Ultrafast Molecular Spectroscopy

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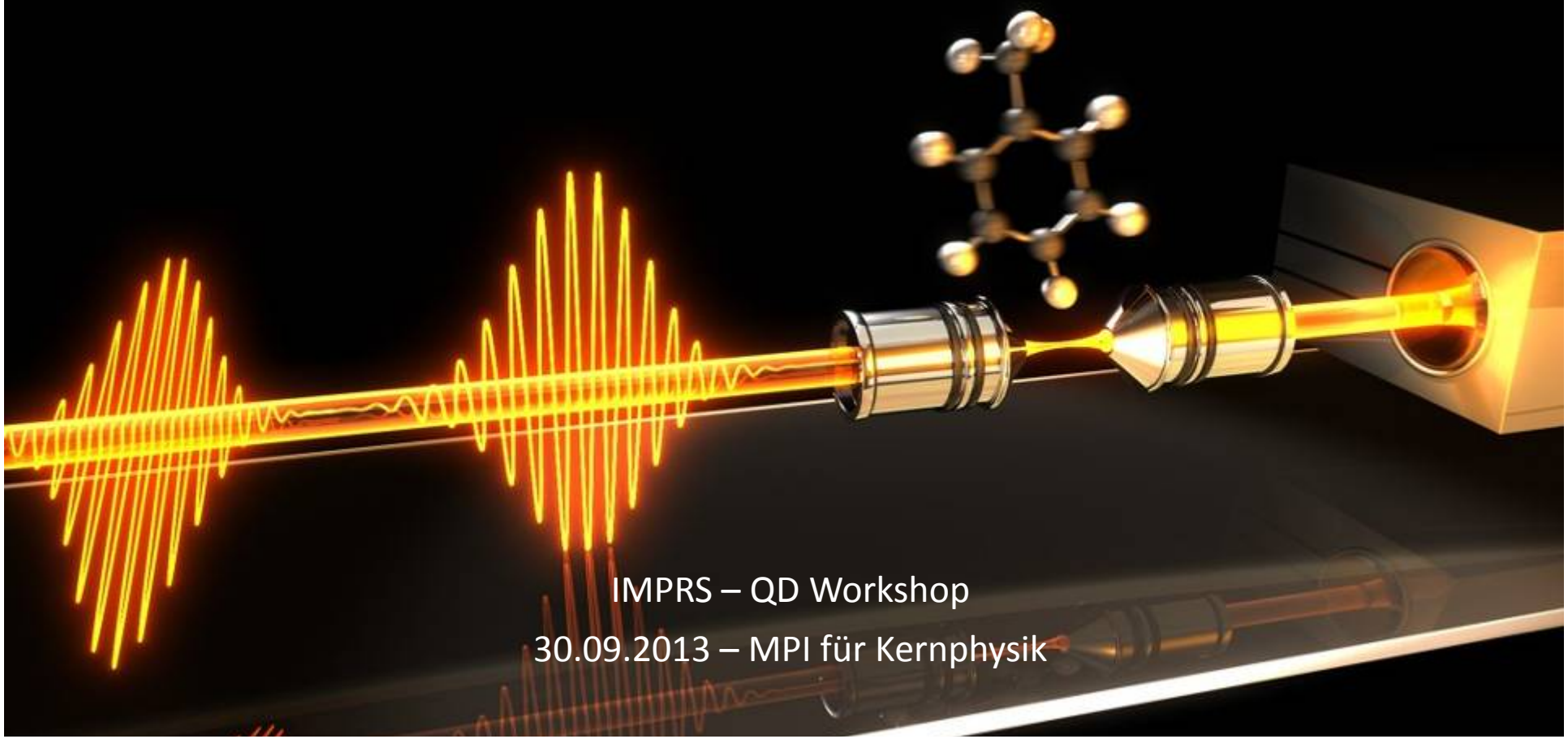


IMPRS – QD Workshop

30.09.2013 – MPI für Kernphysik

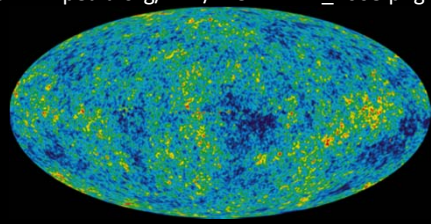
time scales in science

shortest man-made
flash/pulse of light
80 attoseconds

http://www.gettyimages.com/detail/89516567/Photographers-Choice

1 second

http://en.wikipedia.org/wiki/File:WMAP_2008.png



age of the universe
14 billion years

as fs ps ns µs ms

10^{-18} 10^{-12} 10^{-6} 1 10^{6} 10^{12} 10^{18}

electronic timescale

human/biological timescale

molecular timescale

geological/astronomical timescale

cameras

laser pulses

Adapted from T. Pfeifer, MPI-K

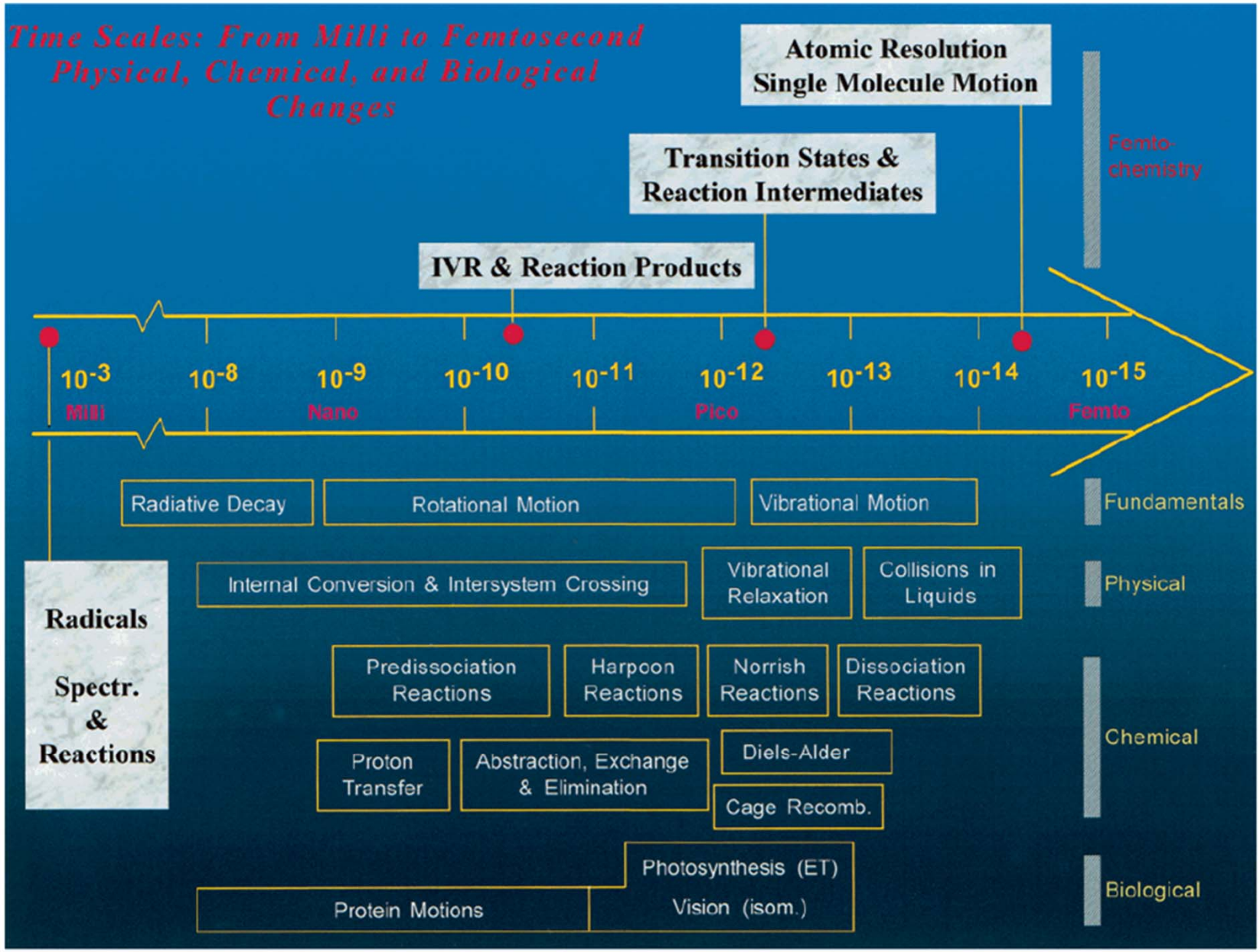


Figure 2. Time scales. The relevance to physical, chemical, and biological changes. The fundamental limit of the vibrational motion defines the regime for femtochemistry. Examples are given for each change and scale.

Ultrafast Molecular Spectroscopy

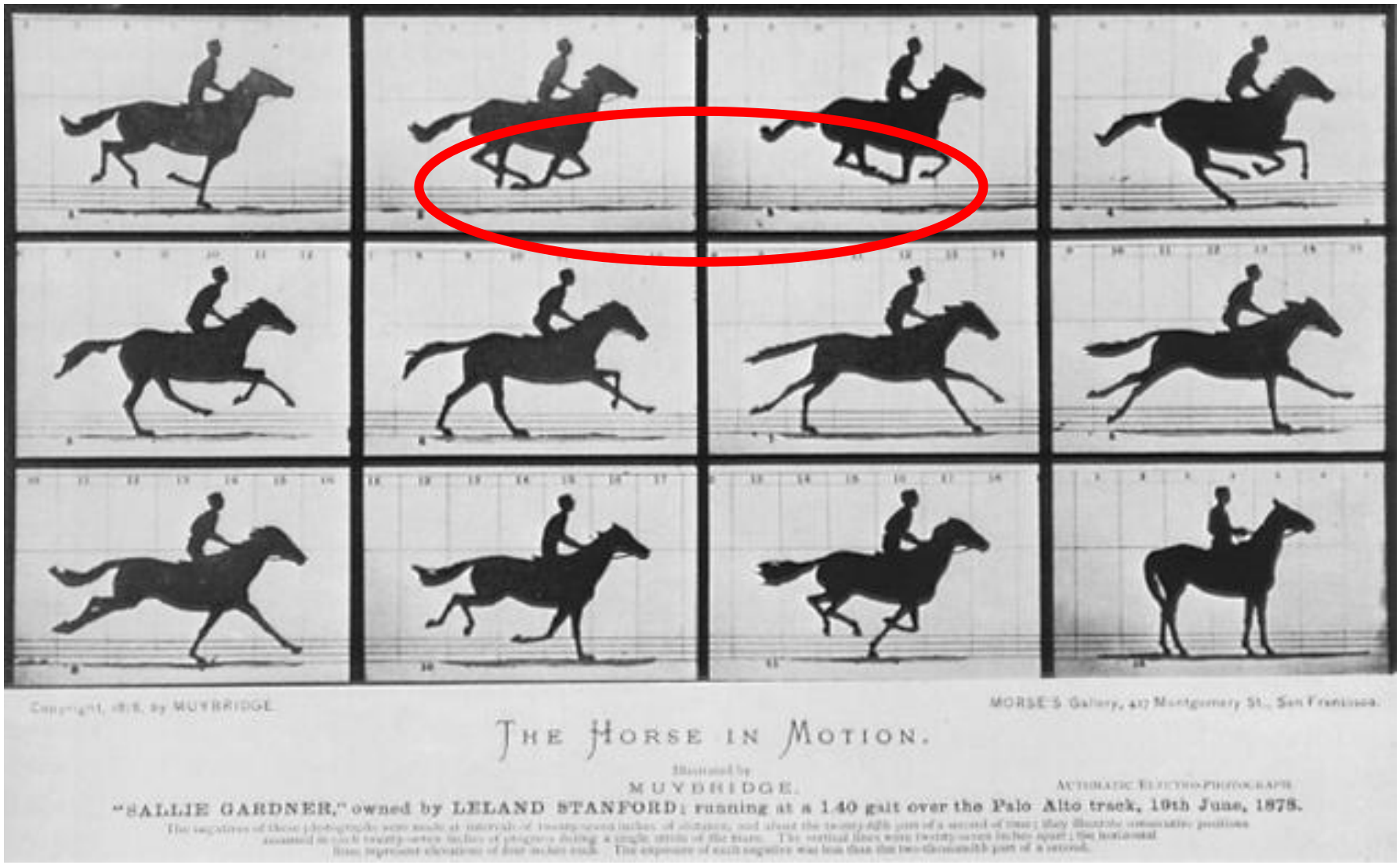
Outline

I. Intro - Ultrafast Molecular Spectroscopy
- Time scale of chemical processes, Overview of methods
- Pump-probe principle
- seminal experiments, applications
- wavepackets

II. Optical Methods of Pump-Probe-Spectroscopy
- Transient Absorption: Population dynamics
- Examples
- Problem of overlapping resonances

III. Multidimensional spectroscopy
- Case study: dynamics on Carotenoids
- Pump-dump-spectroscopy
- Pump-DFWM
- Quantum control spectroscopy

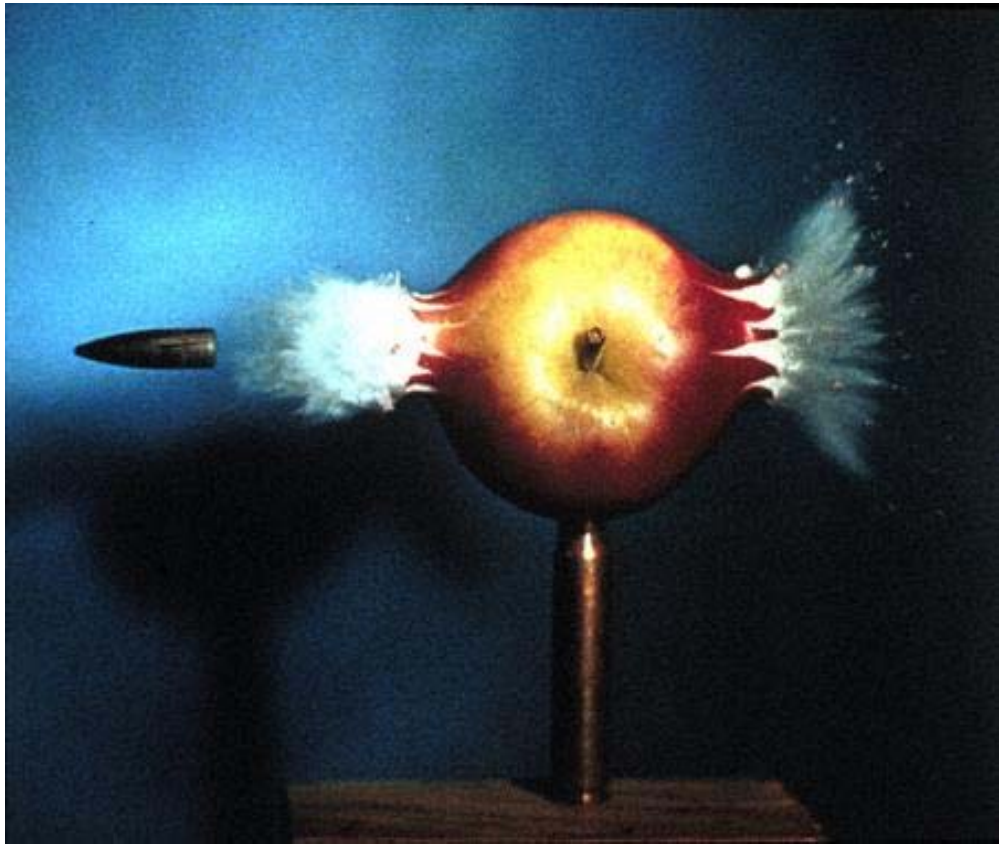
“not observable” fast processes: slow-motion movie



(*Eadweard Muybridge, “The Horse in Motion”, 1878*)

'Doc' Edgerton - Strobe Photography

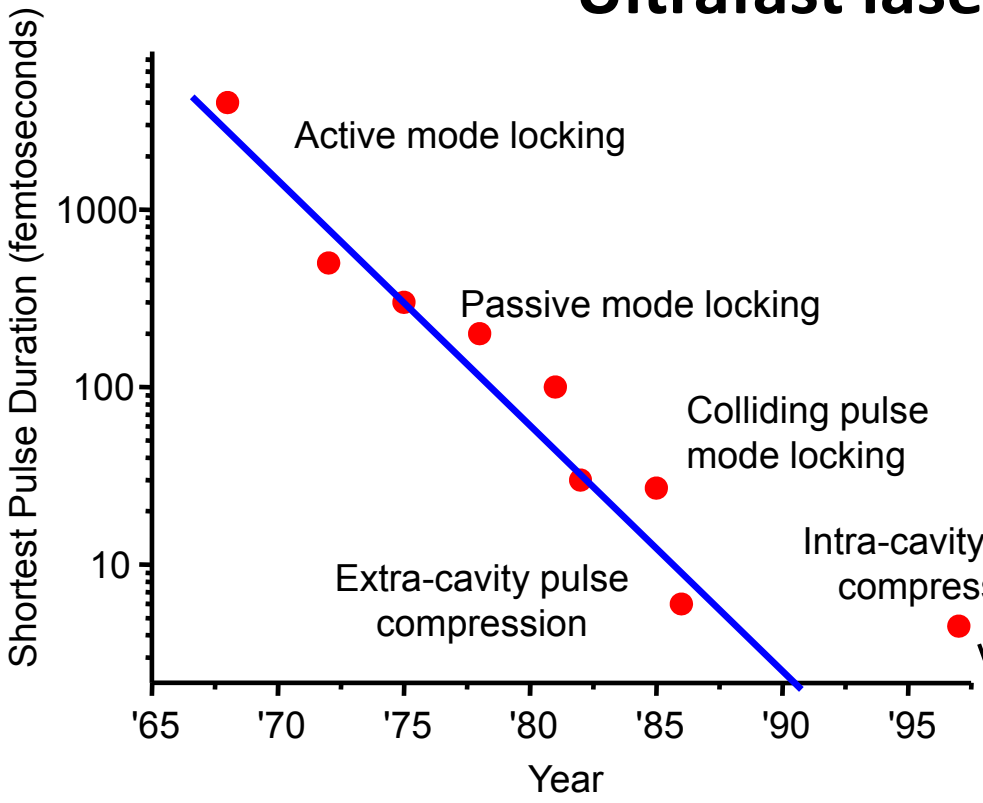
Harold Edgerton
MIT, 1942



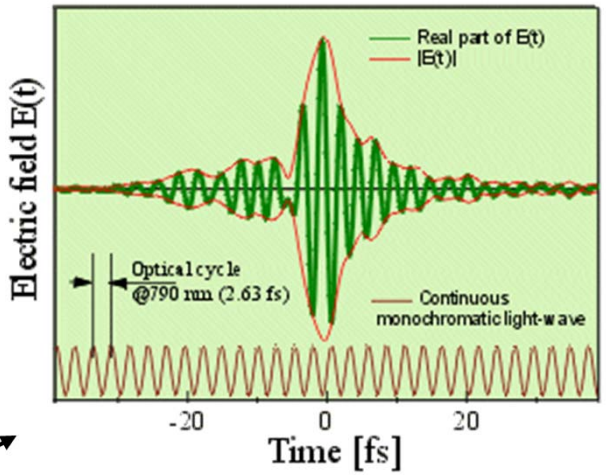
“How to Make Apple sauce at MIT”, 1964

→ Time Resolution: a few microseconds

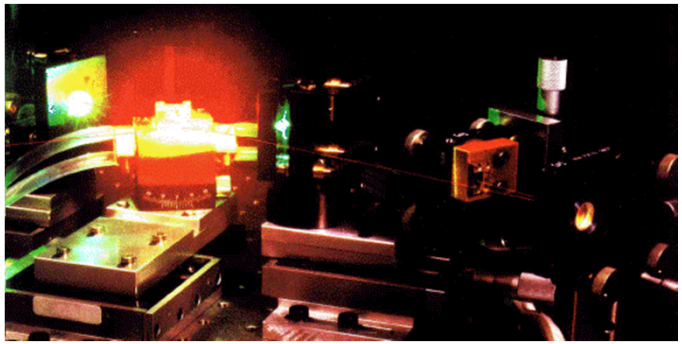
Ultrafast lasers



~4 fs pulse

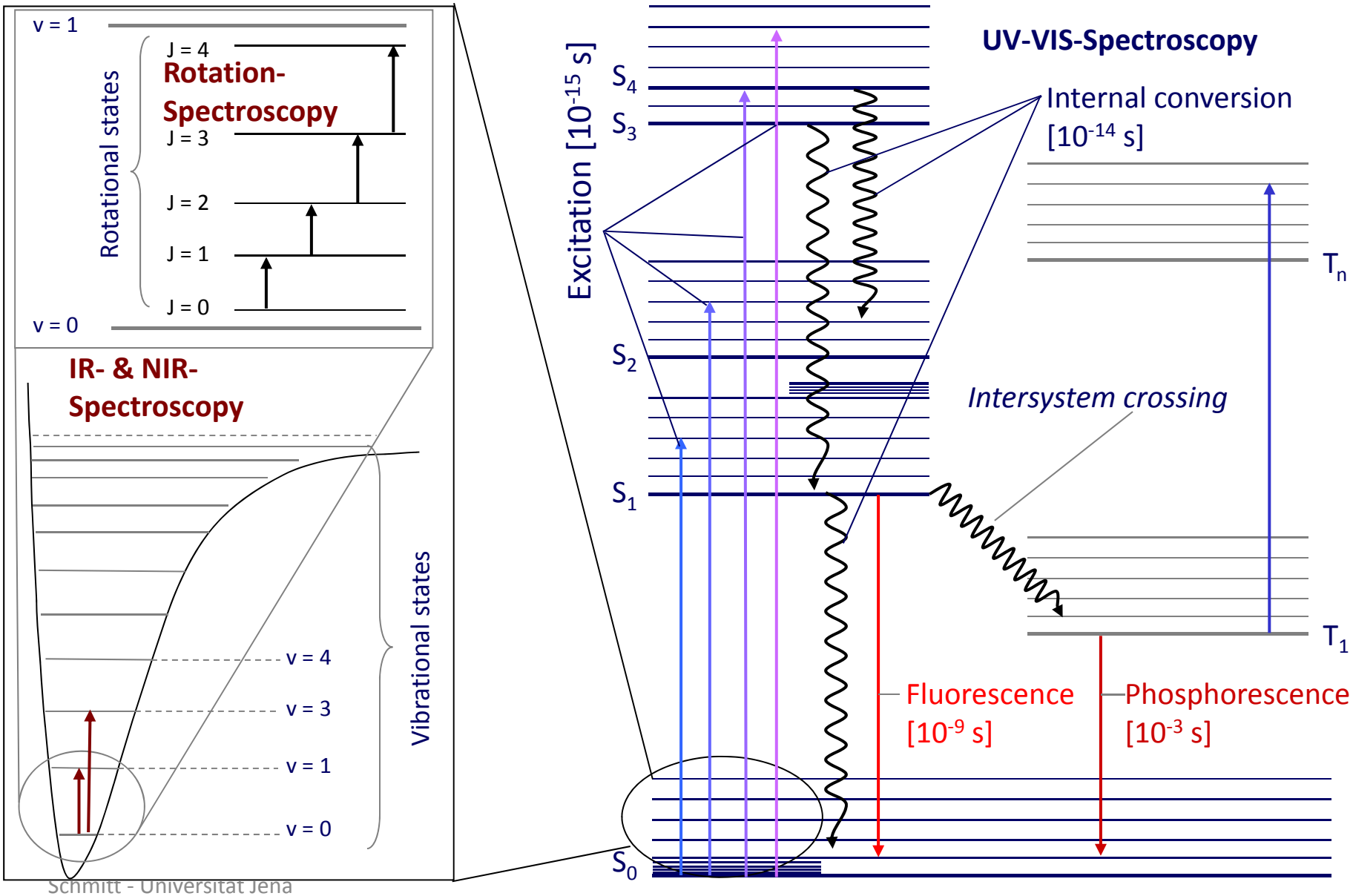


Baltuska et al. 2001



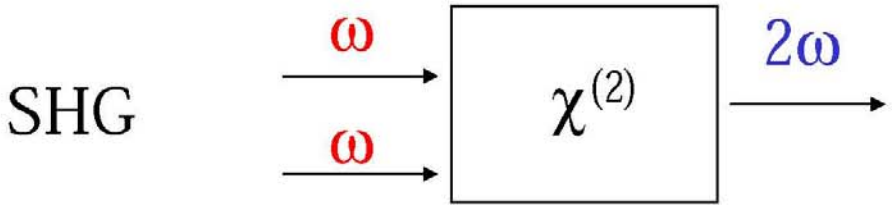
Ultrafast
Ti:sapphire laser

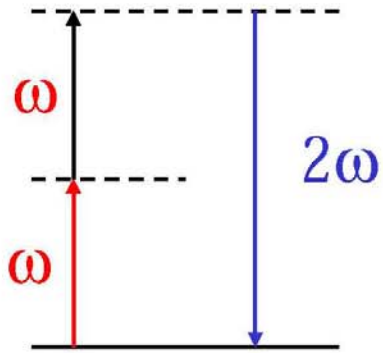
Transitions in a molecule



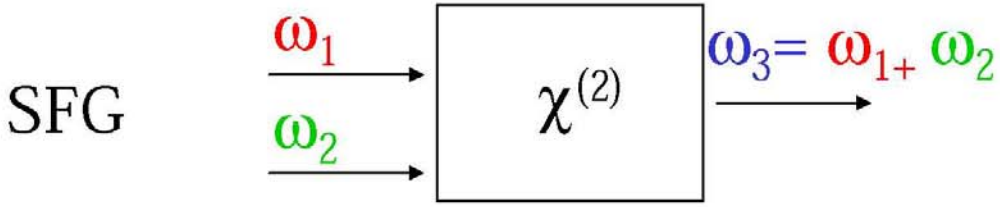
Frequency conversion with nonlinear optics: $\chi^{(2)}$ - Processes

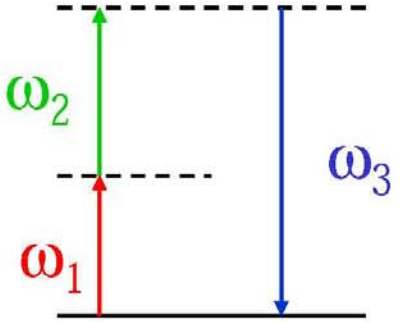
Second harmonic generation:



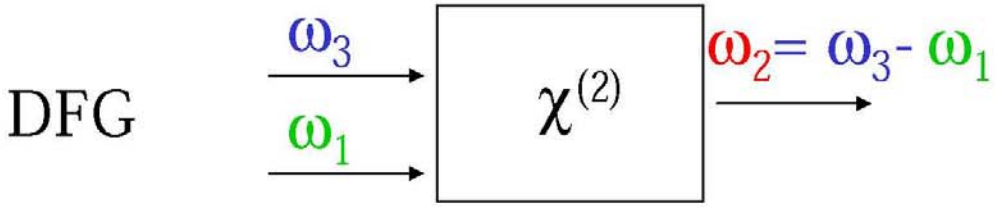


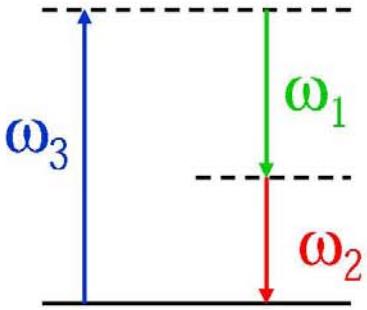
Sum frequency generation:



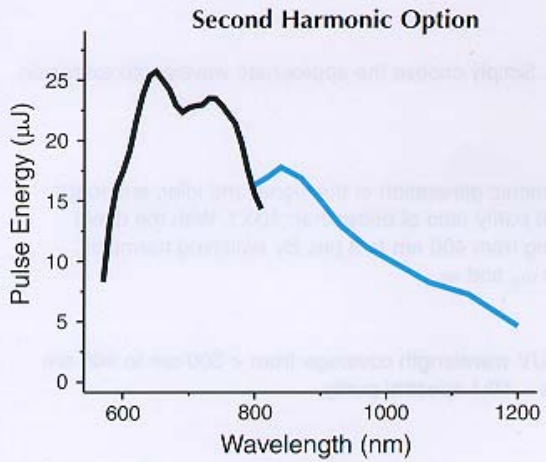


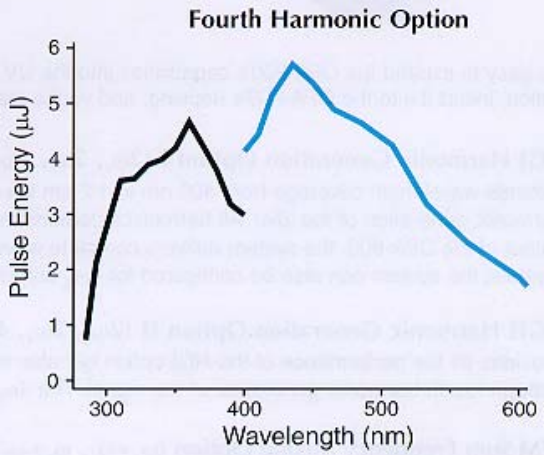
Difference frequency generation:

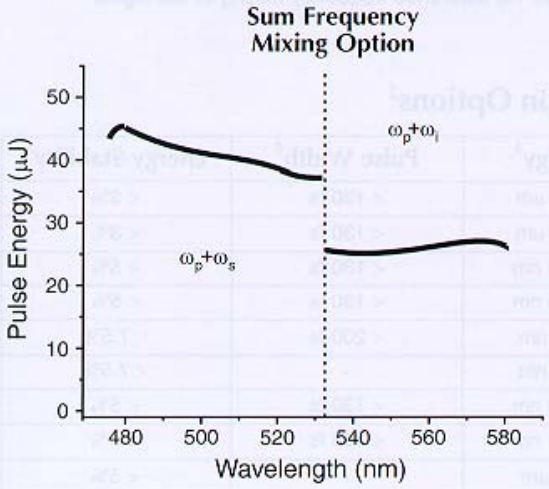


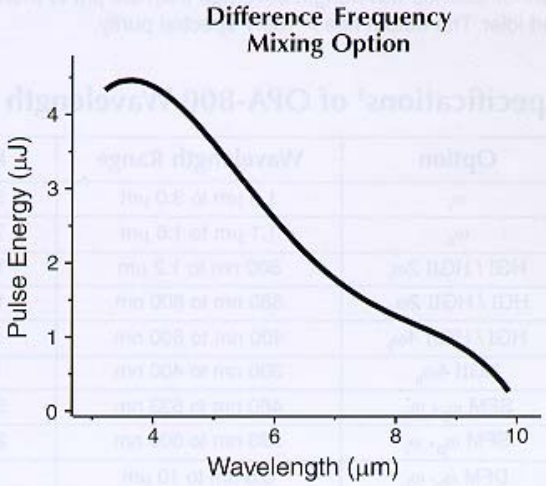


OPA-800 Wavelength Extension Performance



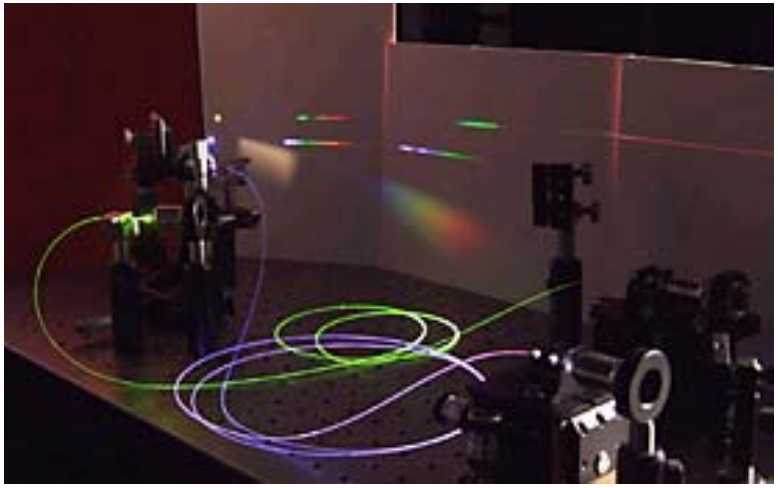




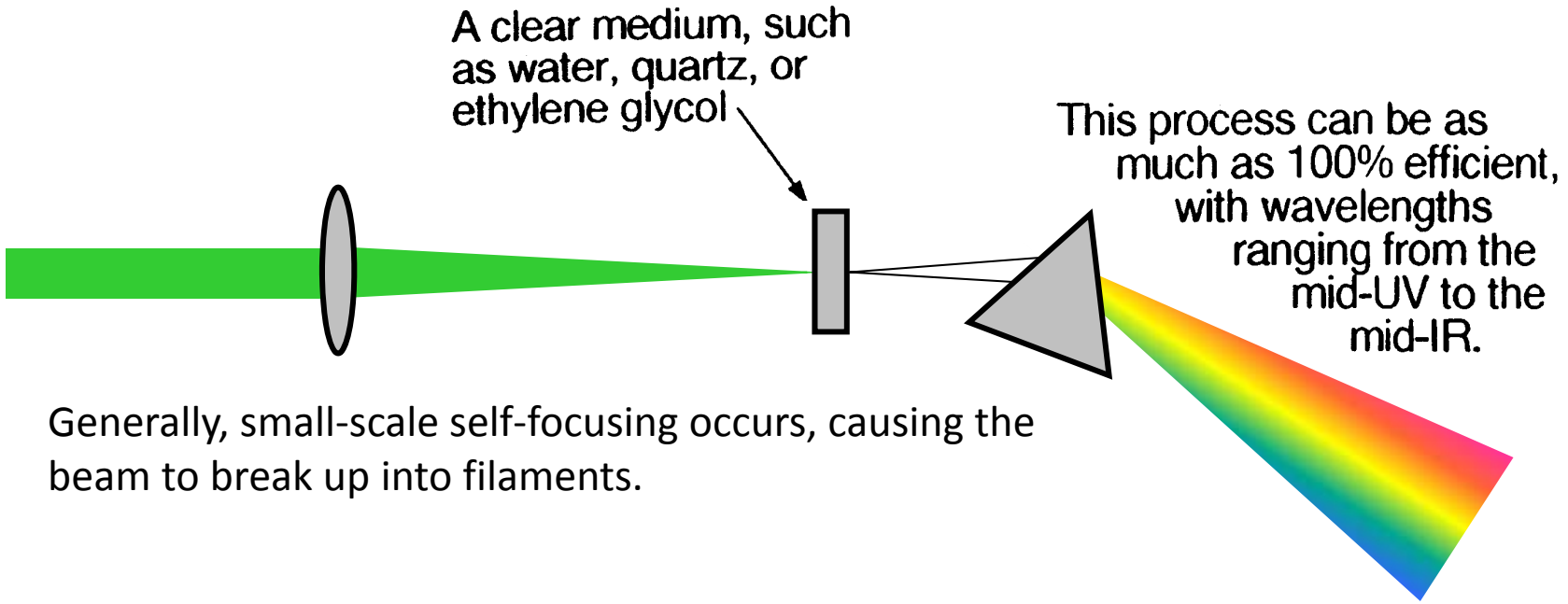


From: Spectra-Physics

Continuum Generation



Continuum Generation: focusing a femtosecond pulse into a clear medium turns the pulse white.

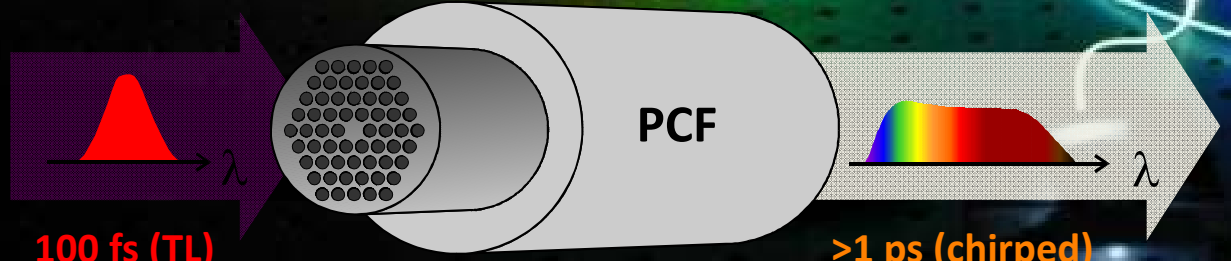


Generally, small-scale self-focusing occurs, causing the beam to break up into filaments.

Recently developed techniques involving optical fibers, hollow fibers, and microstructure fibers produce very broadband continuum, over 500 THz (1000 nm) in spectral width!

