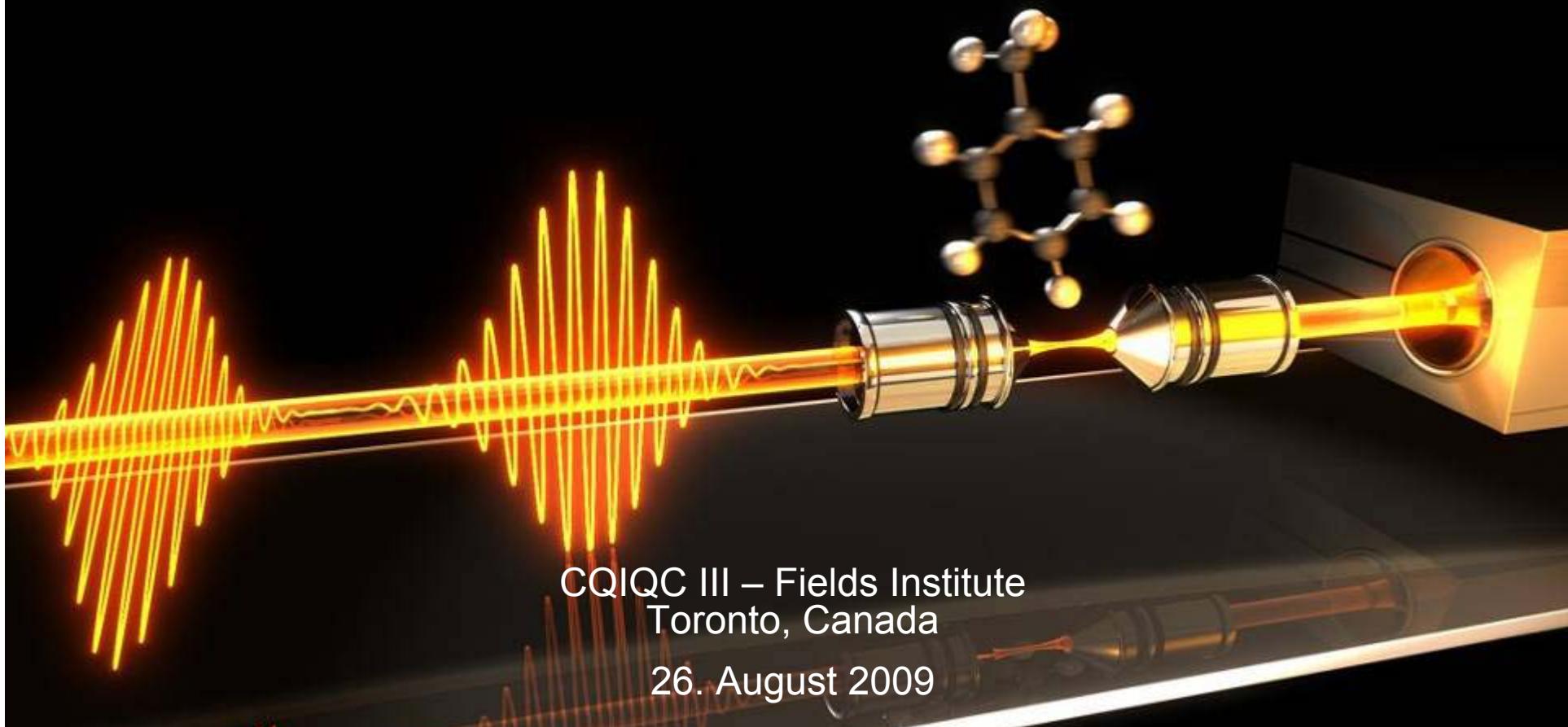


Spectroscopy of biological molecules using coherent control

Marcus Motzkus, Physikalisch-Chemisches Institut
Universität Heidelberg

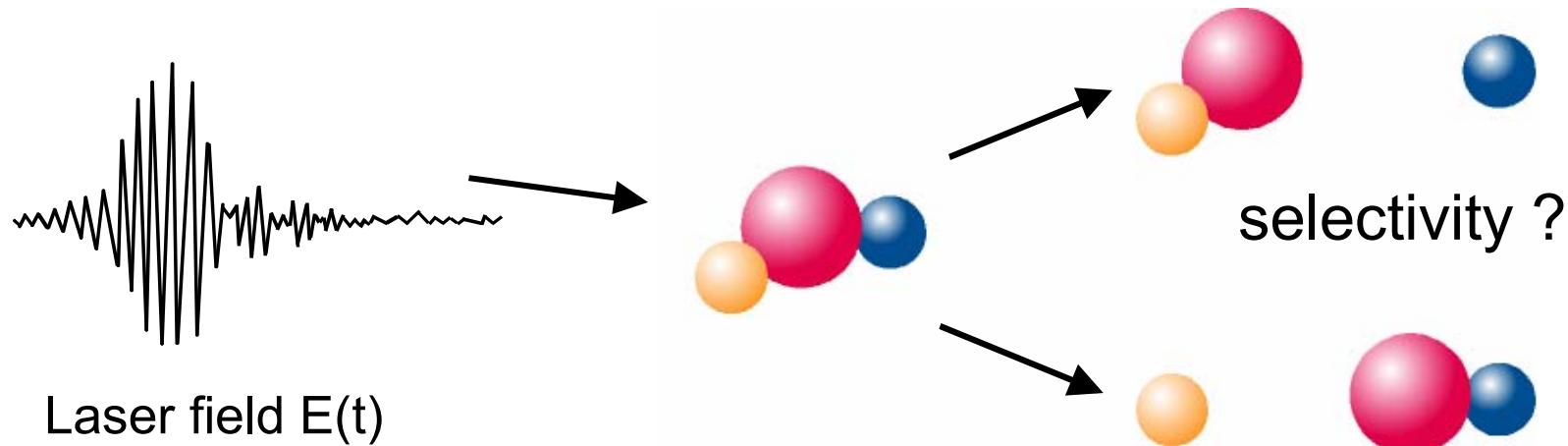




Outline

- Adaptive coherent control of biological systems:
 - playing with the complexity
 - extracting mechanism with parametrization
- Coherent Control with multipulses in the ground state
- Coherent Control with multipulses in the excited states of β -carotene
 - Pump-DFWM spectroscopy
 - Theoretical model of control mechanism

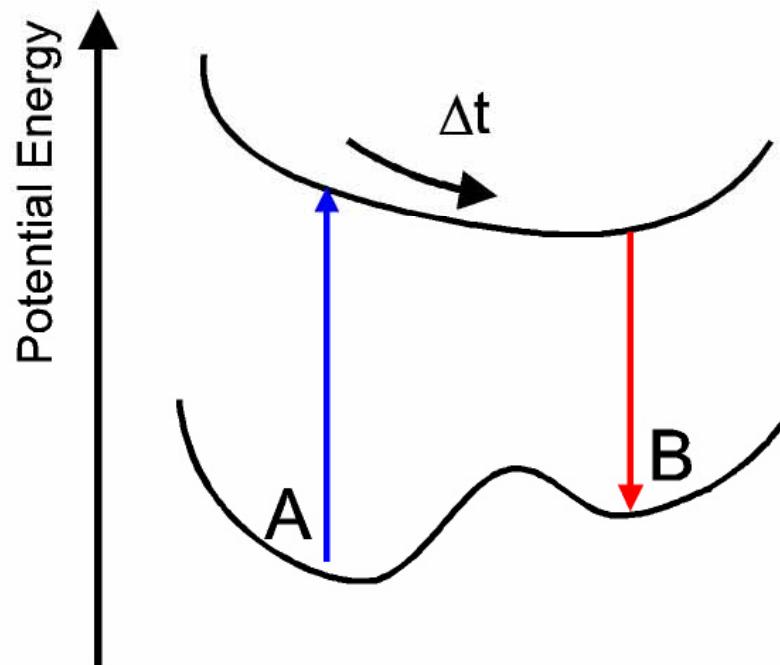
Coherent control of chemical reactions



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

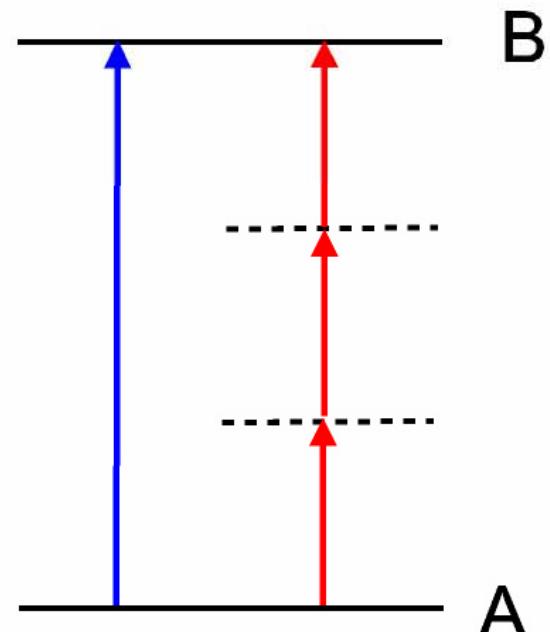
Control strategies

Tannor-Kosloff-Rice
JCP 85, 5805 (1986)



time delay: Δt

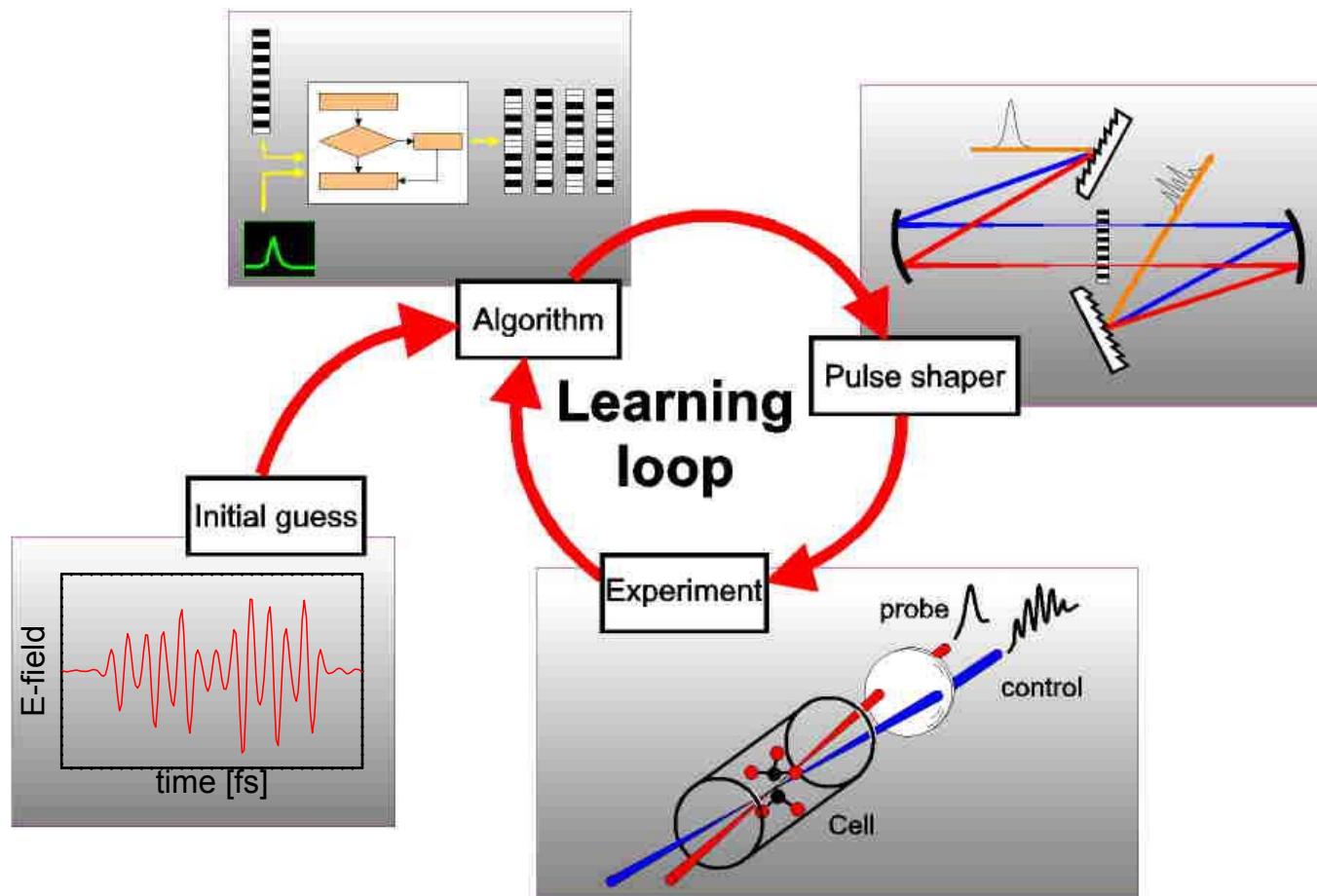
Brumer-Shapiro
CPL 126, 54 (1986)



