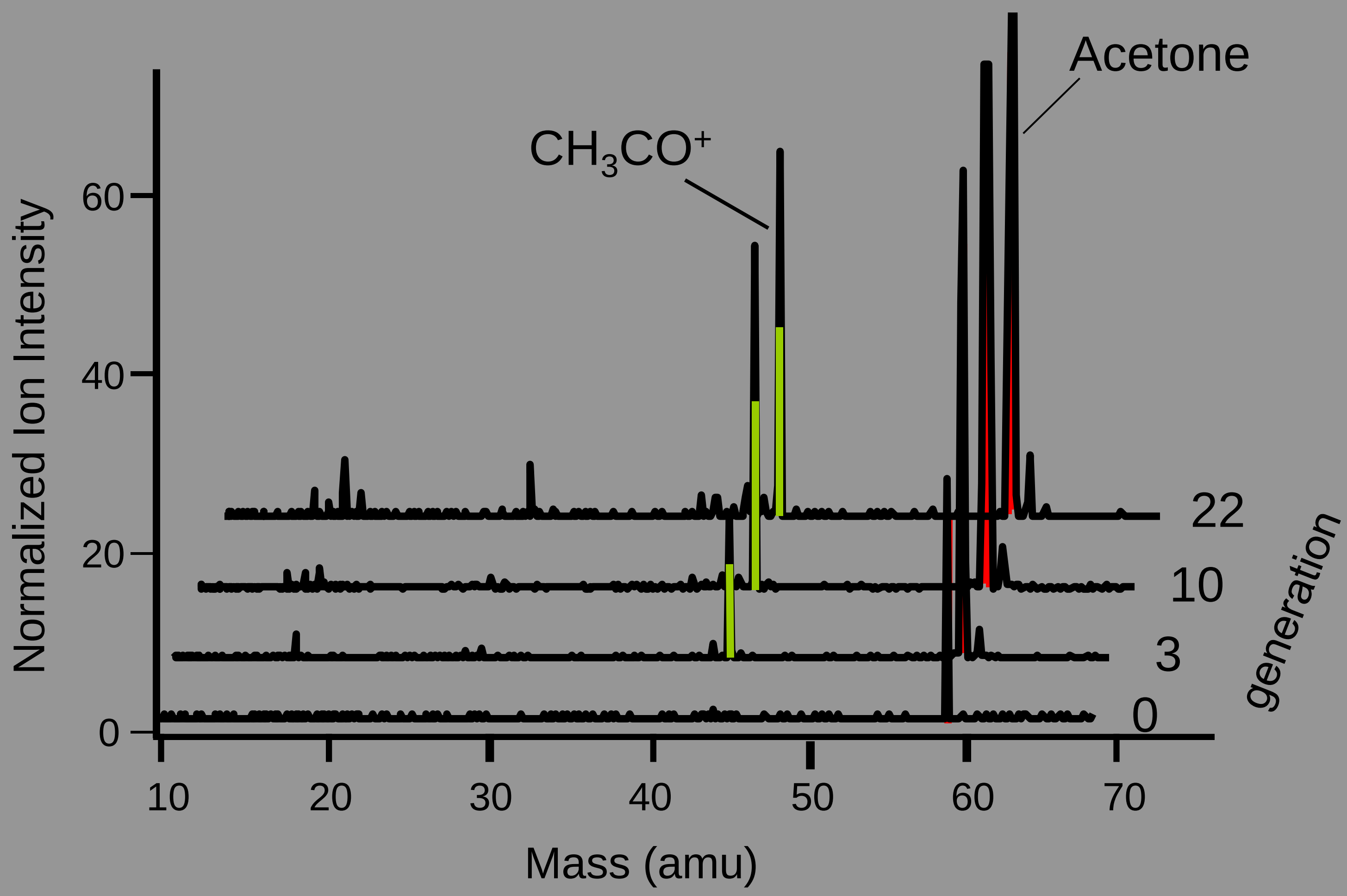




Levis and coworkers

Optimizing one acetone photo-fragment

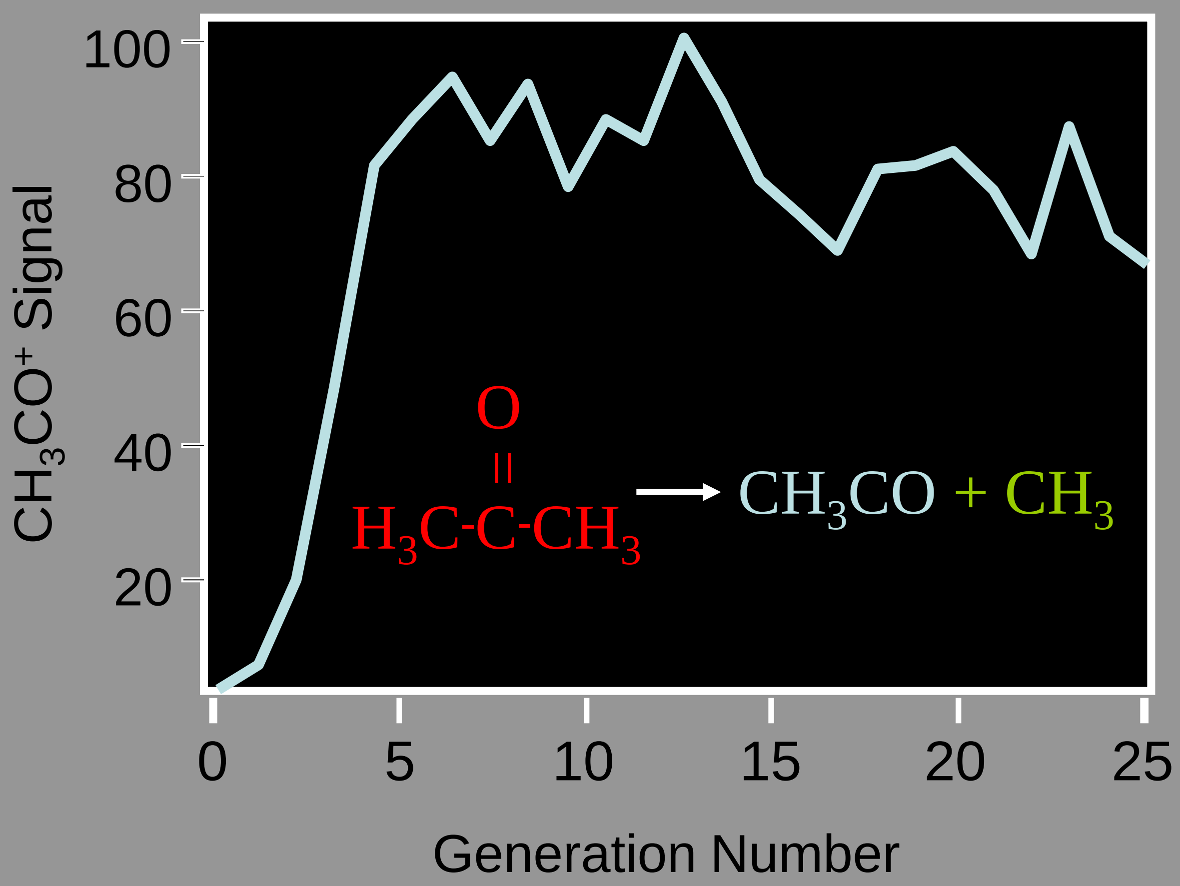
Goal: Optimize CH_3CO^+ at 43 amu



Levis and coworkers

Science 2001, 292, 709

Maximization of the relevant photo-fragment occurs rapidly.