From R. Trebino, GaTech

Supercontinuum Generation in a Photonic Crystal Fiber (PCF)

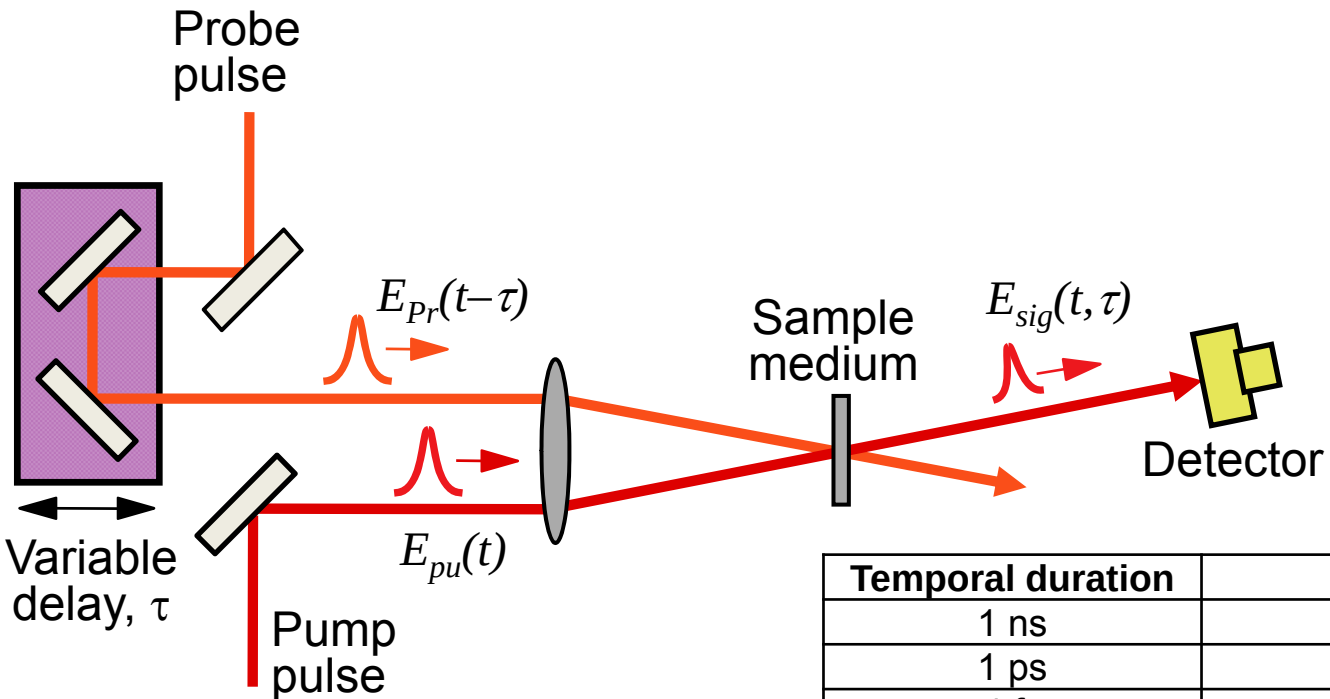


100 fs (TL)
$\Delta\lambda$ = 9 nm @ 800 nm

>1 ps (chirped)
$\Delta\lambda$ > 600 nm

Photo from *www.bath.ac.uk/physics.*

Ultrafast Spectroscopy: Pump and Probe

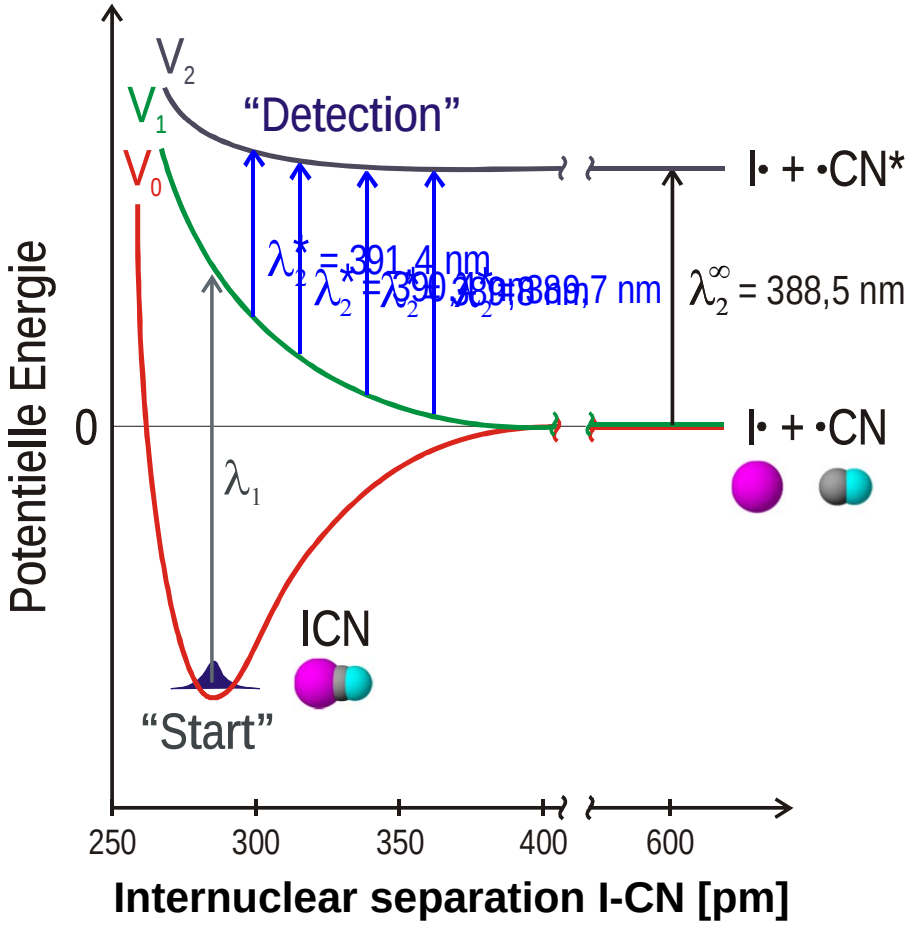


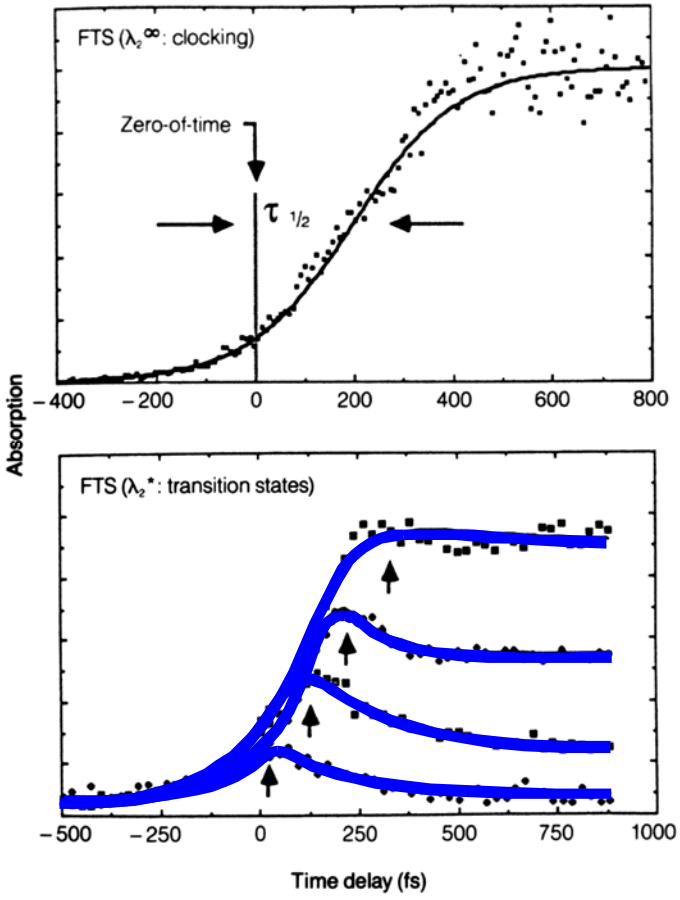
Temporal duration	Path
1 ns	≈ 30.0 cm
1 ps	≈ 0.3 mm
4 fs	≈ 1.2 μm

(Temporal duration corresponds to the time it takes for the pulse to travel along the path which is set by the variable delay stage)

The excite and probe pulses can be different colors.

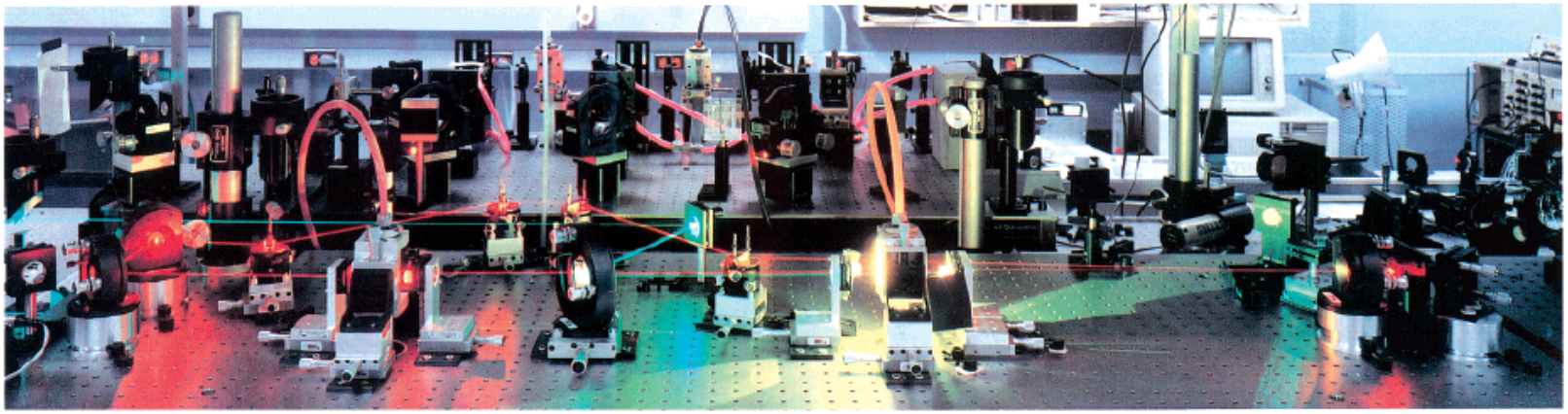
First fs-observation of a transition state: ICN-Dissociation

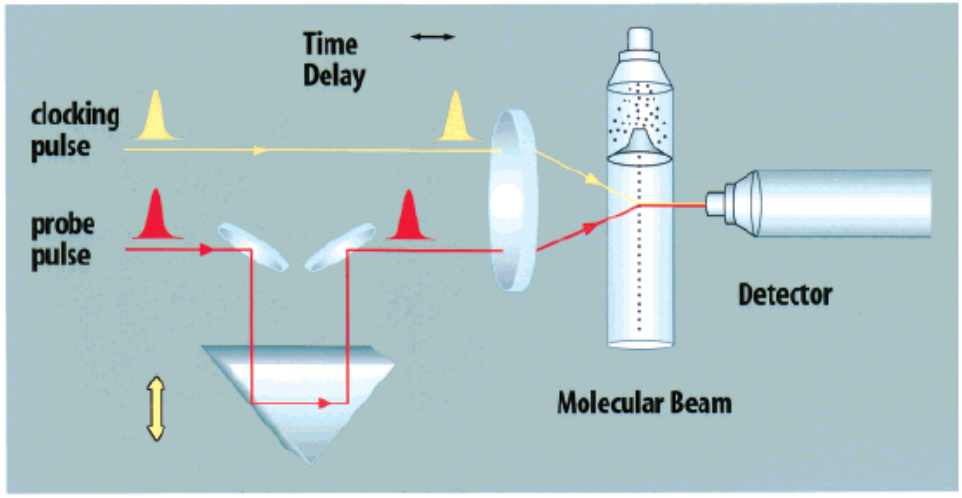


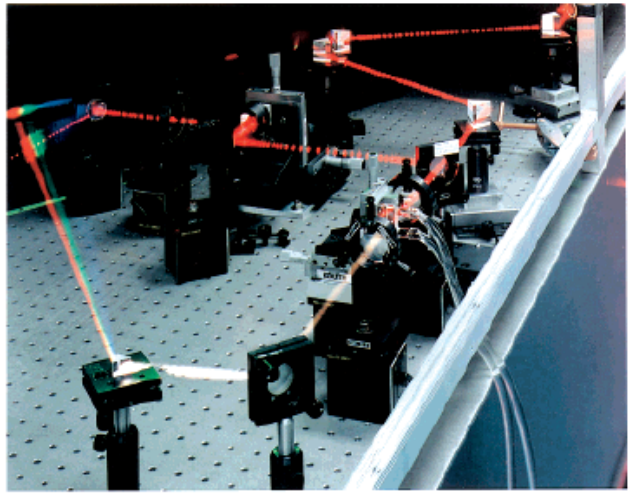


M.J. Rosker et al., J. Chem. Phys. ***89*** *(1988) 6113*

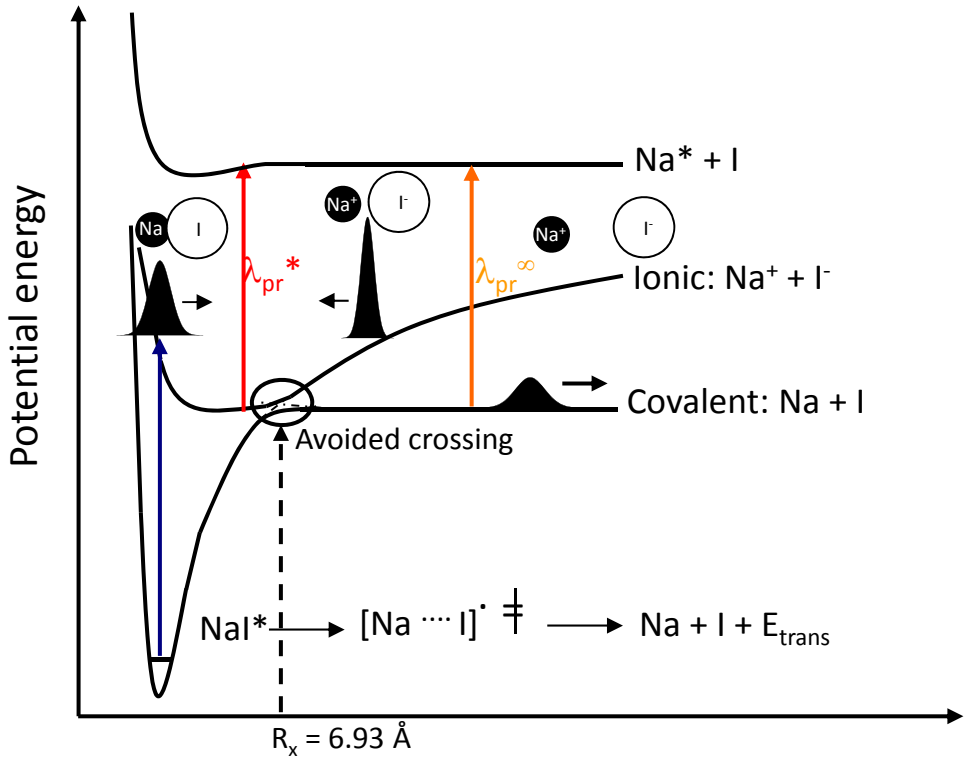
Pump-Probe Femtosecond Experiment (Zewail lab)

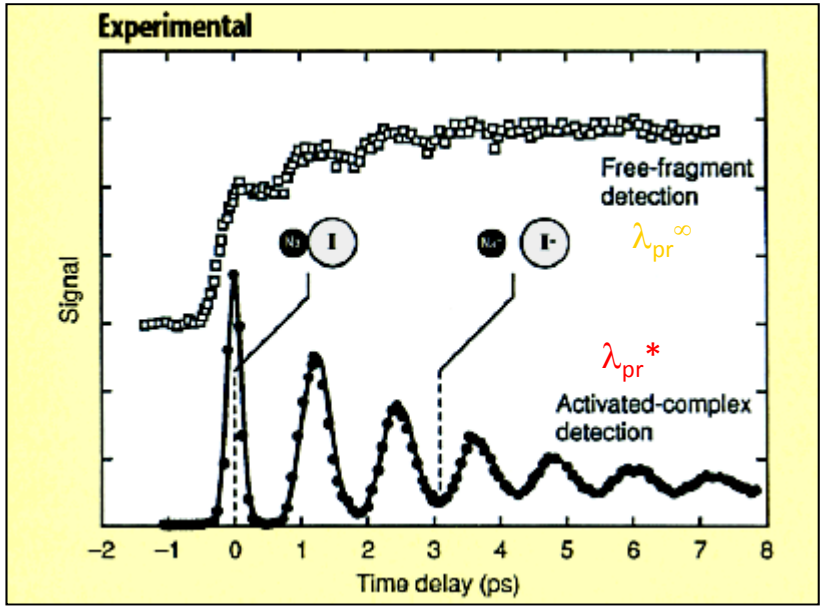






Real-time observation of wavepacket dynamics in a dissociation reaction





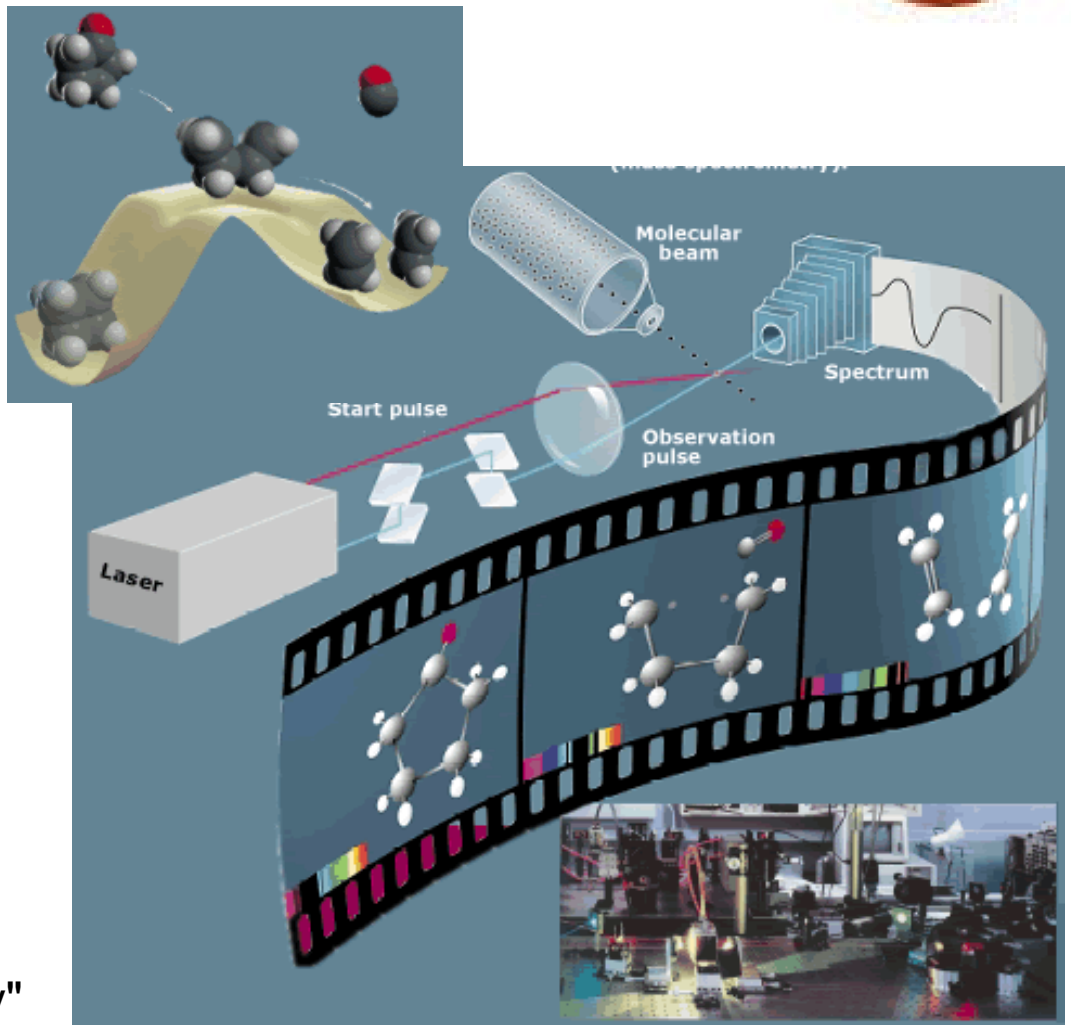
Paradigma: Chemical bond in a two-atomic molecule NaI changes its character (covalent or ionic) with time before dissociation into Na- and I-atoms takes place (bond forms again after an electron was transferred).

T.S. Rose et al. – J. Chem. Phys. ***88*** *(1988) 6672*

1999 Nobel Prize in Chemistry

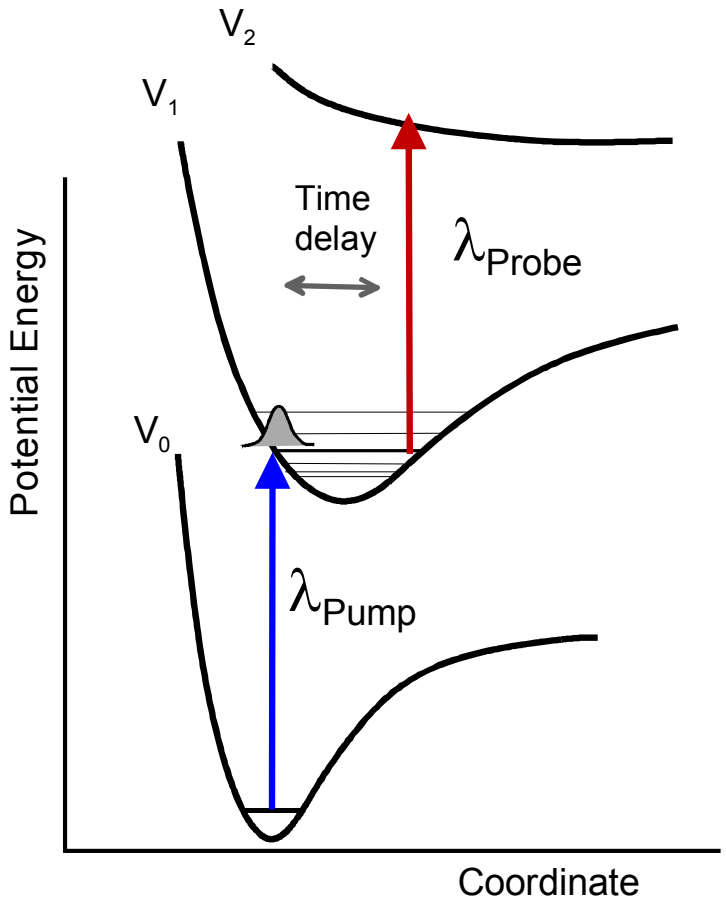
Ahmed H. Zewail

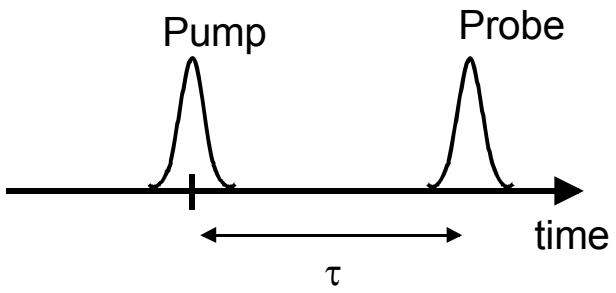
"for his studies of the transition states of chemical reactions using femtosecond spectroscopy"

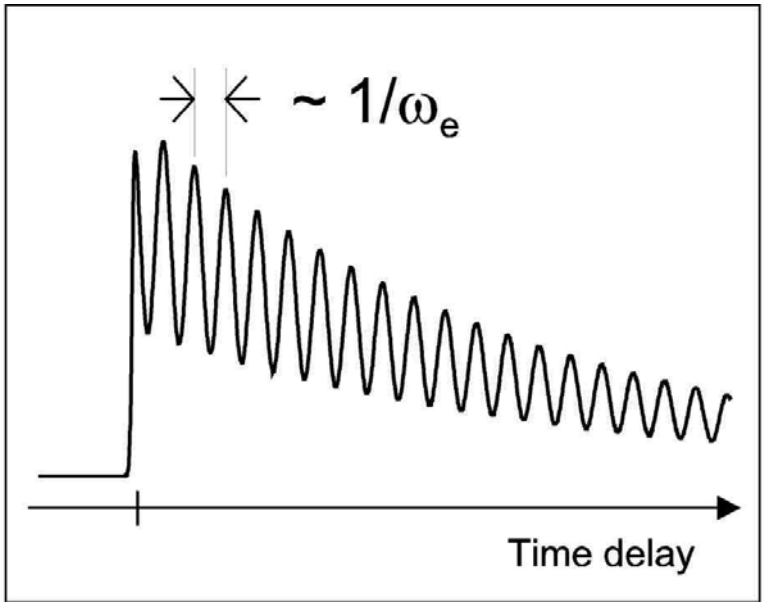


http://nobelprize.org/

Probing of vibrational dynamics in real-time



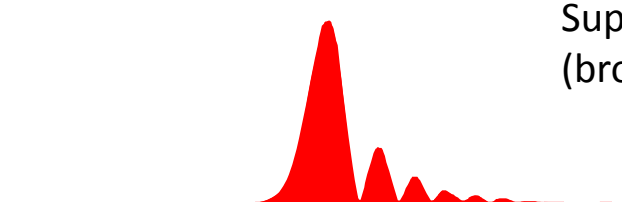


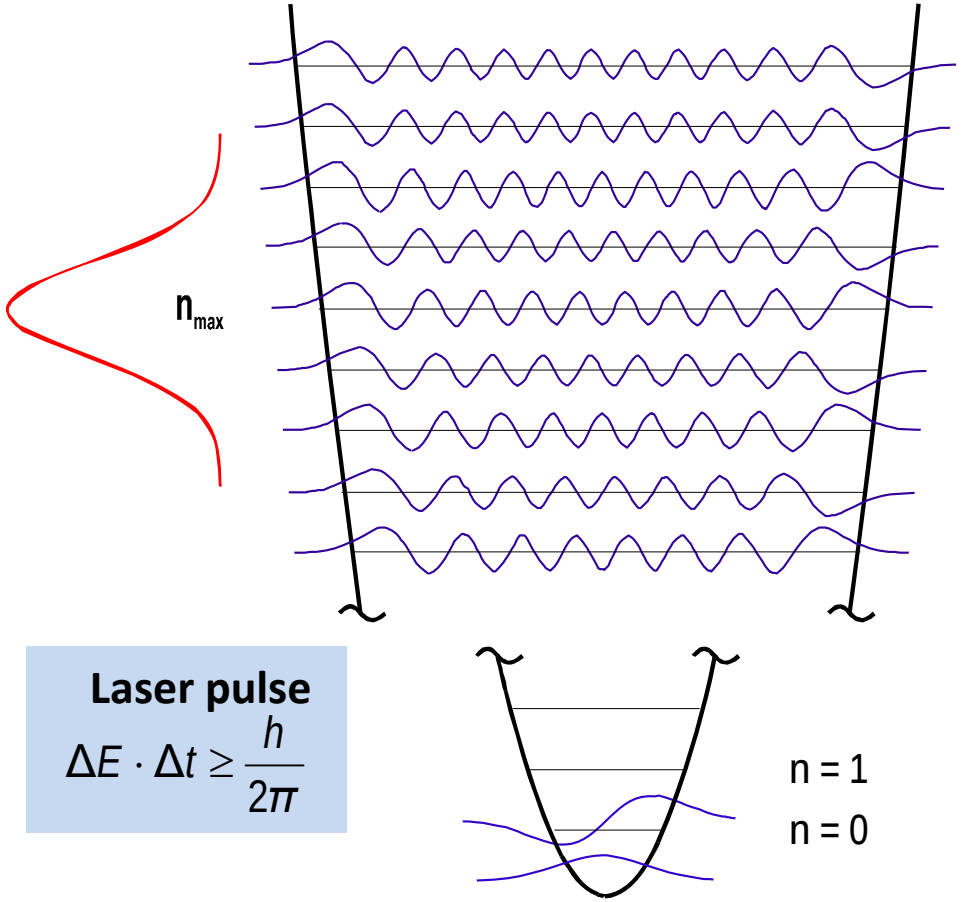


Coherence

Wavepacket

Superposition of time-dependent wavefunctions excited by short (broadband) laser pulse gives oscillating wavepacket.

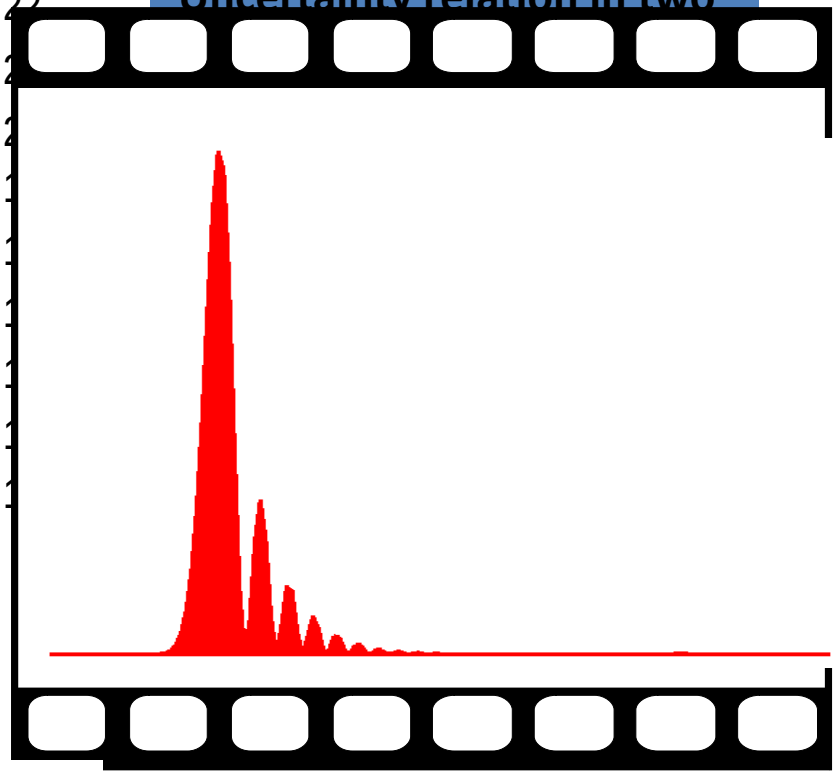




Laser pulse

$$\Delta E \cdot \Delta t \geq \frac{h}{2\pi}$$

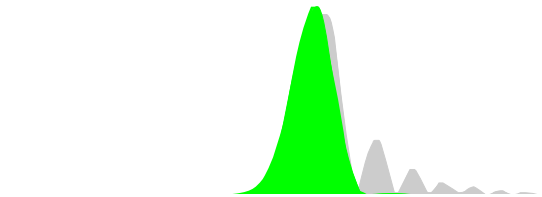
Uncertainty relation in two

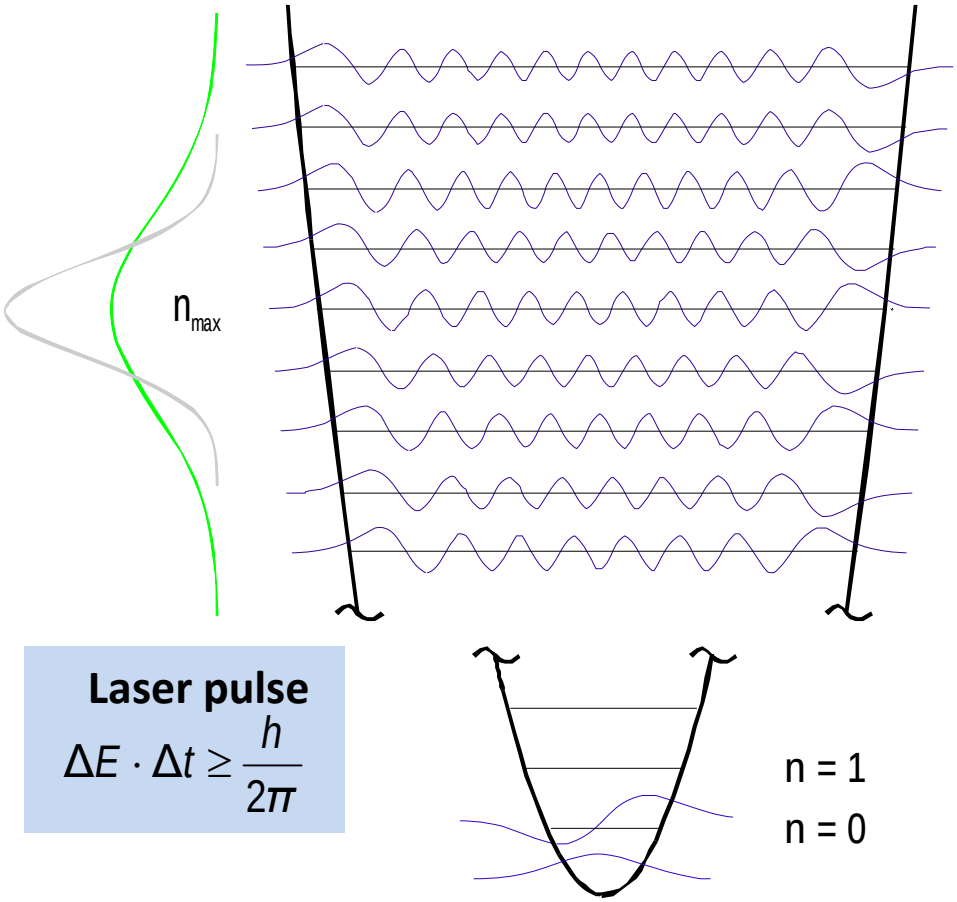


Coherence

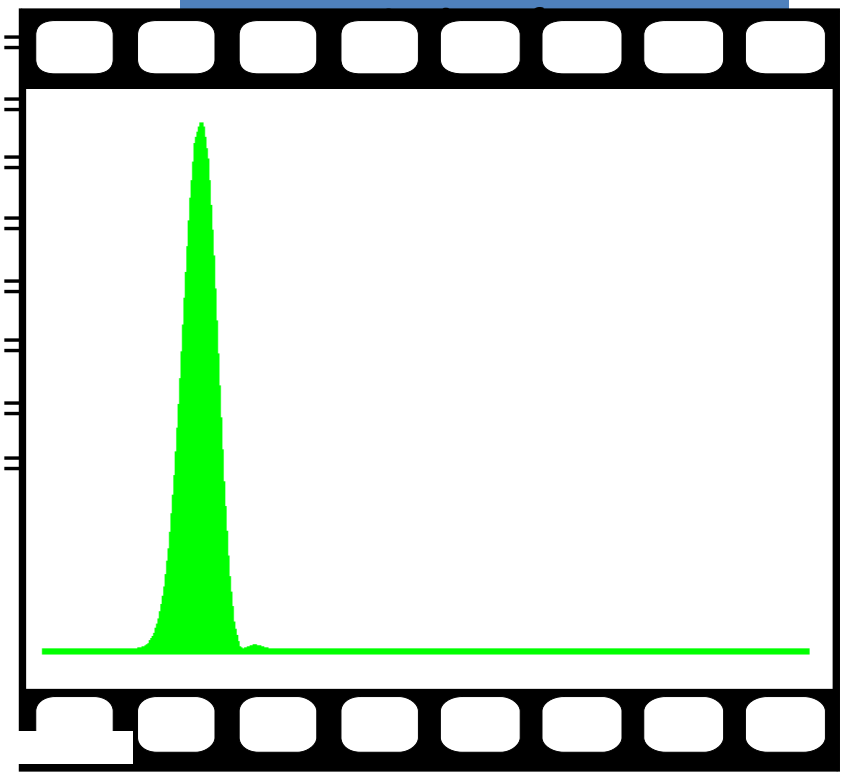
Wavepacket

Shorter Laser pulse → broader laser spectrum → better localised wavepacket





Uncertainty relation in two

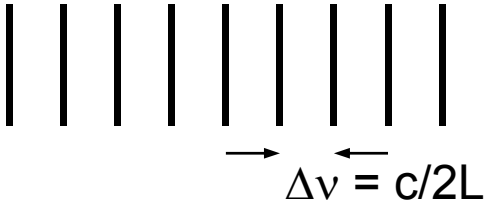


Laser pulse

$$\Delta E \cdot \Delta t \geq \frac{h}{2\pi}$$

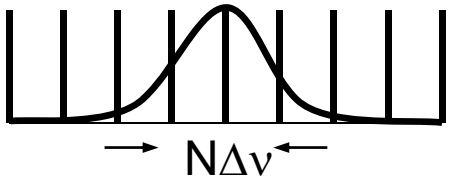
Laser mode locking *vs.* Vibrational wave packet

Laser resonator



One mode
→ single-mode operation
ΔE minimal

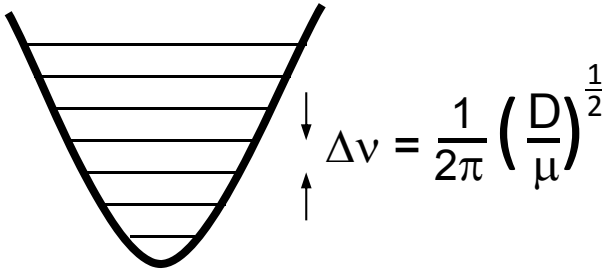
Mode locking:



$T_{repetition} = 1/\Delta\nu$

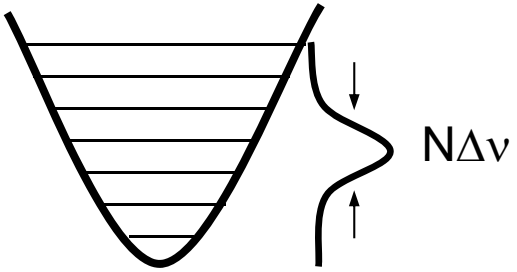
Time-bandwidth product

Harmonic potential



One eigenstate
→ time-independent
ΔE minimal

Coherent superposition:



$T_{oscillation} = 1/\Delta\nu$

Uncertainty relation

Concept of wavepackets

Quantum mechanics ≡ Stationary wavefunctions extending over a relatively large region of space

Classical mechanics ≡ Moving point objects; Localization

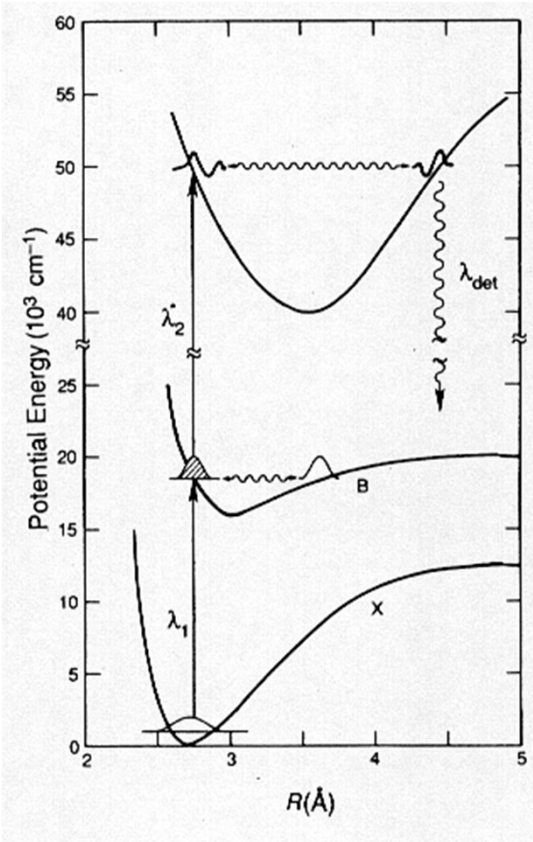
but is it valid?

Erwin Schrödinger, "Der kontinuierliche Übergang von der Mikro zur Makromechanik," Die Naturwissenschaften, Heft 28, 9.7.**1926**, 664-660: (Translation)

...I show, that **a group of eigenmodes** with high quantum number n and relatively small differences in their quantum numbers **describe a point mass which moves according to usual mechanics**...