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



Quantum control with adaptively shaped light

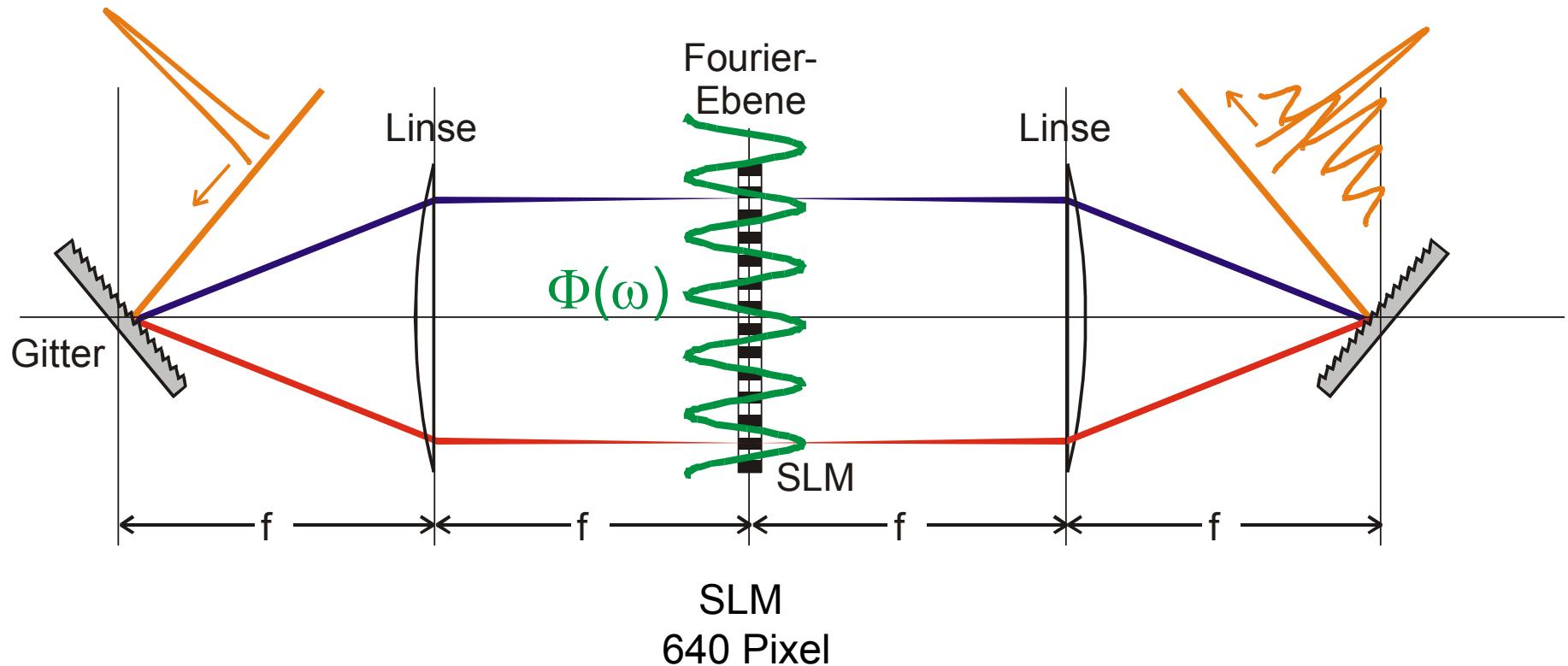


Science 288 (2000) 824

Concept: R.S. Judson and H. Rabitz, Phys. Rev. Lett. **68** (1992) 1500



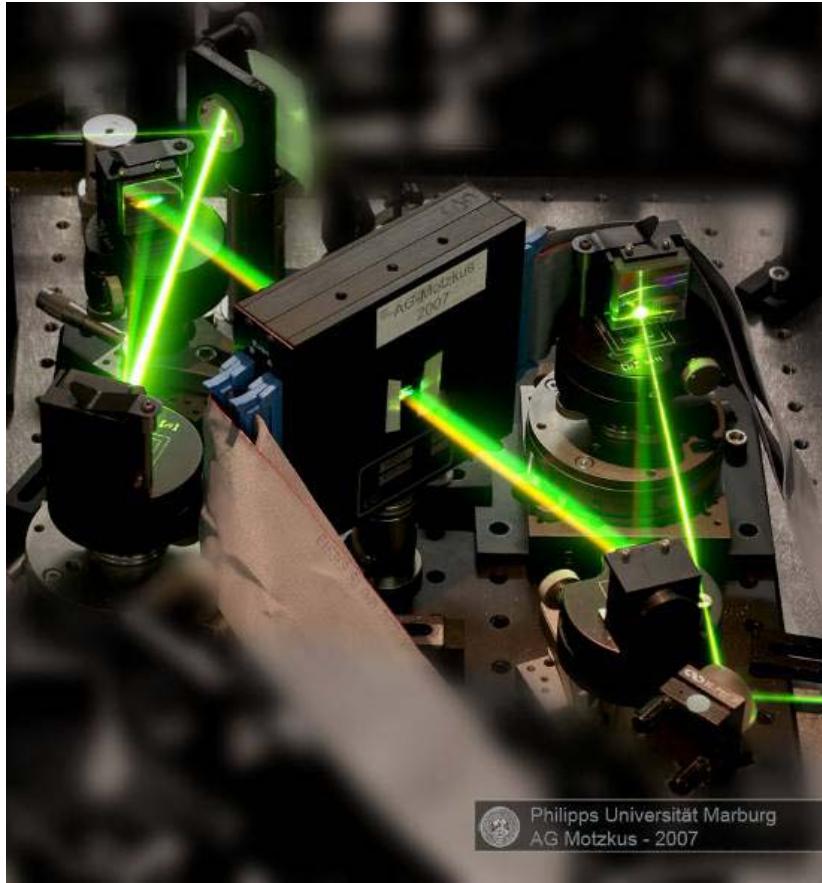
Shaping of fs-Laser Pulses



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



Liquid crystal spatial light modulator



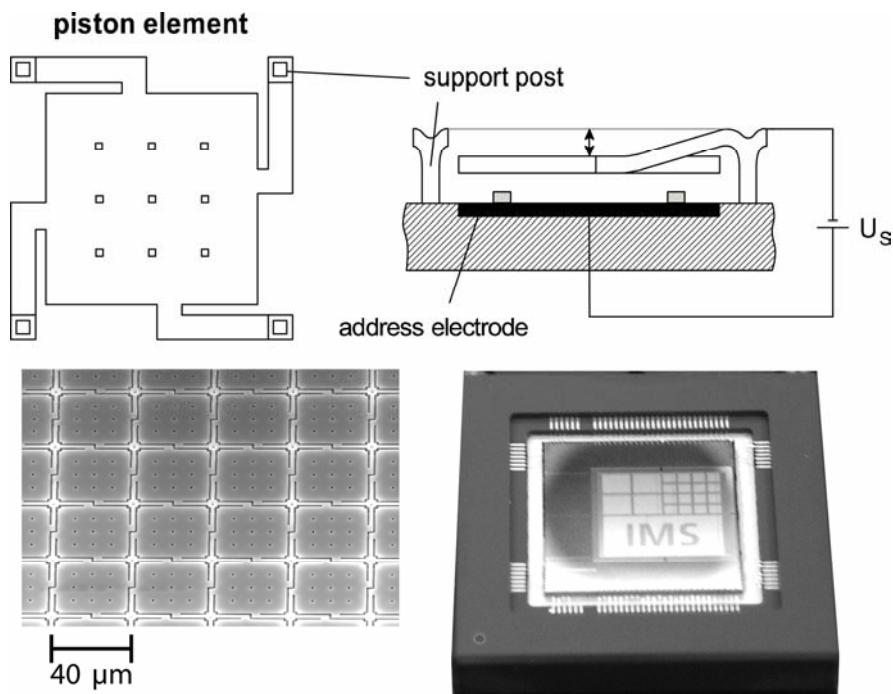
128 pixel device

→ Development of new 640 pixel shaper in cooperation
with University of Jena and Jenoptik:

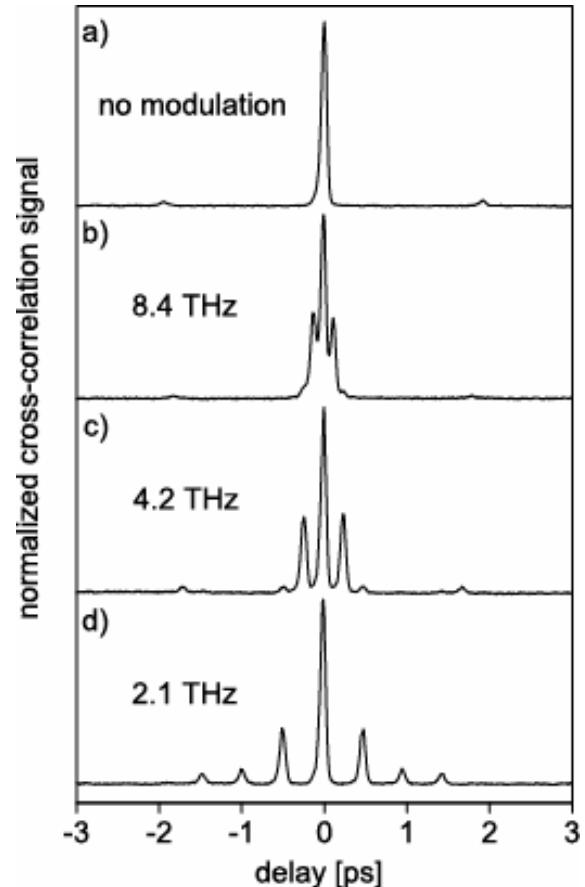
Appl. Phys. B 72 (2001) 627

Direct UV shaping

Micromirror SLM



→ Shaping of 260nm, 25 fs pulses

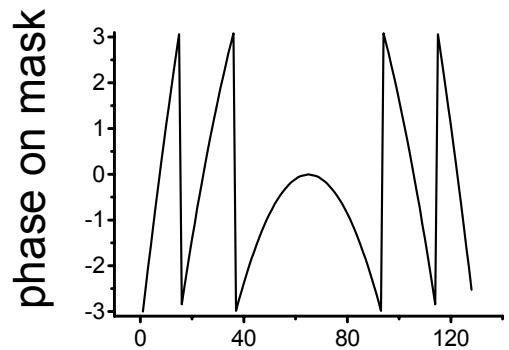


*Appl. Phys. B 76 (2003) 711
JOSA B (2009) in press*

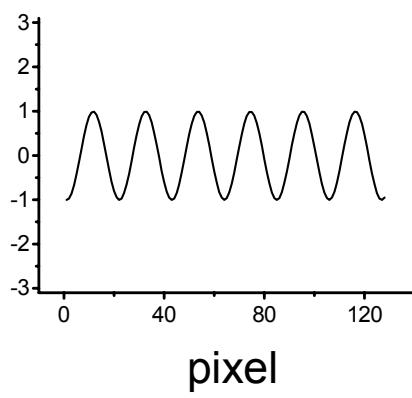


Parameterization of excitation mechanism

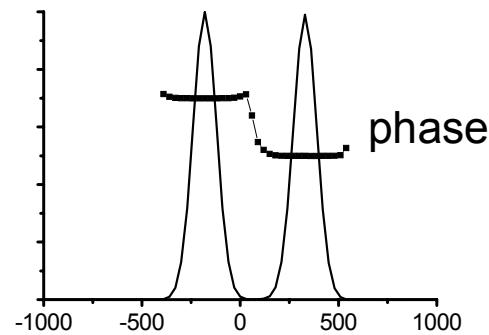
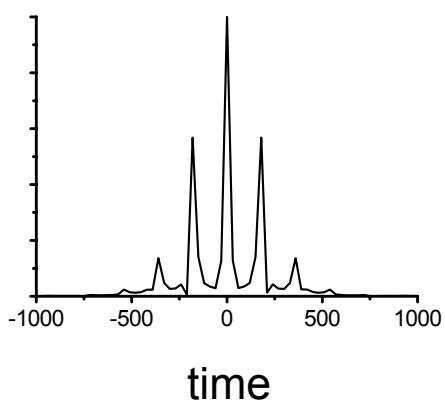
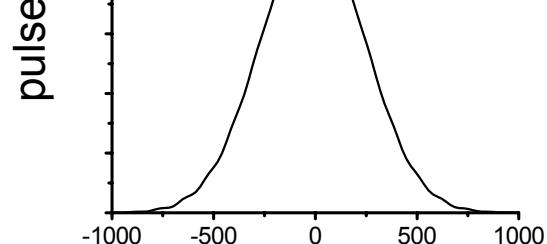
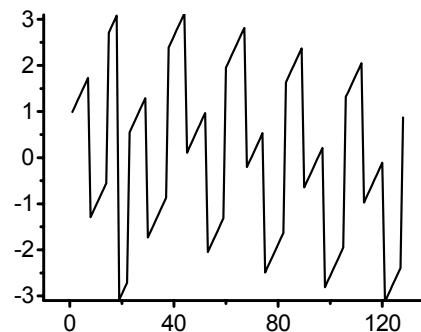
chirped



