Multimodal Quantum Control Micro-Spectroscopy I

Coherent control of ultrafast molecular dynamics

OSA Siegman International School on Lasers,
ICFO, Spain

24 -29 July 2016

Outline

I. Coherent Control

- Concepts of Coherent Control
- Learning Loop: Pulse shaping, algorithms
- Applications:
  - Control of 2-Photon-Absorption
  - Control of energy transfer

II. Single beam CARS

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- Nonlinear Raman spectroscopy
- Shaped CARS
- Multimodal microscopy

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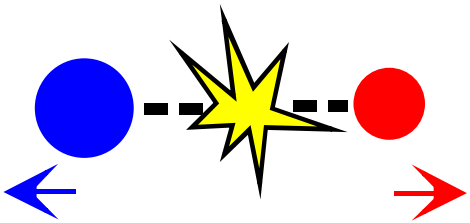
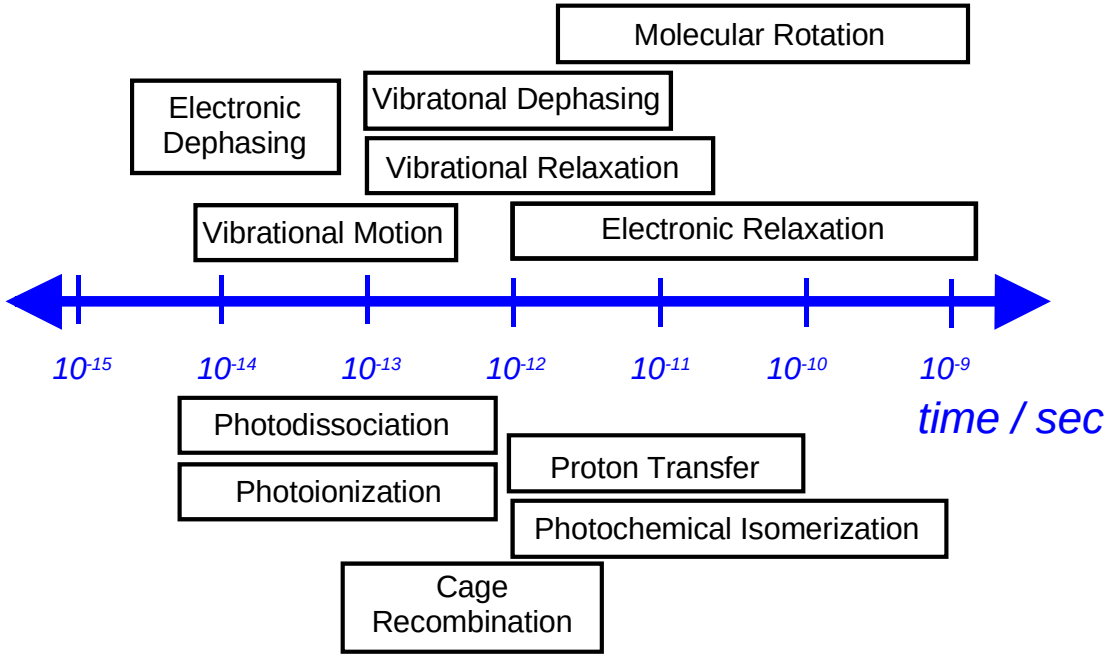
Multimodal Quantum Control Micro-Spectroscopy

Femtochemistry

Ultimate timescale for chemical dynamics

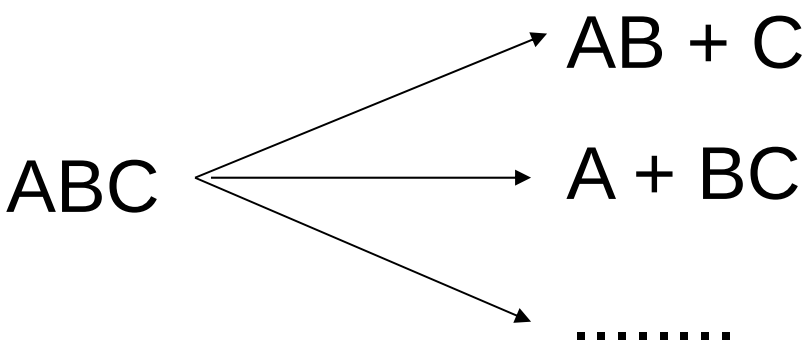


v = 1 km/s
= 0.01 Å/fs



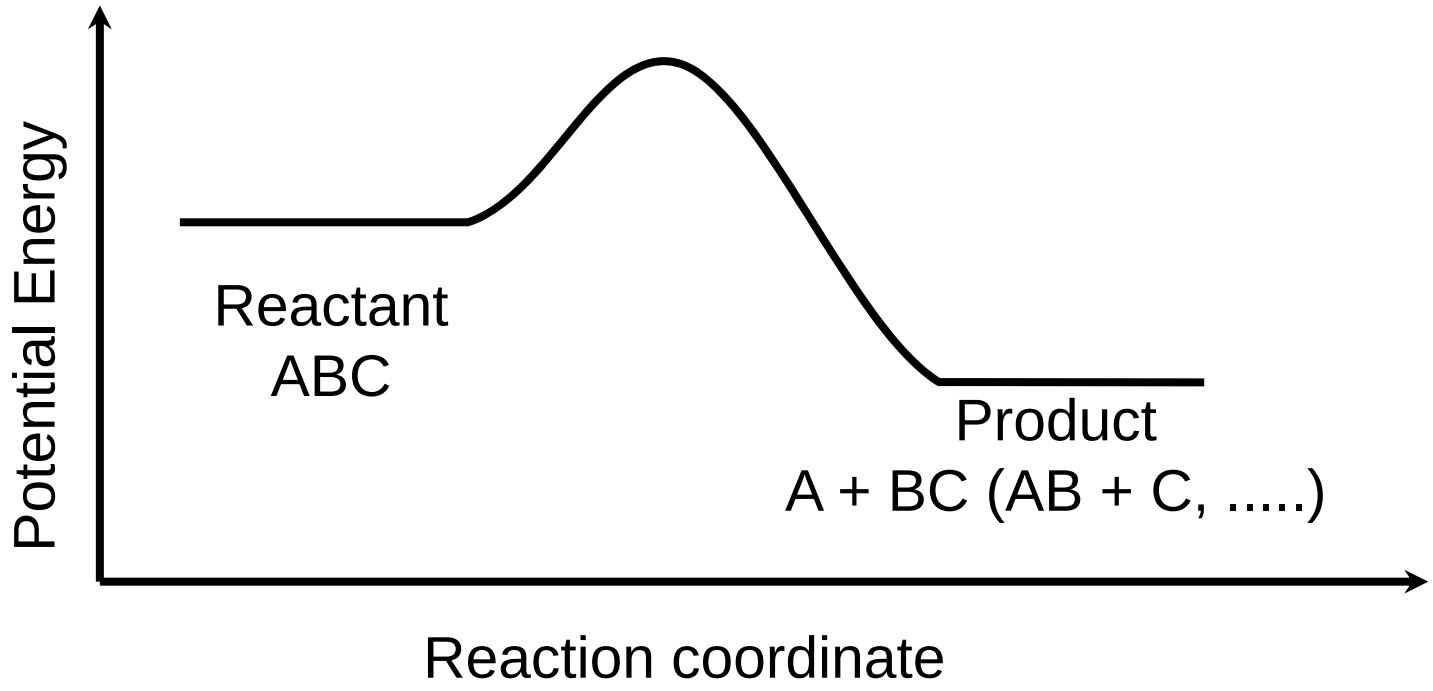
Introduction

Chemistry (microscopic) ≡ Breaking and making bonds



General goal: Maximize yield of desired products and suppress yield of unwanted byproducts

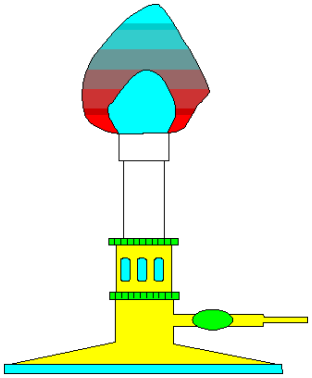
Cut through a multidimensional PES:



How can we supply energy to get over barrier and achieve a specific product?

→ Typical macroscopic approach: Temperature

wanted and unwanted products formed statistically



Passive control *vs.* **Active** control

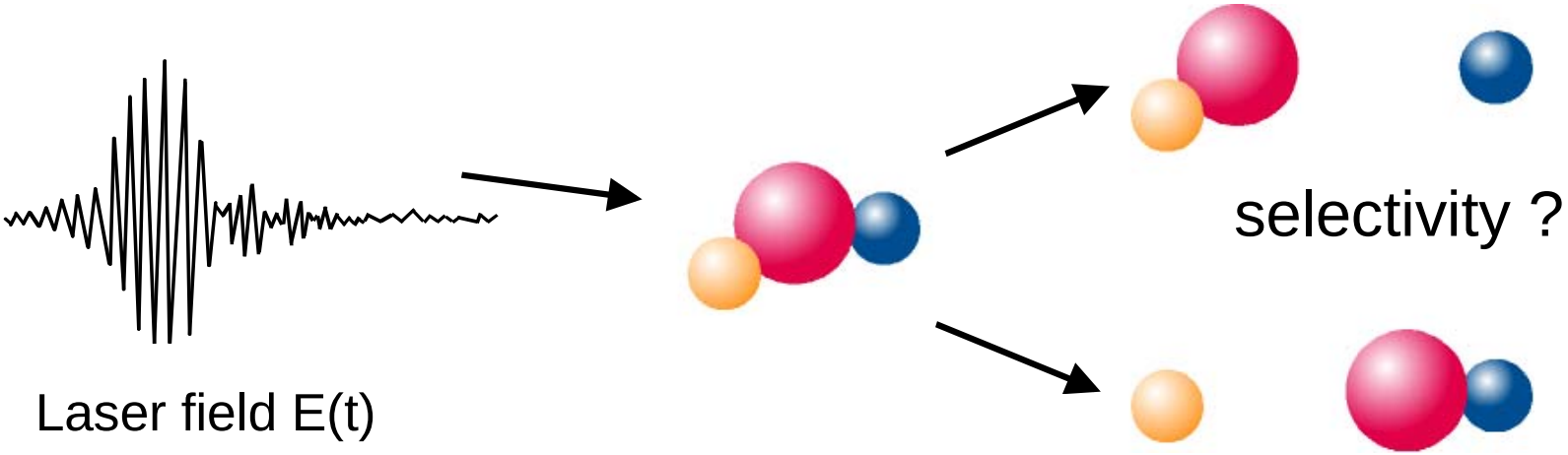
1. *Reactant molecules and any surrounding solvent molecules are* ***not subjected to manipulation by external influences*** *during the evolution from reactants to products.*
2. *Evolution of energized reactant molecules is largely or completely* ***incoherent***
3. *Role of experimenter is to initiate the reaction, without having control of subsequent evolution of the system*

- Concentration
- Temperature
- Pressure
- pH
- Solvent
- Catalyst
- Synthetic criteria

External manipulation *of molecular dynamics so as to* ***influence the evolution*** *of the reactant molecule to generate more or all of a particular product*

- Electric fields
- Optical fields
- .....
  - Intensity
  - Phase
  - Polarization
  - Spectral content
  - Time dependence

Coherent control of chemical reactions

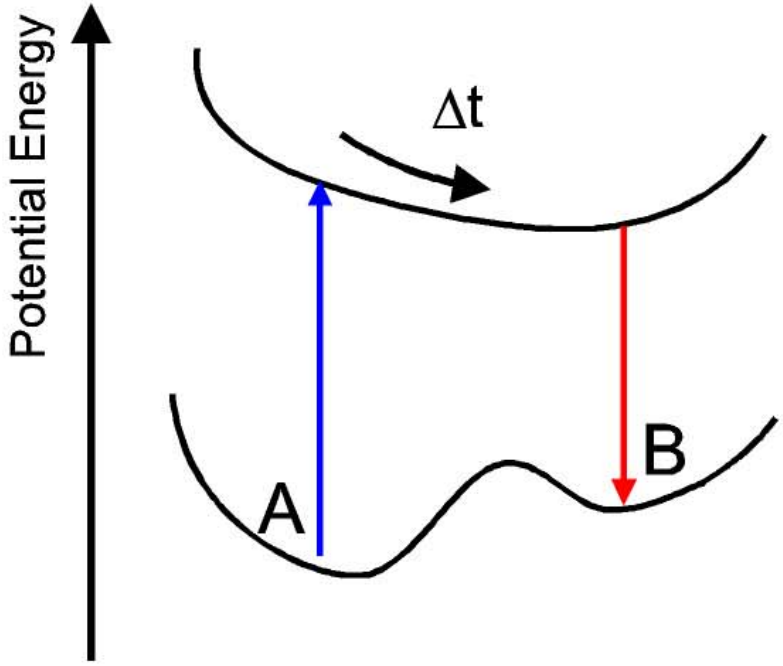


- calculation for real molecules complicated (if not impossible)
- experimental realization of predicted E-fields difficult

Control strategies

Tannor-Kosloff-Rice

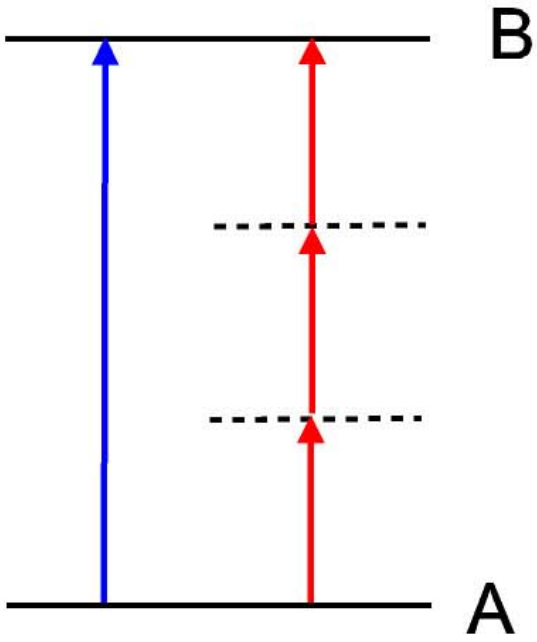
JCP 85, 5805 (1986)



time delay: Δt

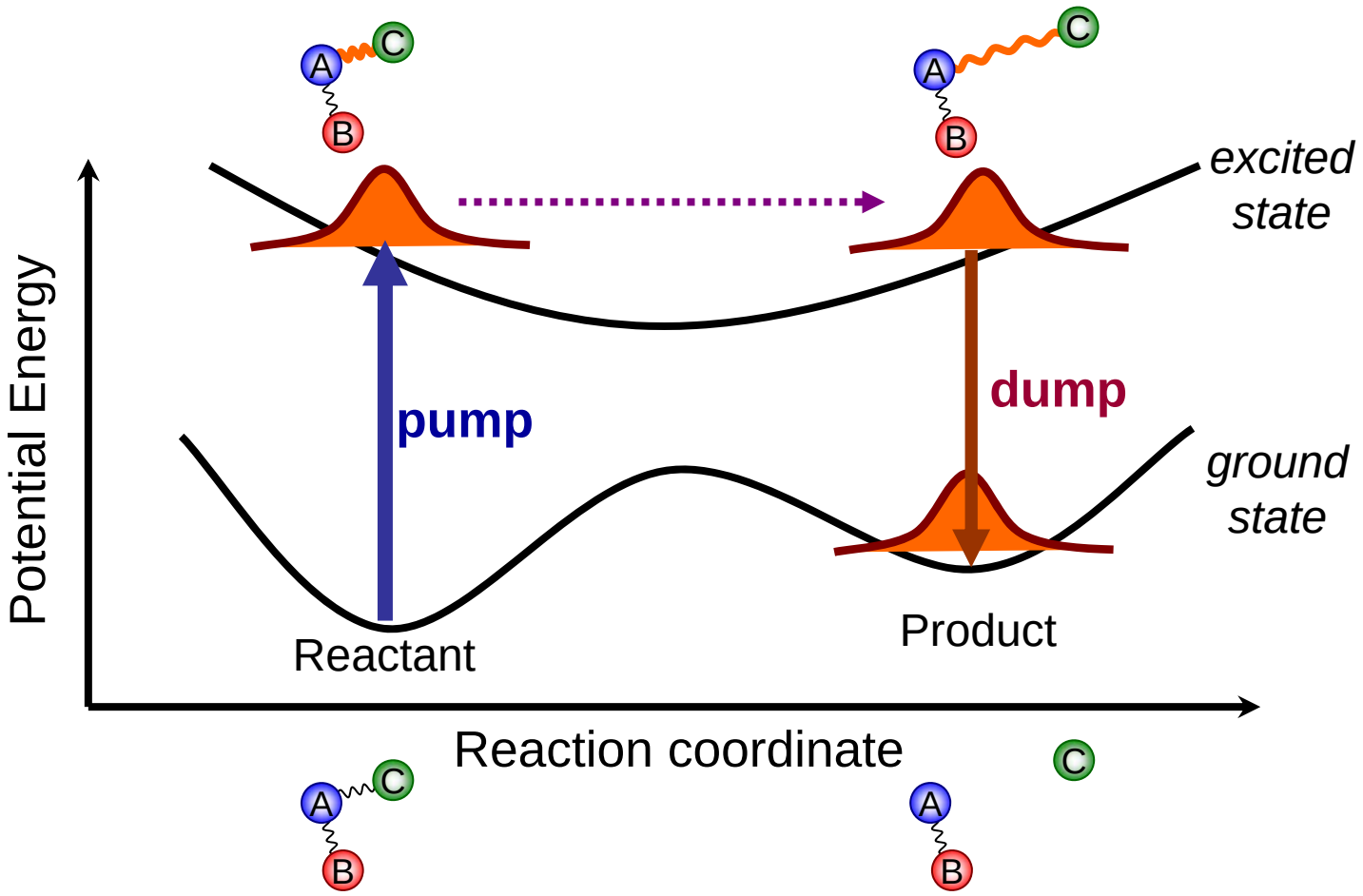
Brumer-Shapiro

CPL 126, 54 (1986)