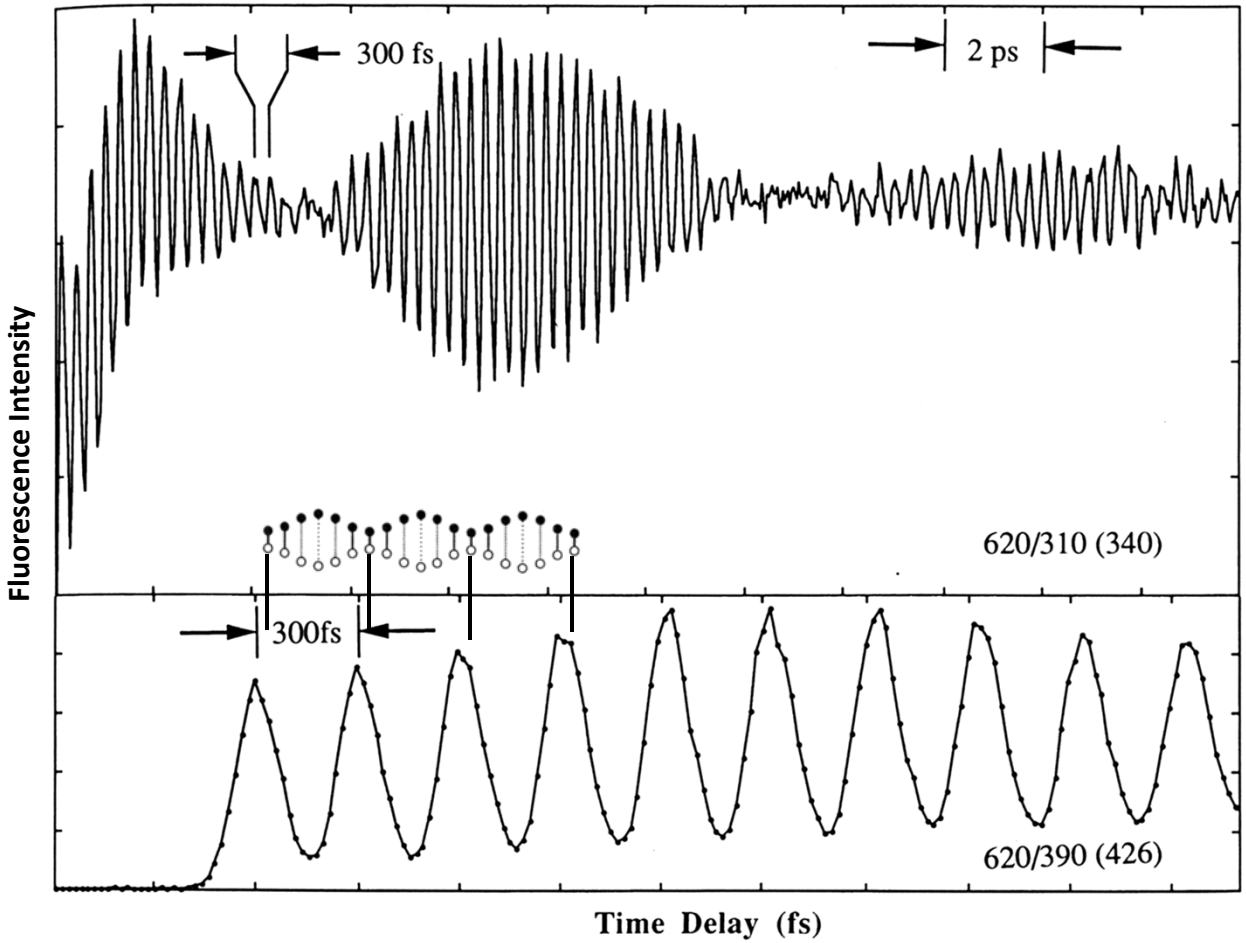
$$\Psi(x,t) = \sum a_n \phi_n e^{-i\frac{E_n}{\hbar}t}$$

Coherent vibration dynamics



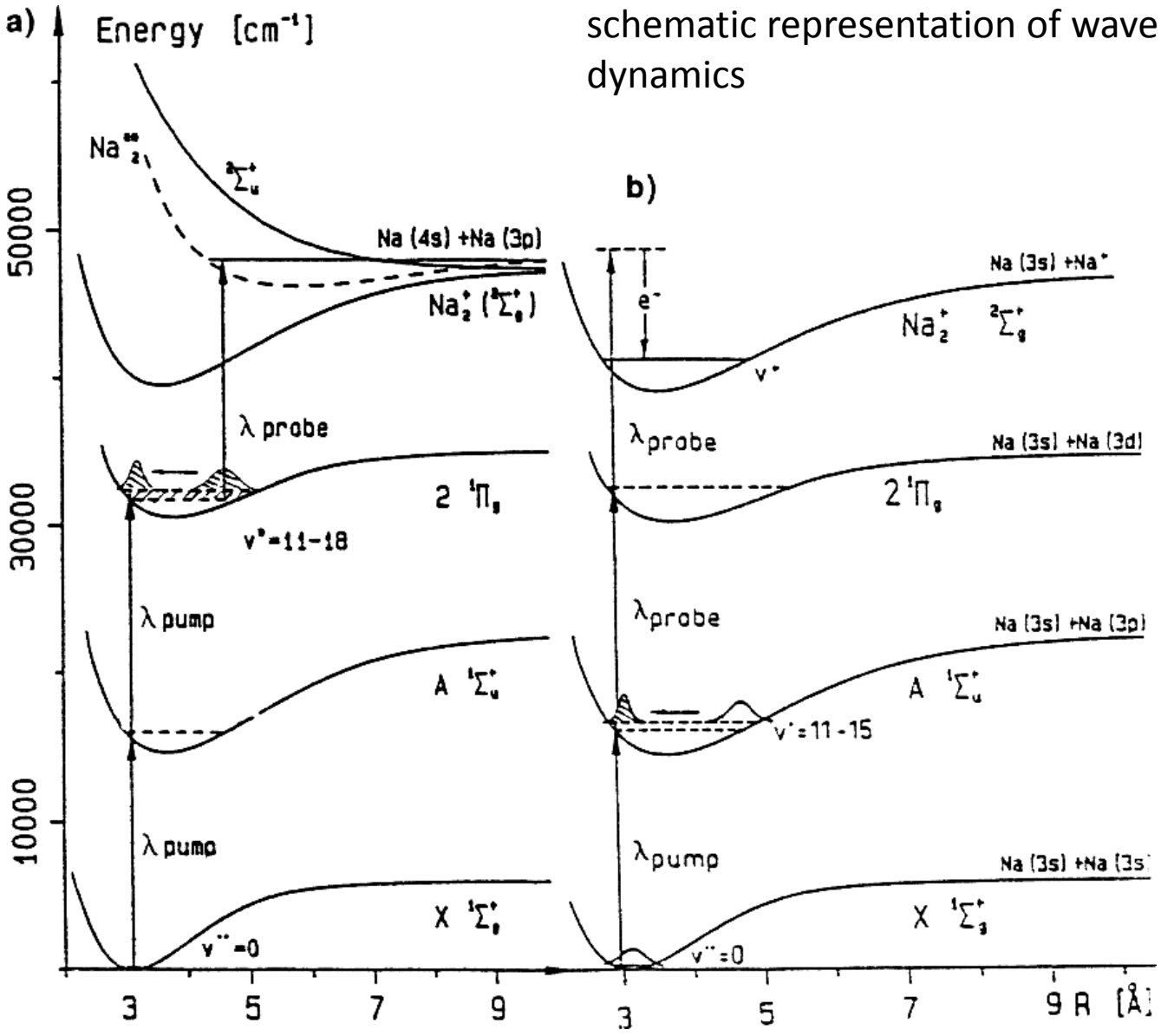
Vibrational wavepacket reflects classic movement of the nuclei

Wavepacket dynamics in the B-state of I_2



R.M. Bowman et al. –Chem. Phys. Lett. ***161*** *(1989) 297*

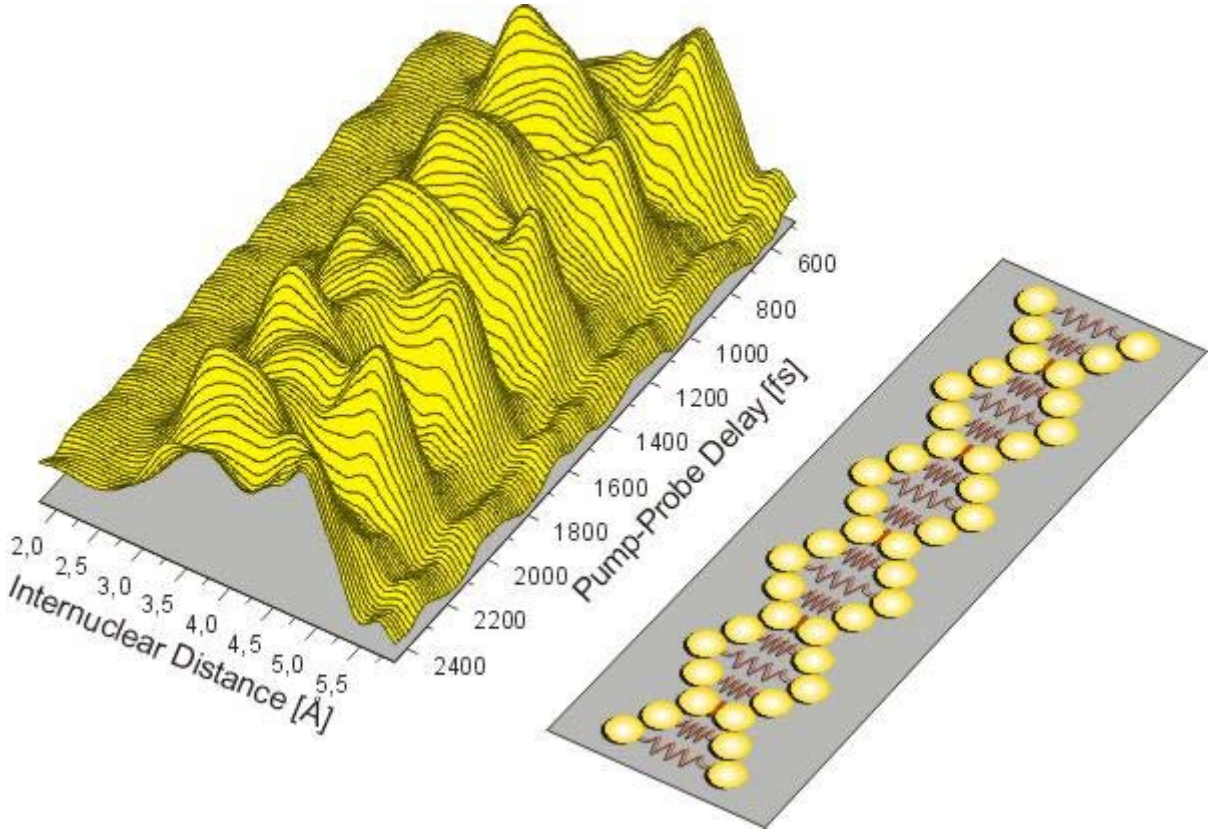
Potential energy curves of Na_2-molecule and schematic representation of wavepacket dynamics



T. Baumert, Universität Kassel

Pump-probe: Time-resolved photoelectron spectroscopy

Visualizing wave packet motion



Left: **Measured photoelectron distribution of Na_2 as a function of the pump-probe delay. The kinetic energy of the photoelectrons has been transformed to the internuclear distance.**
Right: **Classical oscillation of a molecule consisting of two atoms.**

T. Baumert, University of Kassel

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- seminal experiments, applications
- wavepackets

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- Pump-DFWM
- Quantum control spectroscopy

Pump-probe: Time-resolved absorption spectroscopy

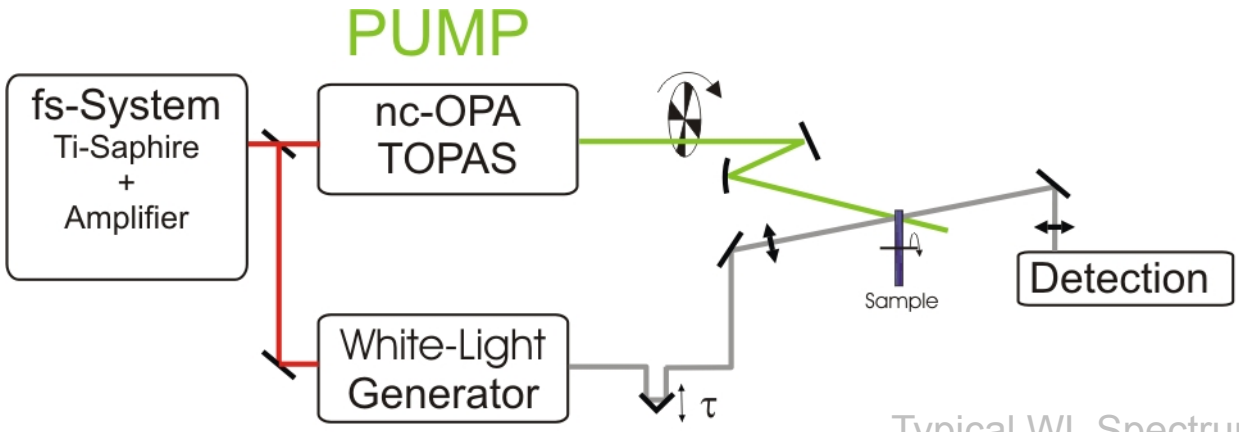
Transient absorption

- One of the most used time-resolved spectroscopical techniques (third-order method).
- A (weak) probe pulse measures the variation of absorption after the interaction with a (strong) pump pulse.

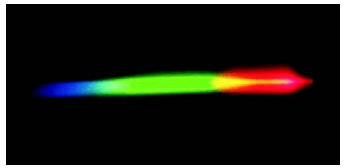
$$\frac{I_{pump}}{I_{probe}} \geq 100$$

- Requires spectral resolution, which is given by the detector (filters, gratings, monochromators, etc).

Typical setup



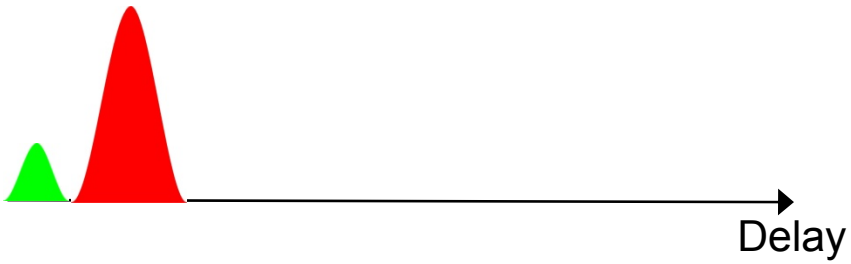
Typical WL Spectrum

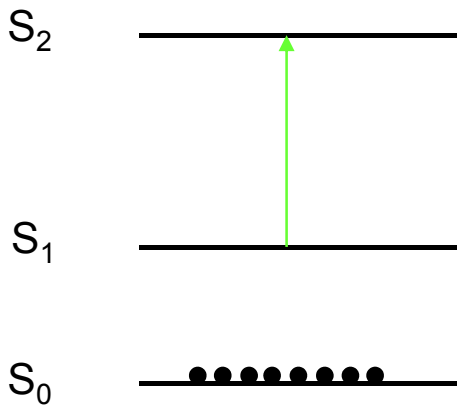


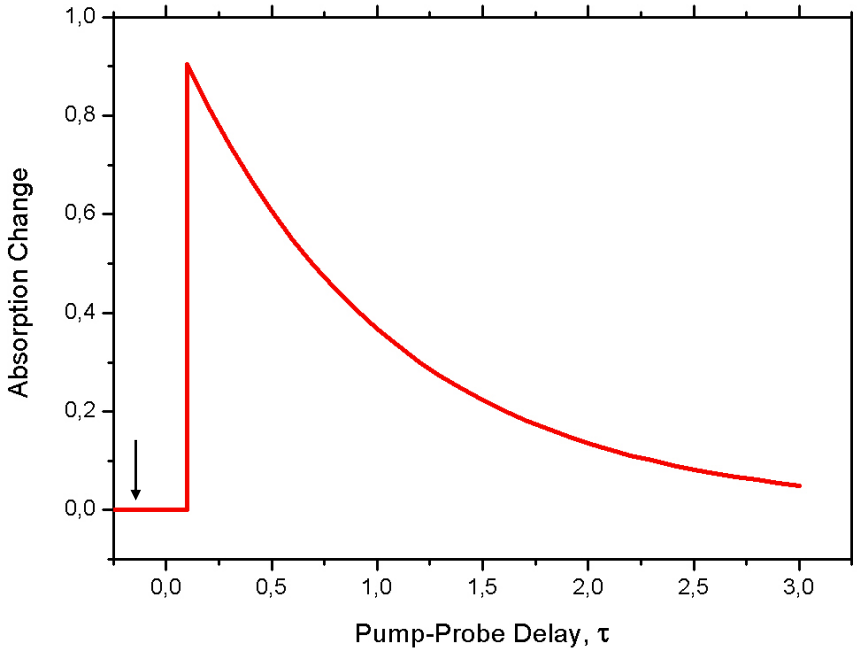
Pump-probe: Time-resolved absorption spectroscopy

• The absorption of the Probe Intensity is measured at different delays (τ):

Probe before the pump: no signal!



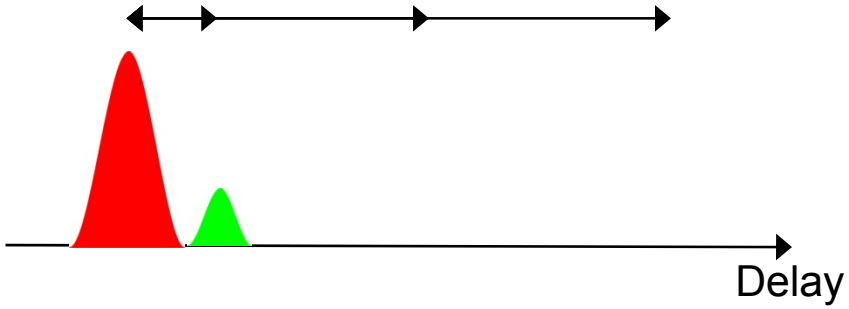


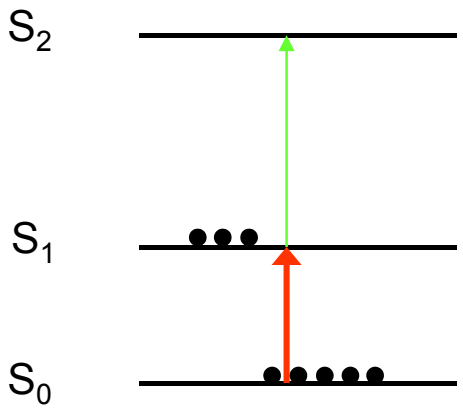


$$S_{TA} = \log\left(\frac{I_{\mathrm{Pr}}^{PumpOff}}{I_{\mathrm{Pr}}^{PumpOn}}\right) = \Delta c \cdot \varepsilon \cdot d$$

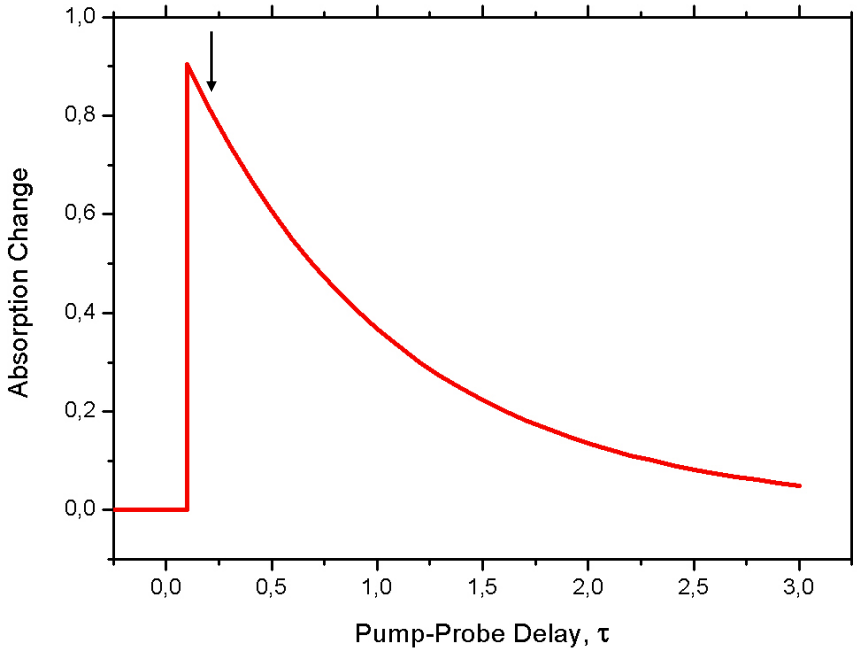
Pump-probe: Time-resolved absorption spectroscopy

- The absorption of the Probe Intensity is measured at different delays (τ):





Excited State Absorption (ESA)

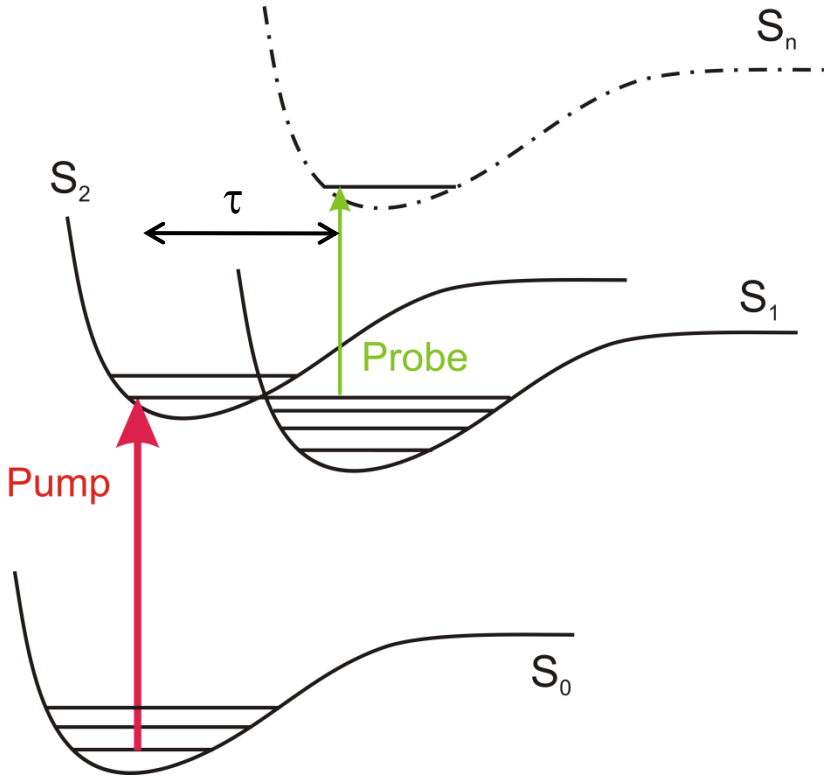


$$S_{TA} = \log\left(\frac{I_{\mathrm{Pr}}^{PumpOff}}{I_{\mathrm{Pr}}^{PumpOn}}\right) = \Delta c \cdot \varepsilon \cdot d$$

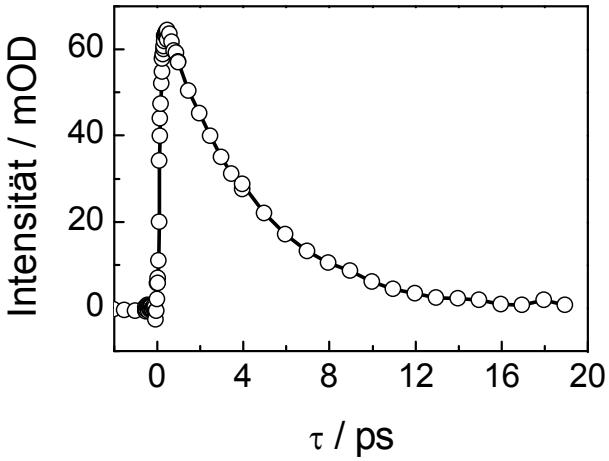
Pump-probe: Time-resolved absorption spectroscopy

Example: Energy flow in carotenoids

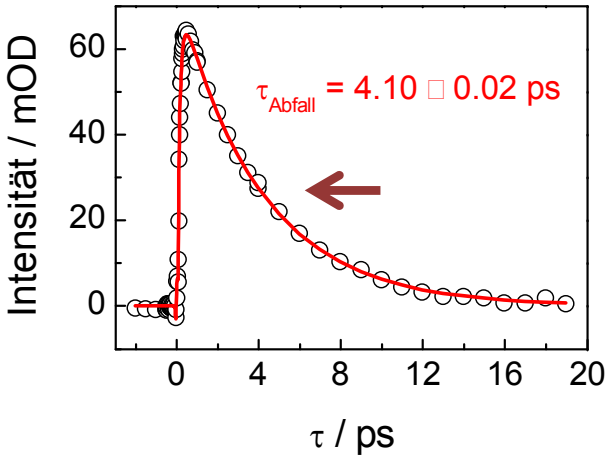
Pump excites S_2, Probe measures population of S_1

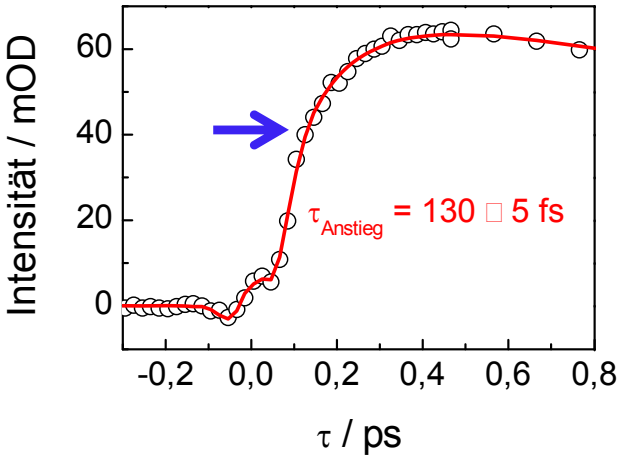


Signal (Lycopin):



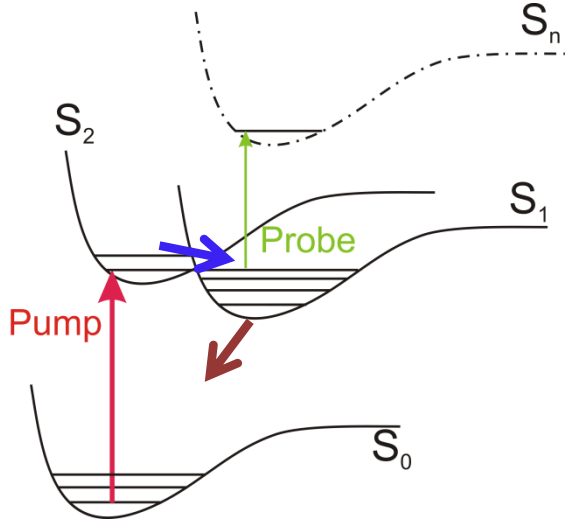
Interpretation of signal: Fit to rise and decay of the transient





4.1 ps → S_1 time constant ←

130 fs → S_2 time constant →

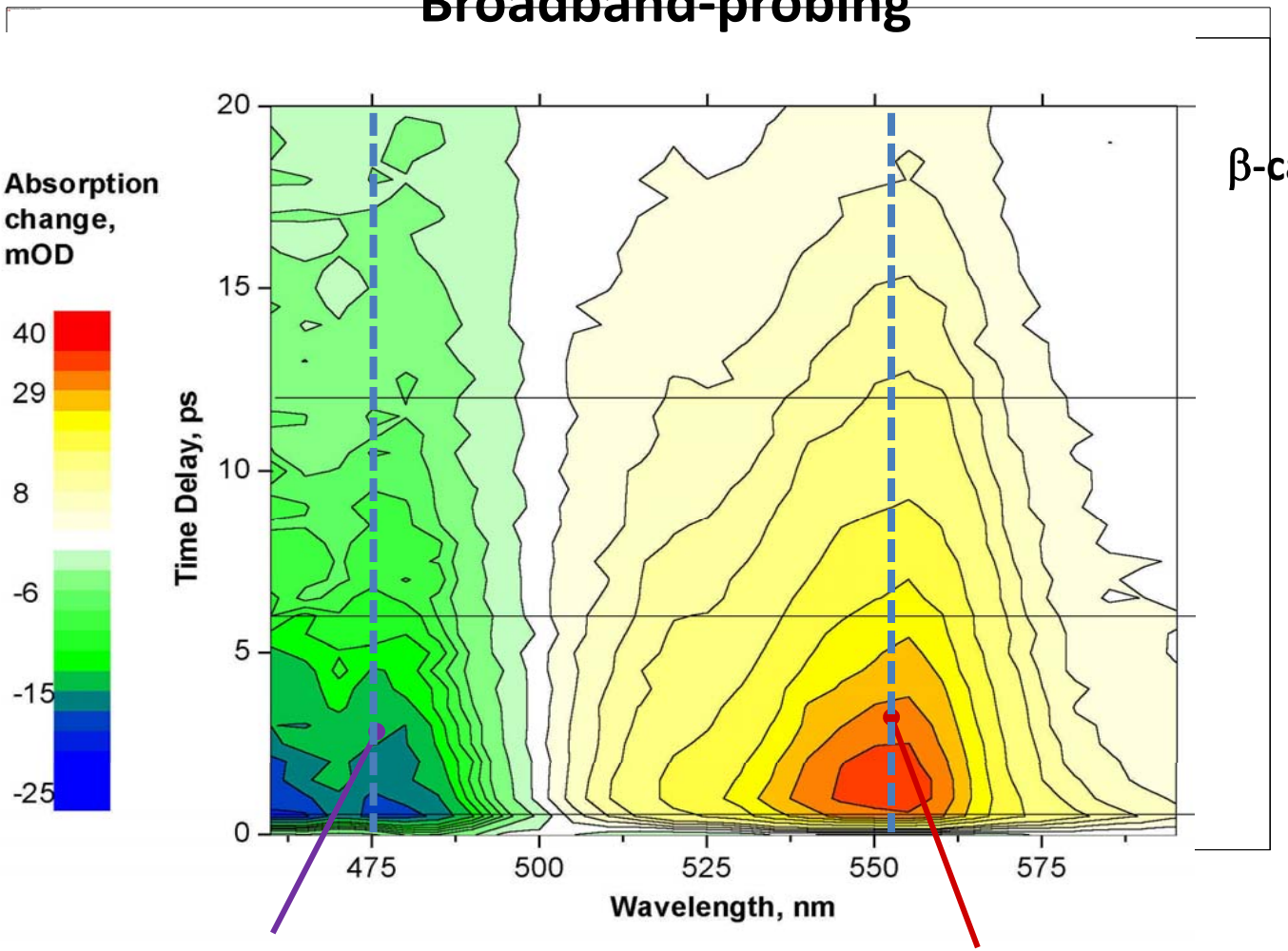


Signal at this wavelength probes S_1 :

→ Excited state absorption (ESA)

Pump-probe: Time-resolved absorption spectroscopy

Broadband-probing

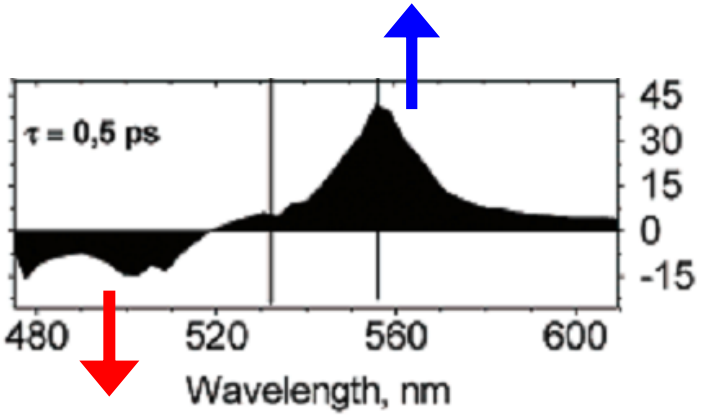


β-carotene

Ground-State Bleach S_0-S_2

Excited State absorption $S_1 \rightarrow S_N$

Transient absorption:
Positive and negative signal contributions



$$S_{TA} = \log\left(\frac{I_{Pr}^{PumpOff}}{I_{Pr}^{PumpOn}}\right) = \Delta c \cdot \varepsilon \cdot d$$

$I_{Pr}^{PumpOff} < I_{Pr}^{PumpOn}$ → Negative signal

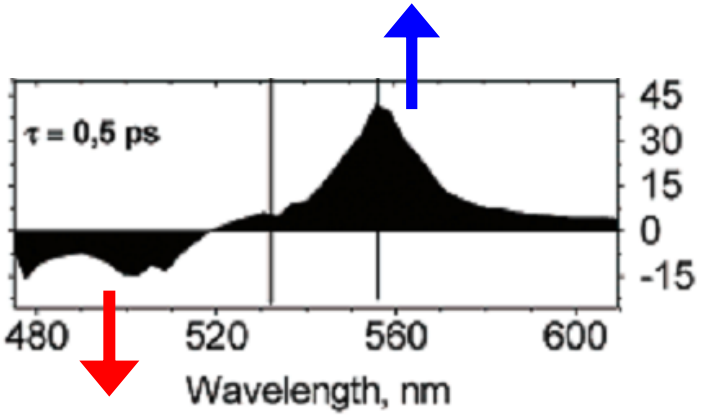
Stimulated Emission (SE)

Groundstate-Bleaching (GB)

$I_{Pr}^{PumpOff} > I_{Pr}^{PumpOn}$ → Positive signal

Excited State Absorption (ESA)

Transient absorption:
Positive and negative signal contributions



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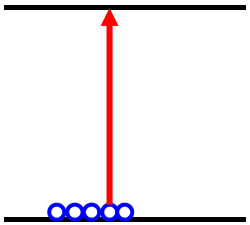
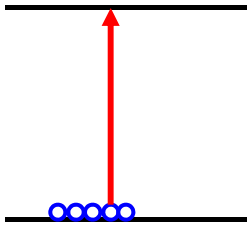
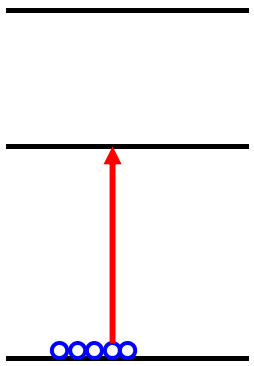


Groundstate-Bleaching (GB)

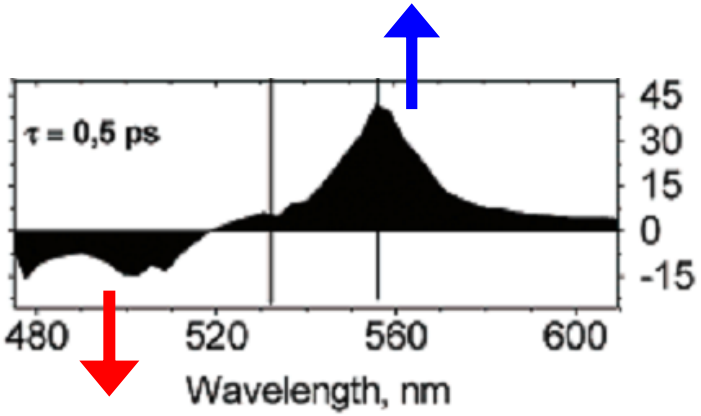


$I_{Pr}^{PumpOff} > I_{Pr}^{PumpOn}$ → Positive signal

Excited State Absorption (ESA)



Transient absorption:
Positive and negative signal contributions



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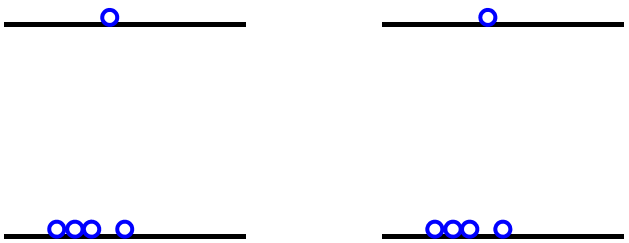
Stimulated Emission (SE)

Groundstate-Bleaching (GB)



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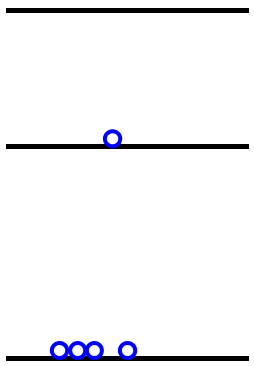
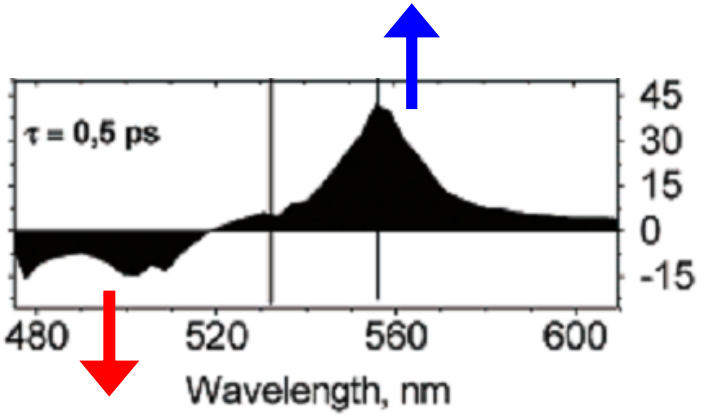
Excited State Absorption (ESA)



Transient absorption:
Positive and negative signal contributions



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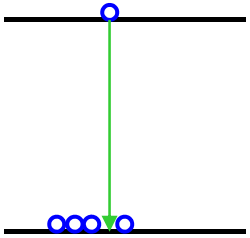
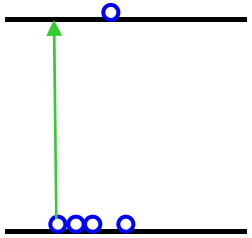


Groundstate-Bleaching (GB)



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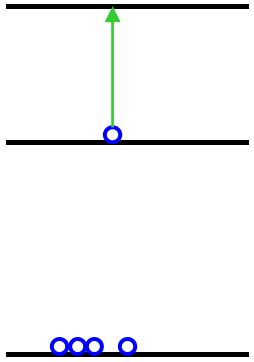
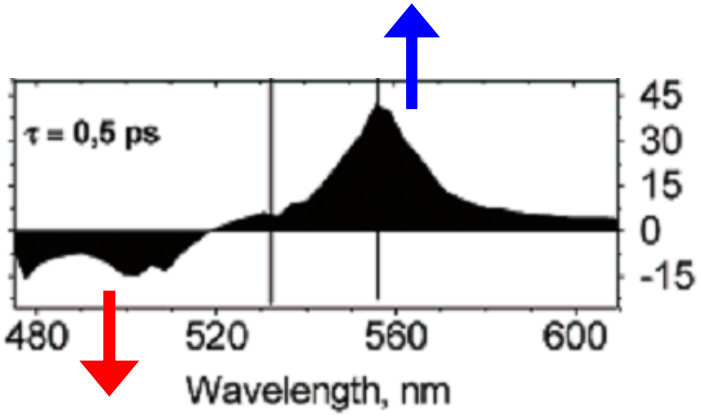
Excited State Absorption (ESA)



Transient absorption:
Positive and negative signal contributions



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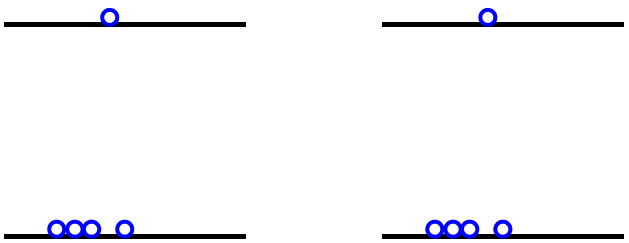
Stimulated Emission (SE)

Groundstate-Bleaching (GB)