impulsive



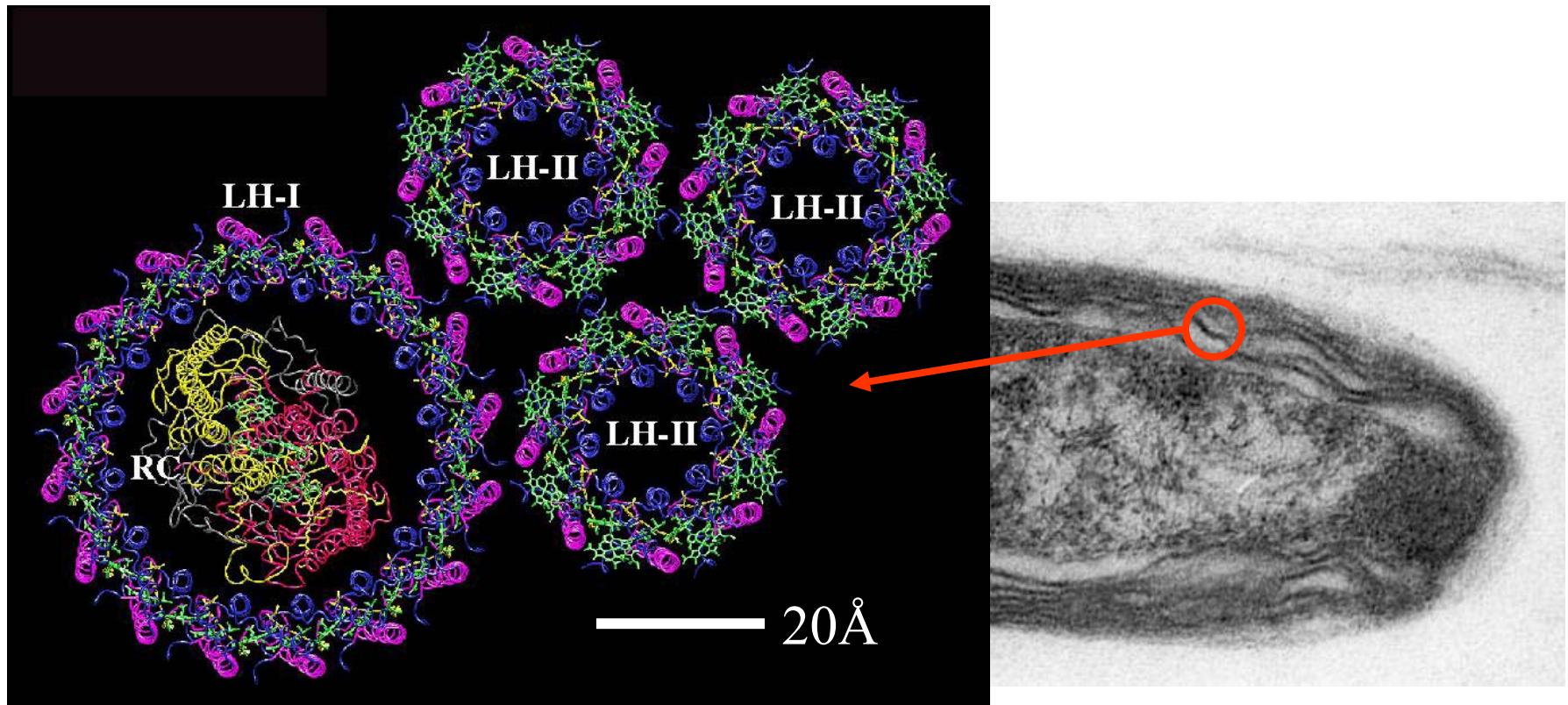
phase-locked





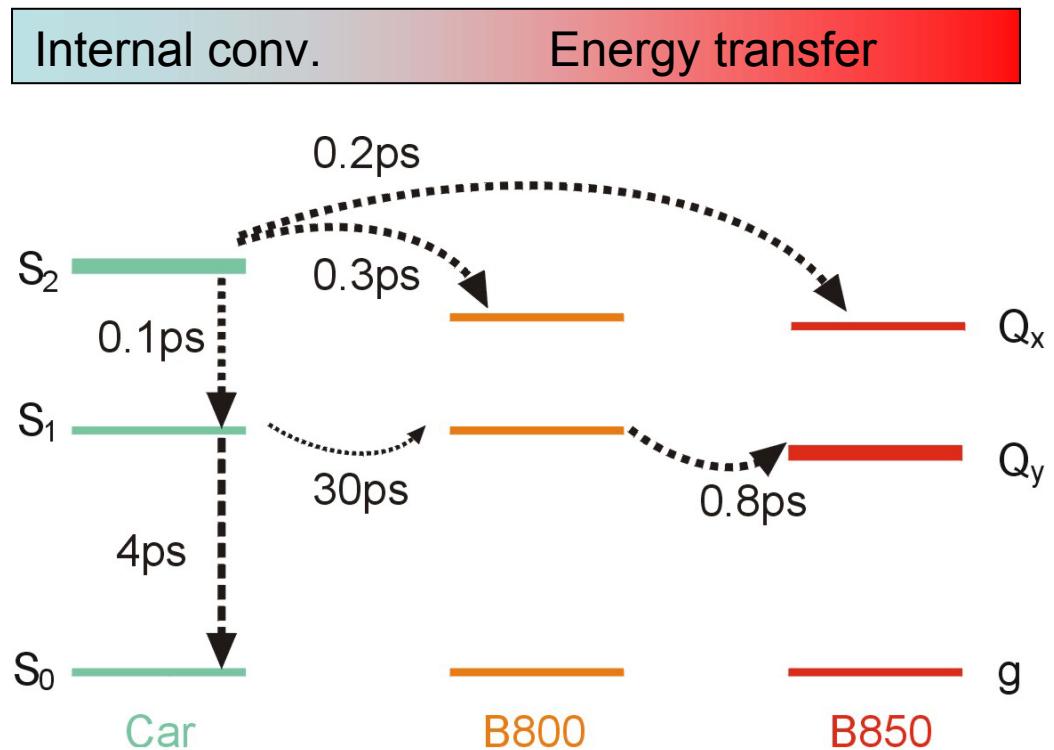
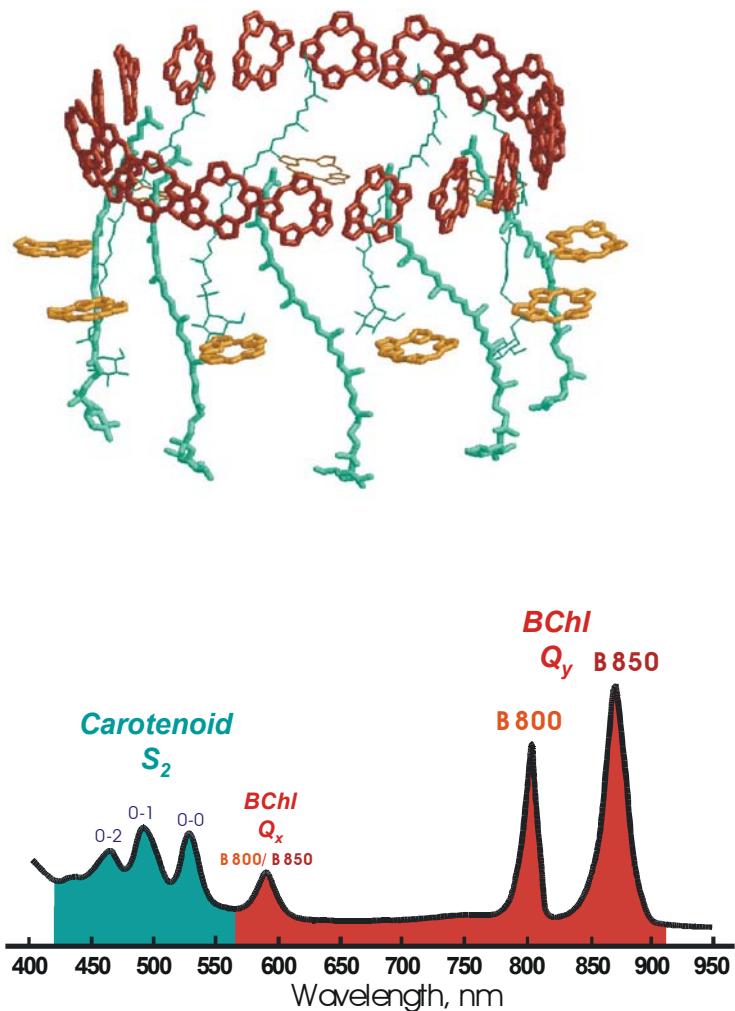
Photosynthetic purple bacteria

Light harvesting + reaction center unit



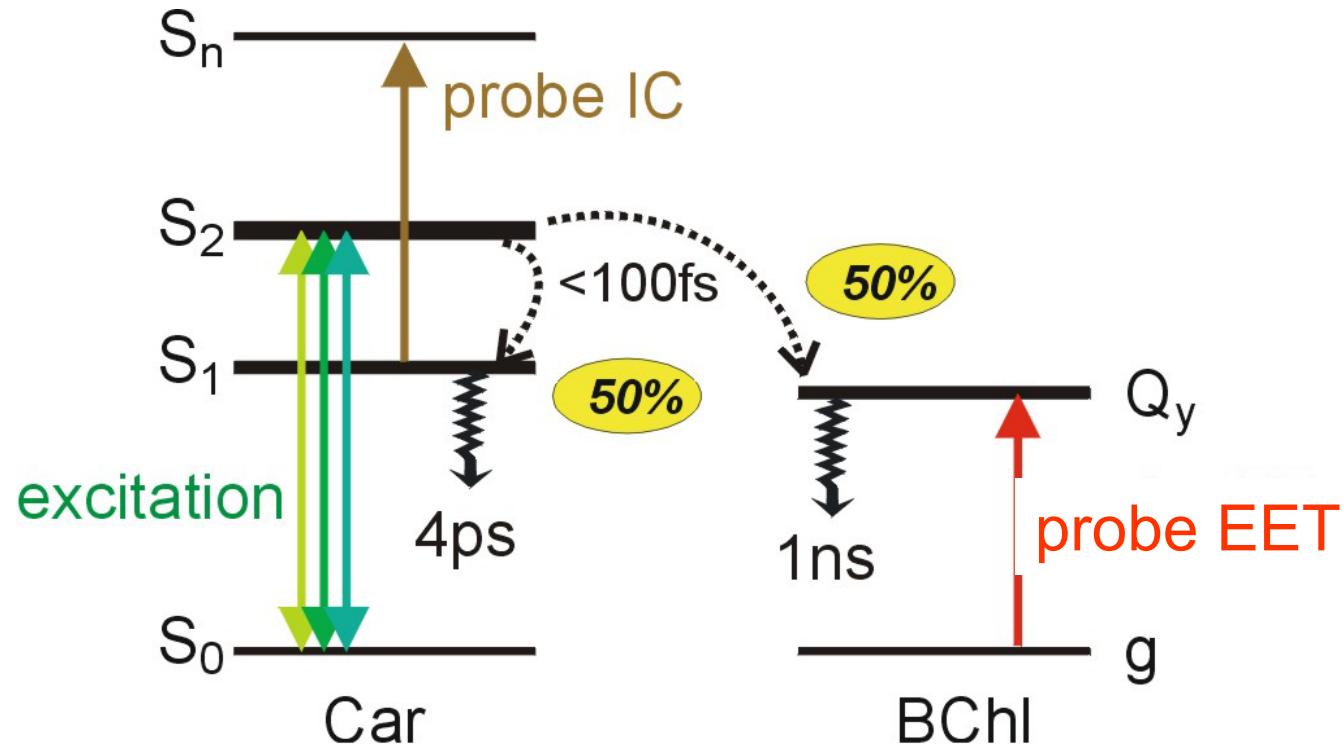


LH2 of *Rps. Acidophila* - Standard model



Polivka & Sundström, Chem. Rev. (2004)

Competing deactivation IC-EET



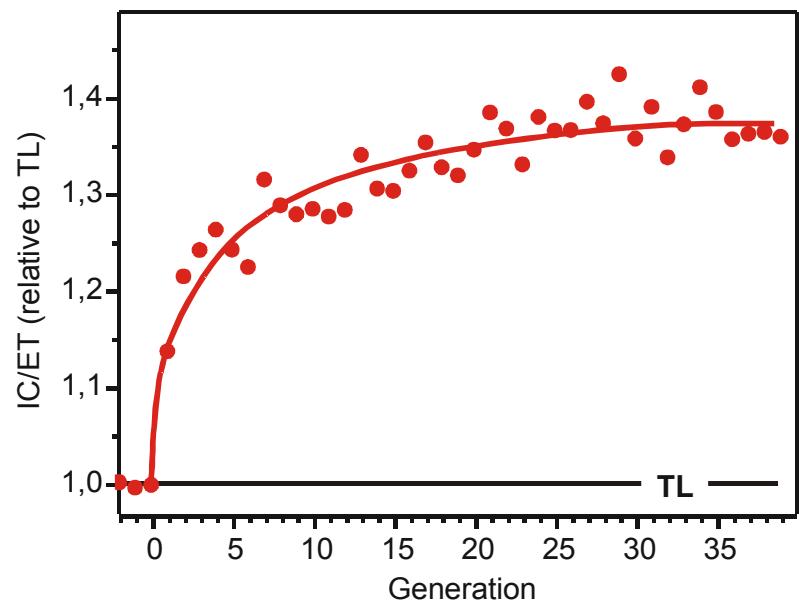
- Significant loss channel IC
- Negligible cross talk IC-EET
- Energy funnel precludes back transfer



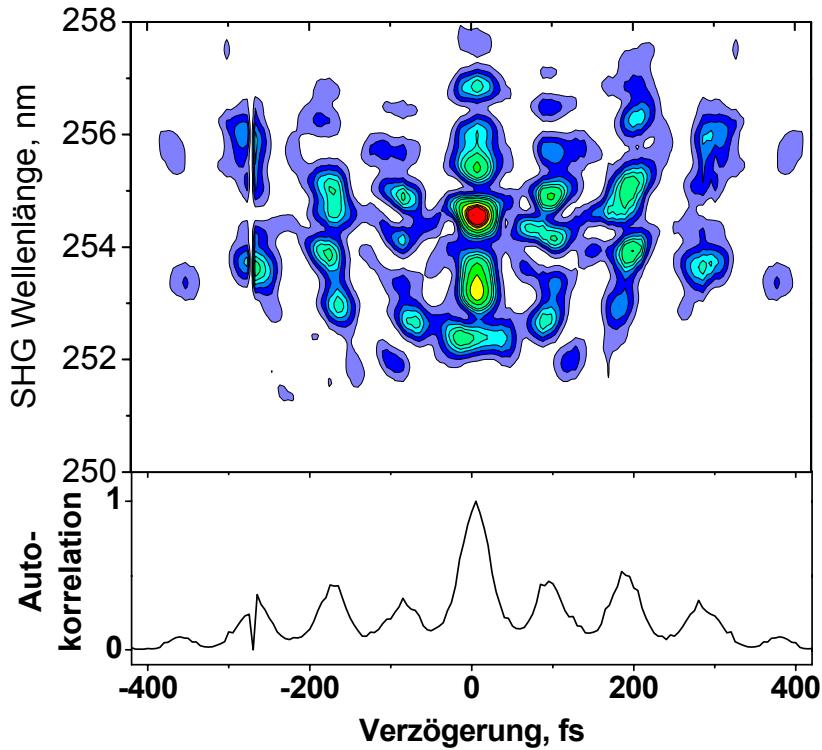


64-parameter optimisation of IC/EET

Convergence curve



Optimal pulse FROG trace



Nature **417** (2002) 533

ChemPhysChem **6** (2005) 850

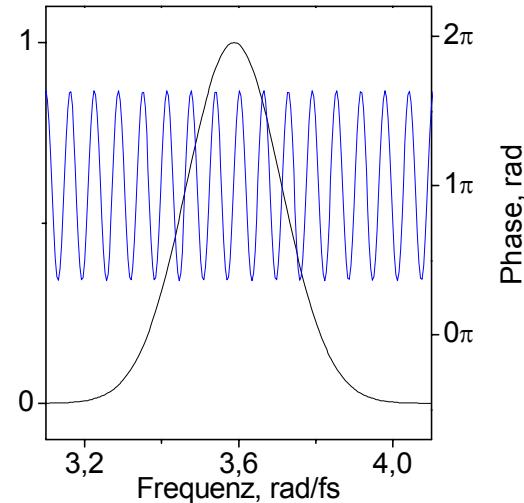


Parameterized multipulses

Sinusoidal SPECTRAL phase:

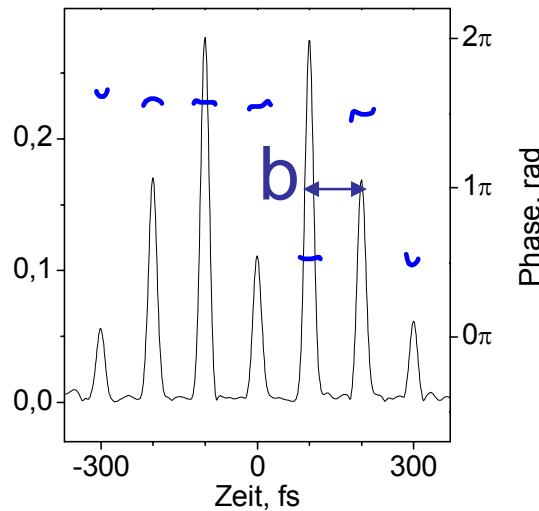
$$\phi(\omega) = \textcolor{red}{a} \cdot \sin(\textcolor{blue}{b} \cdot \omega + \textcolor{green}{c})$$

- a: modulation depth
- b: multipulse spacing
- c: phase offset



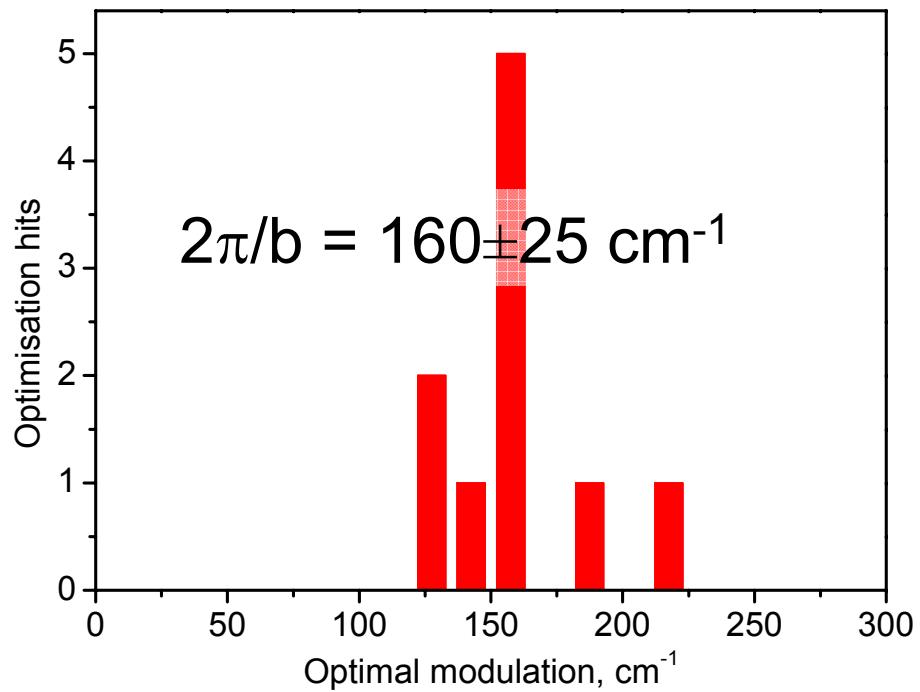
Result in TIME DOMAIN: multipulses

- a: sidepulse intensity
- b: inter-pulse separation
- c: carrier phase pattern





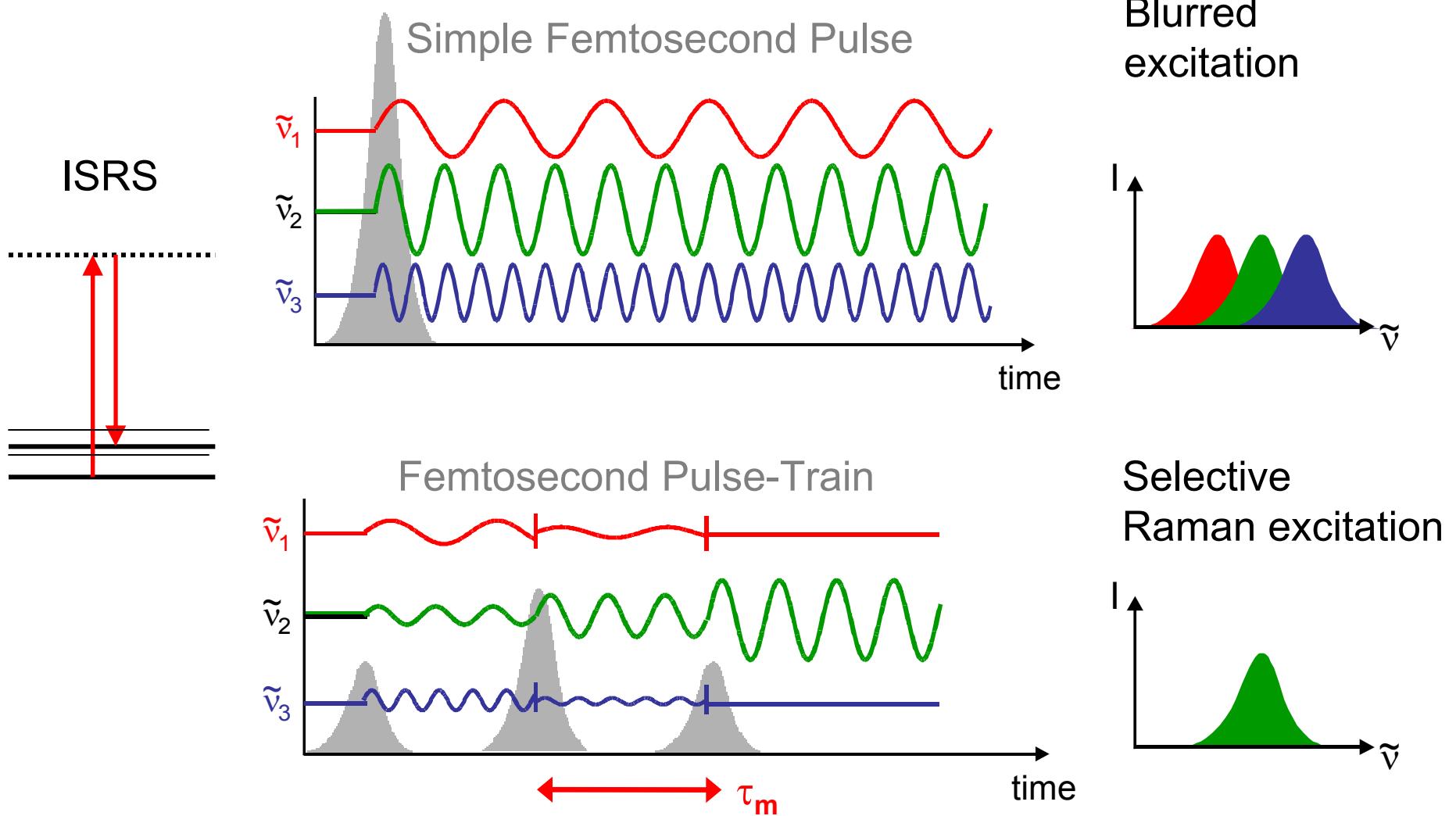
Histogram of successive IC/EET optimisations in LH2



Sub-pulse distance b → vibrational frequency



Multipulses: Impulsive stimulated Raman scattering



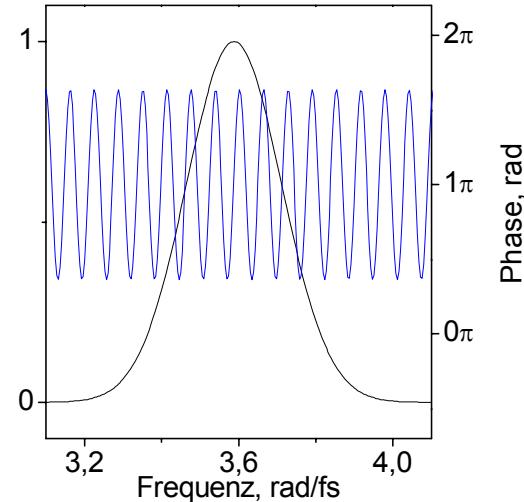


Parameterized multipulses

Sinusoidal SPECTRAL phase:

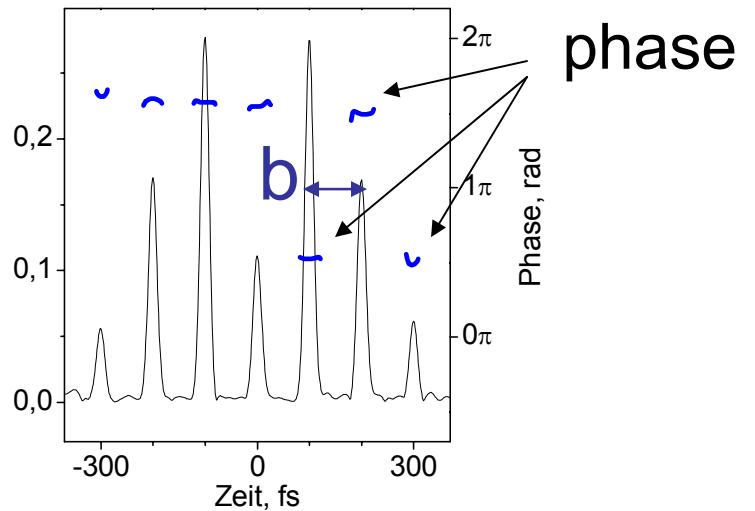
$$\phi(\omega) = \textcolor{red}{a} \cdot \sin(\textcolor{blue}{b} \cdot \omega + \textcolor{green}{c})$$