phase difference: $\Delta\phi=\phi_{\omega}-\phi_{3\omega}$

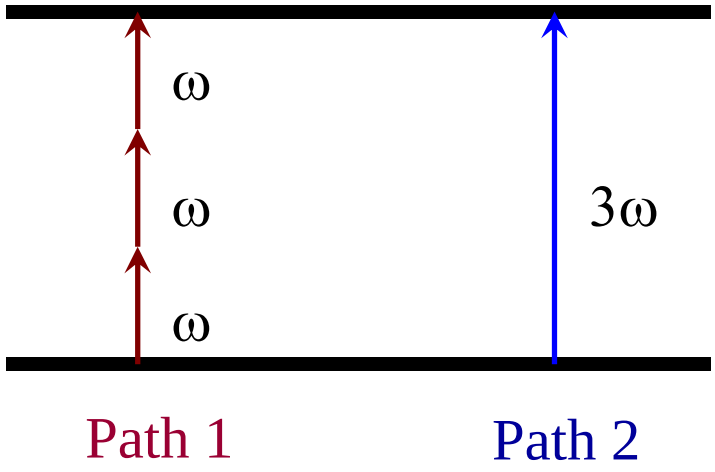
Tannor-Rice scheme
Pulse-timing control



Tannor, D. J., Kosloff, R. & Rice, S. A. Coherent pulse sequence induced control of selectivity of reactions: Exact quantum mechanical calculations.J. Chem. Phys. 85, 5805-5820 (1986)

Brumer-Shapiro scheme:
Multiple-path interference control

Excite the desired product channel via two different pathways:



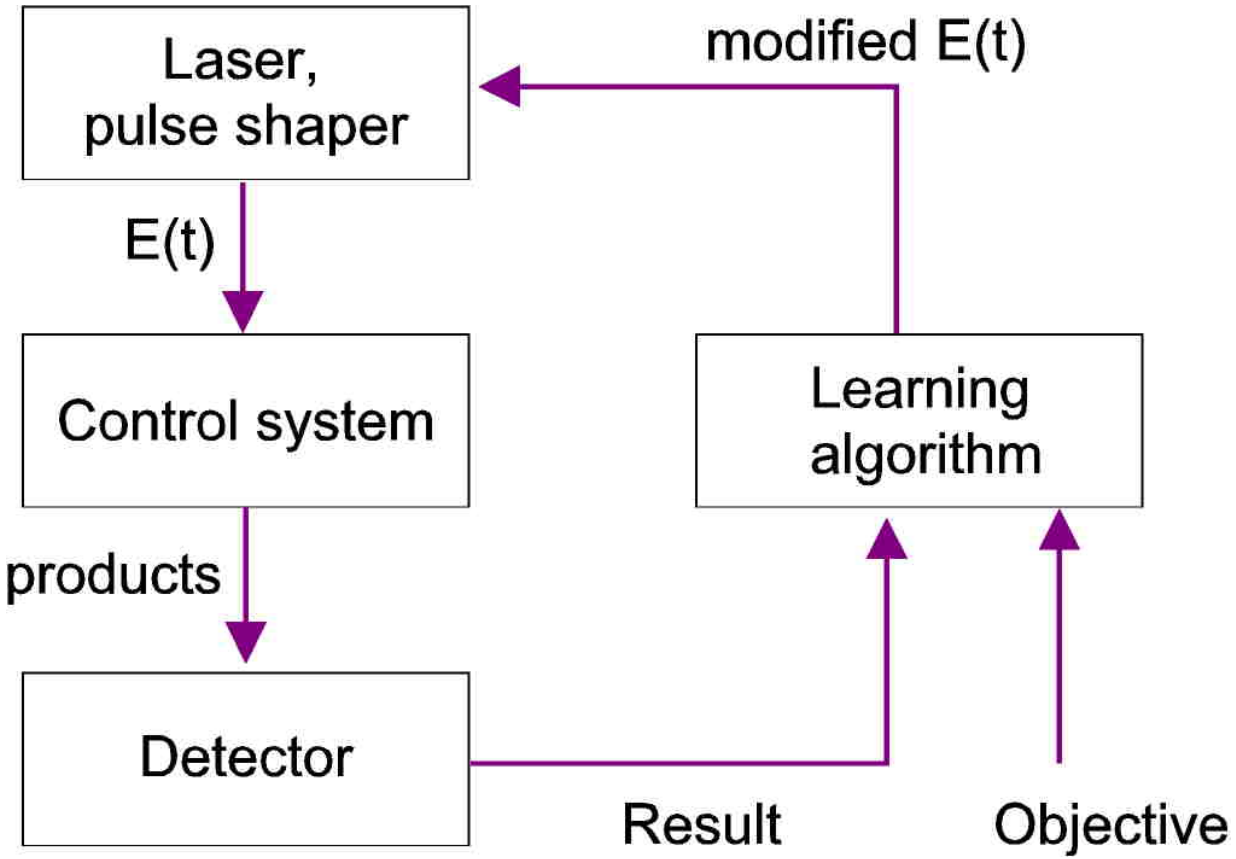
Probability (***P***) of forming a product:

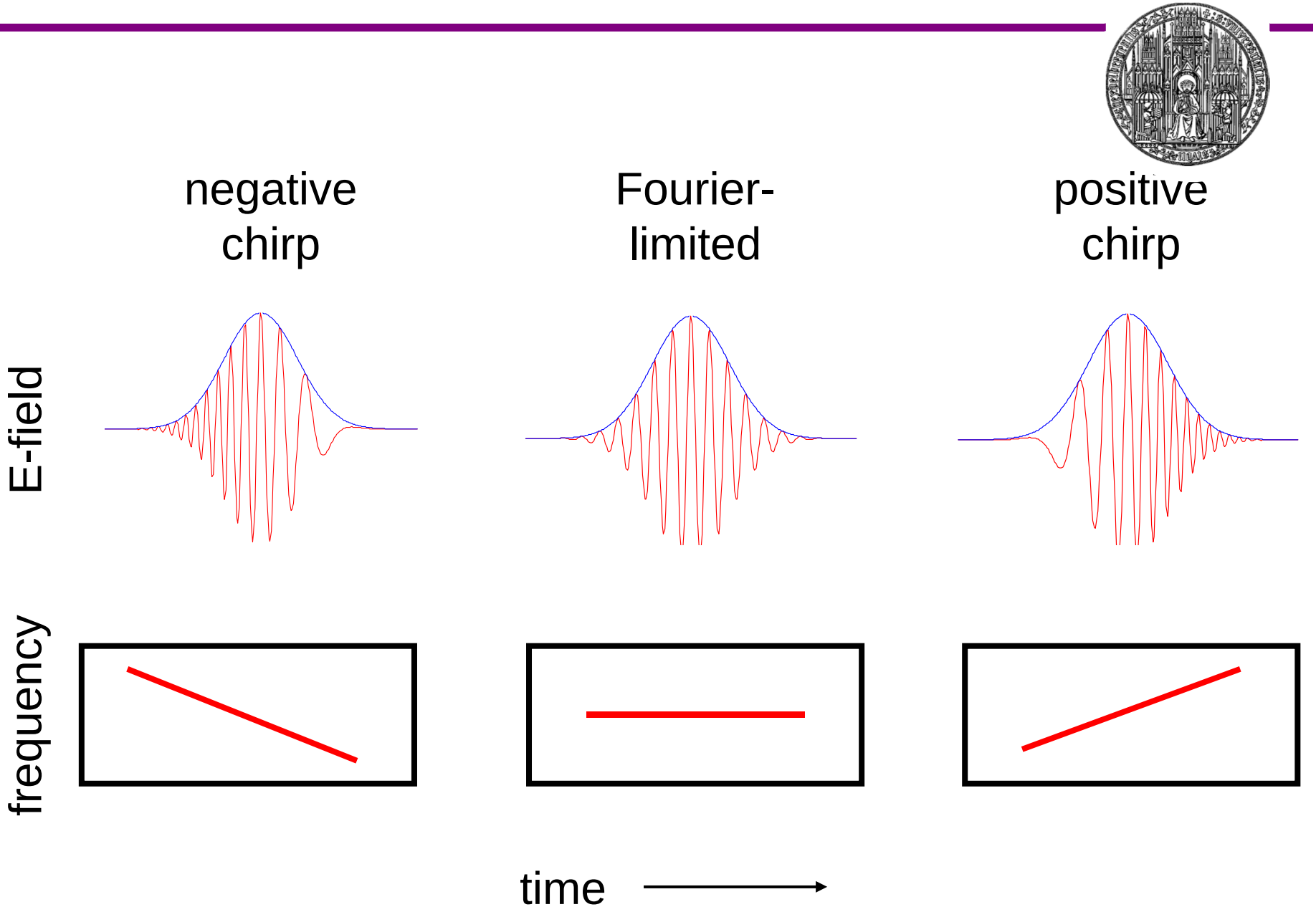
$$P = P_1 + P_3 + 2P_{13}\cos(\phi+\delta_{13})$$

P. Brumer and M. Shapiro, Chem. Phys. Lett. ***126*** *(1986) 541*

"teaching lasers to control molecules"

R.S. Judson and H. Rabitz, PRL 68 (1992) 1500

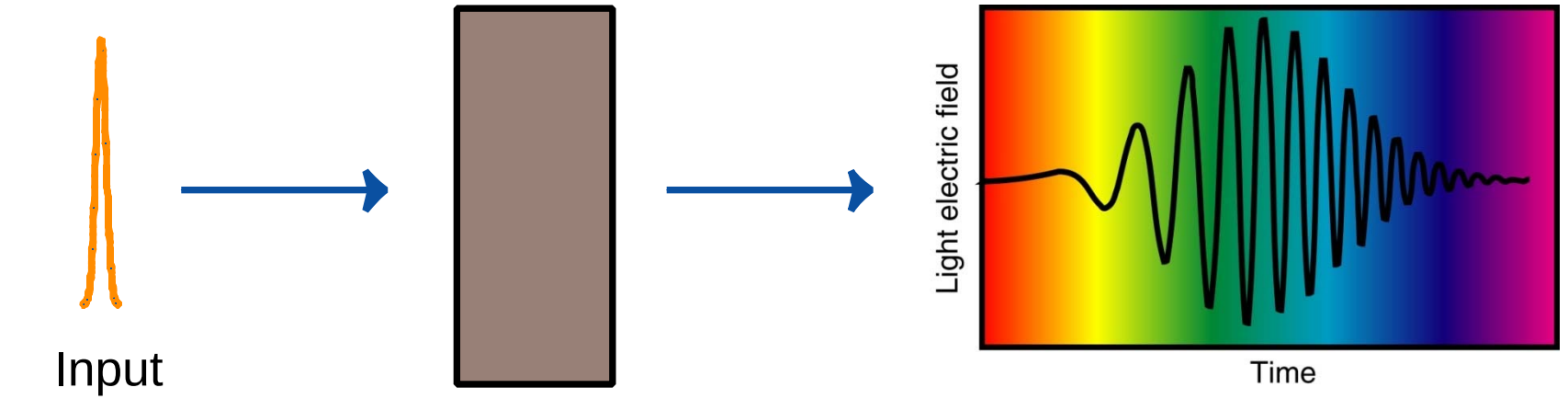




From R. Trebino, GaTech

Simple shaping of fs pulses

Different frequencies travel at different group velocities in materials, causing pulses to expand to highly "chirped" (frequency-swept) pulses.



Input ultrashort pulse

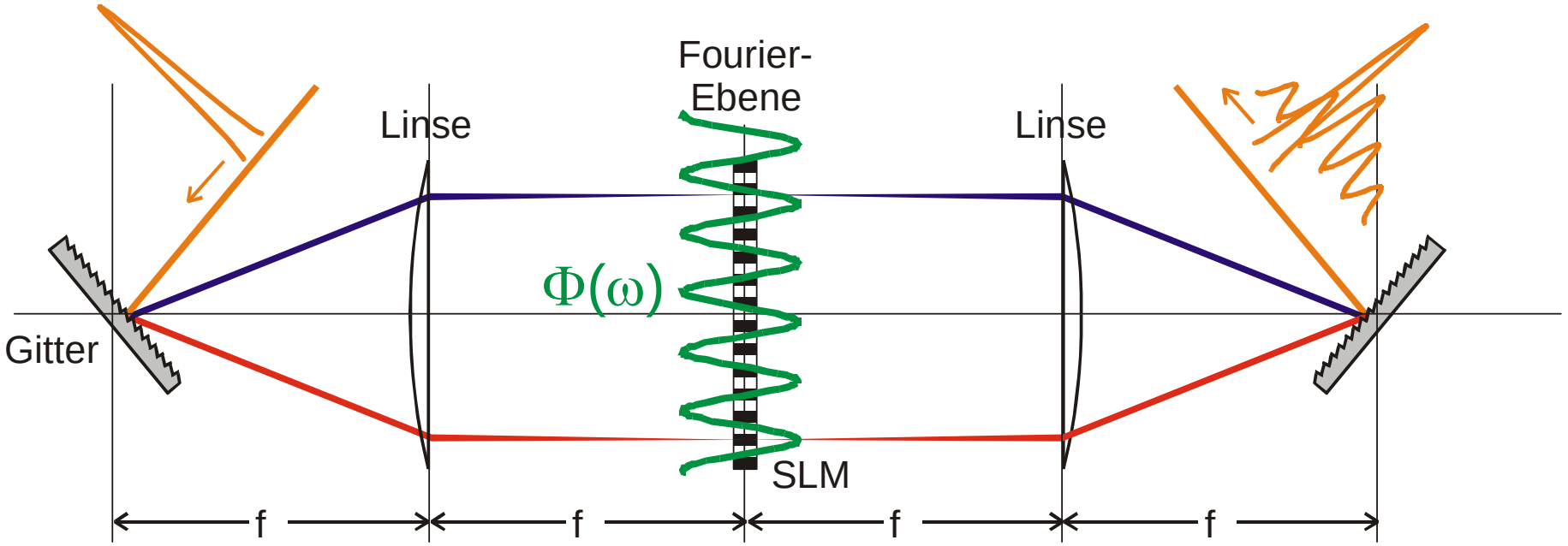
Any medium

Chirped output pulse

Longer wavelengths almost always travel faster than shorter ones.