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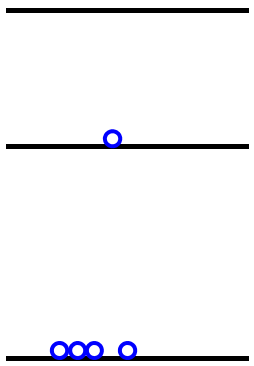
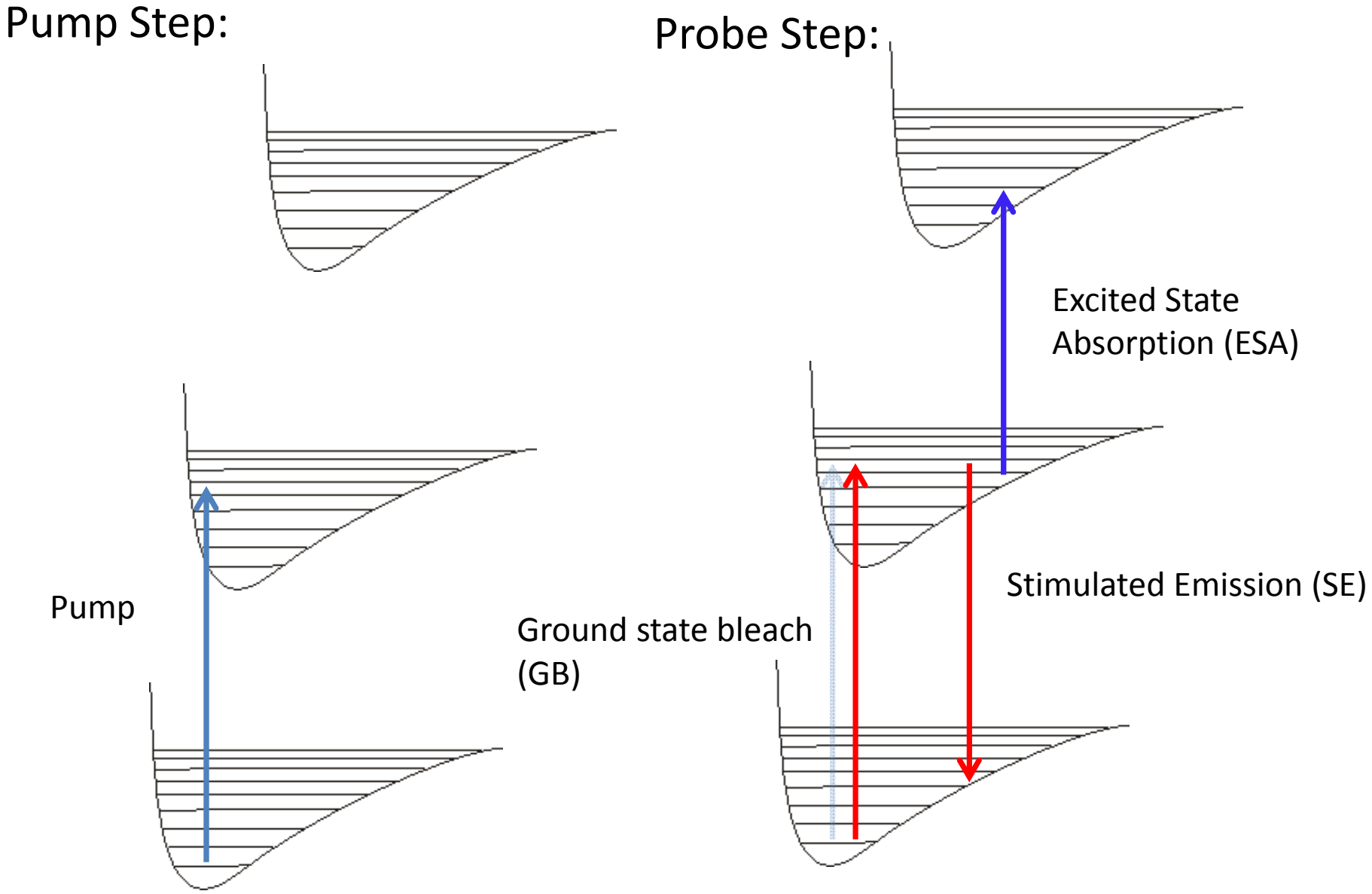


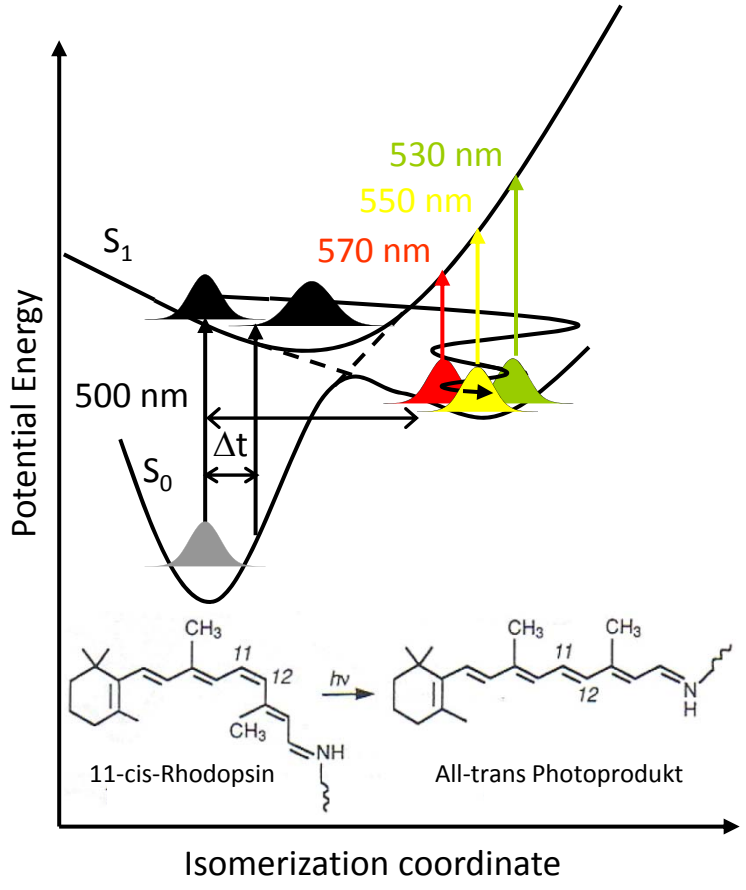
Three contributions in transient absorption

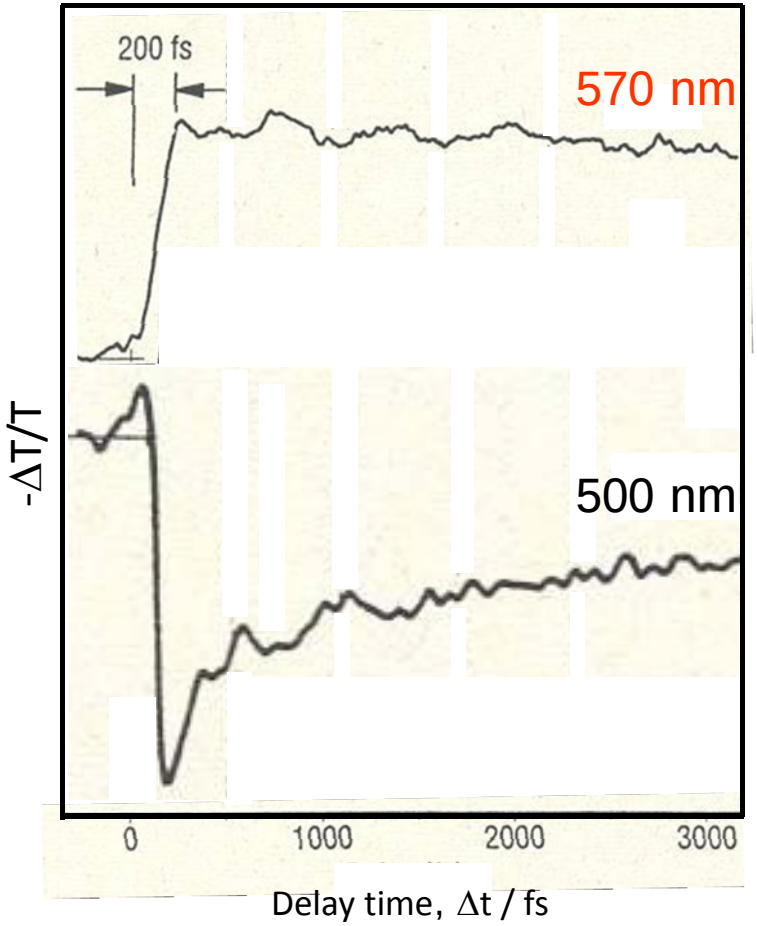


Pump-probe: Time-resolved absorption spectroscopy

Example of Femtobiology:

Observation of first step in vision - Isomerization of Rhodopsin



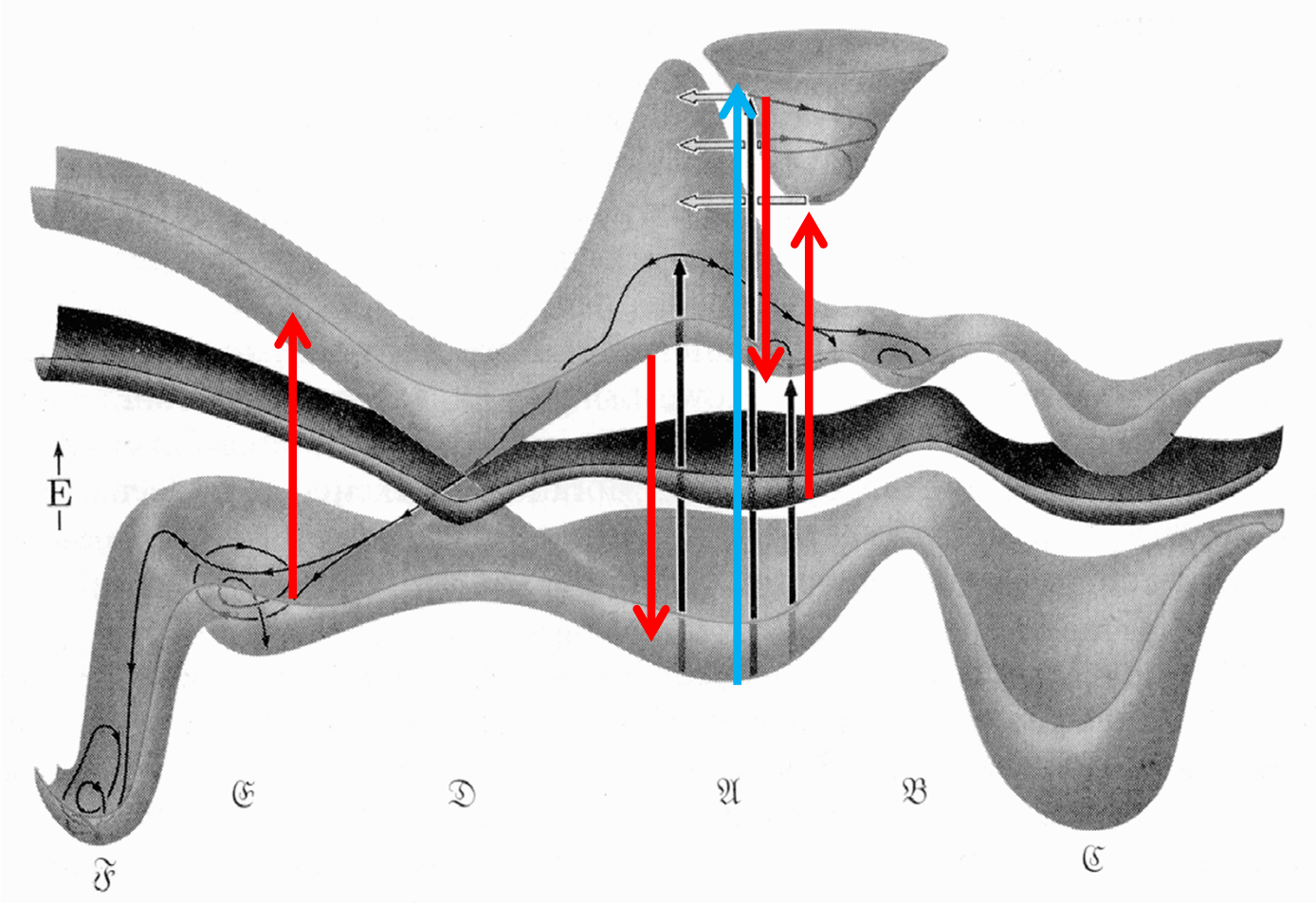


⇨ Photosensivity and high quantum yield due to ultrafast non-adiabatic isomerization reaction

*R.W. Schoenlein et al., Science **254** (1991) 412*
*P. Kukura et al., Science **310** (1990) 1006*

Femtochemistry:

Observation of ultrafast dynamics in complex molecules

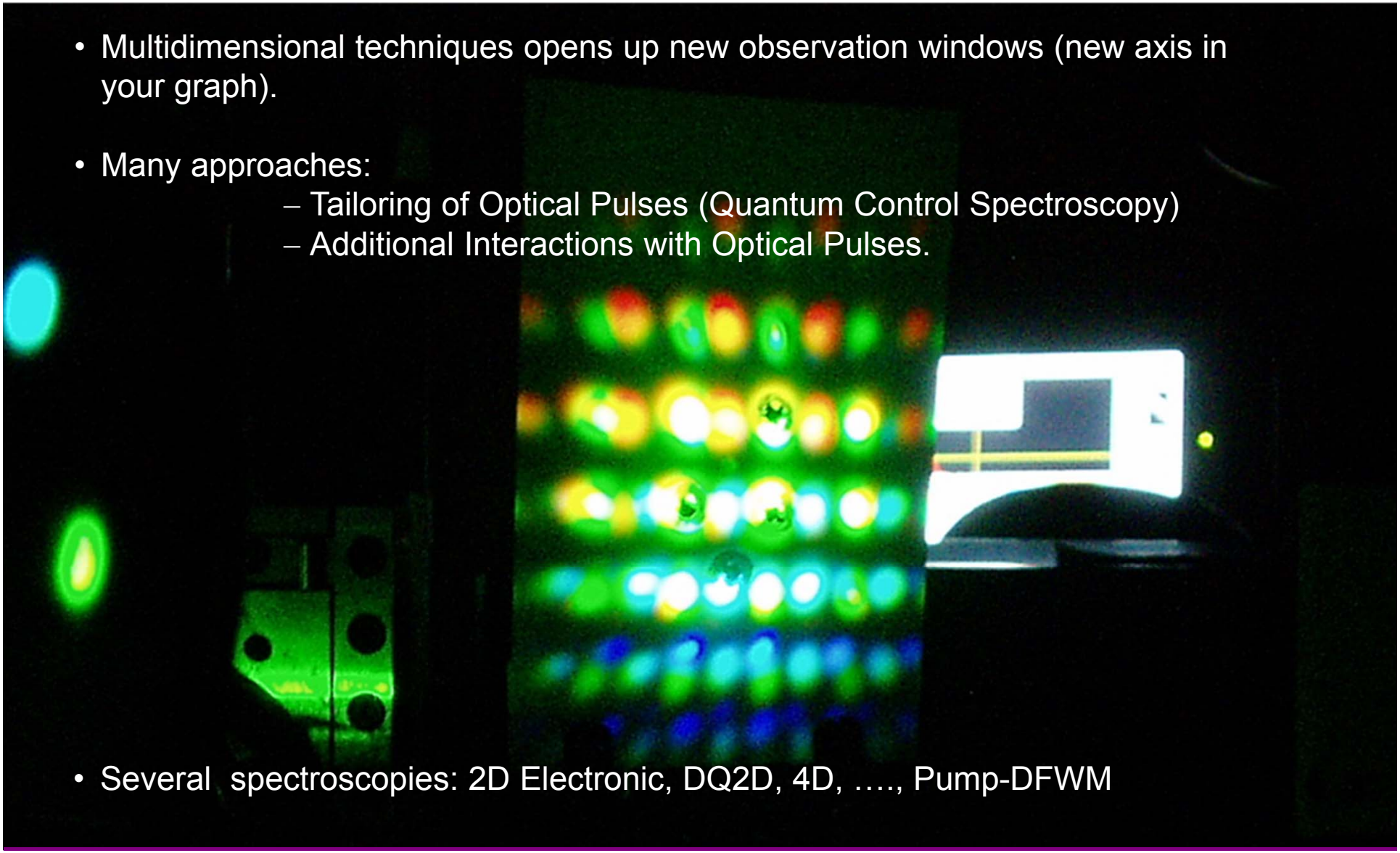


→ Due to overlapping resonances of many contributing states more sophisticated optical techniques are needed !!

→ Multidimensional spectroscopy

Multidimensional Time-Resolved Spectroscopy

- Multidimensional techniques opens up new observation windows (new axis in your graph).
- Many approaches:
  - Tailoring of Optical Pulses (Quantum Control Spectroscopy)
  - Additional Interactions with Optical Pulses.



- Several spectroscopies: 2D Electronic, DQ2D, 4D, …., Pump-DFWM

Ultrafast Molecular Spectroscopy

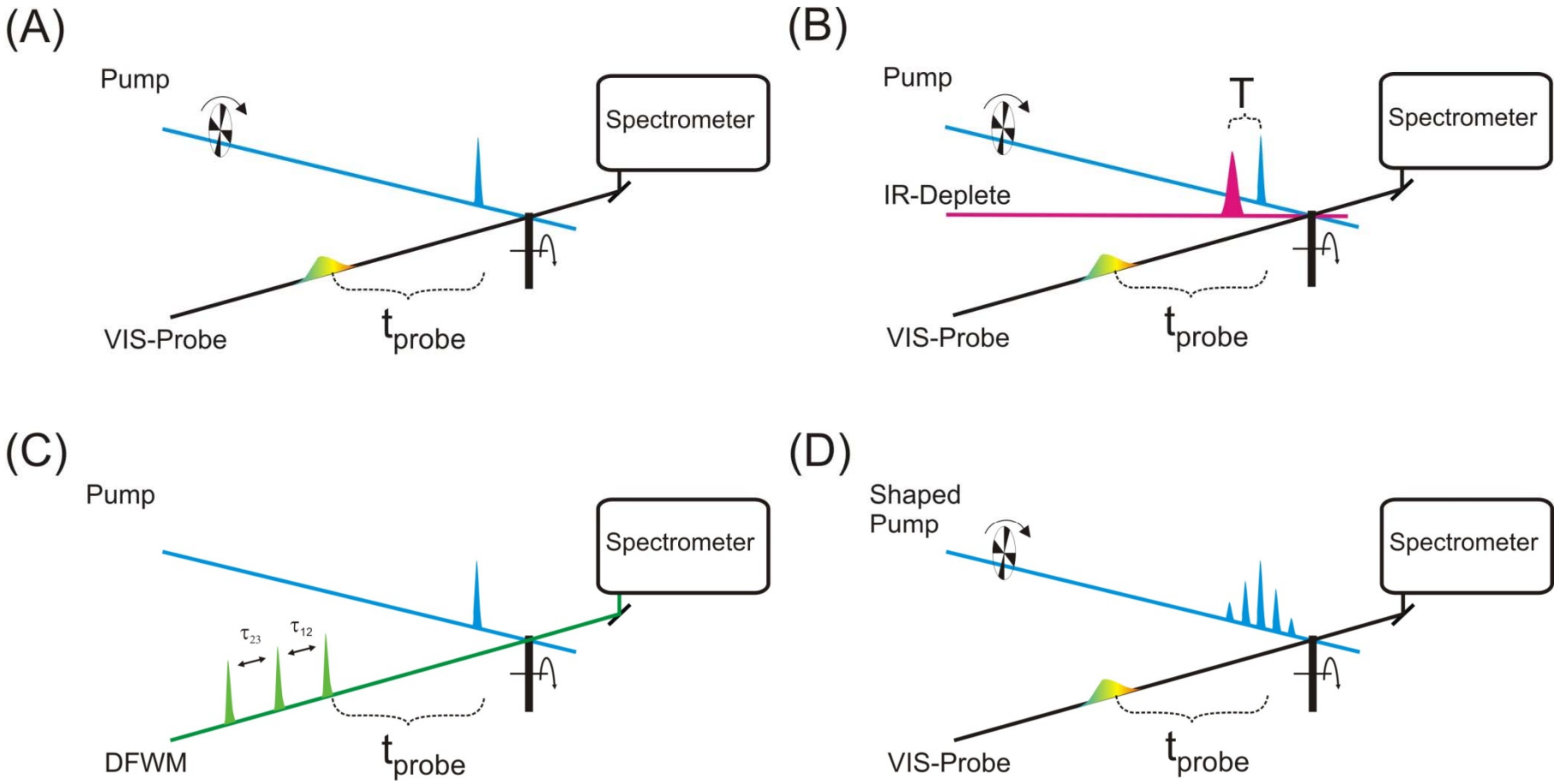
Outline

I. Intro - Ultrafast Molecular Spectroscopy
- Time scale of chemical processes, Overview of methods
- Pump-probe principle
- seminal experiments, applications
- wavepackets

II. Optical Methods of Pump-Probe-Spectroscopy
- Transient Absorption: Population dynamics
- Examples
- Problem of overlapping resonances

III. Multidimensional spectroscopy
- Case study: dynamics on Carotenoids
- Pump-dump-spectroscopy
- Pump-DFWM
- Quantum control spectroscopy

Going beyond simple pump-probe: Complex excitation + complex probe



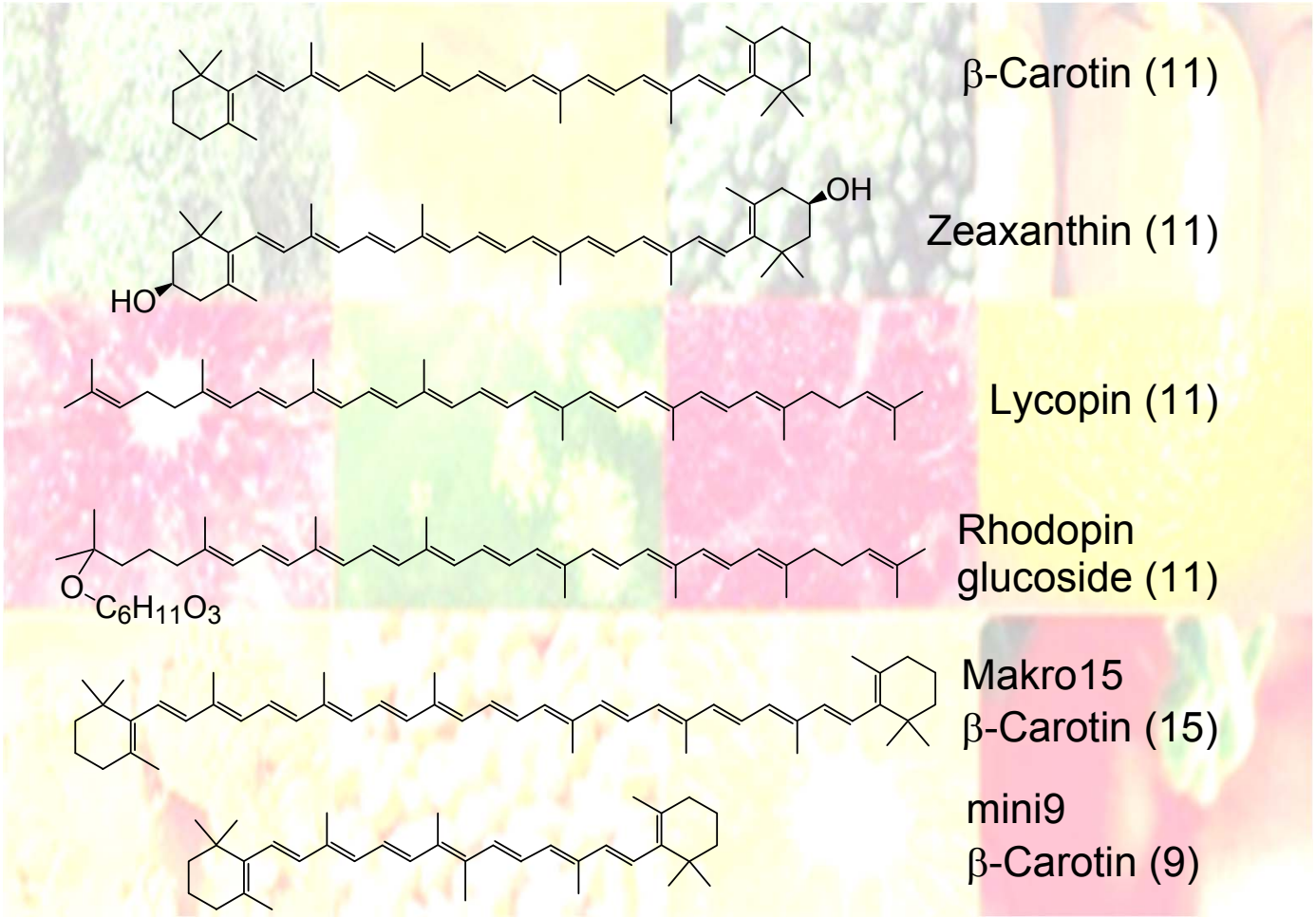
Carotenoids

Carotenoids

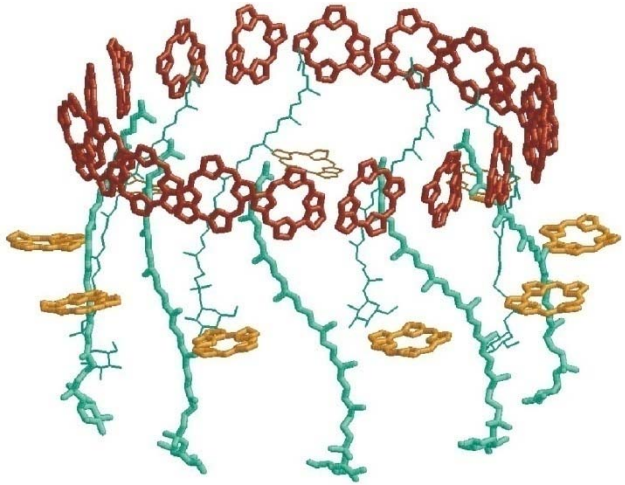
natural, in solution

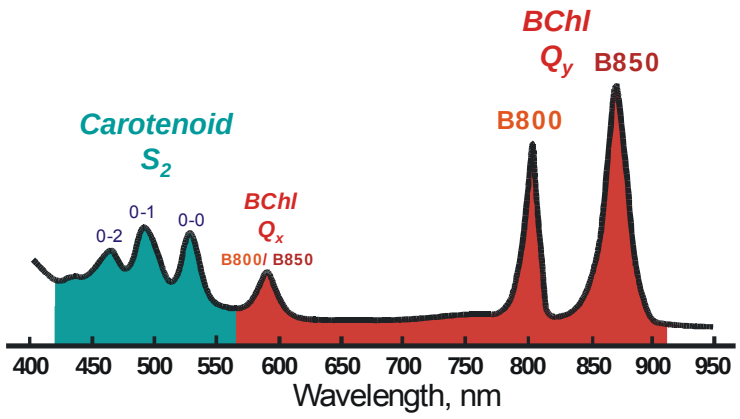
in LH2

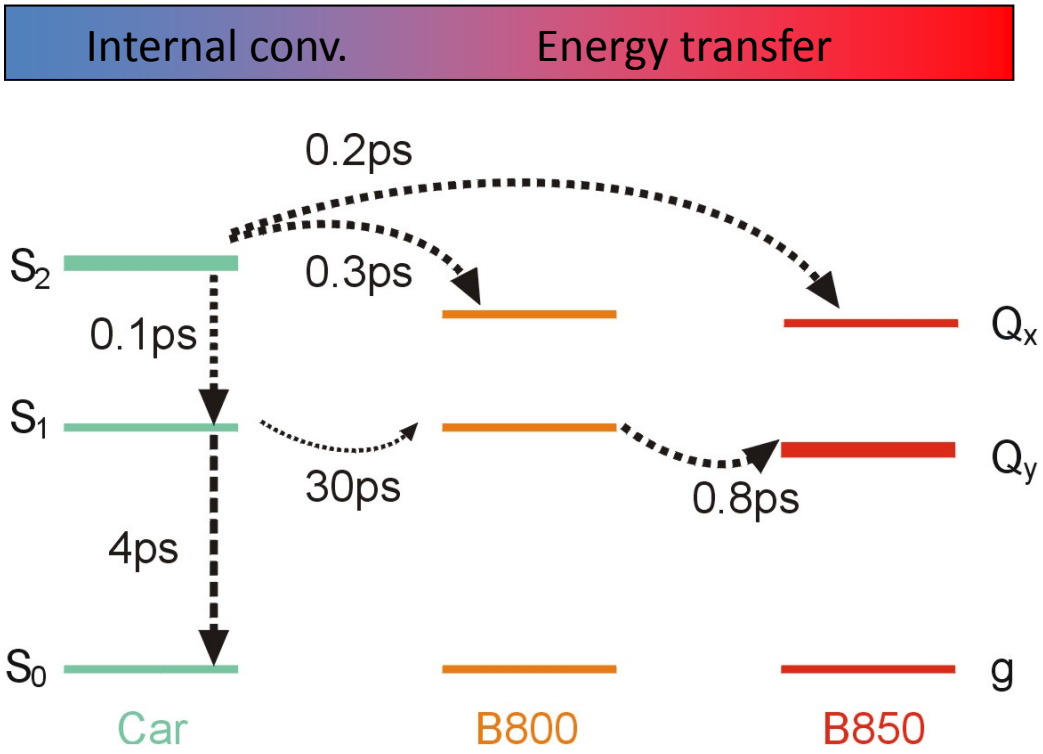
artificial, in solution



Ultrafast dynamics in Light Harvesting







Polivka & Sundström, Chem. Rev. (2004)

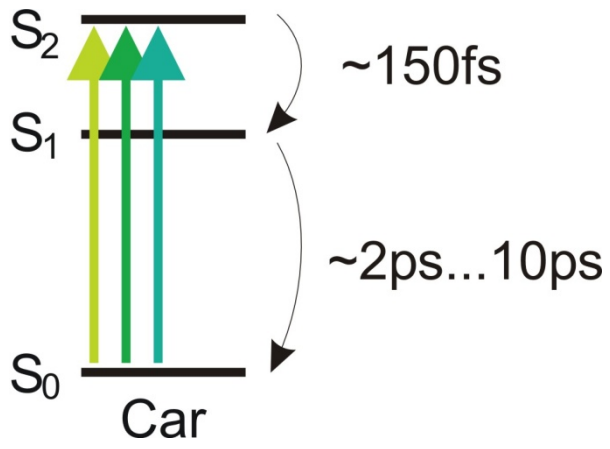
Biological function of carotenoids

Light harvesting
Photoprotection
Quenching
} →

Electronic Energy Transfer: fs-ps

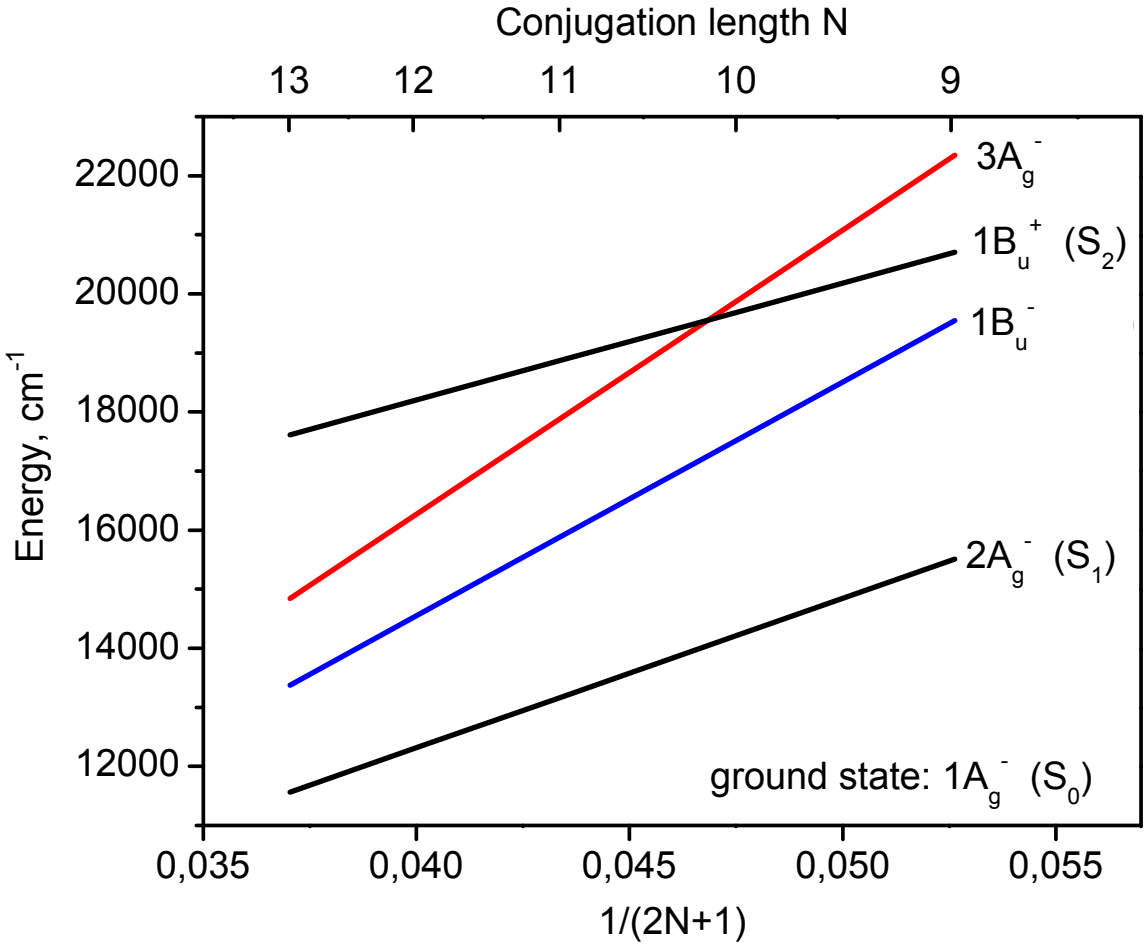
EET between non-degenerate states
→ Excess vibronic excitation: fs-ps

Classical 3-level Scheme



BUT, theory predicts other states between S_2-S_1!

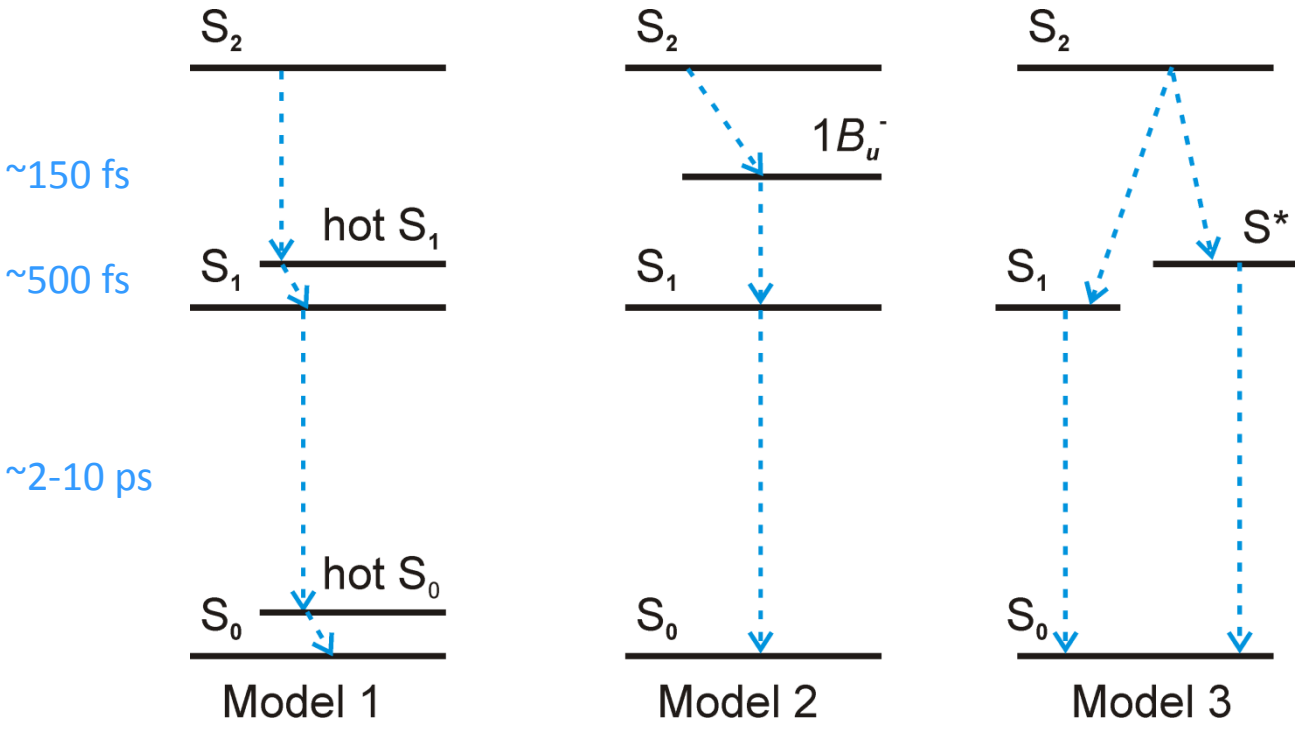
Predicted dark states



Theory: Tavan & Schulten, J. Chem. Phys. **85** (1986) 6602

Carotenoids in solution

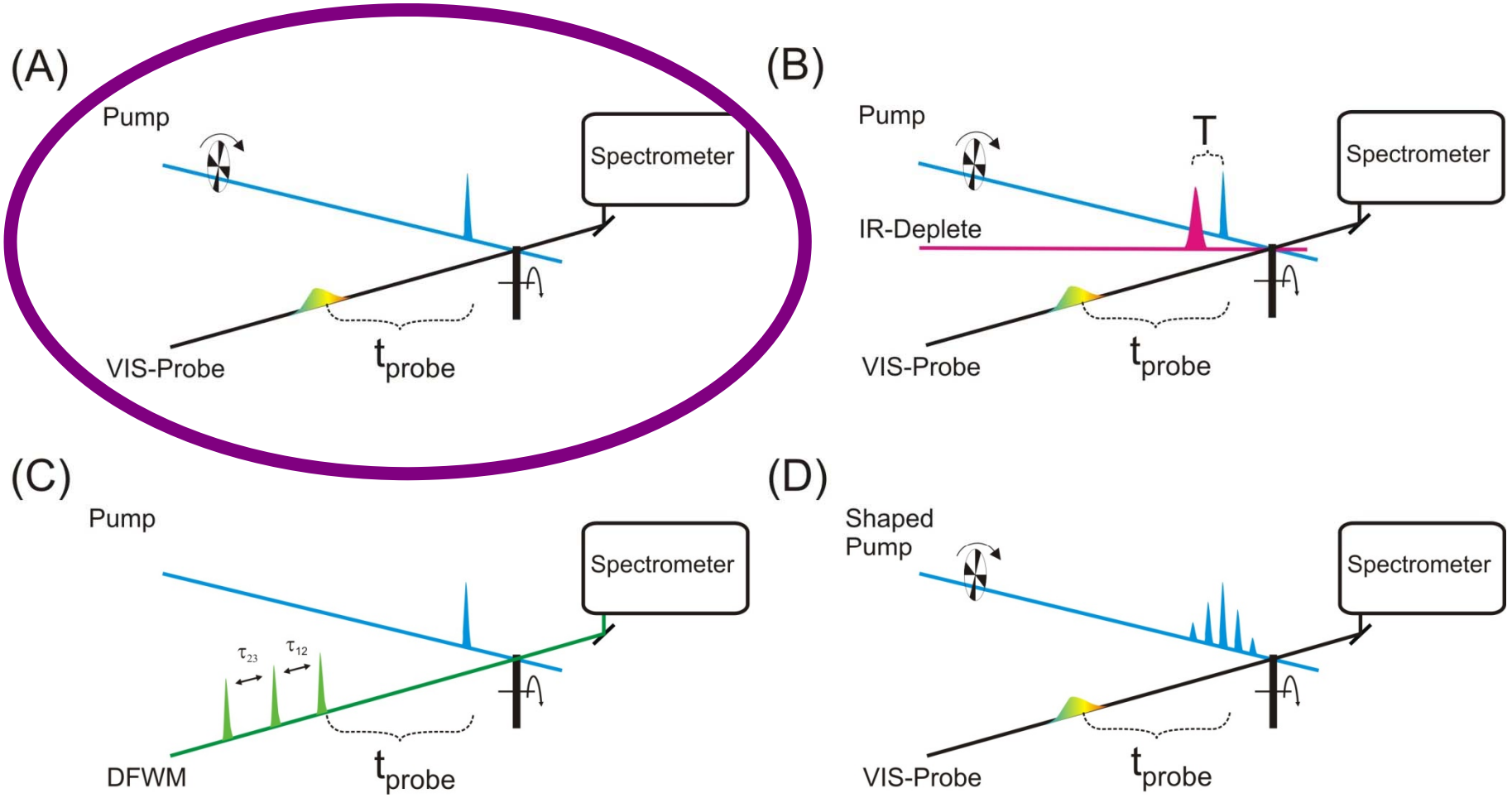
Three different models for relaxation:



Energy level diagram derived from *all-trans*-polyenes with C_{2h} symmetry.