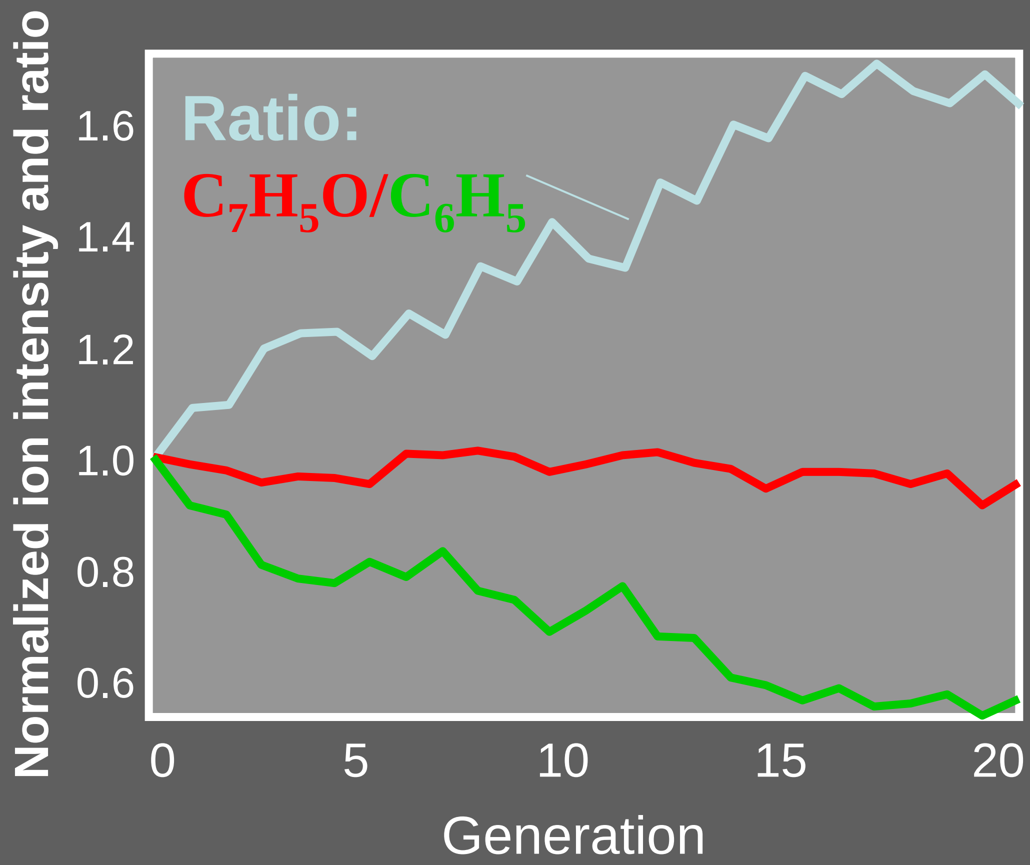


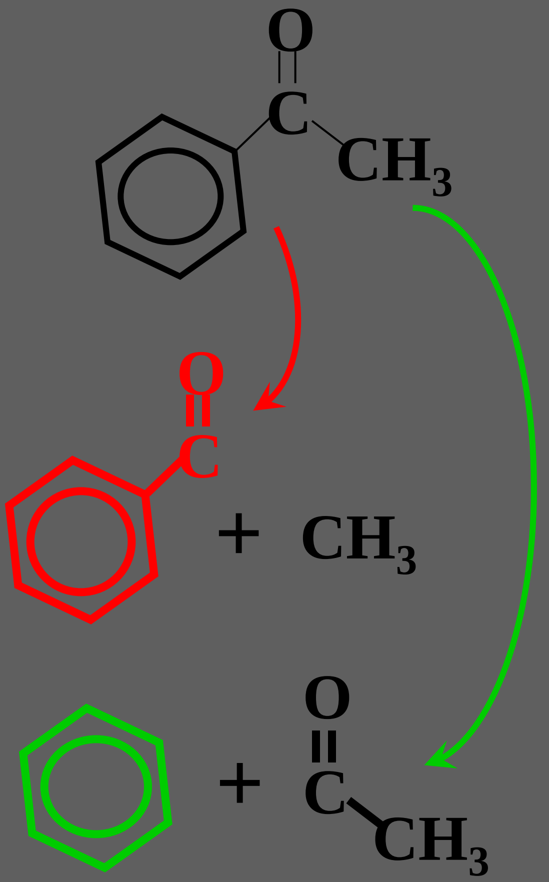
Levis and coworkers

Science 2001, 292, 709

Manipulating the dissociation yields in acetophenone

Different pulse shapes can optimize different photo-fragments.

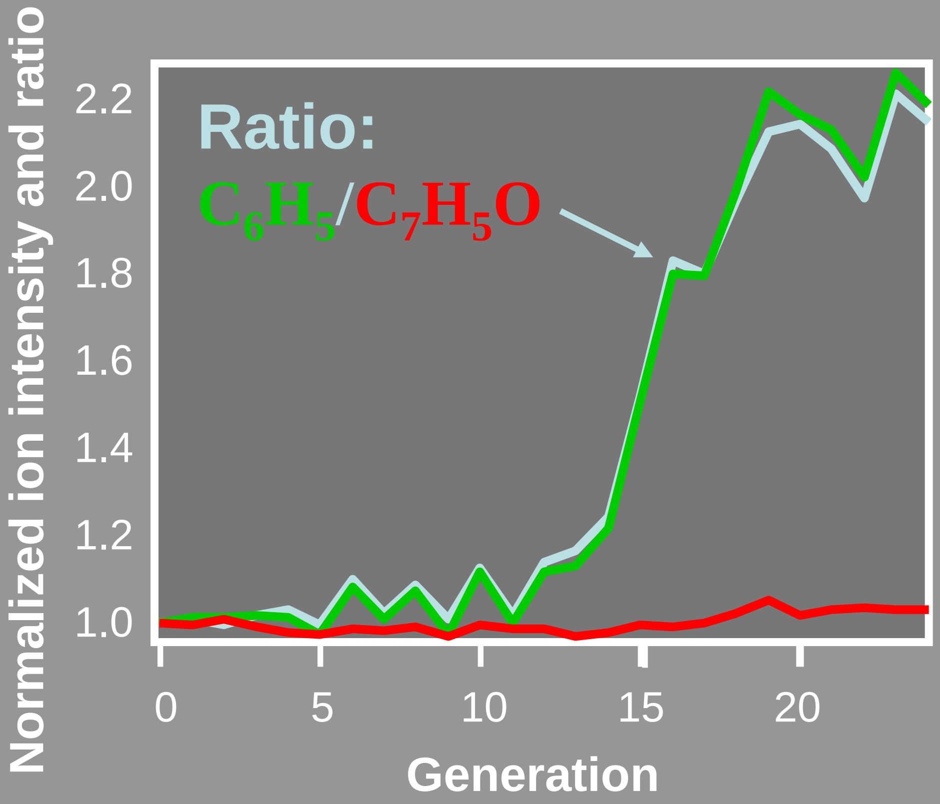


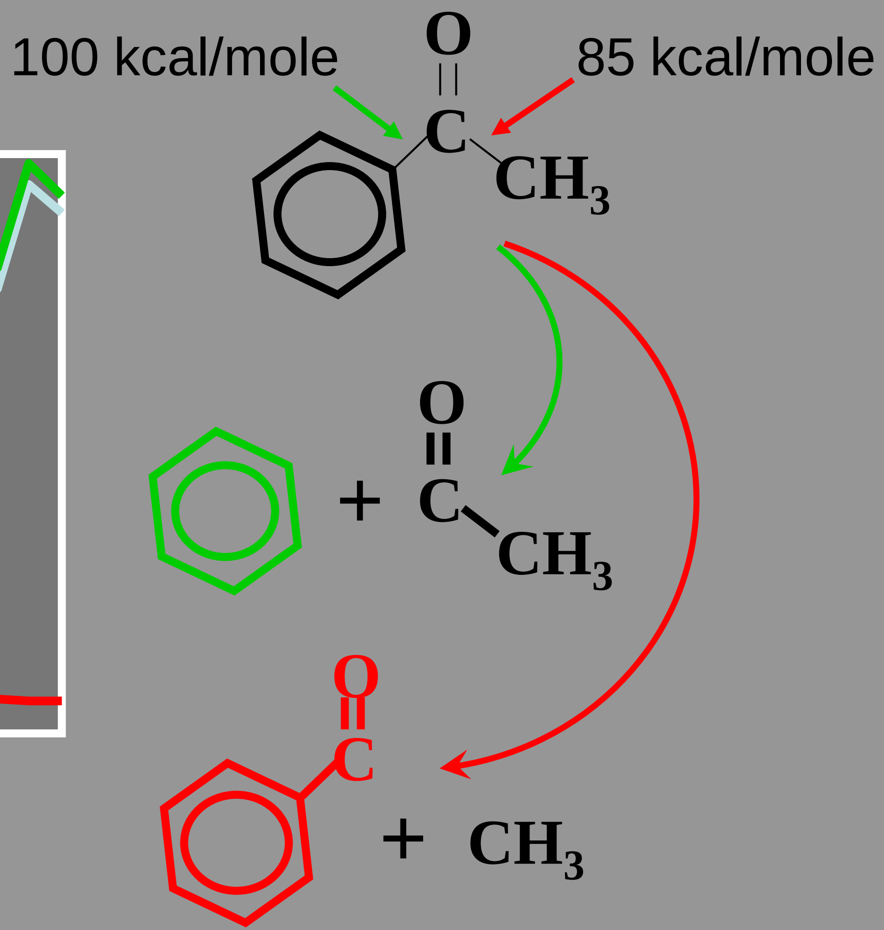


Levis and coworkers

Reversing the ratio: Increasing the phenyl yield

Optimizing the phenyl fragment yield also works.