From R. Trebino, GaTech

Shaping of fs-Laser Pulses

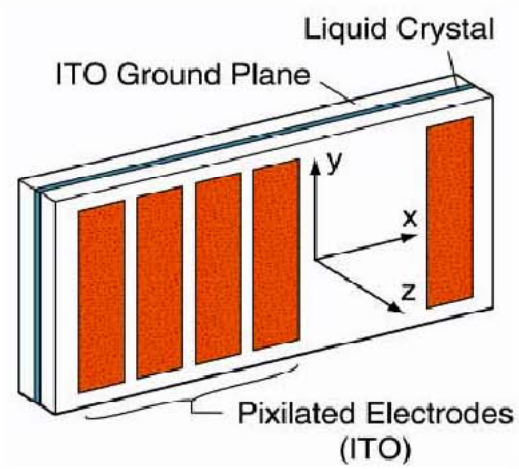


SLM
640 Pixel

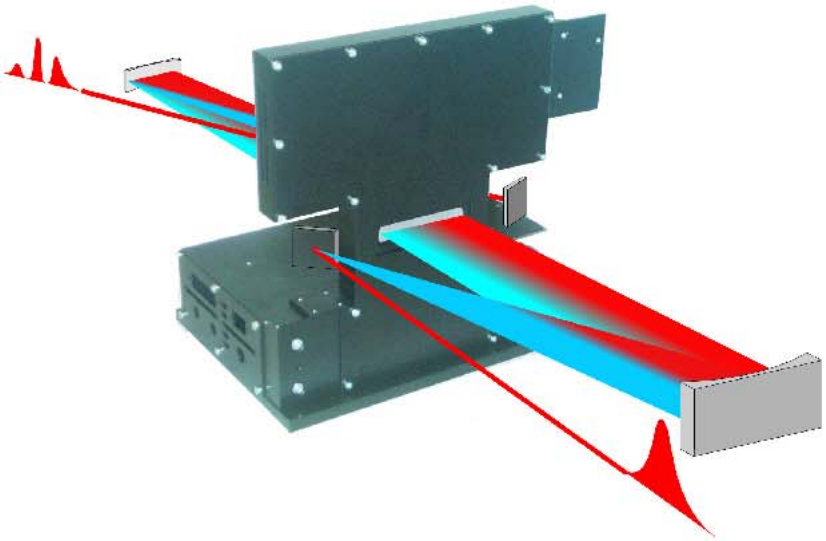
Reference: A.M. Weiner, Rev. Sci. Instrum. 71 (2000) 1929

Liquid crystal spatial light modulator

schematic of liquid crystal



novel shaper with 640 stripes

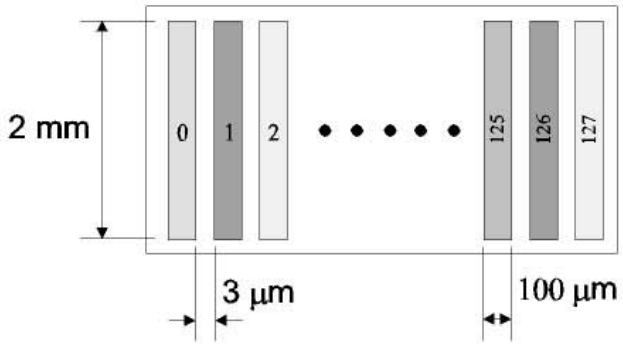


Cooperation with: IOQ-Universität Jena
Jenoptik AG

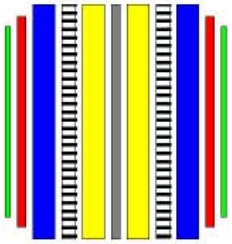
Appl. Phys. B 72 (2001) 627

Liquid crystal spatial light modulator

Front view

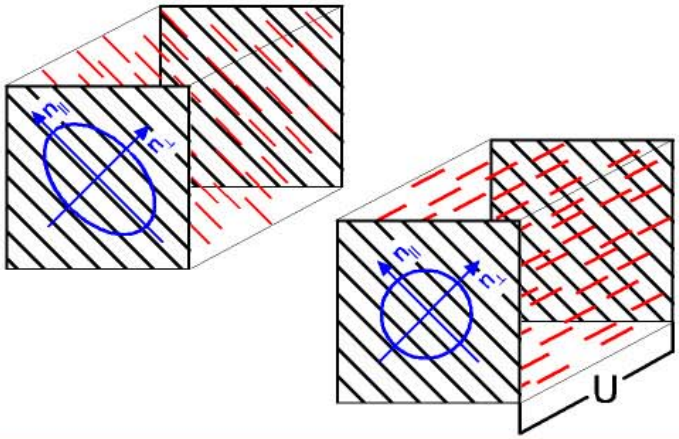


Side view

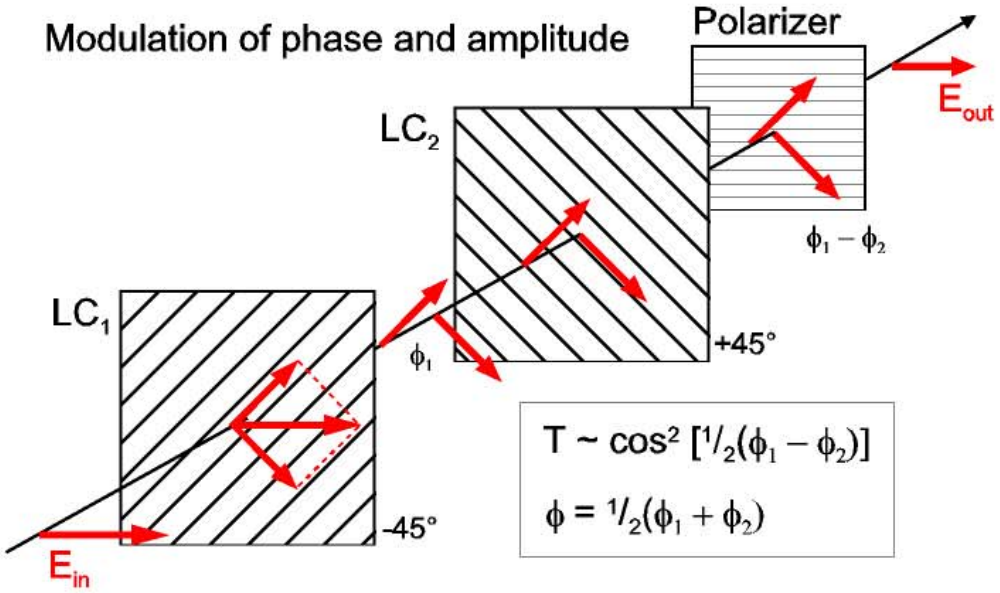


AR-coated cover
polarizer
substrate buffed at +/-45°
liquid crystal
indium tin oxide patterned substrate
index-matching epoxy

Electrically induced birefringence



Modulation of phase and amplitude

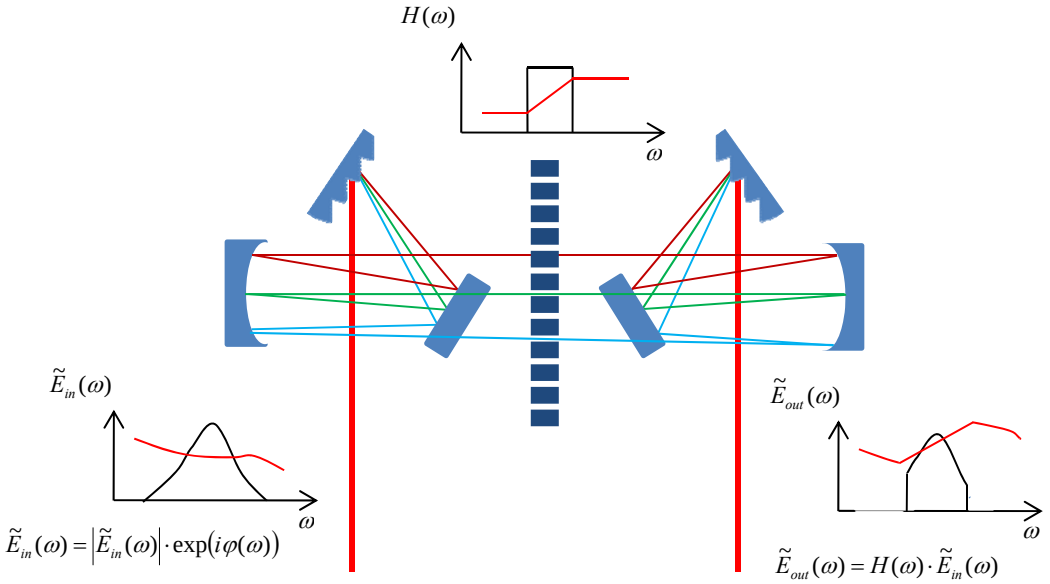


$T \sim \cos^2 [1/2(\phi_1 - \phi_2)]$

$\phi = 1/2(\phi_1 + \phi_2)$

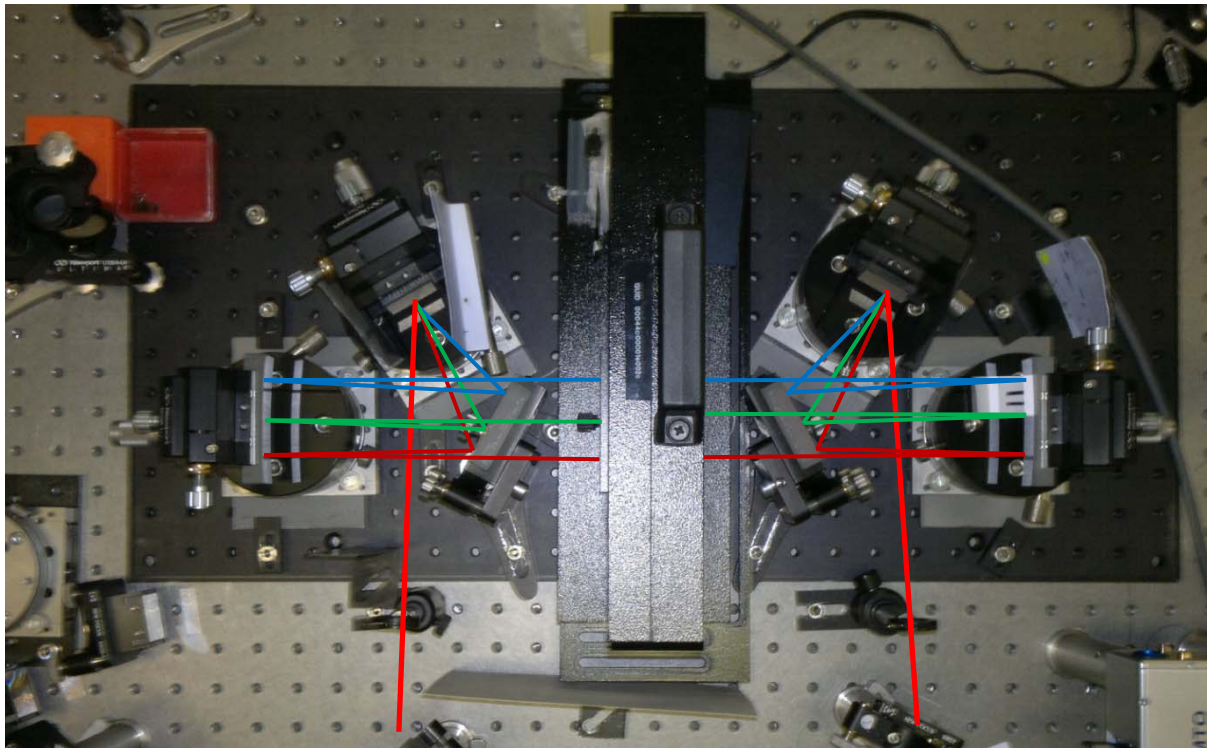
Principles of pulse shaping (cont´d)

- Singlebeam-CARS uses most often femtosecond laser pulses due to their large bandwidth.
- Pulse shaping cannot be accomplished in the time domain, because no modulator is fast enough.



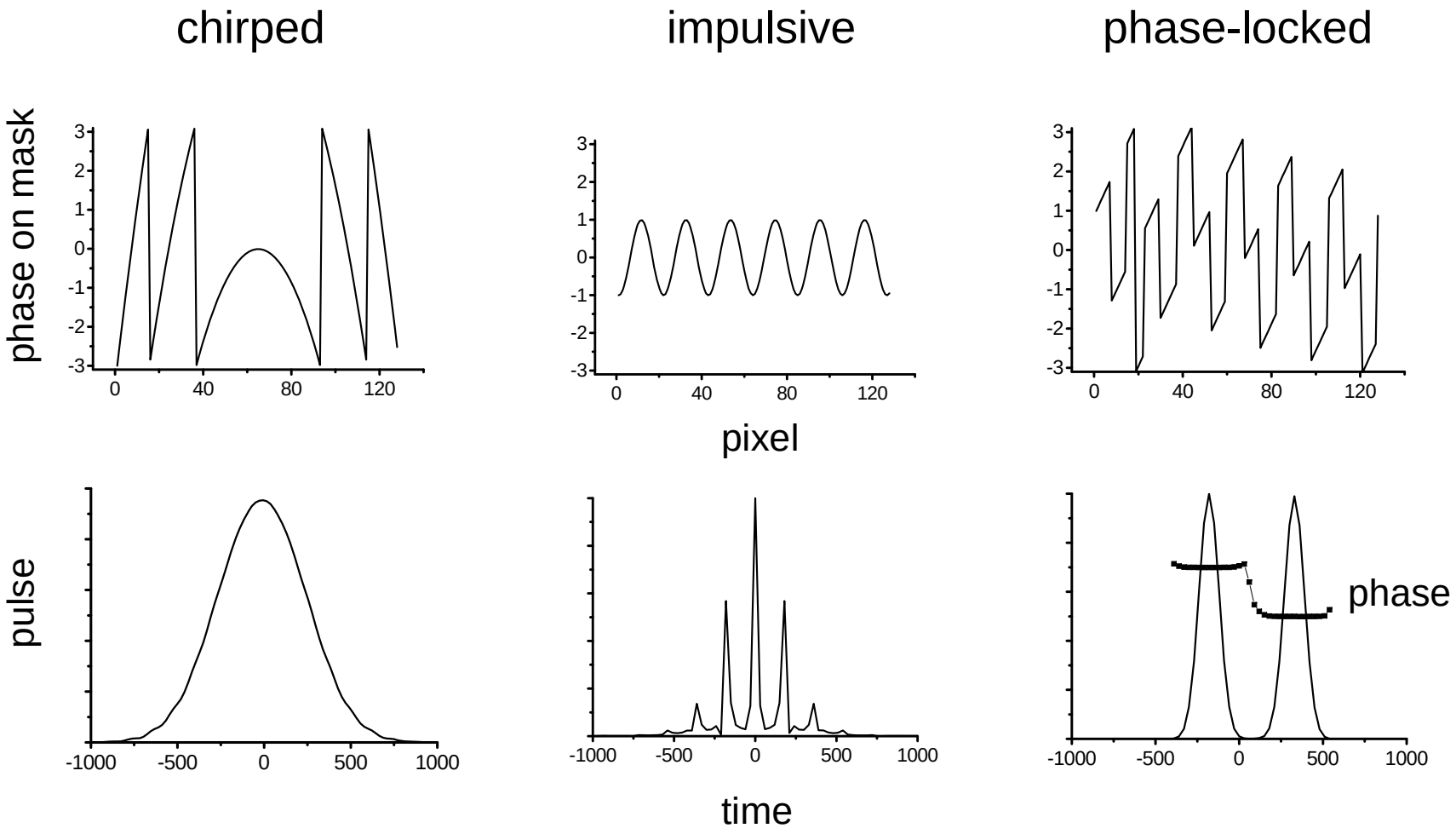
$H(\omega)$ is a complex mask function, this means amplitude an phase can be controlled.