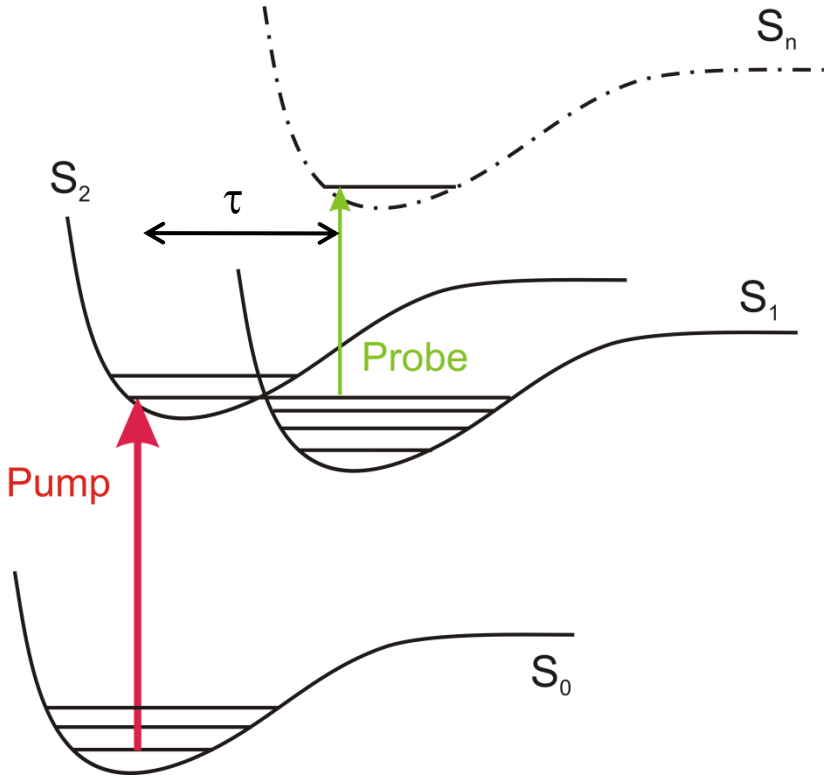
T. Polìvka, V. Sundström; Chem. Rev. ***2004****, 4, 2021*
T. Polìvka, V. Sundström; Chem. Phys. Lett. ***2009****, 477, 1*

Going beyond simple pump-probe: Complex excitation + complex probe

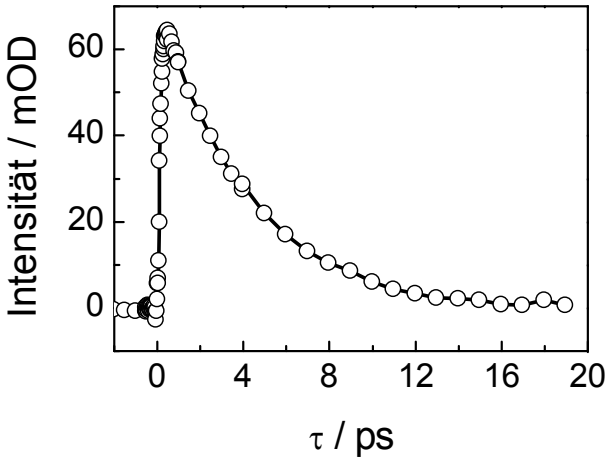


Dynamics in Carotenoids studied with transient absorption

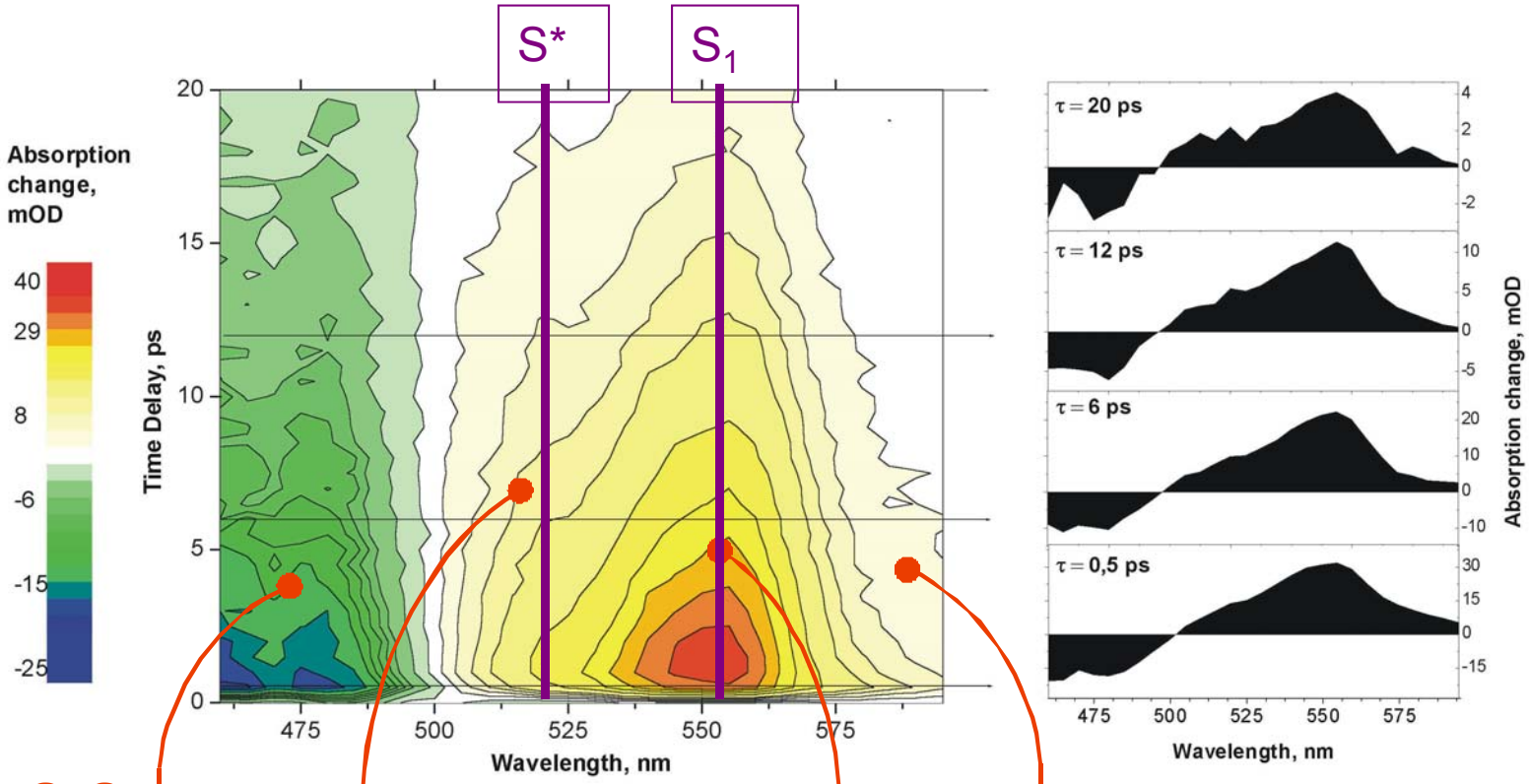
Pump excites S_2, Probe measures population of S_1



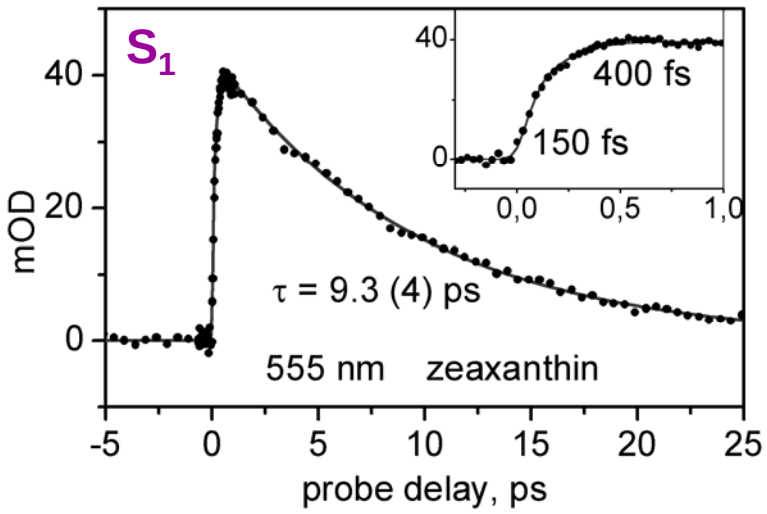
Signal (Lycopin):

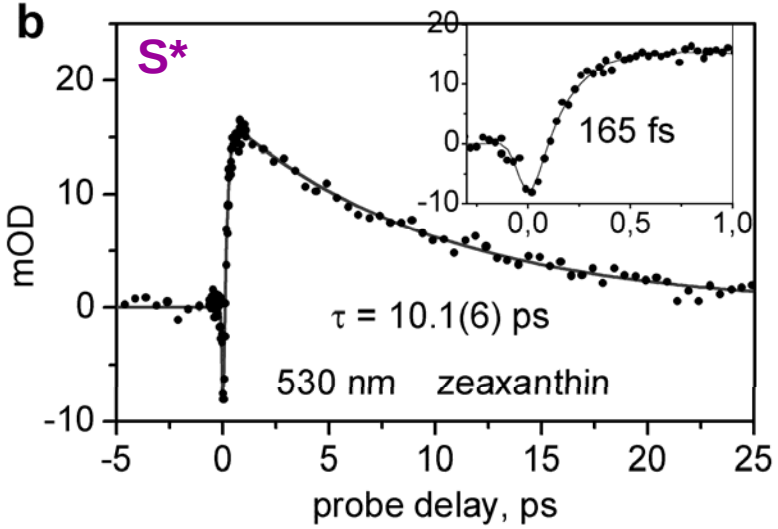


Transient absorption (Zeaxanthin)



Pump&Probe: kinetics traces





S* risetime is the lifetime of S_2 fluorescence!

Two Hypothesis:

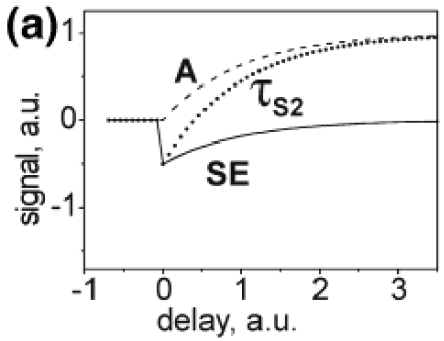
1. **S* does not rise instantaneously, i.e. it starts from S_2**

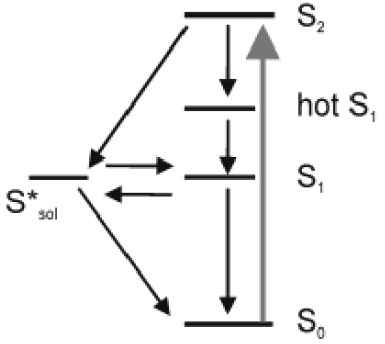
OR

2. **S* rises instantaneously,i.e. it doesn´t depend on the population of S_2**

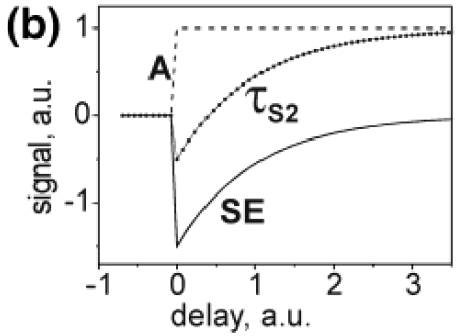
Study of dynamics in carotinoids with transient absorption

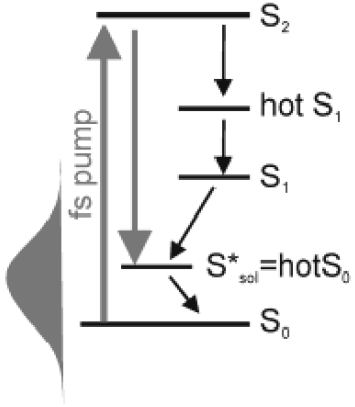
Two possible models which provide an explanation of additional signal:





- Transient absorption (A) increases with τ_{S2}.
- Stimulated emission (SE) decreases with τ_{S2} .



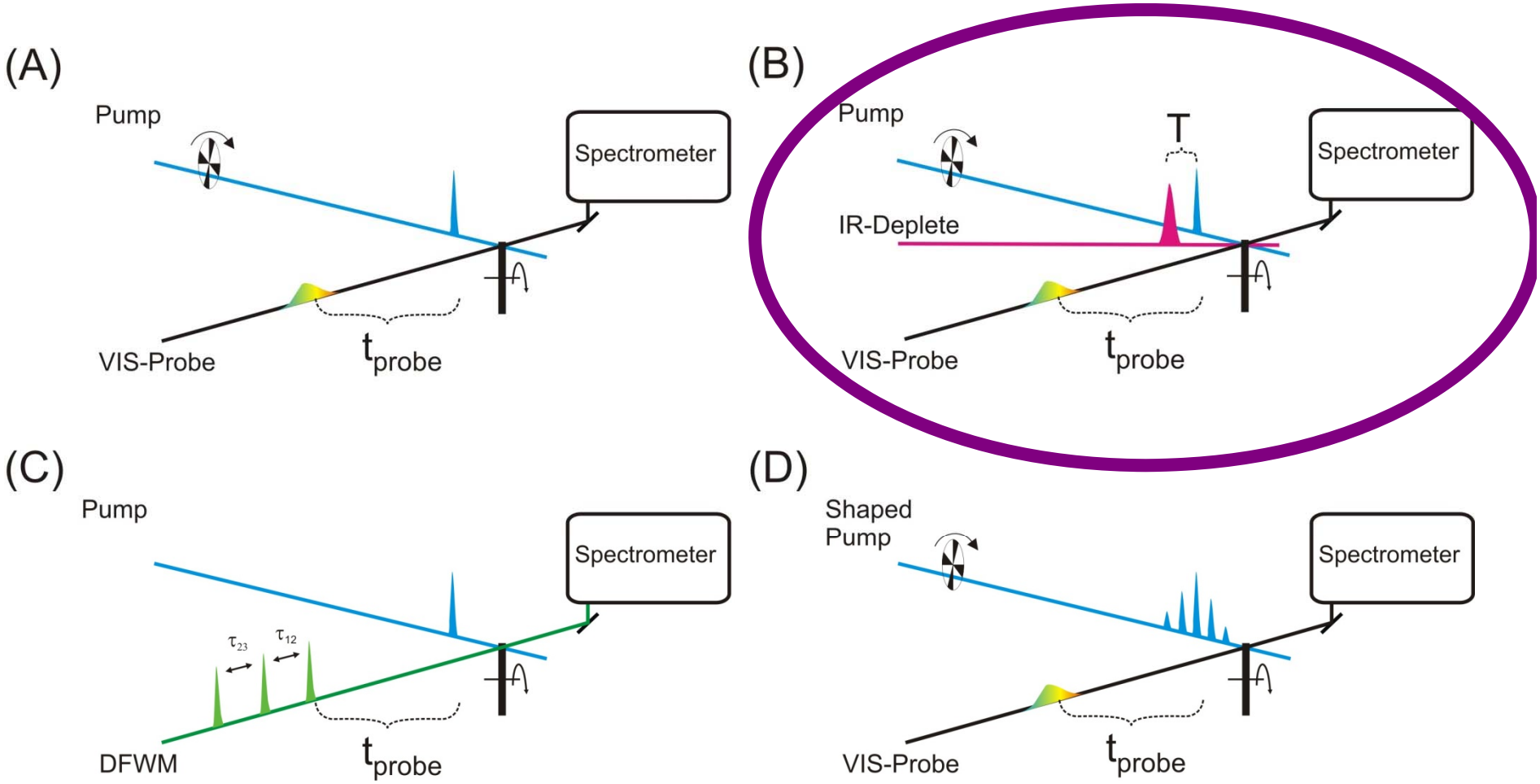


- Transient absorption (A) increases instantaneously.
- Stimuliert emission (SE) decreases with τ_{S2} ab.

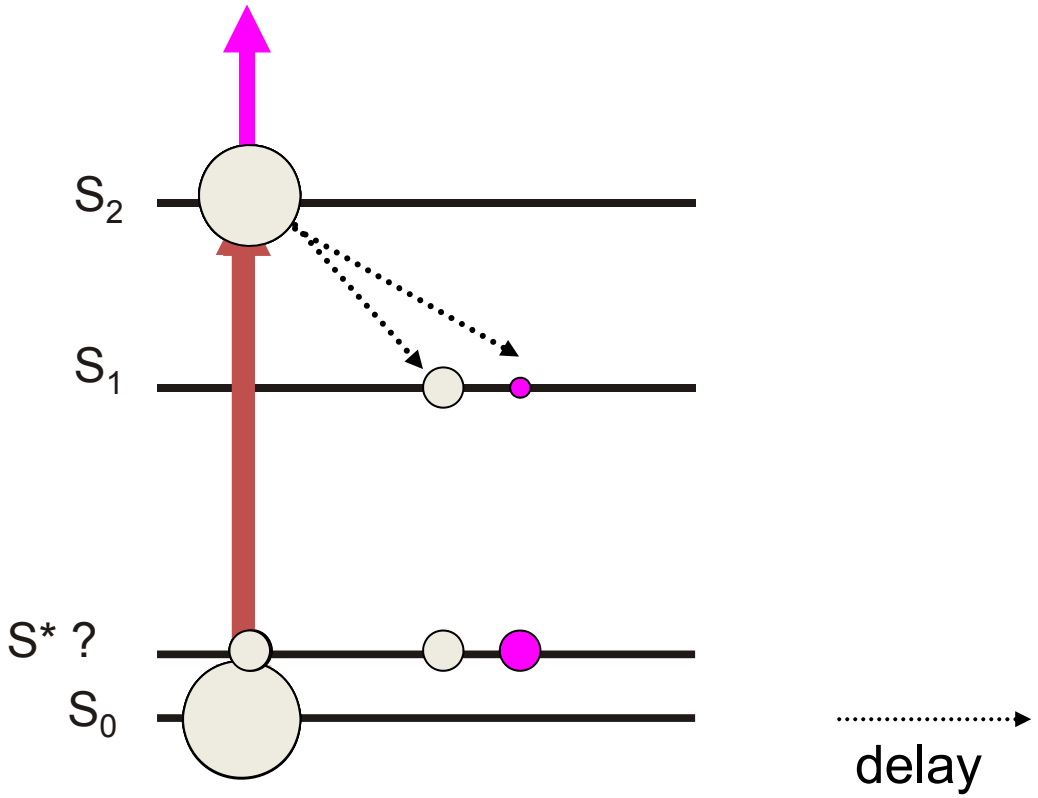
→ In both cases the sum of A und SE give rise to the same result!

W. Wohlleben; *J. Phys. Chem. B* **2004**, *108*, 3320.

Going beyond simple pump-probe: Complex excitation + complex probe



Pump-deplete-probe spectroscopy

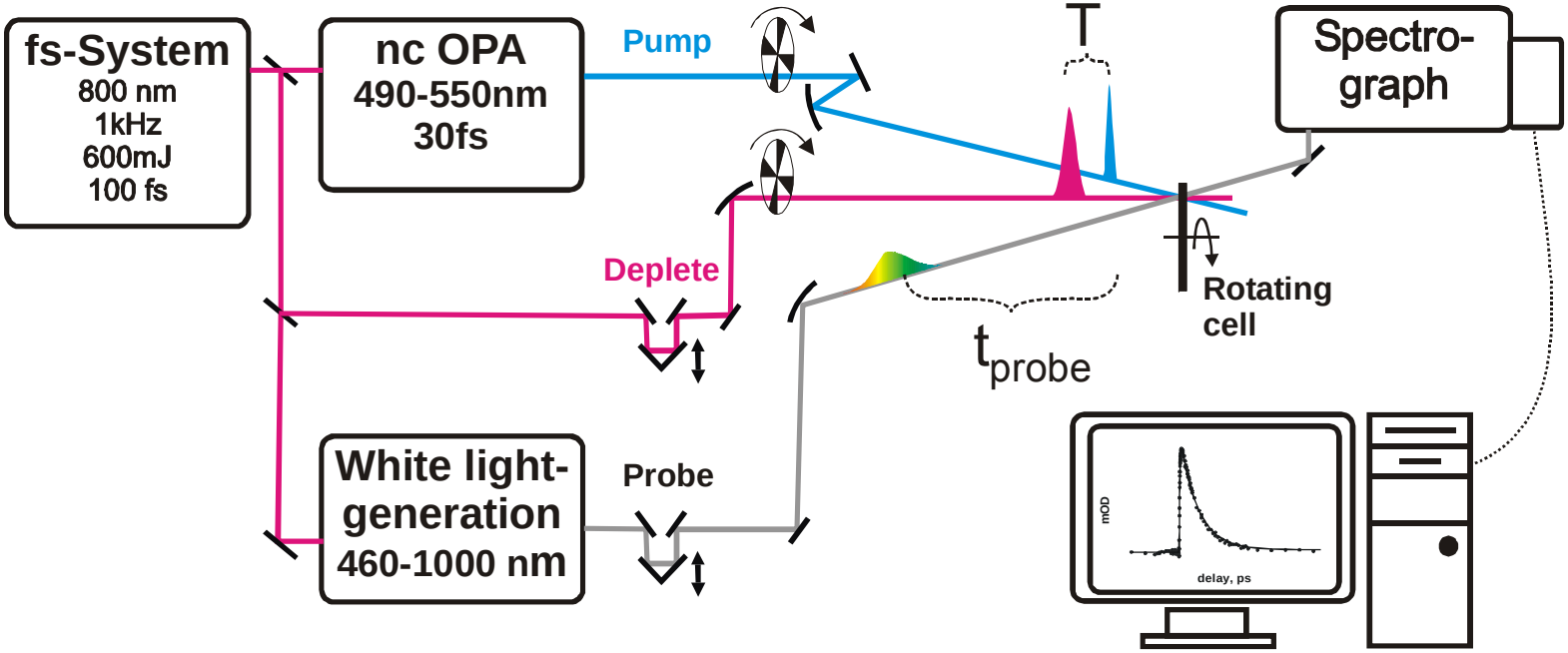


Pump ~490nm S_0-S_2

Deplete 800nm S_2 -S_n (T<200fs; Fujii, CPL 369 (2003) 165)

Probe S_0 bleach, S* and S_1 absorption ⟶ correlation with S_2 ?

Pump-deplete-probe setup

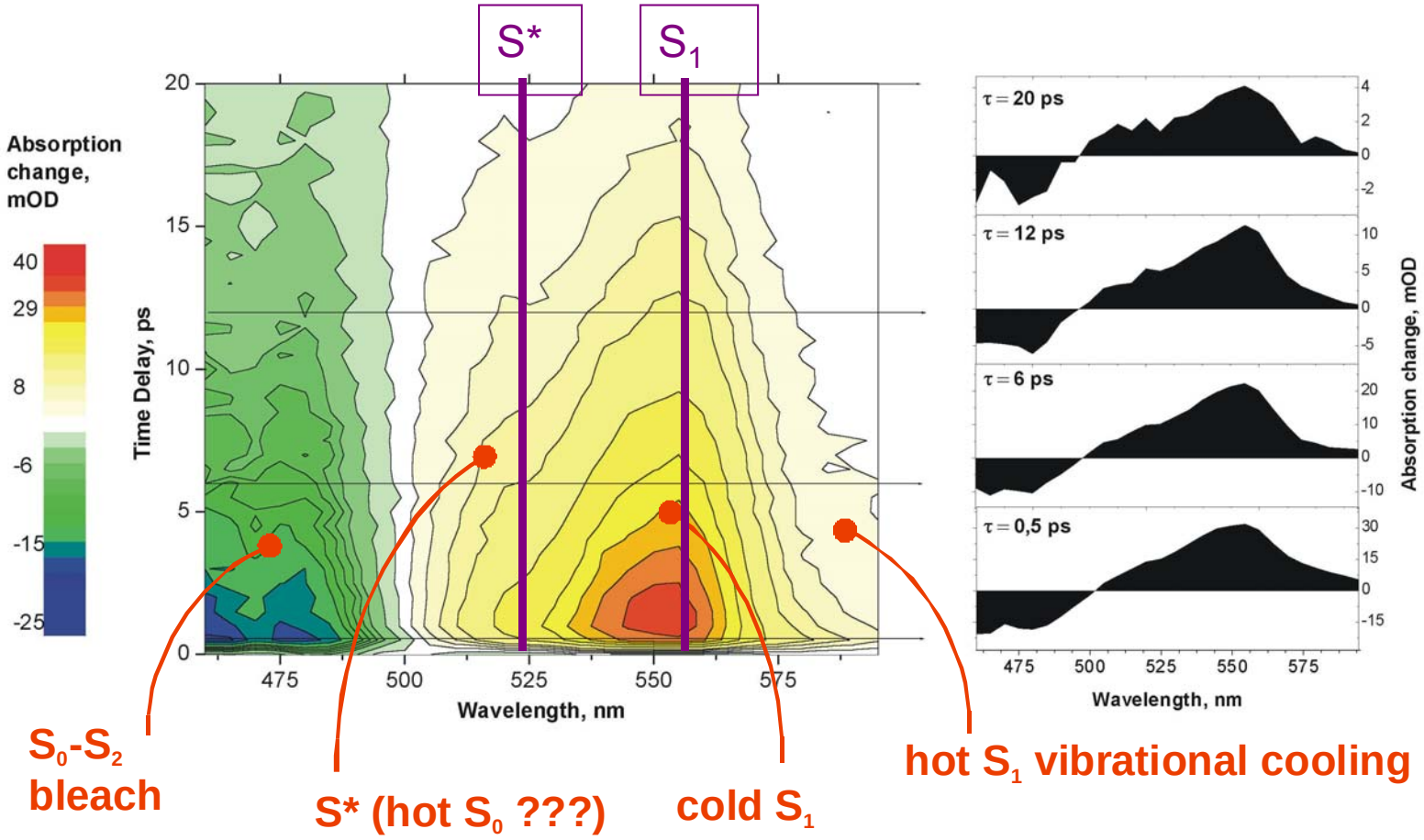


Pump

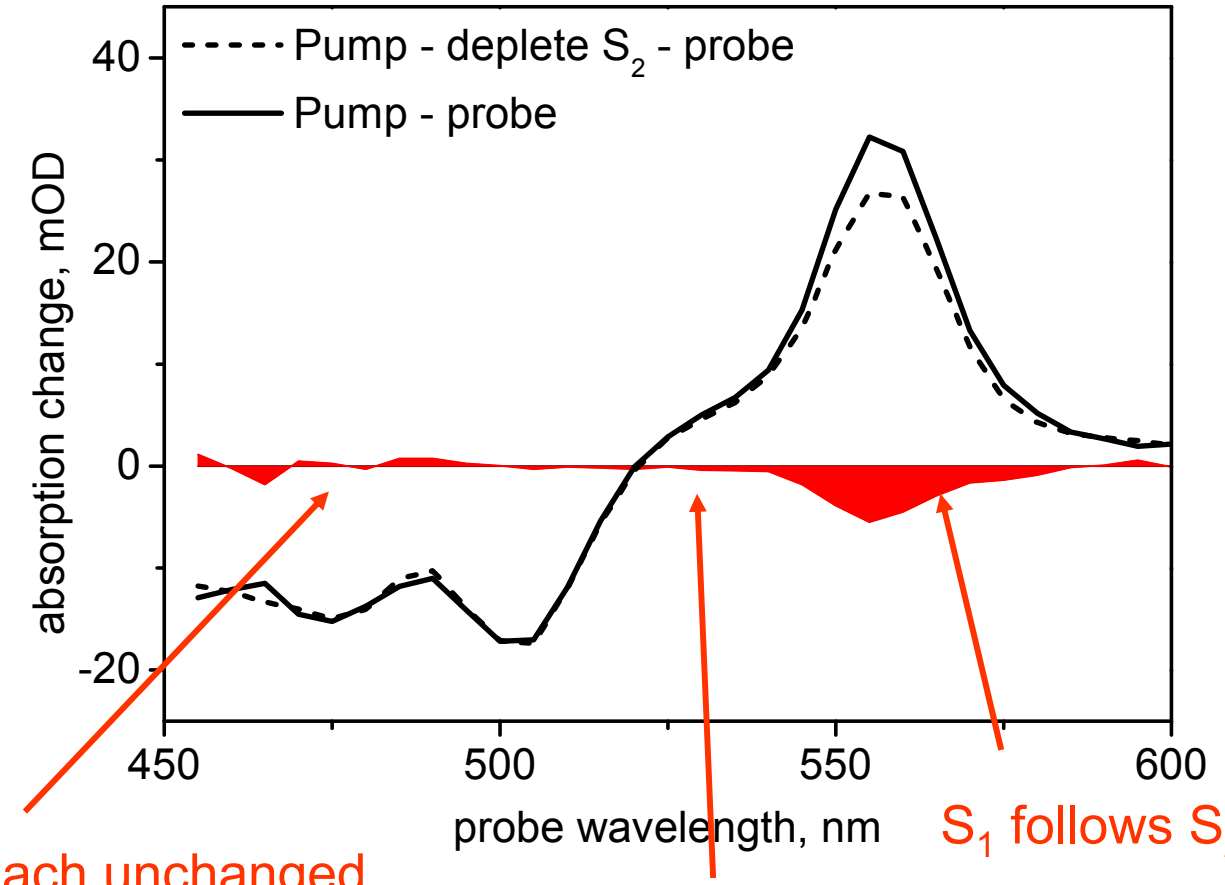
Deplete excited state

Probe manipulated absorption spectra

Transient absorption (reminder)



Pump-deplete-probe spectra (lycopene)



S_0-S_2 bleach unchanged

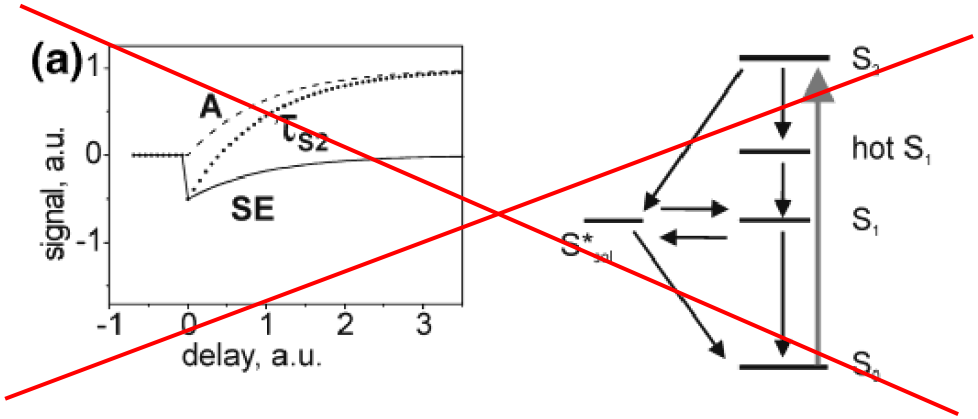
S_1 follows S_2 population

S* signal independent of S_2 population
Confirms assumed IRS mechanism!

J. Phys. Chem. B **108**, 3320 (2004)

Study of dynamics in carotinoids with transient absorption

Two possible models which provide an explanation of additional signal:



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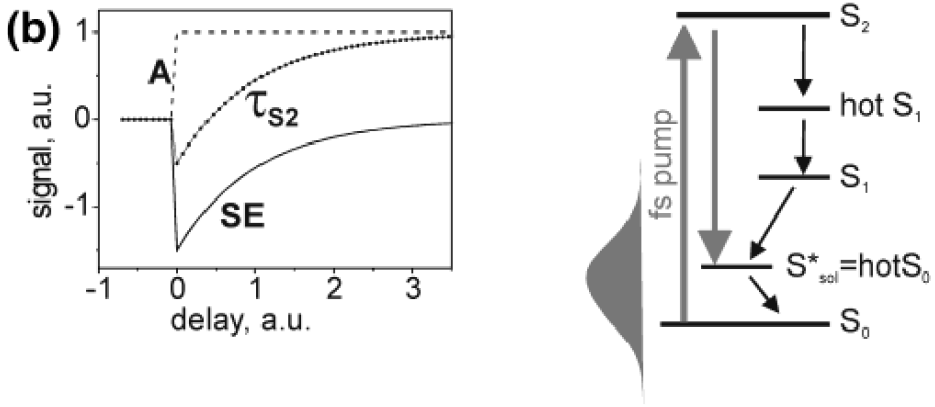

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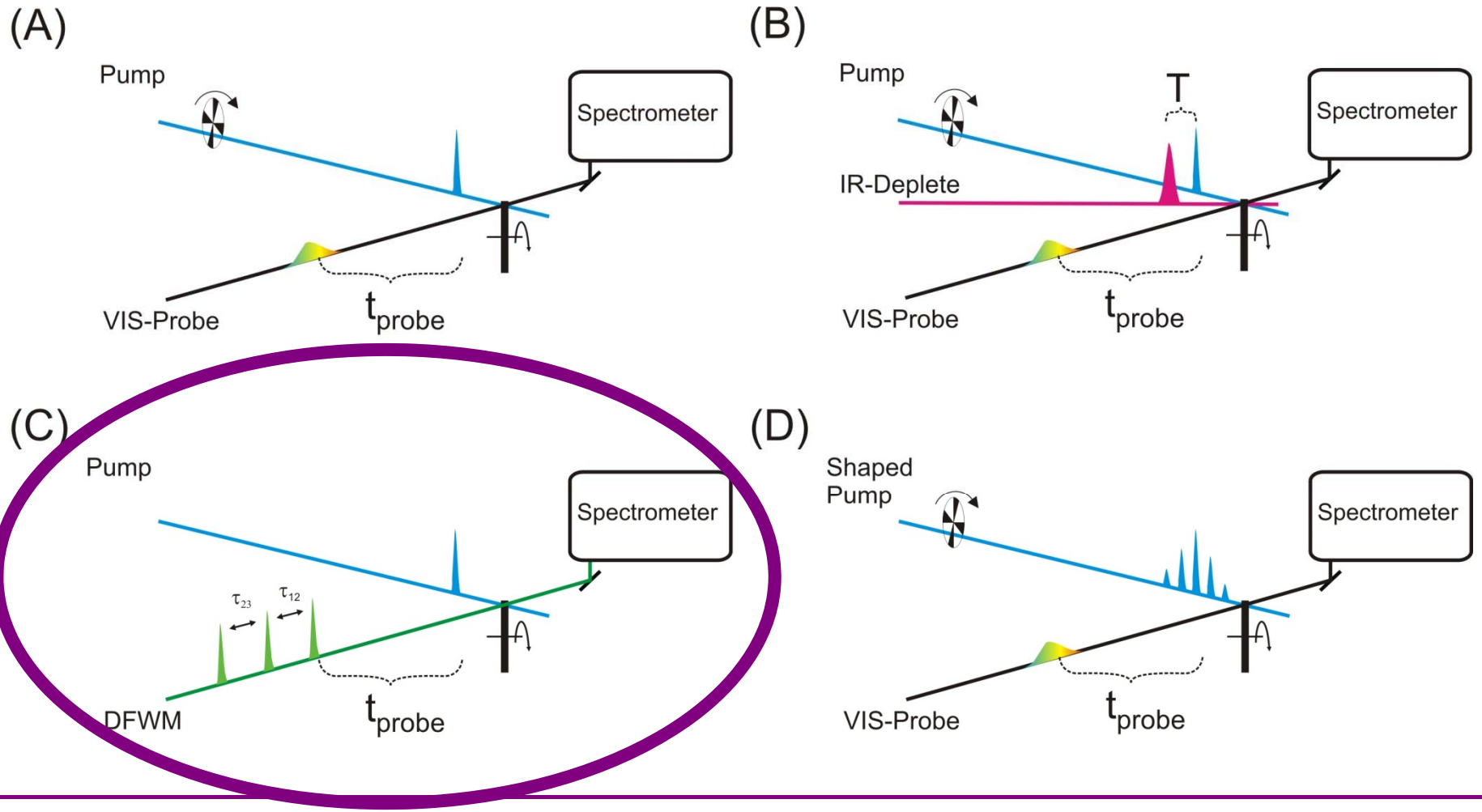
W. Wohlleben; *J. Phys. Chem. B* **2004**, *108*, 3320.