- a: modulation depth
- b: multipulse spacing
- c: phase offset



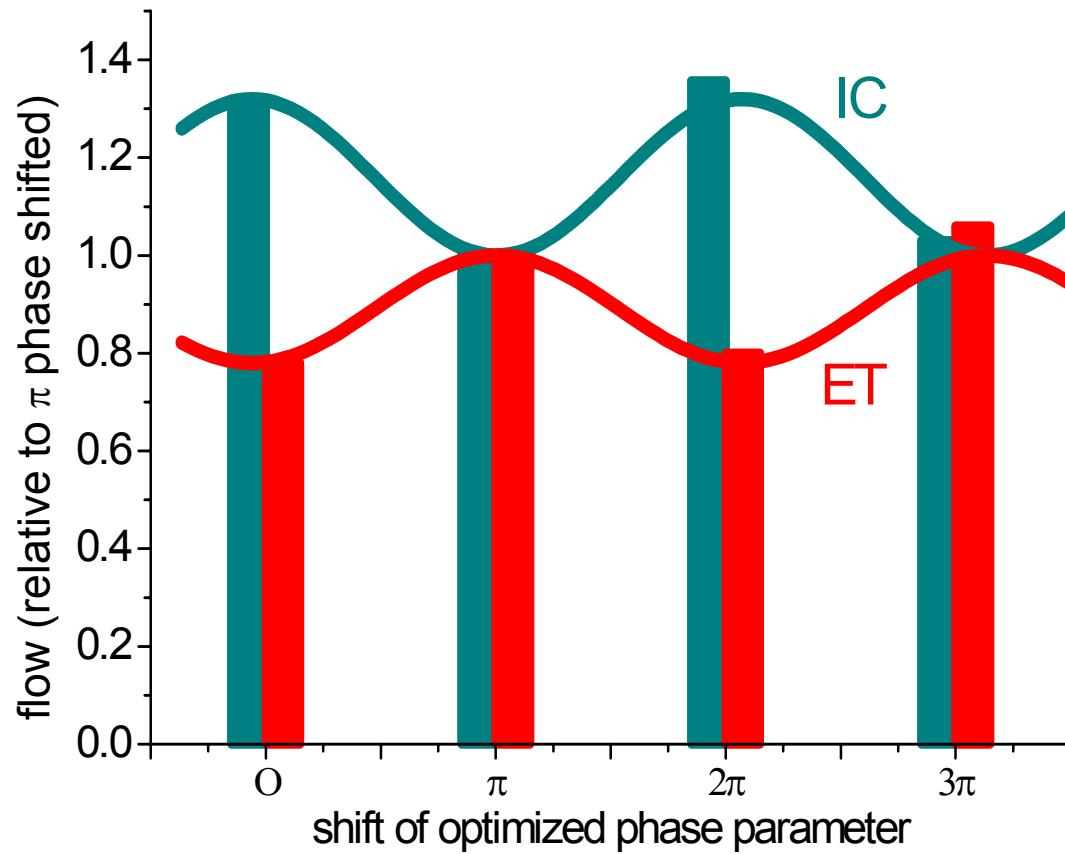
Result in TIME DOMAIN: multipulses

- a: sidepulse intensity
- b: inter-pulse separation
- c: carrier phase pattern





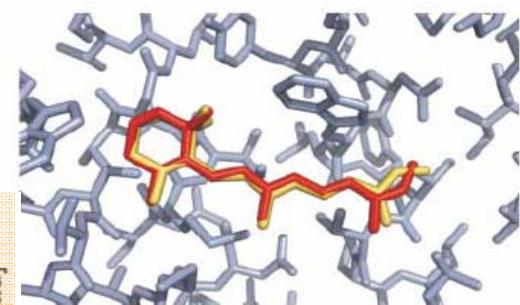
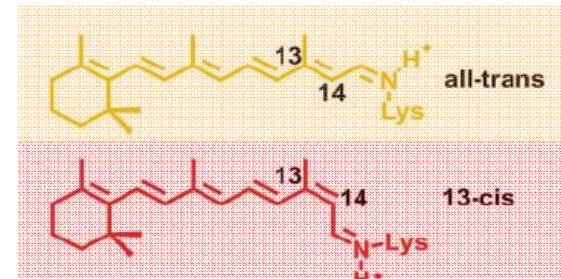
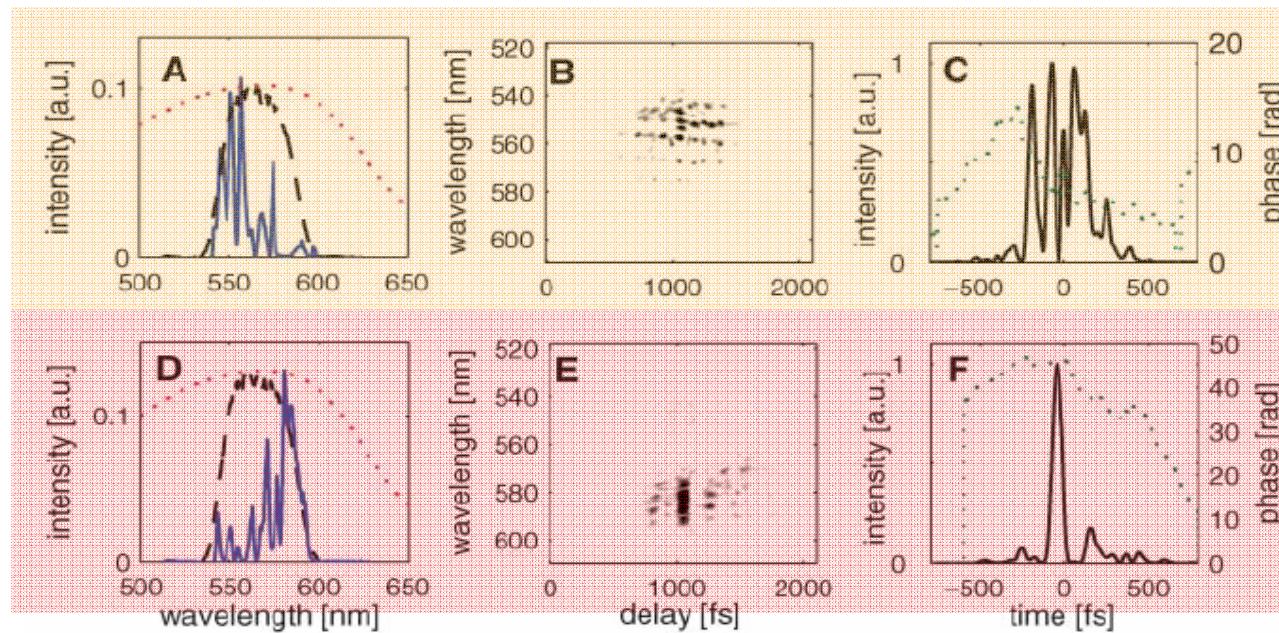
Sub pulse phase phase dependence



Coherent Control of Retinal Isomerization in Bacteriorhodopsin

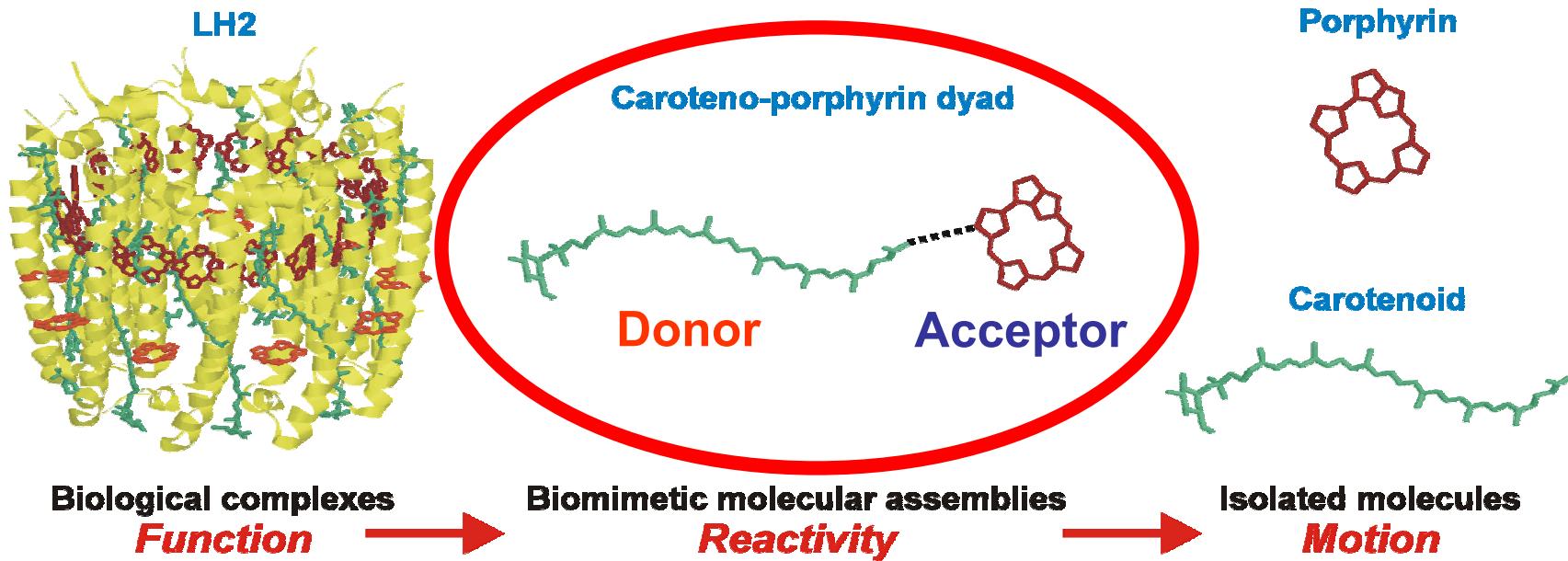
Valentyn I. Prokhorenko,¹ Andrea M. Nagy,¹ Stephen A. Waschuk,² Leonid S. Brown,² Robert R. Birge,³ R. J. Dwayne Miller^{1*}

www.sciencemag.org SCIENCE VOL 313 1 SEPTEMBER 2006





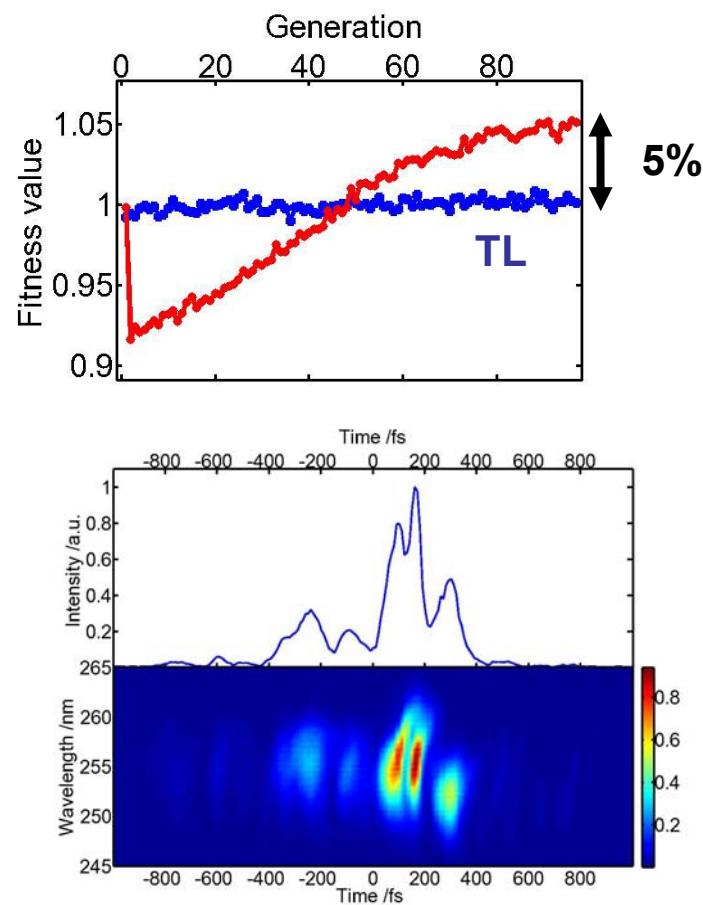
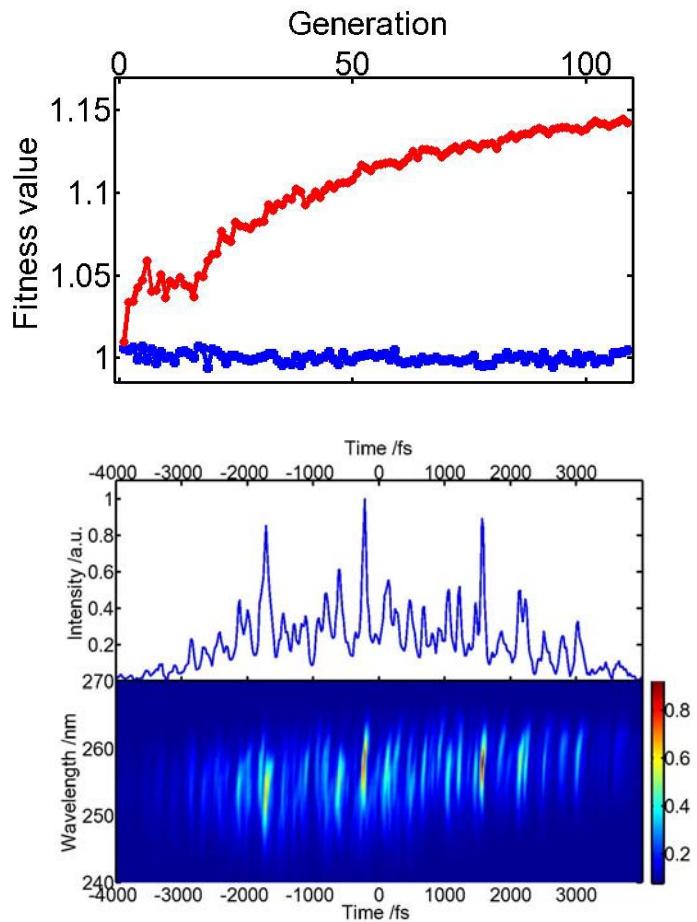
Reducing the complexity





Control of Dyad complex

IC/ET ET/IC

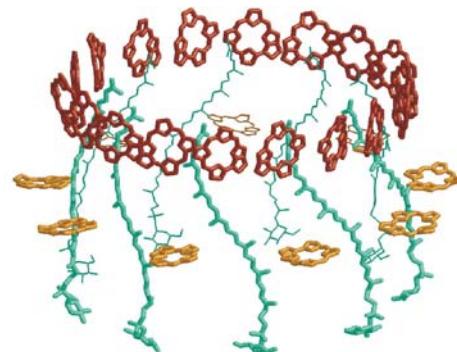


Collaboration with AMOLF/Twente

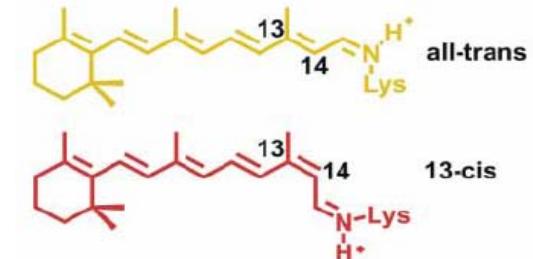
PNAS 105 (2008) 7641

Successful control of large biomolecules

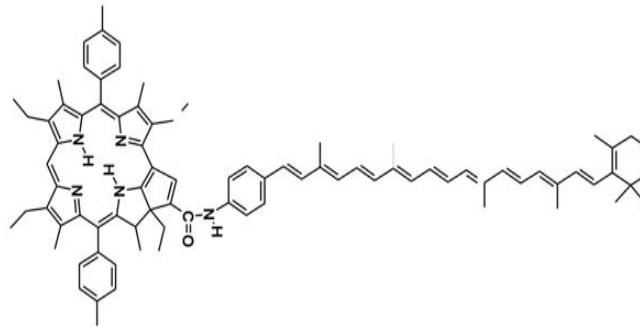
LH2 complex



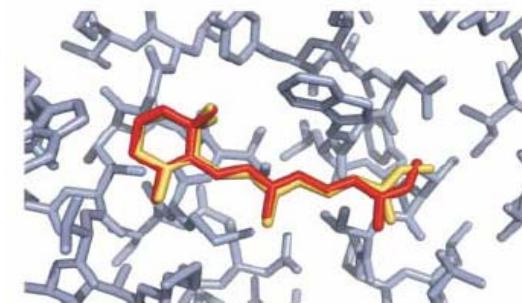
Bacteriorhodopsin



Dyad complex



Others...