Principles of pulse shaping



Appl. Phys. B ***72*** *(2001) 627*

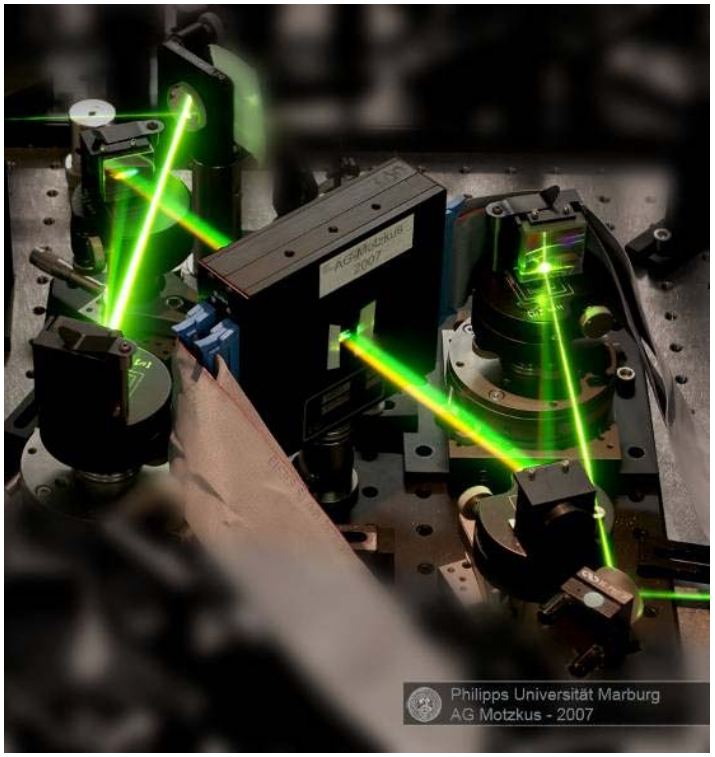
Parameterization of excitation mechanism



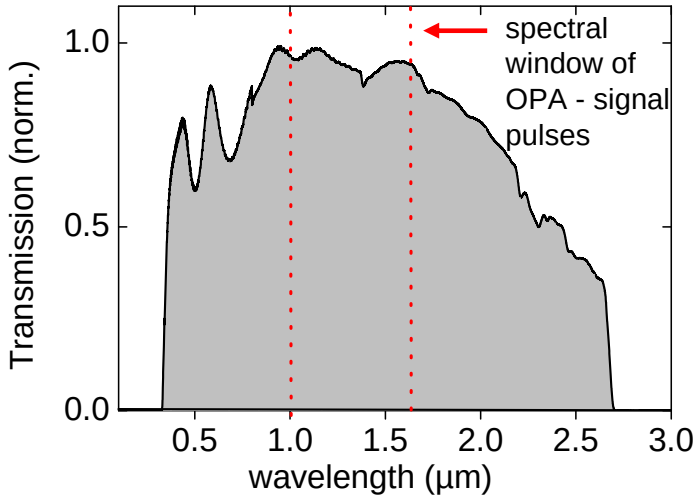
Chem. Phys. Lett. **326** (2000) 445, Phys. Rev. A **64** (2001) 023420

Spectral range of a liquid crystal mask

NIR / VIS: 4-f-setup



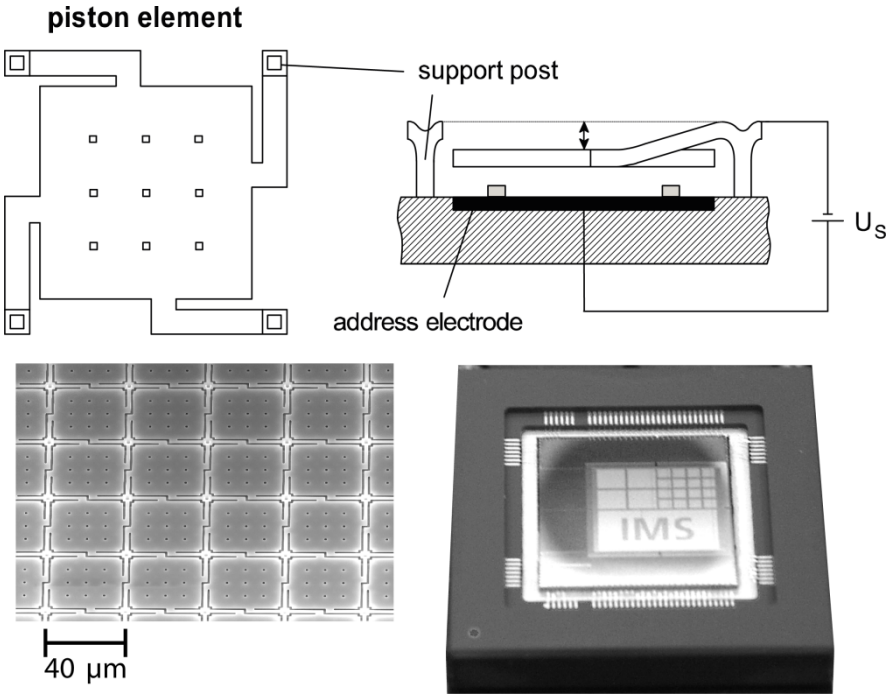
Transmission spectrum of liquid crystal mask CRI-256

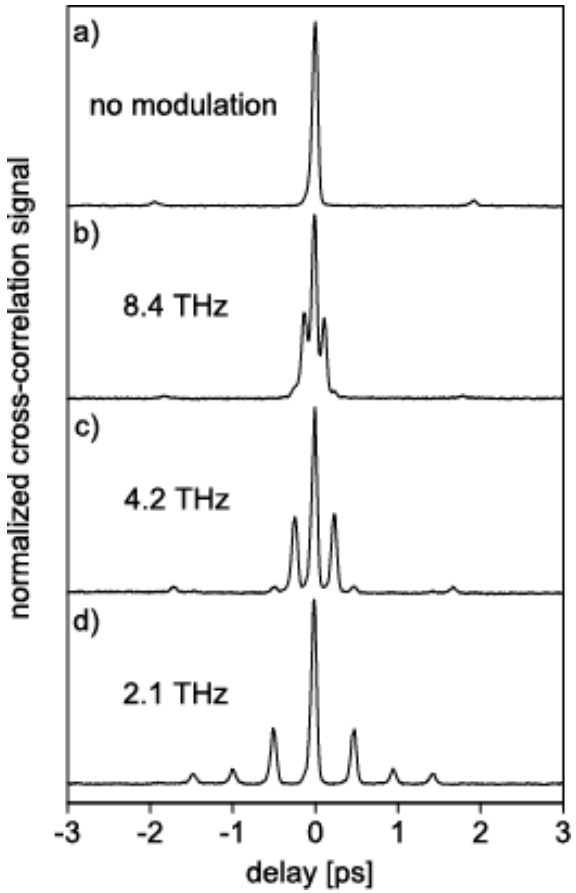


→ No modulation of pulses in the UV and mid IR

Direct UV shaping

Micromirror SLM

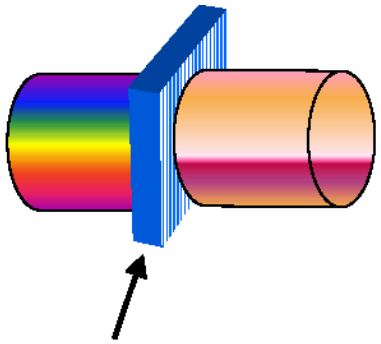




Appl. Phys. B ***76*** *(2003) 711; JOSA B* ***26*** *(2009) 1538*

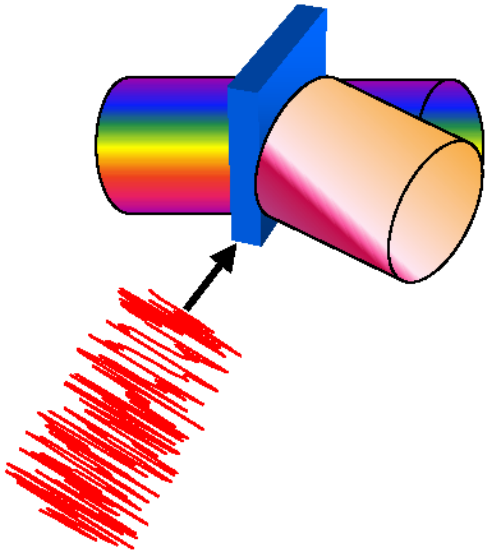
Methods of pulse shaping

Liquid-crystal modulator



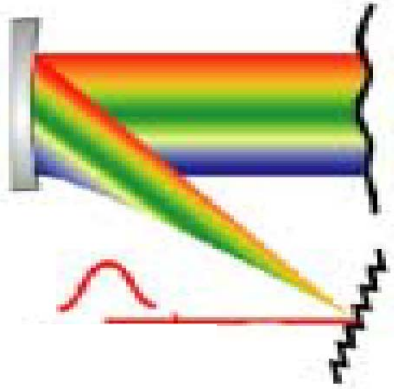
Individually-addressed pixels can vary phase or amplitude

Acousto-optic modulator



Modulated rf field creates an amplitude- and phase-dependent grating

Deformable mirror



Array of movable elements allows phase variations of spectral components

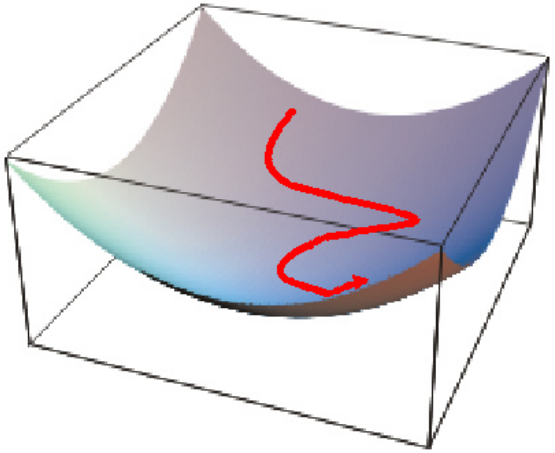
Review: *"Femtosecond pulse shaping using spatial light modulators "*
A. M. Weiner, Rev. Sci. Inst. ***71*** *(2000) 1929-1960*

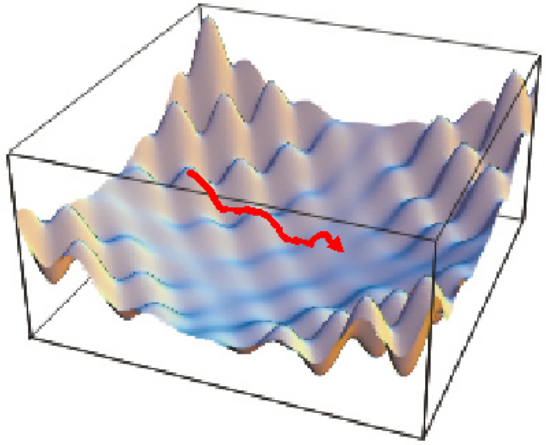
Tutorial: *"A newcomer's guide to ultrashort pulse shaping and characterization"*
A Monmayrant et al., J Phys B - Atom Mol Opt Phys ***43*** *(2010) 103001*

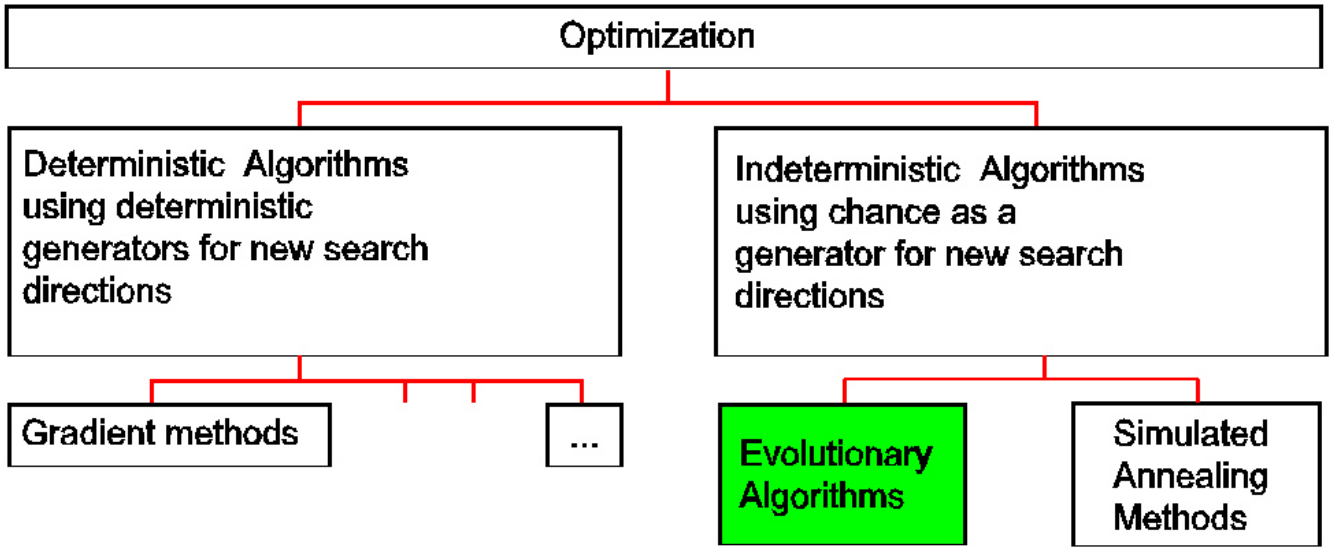
Complex fs-pulse shaping techniques

Pulse shaper	**LCD**	**AOM**	**AOPDF**	**Def. Mirror**
Modulation	Phase, amplitude and polarization	Phase and amplitude	Phase, amplitude and (polarization?)	Phase only
Pixels	128 (650)	1800	450	continous (16 stamps)
Transmission	70 %	30 %	30 %	95 %
Waveform update Rate	10 Hz	100 kHz	100 kHz	few 10 Hz
Group-delay range	4 ps	3 ps	3 ps	few 5 fs
Additional imposed chirp	Negligible (reflective optics)	270000 fs^2	12500 fs^2	No chirp

Optimization Algorithms

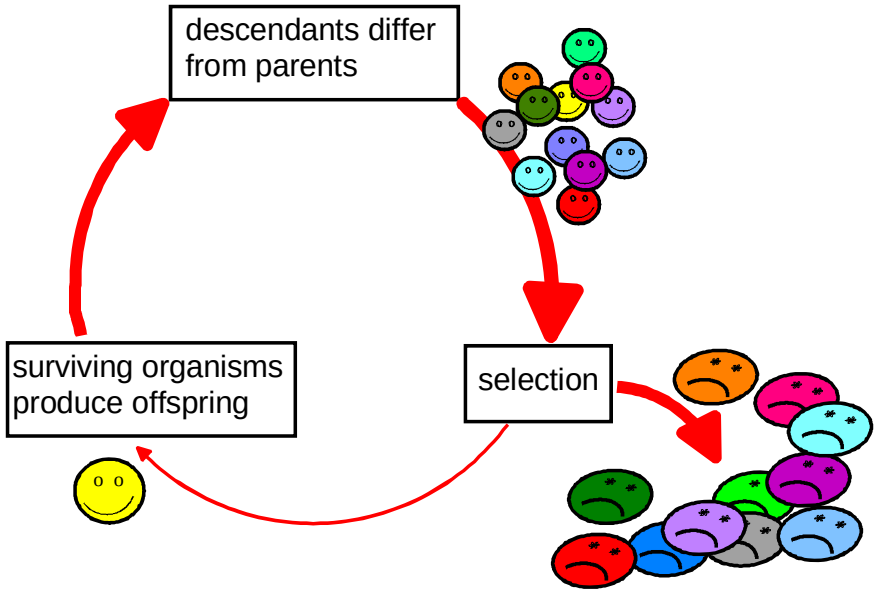






Evolutionary Algorithms

"survival of the fittest"



Chromosome : vector of numbers

...	1.35	0.83	6.22	9.25	2.76	3.28	4.59	3.47	2.39	5.10	...

Recombination : multiple cross-over

...	1.35	0.83	6.22	9.25	2.76	3.28	4.59	3.47	2.39	5.10	...
...	6.34	7.53	9.44	2.98	6.31	0.11	1.52	8.55	8.25	4.72	...
→ ...	1.35	7.53	6.22	9.25	6.31	0.11	1.52	3.47	8.25	4.72	...

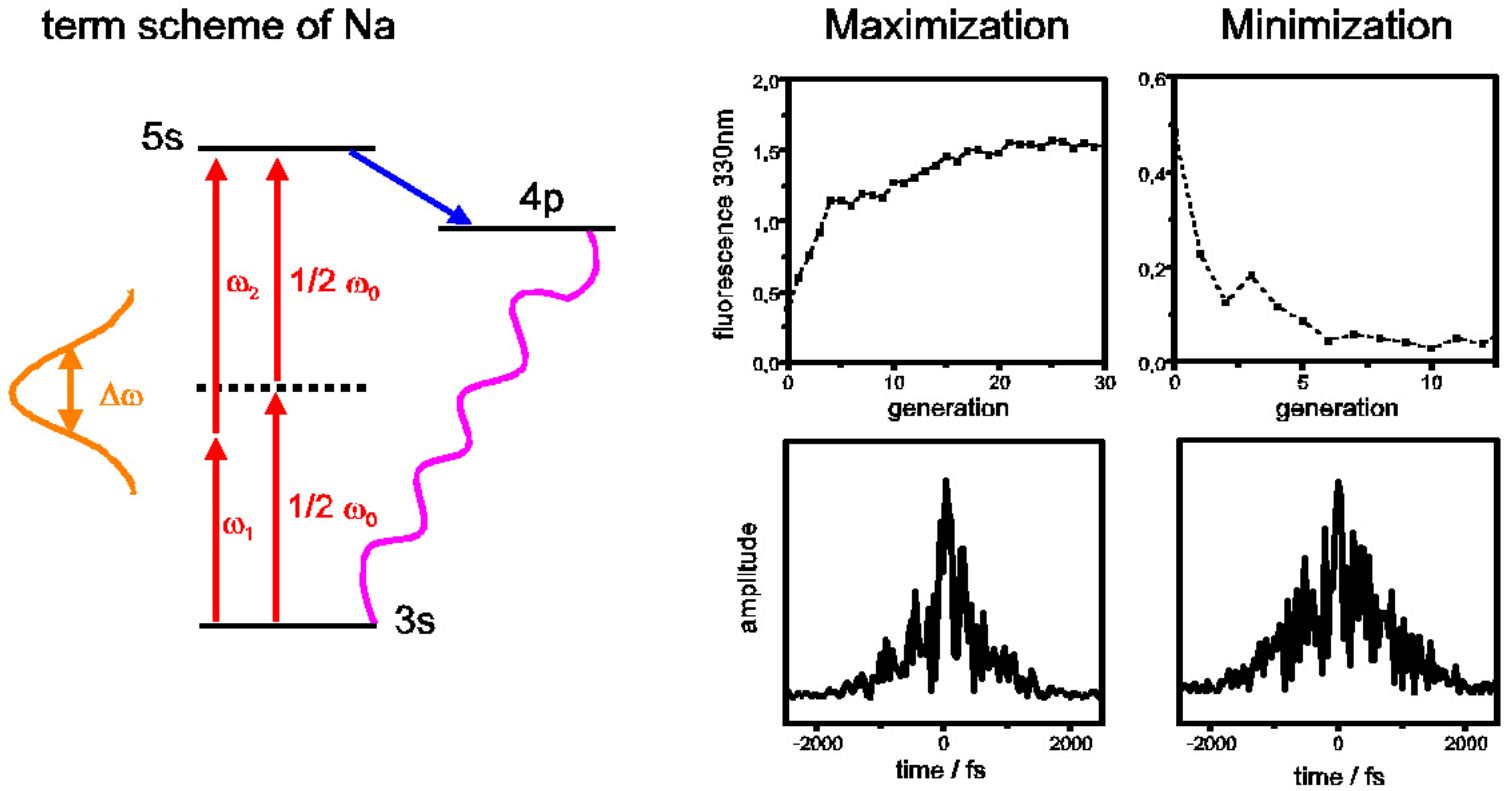
also possible : intermediary recombination

Mutation : Change the value of a vector element

...	1.35	0.83	6.22	9.25	2.76	3.28	4.59	3.47	2.39	5.10	...
→ ...	1.35	0.83	6.84	9.25	2.76	3.28	4.59	3.47	2.39	5.10	...