Going beyond simple pump-probe: Complex excitation + complex probe



Excitation with several pulses (E-Fields):

Nonlinear Interaction

$$\vec{P} = \varepsilon_0 \cdot \left(\chi^{(1)} \cdot \vec{E} + \chi^{(2)} \cdot \vec{E}\vec{E} + \chi^{(3)} \cdot \vec{E}\vec{E}\vec{E} + \ldots \right)$$

Rayleigh-, Raman-scattering	Frequency Mixing SHG, DFG,… 2ω, ω_1-ω_2,…	Four-Wave- Mixing CARS, DFWM, 3ω, …

→ in media with inversion symmetry: $\chi^{(2)}=0$

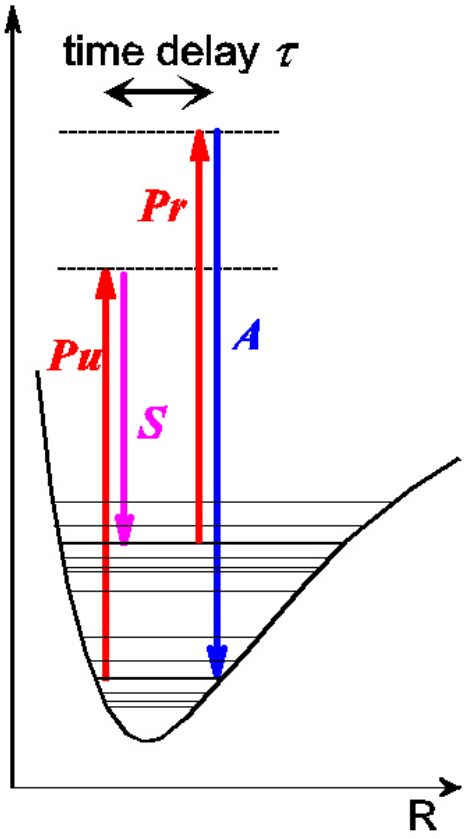
→ first non-linear term in gases and liquids: $\chi^{(3)}$

→ two conditions important:

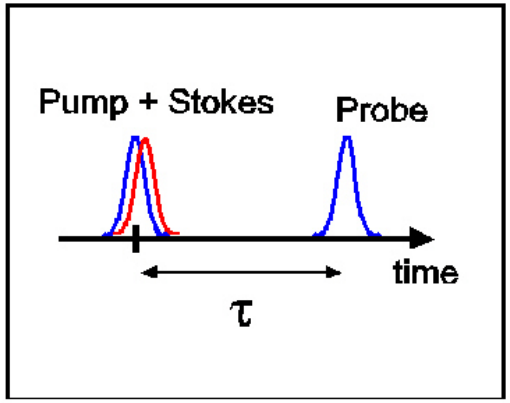
Conservation of energy and momentum

Time-resolved four-wave-mixing

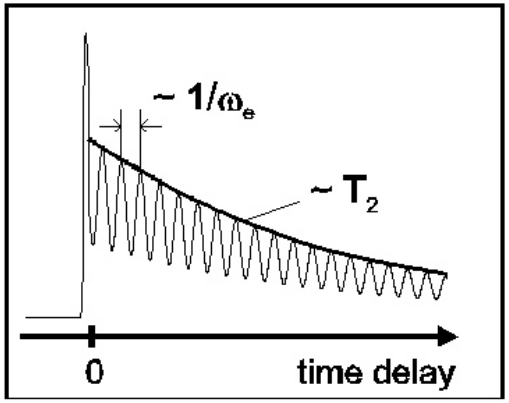
energy scheme



pulse sequence



FWM transient



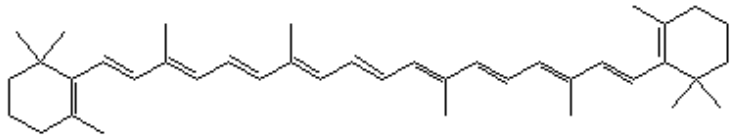
- four-wave-mixing signal

$$I_{\mathrm{FWM}} \sim \int dt \left| P^{(3)}(t) \right|^2$$

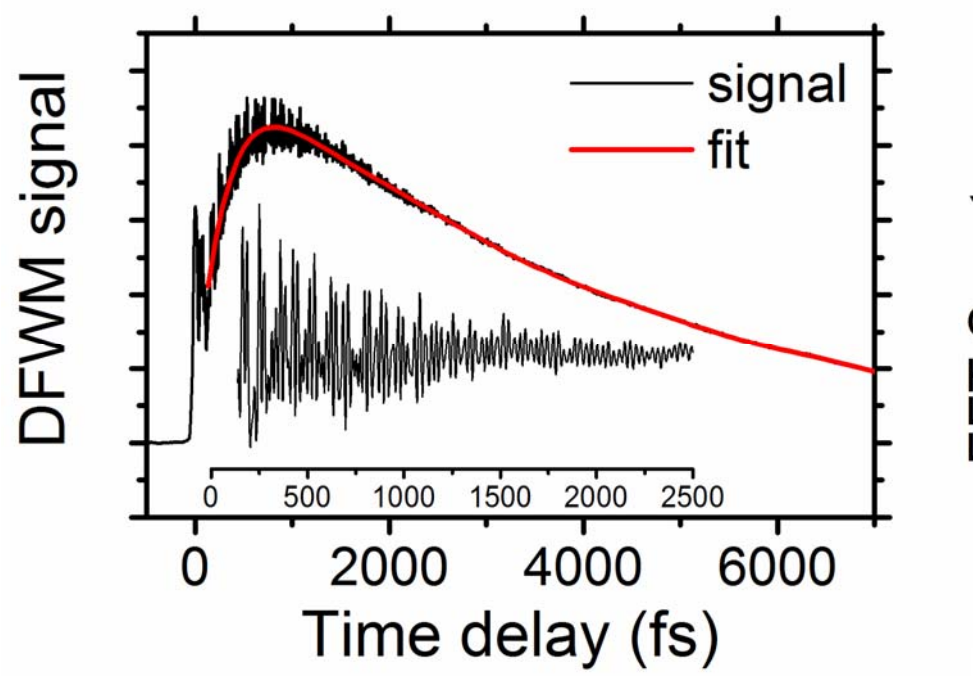
- third order nonlinear polarization

$$P_{\tau}^{(3)}(t) = E_P(t) \cdot \int_{-\infty}^{+\infty} E_L(t-\tau) E_S^*(t-\tau) \cdot R(t) dt$$

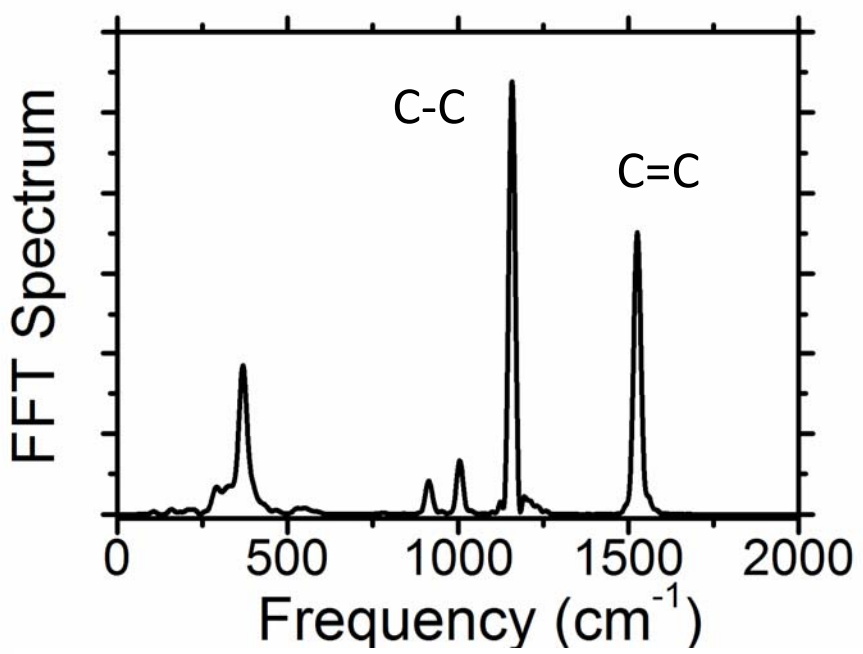
Wavepackets in β–Carotene



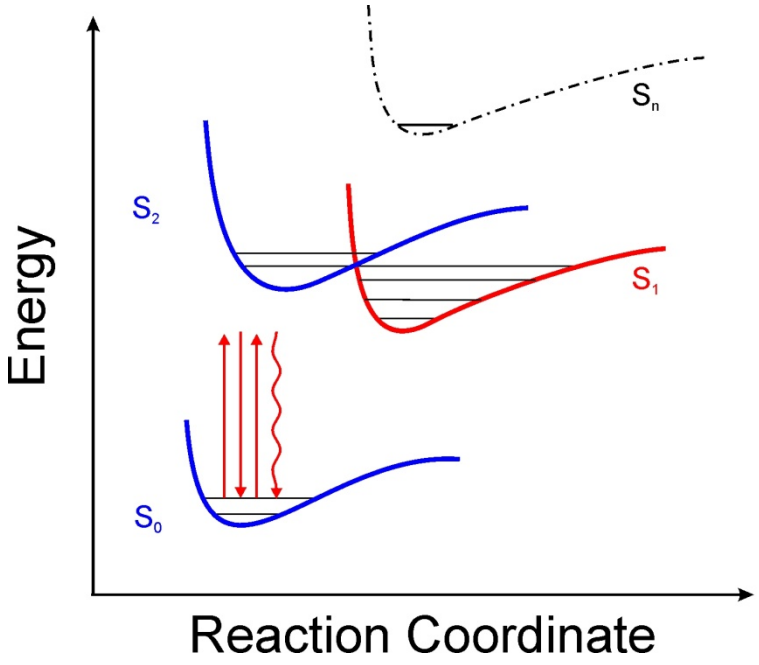
Transient



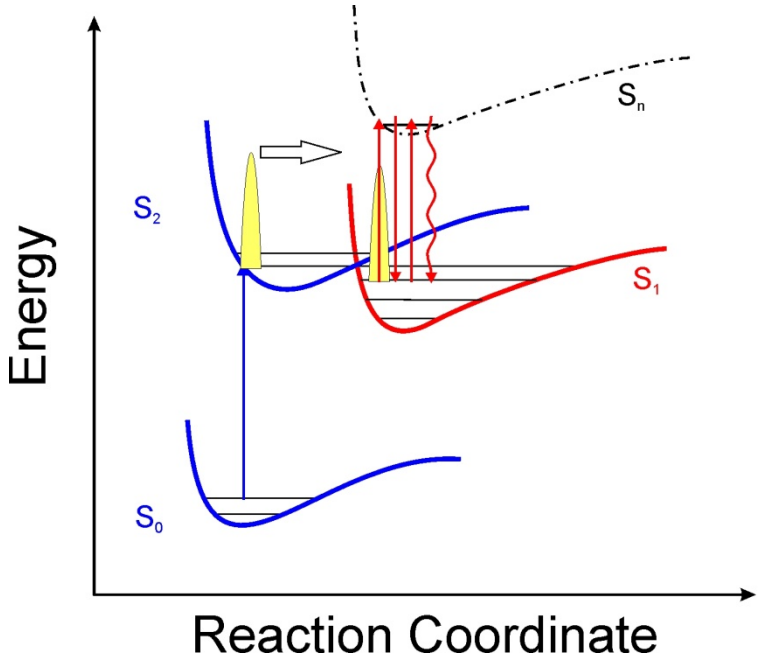
FFT spectrum



Excited State Dynamics Investigated by Pump-DFWM

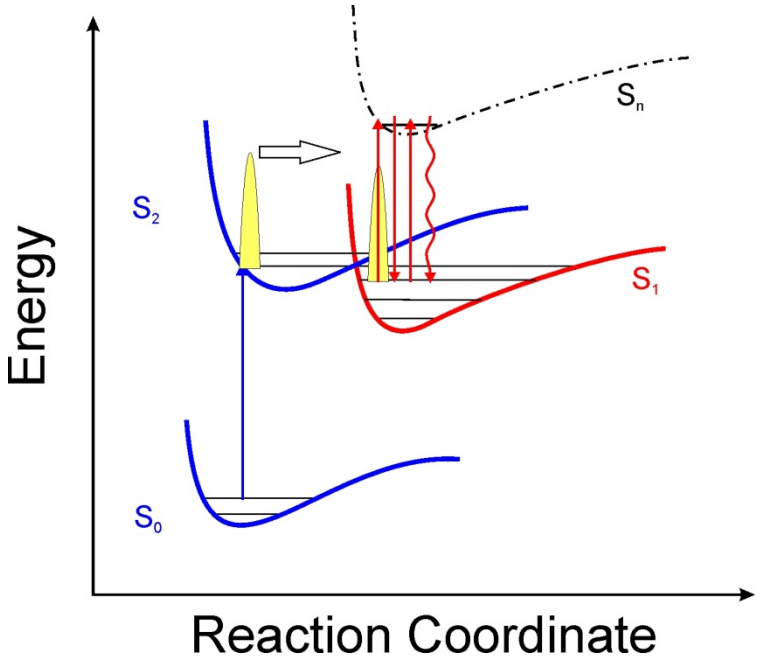


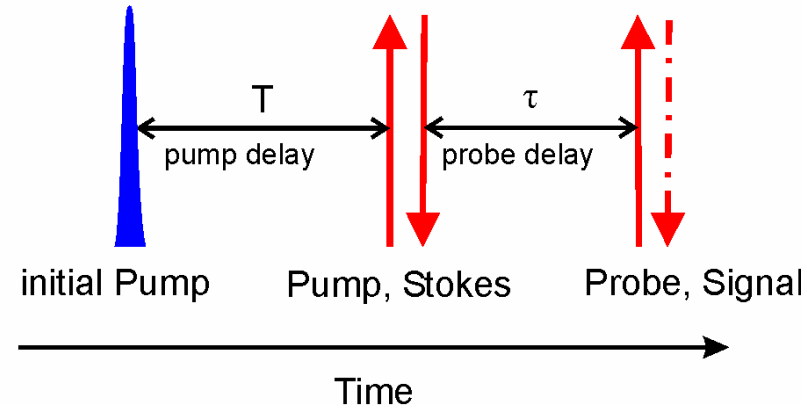
Weak non-resonant signal



Strong resonant signal

Excited State Dynamics Investigated by Pump-DFWM



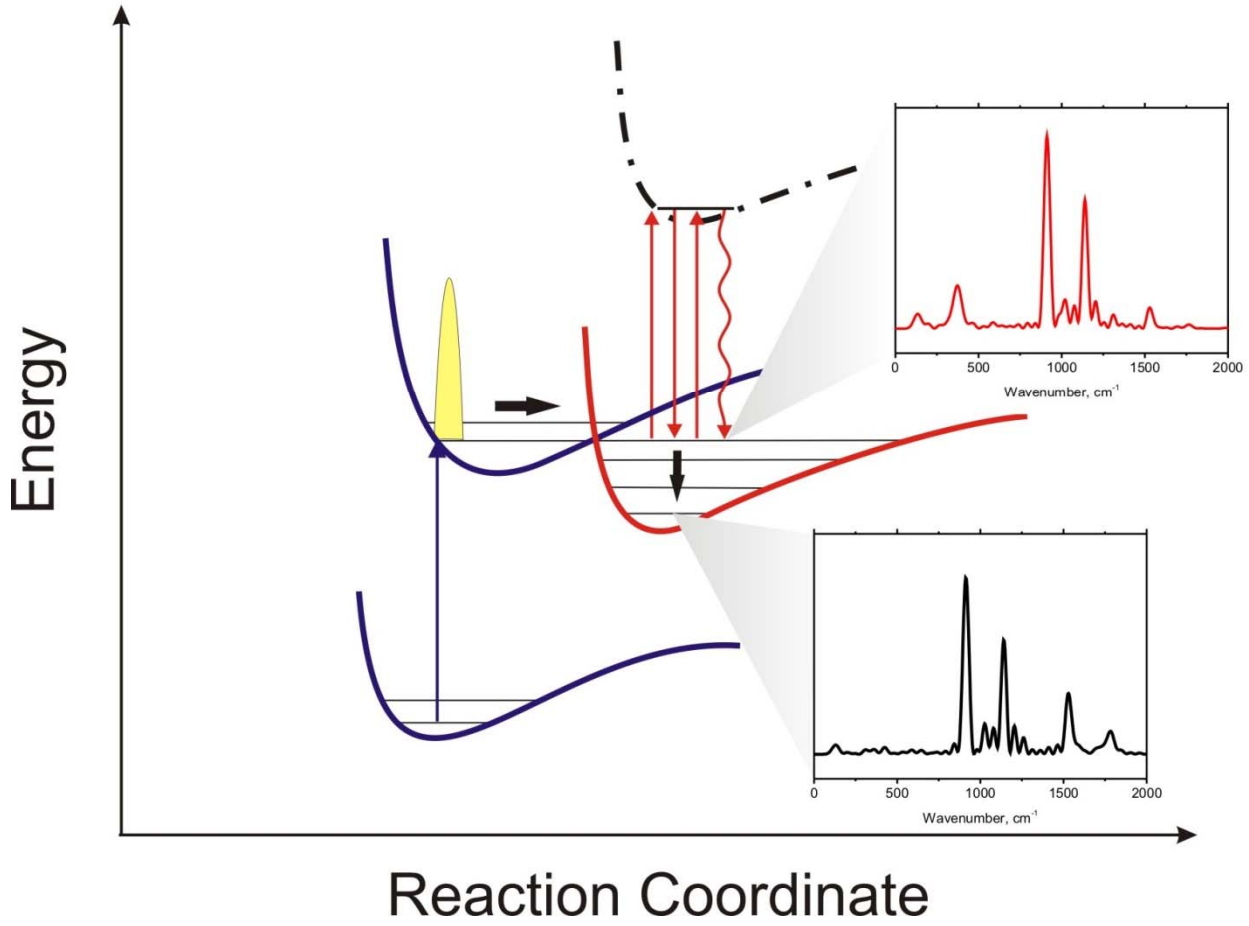


- Pump and Stokes arrive simultaneously
- Transients in τ at different values of T

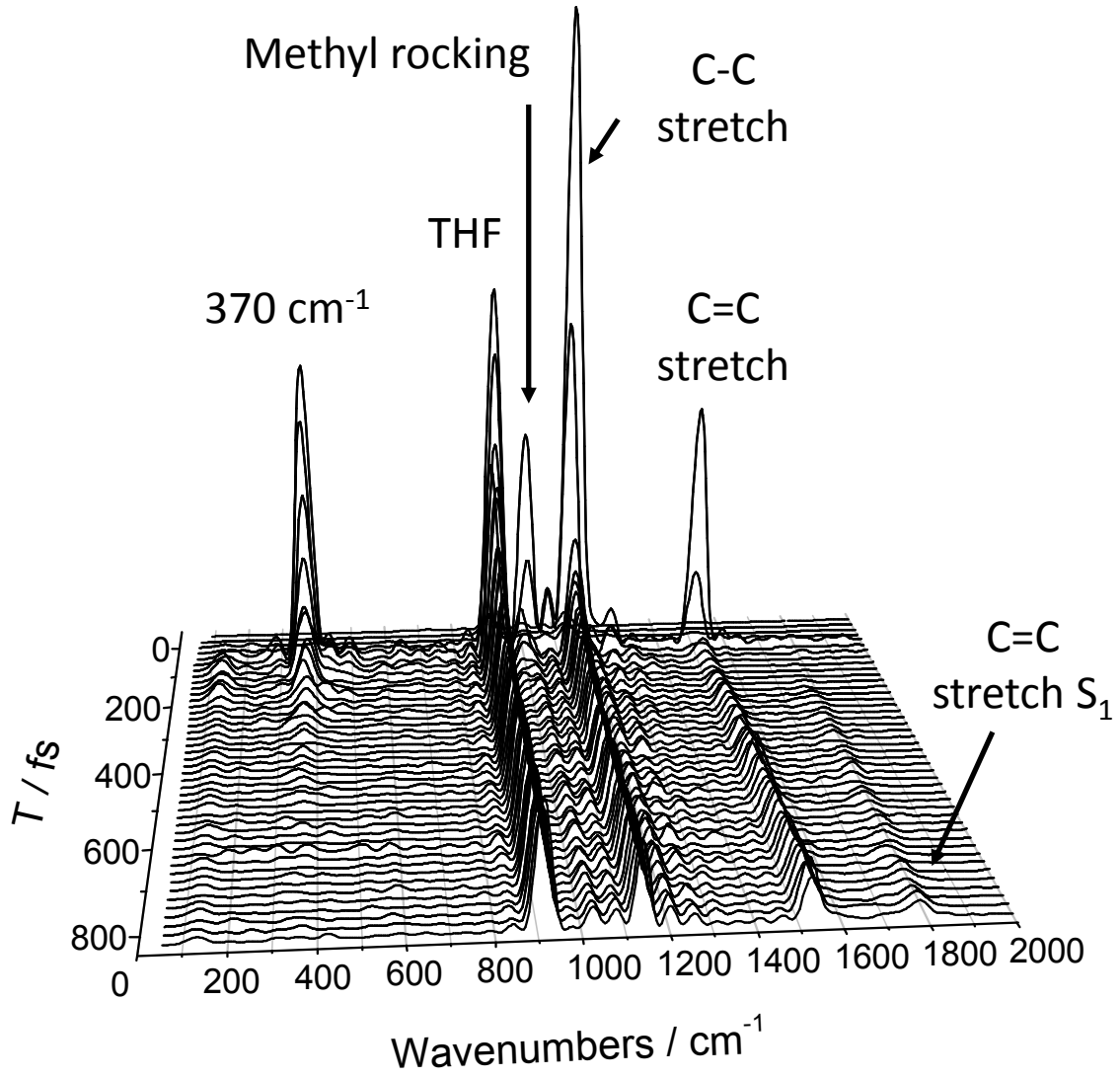
J Phys Chem A ***111*** *(2007) 10517*
Chem Phys Lett ***402*** *(2005) 283*
J Phys Chem ***100*** *(1996) 5620*

Namboodiri et al Laser Phys ***19*** *(2009) 154*
Fujiyoshi et al JPCA ***108*** *(2004) 11165*
Oberle et al CPL ***241*** *(1995) 281*

Probing vibrational dynamics in real-time

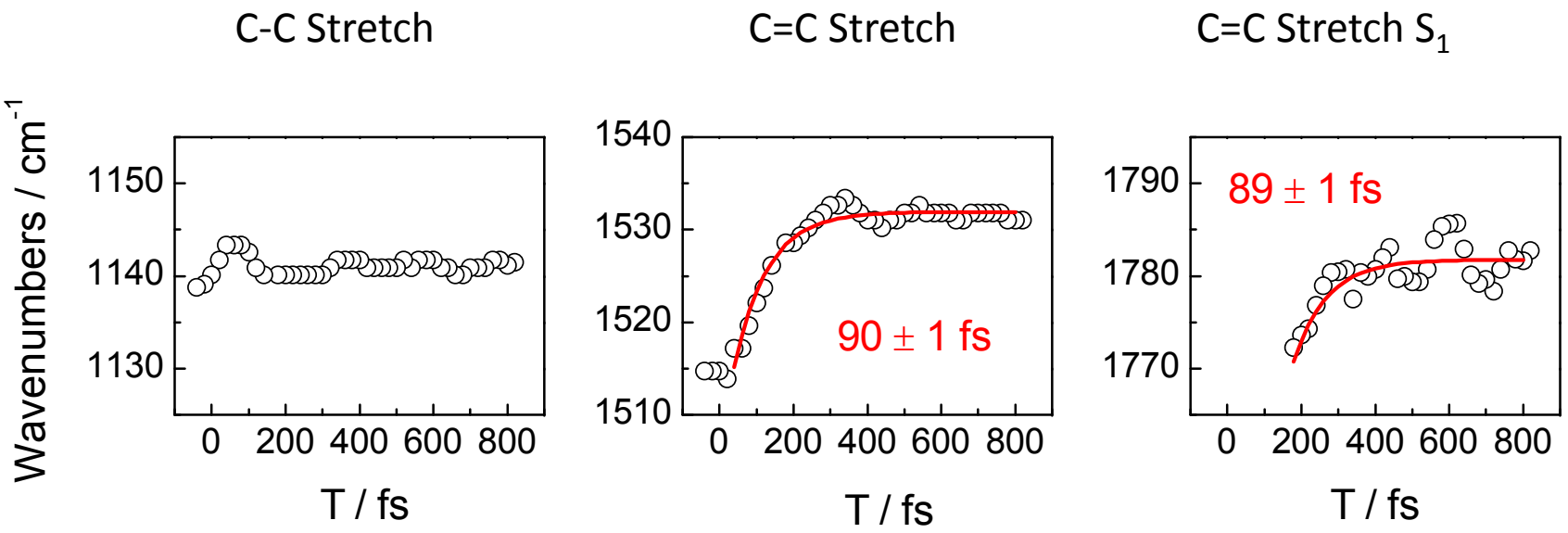


Dynamics of Vibrational Modes

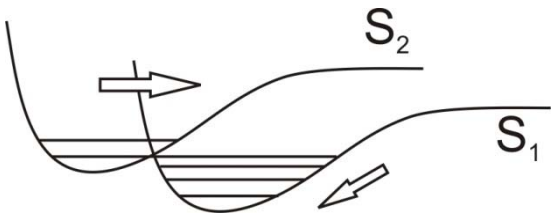


J. Phys. Chem. B ***115*** *(2011) 8328*

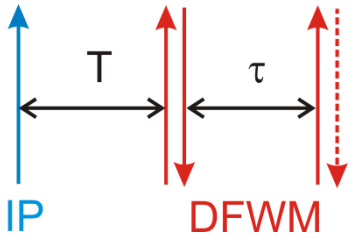
Shift of Vibrational Frequencies



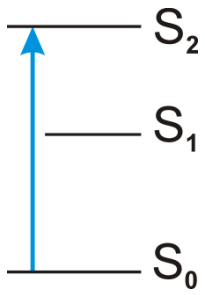
- C=C modes are coupled stronger than C-C mode.
- Intra- /intermolecular energy distribution 90 fs.
- Absence of evolution for the C-C mode.



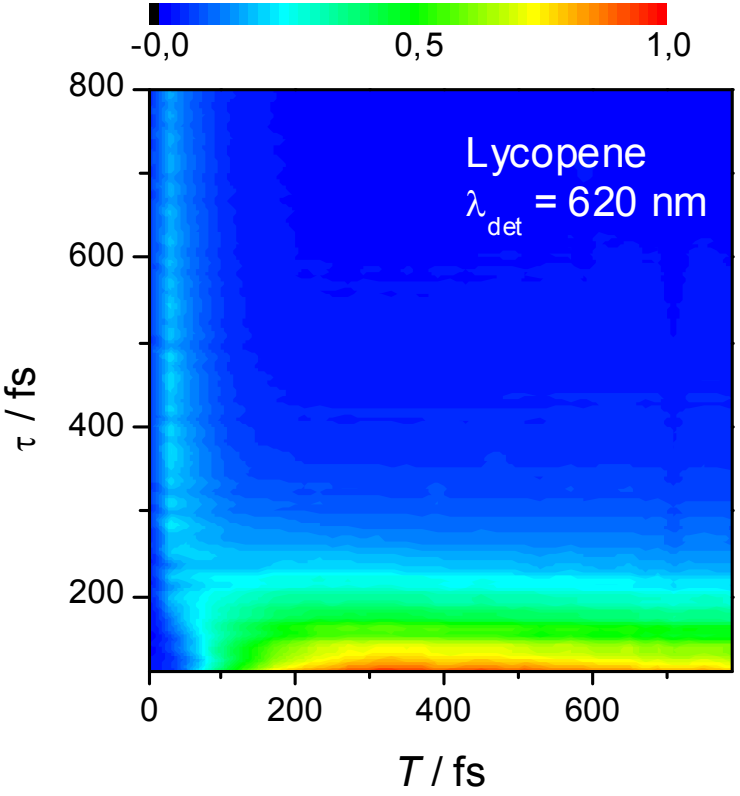
Arch. Biochem. Biophys. **483** (2009) 219.



Lycopene's pump-DFWM signal

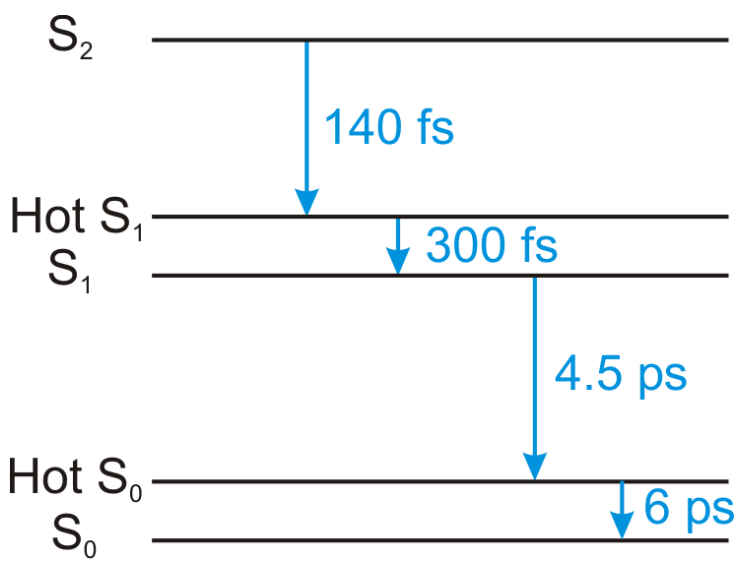


Experimental *T* vs. τ Scan

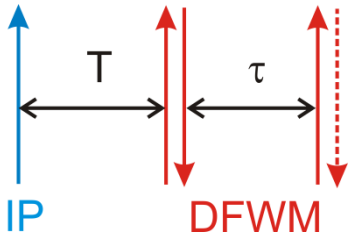


Simulation of the pump-DFWM signal

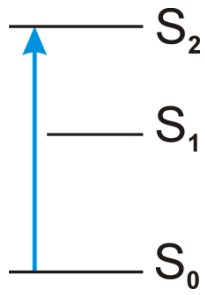
- Pump-DFWM = DFWM on excited state.
- Initial pump: 10% population into S_2, 1% population into hot S_0.
- Simulation of DFWM signal based on Brownian oscillator model.[1]
- Rate model:



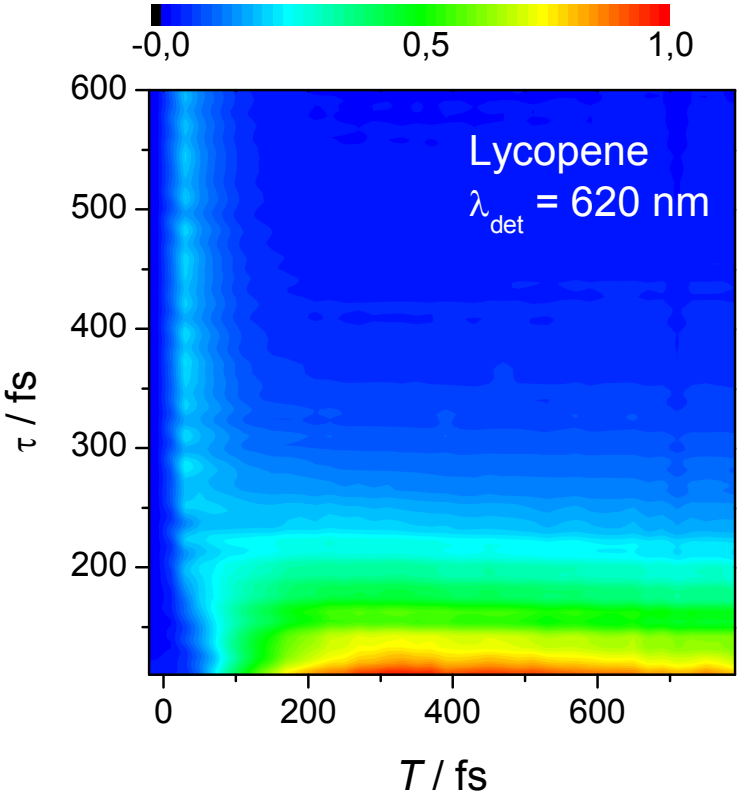
[1]S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995)



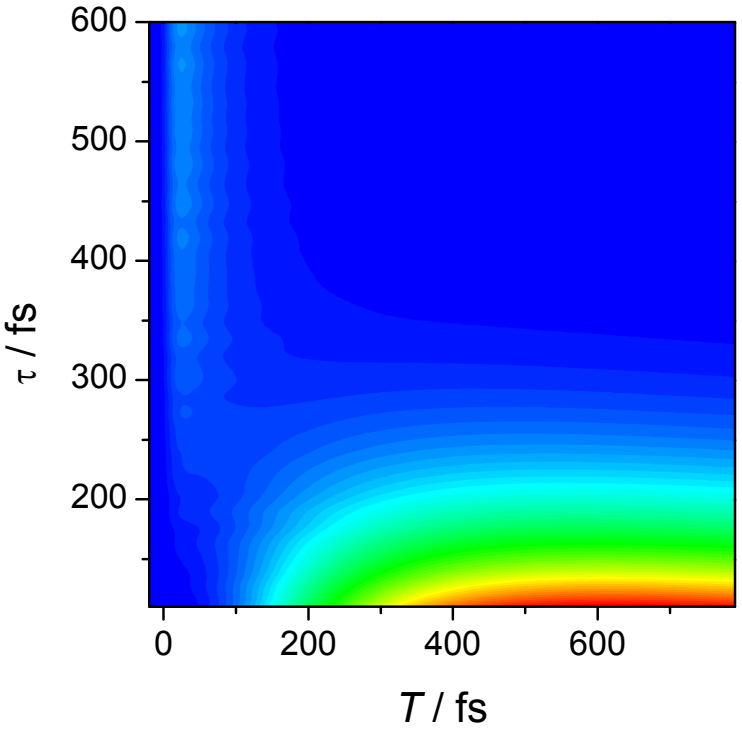
Lycopene's pump-DFWM signal



Experimental *T* vs. τ Scan



Simulation with real pulse duration



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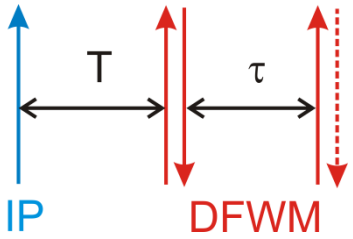

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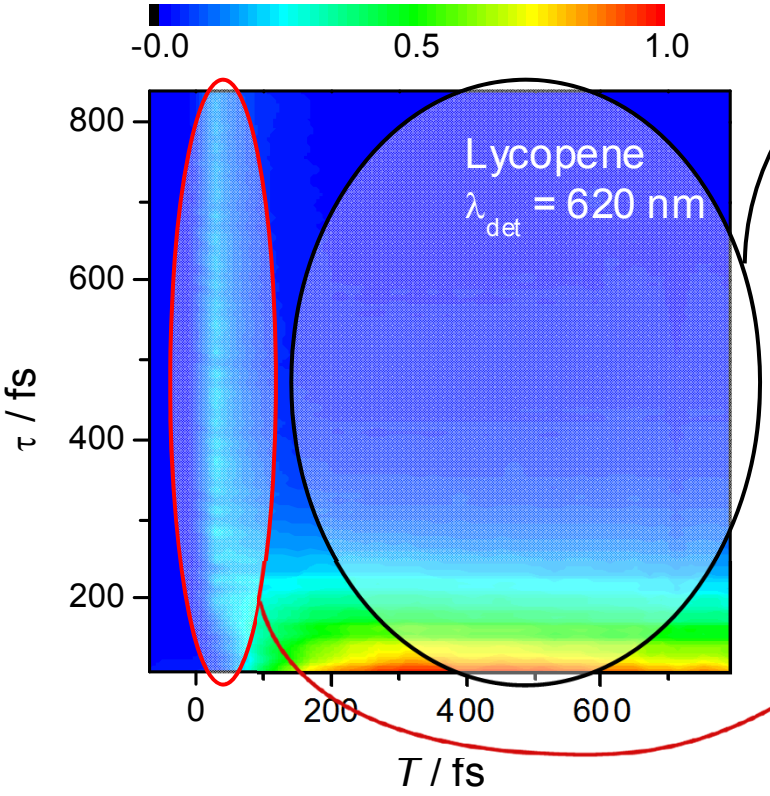
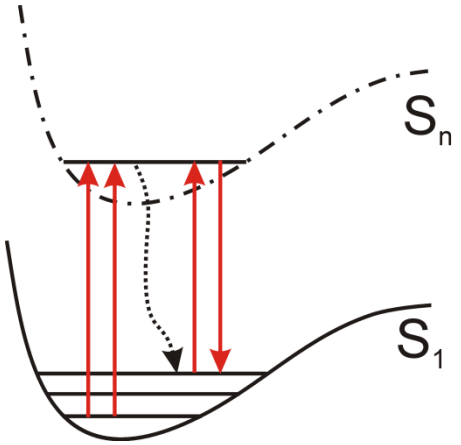
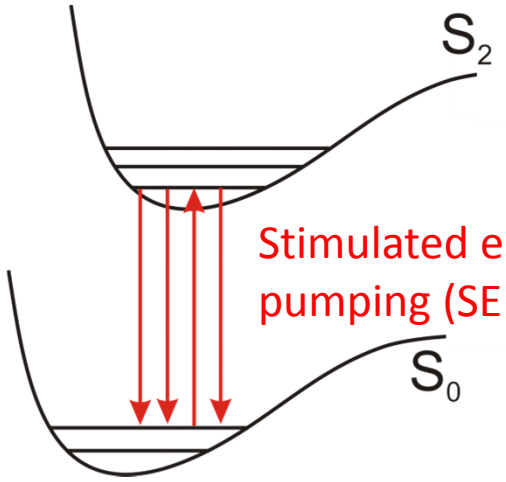




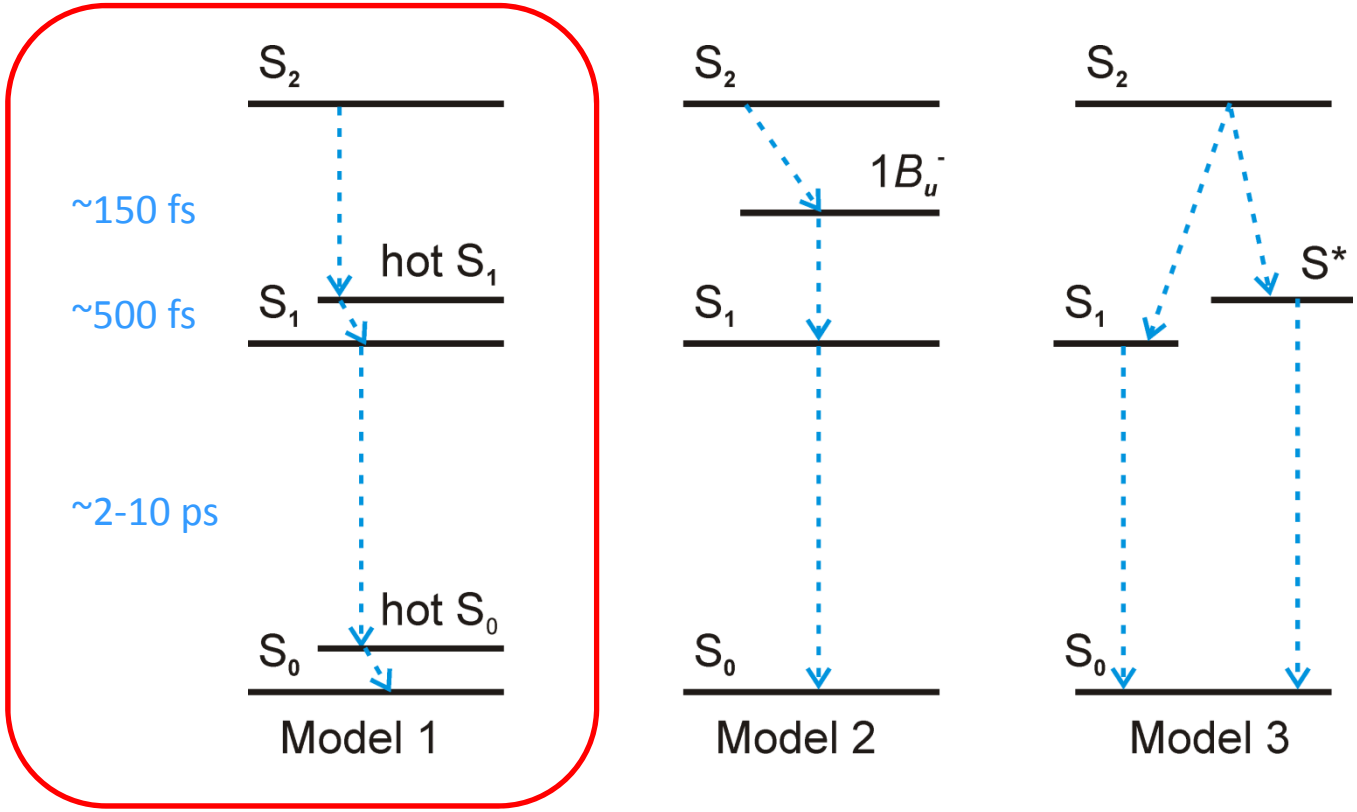
Vibrational cooling



Stimulated emission pumping (SEP) DFWM

Carotenoids in solution

Three different models for relaxation:

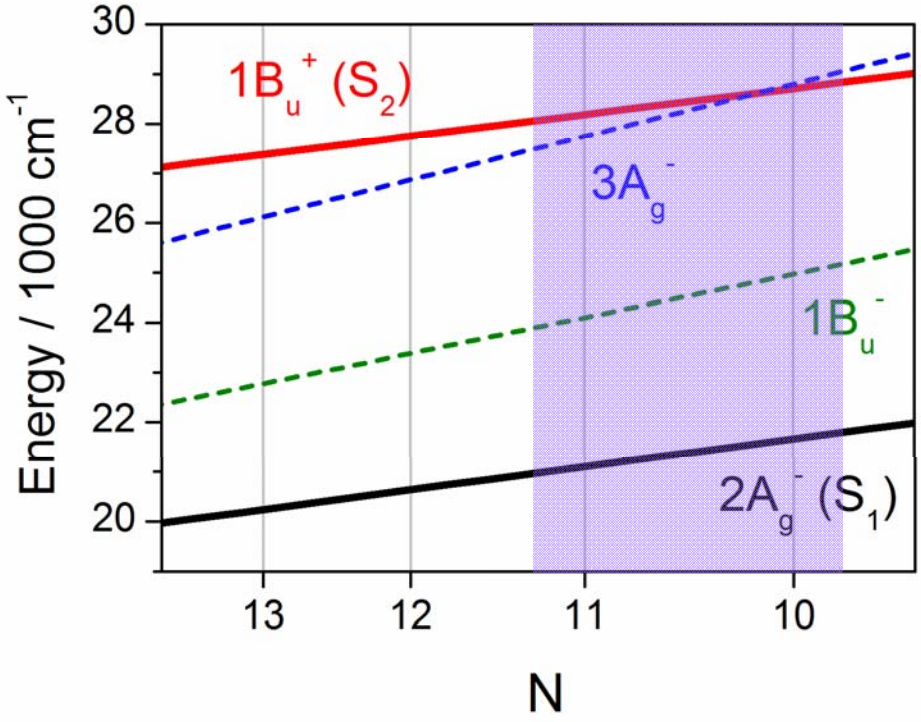


Energy level diagram derived from *all-trans*-polyenes with C_{2h} symmetry.