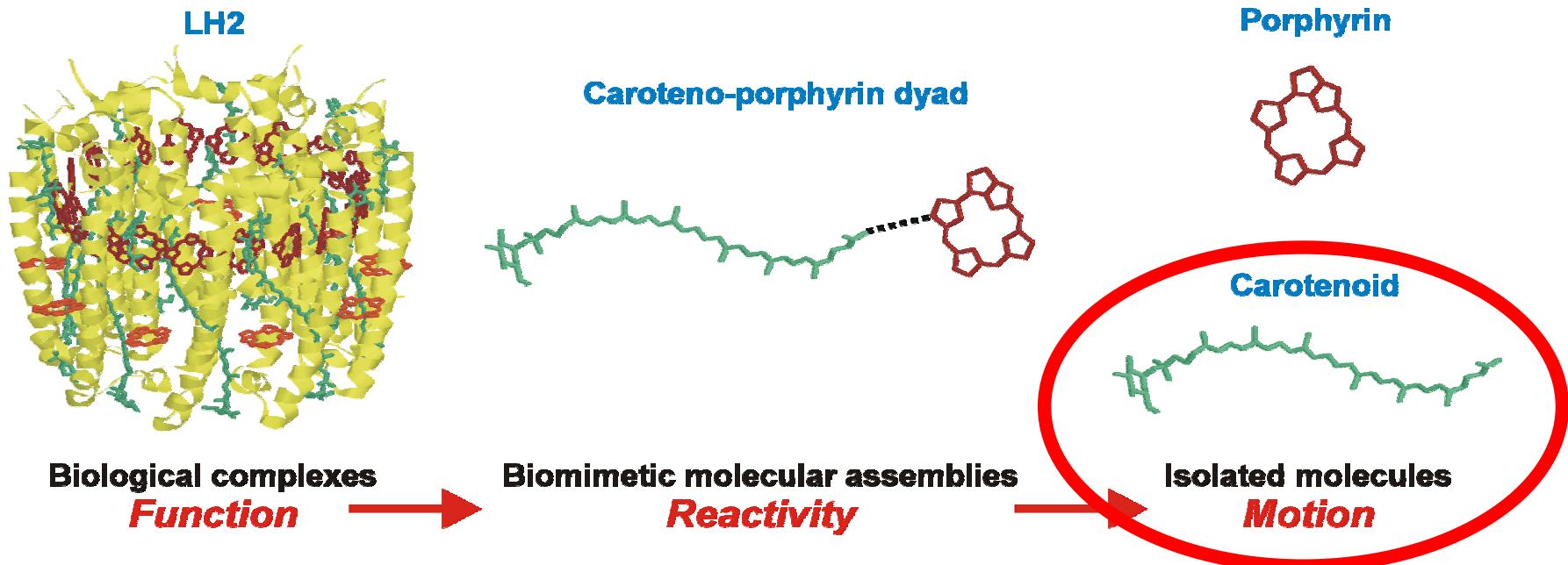


Common features:

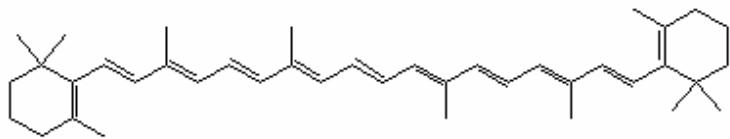
- chromophore consists of a linear chain of conjugated double bonds
- optimized pulse exhibits multipulse structure



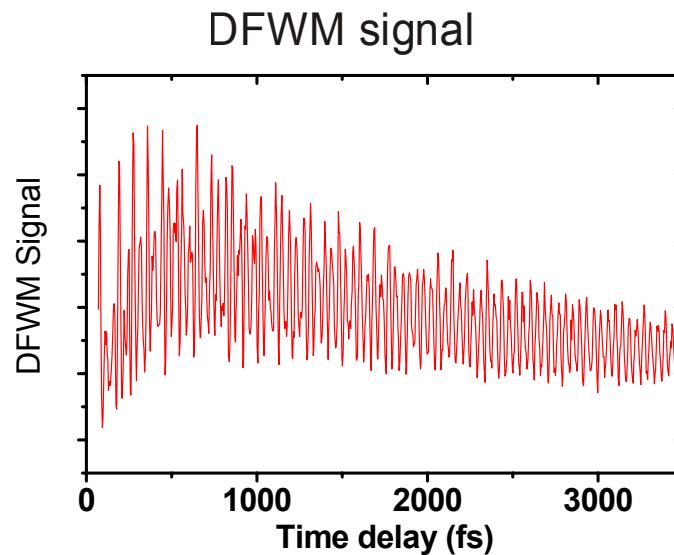
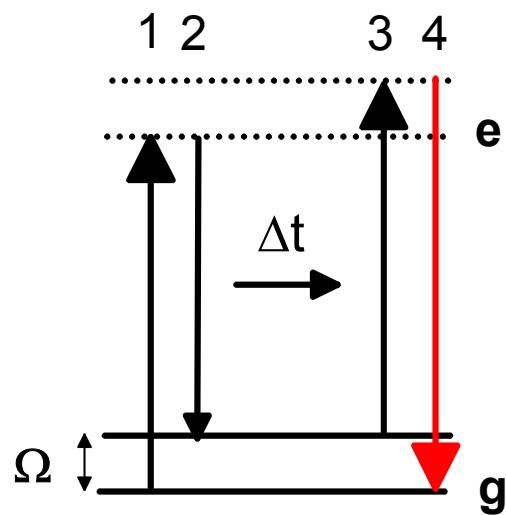
Further reduction of complexity



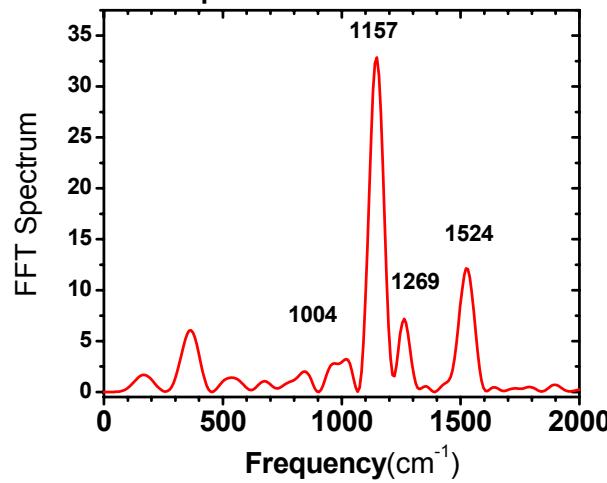
Control of vibrational modes in β -Carotene: ground-state



DFWM scheme

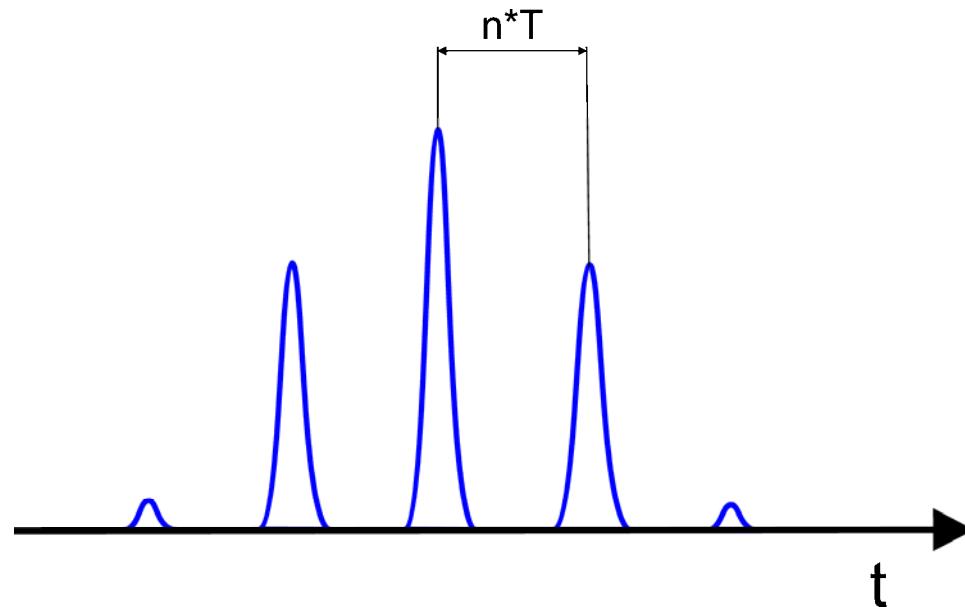


FFT spectrum in FL case



Pulse Spacings

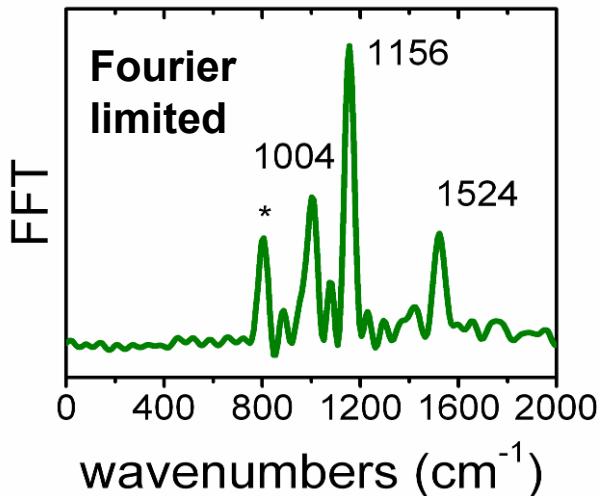
Energy (cm ⁻¹)	T(fs)	2 T(fs)	3 T(fs)	4 T(fs)	5 T(fs)
1524	21.9	43.8	65.7	87.6	109.5
1157	28.8	57.6	86.4	115.2	144
1004	33.2	66.4	99.6		



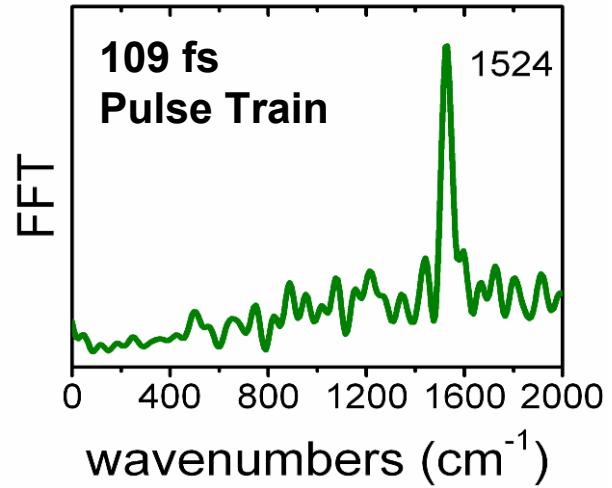
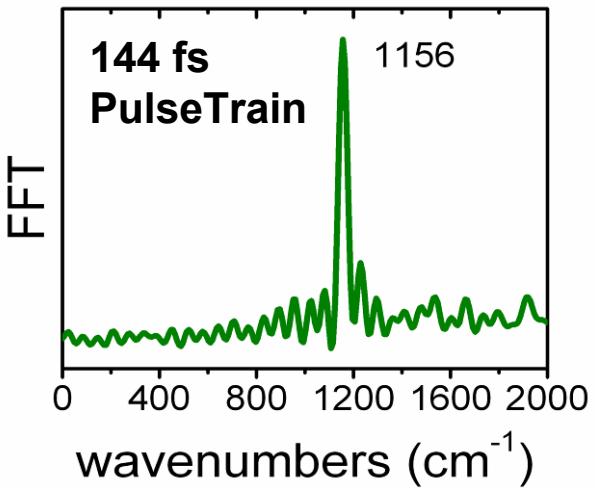
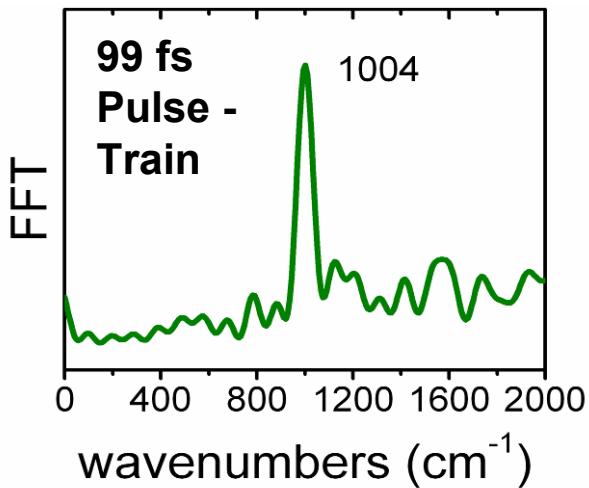


Control of ground state vibrations

Nonlinear Raman spectra

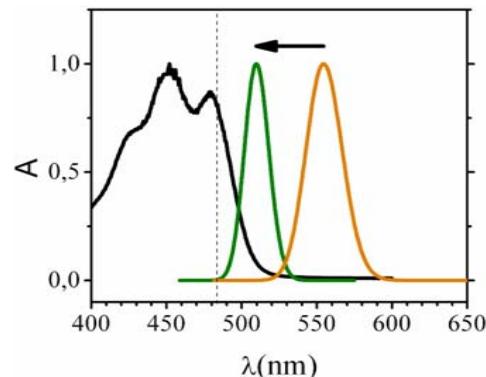


→ Modes can be selectively excited



Resonant Enhancement of Raman modes in β -Carotene

Resonant-nonresonant excitation

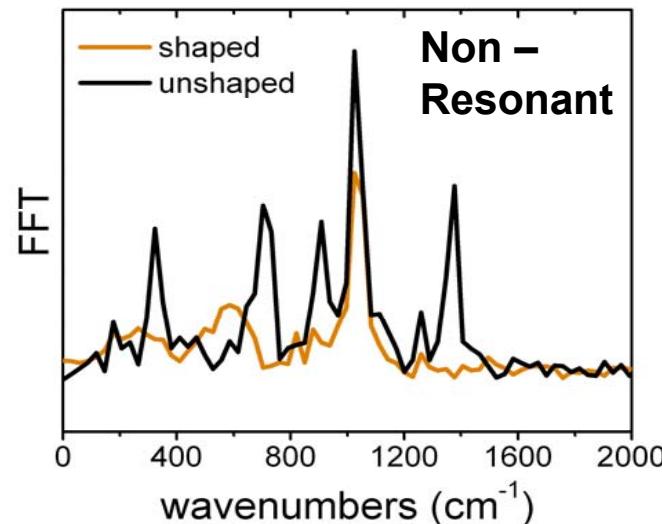
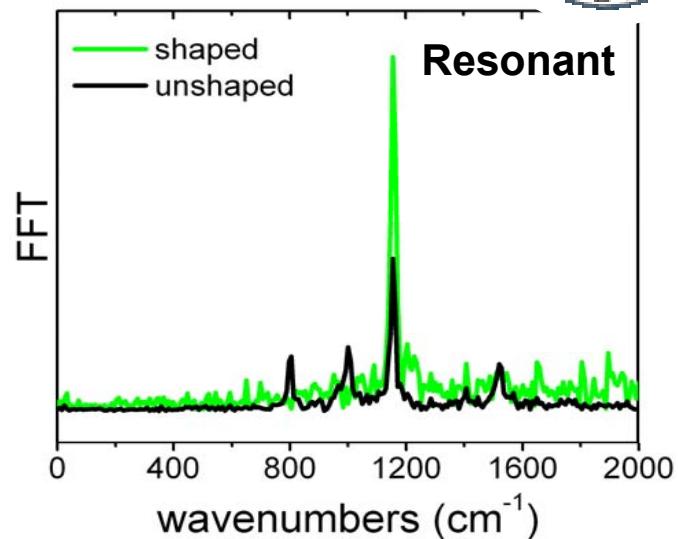