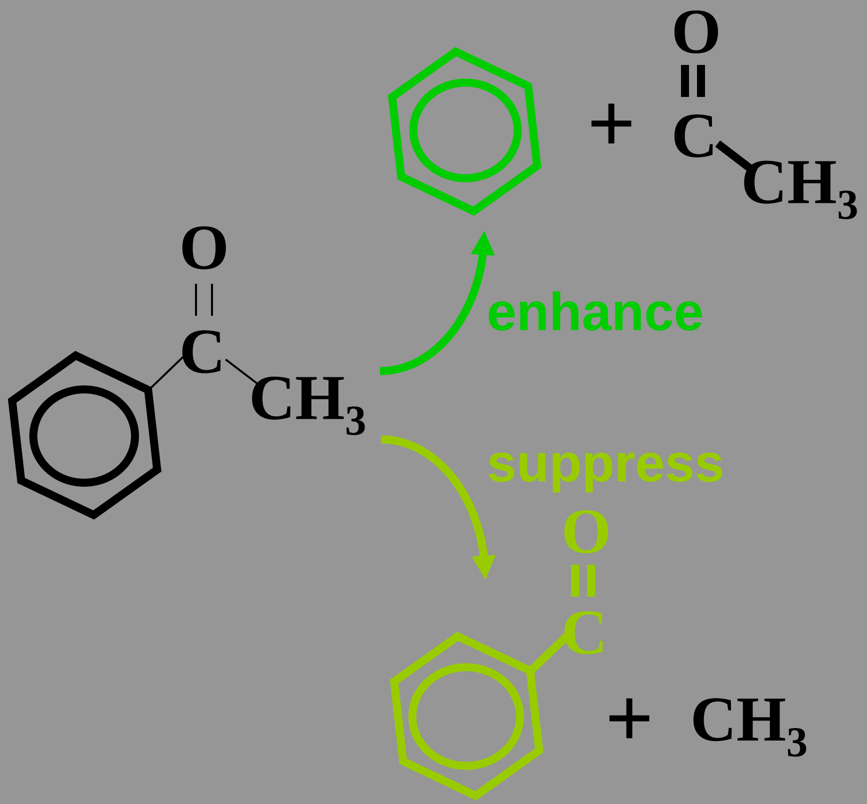


Levis and coworkers

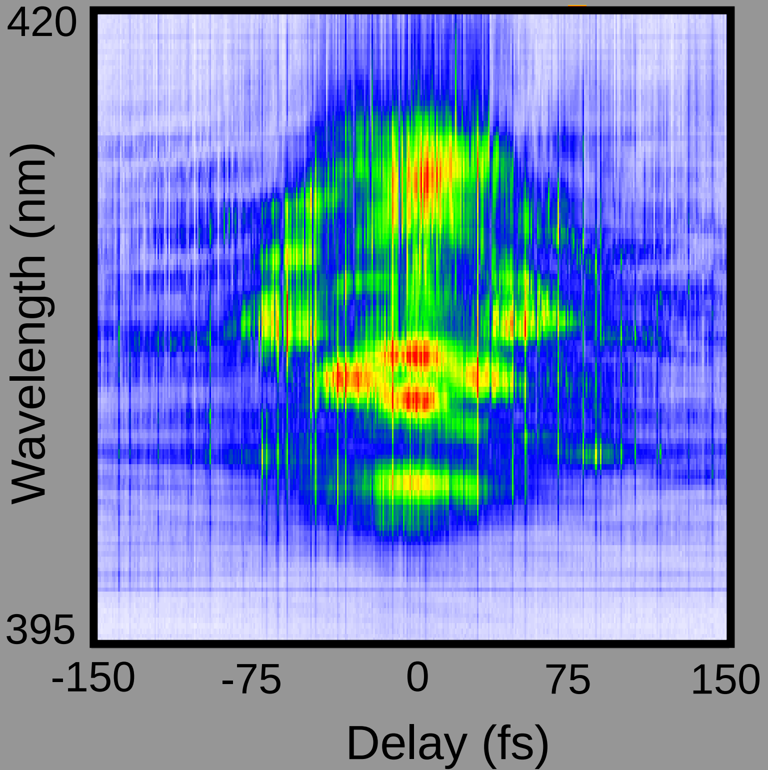
What do these pulses look like?

The pulse that maximizes the ratio of the two fragments.

Interestingly, a very simple pulse maximizes the phenyl radical (but not the ratio).