T. Polìvka, V. Sundström; *Chem. Rev.* **2004**, *4*, 2021.

Energy levels

Excited state energies are dependent on conjugation length N



Interesting region:

- Crossing between states
- Spectral region accessible with fs-pulses

P. Tavan and K. Schulten *J. Chem. Phys*. **1986**, *85*, 6602.

Energy levels

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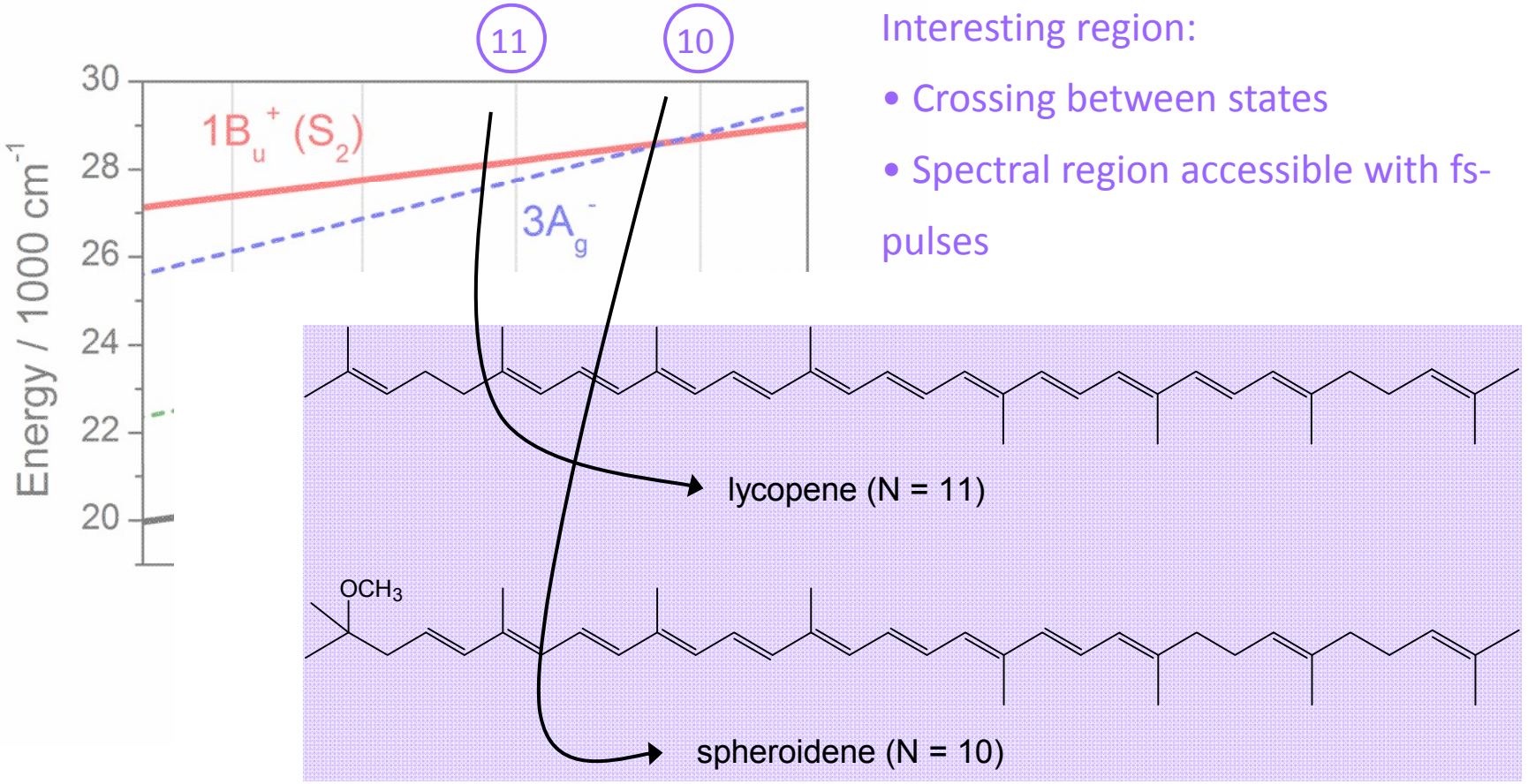
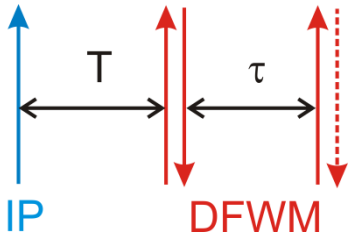
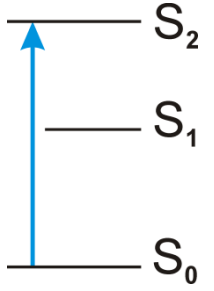


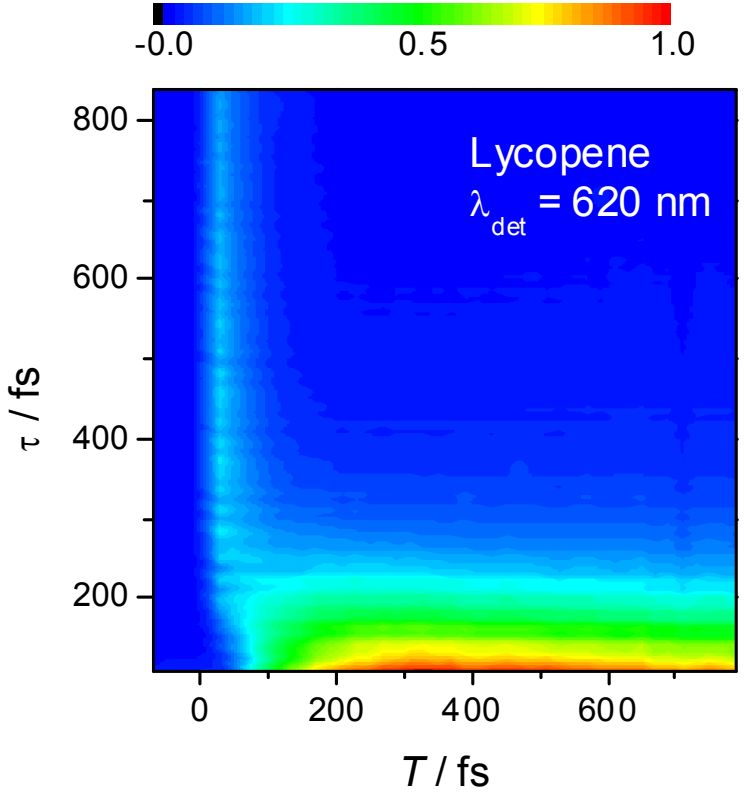
Interesting region:

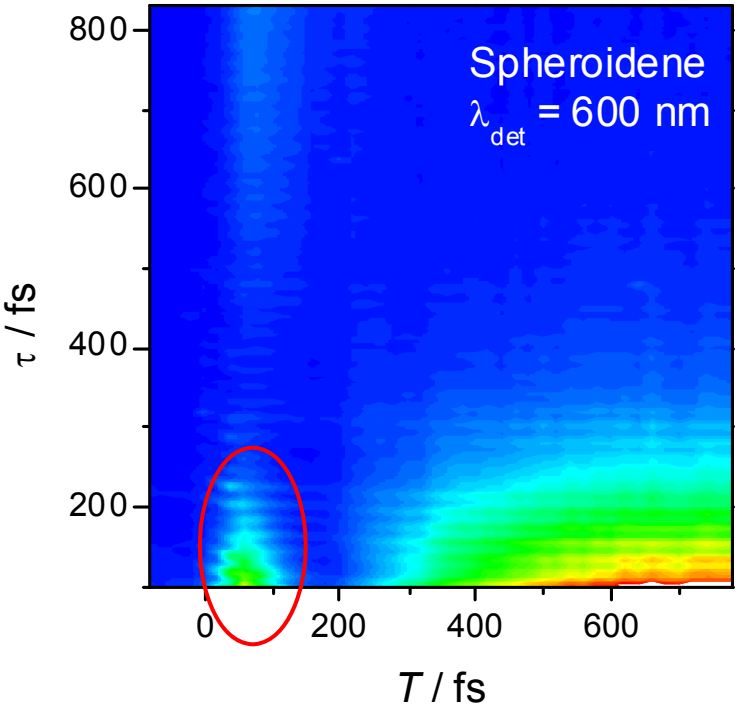
- Crossing between states
- Spectral region accessible with fs-pulses

Lycopene vs. Spheroidene

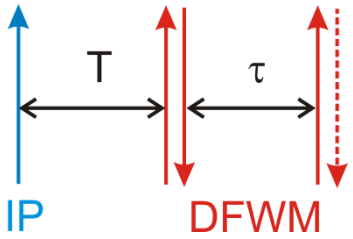






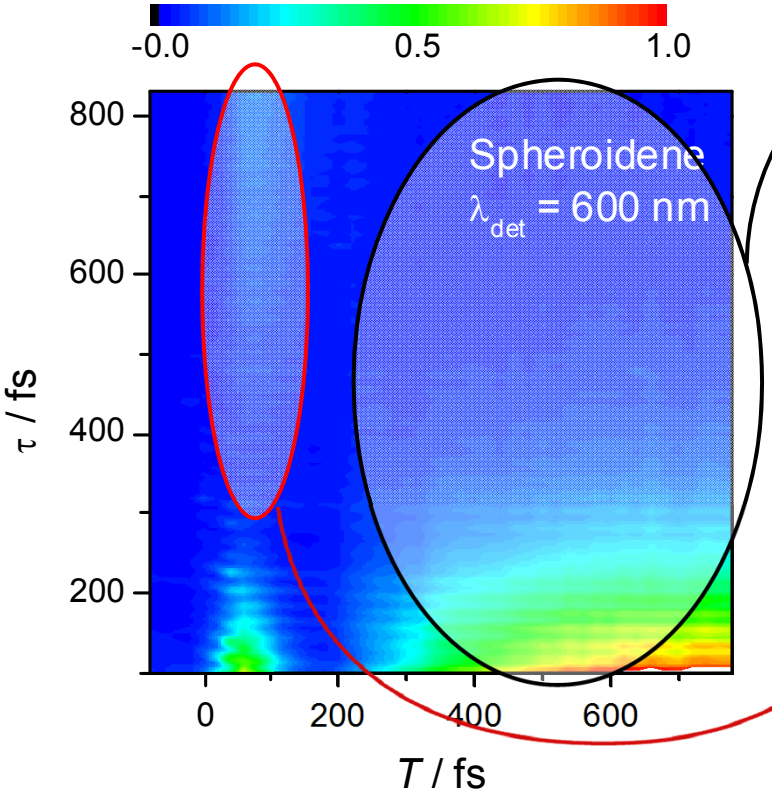


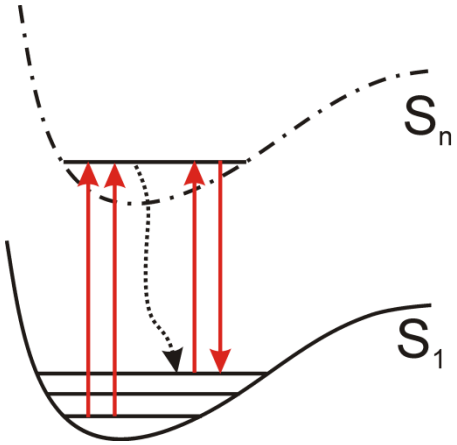
Long living signal in spheroidene at later *T* and overlaid with strong rapidly decaying component.



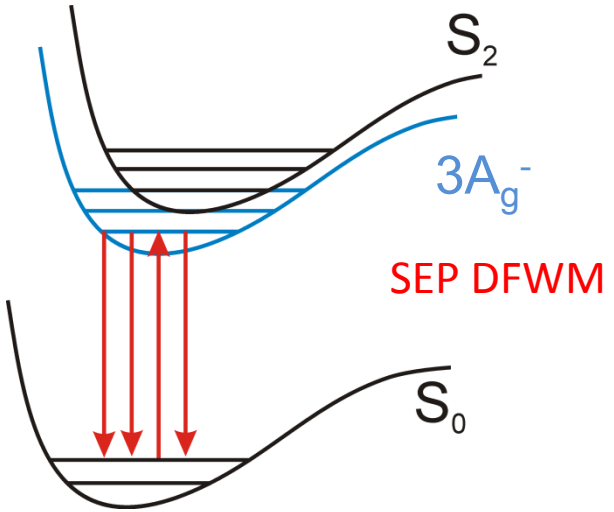
Spheroidene's pump-DFWM signal

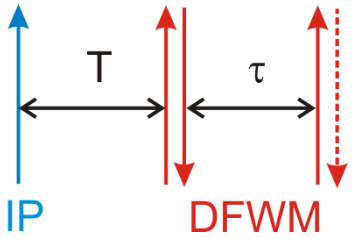
Experimental *T* vs. τ Scan





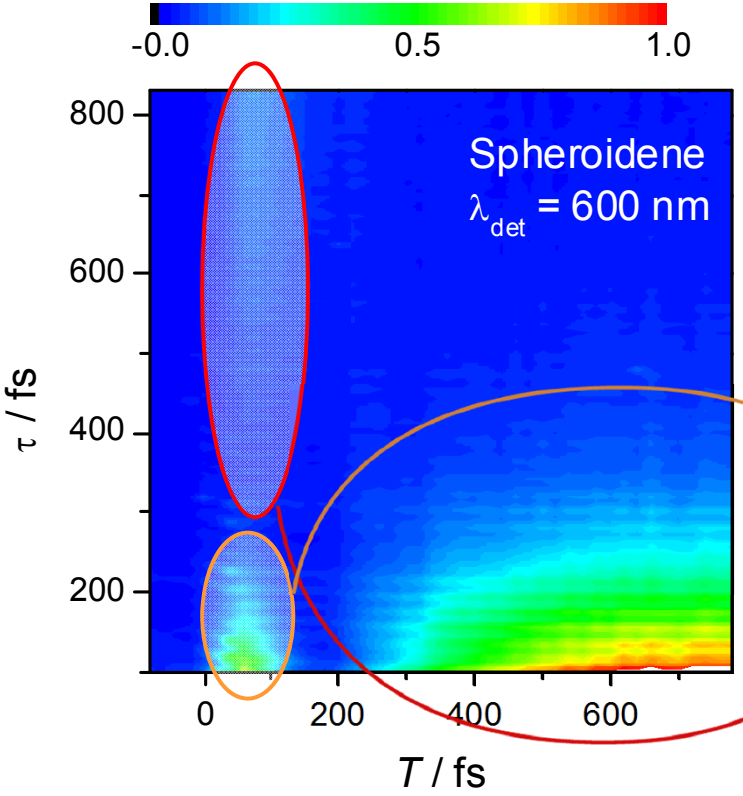
Vibrational cooling



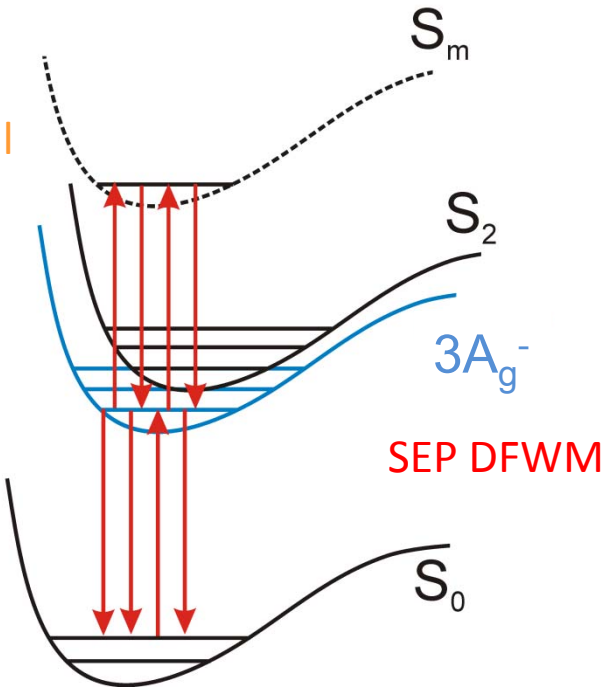


Spheroidene's pump-DFWM signal

Experimental *T* vs. τ Scan



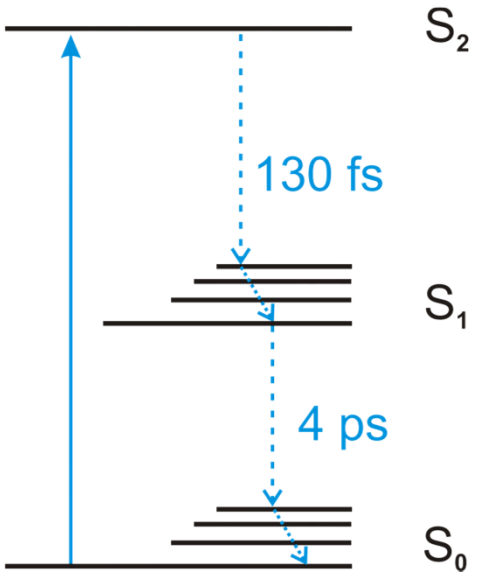
Additional ESA



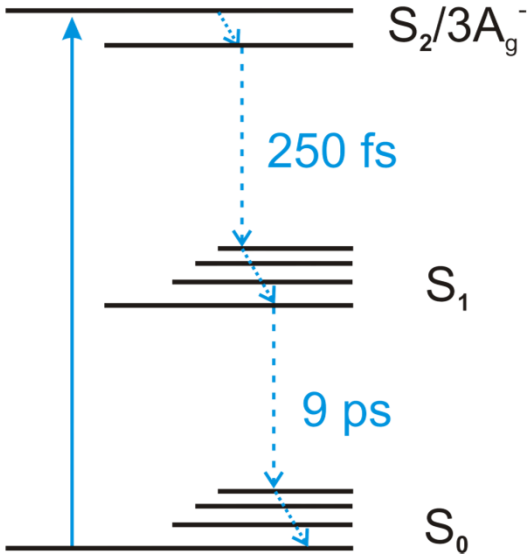
Summary of pump-DFWM

Pump-DFWM in combination with numerical model simulations allows determination of relaxation pathways:

Lycopene (N = 11)

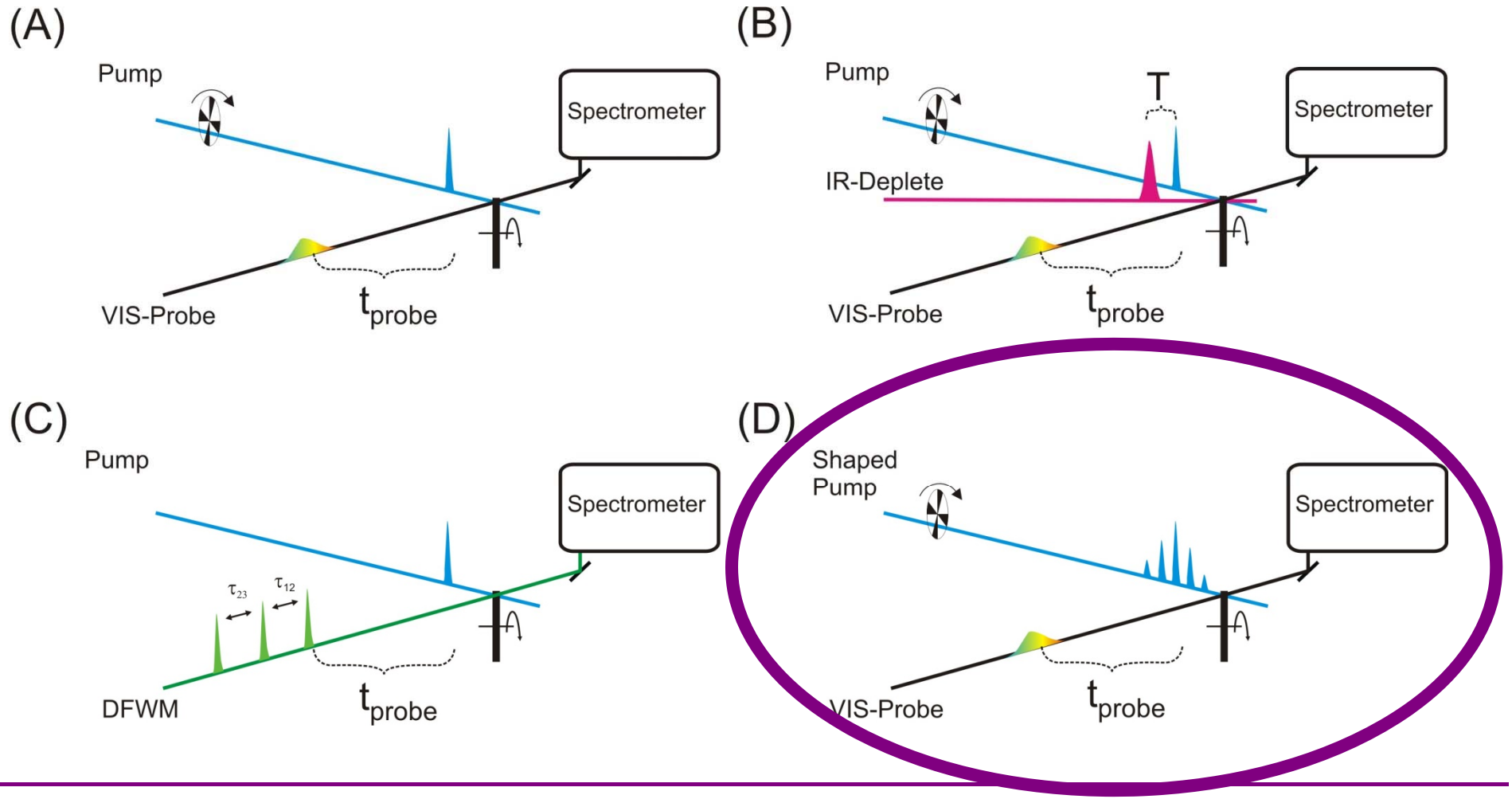


Spheroidene (N = 10)

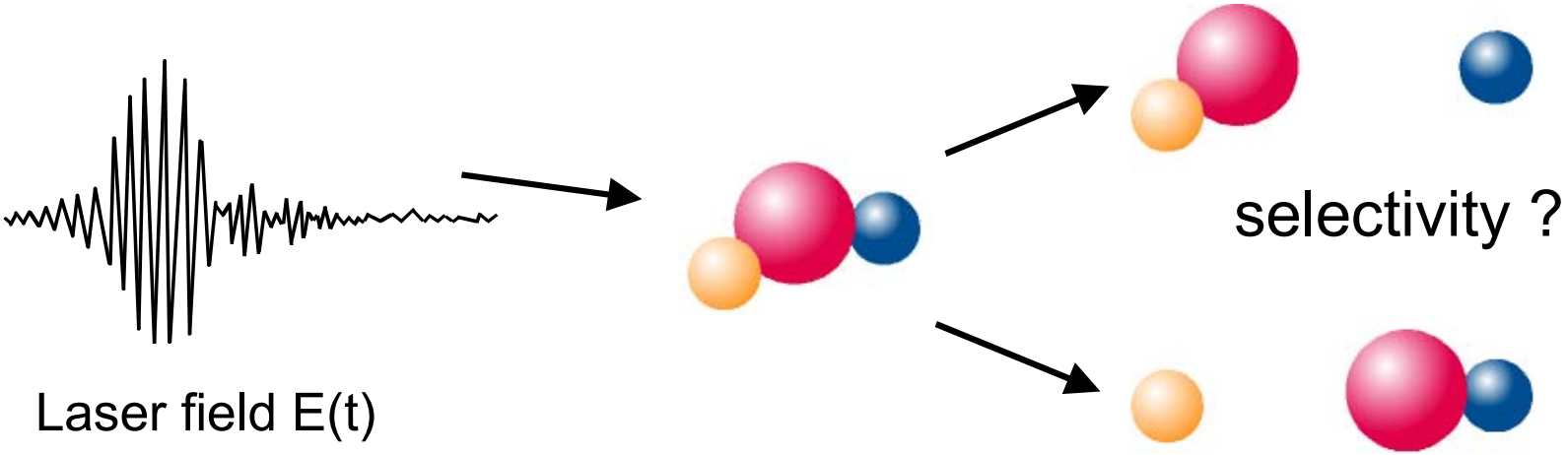


J. Chem. Phys. 139 ***(2013)*** *074202*
Ann. Rev. Phys.Chem., in print

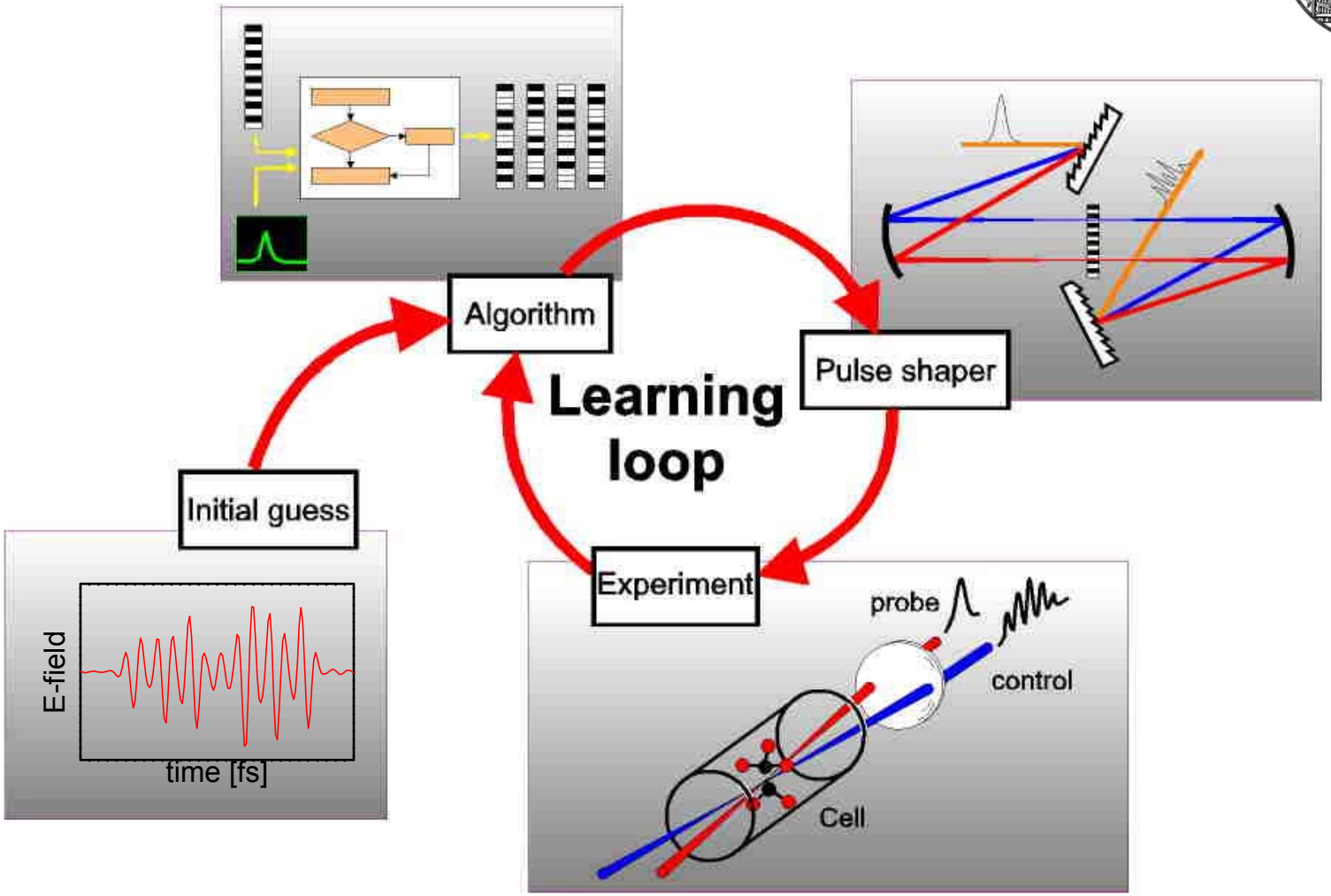
Going beyond simple pump-probe: Complex excitation + complex probe



Coherent control of chemical reactions



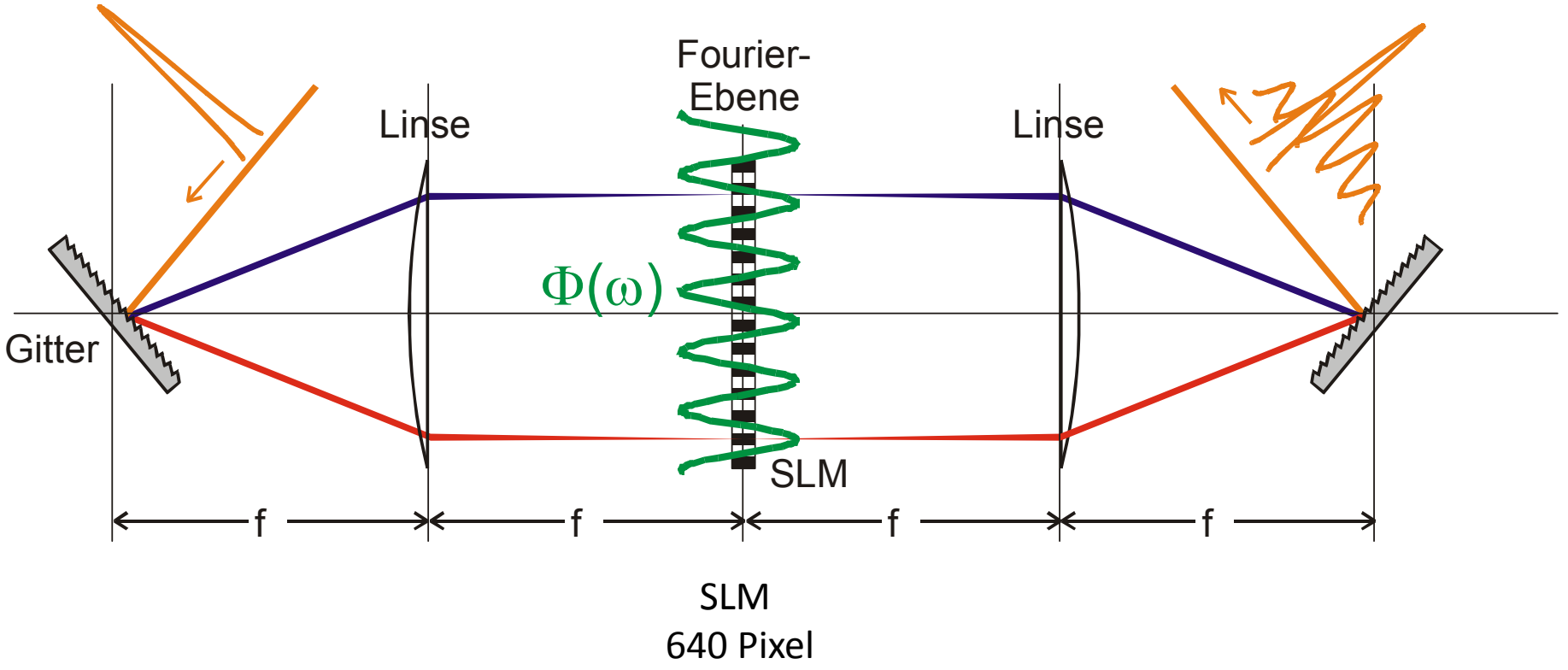
- calculation for real molecules complicated (if not impossible)
- experimental realization of predicted E-fields difficult



Science 288 (2000) 824

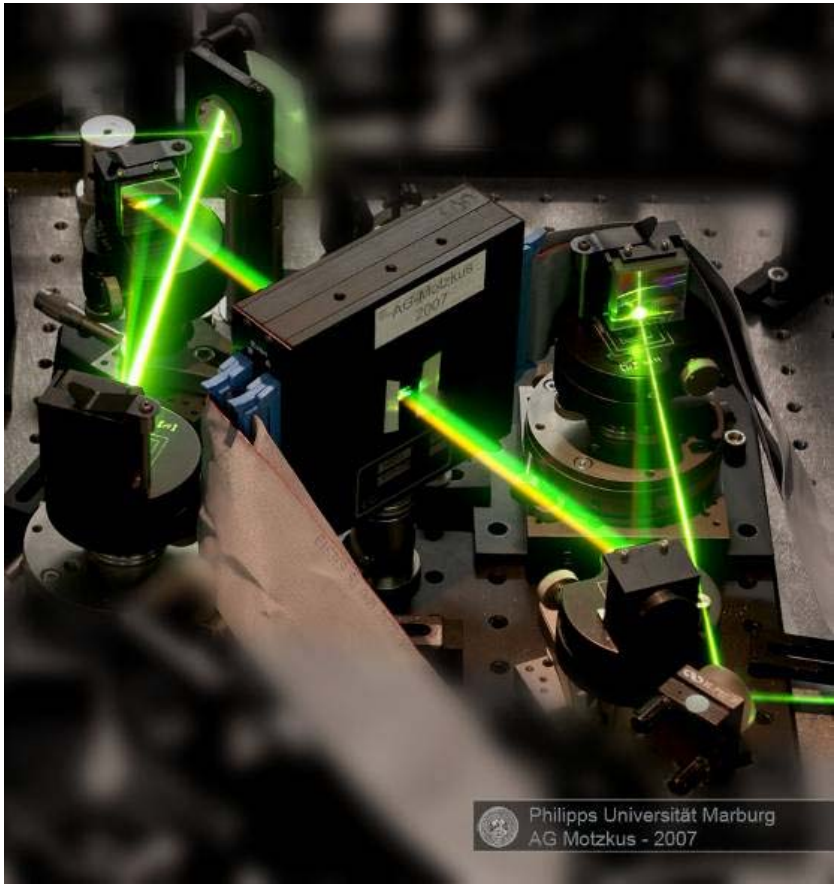
Concept: R.S. Judson and H. Rabitz, Phys. Rev. Lett. **68** (1992) 1500