Phys. Rev. A 64 (2001) 023420

Coherent control of two photon transition

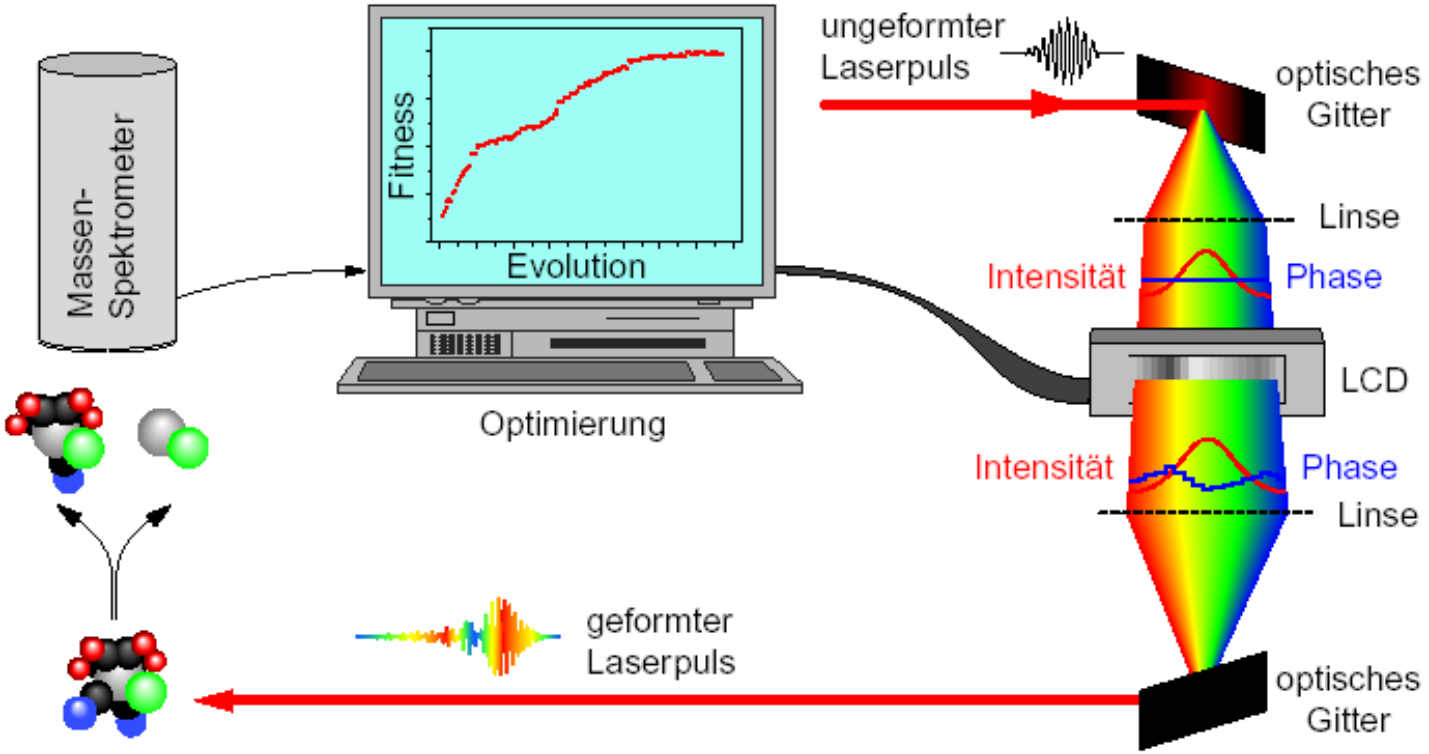


Science **288** (2000) 824; Appl.Phys. **B 71** (2000) 277

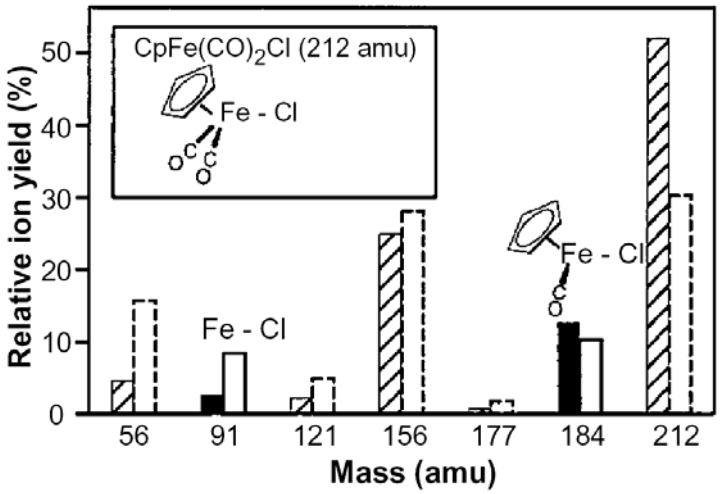
*See also Silberberg group, e.g. Nature **396** (1998)*

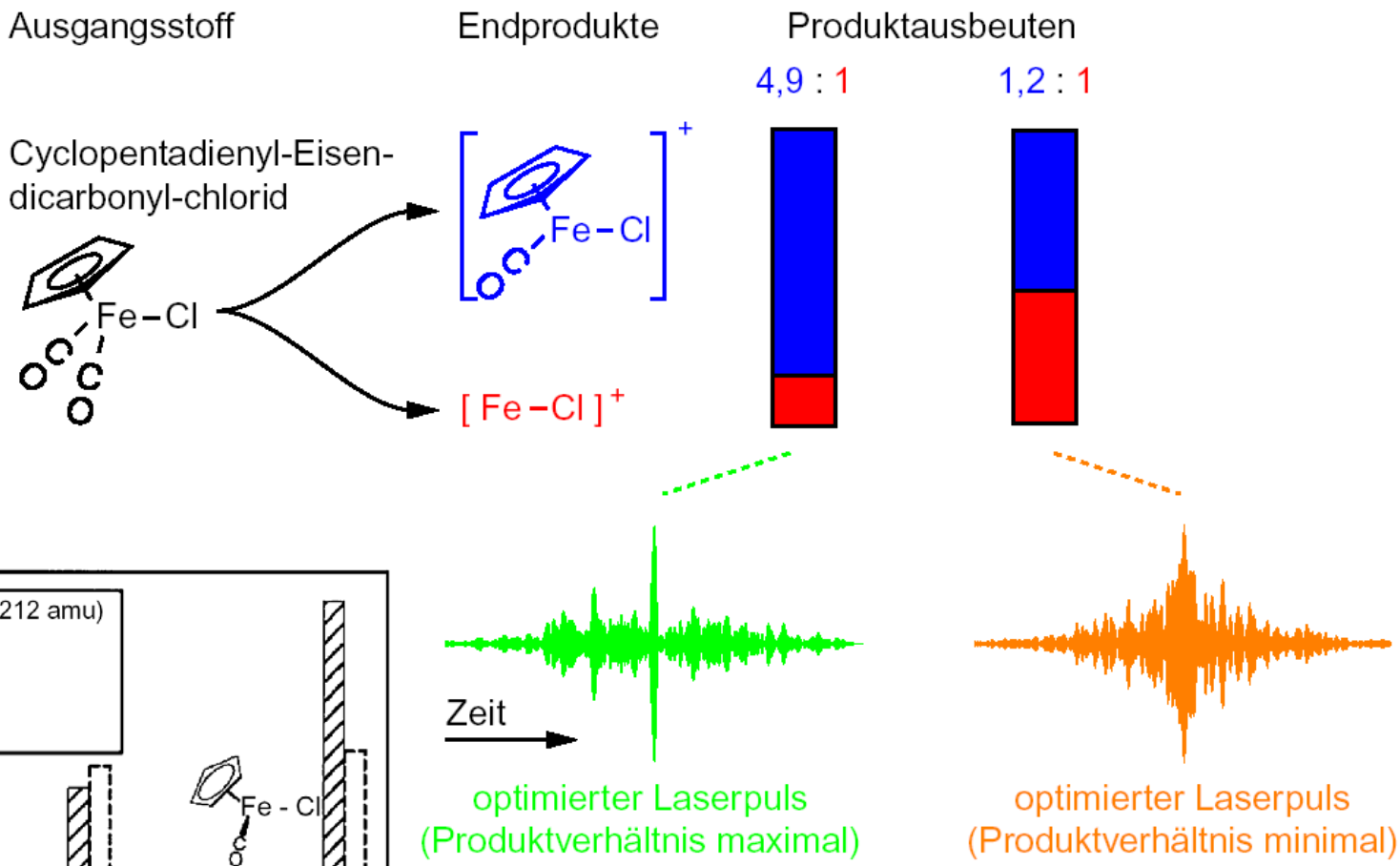
Control of Chemical Reactions by Feedback-Optimized Phase-Shaped Femtosecond Laser Pulses

A. Assion, T. Baumert,* M. Bergt, T. Brixner, B. Kiefer,
V. Seyfried, M. Strehle, G. Gerber



Control of photofragmentation, cont.

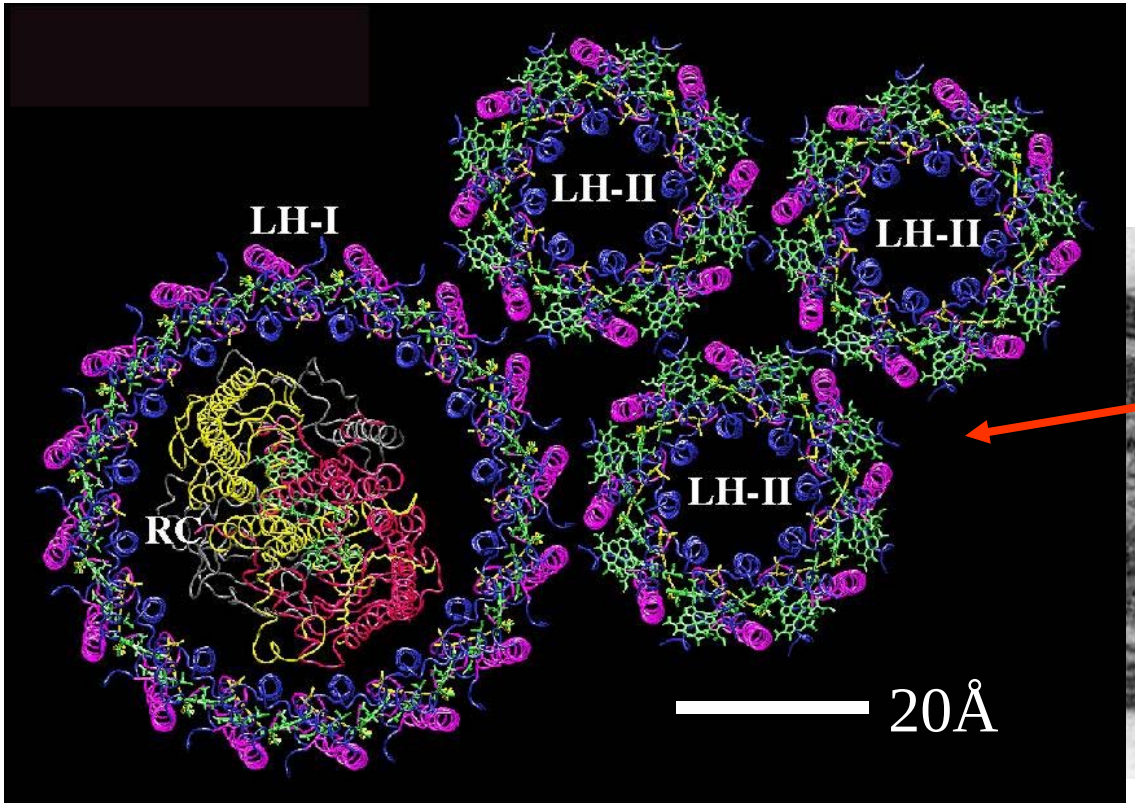




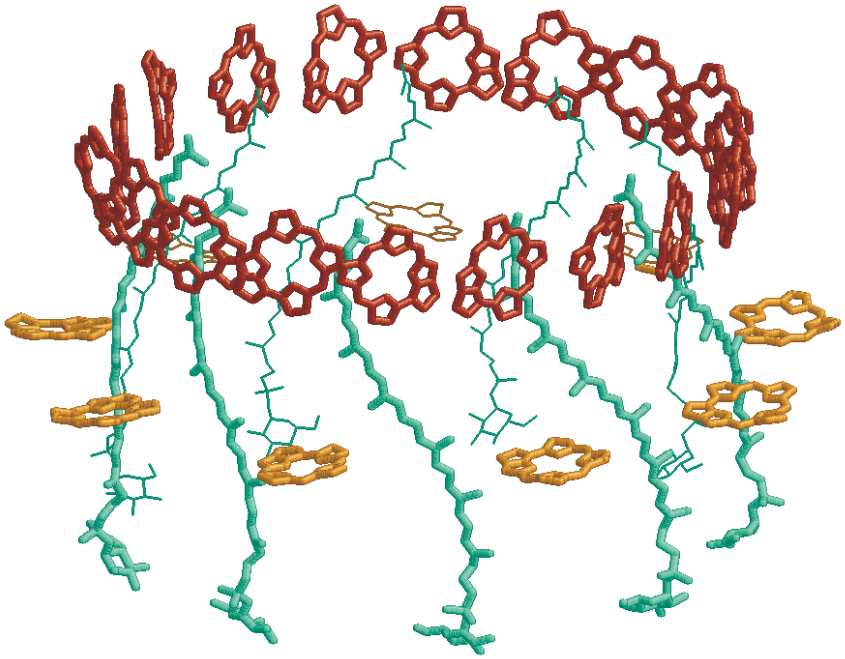
Changing the pulse shape
changes the product ratio

Photosynthetic purple bacteria

Light harvesting + reaction center unit



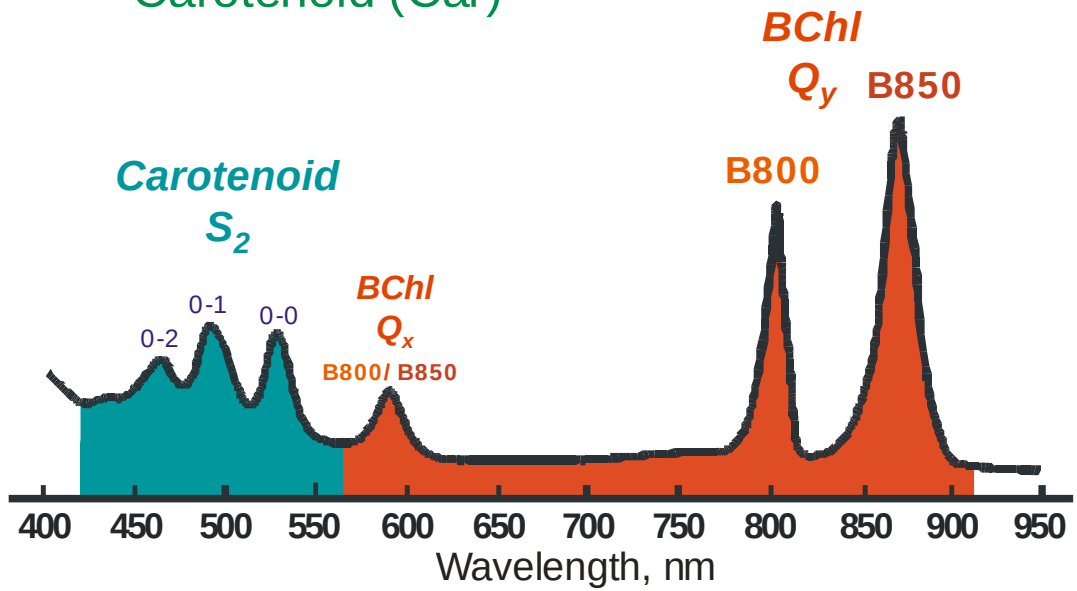
LH2 from Rps. acidophila



B850 Bacterio-chlorophyll (BChl)