- Real enhancement of resonantly excited Raman modes by coherent control

$$E_{\text{multipulse}} = E_{\text{TL}}$$

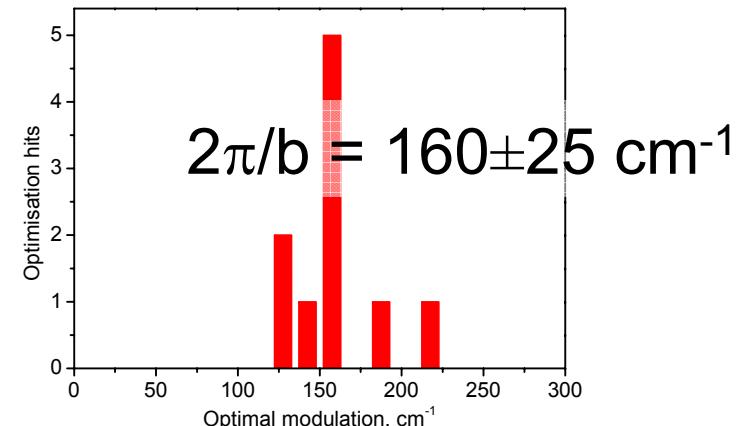
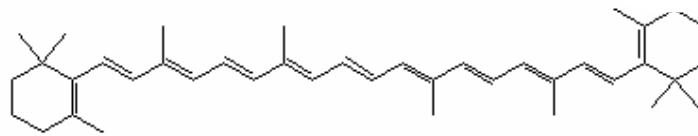
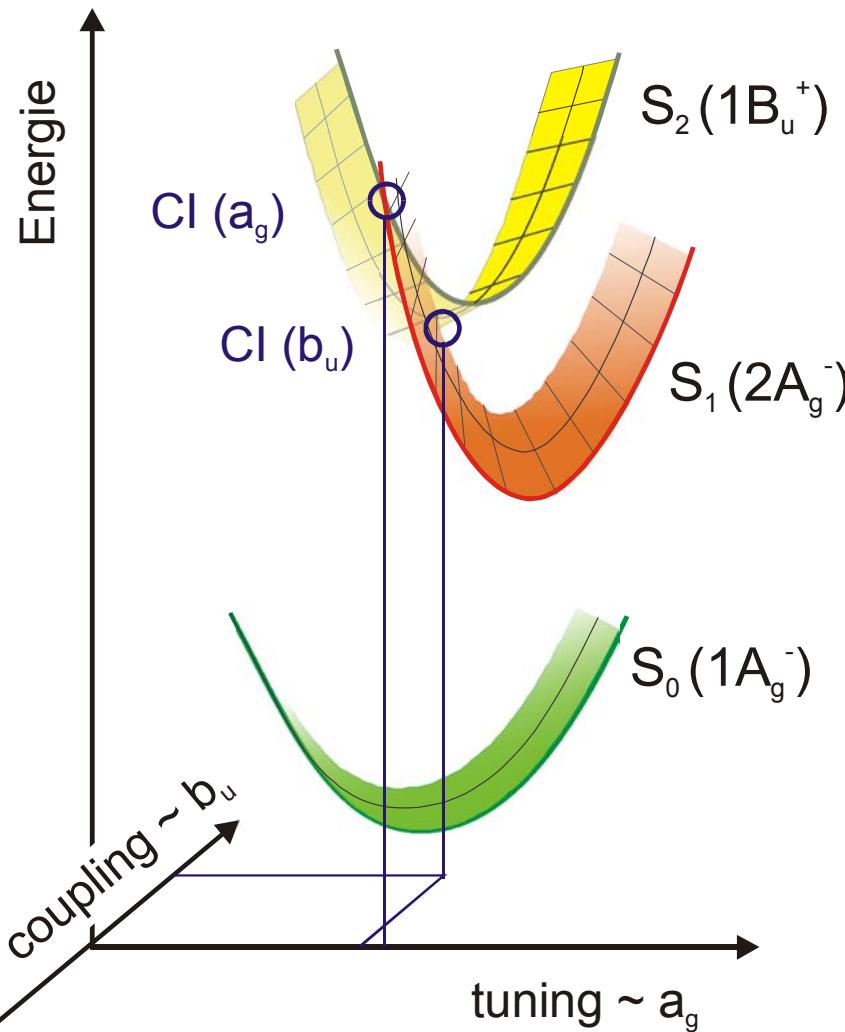
- Enhancement factor of up to 5.7

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





Control of the β -carotene

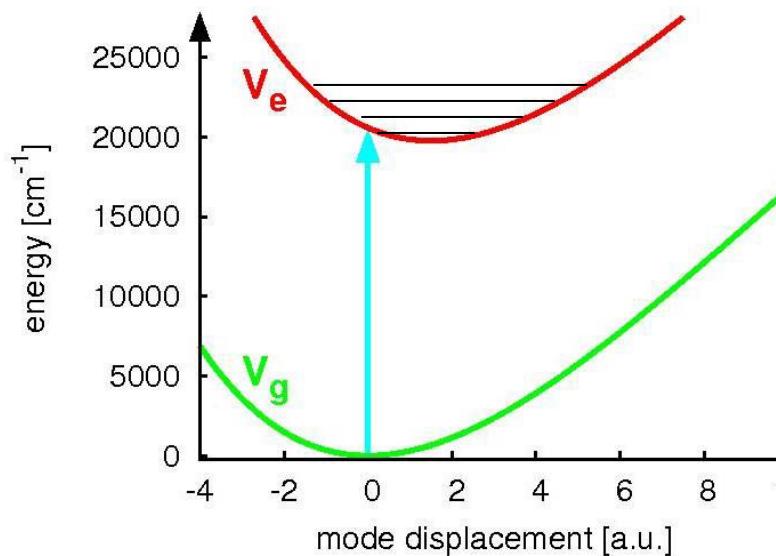


→ Optimized field drives bending modes which are the coupling modes for internal conversion

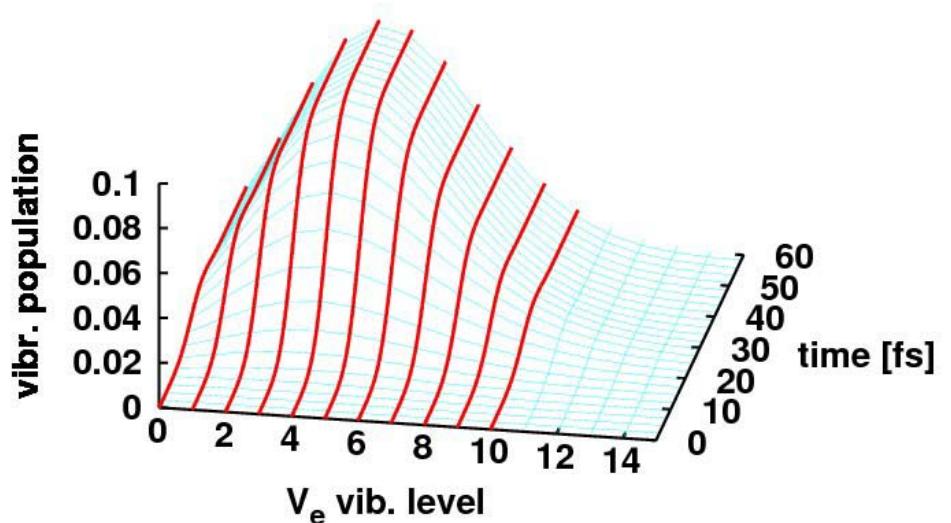
Excitation with multipulses – a theoretical approach

J. Voll and R. de Vivie-Riedle, LMU Munich

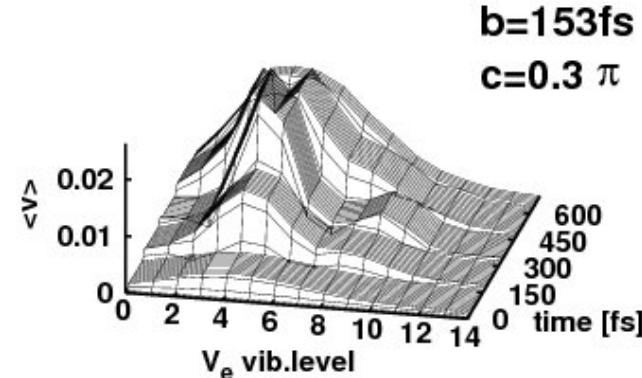
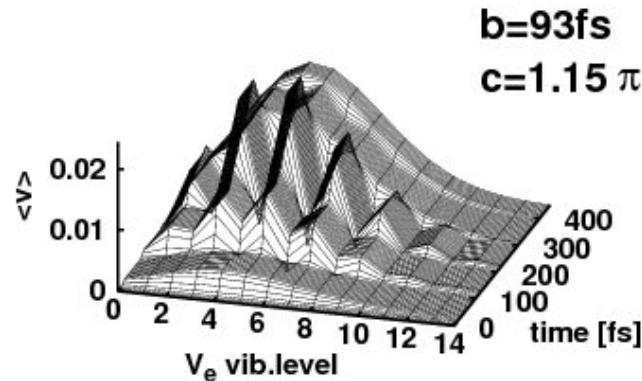
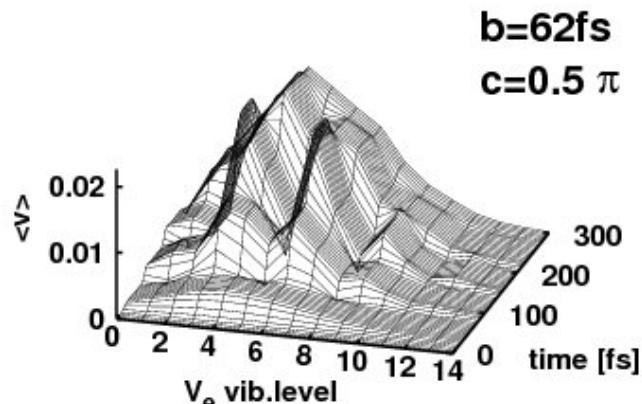
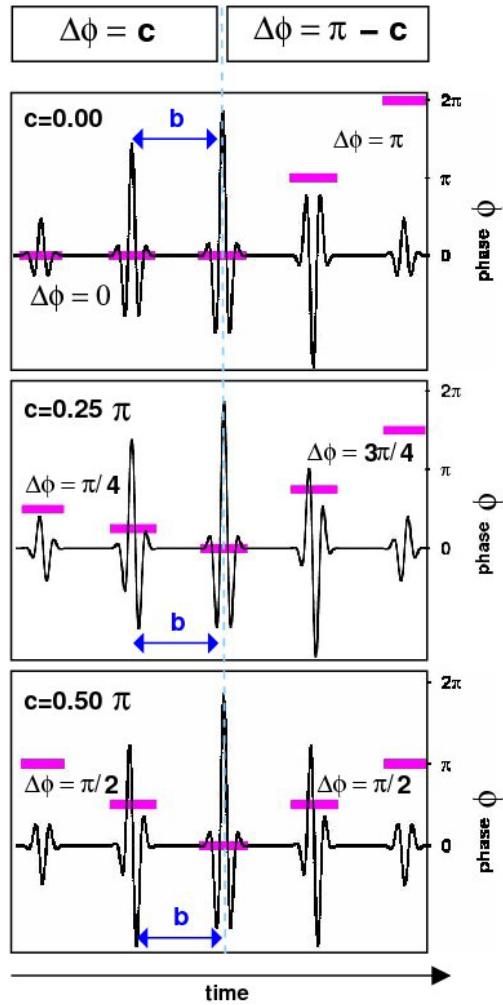
S₀-S₂ Transition