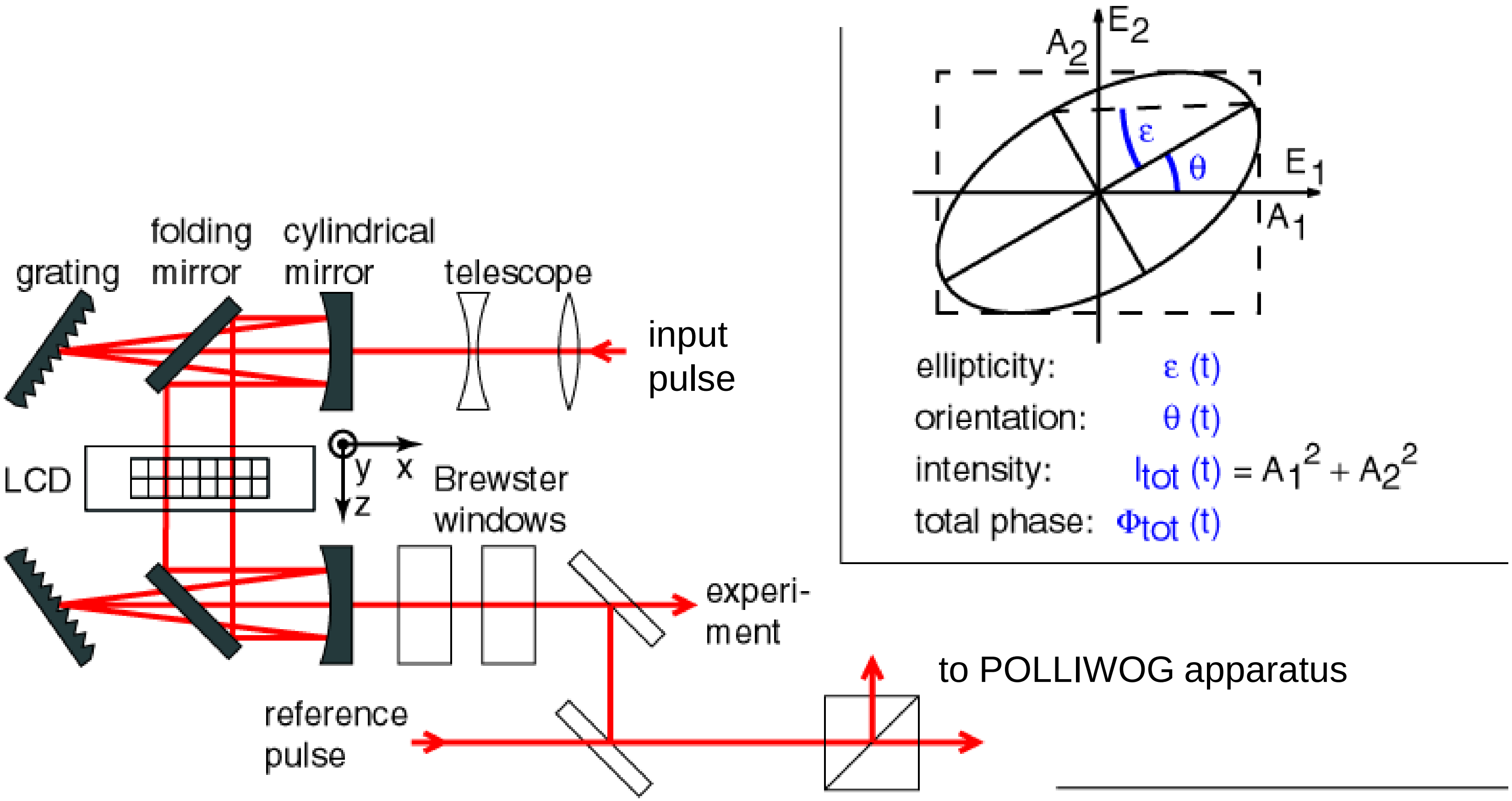


SHG FROG trace



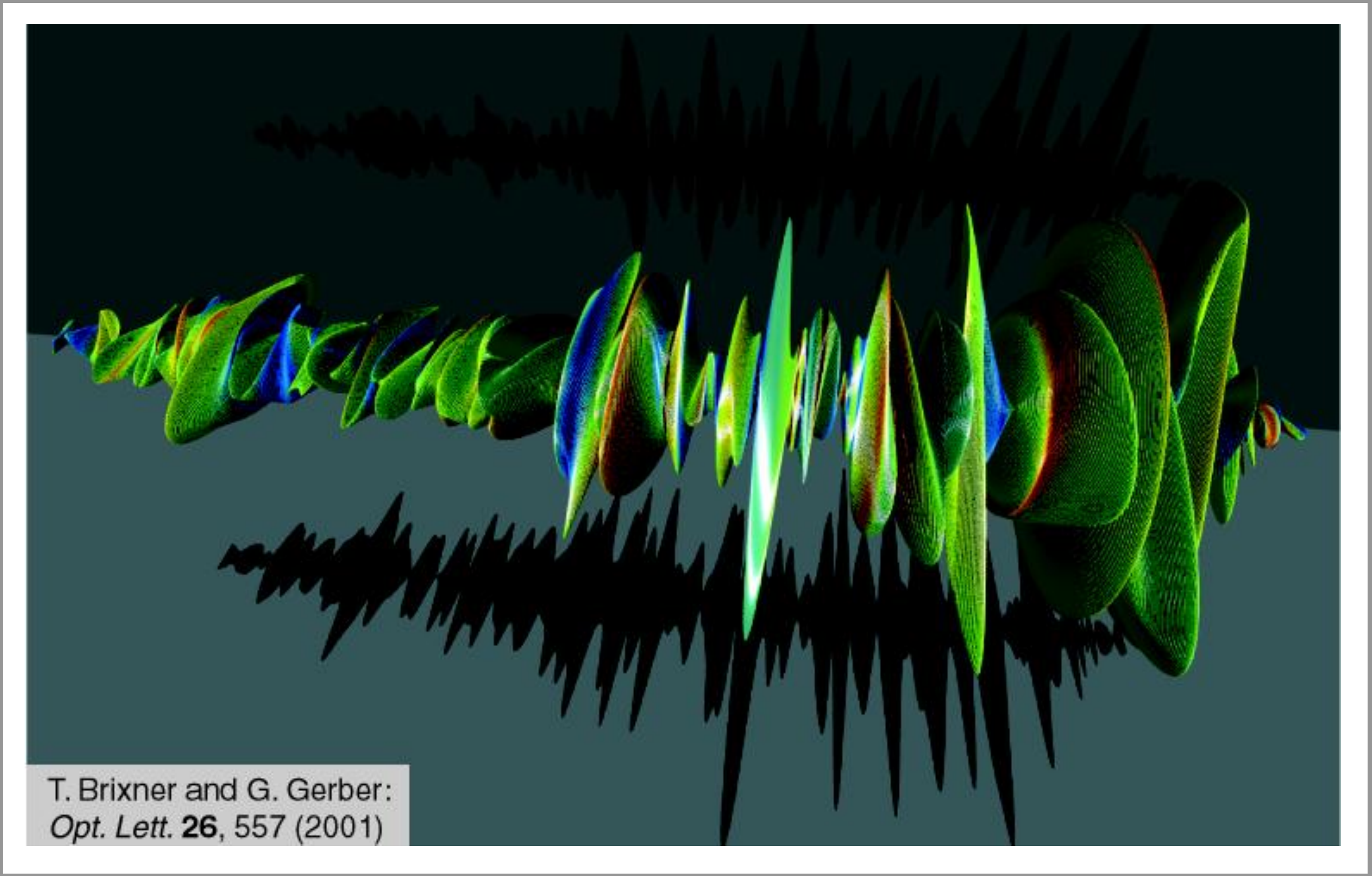
Levis and coworkers

Molecules are not isotropic, so pulse polarization shaping is important.

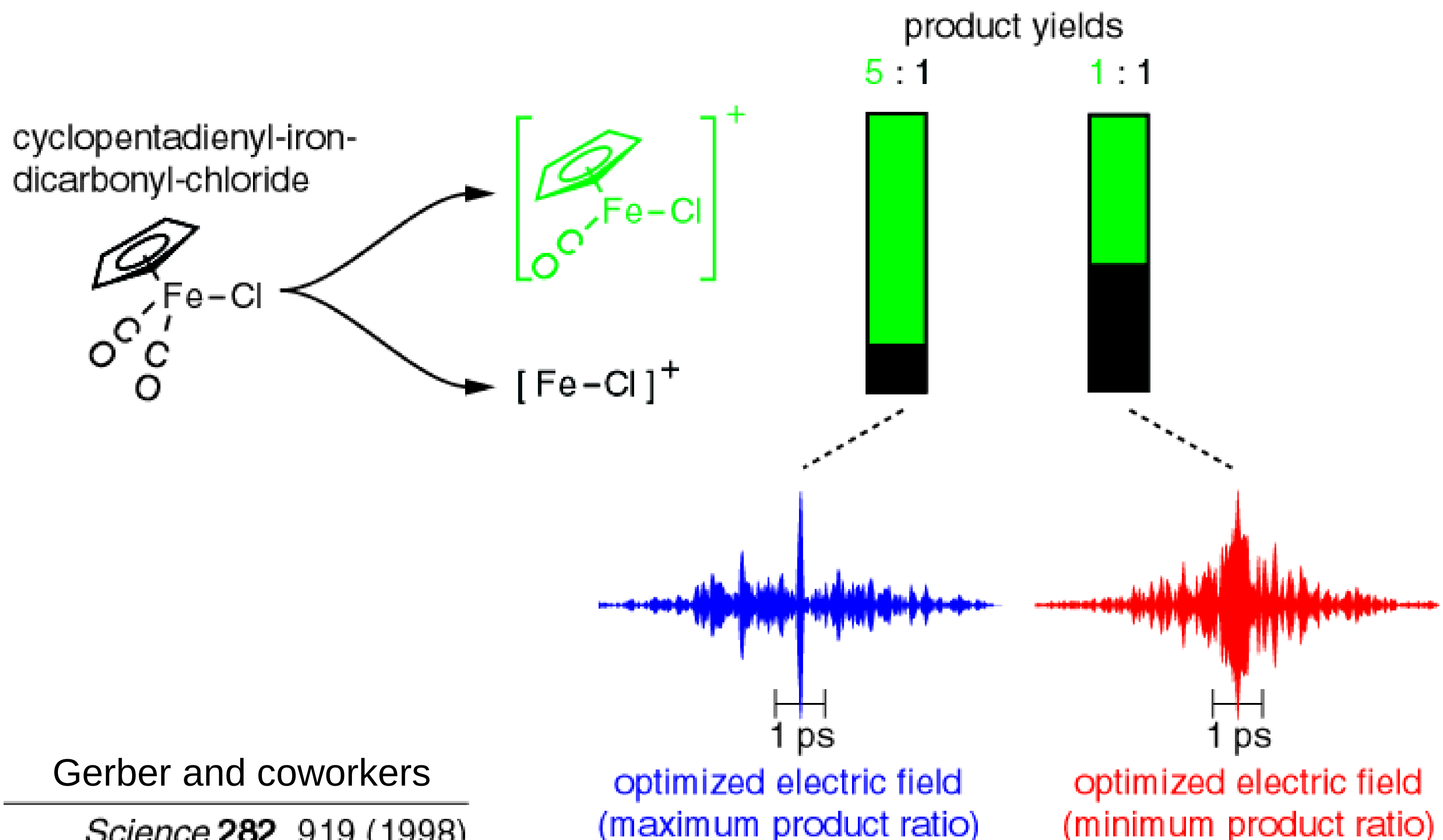


T. Brixner and G. Gerber: *Opt. Lett.* **26**, 557 (2001)

A complex polarization-shaped pulse



Coherent polarization control of a complex molecule in the gas phase



Gerber and coworkers

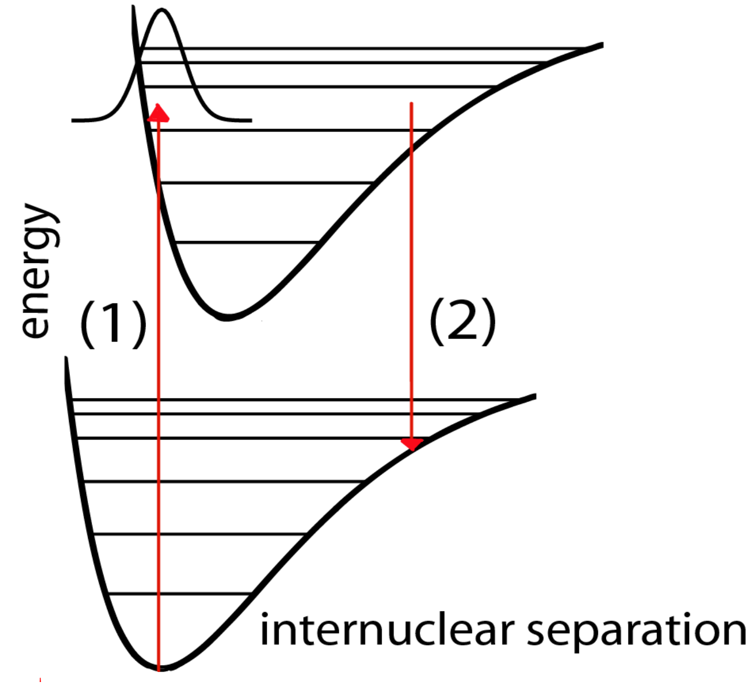
Science **282**, 919 (1998)