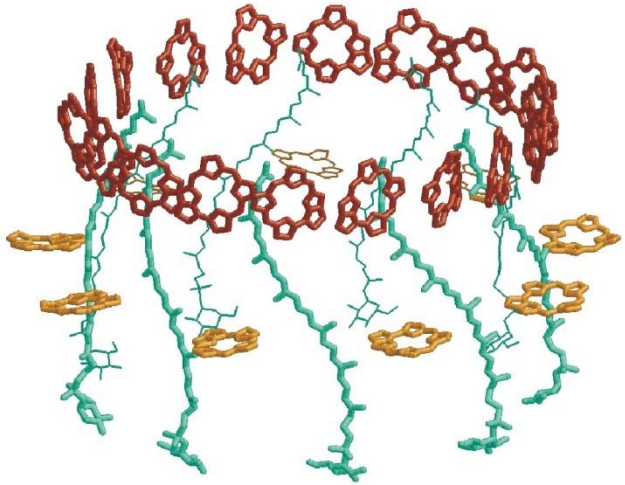
B800 BChl

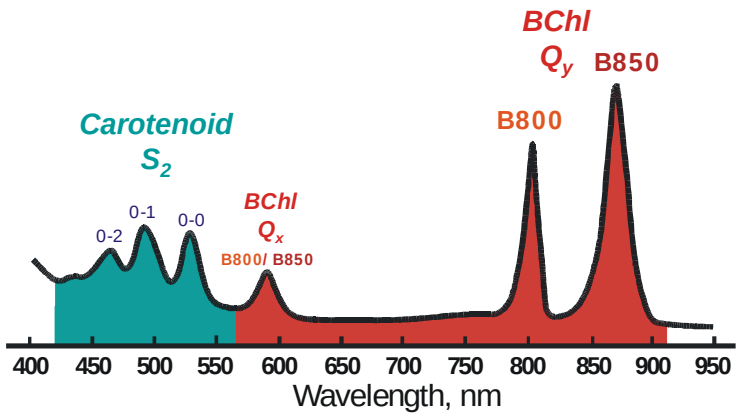
Rhodopin glucoside Carotenoid (Car)

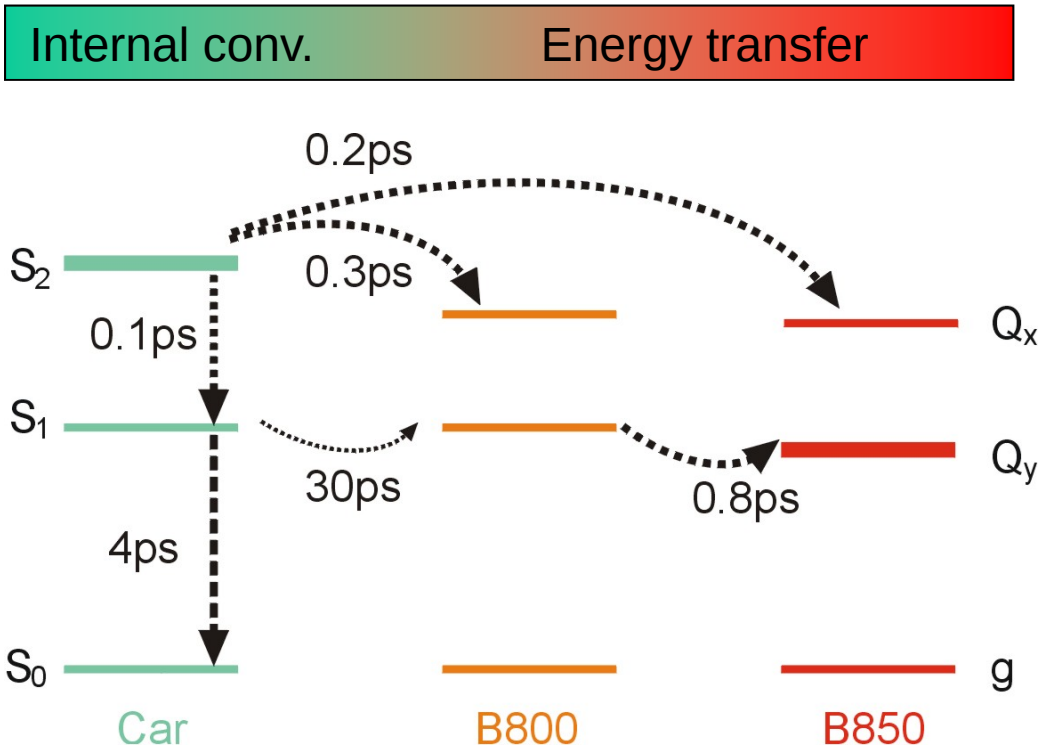


Collaboration with
J.L. Herek, AMOLF
R.J. Cogdell,
University of Glasgow

LH2 of *Rps. Acidophila* - Standard model

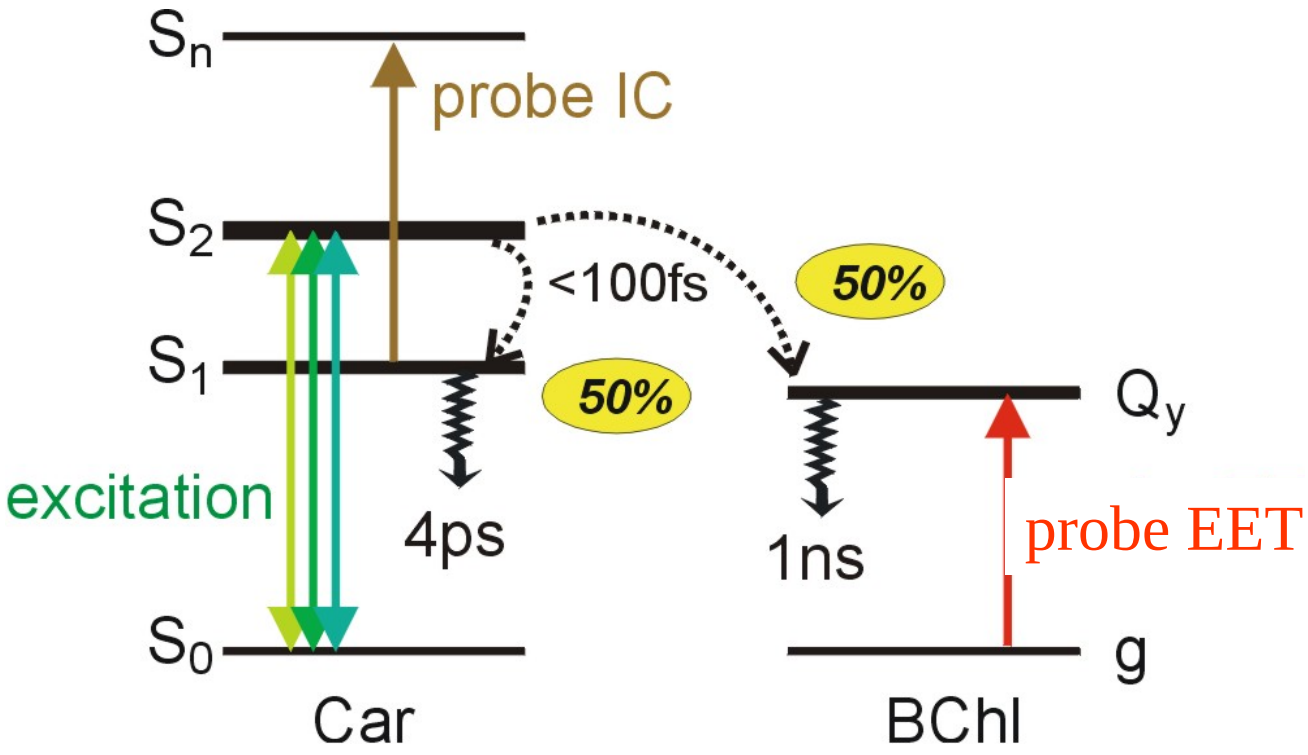






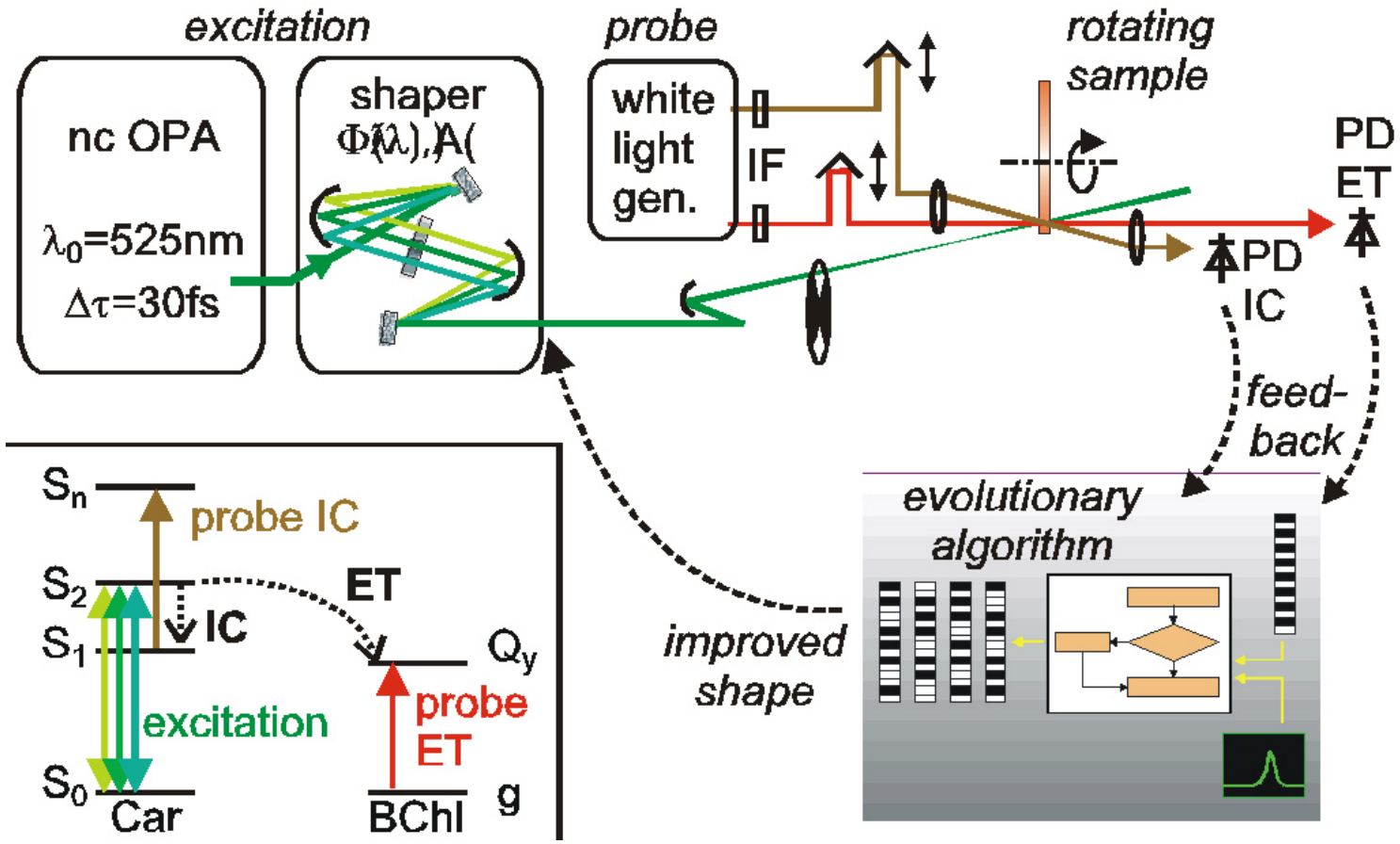
Polivka & Sundström, Chem. Rev. (2004)

Competing deactivation IC-EET



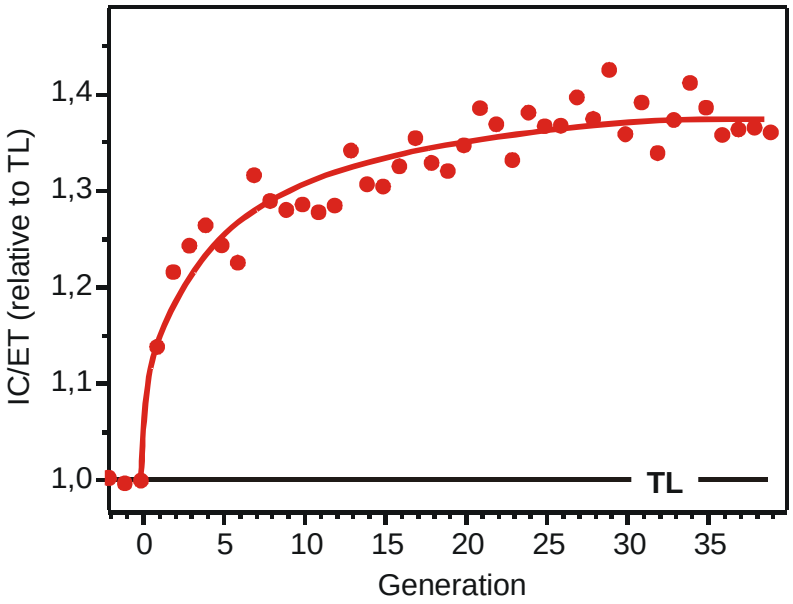
- Significant loss channel IC
- Negligible cross talk IC-EET
- Energy funnel precludes back transfer

Closed-loop approach on LH2

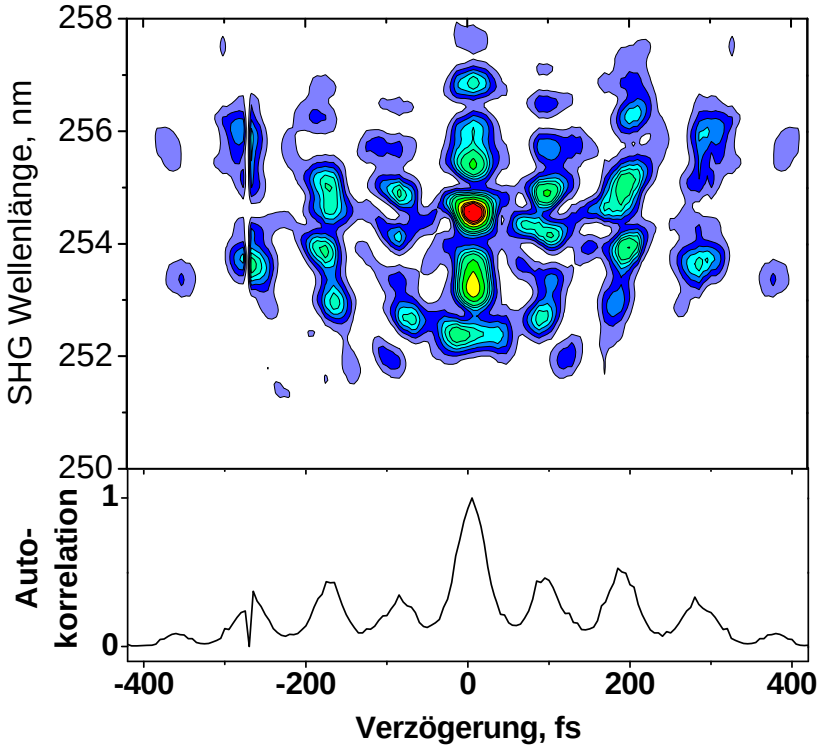


64-parameter optimisation of IC/EET

Convergence curve



Optimal pulse FROG trace



Nature **417** (2002) 533

ChemPhysChem **6** (2005) 850

Coherent Control of Retinal Isomerization in Bacteriorhodopsin

Valentyn I. Prokhorenko,[1] Andrea M. Nagy,[1] Stephen A. Waschuk,[2] Leonid S. Brown,[2] Robert R. Birge,[3] R. J. Dwayne Miller[1]*