Vibrational excitation in S₂ with Fourier-limited-pulses

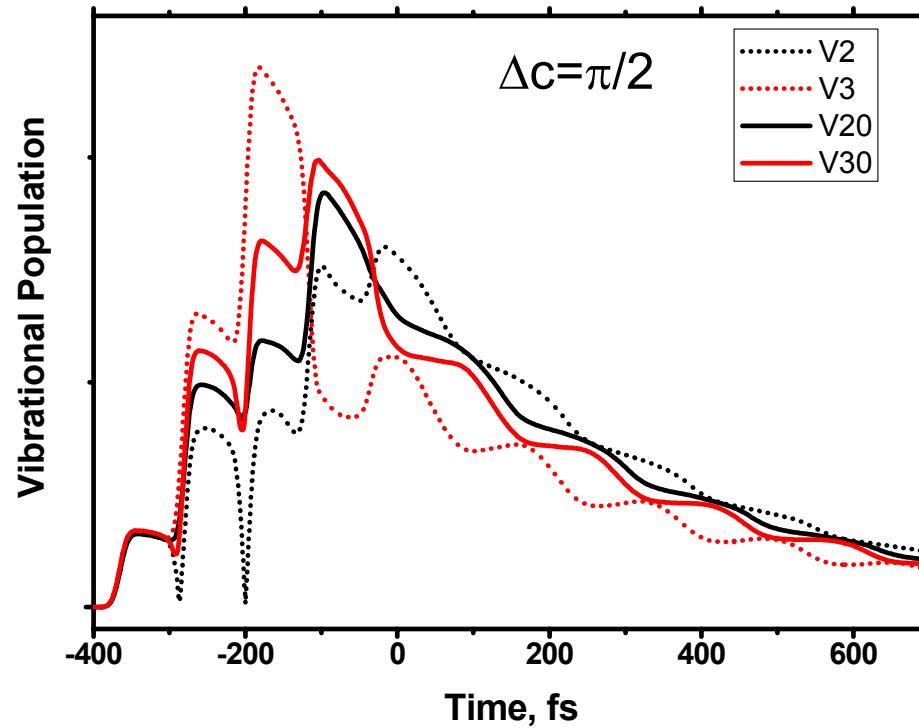


Excitation with multipulses: b- and c-dependance



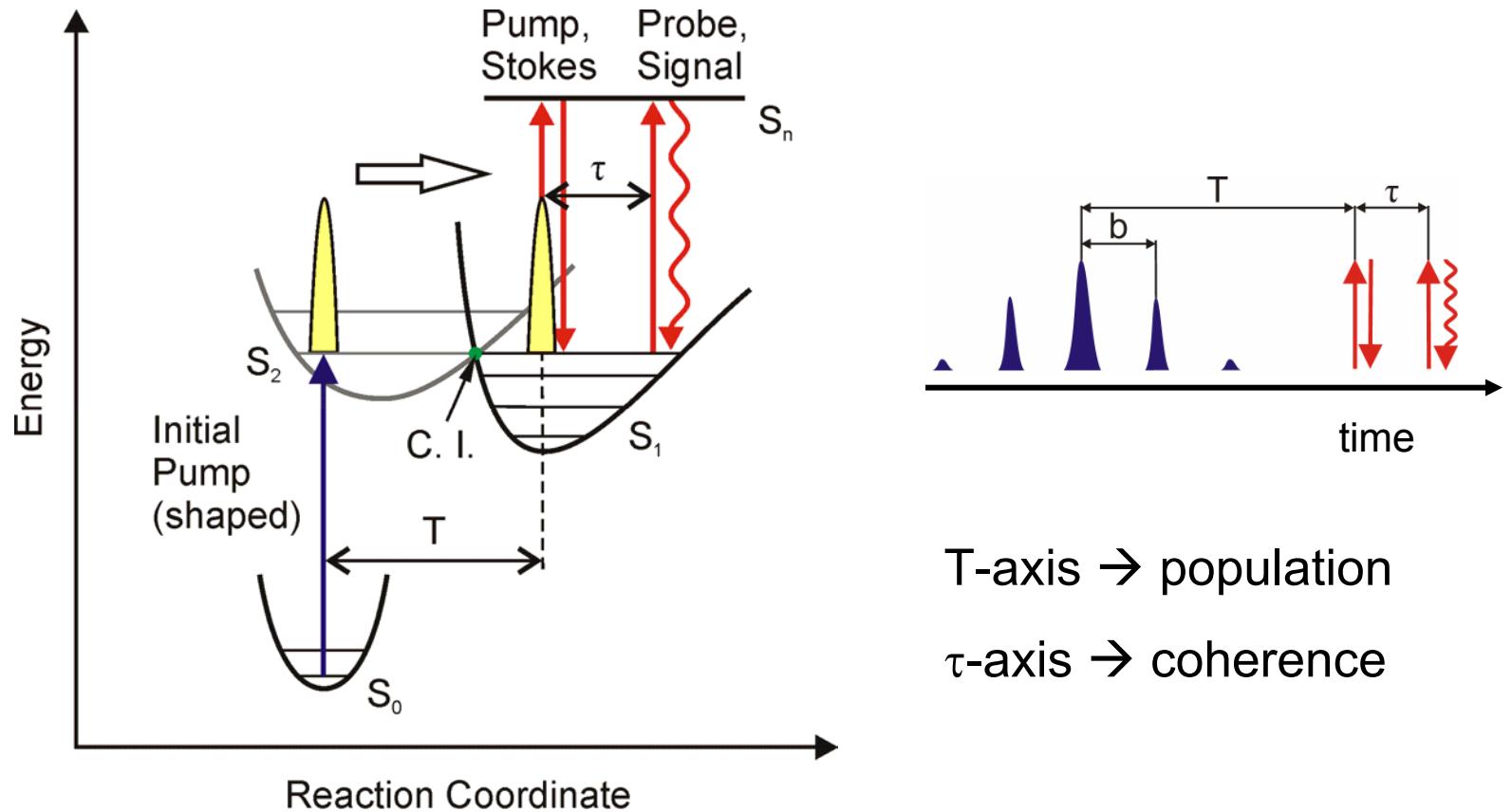


c-dependance of vibrational distribution including coupling



- Transient population in the vibrational levels depends on the pulse relative phase.
- Transient optimization of odd against even (and vice-versa) levels.

Probing dynamics in the excited state



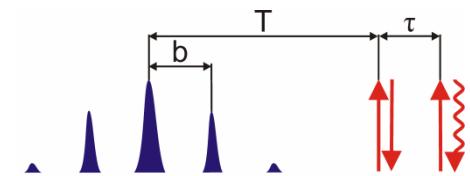
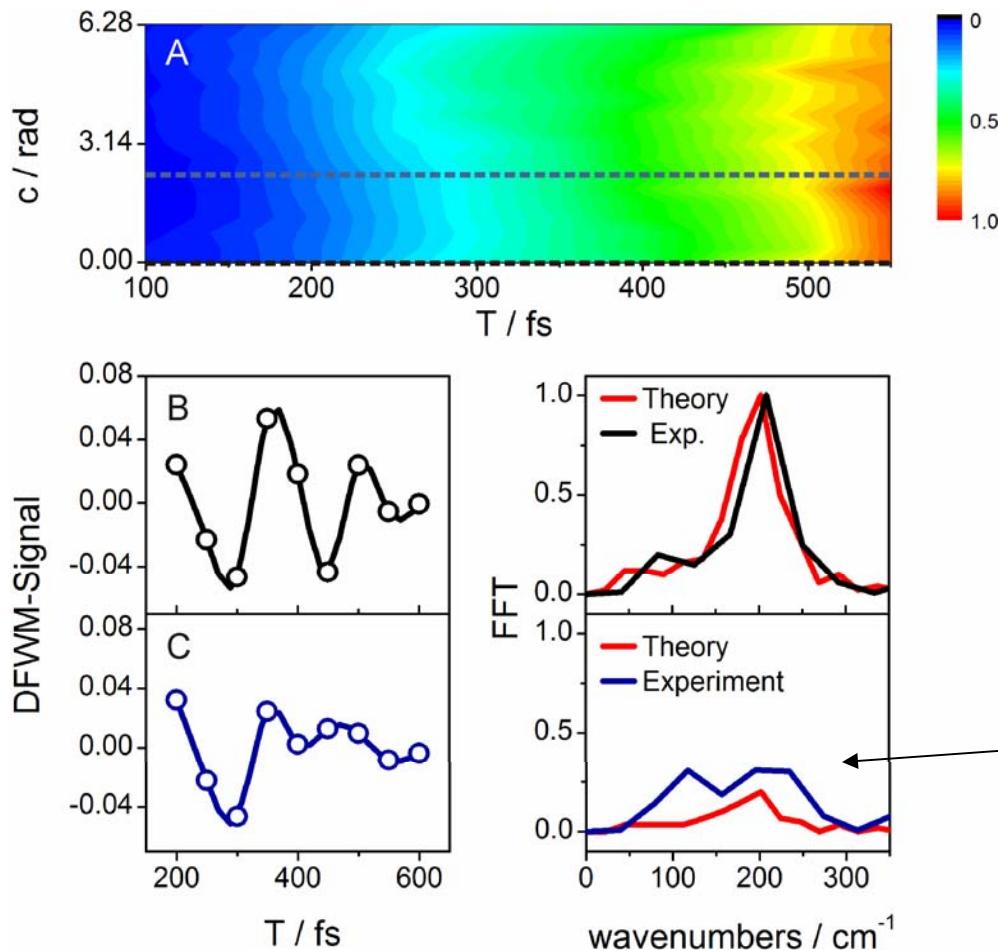
Hornung, T., Skenderovic, H., Motzkus, M. *CPL* **2005**, 402, 283.

Oberle, J.; Jonusauskas, G.; Abraham, E.; Rulliere, C. *CPL* **1995**, 241, 281.

Hauer, J., Buckup, T., Motzkus, M. *JPCA* **2007**, 111, 10517

Motzkus et al., *JCP* **1996**, 100, 5620

Population dynamics in S1



- Signal variation along c is in good agreement with theory
- $b = 55 \text{ fs} \rightarrow T/3$ of coupling mode



Electronic Coherence and Multipulses

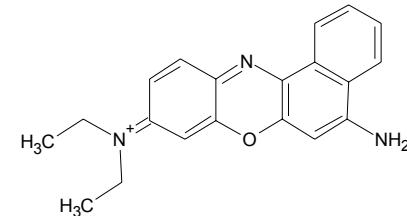
- Decoherence effects:

interaction with the solvent

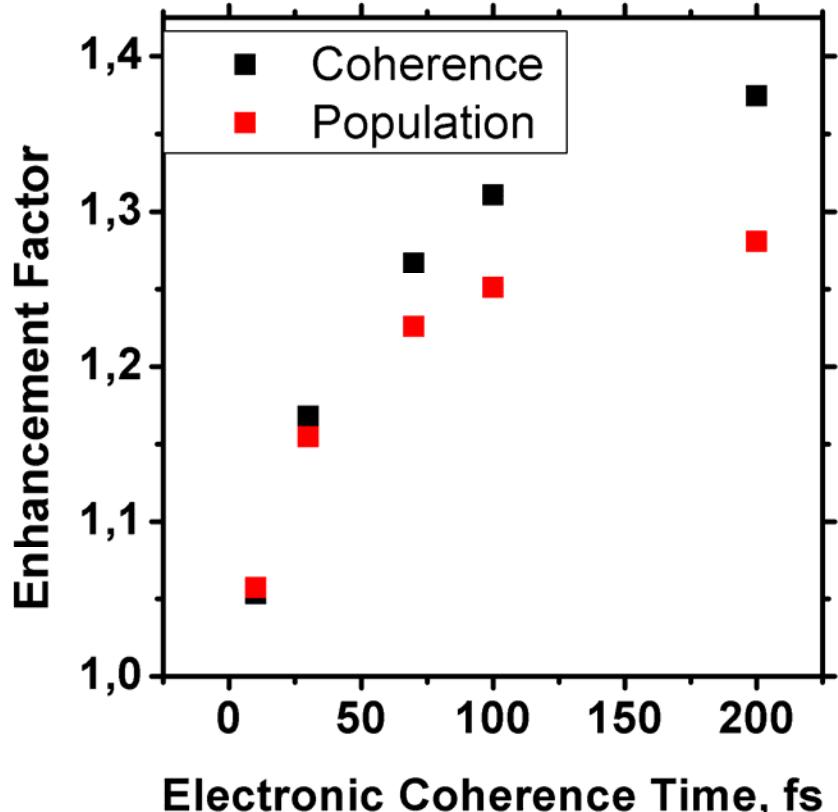
~~incoherence properties of the laser~~

- „....(some references) have generally concluded that some degree of control is indeed possible in solution, depending upon the extent of the coupling between system and solvent, and to which one can manipulate the incident pulses. No quantitative rules have yet emerged on the extent to which control is, in fact, possible.

(Shapiro and Brumer, „Principles of the Quantum Control of Molecular Process“, John Wiley & Sons, p.104)

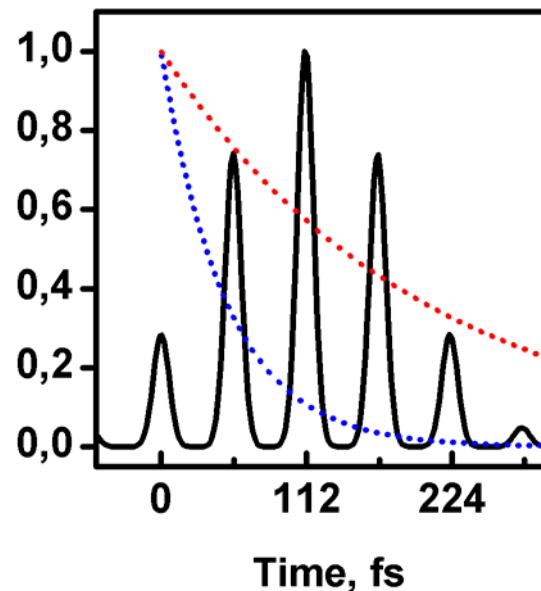


At the Edge of the Enhancement



Explanation:

Sub-pulse separation (b) = 56 fs

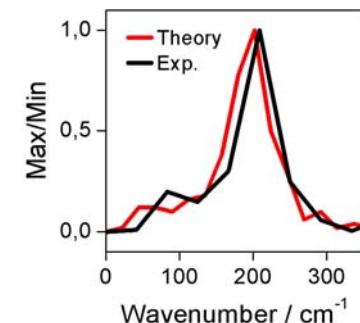
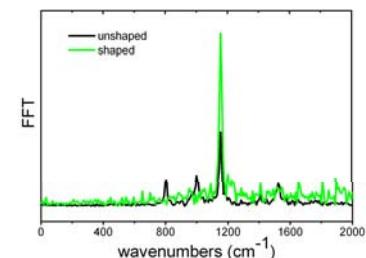
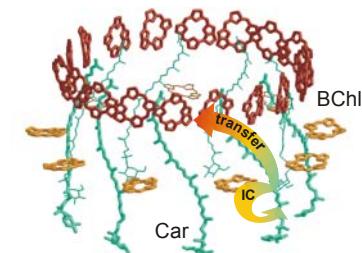


→ If $b \sim T_2$, then enhanc. ~ 50%.



Summary

- Successful coherent control in several large biological systems !
- Control pulses show multipulse structure
- Electronic resonance necessary for real enhancement of coherence and population
- Phase dependence of multipulses influences energy flow in carotenoids
→ shaping of wavepackets in bright state determines passage through a conical intersection





Acknowledgements

Experiment

- Jürgen Hauer
- Tiago Buckup



- Jens Möhring
- Bernhard von Vacano

Theory

- Judith Voll
- Regina de Vivie-Riedle



- Philipps Universität Marburg
- Max Planck Society
- BMBF actIOL

- Ludwig-Maximilians-Universität München
- The Munich-Centre for Advanced Photonics (MAP)
- SFB 749 – Dynamics and Intermediates of molecular transformations