Chem. Phys. **267**, 241 (2001)

Coherent control of decoherence

• Coherent excitation of the vewepacket(1)
• Fluorecence detection (2)

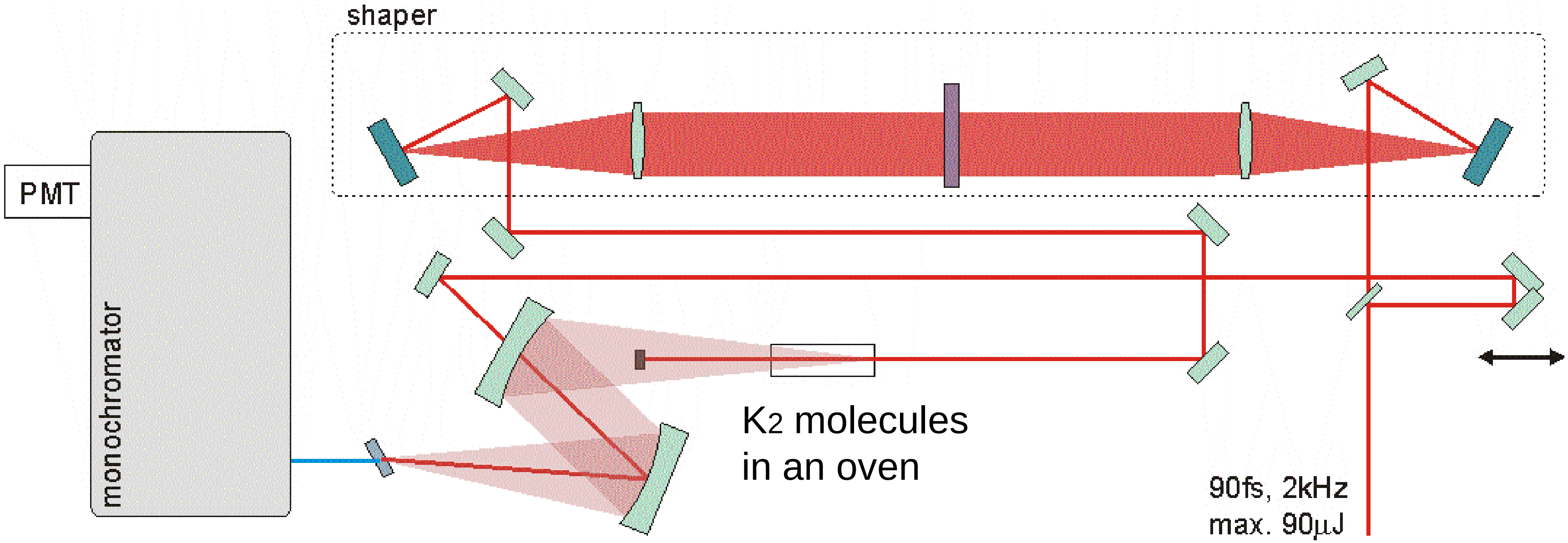
• Time evolution of the wavepacket– decoherence
• visibility as a measure of the wavepacket localization



Can we:

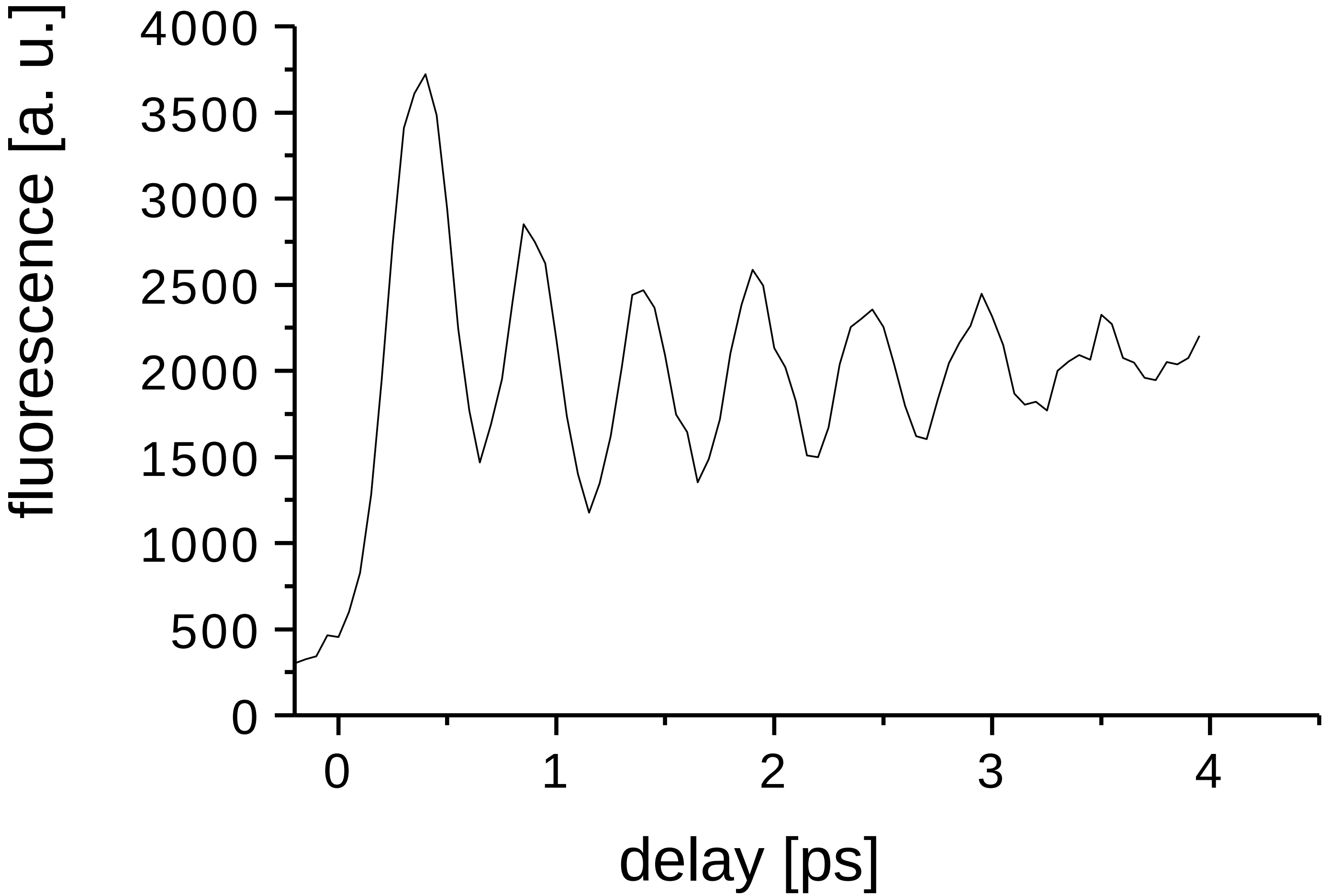
1. Affect the wavepacket lifetime?
2. Prepare the wavepacket with the longest possible lifetime?