Shaping of fs-Laser Pulses



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

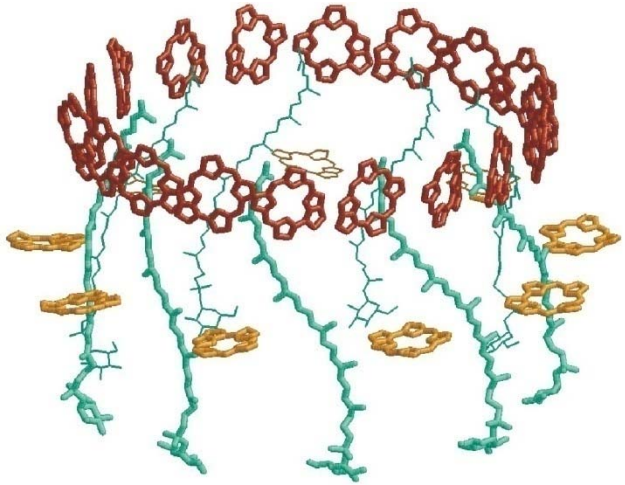
Liquid crystal spatial ligt modulator

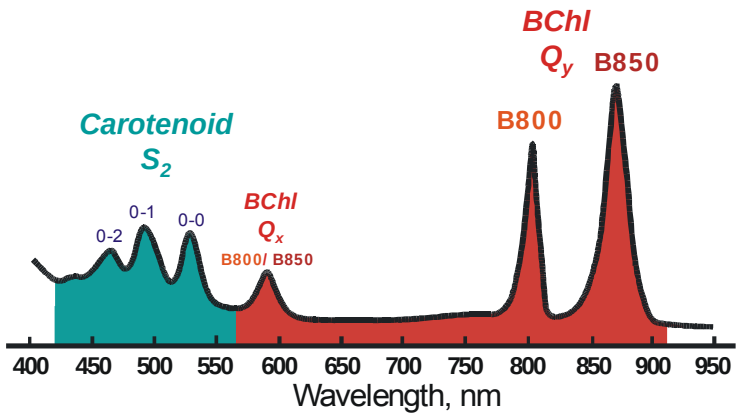


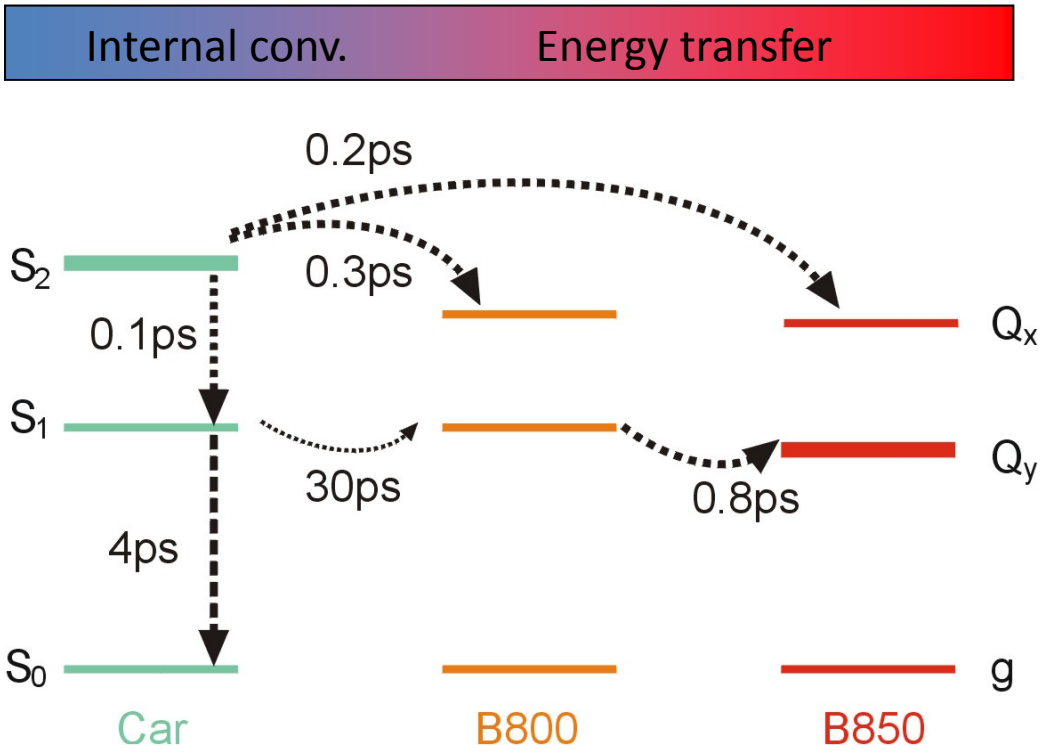
128 pixel device

→ Development of new 640 pixel shaper in cooperation
with University of Jena and Jenoptik: *Appl. Phys. B 72 (2001) 627*

LH2 of *Rps. Acidophila* - Standard model

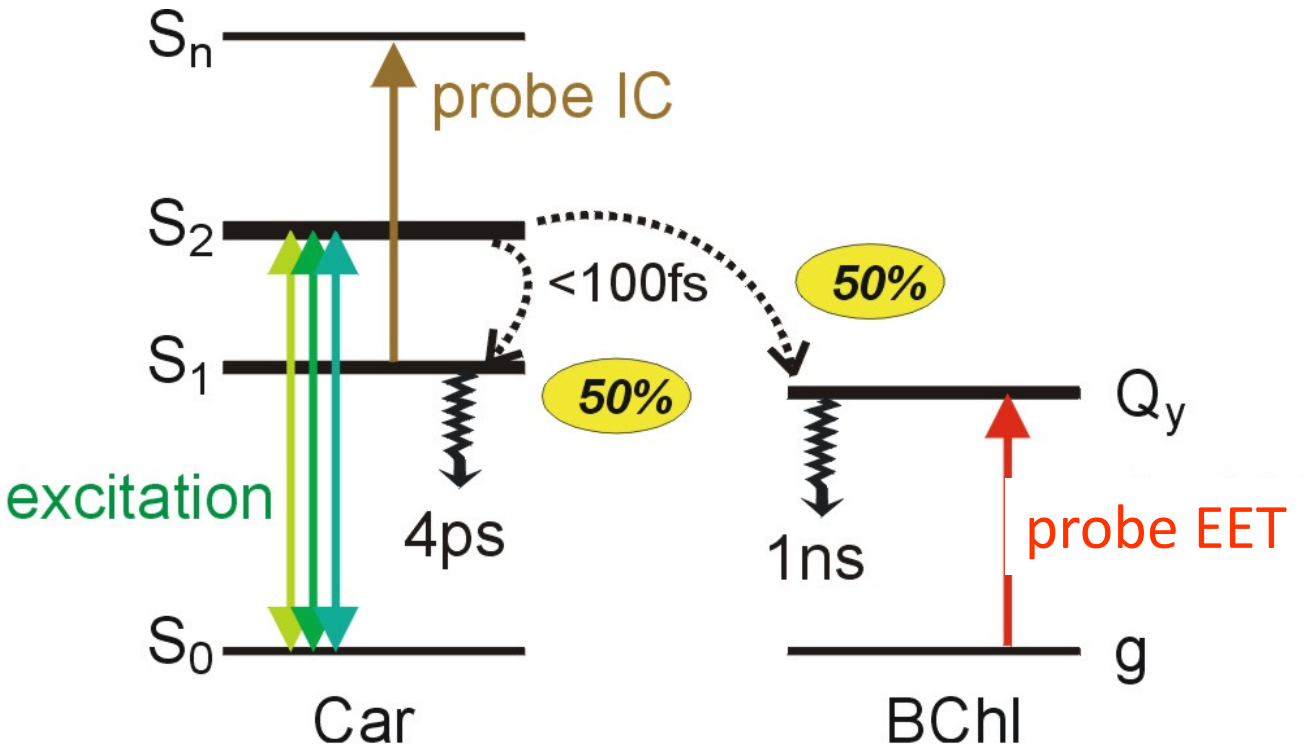






Polivka & Sundström, Chem. Rev. (2004)

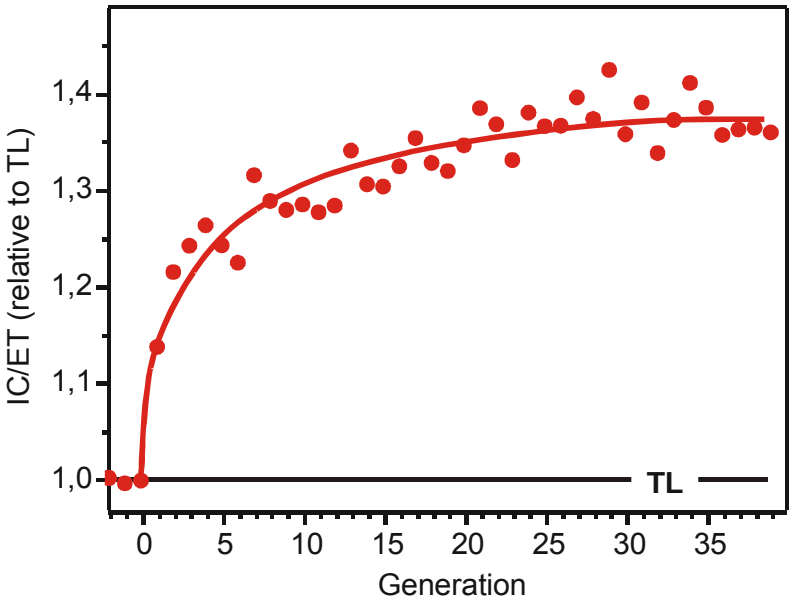
Competing deactivation IC-EET



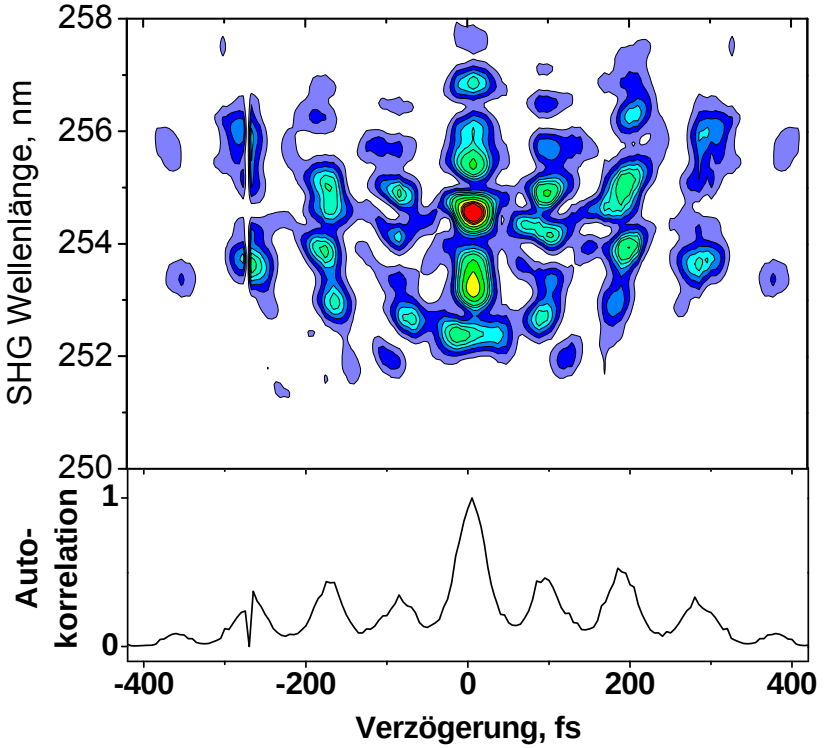
- Significant loss channel IC
- Negligible cross talk IC-EET
- Energy funnel precludes back transfer

64-parameter optimisation of IC/EET

Convergence curve



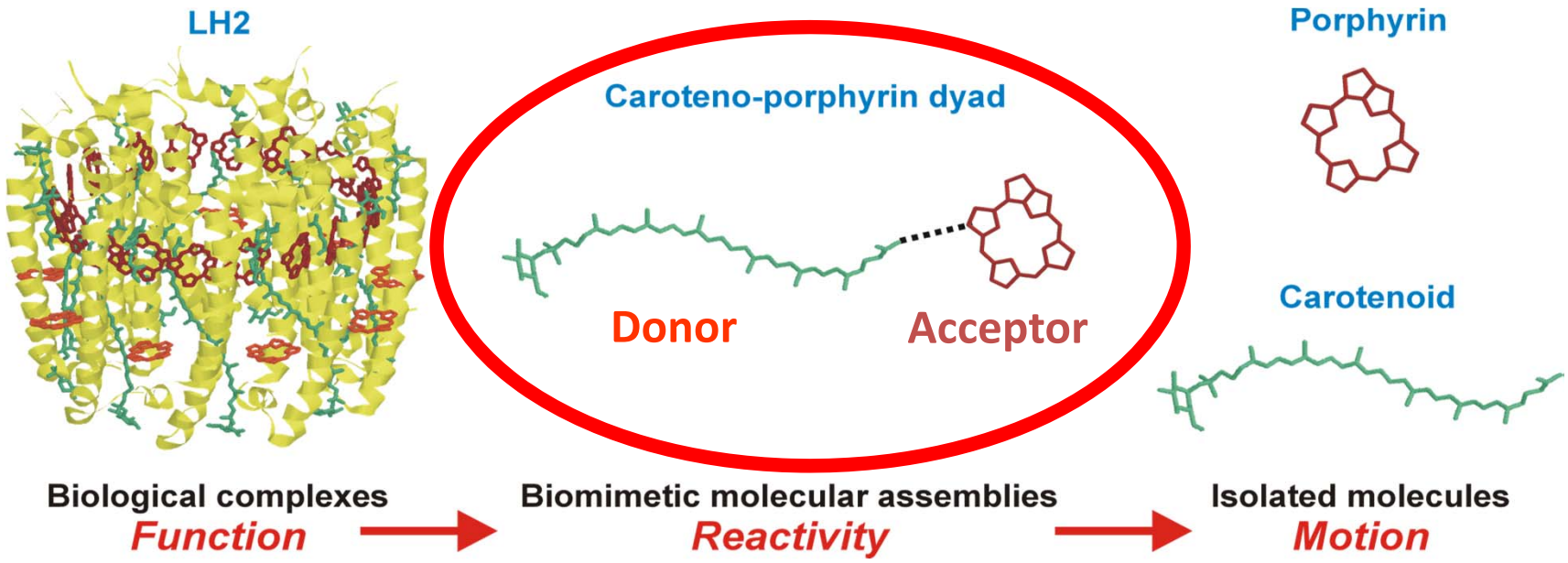
Optimal pulse FROG trace



Nature **417** (2002) 533

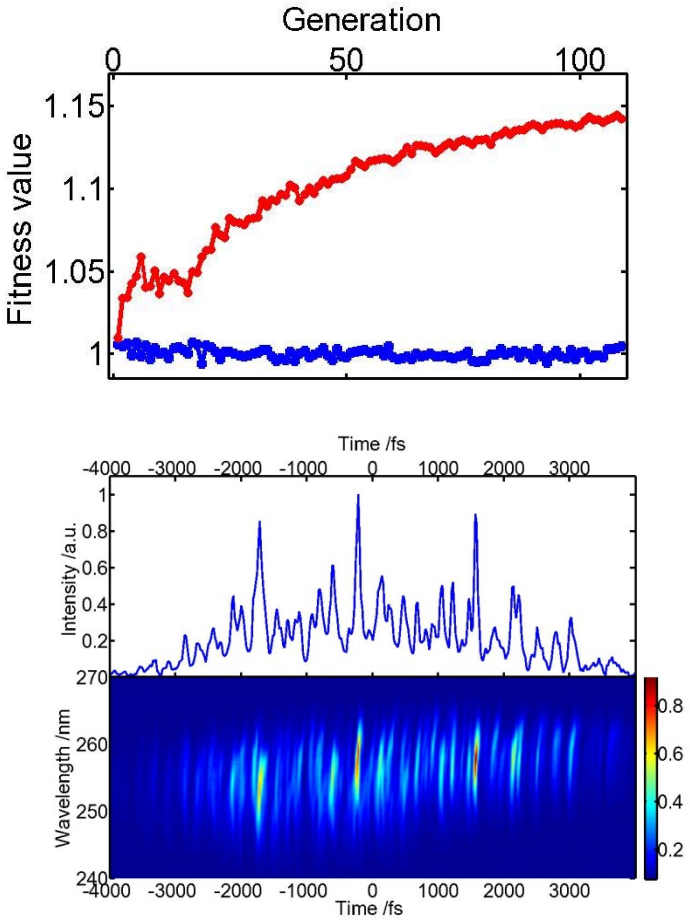
ChemPhysChem **6** (2005) 850

Reducing the complexity

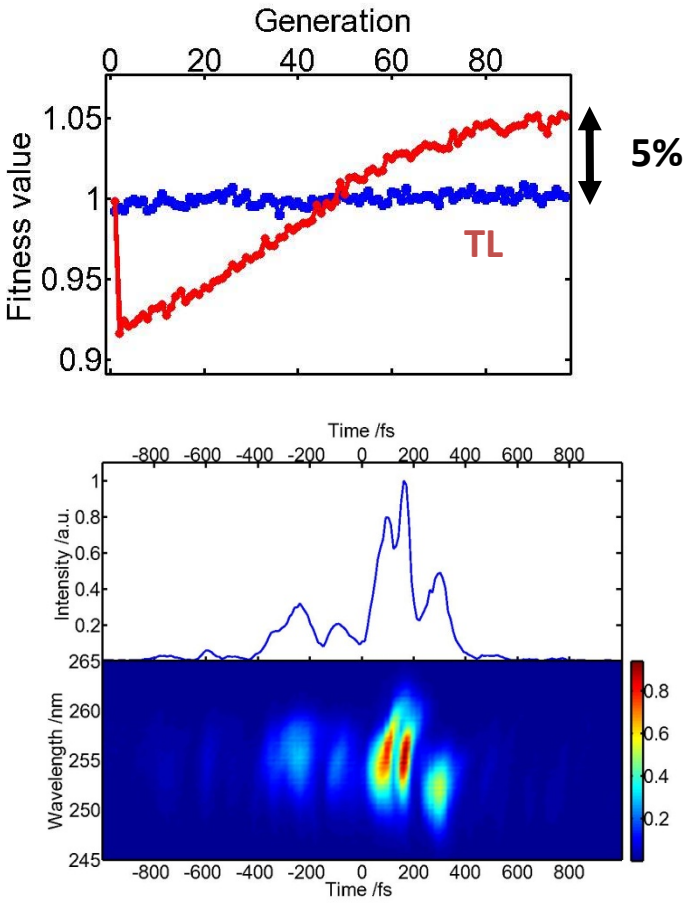


Control of Dyad complex

IC/ET



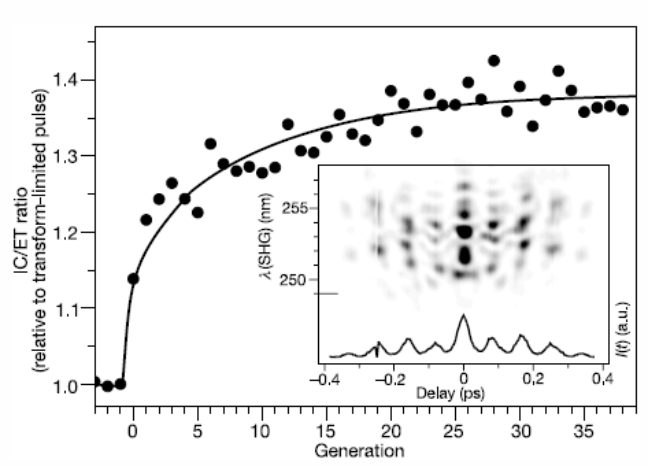
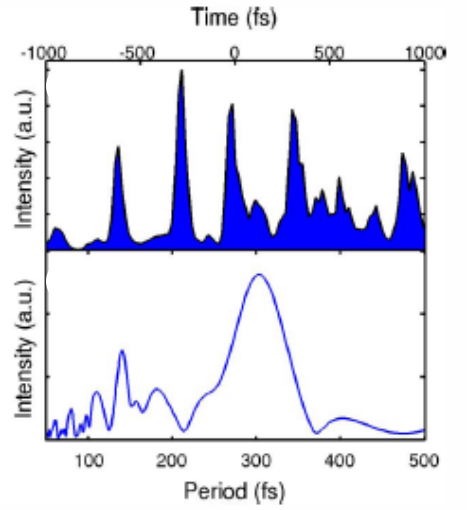
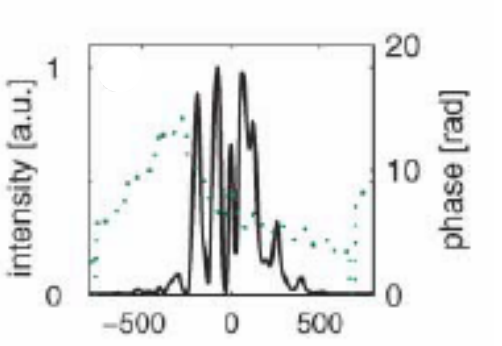
ET/IC



Collaboration with AMOLF/Twente

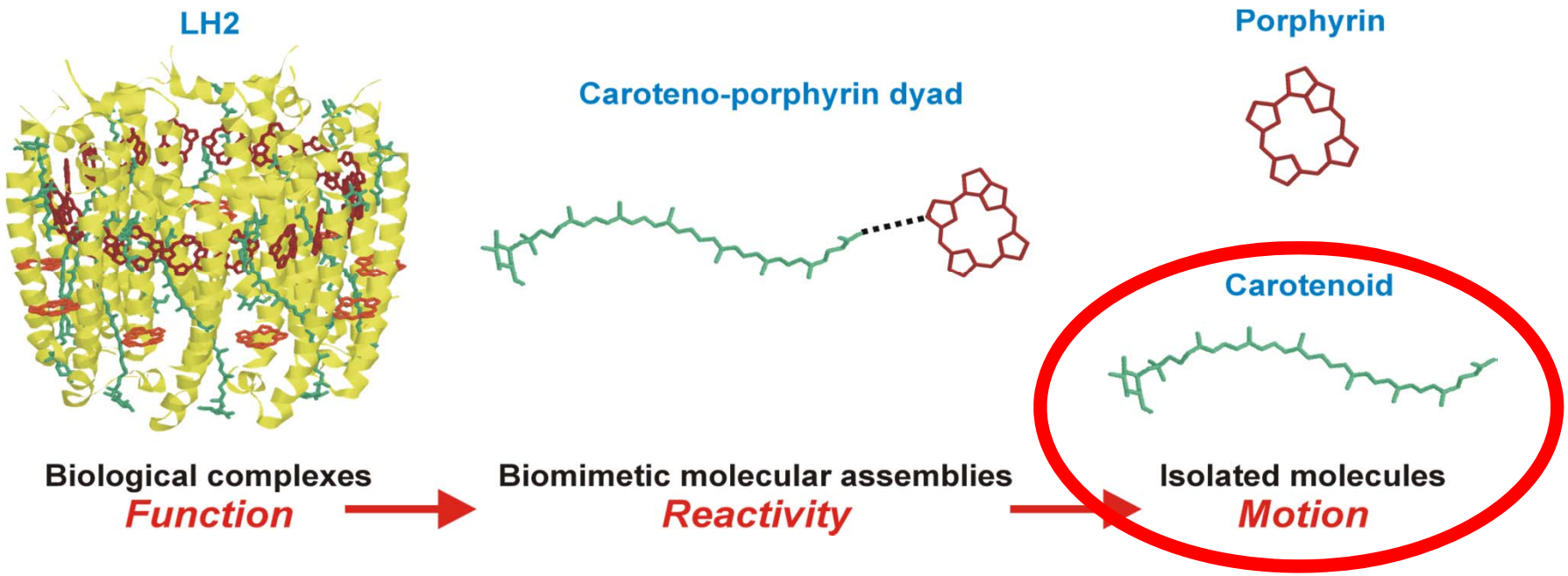
PNAS ***105*** *(2008) 7641*

Optimal Control Results

Natural Light Harvesting: LH2	Artifical Light Harvesting: Dyad	Bacteriorhodopsin
		
Herek et al, Nature 417 (2002) 533.	Savolainen et al, PNAS 105 (2008) 7641.	Prokhorenko et al, Science 313 (2006) 1257.
Optimal: NA	Optimal: 110cm^{-1}(300fs)	Optimal: 230cm^{-1}(145fs)
Anti-Optimal: 160cm^{-1}(210fs)	Anti-Optimal: 166cm^{-1}(200fs)	Anti-Optimal: 155cm^{-1}(215fs)

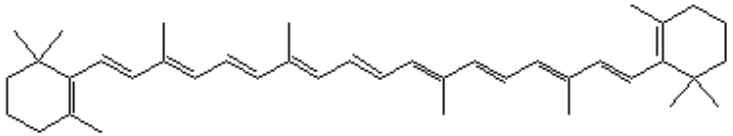
What is the general QM mechanism behind all these results?

Further reduction of complexity

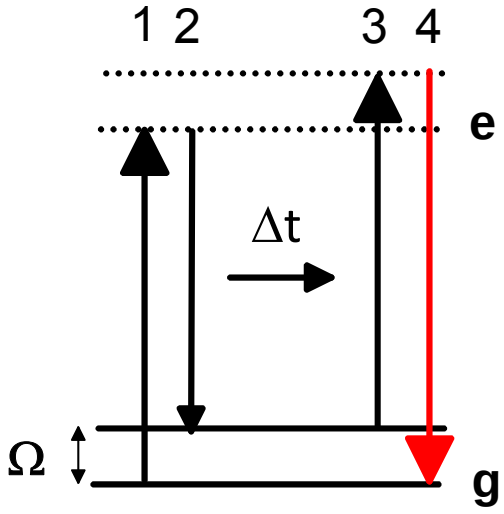


Time-resolved FWM spectroscopy of ground-state dynamics

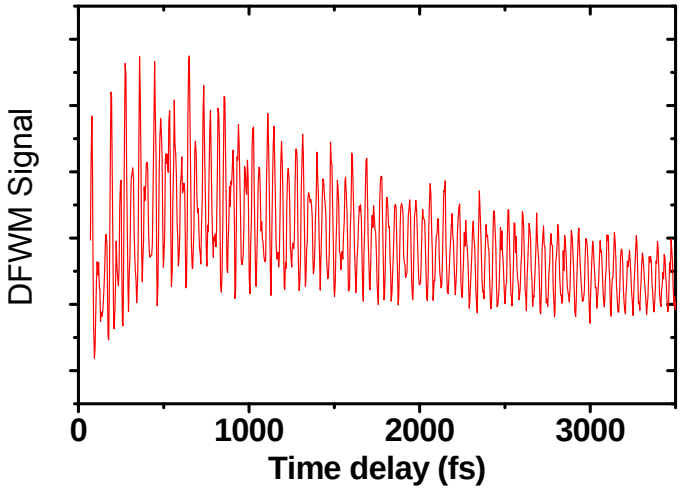
β-carotene



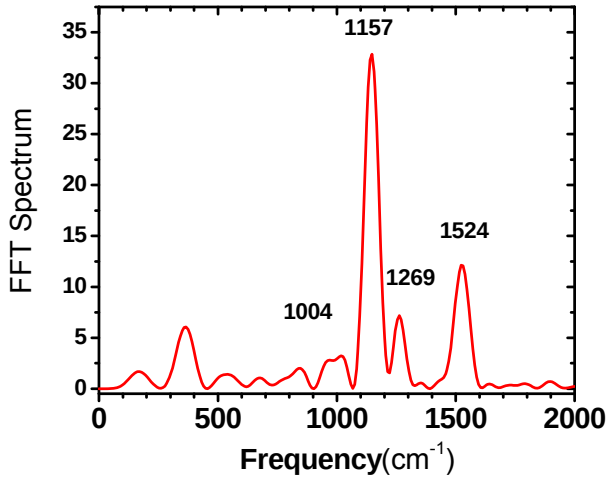
DFWM scheme



DFWM signal

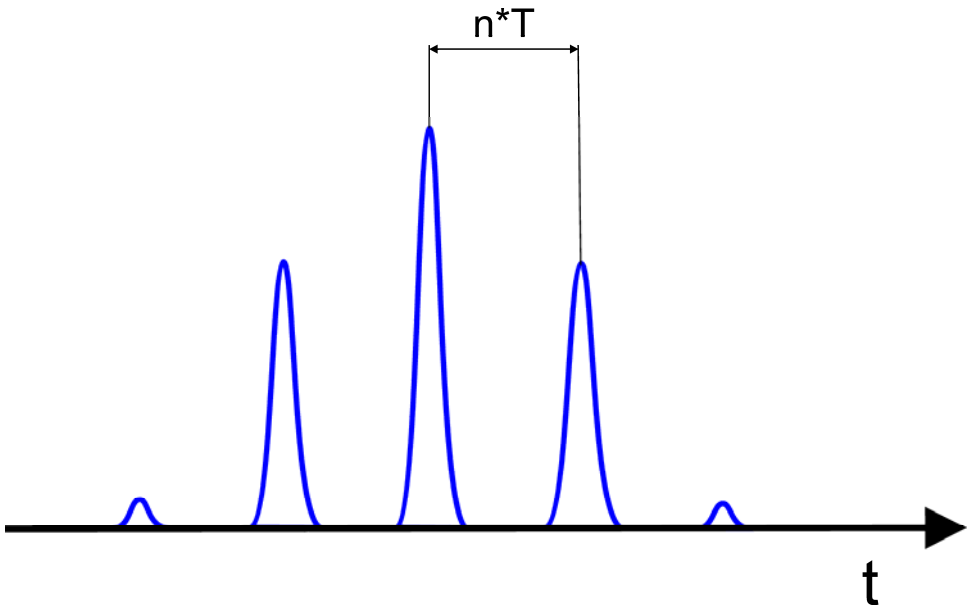


FFT spectrum



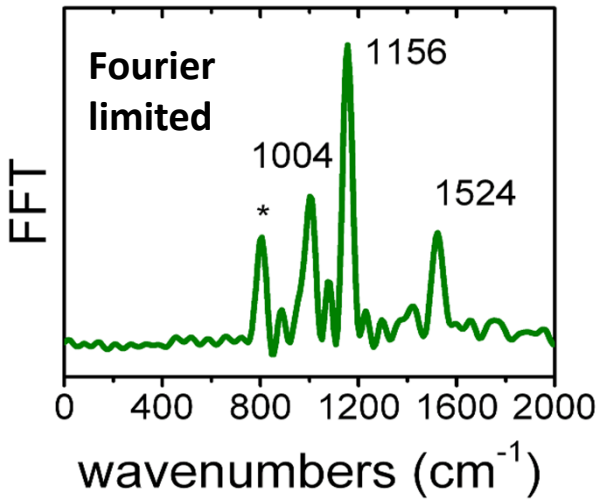
Pulse Spacings

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		



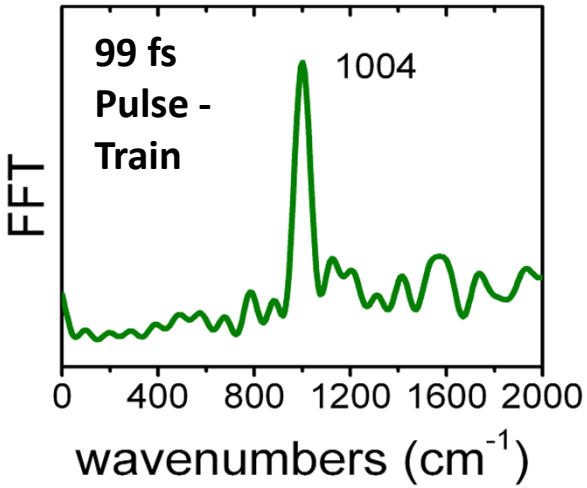
Control of ground state vibrations

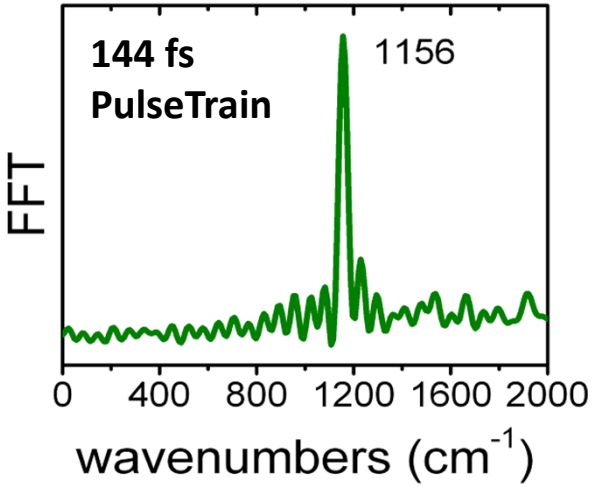
Nonlinear Raman spectra

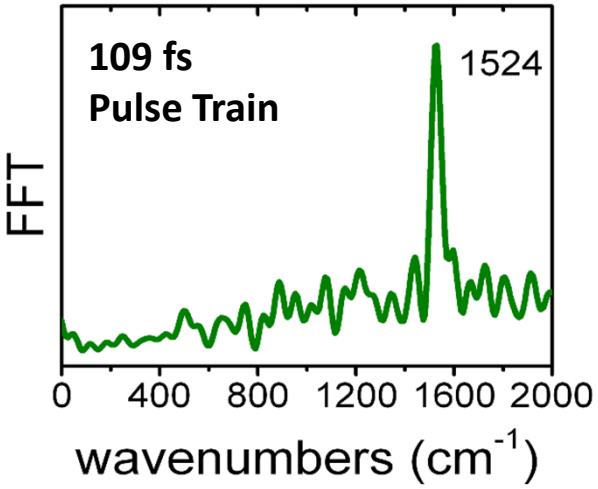


→ *Modes can be selectively excited*

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



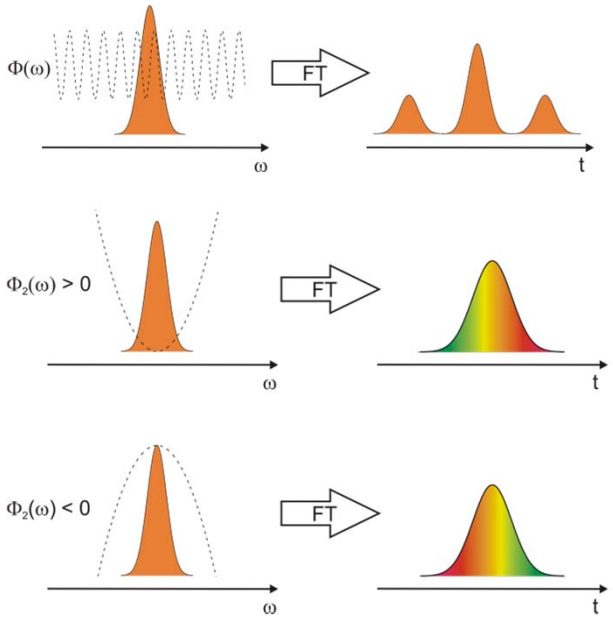




Coherent Control (pulse shaping) + Spectroscopy = Quantum Control Spectroscopy (QCS)

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

→ **Disentanglement of complex dynamics and symplifying experiments**



Nature ***417*** *(2002) 533*
ChemPhysChem ***6*** *(2005) 1*
JPPA ***125*** *(2006) 194505*
PNAS ***105*** *(2008) 7641*
Faraday Discuss. ***153*** *(2011) 213*

PCCP ***10*** *(2008) 168*
Opt. Lett. ***37*** *(2012) 4239*

Quantum Control Spectroscopy

Technology

- Open-loop complex pulse synthesis and characterization
- UV-MIR shaping
- Photonic crystalls
- FWM-spectroscopy

Concepts

- Plurality of closed-/ open-loop control and pump-probe
- Parameterisation of pulse shapes
- Role of coherence and contrability

Systems

- Prototype molecul.: Dimers, Dyes etc.
- Biomolecules: ultrafast energy flow in LH2 and carotenoids
- Nonlinear microscopy
- Medical application

Literature

Basics and Applications:

- **Ultrashort Laser Pulse Phenomena**, J.-C. Diels and W. Rudolph, 2nd ed., Academic Press, 2006
- **Femtosecond Laser Pulses**, ed. by C. Rullière, 2nd ed., Springer, 2005
- **Laser Spectroscopy: Vol. 1 and 2, W. Demtröder,** 4th ed., Springer, 2008

Femtochemistry:

- **Femtochemistry: Atomic-scale dynamics of the chemical bond**, A.H. Zewail, J. Phys. Chem. A , Vol. 104, pp. 5660-5694, 2000
- **Ultrafast Phenomena I - XVII**, Conference Proceedings, Springer and Oxford Press
- **Femtochemistry and Femtobiology**, 1994 – 2011, Proceedings, Elsevier et al.
- **Femtosecond Laser Spectroscopy**, ed. by P. Hannaford, Springer, 2005

Control:

- **Coherence and Control in Chemistry,** Faraday Discuss., 2011, **153**, RSC Publishing
- **Quantum Control of Molecular Processes, P. Brumer and M. Shapiro, 2nd ed., 2011,** Wiley-VCH Verlag
- **Optical Control of Molecular Dynamics, S.A. Rice and M. Zhao, 2000,** John Wiley & Sons

Thanks to …

- Tiago Buckup
- H.-R. Volpp
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- Marie Marek
- Jens Möhring
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- Jean Rehbinder
- Dzmitry Starukhin
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- Jürgen Hauer
- Bernhard von Vacano

Marburg

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Munich

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- Judith Voll

Twente, NL

- Prof. Jennifer Herek

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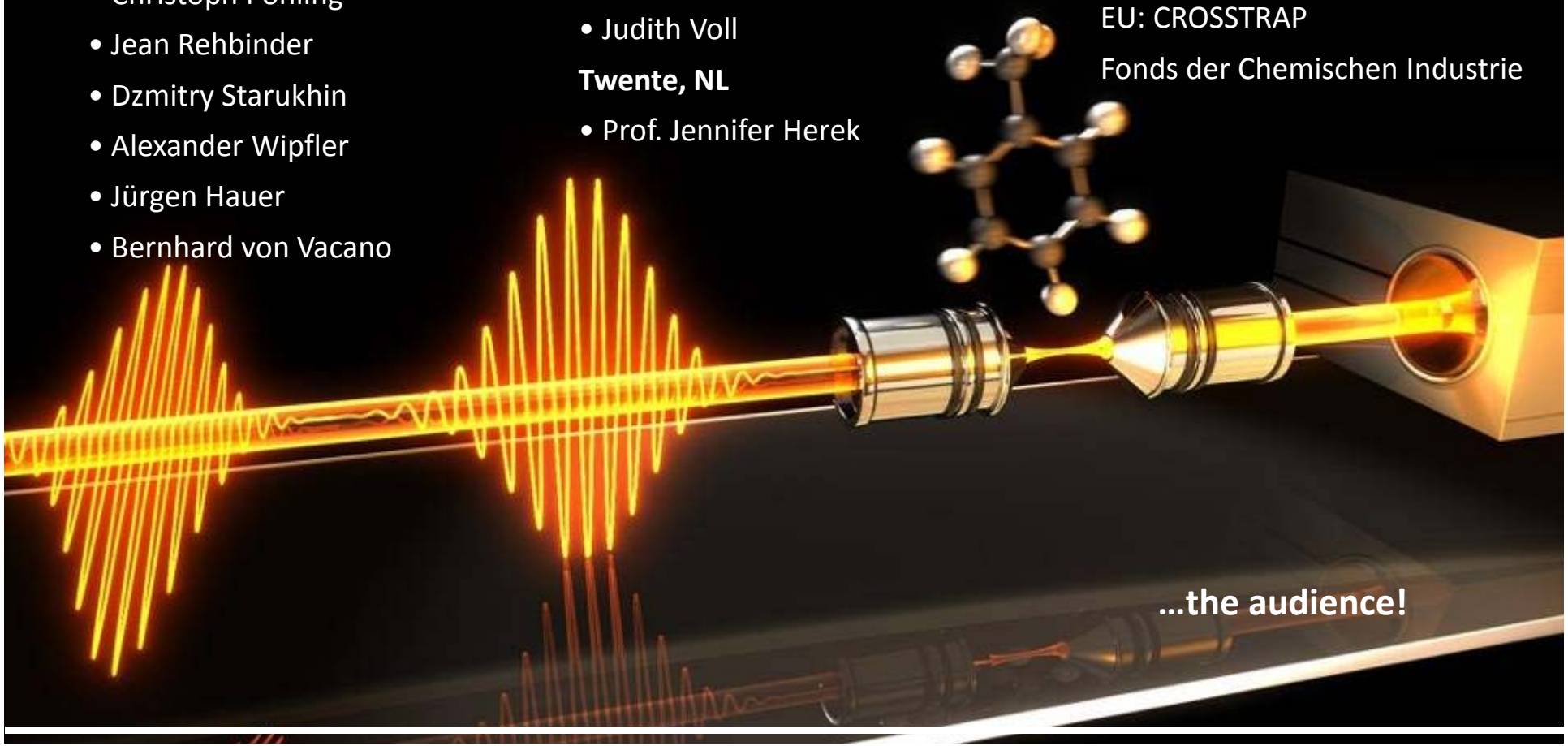
BMBF: ActIOL + MediCARS

EU: CROSSTRAP

Fonds der Chemischen Industrie



…the audience!