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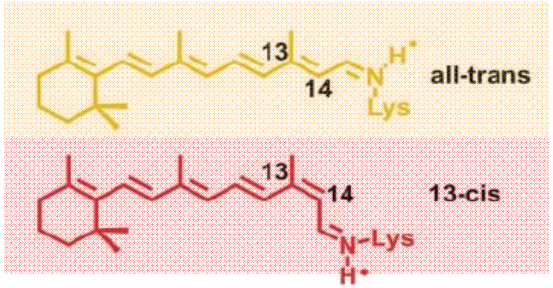
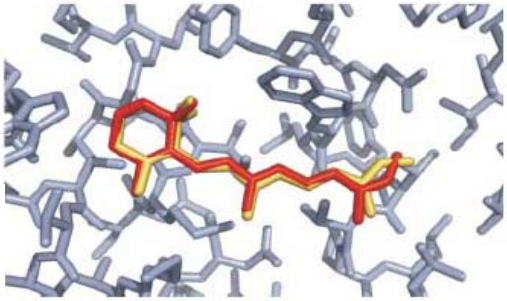
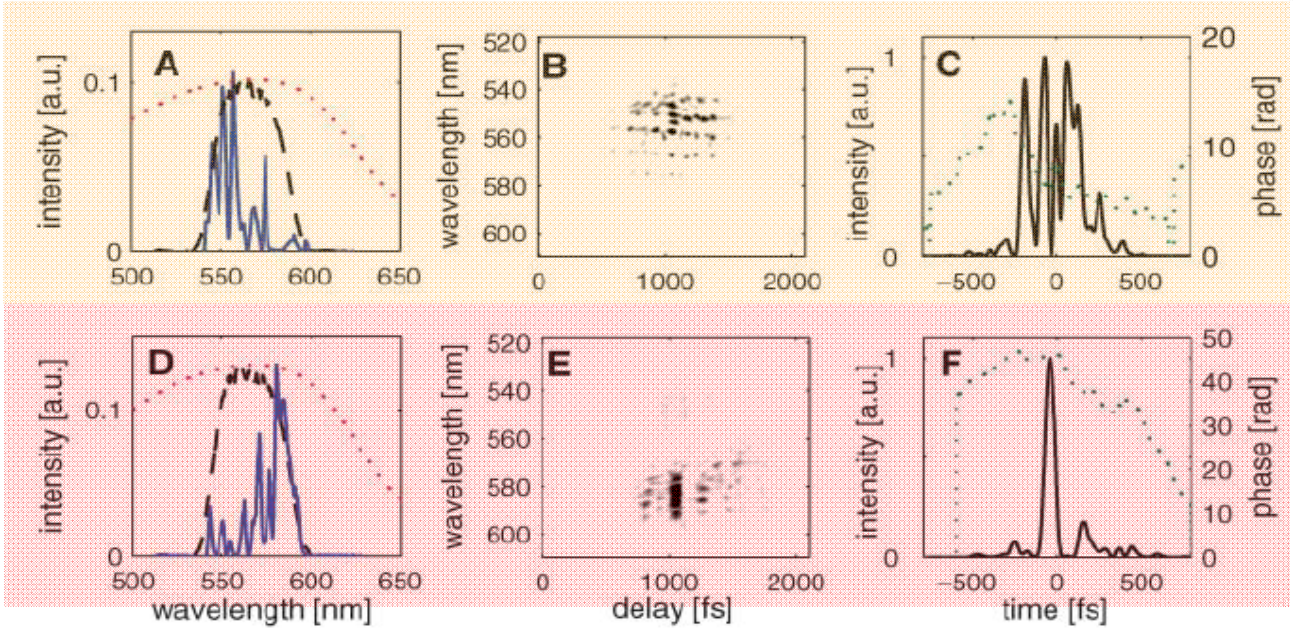
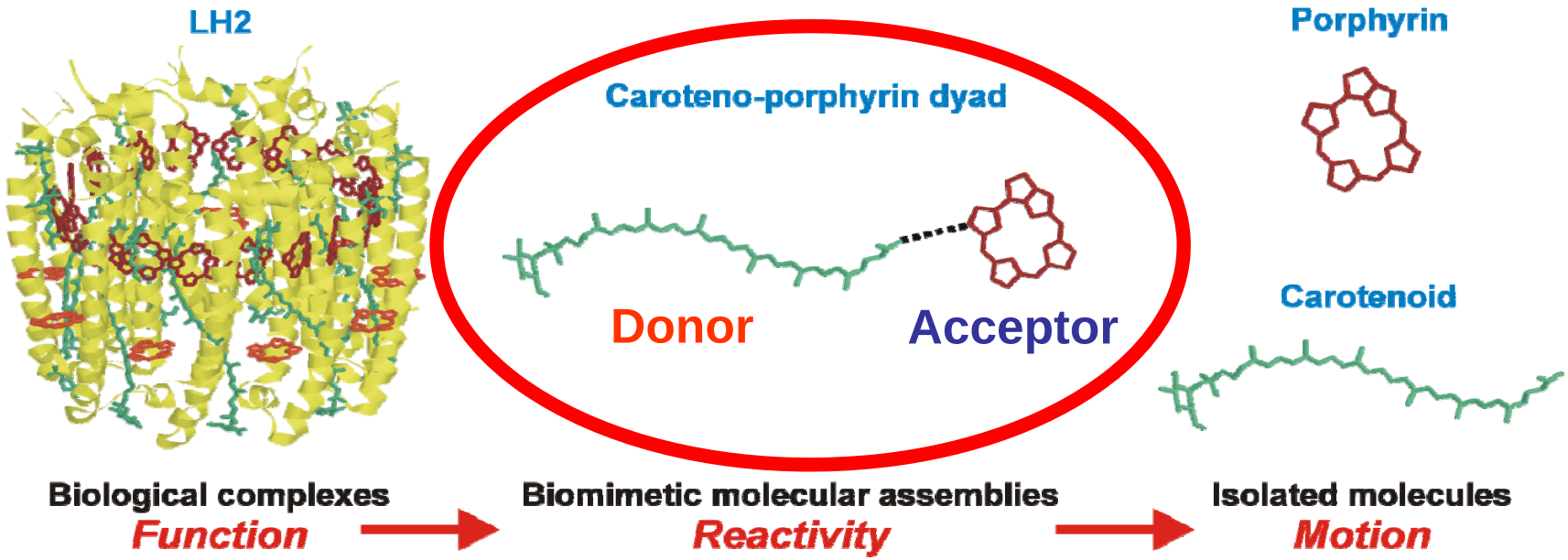




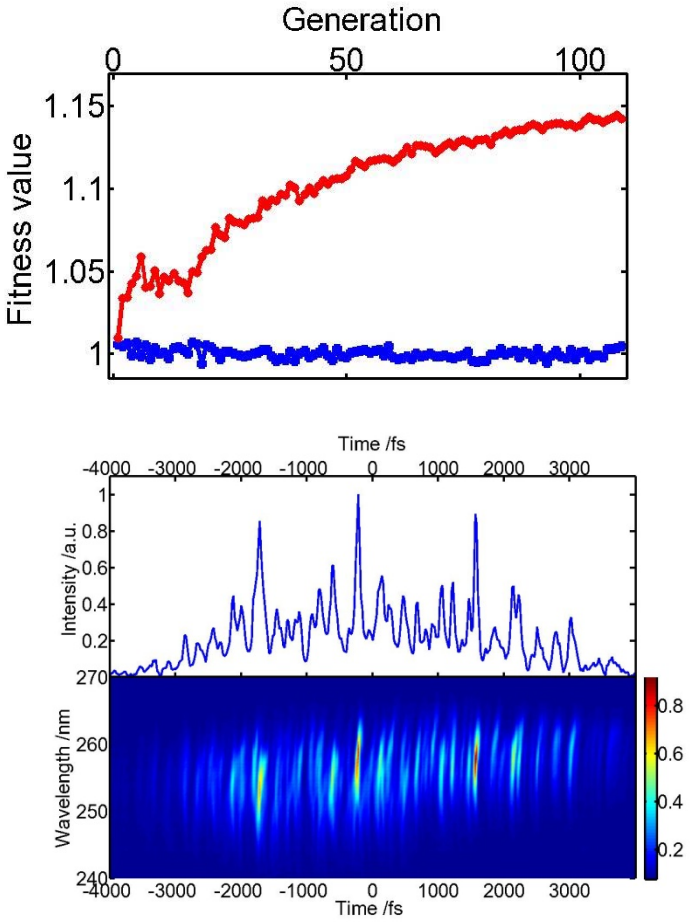


Reducing the complexity

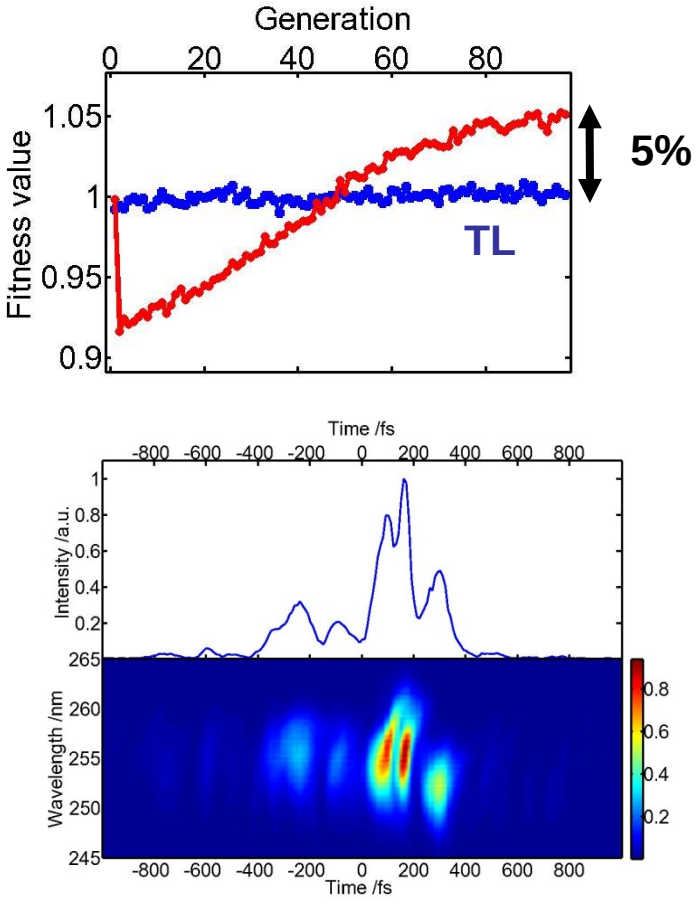


Control of Dyad complex

IC/ET



ET/IC



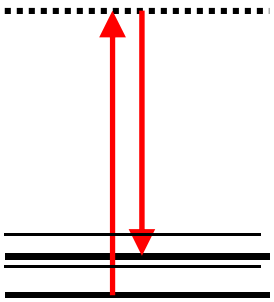
Collaboration with AMOLF/Twente

*PNAS **105** (2008) 7641*

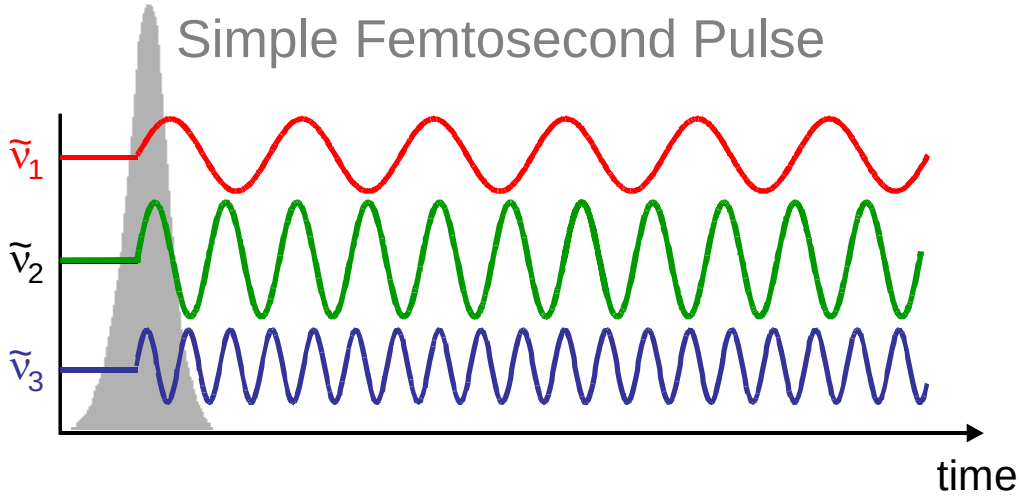
Multipulses:

Impulsive stimulated Raman scattering

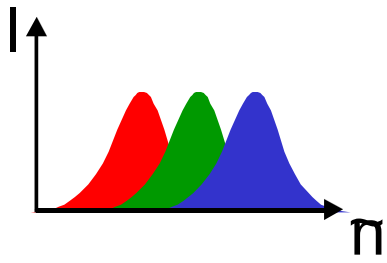
ISRS



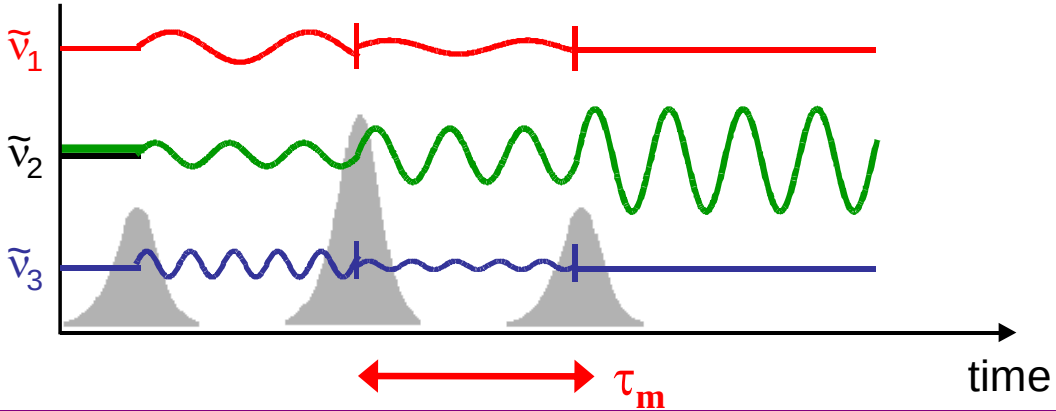
Simple Femtosecond Pulse



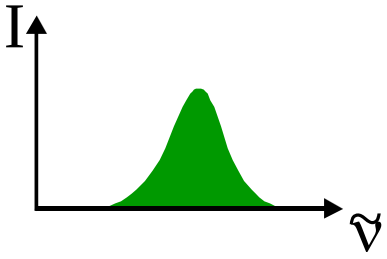
Blurred excitation



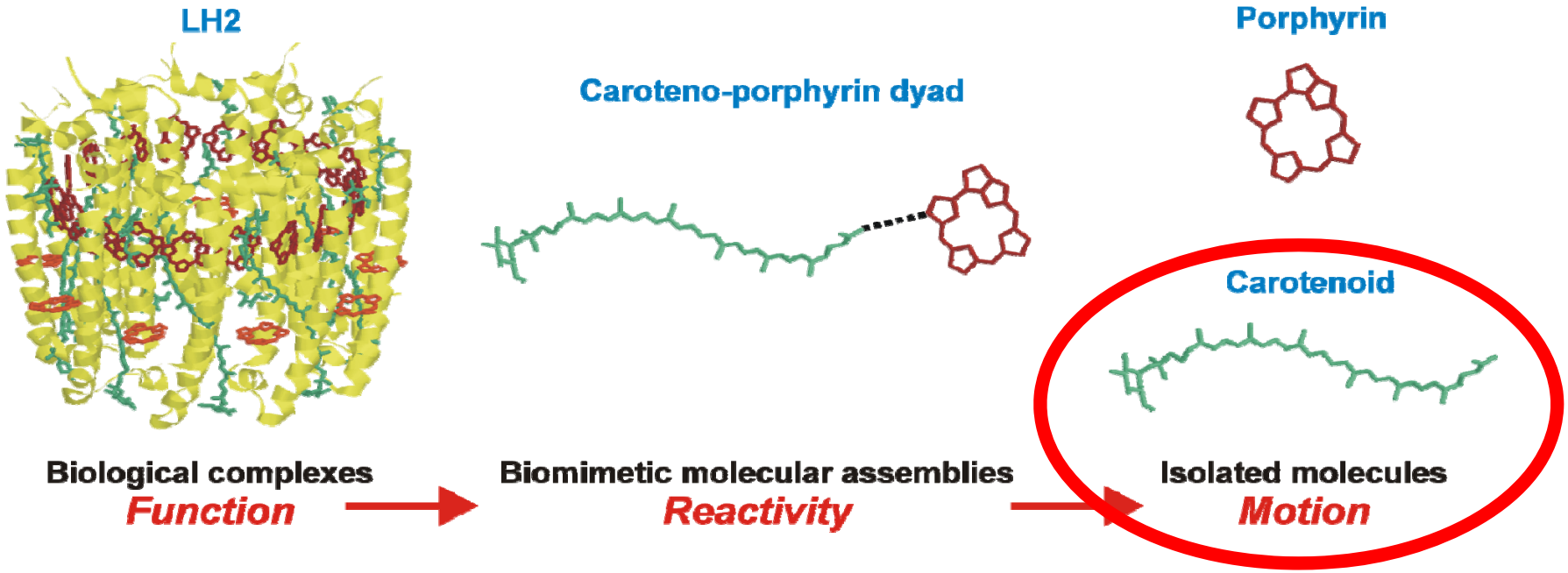
Femtosecond Pulse-Train



Selective Raman excitation

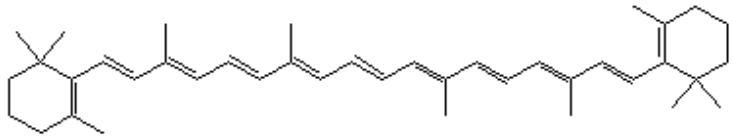


Further reduction of complexity

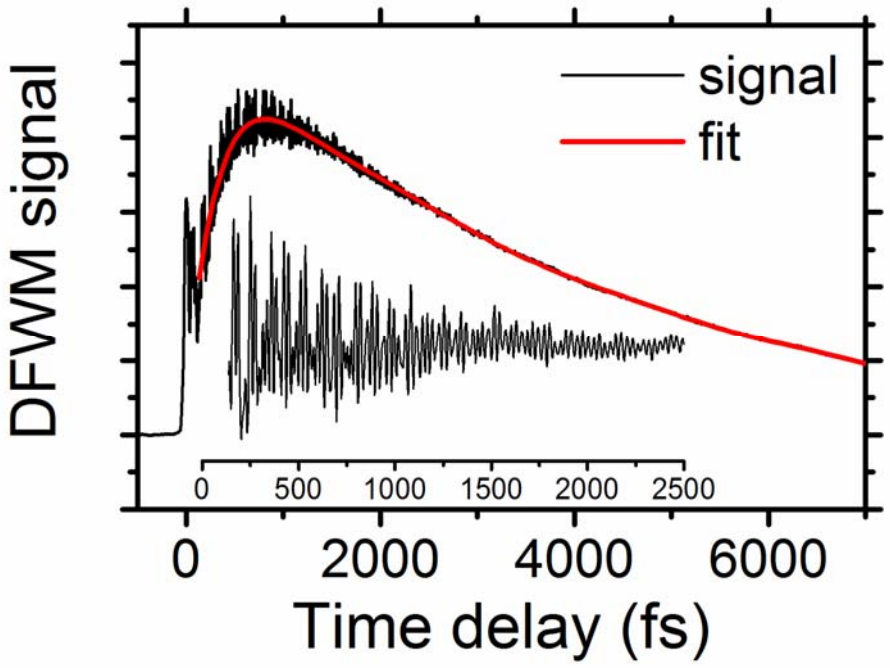


Chem. Phys. Lett. ***421*** *(2006) 523*

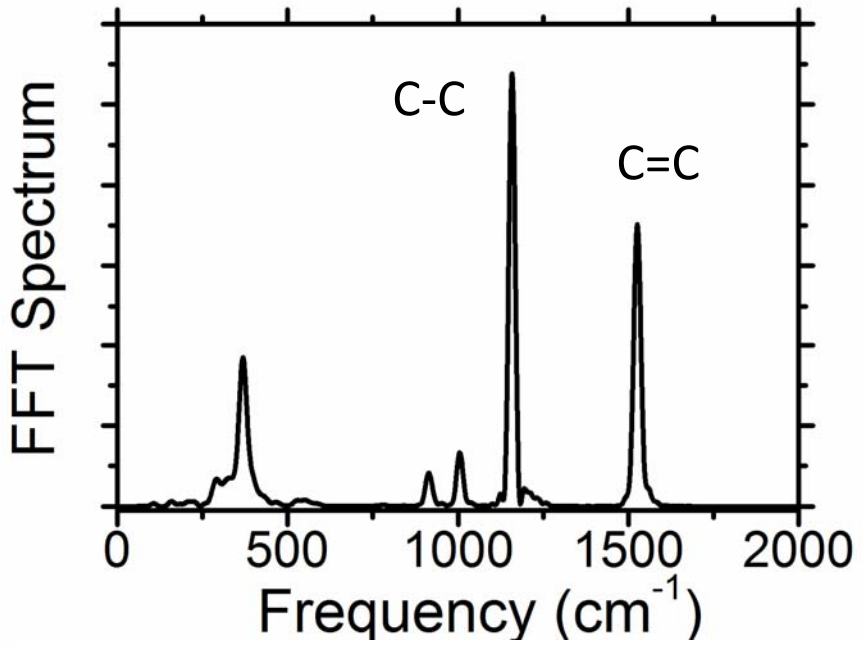
Wavepackets in β–Carotene



Transient



FFT spectrum



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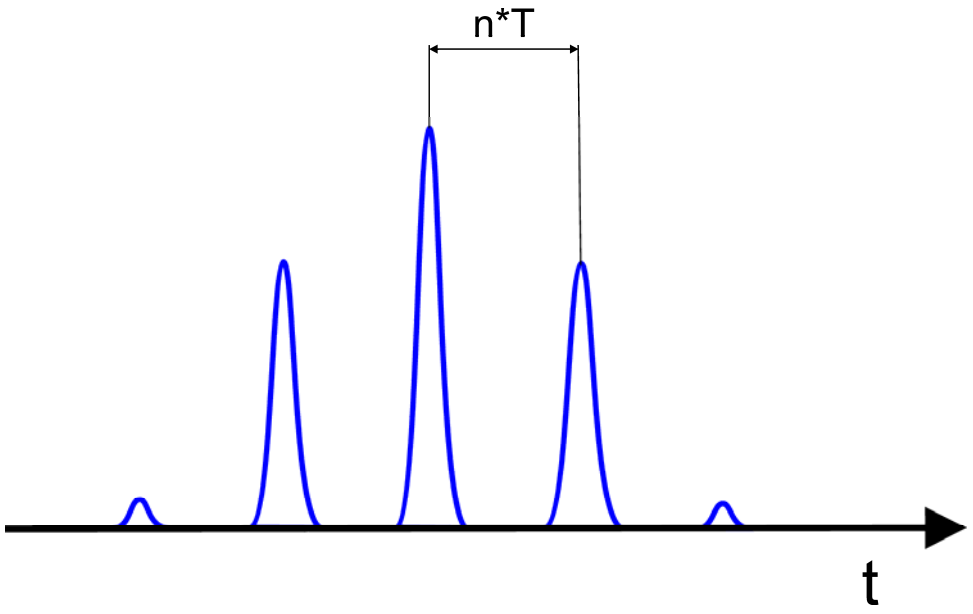
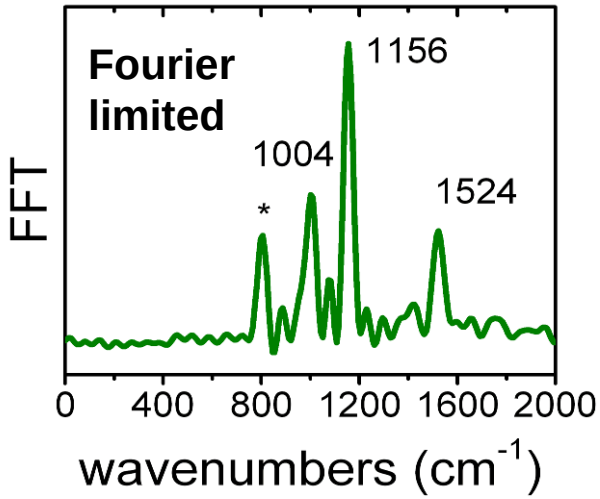
Pulse Spacings

Energy (cm^{-1})	T(fs)	2 T(fs)	3 T(fs)	4 T(fs)	5 T(fs)
1524	21.9	43.8	65.7	87.6	109.5
1157	28.8	57.6	86.4	115.2	144
1004	33.2	66.4	99.6		



Control of ground state vibrations

Nonlinear Raman spectra



→ *Modes can be selectively excited*

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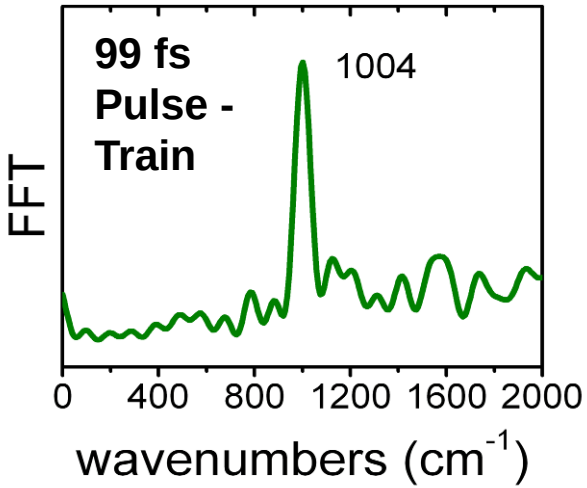
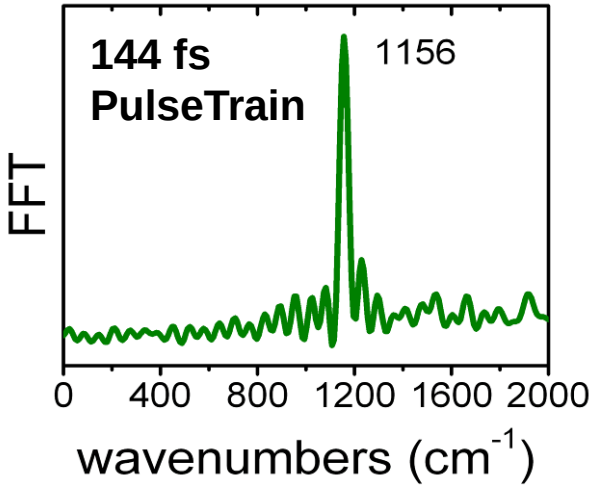
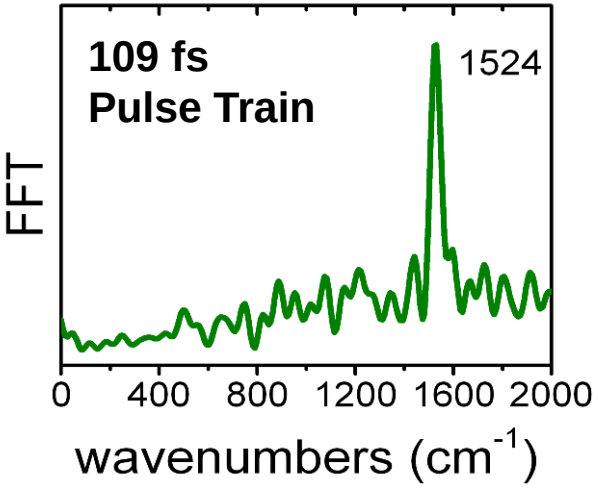
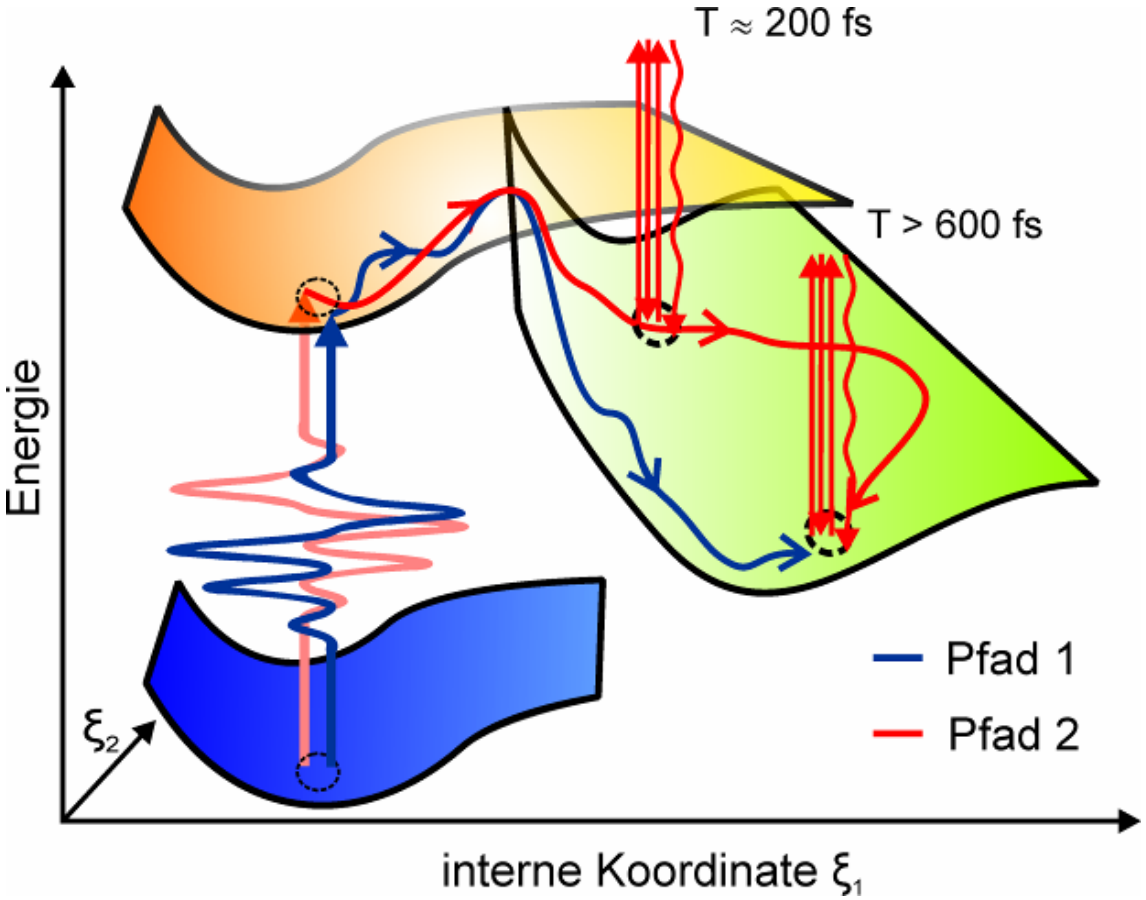






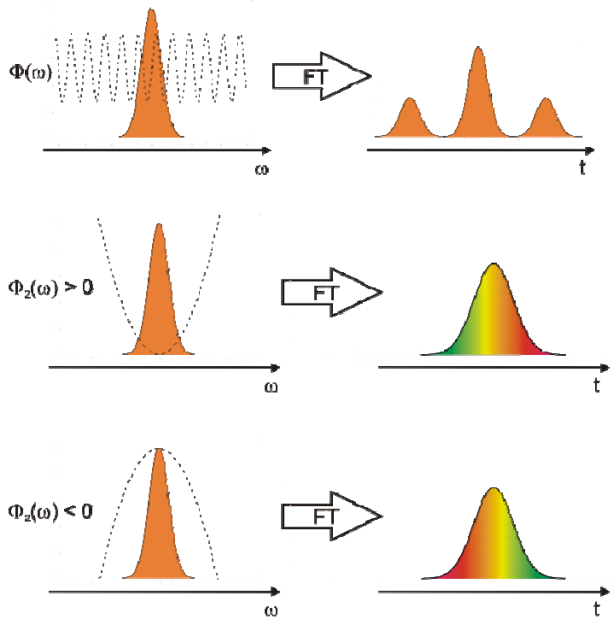
Control of excited state dynamics in carotene



- Additive phase term *c* affecting the wavepacket evolution?
- Need for further theoretical investigation

Coherent Control + Spectroscopy = Quantum Control Spectroscopy (QCS)[1-4]

- Modify the excitation to learn more about the dynamics
- Several possible „new“ molecular responses :



Example of QCS-approach:

→ Disentanglement of complex dynamics in carotenoids!

(1) *Faraday Discus.* ***153*** *(2011) 213*
(2) *IEEE J. Quantum Electronics* ***18*** *(2012) 449*
(3) *Chem. Phys.* ***350*** *(2008) 220*
(4) *PNAS* ***105*** *(2008) 7641*