Experimental setup

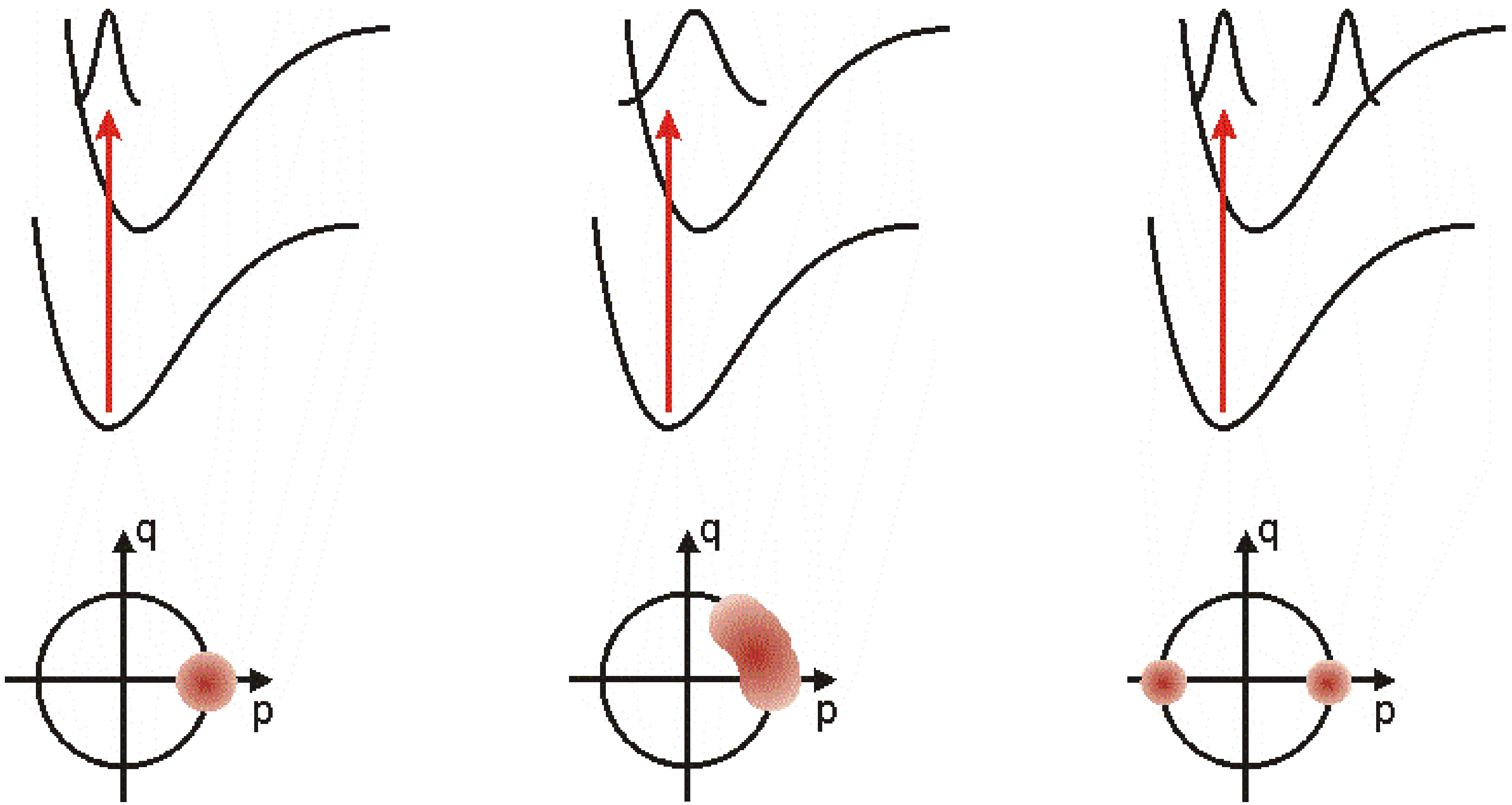


Temporal resolution: 150fs
Spectral resolution: 2 nm

„Real-time” molecular vibrations (wavepacket) measurements

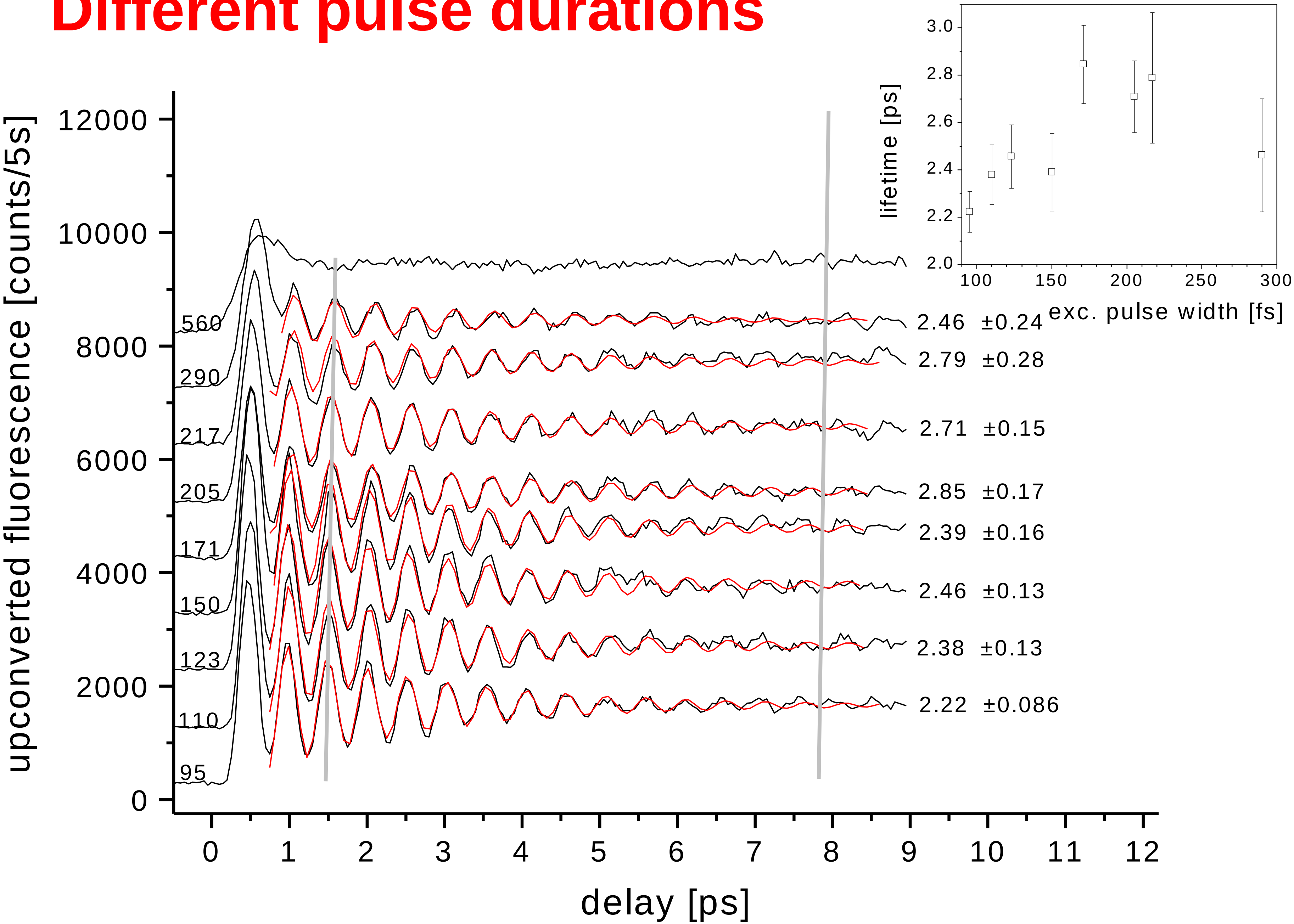


Different pulses excite different wavepackets

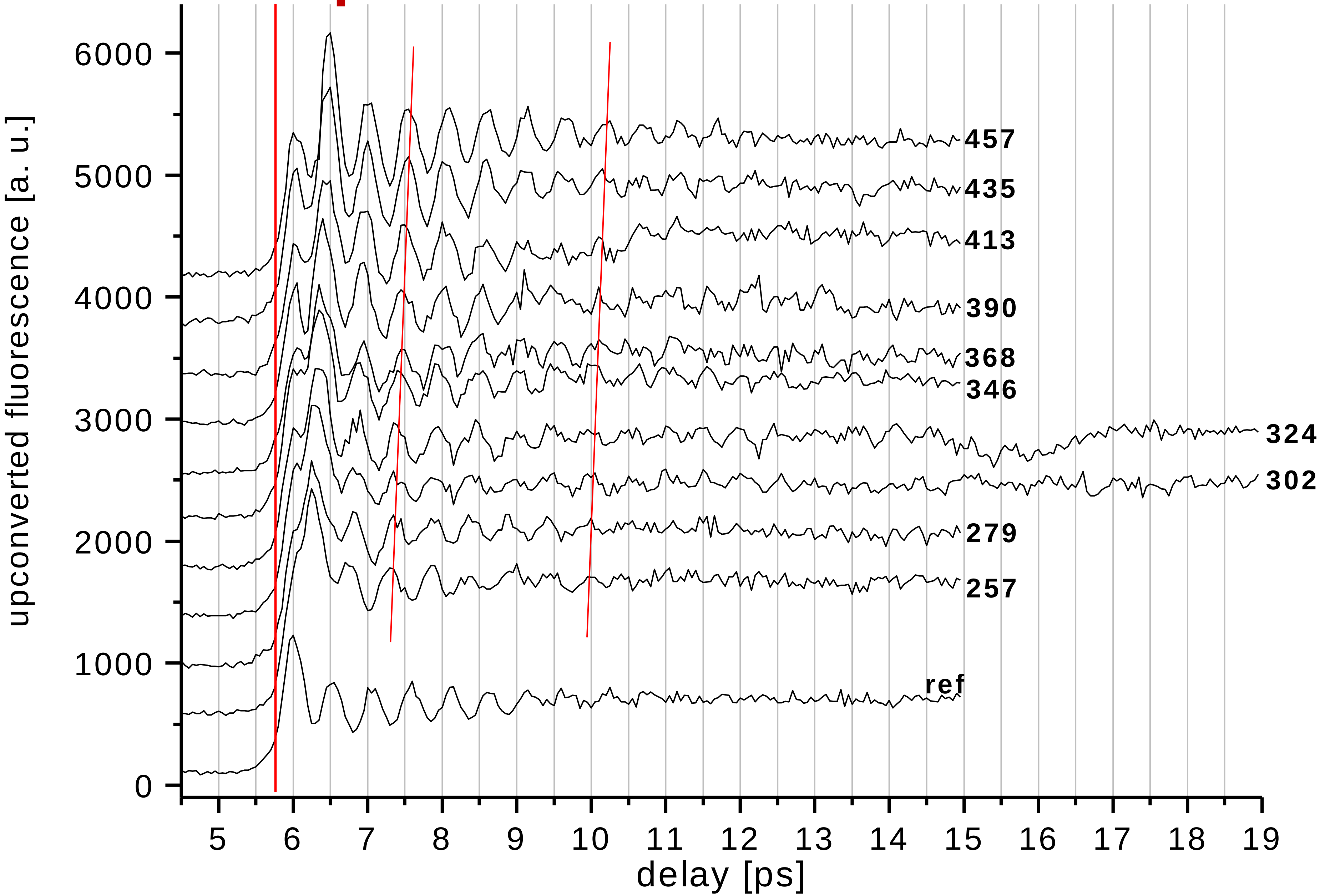


Short pulse… Longer pulse… …or two

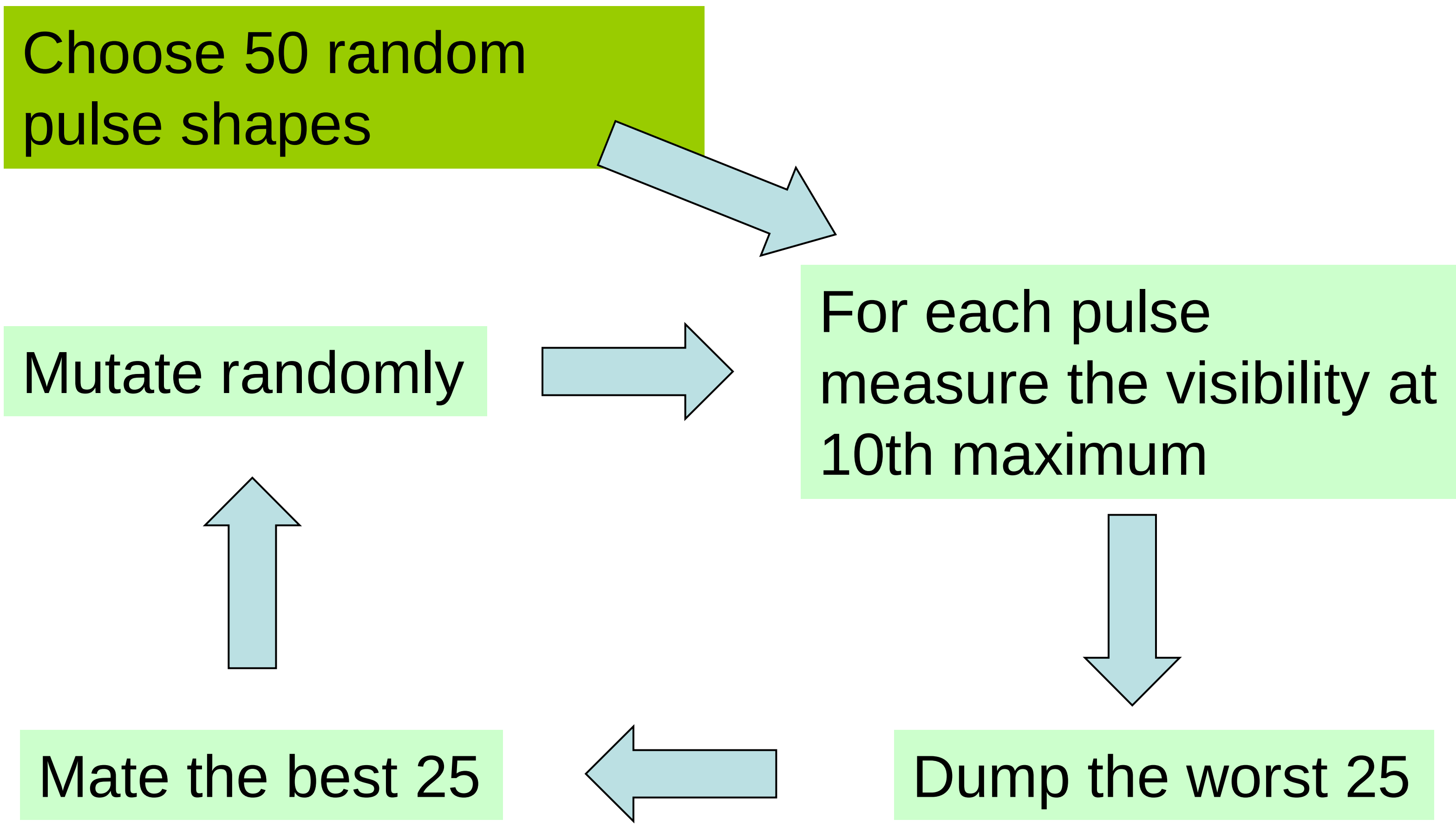
Different pulse durations



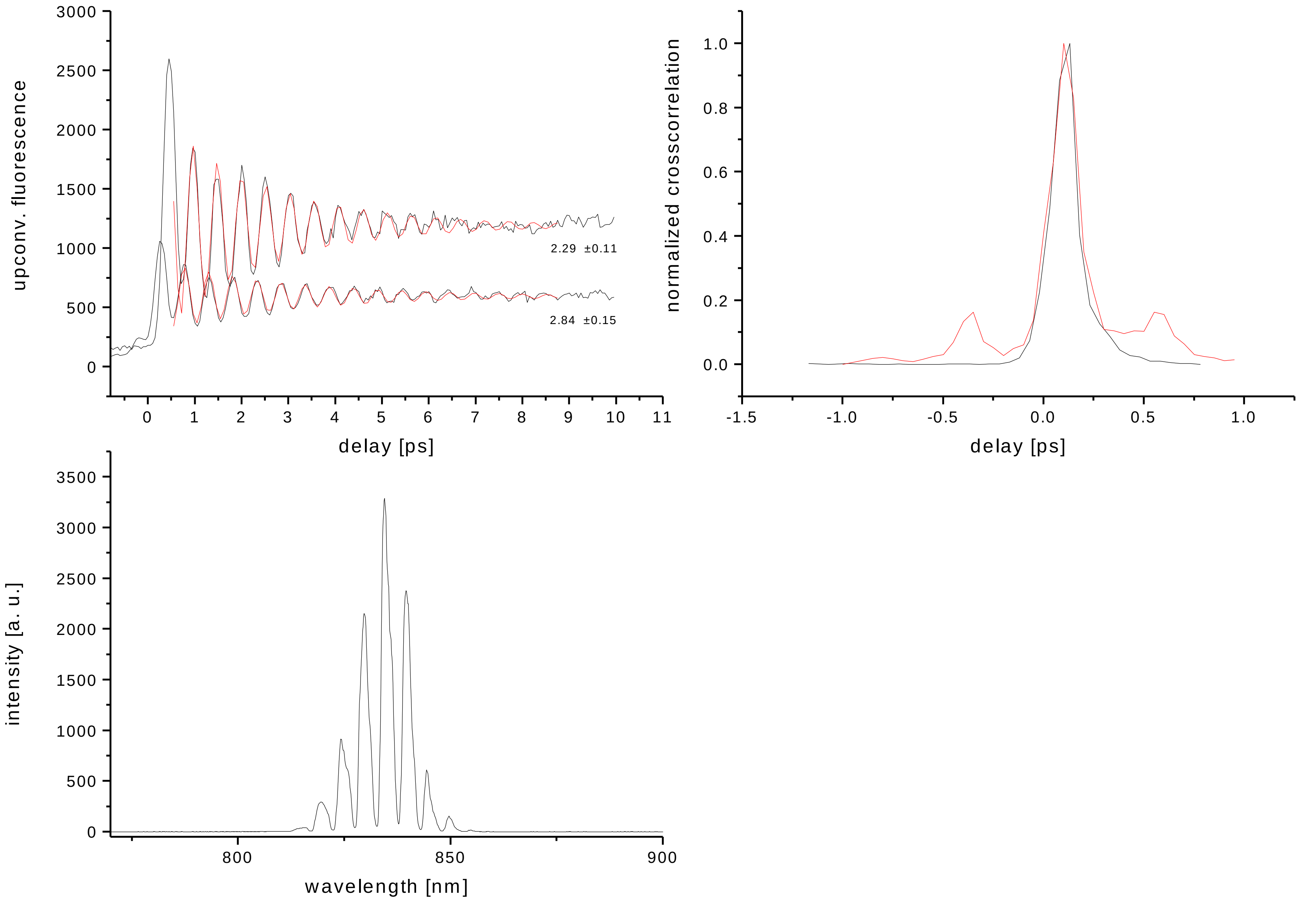
Now two pulses



Now let the genetic algorithm optimize the coherence time

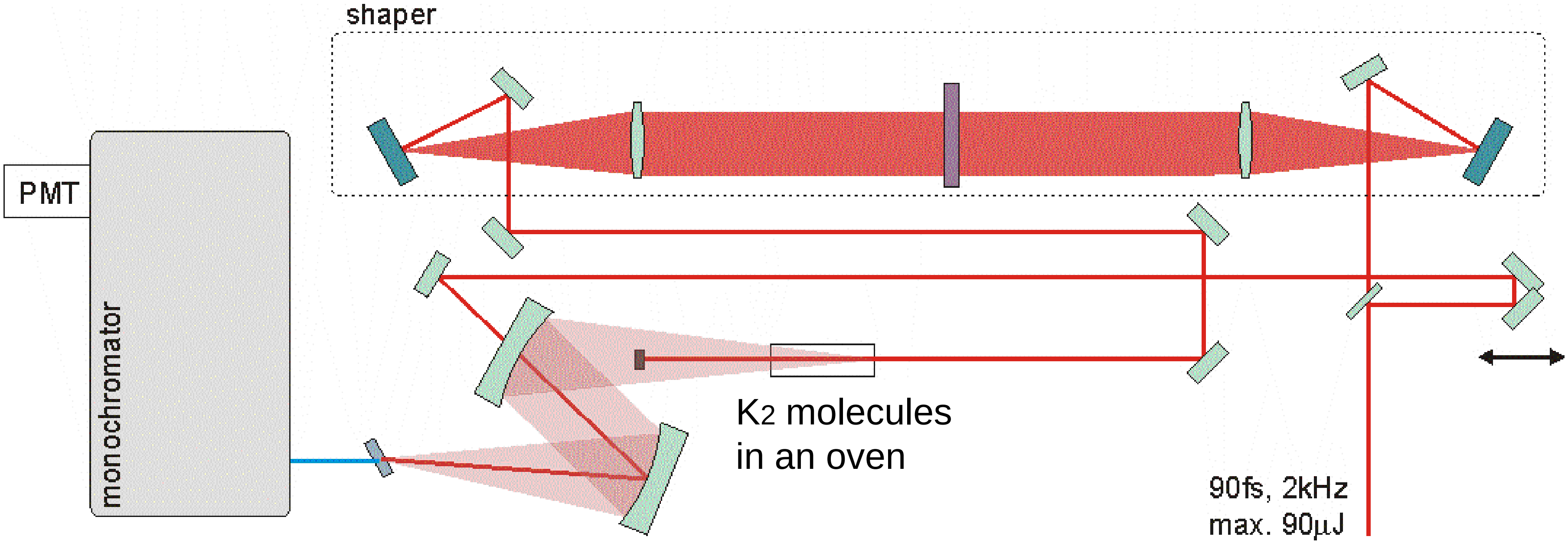


Genetic algorithm - results



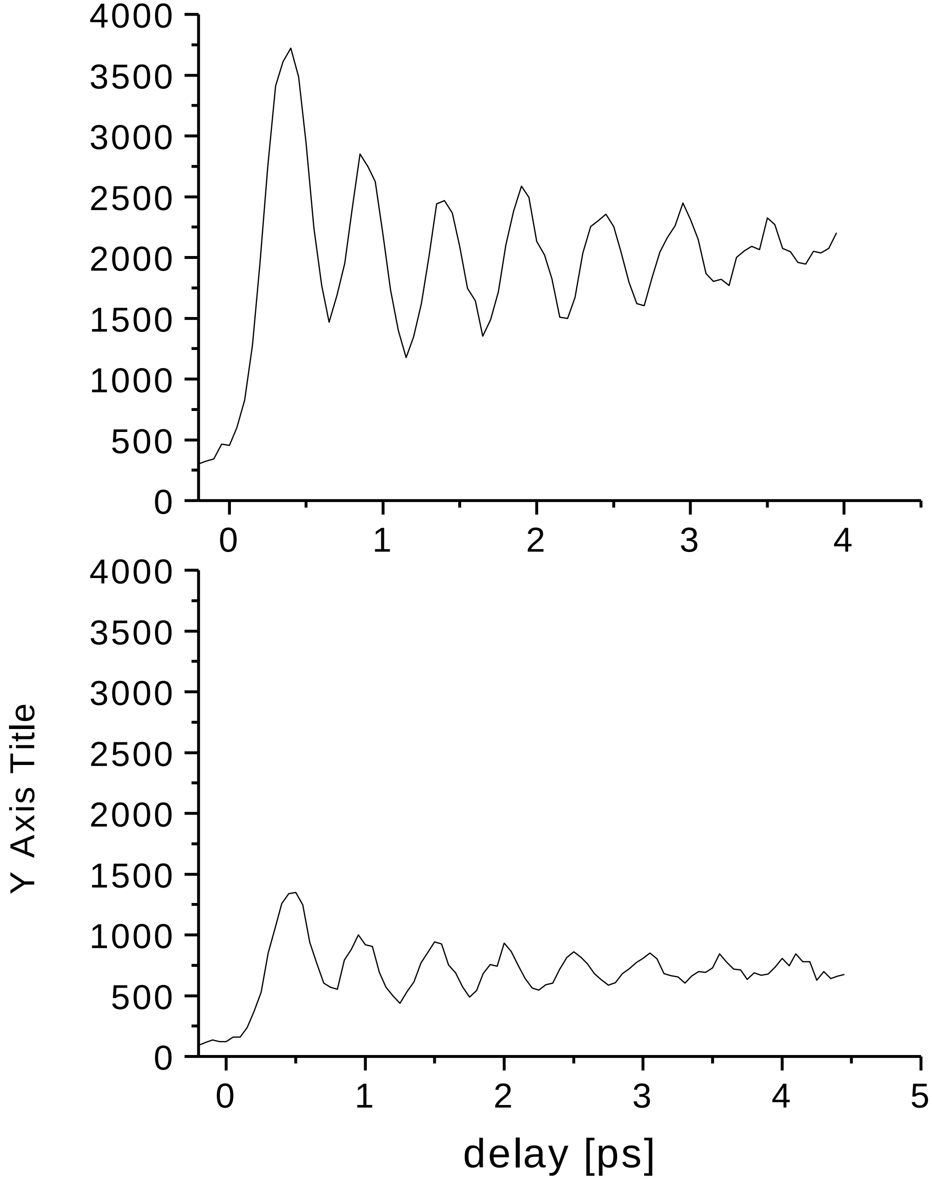
Simpler experiment – thick crystal

Thick SFG crystal = thin one + spectrometer



Simpler experiment – thick crystal

… and better SNR too



Successful closed-loop coherent control experiments in physics and chemistry

(1) Fluorescence spectrum manipulation (Wilson, 1997)

(2) Atomic excitation tailoring (Bucksbaum, 1999)

(3) Vibrational excitation tailoring in polymers (Motzkus, 2002)

(4) Molecular fragmentation selectivity (Gerber, 1998; Levis & Rabitz, 2001)

(5) Molecular rearrangement selectivity (Levis & Rabitz, 2001)

(6) Chemical discrimination (Gerber, 2001)

(7) High harmonic X-ray tailoring (Murnane & Kapteyn, 2000)

(8) Ultrafast solid-state optical switching (Keller, 2000)

(9) Distortion-free transmission of pulses in optical fibers (Omenetto, 2001)

(10) Decoherence management (Walmsley, 2002)

(11) Photosynthetic bacteria energy transfer (Herek and Motzkus 2002)

By 2003, ~ 50 systems have been successfully controlled.